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SRC-I DEMONSTRATION PLANT ANALYTICAL LABORATORY METHODS MANUAL

Final Technical Report

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Allentown, Pennsylvania

and

International Coal Refining Company
Allentown, Pennsylvania

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FINAL TECHNICAL REPORT:

SRC-I DEMONSTRATION PLANT ANALYTICAL LABORATORY METHODS MANUAL

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UNITED STATES DEPARTMENT OF ENERGY
Office of Solvent-Refined Coal Products
under Contract DE-AC05-78-OR-03054

FINAL TECHNICAL REPORT:

SRC-I DEMONSTRATION PLANT ANALYTICAL LABORATORY METHODS MANUAL

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LIST OF ABBREVIATONS

ASTM	American Society for Testing and Materials
APCI	Air Products and Chemicals, Inc.
H.O.	Heavy oil; 650-850°F distillate fraction
HSRC	Heavy solvent-refined coal; first-stage SRC product recovered from the SRC-I process after Kerr-McGee deashing
KMAC	Kerr-McGee ash concentrate
L.O.	Light oil; initial boiling point to 450°F distillate fraction
LSRC	Light solvent-refined coal; intermediate stream derived from the Kerr-McGee deashing process
M.O.	Middle oil; 450-650°F distillate fraction
O.S.H.A.	Occupational Safety and Health Administration
SRC	Solvent-Refined Coal
TSL SRC	Two-stage liquefaction or hydrocracked solvent-refined coal

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ABSTRACT

This manual is a compilation of analytical procedures required for operation of a Solvent-Refined Coal (SRC-I) demonstration or commercial plant. Each method reproduced in full includes a detailed procedure, a list of equipment and reagents, safety precautions, and, where possible, a precision statement. Procedures for the laboratory's environmental and industrial hygiene modules are not included. Required American Society for Testing and Materials (ASTM) methods are cited, and ICRC's suggested modifications to these methods for handling coal-derived products are provided.

SRC-I DEMONSTRATION PLANT
ANALYTICAL LABORATORY METHODS MANUAL

EXECUTIVE SUMMARY

Part of International Coal Refining Company's (ICRC) design for a plant demonstrating the Solvent-Refined Coal (SRC-I) technology includes an analytical laboratory to monitor process streams for process and product quality control during start-up and operation. This manual collates all analytical procedures required to operate an SRC-I plant. It can be used to establish and operate the laboratory, and to train technicians.

Standard Air Products and Chemicals, Inc. procedures, as well as other techniques developed exclusively for SRC-I products and materials, are reproduced, including equipment and reagents and, where possible, precision statements. Applicable standard American Society for Testing and Materials (ASTM) methods are cited but not reproduced in full because of copyright restrictions. However, modifications for handling coal-derived products are included for all methods, as well as general and specific safety precautions that must be adhered to strictly.

Methods are organized in the manual according to the module in the laboratory where they would be used: sample preparation; distillation; ASTM/wet chemical; microanalytical; instrumental; solvent quality testing; and gas chromatography. Although environmental and industrial hygiene modules are also planned for the laboratory, funding restrictions prevented development of appropriate procedures. Because this manual is preliminary, anyone using it should judge the applicability of the methods in light of his own unique requirements.

INTRODUCTION

Under its Cost-Sharing Agreement with the U.S. Department of Energy (DOE), International Coal Refining Co. (ICRC) is designing a coal refinery to demonstrate the Solvent-Refined Coal (SRC-I) technology. Part of the design includes an analytical laboratory planned for construction at the plant site in Newman, Kentucky. The laboratory was included to support plant operation, commercial activity, and environmental monitoring. Specifications for the laboratory include a floor space of about 4,700 ft^2 and a staff of 26 technicians, 4 shift leaders, 2 chemists, and a quality control manager, who will collectively conduct about 880 hr of analysis/week.

This methods manual is a primary tool for establishment and operation of the laboratory. Its purpose is to provide sufficient information on each analytical technique to direct the acquisition of laboratory hardware and reagents and to facilitate their setup. Because the manual contains detailed information on the performance of each analysis, it can be used for both technician training and reference. In conjunction with proper laboratory supervision, this manual should provide the basis for safe, precise, and efficient performance of all laboratory techniques.

BACKGROUND

Effective start-up and operation of the SRC-I Demonstration Plant, or any coal liquefaction plant, will rely on monitoring process streams to provide data for process control and product quality control. Accurate and timely analyses will be particularly vital during plant start-up, when operating conditions are being adjusted and the relationships between product yield and quality and process conditions are not well understood. Therefore, the plant's analytical laboratory must be operating smoothly during the start-up phase.

To achieve this goal, ICRC subcontracted to Air Products and Chemicals, Inc. a 3-year research and development program: "SRC-I Demonstration Plant Analytical Laboratory." The program was designed to provide all necessary planning and technical support to enable the plant's analytical lab to be functioning efficiently prior to plant start-up. The following specific objectives were encompassed:

- Define the scope and physical requirements of the analytical laboratory
- Select and validate methods to analyze all samples associated with the laboratory
- Conduct all necessary methods development work to upgrade available analytical techniques to the required accuracy and precision for coal-derived samples
- Develop an analytical laboratory methods manual
- Specify analytical equipment for the laboratory
- Select and train laboratory personnel
- Assist in start-up of the laboratory
- Help specify on-line plant monitoring instrumentation

Subsequently, DOE decided not to construct a DOE-funded SRC-I Demonstration Plant and requested that this R&D program be halted at a logical stopping point, prior to completion of the program's second year. Thus, the last four program objectives were not initiated, and several methods development programs were either not begun or stopped before completion. Consequently, analytical methods for the environmental laboratory were not compiled for inclusion in this methods manual.

The manual includes methods that were developed, modified, or tested under several other R&D programs performed by Air Products and ICRC in addition to the 3-year program just mentioned: "Development of SRC-I Product Analysis"; "Solid Product Characterization"; and "Liquid Product Characterization." Furthermore, many of the methods selected are standard American Society for Testing and Materials (ASTM) methods or ASTM methods that have been modified to handle coal- rather than petroleum-derived samples. Other analyses were obtained from the Wilsonville Advanced Coal Liquefaction Facility, Conoco, Kerr-McGee, and the Bartlesville Energy Technology Center.

Because neither this R&D program nor the SRC-I Demonstration Plant design was completed, this methods manual cannot be viewed as a finished document. The manual is based upon anticipated needs and assumed facts, which may change by the time an SRC-I plant is operating. Thus, this manual would normally evolve between now and the time an SRC-I plant is operating routinely. Anyone using this manual must appreciate this, by using his own professional judgment and knowledge of individual situations and requirements to ascertain the applicability of these methods.

LABORATORY ANALYTICAL REQUIREMENTS

Tables 1-5, respectively, list comprehensive analytical requirements compiled by ICRC's manufacturing, wastewater treatment, environmental monitoring, and business management groups. Each group estimated the quantity and type of analyses that would be required when the demonstration plant operates at steady-state conditions. Although more analyses and additional types of analysis will be needed during plant start-up, this increased analytical load was not specifically incorporated because these requirements will be temporary. However, the lab modules as sized can accommodate an increased level of analyses, and additional laboratory personnel will be available during start-up.

Although the analytical lists were revised several times and are as accurate and detailed as possible, each group faced uncertainty in projecting its analytical needs for the demonstration plant period. For example, in the wastewater treatment and manufacturing areas, where analysis is performed for process control, some processes and equipment have not yet been selected, or the area contractor has provided insufficient information with which to detail analytical needs. In the business management area, where analysis of the plant's final products provides quality assurance, the extent and type of analysis are affected by shipment frequency, number of customers, and specification parameters to be set out in the sales/use agreements. None of these have yet been fixed. In the environmental monitoring area, actual requirements will be affected both by future regulatory policy and by the quantity and nature of pollutants detected in the plant vicinity.

Despite these uncertainties, the comprehensive list of analytical requirements is believed to fairly represent the analytical load the laboratory will actually experience. No contingency has been included in the analysis list to account for possible future increases of the plant's analytical requirements.

Not all analytical work required in the demonstration plant will be handled by the laboratory. On-line analysis, which will continuously measure certain process parameters, was selected over laboratory analysis whenever a suitable on-line technique was available, and when the required turnaround time or frequency of analysis warranted the capital expenditure. In other instances, quick, simple tests will be performed by operators within battery limits. Outside laboratory subcontractors will be hired to perform analyses that are needed infrequently and require specialized testing, such as catalyst analyses.

LABORATORY MODULES

To promote efficient operation, the laboratory is subdivided into nine modules, each of which contains functionally related analytical equipment: sample preparation; distillation; ASTM/wet chemical; microanalytical; instrumental; solvent quality activity testing; gas chromatography/liquid chromatography (GC/LC); environmental; and industrial hygiene. The laboratory design also includes additional utility areas for sample receiving, storage, and preparation. A computer-implemented laboratory management information system will serve the data tracking, reporting, and correlation functions required to efficiently process almost 130,000 analyses to be conducted annually.

Sample Preparation Laboratory

The Hardgrove grindability test for SRC and TSL SRC fuels and anode coke plus determination of the particle-size distribution of coal and KMAC comprise the bulk of the work to be performed in this area (Table 6).

Distillation Laboratory

If current methods development is successful, many of the projected distillations (Table 7) may be replaced by GC simulated distillation. Consequently, the number of samples that will require spinning-band or flash distillations is unknown.

ASTM/Wet Laboratory

This module will study physical and chemical properties using standard APCI and ASTM methods, to ensure product quality and to analyze process materials (Table 8). A microprocessor-controlled coal analyzer that determines moisture, volatiles, and ash for proximate analysis will greatly reduce labor requirements.

Methods for analyzing either treatment chemicals from the utilities and off-sites area or the corrosion inhibitor concentration in the diethanolamine (DEA) process in the gas-treating area have not yet been determined. In addition, the sample source or frequency of the following tests has not yet been established:

- Mercaptan
- Softening point
- Neutralization number

The labor requirement (Table 8) does not include time for spot-checking pyrite, sulfate, or organic sulfur from batches of incoming coal. Such analyses will increase the needs of this area; the magnitude depends upon sampling frequency. Wet digestion or pretreatment of water samples and SRC-I products to be analyzed in the Environmental and Instrumental Laboratories will also be conducted in this module.

Microanalytical Laboratory

Using automated carbon, hydrogen, nitrogen, oxygen, and sulfur analyzers, the microanalytical laboratory will handle the elemental analyses for a wide variety of samples. High heating values, particle size distribution, and coal tar pitch volatiles will also be calculated (see Table 9).

Instrumental Laboratory

Energy-dispersive X-ray techniques will analyze the ash residue from feed coals and SRC-I products, solid waste materials, and samples being studied for industrial hygiene purposes (Table 10). Metal-bearing water samples and samples containing low atomic weight metals will be analyzed by atomic absorption/atomic emission spectroscopy using a spectrophotometer with inductively coupled plasma (ICP), graphite furnace, hydride generation, and other auxiliary features. A pretreatment step, such as digestion with acid, may be performed prior to analysis on water samples with large concentrations of organics.

Solvent Quality Activity Test (SQAT) Laboratory

Two tests will measure the hydrogen donor quality index (HDQI) of the process recycle solvent and the solvent-separation characteristics of SRC materials (Table 11). The solvent-separation test measures the oil/asphaltene/preasphaltene/residue distribution of a sample using an automated, microprocessor-controlled solvent-separation technique. Sample sources for this test include light and heavy SRC, Kerr-McGee ash concentrate (KMAC), vacuum column bottoms, and the slurries exiting from the fired heater and dissolvers.

GC/LC Laboratory

A capillary-column GC will analyze completely the coker off-gas, the recycle, sponge-absorber, and methanator hydrogen, and other streams. A GC equipped with dual flame ionization and thermal conductivity detectors (and capable of reducing data) will determine the boiling-point distribution of intermediate and product liquids by gas chromatographic simulated distillation. Frequent quantitative analysis of the residual concentration of deashing solvent in various process streams will be accomplished using a packed-column GC and an autosampler. The liquid chromatograph will analyze phenols, polynuclear aromatic hydrocarbons, and mercaptans (see Table 12 for details). However, development of LC procedures ended when the third year of the R&D program was cancelled, so these are not included in the manual.

Environmental Laboratory

The environmental laboratory will analyze water samples from the wastewater treatment system and manufacturing process, and perform tests required by the Resource Conservation and Recovery Act (RCRA) and National Pollutant Discharge Elimination System (NPDES) regulations. Routine water analysis includes measurement of biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, specific conductance, alkalinity, hardness, ammonia, and chlorine. These methods are not included in the manual.

Industrial Hygiene Laboratory

One module of the analytical laboratory will be used by industrial hygiene personnel to prepare chemical absorbing solutions, to recharge and calibrate equipment, and to work with organic chemical detector tubes and monitors. The manual does not include procedures for this module.

INSTRUCTIONS FOR USING MANUAL

Methods selected for use in the analytical laboratory include standard published ASTM methods and standard Air Products and Chemicals, Inc. (APCI) procedures, as well as methods developed exclusively for SRC-I products and materials. The ASTM procedures are not reproduced here because of copyright restrictions. However, for each ASTM method, and for each APCI method as well, the following supplementary information is provided, when available, to describe how a method was adapted or how it relates to SRC material:

- Which SRC-I materials the procedure will be used for.
- The preferred procedure, if more than one is described.
- Major or minor modifications to the procedure, including chemicals, apparatus, sample size, time of analysis, etc.
- Precision and accuracy data as it relates to SRC-I material.

To increase efficiency, we divided the manual into sections corresponding to the laboratory modules described previously, which contain functionally related analytical equipment. Each section contains methods to be performed in the same work area. That way, each area will need only a single section of the manual, not the complete edition.

Procedures are included that may not be performed at the demonstration plant analytical laboratory, such as proton nuclear magnetic resonance. These are included for easy reference if the data are required and the analyses are subcontracted to outside laboratories. Other procedures, for example, corrosion inhibitor concentration and paraffins-olefins-naphthenes-aromatics (PONA) analysis, can be added at a later date when the chemicals or procedures are defined. No environmental or industrial hygiene laboratory procedures are in the manual.

A list of abbreviations used throughout the manual is conveniently located in the introductory pages.

Proper safety awareness is essential for a productive analytical laboratory and is stressed throughout the manual. Special precautions that must be followed carefully are cited for each procedure. Hazards to be aware of include reduced pressures, temperature extremes, flammable or toxic chemicals, etc. The user should not depend solely on noted safety hazards; know all potential chemical and physical hazards and their remedies before proceeding with any analysis. Specific safety procedures should be developed for each method and strictly adhered to.

SRC-I products and related materials contain known carcinogens and should be handled carefully. The following general precautions should be observed:

- Avoid all body contact with SRC-I products. If you do contact a product, wash the affected area thoroughly with soap and water. Do not use solvents because they encourage penetration into the skin.
- Use a respirator (the type for hydrocarbons) and protective clothing when cleaning spills.
- Wear a complete set of clean work clothing every day (underwear, pants, shirt, and socks).

- Do not wear shoes worn on the job for any other purpose.
- Shower after every shift.

The following ICRC Material Safety Data Sheets (on U.S. Department of Labor O.S.H.A. standard forms) provide specific handling procedures and precautions for the major SRC-I liquids and solids. Sections to note in particular include:

- Fire and explosion data (fire fighting procedures and self-ignition data).
- Health hazard data (emergency first aid procedures).
- Spill or leak procedures.
- Special protection and precaution data.

Each safety data sheet should be carefully read and understood before handling SRC-I materials. This is true of any chemical or technique.

Note that the safety recommendations presented here are based on our experience and the experience of others and are believed to be accurate. However, no guarantee of their accuracy or completeness is made. The safety precautions discussed are distributed without warranty, expressed or implied, and the person receiving them should make his or her own determination of the suitability thereof. Each procedure must be carefully read entirely before proceeding with any analysis. Safety precautions must be developed by individual laboratory supervisors in conjunction with technician experience.

Table 1

Manufacturing Analytical Lab Requirements[a]

Sample description	Analysis	Frequency	On-line	Comments
Coker area				
Molten SRC feed (HSRC)	Distillation to 950°F	1/day		Includes analyses required on LC-Finer feed
	Asphaltenes/ preasphaltenes	3/week		
	C, H, S, O, N, Cl, ash	1/day		
	Fe	Spot		
	Isoviscous temperature		+	
	Specific gravity		+	Needed for flow measurements On-line measurement required because specific gravity has strong temperature dependence
Combination tower overhead water	pH		+	
	Oil	1/shift		
	Total sulfur	1/day		
	Fe	1/day		
	Phenols	1/day		
	Ammonia	1/day		
Coker raw naphtha	Distillation end points		+	
	Full distillation	1/day		ASTM procedure
Coker off-gas	GC including C_1 to C_6, CO, CO_2, N_2, O_2, H_2S, NH_3, H_2	1/day		
Compressor discharge gas	GC including C_1 to C_6, CO, CO_2, N_2, O_2, H_2S, NH_3, H_2	1/day		
Coker raw middle distillate	Distillation end points		+	
	Full distillation	1/day		
	Flash point	1/day		
	Pour point	1/week		
	Viscosity	1/week		
Anode grade coke	VCM (wt %)	1/day		
	Moisture (wt %)	1/day		
	Real density	1/day		
	Particle size distribution	1/day		

Table 1 (Continued)[a]

Sample description	Analysis	Frequency	On-line	Comments
Green coke	VCM (wt %)	1/day		
	Moisture (wt %)	1/day		
Slop oil from blowdown tower	Distillation	2/week		
	Specific gravity	2/week		
Overhead water from blowdown tower	Oil	1/day		
	TSS	1/day		
	TDS	1/day		
LC-Finer				
H_2 feed from sponge absorber	Density		•	
	GC including H_2, CO, CO_2, N_2, C_1 to C_3, H_2S	1/day		
Atmospheric tower feeds[b]	Distillation	1/week		
	Viscosity	1/week		
	Pour point	1/week		
Recycle H_2	Density		•	
	GC including H_2, CO, CO_2, N_2, O_2			
	ppm H_2O, H_2S			0-20 ppm H_2O; 0-3 ppm H_2S
Slop water from atmospheric tower	pH		•	
	TDS	1/day		
Slop water from vacuum tower	pH		•	
	TDS	1/day		
Off-gas to fuel gas area treating	GC including inerts and H_2S	1/shift		
LC-Finer raw naphtha	Distillation end points		•	
	Full distillation	1/day		
LC-Finer raw middle distillate[c]	Distillation end points		•	
	Full distillation	1/day		
	Flash point	1/day		
	Pour point	1/week		
	Viscosity	1/week		

Table 1 (Continued)[a]

Sample description	Analysis	Frequency	On-line	Comments
Vacuum tower feed (atmospheric tower bottoms)	Distillation	1/day		
	Viscosity	1/day		
	Pour point	1/day		
Vacuum tower slop oil	Distillation	2/week		
	Viscosity	2/week		
	Pour point	2/week		
	Specific gravity	2/week		
	Water	2/week		
H_2 from methanator	Density		+	
	GC including CO_2, H_2	1/day		
Vacuum tower bottoms	Solvent, SRC, unconverted coal, ash, pour point	1/day		
Spent catalyst	Carbon residue	3/week		
	Metal content (V, Ni, Fe, etc.) (after regeneration)	3/week		
	Pore volume, surface area (after regeneration)	3/week		
	Activity	3/week		
Fresh catalyst	Pore volume, surface area, metal oxide content, metal sulfide content after presulfiding	1/delivered batch		Some catalyst analyses performed by outside analytical lab
Parsons				
GKT				
Coal (pulverized)	Proximate analysis	1/shift		Includes tests for pulverized coal fed in Rust area
	Ash, S, Cl	1/shift		
	Moisture	6/day	+	On-line microwave analysis is likely
	Grain size	1/shift		
	Fe and SiO_2	1/day		
	Other tests to be identified by GKT			

Table 1 (Continued)[a]

Sample description	Analysis	Frequency	On-line	Comments
K-MAC	Moisture	6/day	+	Microwave analysis
	Fe and SiO_2	1/day		
	Grain size			
	Miscellaneous tests to be identified by GKT			
Selexol				
Selexol	Fe and Cl	1/day		
	H_2O	1/day		
Rich Selexol	H_2S, CO_2	1/day		
Lean Selexol	H_2S, CO_2	1/day		
DEA				
DEA	Fe, Cl, hydrocarbon oil concn in solution	1/day		
	H_2O	1/day		
Lean DEA	H_2S, CO_2	1/day		
	Corrosion inhibitor concn	1/day		
Rich DEA	H_2S, CO_2	1/day		
Claus/Beavon sulfur removal unit				
TBD	TBD	TBD		
Rust area				
Coal (as received)	Proximate analysis	1-4/day		
	S, Fe			
	Other coal analyses	Spot		
Coal (as fed to pulverizer)	Moisture	2/shift		
Coal (pulverized)				See tests on pulverized coal in GKT area

Table 1 (Continued)[a]

Sample description	Analysis	Frequency	On-line	Comments
Steam condensate	pH		•	
	TSS		•	
	Silica		•	
	Conductivity		•	
	Fe	1/day		
	Oils	1/day		
Deaerator feed	pH		•	
	TSS		•	
	Silica		•	
	Conductivity		•	
	Fe	1/day		
	Oils	1/day		
	Cu	1/day		
Boiler feedwater	pH, conductivity		•	
	TDS, TSS		•	
	Oils	1/shift		
	Alkalinity, hydroxide	1/shift		
	Fe, Cu	1/shift		
	Dissolved O_2	1/shift		
	Silica		•	
Boiler blowdown	pH, conductivity		•	
	TSS		•	
	Treatment chemicals	1/day		
Potable water treatment	TBD	TBD		
Process water treatment	TBD	TBD		
Heater fuel	Heating value	Spot		Backup of on-line testing
Slurry exchange first dissolver	Conversion	1/day		
Slurry exchange second dissolver	Conversion	1/shift		
Slurry exchange fired heater	Conversion	1/day		
Solids blowdown	Solids	1/day		
HP sour gas	Density		•	
	H_2, S	1/day		

Table I (Continued)[a]

Sample description	Analysis	Frequency	On-line	Comments
HP wastewater	TOC	1/day		
HP water separator liquid	Distillation	1/week		
HP flash slurry	Volatiles	1/day		Distillation to 650°F end point
MP flash vapor	Density		+	
	H_2, S	1/day		
LP flash vapor	Density		+	
	H_2, S	1/day		
Preheated MP liquid	Distillation end points		+	
	Full distillation	1/day		
MP wastewater	TOC	1/day		
MP sour gas	Density		+	
	H_2, S	1/day		
Sour gas condensate	Distillation end points		+	
	GC	1/day		
Solvent column process solvent	Distillation end points		+	
	Full distillation	1/day		
Solvent column off-gas	Density		+	
	H_2, S	1/day		
Solvent column medium oil	Distillation end points		+	
	Full distillation	1/day		
Solvent column wastewater	TOC	1/day		Composite sample
Process solvent feed	Distillation	1/day		
	Donor quality	1/day		
Vacuum column bottoms	Viscosity		+	
	SRC, unconverted coal, ash, process solvent	1/day		
	Asphaltenes/preasphaltenes	3/week		

Table 1 (Continued)^{a}

Sample description	Analysis	Frequency	On-line	Comments
Vacuum column process condensate	TOC	1/week		
Vacuum column precondenser liquid	Distillation end points		•	
	Full distillation	1/day		
Ash concentrate	Critical solvent, process solvent, carbon, SRC	1/day		Critical solvent analysis has on-line potential
	Asphaltenes/ preasphaltenes	3/week		
First-stage light phase	Critical solvent, SRC	1/day		
Recycle critical solvent	Critical solvent, solids, H_2O	1/day		
Second-stage light phase	Critical solvent, SRC	1/day		
Third-stage light phase	Critical solvent, SRC	1/day		
LSRC stripper bottoms	Critical solvent	2/shift		
	Asphaltenes/ preasphaltenes	3/week		
HSRC stripper bottoms	Critical solvent	2/shift		
HSRC stripper overheads	H_2O, critical solvent, SRC	1/day		
LSRC stripper overheads	H_2O, critical solvent, SRC	1/day		
Process condensate	TOC	1/day		
SRC blowdown tank	Solids	1/week		
	Distillation	1/week		
SRC slop tank	Distillation	1/week		

Table I (Continued)[a]

Sample description	Analysis	Frequency	On-line	Comments
CSD blowdown tank	Solids Distillation	2/week		
Decoking drum off-gas	CO_2, O_2	Spot		
Incinerator feed	HHV	1/day		
Product columns	Distillation end points		+	
	Full distillation	1/day		

[a] Abbreviations used are: HSRC, heavy solvent-refined coal; ASTM, American Society for Testing and Materials; IR, infrared; VCM, volatile carbonaceous material; TSS, total suspended solids; TDS, total dissolved solids; DEA, diethanolamine; TBD, to be determined; BFW, boiler feedwater; HP, high pressure; TOC, total organic carbon; GC, gas chromatography; MP medium pressure; LP, low pressure; LSRC, light solvent-refined coal; CSD; critical solvent deashing; HHV, higher heating value.

[b] Three samples, one from each feed stream.

[c] Two samples, one from vacuum tower and one from atmospheric tower.

Table 2

Wastewater Treatment Analytical Lab Requirements[a]

	Oil separator		ASWS	Leachate		Metal precipitator	Biounit 1				Biounit 2			Filters			Reverse osmosis[d]	Evaporator blowdown	Evaporator overhead
	I	E	E	Ash pond	Metal sludge	E	Feed	Aeration basin	Clarifier I	Clarifier E	Aeration basin	Clarifier I	Clarifier E	Sand I	Carbon I	Ozonation I			
Trace elements[b]	III	III	III	IV	IV	III	IV			IV			IV	IV		IV	IV	VI	
Temp							A*			A*						A*	A*		
pH	A					A	A			A*	A*					A*	A	A-I	A-I
TSS	III	III					III	I	III	IA	I	III	I	IA		I	A	VI	
VSS							III	I	III	III	I	III	I			I			
TDS/conductivity																A	A	VI	
Oil	III	III					IV			IV			IV	III	III	I	IV		
TOC	A-III	A-III	A*				A*			A*			A		A*	A	IV	VI	V
COD	III	III					III			III			III		III	I	IV	VI	V
BOD	III	III					II			II			II		II	I	IV	VI	V
Phenolics			I				I			I			I		I	I	IV	VI	V
Mercaptans			III				III			I			I		III	I	IV		
Thiocyanates			III				III						I		III	I	IV	VI	V
H_2S			III				III			III			III		III	I	IV		
Free cyanides			III				III			III			III		III	I	IV		
Cyanides			III				III			III			III		III	I	IV		
Alkalinity							III			III							IV		
PO_4										I			I			IV	IV		
NH_3			A*-II				A*-I			A*-I			I-A*			I	IV		
Dissolved O_2									A*		A*					A			
O_2 uptake									I		I								
Trace organics[c]			IV				IV			IV			IV		IV	IV	IV	VII	
Nitrates/ nitrites										A-I			I			A-I	IV		
Total Kjeldahl nitrogen			II				A-I			A*-I			I			III	IV		
Thiosulfate			III				III			III			III			III	IV		
Color																III			
Coliform bacteria																III			
Na, Ca, Mg, K, Mn, SO_4, Cl, bicarb, carb			IV				IV									IV	IV		

---

[a] Abbreviations used are: I, influent; E, effluent; A*, critical probe or analyzer; A, probe or analyzer; I, once per day, grab or composite; II, twice per week, composite; III, once per week, composite; IV, once per month; V, once per quarter; VI, semiannual; VII, annual; ASWS, ammonia/sulfide water stripper; TSS, total suspended solids; VSS, volatile suspended solids; TDS, total dissolved solids; TOC, total organic carbon; COD, chemical oxygen demand; BOD, biochemical oxygen demand.

[b] Trace element analyses required include: aluminum, antimony, arsenic, barium, boron, beryllium, bromine, cadmium, chromium, cobalt, copper, fluorine (fluoride), iron, lead, manganese, mercury, molybdenum, nickel, phosphorus, selenium, silver, thallium, tellurium, titanium, tin, vanadium, zinc.

[c] EPA priority organic pollutants plus certain polycyclic aromatic hydrocarbons.

[d] Use of reverse osmosis is being studied, although currently it is not included in the wastewater treatment conceptual design.

Table 3

Utility Water Analytical Lab Requirements[a]

	Cooling tower	Potable water	Boiler feedwater	Condensate return	Process water
Chromium					
Total	I (A)				
Cr^{6+}	I (A)				
pH	A	A	A		A
TSS	III	A-II	A		A
Conductivity	A	A-I	A	A	A
PO_4	I				
TOC	A	II		A	
Chlorine					
Free	I	I			
Total	I	I			
Alkalinity (acidity)	III	III	I		III
Dissolved oxygen	A		A	A	
Silica		III	I		
Ca		III			III
Mg		III			III
Total hardness		II			IV
Fe		II			III
Cu		II			IV
Al		II			IV

[a] Abbreviations used are: A, probe or analyzer; I, once per day, grab or composite; II, twice per week, composite; III, once per week, composite; IV, once per month; TSS, total suspended solids; TOC, total organic carbon.

Table 4

Environmental Monitoring Analytical Lab Requirements[a]

Groundwater monitoring[b]			
Analysis	Frequency	Analysis	Frequency
Total organic carbon	V	Hardness	V
Biochemical oxygen demand	V	Phenol	V
Chemical oxygen demand	V	Cyanide	V
Conductivity	V	Nitrates	V
Total dissolved solids	V	Trace elements[c]	VII
Sulfates	V	Trace organics[d] (GC/MS)	VII
Chlorides	V		

	Solid waste testing			
Analysis	Ash	Metal sludge	Biological sludge	Fixed evaporator residue
EPA extraction procedure	V	VII	VII	I
Total organic carbon	V	VII	VII	I
Conductivity	V	VII	VII	I
Sulfates	V	VII	VII	III
Chlorides	V	VII	VII	I
Hardness	V	VII	VII	
Phenol	V	VII	VII	IV
Cyanide	V	VII	VII	IV
Nitrate	V	VII	VII	I
Trace elements[c]	VI	VII	VII	V
Trace organics[d]	VI	VII	VII	V

[a] Abbreviations used are: I, once per day, grab or composite; III, once per week, composite; IV, once per month; V, once per quarter; VI, semiannual; VII, annual; EPA, Environmental Protection Agency; GC/MS, gas chromatography/mass spectrometry.

[b] At least 24 monitoring wells are currently planned. These wells can be sampled in batches of four or more for analysis; each batch would consist of a background and four or more downstream wells. Analyses needed for each well are listed.

[c] Trace element analyses required include: aluminum, antimony, arsenic, barium, boron, beryllium, bromine, cadmium, chromium, cobalt, copper, fluorine (fluoride), iron, lead, manganese, mercury, molybdenum, nickel, phosphorus, selenium, silver, tellurium, thallium, tin, titanium, vanadium, zinc.

[d] EPA priority organic pollutants plus certain polycyclic aromatic hydrocarbons.

Quality Assurance Analytical Lab Requirements

Product	Test	Frequency: Sample per month	Frequency: Actual	Comments
Sulfur	Freezing point	6	2 every 10 days	
	Color	6	2 every 10 days	Potential requirement
	Dissolved H_2S	6	2 every 10 days	Potential requirement
LPG	GC breakdown	On-line		
	Copper strip	4	2 every 15 days	
Anode coke	Bulk density	12	2 every 5 days	
	Real density	12	2 every 5 days	
	Hardgrove grindability	12	2 every 5 days	
	Particle size distribution	12	2 every 5 days	
	Metals (Si, Fe, V, Ni, Ti, B, Ca)	12	2 every 5 days	
	Sulfur	12	2 every 5 days	
	Moisture	On-line		
	Ash	12	2 every 5 days	Probably on-line
SRC solid	Proximate analysis	20	2 every 3 days	
	Higher heating value	20	2 every 3 days	
	Ultimate analysis	20	2 every 3 days	
	Melting point	20	2 every 3 days	
	Hardgrove grindability	20	2 every 3 days	
	Bulk density	20	2 every 3 days	
	Conradson carbon	20	2 every 3 days	
	Metals (Na, K, Ca, Fe, Si, Ti)	20	2 every 3 days	
TSL solid	Proximate analysis	4	2 every 15 days	
	Higher heating value	4	2 every 15 days	
	Ultimate analysis	4	2 every 15 days	
	Melting point	4	2 every 15 days	
	Hardgrove grindability	4	2 every 15 days	
	Bulk density	4	2 every 15 days	
	Conradson carbon	4	2 every 15 days	
	Metals (Na, K, Ca, Fe, Si, Ti)	4	2 every 15 days	
SLM (solid/liquid mixture)	Specific gravity	4		Inclusion of SLM as a product is speculative. No information on the actual sampling frequency is yet available.
	Specific gravity (spot check)	8		
	Flash point	4		
	Isoviscous temperature	4		Temperature required
	Isoviscous temperature (spot check)	8		

Table 5 (continued)

Product	Test	Frequency		Comments
		Sample per month	Actual	
	% solids	4		
	% solids (spot check)	8		
	Higher heating value	4		
	S, N	4		
	Ash	4		
	Carbon residue	4		
Heavy oil	Specific gravity	On-line		
	Viscosity	4	2 every 15 days	
	Simulated distillation	4	2 every 15 days	
	Flash point	4	2 every 15 days	
	Pour point	4	2 every 15 days	
	S, N	4	2 every 15 days	
	Bottoms, sediment, and water	4	2 every 15 days	
	Higher heating value	4	2 every 15 days	
	Carbon residue	4	2 every 15 days	
	Ash	4	2 every 15 days	
	Metals (Na, K, Ca, Fe, Si, Ti)	4	2 every 15 days	
Middle distillate	Specific gravity	On-line		
	Viscosity	12	2 every 5 days	Possibly on-line analysis of tank pumparound
	Dupont stability	12	2 every 5 days	Analysis on tank
	Simulated distillation	12	2 every 5 days	
	Flash point	12	2 every 5 days	
	Pour point	12	2 every 5 days	
	ASTM color	12	2 every 5 days	
	Copper strip	12	2 every 5 days	
	Carbon residue	12	2 every 5 days	
	S, N	12	2 every 5 days	
	Bottoms, sediment, and water	12	2 every 5 days	
	Higher heating value	12	2 every 5 days	
	Ash	12	2 every 5 days	
	Metals (Na, K, Ca, Fe, Si, Ti)	12	2 every 5 days	
Hydrotreated naphtha	95% point distillation	On line		
	Specific gravity	On line		
	Reid vapor pressure	12	2 every 5 days	
	Existent gum	12	2 every 5 days	Analysis on tank
	Accelerated gum stability	12	2 every 5 days	Analysis on tank
	Paraffins, olefins, naphthenes, aromatics	12	2 every 5 days	
	Copper strip	12	2 every 5 days	
	Bromine number	12	2 every 5 days	
	Elemental analysis (C, H, O, N, S)	12	2 every 5 days	
	Color (spot check)			Battery limits test

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[a] Abbreviations uses are: LPG, liquefied petroleum gas, GC, gas chromatography, TSL, two stage liquefaction, ASTM, American Society for Testing and Materials.

Table 6

Sample Preparation Laboratory

Test	No./week	hr/test	hr/week	Linear bench space (ft)
Hardgrove grindability	9	0.4	3.6	4
Gravity sieve	49	0.3	14.7	3
Coal size	Spot			3
Dustiness	Spot			7
Fusibility of coal and coke ash	Spot			5
		Total	18.3 (2.6 hr/day)	Total 22

Table 7

Distillation Laboratory

Source	No./week	hr/test	hr/week
Molten SRC feed	7	1.0	7.0
Slop oil from blowdown tower	2	1.0	2.0
Atmospheric tower feed	1	1.0	1.0
Vacuum tower feed	7	1.0	7.0
Vacuum tower slop oil	2	1.0	2.0
High-pressure separator liquid	1	1.0	1.0
Sour gas condensate	7	1.0	7.0
SRC slop tank	1	1.0	1.0
Product columns	7	1.0	7.0
Vacuum tower precondenser liquid	7	1.0	7.0
SRC blowdown tank	1	1.0	1.0
Critical solvent deashing blowdown tank	2	1.0	2.0
Coker raw naphtha	7	1.0	7.0
Coker raw middle distillate	7	1.0	7.0
LC-Finer raw naphtha	7	1.0	7.0
LC-Finer raw middle distillate	7	1.0	7.0
High-pressure flash slurry	7	1.0	7.0
Preheated medium-pressure liquid	7	1.0	7.0
Solvent column medium oil	7	1.0	7.0
Process solvent feed	7	1.0	7.0
		Total	101
			(14.4 hr/day)

0.5 hr/test, assuming most are simulated distillation

Table 8

ASTM/Wet Laboratory

	Test	No./week	hr/test	hr/week	Linear bench space (ft)
1.	Viscosity	17	0.4	6.8	3
	Isoviscous temp	3	0.4	1.2	--
2.	Water	37	0.4	14.8	4
3.	Moisture	90-111	0.1	9.0-11.1	
	Ash	55-76	0.1	5.5-7.6	5 (coal analyzer)
	Volatiles	81-102	0.1	8.1-10.2	
4.	Specific gravity	7	0.2	1.4	3 (bath)
5.	Cl by Parr bomb	14	1.5	21.0	4
6.	Cl by oxygen bomb	49	0.6	29.4	3
7.	Freeze point	1.5	0.5	0.75	2
	Pour point	14	0.5	7.0	--
8.	Reid vapor pressure	3	1.0	3.0	5 (large bath)
9.	Copper strip corrosion	7	0.5	3.5	4
10.	Conradson carbon	11	0.5	5.5	3
11.	Flash point	19	0.4	7.6	2
12.	Real density	10	0.3	3.0	2
	ASTM color	3	0.05	0.15	--
	Bulk density	9	0.2	1.8	--
13.	H_2SO_4 ash	19-40	0.8	15.2-32.0	5 (furnace)
14.	DuPont stability	3	0.4	1.2	4
15.	Existent gum	3	1.0	3.0	3
16.	Accelerated gum stability	3	1.0	3.0	3
17.	Bromine no.	3	0.5	1.5	3
18.	Bottoms, sediment, and water	7	0.5	3.5	2
	% solids	9	0.25	2.25	--
19.	Volatile carbonaceous material (wt %)	14	0.3	4.2	--
20.	Melting point	6	0.5	3.0	--
21.	Treatment chemicals	7	TBD	--	--
22.	Pyridine extraction	56	0.3	16.8	3
23.	Neutralization no.	TBD			Autotitrator
	Mercaptans				Autotitrator
24.	Softening point	TBD			
25.	Corrosion inhibitor concentration	TBD			
26.	Pyritic sulfur	Spot			
27.	Sulfate sulfur	Spot			
	Organic sulfur	Spot			
28.	Free swelling index	Spot			3
			Total	183.2-206.3 (26.2-29.5 hr/day)	Total 66

Table 9

Microanalytical Laboratory

		No./week	hr/test	hr/week	Linear bench space (ft)
1.	Carbon	16	0.3	4.8	8
	Hydrogen	16	0.3	4.8	
	Nitrogen	21	0.3	6.3	
2.	Sulfur	90-111	0.2	18.0-22.2	6
3.	Oxygen	10	0.4	4.0	7
4.	HHV (Btu/lb)	18 + spot	0.5	9.0	5
5.	CTPV	18	1.0	18.0	6
6.	TGA	TBD		--	
7.	Mol wt (VPO)	TBD		--	4
8.	Particle size distribution	59	0.3	17.7	6
9.	Dust (industrial hygiene)	6	0.2	1.2	--
			Total	83.8-88.0 (12.0-12.6 hr/day)	42

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[a] Abbreviations used are: HHV, higher heating value; CTPV, coal tar pitch volatiles; TGA, thermogravimetric analysis; mol wt, molecular weight; VPO, vapor-phase osmometry.

Table 10

Instrumentation Laboratory

Test	No./week	hr/test	hr/week
X-ray			
Fe on ash	35	0.4	14.0
Metals on spent catalyst	3	0.5	1.5
Metal oxide on fresh catalyst	1/batch	--	
Ash of anode coke (Si, Fe, Ni, B, Ti, V, Ca)	3	1.5	4.5
Ash of SRC and TSL solids (Na, K, Ca, Fe, Si, Ti)	6	1.0	6.0
Ash of heavy oil (Na, K, Ca, Fe, Si, Ti)	1	1.0	1.0
Ash of middle distillate (Na, K, Ca, Fe, Si, Ti)	3	1.0	3.0
Ash of wastewater solids (trace elements: Al, As, Sb, Ba, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, Se, Ag, Th, Te, Ti, Sn, V, Zn)	0.25	2.0	0.5
Industrial hygiene (catalyst additives)		TBD	
Ash of coal (as received or pulverized (Si, Fe, Al, Ti, Ca, Mg)	Spot		
Si on ash	28	0.4	11.2
Atomic absorption			
H_2O samples			
Fe	18	0.05	0.9
Cu	12	0.05	0.6
Mn	1	0.05	0.05
Si	8	0.05	0.4
Al	2	0.05	0.1
Trace elements	20 × 8/week = 160	0.05	8.0
B	8	0.05	0.4
Be	8	0.05	0.4
Cr	14	0.05	0.7
Hg	8	0.05	0.4
Se	8	0.05	0.4
Ash of anode coke, B	3	0.5	1.5
Ash of coal (as received or pulverized)			
Na	Spot		
K	Spot		
		Total	54.1 (7.7 hr/day)

Table 11

Solvent Quality Activity Test Laboratory

Test	No./week	hr/test		hr/week	Linear bench space (ft)
1. Conversion					6
Oils	47	0.75		32.25	
Asphaltenes	47	0.75		32.25	
Preasphaltenes	47	0.75		32.25	
Residue	47	0.50		23.5	
2. Hydrogen donor quality index	7	1.5		10.5	8
			Total	130.75 (18.7 hr/day)	

Table 12

GC/LC Laboratory

	GC		
Test	No./week	hr/test	hr/week
GC analysis	56	0.75	42.0
Simulated distillation	4	0.4	1.6
Critical solvent	147	0.1	14.7
H_2S	28	0.1	2.8
CO_2	28 + spot	0.1	2.8
H_2	35	0.2	7.0
O_2	Spot	--	--
Benzene (industrial hygiene)	5	0.2	1.0
Toluene	5	0.2	1.0
Xylenes	5	0.2	1.0
Amines	4	0.3	1.2
Phenols	5	0.3	1.5
Process solvent	7	0.1	0.7
Paraffins, olefins, naphthenes, aromatics	3	TBD	--
		Total	77.3
			(11.0 hr/day)

	LC			
Source	Test	No./week	hr/test	hr/week
Wastewater treatment	Phenols	42	0.2	8.4
Combination tower overhead H_2O	Phenols	7	0.2	1.4
Environmental licensing and monitoring	Phenols	1.5	0.2	0.3
Wastewater treatment	Mercaptans	24	0.2	4.8
	Polynuclear aromatics 2-Methylnaphthalene Dibenzo(ac)anthracene Dibenzothiophene Benzo(c)phenanthrene Benzo(j)fluoranthene Benzo(a)pyrene o-Phenylene purene Benzo(g,h,i)perylene Chrysene Dibenzo(a,h)anthracene Benzo(a)anthracene Fluoranthene 5-Methylchrysene Benzo(b)fluoranthene 2-Methylfluoranthene	3	1.0	3.0
			Total	17.9
				(2.6 hr/day)

International Coal Refining Company

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
MATERIAL SAFETY DATA SHEET

SRC I MATERIAL

SECTION I

SUPPLIER'S NAME
International Coal Refining Company

EMERGENCY TELEPHONE NO
PA-800-322-9092 Foreign
US-800-523-9374 215-481-4911

ADDRESS (NUMBER STREET CITY STATE & ZIP CODE)
Mailing: P.O. Box 2752, Allentown, PA 18001; Location: 2141 Downyflake Ln., Allentown, PA 18103

CHEMICAL NAME & SYNONYMS: Solvent Refined Coal-I (SRC-I) Naphtha; Light Oil

TRADE NAMES & SYNONYMS: NA

CHEMICAL FAMILY: Coal derived aromatic naphtha

FORMULA: Mixture

CAS NUMBER: 68476-79-9

TSCA REGISTRY ENTRY: 30814099

SECTION II - HAZARDOUS INGREDIENTS

MATERIALS	%	TLV (Units)	MATERIALS	%	TLV (Units)
Phenols and Cresols	15-35	5 ppm	Benzene	<1.0	10 ppm
Hydrogen Sulfide	<1.0	10 ppm			

DOT HAZARD CLASS: FLAMMABLE LIQUID

SECTION III - PHYSICAL DATA

BOILING POINT °C (°F) 60-232°C (140-450°F)	SPECIFIC GRAVITY (H_2O = 1) 15.6°C 15.6°C 0.83-0.89
VAPOR PRESSURE (mm Hg.) Reid 185-225	VOLATILES, VOLUME PERCENT (%) 99
VAPOR DENSITY (AIR = 1) ND	EVAPORATION RATE ND
SOLUBILITY IN WATER Negligible	

APPEARANCE AND ODOR
Colorless to dark amber (darkens with age and air contact); intense phenolic and sulfurous odor

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT: -28.9°C (-20°F)

FLAMMABLE LIMITS. LEL: ND UEL: ND

EXTINGUISHING MEDIA
☐ ALCOHOL FOAM ☒ CARBON DIOXIDE ☒ DRY CHEMICAL ☒ FOAM ☒ WATER SPRAY (FOG)
☐ OTHER

SPECIAL FIRE FIGHTING PROCEDURES
Treat as Class B fire. Treat like gasoline or light petroleum naphtha. Use water spray to keep fire-exposed containers cool, flush spills away from fire exposure, and to disperse vapors. Wear self-contained breathing apparatus for fires in enclosed or contained spaces. This material floats on water.

FIRE AND EXPLOSION HAZARDS
Highly volatile and flammable. Material can be ignited by flame or incendiary sparks under almost all normal atmospheric temperature conditions due to its low flash point.

NA = Not Applicable ND = No Data Available

Modified Form OSHA-20
11/81 REV. 0

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE See Section II

EFFECTS OF OVEREXPOSURE

Irritating to eyes, lungs, and skin. Depending on the intensity and duration of exposure, effects may vary from mild irritation to systemic toxicity due to the presence of phenolic compounds and aromatic hydrocarbons.

EMERGENCY AND FIRST AID PROCEDURES INHALATION: Remove to fresh air. If breathing is difficult give oxygen and call for medical assistance. EYE CONTACT: Flush eyes immediately with copious amounts of water or mineral oil. Call a physician. SKIN CONTACT: Wash thoroughly with soap and water or waterless hand cleaner. Avoid solvents. INGESTION: DO NOT INDUCE VOMITING. Give 2 tablespoons of activated charcoal USP in water. Call medical assistance.

SECTION VI - REACTIVITY DATA

STABILITY Stable

CONDITIONS TO AVOID NA

INCOMPATABILITY (Materials to avoid) Strong oxidants

HAZARDOUS DECOMPOSITION PRODUCTS Irritating and toxic fumes, smoke, carbon monoxide, and sulfur oxides, in the case of incomplete combustion

HAZARDOUS POLYMERIZATION will not occur

CONDITIONS TO AVOID NA

SECTION VII - SPILL OR LEAK PROCEDURES

☐ EVACUATE AREA
☒ STOP FLOW
☒ ELIMINATE ALL SOURCES OF IGNITION FLAMMABLES
☒ AVOID INHALATION
☒ AVOID DERMAL CONTACT
☒ RESPIRATORY PROTECTION (AS PER SECTION VIII)
☒ SKIN PROTECTION (AS PER SECTION VIII)
☒ ABSORB OR SCRAPE UP
☐ VACUUM UP
☐ EVAPORATE SMALL AMOUNTS IN HOOD
☒ INCINERATE UNDER CONTROLLED CONDITIONS
☐ INCINERATE USING AFTER BURNER & SCRUBBER
☐ BURY IN REMOTE AREA OR USE AS LANDFILL
☐ NEUTRALIZE AND WASH AWAY WITH WATER
☒ OBSERVE GOVERNMENTAL SPILL & WATER QUALITY REGULATIONS
☒ REMOVE SOILED CLOTHING
☐ OTHER

SECTION VIII - SPECIAL PROTECTION INFORMATION

	DURING NORMAL USE	FOR GASES VAPORS, DUSTS, FUMES, MISTS EXCEEDING TLV	SPECIAL (E.G. THERMAL PROCESSING SPRAY APPLICATIONS)
GENERAL VENTILATION	Yes	Yes	
LOCAL EXHAUST	Yes	Yes	
RESPIRATORY PROTECTION (1-3)		2, if needed	3, large spills

1 *Particle-Removing Air Purifying Air Respirator (Mechanical Filter)*
2. *Gas and Vapor-Removing Air Purifying Respirator (Canister)*
3. *Full Face Mask Positive Pressure-Demand Type Supplied Air*

EYE PROTECTION	SAFETY GLASSES		CHEMICAL GOGGLES	X	FACE SHIELD		*(E) EXCELLENT* *(G) GOOD* *(F) FAIR* *(P) POOR* *(NR) NOT RECOMMENDED*
PROTECTIVE GLOVES	NEOPRENE	G	POLYVINYL ALCOHOL	NR	POLYETHYLENE	NR	
	NATURAL RUBBER	P	BUTYL RUBBER	NR	POLYVINYL CHLORIDE	NR	

OTHER PROTECTIVE EQUIPMENT Wear full, long-sleeved clothing closed at the neck. The application of a skin barrier cream before work is recommended.

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING Avoid skin and eye contact and inhalation of mists or vapors. Maintain good ventilation. Empty drums may contain flammable hydrocarbon vapors. Wash out drums with water before discarding. May dissolve plastics and rubbers. Therefore, do not use transfer lines or storage vessels made of these materials. Upon standing or being cooled a foul-smelling mercaptan water layer may settle out. This layer should be discarded before use. Showering and clothing change recommended after each shift.

NOTICE

The data and recommendations presented herein are based upon our research and the research of others, and are believed to be accurate; however, no guarantee of their accuracy is made. The products discussed are distributed without warranty, express or implied, and the person receiving them shall make his own determination of the suitability thereof for his particular purpose.

FOR TRANSPORTATION SPILLS OR LEAK EMERGENCIES, CALL: CHEMTREC - 800-424-9300 (CHEMICAL TRANSPORTATION EMERGENCY CENTER).

International Coal Refining Company

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
MATERIAL SAFETY DATA SHEET

SRC I MATERIAL

SECTION I

SUPPLIER'S NAME International Coal Refining Co.	EMERGENCY TELEPHONE NO. PA-800-322-9092 Foreign US-800-523-9374 215-481-4911
ADDRESS (NUMBER, STREET, CITY, STATE & ZIP CODE) Mailing: P.O. Box 2752, Allentown, PA 18001;	Location: 2141 Downyflake Lane, Allentown, PA 18103
CHEMICAL NAME & SYNONYMS Solvent Refined Coal-I (SRC-I) Middle Distillate; Medium Oil	TRADE NAMES & SYNONYMS NA
CHEMICAL FAMILY Coal derived aromatic distillate	FORMULA Mixture
CAS NUMBER 68911-57-9	TSCA REGISTRY ENTRY ND

SECTION II - HAZARDOUS INGREDIENTS

MATERIALS	%	TLV (Units)	MATERIALS	%	TLV (Units)
Phenols and Cresols	10-20	5 ppm			
Benzene	<1	10 ppm			

Contains aromatic hydrocarbon and phenolic compounds. Long-term exposure may lead to serious long-term health problems.

DOT HAZARD CLASS: Excepted from regulations

SECTION III - PHYSICAL DATA

BOILING POINT °C (°F) 204-343°C (400-650°F)	SPECIFIC GRAVITY (H_2O = 1) 15.6°C/15.6°C 1.0
VAPOR PRESSURE (mm Hg) 0 psia Reid	VOLATILES, VOLUME PERCENT (%) ND
VAPOR DENSITY (AIR = 1) ND	EVAPORATION RATE ND
SOLUBILITY IN WATER Negligible	
APPEARANCE AND ODOR Amber to black oil; faint oily odor	

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT 97°C (206°F) closed cup	FLAMMABLE LIMITS LEL ND UEL ND

EXTINGUISHING MEDIA
☐ ALCOHOL FOAM ☒ CARBON DIOXIDE ☒ DRY CHEMICAL ☒ FOAM ☒ WATER SPRAY (FOG)
☐ OTHER

SPECIAL FIRE FIGHTING PROCEDURES Treat as Class B fire. Use water spray to keep fire-exposed containers cool, flush spills away from fire exposure, and to disperse vapors. Wear self-contained breathing apparatus for fires in enclosed or contained spaces. This material may float on water.

FIRE AND EXPLOSION HAZARDS

Combustible. Heating this material to its flash point is likely to give sufficient vapors for ignition upon exposure to flame or incendiary sparks.

NA = Not Applicable ND = No Data Available

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11-81 REV 0

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE Suggested guideline for airborne exposure to coal derived materials: 0.2 mg/m^3 as benzene solubles. See Section II.

EFFECTS OF OVEREXPOSURE
Irritating to eyes, lungs, and skin. Depending on the intensity and duration of exposure effects may vary from mild irritation to systemic toxicity due to the presence of phenolic compounds and aromatic hydrocarbons.

EMERGENCY AND FIRST AID PROCEDURES INHALATION: Remove to fresh air. If breathing is difficult give oxygen and call for medical assistance. EYE CONTACT: Flush eyes immediately with copious amounts of water or mineral oil. Call a physician. SKIN CONTACT: Wash thoroughly with soap and water or waterless hand cleaner. Avoid solvents. INGESTION: DO NOT INDUCE VOMITING. Give 2 tablespoons of activated charcoal USP in water. Call medical assistance.

SECTION VI - REACTIVITY DATA

STABILITY Stable	CONDITIONS TO AVOID NA

INCOMPATABILITY (Materials to avoid) Strong oxidants

HAZARDOUS DECOMPOSITION PRODUCTS
Fumes, smoke, carbon monoxide, and sulfur oxides, in the case of incomplete combustion.

HAZARDOUS POLYMERIZATION Will not occur	CONDITIONS TO AVOID NA

SECTION VII - SPILL OR LEAK PROCEDURES

☐ EVACUATE AREA
☒ STOP FLOW
☐ ELIMINATE ALL SOURCES OF IGNITION FLAMMABLES
☒ AVOID INHALATION
☒ AVOID DERMAL CONTACT
☐ RESPIRATORY PROTECTION (AS PER SECTION VIII)
☒ SKIN PROTECTION (AS PER SECTION VIII)
☒ ABSORB OR SCRAPE UP
☐ VACUUM UP
☐ EVAPORATE SMALL AMOUNTS IN HOOD
☒ INCINERATE UNDER CONTROLLED CONDITIONS
☐ INCINERATE USING AFTER BURNER & SCRUBBER
☐ BURY IN REMOTE AREA OR USE AS LANDFILL
☐ NEUTRALIZE AND WASH AWAY WITH WATER
☒ OBSERVE GOVERNMENTAL SPILLS & WATER QUALITY REGULATIONS
☒ REMOVE SOILED CLOTHING
☐ OTHER

SECTION VIII - SPECIAL PROTECTION INFORMATION

	DURING NORMAL USE	FOR GASES VAPORS DUSTS FUMES, MISTS EXCEEDING TLV	SPECIAL (E.G. THERMAL PROCESSING SPRAY APPLICATIONS)
GENERAL VENTILATION	Yes	Yes	NA
LOCAL EXHAUST	Yes	Yes	NA
RESPIRATORY PROTECTION (1-3)	Not required	1 & 2, if needed	3, large spills

1 *Particle-Removing Air Purifying Air Respirator (Mechanical Filter)*
2. *Gas and Vapor-Removing Air Purifying Respirator (Canister)*
3. *Full Face Mask Positive Pressure-Demand Type Supplied Air*

EYE PROTECTION	SAFETY GLASSES		CHEMICAL GOGGLES	X	FACE SHIELD		*(E) EXCELLENT* *(G) GOOD*
PROTECTIVE GLOVES	NEOPRENE	G	POLYVINYL ALCOHOL	NR	POLYETHYLENE	NR	*(F) FAIR* *(P) POOR*
	NATURAL RUBBER	P	BUTYL RUBBER	NR	POLYVINYL CHLORIDE	NR	*(NR) NOT RECOMMENDED*

OTHER PROTECTIVE EQUIPMENT Wear full, long-sleeved clothing closed at the neck. The application of skin barrier cream before work is recommended.

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING Avoid skin and eye contact and inhalation of mists or vapors. Maintain good ventilation. Empty drums may contain flammable hydrocarbon vapors. Wash out drums with water before discarding. May dissolve plastics and rubbers. Therefore, do not use transfer lines or storage vessels made of these materials. Upon standing or being cooled a foul-smelling mercaptan water layer may settle out. This layer should be discarded before use. Showering and clothing change recommended after each shift.

NOTICE

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FOR TRANSPORTATION SPILLS OR LEAK EMERGENCIES, CALL: CHEMTREC - 800-424-9300 (CHEMICAL TRANSPORTATION EMERGENCY CENTER).

International Coal Refining Company

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
MATERIAL SAFETY DATA SHEET

SRC I MATERIAL

SECTION I

SUPPLIER'S NAME International Coal Refining Co.	EMERGENCY TELEPHONE NO PA-800-322-9092 Foreign US-800-523-9374 215-481-4911
ADDRESS (NUMBER, STREET, CITY, STATE & ZIP CODE) Mailing: P.O. Box 2752, Allentown, PA 18001;	Location: 2141 Downyflake Ln., Allentown, PA 18103
CHEMICAL NAME & SYNONYMS Solvent Refined Coal-I (SRC-I) Heavy Distillate; Heavy Oil	TRADE NAMES & SYNONYMS NA
CHEMICAL FAMILY Coal derived aromatic distillate	FORMULA Mixture
CAS NUMBER 68410-07-1	TSCA REGISTRY ENTRY ND

SECTION II - HAZARDOUS INGREDIENTS

MATERIALS	%	TLV (Units)	MATERIALS	%	TLV (Units)
Phenols and other hydroxy-aromatics	>40	5 ppm			
Benzene	<1	10 ppm			

The health hazards, particularly skin lesions (including skin cancer), associated with coal liquefaction processes are recognized as potential health problems. Also, the chemical composition is such that the possibility of causing cancer at other body sites and of other health hazards such as fetotoxicity cannot be ruled out. It is strongly recommended that inhalation and skin exposure be kept to a minimum and that all recommended precautions be observed when handling this material. See Sections V and IX.

DOT HAZARD CLASS: Excepted from regulations.

SECTION III - PHYSICAL DATA

BOILING POINT (°C °F) 343-454°C (650-850°F)	SPECIFIC GRAVITY (H_2O = 1) 15.6°C/15.6°C 1.1
VAPOR PRESSURE (mm Hg) 0 psia (Reid)	VOLATILES VOLUME PERCENT (%) ND
VAPOR DENSITY (AIR = 1) ND	EVAPORATION RATE ND
SOLUBILITY IN WATER Negligible	
APPEARANCE AND ODOR Amber to black tar; faint, oily odor	

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT >110°C (230°F) closed cup	FLAMMABLE LIMITS LEL ND UEL ND

EXTINGUISHING MEDIA
☐ ALCOHOL FOAM ☒ CARBON DIOXIDE ☒ DRY CHEMICAL ☒ FOAM ☒ WATER SPRAY FOG
☐ OTHER

SPECIAL FIRE FIGHTING PROCEDURES Treat as Class B fire. Use water spray to keep fire-exposed containers cool. Flush spills away from fire exposure, and to disperse vapors. Wear self-contained breathing apparatus for fires in enclosed or contained spaces. This material sinks in water.

FIRE AND EXPLOSION HAZARDS

Combustible. Heating this material to its flash point is likely to give sufficient vapors for ignition upon exposure to flame or incendiary sparks.

NA = Not Applicable ND = No Data Available

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE Suggested guideline for airborne exposure to coal derived materials: 0.2 mg/m^3 as benzene solubles. See Section II.

EFFECTS OF OVEREXPOSURE Irritating to eyes and lungs. Minor irritation and dermatitis may occur after prolonged or repeated skin contact. Although the inhalation hazard is low due to the relatively low volatility of the products, inhalation of mists or vapors released upon heating should be avoided. Prolonged and repeated exposure in the absence of proper hygiene practices may lead to serious skin disorders and possibly skin cancer.

EMERGENCY AND FIRST AID PROCEDURES INHALATION: Remove to fresh air. If breathing is difficult give oxygen and call for medical assistance. EYE CONTACT: Flush eyes immediately with copious amounts of water or mineral oil. Call a physician. SKIN CONTACT: Wash thoroughly with soap and water or waterless hand cleaner. Avoid solvents. INGESTION: Induce vomiting then give 2 tablespoons of activated charcoal USP in water. Call medical assistance.

SECTION VI - REACTIVITY DATA

STABILITY Stable

CONDITIONS TO AVOID NA

INCOMPATABILITY (Materials to avoid) Strong oxidants

HAZARDOUS DECOMPOSITION PRODUCTS Fumes, smoke, carbon monoxide, and sulfur oxides, in the case of incomplete combustion.

HAZARDOUS POLYMERIZATION Will not occur.

CONDITIONS TO AVOID NA

SECTION VII - SPILL OR LEAK PROCEDURES

☐ EVACUATE AREA
☒ STOP FLOW
☒ ELIMINATE ALL SOURCES OF IGNITION FLAMMABLES
☒ AVOID INHALATION
☒ AVOID DERMAL CONTACT
☐ RESPIRATORY PROTECTION (AS PER SECTION VIII)
☒ SKIN PROTECTION (AS PER SECTION VIII)
☒ ABSORB OR SCRAPE UP
☐ VACUUM UP
☐ EVAPORATE SMALL AMOUNTS IN HOOD
☒ INCINERATE UNDER CONTROLLED CONDITIONS
☐ INCINERATE USING AFTER BURNER & SCRUBBER
☐ BURY IN REMOTE AREA OR USE AS LANDFILL
☐ NEUTRALIZE AND WASH AWAY WITH WATER
☒ OBSERVE GOVERNMENTAL SPILL & WATER QUALITY REGULATIONS
☒ REMOVE SOILED CLOTHING
☐ OTHER

SECTION VIII - SPECIAL PROTECTION INFORMATION

	DURING NORMAL USE	FOR GASES, VAPORS DUSTS, FUMES, MISTS EXCEEDING TLV	SPECIAL (E.G. THERMAL PROCESSING, SPRAY APPLICATIONS)
GENERAL VENTILATION	Yes	Yes	NA
LOCAL EXHAUST	Preferred	Yes	NA
RESPIRATORY PROTECTION (1-3)	Not Required	1 & 2, if needed	NA

1. Particle-Removing Air Purifying Air Respirator (Mechanical Filter)

2. Gas and Vapor-Removing Air Purifying Respirator (Canister)

3. Full Face Mask Positive Pressure-Demand Type Supplied Air

EYE PROTECTION	SAFETY GLASSES		CHEMICAL GOGGLES	X	FACE SHIELD		*(E) EXCELLENT* *(G) GOOD* *(F) FAIR* *(P) POOR* *(NR) NOT RECOMMENDED*
PROTECTIVE GLOVES	NEOPRENE	G	POLYVINYL ALCOHOL	NR	POLYETHYLENE	NR	
	NATURAL RUBBER	P	BUTYL RUBBER	NR	POLYVINYL CHLORIDE	NR	

OTHER PROTECTIVE EQUIPMENT Wear full, long-sleeved clothing, closed at neck. The application of a skin barrier cream before work is recommended.

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING Avoid skin and eye contact and inhalation of mists or vapors. Maintain good ventilation. Empty drums may contain flammable hydrocarbon vapors. Wash out drums with water before discarding. May dissolve plastics and rubbers. Therefore, do not use transfer lines or storage vessels made of these materials. Upon standing or being cooled a foul-smelling mercaptan water layer may settle out. This layer should be discarded before use. Showering and clothing change recommended after each shift.

NOTICE

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FOR TRANSPORTATION SPILLS OR LEAK EMERGENCIES, CALL: CHEMTREC - 800-424-9300 (CHEMICAL TRANSPORTATION EMERGENCY CENTER).

International Coal Refining Company

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
MATERIAL SAFETY DATA SHEET

SRC I MATERIAL

SECTION I

SUPPLIER'S NAME International Coal Refining Co.	EMERGENCY TELEPHONE NO. PA-800-322-9092 Foreign US-800-523-9374 215-481-4911
ADDRESS (NUMBER, STREET, CITY, STATE & ZIP CODE) Mailing: P.O. Box 2752, Allentown, PA 18001;	Location: 2141 Downyflake Ln., Allentown, PA 18103
CHEMICAL NAME & SYNONYMS Solvent Refined Coal, SRC, SRC Solid	TRADE NAMES & SYNONYMS NA
CHEMICAL FAMILY Coal derived vacuum residue	FORMULA Mixture
CAS NUMBER 68409-94-9	TSCA REGISTRY ENTRY 30814040

SECTION II - HAZARDOUS INGREDIENTS

MATERIALS	%	TLV (Units)	MATERIALS	%	TLV (Units)
SRC Dust		2 mg/m^3			

Should significant fumes or vapors be generated from SRC in molten form, it is suggested that the airborne exposure of 0.2 mg/m^3, as benzene solubles, be observed. See sections V and IX.

DOT HAZARD CLASS: Excepted from regulations

SECTION III - PHYSICAL DATA

BOILING POINT (°C/°F) $>454^{\circ}$C (850°F)	SPECIFIC GRAVITY (H_2O = 1) 15.6°C/15.6°C 1.2
VAPOR PRESSURE (mm Hg) <1	VOLATILES, VOLUME PERCENT (%) Negligible
VAPOR DENSITY (AIR = 1) ND	EVAPORATION RATE Negligible
SOLUBILITY IN WATER Negligible	Softening point: 155°C (310°F)
APPEARANCE AND ODOR Black, shiny, pitchlike solid; odorless	

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT $>300^{\circ}$C (572°F) open cup	FLAMMABLE LIMITS LEL ND UEL ND

EXTINGUISHING MEDIA
☐ ALCOHOL FOAM ☒ CARBON DIOXIDE ☒ DRY CHEMICAL ☒ FOAM ☒ WATER SPRAY (FOG)
☐ OTHER

SPECIAL FIRE FIGHTING PROCEDURES

Material may become liquid during fire. Wear self-contained breathing apparatus for fires in enclosed or confined spaces.

FIRE AND EXPLOSION HAZARDS

Explosion hazard when SRC dust is in contact with an ignition source.

NA = Not Applicable ND = No Data Available

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
See Section II. Respirable mass: 2 mg/m^3

EFFECTS OF OVEREXPOSURE
May cause mild eye, skin, and lung irritation.

EMERGENCY AND FIRST AID PROCEDURES
INHALATION: Remove to fresh air.
EYE CONTACT: Flush eyes immediately with copious amounts of water.
SKIN CONTACT: Wash thoroughly with soap and water or waterless hand cleaner.

SECTION VI - REACTIVITY DATA

STABILITY
Stable

CONDITIONS TO AVOID
Contact with oxygen-containing atmosphere at elevated temperatures.

INCOMPATABILITY (Materials to avoid)
None

HAZARDOUS DECOMPOSITION PRODUCTS
Formation of CO during fire is possible.

HAZARDOUS POLYMERIZATION
Will not occur.

CONDITIONS TO AVOID
NA

SECTION VII - SPILL OR LEAK PROCEDURES

☐ EVACUATE AREA
☐ STOP FLOW
☐ ELIMINATE ALL SOURCES OF IGNITION FLAMMABLES
☒ AVOID INHALATION
☒ AVOID DERMAL CONTACT
☒ RESPIRATORY PROTECTION (AS PER SECTION VIII)
☒ SKIN PROTECTION (AS PER SECTION VIII)
☐ ABSORB OR SCRAPE UP
☒ VACUUM UP
☐ EVAPORATE SMALL AMOUNTS IN HOOD
☒ INCINERATE UNDER CONTROLLED CONDITIONS
☐ INCINERATE USING AFTER BURNER & SCRUBBER
☐ BURY IN REMOTE AREA OR USE AS LANDFILL
☐ NEUTRALIZE AND WASH AWAY WITH WATER
☒ OBSERVE GOVERNMENTAL SPILL & WATER QUALITY REGULATIONS
☐ REMOVE SOILED CLOTHING
☐ OTHER

SECTION VIII - SPECIAL PROTECTION INFORMATION

	DURING NORMAL USE	FOR GASES, VAPORS DUSTS, FUMES, MISTS EXCEEDING TLV	SPECIAL (E.G. THERMAL PROCESSING, SPRAY APPLICATIONS)
GENERAL VENTILATION	Not required	Yes	NA
LOCAL EXHAUST	Not required	Not required	NA
RESPIRATORY PROTECTION (1-3)	Not required	1 & 2, if needed	NA

1. Particle-Removing Air Purifying Air Respirator (Mechanical Filter)
2. Gas and Vapor-Removing Air Purifying Respirator (Canister)
3. Full Face Mask Positive Pressure-Demand Type Supplied Air

EYE PROTECTION	SAFETY GLASSES		CHEMICAL GOGGLES	X	FACE SHIELD		*(E) EXCELLENT* *(G) GOOD*
PROTECTIVE GLOVES	NEOPRENE	G	POLYVINYL ALCOHOL	G	POLYETHYLENE	F	*(F) FAIR* *(P) POOR*
	NATURAL RUBBER	G	BUTYL RUBBER	G	POLYVINYL CHLORIDE	F	*(NR) NOT RECOMMENDED*

OTHER PROTECTIVE EQUIPMENT
Full long-sleeved clothing closed at the neck.

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
Avoid repeated inhalation, skin, and eye contact with dust and vapors. Maintain good ventilation.

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SRC-I Process Solvent

International Coal Refining Company

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
MATERIAL SAFETY DATA SHEET

SRC I MATERIAL

SECTION I

SUPPLIER'S NAME International Coal Refining Co.	EMERGENCY TELEPHONE NO PA-800-322-9092 Foreign US-800-523-9374 215-841-4911
ADDRESS (NUMBER, STREET, CITY, STATE & ZIP CODE) Mailing: P.O. Box 2752, Allentown, PA 18001;	Location: 2141 Downyflake Lane, Allentown, PA 18103
CHEMICAL NAME & SYNONYMS Solvent Refined Coal-I (SRC-I) Process Solvent; Recycle Solvent	TRADE NAMES & SYNONYMS NA
CHEMICAL FAMILY Coal derived aromatic distillate	FORMULA Mixture
CAS NUMBER 68410-08-2	TSCA REGISTRY ENTRY 30814057

SECTION II - HAZARDOUS INGREDIENTS

MATERIALS	%	TLV (Units)	MATERIALS	%	TLV (Units)
Phenols and Cresols	20-40	5 ppm			
Benzene	<1	10 ppm			

The health hazards, particularly skin lesions (including skin cancer) associated with coal liquefaction processes are recognized as potential health problems. Also the chemical composition is such that the possibility of causing cancer at other body sites, and of other health hazards such as fetotoxicity, cannot be ruled out. It is strongly recommended that inhalation and skin exposure be kept to a minimum and that all recommended precautions be observed when handling this material. See Sections V and IX.

DOT HAZARD CLASS: Excepted from regulations

SECTION III - PHYSICAL DATA

BOILING POINT (°C) (°F) 232-454°C (450-850°F)	SPECIFIC GRAVITY (H_2O = 1) 15.6°C/15.6°C 1.06
VAPOR PRESSURE (mm Hg.) 0 psia (Reid)	VOLATILES, VOLUME PERCENT (%) ND
VAPOR DENSITY (AIR = 1) ND	EVAPORATION RATE ND
SOLUBILITY IN WATER Negligible	
APPEARANCE AND ODOR Amber to black oil; faint oily odor	

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT >110°C (230°F) closed cup	FLAMMABLE LIMITS LEL ND UEL ND

EXTINGUISHING MEDIA
☐ ALCOHOL FOAM ☒ CARBON DIOXIDE ☒ DRY CHEMICAL ☒ FOAM ☒ WATER SPRAY (FOG)
☐ OTHER

SPECIAL FIRE FIGHTING PROCEDURES Treat as Class B fire. Use water spray to keep fire-exposed containers cool, flush spills away from fire exposure, and to disperse vapors. Wear self-contained breathing apparatus for fires in enclosed or contained spaces. This material sinks in water.

FIRE AND EXPLOSION HAZARDS Combustible. Heating this material to its flash point is likely to give sufficient vapors for ignition upon exposure to flame or incendiary sparks.

NA = Not Applicable ND – No Data Available

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11/81 REV. 0

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE Suggested guideline for airborne exposure to coal derived materials: 0.2 mg/m^3 as benzene solubles. See Section II.

EFFECTS OF OVEREXPOSURE Irritating to eyes and lungs. Minor irritation and dermatitis may occur after prolonged or repeated skin contact. Although the inhalation hazard is low due to the relatively low volatility of the product, inhalation of mists or vapors released upon heating should be avoided. Prolonged and repeated exposure in the absence of proper hygiene practices may lead to serious skin disorder and possibly skin cancer.

EMERGENCY AND FIRST AID PROCEDURES INHALATION: Remove to fresh air. If breathing is difficult, give oxygen and call for medical assistance. EYE CONTACT: Flush eyes immediately with copious amounts of water or mineral oil. Call a physician. SKIN CONTACT: Wash thoroughly with soap and water or waterless hand cleaner. Avoid solvents. INGESTION: Induce vomiting then give 2 tablespoons of activated charcoal USP in water. Call medical assistance.

SECTION VI - REACTIVITY DATA

STABILITY	Stable	CONDITIONS TO AVOID	NA
INCOMPATABILITY (Materials to avoid)	Strong oxidants		
HAZARDOUS DECOMPOSITION PRODUCTS	Fumes, smoke, carbon monoxide, and sulfur oxides, in the case of incomplete combustion.		
HAZARDOUS POLYMERIZATION	Will not occur.	CONDITIONS TO AVOID	NA

SECTION VII - SPILL OR LEAK PROCEDURES

☐ EVACUATE AREA
☒ STOP FLOW
☐ ELIMINATE ALL SOURCES OF IGNITION FLAMMABLES
☒ AVOID INHALATION
☒ AVOID DERMAL CONTACT
☐ RESPIRATORY PROTECTION (AS PER SECTION VIII)
☒ SKIN PROTECTION (AS PER SECTION VIII)
☒ ABSORB OR SCRAPE UP
☐ VACUUM UP
☐ EVAPORATE SMALL AMOUNTS IN HOOD
☒ INCINERATE UNDER CONTROLLED CONDITIONS
☐ INCINERATE USING AFTER BURNER & SCRUBBER
☐ BURY IN REMOTE AREA OR USE AS LANDFILL
☐ NEUTRALIZE AND WASH AWAY WITH WATER
☒ OBSERVE GOVERNMENTAL SPILLS WATER QUALITY REGULATIONS
☒ REMOVE SOILED CLOTHING
☐ OTHER

SECTION VIII - SPECIAL PROTECTION INFORMATION

	DURING NORMAL USE	FOR CAGED VAPORS DUSTS FUMES, MISTS EXCEEDING TLV	SPECIAL E.G. THERMAL, PROCESSING SPRAY APPLICATIONS
GENERAL VENTILATION	Yes	Yes	NA
LOCAL EXHAUST	Preferred	Yes	NA
RESPIRATORY PROTECTION (1-3)	Not Required	1 & 2, if needed	NA

1. Particle-Removing Air Purifying Air Respirator (Mechanical Filter)
2 Gas and Vapor-Removing Air Purifying Respirator (Canister)
3. Full Face Mask Positive Pressure-Demand Type Supplied Air

EYE PROTECTION	SAFETY GLASSES		CHEMICAL GOGGLES	X	FACE SHIELD		*(E) EXCELLENT* *(G) GOOD*
PROTECTIVE GLOVES	NEOPRENE	G	POLYVINYL ALCOHOL	NR	POLYETHYLENE	NR	*(F) FAIR* *(P) POOR*
	NATURAL RUBBER	P	BUTYL RUBBER	NR	POLYVINYL CHLORIDE	NR	*(NR) NOT RECOMMENDED*

OTHER PROTECTIVE EQUIPMENT Wear full, long-sleeved clothing closed at the neck. The application of a skin barrier cream before work is recommended.

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING Avoid skin and eye contact and inhalation of mists or vapors. Maintain good ventilation. Empty drums may contain flammable hydrocarbon vapors. Wash out drums with water before discarding. Upon standing or being cooled a foul-smelling mercaptan water layer may settle out. This layer should be discarded before use. Showering and clothing change recommended after each shift.

NOTICE

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International Coal Refining Company

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
MATERIAL SAFETY DATA SHEET

SRC I MATERIAL

SECTION I

SUPPLIER'S NAME International Coal Refining Co.	EMERGENCY TELEPHONE NO. PA-800-322-9092 Foreign US-800-523-9374 215-481-4911

ADDRESS (NUMBER, STREET, CITY, STATE & ZIP CODE)
Mailing: P.O. Box 2752, Allentown, PA 18001; Location: 2141 Downyflake Lane, Allentown, PA 18103

CHEMICAL NAME & SYNONYMS Kerr-McGee Ash Concentrate (KMAC)	TRADE NAMES & SYNONYMS NA
CHEMICAL FAMILY Inorganic minerals & hydrocarbons	FORMULA Mixture
CAS NUMBER NA	TSCA REGISTRY ENTRY NA

SECTION II - HAZARDOUS INGREDIENTS

MATERIALS	%	TLV (Units)	MATERIALS	%	TLV (Units)
KMAC Dust		2 mg/m^3			
Toluene	<1	100 ppm			

DOT HAZARD CLASS: ORM-A

SECTION III - PHYSICAL DATA

BOILING POINT (°C) (°F) NA	SPECIFIC GRAVITY (H_2O = 1) 15.6°C/15.6°C 1.6
VAPOR PRESSURE (mm Hg) 0	VOLATILES, VOLUME PERCENT (%) 0
VAPOR DENSITY (AIR = 1) NA	EVAPORATION RATE 0
SOLUBILITY IN WATER Negligible	Bulk density lb./cu. ft.: 25

APPEARANCE AND ODOR
Fine, black dull particulate (like carbon black); generally odorless but may contain odorous aromatic residue.

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT N.A. Glow Temp.: 280°C Ignition Temp.: 560°C	FLAMMABLE LIMITS. LEL ND UEL ND

EXTINGUISHING MEDIA
☐ ALCOHOL FOAM ☒ CARBON DIOXIDE ☒ DRY CHEMICAL ☒ FOAM ☒ WATER SPRAY (FOG)
☐ OTHER

SPECIAL FIRE FIGHTING PROCEDURES Treat as Class A fire. Wear self-contained breathing apparatus for fires in enclosed or contained spaces. To prevent reignition of the material, care must be taken during fire fighting to insure all glowing embers are extinguished. Stirring the material while applying the extinguishing medium is recommended.

FIRE AND EXPLOSION HAZARDS Pyrophoric at elevated temperatures. Dusting in atmosphere can create dust explosion hazard where sources of ignition are present. Self-ignition may occur in atmospheres containing more than 15% oxygen.

NA = Not Applicable ND = No Data Available

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE Respirable Mass: 2.0 mg/m^3. See Section II.

EFFECTS OF OVEREXPOSURE

Dist and fumes may cause minor irritation to the eyes and lungs. Minor irritation and dermatitis may occur after prolonged or repeated skin contact. Prolonged or repeated exposure to SRC dust and fumes may lead to more serious pulmonary and skin disorders.

EMERGENCY AND FIRST AID PROCEDURES INHALATION: Remove to fresh air. If breathing is difficult, give oxygen and call for medical assistance. EYE CONTACT: Flush eyes immediately with copious amounts of water or mineral oil. Call a physician. SKIN CONTACT: Wash thoroughly with soap and water or waterless hand cleaner. Avoid solvents. INGESTION: Induce vomiting, then give 2 tablespoons of activated charcoal USP in water. Call medical assistance.

SECTION VI - REACTIVITY DATA

STABILITY Stable	CONDITIONS TO AVOID NA

INCOMPATABILITY (Materials to avoid) Strong oxidants

HAZARDOUS DECOMPOSITION PRODUCTS
Fumes, smoke, carbon monoxide, and sulfur oxides, in the case of incomplete combustion.

HAZARDOUS POLYMERIZATION Will not occur.	CONDITIONS TO AVOID NA

SECTION VII - SPILL OR LEAK PROCEDURES

☐ EVACUATE AREA
☐ STOP FLOW
☐ ELIMINATE ALL SOURCES OF IGNITION FLAMMABLES
☒ AVOID INHALATION
☒ AVOID DERMAL CONTACT
☒ RESPIRATORY PROTECTION (AS PER SECTION VIII)
☒ SKIN PROTECTION (AS PER SECTION VIII)
☐ ABSORB OR SCRAPE UP
☒ VACUUM UP
☐ EVAPORATE SMALL AMOUNTS IN HOOD
☒ INCINERATE UNDER CONTROLLED CONDITIONS
☐ INCINERATE USING AFTER BURNER & SCRUBBER
☐ BURY IN REMOTE AREA OR USE AS LANDFILL
☐ NEUTRALIZE AND WASH AWAY WITH WATER
☒ OBSERVE GOVERNMENTAL SPILLS WATER QUALITY REGULATIONS
☐ REMOVE SOILED CLOTHING
☐ OTHER

SECTION VIII - SPECIAL PROTECTION INFORMATION

	DURING NORMAL USE	FOR GASES VAPORS DUSTS FUMES MISTS EXCEEDING TLV	SPECIAL (E.G. THERMAL PROCESSING SPRAY APPLICATIONS)
GENERAL VENTILATION	Recommended	Recommended	NA
LOCAL EXHAUST	Not required	Yes	NA
RESPIRATORY PROTECTION (1-3)	Not required	1, if needed	NA

1. Particle-Removing Air Purifying Air Respirator (Mechanical Filter)

2. Gas and Vapor-Removing Air Purifying Respirator (Canister)

3. Full Face Mask Positive Pressure-Demand Type Supplied Air

EYE PROTECTION	SAFETY GLASSES		CHEMICAL GOGGLES	X	FACE SHIELD	
PROTECTIVE GLOVES	NEOPRENE	G	POLYVINYL ALCOHOL	G	POLYETHYLENE	F
	NATURAL RUBBER	G	BUTYL RUBBER	G	POLYVINYL CHLORIDE	F

(E) EXCELLENT
(G) GOOD
(F) FAIR
(P) POOR
(NR) NOT RECOMMENDED

OTHER PROTECTIVE EQUIPMENT Full long-sleeved clothing closed at the neck.

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING Avoid prolonged and repeated skin and eye contact with dust and fumes. Avoid inhalation of dust and fumes. Maintain good ventilation. Showering and clothing change recommended after each shift. This material is a brittle solid so dusting may occur. Finely divided SRC dust presents a strong explosion hazard.

NOTICE

The data and recommendations presented herein are based upon our research and the research of others, and are believed to be accurate; however, no guarantee of their accuracy is made. The products discussed are distributed without warranty, express or implied, and the person receiving them shall make his own determination of the suitability thereof for his particular purpose.

FOR TRANSPORTATION SPILLS OR LEAK EMERGENCIES, CALL: CHEMTREC - 800-424-9300 (CHEMICAL TRANSPORTATION EMERGENCY CENTER).

SAMPLE PREPARATION LABORATORY PROCEDURES

GRINDABILITY OF COAL BY THE HARDGROVE-MACHINE METHOD

(ASTM D 409)

The procedure is applicable to HSRC, LSRC, TSL SRC, coal and coke as written.

Safety

The procedure should be completed in a well-ventilated area and a dust mask worn by the analyst if coal dust is present.

SIEVE ANALYSIS OF COAL
(ASTM D 410)

The procedure, including exceptions noted therein, is applicable to coal samples as written. The method is used if ASTM D 431 is insufficient to provide a complete sieve analysis of coal sizes.

Safety

The procedure should be completed in a well-ventilated area and a dust mask worn by the analyst if coal dust is present.

DESIGNATING THE SIZE OF COAL FROM ITS SIEVE ANALYSIS
(ASTM D 431)

This procedure is applicable to coal samples with natural continuous ranges of sizes as produced by mining, handling, crushing, screening, etc. ASTM D 410 is to be used if a complete sieve analysis is required to describe coal sizes.

Safety

The procedure should be completed in a well-ventilated area and a dust mask worn by the analyst if coal dust is present.

INDEX OF DUSTINESS OF COAL AND COKE
(ASTM D 547)

The method is applicable to coal or coke samples as written.

Safety

The procedure should be completed in a well-ventilated area and a dust mask worn by the analyst if coal dust is present.

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DISTILLATION LABORATORY PROCEDURES

DISTILLATION OF PETROLEUM PRODUCTS

(ASTM D 86)

This procedure (Engler distillation) is applicable to all SRC-1 liquids and blends as written. The glass still is charged with 100 ml of sample and contains one theoretical plate. The sample is distilled at atmospheric pressure and the results obtained are not comparable with those obtained from ASTM D 1160, a vacuum distillation.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Distillations must be completed in a well-ventilated area and the analyst must avoid inhalation of chemical vapors.

The distillation vessel reaches high temperatures and care must be taken to avoid contact.

DISTILLATION OF PETROLEUM PRODUCTS AT REDUCED PRESSURES
(ASTM D 1160)

Some fuel products decompose when distilled at atmospheric pressure. This distillation method determines the distillation characteristics of such materials.

The procedure is applicable to all SRC-1 liquids and blends as written. Results by this method are not comparable with those of other ASTM procedures for determining boiling ranges of fuel products, such as ASTM Method B86; ASTM Method D216: Distillation of Natural Gasoline; and ASTM Method D285: Distillation of Crude Petroleum.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Distillations must be completed in a well-ventilated area and the analyst must avoid inhalation of chemical vapors.

The distillation vessel reaches high temperatures and care must be taken to avoid contact.

SOLVENT REFINED COAL LIQUID PRODUCT WORK-UP DISTILLATION

1. SCOPE:

This distillation system is used to fractionate the total effluent generated by the solvent refined coal process. Selected fractions are collected to determine yield and are available for characterization studies.

2. PRINCIPLE:

The fractions are obtained by distilling a quantity of effluent, usually 300 grams to 2000 grams, through a fifteen theoretical plate column. The conventional type petroleum fractions, 420°F, 550°F and 650°F are removed at a 10:1 reflux ratio using normal distillation conditions. The solvent fraction, 650°F - 1000°F is removed using total liquid takeoff and increasing the temperatures of the column and head corresponding to the temperature rise of the pot. Reduced pressure is used to prevent degredation of the recovered products. An absolute pressure of 100 mm Hg is maintained to 550°F, 50 mm Hg to 650°F and lowest possible pressure to 1000°F, which is usually below 1 mm Hg. All fraction temperatures are measured at the head above the column except for the final fraction (1000°F), where the temperature in the flask at the lowest pressure is converted to a 1000°F atmospheric equivalent. The simulated distillation technique including ASTM D86 or D1160 correlation is used to determine the temperature profiles on all the fractions.

3. APPARATUS:

A. Column

The column (Figure 1) is constructed from a section of standard Pyrex glass tubing 25mm ID x 8" long. The middle 6" is packed with Reliance Glass Works Heli-Pak Packing, size .050 x 0.100 x 0.100 inches (ss). Catalog No. 3013.

A 45/50 standard taper male joint is joined to the bottom of the column for attachment of the pot. The head assembly is joined to the top of the column. The column also incorporates a thermowell which enters at the top of the packed section and extends to the center of the packing, close to the wall.

The total length (8") of the column is lagged with No. 22 nichrome insulated heating wire spaced at 1/4" intervals and the power to this heating wire is controlled by a 10 amp Variac. The column is then insulated to prevent heat loss.

3. APPARATUS (Contd.)

B. Flask

The pot is a 500 ml or 2000 ml round bottom flask with a 45/50 standard taper female joint and a thermowell. Controlled heating is applied to the 500 ml or 2000 ml flask by using the appropriate Glascol heating mantle.

C. Head

The head (Figure 2) is a typical total condenser assembly with facility for measuring vapor temperatures and controlling reflux ratios. It was constructed at Air Products Glass Shop at Linwwod, Pa. The vapor path is lagged with No. 22 nichrome insulated heating wire spaced 1/4" and controlled by a 10 amp Variac.

D. Receiver

The receiver (Figure 3) is a length of Pyrex tubing calibrated in 10 ml increments to 400 ml. It is constructed for draining through a suitable stopcock and has provisions for attaching it to the head and to a vacuum system. Stopcocks are provided for raising the pressure to atmospheric pressure for draining and reevacuating to run pressure. It was constructed at Air Products Glass Shop at Linwood Pa.

E. Auxilliary Equipment

1. Vacuum Pump -- Sargent-Welsh Scientific Co.-Model 1400
2. Magnetic Stirrer -- Corning Glass Works-Hot-Plate-Stirrer-PC351
3. Closed-end Hg Manometer 0-200mm -- Air Products-Linwood Pa.
   Drawing No. RS-349, Rev. 1
4. Gilmont manometer -- Low pressure-Mercury tilt-(0-5mm)
   Arthur H. Thomas
5. Nitrogen bleed valve -- any fine needle valve-Hoke Inc.-1/4" needle.
6. Nitrogen rotometer -- Low volume tube insert-Brooks Instrument
7. Nitrogen regulator -- Low pressure (10 lb.) Air Products-Model 2200

3. APPARATUS (Contd.)

E. Auxilliary Equipment (Contd.)

8. Digimite -- Temperature readout-3 needed-Thermo Electric Co.
Iron constantan, thermocouples rated at -300°F-+1600°F

9. Parr Instrument -- Pressure reactor filter-Catalog No. 4551
Parr Instrument Co.

4. PROCEDURE

A. Operation (Figure 4) - Review Safety Preparations

1. After melting and thoroughly mixing to insure sample homogenity, weigh up to 2,000 grams of sample into the appropriate tared 500 ml or 2,000 ml flask into which a stirring bar has been placed.

2. Activate magnetic stirrer at a sensible speed.

3. Put water into head condenser and ice down dry ice trap.

4. Start vacuum pump and reduce pressure to 100 mm by way of the nitrogen bleed system.

5. Apply heat to the flask through the heating mantle (Note 1). Adjust the heat to regulate the reflux return to the column to 165-180 drops per minute.

6. Position product take-off stopcock so that 1 drop is collected as product while 10 drops are returned to the column. (10:1 R.R.)

7. Maintain this condition (10:1 reflux-ratio at 100 mm pressure) until head vapor rises to 420°F equivalent at this pressure (Note 2)

8. Close product take-off stopcock and drain accumulated product into tared bottle and weigh. (Note 3)

9. Open stopcock wide and continue the distillation using total take-off until an atmospheric equivalent head vapor temperature of 500°F is reached.

10. Return to the 10:1 reflux ratio mode and make the cut point at a 550°F atmospheric equivalent.

11. At the 550°F cut point, put still on total-reflux, isolate the receiver, collect and weigh this cut as before.

12. If a 550°F to 650°F fraction is desired, repeat steps 9 to 11 using a pressure of 50 mm Hg. (Note 4)

4. PROCEDURE (Contd.)

A. Operation (Figure 4) - Review Safety Preparations (Contd.)

13. Turn off the heat to flask and cool the pot to 250°F. An external air jet may be used after initial cooling of flask.

14. Close nitrogen bleed and pump still to lowest possible pressure (usually below 1 mm).

15. Adjust the heat to control drops from head condenser as before, using a drop rate at 65-80 drops/minute. Open the stopcock to the total take-off mode. Maintain 65-80 drops/minute to the product receiver. As the pot temperature rises, apply heat to both the column and the head maintaining the same temperature as pot.

16. When pot temperature rises to an atmospheric equivalent of 1000°F and column and head temperatures are at the same temperature, ± 10°F, hold this condition until product stops coming over (approx. 10-15 minutes). This is the final cut point. If the pressure begins to rise as indicated on the low pressure manometer, before this condition is reached, it is a sign of decomposition and the run should be terminated immediately. This cut point is considered acceptable even if only a 900°F equivalent head temperature is reached, because this should remove essentially all the solvent. The actual boiling range of the solvent is determined by simulated distillation.

17. As soon as the heat is removed from the flask, raise the pressure to atmospheric with the nitrogen bleed. Now immediately tap the pot free from the column.

18. Allow the flask to cool under a nitrogen blanket and weigh.

19. To remove contents from flask, chill it with liquid nitrogen and gently tap it to break and dislodge the solid mass for transfer to a suitable container.

20. Clean the column by refluxing 200 ml of pyridine. Repeat using a charge of acetone and blow dry.

21. All products should be stored at 4°C under nitrogen blanket.

B. Operational Notes

1. Flooding caused by too much heat may be quickly stopped by raising the pressure on the system through the nitrogen bleed valve.

2. Solids may build up in the head but may be prevented by only intermittently supplying water to the head condenser. Hold the condenser at approximately 150°F. Heat lamps will be needed to keep remainder of the product system fluid.

3. APPARATUS (Contd.)

B. Operational Notes (Contd.)

3. All drainings from the receiver under vacuum must include isolating receiver from the rest of the system then raising pressure to atmospheric with separate nitrogen source, draining, then reevacuating to run pressure before reintroducing to the system.

4. The temperature of cut points of fractions ofttimes deviate from the standard cut points (int.420-550-850°F). This writeup implies that up to 650°F a 10:1 reflux ratio is normally used with a pressure of 50 mm Hg and total take-off is used from 650°F-850°F (1000°F equivalent) at the lowest possible pressure.

C. Post Distillation Work-Up - Review Safety Precautions

1. Bottoms Work-Up

a. After the bottoms have been removed from the flask, grind the total bottoms by first breaking up the bulk using a plastic bag containing the sample and a mallet. Further grinding may be necessary with a motar and pestle. This grinding should be performed in a hood and use of a dust mask is advised.

b. Mix thoroughly and remove approximately 90 grams. Weigh into the filter apparatus approximately 90 grams of sample and add 1200 ml pyridine. Hold the temperature on the filter at 115°C for one hour shaking frequently before positioning the apparatus in the filter mode. Allow filtering to continue at 2-3 lb pressure until liquid recovery ceases. Now add 400 ml of toluene to the filter for the purpose of removing the residual pyridine.

c. Remove the filter cake from the filter, weigh and dry in a vacuum oven at 100°C for four hours. Remove from oven and weigh the dried cake. This weight is the amount of insolubles and is reported as weight percent of the charge to the still.

2. Pyridine Distillation to Recover SRC

a. Charge all of the pyridine plus SRC recovered from the filter back into the still.

b. Run at total take-off conditions as described earlier.

c. Use atmospheric pressure to a pot temperature of 400°F. Cool still, reduce pressure to 150 mm and continue removing product.

d. During the 150 mm pressure stage of the distillation, maintain the column and head temperatures the same as the pot.

e. Bring all three temperatures to 400-425°F and hold this condition until all signs of boiling in the flask stops.

3. APPARATUS (Contd.)

C. Post Distillation Work-Up - Review Safety Precautions (Contd.)

f. Remove flask and recover solids as described earlier (Steps F-16 to F-20). This weight of solids represents the amount of SRC in the charge and may be then calculated as a weight percent.

g. Pyridine plus toluene recovered should be discarded.

D. Safety Precautions

1. Solvent refined coal products are harmful to the skin, or if inhaled or swallowed causes burns of eyes and skin and may cause cancer.
2. Avoid all body contact. Wash thoroughly with soap and water. Do not use solvents to wash affected areas. Solvents encourage penetration into the skin.
3. Use respirator (hydrocarbon) and protective clothing when cleaning spills.
4. Shower and change clothing at end of the day.

SOLVENT REFINED COAL LIQUID PRODUCT WORK-UP DISTILLATION COLUMN

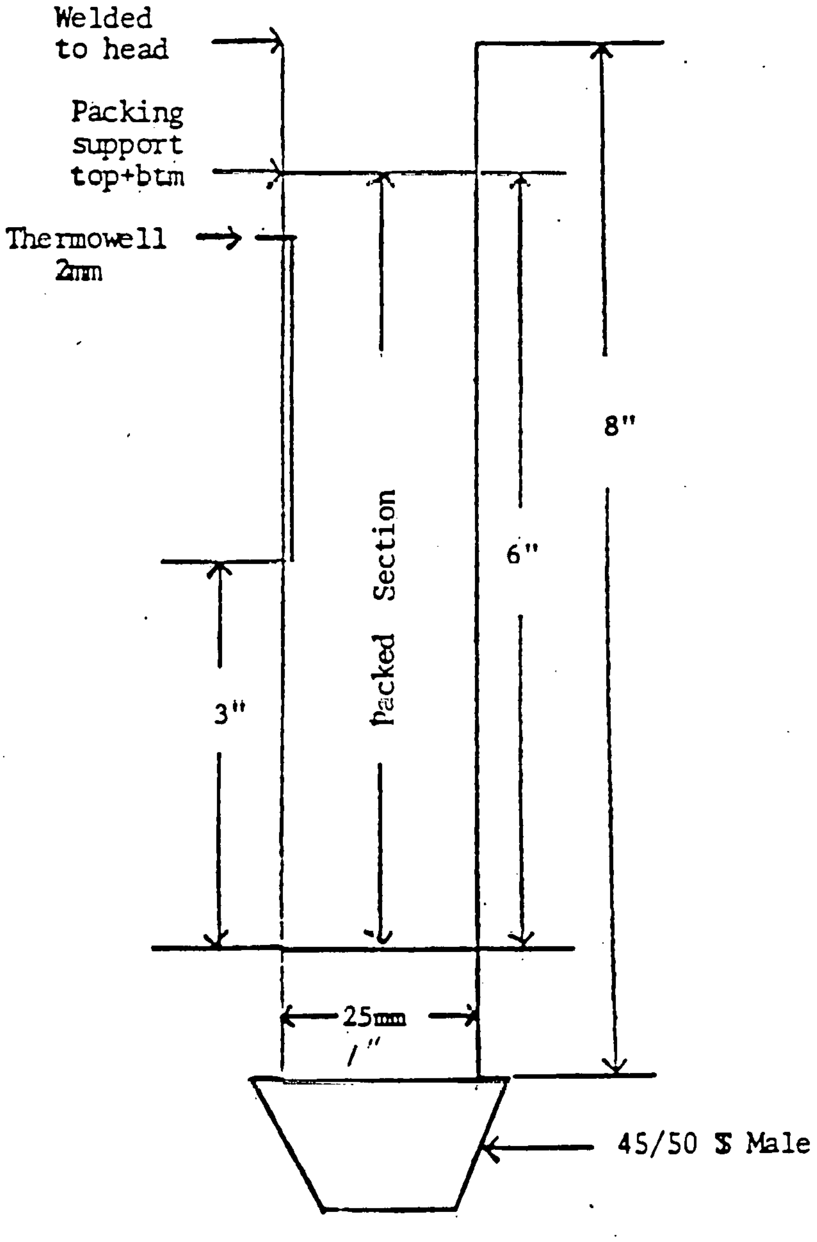


FIGURE 1

SOLVENT REFINED COAL LIQUID PRODUCT WORK-UP DISTILLATION

HEAD ASSEMBLY

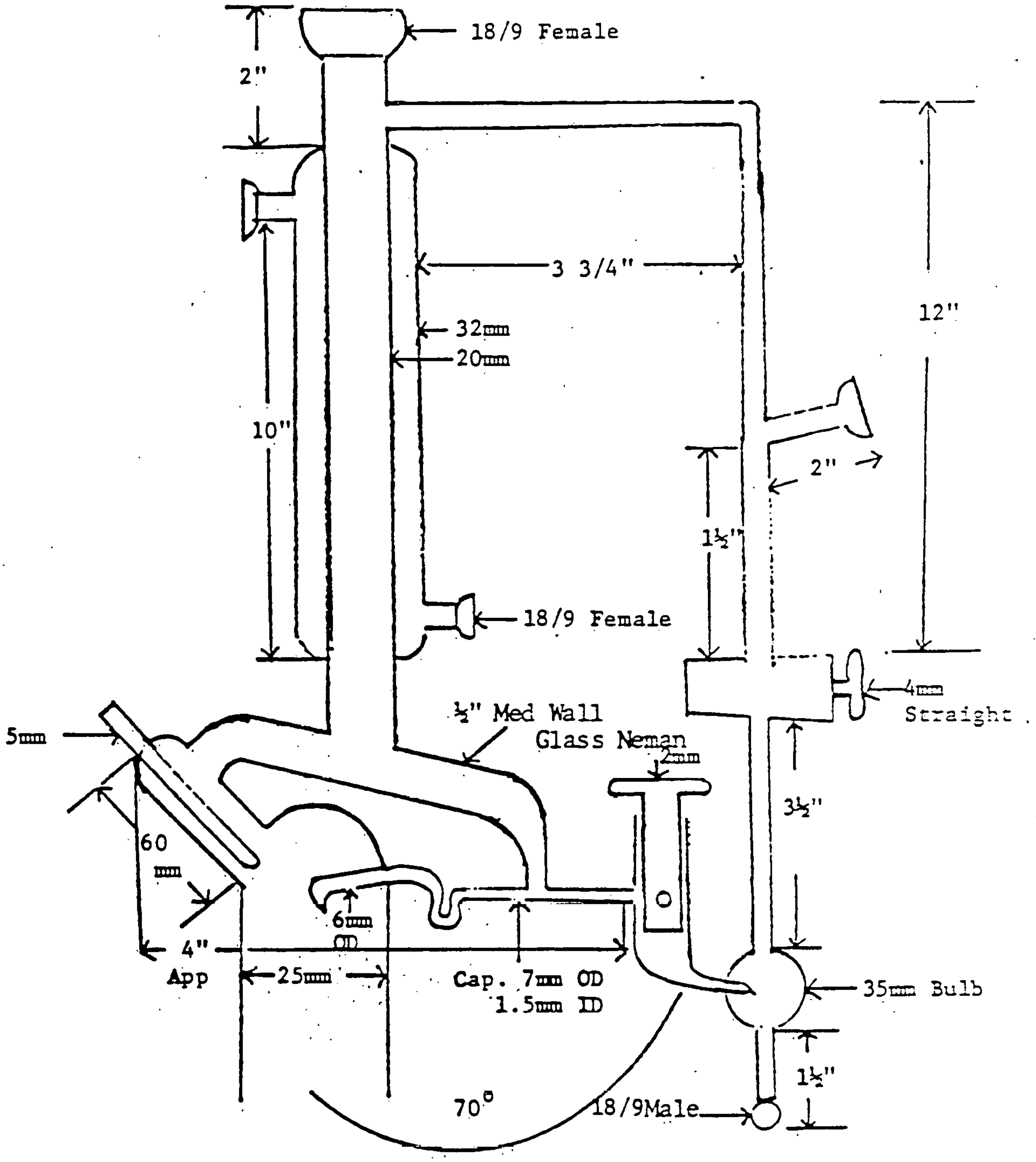


FIGURE 2

SOLVENT REFINED COAL LIQUID PRODUCT WORK-UP DISTILLATION

RECEIVER

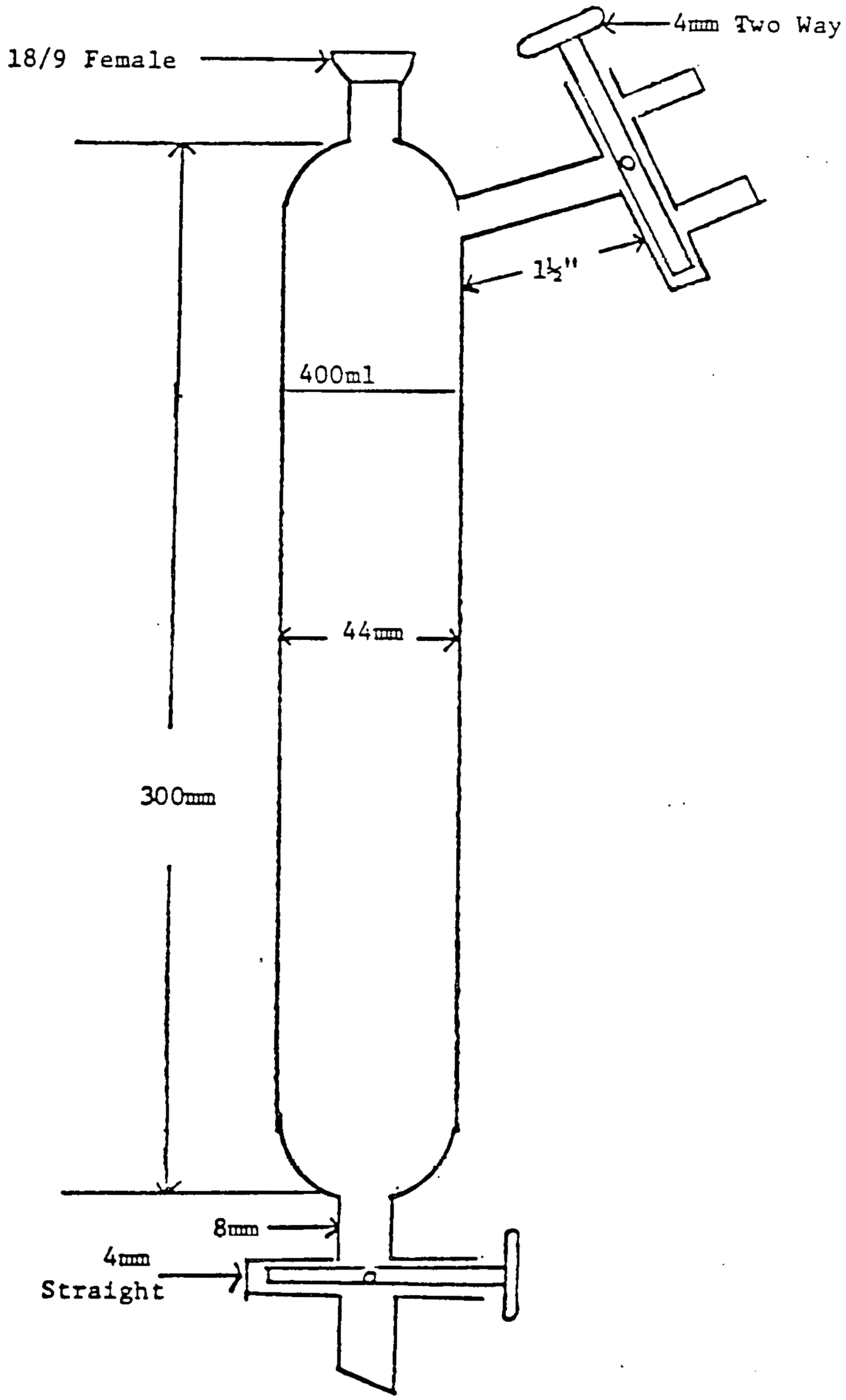


FIGURE 3

SOLVENT REFINED COAL LIQUID PRODUCT WORK-UP DISTILLATION

FLOW DIAGRAM

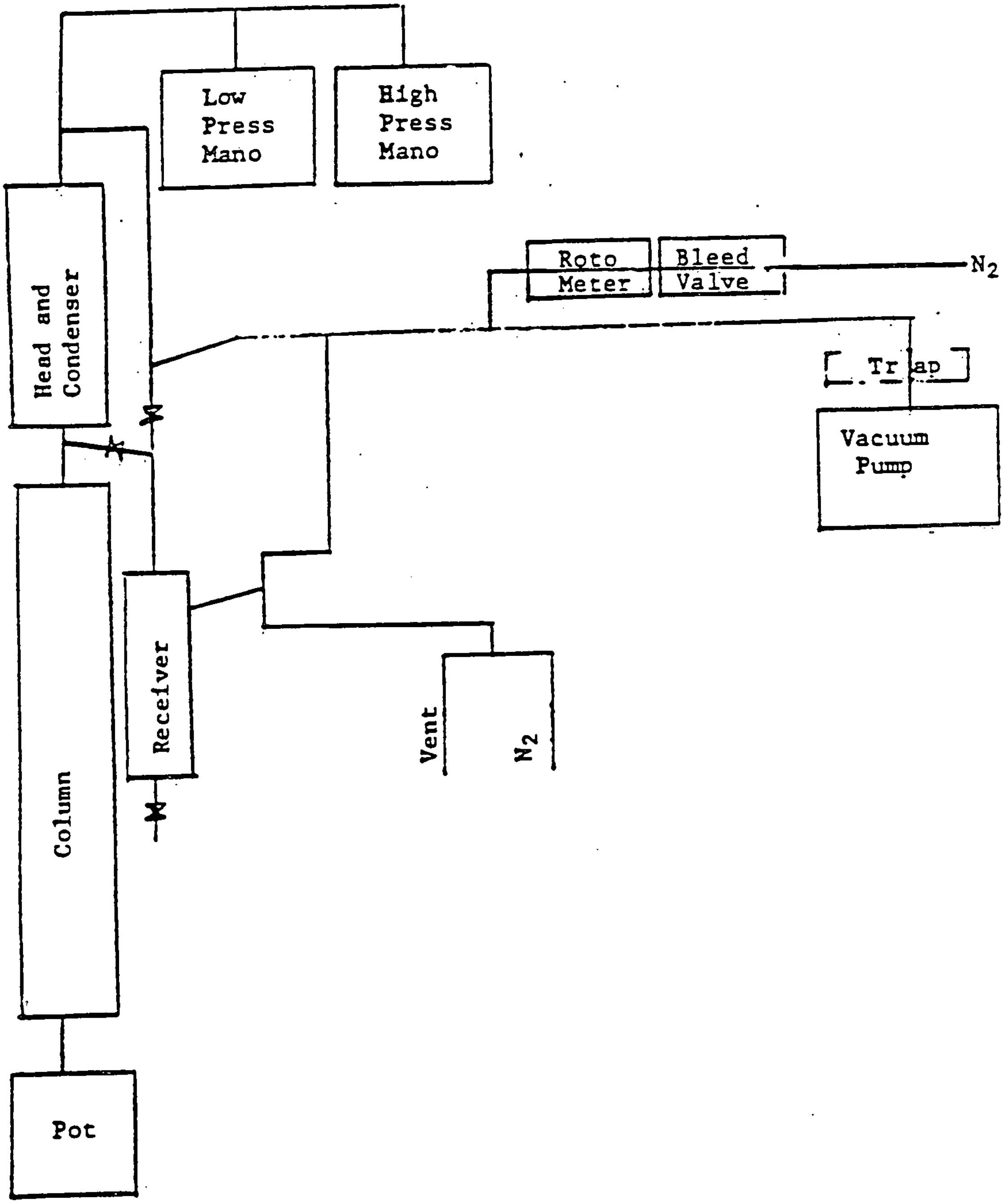


FIGURE 4

Determination of Percent Distillate by Vacuum Distillation
(Wilsonville Procedure No. 36025-9)

SCOPE: This method determines that fraction of the sample defined as solvent. Solvent refers to the hydrocarbon portion that can be distilled up to a corrected temperature of 925°F.

PRINCIPLE: The SRC, which is usually solid, is broken and then heated under 1-mmHg pressure to a final pot temperature of 600°F. Under these conditions, the solvent in the sample will be distilled.[a] For deashing solvent determination, the receiver is immersed in a dry ice/methanol bath.

PROCEDURE:

A. Sample is ground or broken; between 100 and 200 g is added to a tared distilling flask. Sample weight is recorded.

B. Distillation flask is attached to an apparatus assembled as in Figure 1.

C. Vacuum is applied (0.1 mm or better).

D. Apparatus is fully insulated with glass wool and the powerstats are turned on. Temperature is raised to the final temperature of 600°F.[c]

E. Powerstats are turned off and insulation is removed to facilitate cooling. To avoid explosions, sample must be cooled below 200°F before air is admitted to system.

F. Distillation flask containing nondistillables is removed from apparatus and weighed. Weight difference from original sample weight is taken to be weight of solvent removed by distillation.[d]

---

[a] This procedure may be modified readily to accommodate other SRC process samples (solid or liquid). For liquid samples (including various laboratory filtrates), the vacuum may have to be raised very slowly to prevent the lower boiling solvent fractions from flashing over. In some instances, an atmospheric cut to 600°F is necessary to prevent flashing. If, during any distillation, any part of the contents flashes over, the test must be rerun.

[b] Before vacuum is applied, a safety shield should be in position to protect the analyst from implosion and explosion. Do not manipulate the distillation apparatus while it is hot and evacuated--allow it to cool.

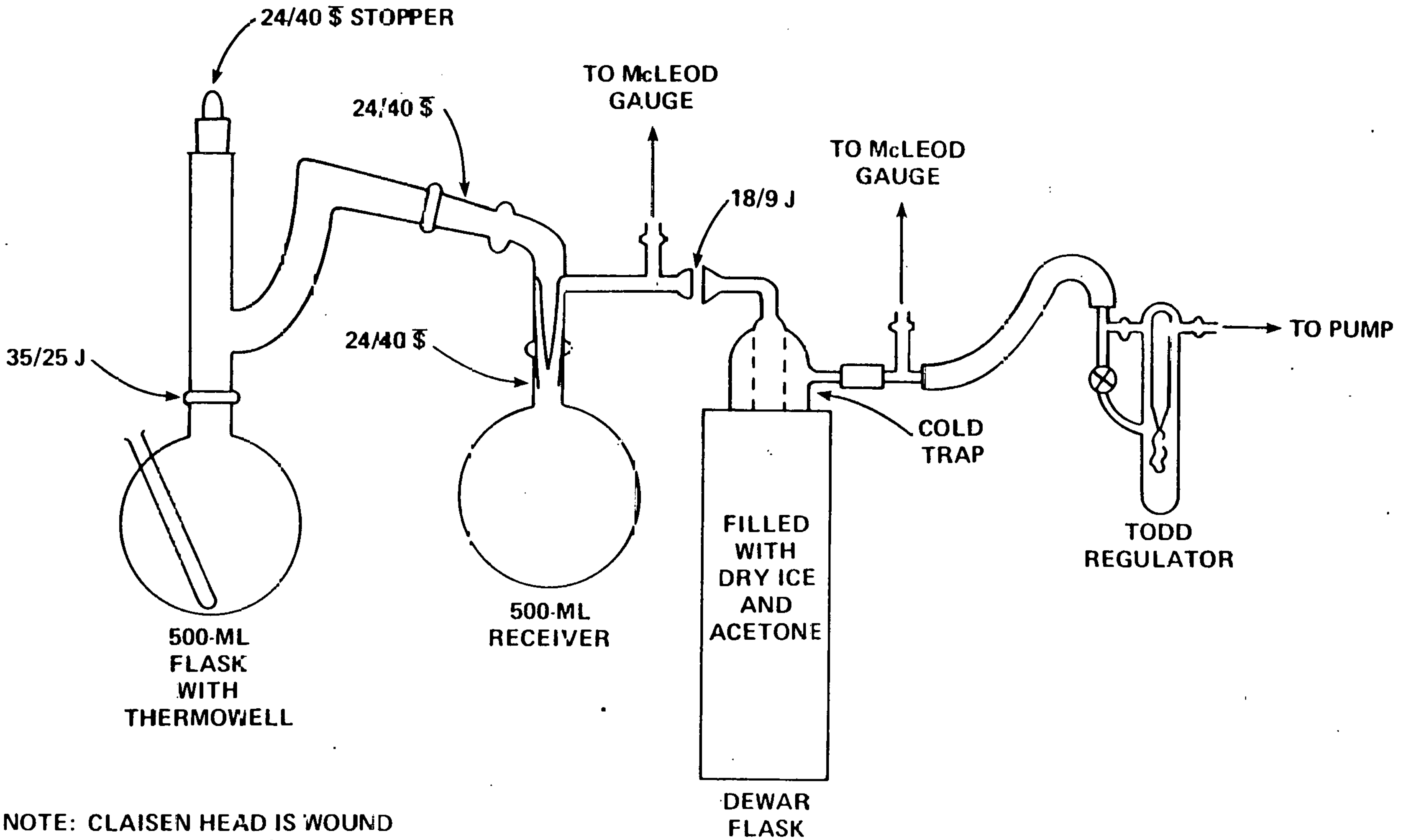
[c] Temperature may be monitored manually using a thermometer (no mercury in thermowell) or by using a temperature controller including a thermocouple in conjunction with the heating mantles.

[d] Depending on the time available for analysis and the degree of accuracy required, the percent solvent can be verified by using clean glassware and weighing each piece (Claisen head, adapter, receiver, tubing, and cold trap) before distillation. After distillation, reweighing of all apparatus should yield an additional weight equal to the loss of weight from the sample. Use of proper techniques should yield balances within 0.5 g.

EQUIPMENT: Apparatus is illustrated in Figure 1.

CALCULATION: $$\% \text{ solvent} = \frac{(\text{sample wt} - \text{solvent-free residue wt}) \times 100}{\text{sample wt}}$$

Figure 1
Apparatus for Vacuum Distillation
(Wilsonville Procedure No. 36025-9)



NOTE: CLAISEN HEAD IS WOUND WITH ASBESTOS TAPE AND HEATING WIRE (24 BS)

Determination of Distillables by Vacuum Distillation
(Kerr-McGee Procedure No. ACL85-3)

INTRODUCTION: This method is used to determine the percentage of distillable organic matter in a coal-derived feed or product. The sample is distilled at a pressure of about 0.1 mmHg and a distillation pot temperature of 600°F.

SAFETY: In this procedure, the apparatus must be evacuated to 1 mmHg. Care must be taken to prevent injury from implosion.

EQUIPMENT:
Distillation flask with thermowell
Column
Condenser
Product receiver
Heating mantle
Thermometers for measuring vapor and pot temperature
McLeod gauge for pressure measurement
Heat tape
Rheostats for controlling temperature
Silicone grease

METHOD:

A. Place a small plug of glass wool in the distillation flask thermowell and insert the thermometer.

B. Tare the distillation flask, column, condenser, and product receivers.

C. Measure about 100 g, weighed to the nearest 0.01 g, into the distillation flask.

D. Lubricate the spherical joints of the distillation apparatus with a high-temperature silicone grease and connect the joints of the apparatus. Clamp the joints by means of adjustable spring clamps.

E. Wrap the neck of the distillation flask and the column with heat tape and insulate with fiberglass wool.

F. Start the vacuum pump and evacuate the apparatus to about 0.1 mmHg to degas the sample and then increase the pressure to about 5 mm to start the distillation.

G. Turn on the heater and heat tracing and set the rheostats at about 60%. This will give a temperature increase of about 5°C/min.

H. After the sample starts to melt, the distillation flask temperature will increase rapidly. Evacuate the apparatus to 0.1 mmHg after the sample is melted.

I. Adjust the heat tracing so that the vapor temperature in the head is from 10 to 20°C less than the temperature in the distillation flask.

J. During distillation, it may be necessary to use heat lamps and steam in the condenser jacket to keep the distillate fluid enough to flow into the receiver.

K. Continue distillation until the distillation flask has reached 600°F at a pressure of 0.1 mmHg.

L. Continue distillation at settings of (11) for 1 hr.

M. After the end point has been reached, cool and disassemble the apparatus. Weigh and record the weights of the distillation flask, column, condenser, and receiver.

REPORTING: Report the percent of distillable (sample basis) in the column, condenser, and receiver. Also report the total percent distilled (sample basis), which is the sum of the three percentages previously reported.

Air Products

TENTATIVE ANALYTICAL METHOD 251
January, 1983
Page 1 of 22
By: F. Troxell
W. W. Stawasz
W. F. Tiedge

VACUUM DISTILLATION OF T-102 BOTTOMS TO DETERMINE RESIDUAL PROCESS SOLVENT

I. SCOPE

Solvent Refined Coal (SRC) may contain residual amounts of process solvent, which is defined as material having a boiling point of less than 1000°F at atmospheric pressure. This distillation procedure is used to determine the amount of residual process solvent in a T-102 Bottoms material. Process solvent levels up to 15% can be present.

Higher levels of solvent may also be determined using this procedure; however, modifications of the method may be necessary.

II. PRINCIPLE

The T-102 Bottoms is placed in a specially constructed fractionation apparatus (see Figure 1), and the process solvent is distilled under low vacuum (0.1 - 1 mm Hg). The process solvent is taken overhead until a pot temperature of 600°F (at <1 mm Hg pressure) is attained. This temperature is defined as the end-point equivalent to an atmospheric boiling point of 1000°F. The material taken overhead is accurately weighed and calculated as a fraction of the still charge. Material remaining in the still pot is weighed to obtain a mass balance, which should be greater than 95%.

III. APPARATUS

A. Distillation column, glass, JBS 10 (J. Blomquist Co., 680 Bethel Church Road, North East, MD 21901).

B. Distillation Head, glass, JBS 100 (J. Blomquist Co., 680 Bethel Church Road, North East, MD 21901).

C. Receiver, glass, 25 ml, with 18/9 female joint (J. Blomquist Co., 680 Bethel Church Road, North East, MD 21901).

D. Flask, 200 ml, round bottom, glass, with 24/40 standard taper joint and thermowell.

E. Vacuum pump, Duo-Seal-Model No. 1400 (Welch Scientific Co., 7300 N. Linder Ave., Chicago, IL) or equivalent.

F. Gilmont Swivel (McLeod) mercury, vacuum gage (Catalog No. 5654-010, 0-5 mm), (Arthur H. Thomas Co., Vine and Third Streets, Philadelphia, PA, modified by J. Blomquist Co., 680 Bethel Church Road, North East, MD 21901).

VACUUM DISTILLATION OF T-102 BOTTOMS TO DETERMINE RESIDUAL PROCESS SOLVENT

III. APPARATUS (continued)

G. Magnetic stirrer and three-eights inch, glass, magnetic spinbar.

H. Three Digimite or equivalent temperature indicators with iron-constantan, Type J, 24AWG thermocouples.

I. Heating mantle, for 200 ml round bottom flask.

J. Nichrome wire, #22AWG, asbestos covered, (Molecule Wire Co., Farmingdale, NJ).

K. Variac transformer, 5 amps, 120 volt.

L. Fiberglas cloth, 1.5 inch wide.

M. Heat lamp or heat gun (500 watts).

N. Aluminum foil.

O. Stainless steel packing, 0.50 x 0.100 x 0.100 inches Heli-Pak Catalog No. 2917 and 0.92 x 0.175 x 0.175 inches Heli-Pak Catalog No. 2918, (Reliance Glass Co., P. O. Box 825, Bensonville, IL 60106).

P. Stainless steel sponge, (Schnitzer Alloy Products Co., 325 Pine Street, Elizabeth, NJ).

R. Balance, Mettler, top loading, with accuracy of 0.01 grams or equivalent.

S. Balance, Mettler, analytical, with accuracy of 0.001 grams or equivalent.

T. Silicone grease, high vacuum, Dow Corning.

IV. REAGENTS

A. Acetone, histological grade (Fischer Scientific, Catalog No. ΔA-16-P, King of Prussia, PA) or equivalent.

B. Methylene chloride, HPLC grade (Fischer Scientific, Catalog No. D143, King of Prussia, PA) or equivalent.

C. Pyridine, technical grade (Fischer Scientific, Catalog No. ΔP-369, King of Prussia, PA) or equivalent.

D. Mercury, high purity ACS reagent grade (Process Chemicals, Inc., 89 Lincoln Ave., Fairlawn, NJ 07410).

VACUUM DISTILLATION OF T-102 BOTTOMS TO DETERMINE RESIDUAL PROCESS SOLVENT

V. PROCEDURE

A. The column (see Figure 2) is prepared for distillation by adding approximately one-quarter inch of stainless steel sponge (turnings) to the inside, until the glass indentations are reached. A metal or glass rod can be used to pack the turnings. A small amount of the large stainless steel packing (Catalog No. 2918) is inserted, followed by approximately three inches of the smaller stainless steel packing (Catalog No. 2917). The larger packing and additional turnings are again placed as a top layer.

An iron-constantan thermocouple wire is fused with an oxygen torch and inserted into the thermowell built into the center of the packed area.

The column is then wrapped with an asbestos covered nichrome heating wire (approximately 11 turns per inch) having a male electrical clip at the two ends. The male clips are connected to two female clips of an electrical plug leading from the Variac transformer.

The temperature indicating and heating wires are finally covered with 1.5 inch wide fiberglas cloth.

B. The distillation head was designed to eliminate as many joints as possible (see Figure 3). A thermowell was built into the vapor stream for placing an iron-constantan wire connected to a second temperature indicator. The glass area below the condenser is wired in the same manner as the column to provide heating and additional temperature control. Fiberglas cloth also covers these wires.

C. Weigh the empty 25 ml glass receiver (see Figure 4) to the nearest milligram on the Mettler analytical balance, record the weight on the distillation record form (see Appendix I, page 12). Attach the receiver to the still using a very small amount of high vacuum silicon grease on the ball joints.

D. The T-102 Bottoms are solid at room temperature. If not preground when received, a sample can be broken up by freezing in a container with liquid N_2 and hitting with a spatula or placing in a polyethylene bag (do not use plasticized vinyl) and smashed with a mallet into pieces approximately 2 cm in size or less. Dust particles should be removed by screening through a 10 mesh screen. Store any unused material in a glass jar and blanket with nitrogen gas.

E. Insert the glass magnetic stirring bar into the 200 ml flask and weigh to the nearest 10 milligrams on the Mettler top loading balance and record the weight on the distillation record form.

V. PROCEDURE (continued)

F. Weigh 100 grams (to the nearest 10 milligrams) of the crushed T-102 Bottoms into the flask and again record the total weight.

G. Connect the flask to the distillation column using a small amount of silicon grease to the tapered joints. Cover the top of the flask with fiberglas pipe insulation. Raise heating mantle to pot and insulate remainder of flask with pipe insulation. Also cover column and head with several layers of pipe insulation.

H. Circulate cold tap water in the head condenser. Weigh and record the mass of the condensate trap and connect to still (do not add liquid N_2 to Dewar flask until distillation unit is evacuated). Connect column and head wiring to individual Variacs.

I. Fill manometer with mercury up to the marked line (see additional details on McLeod swivel gage in appendix - page 12). The bulb containing the mercury has been enlarged, therefore disregard filling volume recommended by the manufacturer.

J. Connect manometer, vacuum and N_2 bleed lines. The N_2 bleed is used only at the end of the run to stop the distillation.

K. Start vacuum pump and reduce pressure to less than 1 mm Hg. With tight glass connections initial pressures of 20 to 50 microns can be obtained. To read the pressure on the Gilmont swivel gage see directions in Appendix II, page 14. Fill Dewar flask with liquid N_2.

L. Record the time, temperature, pressures and Variac settings on the distillation record form.

M. Set Variac at 100 volts to the flask through the mantle. Start heat on column (10-12 volts) and head (12-14 volts) at the same time. Record time, temperatures, pressure and Variac settings at each change or at 5 minute intervals. As solid SRC melts it will start to degas and pressure will increase to about 600 microns and decrease again to about 200 microns when completely melted.

N. Turn magnetic stirrer on when the sample has liquified (at approximately 450°F pot temperature).

O. When vapors approach head (as noted by increased head temperature) put heat lamp on take-off line (backed by aluminum foil to distribute heat evenly). Set mantle Variac at 80-90 volts.

VACUUM DISTILLATION OF T-102 BOTTOMS
TO DETERMINE RESIDUAL PROCESS SOLVENT

V. PROCEDURE (continued)

P. Continue to decrease voltage on the mantle to approximately 65 volts till vapors are noted in receiver. It takes about 30 minutes to reach this stage. When overhead flows into the receiver turn off condenser water for remainder of distillation to prevent solids from building up on condenser walls. Increase the voltage on the head and column to maintain temperature within 10°F of still pot (14-16 volts).

Q. Bring the three temperatures up slowly until the pot temperature reaches approximately 598°F. Pressure will usually increase from 200 microns at melting stage to 700 microns at completion. Shut heating mantle off and reduce column and head voltage in half. Allow pot temperature to creep up to 600°F and maintain for only one minute. The distillation is stopped quickly by closing vacuum valve while opening N_2 bleed inlet valve at the same time.

R. The time for completion of the distillation is approximately one hour. A typical distillation record is shown in Appendix III.

S. Heat receiver lines with heat lamp to drain all product into receiver. Drain column back to pot. Cool pot to below 200°F.

T. Remove pot receiver and trap, wipe off vacuum grease with lens paper and reweigh on appropriate balances. Record weights on the distillation record form. Any material in trap should be physically added to overhead and the mass totaled.

U. Place flask in ring stand and support firmly. Use liquid N_2 to freeze SRC solid in flask. When SRC becomes brittle hit gently with a metal spatula to shatter. Be careful not to break thermowell or bottom of flask. Pour broken pieces of SRC out of flask.

V. Clean the flask column and head by initially boiling toluene then methylene chloride through the glassware. Dry with a N_2 sweep upon completion. A film of SRC usually remains even after solvent cleaning and requires wiping with soft glassware brushes and laboratory cleaning cloths. Care must be taken not to break thermowells and other glassware. Boiling pyridine through the still is a final step that can be taken if necessary to clean remaining residues.

VI. CALCULATIONS

A. $\% \text{ Solvent} = \frac{\text{Total Overhead Wt.} \times 100}{\text{Charge Wt.}}$

B. $\% \text{ Recovered SRC} = \frac{\text{Total Recovered Wt.} \times 100}{\text{Charge Wt.}}$

C. % Loss = 100.00 - (% Recovered SRC)

VII. PRECISION AND ACCURACY

A. Precision

With proper care and strict attention to details, duplicate results obtained for solvent yields of 6 to 7% on the T-102 Bottoms should be within 1%. Losses also should not exceed 1.0%. These percentages may differ with other products.

B. Accuracy

Standards of accuracy for process solvent in SRC are not available, and spiking studies have not been performed. The APCI Encapsulated GC-Simulated Distillation procedure has been utilized to determine the efficiency of process solvent removal from the SRC, and whether material boiling at >1000°F has been taken overhead. Preliminary data indicates that less than 5% of the material taken overhead has a boiling point >1000°F, and only trace levels of material boiling at <1000°F remains in the SRC.

VIII. QUALITY ASSURANCE

A. Pressure Measurements

Initial pressures should be below 1 mm Hg since pressure will increase as material is heated and vapors approach head. Pressures should not rise above 1.2 mm Hg in order to distill solvent below 1000°F (at atmospheric pressures). If low pressures cannot be maintained regrease all glass joints and determine sources for other possible air leaks.

B. Temperature Measurements

The temperature indicators should be calibrated as per the instrument manual. In all cases allow instrument to warm up for 30 minutes before calibrating. The Digimite temperature indicator has a temperature range from -310°F to 1600°F with a Type J iron-constantan thermocouple. By pushing the check button the temperature reading specified on the top label by the manufacturer should be read. If temperature is not obtained make adjustments as specified by manufacturer.

VACUUM DISTILLATION OF T-102 BOTTOMS
TO DETERMINE RESIDUAL PROCESS SOLVENT

IX. SAFETY

A. Wear vinyl or rubber gloves and other protective clothing when handling SRC materials and cleaning spills. Avoid all skin contact with SRC products; however, if contact is made, wash skin thoroughly with soap and water or use waterless hand cleaner. Do not use solvents to wash affected areas since they enhance penetration into the skin.

B. For additional precautions see attached material safety data sheets in Appendix IV A, B and C.

C. The distillation unit should be placed in a hood. A laboratory safety shield should be placed in front of the apparatus to prevent injury from possible implosions.

D. Wear safety glasses at all times.

X. REFERENCES

A. Vacuum Distillation of SRC-1 Process Stream Samples (APCI Analytical Method No. 1161).

B. Determination of Percent Distillate by Vacuum Distillation (Wilsonville Procedure No. 36025-9).

WWS:bas:967
ANA19

Figure 1

Vacuum Distillation Apparatus

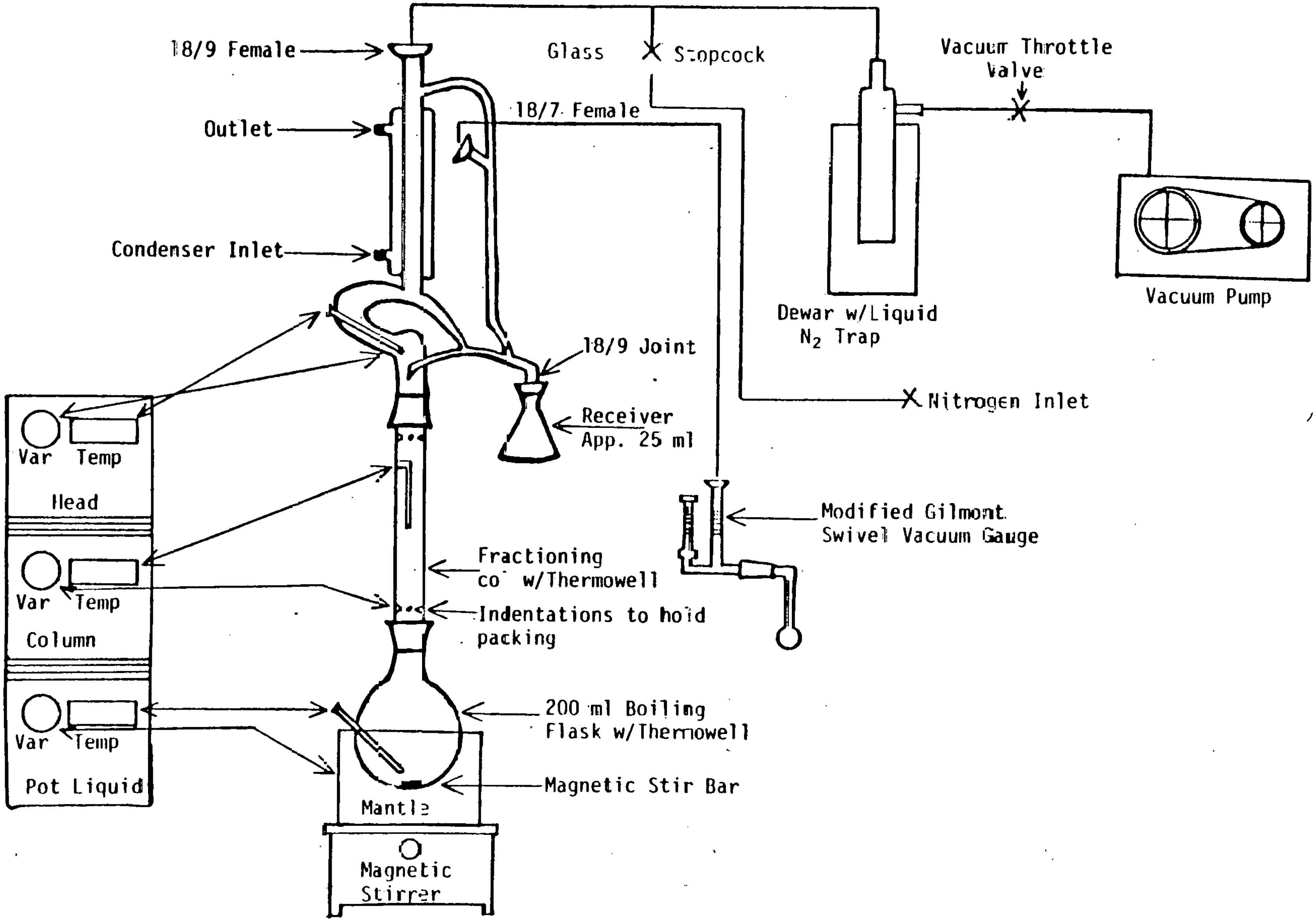


Figure 2

Vacuum Distillation Column

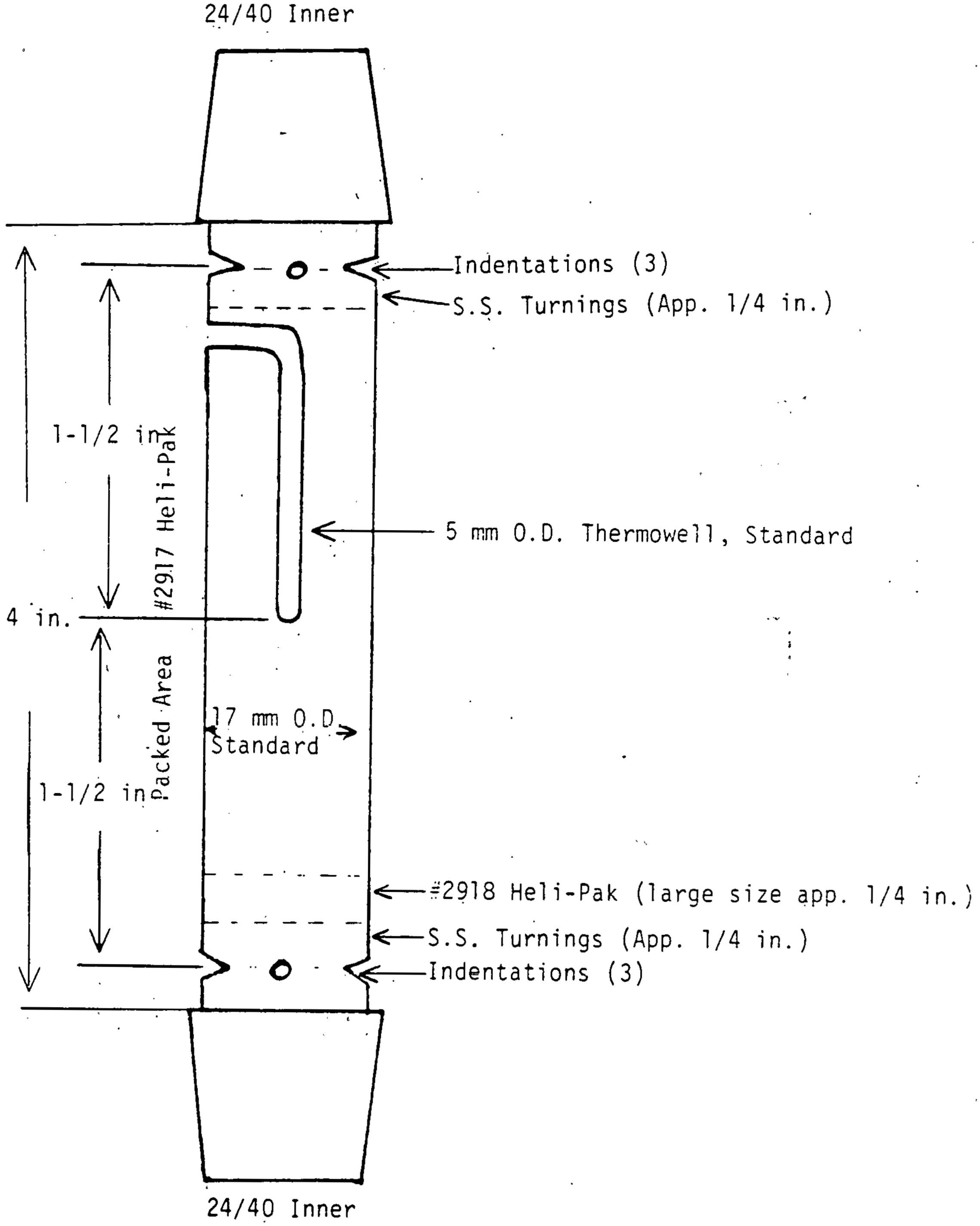
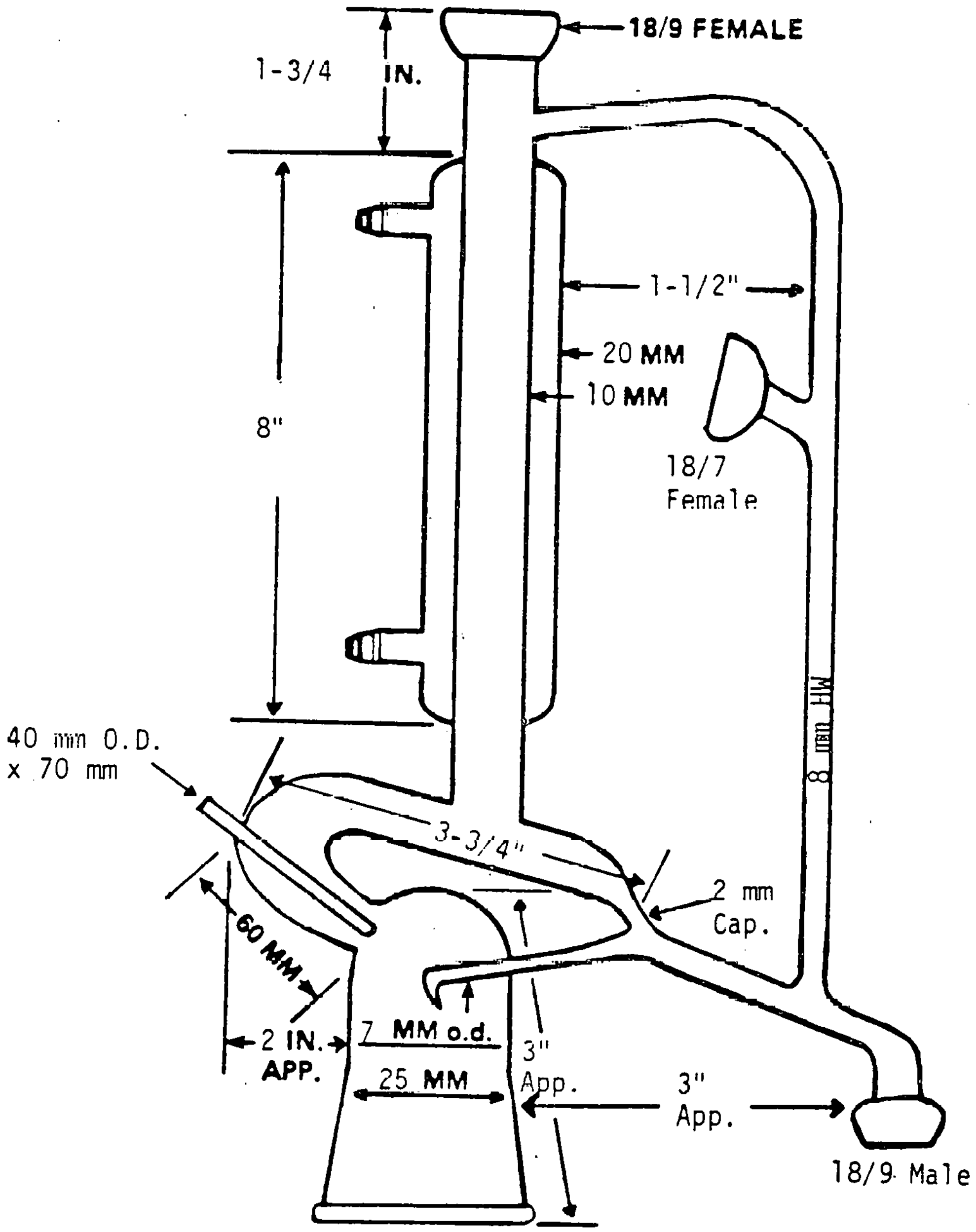


Figure 3

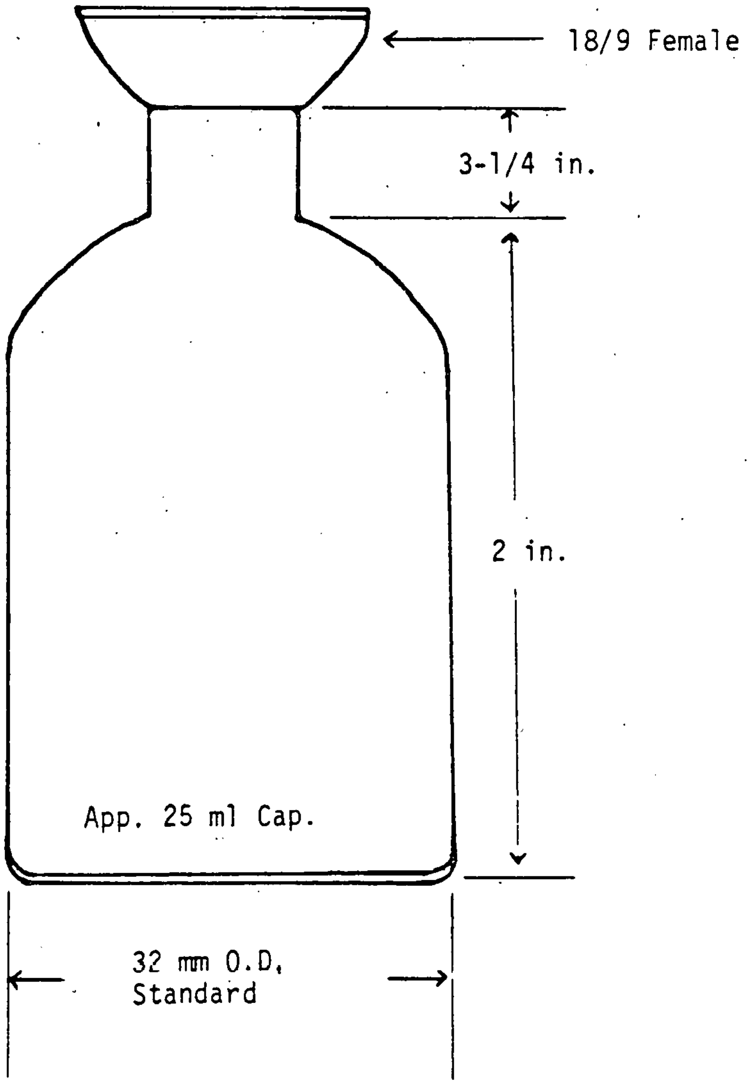
Vacuum Distillation Head Assembly



24/40 Outer

Figure 4

Vacuum Distillation Receiver



Air Products

DATE ____________________

VACUUM DISTILLATION

Product: ____________________ Lot or I.D. No. ____________________

Calculations

A) Charge & Tare Wt.	________	B) Bottoms & Tare Wt.	________
Dist. Flask Tare Wt.	________	Dist. Flask Tare Wt.	________
Charge Weight	________	Wt. of Bottoms	________

C) Wt. of Rec. Flask & Overhead	________	D) Wt. of Trap (after Distillation)	________
Rec. Flask Tare Wt.	________	Trap Tare Wt.	________
Overhead Wt.	________	Distillate Wt. in Trap	________

E) Overhead Wt. ________ + Distillate Wt. in Trap ________ = Total Overhead Wt. ________

$$\% \text{ Solvent} = \frac{\text{Total Overhead Wt.}}{\text{Charge Wt.}} \quad \frac{\_\_\_\_\_\_}{\_\_\_\_\_\_} \quad \times 100$$

F) Wt. of Bottoms ________ + Total Overhead Wt. ________ = Total Recovered Wt. ________

$$\% \text{ Recovered SRC} = \frac{\text{Total Recovered Wt.}}{\text{Charge Wt.}} \quad \frac{\_\_\_\_\_\_}{\_\_\_\_\_\_} \quad \times 100$$

G) % loss = 100.00 - (% Recovered SRC ________) = ________

H) Distillation Time: Start ________ Finish ________ = ________ Minutes

WWS:bas:968
ANA19

TENTATIVE ANALYTICAL METHOD 251
January, 1983
APPENDIX I
Page 13 of 22
Date ________

Air Products

VACUUM DISTILLATION

Product: ____________________ Lot or ID No.: ____________

Operating Data

Time	Head Temp,°F	Variac Setting (Head)	Column Temp,°F	Variac Setting (Column)	Pot Temp,°F	Variac Setting (Pot)	Pressure μ Hg	Remarks

Comments: ____

WWS:bas:968

SWIVEL McLEOD GAGE*

This latest addition to the GILMONT line of vacuum gages represents the first significant advance in McLeod Gages since the tilting type was developed at the turn of the century. Its remarkably simple design, combined with its ease of operation and cleaning, make this apparatus by far the best buy among the compact McLeod gage instruments presently available.

The novel swivel arrangement achieves three features heretofore unattainable in the tilting types:

1. **Rigid connection to the vacuum system with the scales vertical at all times.**
2. **A combination of linear and square root scales which allows comparable accuracy in a much shorter over-all scale length.**
3. **A considerably smaller instrument for the same over-all scale length.**

The closed end is made with a unique plastic plug that includes these additional features: greater ease of cleaning and a tapered point that exactly compensates for meniscus curvature giving full accuracy at higher vacua.

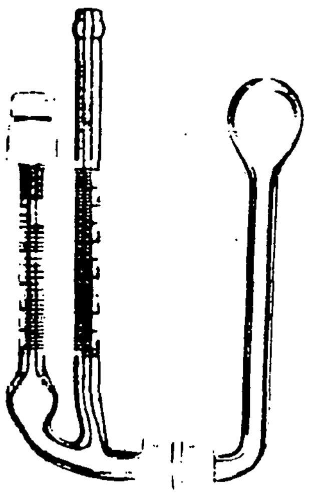
The instrument is fabricated to the high standards that have become typical of all GILMONT products and is supplied with complete instructions and a convenient storage case to prevent accidental breakage when not in use. Technical specifications are as follows:

- **High vacuum O-ring seals throughout.**
- **Precision bore capillaries.**
- **Permanent ceramic scales and white background.**
- **Corrosion resistant plastic parts of polypropylene.**
- **Metal parts of black anodized aluminum.**
- **Linear Scale: 0-5 mm. in 0.1 mm. divisions.**
- **Square Root Scale: From 2 microns to 5 mm.**
- **Accuracy: ± 3% of reading or 1 mm. of scale division whichever is the greater.**
- **Requires approximately 4 ml. of mercury.**

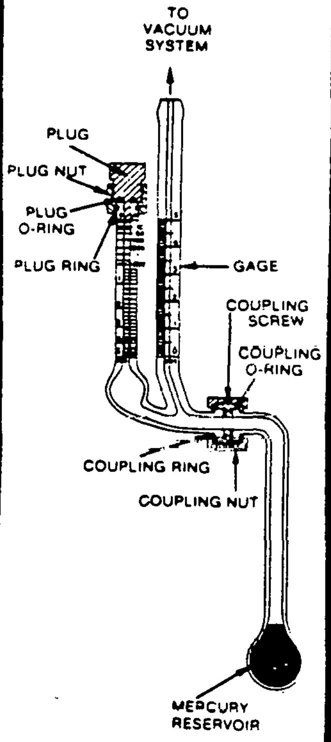
G-1700 Swivel McLeod Gage complete as described above without mercury $49.75

SPARE PARTS LIST

DESCRIPTION	CAT. NO.	PRICE
Glass Part	G-1701	32.30
Gage Glass	G-1701-A	25.50
Reservoir Glass	G-1701-B	6.80
Plug Assembly	G-1702-A	11.15
Consisting of:		
Plug	G-1711	6.25
Plug Nut	G-1712	3.90
Plug Ring	G-1713	1.30
Plug O-ring	G-1721	.65
Coupling Assembly	G-1702-B	11.00
Consisting of		
Coupling Nut (2)	G-1714	3.60
Coupling Ring (2)	G-1715	1.30
Coupling Screw	G-1716	4.40
Coupling O-ring (2)	G-1722	.40



* U.S. Patent No. 3,417,622



REST POSITION

OVERALL DIMENSIONS
5½" x 3½" x ¾"

67N

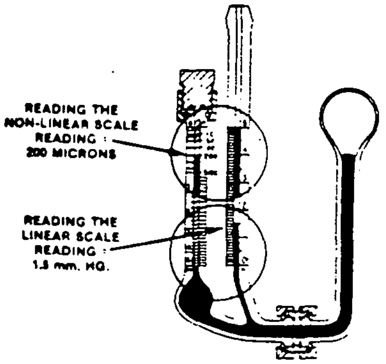
DIRECTIONS

Filling with Mercury—The recommended procedure is to disconnect the coupling assembly and carefully add approximately 4 ml. of clean dry instrument grade mercury to the reservoir bulb. The reservoir bulb with its volume of mercury is reconnected to the coupling as shown in the rest position. The instrument is now ready for mounting and connection to the vacuum system. A standard buret clamp fastened around the coupling assembly is an excellent means of support. It may be found desirable to add or subtract mercury from the reservoir bulb after readings have been made on the non-linear scale. The exact volume of mercury is not critical, however, there should be sufficient quantity present so that when reading the non-linear scale the mercury level in the open capillary can be made to reach the top line.

Reading the Linear Scale—When turning on the vacuum system the gage should be in the rest position. Gases and vapors that may be trapped in the mercury are more readily removed by gently tilting and tapping the reservoir bulb. To read the linear scale after equilibrium has been reached, the reservoir bulb is carefully swiveled beyond its horizontal position until the mercury level in the closed capillary reaches the lowest line as shown. The level of the mercury column is now read in the open capillary. When the reading is less than 1 mm. Hg. a more accurate measurement is obtained by reading the non-linear scale as follows.

Reading the Non-Linear Scale—Continue to swivel the reservoir until it reaches its vertical positon, then carefully adjust the mercury level in the open capillary until it reads at the top line. Gentle tapping of the capillaries will improve the accuracy of the reading, which is taken by the level of the mercury column in the closed capillary. Below 1 mm Hg. the scale is graduated in microns (μ). The minimum reading is 2 μ in which case the meniscus will just make contact with the point of the plug. Accuracy of the readings will be 3% or 1 mm. of scale division whichever is the greater. Thus at 5 mm. the reading is within ±0.15 mm., at 1 mm. within ±0.10 and at 2 μ within ±2 μ. With clean mercury and careful technique, reproducibility should be from 2 to 5 times better than the accuracy.

Cleaning—When the mercury levels in each capillary no longer give reproducible hemispherical menisci, it is time to clean the gage and replace or clean the mercury. Once the coupling and plug assemblies are dismantled the glass parts can be easily and thoroughly cleaned in the usual manner (dilute nitric acid and rinsing with distilled water). Plastic and rubber parts may be cleaned with the usual laboratory detergent solutions. An extremely thin film of silicone grease applied to the O-rings and wiped dry with a rag or tissue will assure a high vacuum seal together with easy operation of the swivel coupling. The glass parts should be thoroughly dried before reassembly at which point the instrument is ready for filling with mercury.



TAKING A READING

Air Products

DATE 1/31/83

TYPICAL VACUUM DISTILLATION

Product: T-102 Bottoms

Lot or I.D. No. 2129CB-0

Calculations

A) Charge & Tare Wt.	268.48	B) Bottoms & Tare Wt.	260.86
Dist Flask Tare Wt.	168.45	Dist. Flask Tare Wt.	168.45
Charge Weight	100.03	Wt. of Bottoms	92.41

C) Wt. of Rec. Flask & Overhead	33.946	D) Wt. of Trap (after Distillation)	183.35
Rec. Flask Tare Wt.	27.142	Trap Tare Wt.	183.35
Overhead Wt.	6.804	Distillate Wt. in Trap	0.00

E) Overhead Wt. 6.804 + Distillate Wt.in Trap 0 = Total Overhead Wt. 6.804

$$\% \text{ Solvent} = \frac{\text{Total Overhead Wt.}}{\text{Charge Wt.}} \quad \frac{6.804}{100.03} \quad \times 100 = 6.80$$

F) Wt.of Bottoms 92.41 + Total Overhead Wt. 6.804 = Total Recovered Wt. 99.214

$$\% \text{ Recovered SRC} = \frac{\text{Total Recovered Wt.}}{\text{Charge Wt.}} \quad \frac{99.214}{100.03} \quad \times 100 = 99.18$$

G) % loss = 100.00 - (% Recovered SRC 99.18) = 0.82

H) Distillation Time: Start 10:15 Finish 11:16 = 61 Minutes

WWS:bas:971
ANA19

Air Products

TYPICAL VACUUM DISTILLATION

Product: T-102 Bottoms

Lot or ID No.: 2129CB-0

Operating Data

Time	Head Temp,°F	Variac Setting (Head)	Column Temp,°F	Variac Setting (Column)	Pot Temp,°F	Variac Setting (Pot)	Pressure μ Hg	Remarks
10:15	74	12	74	12	77	100	50	Heat on LIN in trap
10:20	165	14	225	12	250	90	600	Degassing
10:30	350	14	385	12	400	75	500	"
10:40	440	14	498	13	480	70	200	Condenser water off lamp on ovhd lines
10:45	455	12	500	15	501	65	200	Stirrer on, ovhd in recr. Total take off
10:50	505	14	520	14	525	60	200	Total take off
10:55	532	15	534	10	538	60	250	" "
11:00	555	16	551	12	558	65	300	" "
11:05	573	15	565	14	573	68	400	" "
11:10	585	15	584	14	588	68	500	" "
11:15	598	7	598	7	590	Off	600	Mantle heat off
11:16	600	Off	600	Off	600	Off	700	Stopped distillation

Comments:

International Coal Refining Company

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
MATERIAL SAFETY DATA SHEET

SRC I MATERIAL

SECTION I

SUPPLIER S NAME International Coal Refining Co.	EMERGENCY TELEPHONE NO PA-800-322-9092 Foreign US-800-523-9374 215-481-4911
ADDRESS (NUMBER, STREET, CITY, STATE & ZIP CODE) Mailing: P.O. Box 2752, Allentown, PA 18001;	Location: 2141 Downyflake Ln., Allentown, PA 18103
CHEMICAL NAME & SYNONYMS Solvent Refined Coal, SRC, SRC Solid	TRADE NAMES & SYNONYMS NA.
CHEMICAL FAMILY Coal derived vacuum residue	FORMULA Mixture
CAS NUMBER 68409-94-9	TSCA REGISTRY ENTRY 30814040

SECTION II - HAZARDOUS INGREDIENTS

MATERIALS	%	TLV (Units)	MATERIALS	%	TLV (Units)
SRC Dust		2 mg/m^3			

Should significant fumes or vapors be generated from SRC in molten form, it is suggested that the airborne exposure of 0.2 mg/m^3, as benzene solubles, be observed. See sections V and IX.

DOT HAZARD CLASS: Excepted from regulations

SECTION III - PHYSICAL DATA

BOILING POINT °C (°F) >454°C (850°F)	SPECIFIC GRAVITY (H_2O = 1) 15.6°C / 15.6°C 1.2
VAPOR PRESSURE (mm Hg.) <1	VOLATILES, VOLUME PERCENT (%) Negligible
VAPOR DENSITY (AIR = 1) ND	EVAPORATION RATE Negligible
SOLUBILITY IN WATER Negligible	Softening point: 155°C (310°F)

APPEARANCE AND ODOR
Black, shiny, pitchlike solid; odorless

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT >300°C (572°F) open cup	FLAMMABLE LIMITS LEL ND UEL ND

EXTINGUISHING MEDIA
☐ ALCOHOL FOAM ☒ CARBON DIOXIDE ☒ DRY CHEMICAL ☒ FOAM ☒ WATER SPRAY (FOG)
☐ OTHER

SPECIAL FIRE FIGHTING PROCEDURES

Material may become liquid during fire. Wear self-contained breathing apparatus for fires in enclosed or confined spaces.

FIRE AND EXPLOSION HAZARDS

Explosion hazard when SRC dust is in contact with an ignition source.

NA = Not Applicable ND = No Data Available

Modified Form OSHA-20
11/81 REV. 0

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
Respirable Mass: 2.0 mg/m^3. See Section II.

EFFECTS OF OVEREXPOSURE
Dist and fumes may cause minor irritation to the eyes and lungs. Minor irritation and dermatitis may occur after prolonged or repeated skin contact. Prolonged or repeated exposure to SRC dust and fumes may lead to more serious pulmonary and skin disorders.

EMERGENCY AND FIRST AID PROCEDURES INHALATION: Remove to fresh air. If breathing is difficult, give oxygen and call for medical assistance. EYE CONTACT: Flush eyes immediately with copious amounts of water or mineral oil. Call a physician. SKIN CONTACT: Wash thoroughly with soap and water or waterless hand cleaner. Avoid solvents. INGESTION: Induce vomiting, then give 2 tablespoons of activated charcoal USP in water. Call medical assistance.

SECTION VI - REACTIVITY DATA

STABILITY Stable
CONDITIONS TO AVOID NA
INCOMPATABILITY (Materials to avoid) Strong oxidants
HAZARDOUS DECOMPOSITION PRODUCTS
Fumes, smoke, carbon monoxide, and sulfur oxides, in the case of incomplete combustion.
HAZARDOUS POLYMERIZATION Will not occur.
CONDITIONS TO AVOID NA

SECTION VII - SPILL OR LEAK PROCEDURES

☐ EVACUATE AREA
☐ STOP FLOW
☐ ELIMINATE ALL SOURCES OF IGNITION FLAMMABLES
☒ AVOID INHALATION
☒ AVOID DERMAL CONTACT
☒ RESPIRATORY PROTECTION (AS PER SECTION VIII)
☒ SKIN PROTECTION (AS PER SECTION VIII)
☐ ABSORB OR SCRAPE UP
☒ VACUUM UP
☐ EVAPORATE SMALL AMOUNTS IN HOOD
☒ INCINERATE UNDER CONTROLLED CONDITIONS
☐ INCINERATE USING AFTER BURNER & SCRUBBER
☐ BURY IN REMOTE AREA OR USE AS LANDFILL
☐ NEUTRALIZE AND WASH AWAY WITH WATER
☒ OBSERVE GOVERNMENTAL SPILL & WATER QUALITY REGULATIONS
☐ REMOVE SOILED CLOTHING
☐ OTHER

SECTION VIII - SPECIAL PROTECTION INFORMATION

	DURING NORMAL USE	FOR GASES, VAPORS, DUSTS, FUMES, MISTS EXCEEDING TLV	SPECIAL (E.G. THERMAL PROCESSING, SPRAY APPLICATIONS)
GENERAL VENTILATION	Recommended	Recommended	NA
LOCAL EXHAUST	Not required	Yes	NA
RESPIRATORY PROTECTION (1-3)	Not required	1, if needed	NA

1. Particle-Removing Air Purifying Air Respirator (Mechanical Filter)
2. Gas and Vapor-Removing Air Purifying Respirator (Canister)
3. Full Face Mask Positive Pressure-Demand Type Supplied Air

EYE PROTECTION	SAFETY GLASSES		CHEMICAL GOGGLES	X	FACE SHIELD	
PROTECTIVE GLOVES	NEOPRENE	G	POLYVINYL ALCOHOL	G	POLYETHYLENE	F
	NATURAL RUBBER	G	BUTYL RUBBER	G	POLYVINYL CHLORIDE	F

(E) EXCELLENT
(G) GOOD
(F) FAIR
(P) POOR
(NR) NOT RECOMMENDED

OTHER PROTECTIVE EQUIPMENT Full long-sleeved clothing closed at the neck.

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING Avoid prolonged and repeated skin and eye contact with dust and fumes. Avoid inhalation of dust and fumes. Maintain good ventilation. Showering and clothing change recommended after each shift. This material is a brittle solid so dusting may occur. Finely divided SRC dust presents a strong explosion hazard.

NOTICE

The data and recommendations presented herein are based upon our research and the research of others, and are believed to be accurate; however, no guarantee of their accuracy is made. The products discussed are distributed without warranty, express or implied, and the person receiving them shall make his own determination of the suitability thereof for his particular purpose.

FOR TRANSPORTATION SPILLS OR LEAK EMERGENCIES, CALL: CHEMTREC - 800-424-9300 (CHEMICAL TRANSPORTATION EMERGENCY CENTER).

International Coal Refining Company

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
MATERIAL SAFETY DATA SHEET

SRC I MATERIAL

SECTION I

SUPPLIER'S NAME International Coal Refining Co.	EMERGENCY TELEPHONE NO. PA-800-322-9092 Foreign US-800-523-9374 215-841-4911
ADDRESS (NUMBER, STREET, CITY, STATE & ZIP CODE) Mailing: P.O. Box 2752, Allentown, PA 18001 Location: 2141 Downyflake Lane, Allentown, PA 18103	
CHEMICAL NAME & SYNONYMS Solvent Refined Coal-I (SRC-I) Process Solvent: Recycle Solvent	TRADE NAMES & SYNONYMS NA
CHEMICAL FAMILY Coal derived aromatic distillate	FORMULA Mixture
CAS NUMBER 68410-08-2	TSCA REGISTRY ENTRY 30814057

SECTION II - HAZARDOUS INGREDIENTS

MATERIALS	%	TLV (Units)	MATERIALS	%	TLV (Units)
Phenols and Cresols	20-40	5 ppm			
Benzene	<1	10 ppm			

The health hazards, particularly skin lesions (including skin cancer) associated with coal liquefaction processes are recognized as potential health problems. Also the chemical composition is such that the possibility of causing cancer at other body sites, and of other health hazards such as fetotoxicity, cannot be ruled out. It is strongly recommended that inhalation and skin exposure be kept to a minimum and that all recommended precautions be observed when handling this material. See Sections V and IX.

DOT HAZARD CLASS: Excepted from regulations

SECTION III - PHYSICAL DATA

BOILING POINT °C (°F) 232-454°C (450-850°F)	SPECIFIC GRAVITY (H_2O = 1) 15.6°C / 15.6°C 1.06
VAPOR PRESSURE (mm Hg.) 0 psia (Reid)	VOLATILES, VOLUME PERCENT (%) ND
VAPOR DENSITY (AIR = 1) ND	EVAPORATION RATE ND
SOLUBILITY IN WATER Negligible	
APPEARANCE AND ODOR Amber to black oil; faint oily odor	

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT 121°C (250°F) closed cup	FLAMMABLE LIMITS: LEL ND UEL ND

EXTINGUISHING MEDIA
☐ ALCOHOL FOAM ☒ CARBON DIOXIDE ☒ DRY CHEMICAL ☒ FOAM ☒ WATER SPRAY (FOG)
☐ OTHER

SPECIAL FIRE FIGHTING PROCEDURES Treat as Class B fire. Use water spray to keep fire-exposed containers cool, flush spills away from fire exposure, and to disperse vapors. Wear self-contained breathing apparatus for fires in enclosed or contained spaces. This material sinks in water.

FIRE AND EXPLOSION HAZARDS Combustible. Heating this material to its flash point is likely to give sufficient vapors for ignition upon exposure to flame or incendiary sparks.

NA = Not Applicable ND = No Data Available

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE Suggested guideline for airborne exposure to coal derived materials: 0.2 mg/m^3 as benzene solubles. See Section II

EFFECTS OF OVEREXPOSURE Irritating to eyes and lungs. Minor irritation and dermatitis may occur after prolonged or repeated skin contact. Although the inhalation hazard is low due to the relatively low volatility of the products, inhalation of mists or vapors released upon heating should be avoided. Prolonged and repeated exposure in the absence of proper hygiene practices may lead to serious skin disorder and possibly skin cancer.

EMERGENCY AND FIRST AID PROCEDURES INHALATION: Remove to fresh air. If breathing is difficult, give oxygen and call for medical assistance. EYE CONTACT: Flush eyes immediately with copious amounts of water or mineral oil. Call a physician. SKIN CONTACT: Wash thoroughly with soap and water or waterless hand cleaner. Avoid solvents. INGESTION: Induce vomiting then give 2 tablespoons of activated charcoal USP in water. Call medical assistance.

SECTION VI - REACTIVITY DATA

STABILITY Stable

CONDITIONS TO AVOID

INCOMPATABILITY (Materials to avoid) Strong oxidants

HAZARDOUS DECOMPOSITION PRODUCTS Fumes, smoke, carbon monoxide, and sulfur oxides, in the case of incomplete combustion.

HAZARDOUS POLYMERIZATION Will not occur.

CONDITIONS TO AVOID

SECTION VII - SPILL OR LEAK PROCEDURES

☐ EVACUATE AREA
☒ STOP FLOW
☐ ELIMINATE ALL SOURCES OF IGNITION, FLAMMABLES
☒ AVOID INHALATION
☒ AVOID DERMAL CONTACT
☐ RESPIRATORY PROTECTION (AS PER SECTION VIII)
☒ SKIN PROTECTION (AS PER SECTION VIII)
☒ ABSORB OR SCRAPE UP
☐ VACUUM UP
☐ EVAPORATE SMALL AMOUNTS IN HOOD
☒ INCINERATE UNDER CONTROLLED CONDITIONS
☐ INCINERATE USING AFTER BURNER & SCRUBBER
☐ BURY IN REMOTE AREA OR USE AS LANDFILL
☐ NEUTRALIZE AND WASH AWAY WITH WATER
☒ OBSERVE GOVERNMENTAL SPILL & WATER QUALITY REGULATIONS
☒ REMOVE SOILED CLOTHING
☐ OTHER

SECTION VIII - SPECIAL PROTECTION INFORMATION

	DURING NORMAL USE	FOR GASES, VAPORS, DUSTS, FUMES, MISTS EXCEEDING TLV	SPECIAL (E.G. THERMAL PROCESSING SPRAY APPLICATIONS)
GENERAL VENTILATION	Yes	Yes	NA
LOCAL EXHAUST	Preferred	Yes	NA
RESPIRATORY PROTECTION (1-3)	Not Required	1 & 2, if needed	NA

1. *Particle-Removing Air Purifying Air Respirator (Mechanical Filter)*
2. *Gas and Vapor-Removing Air Purifying Respirator (Canister)*
3. *Full Face Mask Positive Pressure-Demand Type Supplied Air*

EYE PROTECTION	SAFETY GLASSES		CHEMICAL GOGGLES	X	FACE SHIELD		*(E) EXCELLENT* *(G) GOOD*
PROTECTIVE GLOVES	NEOPRENE	G	POLYVINYL ALCOHOL	NR	POLYETHYLENE	NR	*(F) FAIR* *(P) POOR*
	NATURAL RUBBER	P	BUTYL RUBBER	NR	POLYVINYL CHLORIDE	NR	*(NR) NOT RECOMMENDED*

OTHER PROTECTIVE EQUIPMENT Wear full, long-sleeved clothing closed at the neck. The application of a skin barrier cream before work is recommended.

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING: Avoid skin and eye contact and inhalation of mists or vapors. Maintain good ventilation. Empty drums may contain flammable hydrocarbon vapors. Wash out drums with water before discarding. Upon standing or being cooled a foul-smelling mercaptan water layer may settle out. This layer should be discarded before use. Showering and clothing change recommended after each shift.

NOTICE

The data and recommendations presented herein are based upon our research and the research of others, and are believed to be accurate; however, no guarantee of their accuracy is made. The products discussed are distributed without warranty, express or implied, and the person receiving them shall make his own determination of the suitability thereof for his particular purpose.

FOR TRANSPORTATION SPILLS OR LEAK EMERGENCIES, CALL: CHEMTREC - 800-424-9300 (CHEMICAL TRANSPORTATION EMERGENCY CENTER).

International Coal Refining Company

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
MATERIAL SAFETY DATA SHEET

SRC I MATERIAL 1/81

SECTION I

MANUFACTURER'S NAME International Coal Refining Co.	EMERGENCY TELEPHONE NO PA – 800-322-9092 Foreign – US – 800-523-9374 215-481-4911
ADDRESS (NUMBER STREET CITY STATE & ZIP CODE) Box 2752, Allentown, PA 18001	
CHEMICAL NAME & SYNONYMS Light Oil, Naphtha	TRADE NAMES & SYNONYMS Light Oil
CHEMICAL FAMILY Coal derived aromatic naphtha	FORMULA NA
CAS NUMBER 68476-79-9	TSCA REGISTRY ENTRY 30814099

SECTION II - HAZARDOUS INGREDIENTS

MATERIALS	%	TLV (Units)	MATERIALS	%	TLV (Units)
Light Oil Naphtha	99+	•	Hydrogen Sulfide	<0.1	10 ppm
Phenols and Cresols	5-10	5 ppm	Benzene	<1.0	10 ppm

DOT HAZARD CLASS: Flammable liquid

SECTION III - PHYSICAL DATA

BOILING POINT (°C / °F)	60-193°C (140-380°F)	SPECIFIC GRAVITY (H_2O = 1) 15.6° / 15.6°C	0.85
VAPOR PRESSURE (mm Hg)	ND	PERCENT VOLATILE BY VOLUME (%)	99
VAPOR DENSITY (AIR = 1)	ND	EVAPORATION RATE	ND
SOLUBILITY IN WATER	Negligible		
APPEARANCE AND ODOR	Colorless to dark amber (darkens with age and air contact)		

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT -35.6°C (-32°F) closed cup	FLAMMABLE LIMITS ND	LEL	UEL

EXTINGUISHING MEDIA
☐ ALCOHOL FOAM ☒ CARBON DIOXIDE ☒ DRY CHEMICAL ☒ FOAM ☒ WATER SPRAY (FOG)
☐ OTHER

SPECIAL FIRE FIGHTING PROCEDURES

Treat like gasoline or light petroleum naphtha. Floats on water. Use water to cool fire-exposed containers, disperse vapors, and protect personnel. Use air-supplied rescue equipment for enclosed areas.

FIRE AND EXPLOSION HAZARDS

Highly volatile and flammable. Material can be ignited by flame or incendiary sparks under almost all normal atmospheric temperature conditions due to its low flash point.

NA = Not Applicable ND = No Data Available

Modified Form OSHA-20

LIGHT OIL

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE See Section II.

EFFECTS OF OVEREXPOSURE

Irritating to eyes, lungs, and skin. Depending on the intensity and duration of exposure, effects may vary from mild irritation to systemic toxicity due to the presence of phenolic compounds. High concentrations of H_2S in an enclosed space will produce central nervous system depression, unconsciousness and death.

EMERGENCY AND FIRST AID PROCEDURES

EYE CONTACT: Treat by immediate and prolonged flushing with water. Obtain medical assistance at once. SKIN CONTACT: Flush the affected area with large quantities of water, followed by an application of skin oil. INHALATION: Remove from exposure, apply artificial respiration if necessary. INGESTION: DO NOT INDUCE VOMITING. Give 1-2 ounces of activated charcoal if available followed by 1-2 glasses of milk. Obtain immediate medical aid.

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		STABLE	X	CONDITIONS TO AVOID
HAZARDOUS POLYMERIZATION	MAY OCCUR		WILL NOT OCCUR	X	CONDITIONS TO AVOID

INCOMPATABILITY (Materials to avoid) Reacts with strong oxidizing materials

HAZARDOUS DECOMPOSITION PRODUCTS When heated to decomposition, it may emit irritating and toxic fumes

SECTION VII - SPILL OR LEAK PROCEDURES

☐ EVACUATE AREA

☒ STOP FLOW

☒ ELIMINATE ALL SOURCES OF IGNITION, FLAMMABLES

☒ AVOID INHALATION

☒ AVOID DERMAL CONTACT

☒ RESPIRATORY PROTECTION (AS PER SECTION VIII)

☒ SKIN PROTECTION (AS PER SECTION VIII)

☒ ABSORB OR SCRAPE UP

☐ VACUUM UP

☐ EVAPORATE SMALL AMOUNTS IN HOOD

☒ INCINERATE UNDER CONTROLLED CONDITIONS

☐ INCINERATE USING AFTER BURNER & SCRUBBER

☐ BURY IN REMOTE AREA OR USE AS LANDFILL

☐ NEUTRALIZE AND WASH AWAY WITH WATER

☒ OBSERVE GOVERNMENTAL SPILL & WATER QUALITY REGULATIONS

☒ REMOVE SOILED CLOTHING

☐ OTHER

SECTION VIII - SPECIAL PROTECTION INFORMATION

	DURING NORMAL USE	FOR GASES, VAPORS, DUSTS, FUMES, MISTS EXCEEDING TLV	SPECIAL (E.G. THERMAL PROCESSING, SPRAY APPLICATIONS)
GENERAL VENTILATION	Yes	Yes	
LOCAL EXHAUST	Yes	Yes	
RESPIRATORY PROTECTION (1-3)		2, if needed	3, large spills

1. Particle-Removing Air Purifying Air Respirator (Mechanical Filter) *2. Gas and Vapor-Removing Air Purifying Respirator (Canister)* *3. Full Face Mask Positive Pressure-Demand Type Supplied Air*

EYE PROTECTION	SAFETY GLASSES		CHEMICAL GOGGLES	X	FACE SHIELD		*(E) EXCELLENT*
PROTECTIVE GLOVES	NEOPRENE	G	POLYVINYL ALCOHOL	NR	POLYETHYLENE	NR	*(G) GOOD* *(F) FAIR*
	NATURAL RUBBER	P	BUTYL RUBBER	NR	POLYVINYL CHLORIDE	NR	*(P) POOR* *(NR) NOT RECOMMENDED*

OTHER PROTECTIVE EQUIPMENT The application of a skin barrier cream before work and several times during work is recommended.

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING

Avoid skin and eye contact. Avoid the inhalation of mists, fumes, or vapors. Maintain good ventilation. Flammable hydrocarbons, empty drums may contain flammable vapors. Wash out drums with water before discarding. May dissolve most plastics and rubbers. Do not transfer lines or storage vessels made of these materials. Upon standing or being cooled a sour, obnoxious-smelling mercaptan water layer may settle out. This layer should be discarded before use.

NOTICE

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ASTM/WET LABORATORY PROCEDURES

SOFTENING POINT OF BITUMEN
(RING-AND-BALL APPARATUS)
(ASTM D 36)

The procedure is applicable to coke and coke samples as written. It is recommended that a glycerin temperature bath be used, since it can be used to cover a large temperature range. Initial heating of sample to prepare test specimens must be completed slowly to avoid overheating at localized areas.

Safety

Grinding of any coal, coke or KMAC must be completed in a well-ventilated area and the analyst be required to wear a lab coat and dust mask. See the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet located in the front section of the manual for special precautions when handling SRC KMAC.

Place the glycerin temperature bath in a well-ventilated area and avoid inhalation of hot vapors. Use protective equipment when working near temperatures of 100°C.

SAYBOLT VISCOSITY

(ASTM D 88)

This procedure is applicable to SRC-1 H.O. as written. ASTM D'445, a kinematic viscosity procedure, is to be used when analyzing SRC-1 L.O. and M.O. The value can be converted to kinematic viscosity values by using ASTM D 2161. H.O. usually require temperatures above 100°F to flow through either the Universal or Furol orifice.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Wear protective equipment when working at temperatures above 60°C.

FLASH POINT BY PENSKY-MARTENS CLOSED TESTER
(ASTM D 93)
OR
FLASH POINT BY SETAFLASH CLOSED TESTER
(ASTM D 3828)

ASTM D 93 and Method B of ASTM D 3828 can be used for all SRC-1 liquids as written. Previously observed flash points are <-30°C, 100°C and >110°C for L.O., M.O. and H.O., respectively.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Complete flash point analyses in a well-ventilated area. Keep organic vapors away from open flames.

POUR POINT OF PETROLEUM OILS

(ASTM D 97)

The procedure is applicable to SRC-1 M.O. and H.O. as written. The L.O. was always pourable at -80°F (-60°C), which is the low temperature reached when using a slurry of solid carbon dioxide and acetone. Results are variable, but most M.O. and H.O. pour points occur between 32 and -34°C or by using Procedure 5.3.1.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Cold resistent gloves must be worn when handling solid carbon dioxide.

DETECTION OF COPPER CORROSION FROM PETROLEUM PRODUCTS BY THE COPPER STRIP TARNISH TEST

(ASTM D 130)

The method applies to all SRC-1 liquids when using the natural gasoline conditions. The polished copper strip is immersed in the sample at 40°C for three hours before comparison to ASTM Copper Strip Corrosion Standards. The wash solvent may be either toluene or a mixture of xylene isomers.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Avoid inhalation of wash solvent and use in a well-ventilated area. Keep organic vapors from open flames.

CONRADSON CARBON RESIDUE OF PETROLEUM PRODUCTS
(ASTM D 189)

The procedure is applicable to all SRC-1 liquids and blends as written. SRC-1 L.O. and M.O. samples have less than 0.10 wt% (1000 ppm) carbonaceous residue formed after evaporation and pyrolysis. H.O. samples generally contain greater than 1.0 wt% residue after the same treatment.

Safety

SRC liquids and related material should be treated as toxic material. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Apply the destructive distillation in a well-ventilated area. Use appropriate protective equipment when working with hot crucibles and avoid contact of hot surfaces with skin.

VAPOR PRESSURE OF PETROLEUM PRODUCTS
(REID METHOD)
(ASTM D 323)

This method is applicable to SRC-1 naphtha as written. The method is not recommended for analysis of viscous petroleum products or liquefied petroleum gases.

Safety

SRC-1 liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

EXISTENT GUM IN FUELS BY JET EVAPORATION
(ASTM D 381)

The procedure is applicable to SRC-1 naphtha as written. Operating conditions recommended for naphtha are the same as those for aircraft turbine fuel which appear in Table 2 of the procedure.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Heptane is very volatile and must be handled in a well-ventilated area away from open flames.

Wear protective equipment and avoid skin contact with open hot surfaces of the drying oven and air-jet apparatus.

KINEMATIC VISCOSITY OF TRANSPARENT AND OPAQUE LIQUIDS
(and the Calculation of Dynamic Viscosity)
(ASTM D 445)

The procedure is applicable to SRC-1 L.O. and M.O. as written. ASTM D 88 (Saybolt Viscosity) is recommended when analyzing SRC-1 H.O.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

When analyzing samples at elevated temperatures avoid skin contact with hot surfaces and samples.

ASH FROM PETROLEUM PRODUCTS

(ASTM D 482)

This method covers the determination of ash in SRC-1 L.O., M.O. and H.O. as written. A platinum dish is recommended for the procedure if the ash is to be further analyzed (metal analysis). A sample weight of 50-100 grams is needed to obtain sufficient ash to weigh.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Wear protective clothing when working near temperatures of 775°C.

NEUTRALIZATION NUMBER BY POTENTIOMETRIC TITRATION
(ASTM D 664)

The method applies to all SRC liquids as written, although an automatic titrator can be used in place of the manual titration procedure.

All SRC liquids typically contain high base numbers. No precision and accuracy values were determined, but duplicate analyses of naphtha samples with a base number between 2.00 and 7.00 mg KOH/g sample did not vary above 0.10. Higher density SRC liquids contained base numbers between 18 and 30 mg KOH/g sample and duplicate analyses did not vary by more than 0.5.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

FREE-SWELLING INDEX OF COAL
(ASTM D 720)

The method applies to LSRC, HSRC and TSL SRC as written. Grind enough material to produce five grams of working sample.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Grinding of solid samples should be completed in a well-ventilated area and a dust mask must be worn by the analyst.

Wear appropriate protective equipment when working near a hot burner or furnace.

DENSITY AND RELATIVE DENSITY (SPECIFIC GRAVITY)
OF LIQUIDS BY LIPKIN BICAPILLARY PYCNOMETER
(ASTM D 941)

The bicapillary Lipkin pycnometer density Procedure A is applicable to SRC-1 L.O. and M.O. The temperature at which the specific gravities are obtained is 60°F.

To speed the filling of the pycnometer, a vacuum line is attached to a capillary column while the other end is immersed in the sample. DO NOT turn on vacuum until the capillary column is immersed in the sample.

Specific gravity results are reported to the nearest 0.0001 and have a precision of ±0.02% relative standard deviation.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

BROMINE NUMBER OF PETROLEUM DISTILLATES AND COMMERCIAL ALIPHATIC OLEFINS BY ELECTROMETRIC TITRATION

(ASTM D 1159)

The bromine number results can be misinterpreted when equated to the olefin content of a sample because of the interfering substances in SRC liquids. Therefore, the procedure is appropriate for only the SRC hydrotreated naphtha. The precision and accuracy of the procedure are unknown for hydrotreated naphtha.

Safety

SRC hydrotreated naphtha should be treated as a toxic material and only used in a well-ventilated area. Gloves and protective outerwear must be worn by the analyst.

Methanol is a volatile flammable chemical and should be used in a well-ventilated area away from all open flames.

DENSITY, SPECIFIC GRAVITY OR API GRAVITY OF CRUDE PETROLEUM AND LIQUID PETROLEUM PRODUCTS BY HYDROMETER METHOD

(ASTM D 1298)

The procedure is applicable to all SRC-1 liquids and blends as written.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

SMOKE POINT OF AVIATION TURBINE FUELS
(ASTM D 1322)

The procedure is applicable to all SRC-1 liquids and blends as written. The wicks were extracted with toluene and methanol at a vigorous rate for a period of time no less than 16 hours.

Safety

SRC liquids and related material should be treated as gas toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Complete extraction of wicks in a well-ventilated area and keep hot methanol and toluene away from open flames. Avoid inhalation of hot organic vapors.

MERCAPTAN SULFUR IN AVIATION TURBINE FUELS
(AMPEROMETRIC AND POTENTIOMETRIC METHODS)
(ASTM D 1323)

The potentiometric procedure applies to SRC naphtha M.O. and H.O. as written, although to obtain results in the detectable range, a smaller sample than is designated by the method is analyzed. One gram of SRC liquid is generally required for obtaining results in the detectable range. Hydrotreated liquids require the sample size specified in the procedure.

A solution of cadmium chloride can be used in place of cadmium sulfate to remove hydrogen sulfide from SRC liquids.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing. For

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Isopropyl alcohol is flammable and should be kept away from open flames.

ASTM COLOR OF PETROLEUM PRODUCTS
(ASTM COLOR SCALE) (ASTM D 1500)

The procedure is applicable to all SRC-1 liquids and blends as written.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

If solvent kerosine is used as a diluent, keep away from open flames and avoid inhalation of vapors.

WATER AND SEDIMENT IN CRUDE OILS BY CENTRIFUGE
(ASTM D 1796)

The procedure is applicable to SRC-1 L.O., M.O. and H.O. as written. L.O. and M.O. were found to contain less than 0.05 milliliters of water and sediment for a 50 milliliter sample. H.O. were found to contain a trace quantity of water and sediment, but usually less than 0.1 milliliters.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Do not attempt to stop centrifuge with hands or any other object.

FUSIBILITY OF COAL AND COKE ASH
(ASTM D 1857)
ALSO, SINTERING TEMPERATURE

The method is applicable to coal, coke, LSRC and HSRC as written. Thermomechanical analysis (TMA) is used to determine the fusion (melting) point of the samples. The experiments are run under an inert atmosphere (nitrogen) and not an oxidizing or reducing atmosphere.

A sample of SRC is ground and screened to obtain a sample of uniform particle size. Part of the sample is placed in the apparatus under a 5-g load and heated at a constant rate through the temperature range that initiates the first dimensional change of the sample. The instrument is placed on isothermal hold for several minutes; then the condition of the sample is visually observed to determine whether it has fused into a solid disk. If not, a fresh sample is analyzed with the isothermal hold temperature raised several degrees. If the sample has already fused, the isothermal hold temperature is lowered.

The sintering temperature of LSRC and HSRC can also be determined by TMA. The SRC sintering temperature has been defined as the temperature at which SRC can no longer be ground or when SRC first undergoes a dimensional change under the sintering temperatures; a test procedure is needed to measure this property.

The analytical method used for this test is thermomechanical analysis (TMA), which measures dimensional changes in a sample as its temperature is increased at a constant rate, while under load. A sample of SRC is ground up, and a screened, uniformly sized portion of the sample is placed in the apparatus under a 5-g load. The temperature is increased at a uniform rate. When the sample changes from a glossy, brittle solid to a soft, amorphous mass, its change in volume is automatically recorded. Preliminary work with this method indicates that this critical temperature is reproducible to about ±2°C.

Safety

Grinding of any coal, coke, KMAC, LSRC and HSRC must be completed in a well-ventilated area and the analyst be required to wear a lab coat and dust mask. See the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet located in the front section of the manual for special precautions when handling SRC KMAC.

Wear protective equipment when working near temperatures of 800 to 900°C.

CONVERSION OF KINEMATIC VISCOSITY TO SAYBOLT UNIVERSAL VISCOSITY OR TO SAYBOLT FUROL VISCOSITY

(ASTM D 2161)

The conversion procedure is used to convert results obtained from method ASTM D 445, kinematic viscosity values, to Saybolt Universal viscosity in Saybolt Universal seconds.

BENZENE-INSOLUBLE (BI) CONTENT OF TAR AND PITCH
(ASTM D 2317)

The method applies to LSRC, HSRC and TSL SRC with a slight modification. The extraction apparatus shown in Figure 1 of the procedure is replaced by the extraction set-up shown in Figure 2. The alundum thimble is held 25 mm above the hot benzene by a 0.64 mm diameter copper wire attached to a condensor and holes drilled in the thimble.

No precision and accuracy data was accumulated for SRC solids, but duplicate determinations by the same operator did not vary by more than 0.5 wt% if the sample contained between 10 and 15 wt% BI material.

Safety

SRC solids and related material should be treated as toxic chemicals. Gloves and a lab coat must be worn to protect hands and clothing. Grinding of samples must be done in a hood and a dust mask worn by the analyst.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Avoid inhalation of hot benzene vapors.

QUINOLINE-INSOLUBLE (QI) CONTENT OF TAR AND PITCH
(ASTM D 2318)

The procedure applies to LSRC, HSRC and TSL SRC as written. No precision and accuracy data is available for SRC material, because only low levels (<1.0 wt%) of QI material were found in the SRC samples analyzed. A working sample between 5-10 grams is adequate when working at the low detection limit of the procedure. A value of <0.2 wt% is reported when no QI material is found in the SRC sample.

Safety

SRC solids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Grinding of SRC solids must be completed in a well-ventilated area and a dust mask worn by the analyst. Do not inhale hot quinoline vapors and perform all washings in a hood. Benzene is a carcinogenic chemical and contact with skin or inhalation of vapors must be avoided.

FREEZING POINT OF AVIATION FUELS

(ASTM D 2386)

This method is applicable to SRC naphtha, M.O. and H.O. as written. The recommended coolant is finely crushed solid carbon dioxide and acetone which are added in the proper proportions to form a slurry.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

The coolant bath is extremely cold (-78°C) and care must be taken not to expose unprotected parts of the body to this temperature.

FORMS OF SULFUR IN COAL
(ASTM D 2492)

This method covers the determination of three commonly recognized forms of sulfur in coal: sulfate sulfur, pyritic sulfur and organic sulfur. The method is applicable to coal, coke and KMAC as written. The pyritic sulfur is determined by the titration with standard 0.05 N potassium permanganate solution procedure.

Safety

Grinding of any coal, coke or KMAC must be completed in a well-ventilated area and the analyst be required to wear a lab coat and dust mask. See the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet located in the front section of the manual for special precautions when handling SRC KMAC.

Care must be taken when handling concentrated acids and bases to avoid contact with skin or inhalation of vapors. Keep hydrogen peroxide away from oxidizable materials and store in a cold atmosphere.

COMPATIBILITY OF FUEL OIL BLENDS BY SPOT TEST
(ASTM D 2781)

The procedure applies to SRC-1 liquids and blends as written. For L.O. and M.O. samples, ratings of 1 and 1 to 3 are found, respectively. H.O. samples have compatibility ratings near 5.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

PROXIMATE ANALYSIS OF COAL AND COKE
(ASTM D 3172)

The procedures for the analysis of moisture, ash and volatile matter are discussed separately. The procedure is not used for classification of coal by rank; therefore, strict adherence to sample collection and preparation is not required.

The fixed carbon content of coal, coke or SRC solids is calculated by the equation given in the method. It should be noted that the fixed carbon value incorporates all the errors involved in each separate analysis. This will adversely affect the precision of the reported value.

MOISTURE IN THE ANALYSIS SAMPLE OF COAL AND COKE
(ASTM D 3173)

The method is applicable to coal or coke samples as written. The procedure is also used for the analysis of HSRC, LSRC and TSL SRC with a slight modification. In place of a current of air passing through the sulfuric acid (used as a desiccant) and oven, use an inert gas: nitrogen is recommended. The SRC-1 solids oxidize in air and this will cause a weight increase. Avoid use of any perchlorate as a desiccant.

Grind enough material to produce five grams of working sample.

The moisture level found in HSRC or SRC TSL is typically less than 0.1 wt% (1000 ppm). LSRC contains less than 0.5 wt% (500 ppm) moisture. Results are considered suspect if duplicate results by the same analyst differ by more than ±0.02 wt% in the 0.5 to 0.1 wt% range.

Safety

Grinding of any coal, coke or SRC-1 solid must be completed in a well-ventilated area and the analyst be required to wear a lab coat and dust mask. See the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet located in the front section of the manual for special precautions when handling SRC solid.

When handling concentrated sulfuric acid, care must be taken to avoid contact with skin. Also, use protective equipment when working near hot oven.

ASH IN THE ANALYSIS SAMPLE OF COAL AND COKE
(ASTM D 3174)

This method is applicable to coal, coke, LSRC, HSRC or TSL SRC as written. Since LSRC and HSRC typically contain less than 0.1 wt% ash and TSL SRC less than 0.05 wt% ash the use of a five gram sample is recommended. Porcelain capsules are used for analysis, unless further testing is required (metal determination); then a platinum crucible should be used.

Grind enough material to produce twenty grams of working sample if each analysis requires five grams.

Safety

Grinding of any coal, coke or SRC-1 solid must be completed in a well-ventilated area and the analyst be required to wear a lab coat and dust mask. See the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet located in the front section of the manual for special precautions when handling SRC solid.

Wear protective clothing when working near temperatures of 750°C.

VOLATILE MATTER IN THE ANALYSIS SAMPLE OF COAL AND COKE
(ASTM D 3175)

This method is applicable to coal, coke, LSRC, HSRC and TSL SRC as written. SRC-1 solids did not spark during heating so the conditions in Procedure 6.1 are used for analysis. Volatile matter results for HSRC, LSRC and TSL SRC are found to be between 60-70, 82-87 and 70-80 wt%, respectively. Results between 60-90 wt% are considered suspect if duplicate results by the same analyst differ by more than ±0.4 wt% volatile matter.

Safety

Grinding of any coal, coke or SRC-1 solid must be completed in a well-ventilated area and the analyst be required to wear a lab coat and dust mask. See the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet located in the front section of the manual for special precautions when handling SRC solid.

Wear protective clothing when working near temperatures of 950°C.

THERMAL OXIDATION STABILITY OF AVIATION TURBINE FUELS
(JFTOT PROCEDURE)
(ASTM D 3241)

This procedure applies to L.O., M.O. and H.O. as written. L.O. samples previously analyzed had a deposit rating of +4 at 254 mm Hg.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

SPECIFIC GRAVITY BY MEANS OF A WALKER TYPE PYCNOMETER
(APCI METHOD NO. 20)

This method is applicable to LSRC, HSRC, and SRC-1 H.O., which is too viscous to measure by a bicapillary Lipkin pycnometer. Use procedure 5-B entitled "For Solids and Semisolids".

If the sample can not be heated to produce a fluid, the solid material can be placed directly in the pycnometer using the largest pieces available (the sample must be water insoluble). Specific gravity results obtained in this fashion are referred to as bulk densities, because of the random air bubbles in the solid sample. This procedure should be completed in duplicate and the values should not differ by more than ±0.002.

Safety

SRC solids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

SPECIFIC GRAVITY BY MEANS OF A WALKER TYPE PYCNOMETER

1. SCOPE:

This method is intended for the determination of the specific gravity of liquid petroleum products when greater accuracy is required or when the hydrometer is unsuitable because of insufficient material, or because of the viscous nature of the sample. The test is applicable to solid samples, semisolids, and polymeric materials such as FS-100 that are insoluble in water (Note 1).

2. PRINCIPLE:

The specific gravity shall be expressed as the ratio of the weight of a given volume of sample to that of an equal volume of water at the same temperature.

3. APPARATUS:

A. Specific Gravity Bottle of the Walker Type

Approximately 25 ml. capacity. (A. H. Thomas Co., No. 9033)

B. Constant Temperature Bath

With thermostatic control, capable of maintaining a temperature of 20°C ± 0.1°C.

C. Thermometer

Centigrade, graduated in 0.1 degrees.

D. Analytical Balance

Accurate to 0.1 mg.

4. CALIBRATION OF THE PYCNOMETER:

Before a test can be performed, the water equivalent of the pycnometer at 20°C must be determined. Clean and dry the pycnometer (bottle, capillary and cap), allow it to come to room temperature, and weigh it on the analytical balance to 0.1 mg. Fill the bottle with freshly boiled and cooled distilled water, but do not insert the capillary and cap. The bottle is then suspended in the constant temperature bath maintained at 20°C ± 0.1°C. The top of the bottle should be slightly

Calibration of the Pycnometer (Continued)

above the level of the water in the bath. However, it must not be immersed so far that there is danger of contamination from the bath water. After 1/2 hour, insert capillary, wipe the excess moisture from the outside of the capillary stem, and set cap in place. Remove from bath. Wipe the outside of the pycnometer with a clean cloth moistened with acetone, then wipe dry. Allow it to stand approximately 2 minutes so that the outside of the pycnometer will be thoroughly dry. Weigh the pycnometer and water on the analytical balance to 0.1 mg. The difference between the weight of the pycnometer and the pycnometer plus the water is the water equivalent at 20°C. This calibration should be checked frequently.

5. PROCEDURE:

A. For Liquids

To determine the specific gravity of a liquid, weigh the clean, dry, calibrated pycnometer (bottle, capillary and cap) on the analytical balance to 0.1 mg. If the sample contains entrapped air, heat gently on a hot plate while stirring constantly. Care should be taken to prevent loss of material by evaporation. If it is necessary to warm the sample, also warm the bottle. Using a funnel, fill it carefully with sample avoiding the inclusion of air bubbles. Add enough sample to the bottle to allow for contraction in cooling. Suspend the bottle containing the sample in the constant temperature bath so that the top of the bottle is slightly above the level of the water in the bath. It must not be immersed so far that there is danger of contamination from the bath water. After one-half hour, insert the capillary in the neck of the bottle forcing all excess sample through the opening. Wipe the excess material from the outside of the capillary with a clean, dry cloth and set the cap in place. Remove from bath and wipe the outside of the pycnometer with a clean cloth moistened with acetone. Wipe dry. After allowing it to stand approximately 2 minutes, weigh to 0.1 mg.

Calculation:

$$\text{Specific Gravity } (20/20^\circ\text{C}) = \frac{\text{Wt. of sample at } 20^\circ\text{C, g.}}{\text{Water equivalent at } 20^\circ\text{C, g.}}$$

B. For Solids and Semisolids

Determine the tare weight of the clean, dry calibrated pycnometer (bottle, capillary and cap). Heat the sample on a hot plate until it is fluid, stirring constantly to remove all air bubbles.

SPECIFIC GRAVITY BY MEANS OF A WALKER TYPE PYCNOMETER

For Solids and Semisolids (Continued)

Heat carefully so that none of the sample is lost through evaporation. Warm the pycnometer and funnel in the electric oven. Introduce the sample into the bottle until it is one-half filled. Take precautions to prevent the fluid from touching the sides of the bottle above the final level and pour carefully to prevent the inclusion of air bubbles. Allow the bottle and contents to cool to room temperature. A few air bubbles can be removed from the surface of the sample by using a piece of wire to lift a small amount of the sample containing the bubble or bubbles from the bottle. After the sample is free from air bubbles and cool, weigh to 0.1 mg. Then fill the pycnometer with freshly boiled and cooled distilled water. Suspend the bottle and its contents in the constant temperature bath at 20°C so that the entire contents (both sample and distilled water) is immersed in the bath. The bottle should not be immersed so far that there is danger of contamination from the bath water. After one-half hour, set the capillary in place, wipe excess water from the outside of the capillary with a clean, dry cloth and place the cap on the capillary. Remove from bath and wipe the outside of the pycnometer with a clean cloth moistened with acetone and dry. After the pycnometer has stood approximately 2 minutes, weigh to 0.1 mg.

Calculation:

$$\text{Specific Gravity } (20/20^\circ\text{C}) = \frac{W_P - W_B}{W - (W_F - W_P)}$$

where:

W = water equivalent of pycnometer, g.

W_B = weight of pycnometer, g.

W_P = weight of pycnometer + solid, g.

W_F = weight of pycnometer + solid + distilled H_2O, g.

Knowing the specific gravity, the density may be calculated as follows:

Density 20/4°C = specific gravity x density of H_2O @ 20°C (.99823)

SPECIFIC GRAVITY BY MEANS OF A WALKER TYPE PYCNOMETER

6. PRECAUTIONS:

A. Exercise care to prevent the expansion and overflow of the contents from the heat of the hand or atmosphere when wiping the excess sample from the capillary.

B. To prevent breakage of the pycnometer after a determination on a viscous or semisolid material has been made, it is advisable to warm it in an electric oven not over 100°C until most of the material can be poured or swabbed out with a soft cloth or cotton waste. When it is cool, rinse with benzol and acetone or other suitable solvents. Then use chromic acid cleaning solution followed by distilled water rinsings.

NOTE:

1. Since the FS-100 material is very viscous, the specific gravity should be determined by using the procedure described in 5(B).

SPECIFIC GRAVITY BY MEANS OF A WALKER TYPE PYCNOMETER

BIBLIOGRAPHY

1. ASTM Standards on Petroleum Products and Lubricants, Method D70-52.
2. Standard Methods for Testing Petroleum and Its Products, Institute of Petroleum, London (1962), Method IP-59/57, pp. 526-528.

DETERMINATION OF WATER IN ORGANIC AND INORGANIC COMPOUNDS
(APCI METHOD NO. 101)

The procedure is applicable to SRC-1 liquids as written. SRC-1 liquids can contain amines; therefore, the solvent system is 75 milliliters of chloroform and 50 milliliters of 15 percent salicylic acid in methanol. The salicylic acid blocks many amines from reacting with the Karl Fischer reagent and producing an additive effect to the water value. Procedure 5B, automatic titrimeter, is recommended to provide the most precise data and is less time consuming than the manual procedure.

The water content of SRC-1 liquids is typically less than 0.5 wt%. Therefore, a sample weight of five grams is used for each analysis. The sample is best introduced into the titration vessel by a syringe which is weighed full and after each injection to determine the sample weight.

Duplicate determinations by the same analyst should not vary by more than 0.02 wt% absolute for values less than 0.50 wt% water in SRC-1 liquids.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Use methanol and chloroform in a well-ventilated area and away from open flames.

Karl Fischer reagent is very toxic and flammable and should be carefully handled.

ANALYTICAL METHOD #101

Air Products and Chemicals inc

DETERMINATION OF WATER IN ORGANIC AND INORGANIC COMPOUNDS

1. SCOPE:

This method describes a procedure for the determination of free water and water of hydration in most solid or liquid organic and inorganic compounds. By proper choice of sample size and Karl Fischer reagent concentration, the method is suitable for the measurement of water over a range of parts per million to pure water.

2. PRINCIPLE:

The sample is dissolved in a solvent of methanol and chloroform. If the sample is an amine, the methanol used in the solvent should contain 15 percent salicylic acid. The water content is determined by either manual amperometric titration equipment or an automatic titrimeter using Karl Fischer reagent. The end point is the first appearance of free iodine determined electrometrically.

3. APPARATUS:

A. Manual Amperometric Equipment (shown schematically in Figure 1)

(1) Buret Assembly

A 10 ml. semi-micro buret provided with a 28/15 ball joint as shown in Figure 1. A closed-system reservoir is fitted to the top of the buret. The top of the reservoir is connected to a tube filled with Indicating Drierite by a two-foot length of 2 mm. ID tubing.

(2) Electrode Assembly

Two 0.5 mm. diameter platinum wires sealed through the end of a suitable soft glass tube and extending for one-half inch in a horizontal plane just above the magnetic stirring bar. The two wires shall be parallel to each other and spaced several millimeters apart. The glass tube containing the leads shall be cemented into a 35/20 ball joint having a connection to a Drierite tube.

(3) Meter

An electron tube voltmeter with a range of 500 millivolts, full scale. A line operated pH meter with a range of 700 millivolts, full scale, may be used.

(4) Titration Vessel

A suitable design is shown in Figure 2, however, other designs may be used provided that they permit several successive determinations in the same container. The constricted, flat-bottomed section permits thorough agitation with a magnetic stirrer.

B. Automatic Titrimeter Equipment

Metrohm - Karl Fischer Titrator E-452.

4. REAGENTS:

All chemicals used shall be reagent grade. All water used shall be distilled water.

A. Chloroform

Code #C360 (Lehigh Valley Chemical Company, Easton, Pa.)

B. Methanol

Code #M370 (Lehigh Valley Chemical Company, Easton, Pa.)

C. Salicylic Acid

Code SX60-CB664 (Matheson Coleman and Bell, Philadelphia, Pa.)

D. Karl Fischer Reagent

Code #KX10-B806 (Matheson Coleman and Bell, Philadelphia, Pa.)

E. Karl Fischer Reagent - Working Solution

Dilute 500 ml. of stock solution with 500 ml. of methanol and store for at least one day before use. When freshly prepared, 1 ml. of this solution is approximately equivalent to 2 mg. of water, but changes on standing.

F. Methanol - Salicylic Acid

Dissolve 150 g. of salicylic acid in 1 liter of methanol. Use for amines.

5. PREPARATION AND STANDARDIZATION:

A. Manual Amperometric Equipment

(1) Assemble the apparatus as shown in Figure 1 and fill the reservoir and buret with the Karl Fischer working solution.

(2) Introduce 100 ml. of chloroform and 25 ml. of methanol into the titration vessel through the 28/15 sampling joint. Stopper with the sealed end ball member and start the magnetic stirrer. Measure the voltage across the electrodes with the millivoltmeter.

(3) Add the Karl Fischer reagent in 1 ml. portions, the additions being made in rapid succession at first, then more slowly. The voltage, as measured on the meter, will drop sharply after each addition and then increase. Using a stopwatch, measure the time required for the voltage to increase by 10 millivolts after each addition. Continue the additions of titrant in 1 ml. increments until the increase in voltage after an addition approximates 10 millivolts in 10 seconds.

(4) Decrease the additions to 10 drops then to 5 drops as long as the voltage increases by more than 10 millivolts in 10 seconds. Then add the titrant in 2-drop increments as long as the voltage increases by more than 10 millivolts in 30 seconds. The end point of the titration will have been

reached at the first two-drop addition after which more than 30 seconds will be required for an increase of 10 millivolts. With normally fresh, dry chloroform and methanol, not more than 10-15 ml. of titrant are required for the water present in these reagents.

(5) Immediately after adjustment of the solvents, introduce one-two drops of water from a tared weighing pipet into the titration vessel. Close the vessel and start the magnetic stirrer, then reweigh the weighing pipet to the nearest 0.1 mg. Again titrate with Karl Fischer reagent, following the same procedures specified in (3) and (4) above. Record the values of titrant used to the nearest 0.01 ml.

(6) Repeat section (5) above until successive standardization determinations indicate an equivalence of 1 ml. = X ± 0.01 mg. water.

(7) Standardize the Karl Fischer reagent at least once a week, if the apparatus is in constant use. If the apparatus is idle several days or more, standardize before testing samples.

B. Automatic Titrimeter Equipment

(1) Introduce 100 ml. of chloroform and 25 ml. of methanol into the titration vessel through the sampling joint.

(2) Before the solvents are adjusted for water content, set the various switches on the titrator as follows: (See Figure 4)

   (a) Throw toggle switch #2 to "I", the pilot light #1 comes on.

   (b) Adjust stirrer, switch #11, so that the stirring bar mixes the solution thoroughly but not so violently that a vortex (cavitation) is created, causing air bubbles to contact the electrodes.

(c) Set selector switch #13 to "automatic" for left-hand Dosimat.

(d) Set switch #12 to 15/25, the end point potentiometer.

(e) Set switch #9 to 20-60 seconds.

(f) Set potentiometer #5 for 30 second end point.

(g) Turn the left-hand switch on left Dosimat to "on" (see Figure 3).

(h) Fill the buret and turn stopcock to allow Karl Fischer solution to be fed into titration vessel.

(i) Set titration speed to slow by adjusting the right-hand switch on the left Dosimat (see Figure 3).

(j) Adjustment of the water content of the solvents can now be completed by depressing the "start" button #6. The "stop" pilot light #7 goes out and the titration proceeds automatically. The "stop" pilot light #7 comes on again when the delay period set by switch #5 has elapsed after the last signal has been transmitted.

(k) Immediately after adjustment of the solvents, introduce one-two drops of water from a tared weighing pipet into the titration vessel. Close the vessel and adjust stirrer switch #11.

(l) Proceed according to steps (h), (i) and (j) above and record the volume of Karl Fischer solution.

C. <u>Calculation of Karl Fischer Factor</u>

$$(\text{g. } H_2O/\text{ml. K.F.}) = \frac{\text{Wt. of } H_2O \text{ (g.)}}{\text{Volume of K.F. Solution}}$$

Calculate standardization to six decimal places.

DETERMINATION OF WATER IN ORGANIC AND INORGANIC COMPOUNDS

6. PROCEDURE:

A. To the adjusted solvents (Note 1) add an appropriate weight of sample to the titration vessel according to Table I.

B. When using the manual equipment, start the stirrer, add the Karl Fischer solution in small increments, and proceed according to sections 5(A)3 and 5(A)4.

C. When using the automatic equipment, adjust stirrer switch #11 and proceed according to steps 5(B)h, 5(B)i, and 5(B)j, and record the volume of the Karl Fischer solution.

7. CALCULATION:

$$\frac{\text{Volume of K.F. solution} \times \text{K.F. Factor} \times 100}{\text{Wt. of Sample}} = \text{Wt. \% } H_2O$$

8. REPEATABILITY:

Depending upon the amount of water present in the sample, the results obtained by the same analyst should be considered suspect if they differ by more than the following:

% H_2O	Repeatability
0 - 1.0	±0.01% absolute
1 - 5.0	±0.03%
5 - 50.0	±0.10%
over 50.0	±0.30%

TABLE I

Wt. % H_2O	Wt. Sample	Vol. K.F. Solution*
0.001 - 0.01	50.0 g.	.25 - 2.5 ml.
0.01 - 0.1	20.0 g.	1 - 10 ml.
0.1 - 1.0	5.0 g.	2.5 - 25 ml.
1.0 - 10.0	0.5 g.	2.5 - 25 ml.
10.0 - 100.0	0.1 g.	5 - 50 ml.

* Based on a K.F. Factor of .002 g. H_2O/ml. K.F.

DETERMINATION OF WATER IN ORGANIC AND INORGANIC COMPOUNDS

NOTE 1: If the sample is an amine run the duplicate test with 75 ml. of chloroform and 50 ml. of methanol with 15 percent salicylic acid added.

FIGURE 1

SCHEMATIC ARRANGEMENT OF
APPARATUS FOR WATER
DETERMINATION
(NOT SCALED)

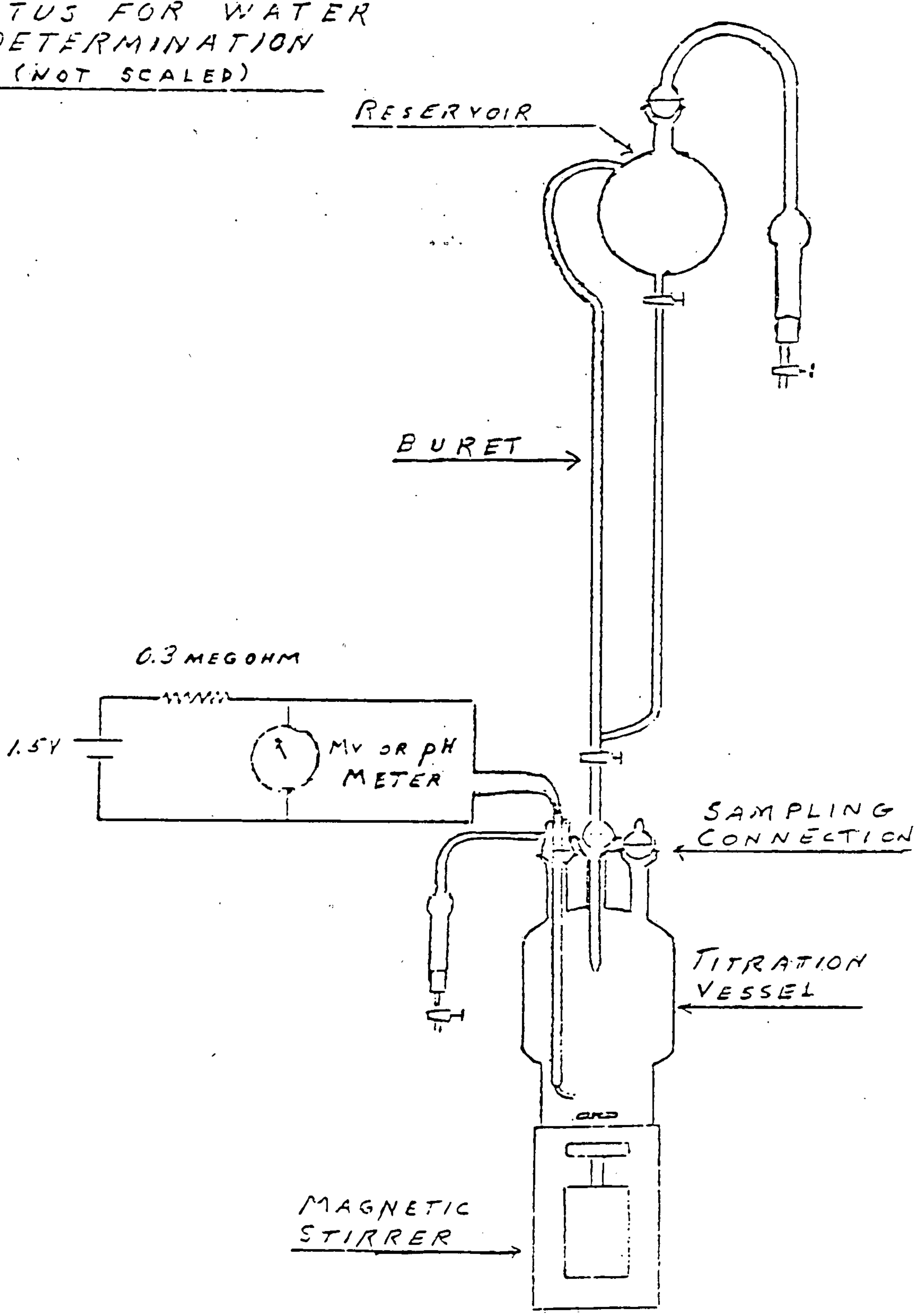
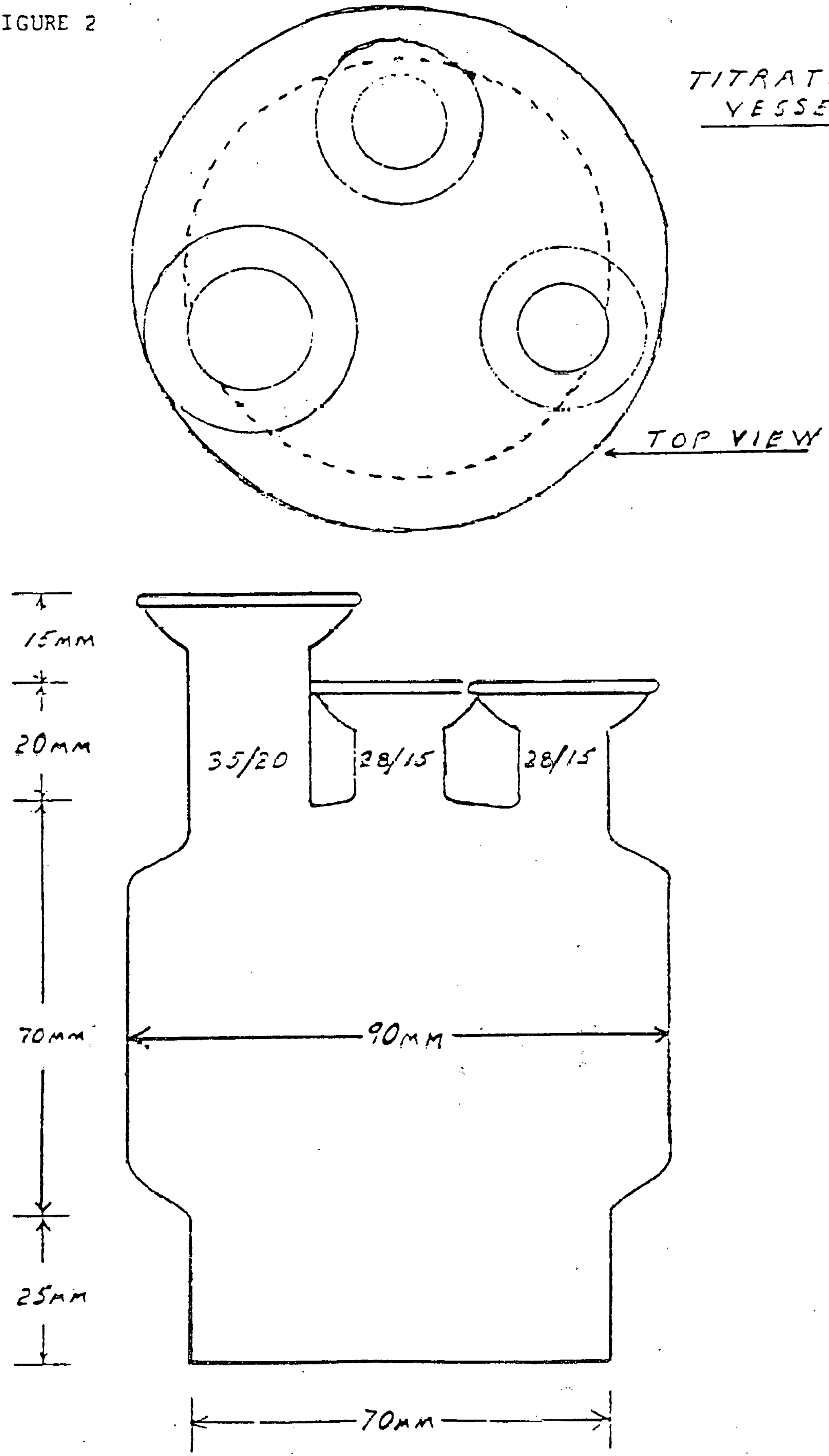


FIGURE 2



TITRATION VESSEL

FIGURE 3

KARL-FISCHER-TITRATOR E 452

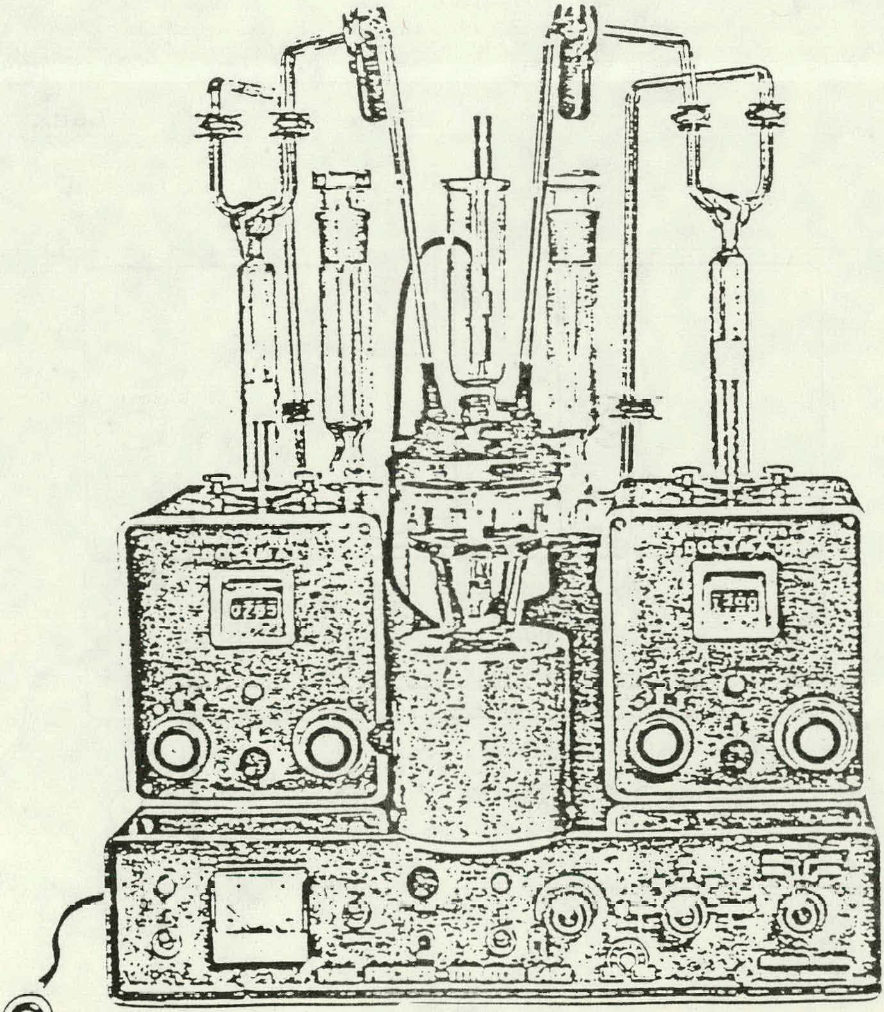
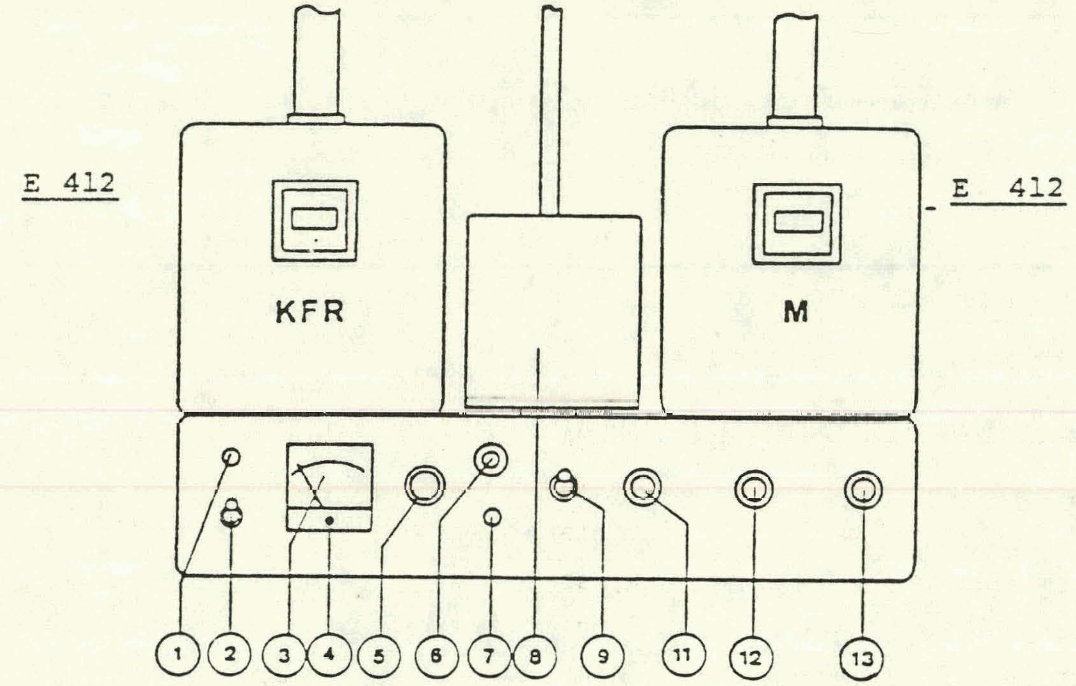
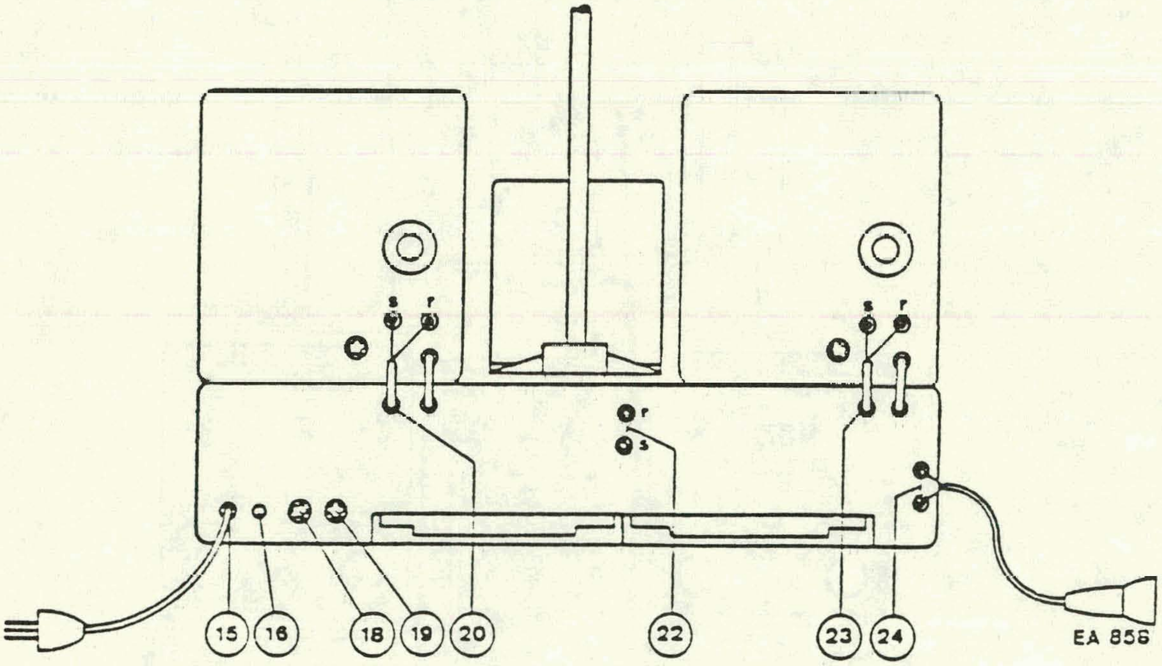


FIGURE 4

Front view



Back view



DETERMINATION OF CHLORIDE BY PARR PEROXIDE BOMB
(APCI METHOD NO. 104)

The procedure is applicable to coal, coke and KMAC samples as written. For samples containing less than 2.0 wt% chlorine use a 0.4 gram sample and add only 25 milliliters of the 0.1N silver nitrate solution. See APCI Method No. 208 for the preparation and standardization of 0.1N solutions of silver nitrate and ammonium thiocyanate.

Grind enough material to produce a five gram working sample.

Safety

Grinding of any coal, coke or KMAC must be completed in a well-ventilated area and the analyst be required to wear a lab coat and dust mask. See the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet located in the front section of the manual for the special precautions when handling SRC KMAC.

Care must be taken when handling concentrated acids and bases to avoid contact with skin or inhalation of vapors.

Keep sodium peroxide stored in a desiccator containing desiccant and away from water. If sodium peroxide spills, do not clean up with a combustible material. e.g., paper towels, because they can ignite.

DETERMINATION OF CHLORIDE BY THE PARR PEROXIDE BOMB

1. SCOPE:

This method describes a procedure for the determination of chloride in organic compounds in the range of 0.5 to 95.0 percent.

2. PRINCIPLE:

The sample is decomposed with sodium peroxide and sodium carbonate in the Parr bomb. The chloride present is determined by titration using ammonium thiocyanate in the presence of an excess of silver nitrate.

3. APPARATUS:

A. Parr Peroxide Bomb (1)

Assembly complete with lead gaskets (Arthur H. Thomas Co., Philadelphia, Pennsylvania).

B. Graduate Cylinder (1)

10 ml. (Arthur H. Thomas Co., Philadelphia, Pennsylvania).

C. Tripod (1)

With transite pad.

D. Bunsen Burner (1)

E. Explosion Proof Shelter (1)

F. Beaker (1)

400 ml. (Arthur H. Thomas Co., Philadelphia, Pennsylvania).

G. Watchglass (1)

100 mm. diameter (Arthur H. Thomas Co., Philadelphia, Pennsylvania).

H. Pipettes

(1) 50 ml., (1) 25 ml. (Arthur H. Thomas Co., Philadelphia, Pennsylvania).

I. Flask (1)

Iodine, 500 ml. (Arthur H. Thomas Co., Philadelphia, Pennsylvania).

J. Burettes

(1) 50 ml., (1) 10 ml. (Arthur H. Thomas Co., Philadelphia, Pennsylvania).

4. REAGENTS:

A. Silver Nitrate

Reagent grade (Baker and Adamson, Moorestown, New Jersey). Prepare a 0.1 N solution and standardize.

B. Ammonium Thiocyanate

Reagent grade (Baker and Adamson, Moorestown, New Jersey). Prepare a 0.1 N solution and standardize.

C. Sodium Carbonate

Reagent grade (Baker and Adamson, Moorestown, New Jersey).

D. Sulfuric Acid

Reagent grade (E. I. DuPont de Nemours & Co., Wilmington, Delaware). Prepare a 40 percent solution.

E. Sodium Peroxide

Reagent grade (Baker and Adamson, Moorestown, New Jersey).

F. Ferric Ammonium Sulfate Indicator

Reagent grade (Baker and Adamson, Moorestown, New Jersey).

C. Nitrobenzene

Reagent grade (Baker and Adamson, Moorestown, New Jersey).

H. Sodium Sulfite

Reagent grade (Baker and Adamson, Moorestown, New Jersey). Prepare a saturated solution.

I. Distilled Water

J. Nitric Acid

Reagent grade (Baker and Adamson, Moorestown, New Jersey).

5. PROCEDURE:

Before proceeding with the analysis see note on safety requirements at the end of the method.

A. Solid Samples

(1) Weight 0.2 to 0.4 g. of sample into the fusion cup containing approximately 1/16 inch of sodium carbonate.

(2) Using the dipper supplied with the bomb, add 5 grams (one-half dipper) of sodium peroxide to the fusion cup. Place the cover on the bomb and shake well.

(3) Remove the cover and add 5 grams (one-half dipper) of additional sodium peroxide. Do not shake.

(4) Assemble the Parr bomb and tighten with the wrench which is provided.

(5) Proceed as outlined in Section C.

DETERMINATION OF CHLORIDE BY THE PARR PEROXIDE BOMB

B. Liquid Samples

(1) Weight 0.1 to 0.4 g. of sample into the fusion cup containing approximately 1/16 inch of sodium carbonate.

(2) Using the dipper provided, add 10 grams (one full dipper) of sodium peroxide to the fusion cup. Place the cover on the bomb. Do not shake.

(3) Assemble the Parr bomb and tighten with the wrench which is provided.

(4) Proceed as outlined in Section C.

C. Firing of Bomb

(1) Place the assembled bomb in a close fitting transit board supported by a tripod and surrounded by an explosion-proof shelter.

(2) Fill depression on top of the bomb with water.

(3) Before heating the bomb in the explosion-proof shelter, have the Bunsen burner adjusted so that the tip of the blue flame covers about one-half of the bottom of the fusion cup.

(4) Heat the bottom surface of the bomb until the water on top boils.

(5) Remove the bomb and cool it in a pan containing about on-half inch of water.

D. Analysis of Fusion Products

(1) Rinse the cup cover into a 400 ml. beaker. Place the fusion cup on its side in the 400 ml. beaker and add about 100 ml. of water. Cover the beaker with a watchglass.

(2) When effervescence ceases, add 5 ml. of a saturated solution of sodium sulfite.

(3) By means of a pipette, add 40-50 ml. of a 40 percent sulfuric acid.

(4) When effervescence ceases, remove the fusion cup and evaporate to about 100 ml.

(5) Transfer the solution to 500 ml. iodine flask and add 10 ml. of concentrated nitric acid.

(6) Using a 25 or 50 ml. pipette, add an excess (10 to 20 ml.) of standard 0.1 N silver nitrate solution.

(7) Add 5.0 ml. of nitrobenzene and 3 ml. of ferric ammonium sulfate indicator.

(8) Shake thoroughly and titrate the excess silver nitrate with standard 0.1 N ammonium thiocyanate solution to a pink end point.

E. Calculation

$$\frac{(\text{ml. } AgNO_3 \times N) - (\text{ml. } NH_4SCN \times N) \times 3.546}{\text{Wt. of Sample}} = \%\ Cl$$

6. SAFETY NOTES:

A. Apparatus

(1) Explosion-Proof Shelter

Made of shatter-proof glass in which to ignite the bomb.

(2) Safety Shield

For the face - shatter-proof and resistant to acid and alkali.

(3) Fusion Cup

The fusion cup shall be carefully inspected after each ignition, and shall be discarded whenever bulging has occurred or whenever inspection reveals any fine-line cracks or other weakness of any kind.

(4) Peroxide Measuring Dipper

The correct sodium peroxide measuring dipper should be used for measuring out the sodium peroxide.

DETERMINATION OF CHLORIDE BY THE PARR PEROXIDE BOMB

(5) Gaskets

Inspect the gasket. If it appears at all worn or channeled, replace it with a new one.

B. Sodium Peroxide

(1) Store sodium peroxide in a tightly stoppered bottle.

(2) In storage and handling, keep to an absolute minimum the exposure of the reagent to the air.

(3) Never put mixtures containing sodium peroxide together with other refuse containing carbonaceous matter or paper; such mixtures may ignite spontaneously.

C. Fusion Procedure

(1) If the sample is mostly organic in nature, the sample size shall not exceed 0.4 g.

NOTE: Samples of solid materials must be finely powdered, or if this is not possible, thoroughly dried and finely shreaded. Liquid samples, especially those of high volatility which may react spontaneously with the peroxide, must be handled with care in sealed ampoules or capsules.

(2) Wear a face shield when making the fusion.

Air Products

STANDARDIZATION OF 0.1N $AgNO_3$ and 0.1N NH_4SCN FOR USE IN THE DETERMINATION OF CHLORINE, BROMINE AND IODINE IN FUSION PROCEDURES

I. SCOPE

This method is to be used to determine the normalities of 0.1N $AgNO_3$ and 0.1N NH_4SCN solutions. These solutions are used when chloride is determined by a carbonate fusion or when chloride, bromide, or iodide is determined by Parr Peroxide Bomb.

II. PRINCIPLE

A measured amount of standard 0.1N NaCl solution is added to a 500 ml iodine flask. An excess of 0.1N $AgNO_3$ solution is then added to the flask. The excess $AgNO_3$ is titrated with 0.1N NH_4SCN solution in the presence of ferric ammonium sulfate indicator and nitrobenzene.

III. APPARATUS

A. Flasks Volumetric
250 ml (2)
(Fisher Scientific Co., King of Prussia, Pennsylvania)

B. Flasks Iodine
500 ml (2)
(Fisher Scientific Co., King of Prussia, Pennsylvania)

C. Pipets Volumetric
25 ml (2) 30 ml (1) 50 ml (1)
(Fisher Scientific Co., King of Prussia, Pennsylvania)

D. Buret
50 ml (1)
(Fisher Scientific Co., King of Prussia, Pennsylvania)

E. Graduated Cylinder
10 ml (1)
(Fisher Scientific Co., King of Prussia, Pennsylvania)

F. Flasks Iodine
250 ml (2)
(Fisher Scientific Co., King of Prussia, Pennsylvania)

IV. REAGENTS

A. Sodium Chloride
Reagent grade code S-271 (Fisher Scientific Co., King of Prussia, Pennsylvania)

B. Silver Nitrate
Reagent grade, code S-181 (Fisher Scientific Co., King of Prussia, Pennsylvania)

C. Ammonium Thiocyanate
Reagent grade code 1-0818 (J. T. Baker Chemical Co. Phillipsburg, New Jersey)

D. Ferric Ammonium Sulfate
Reagent grade code 1-75 (Fisher Scientific Co. King of Prussia, Pennsylvania)

E. Distilled Water

F. Nitric Acid
Reagent grade (Baker and Adamson, Moorestown, New Jersey)

G. Nitrobenzene
Reagent grade (Baker and Adamson, Moorestown, New Jersey)

V. PREPARATION OF SOLUTIONS

A. Sodium Chloride Solution

1. Prepare two 0.1N NaCl solutions as follows: To a 250 ml volumetric flask add 1.47 ± 0.01g NaCl previously dried for 1 hour at 105°C. To a second flask add 1.61 ± 0.01g of dried NaCl. Dilute both flasks to volume with distilled water.

2. Calculation of Normality

$$\frac{\text{wt. of NaCl} \times 4}{58.45} = \text{N of NaCl}$$

B. Silver Nitrate Solution

1. Prepare a 0.1N solution of $AgNO_3$ as follows:
To a 1 liter volumetric flask, add 17g of $Ag\ NO_3$ and dilute to volume with distilled water.

C. Ammonium Thiocyanate Solution

1. Prepare a 0.1N solution of NH_4SCN as follows:
To a 1 liter volumetric flask add 7.6g of NH_4SCN and dilute to volume with distilled water.

D. Ferric Ammonium Sulfate Indicator (Ferric Alum)

1. Add 35g of $Fe_2 (SO_4)_3 (NH_4)_2 SO_4 \cdot 24H_2O$ to 100 cc of H_2O and acidify with conc. HNO_3 until a straw color is obtained.

2. Boil for 10 minutes to remove the oxides of nitorgen.

VI. PROCEDURE

A. By means of a pipette add 25 and 30 cc of the 0.1N Ag NO_3 solution to 250 cc iodine flasks.

B. Add 3.0 cc of the ferric ammonium sulfate indicator by graduated cylinder.

C. Titrate, using a 50 cc buret, with 0.1N NH_4SCN to a pink end point.

D. Calculate a standardization factor.

E. Using a pipette, add 25cc of each 0.1N NaCl solution to two 500 cc iodine flasks.

F. Heat to boiling on a hot plate.

G. Add two drops of conc HNO_3.

H. Boil for 15 additonal minutes and let cool to room temperature.

I. Add 50 cc of 0.1N Ag NO_3 to each iodine flask.

J. Add 5.0 cc of nitrobenzene and 3.0 cc of ferric ammonium sulfate indicator.

K. Shake thoroughly and titrate excess silver nitrate with 0.1N NH_4SCN solution to a pink end point.

VII. CALCULATIONS

A. Standardization Factor (S.F.)

$$\frac{\text{cc of 0.1N } AgNO_3 \text{ added to flask}}{\text{cc of 0.1N } NH_4SCN \text{ required for titration}} = \text{S.F.}$$

Example:

$$\frac{25.00}{24.24} = 1.0314 \text{ S.F.}$$

B. Normality of Ag NO_3

$$\frac{25.00 \times N}{50.00 - (A \times S.F.)} = N \text{ of Ag } NO_3$$

Where:

N = normality of NaCl solution
A = cc of NH_4SCN required
S.F. = standardization factor

Example:

$$\frac{25.00 \times .10056}{50.00 - (24.38 \times 1.0314)} = 0.1011N \text{ Ag } NO_3$$

C. Normality of NH_4SCN

$$\frac{A \times M}{B} = N \text{ of } NH_4SCN$$

Where:
A = cc of Ag NO_3 added in step VI A.
M = normality of Ag NO_3
B = cc of NH_4SCN required in step VI C.

Example:

$$\frac{25.00 \times 0.1011}{24.24} = 0.1043 \text{ N } NH_4SCN$$

Analytical Method #240

Air Products

HOT SEDIMENT FILTRATION OF SRC-I DISTILLATE FUEL OILS

I. SCOPE

This method covers the determination of total hot filtration sediment in SRC-I distillate fuel oils. The minimum detectable sediment is 1 mg/100 ml of sample and can be decreased by increasing the recommended sample size. The method is intended for filterable SRC-I liquids and no provisions have been made for viscous liquids not suitable for the glass filters used in the procedure.

II. APPARATUS

A. Crucibles, Gooch
25 ml, Catalog No. 08-195D (Fisher Scientific Co., King of Prussia, Pa.)

B. Crucible Holders, Walter
Catalog No. 08-285 (Fisher Scientific Co., King of Prussia, Pa.)

C. Filter
250 ml, Catalog No. 10-180D (Fisher Scientific Co., King of Prussia, Pa.)

D. Glass Filters, Whatman
2.4 cm diameter (934-AH) Catalog No. 1827 024 (Whatman Inc., Clifton, NJ)

E. Volumetric Pipettes, Class A
50 ml, Catalog No. 13-650S (Fisher Scientific Co., King of Prussia, Pa.)

F. Graduated Cylinder
25 ml, Catalog No. 08-548B (Fisher Scientific Co., King of Prussia, Pa.)

G. Desiccator
160 mm, Catalog No. 08-632 (Fisher Scientific Co., King of Prussia, Pa.)

H. Jars, French Squares
8 oz, Catalog No. 1724-C52
(Arthur H. Thomas Co., Philadelphia, Pa.)

I. Drying Oven, Gravity Convection
Explosion-proof, Model No. 70, Catalog No. 13-258-13F (Fisher Scientific Co., King of Prussia, Pa.)

HOT SEDIMENT FILTRATION OF SRC-I DISTILLATE FUEL OILS

II. APPARATUS (Cont.)

J. Balance, Mettler
0.01 mg, Catalog No. 01-909-105 (Fisher Scientific Co., King of Prussia, Pa.)

K. Flask, Filtering
500 ml, Catalog No. 10-180E (Fisher Scientific Co., King of Prussia, Pa.)

L. Gloves, Insulating
Catalog No. 11-392-15 (Fisher Scientific Co., King of Prussia, Pa.)

III. REAGENTS

A. Drierite Absorbent, Indicating
8 mesh, Catalog No. 07-578-3B
(Fisher Scientific Co., King of Prussia, Pa.)

B. Naphtha, Xylenes
Catalog No. X-4
(Fisher Scientific Co., King of Prussia, Pa.)

C. Molecular Sieves
10-16 Mesh, Beads, Catalog No. M-518
(Fisher Scientific Co., King of Prussia, Pa.)

IV. SAFETY

All standard procedures when working with SRC liquids or oils must be adhered to, including the wearing of gloves and laboratory coat. The oven treatment of samples and all filtering and washing operations must be performed in a hood. The insulating gloves must be worn when filtering hot samples. SRC-I material contain possible carcinogens.

For specific handling precautions refer to the U.S. Dept of Labor O.S.H.A. Material Safety Data sheet for SRC-I Middle Distillates.

V. PROCEDURE

A. Pipet 50 ml of sample into an eight ounce jar. If the sample cannot be pipetted at room temperature weigh approximately 50 grams to the nearest 0.1 mg into a tared eight ounce jar.

B. Place the uncovered jar into an explosion-proof oven which has been set at 200°F (94°C) for two hours. The oven should be placed in a well-ventilated hood.

HOT SEDIMENT FILTRATION OF SRC-I
DISTILLATE FUEL OILS

V. PROCEDURE (Cont.)

C. While the jar is in the oven, place a glass filter into a Gooch crucible, allowing one crucible per sample jar and providing two crucibles with filters for use as reagent or moisture blanks.

D. Place the crucibles containing the filters in a forced convection drying oven for two hours at a temperature of 105°C.

E. Remove crucibles and place in a desiccator containing indicating Drierite and allow to cool to room temperature.

F. Weigh crucibles to the nearest 0.01 mg.

G. Place a crucible in holder on filtering flask and return to oven for an additional 10 minutes.

H. Remove equipment from oven and quickly secure and proceed to Step I. (Wear insulating gloves when handling hot equipment.)

I. Slowly filter the sample <u>while</u> <u>hot</u> through the Gooch crucible by placing the sample on the glass filter until the crucible is one-third full and slowly turning on the vacuum. (Wear insulating gloves when handling hot samples.

J. Repeat Step I until the total sample is filtered.

K. Measure 20 ml of naphtha by graduated cylinder and add to the eight ounce jar to remove any residue.

L. Transfer wash naphtha from the jar into the crucible and slowly turn on vacuum to remove any soluble residue from the glass filter.

M. Repeat Steps K and L three additional times with 20 ml of naphtha.

N. Filter 80 ml of naphtha through a crucible containing a clean glass filter to serve as a moisture blank.

O. Repeat Step N with second clean crucible.

P. Place all crucibles in explosion-proof oven for two hours at 105°C.

Q. Repeat Steps E and F.

VI. CALCULATIONS

A. If the sample was measured by pipette, the amount of residue is calculated by the following equation:

VI. CALCULATIONS (Cont.)

$$\frac{\text{mg of sediment}}{\text{100 ml of sample}} = \frac{[(B-A) \times 100 \text{ ml}]}{50 \text{ ml}}$$

or

$$\frac{\text{mg of sediment}}{\text{100 ml of sample}} = [(B-A) \times 2]$$

where:

A = average weight of residue from moisture blank crucibles (mg)
B = weight of residue from samples (mg)

B. If the sample was weighed before filtering, the amount of residue is calculated by the following equation:

$$\frac{\text{mg of sediment}}{\text{100 ml of sample}} = \frac{[(B-A) \times 100 \text{ ml}]}{C}$$

where:

A = average weight of residue from moisture blank crucibles (mg)
B = weight of residue from samples (mg)
C = volume of sample used (ml)

The volume of sample used can be calculated by the following equation:

$$\text{ml of sample} = \frac{\text{weight of sample used (g)}}{\text{density of sample (g/ml)}}$$

VII. PRECISION AND ACCURACY

An SRC-I middle oil, Sample No. 2008CB, was analyzed in duplicate and determined to contain no detectable residue. A known quantity of dried carbon black, 28.3 mg, was added to 500 ml of the middle oil. This mixture served as a known standard for determing the precision and accuracy of the procedure. The mixture was not intended to simulate actual SRC-I middle oil residue, but only to serve as a sample to determine the repeatability of the experimental manipulations at the expected residue levels.

The results of seven determinations on the blend are listed below:

Experimental Mean (mg residue/100 ml sample) = 5.44
Standard Deviation (mg residue/100 ml sample) = 0.36
Expected Value (mg residue/100 ml sample) = 5.70

HOT SEDIMENT FILTRATION OF SRC-I DISTILLATE FUEL OILS

VII. PRECISION AND ACCURACY (Cont.)

Three additional blends were prepared and the results of duplicate determinations are listed below:

Sample	Sediment (mg residue/100 ml sample)	
	Experimental	Calculated
Blend A	2.4	3.2
Blend B	10.3	11.2
Blend C	20.3	19.0

VIII. QUALITY ASSURANCE

A. All balances must be quality assured in accordance with the CRSD Analytical Services Quality Assurance Program Guidelines on page 32.

B. Naphtha should be stored over molecular sieves to ensure dryness.

C. Indicating Drierite in desiccator should be checked before starting analysis and replaced if hydrated.

D. All samples should be analyzed in duplicate and if the determined level of precision expected is not reached, the sample analysis should be repeated.

IX. PRINCIPLE

Fifty ml of sample is pipetted or weighed into 8 oz jars and placed in an oven set at 200°F (94°C) for two hours. The sample is filtered while hot through a Gooch crucible containing a glass filter and is washed with naphtha. The crucible is dried in an oven set at 105°C for two hours, cooled in a desiccator and weighed to determine the mg of sediment present.

The sediment formed can be due to either organic or inorganic material. The hot filtration sediment is an indication of either contamination, deterioration of the oil, separation upon blending or precipitation of substances after distillation.

X. REFERENCES

A. ASTM Manual, ASTM D 1698-64, Sediment and Soluble Sludge in Service Aged Insulating Oils.

ANALYTICAL METHOD NO. 241

Air Products

PENTANE INSOLUBLES OF SRC SOLIDS

I. SCOPE

The determination of pentane insoluble material above the level of one percent is possible using this method based upon initial weight of sample. The method was developed for HSRC, LSRC and LC Finer solids but is applicable to coke and coal samples.

II. APPARATUS

A. Balance
Analytical, Mettler H542 (Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #01-909-542

B. Beaker
100 ml (Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #02-612A

C. Stirring Rod
150 mm, Kimax (Sargent-Welch, Skokie, Illinois) Catalog #S-40097-B

D. Mortar
75/60 (OD/ID) Agate, with Pestle (Sargent-Welch, Skokie, Illinois) Catalog #S-62205-B

E. Watch Glass
66 mm (Fisher Scientific Company, Pittsburgh, Pennsylvania)

F. Hot Plate
Electric, Adjustable Heat (Sargent Welch, Skokie, Illinois) Catalog #S-41043

G. Extraction Thimble
Alundum, AN889 Medium, 34 mm x 100 mm (Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #09-660D
Two holes (1 mm in dia.) are drilled on opposite sides of the thimble, one-half inch from the top. (See Figure 1)

H. Filter Paper
7 cm, Medium Porosity, Circles (Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #09-805C

II. APPARATUS (Cont.)

I. Drying Oven
200°C Maximum (Fisher Scientific Company, Pittsburgh, Pennsylvania)
Catalog #13-245-116G

J. Tubing
5/16" ID-3/32", Amber Wall (Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #14-178-5E

K. Condenser
40 mm, 45/50 (Fisher Scientific Company, Pittsburgh, Pennsylvania)
Catalog #09-551 10B
A glassblower must curve the bottom of the inner tip of the condenser to be able to hold the thimble. (See Figure 1)

L. Flask
1000 ml, with Joint (45/50) (Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #10-048C

M. Flask
500 ml, Filtering (Fisher Scientific Company, Pittsburgh, Pennsylvania)
Catalog #10-180C

N. Rubber Stopper
Size No. 7, Hole 5 mm, Non-corrosive (Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #14-135H

O. Graduated Cylinder
100 ml (Fisher Scientific Company, Pittsburgh, Pennsylvania)
Catalog #08-549-5E

P. Boiling Stones
(Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #B-365

Q. Thermometer
305 mm, (Fisher Scientific Company, Pittsburgh, Pennsylvania)
Catalog #14-983-10C

R. Copper Wire
0.64 mm Diameter, (Fisher Scientific Company, Pittsburgh, Pennsylvania)
Catalog #15-545-2D

S. Furnace
3-wall heat. (Fisher Scientific Company, Pittsburgh, Pennsylvania)
Catalog #10-552

PENTANE INSOLUBLES OF SRC SOLIDS

II. APPARATUS (Cont.)

T. Tube
Filtering, 42 x 160 mm, (Arthur H. Thomas Company, Philadelphia, Pennsylvania) Catalog #4797-R34.

III. REAGENTS

A. Pentane
Reagent Grade (Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #0-4062

B. Hydrochloric Acid
Reagent Grade (Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #A-144

C. Drierite
Indicating, 8 mesh (Fisher Scientific Company, Pittsburgh, Pennsylvania) Catalog #07-578-3B

D. Distilled Water

IV. SAFETY

SRC solids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing. Grinding of samples should be done in a hood and a dust mask worn by the analyst. For specific handling precautions of SRC-1 solids see the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet.

Pentane is a hazardous material because of its volatility and flammability. When refluxing pentane, extreme care must be taken to avoid overheating and causing the flask to go to dryness. Also, the refluxing pentane must be in an area where all open flames are avoided.

The pentane containing the soluble oils and the residue remaining in the alundum thimble must be properly disposed. Do not pour down sink.

V. PROCEDURE

A. Preparation of Sample

Prepare a 10 gram working sample by crushing and grinding with an agate mortar and pestle. Store the sample under nitrogen in a tightly closed container. Use the sample within 48 hours because changes in composition may occur in pulverized SRC-1 solids. (See Safety Section.)

A tarry sample that can not be ground with a mortar and pestle can be analyzed as received.

V. PROCEDURE (Cont)

B. Preparation of Thimble

1. Ignite an alundum thimble at 700°C for one hour in a muffle furnace.

2. Remove the thimble from the furnace and place directly into a drying oven set at 105 ± 5°C for 30 minutes. (This will prevent rapid cooling and cracking of the thimble.)

3. Remove thimble from oven and place directly into a desiccator containing Drierite.

4. Allow the thimble to cool.

5. Attach the copper wire as shown in Figure 1.

6. Place thimble and copper wire in a drying oven for 30 additional minutes.

7. Repeat Steps 3 and 4.

8. Weigh the thimble to the nearest 0.1 mg and record the weight.

9. After each use the thimble should be soaked with 1:1 hydrochloric acid and rinse with distilled water before igniting in furnace.

C. Analysis of Sample

1. One gram of the working sample is weighed to the nearest 0.1 mg in a 100 ml beaker.

2. By graduated cylinder, 60 ml of reagent grade pentane is added to the beaker with constant stirring using a stirring rod.

3. Heat the beaker to 40±2°C and occasionally stir the mixture to ensure complete dispersion for 30 minutes on a hot plate. (Check temperature with thermometer.)

4. Place the tared thimble into a filter tube supported over a filtering flask.

5. Wet the thimble with approximately 50 ml of pentane and carefully decant the sample/pentane mixture into the wetted thimble. (Do not permit the level of pentane to rise higher than 20 mm from the top of the thimble.)

6. Transfer the insoluble matter from the beaker with small quantities (10 ml) of pentane.

7. Place the thimble containing the residue in the wire support of the condenser.

V. PROCEDURE (Cont)

8. Fold the filter paper to form a cone. Cover the thimble with the paper cone prepared from medium porosity, 7 cm filter paper, point down. (See Figure 1)

9. Add six boiling stones and 200 ml of pentane to the 1000 ml flask and assemble the extraction apparatus shown in Figure 1. (The surface of the pentane in the flask should be 25 mm below the bottom of the thimble.)

10. Conduct the extraction for a period of 18 hours. (Avoid loss of pentane by adjusting the heat low and keeping a steady flow of cold water through the condenser.)

11. After 18 hours shut off heat and allow reflux apparatus to cool to room temperature.

12. Set thimble in a 100 ml beaker in a hooded area until its appearance is dry.

13. Place dry thimble and beaker in an oven at 105 ± 5°C for 1 hour.

14. Remove the thimble and beaker and immediately place in a desiccator containing Drierite and allow to cool to room temperature.

15. When cool, weigh the thimble and contents to the nearest 0.1 mg and record the weight.

VI. CALCULATIONS

The pentane insoluble content of the material can be calculated from the following equation:

$$\text{wt \% Pentane Insolubles} = [(B-A)/C] \times 100$$

where:

A = weight of alundum thimble empty (grams)
B = weight of alundum thimble plus pentane insoluble material (grams), and
C = weight of sample

Report the pentane insoluble content to the nearest 0.1%.

PENTANE INSOLUBLES OF SRC SOLIDS

VII. PRECISION AND ACCURACY

A. Precision

An SRC solid and LC Finer solid were analyzed in replicate (six determinations) to determine the repeatability of the procedure. The results of the analyses are listed in the table below.

Sample	Pentane Insolubles Mean (wt%)	Standard Deviation (wt%)	% Standard Deviation
SRC Solid	40.83	1.11	2.72
LC Finer Solid	41.09	2.40	5.84

B. Accuracy

The method is empirical and changes in the procedure will result in variations in results. Also, no certified standards exists for pentane-insolubles of coals or SRC material. Therefore, there is no way of determing the accuracy of the procedure.

The results were compared to a procedure using solvent fractionation in an ultrasonic environment. The comparison of results are listed below and there is a consistency between the values for each procedure. The solvent fractionation is lengthy, but the results are considered a good determinate of oil content in SRC solids.

Sample No.	Pentane Extraction Procedure	Solvent Fractionation Procedure (SFP)	% Difference
1914CB (HSRC Run 225)	87.5	96.3	-9.14
1915CB (LSRC Run 220)	40.8	43.3	-5.77
1951CB (LC Finer Solid)	41.1	39.7	3.53
1913CB (LSRC Run 225)	41.9	42.3	-0.95
1916CB (HSRC Run 220)	22.6	38.3	-6.46
1943CB (LC Finer Solid)	39.7	35.4	12.15

% Difference is calculated $\left(\frac{\text{Pentane Extraction Result - SFP Result}}{\text{SFP Result}}\right) \times 100$

PENTANE INSOLUBLES OF SRC SOLIDS

VIII. QUALITY ASSURANCE

A. All balances must be quality assured in accordance with the CRSD Analytical Services Quality Assurance Program Guidelines on page 32.

B. Pentane should be stored over molecular sieves to ensure dryness.

C. Indicating Drierite in desiccator should be checked before starting analysis and replaced if hydrated.

D. All samples should be analyzed in duplicate and if the determined level of precision expected is not reached, the sample analysis should be repeated.

E. The method is empirical, therefore strict adherence to all details of the procedure is necessary.

IX. PRINCIPLE

One gram of a working sample of SRC solid is placed in a beaker with 60 ml of pentane. The solution is heated to 40°C for 30 minutes and the mixture is filtered through a tared, medium porosity alundum thimble. The thimble is placed over 200 ml of pentane and extracted in the hot pentane vapors for 18 hours. The thimble is dried and reweighed to determine pentane insoluble residue.

The test is one measurement useful in evaluating and characterizing solids and detecting changes that have occurred during downstream processing.

X. REFERENCES

A. ASTM Manual, ASTM D 2317-76, Benzene-Insoluble Content of Tar and Pitch.

B. W. W. Stawasz, T. L. Slager and W. F. Tiedge, SRC Solid Product Characterization, RRRS APCI/CRS-82-006

MLK:bas:775
ANAL8

FILTERABLE AND ADHERENT INSOLUBLE CONTENT OF ACCELERATED AGED MATERIAL

(BARTLESVILLE ENERGY TECHNOLOGY CENTER)

This method is abstracted from the U.S. Department of Energy report "Accelerated Stability Test Techniques for Middle Distillate Fuels," DOE/BC/10043-12.

The method is applicable to M.O., M.O. blends or coal liquid samples having a density of less than 0.98 g/ml at 60°F. Samples having larger densities, like SRC-1 H.O., required excessively long filtration times or could not be filtered. No precision or accuracy data is available for SRC-1 liquids.

Note: The Bartlesville Energy Technology Center has improved the precision of this procedure since ICRC adopted it. Changes in the procedure are described in two publications: "Optimization of Accelerated Stability Test Techniques for Diesel Fuels," DOE/BC/10043-25, June 1981; "Fundamental Synthetic Fuel Stability Study," DOE/BC/10045-23, March 1982. ICRC has not incorporated recent changes into the method, since they have not been evaluated on SRC-I samples.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Isooctane and the adherent insolubles solvent containing equal parts of acetone, methanol and toluene are extremely flammable and vapors may cause flash fire. Avoid inhalation of vapors.

The drying oven contains exposed hot surfaces which may be avoided by wearing protective equipment as required.

FILTERABLE AND ADHERENT INSOLUBLE CONTENT OF ACCELERATED AGED MATERIAL

1. Scope

This method covers the measurement of insoluble material in a distillate fuel. The fuel is stored at a slightly elevated temperature over an extended period to give an indication of the fuel's potential long-term storage stability when stored at lower temperatures.

2. Summary of Method

A measured volume of filtered fuel in several glass containers is stored at 43.3°C for up to 24 weeks. After aging for various time intervals, one set of samples is removed from storage, cooled to room temperature, and analyzed for particulates by filtration. Adherent gum on the wall of the aging container is also measured.

3. Significance

Past research has indicated that storage at 43.3°C for one week is approximately equivalent to storage at average ambient (21°C) conditions for four weeks, assuming all other factors are equivalent. This test does not account for any environmental effects or container effects that may be encountered under a given field storage condition.

4. Apparatus

A. Sample containers are borosilicate glass bottles. The containers should preferably have a lid or cover with a Teflon insert and a hole for a borosilicate glass vent. The total capacity of the container is 500 ml.

B. Storage oven should be large enough to contain all sample bottles. It should be thermostatically controlled to maintain a temperature of 43.3°±1°C.

It shall be as dark as possible to prevent degradation due to photolytic reactions and shall also be "explosion proof."

C. Drying oven, maintained at 99°±1°C.

D. Gooch crucible, porcelain, No. 4

E. Filter flash assembly, as shown in Figure 1.

5. Reagents and Materials

A. Glass fiber filter, 2.4 cm circle

B. Hydrocarbon solvent, isooctane, ASTM knock test reference fuel grade, filtered through two glass-fiber filter papers.

C. Adherent insolubles solvent--Mix equal parts of reagent grade acetone, methanol, and toluene.

6. Sampling Procedure

Sample containers should preferably be one gallon or larger epoxy-lined cans. These containers should be filled almost to the top to avoid a significant air space, and then the ullage should be purged with nitrogen. Where possible, samples should be stored at reduced temperature, -7° to 4°C, prior to use.

7. Preparation of Apparatus

A. Sample storage bottles--Scrub each bottle with a detergent solution, and rinse it with water. Soak the bottle overnight in an alkaline laboratory glassware cleaning solution. Rinse the bottle with tapwater, then invert and flush with a stream of distilled water. Allow the bottles to dry, and rinse the bottles with 50 ml of the fuel sample. Bottles are vented during storage preferably by a Teflon insert and a glass tube bent in a u-shape to prevent contamination of the sample from airborne particulates (See Figure 2).

B. Insert two glass-fiber filter disks into each of three clean Gooch crucibles (Note 1). Wash the filters by pouring 200 ml of isooctane through the Gooch crucible. Dry the crucible and filters for one hour in an oven maintained at 99°±1°C. After drying, place the crucible and filters in a dessicator (without dessicant) for at least 30 minutes (Note 2). Weigh to the nearest 0.1 mg and retain for sample analysis. This procedure must be followed for the original sample and for each test sample interval. Prepare one crucible with filters for each bottle to be analyzed at each test sample interval and one crucible with filters to be used as a moisture correction. When a set of bottles is being analyzed, only one "moisture blank" is required. The "moisture blank" crucible should be weighed whenever the other crucibles are weighed and its change in weight subtracted from the final sample weight to give a sample weight that is corrected for atmospheric moisture.

8. Preparation of Sample

Prior to storage, the fuel oil shall be filtered through two glass fiber filters. It is suggested that a filtration system as shown in Figure 1 be used to filter the fuel (Note 3).

9. Procedure

A. Adjust the storage oven for sample storage to a temperature of 43.3°±1°C.

B. Prepare the fuel for storage (Section 8).

C. Place 400 ml of filtered fuel into each bottle. Use two bottles for each sampling period. (The suggested sampling periods are 4, 8, 12, 16, and 24 weeks). Also, fill two bottles with fuel to be used as extras. These extra bottles may be used in the case of accidents, if extra fuel is needed for futher tests, or if desired to extend the overall storage test duration. Also filter enough fuel to be analyzed for zero-week data. These analyses should be performed on the same day that the other samples are placed in storage. Label each storage bottle completely.

D. At the end of each prescribed period, remove two bottles and allow them to cool at 21°-27°C for 4-24 hours in a dark environment.

E. Analysis of the fuel, after it has cooled, should be performed in the following manner. Pour the sample from one bottle into a clean separatory funnel, using a glass funnel (Note 4), and filter through a tared Gooch crucible containing two glass-fiber filter papers (Note 4). Use a self-feeding system as illustrated in Figure 1. Repeat this procedure with the other bottle of fuel using a different crucible and filters (Note 5). Rinse the bottles used during aging with filtered hydrocarbon solvent (use three rinsings of approximately 50 ml each) to remove all traces of fuel from the bottle.

F. Filter these rinsings through the Gooch crucible. After the crucible is washed oil-free on the inside, turn off the suction and remove the crucible. Then rinse the outside of the crucible (using a wash bottle) with additional hydrocarbon solvent until its surface is oil free. The filtrate can be discarded.

G. Place the crucibles, including the "moisture blank" in the drying oven for four to six hours. Then place in a dessicator without dessicant and allow to cool to room temperature; requires at least one hour (Note 2). Weigh to nearest 0.1 mg.

H. After the final washing with the hydrocarbon solvent, dissolve any adherent gum on the sample container walls with two washings of 30 to 35 ml of the adherent insolubles solvent.

I. Place solvent in a clean, 150 ml beaker weighed to the nearest 0.1 mg and evaporate to dryness on a steambath. Place the apparently dry beaker in an oven at 105°±2°C for three hours. Remove the beakers to a dessicator without dessicant, allow to cool and weigh to the nearest 0.1 mg.

10. Calculation

A. Calculate the total insolubles after aging, in milligrams per 100 ml, as follows:

$$A = B+C/4.0$$

where:

A = Total insolubles, mg/100 ml,

B = Weight of filterable insolubles, mg, and

C = Weight of adherent insolubles, mg, as determined in Section 9F. Correct values B and C for moisture blank.

B. For the aged fuel, report A, B, and C for both bottles to show repeatability of tests at each aging period.

11. Notes

Note 1: A single paper will not prove satisfactory since it may rupture under strong vacuum.

Note 2: A dessicator is used to protect the crucible and filters from airborne particulates. The dessicant is removed from the dessicator to allow the crucible to cool in an environment similar to the surrounding environment and thereby prevent possible errors due to sudden absorption of moisture from the atmosphere when the crucible is removed from the dessicator. The crucible used as a "moisture blank" will correct for the atmospheric moisture.

Note 3: The receiving flask, separatory funnel, and glass funnel should be as clean as the storage bottles (Section 8.1). These items should also be rinsed with filtered isooctane.

Note 4: If severe filter plugging is encountered so that filtration is not complete in three hours, discontinue the test with the notation that filter plugging occurred.

Note 5: ASTM D 1500 color and D 381 Steam Jet Gum can be determined on the filtered fuel if desired. If these analyses are to be carried out, do not add rinsings or contaminate the filtered fuel in any manner, and protect the sample from light until these tests are completed.

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MICROANALYTICAL LABORATORY PROCEDURES

HEAT OF COMBUSTION OF LIQUID HYDROCARBON BY BOMB CALORIMETER

(ASTM D 240)

The procedure is applicable to all SRC-1 liquids and blends as written. Heats of combustion are generally referred to as higher (gross) heating values. A Parr Adiabatic Calorimeter with oxygen bomb is recommended for use in this method.

The higher heating values for SRC-I liquids are generally between 17,800 and 16,700 BTU/lb; the L.O. samples are near the upper value, the H.O. are near the lower value, and SRC-1 M.O. are approximately 17,200 BTU/lb.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Keep 2,2,4-trimethylpentane from open flames if using as a standard.

GROSS CALORIFIC VALUE OF SOLID FUEL BY THE ADIABATIC BOMB CALORIMETER

(ASTM D 2015)

The procedure applies to all solid fuels as written, including coal, coke, HSRC, LSRC, TSL SRC and KMAC. Grind enough material to produce five grams of working sample.

Safety

SRC solids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Grinding of solid samples should be completed in a well-ventilated area and a dust mask must be worn by the analyst.

MOLECULAR WEIGHT OF HYDROCARBONS BY THERMOELECTRIC MEASUREMENT OF VAPOR PRESSURE

(ASTM D 2503)

The procedure is applicable to SRC-1 solvent fractionalized subfractions (preasphaltenes, asphaltenes and pentane-soluble oils) and distillate liquids with an initial boiling point greater than 400°F.

SRC derived solid and liquid fractions associate in dilute, polar solvents. Therefore, the experimental concentration range is maintained between four to seven grams per liter.

The following are the solvent and experimental temperature range for each fraction:

FRACTION	SOLVENT	TEMPERATURE
1. Preasphaltenes, asphaltenes, and heavy distillates	Pyridine	85 - 90°C
2. Pentanesoluble oils and low boiling range distillation	Methylene chloride	28 - 32°C

SRC-1 M.O. and H.O. have molecular weights of approximately 150 and 250, respectively. Molecular weight values for SRC-1 solids are between 400-650.

Safety

SRC-1 material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Grinding of SRC-1 solid must be completed in a well-ventilated area and the analyst must be required to wear a lab coat and a dust mask.

Methylene chloride and pyridine should be used in a well-ventilated area. Pyridine has a permissible exposure limit of 5 ppm (15 mg/m^3).

SPECIFIC HEAT OF AIRCRAFT TURBINE LUBRICANTS BY THERMAL ANALYSIS
(ASTM D 3947)

The thermal analysis procedure applies to all SRC-1 products as written. The temperature calibration of the thermal analyzer is completed with pure indium. Sapphire has a well characterized specific heat and is used to quality assure the instrumentation.

Grind at least one gram of solids to use as a working sample.

Safety

SRC liquids and solids should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Grinding of any coal, coke or KMAC must be completed in a well-ventilated area and the analyst be required to wear a lab coat and dust mask.

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

(APCI METHOD NO. 156)

The method is applicable to SRC-1 hydrotreated liquids which contain low heteroatom content. Procedure 6-C, " Single Boat Injection System into a High Capacity Combustion Tube", is recommended for samples with complex matrices like SRC-1 liquids.

The SRC-1 liquids are highly aromatic. Therefore, a sulfur standard in toluene or a xylene isomer would be more appropriate than isooctane when determining the response factor. This type of solution parallels SRC-1 samples and will help eliminate errors due to matrix effects.

Samples

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

When using organic solvents, avoid inhalation of vapors and keep awa open flames. Use isooctane and other organic solvents in a well-ventilat

Glacial acetic acid has a permissible exposure limit of 10 ppm (25 mg and should only be handled in a well-ventilated area. Avoid skin contact all acids.

Air Products and Chemicals INC.

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES
ABSTRACTED FROM ASTM D-3120 AND THE DOHRMANN INSTRUMENT MANUAL

1. SCOPE:

This method is for the determination of total sulfur in the range of 0.1 ppm to 10,000 ppm for samples having an organic matrix. It is limited to samples having a chlorine level less than 10 times the sulfur content, the nitrogen level less than 10 wt percent absolute and the heavy metal concentration less than 500 ppm.

2. PRINCIPLE:

The sample is introduced into a combustion tube maintained at about 800°C having a flowing gas stream containing 80% oxygen and 20% inert gas (helium or argon). Oxidative pyrolysis converts the sulfur to sulfur dioxide which flows into a titration cell where it reacts with the triiodide ion present in the electrolyte. The triiodide consumed is coulometrically replaced and the total current required to replace the triiodide is a measure of the sulfur present in the sample injected. The reactions occuring in the titration cell are cited below.

$$I_3^- + SO_2 + H_2O \longrightarrow SO_3 + 3I^- + 2H^+$$

$$3I^- \longrightarrow I_3^- + 2e^-$$

3. APPARATUS

A. Dohrmann MCTS-30 Sulfur System or Equivalent

1. Pyrolysis Furnace (S-300)
2. Titration System (T-300-P)
3. Digital Microcoulometer (C-300)

(Dohrmann Division of Envirotech Corp., Santa Clara, Ca.)

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

B. Sampling Syringe

Syringe, 10 µl and 50 µl (P/N 523901 and P/N 523851)
(Dohrmann Division of Envirotech Corp., Santa Clara, Ca).

C. Single Boat Inlet System (SBI)

Single Boat Inlet System (P/N 526005)
(Dohrmann Division of Envirotech Corp., Santa Clara, Ca.)

D. Pyrolysis Tube

1. COT Pyrolysis tube, quartz (P/N 511778)
2. COT-H High capacity oxidative pyrolysis tube (P/N 511300)

(Dohrmann Division of Envirotech Corp., Santa Clara, Ca.)

E. Purge Value

Safety purge valve for use with COT-H pyrolysis tube (P/N 899434)
(Dohrmann Division of Envirotech Corp., Santa Clara, Ca.)

F. Exit Tube

Quartz exit tube kit (P/N 511760): Includes exit tube inserts (P/N 511776) Quartz Wool (P/N 511735, "O"-rings (P/N 511762) and a reducing joint (P/N 523733).
(Dohrmann Division of Envirotech Corp., Santa Clara, Ca.)

G. Septa

Septa, Teflon backed (P/N 517787 and P/N 517798)

H. Volumetric Flask

Kimax No. 28014 (Class A), 100 ml capacity
(Kimble Products, Owens-Illinois, Inc., Toledo, Ohio)

I. Analytical Balance

Analytical Balance capable of weighing to 0.01 gm, Mettler #H54AR.
(Fisher Scientific Co., King of Prussia, Pa.)

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

J. Vials

2 dr, Fisher #3-338C
(Fisher Scientific Co., King of Prussia, Pa.)

K. Pipet, Volumetric

4 ml capacity, Kimax #37010
(Kimble Products, Owens-Illinois, Inc., Toledo, Oh)

L. Automatic Injection Adaptor

Hamilton Repeating Dispensor (P/N 899145)
(Dohrmann Division of Envirotech Corp., Santa Clara, Ca.)

REAGENTS AND MATERIALS

A. Water

Deionized, distilled water

B. Acetic Acid

Acetic Acid, Reagent Glacial (P/N AX0073)
(Matheson, Coleman and Bell, Norwood, Ohio)

C. Gases

Oxygen and Helium, zero grade
(Air Products and Chemicals, Inc., Trexlertown, Pa.)

D. Potassium Iodide

KI, Reagent, Crystals (P/N PX1505)
(Matheson, Coleman and Bell, Norwood, Ohio)

E. Sodium Azide

NaN_3, Reagent (P/N SX0299)
Matheson, Coleman and Bell, Norwood, Ohio)

F. Isooctane

C_8H_{18} Pure Grade
(Philips Petroleum Co., Bartlesville, Ok.)

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

G. Butyl Sulfide

C_8H_9S, Reagent (P/N BX2075)
(Matheson, Coleman and Bell, Norwood, Oh.)

H. Cell Electrolyte Solution

Dissolve 0.5 gm of potassium iodide (KI) and 0.6 gm of sodium azide (NaN_3) in approximately 500 ml of high-purity water, add 5 ml of acetic acid (CH_3COOH) and dilute to 1000 ml. (Note 1)

I. Sulfur Standard (1000µg/ml or 1445µg/gm)

Tare a 100 ml volumetric flask, add about 0.4562 gm of N-butyl sulfide, reweigh and dilute to 100 ml with isoostane (Note 2)

$$S\ (\mu g/ml) = \frac{(\text{wt. of N-butyl sulfide})\ (0.2192)\ (1X10^6)}{(100ml)}$$

$$S\ (\mu g/gm) = \frac{(\text{wt. of N-butyl sulfide})\ (0.2193)\ (1X10^6)}{(100\ ml)\ (0.6918\ gm/ml)}$$

where 0.2192 = wt. fraction of sulfur in N-butyl sulfide
0.6918 = density of isooctane

J. Sulfur Standards

To prepare standards of less than 1000 µg/ml dilute the above solution V/V with isooctane to reach the appropiate concentration.

5 INSTRUMENT START-UP AND CALIBRATION

A. Start-up

1. Set the instrument conditions according to one of the three procedures to be used, as presented in Section 6.
2. Attach the cell.
3. Push the generator read button.
4. Flush the cell with electrolyte until the generator read signal is negative.
5. Switch to single cycle operation and base line read.

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

6. The base line should be highly negative. It will rapidly come to an equilibrium reading which should be slightly negative.

7. Switch to integrate ng.

8. Run 3 analyses according to the selected procedure to condition the instrument.

B. Calibration

1. Select the standard to be used. (Note 2)

2. Following the procedure selected below analyze the sample in triplicate and record the sulfur level (S_2). The calculated recovery factors should be within ± 2% or further standardization analyses should be performed.

3. Every 2 hours of operation a standard should be run to check the system stability.

4. Every 4 hours of operation the cell electrolyte should be changed and the system calibration rechecked.

6. PROCEDURE

This system can be operated in three different configurations: A. Syringe injection, B. Boat injection and C. Boat injection into a high capacity combustion tube. Each will be described below.

A. Syringe Injection

1. Instrumental conditions: (Note 3)
   Figure 1 = instrumental set-up
   Inlet Temperature = 700°C
   Center Temperature = 800°C
   Outlet Temperature = 800°C
   Exit Tube = Packed with 1/2 in. of quartz wool
   Heating Tape = On
   Reactant Gas (Oxygen) = 160 cc/min.
   Inert Gas (Helium) = 40 cc/min.
   Bias Voltage = 160 mV
   Gain = 100
   Integration Time = Variable (Typical 180 sec.)
   Range = x 1 for 2,000 μg of S or x 10 for 10,000 μg to 2,000 μg of S.

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

2. Fill the 10 μl or 50 μl syringe with an appropiate volume of sample (less than 80% of the syringe capacity) (Note 4).

3. Draw air into the syringe until the lower maniscus falls on the 1 μl or 10 μl mark of the syringe and record the volume (V_1).

4. Insert the needle into the pyrolysis tube and wait 15 sec. for the signal due to the material in the needle to be titrated.

5. Press the integrate start button.

6. When the blue light goes on, inject the sample at a rate of less than 0.2 μl/sec. with a pause of 1 sec. between each pulse. (Note 5).

7. Remove the syringe, draw air into the syringe setting the lower maniscus on the 1 μl or 10 μl mark and record the volume of sample remaining in the syringe (V_2).

8. Record the ng of sulfur detected by the analyzer at the end of integration time (S_1). If the DVM is still increasing when integration stops, increase the integration time and repeat the analysis.

9. Each sample should be analyzed in triplicate.

B. Single Boat Injection System (Note 6)

1. Instrument Conditions (Note 3).
Figure 2 = hook-up of gases and boat to the pyrolysis tube
Inlet Temperature = 700°C
Center Temperature = 800°C
Outlet Temperature = 800°C
Exit Tube = Packed with 1/2 in. of quartz wool
Heating Tape = On
Reactant Gas (Oxygen) = 160 cc/min.
Inert Carrier (Helium) = 20 cc/min.
Auxiliary Carrier (Helium) = 20 cc/min.
Bias Voltage = 160 mV
Gain = 100
Integration Time = Variable (Typical 300 sec.)
Range = x 1 for 2,000 μg of S or x 10 for 10,000 μg to 2,000 μg of S.

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

2. Place the sample boat in position A (Figure 2) Note 6).

3. Fill the 10 µl or 50 µl syringe with an appropiate volume of sample (less than 80% of the syringe capacity) (Note 4)

4. Draw air into the syringe until the lower maniscus falls on the 1 µl or 10 µl mark and record the volume. (V_1).

5. Press the integrate start button

6. Inject the sample into the quartz boat when the blue lamp comes on. Touch the side of the boat to remove the last drop of sample.

7. Before withdrawing the syringe back the syringe tip away from the boat and draw in some gas. Then withdraw the syringe. Set the lower maniscus on the 1 µl or 10 µl mark and record the volume. (V_2).

8. Place the boat into the warm space (Position D of Figure 2) so that the furnace can warm the sample to drive off the low boiling materials or until the solvent peak has been titrated as noted by a decrease in the rate of titration. (Note 5)

9. Slowly insert the boat into the hot zone (Position E of Figure 2) until the integration time has elapsed. The gas selector valve is pushed in to put oxygen into thc SBI after about one minute. If the DVM is still increasing at termination of integration increase the integration time and repeat the analysis.

10. Withdraw the boat to position B (Heat Sink) for 30 seconds, pull out the selector valve and record the sulfur level (S_1).

11. Analyze each sample in triplicate.

C. Single Boat Injection System into a High Capacity Combustion Tube

1. Instrument Conditions (Note 3)
Figure 3 shows the hook-up of the gases and the SBI to the high capacity pyrolysis tube.
Inlet Temperature = 700°C
Center Temperature = 800°C
Outlet Temperature = 850°C
Exit Tube = Packed with 1/2 in. of quartz wool
Heating Tape = On
Reactant Gas (Oxygen) = 110 ml/min.
Auxiliary Gas (Oxygen) = 10 to 14 ml/min.
Carrier gas (Helium) = 8 to 10 ml/min.

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

Range = x1 for 2,000 μg of S or x10 for 10,000 μg to 2,000 μg of S.
Bias Voltage = 160 mV
Gain = 100
Integration Time = Variable (Typical 480 sec.)

2. Place the sample boat in position A (Figure 3)(Note 6)

3. Fill the 10 μl or 50 μl syringe with an appropiate volume of sample (less than 80% of syringe capacity) (Note 4).

4. Draw air into the syringe until the lower maniscus falls on the 1 μl or 10 μl mark and record the volume (V_1).

5. Press the integrate button

6. Inject the sample into the quartz boat when the blue lamp comes on. Touch the side of the boat to remove the last drop of sample.

7. Before withdrawing the syringe back the syringe tip away from the boat and draw in some gas. Then withdraw the syringe, set the lower maniscus on 1 μl or 10 μl and record the volume (V_2).

8. Move the boat to position D of Figure 3 (warm zone) so that the furnace can warm the sample driving off the low boiling materials usually about 1 minute or until the solvent peak has been titrated as noted by a decrease in the rate of titration.

9. Insert the boat into the hot zone (Position E of Figure 3) until the integration time has elapsed. At about four minutes the flow reversal valve is depressed for 45 sec. and returned to the out position. The purge toggle valve is then actuated for 1 min.

10. If the DVM is still increasing the integration time and repeat the analysis.

11. Withdraw the boat to position B (heat sink) for 1 minute and record the sulfur level (S_1).

12. Each sample should be analyzed in triplicate.

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

7. DENSITY MEASUREMENT

A. Tare a 2 dram vial and cap on an analytical balance to the nearest 0.01 mg (W_1).

B. Pipette 4 ml. of sample into the vial, cap the vial and reweigh to the nearest 0.01 mg (W_2).

8. CALCULATIONS (Note 7)

A. Density

$$d\ (\text{gm/ml}) = (W_2 - W_1)/4$$

where W_2 = weight of full vial (g)

W_1 = weight of empty vial (g)

4 = volume of pipette (ml)

B. Response Factor

$$RF = \frac{S_2}{(V_1 - V_2)\ (S_v)} = \frac{S_2}{(V_1 - V_2)(d)\ (S_w)}$$

where S_2 = sulfur recorded for the analysis of the standard (ng)

V_1 = volume of liquid in syringe before injection (µl)

V_2 = volume of liquid in syringe after injection (µl)

S_v = sulfur in standard (µg/ml)

S_w = sulfur in standard (µg/g)

Use the average RF for all standards run.

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

C. Sulfur Content

$$S\ (\mu g/g) = \frac{S_1}{(V_1 - V_2)\ (d)\ (RF)}$$

where S_1 = sulfur recorded for the analysis of the sample (ng)

V_1 = volume of liquid in syringe before injection (μl)

V_2 = volume of liquid in syringe after injection (μl)

d = density of sample

RF = average response factor.

9. PRECISION AND ACCURACY

The precision and accuracy depend on the level of sulfur being analyzed. The following Table summarizes this data. (Note 8).

S (ppm)	Precision (1σ)	Accuracy (1σ)
0.1	0.05 (ppm)	0.05 (ppm)
0.5	0.07 (ppm)	0.07 (ppm)
1.0	0.10 (ppm)	0.10 (ppm)
10.0	0.50 (ppm)	0.50 (ppm)
100.0	3.2 (ppm)	3.2 (ppm)
>500.0	3.0% relative (ppm)	3.0% relative (ppm)

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

10. NOTES

Note 1. This solution should be prepared 24 hours prior to use and if stored in a dark place should be usable for 3 months.

Note 2. The standards used for calibration should be of the same type as the sulfur species expected in the sample and the level of the sulfur content should be similar. If the level of sulfur is expected to be greater than 1,000 µg/ml, increase the amount of butyl sulfide or other appropiate sulfur species by the appropiate amount.

Note 3. The Bias voltage, gain, and integration time may vary depending on the sample and instrument. Each should be maximized prior to use.

Note 4. The volume of sample injected depends on the range, setting of the instrument and the sulfur content of the sample. For various levels of sulfur, the volume to be injected can be approximated by the following formulas. If the integrated value exceeds 2,000 ng of S on Range X1 or 10,000 ng of S on Range X10, increase the Range setting, reduce the amount injected or dilute the sample with a sulfur free solvent of the same matrix and boiling range of the sample.

(Range X1): (µl injected)=(1,000)/(Sulfur level expected (ppm)).

(Range X10): (µl injected)=(5,000)/(Sulfur level expected (ppm)).

Note 5. Extreme care must be taken to avoid injecting the sample too rapidly, since the sample may form pyrolysis products rather than combustion products. The pyrolysis materials will coke up the cell and prevent further operation until a clean-up has been performed.

DETERMINATION OF TRACE LEVELS OF SULFUR IN ORGANIC MATRICES

Note 6. The sample boat must be conditioned by pushing it into the hot zone of the pyrolysis tube. Proper conditioning is acheived when a blank of less than 3 ng is obtained.

Note 7. The instrument normally reads in ng of sulfur. It can be operated in the ppm mode if the standard and the samples have the same matrix composition and the sulfur compounds in the samples give similar recoveries to those of the standards. For operation in this mode, follow the manufactures directions during calibration. The instrument is then direct reading.

Note 8. Without having the absolute sulfur levels determined by another more accurate technique the accuracy is assumed to be equal to the precision. This should be valid if the matrix of the standard and the sample are similar.

11. REFERENCES

1. ASTM D3120-72T "Tentative Method of Test for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry", ASTM, Philadelphia, Pa. 1976.

2. Dohrmann Equipment Manual, Edition May 17, 1976, P/N 915-025; M14E6, Dohrmann Instrument Division of Envirotech Corp., Santa Clara, Ca.

FIGURE 1

CONFIGURATION FOR OXIDATIVE ANALYSIS - SYRINGE INJECTION

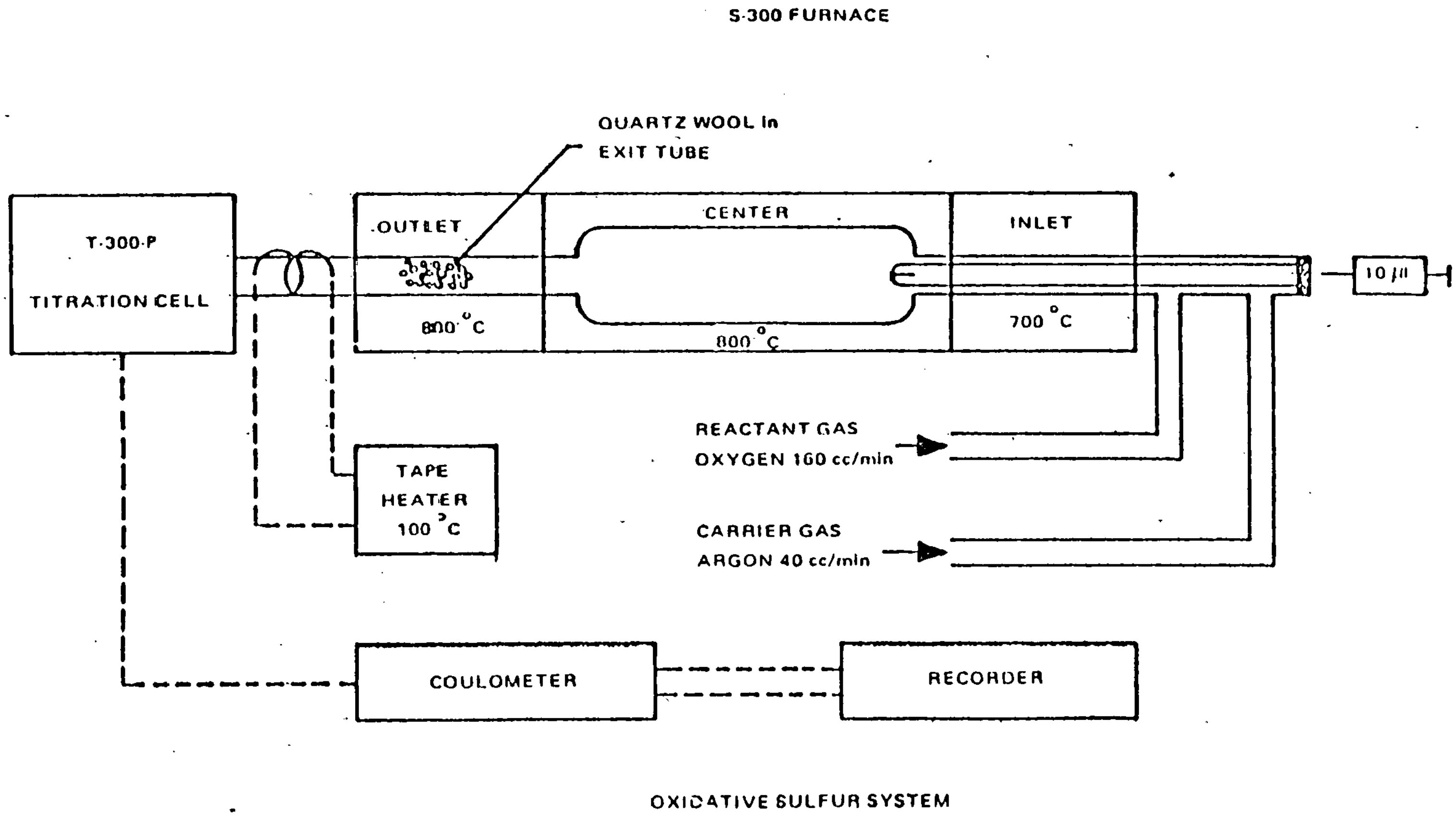
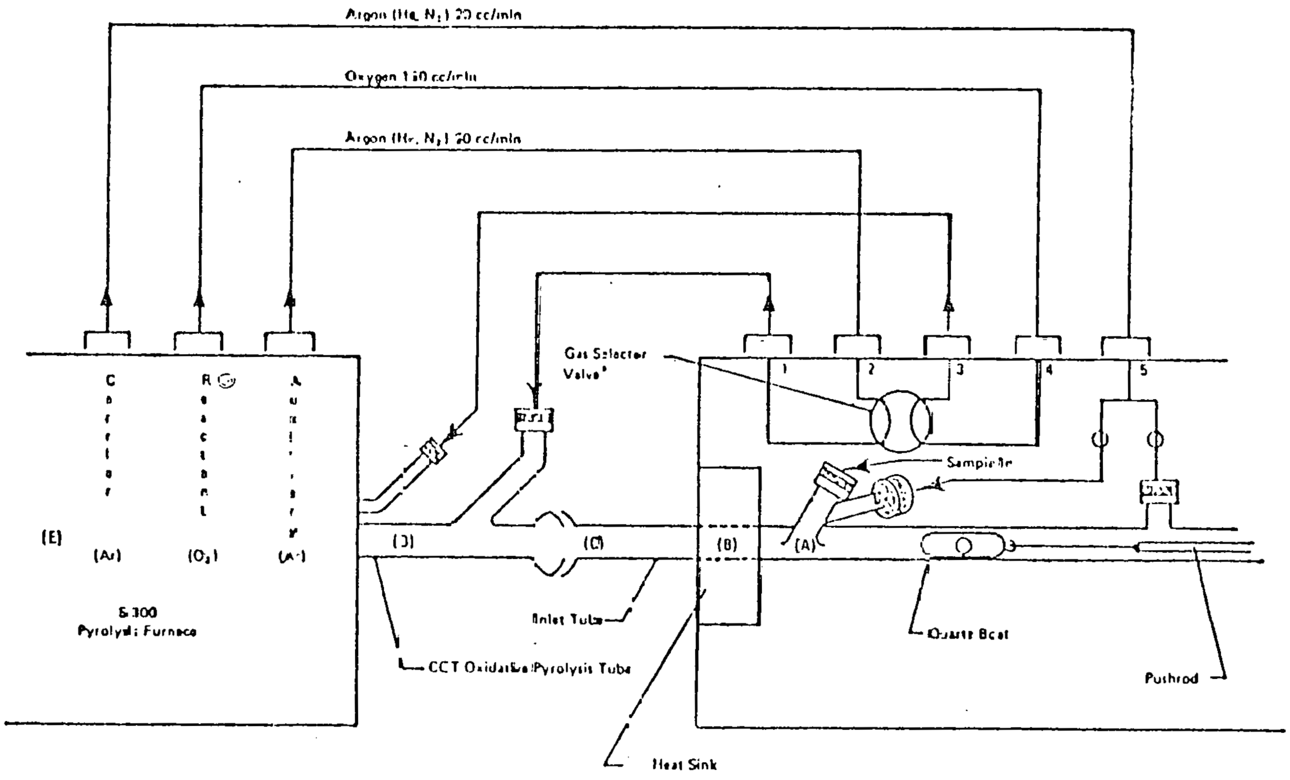


FIGURE 2

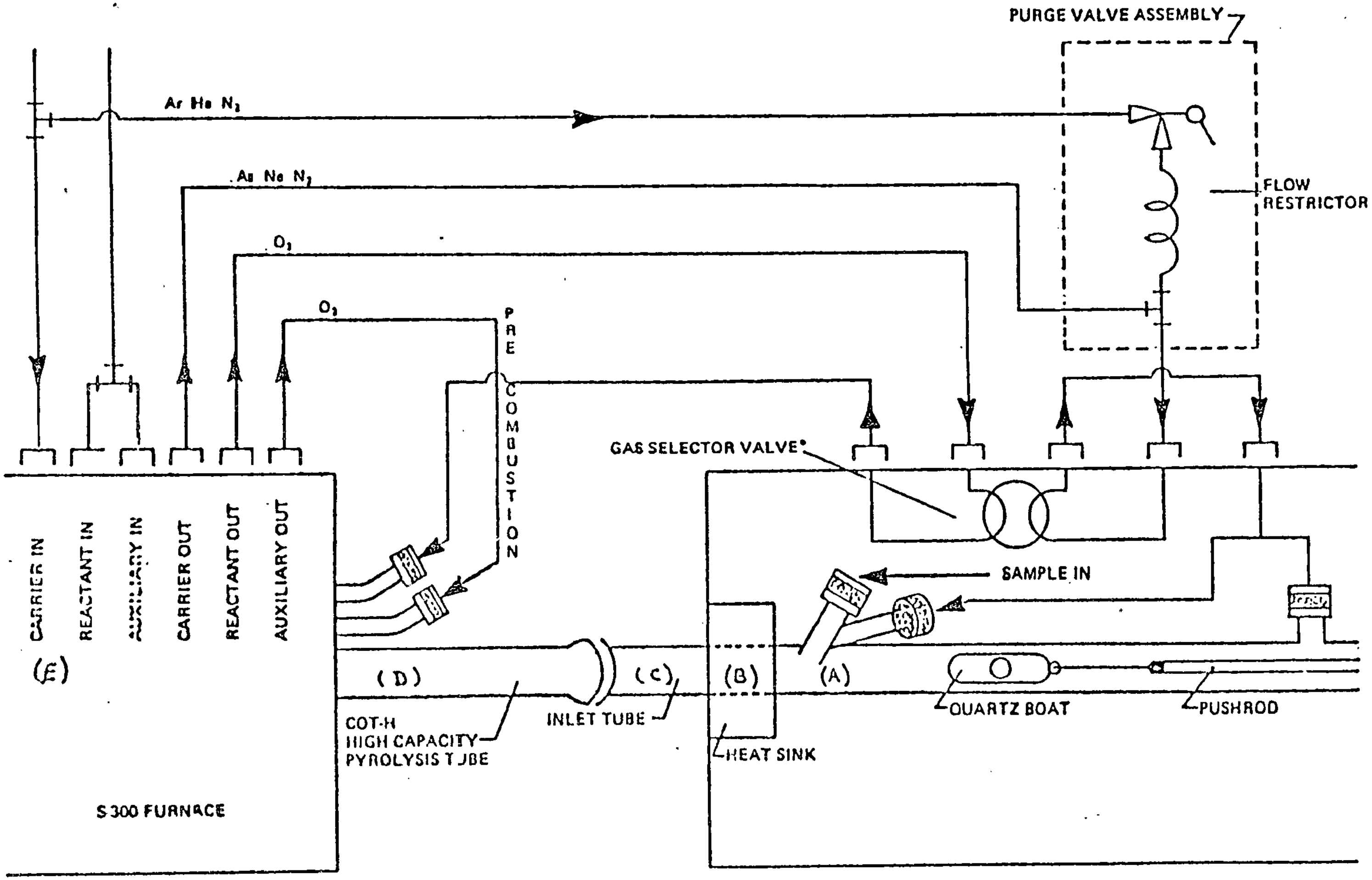
SB1 CONFIGURATION FOR OXIDATIVE ANALYSIS



* Gas Selector Valve shown in the "OUT" Position

FIGURE 3

SB1 SINGLE BOAT INLET CONFIGURATION FOR OXIDATIVE ANALYSIS USING THE COT-H HIGH CAPACITY PYROLYSIS TUBE (P/N 5113000)



* Shown in "O[illegible]" position

COAL TAR PITCH VOLATILES
(APCI METHOD NO. 195)

This procedure is for the analysis of atmospheric monitoring samples collected by an industrial hygienist. The samples must be analyzed in a clean area to avoid atmospheric contamination during analysis.

Safety

Prepare chromic acid while wearing a face mask, gloves and acid resistant lab coat. Add sulfuric acid slowly with constant stirring.

Use benzene and acetone in a well-ventilated area away from open flames. Benzene is a known carcinogen with a permissible exposure limit of 1 ppm.

ANALYTICAL METHOD # 195

COAL TAR PITCH VOLATILES

I. SCOPE

This method is for the quantitative determination of coal tar pitch volatiles collected on a prefilter and silver membrane filter during atmospheric monitoring.

II. PRINCIPLE

The prefilter and silver membrane filter are extracted with benzene (Note 1). The extracted coal tar pitch volatiles are concentrated by evaporation of the solvent. The benzene concentrate is transferred to a glass cup and evaporated to dryness. The weight of the residue is reported as micrograms of coal tar pitch volatiles.

III. APPARATUS

A. Sample beaker, pH meter, glass - 5 ml Cap. Cat. S530134 Sargent Welch Scientific Co., Springfield, New Jersey. Using a wet glass cut-off saw reduce the size of the beaker to approximately 3 ml with a tare weight of 2.800 ± 0.005 g.

B. Evaporative Concentrator 10 ml graduated evaporative concentrator plus a 1 ml tube. 14/20 joint Cat. #K-569000-0314 Kontes Glass Co., Vineland, New Jersey.

C. Sintered Glass Funnel (Buchner) 15 ml medium porosity Cat.#D-955000-0144 Kontes Glass Co., Vineland, New Jersey

D. Balance Micro - Autobalance AD-2 Perkin-Elmer, Norwalk, Connecticut.

E. Test tube 15 ml, Arthur H. Thomas Co., Philadelphia, Pa.

F. Graduate Cylinder 10 ml, Arthur H. Thomas Co., Philadelphia, Pa.

G. Ultrasonic Bath Ultrasonic Cleaner -Cole Palmer Instrument, Inc., Chicago, Ill.

H. Filter Apparatus Fisher Filtrator Cat. #9-788, Fisher Scientific Co., King of Prussia, Pa.

I. Pipettes, disposable, Pasteur 5-3/4" length Cat. #13-678-6A Fisher Scientific Co., King of Prussia, Pa.

J. Analytical Balance Weights Cat. #2-214B
Fisher Scientific Co., King of Prussia, Pa.

K. Vacuum Oven 40°C.

L. Tweezers.

M. Beakers 100 ml, 30 ml, Arthur H. Thomas Co., Philadelphia, Pa.

IV. REAGENTS

A. Chromium Trioxide (Chromic Acid) Cat. #C-391, Lehigh Valley Chemical Co., Easton, Pa.

1. Prepare a solution of 100 g chromic acid and 100 ml of water.
2. Add to this solution, carefully, 13-1/2 lbs. of 66°B sulfuric acid.

B. Benzene Cat. #C093-L95 Nonograde
Arthur H. Thomas Co., Philadelphia, Pa.

C. Acetone - Cat. #C006-T53
Arthur H. Thomas Co., Philadelphia, Pa.

D. Sulfuric Acid Cat. #746-C96 66°B.
Arthur H. Thomas Co., Philadelphia, Pa.

E. Drierite, indicating, 8 mesh W. A. Hammond Co., Xenia, Ohio.

V. PROCEDURE

A. Pretreatment of Equipment

1. Clean all glassware with chromic acid.
2. Rinse with deionized-distilled water.
3. Rinse with acetone. Dry with air.
4. Rinse all glassware with nonograde benzene.
5. Place 80 cc of indicating drierite in a 100 ml beaker and set the beaker in the microbalance weighing chamber.

B. Extraction (All work should be done in an exhaust hood).

1. Transfer the glass prefilter and the silver membrane filter to a 15 ml test tube using tweezers.

2. To the test tubes, add 5 ml of benzene and place the test tube in an ultrasonic bath for 5 min.

3. Filter the benzene through the 15 ml sintered-glass funnel into the base of the Kontes evaporator using the Fisher Filtrator with the vacuum on (Note 2).

4. With the vacuum on, evaporate approximately 1 ml of the benzene from the base of the Kontes evaporator.

5. Rinse the test tube with 1.5 ml of benzene using a Pasteur disposable pipette.

6. Transfer the benzene to the sintered-glass funnel with the vacuum on. Evaporate approximately 1 ml of benzene from the base of the Kontes evaporator.

7. Repeat steps 5 and 6.

8. Remove the base of the Kontes evaporator from the Fisher Filtrator. Connect the base to the distillation column and evaporate the sample to approximately 1 ml using house vacuum.

9. Set the analytical microbalance at zero as follows:

   Place a 3-ml beaker cup on the right-hand pan as a reference weight. To the left-hand pan add 2.8 grams of analytical weights. With the range control in the auto position, adjust the course and fine pots until the balance reads zero µg (Note 3).

10. Remove the weights from the left-hand pan and add a 3-ml beaker cup. Set the range control at 10 and read the weight of the cup.

11. Repeat steps 9 and 10 four more times. Record the weight of the cup each time. Average these weights as the tare of the cup. Discard any weight that appears to be substantially different from the other weights (> 0.020 mg from the average).

12. Using a disposable pipette, transfer the benzene concentrate from the base of the Kontes evaporator to the tared beaker cup. Wash down the sides of the base of the Kontes evaporator with approximately 0.5 ml of benzene using a disposable pipette. Transfer this to the tared cup using the first disposable pipette.

13. Transfer the beaker cup to the Fisher Filtrator with a sintered-glass funnel in its top. Apply the vacuum slowly, and evaporate to dryness.

14. Transfer the beaker cup to a 40°C vacuum oven for 1 hour.

15. Transfer the beaker cup to the micro analytical balance and allow it to come to room temperature (1 hour).

16. Weigh the beaker cup as described in steps 9 thru 11.

VI. CALCULATION

Report the difference between the tare weight of the cup and the final weight as milligrams of coal tar pitch volatiles.

VII. PRECISION AND ACCURACY

Government specification is less than 200 $\mu g/m^3$. Without absolute standards the value for the accuracy of this test cannot be established. It is assumed to be equal to the precision which is ± 15 μg. A reading < 30 μg is reported as < 30 μg.

VIII. REFERENCES

1910-1499, S-106, 31:8345 Appendix B of Industrial Hygiene Guidelines.

Note 1: Benzene is a known carcinogen and should be handled carefully. The use of plastic throw-away-gloves, an efficient exhaust hood, and periodic monitoring of body exposure is recommended.

Note 2: The base of the Kontes evaporator can be supported with a one-hole No. 7 rubber stopper in a 30 ml beaker. The height should be adjusted so that the tip of the filter is inside the base.

Note 3: Extreme care should be exercised when adding or subtracting the beaker cups or the weights from the balance pans since jarring the balance beam may change the zero position.

Analytical Method No. 244

Air Products

DETERMINATION OF TRACE LEVELS OF CHLORINE IN ORGANIC MATRICES

I. SCOPE

This method is for the determination of total chlorine in liquid samples having an organic matrix. The range of the method is 1.0 to 500 ppm (µg/g) total chlorine. The working range of the procedure can be extended to higher chlorine levels by diluting the sample with an appropriate solvent. Solid samples can be analyzed by dissolution in a suitable solvent, i.e., totally dissolves the sample and is not a chlorinated chemical. The final concentration of chlorine in the solution must be in the working range of the procedure. See Section X for a complete discussion of interferences.

II. APPARATUS

A. Pyrolysis Furnace

S-300 (Dohrmann Division of Envirotech Corp., Santa Clara, Ca)

B. Titration System

T-300-P (Dohrmann Division of Envirotech Corp., Santa Clara, Ca)

C. Microcoulometer

C-300 (Dohrmann Division of Envirotech Corp., Santa Clara, Ca)

D. Syringe

10 and 50 µl graduated
P/N 523901 and P/N 523851
(Dohrmann Division of Envirotech Corp., Santa Clara, Ca)

E. Single Boat Inlet (SBI) System

P/N 526005
(Dohrmann Division of Envirotech Corp., Santa Clara, Ca)

F. Pyrolysis Tube

COT, quartz P/N 511778
(Dohrmann Division of Envirotech Corp., Santa Clara, Ca)

G. Quartz Exit Tube Kit

Includes:
- Exit tube inserts (P/N 511776)
- Quartz Wool (P/N 511735)
- O-Rings (P/N 511762)
- Reducing Joint (P/N 523733)

(Dohrmann Division of Envirotech Corp., Santa Clara, Ca)
Pack the quartz exit tube with one inch of cupric oxide and quartz wool at both ends, if the sample is expected to contain sulfur or nitrogen (See Section X). The cupric oxide accelerates complete combustion of the sample to the oxides and decreases the probability of producing titratable species, e.g., cyanide.

H. Septa

Teflon Backed, P/N 517787
(Dohrmann Division of Envirotech Corp., Santa Clara, Ca)

I. Volumetric Flask

100 ml, Class A, Kimax No. 28014
(Kimble Products, Owen-Illinois, Inc., Toledo, Ohio)

J. Volumetric Flask

1000 ml, Class A, Kimax No. 28015
(Kimble Products, Owen-Illinois, Inc., Toledo, Ohio)

K. Graduated Cylinder

1000 ml, 10 ml subdivision, No. 08550H
(Fisher Scientific Company, Pittsburgh, Pennsylvania)

L. Pipet, Volumetric

4 ml, No. 13-650-5D 10 ml, No. 13-650-5F (Fisher Scientific Company, Pittsburg, Pennsylvania)

M. Balance

Mettler H542 or equivalent. Precision ±0.01 mg, No. 01-909-542
(Fisher Scientific Company, Pittsburgh, Pennsylvania)

N. Vial

2 dram, No. 3-338C
(Fisher Scientific Company, Pittsburgh, Pennsylvania)

III. REAGENTS

A. 2,2,4-Trimethylpentane (Isooctane)

Certified ACS, Catalog No. 0-299
(Fisher Scientific Company, Pittsburgh, Pennsylvania)

B. Chlorobenzene

Certified ACS, Catalog No. B-255
(Fisher Scientific Company, Pittsburgh, Pennsylvania)

C. 2,4-Dichlorophenol

Reagent, Catalog No. 1933
(Fisher Scientific Company, Pittsburgh, Pennsylvania)

D. Toluene

Certified ACS, Catalog No. T-289
(Fisher Scientific Company, Pittsburgh, Pennsylvania)

E. Water

Deionized, Distilled

F. Acetic Acid, Glacial

Reagent, Catalog No. A-38
(Fisher Scientific Company, Pittsburgh, Pennsylvania)

Preparation of 70% Acetic Acid
Add 700 ml of glacial acetic acid to a 1 liter volumetric flask containing about 200 ml of distilled water by a graduated cylinder. Dilute to volume with distilled water.

G. Acetone

Certified ACS, Catalog No. A-18
(Fisher Scientific Company, Pittsburgh, Pennsylvania)

H. Oxygen Gas

Zero Grade
(Air Products and Chemicals, Inc. Trexlertown, Pennsylvania)

I. Cupric Oxide Wire

Catalog No. P/N 511866 (Dohrmann Division of Envirotech Corp., Santa Clara, California)

J. Helium Gas

Zero Grade
(Air Products and Chemicals, Inc. Trexlertown, Pennsylvania)

IV. SAFETY

The pyrolysis tube at the boat inlet and the outlet connection to the titration cell is very hot when furnace compartments are turned on. (The glass looks the same cool or hot.)

Chlorobenzene has a permissible exposure limit of 75 ppm (350 mg/m^3) and should be handled in a well ventilated area. If skin contact is made, immediately wash with soap and water. Use toluene and 2,2,4-trimethylpentane in a well ventilated area. Avoid skin contact with 2,4-dichlorophenol. Glacial acetic acid has a permissible exposure limit of 10 ppm (25 mg/m^3) and should only be handled in a well ventilated area.

V. PROCEDURE

A. Preparation of Standards

1. Chlorobenzene in 2,2,4-Trimethylpentane (500 μg/ml or 723 μg/g)

Weigh about 0.16 g of chlorobenzene to the nearest 0.1 mg in a 100 ml volumetric flask. Dilute to 100 ml with 2,2,4 - trimethylpentane. The concentration of chlorine can be calculated from the following equations:

$$\text{Cl } (\mu g/ml) = \frac{(A)\ (0.3150)\ (1 \times 10^{6})}{(100 \text{ ml})}$$

$$\text{Cl } (\mu g/g) = \frac{(A)\ (0.3150)\ (1 \times 10^{6})}{(100 \text{ ml})\ (0.6918 \text{ g/ml})}$$

where: A = wt of chlorobenzene added to flask (g)
0.3150 = wt fraction of chlorine in chlorobenzene
0.6918 = density of 2,2,4-trimethylpentane (g/ml)

2. 2,4-Dichlorophenol in Toluene (500 μg/ml or 577 μg/g)

Weigh about 0.115 g of 2,4-dichlorophenol to the nearest 0.1 mg in a 100 ml volumetric flask. Dilute to volume with toluene. The concentration of chlorine can be calculated form the following equations:

$$\text{Cl } (\mu g/ml) = \frac{(B)\ (0.4350)\ (1 \times 10^6)}{(100 \text{ ml})}$$

$$\text{Cl } (\mu g/g) = \frac{(B)\ (0.4350)\ (1 \times 10^6)}{(100 \text{ ml})\ (0.8669 \text{ g/ml})}$$

where: B = wt of 2,4-dichlorophenol added to flask (g)
0.4350 = wt fraction of chlorine in 2,4-dichlorophenol
0.8669 = density of toluene (g/ml)

3. Lower Chlorine Standards

To prepare chlorine standards less than 500 µg/ml dilute the above standards on a volume basis with the appropriate solvent. For example, to prepare a 50 µg/ml standard add 10 ml of a 500 µg/ml standard by pipet and dilute to 100 ml with the appropriate solvent.

B. Preparation of Samples

Liquid Samples

Liquid samples are used as received but may be diluted in a suitable solvent to extend the range of the microcoulometric procedure.

Solid Samples

Solid samples to be analyzed should be dissolved in a suitable solvent. The final solution must have a chlorine concentration between 1.0 and 500 ppm.

A suitable solvent for both liquid and solid samples must form a homogeneous solution and not be a chlorinated chemical. Trace chlorine levels in the solvent must be subtracted out as a reagent blank. Solvents containing sulfur, nitrogen, bromine and iodine should also be avoided (See Section X).

C. Instrument Set-Up (See Reference C for complete installation procedure)

1. Attach gas lines to pyrolysis tube and furnace according to the configuration shown in Figure 1.

2. Set furnace temperatures as follows:

Inlet Temperature = 850-900°C
Center Temperature = 850°C
Outlet Temperature = 800°C

It is important to note that chlorine recovery is a function of inlet temperature. Figure 2 is a plot of percent recovery of chlorine in pure compounds dissolved in water or toluene as a function of furnace inlet temperature. Chlorobenzene gave the theoretical yield of chlorine at 400°C. However, inorganic chloride required higher temperature because they do not decompose or volatilize at 400°C. Therefore, an inlet temperature at or above 850°C is suggested for total chlorine determination. The results of using a lower inlet temperature, 350°C, might give an indication of inorganic or organic chlorides present in the sample. Also, if the chlorine in the sample is present entirely as an organic species a lower inlet temperature can be used to increase furnace life.

3. Set gas flow rates as follows:

   Reactant (Oxygen) = 150 cc/min
   Inert (Helium) = 50 cc/min
   Auxiliary (Helium) = 50 cc/min

4. Set instrument parameters as follows:

   Bias Voltage = 245-265
   Gain = 2000-3500
   Integration Time = Variable (200 Sec.)
   Range = X 1

   The bias voltage is set to be exactly opposite the potential formed across the sensor electrode pair. This voltage will vary slightly from cell to cell and with different concentrations of electrolyte solutions. The gain and integration time vary depending upon instrument and sample. Each should be maximized prior to use.

5 Attach titration cell containing cell electrolyte solution. Wrap heating tape around tube from pyrolysis tube exit to titration cell entrance and turn on.

D. Instrument Calibration - Response Factor

1. Turn the microcoulometer on.

2. Push the generator read button.

3. Flush the titration cell with 70% acetic acid until the generator read signal is negative. (The sensor electrodes are therefore detecting no titration with silver ions.)

4. Depress the single cycle operation and base line read buttons.

   Immediately upon switching instrument modes the base line will be highly negative on the digital microcoulometer. Equilibrium will be quickly reached and the baseline reading should be slightly negative.

5. Depress integrate ng.

6. Place the sample boat in position A (Figure 1). Extreme care must be taken to avoid injecting the sample or standard too rapidly, since the sample may form pyrolysis products rather than combustion products. The pyrolysis materials will coke up the cell and prevent further operation until a lengthy clean-up of the titration cell has been performed.

7. Fill the 10 μl or 50 μl syringe with an appropriate volume of standard.

   Three factors must be considered when selecting a proper standard. The standard used should be of a similar concentration, a similar chlorine species and in a similar matrix. It is usually sufficient to know if the chlorine is present as inorganic or organic chlorine. The approximate concentration can be determined by a preliminary injection of the sample (See Section VE2). Matrix corrections can be made for complex mixtures by using either an aromatic (toluene), aliphatic (2,2,4-trimethylpentane) or combination solvent, depending upon the nature of the sample matrix. Proper matrix matching will also avoid small errors due to the amount of water produced from the combustion when analyzing for low chlorine levels. (See P. Gouverneur, Anal. Chim. Acta, V.50, pg 219, 1970).

8. Draw air into the syringe until the lower maniscus falls on the 1 μl or 10 μl (50 μl if using 50 μl syringe) mark and record the volume. (V_1).

9. Press the integrate start button.

10. Inject the standard into the quartz boat when the blue lamp comes on. Touch the side of the boat with syringe tip to remove the last drop of standard.

11. Before completely withdrawing the syringe, back the syringe tip away from the boat and draw in some gas. Then withdraw the syringe. Set the lower maniscus on the 1 μl or 10 μl (or 50 μl) mark and record the volume. (V_2).

12. Place the boat into the warm space (Position D of Figure 1) so that the furnace can warm the standard to drive off the low boiling materials or until the solvent peak has been titrated as noted by a decrease in the rate of titration.

13. Slowly insert the boat into the hot zone (Position E of Figure 1) until the integration time has elapsed. The gas selector valve is pushed in to put oxygen into the SBI after the boat has been in the hot zone for about one minute. If the digital counter is still increasing at termination of integration increase the integration time or gain and repeat the analysis.

14. Withdraw the boat to position B of Figure 1 (Heat Sink) for 30 seconds, pull out the selector valve and record the chlorine level (Clg).

15. Analyze standard in triplicate.

16. Calculation the response factor (RF) as follows:

$$RF = \frac{Cl_a}{(V_1-V_2) \times Cl_s}$$

Where Cl_a = actual chlorine value recorded for the analysis of the standard (ng):

V_1 = Volume of liquid in syringe before injection (ul).

V_2 = Volume of liquid in syringe after injection (ul).

Cl_s = Chlorine concentration in standard (ug/ml).

17. Average the three results and use in the final calculation for samples.

C. Analyses of Samples

1. Depress single cycle operation and baseline read. After equilibrium is reached, the baseline should be slightly negative. If the baseline is not negative, complete Steps 2 thru 4 in Section V-D.

2. Complete Steps 5 thru 14 in Section V-D with an appropriate sample size. Add the sample volume to produce between 100-1000 ng of total chlorine. If the chlorine content is unknown, inject a small volume of sample (<10 µl) and adjust volume accordingly. If the chlorine content is very high, a large injection volume will result in a very long titration time.

3. Analyze the sample in triplicate and report the average value.

F. Density Determination

1. Tare a 2 dram vial and cap on an analytical balance to the nearest 0.01 mg (W_1).
2. Pipette 4 ml. of sample into the vial, cap the vial and reweigh to the nearest 0.01 mg (W_2).
3. Calculate the density as follows:

   $d\ (gm/ml) = (W_2 - W_1)/4$

   where W_2 = weight of full vial (g)

   W_1 = weight of empty vial (g)

   4 = volume of pipette (ml)

4. Complete the determination in duplicate and use the average value for calculations.

VI. CALCULATION

The chlorine content of the sample can be calculated from the following equation:

$$Cl\ (\mu g/g) = \frac{Cl_a}{(V_1 - V_2) \times d \times RF}$$

where:

Cl_a = chlorine value recorded for analysis of the sample (ng).

V_1 = volume of liquid in syringe before injection (μl)

V_2 = volume of liquid in syringe after injection (μl)

d = average density of sample obtained from Section V F-4 (g/ml)

RF = average response factor obtained from Section V D-16

VII. PRECISION AND ACCURACY

To examine the accuracy and precision of the instrument, a Dohrmann standard was analyzed seven times. The standard, chlorobenzene in 2,2,4-trimethylpentane, contained 45.36 µg of chlorine/g. The average chlorine content for seven analyses was 43.9 µg/g; the standard deviation (SD) was 2.8 µg/g or 6.38%. Instrument specifications at this chlorine level are about 4.0% relative SD. Response factors were similar to published instrumental data, which show a typical system recovery of 80%.

The procedure was specifically developed for coal liquids or samples containing complex matrices. Therefore, the precision of chlorine analyses on selected SRC-1 (Solvent Refined Coal) liquids was determined. The data from five analyses of various SRC-1 liquids, using either chlorobenzene or 2,4-dichlorophenol as the calibration standard, are listed in Table 1. The standard deviation was about 10% at the 25-ppm chlorine level and increased at lower chlorine levels; these values are typical of those found for similar SRC-I liquids.

Table 1

Precision of Chlorine Analysis on Selected SRC-I Liquid Products

Sample	Density at 25°C (g/ml)		Chlorine (μg/g)
Light Oil (IBP[a]-400°F)	0.810		20.3
			23.0
			17.7
			18.7
			20.2
		Average	20.0
		Standard Deviation	2.0
Middle Distillate (400-650°F)	0.956		27.4
			26.8
			23.7
			26.0
			30.1
		Average	26.8
		Standard Deviation	2.3
Heavy Distillate (650°F-FBP[a])	1.02		3.0
			5.9
			2.6
			3.8
			3.9
		Average	3.8
		Standard Deviation	1.3

[a] IBP, initial boiling point; FBP, final boiling point.

The results of a spiking study to determine recovery factors in an SRC-I liquid matrix appear in Table 2. The study also determined whether the instrument can detect higher levels of chlorine without saturating the detector and losing linearity. The precision of the recovery factors measured is similar to that measured for lower levels of chlorine in 2,2,4-trimethylpentane.

Table 2

Results of a Spiking Study for Chlorine Determination Using SRC Liquids and 2,2,4-Trimethylpentane Containing Chlorobenzene

Sample	Expected Chlorine Value (ng)			Chlorine Found (ng)	% Error
	From Sample	From Spike	Total		
Light Oil-1	81.0	157.6	238.6	234.3	-1.80
Light Oil-2	74.3	157.6	231.9	224.0	-3.41
Middle Distillate-1	67.7	157.6	225.3	233.2	3.09
Middle Distillate-2	96.0	157.6	253.6	238.9	-5.80
Heavy Distillate	83.1	157.6	240.7	251.6	4.53
Hydrotreated Naphtha	0.0	157.6	157.6	163.9	4.00
Hydrotreated Low-Conversion Naphtha	0.0	49.0	49.0	53.9	10.0
Hydrotreated Low-Conversion Naphtha	0.0	73.5	73.5	69.6	-5.31
Hydrotreated High-Conversion Middle Oil	43.0	24.5	67.5	68.4	1.33
Hydrotreated High-Conversion Middle OIl	86.0	73.5	159.5	154.8	-2.95

VIII. QUALITY ASSURANCE

A. The response factor should be determined daily and checked after analyzing every third sample in duplicate. The results are recorded in the Dohrmann QA Manual and the values compared to previously recorded response factors. Major variations are an indication the instrument is not properly functioning. When large variations occur refer to the Troubleshooting section in Reference C.

B. The 70% glacial acetic acid in the titration cell should be changed daily or while analyzing samples if a steady negative baseline cannot be achieved. The titration solution should be changed after incomplete combustion of a sample.

C. All balances must be quality assured in accordance with the CRSD Analytical Services Quality Assurance Program on Page 32.

D. Once opened, all solvents should be stored over molecular sieves to ensure dryness.

E. All samples should be analyzed in triplicate and if the determined level of precision expected is not reached, the sample analysis should be repeated.

F. The quartz pyrolysis tube should be checked every month to determine if the tube devitrified. The tube should be changed if it devitrifies.

IX. PRINCIPLE

The sample is injected into a sample boat, which is placed in a flowing stream of 80% oxygen and 20% inert gas. The inert gas recommended is helium, but nitrogen or argon can be substituted. The gas and sample flow through a combustion tube maintained at 850°C at its inlet and center compartments and 800°C at the outlet. In the tube, the chlorine in the liquid is converted to either chloride or oxychlorides, depending on the initial sample matrix and chemical form of the chlorine. The combustion products flow into a titration cell, where they react with silver ions. The silver ions thus consumed by chloride are coulometrically replaced. The total current required to replace the silver ions is displayed on a digital microcoulometer; this value represents the amount of chlorine present in the samples. The value obtained is corrected by a response factor, previously determined for a sample with a similar matrix.

X. INTERFERENCES

Incomplete combustion products of sulfur and nitrogen interfere with the chlorine determination to different extents. The effects of the S and N interference is shown in Figures 3 and 4, which were generated by Matsuzaki and Koyano. Using the cupric oxide wire-packed scrubber tube nitrogen does not interfere up to 8% in the sample and sulfur does not additively interfere until it is present at the 10% level in the original sample. Using a small sample size and a slow injection rate will ensure reported interference levels.

Bromine and iodine are partly titrated in the silver cell. About 37% of the bromine content and 20% of the iodine content is determined as if it is chlorine content.

XI. REFERENCES

A. Matsuzaki, A. and Koyano, K., Anal. Chem., Vol. 52, 146-149 (1980).

B. Ladrach, W., van deCraats, F., and Gouverneur, P., Anal. Chem. Acta., Vol. 50, 219-228 (1970).

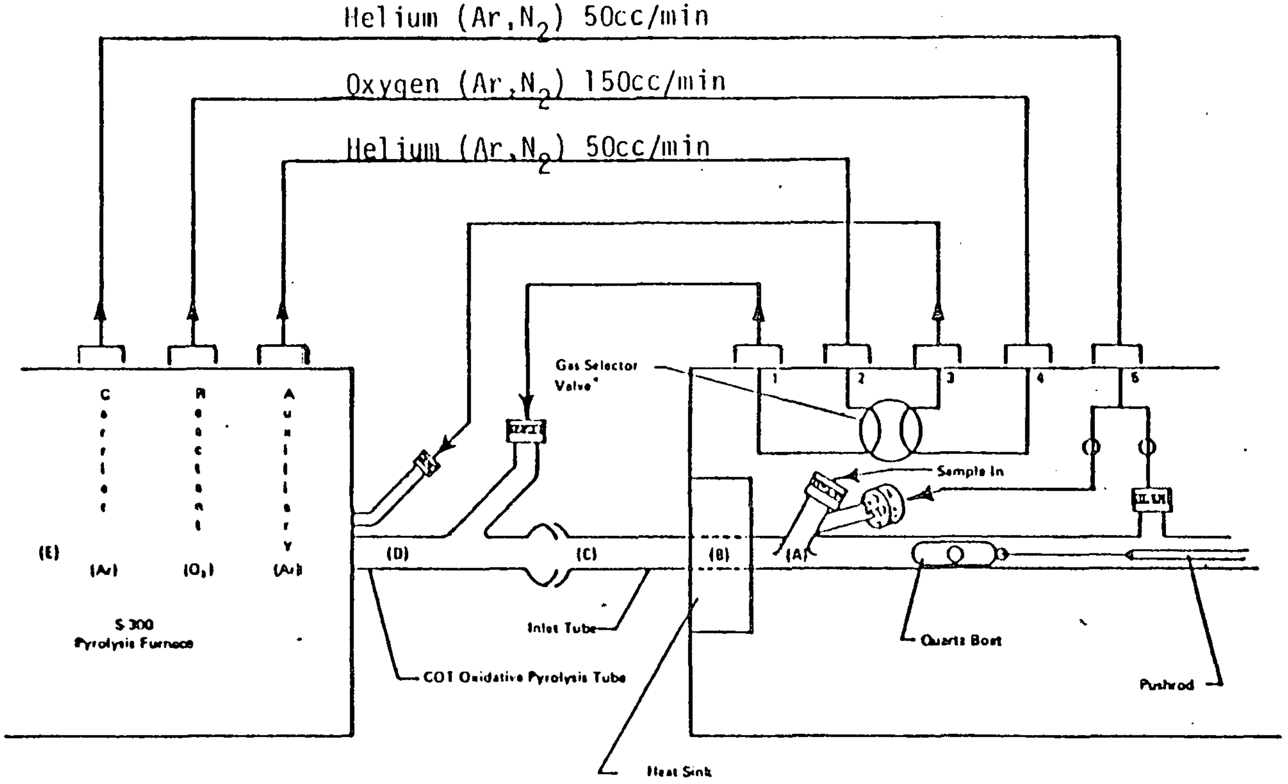
C. Dohrmann Equipment Manual, Edition May 17, 1976, P/N 915-025, M14E6, Dohrmann Instrument Division of Envirotech Corp., Santa Clara, Ca.

D. Slager, T. L., APCI Method No. 156, Determination of Trace Levels of Sulfur in Organic Matrices (1978).

F. CRSD Analytical Services Guideline Quality Assurance Manual.

FIGURE 1

SB1 CONFIGURATION FOR OXIDATIVE ANALYSIS



* Gas Selector Valve shown in the "OUT" Position

FIGURE 2

Percent Recovery of Chlorine in Pure Compounds as a Function of Furnace Inlet Temperature

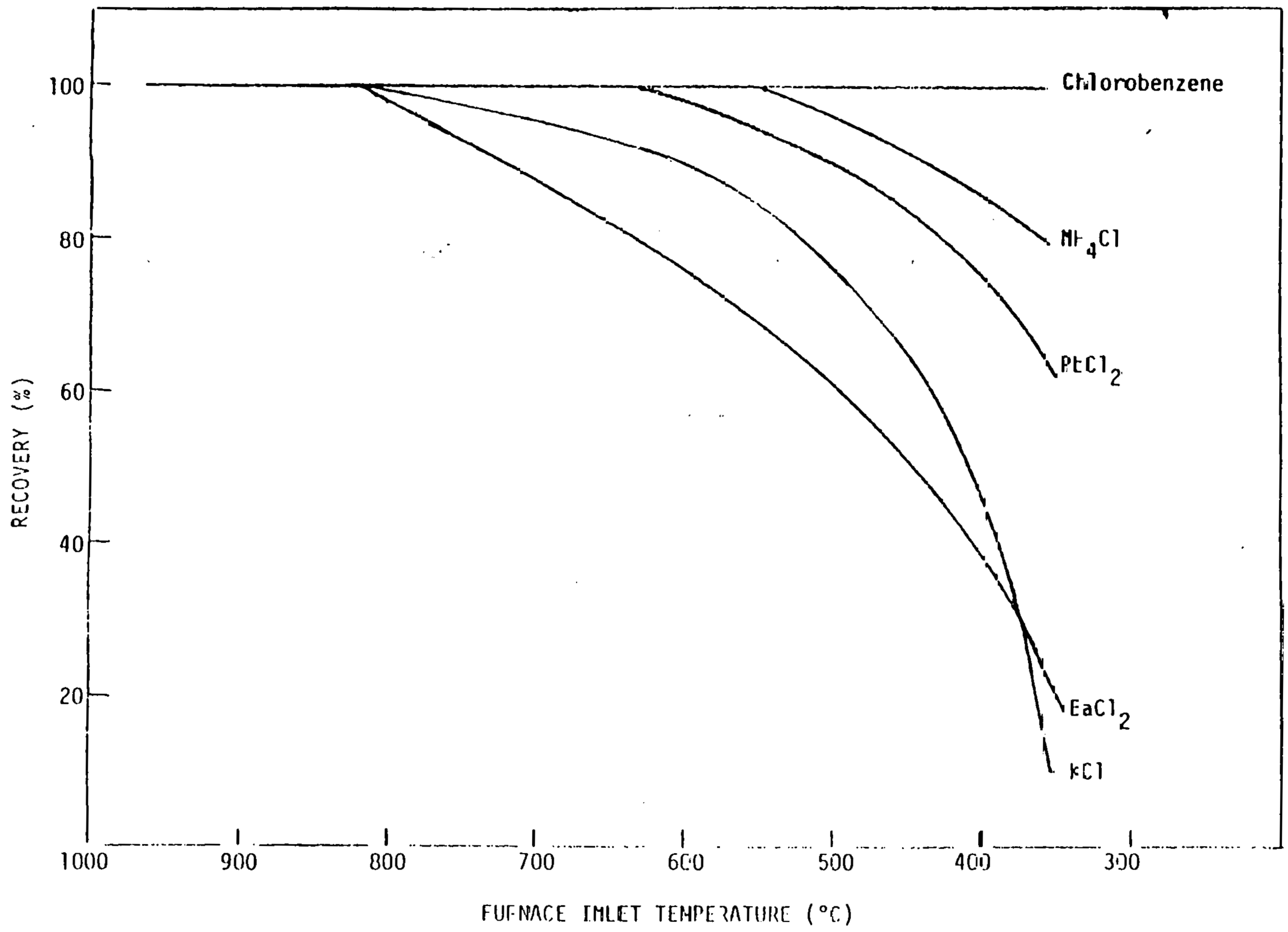
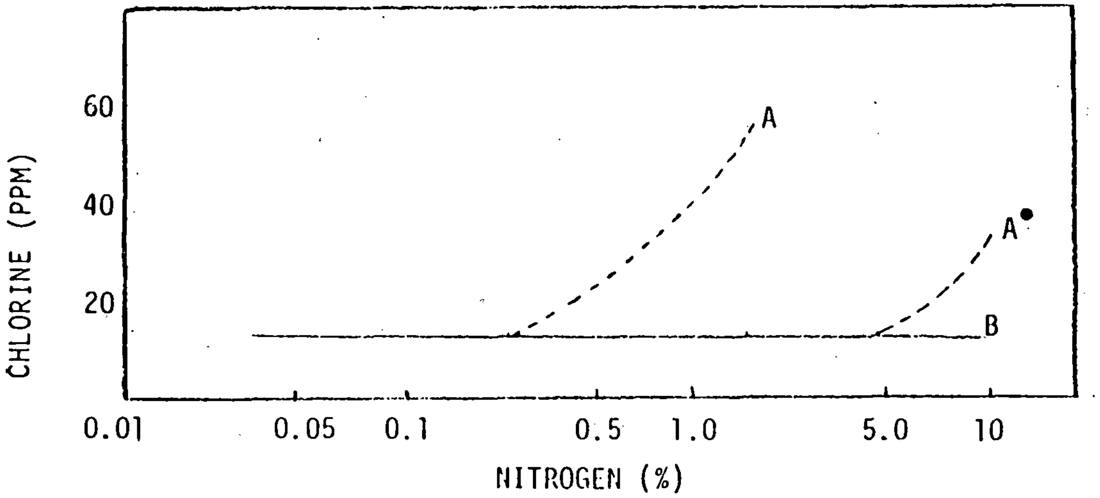


FIGURE 3

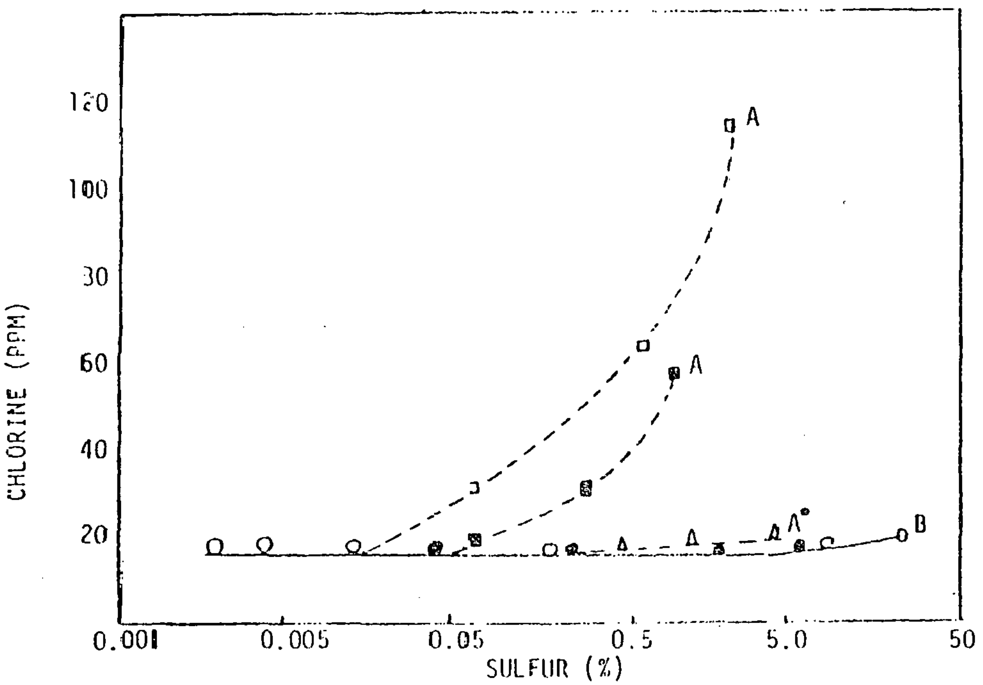
Effects of Nitrogen
On
Chlorine Determination



Effect of scrubber tube on chlorine determination of nitrogen-containing sample. Sample: Toluene and white oil (1:1) solution with added p-chlorobenzoic acid and quinoline. Chlorine concentration: 14 ppm. Curve A: Quartz wool-packed scrubber; sample size, 20 μL. Curve A°: Quartz wool-packed scrubber; sample size, 10 μL. Curve B: Cupric oxide wire-packed scrubber; sample size, 20 μL.

FIGURE 4

Effects of Sulfur
On
Chlorine Determination



Effect of scrubber tube on chlorine determination of sulfur-containing sample. Sample: (□), (△), (○) Toluene and white oil (1:1) solution with added p-chlorobenzoic acid and di-n-butyl-disulfide. (■), (●) toluene and white oil (1:1) solution with added p-chlorobenzoic acid and benzothiophene. Chlorine concentration: 15 ppm. Curve A: Quartz wool-packed scrubber; sample size. 10 μL. Curve A°: Quartz wool-packed scrubber; sample size. 5 μL. Curve B: Cupric oxide wire-packed scrubber; sample size. 10 μL.

Air Products

METHOD FOR THE DETERMINATION OF CARBON, HYDROGEN, NITROGEN AND LOW NITROGEN

I. SCOPE

This method covers the simultaneous determination of the weight percent carbon, hydrogen and nitrogen and the determination of the weight percent low nitrogen (0.2%-1.0%) in solid and liquid samples using a Control Equipment Corp. (CEC) 240-X Elemental Analyzer.

II. PRINCIPLE

The carbon, hydrogen and nitrogen content of organic and inorganic compounds (inorganic forms can be determined provided the sample can be combusted at 950°C) is obtained by combusting a weighed sample (1-3 mg) in pure oxygen under static conditions and detecting the products of combustion (CO_2, H_2O, N_2).

The combustion products are pased over reagents via helium carrier gas in a combustion tube to ensure complete oxidation and removal of by-products (sulfur, phosphorous, and halogens). In a reduction tube, oxides of nitrogen are reduced to molecular nitrogen (N_2) and residual oxygen is removed. The CO_2, H_2O, and N_2 gases are flushed into a mixing volume where they are homogenized at a precise temperature and pressure (~80°C-1500 mm Hg). This mixture is released through a sample volume into the detector block which contains three pairs of thermal conductivity detectors, five of which are connected in series. The last detector is a reference detector through which He flows. Between the first pair of detectors there is an absorption trap which removes water from the sample gas. The differential signal read before and after the trap indicates the water concentration and, therefore, the hydrogen content of the original sample. Similar measurements are made of the signal output of the two remaining pairs of thermal conductivity detectors. Between the second pair of detectors is a trap which removes CO_2 giving the carbon content of the sample. The combustion gases now contain only helium and nitrogen. These pass through the last of the five series detectors and the output signal is referenced to pure helium flowing through the last detector resulting in the nitrogen concentration. The combustion train and analytical system appear in Figure #1.

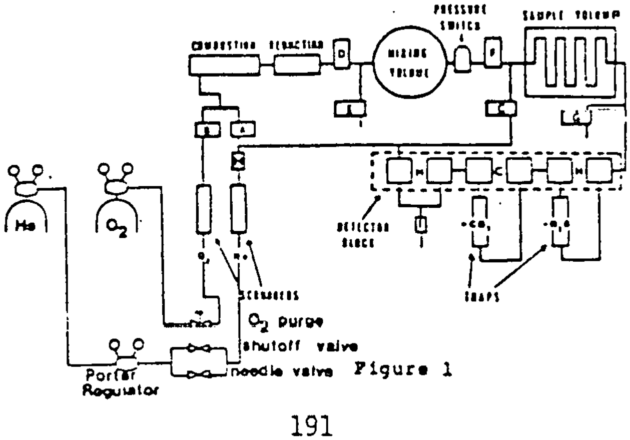


Figure 1

III. APPARATUS

A. Analyzer

1. Control Equipment Corp. Model 240-X elemental analyzer, MC-341 microjector, and silent 700 printer (the analyzer has the capability of running 64 samples automatically or single samples manually).

B. Balance

1. Perkin-Elmer Model AD-2 Autobalance or equivalent. The balance should be accurate to ±5 μg.

C. Glassware

1. Combustion tube - Manual (Control Equipment, Part # 0240-1225 or the APCI Glass Shop).
2. Combustion tube - Microjector (Control Equipment, Part # 6703-0378 or the APCI Glass Shop).
3. Reduction Tube, large diameter (Control Equipment, Part # 0240-1573 or the APCI Glass Shop).
4. Connector Tube, microjector (Control Equipment, Part # 6703-0392 or the APCI Glass Shop).
5. Scrubber and Trap tube (Control Equipment, Part # 0240-1217 or the APCI Glass Shop).
6. Ladel, manual, without cut-out (Control Equipment, Part # 0240-1321B or the APCI Glass Shop).
7. Ladel, automatic operation, microjector (Control Equipment, Part # 6703-0376 or the APCI Glass Shop).

D. Sample Handling Apparatus

1. Aluminum sample capsule, 7 x 3 mm (Control Equipment, Part #6703-0411).
2. Tin capsule, smooth wall, 6 x 2.9 mm diameter (Control Equipment, Part #6703-0418).
3. Nickel Sleeve (Control Equipment, Part #6703-0412).
4. Sample Sealer accessory (Perkin-Elmer, Part #219-0061).
5. Micro Spatula (Fisher Scientific, Part #21-401-25B.

6. 10 µl Syringe (Hamilton).

7. Single Quill Brushes (P-E, Part #0240-1296).

8. Dumont forceps (VWR Scientific, Part #25729-081).

9. ASTM Micro dessicator (P-E, Part #0240-1289).

E. Miscellaneous

1. Two stage stainless steel diaphragm regulator for He cylinder (Part #E12-6-C445A, CGA fitting #580; APCI Specialty Gas Div.).

2. Matheson two stage stainless steel diaphragm regulator for O_2 cylinder (Part #3104, CGA fitting #540, Matheson).

3. 0-60 PSIG Porter Regulator (Model #8290, Porter Instrument Co.).

IV. REAGENTS

A. Cuprin (Control Equipment; Part #0240-1362).

B. Ascarite (A. H. Thomas Co., Part #C049-U90 or Allentown Labs Staging Area).

C. Magnesium Perchlorate (Fisher Scientific, Part #M-54).

D. Silver Vanadate (Control Equipment, Part #0240-1117).

E. Silver Oxide/Silver Tungstate on Chromosorb P (Control Equipment, Part #0240-0113).

F. Silver Tungstate on Magnesium Oxide (Control Equipment, Part #0240-1344).

G. Quartz Wool (Control Equipment, Part #0240-1118).

H. Helium (Zero Grade, APCI Specialty Gas Div.).

I. Oxygen (Zero Grade, APCI Specialty Gas Div.).

J. Acetanilide (NBS - #141C).

K. Benzoic Acid (NBS - #140B).

L. Platinum Gauze (Control Equipment, Part #0240-1147B).

V. PROCEDURE

A. Filling and installing combustion tube, reduction tube, traps, and scrubbers.

1. Filling Procedure

   Follow the procedure as given in the CEC 240-X 341 HA-SAI Operation Manual pages 25-26 with the following changes:

   a. Combustion Tube

      (i) Instead of using Pt gauze at the indentation, a similar size wad of quartz wool is used.

      (ii) Pt gauze is used at the end of the packing instead of the recommended silver gauze.

   b. Reduction Tube

      (i) Pt gauze is used instead of Ag gauze.

      (ii) Only 1/16" of quartz wool is used instead of 3/4".

   c. CO$_2$ Trap and Scrubbers (Ascarite 20-30 mesh; MgClO$_4$ 8-14 mesh)

      (i) The 1/8" wad of quartz wool is reduced to 1/16".

2. Installation Procedure

   Follow the procedure as given in the CEC 240-X 341 HA-SAI Operation Manual pages 44-45.

D. Sample Handling

1. Capsule and Sleeve Preparation

   a. Nickel sleeves are either flamed or placed in a furnace and heated until red hot ($\geq$ 1000°C).

   b. Tin capsules are washed with acetone without sonication four times making sure that each capsule washed is totally immersed in the acetone (some capsules will float due to air trapped inside the capsule). The capsules are dried under vacuum at 50°C in a vacuum oven for about 1 hour and are stored in a dessicator. After cleaning, capsules are handled only with a forceps.

   c. Aluminum capsules are washed four times in acetone, but are sonicated in an Ultrasonic bath. After washing, the capsules are dried and stored as indicated above.

2. Nonvolatile Samples

   A tin capsule is weighed empty on a microbalance. After weighing, the capsule is placed on a clean, solid surface and 1-3 mg of sample is weighed in the capsule. If possible, the sample weight should be such that its read signal corresponds to the hydrogen content in the standard material used to calibrate the instrument [Sample Weight = $\% \ H_{std.}/\% \ H_{sample}$) x Wt. of standard]. All weights are to the nearest microgram and the capsule is sealed before reweighing. The reweighed tin capsule is placed in a nickel sleeve. For low nitrogen measurements, aluminum capsules are used (these generate more consistent nitrogen blanks) and the sample weight is increased to approximately 5 mg. A low nitrogen reference material (latex emulsion) is used to check low nitrogen accuracy. Aluminum capsules are used without Ni sleeves.

3. Volatile Samples

An aluminum capsule is weighed empty on a microbalance. After weighing, the capsule is placed in the Volatile Sample Sealer Accessory and pressed into the die as far as it will go with the side of a forceps. Using a 10 µl syringe, 2.0 to 3.0 µl of sample are added to the capsule or such a volume as to give a sample weight of 1-3 mg as above. The sample weight is adjusted to the hydrogen content of the standard as above. The capsule is crimped (as low and consistent as possible) and the sample is reweighed.

4. Capsule Sealing

a. Aluminum capsules are sealed using the sample sealer accessory (D.4).

b. Tin capsules are sealed by crimping with a forceps. The crimp should be such that almost all air is expelled from the capsule. The crimped section is then folded over so that the capsule can be placed in a nickel sleeve after reweighing.

C. Operation Procedure

Before starting check/perform the following:

He Pressure: ~17 psig (Porter regulator)

O_2 Pressure: ~40 psig - purge O_2 line to remove any air that may have leaked into line through the regulator.

Open shutoff valve (see Figure #1).

Follow Quality Assurance Program (Section VIII).

Instrument operation is commenced with the analyzer in the overnight standby mode. If not in this condition, refer to the end of this section for standby procedure.

Generate capsule blanks by running empty, crimped capsules (tin capsules must be placed in nickel sleeves to prevent devitrification of tubes and ladels) until the values obtained are stable (for approximate values see the values generated the previous operating day). Blanks are generated by resetting the microprocessor (run/halt switch on halt) and pushing key (6) on the terminal. This allows entry of blank and K factors. Zeroes are entered for all blanks and 1000 is entered for all K factors. After entering the above, key (8) is pushed, 1000 is entered as the sample weight and the date is entered as the sample I.D. The empty capsule is placed into the ladel and the run/halt switch turned to run. The instrument automatically proceeds through one cycle, calculates the results and prints the results (in percent) and SELECT MODE in preparation for the next run. Key (6) is pushed and the blanks generated above are entered along with the C, H, N content (in percent) of the standard material being entered as the K factors. During the generation of the blank values, three (3) standards are weighed (2000 ± 20 μg). These are now run successively, by pushing key (8), to generate the calibration factors which will be used for the day (first std. acts as a conditioner). Standards are selected on the basis of the C, H, N content of the samples to be analyzed with one using the standard that contains C, H, N concentrations similar to those expected in the samples. A single blank capsule is run afterward to determine blank values to be used during the analysis of samples. After entering the actual calibration factors and calibration blank (see calculations section for calculations involving blanks and K factors) samples can be analyzed (precision ± 0.1% absolute). Samples are grouped together on the basis of similar expected C, H, N content. A capsule blank is run after each unique type of sample and the values corrected (see calculations section, e.g. - preasphaltenes, amines, etc.). The sample blank will differ from the calibration blank, due to adsorption and desorption effects in the analyzer, if the relative concentrations of the component combustion gases differ from that of the calibration standard. At some point during the day, instrument calibration and the calibration blank are checked (see Quality Assurance Section - Pg. 14). After all analyses are completed, the instrument is shut down as follows:

<u>System Pressure</u> - ~1200 mm Hg - after final analysis, program is started and permitted to run until system pressure reaches ~1200 mm during "fill time". After the system pressure reaches 1200 mm the system is reset to halt the program.

<u>Program Mode</u> - Standby (C valve open).

<u>He Flow</u> - Reduced to ~58 cc/min by closing shutoff valve after Porter regulator - metering valve preset at ~58 cc/min. This is done so as to maintain a constant effective flow through the detectors while the instrument is not in operation and to keep the detectors at a constant temperature. This eliminates equilibration of detectors when the instrument is started the next day. Open shutoff valve for normal operation (see Figure #1).

VI. CALCULATIONS

Initial blank values (B_I) - the last three (3) blanks are summed and divided by three.

For Carbon: $$\frac{\Sigma_n B_{CI}}{n} = \overline{B_{CI}}$$

For Hydrogen: $$\frac{\Sigma_n B_{HI}}{n} = \overline{B_{HI}}$$

For Nitrogen: $$\frac{\Sigma_n B_{NI}}{n} = \overline{B_{NI}}$$

Calibration Factors (K) are calculated as follows:

The mean weights of each component (C,H,N) in the standard are calculated:

$$\frac{\Sigma_n \text{ µg of C}}{n} = \frac{\Sigma_n \text{ µg Standard x (\%C)}}{n}$$

$$\frac{\Sigma_n \text{ µg of H}}{n} = \frac{\Sigma_n \text{ µg Standard x (\%H)}}{n}$$

$$\frac{\Sigma_n \text{ µg of N}}{n} = \frac{\Sigma_n \text{ µg Standard x (\%N)}}{n}$$

The blank run after the standards is reduced by the initial blank and divided by the mean weight of each component. This value is subtracted from the mean of the K factors obtained in calibration resulting in the K factors used for anlaysis:

$$K_{C_{Actual}} = K_{C_{Observed}} - \left(\frac{B_{Cc} - B_{CI}}{\overline{Wt}_C}\right)$$

$$K_{H_{Actual}} = K_{H_{Observed}} - \left(\frac{B_{Hc} - B_{HI}}{\overline{Wt}_C}\right)$$

$$K_{N_{Actual}} = K_{N_{Observed}} - \left(\frac{B_{Nc} - B_{NI}}{\overline{Wt}_C}\right)$$

If the capsule blank run after each type of sample (B_S) is significantly different from that which is entered ($[\pm 1\ K_{Actual}\ (wt/2000)] = \pm 0.05\% =$ 1 µg absolute), then the values are recalculated as follows:

$$\left(\frac{B_C - B_S}{K_{C_{Actual}}}\right)\left(\frac{100}{\mu g \text{ of sample}}\right) + \%C = \text{corrected } \%C$$

and similarly with the H, N values obtained.

The microcomputer computes values as follows:

K factors:

$$K_C = \frac{\text{Read Signal - Baseline Signal - Blank}}{\mu g\ C}$$ and similarly with H and N.

% C:

$$\frac{(\text{Read Signal - Baseline Signal - Blank})\ (100)}{(K_C)\ (\mu g \text{ of sample})}$$

and similarly with H and N

Examples of calculations appear in Table #1.

VII. PRECISION AND ACCURACY

The precision between replicate analyses should be ±0.1% absolute. If not, then the analysis should be repeated (sample homogeneity and composition will determine whether this is achievable).

The obtainable accuracy (±2σ) based on standard organic compounds during an eight (8) hour operating day are as follows:

C - ±0.07% Absolute
H - ±0.03% Absolute
N - ±0.05% Absolute
Low N - ±0.02% Absolute

Accuracy can be checked by analyzing an organic standard.

VIII. QUALITY ASSURANCE

The following items are performed on a daily basis to assure the accuracy and precision of the method:

1. Check detector baseline voltages at the start and end of the day (must be greater than zero).
2. Indicate the type of capsule being used.
3. Record the fill time.

4. Record the initial system blank values.
5. Record the calibration factors.
6. Record the values of the calibration check.
7. Record the detector oven temperature.
8. Record the combustion and reduction oven temperatures.
9. Check the condition of all tubes and traps.
10. Check pressures of helium and oxygen cylinders (change at $\leq$200 psig).
11. Check instrument calibration and calibration blank twice daily (after initial calibration and at the end of the day).

Space is provided in the C, H, N Quality Assurance Manual for each of the above items. These values are compared to previously recorded values and any major deviations may be an indication of the instrument developing a problem. If problem symptoms occur refer to operation manual or Quality Assurance Troubleshooting section.

When samples are received in the laboratory, they are visually inspected for any contamination. If any is found it is removed from the sample and/or a comment to that effect is included with the analytical report. Solid samples are homogenized by grinding in a vibratory mill (wiggle-bug) to less than 150 mesh and stored in a capped vial until analyzed. Before being analyzed, liquid samples are mixed on a Vortex-Genie and solid samples are mixed by moving the sample container in a figure eight motion.

IX. SAFETY

Items which are to be considered for the safe operation of the instrument include:

1. Gases in the cylinders are under high pressure and should be handled accordingly.
2. Combustion and reduction zones are very hot and should be handled with appropriate protection.
3. Toxicity of samples should be checked by referring to the sample request form and handled accordingly.
4. Some of the materials used in the tube and trap packings should be handled with care as they may cause burns and are also dust hazards.

X. REFERENCES

1. CEC 240-X 341 HA-SAI Operation Manual; CEC, Lowell, Mass.; July 1981.

2. Perkin-Elmer Model 240 Elemental Analyzer Manual; Perkin-Elmer, Norwalk, Conn.; April 1974.

3. Quality Assurance Program Guidelines, CRSD Analytical Services; May 1982, pp. 72.

TABLE #1

The following data are typical values that one may see during an 8 hour operating day. (Note: the absolute values will change, but the order of magnitude is the same.)

Tin Capsule Inherent Blanks (B_I) -	C	-	42, 30, 28, 29, 30
(Values in sequential order,	H	-	317, 196, 139, 137, 140
indicating system purging)	N	-	222, 179, 175, 172, 174
Calibration Factors (K) -	C	-	19.04, 19.04, 19.06
(Values in sequential order,	H	-	57.57, 59.28, 59.42
indicating system conditioning and equilibration)	N	-	7.15, 7.15, 7.14
Tin Capsule Calibration Blanks (B_C) -	C	-	51
	H	-	229
	N	-	173

Observed K Factor Calculations (Performed by Instrument):

$$K_{C_{\text{Observed}}} = \frac{(31588 - 4348 - 28)\mu V}{1428.91\ \mu g} = 19.04\ \mu V/\mu g$$

$$K_{H_{\text{Observed}}} = \frac{(12985 - 4859 - 139)\mu V}{134.74\ \mu g} = 59.28\ \mu V/\mu g$$

$$K_{N_{\text{Observed}}} = \frac{(4692 - 3029 - 175)\mu V}{208.03\ \mu g} = 7.15\ \mu V/\mu g$$

TABLE #1 (Continued)

Actual K Factor Calculations (Performed by Analyst):

$$K_{C_{\text{Actual}}} = 19.05\ \mu V/\mu g - \frac{(51 - 28)\mu V}{1426.78\ \mu g} = 19.03\ \mu V/\mu g$$

$$K_{H_{\text{Actual}}} = 59.35\ \mu V/\mu g - \frac{(229 - 139)\mu V}{134.67\ \mu g} = 58.68\ \mu V/\mu g$$

$$K_{N_{\text{Actual}}} = 7.15\ \mu V/\mu g - \frac{(173 - 175)\mu V}{207.93\ \mu g} = 7.16\ \mu V/\mu g$$

Component Concentration Calculation (Performed by Instrument): Following data for calculations is not specifically related to previous calibration data presented. This data was chosen to exemplify the following corrections.

$$\%\ C = \frac{(39498 - 4362 - 58)\mu V(100)}{(19.03\ \mu V/\mu g)\ (2120\ \mu g)} = 86.95\%$$

$$\%\ H = \frac{(12468 - 4824 - 237)\mu V(100)}{(59.24\ \mu V/\mu g)\ (2120\ \mu g)} = 5.90\%$$

$$\%\ N = \frac{(3374 - 3008 - 43)\mu V(100)}{(7.17\ \mu V/\mu g)\ (2120\ \mu g)} = 2.12\%$$

Correction Sample Calculations:

$B_C = 58$

$B_S = 80$

$$\text{Corrected } \%\ C = \left[\frac{(58 - 80)\mu V}{19.03\ \mu V/\mu g}\right]\left[\frac{100}{2120\ \mu g}\right] + 86.95\% = 86.90\%$$

$B_H = 237$

$B_S = 304$

$$\text{Corrected } \%\ H = \left[\frac{(237 - 304)\mu V}{59.24\ \mu V/\mu g}\right]\left[\frac{100}{2120\ \mu g}\right] + 5.90\% = 5.85\%$$

$B_N = 43$

$B_S - 33$

$$\text{Corrected } \%\ N = \left[\frac{43 - 33\ \mu V}{7.17\ \mu V/\mu g}\right]\left[\frac{100}{2120\ \mu g}\right] + 2.12\%$$

Air Products

ANALYTICAL METHOD #317

OXYGEN ANALYSIS OF ORGANIC COMPOUNDS WITH THE COULOMETRICS CO_2 COULOMETER

I. Scope:

This method is used for the determination of organic oxygen in a range of 0.5 to 100%. Inorganic forms of oxygen may interfere if the compounds are reduced or the oxygen is displaced at 1120°C. Reducible oxides interfere if the sample contains sufficient carbon to reduce the oxide or if a reducing or displacing agent is added to the sample. The instrument can be used to analyze for the oxygen content of inorganic oxides if it is operated under different experimental conditions.

II. Principle:

Samples are pyrolyzed in a stream of nitrogen. The pyrolysis products are swept over a carbon bed at 1120°C converting all oxygen to CO. After acidic gases are scrubbed from the gas stream by Ascarite and magnesium perchlorate, the CO is oxidized with copper oxide at 450°C to CO_2. The CO_2 is quantitatively absorbed with a partially aqueous solution containing monoethanolamine and a colorimetric indicator. The reaction produces a strong titratable acid, causing the indicator to fade. A coulometer electrically generates a base to return the solutions to the original color.

III. Apparatus:

A. Coulometerics CO_2 Coulometer System

Model 5010 Coulometer and 5060 Oxygen Apparatus (Coulometerics Incoporated) Wheat Ridge, CO.

B. Quartz Wool

P/N 240-1118 (Control Equipment) Lowell, MA.

C. Silver Capsules (9 x 3.5 mm)

P/N 6703-0416 (Control Equipment) Lowell, MA.

D. Scoop Ladle

P/N 201-014 (Coulometrics Incorporated) Wheat Ridge, CO
or Glass Blowing Shop (APCI)

E. Combustion Tube

P/N 201-004 (Coulometrics Incoporated) Wheat Ridge, CO.
or Glass Blowing Shop (APCI)

F. Scrubber Tubes

P/N 200-014 (Coulometrics Incoporated) Wheat Ridge, CO
or Glass Blowing Shop (APCI)

G. Coors Porcelain Boats (17 x 6 x 4 mm)

P/N 3183-B05 (Thomas) Philadelphia, PA

H. Capsule Crimper

P/N 043680 (Perkin-Elmer) Newton Square, PA

I. Time Switch, 1 Hour

P/N 3048-E-25 (Thomas) Philadelphia, PA

J. Carrier Gas Drying Tube

P/N 2-0618 (Supleco Incorporated) Bellefonte, PA

K. Indicating Oxy-Trap

P/N 4004 (Alltech Association) Kennett Square, PA

L. Micro Balance

Cahn-26 (Fisher) Philadelphia, PA or equivalent

M. Variable Transformer

P/N 09-521-110 (Fisher) Philadelphia, PA

N. Electric Furnace

(Basic Products Company) Milwaukee, WI or equivalent

O. General Electric Gc-Getter

P/N 4015 (Alltech) Kennett Square, PA

IV. Reagents:

A. Carrier Gas - Nitrogen

99.998% pure, Low O_2, Low H_2O (APCI) Hometown, PA

B. Benzoic Acid

(>99.5% purity), (BDH) Poole England or equivalent. High purity sucrose, cholesterol, 2-naphthol and - acetanilide may also be used for a standard.

C. Magnesium Perchlorate Anhydrous (8-10 mesh)

P/N 300-010 (Coulometrics Incorporated) Wheat Ridge, CO

D. Coulometer Cell Reagents

1. Coulometer Solution
2. Anode Solution
3. Postassium Iodide

P/N 101-040 (Coulometrics Incoporated) Wheat Ridge, CO

E. Ascarite (20-30 mesh)

P/N 300-017 (Coulometrics Incoporated) Wheat Ridge, CO

F. Cuprox

P/N 240-1092 (Control Equipment) Lowell, MA

V. Procedure:

A. Preparation Setup[1]

1. Attach carrier gas drying scrubber tube at N_2 cylinder.
2. Connect go-getter after carrier gas drying tube.
3. Attach indicating oxy-trap close to the flowmeter. (Don't exceed 10 psig.)
4. Check remaining set-up procedure in the oxygen section of the manual. (Ref. 1)

B. Instrument Startup[1]

1. Be sure scrubbers and pyrolysis tubes are assembled.
2. Set carrier gas flow to 80 cc/min. with the exit rotameter, having the toggle valve (TV1) open.
3. Close TV1, set gas flow to 20 cc/min at exit rotameter with the flow metering valve.
4. Set pyrolysis furnace temperature for 1120°C and allow temperature to equilibrate.
5. Check system for leaks by blocking sample line at inlet of coulometric cell and observe stopped flow on rotameter.

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[1] A schematic diagram of the apparatus is in Figure I.

6. For filling and connecting coulometer cell, follow the CO_2 section of the manual. (Ref. 1)

   Note: Gas flow is controlled by TV1 after the flows are set.

C. Blank Runs

1. Switch TV1 to set gas flow to 80 cc/min.
2. Direct carrier gas flow with the ball valve to a back sweep purge.
3. Remove end cap, place an empty crimped silver capsule in a ceramic boat, on a ladle. Avoid contamination of the ladle during handling (remember water is 88% oxygen).
4. Insert the ladle with boat and capsule into the pyrolysis tube but not into the furnace.
5. Place end cap loosely on breech block and set time switch to 2 1/2 min. For thirty seconds the air introduced by the ladle, boat, and capsule are backswept out of the system.
6. Tighten end cap, switch the ball valve to the front end purge for the remaining 2 minutes.
7. The instrument has a 15 second counting cycle. After a 2 minute purge, the instrument should be counting less than 3 micrograms of oxygen for each 15 second counting cycle. To prevent the cell solution from backing up the sample line and causing errors in the analysis , close the toggle valve, TV2, at the inlet of the copper oxide tube, immediately after a counting cycle. Inject the ladle into the furnace with the magnet, open TV2, reduce the carrier gas flow to 20 cc/min with TV1, reset the coulometer counter and set the time switch to 7 minutes.
8. Four minutes after inserting the ladle, the carrier gas flow is increased to 80 cc/min with TV1 and the ladle removed from the furnace.
9. At the end of the 7 minute analysis, record the micrograms of oxygen. The last 2 minutes, the detector counts micrograms approximately every 10 to 15 seconds. To improve the accuracy, a 1 microgram oxygen value is added to the micrograms of oxygen at the end of the analysis, for every five seconds less than the 7 min. analysis time. The opposite is performed for every five seconds over the 7 min. analysis time. This value is added or subtracted when the 7 minute analysis time ends in between the 10-15 seconds detection intervals.
10. Three or four blank runs are required to insure consistent reasonable blank values. The blank should generally be less than 60 micrograms of oxygen with a 3 microgram absolute deviation.

Note-1: If cell solution backs up, the cell has to be cleaned

D. Standard and Sample Runs

1. Weigh a benzoic acid standard, (26.20% oxygen) in a range of 2.6-3.6 mg to within .01 mg on the micro balance into a silver capsule.
2. Follow the same procedure for the standard and samples as blank runs.
3. Three standard samples are run with the first run being a conditioner. A standard and blank check are run after four hours of operating the instrument and at the end of the day.
4. If the standard value is off by .30% absolute, restandardization is performed.
5. Analyze 3-13 mg of sample, depending on the amount of oxygen in the sample. The samples are weighed to detect 1000 micrograms of oxygen. (Samples with unknown oxygen content are preanalyzed.)

Note: Standards and samples are weighed to achieve 1000 micrograms of oxygen, unless they contain water or carboxylic acids. Then they are weighed to obtain 500 to 900 micrograms of oxygen.

E. Shutdown of Instrument

1. Turn cell switch off.
2. Keep temperature at 1120°C.
3. Adjust flow rate to 20 cc/min
4. Remove cell and empty anode and cell solutions into a poly bottle for waste disposal. Wash cell with soap and water.
5. Rinse silver electrode with acetone and wipe dry.
6. Rinse anode compartment with acetone. Use test tube brush to remove KI and deposits on top of the glass frit if necessary.
7. Pull acetone through frit with aspirator or other vacuum source. If acetone does not flow through the frit rapidly, the frit should be more thoroughly cleaned or replaced. Anode deposits can be removed with a saturated KI solution.
8. If deposit is evident on the platinum electrode, this should be dissolved with 1:1 HNO$_3$. In order to prevent deposits on the platinum electrode, the cell assembly should be disassembled when not in use.
9. Dry all cell components with air or nitrogen.

VI. Calculation

$$\%\ \text{Total Oxygen} = \frac{\text{micrograms read} - \text{micrograms blank}}{\text{sample weight (micrograms)}} \times 100$$

VII. Precision and Accuracy

Values obtained from benzoic acid and 2-naphthol standards showed that the analysis has a precision of 0.4% relative with an accuracy of 0.3% absolute for simple organic compounds, provided the micrograms of oxygen detected is between 400 and 1300 micrograms. The precision and accuracy values are variable for complex organic compounds.

VIII. Quality Assurance

- To obtain the maximum accuracy and precision, the samples should be weighed as accurately as possible with a four place micro balance.
- The carrier gas, pyrolysis scrubbers and copper oxide tubes are replaced after three, two and one weeks, respectively.
- The coulometer solution is changed daily.
- The carbon and quartz pyrolysis tube are changed once a month. The pyrolysis tube devitrifies, causing a increase in blank values. The pyrolysis tube is cleaned, removing fingerprints which may cause a shorter life span of the tube, before being installed.
- The electronics cooling fan screening is cleaned twice a month.
- The carbon is burned off the ladle with a bunsen burner every day.
- Consistent performance of the procedure reduces errors in the analysis.
- A trouble shooting guide is listed in the manual; Section "Total Carbon", pg. 13-14 and Section "CO_2 Coulometer", pg. 9-11.
- Operation of the Coulometerics Oxygen Analyzer should be maintained according to standard APCI QA procedures. (Ref. 2)
- Typical Blank runs are 60 micrograms.
- Samples are analyzed in duplicate.
- Typical standard values for Benzoic Acid and 2-napthol are 26.00% and 11.05% respectively.

IX. Interferences:

Samples containing fluorine cannot be analyzed, due to the displacement of oxygen in the pyrolysis tube. Oxygen in refractory metal oxides cannot be determined. Samples with high sulfur content have been reported to cause interferences.

X. Safety:

The Ascarite and magnesium perchlorate are skin irritants, gloves should be worn when handling these reagents. The coulometer solution has an ammoniocal oder due to the monoethanolamine contained in the solution. A hood should be used when working with this solution. Precaution is needed while operating the high temperature furnaces.

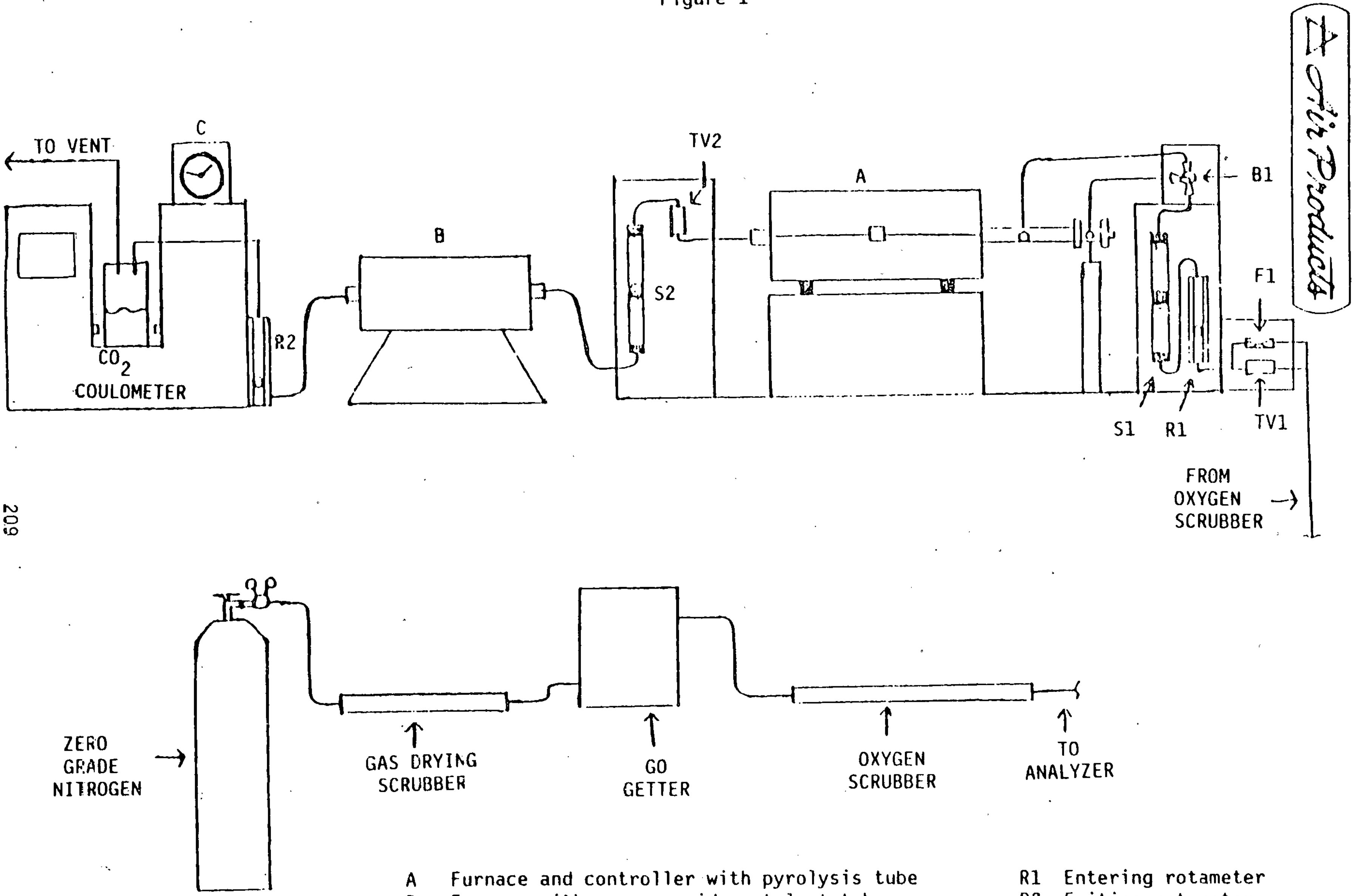
Note: A waste material survey must be filled out for the disposal of the anode and coulometer solutions, Ascarite and magnesium perchlorate.

XI. Reference:

1. Coulometrics Incorporated Instruction Manual, Issue D
2. Air Products CRSDA QA Manual.

45-AL

Figure 1



A	Furnace and controller with pyrolysis tube	R1	Entering rotameter
B	Furnace with copper oxide catalyst tube	R2	Exiting rotameter
C	Time switch	S1	Prescrubber
F1	Fine metering valve	S2	Postscrubber
B1	Ball valve	TV1, TV2	Toggle valves

DETERMINATION OF SULFUR BY THE LECO-132 SULFUR ANALYZER

The Leco sulfur analysis, a modified standard high-temperature combustion procedure, offers a rapid, reliable method for determining total sulfur in solid and liquid SRC-1 products. The analyzer is a microprocessor-based instrument for determining the amount of sulfur contained in coal, coke and petroleum products.

The instrument combusts samples at 2,500°F in a furnace swept with oxygen, which oxidizes the sulfur to SO_2 gas. The microprocessor formulates the analytical results, which are displayed and printed on the control console by combining the outputs from the infrared detector and the system's ambient sensors with preprogrammed factors of calibration, linearization, and weight compensation.

The analyzer has an analytical range of 0.005 - 99.99% sulfur and accuracy to within ±1% of the sulfur content. For this model the upper limit of linear detection is 0.02 g of sulfur.

The analyzer is capable of excellent analytical precision and can be applied to analyze SRC-1 related products with a standard deviation less than ±0.04%

Precautions

SRC-1 solids must be thoroughly ground (200 mesh) and mixed to produce representative samples.

The volatility of SRC-1 liquids requires that liquids be sealed in tin capsules and should be analyzed within two minutes of weighing.

Samples analyzed with less than 0.5 g sample weight must be weighed on an analytical balance with ±0.00005 g accuracy.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing. For specific handling precautions of SRC liquids, see the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet located in the front section of the manual.

INSTRUMENTAL LABORATORY PROCEDURES

ETHOD #237

Air Products

BORON BY GRAPHITE FURNACE ATOMIC ABSORPTION USING PARR OXYGEN BOMB DIGESTION

I. SCOPE

The determination of trace quantities of boron in an organic matrix is possible by this method. The digestion is a very clean, quick procedure. The graphite furnace is utilized because the concentrations of interest are very near the detection limits of conventional flame Atomic Absorption. Samples analyzed by this procedure to date ranged from 10 to 60 ppm boron. The detection limit using the graphite furnace is approximately 4 ug/g by this method. A lower detection limit can be achieved by adjusting various experimental parameters, e.g., final sample injection volume, initial sample weight and final dilution volume. Furnace program times may need to be adjusted when experimental parameters are changed.

II. APPARATUS

A. Parr 1241 Adiabatic Calorimeter, Parr Instrument Company, Moline, IL 61265.

B. Parr 1108 Oxygen Bomb, Parr Instrument Company, Moline, IL 61265.

C. Parr 43As stainless steel combustion capsules. Parr Instrument Company, Moline, IL 61265.

D. Fuse Wire (nickel alloy wire) 45C10 Parr Instrument Company, Moline, IL 61265.

E. Bomb Head Support Stand, A38A, Parr Instrument Company, Moline, IL 61265.

F. Oxygen Filling Connection, 1825, Parr Instrument Company, Moline, IL 61265.

G. Perkin Elmer 5000 Atomic Absorption Spectrophotometer, Perkin Elmer Corporation, Norwalk, CT 06856.

H. Perkin Elmer HGA 500 Graphite Furnace, Perkin Elmer Corporation, Norwalk, CT 06856.

I. Graphite Tubes, Pyrolytically Coated, 0290-1807, Perkin Elmer Corporation, Norwalk, CT 06856.

J. 20 microliter Eppendorf pipet, 21-278-8, Fisher Scientific Company, King of Prussia, PA 19406.

K. Disposable pipet tips, 21-371 Fisher Scientific Company, King of Prussia, PA 19406.

BORON BY GRAPHITE FURNACE ATOMIC ABSORPTION USING PARR OXYGEN BOMB DIGESTION

II. APPARATUS (Cont)

L. 100 ml polypropylene flasks, 50 ml polypropylene volumetric flasks, Fisher Scientific Company, King of Prussia, PA 19406

M. 250 ml polyethelene beakers, Fisher Scientific Company, King of Prussia. PA 19406.

N. Volumetric pipets, 1 ml, 2 ml, 3 ml and 10 ml, Fisher Scientific Company, King of Prussia, PA 19406.

O. Volumetric flasks, 10 ml, Class A, Fisher Scientific Company, King of Prussia, PA 19406.

III. REAGENTS

A. Calcium Nitrate 4-Hydrate, reagent grade, J. T. Baker Chemical Company, Phillipsburg, NJ.

B. One Percent Calcium (1% Ca) Solution
Prepare a 1% Ca solution by dissolving 15.7 g of calcium nitrate 4-hydrate in 250 ml of distilled, deionized water.

C. Boron Atomic Absorption Reference Solution 1000 ppm, Fisher Scientific Company, King of Prussia, PA 19406

D. 100 ppm Boron Solution: Pipet 10 ml of the 1000 ppm AA Reference solution into a 100 ml polypropylene volumetric flask. Dilute to volume with distilled water.

E. Boron Standards:
Pipet 0, 1, 2, and 3 milliliters of 100 ppm Boron solution into 4 respective polypropylene volumetrics. Pipet 10 ml of the 1% Ca solution into each of the volumetrics. Acidify with 2 drops of concentrated nitric acid. Dilute to 100 ml with distilled water. (0, 1, 2 and 3 ppm Boron)

F. Water, distilled, deionized and filtered through a 0.2 u filter.

G. Argon, commercial grade, APCI, Trexlertown, PA 18105.

H. Sodium Hydroxide. NaOH, reagent grade. 50% W/W Solution, Fisher Scientific Company, King of Prussia, PA 19406.

BORON BY GRAPHITE FURNACE ATOMIC ABSORPTION USING PARR OXYGEN BOMB DIGESTION

III. REAGENTS (Cont.)

I. Nitric Acid, HNO_3, reagent grade, Fisher Scientific Company, King of Prussia, PA 19406.

J. Methanol, reagent grade, Fisher Scientific Company, King of Prussia, PA 19406.

K. Oxygen, commercial grade, APCI, Trexlertown, PA 18106.

IV. SAFETY

Caution should be exercised when using the oxygen combustion bomb. Not more than one gram of sample should be used when firing. Also pressurizing the bomb should be done slowly. All recommended procedures in handling mineral acids and caustics should be followed. Finally, the graphite tubes of the furnace reach temperatures of up to 3000°C and should be allowed to cool between analysis.

Methanol is a flammable and toxic chemical. It should be used in a well-ventilated area and kept away from all open flames.

V. PROCEDURE

A. Preparation of Sample

1. Weigh one gram of sample to the nearest 0.1 milligram into the tared stainless steel sample cups. (The concentration of boron in the final sample volume should be between 0.2 ug/ml and 1.2 ug/ml.)
2. Add to sample one ml methyl alcohol slowly by pipette, and place cup in bomb head support stand.
3. Cut 10 cm of fuse wire and attach to the electrodes as illustrated in Figure 1. (It is not necessary to submerge wire in a powdered sample, slightly above should be sufficient. Tilt cup slightly away from straight electrode.)
4. Pipet 10 ml of distilled water into bomb cylinder.
5. Carefully place the bomb head into the bomb cylinder.
6. Set the screw cap on the cylinder and turn it down by hand.
7. Place the fitting on the end of the oxygen hose into the inlet valve socket of bomb. Open oxygen valve not more than one quarter turn. Pressurize to 30 psi, close valve and release pressure by pushing down on relief valve.

BORON BY GRAPHITE FURNACE ATOMIC ABSORPTION
USING PARR OXYGEN BOMB DIGESTION

V. PROCEDURE (Cont.)

A. Preparation of Sample

8. Fill stainless steel bucket with two liters of distilled water and place into calorimeter.

9. Place bomb inside bucket using tongs provided by Parr, attach lead wires to bomb head, and close lid.

10. Allow a few minutes for equilibration and ignite sample, allow five minutes for equilibration after ignition.

11. Remove bomb from water, thoroughly shake the bomb for one minute to absorb all of the combustion products.

12. Slowly and carefully release the bomb pressure by turning knurled screw on bomb head.

13. Wash bomb contents into 250 ml polyethylene beakers with distilled water.

14. Neutralize sample with NaOH and place on a steam bath to evaporate sample to about five ml.

15. Quantitatively transfer contents of beaker into a 50 ml polypropylene volumetric. Rinse three times with three milliliter aliquots of distilled water. If the sample is expected to have a concentration less than 10 ug/g, a 10 ml glass volumetric would be advisable.

16. Dilute to volume with distilled water.

17. Prepare a blank in same manner using one ml methanol for blank combustion.

B. Analysis of Sample by Graphite Furnace

1. The graphite furnace is installed and aligned in accordance with the manufacturer's reference manual.

2. The boron lamp is aligned with furnace tilted out of sample beam.

3. Be sure water is flowing through furnace coolant system and argon is on.

BORON BY GRAPHITE FURNACE ATOMIC ABSORPTION USING PARR OXYGEN BOMB DIGESTION

V. PROCEDURE (Cont.)

4. Program for furnace:

1)Dry	130°C	2)Char	1000°C	3)Atom	2700°
Ramp	10 sec	Ramp	10 sec	Ramp	0 sec*
Hold	50 sec	Hold	20 sec	Hold	5 sec
				Read	-5
				Rec	-5
				Int Flow	150

4th step cleanout Temp 2700°C Rec on
Ramp 2 sec
Hold 2 sec

5. Spectrophotometer should be in Hold, Peak Height, and AA-BG modes.

6. Use a fresh pyrolitically coated graphite tube, install and condition as outlined in manufacturer's operator manual.

7. Sample will be analyzed by method of standard additions.

8. With 20 microliter Eppendorf pipet, pipet 20 microliters of sample and 20 microliters of 0 ppm B standard containing 1000 ppm Ca^{+2}.

9. Hit start/stop button on Furnace Programmer to initiate Furnace Program.

10. Record peak height on spectrophotometer.

11. Repeat steps 8-10 for sample 1, substituting 1, 2, and 3 microgram per milliter boron standards containing 1000 ppm Ca^{+2} for 0 standard.

12. Analyze blank and samples in same manner.

VI. CALCULATIONS

A. Determine the peak height readings for each addition. Plot the readings against the added concentration. Extrapolate the resulting straight line through zero absorbance. The intercept on the concentration axis gives the concentration of the metal in the diluted sample solution. Exemplified in Figure 2.

BORON BY GRAPHITE FURNACE ATOMIC ABSORPTION USING PARR OXYGEN BOMB DIGESTION

VI. CALCULATIONS (Cont)

B. Calculate the concentration of boron in the original sample as follows:

$$\frac{C \times V}{W} = \frac{\text{micrograms}}{\text{gram}} \text{ (ppm)}$$

C = concentration from standard additions in micrograms/milliliter
V = dilution volume in milliliters
W = weight of sample in grams

VII. PRECISION AND ACCURACY

A. Precision was determined from 7 replicate determinations of NBS SRM 1571 Orchard Leaves. The results of these determinations:

Mean	S.D.	% S.D.
32.8	2.8	8.5%

B. Accuracy was determined by comparing the 7 replicate values of NBS SRM 1571 to the reported certified value. The Mean value of the 7 determinations was 32.8±2.8 ug/g compared with the NBS value of 33±3 ug/g.

Along with the above procedures, some of our actual samples were analyzed by an outside laboratory and the values were compared. The analytical method used by the outside laboratory was colorimetric. The results of this comparison are from single determinations for both labs except where indicated.

	GFAAS	Colorimetric
1.	60 ug/g*	52 ug/g
2.	53 ug/g*	39 ug/g
3.	35 ug/g	38 ug/g
4.	10 ug/g	12 ug/g

*duplicate results

As exemplified by the data for the NBS SRM 1571 recovery was about 100% the actual figure is 99 ± 8%. Also an organometallic standard was used to check recovery. To facilitate the use of this standard methyl isobutyl ketone was substituted for methanol since the oil base in which the organic sulfonate was dissolved in was not soluble in methanol. Data for this is listed in Table 1 and Table 2.

BORON BY GRAPHITE FURNACE ATOMIC ABSORPTION USING PARR OXYGEN BOMB DIGESTION

VIII. QUALITY ASSURANCE

A. The results should not be considered suspect unless duplicate determinations differ by more than 2 times the standard deviation (2σ) or 17.0%. The following chart should serve as a guide to acceptable limits.

Boron ug/g	Precision (2σ)
10	2
20	3
30	5
40	7
50	9
60	10

B. The quality assurance of the atomic absorption spectrophotometer and balance should be completed in accordance with the CRSD Analytical Services Q.A. Program Guidelines Manual.

C. Boron standards should be prepared from the 1000 ppm reference solution weekly.

D. The temperature profile for each different atomic absorption spectrophotometer should be adjusted to achieve optimum sensitivity.

IX. PRINCIPLE

The sample is combusted in a 30 psi oxygen atmosphere and the boron is absorbed into 10 milliliters of water. The combustion is done in a sealed stainless steel combustion bomb which is immersed in a cooling bath. Ignition of the sample is done electronically. The sample is then diluted to volume and the boron analyzed by Graphite Furnace/Atomic Absorption Spectrophotometry.

TABLE 1

RESULTS OF ANALYSIS OF AN ORGANOMETALLIC BORON STANDARD

Standard only	Micrograms added	Micrograms found	% Recovery
1	26.5	16	60%
2	52.4	46	89%
3	101.0	105	104%
Recheck 1	26.5	26	98%
		avg of 4 = 88%	

TABLE 2

RESULTS OF ALCOA SOLIDS SPIKED WITH AN ORGANOMETALLIC BORON STANDARD

Sample	Micrograms from sample	Micrograms added	Micrograms actual	Micrograms found	% Recovery
2096CB	16	26	42	37	88
	16	52	68	60	88
2097CB	50	26	76	52	82
	50	52	102	62	61*
2098CB	30	26	56	44	79
	30	52	82	62	76%
2099CB	31	26	57	44	77%
	31	52	83	69	81%
				avg of 7 =	82±5

*By Q test data point can be disregarded.
Quantitative Analytical Chemistry, 3rd Edition,
James S. Fritz and George H. Schenk, Allyn and Bacon Inc. 1974, pp 37-39

Recovery using NBS SRM 1571 orchard leaves 99 ± 8% in methanol.

ETS:bas:843
ANALS

METHOD #237

Air Products

BORON BY GRAPHITE FURNACE ATOMIC ABSORPTION USING PARR OXYGEN BOMB DIGESTION

X. REFERENCES

A. Parr Instrument Co., Moline IL, Instructions for the 1241 and 1242 Adiabatic Calorimeters.

B. Bailey, J. J., Gehring, D. G., Anal. Chem. 33, 1760-2 (1961).

C. Nadkarni, R. A., American Laboratory, August 1981.

D. Lindahl, P. C., Paper No. 679 at 1981 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ.

E. Perkin Elmer Corporation, Norwalk, CT, HGA 500, Graphite Furnace Operator's Manual.

F. Perkin Elmer Corporation, Norwalk, CT, Analytical Methods for Atomic Absorption Spectrophotometry.

H. CRSD Analytical Services QA Program Guidelines

ES MK:bas:563
Anal3

ANALYTICAL METHOD #301

Air Products

PROTON DISTRIBUTION OF COAL-DERIVED LIQUIDS BY NUCLEAR MAGNETIC RESONANCE

1. SCOPE:

This method is for the determination of the proton distribution in coal-derived liquids by nuclear magnetic resonance (NMR).

2. PRINCIPLE:

The sample, diluted to 25% with deuterated chloroform, is placed in a highly homogeneous magnetic field of about 14,000 gauss. A coil surrounds the sample and is used to subject the sample to a weak radio-frequency signal. The intensity of absorption of the radio frequency signal is plotted as a function of increasing magnetic field strength. The magnetic field strength at which a nucleus absorbs energy of a particular radio frequency is dependant on the chemical environment of the nucleus. Thus, protons in different locations in the molecule (for example, aromatic vs. aliphatic locations) absorb a signal at slightly different magnetic field strengths. Also, the intensity of absorption of the radio frequency signal is proportional to the number of nuclei causing the absorption. Consequently, the percentage of the various types of hydrogen atoms present in a coal-derived liquid can be determined by interpreting the NMR spectrum. The hydrogen are divided into the following four groups:

(1) H_{AR}: aromatic hydrogen (may also contain some of the phenolic compounds); δ = 6.0 to 9.0 ppm

(2) H_α : hydrogen on saturated carbon adjacent to an aromatic ring (included are methylene and methine protons of hydroaromatic rings, α methylene and methine protons of aliphatic side chains and α methyl groups; not included are methylene α to two aromatic rings such as the methylene group in 9,10-dihydroanthracene, diphenylmethane or fluorene since they absorb from δ = 3.6 to δ = 4.3); δ = 2.0 to 3.5 ppm.

(3) H_β : methylene or methine protons of saturated compounds, side chains methylene or methine groups β or further from an aromatic ring, and β methyl groups; δ = 1.0 to 2.0 ppm.

(4) H_γ : methyl groups of saturated compounds or methyl groups γ or further from an aromatic ring; δ = 0 to 1.0 ppm.

The H_β and H_γ peaks are not well resolved and the division, 1.0 ppm, is somewhat arbitrary.

PROTON DISTRIBUTION OF COAL-DERIVED LIQUIDS BY NUCLEAR MAGNETIC RESONANCE

3. APPARATUS:

A. High Resolution Nuclear Magnetic Resonance Spectrometer

Equipped for proton resonance

B. NMR Tubes

5 mm thin wall tubes (Stohler Isotope Chemicals, Waltham, Massachusetts, Catalogue No. S-5).

C. Caps for NMR Tubes

5 mm caps (Stohler Isotope Chemicals, Waltham, Massachusetts, Catalogue No. SPC-5).

D. Syringe and Syringe Needle

2 cc capacity syringe with 2" length needle (Stohler Isotope Chemicals, Waltham, Massachusetts, Catalogue Nos. S27500-2 and SSN-55).

E. Vials

Specimen, screw cap, 5 ml capacity (A.H. Thomas Co, Philadelphia, Pa., Catalogue No. 9710-D24).

F. Pasteur Disposable Pipets

A. H. Thomas Co., Catalogue No. 7760-B26.

4. REAGENTS

A. Chloroform - d_1 & 1% TMS

Stohler Isotope Chemcicals Waltham, Massachusetts, Catalogue No. D322.

B. Tetramethylsilane (TMS)

Stohler Isotope Chemicals, Waltham, Massachusetts, Catalogue No. 327S.

PROTON DISTRIBUTION OF COAL-DERIVED LIQUIDS BY NUCLEAR MAGNETIC RESONANCE

5. PROCEDURE

A. Sample Preparation

Using a 2 cc syringe, transfer 0.5 ml of sample to a 5 ml glass vial. Then, add 1.5 ml of chloroform d_1 & 1% TMS to the vial. Swirl the vial until a uniform solution is obtained. Transfer approximately half of the diluted sample to an NMR tube (using a disposable Pasteur pipette) and cap the tube.

B. NMR Spectrum

For the basic operation of the NMR spectrometer, refer to Perkin-Elmer Manual No. 5600-3064B, "Model R12B NMR Spectrometer, Operator's Manual".

(1) Insert the NMR tube containing the diluted sample into the probe and adjust the spinner air control so that the sample spins smoothly between 30 and 60 rev/sec.

(2) Position the TMS peak at 0 δ, using the fine and coarse field shift controls.

(3) The following are the normal NMR control settings:

Sweep Range: 0 - 10 ppm

Sweep Time: 5 min

Filter: 2

H_1 Level: 8

Sensitivity: 2

(4) Record the spectrum of the sample.

(5) Immediately after the spectrum is recorded, integrate the peaks. If the baseline is not level before and after a group of peaks, i.e., the integration baseline is not level when there are no peaks in the spectrum, the phase may need to be adjusted. The correct phase adjustment is critical to the accuracy of the integration.

PROTON DISTRIBUTION OF COAL-DERIVED LIQUIDS BY NUCLEAR MAGNETIC RESONANCE

6. CALCULATIONS

A. Record the magnitude of the drop in the integrator trace between the following field shifts:

(1) δ = 6.0 ppm to 9.0 ppm (H_{AR})

(2) δ = 2.0 ppm to 3.5 ppm (H_{α})

(3) δ = 1.0 ppm to 2.0 ppm (H_{β})

(4) δ = 0.0 ppm (not including the TSM integration) to 1.0 ppm (H_{γ})

B. Normalize the integrated areas to 100% and report the results.

7. REPEATABILITY

Although a repeatability study has not been performed with this method, literature values for the error measurement of this method do not exceed ±5 percent, relative.

Bibliography

1. Anderson, R. P., Evolution of Steady State Process Solvent in the Pittsburg and Midway Solvent Refined Coal Process, Symposium on Coal Processing, AIChE, 20 August 1974.

2. Brown, J. K., Ladner, W. R. and Sheppard, N., Hydrogen Distribution of Coal-like Materials, Fuel; Vol. 39, 1959.

ANALYTICAL METHOD #1160

Air Products

Estimation of OH, NH and NH_2 Concentration in Methylene Chloride Soluble Materials
(SRC Liquifaction Products)

I. SCOPE:

This method is designed to quantatively measure by near infrared spectroscopy the amount of OH, NH and NH_2 functional groups present in a sample of material soluble in methylene chloride (typically SRC liquifaction products) by comparison to reference materials. (Safety: See Note 1)

II. PRINCIPLE

A weighed amount of sample is dissolved in 10 ml of methylene chloride transferred to a 1 cm path-cell and measured by the near infrared spectrophotometry The absorbance of the OH, NH and NH_2 functional groups are measured at the wavelength maximum for OH (~ 2790), NH (~2885) and NH_2 (~2950). Since the absorbance of each functional group in heterogeneous samples, such as SRC liquifaction products, is the average of many compounds containing one or more of the above functional groups, the peak maximum and the absorbance of any functional group is the average of all compounds having that one functional group. For the purpose of this test the absorbance of the each functional group at the wavelength maximum is assumed to equal to that of β-naphthol (OH), carbazole (NH) or 1-aminonapthalene (NH_2). These compounds are used as standard reference materials to estimate the weight percent of O as OH, N as NH and N as NH_2.

III. REAGENTS

A. Methylene Chloride

HPLC Grade, Cat. No. 450 (Bodman Chemical Co., Media, Pa.)

B. β-Napththol

>99% pure, Cat. No. 18550-7 (Aldrich Chemical Co., Milwaukee, Wis.)

C. Carbazole

>99% pure, Cat. No. C-308-1 (Aldrich Chemical Co., Milwaukee, Wis.)

D. 1-Aminonaphthalene

>99% pure, Cat. No. A6639-1 (Aldrich Chemical Co., Milwaukee, Wis.)

Estimation of CH, NH and NH_2 Concentration in Methylene Chloride Soluble Material (SRC Liquifaction Products)

IV. EQUIPMENT

A. Volumetric Flasks

10 ml, Class A, Cat. No. 10-209A (Fisher Scientific Co., King of Prussia, Pa.)

B. Pipettes

Pasteur, Cat. No. 13-678-20A (Fisher Scientific Co., King of Prussia, Pa.)

C. Pipet Bulb

1 ml bulb, Cat. No. 13-678-9A (Fisher Scientific Co., King of Prussia, Pa.)

D. Spatula

Narrow blade, Cat. No. 14-374 (Fisher Scientific Co., King of Prussia, Pa.)

E. NIR Spectrometer

UV, Vis, NIR Spectrometer, Beckman Model No. ACTA MVII or equivalent (Beckman Instrument, Inc., Irvine, Calif.)

F. Analytical Balance

Analytical Balance able to read to ± 0.01 mg, Mettler Model No. HL 52, Cat. No. 1-909-105 (Fisher Scientific Co., King of Prussia, Pa.)

G. Gloves

Disposable Latex Gloves, Cat. No. DF0488, (Dayton Flexible Products, Dayton Ohio)

H. Autopipet

Repipet, Cat. No. 13-687-55, (Fisher Scientific Co., King of Prussia, Pa.)

I. Cells

Infrasil, Cat. No. 14-385-906C (Fisher Scientific Co., King of Prussia, Pa.)

Air Products

Estimation of OH, NH, and NH_2 Concentration in Methylene Chloride Soluble Materials (SRC Liquifaction Products)

V. PROCEDURE

A. Instrument Start Up - ACTA MVII

1. Push in power button.
2. Turn on W lamp.
3. Set lamp source to auto.
4. Set spectral range to NIR.
5. Set NIR senisitivity to 2X10.
6. Adjust chart speed to 40 nm/in and scan speed to 2 nm/sec.
7. Set period = 4.
8. Set slit to DB servo and program.
9. Push display button.
10. With wavelength @ 2800 nm and both beams empty check that energy level is in the green area. If not see manual.
11. Set span to 3.0 and adjust the display to 0.000 using the top dial.
12. Turn the shutter to R open & S closed, set to calibrate and adjust to 0.000.
13. Return shutter to R open, S open and span switch to 3.0 and check zero.
14. Repeat steps 11 to 13 until both setting are 0.000.
15. To scan adjust paper to start line by rolling the paper out or by scanning to a line and adjust the wavelength to 3000 nm from a position >3000 nm.
16. Push the scan button and the start button.

B. Preparation of Standard Calibration Curves (Note 2)

The preparation of calibration curves for the OH, NH and NH_2 species are identical with a-naphthol the reference for OH, carbazole the reference for NH and 1-aminonaphthalene the reference for NH_2.

1. Weigh clean dry 10 ml volumetric flasks to the nearest 0.01 mg.
2. Using a spatula place approximately 0.5, 2.0, 4.0, 7.0, 10.0 and 15.0 mg of standard reference material into the seperate tared 10 ml flasks.
3. Reweigh each volumetric flask to the nearest 0.01 mg and record the weight of sample in mg. introduced into the volumetric flask.
4. Using the autopipet fill the volumetric flask to the 10 ml mark and shake the sample until everything has gone into solution.

V. PROCEDURE (Continued)

B. Preparation of Standard Calbration Curves (Note 2) (Continued)

5. Set instrument according to the instrument start up (VA)
6. Place a 1 cm cell containing clean dry methlene chloride in the reference side of the spectrometer and a 1 cm cell containing the sample in the sample chamber.
7. Read the absorbance at 3000 nm and 2750 nm for base line correction.
8. Read the absorbance at 2793 nm for β-naphthol (OH), 2887 nm for carbazole (NH) and 2950 nm for 1-aminonaphthalene (NH_2).
9. See the calculation section for the proper means of determing the baseline correction at each of the maxima for the reference materials.
10. Using the corrected absorbances (Abs - bkg) plot these values against the mg of O([0.111] [mg of β-naphthol]), mg of N ([0.0837] [mg carbazole]) or mg of N ([0.0987] [mg of 1-aminoaphthalene]). A typical calibration plot for mg of O as OH, mg of N as NH or mg of N as NH_2 is shown in Figure 1.
11. For most practical purposes it is easier to perform a linear regression on this data and use the equation of the line to calculate the mg of the unknown species of interest (See the calculation section).

C. Analysis of Unknown Samples

This method was originally set up to analyze effluent from SRC liquifaction experiments, however, any organic sample could be analyzed as long as it contains no interfering peaks. (Note 3) The effluents may come as liquids (SRC oils) or solids (SRC asphaltenes or SRC preasphaltenes). As long as the sample is completely soluable in methylene chloride and transparent in the NIR it can be analyzed.

1. Weigh a clean dry 10 ml volumetric flask to the nearest 0.01 mg.
2. Using a disposable pasteur pipet for liquids or a spatula for solids transfer about 50 mg of liquid or 10 to 20 mg of solid to the volumetric flask.
3. Reweigh the volumetric flask to the nearest 0.01 mg and record the amount of sample added to the flask.
4. Using the autopipet fill the volumetric flask to the 10 ml mark and shake the sample until it has gone into solution and mixed well.
5. Place a portion of the solution in this 10 ml volumetric flask into the 1 cm sample cell.
6. Scan the sample at 2 nm/sec, 40 nm/in and 3.0 abs full scale with all other instrument parameters the same as in the instrument set up section (VA). This scan must be attached to the reports of analysis. A typical scan is presented as Figure 2.

Estimation of OH, NH and NH_2 Concentration
in Methylene Chloride Soluble Materials
(SRC Liquifaction Products)

V. PROCEDURE

C. Analysis of Unknown Samples (Continued)

8. Record the absorbance and the wavelength at the peak maximum or if the peak is very flat and the maximum cannot be defined, at the maximum of the standard reference material OH(2793 nm), NH(2887 nm) or NH_2(2950 nm).
9. Rinse the sample cell with methylene chloride and allow to dry prior to analyzing the next sample.

VI. CALCULATION

A computer program ($CHNHNH_2$) has been written to perform the following calculations. The data input sheet is presented as Figure 3 and a typical report as Figure 4.

A. Background Correction

The background absorbance is recorded at 3000 nm and 2752 nm. The background between these two points is assumed to be linear.

$$\Delta A = A\ (@\ 2752) - A\ (@\ 3000)$$

$$BA\ (X) = A\ (@\ 3000) + \frac{(\Delta A)\ (3000 - X)}{248}$$

Where:

BA (X) = Calculated background absorbance at wavelength X.

X = Wavelength at maximum absorbance of the OH, NH or NH_2 functional group.

A = Absorbance.

B. Corrected Absorbance

$$AC\ (X) = A\ (X) - BA\ (X)$$

Where:

AC (X) = Corrected Absorbance at wavelength X.

A (X) = Absorbance recorded at wavelength X.

Estimation of OH, NH and NH_2 Concentration in Methylene Chloride Soluble Materials
(SRC Liquifaction Products)

VI. CALCULATION (Continued)

C. Correction of NH_2 Interference on NH Measurement

$$IAC\ (NH) = AC\ (X) - (AC\ [NH_2]\ [y])$$

Where:

IAC (NH) = Absorbance at the NH maximum corrected for background and NH_2 interference.

AC (NH) = Absorbance at the NH maximum corrected for background.

AC (NH_2) = Absorbance at the NH_2 maximum corrected for background as in in step B.

y = A (@2877)/ A (@2950) = 0.668

A (@2877) = Absorbance at 2887 nm for 1-aminonaphthalene.

A (@2950) = Absorbance at 2950 nm for 1-aminonaphthalene.

D. Calculation of Weight %O as OH, N as NH and N as NH_2

1. % O as OH

$$\%\ O\ \text{as}\ OH = \frac{([ACOH]\ [MOH] + BOH)\ [100]}{W}$$

Where:

ACOH = Corrected absorbance AC (X) at the OH maximum as calculated in step B.

MOH = Slope of the OH Calibration curve from β-naphthol.

BOH = Intercept of the slope of the OH Calibration curve from β-naphthol.

W = Weight of sample placed in the 10 ml volumetric.

Estimation of OH, NH and NH_2 Concentration in Methylene Chloride Soluble Materials
(SRC Liquifaction Products)

D. Calculation of Weight % O as OH, N as NH and N as NH_2 (Continued)

2. % N as NH

$$\% \text{ N as NH} = \frac{([IACHN]\ [MNH] + BNH)\ 100}{W}$$

Where:

IACHN = Absorbance at the maximum for NH, corrected for background and NH_2 interference as in steps B and C.

MNH = Slope of the NH calibration curve from carbazole.

BNH = Intercept of the NH calibration curve from carbazole.

W = Weight of sample.

3. % N as NH_2

$$\% \text{ N as } NH_2 = \frac{([ACNH_2]\ [MNH_2] + BNH_2)\ 100}{W}$$

Where:

$ACNH_2$ = Absorbance at the maximum for NH_2 corrected for background as in step B.

MNH_2 = Slope of NH_2 calibration curve from 1-aminonaphthalene.

BNH_2 = Intercept of the NH_2 calibration curve from 1-aminonaphthalene.

W = Weight of sample.

NOTES

Note 1: SRC materials are suspected carcinogens. They should be kept in an adaquate hood and the appropriate safety apparatus should be worn to prevent contact.

Note 2: Although not labeled as such the materials should be handled as suspected carcinogins. The calibration curves need only be prepared when using a new instrument or if a substantial difference between the actual % O in β-naphthol (11.1%), % N in carbazole (8.37%) or % N in 1-aminonaphthalene (9.37%) is found when a sample of each reference materials is analyzed with each batch of unknown samples.

NOTES (Continued)

Note 3: Water seriously interfers with this analysis. Thus every effort should be made to avoid getting water in the HPLC grade methylene chloride or in the sample. The height of the trace at 2700 nm gives a qualtitative indication of problems with a wet sample. On very humid days replace the methylene chloride in the reference cell frequently.

VII. ACCURACY AND PRECISION

1. ACCURACY

The accuracy of the data in unknown since this test compares a pure compound to an average of many compounds. Test methods are available to analyze for these functional groups but no comparative testing has been performed.

2. PRECISION

Replicate analyses of samples show that the repeatability of this test is ± 0.02 wt. % for all three functional groups.

VIII. REFERENCES

1. D. Finseth, unpublished paper, PETC, Pittsburgh, Pa.
2. F. K. Schweighardt, comments during method development.

FIGURE I

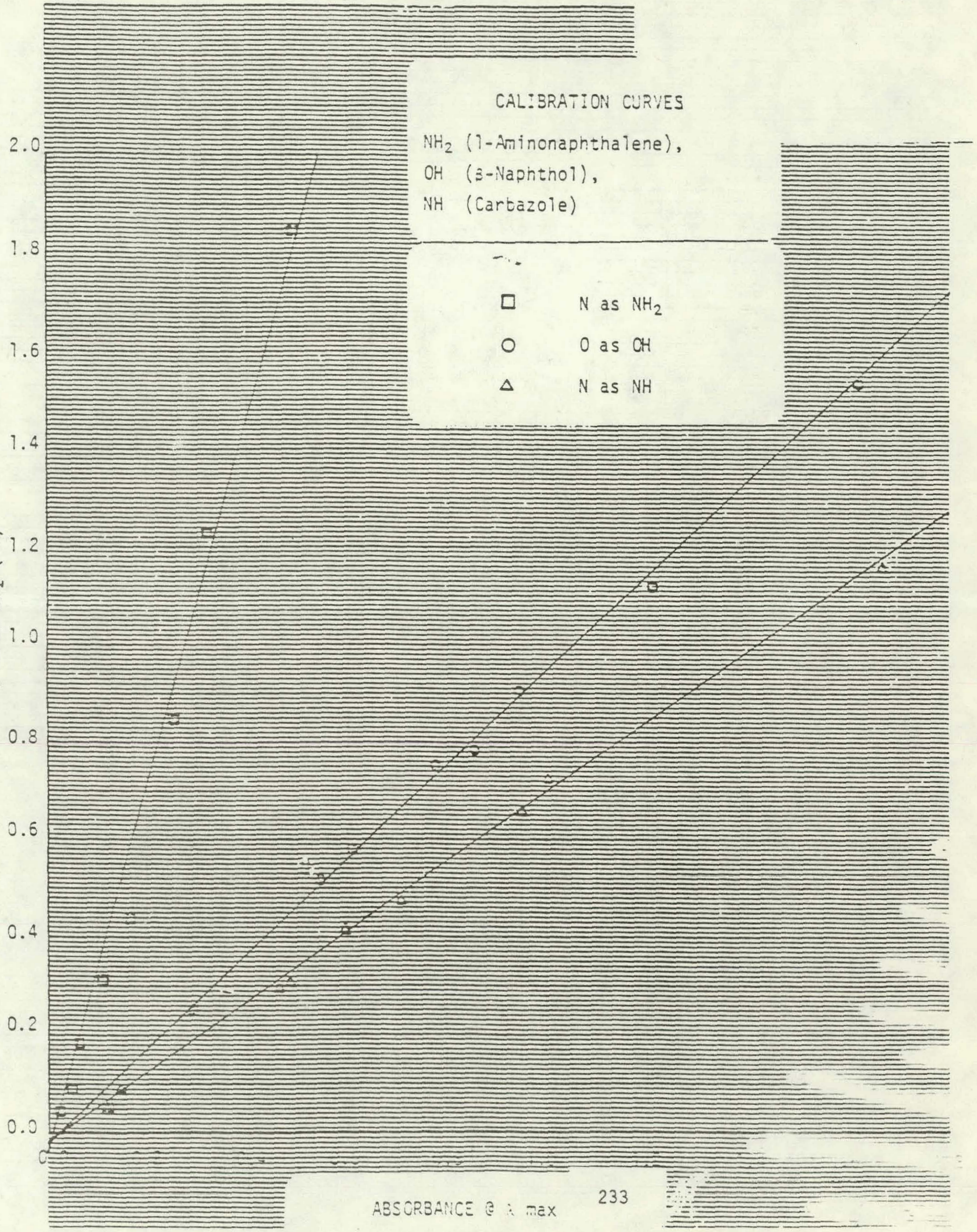
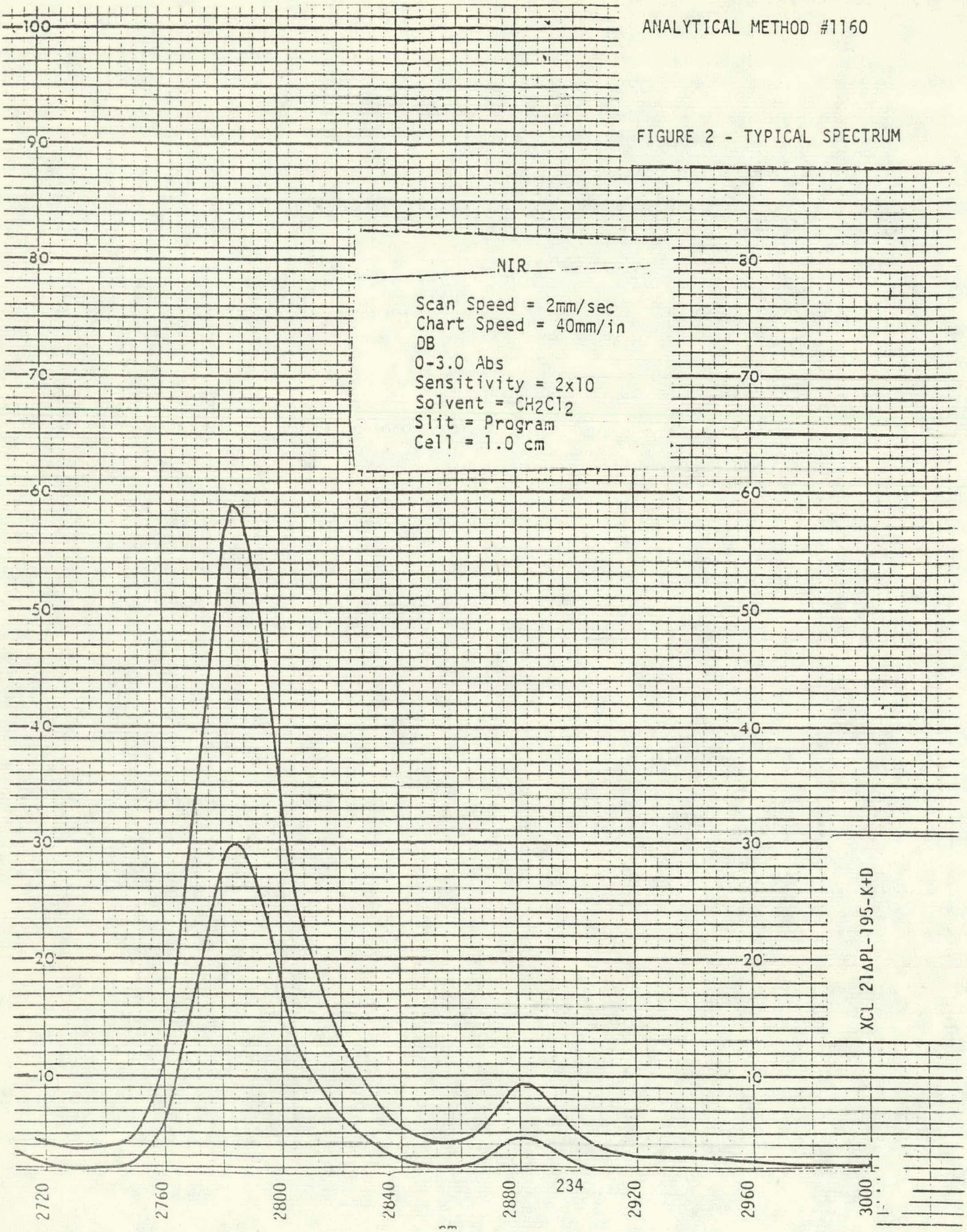

CALIBRATION CURVES
NH2 (1-Aminonaphthalene),
OH (β-Naphthol),
NH (Carbazole)
□ N as NH2
○ O as OH
△ N as NH
OH, NH or NH2 (MG)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
ABSORBANCE @ λ max

FIGURE 2 - TYPICAL SPECTRUM



NIR

Scan Speed = 2mm/sec
Chart Speed = 40mm/in
DB
0-3.0 Abs
Sensitivity = 2x10
Solvent = CH_2Cl_2
Slit = Program
Cell = 1.0 cm

XCL 21ΔPL-195-K+D

FIGURE 3

DATA INPUT FOR PROGRAM
OHNHNH$_2$

CARD 1

Code A (1) (1A1), Analyst Name T. L. Slager (2-26) (25A1), Approved By T. L. Slager (27-50) (24A1), BB No. 5278 (51-62) (12A1), Charge No. XU-2268 (63-72) (10A1), Date 3/24 1980 (73-80) (mm/dd/yy)

CARD 2

Code B (1) (1A1), Requestors S. Dukett, K. Grasso, A. Kamzelski, D. Kang, R. Skinner, F. Schweighardt (2-80) (79A1)

CARD 3 (Semipermanant Data)

Code C (1), Slope-OH 0.96546 (11-20) (F 10.5), Intercept-0.0209 (21-30) (F 10.5), Slope-NH 0.71586 (31-40) (F 10.5), Intercept-NH-0.0207 (41-50) (F 10.5), Slope-NH$_2$ 3.8634 (51-60) (F 10.5),

Intercept-NH$_2$=0.0801 (61-70) (F 10.5), Ratio(NH/NH$_2$) 0.668 (71-77) (F 6.3)

SAMPLE CARDS (Code "D" in cc1) (1 card/sample)

	Sample ID (21A1) (2-22)	Bkg @ 3000 (F 6.3) (25-30)	Bkg @ 2752 (F 6.3) (31-36)	λ max-OH (F 6.3) (37-42)	Abs.-OH (F 6.3) (43-48)	λ max-NH (F 6.3) (49-54)	Abs.-NH (F 6.3) (55-60)	λ max-NH$_2$ (F 6.3) (61-66)	Abs.-NH$_2$ (F 6.3) (67-72)	Sample wt. (mg) (F 6.3) (73-78)
D	XCL 21-195-PL+K+D	0.026	0.072	2788.	0.900	2885.	0.140	2950.	0.040	50.74
D	XCL 21-195-PL+K+D	0.064	0.142	2788.	1.790	2885.	0.283	2950.	0.085	106.24
D	X23-15 B Oils	0.038	0.080	2788.	0.942	2885.	0.209	2950	0.056	62.94
D	X23-15 B Oils	0.023	0.055	2788.	0.627	2885.	0.138	2950.	0.036	42.13
D	C25-52 Oils	0.031	0.064	2789.	0.642	2885.	0.376	2950.	0.060	69.43
D	C25-52 Oils	0.020	0.046	2789.	0.439	2885.	0.255	2950.	0.042	46.69
D	M64 Oils	0.047	0.061	2787.	1.412	2884.	0.190	2950.	0.067	83.03
D	M64 Oils	0.105	0.125	2787.	1.776	2884.	0.240	2950.	0.087	107.50
D	X23-120 PL Oils	0.025	0.100	2787.	0.826	2885.	0.152	2950.	0.036	50.74
D	X23-120 PL Oils	0.045	0.142	2787.	1.319	2885.	0.249	2950.	0.064	82.91
D										
D										
D										
D										
D										
D										
D										
D										

X (LAST CARD)

FIGURE 4 - TYPICAL COMPUTER PRINTOUT

```
                CALCULATING  CONCENTRATIONS OF  OH,NH,NH2  IN  SRC  SAMPLES

REQUESTOR(S):   S.DUKETT,K.GRASSO,A,KAMZELSKI,D.KANG,H.SKINNER,F,SCHWEIGHARDT
ANALYST:   T.SLAGER                         APPROVED BY: , T.SLAGER
CHARGE NUMBER:  XC2268          BLACKBOOK NUMBER: 5270-17-22                     DATE:  3-20-80

     THE ESTIMATE OF THE OH,NH,AND NH2 CONCENTRATION ISDETERMINED BY COMPARISON TO STANDARD CURVES.
     THE STANDARD CURVES ARE PREPARED FROM PURE COMPOUNDS SIMILAR TO THE TYPICAL MATERIAL IN SRC LIQUIDS
     THE NIR STANDARD FOR OH IS BETA-NAPHTHOL
     THE NIR STANDARD FOR NH IS CARBAZOLE
     THE NIR STANDARD FOR NH2 IS 1-AMINONAPHTHALENE

                              SAMPLE                        ABSORBANCE
          SAMPLE  I.D.        WEIGHT          WAVELENGTH     READ IN        WT %


        XCC21-195-PLBKBD       50.74  OH       2781.         0.900          1.55
                                      NH       2005.         0.140          0.09
                                      NH2      2950.         0.040        < 0.01

        XCC21-195-PLBKBD      106.24  OH       2786.         1.790          1.49
                                      NH       2005.         0.283          0.10
                                      NH2      2950.         0.085        < 0.01

        X23-15 B OILS          62.94  OH       2786.         0.942          1.50
                                      NH       2005.         0.209          0.14
                                      NH2      2950.         0.056        < 0.01

        X23-15 B OILS          42.13  OH       2781.         0.627          1.27
                                      NH       2005.         0.138          0.12
                                      NH2      2950.         0.036        < 0.01

        C25-52 OILS            69.43  OH       2789.         0.642          0.70
                                      NH       2005.         0.176          0.51
                                      NH2      2950.         0.060        < 0.01

        C25-52 OILS            46.69  OH       2789.         0.439          0.70
                                      NH       2005.         0.255          0.50
                                      NH2      2950.         0.042        < 0.01

        M64 OILS               83.03  OH       2787.         1.412          1.55
                                      NH       2007.         0.190          0.09
                                      NH2      2850.         0.067        < 0.01

        M64 OILS              107.50  OH       2787.         1.770          1.47
                                      NH       2007.         0.240          0.06
                                      NH2      2950.         0.067        < 0.01

        X23-120 PL OILS        50.74  OH       2787.         0.826          1.36
                                      NH       2005.         0.152          0.09
                                      NH2      2950.         0.036        < 0.01

        X23-120 PL OILS        82.91  OH       2787.         1.319          1.36
                                      NH       2005.         0.249          0.11
                                      NH2      2950.         0.064        < 0.01
```

APPENDIX I

```
FORTRAN IV G LEVEL  21                  MAIN               DATE = 80084          13/04/53

                    C
                    C   MAIN
                    C      ----------------------------------------------------------------
                    C      -                                                              -
                    C      -   CALCULATING  CONCENTRATIONS OF OH,NH,NH2  IN SRC SAMPLES   -
                    C      -                                                (BY SLAGER)   -
                    C      -                                                              -
                    C      -   CARD INPUT:                                                -
                    C      -      1. DATA FOR REPORT HEADINGS                             -
                    C      -      2. CONSTANT DATA FOR CALCULATIONS (SLOPES,INTERCEPTS)   -
                    C      -      3. SAMPLE DATA - 1 CARD PER SAMPLE                      -
                    C      -                                                              -
                    C      -   REPORT OUTPUT                                              -
                    C      ----------------------------------------------------------------
                    C
                    C  COMMON FIELDS FOR INFORMATION USED IN HEADING RTN :
0001                       COMMON IPGCNT,ILNCNT
0002                       COMMON ANAME,APPROV,ABLACK,CHRG,DAT,REGSTR
                    C
0003                       DIMENSION ANAME(25),APPROV(24),ABLACK(12),CHRG(10),DAT(8)
0004                       DIMENSION REGSTR(79)
                    C
                    C      ----------------------------------------------------------------
                    C
                    C  FIELDS USED FOR SAMPLE CALCULATIONS:
0005                       DIMENSION SAMPID(21)
                    C
0006                       REAL INTOH,INTNH,INTNH2
0007                       DATA A,B,C,D,X/'A','B','C','D','X'/
                    C
                    C      ----------------------------------------------------------------
                    C  -                                                                  -
                    C  -                  I N I T I A L I Z A T I O N                     -
                    C  -                                                                  -
                    C      ----------------------------------------------------------------
                    C
0008                     1 IPGCNT = 0
0009                       ILNCNT = 99
                    C                  WHERE IPGCNT NUMBERS THE PAGES
                    C                    AND ILNCNT COUNTS LINES PER PAGE
                    C
                    C      ----------------------------------------------------------------
                    C  -                                                                  -
                    C  -                 R E A D   C A R D   "A"   (FOR HEADING)          -
                    C  -                                                                  -
                    C      ------------------------------------------ --------------------
                    C
0010                    50 READ(5,51,END=9000) CODE,(ANAME(I),I=1,25),(APPROV(I),I=1,24),
                          1(ABLACK(I),I=1,12),(CHRG(I),I=1,10),(DAT(I),I=1,8)
0011                    51 FORMAT(80A1)
                    C                WHERE ANAME  = ANALYST NAME(S)
                    C                      APPROV = APPROVED BY
                    C                      ABLACK = ANALYST'S BLACKBOOK NUMBER
                    C                      CHRG   = CHARGE NUMBER
                    C                      DAT    = DATE (MM/DD/YY)
0012                       IF (CODE.NE.A)  GO TO 9000
                    C
```

APPENDIX I

```
FORTRAN IV G LEVEL  21                 MAIN               DATE = 80084          13/04/53
                C
                C
                C  -----------------------------------------------------------------
                C     -                                                            -
                C     -           R E A D   C A R D   "B"   (FOR HEADING)          -
                C     -                                                            -
                C     --------------------------------------------------------------
                C
 0013             100 READ(5,101,END=9010) CODE,(REQSTR(I),I=1,79)
 0014             101 FORMAT(80A1)
                C                 WHERE REQSTR = REQUESTOR(S) NAME(S)
 0015                 IF (CODE.NE.B)  GO TO 9010
                C  -----------------------------------------------------------------
                C     -                                                            -
                C     -           R E A D   C A R D   "C"   (CONSTANTS FOR CALCS)  -
                C     -                                                            -
                C     --------------------------------------------------------------
                C
 0016             200 READ(5,201,END=9020) CODE,SLPOH,INTOH,SLPNH,INTNH,SLPNH2,INTNH2,
                     1RATIO
 0017             201 FORMAT(A1,9X,6F10.5,F6.3)
                C                 WHERE SLPOH  = SLPOH FOR OH
                C                       INTOH  = INTERCEPT FOR OH
                C                    SIMILARY FOR SLPNH,INTNH FOR NH
                C                    SIMILARY FOR SLPNH2,INTNH2 FOR NH2
                C                        RATIO  = RATIO OF NH TO NH2 IN STANDARD
                C
 0018                 IF (CODE.NE.C)  GO TO 9020
                C  ******************************************************************
                C  ***                                                              *
                C  ***            S A M P L E   L O O P                             *
                C  ***                                                              *
                C  ******************************************************************
                C
                C
                C
                C  -----------------------------------------------------------------
                C  -                                                               -
                C  -      1.   R E A D   S A M P L E   C A R D   "D"               -
                C  -                                                               -
                C  -----------------------------------------------------------------
                C
 0019            1000 READ(5,1001,END=9030) CODE,(SAMPID(I),I=1,21),BK3000,BK2752,WAVOH,
                    1ABSOH,WAVNH,ABSNH,WAVNH2,ABSNH2,SMPLWT
 0020            1001 FORMAT (22A1,2X,2F6.3,3(F6.0,F6.3),F6.2)
                C                WHERE SAMPID = SAMPLE ID NUMBER
                C                      SBLACK = REQUESTOR'S SAMPLE BLACKBOOK NUMBER
                C                      SMPLWT = SAMPLE WEIGHT, MG.
                C                      BK3000 = BACKGROUND ABSORBANCE AT WAVELENGTH 3000
                C                      BK2752 = BACKGROUND ABSORBANCE AT WAVELENGTH 2752
                C                      WAVOH  = WAVELENGTH, MAX. FOR OH
                C                      ABSOH  = ABSORBANCE FOR OH
                C                   SIMILAR WAV AND ABS FOR NH AND NH2
                C            NOTE:  AN "X" CARD SIGNALS END OF JOB
 0021                 IF (CODE.EQ.X)  GO TO 8000
                C
 0022                 IF (CODE.NE.D)  GO TO 9040
```

APPENDIX I

```
FORTRAN IV G LEVEL  21                MAIN              DATE = 80084        13/04/53

                 C   ----------------------------------------------------------------
                 C   -                                                              -
                 C   -         2  C A L C.  B A C K G R O U N D   C O R R E C T I O N -
                 C   -                                                              -
                 C   ----------------------------------------------------------------
                 C
0023              1500 COROH = BK3000 + (((BK2752-BK3000) * (3000 - WAVOH)) / 248)
0024                   CORNH = BK3000 + (((BK2752-BK3000) * (3000 - WAVNH)) / 248)
0025                   CORNH2 = BK3000 + (((BK2752-BK3000) * (3000 - WAVNH2)) / 248)
                 C               WHERE  COROH,CORNH,CORNH2 = BACKGROUND CORRECTION FACTORS
                 C
                 C   ----------------------------------------------------------------
                 C   -                                                              -
                 C   -         3.  O H   C A L C U L A T I O N S                    -
                 C   -                                                              -
                 C   ----------------------------------------------------------------
                 C
0026              2000 TRUOH = ABSOH - COROH
0027                   WTOH = (TRUOH * SLPOH)+ INTOH
0028                   PCTOH = (WTOH / SMPLWT) * 100
                 C               WHERE TRUOH  = TRUE ABSORBANCE FOR OH, MAX.
                 C                     ABSOH  = OH ABSORBANCE READ ON CARD "D"
                 C                     COROH  = BACKGROUND CORRECTION FACTOR (PREV. STEP)
                 C                     WTOH   = WEIGHT OF O AS OH IN SAMPLE (MG.)
                 C                     SLPOH  = SLOPE OF OH READ ON CARD "C"
                 C                     INTOH  = INTERCEPT OF OH IN SAMPLE
                 C                     PCTOH  = PER CENT OH IN SAMPLE
                 C                     SMPLWT = SAMPLE WEIGHT READ ON CARD "D"
                 C
                 C   ----------------------------------------------------------------
                 C   -                                                              -
                 C   -         4.   SIMILARLY, N H 2   C A L C U L A T I O N S      -
                 C   -                                                              -
                 C   ----------------------------------------------------------------
                 C
0029              2500 TRUNH2 = ABSNH2 - CORNH2
0030                   WTNH2 = (TRUNH2 * SLPNH2) + INTNH2
0031                   PCTNH2 = (WTNH2 / SMPLWT) * 100
                 C   ----------------------------------------------------------------
                 C   -                                                              -
                 C   -         5.   SIMILARLY,  N H   C A L C U L A T I O N S       -
                 C   -                                                              -
                 C   ----------------------------------------------------------------
                 C
0032                   IF (PCTNH2.GT.0.01) GO TO 3000
0033                   TRUNH2 = 0
0034              3000 TRUNH = ABSNH - CORNH - (TRUNH2 * RATIO)
                 C         NOTE : NH2 INTERFERERES WITH NH & THIS INTERFERENCE
                 C                MUST BE NEGATED     (RATIO WAS READ IN ON CARD "C")
0035                   WTNH = (TRUNH * SLPNH) + INTNH
0036                   PCTNH = (WTNH / SMPLWT) * 100
                 C
                 C   ----------------------------------------------------------------
                 C   -                                                              -
                 C   -         6.   P R I N T   3   L I N E S   O F   R E P O R T   -
                 C   -                                                              -
                     ----------------------------------------------------------------
```

```
FORTRAN IV G LEVEL  21                   MAIN              DATE = 80084         13/04/53

                C          CHECK FOR PAGE OVERFLOW :
 0037            4000 IF (ILNCNT.LT.45)  GO TO 4020
 0038                 CALL HEAD
                C
                C  NOTE : ANY PER CENTS LESS THAN .01% WILL PRINT AS '< 0.01'
                C                ***  OH  LINE  ***
 0039            4020 IF (PCTOH.LT.0.01) GO TO 4025
 0040                 WRITE(6,4022) (SAMPID(I),I=1,21),SMPLWT,WAVOH,ABSOH,PCTOH
 0041            4022 FORMAT(/,15X,21A1,1X,F6.2,'  OH',7X,F5.0,7X,F5.3,5X,F6.2)
 0042                 GO TO 4120
 0043            4025 WRITE(6,4027) (SAMPID(I),I=1,21),SMPLWT,WAVOH ,ABSOH
 0044            4027 FORMAT(/,15X,21A1,1X,F6.2,'  OH',7X,F5.0,7X,F5.3,5X,'< 0.01')
                C
                C                ***  NH  LINE  ***
 0045            4120 IF (PCTNH.LT.0.01)  GO TO 4125
 0046                 WRITE(6,4122) WAVNH,ABSNH,PCTNH
 0047            4122 FORMAT(44X,' NH',7X,F5.0,7X,F5.3,5X,F6.2)
 0048                 GO TO 4220
 0049            4125 WRITE(6,4127) WAVNH,ABSNH
 0050            4127 FORMAT(44X,' NH',7X,F5.0,7X,F5.3,5X,'< 0.01')
                C
                C              - ***  NH2  LINE  ***
 0051            4220 IF (PCTNH2.LT.0.01)  GO TO 4225
 0052                 WRITE(6,4222) WAVNH2,ABSNH2,PCTNH2
 0053            4222 FORMAT(44X,' NH2',6X,F5.0,7X,F5.3,5X,F6.2)
 0054                 GO TO 5000
 0055            4225 WRITE(6,4227) WAVNH2,ABSNH2
 0056            4227 FORMAT(44X,' NH2',6X,F5.0,7X,F5.3,5X,'< 0.01')
                C
 0057            5000 ILNCNT = ILNCNT + 4
                C     ***  FINISHED  THIS  SAMPLE  - GO TO READ NEXT SAMPLE  ***
 0058                 GO TO 1000
                C
                C  ***************************************************************
                C  *                                                             *
                C  *                 E N D   S A M P L E   L O O P               *
                C  *                                                             *
                C  ***************************************************************
                C
                C
 0059            8000 STOP
                C
                C  ---------------------------------------------------------------
                C  -                                                             -
                C  -                 E R R O R   R O U T I N E S                 -
                C  -                                                             -
                C  ---------------------------------------------------------------
                C
 0060            9000 WRITE(6,9002)
 0061            9002 FORMAT(1H1,'  NO CARD TYPE "A"  ANALYST NAME,ETC.')
 0062                 GO TO 9900
                C
 0063            9010 WRITE(6,9012)
 0064            9012 FORMAT(1H1,' NO CARD TYPE "B"  REQUESTOR')
 0065                 GO TO 9900
                C
 0066            9020 WRITE(6,9022)
 0067            9022 FORMAT(1H1,' NO CARD TYPE "C"  SLOPES/INTERCEPTS')
```

```
FORTRAN IV G LEVEL  21                MAIN               DATE = 80084         13/04/53

                 GO TO 9900
           C
            9030 WRITE(6,9032)
            9032 FORMAT(1H1,'  NO END CARD (TYPE "X")')
                 WRITE(6,9034)
            9034 FORMAT('  -- CHECK TO SEE IF ALL SAMPLES ARE REPORTED')
                 GO TO 8000
           C
            9040 WRITE(6,9042)
            9042 FORMAT(1H1,'  INVALID CARD - WAS EXPECTING CARD TYPE "D"')
                 GO TO 9900
           C
            9900 WRITE(6,9902)
            9902 FORMAT(//,'  FATAL ERROR ****************************************')
           C  ------------------------------------------------------------------
           C  -                                                                -
           C  -        T H E   E N D  -  CALC CONC OH,NH,NH2 IN SRC SAMPLES    -
           C  -                                                                -
           C  ------------------------------------------------------------------
                 END
```

```
 FORTRAN IV G LEVEL  21                 MAIN               DATE = 80084         13/04/53

                                 COMMON BLOCK /         / MAP SIZE      280
SYMBOL      LOCATION        SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
IPGCNT          0           ILNCNT         4         ANAME          8         APPROV        EC         ABLACK        CC
CHRG           FC           DAT          124         REGSTR       144

                                 SUBPROGRAMS CALLED
SYMBOL      LOCATION        SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
IBCOM#        160           READ         164

                                 SCALAR MAP
SYMBOL      LOCATION        SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
A             168           B            16C         C            170         D            174         X            178
CODE          17C           I            180         SLPOH        184         INTOH        188         SLPNH        18C
INTNH         190           SLPNH2       194         INTNH2       198         RATIO        19C         BK3000       1A0
BK2752        1A4           WAVOH        1A8         ABSOH        1AC         WAVNH        1B0         ABSNH        1B4
WAVNH2        1B8           ABSNH2       1BC         SMPLWT       1C0         CONOH        1C4         CONNH        1C8
CONNH2        1CC           TRUOH        1D0         WTOH         1D4         PCTOH        1D8         TRUNH2       1DC
WTNH2         1E0           PCTNH2       1E4         TRUNH        1E8         WTNH         1EC         PCTNH        1F0

                                 ARRAY MAP
SYMBOL      LOCATION        SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
SAMPID        1F4

                                 FORMAT STATEMENT MAP
SYMBOL      LOCATION        SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION      SYMBOL     LOCATION
   51         248              101       24E            201       254           1001       262           4022       270
 4027         29E             4122       2C6           4127       2DE           4222       2F8           4227       314
 9002         332             9012       35E           9022       384           9032       3A0           9034       3CC
 9042         3F0             9992       430

    *OPTIONS IN EFFECT*  NOID,EBCDIC,SOURCE,NOLIST,NODECK,LOAD,MAP
    *OPTIONS IN EFFECT*  NAME = MAIN     , LINECNT =        60
    *STATISTICS*    SOURCE STATEMENTS =        74,PROGRAM SIZE =       2870
    *STATISTICS*  NO DIAGNOSTICS GENERATED
```

```
FORTRAN IV G LEVEL  21                 MAIN               DATE = 80004          13/04/53

          C
          C  ---------------------------------------------------------------------
          C  -                                                                   -
          C  -               H E A D I N G     S U B R O U T I N E               -
          C  -                                                                   -
          C  ---------------------------------------------------------------------
                SUBROUTINE HEAD
          C
                COMMON IPGCNT,ILNCNT
                COMMON ANAME,APPROV,ABLACK,CHRG,DAT,REQSTR
                DIMENSION ANAME(25),APPROV(24),ABLACK(12),CHRG(10),DAT(8)
                DIMENSION REQSTR(79)
          C
              1 IPGCNT = IPGCNT + 1
                ILNCNT = 0
          C
                WRITE(6,10) IPGCNT
             10 FORMAT(1H1,21X,' CALCULATING  CONCENTRATIONS OF  OH,NH,NH2',
               1'  IN  SRC  SAMPLES',28X,'PAGE ',I3)
          C
                WRITE(6,20) (REQSTR(I),I=1,79)
             20 FORMAT(/,4X,'REQUESTOR(S):   ',79A1)
          C
                WRITE(6,30) (ANAME(I),I=1,25),(APPROV(I),I=1,24)
             30 FORMAT(4X,'ANALYST:    ',25A1,6X,'APPROVED BY:   ',24A1)
          C
                WRITE(6,40) (CHRG(I),I=1,10),(ABLACK(I),I=1,12),(DAT(I),I=1,8)
             40 FORMAT(4X,'CHARGE NUMBER:   ',10A1,5X,'BLACKBOOK NUMBER:   ',12A1,
               117X,'DATE:   ',8A1,/)
          C
             45 IF (IPGCNT.NE.1)   GO TO 100
                WRITE(6,50)
             50 FORMAT(10X,' THE ESTIMATE OF  THE OH,NH,AND NH2 CONCENTRATION IS',
               1'DETERMINED BY COMPARISON TO STANDARD CURVES.   ')
                WRITE(6,52)
             52 FORMAT(10X,' THE STANDARD CURVES ARE PREPARED FROM PURE COMPOUND',
               1'S SIMILAR TO THE TYPICAL MATERIAL IN SRC LIQUIDS')
                WRITE(6,54)
             54 FORMAT(10X,' THE NIR STANDARD FOR OH IS BETA-NAPHTHOL
               1'                                                      ')
                WRITE(6,56)
             56 FORMAT(10X,' THE NIR STANDARD FOR NH IS CARBAZOLE
               1'                                                      ')
                WRITE(6,58)
             58 FORMAT(10X,' THE NIR STANDARD FOR NH2 IS 1-AMINONAPHTHALENE
               1'                                                      ')
          C
                ILNCNT = ILNCNT + 6
          C
            100 WRITE(6,102)
            102 FORMAT(/,'                ',25X,'SAMPLE',20X,'ABSORBANCE')
          C
                WRITE(6,105)
            105 FORMAT('                          SAMPLE  I.D.        WEIGHT
               1'WAVELENGTH     READ IN         WT X',/)
          C
            500 RETURN
```

```
FORTRAN IV G LEVEL  21                 READ                DATE = 80084          13/04/53
                C  -----------------------------------------------------------------------
                C  -                                                                     -
                C  -       T H E   E N D  -  READING ROUTINE CALC CONC
                C  -                                                                     -
                C  -----------------------------------------------------------------------
 0033                END
```

Determining Metals in SRC-Related Materials Using Energy-Dispersive X-Ray Fluorescence (EDXRF): The 10-mg Micropellet Method

(APCI Method)

I. SCOPE

The 10-mg micropellet method quantitatively analyzes the major elements Al, Si, K, Ca, Ti, and Fe and semiquantitatively analyzes any additional elements of atomic number 11 or above in a sample. Dry ash residues obtained from SRC and TSL solids and liquids, cokes, coals, and Kerr-McGee ash concentrate (KMAC) can be analyzed.

The method was developed to analyze small samples (10 mg) and is best applied to samples with low ash contents. Typically, SRC solids, liquids, and cokes have low ash contents of 0.1% or less; the dry-ashing procedure in this method concentrates the sample's inorganic components for analysis. Samples with high ash contents such as coals and KMAC are best analyzed by other methods.

II. APPARATUS

A. Muffle furnace, Thermolyne Model FA1630-1, 2,150°F maximum (Fisher Scientific Co., King of Prussia, Pa.)

B. Platinum dish, 100-mL capacity (Fisher Scientific Co., King of Prussia, Pa.)

C. Analytical balance, Mettler Model H542, 0.01-mg readability (Fisher Scientific Co., King of Prussia, Pa.)

D. Mortar and pestle, agate, 65-mm o.d. (Fisher Scientific Co., King of Prussia, Pa.)

E. Specimen mold, Angstrom 1/2-in., Model 4451-1/2-SE (Angstrom, Inc., Belleville, Mich.)

F. Hydraulic press, 30 ton, Loomis Model 341-30S with Loomis Power Unit #341-AP (Loomis Products Company Co., Levittown, Pa.)

G. Energy-dispersive X-ray fluorescence analyzer, EDAX, Model 9500 with 9100 analyzer, Rh tube continuous excitation, vacuum capability, 1-mm microcollimator attachment, and Al foil filter.

III. REAGENTS

A. X-ray powder, grinding briquetting additive, Chemplex Catalog No. 600 (Chemplex Industries, Inc., Eastchester, N.Y.)

B. Magic transparent tape, Scotch, No. 021200-07378 (3M Corp., St. Paul, Minn.)

C. Standard reference material 1259, aluminum alloy 7075 (National Bureau of Standards, Washington, D.C.)

D. Standard reference material 1633a, trace elements in coal fly ash (National Bureau of Standards, Washington, D.C.)

E. Certified reference material SARM1, granite (SA Bureau of Standards, Republic of South Africa)

F. Certified reference material SARM3, lujauriet (SA Bureau of Standards, Republic of South Africa)

G. Certified reference material SARM4, norite (SA Bureau of Standards, Republic of South Africa)

IV. SAFETY

Caution! Samples analyzed by this method include SRC materials and products. The analyst should avoid direct contact with skin and eyes.

Caution! The X-ray equipment used in this analysis produces hazardous radiation and should not be operated by unauthorized or untrained personnel. In operating the equipment, all safety recommendations set by the instrument manufacturer and all safety regulations set by the on-site X-ray Radiation Safety Officer must be followed. Do not under any circumstances operate the equipment if any safety shields or cover plates have been removed or if any safety circuits or switches have been bypassed or defeated.

V. PROCEDURES

A. Ashing

1. SRC Solids, Anode Coke, Coals, KMAC, and Reference Standards

Dry-ash about 15 to 20 g according to American Society for Testing and Materials (ASTM) Procedure D-3174-73 (Ash in the Analysis Sample of Coal and Coke). Repeat the procedure if necessary to obtain approximately 20 mg of ash.

2. SRC Heavy Oils and Middle Distillates

Dry ash from 1 to 100 g by using ASTM Procedure D 428-80 (Ash from Petroleum Products) to obtain about 20 mg of dry ash.

B. Grinding and Pelletizing

1. Grinding Standards and Samples

Using the analytical balance, weigh 10.00 ± 0.10 mg of dry ash standard or previously obtained sample and 40.00 ± 0.10 mg of

X-ray mix powder. Quantitatively transfer material to the agate mortar.

Thoroughly grind and mix the ash and powder in the mortar and then alternately grind and scrape the packed powder from the sides of the mortar for a minimum of 5 min to obtain a suitable mixture.

2. Pelletizing Standards and Samples

Transfer all of the sample mixture to the assembled specimen mold. Distribute the material evenly over the surface of the mold and insert the mold plunger. Press the material with a hydraulic press for 10 sec at 20,000 psi.

Place the pellet on a 3-in. piece of Scotch Magic Tape; avoid touching the pellet.

C. Semiquantitative Analysis

1. Calibrate the 9500 spectrometer using the NBS aluminum alloy 1259. 20 kV and 500 μA, 10,000 counts, peak 1 = 1.486 keV (Al Kα), peak 2 = 8.636 keV (Zn Kα). See EDAX 9500 Users Manual, Chapter 3, Section 3, p. 4 for instructions.

2. Instrument Conditions

Collimator with 1-mm attachment; Al filter in; 35 kV; 500 μA; 10 eV/channel; 300 sec, live time; vacuum less than 200 millitorr.

3. Collect the sample spectra using the instrument conditions above, identify, and save all elements found in the sample. See EDAX 9500 Users Manual, Chapter 3, Section 5, p. 1.

4. Remove escape peaks. See EDAX 9500 Users Manual, Chapter 4, Section 1, p. 2.

5. Set a linear background and collect net intensity for each peak. See EDAX 9500 Users Manual, Chapter 4, Section 1, p. 4.

6. Collect a spectra (using the conditions in step 2) for the NBS 1633a standard. Identify and save the following elements: Al, Si, P, K, Ca, Ti, V, Cr, Fe, Cu, Zn, Ga, Sr. Remove the excape peaks and collect the net intensity for each element (steps V.C. 3, 4, 5).

7. Change the instrument conditions to the following: micro-collimator with 1-mm attachment; no Al filter; 20 kV; 500 μA; 10 eV/channel; 200 sec live time; vacuum less than 200 milli-torr.

8. Collect the sample spectra (step V.C.3.) according to the conditions in step V.C.7, identify, and save Na, Mg, and P. Remove the escape peaks (step V.C.4), and set a linear background and collect the net intensity (step V.C.5).

9. Repeat step V.C.8 for the SARM4 standard.

10. Determine elemental sensitivity curves. Calculate the sensitivity for each element identified in Standards NBS 1633a and SARM4, as follows:

$$SEN = \text{net } I/\%\ \text{element}$$

where SEN = sensitivity; net I = net intensity in counts per second; and % element = percent of element present in standard. Plot the SEN for each element (Al or heavier) (Y axis) vs. the energy (keV) (X axis) for each element; see Figure 1. Obtain the SEN for elements identified in the samples but not in the standards from the sensitivity curves.

11. Calculate the semiquantitative concentration of each element in the sample as follows:

$$\text{est \% A} = \frac{1}{\text{SEN}} \times \text{net } I_A$$

where est % A = estimated percent analyte A; SEN = sensitivity for analyte A; and net I_A = net intensity of analyte A.

12. Determine the total additional elements present by adding the estimated percentage of all elements identified in the sample, excluding Al, Si, K, Ca, Ti, and Fe.

D. Quantitative Analysis (Al, Si, K, Ca, Ti, Fe)

1. Calibrate the spectrometer; see step V.C.1.

2. Instrument conditions: microcollimator with 1-mm attachment; no filter; 20 kV; 500 μA; 10 eV/channel; 200 sec live time; vacuum less than 200 millitorr.

3. Establish the MCA file. See EDAX 9500 Users Manual, Chapter 3, Section 2.

4. Establish the Material file. See EDAX 9500 Users Manual, Chapter 3, Section 8.

5. Collect net I using the conditions in step V.D.2 and directions from steps V.C.3, 4, and 5 for the following standard pellets: NBS 1633a, SARM1, and SARM3.

6. Collect net I for the samples as in step V.D.5.

7. Following the directions in the EDAX Users Manual (Chapter 4, Section 3, pp. 1 to 7) for Quantitative Analysis Theoretical

Parameters, calculate the concentrations of Al, Si, K, Ca, Ti, and Fe in the samples. Note: Enter all three standards (NBS 1633a, SARM1, and SARM3) in the THEO section of the program. Standards and samples contain 0.0377 g/cm^3.

8. Normalize the calculted results to 100% minus the percent additional elements (step V.C.12). Note: The concentration of each element in the sample is automatically calculated by the THEO program. A basic form of the equation used for this calculation is:

$$I = C \cdot S \cdot F$$

where I = the measured intensity for the analyte; C = the concentration of the analyte; S = the sensitivity factor for the analyte for the instrument; and F = a function that describes the influence of all the other elements present in the sample on the analyte.

I and S are measured for each analyte when the standards are analyzed. F is determined theoretically from fundamental X-ray theories using tables of wavelength emission lines, mass absorption coefficients, fluorescent yields, absorption edges, and calculated tube spectra. The composition of a sample is calculated as follows:

- The approximate composition of the sample is calculated from the measured intensities and the calculated F factors.

- A fundamental parameters calculation is made to predict intensities that would be obtained from a sample with that composition.

- The calculated intensities are adjusted to agree with the analyzed standards.

- The calculated, adjusted intensities are compared to the measured intensities for the sample.

- If there is disagreement, the program makes a refined estimate of composition and predicts the intensities again.

- The iteration stops when there is no significant change in calculated composition.

VI. PRECISION AND ACCURACY

Accuracy

Tables 10-15 of the main report list the accuracies of quantitative results for Al_2O_3, SiO_2, K_2O, CaO, TiO_2, and Fe_2O_3 for five analytical standards. The mean concentration is the average concentration of the five standards. One σ is the standard deviation for the difference between the true concentration and the calculated concentration. For the major elements present in these check materials (Al_2O_3, SiO_2, K_2O, and Fe_2O_3), the average percent relative errors (1σ divided by the mean concentration) are ±4.21, ±2.26, ±6.01, and 6.77%, respectively. For the minor elements, CaO and TiO_2, the average percent relative errors are ±13.6 and ±18.4, respectively.

Precision

Table 16 of the main report shows the typical precision obtained from triplicate sample analyses. Listed are the mean concentrations of the three analyses, 1σ for the differences between the mean concentration and the calculated concentration, and the percent relative error (1σ divided by the mean concentration). For all of the elements, the method's reproducibility (percent relative error) is better than the accuracy and is on the order of 1 to 10% relative.

Round-Robin Analysis

The XRF micropellet method was applied to four samples from Wilsonville Run 235 (one Kerr-McGee ash and three SRC solid samples) and the results were compared to those obtained by three other laboratories: Alcoa, Alcoa Center, Pa.; IMMR (Institute for Mining and Minerals Research), Lexington, Ky.; and Galbraith Laboratories, Knoxville, Tenn. The samples were also analyzed by atomic absorption spectroscopy at Air Products, Trexlertown, Pa. Results are summarized in Table 3 of the main report.

Because Alcoa and IMMR generally reported the most consistent results, their values were averaged as representing the best results. For the SRC solid samples, the XRF method shows very good agreement with the Alcoa and IMMR values for Si, Ca, K (better with IMMR), V, and Ni (better with Alcoa). For Fe, the XRF method is about 0.01% absolute high at the 0.004% Fe level, and for Ti, the XRF method is about 0.01% absolute high at the 0.01% Ti level. For Na, the XRF estimate is about 0.01% absolute low at the 0.015% Na level. For Al, the XRF value is about 0.003% absolute high at the 0.006% Al level.

For the KMAC sample, the XRF method shows very good agreement for K, Ca, Ti, Fe, and Na. For KMAC Al, the XRF method is about 0.5% absolute high at the 2.7% Al level and for Si, the XRF method is about 0.6% absolute high at the 6.2% Si level. For KMAC Ni and V, the XRF method values are both low. As noted earlier, the XRF micropellet method is not the preferred method for a high-ash-content sample such as KMAC. Such samples can be more accurately analyzed by direct XRF analysis, as in whole coal.

For the SRC solid samples, agreement between the XRF method and the Alcoa/IMMR values is generally acceptable for all metals of interest, except Fe and Ti. For these elements, the method gives somewhat high results. This is thought to be due to a small positive error in measuring and accounting for the thickness of the pressed micropellet used in the analysis.

VII. PRINCIPLE

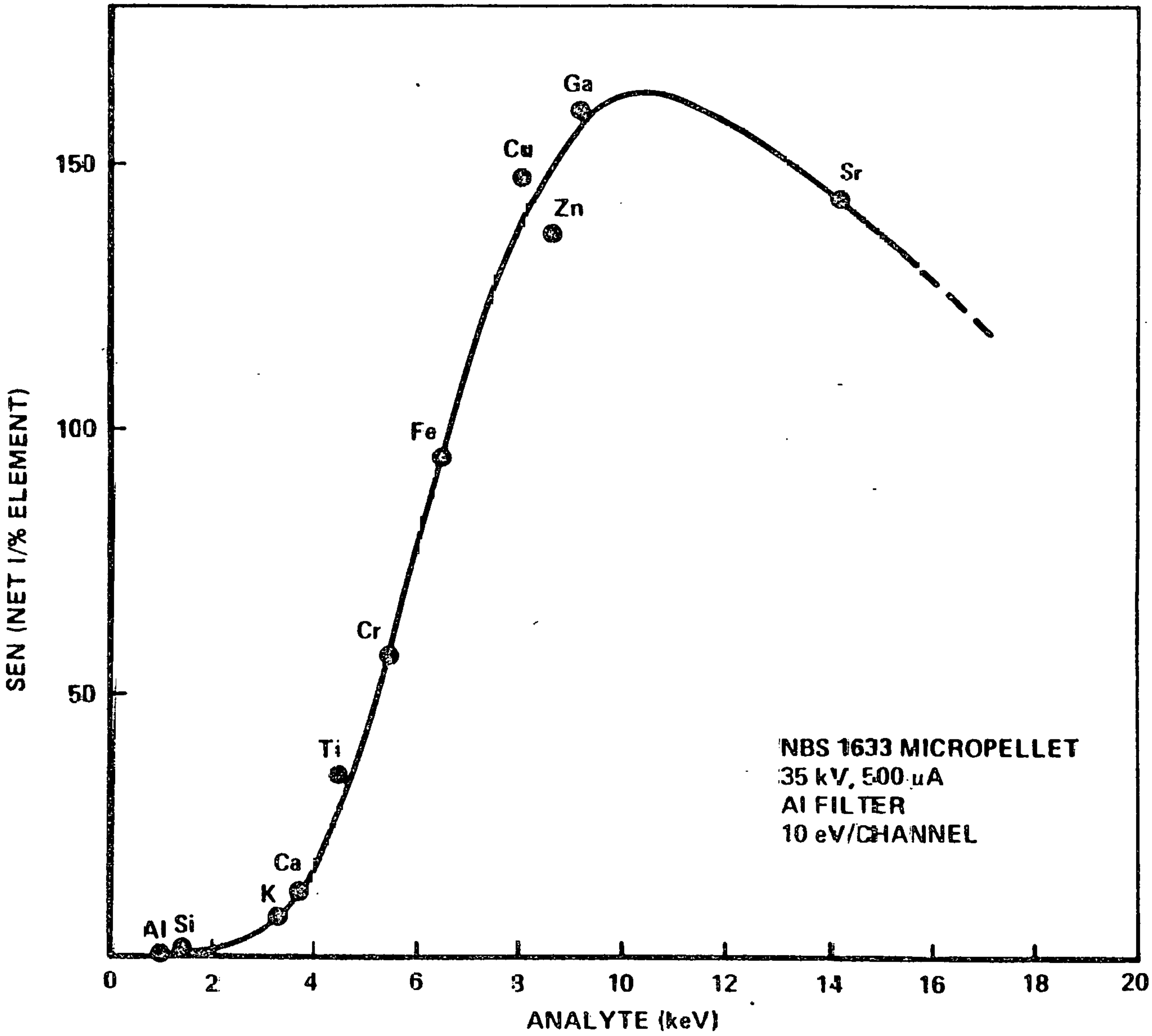
This method determines the elemental content of SRC-related materials using energy dispersive X-ray fluorescence (EDXRF), which rapidly analyzes all elements of atomic number 11 or above and is unaffected by an element's oxidation state. This nondestructive, direct-analysis technique provides simultaneous multielement information from a single sample spectrum. The typical energy resolution for an EDXRF system is 160 eV full width at half-maximum for Mn Kα X-rays. This resolves all but the most severe of spectral overlaps (Mo Lα and S Kα, for example).

Samples are dry-ashed at 750°C to concentrate inorganic components, which are usually present at levels lower than the detection limits of EDXRF by direct analysis. For a typical SRC-related material, the ash content is small, 0.1% or less; as a result, only a small quantity of ash is obtained for analysis. Ten milligrams of ash is pelletized, and net intensities for all the elements of interest are collected. Three standards are used to calibrate the system and the analyte concentrations are calculated.

The actual concentrations are done using a fundamental parameters program (XRF-11), which determines theoretical interelemental influence coefficients that are then used to correct for matrix effects and calculate analyte concentrations in a sample. Th XRF-11 program is used because it provides rapid analyses and requires only a few standards to cover a broad range of analyte concentrations. The results obtained are not as accurate as can be obtained with a large series of standards, but they are acceptable (typical accuracy is ±5 to 10% relative).

Special care should be taken to ensure that the ashing procedure provides accurate results. Contamination in the samples or from the equipment used will be magnified when the whole sample is ashed to a small residue. Results are determined on the ash and then back-calculated using the percent dry ash to determine the elemental content in the "as-received" sample. An error in the ash content will lead to an error in all of the back-calculated analyte results.

Figure 1
Semiquantitative Elemental Sensitivity Curve



Gas Chromatographic Method for Coal Liquids Analysis
(APCI Method)

I. SCOPE

This method is a qualitative capillary column gas chromatographic (GC) procedure for analyzing distillates from the SRC-I process, the hydrotreater unit, or the "oils" fraction from solvent separation of total product liquids. The technique is generally applicable to all coal-derived liquids with distillation upper temperature limits of 850°F (at atmospheric pressure, or corrected to atmospheric pressure for vacuum distillation). The chromatograms generated for each sample type can be used for comparison to other similar samples. Although not strictly quantitative without response factors, sample-to-sample concentration differences of specific chromatographic peaks can be monitored.

In addition to a "universally responsive" flame ionization detector (FID), element-selective detectors provide data on important classes of compounds present in many of these samples (1-3). This is particularly true of nitrogen-selective detectors, although some sulfur-selective detectors are also sensitive enough to be useful. A gas chromatograph/mass spectrometer (GC/MS) also aids in identifying the species present, detecting nonresolved mixtures (and their individual quantitation), and studying changes in samples, including new components being formed that are not chromatographically resolved from already existing components.

Naphtha samples can also be analyzed using a different temperature program. Such samples are typically a volatile fraction, defined as distilling from the "initial boiling point" to about 400°F or 177°C.

Undiluted or diluted samples (as appropriate) are injected into a capillary gas chromatographic column, where the sample is separated into hundreds of peaks. When an FID is used, the most complex samples have produced over 500 peaks.

II. APPARATUS

A. Gas Chromatograph

A modern instrument, equipped with an FID, a splitting capillary injection port, a programmable column oven temperature, and separately controlled injector and detector temperatures, is acceptable. The naphtha samples require subambient programming capability (the liquid carbon dioxide type achieves a sufficiently low temperature). As noted above, the availability of element-selective detectors is useful.

B. Integrator

Any electronic integrator capable of integrating peaks as narrow as 1 sec wide at half-height and as close together as 3 sec is sufficient. Information on the sampling rates of modern integrators shows that all are capable of performing this job. However, memory capacity can be a limitation. The Spectra-Physics SP4100 has insufficient capacity for many of the typically complex chromatograms in this work. It is useful to have the capability to store the chromatograms for replotting and reintegration. Depending on the data desired, peak shoulders and other features of these complex chromatograms can cause problems with integration reproducibility. The ability to expand, replot, draw baselines, and change integration parameters allows facile optimization of integration results. A Varian CDS 401 data station was used in this work. Other computer integrators that have recently entered the market (Perkin-Elmer, Nelson Analytical, and IBM) may be superior for some functions, but so far they have not been able to handle complex chromatograms such as those produced in this work.

C. Capillary Column

A 60-m x 0.25-mm internal diameter fused-silica DB-5 column with a stationary phase film thickness of 0.25 μm was used (J&W Scientific, Inc.). This is a cross-linked stationary phase. SE-52, a similar phase, can also be used.

D. Injection Syringe

A 1-μL positive displacement syringe (plunger through the needle; type 7001 Hamilton) and 22° bevel (narrow gauge) needles were used. A Chaney adapter improved precision slightly (2). We found that supposedly equivalent Scientific Glass Engineering Co. syringes produced results that were distinctly less precise and do not recommend their use for these analyses.

Syringes were cleaned with a Hamilton syringe cleaner and solvents appropriate for the samples such as dichloromethane. A vacuum source must be available; presumably, an autosampler could be substituted, but none were used for this work.

E. Pressure Regulators; Helium and Air

One each, 0-200 psig, two stage, No. E12-Q-N515C (Air Products and Chemicals, Inc.) or equivalent.

F. Hydrogen Generator

A hydrogen generator such as the Milton-Roy Elhygen type (Applied Science Co.) is a good source for FID hydrogen.

G. Gas Filters

All gases should have molecular sieve and calcium carbonate drying traps placed in line before the chromatograph. All chromatographic supply houses stock these filters. In addition, an oxygen scrubber on the helium line is a good precautionary measure. Heated high-capacity traps are available from most chromatography supply companies. Alltech and Chrompack supply indicating oxygen traps.

H. Gas Leak Detector

A GOW-MAC gas leak detector (or similar), available from most chromatographic supply companies, should be used to check all fittings for leaks. If necessary, helium should be plumbed into the suspect line to allow sensitive detection of leaks. The column fittings, septum, and septum nut should be checked periodically.

I. Septa

Supelco Thermogreen LB-1 high temperature septa were used.

J. Bubble Flow Meter

A variable-range bubble flow meter or individual meters usable in the ranges of 1-5, 20-40, and 200-400 mL/min are needed to set up the gas flows. A Flowrater (Spectrum Scientific, Inc.) may also be used, eliminating the need for a stopwatch because it provides a direct readout.

K. Miscellaneous

A stopwatch (if using bubble flow meters), a butane cigarette lighter, a carbide-tipped or diamond-tipped capillary column cutter, and spare column ferrules (15% graphite/Vespel, 0.4-mm-i.d. hole) should be available (Supeltex M-2A by Supelco or equivalent). Do not use graphite ferrules because they are soft and have a tendency to clog tubing and fittings. Silylated glass wool may be recommended for use in the injection port, depending on the specific gas chromatograph chosen and the type of injection port liner in use. This is available from Supelco and many other supply houses. Some injection port liners may also require silylated glass bead packing. 70/80 mesh beads are available from Analabs, Inc. (GCS-020B).

III. REAGENTS (GASES, SOLVENTS, AND STANDARDS)

A. Helium, Air, and Hydrogen

Available from Air Products and Chemicals, Inc. or other suppliers of high-purity gases:

Helium, zero grade, size A; ultra-pure carrier grade may also be used.

Air, zero grade, size A.

Hydrogen, zero grade, size A; use if cylinder hydrogen is chosen instead of a hydrogen generator.

B. Solvents

Dichloromethane is a good general solvent for cleaning syringes, making standard solutions, and diluting viscous samples. ACS Reagent grade solvent is sufficiently pure, but any purchased solvent should be screened first by the analysis system that it will be used with to determine acceptability. Higher grades (HPLC, nanograde, distilled-in-glass, etc.) are available. Other solvents such as toluene may be useful in some cases.

C. Standard Chemicals Representative of Coal Liquid Compounds

Many suppliers stock chemicals such as those listed below, or other aromatic or aliphatic species that may be of interest in coal liquids. This list of chemicals, available from Aldrich Chemical Co., is representative of species used to make standard blends to check retention times or system behavior. Other standards are available from this and other companies.

Acenaphthene, 99%, No. 21,537-6
Biphenyl, 99%, No. B3,465-6
Carbazole, 99%, No. C308-1
m-Cresol, 99+%, Gold Label, No. C8-572-7
Dibenzofuran, 99+%, Gold Label, No. 23,637-3
Dibenzothiophene, 95%, No. D3,220-2
9,10-Dihydrophenanthrene, 97%, No. D10,600-3
2,6-Dimethylnaphthalene, No. 12,653-5
3,4-Dimethylphenol, 99%, No. D17,540-4
Dodecane, 99%, No. D22,110-4
Fluorene, 98%, No. 12,833-3
Fluoranthene, 98%, No. F80-7
Hexacosane, No. 24,168-7
Indan, 97%, No. I-180-4
2-Methylnaphthalene, 98%, No. M5,700-6
1-Methylphenanthrene, No. M6,820-2
Naphthalene, 99+%, Gold Label, No. 18,450-0
1-Naphthol, 99%, No. N199-2
Nonadecane, 99%, No. N2,890-6
Phenanthrene, 98+%, No. P1,140-9
Pyrene, 99+%, No. 18,551-5
Quinoline, 99%, No. 24,157-1
Tetralin, 99%, No. 10,241-5
Triphenylene, 98%, No. T-8,260-0

IV. SAFETY

Most coal liquids contain individual components that are known carcinogens. Thus, coal liquids should be viewed as suspected carcinogens and handled accordingly. This implies the use of fume hoods, gloves, care to avoid contamination of porous surfaces, rapid cleanup of spills, a neat laboratory, and proper disposal of all discarded samples and contaminated materials leaving the laboratory.

Personnel should have annual physicals that include tests appropriate for chemical workers (e.g., enzyme activity).

All instrument exit points should be ventilated directly to a fume hood (e.g., ventilation snorkels for the GC detectors), or a tubing connection should confine the effluent and vent into a hood or snorkel. Although gas chromatographs should have carbon filters before the splitter exit, venting of the splitter is a reasonable precaution. If a septum sweep is present, it too should be vented, although it is typically not used during split analysis.

V. PROCEDURE

A. Preparation of Chromatograph

1. Assemble the chromatograph and integrator according to the manufacturer's instructions.
2. Install the gas filters in the gas lines between the cylinder regulators (or hydrogen generator exit) and the GC.
3. Insert a split-mode injection port liner in the injection port. Pack it with glass beads and glass wool as directed by the GC manufacturer if it is a straight tube design. Although this packing may not be necessary, it prevents nonvolatile material from entering the column.
4. Install a Thermogreen septum in the septum cap; be certain to use the correct size.
5. Many compounds in typical coal liquids are carcinogenic. See appropriate safety recommendations for instrument setup in Section IV.

B. Column Installation

Install the column using the specified ferrules. Note the instrument manufacturer's instructions regarding the direction of the ferrules; some install the ferrules in the reverse direction from others. Special nuts are usually required. After the nuts and ferrules have been installed on the column, break off about 1 cm from each end of the column using the special glass cutter. This avoids possible problems with ferrule material clogging the column.

Install the column in the injection port to the position recommended by the manufacturer. If guidelines are unavailable, have the syringe needle penetrate the injection port until there is a 1- to 2-cm gap between the end of the needle and the column entrance. Install the column exit to just below the detector flame jet exit. Do not overtighten the column fittings. Apply head pressure to the column (40 psig for 60-m column) to produce appropriate column flow rate. Use the leak detector (never use snoop or similar liquid leak detectors) to guide to the proper degree of tightness to prevent leaks. The column fittings must be checked for leaks again after the first couple of heating cycles. Column conditioning using a slow temperature program to 300°C and holding at that temperature for 2 hr is recommended. Be certain that all air has been flushed from the system before the column is heated.

Note: See Section C; zones should be at operating temperatures for column conditioning.

C. Operating Conditions

1. Air and Hydrogen Flows

Set air and hydrogen flow rates according to the GC manufacturer's instructions.

2. Helium Makeup Flow

Using the flow meter, set the flow at about 30 mL/min; be sure that the air and hydrogen are turned off. The column helium flow rate must be accounted for in the calculation. Note that some instruments do not have a makeup gas.

3. Zone Temperatures

Note: Before heating the injector and detector zones, be sure that there is flow through the column and that all air has been purged from the system (10 min will be sufficient if the splitter is open and set properly--see below).

Injector: Different instruments may require different temperatures. Perkin-Elmer instruments in this work required 300°C, and the Varian 4600 GC required 350°C to achieve similar results.

Detector: 310°C.

Initial column oven temperature: The starting temperature varies with the samples: naphtha, 0°C; middle and total product distillate samples (approximate initial boiling point about 175°C, corrected to atmospheric pressure), 50°C; heavy distillates (initial boiling point about 350°C, corrected to atmospheric pressure), 100°C. The oven should not be left at 0°C overnight because the carbon dioxide supply will be rapidly drained; 50 or 100°C are acceptable overnight temperatures.

4. Column Flow

Set the detector range at x1 (1×10^{-12} amps full scale) and the plotter attenuation to x16. Turn the splitter on and adjust it to about 50 mL/min. Set the column head pressure to about 40 psig. Inject butane gas from the lighter (a few microliters) with the column temperature at 50°C to determine the dead volume from the retention time of butane. Butane is considered to be nonretained. Butane can be withdrawn from the lighter by inserting the syringe needle into the flame hole and drawing back the plunger while depressing the lighter valve switch. Make at least three injections and use the average retention time in the following equation to calculate the carrier gas flow rate (CFR):

$$CFR = \frac{\pi r^2 L}{t_b \times C_f}$$

r = internal radius of the column in centimeters
L = length of column in centimeters
t_b = retention time of butane in minutes
C_f is the gas compressibility factor: $1.5(P^2 - 1)/(P^3 - 1)$, where P is the ratio of the column inlet pressure divided by the column outlet pressure. The outlet pressure is normally about 14.7 psia and the inlet pressure will be the column head pressure (gauge reading plus the prevailing atmospheric pressure).
The flow rate should be about 2-3 mL/min.

5. Setting the Split Ratio

Attach the Flowrater or bubble flow meter to the splitter vent and adjust the splitter flow to get a split ratio of about 25:1 to 50:1. The calculation is as follows:

$$\text{split ratio} = \frac{CFR + SFR}{CFR}$$

SFR = splitter flow rate

Make certain the splitter is open before each run.

6. Integrator and Plotting Parameters

Many parameters must be set for proper integration.

The peak width must be fairly narrow, to ensure an adequate number of data points across each peak. A minimum of six is acceptable. A set point of 8 for the peak width in the CDS 401 provides 2.5 data values per second. If data are saved on computer disks, the space required will depend on the sampling rate chosen. A minimum area of 1000 will eliminate small peaks from the report and still provide data on 300-400 peaks in most typical samples. If the data are saved via computer, recalculation can include deleted components by changing the restrictions.

The choice of data system and plotter will dictate the most useful display. The CDS 401 prevents peak retention times from being printed on top of each other. They can also be eliminated either for a clear chromatogram or for replotting from a data file. A computer-assisted display system will provide capabilities of display and manipulation to allow optimization of peak integration. In general, a chart speed of 0.5 cm/min and a chart attenuation of x64 are suitable. Faster chart speeds, especially for replots for close examination of complex chromatograms, may be necessary. Attenuations from x4 to x256 may be useful depending on the sample's complexity, boiling point distribution, percent of volatile components, and extent of dilution in a solvent.

7. Daily Blank Temperature Program

Every day before any analyses are performed, a temperature program should be run without an injection. This elutes any residual coal liquid components or system contaminants (for instance, from the septum) that may condense at the beginning of the column. The column is heated from 50 to 300°C at 10°C/min and this temperature is held for 20 min.

8. Temperature Program for Samples

The column oven temperature is programmed at 2°C/min for all samples; starting temperatures for different types are listed in Section V.C.3. The final temperature for a naphtha is 200°C, although some distillates may have volatile portions like a naphtha and also higher boiling components requiring higher elution temperatures. Middle and total distillate samples require an upper temperature of 280°C and heavy distillates are run with a program upper limit of 300°C. Generally, no final hold time is necessary, although 5-10 min is sometimes used. There is no initial hold time.

D. Test Solution

1. Preparation of the Test Solution

Coal liquids are a complex mixture of many types of compounds. Aromatic hydrocarbons, alkyl-aromatic hydrocarbons, partially hydrogenated aromatic hydrocarbons, alkanes, hydroxyaromatics, aromatic ethers, and heteroatomic species containing nitrogen and sulfur in a diverse range of compound types have been found in coal liquids (2,4-6). Two test solutions were made, to avoid most closely eluting compounds.

The suggested test solutions contain model compounds covering all major classes of compounds found in coal liquids. Other mixtures representative of coal liquid diversity would also be acceptable. Make certain that all components in the test solution are in solution before using it. The test solutions should be stored in the dark, in a number of small amber vials with Teflon cap liners. By dividing the standard solution among multiple bottles, the isolated test solution vials will be unaffected by repeated openings and closings during periodic testing of the chromatographic system. The vials should be weighed so that a vial to be used can be checked to ensure that solvent loss is not extreme. The test solution should not be refrigerated, because this may cause some components to precipitate. Although a few components may degrade slightly over time, this is of little consequence. The standards are to be used for checking retention time shifts, resolution changes, and peak tailing, not for quantitative comparisons. The test solutions should be remade periodically, as needed, although with care, an initial group of vials should last at least 2 years.

2. Sample Injection

Inject 0.2 μL of a test solution into the injection port and start the oven temperature program and data system. Leave the syringe needle in the injection port for 10 sec before withdrawing it. Identify the components based on their elution order and retention times, as shown in Tables I and II. Figures 1 and 2 show the chromatograms of the two standard mixtures.

A test solution should be analyzed at least once a month, and whenever the retention times need to be checked, for example, after changing columns or resetting the head pressure.

E. Samples

1. Sample Preparation

In most cases, these samples can be injected "neat" ("as received" or without dilution) into the chromatograph. Viscous, tarry, or solid samples must be diluted or extracted so that they can be injected with the syringe. Dichloromethane readily dissolves heavy distillates and is never needed in amounts greater than the sample itself to produce a suitable solution. Extraction or solution in pentane may also be suitable. The recorder attenuation should be adjusted for the expected extent of dilution.

2. Sample Injection

Inject 0.2 μL of the sample into the injection port and start the oven temperature program and data system. Leave the syringe needle in the injection port 10 sec before withdrawing it.

Note: A smoky vapor that may be visible when the needle is withdrawn from the injection port should be removed by a ventilation snorkel.

Allow the chromatograph to run until the temperature programs appropriate for each sample type (as discussed in Section V.C.8) are complete. This varies from 100 min for naphtha samples to about 120-130 min for other sample types. Narrower distillate cuts may require less time. There is no substitute for building experience with a large and diverse group of samples

3. Interpretation of Chromatograms

Figure 3, a chromatogram of a typical SRC-I process naphtha, shows that 20 peaks have been identified; the numbers correspond to the list in Table III. Peaks were identified by using gas chromatography/mass spectrometry (GC/MS). Hydrotreated naphthas are typically similar to nonhydrotreated naphthas, except that the hydroxy-aromatics may be greatly diminished or completely removed, and species such as octahydroindenes, dihydroindenes, decalins, and tetralin are more common and more concentrated.

Figure 4 is an SRC-I process solvent distillate (350-850°F, corrected to atmospheric pressure). The distillation cut points may change with process definition and the overall look of the chromatogram may change somewhat as the coal feed or process conditions are changed. However, the major peaks, shown in Table IV, can be expected to be present in all samples of this type (not hydrotreated). Figure 5 is an SRC-I and hydrotreater unit composite middle distillate. The presence of many isomeric partially hydrogenated species increases the complexity of the sample. Table V lists the components identified.

Figures 6 and 7 are chromatograms of an SRC-I process solvent heavy distillate (650-850°F) and a hydrotreated heavy distillate, respectively. These samples are extremely complex. The SRC-I heavy distillate starts in the phenanthrene region. Fluoranthene and pyrene are major components, and heavier aromatics such as methylpyrenes, chrysene, and long-chain alkanes are typical, along with alkylphenanthrenes and phenylnaphthalenes. Hydrotreated heavy distillates and composite samples containing them (see Figure 7) are even more complex. Other than pyrene and the methylpyrenes, which appear to resist hydrogenation, most other peaks are unknowns or mixtures of unknowns with typical molecular weights of 200-280. Although structures can be suggested for many of the components, evidence is scanty. A series of higher molecular weight alkanes (up to about C_{35}) is also readily visible, especially at the end of this chromatogram. Such complex chromatograms can be used for comparison, but identification beyond a very limited extent will require new fundamental investigations.

The hump of nonresolved components obvious in Figure 7 is present in most samples to some degree. Integration is done to a baseline, which extends in most cases from the beginning to the end of the chromatogram. This can lead to substantial areas assigned to small peaks on the hump. Such data must be used with care. Narrow distillate cuts are also very likely to contain nonresolved humps in the chromatograms.

Full-range distillates, especially those from the hydrotreatment process, are extremely complex (see Figure 8) and few species dominate the sample. Table VI lists some typical components. Many chromatographic peaks contain two or more components, as shown by mass spectrometry.

Reproducible assignment of peaks without mass spectrometry or confirmation of retention times on two capillary columns of different polarities depends on being able to match similar chromatographic "fingerprints" where mass spectral evidence (at a minimum) has been used to "identify" components. Then, the peaks may be "identified" by retention time. There are many ways to do this, some of which have been discussed by Lee et al. (7). Although a system of retention indices (8) has been demonstrated to provide some advantages, matrix-specific shifts in the assigned values have been noted (3, 7). We found that relative retention times vs. phenanthrene provided sufficient correction and precision to reproducibly assign peaks in most samples. The effects of matrix were less apparent. In a series of similar samples, for which this method is most appropriate, no problems of this type should occur. However, because naphthas and heavy distillates were not studied, care should be exercised in assigning their peaks.

Retention index calculations require an external computer and appropriate programs. The Varian CDS 401 data system can calculate relative retention times, but does not use them to assign peaks. It also only calculates them to two significant figures, which is insufficient to distinguish many closely eluting components. This data system does allow for correction of raw retention times by using a system of reference peaks. This has been used successfully to assign identities to about 80 peaks in a series of samples that produce chromatograms similar to Figure 8.

VI. CALCULATIONS (QUANTITATION)

The measurement of chromatographic peak areas and use of these data to document the composition of coal liquids and compare one sample to another add an important extra dimension to qualitative comparisons. For the most part, apparently, the same components are formed even when different coal feedstocks or process conditions are used. However, the relative amounts of species vary considerably. Therefore, to use these detailed chromatograms to understand and optimize the liquefaction process, quantitative data should be used. Raw area percentages can be compared from one sample to another. These values will not give an accurate measure of the relative amounts of all components because of different FID responses and injection discrimination between components of widely varying boiling points (7, 9), but such problems can be considered as constants in the analyses.

Even more information can be gained by using normalized area percentages. This requires dissolving weighed samples (100 mg) in n-pentane and the presence of an internal standard. In the work accomplished to date, 4-octyne has been used as the internal standard (available from Aldrich Chemical Co.); it was made up in the pentane at the 0.20 wt % level before the pentane was used to make sample solutions. Generally, all components soluble in pentane can be gas-chromatographed under the conditions used, and, at the levels found in these samples, all volatile species are soluble in pentane. 4-Octyne elutes in one of the few gaps in the complex chromatogram of a hydrotreated coal liquid full distillate (at about 9.5 min under the conditions specified). The weight of 4-octyne to sample can then be calculated, and with the solvent peak inhibited, the data system can be used to calculate all components as percentages relative to the calculated percentage of 4-octyne (1.13 mg in 0.9 mL of pentane). This method accounts for nonvolatile components. The presence of nonvolatile components in a sample would produce a larger area percentage for a given peak size, because the nonvolatile material would not be included in the area normalization using the total area of the chromatogram. With the internal standard, a given peak size will always be assigned the same weight percentage, regardless of the area of the other peaks.

Selected components from throughout a sample similar to one that produced the chromatogram shown in Figure 8 were studied for precision. Fourteen peaks were studied after triplicate analyses. The average peak areas ranged from 0.07 to 2.5% area and the standard deviations ranged from 0.6 to 7.8% (relative). The average relative standard deviation was 4.2%. In general, early eluting components were less precise. Components chosen for study included well-resolved peaks and some that were fused with neighboring peaks to the extent of about 50% valley. Weight percent data precision relative to an internal standard should be similar. This method cannot readily be used for naphtha samples, because n-pentane is a component of these samples and the presence of many low-boiling components means that any solvent used would obscure sample components. Also, see the following section.

VII. PRECISION AND ACCURACY

When a 1.0-μL syringe with a Chaney adapter was used, the average mean standard deviation of the area percentages of selected components in a process solvent was 1.27% (analyzed in triplicate using a 15-m column under conditions similar to those suggested in this method). Without the Chaney adapter, the value was 1.78% (1). Recent work with very complex hydrotreated coal liquids, using the method discussed here, produced an average area percent precision of 4.2% (see Section VI).

The precision may be far worse for components present at low levels, particularly if they are poorly resolved. As discussed below, specialized integration for poorly resolved peaks of interest may be required to provide optimal precision.

Quantitative accuracy is discussed in section VI. The analysis of an SRC-I process solvent distillate (350-850°F, corrected to atmospheric pressure) illustrates what can be accomplished. The sample was analyzed without dilution. Table VII shows the results for selected components, all of which were present at 1.0 or more area percentages (15 peaks). Two components had poor precision due to shoulders. After custom integration in the regions around those peaks, one fell to less than 1.0% and the other fell to just over 1.0%, but was unavailable as a standard. Note that only components present at levels above 1.0% were considered because that was a constraint agreed to during the methods development, even though it eliminates whole classes of compounds. Two other components (biphenyl and diphenyl ether) were disregarded because they were caused by Dowtherm heat transfer fluid contamination. Two other components were also unavailable as standards. The remaining ten species were analyzed for area percent precision. Retention time precision was also analyzed, although as discussed in Section V.E relative retention times of some type should be used to correct for slight changes. These data are shown in Table VII. The coal liquid was also diluted 1:1 in toluene as if it were a viscous sample, to check for possible solvent effects. Table VIII contains these data. The solvent (when not counted in the area integration) does not affect the area percentages. For most of these components, precision was excellent, better in fact than in the nondiluted coal liquid.

High-purity standards of the ten compounds were then mixed in toluene to levels similar to the coal liquid. Table IX gives the results. Area percentages are similar to weight percentages in all cases, except perhaps dibenzofuran, for which the heteroatom would be expected to cause a reduced FID response. It appears from these results that area percentages closely approximate weight percentages without response factors, at least for the component range from naphthalene to pyrene.

Finally, a 1:1 solution of the diluted coal liquid and the standard blend was analyzed. The expected area percentages would be the average of those listed in Tables VIII and IX. Results were similar to those expected (Table X). The technique used here is similar to standard addition techniques. Such techniques are not generally applicable to such complex samples, where there are many components of interest. Readers should consult textbooks of quantitative analysis for more information if interested.

VIII. QUALITY ASSURANCE

The gas chromatograph and integrator should be maintained according to the manufacturer's instructions. During constant use, the septum should be replaced about every 3-5 days, and the injection port liner should be checked weekly. A clean liner with new packing (if the packed type is used) should be installed when the liner or its packing is dirty. More frequent injections may require more frequent septum or liner changes. Analyzing many samples containing a large percentage of nonvolatile material may also necessitate more frequent liner changes. Be alert to septum leaks, head pressure changes, retention time changes, peak size changes, or changes in chromatographic behavior. Although it often does not appear necessary, the injection port should be cooled to perform this maintenance to prevent possible damage to the beginning of the column. Without cooling, air will enter the open port, become heated, and then enters the column, where the hot oxygen might react with the column.

Columns used for work similar to that described in this method have been in use continually for over 2 years and do not appear to be degrading. However, the column should be replaced if a loss of resolution occurs that cannot be rectified, or if tailing of polar compound peaks is determined to be due to the column. The latter problem may lie elsewhere. If tailing is due to the column, this can sometimes be corrected by removing a small piece of the inlet end of the column or by using a silylating reagent.

IX. PRINCIPLE

Samples are analyzed by injecting them (undiluted or diluted, as appropriate) into a gas chromatographic capillary column. The primary separation mechanism depends on boiling point differences, but relative solubilities in the column stationary phase are also involved. Essentially, a very high efficiency distillation occurs, and components are detected as they leave the column. The flame ionization detector responds to mass and is almost universal. The signal generated is proportional to the concentration of ions generated in the detector flame. These ions allow a current to pass between the electrodes in the detector. A voltage proportional to the current is measured and plotted. Areas under the plotted chromatographic peaks are proportional to the concentrations of components in the sample. In this work, typical samples produce hundreds of peaks; the most complex samples produce over 500 peaks. Because these peaks may not represent individual components and response may differ, area percentages must be used carefully.

X. FUTURE WORK

Development of this method is incomplete. For this reason, and because a specific requirement for this method in the demonstration plant analytical laboratory has not been identified, this method is written in general terms. More model compounds should be analyzed, to assign specific isomers and add generally to the list of identifiable peaks. Hydroaromatic species should be studied more thoroughly, particularly to better define heavy distillates from the hydrotreater. Additional work is also required to identify and assign more heteroatomic components. Element-selective detectors (nitrogen and sulfur) should be used side by side with the FID to provide other detailed and meaningful chromatograms. In addition, mass balance, especially regarding polar functionalities present at low levels (amines and sulfur species), is needed. Furthermore, it has been documented that response factors are needed for accurate quantitation, because of both injection port discrimination and true differences in responses, particularly for heteroatomic species. If accurate quantitation is required, as in mass balance studies, more data will be needed.

Finally, any data base can be subjected to pattern recognition analysis. When a sufficient data base is assembled and analyzed, peak data from these complex chromatograms may be found to correlate with feed characteristics or process parameters. This will require computer capability and appropriate software for pattern recognition, but it is probably the fastest, surest way to make this work routine once a data base is collected and key variables are identified.

XI. REFERENCES

1. D. M. Parees and A. Z. Kamzelski in "SRC-I Quarterly Technical Report," October-December 1981. Pgs. 47-120. DOE/OR/03054-6. International Coal Refining Company, Allentown, PA.

2. D. W. Later, M. L. Lee, K. D. Bartle, R. C. Kong, and D. L. Vassilaros, Anal. Chem. 53 (1981) 1612-20.

3. M. L. Lee, D. L. Vassilaros, C. M. White, and M. Novotny, Anal. Chem. 51 (1979) 768-74.

4. D. M. Parees and A. Z. Kamzelski, J. Chrom. Sci. 20 (1982) 441-8.

5. C. Willey, M. Iwao, R. N. Castle, and M. L. Lee, Anal. Chem. 53 (1981) 400-7.

6. F. Merli, M. Novotny, and M. L. Lee, J. Chromatogr. 199 (1980) 371-8.

7. M. L. Lee, D. L. Vassilaros, R. C. Kong, and D. W. Later, J. Chromatogr. 252 (1982) 1-20.

8. D. M. Parees and A. Z. Kamzelski in "SRC-I Quarterly Technical Report," July-September 1982. Pgs. 295-342. DOE/OR/03054-9. International Coal Refining Co., Allentown, PA.

9. D. R. Elliot, A. Z. Kamzelski, M. L. Klusaritz, D. M. Parees, T. L. Slager, and K. C. Tewari in "SRC-I Quarterly Technical Report," January-March 1982. Pgs. 229-336. DOE/OR/03054-7. International Coal Refining Co., Allentown, PA.

10. D. M. Parees in "Draft SRC-I Quarterly Technical Report," October-December 1982. Pgs. 105-26. DOE/OR/03054-11. International Coal Refining Co., Allentown, PA.

Table I

Components Identified in Standard Mixture #1[a] (See Figure 1 for Peaks)

Peak number	Compound	Retention time (min)
1	toluene	6.71
2	phenol	16.46
3	2,3-dihydro-1H-indene (indan)	20.11
4	3-methylphenol	22.86
5	2-ethylaniline	28.63
6	naphthalene	30.63
7	3,4-dimethylphenol	31.19
8	dodecane	31.65
9	1-methylnaphthalene	39.73
10	1,2,3,4-tetrahydroquinoline	40.97
11	biphenyl	44.34
12	2,6-dimethylnaphthalene	45.96
13	1,2-dihydroacenaphthylene (acenaphthene)	51.29
14	1-naphthol	52.69
15	9H-fluorene (fluorene)	57.42
16	xanthene	61.47
17	dibenzothiophene	67.35
18	phenanthrene	69.03
19	phenanthridine	71.29
20	1-methylphenanthrene	74.98
21	nonadecane	76.60
22	pyrene	86.16
23	triphenylene	101.54
24	hexacosane	106.68
25	perylene	118.63

[a] Performed on a 60-m SE-52 capillary column. Conditions are discussed in Section V. Tailing of species such as the phenols, 2-ethylaniline, and 1-naphthol typically indicates adsorptive activity detrimental to the analysis. This problem should be minimized for best results. Xanthene is not found in actual samples.

Table II

Components Identified in Standard Mixture #2[a] (See Figure 2 for Peaks)

Peak number	Compound	Retention time (min)
1	toluene	6.68
2	2,4,6-trimethylpyridine	17.17
3	3-methylphenol	22.96
4	1,2,3,4-tetrahydronaphthalene (tetralin)	29.05
5	naphthalene	30.68
6	quinoline	34.51
7	3-methylindole	44.78
8	dibenzofuran	53.24
9	9,10-dihydroanthracene	63.01
10	9H-Carbazole	71.99

[a] Work performed on a 60-m SE-52 capillary column. Conditions are discussed in Section V. Many of these components should be watched carefully for signs of system activity, as evidenced by tailing. In particular, the pyridine and phenol often exhibit nonideal behavior. In this chromatogram, the phenol looks excellent, but the pyridine tails some, as it has on many of our experimental columns. This tailing may be caused, at least in part, by a possible impurity on the trailing edge of the peak.

Table III

Components Identified in an SRC-I Composite Naphtha (Initial Boiling Point to 400°F)[a] (See Figure 3)

Peak number	Compound	Retention time (min)
1	cyclohexane	11.38
2	heptane	14.39
3	methylcyclohexane	15.81
4	methylbenzene (toluene)	19.55
5	octane	22.75
6	ethylcyclohexane	25.26
7	ethylbenzene	27.82
8	a dimethylbenzene	28.53
9	a dimethylbenzene	30.54
10	nonane	31.56
11	propylcyclohexane	33.82
12	an ethylmethylbenzene	36.61
13	phenol and a C_3-alkylbenzene	38.79
14	2,3-dihydro-1H-indene (indan)	42.64
15	2-methylphenol	44.53
16	3- and 4-methylphenols	46.25
17	a methylindan and a C_4-alkylbenzene	46.79
18	undecane	48.10
19	a methylindan	51.68
20	1,2,3,4-tetrahydronaphthalene (tetralin)	52.57

[a] Identifications are based on GC/MS work.

Table IV

Components Identified in 350-850°F Process Solvent Distillate[a] (See Figure 4)

Peak number	Compound	Retention time (min)
1	1,2,3,4-tetrahydronaphthalene (tetralin)	29.06
2	naphthalene	30.22
3	6-methyltetralin	35.87
4	2-methylnaphthalene	37.93
5	1-methylnaphthalene	39.00
6	biphenyl	43.54
7	an ethylnaphthalene	44.44
8	diphenyl ether	45.11
9	dimethylnaphthalenes	46.11, 46.32, 46.80, 47.32
10	1,2-dihydroacenaphthylene (acenaphthene)	50.22
11	dibenzofuran	52.15
12	9H-fluorene	56.17
13	benz-indans or isomers	56.90, 57.00, 57.25, etc.
14	dibenzothiophene	65.61
15	phenanthrene	67.36
16	9H-carbazole	70.14
17	methylphenanthrenes	73.19, 73.48, 74.31, 74.70
18	fluoranthene	81.35
19	pyrene	83.79
20	methylfluoranthenes/methylpyrenes	88.15, 88.94, 89.25, etc.

[a] Note that the large amount of biphenyl and the diphenyl ether present in this sample are due to contamination from Dowtherm transfer fluid.

Table V

Some Components Identified in a Composite Middle Distillate
(SRC-I and Hydrotreater Processes, 450-650°F)
(See Figure 5)

Peak number	Compound	Retention time (min)
1	3- and 4-methylphenols	22.59
2	1,2,3,4-tetrahydronaphthalene (tetralin)	28.62
3	an ethylphenol	29.09
4	naphthalene	30.16
5	an ethylmethylphenol	35.41
6	6-methyltetralin	35.84
7	2-methylnaphthalene	37.87
8	1-methylnaphthalene	38.90
9	a dimethyltetralin	39.43
10	tetradecane	44.37
11	a dimethylnaphthalene	44.73
12	a dimethylnaphthalene	45.10
13	a dimethylnaphthalene	46.00
14	an ethylmethylnaphthalene	50.10
15	a benzo-2,3-dihydro-1H-indene (benzindan)	56.81
16	a methyl-9H-fluorene	63.11
17	phenanthrene	67.17

Table VI

Components Identified in a Total Distillate of a Hydrotreated Liquid Product (See Figure 8)[a]

Peak number	Compound	Retention time (min)
1	cyclohexane and benzene	4.56
2	methylcyclohexane	5.57
3	toluene	6.63
4	ethylcyclohexane	8.81
5	a dimethylbenzene	10.35
6	propylcyclohexane	13.38
7	phenol and an ethylmethylbenzene	16.40
8	2,3-dihydro-1H-indene (indan)	20.06
9	trans-decalin	21.30
10	a methyldecalin	25.19
11	a chromatographic artifact and a dimethylindan	27.28
12	1,2,3,4-tetrahydronaphthalene (tetralin)	28.94
13	naphthalene	30.50
14	2-methyltetralin	32.79
15	6-methyltetralin	36.33
16	2-methylnaphthalene and 5-methyltetralin	38.32
17	1,1'-bicyclohexyl	38.95
18	2,6- or 2,7-dimethyltetralin	40.06
19	2-methyl-1,1'-bicyclohexyl	42.56
20	an ethyltetralin	42.86
21	1,1'-methylenebiscyclohexane or a methyl-1,1'-bicyclohexyl and (methylcyclohexyl)cyclohexene	43.83
22	an ethylnaphthalene and a dimethyltetralin	45.16
23	a dimethylnaphthalene and a methylcyclohexylbenzene	46.87
24	a butyldecalin	47.62
25	a methylhexahydroacenaphthylene	47.90
26	1,2-dihydro-acenaphthylene and a tetradecahydrophenanthrene	51.17
27	a butyltetralin	55.67
28	a methylhexahydroacenaphthylene or a tetrahydrobenzindan or 2,3-dihydro-1H-phenalene	56.47
29	9H-fluorene	57.24
30	see #28	58.06

Table VI (continued)

Peak number	Compound	Retention time (min)
31	see #28 and a methyltetrahydrobenzindan or an ethylhexahydroacenaphthylene	58.39
32	a methylbenzindan and a methylfluorene	64.56
33	a methyltetrahydrobenzindan or isomer, a methylbenzindan or isomer and an ethyltetrahydrobenzindan or methyloctahydrophenanthrene	65.49
34	tetrahydrophenanthrene	67.42
35	phenanthrene	68.70
36	a chromatographic artifact	68.95
37	a methyltetrahydrophenanthrene or isomer and an ethyltetrahydrophenanthrene or isomer	73.38
38	artifact	74.57
39	a methylphenanthrene	74.94
40	a methylphenanthrene	75.22
41	an ethylphenanthrene and a C_3-dihydrophenanthrene	80.59
42	pyrene	85.92
43	a methylpyrene	91.68
44	a methylphenylnaphthylene or a methyldihydropyrene	92.19

[a] As shown in the table, other isomeric structures are possible in many cases (other possibilities besides those listed may also exist in some cases). The chromatographic artifacts have existed for some time on this instrument, but could not be traced to a specific cause and eliminated.

Table VII

Area Percentages and Precision Data for Components Present in an SRC-I Process Distillate (350-850°F) at a Level of 1.0% and Greater[a] (See Figure 4)

Compound	Retention time	Area percentage
naphthalene	30.18 ± 0.06 (0.2%)	1.99 ± 0.03
2-methylnaphthalene	37.90 ± 0.07 (0.2%)	6.92 ± 0.09
1-methylnaphthalene	38.89 ± 0.11 (0.3%)	1.90 ± 0.02
2-ethylnaphthalene	44.40 ± 0.07 (0.2%)	1.37 ± 0.01
1,2-dihydroacenaphthylene	50.17 ± 0.08 (0.2%)	2.38 ± 0.03
dibenzofuran	52.11 ± 0.08 (0.2%)	2.06 ± 0.02
9H-fluorene	56.12 ± 0.08 (0.1%)	1.86 ± 0.02
phenanthrene	67.31 ± 0.07 (0.1%)	5.37 ± 0.06
fluoranthene	81.30 ± 0.08 (0.1%)	1.40 ± 0.04
pyrene	83.74 ± 0.08 (0.1%)	1.11 ± 0.04

[a] 60-m DB-5 column. Other components present at 1.0% or greater included 4-ethyl-2-methylphenol, 6-methyltetralin, a benzindan (probable), biphenyl and diphenyl ether.

Table VIII

Area Percentages and Precision Data for Components Present in an SRC-I Process Distillate (350-850°F) Diluted in Toluene 1:1[a]

Compound	Area percentage
naphthalene	1.95 ± 0.01
2-methylnaphthalene	6.84 ± 0.02
1-methylnaphthalene	1.88 ± 0.04
2-ethylnaphthalene	1.36 ± 0.002
1,2-dihydroacenaphthylene	2.36 ± 0.004
dibenzofuran	2.01 ± 0.01
9H-fluorene	1.83 ± 0.005
phenanthrene	5.29 ± 0.02
fluoranthene	1.41 ± 0.003
pyrene	1.12 ± 0.003

[a] Toluene area disregarded.

Table IX

Standard Blend of Components Present in a Process Solvent

Compound	Weight percentage[a]	Area percentage[b]	Percent difference[c]
naphthalene	7.52	7.06	6.1
2-methylnaphthalene	26.36	25.45	3.4
1-methylnaphthalene	7.40	6.93	6.4
2-ethylnaphthalene	5.63	5.16	8.3
1,2-dihydroacenaphthylene	8.74	8.81	-0.8
dibenzofuran	7.84	6.59	16
9H-fluorene	7.01	7.11	-1.4
phenanthrene	20.12	20.36	-1.2
fluoranthene	5.44	5.73	-5.3
pyrene	4.32	4.39	-1.6

[a] Toluene weight disregarded.

[b] Toluene area disregarded. Because of the small number of components in this solution, the area percentages are much larger than in the coal liquid.

[c] $$\text{Percent difference} = \frac{100 \times (\text{weight \%} - \text{area \%})}{\text{weight \%}}$$

The actual weight percentages used were similar to the area percentages listed in Table VII.

Table X

Mixture of Coal Liquid and Standard Blend
Area Percent Data for Selected Compounds[a]

Compound	1 area percentage diluted coal liquid	2 Area percentage standard blend	3 Average of columns 1 and 2	4 Area percentage of 1:1 solution
naphthalene	1.95	7.06	4.50	4.71
2-methylnaphthalene	6.84	25.45	16.15	16.33
1-methylnaphthalene	1.88	6.93	4.40	4.43
2-ethylnaphthalene	1.36	5.16	3.26	3.22
1,2-dihydroacenaphthylene	2.36	8.81	5.58	5.45
dibenzofuran	2.01	6.59	4.30	4.66
9H-fluorene	1.83	7.11	4.47	4.53
phenanthrene	5.29	20.36	12.83	12.61
fluoranthene	1.41	5.73	3.57	3.50
pyrene	1.12	4.39	2.75	2.69

[a] Toluene solvent area disregarded in all cases. It should be noted that the peaks in the combined solution are twice as large as those in the original coal liquid. The area percentages in Column 4 are more than twice those in Column 1 because all other components were not similarly "spiked".

Figure 1
Standard Mixture #1
60-M SE-52 Column
Starting Temperature = 50°C
See Table I

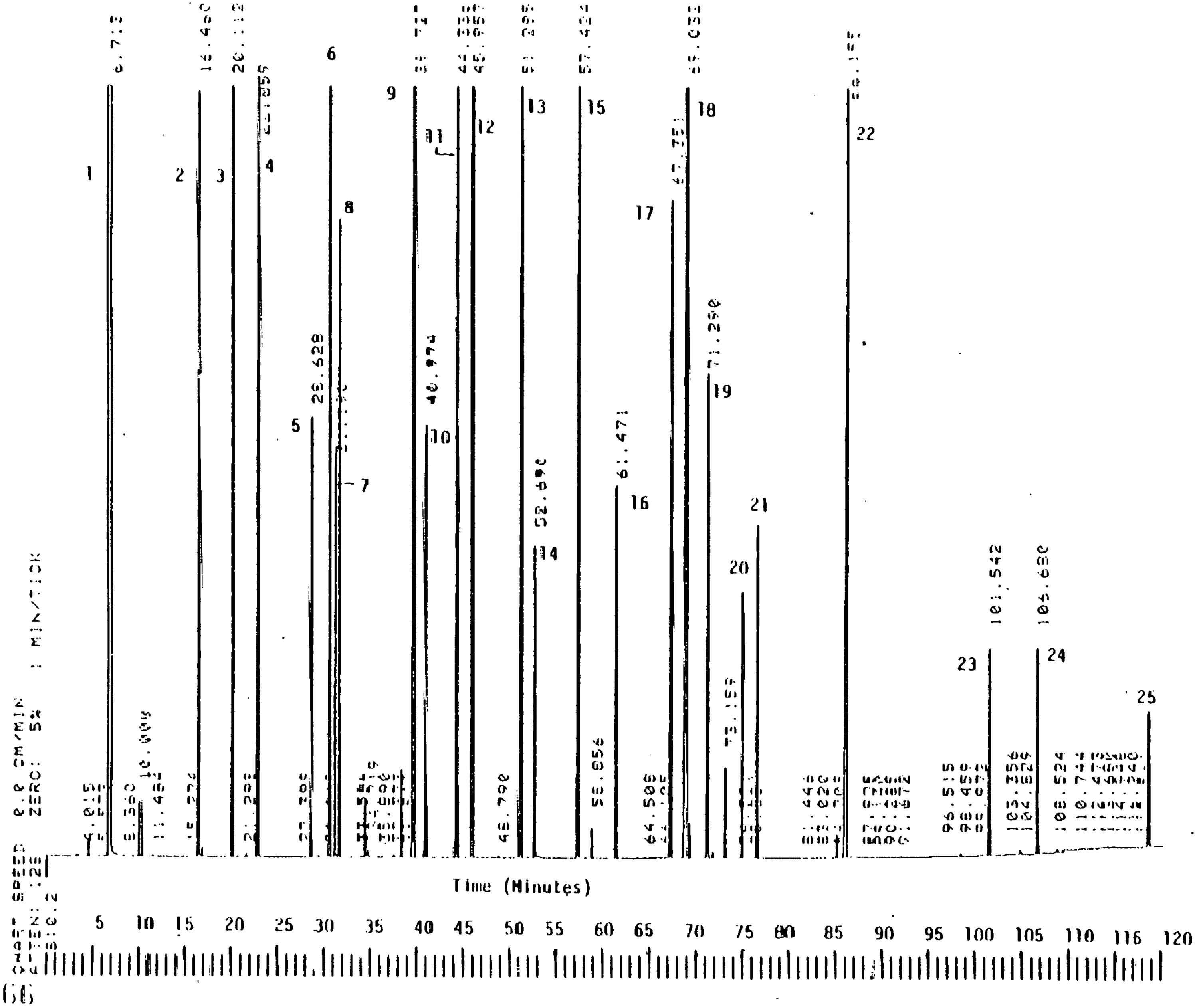


Figure 2

Standard Mixture #2
60-M SE-52 Column
Starting Temperature = 50°C
See Table 2

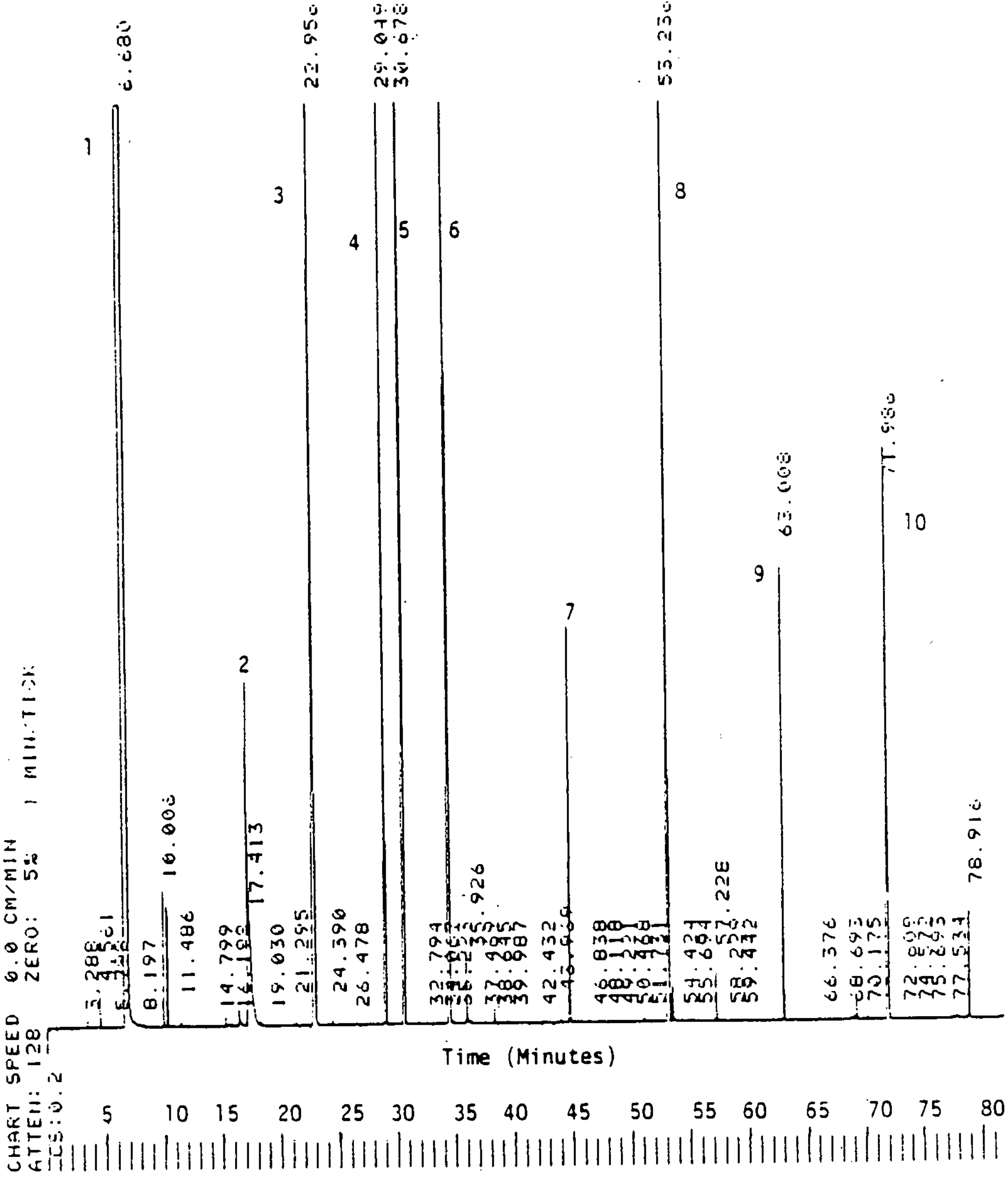
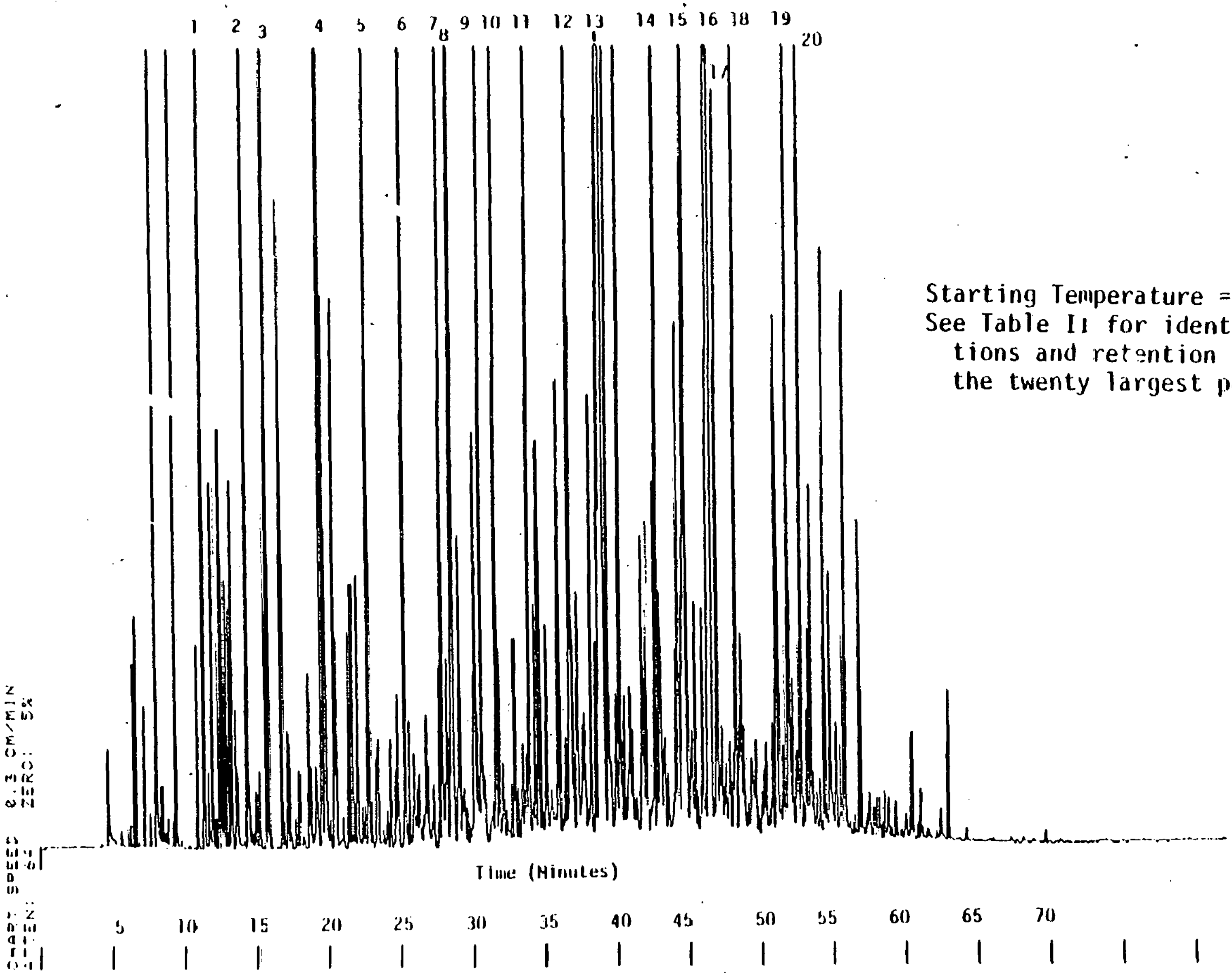


Figure 3

An SRC-I Composite Naphtha
(Initial Boiling Point to
400°F)
60-M DB-5 Column



Starting Temperature = 0°C
See Table II for identifica-
tions and retention times of
the twenty largest peaks

Figure 4

350-850°F Process Solvent Distillate
60-M DB-5 Column
The Split Ratio was about 75:1
Starting Temperature = 50°C
See Table IV For Compound Identifications

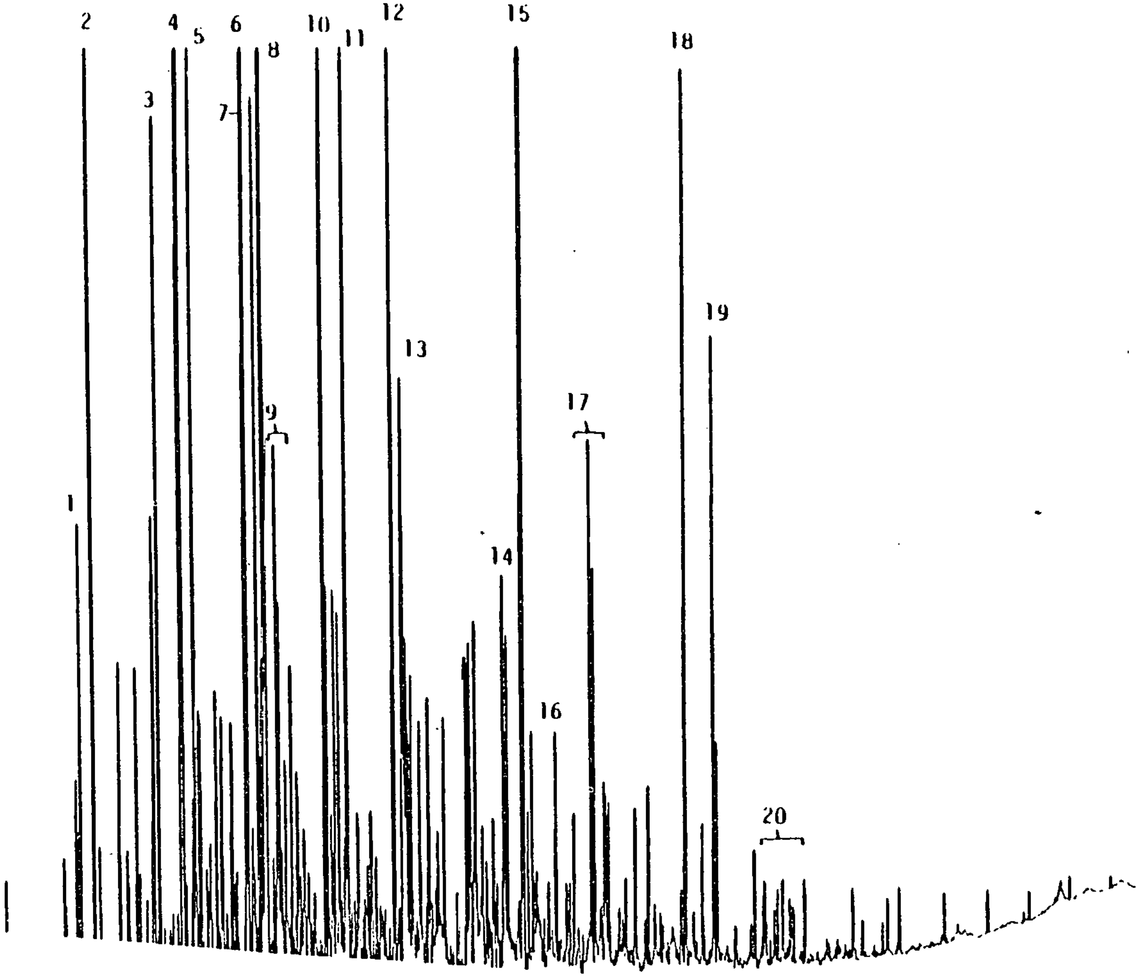


Figure 5

SRC-I and Hydrotreater Processes
Composite Middle Distillate (450-650°F)
60-M DB-5 Column
Starting Temperature = 50°C
See Table V

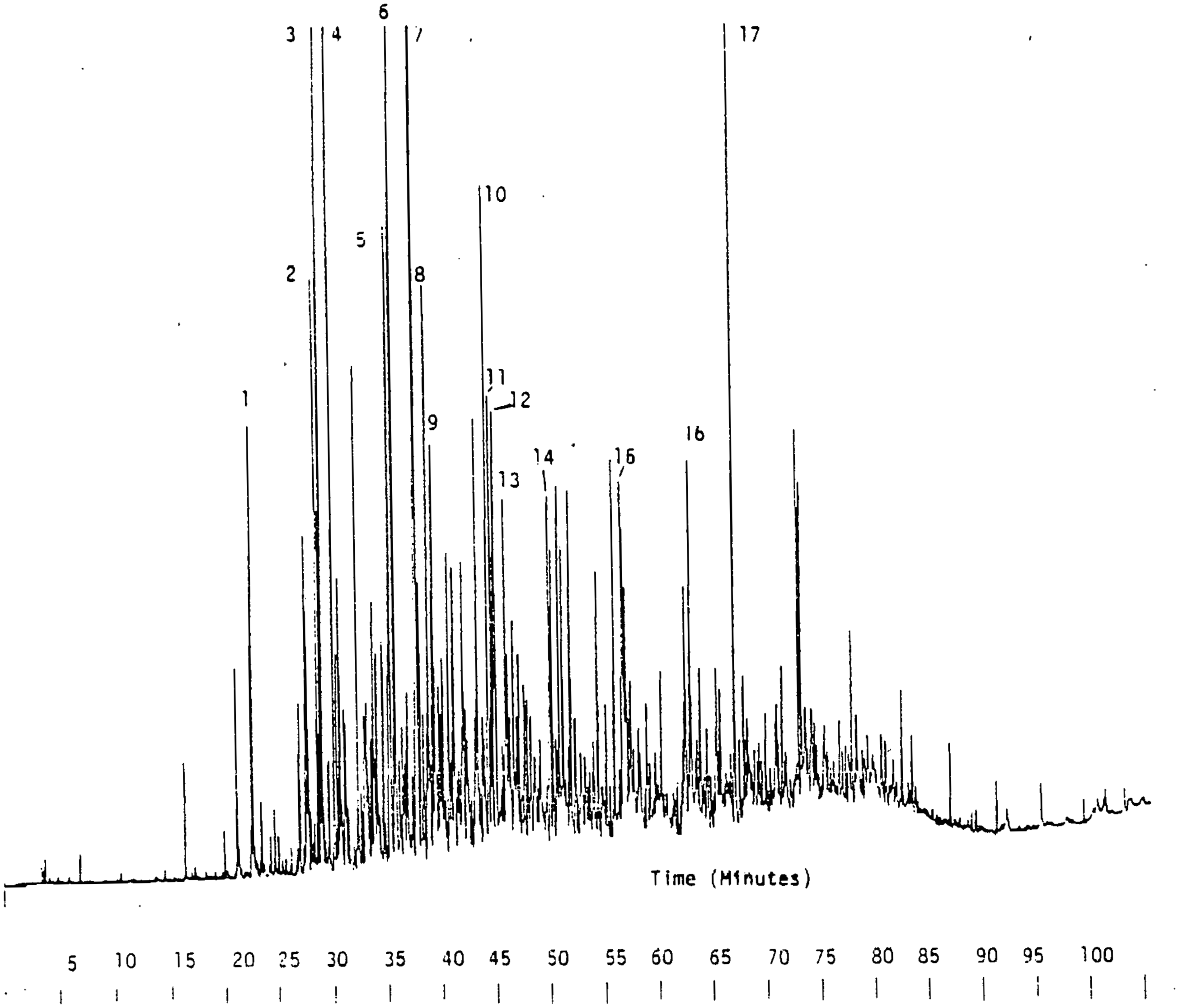


Figure 6

SRC-I Heavy Distillate
60-M DB-5 Column
Sample Diluted for Injection
Note that the beginning of the chromatogram
is not shown. No components elute in that
region.
Starting temperature = 100°C

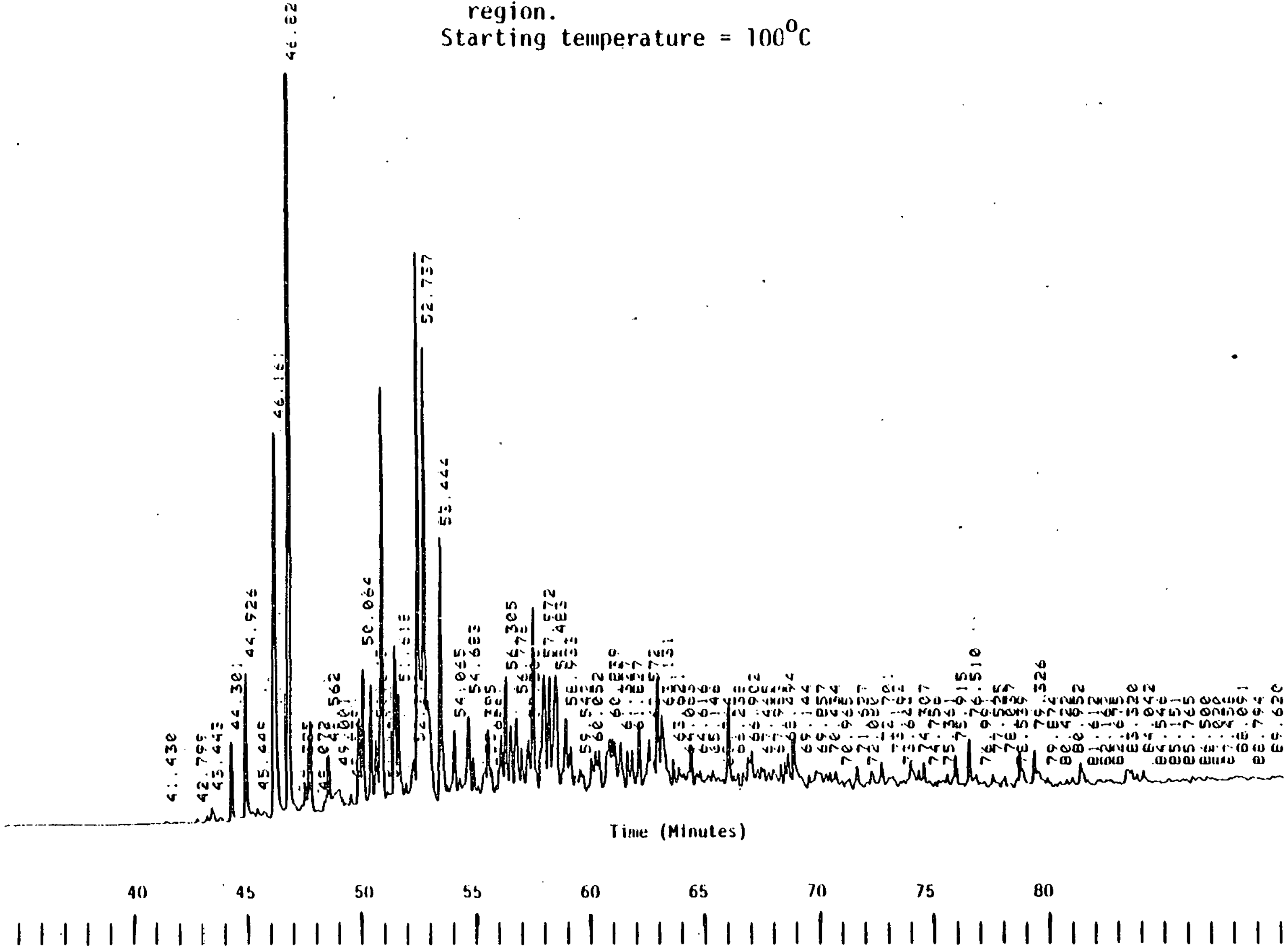


Figure 7

SRC-I and Hydrotreater Unit Composite Heavy Distillate
60-M DB-5 Column
Sample Diluted for Injection
Note that the beginning of the Chromatogram is not shown.
No components at significant concentration
Levels elute in that region
Starting temperature = 100°C

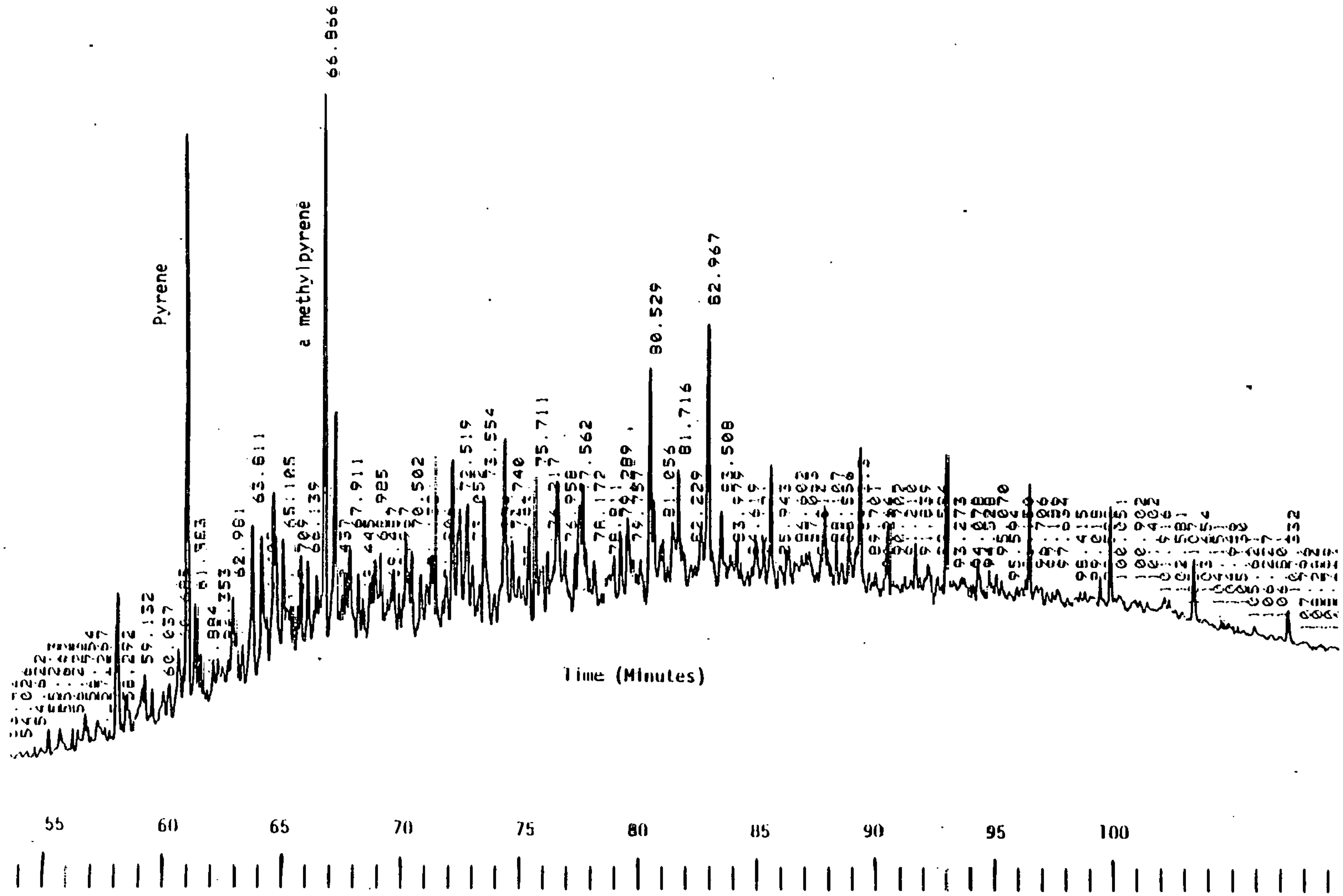
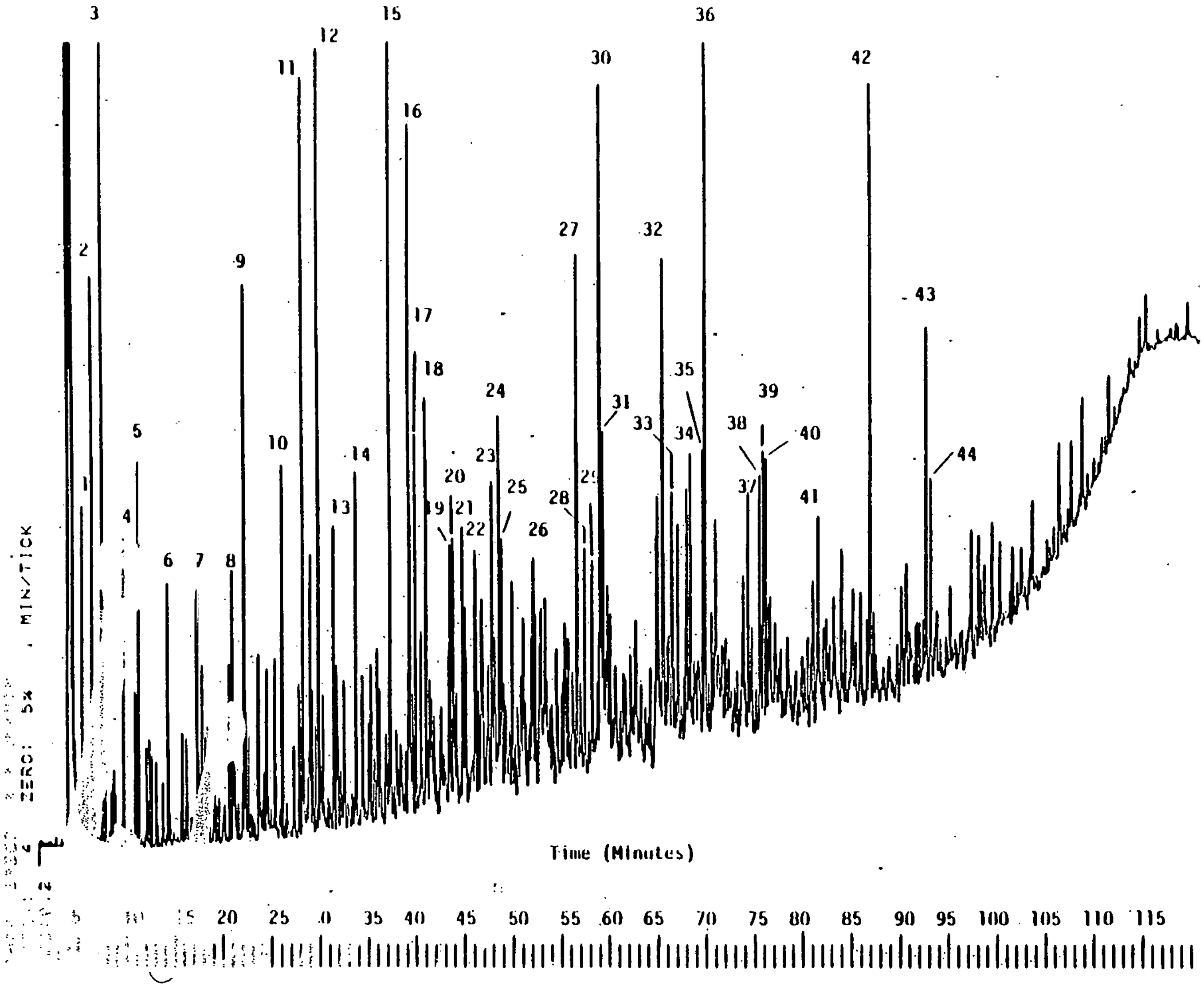


Figure 8

Hydrotreated Liquid Product
(Total Distillate)
60-M SE-52 Column
Starting Temperature = 50°C



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SOLVENT QUALITY ACTIVITY TEST LABORATORY PROCEDURES

Determination of Solvent or Coal Quality by Microautoclave
(ICRC Analytical Procedure)

I. SCOPE — This method applies to raw coal and hydogenated recycle solvent for SRC conversion.

II. PRINCIPLE: The conversion potential of raw coal or hydrogenated solvent is determined by using a microautoclave under specified conditions.

III. SAFETY: SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hand and clothing. For specific handling precautions of SRC liquids, see the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet located in the front section of the manual.

Wear protective equipment when working near tempertures of 750°F.

Tetrahydrofuran has a permissible exposure limit 200 ppm (590 mg/m^3) and must be handled in a well ventilated area.

IV. PROCEDURE:

A. Weigh (to 0.1 mg) 5 g of a standard coal of known moisture and ash content.

B. Weigh 10 g of the solvent to be tested into a previously tared autoclave containing a stainless-steel ball bearing.[a]

C. Transfer coal to autoclave and then seal autoclave.

D. Attach one end of type-K thermocouple wire to thermowell of autoclave, and the other end of the wire to a potentiometer.

E. Attach autoclave to drive mechanism.

F. Turn on the oil to drive mechanism; check operation.

G. Turn on autoclave; lower autoclave into preheated fluidized sandbath.[b]

H. By adjusting sandbath, control temperature of autoclave so that 750 ± 5°F is attained within 90 sec.

I. Control temperature at 750 ± 5°F for 30 min.

J. Remove autoclave from sandbath; immerse immediately in reservoir to cold water to stop reaction and cool microautoclave to room temperature as quickly as possible.

K. Remove contents of autoclave by washing with tetrahydrofuran (THF) (~600 mL) until THF is clear.

L. Stir sample and THF washings for 30 min. to allow maximum mixing with THF.

M. Weigh filter paper, record weight, and place paper in steam-jacketed Buchner funnel.

N. Pour sample into the steam-jacketed Buchner funnel under vacuum and wash with THF until THF washes clear.

O. Transfer filter paper to heated vacuum desiccator and dry for 1 hr at 110°C.

P. Allow sample to cool in desiccator for 1 hr.

Q. Remove filter paper from desiccator, weigh to 0.1 mg and record weight.

R. Calculate conversion by using the formula in the calculations section of this procedure.

V. REAGENTS:

Tetrahydrofuran
Dessicant for desiccator
Standard coal of known moisture and ash
1-Methylnaphthalene
1,2,3,4-Tetrahydronaphthalene (tetralin)

VI. EQUIPMENT:

Microautoclave
Driving mechanism for microautoclave adjusted to 1,000 rpm and a 1.5-in. stroke
Type K thermocouple wire
Potentiometer
Fluidized sandbath (Tecam fluidized bath SBL-2)
Nitrogen source
Heated vacuum desiccator
Desiccator
Steam-jacketed Buchner funnel
1,000-mL side-arm Erlenmyer flask
Rubber vacuum tubing
3/8-in.-diameter stainless steel ball bearing
11-cm quantitative filter paper

VII. CALCULATIONS:

A. Coal sample size x percent H_2O in coal sample = grams of H_2O

B. Coal sample size x percent ash in coal sample = grams of ash

C. Filter paper weight + insolubles - filter paper weight = insolubles

D. Original sample weight - grams of H_2O - grams of ash = grams of moisture - and ash-free coal

E. Percent conversion =

$$\frac{\text{grams of moisture-free coal - insolubles}}{\text{grams of moisture- and ash-free coal in std.}} \times 100$$

VIII. REMARKS: The procedure outlined above is for use in a long run on the autoclave. A short run consists of using an 8:1 solvent-to-coal ratio. The weight of solvent for a short run is 12 g, and the weight of coal is 1.5 g weighted to 0.1 mg. Raw coals may be tested using this procedures if percent moisture and ash are known. Conversions using this procedure are compared to a curve using concentrations of 0, 5, 10, 25, and 50% tetralin in 1-methylnaphthalene and Indiana V coal standard.

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[a] Stainless steel ball bearings (3/8-in. diameter) are placed in each of the two autoclaves for mixing. If ball bearings are not placed in the autoclave, mixing will not be sufficient; as a result, the conversion may be lower than normal.

[b] Temperatures for the sandbath before the autoclaves are introduced may vary; however, under normal conditions, this temperature should be between 810 and 830°F. Such a temperature range should allow for heat transfer from the sandbath to the autoclave and give the necessary 750 ± 5°F within 90 sec.

Sequential Solvent Extraction
(ICRC Analytical Procedure)

SCOPE: This procedure is designed to separate a total product sample into the following fractions:

- oils: pentane soluble
- asphaltenes: pentane insoluble and benzene insoluble
- preasphaltenes: pyridine soluble and benzene insoluble
- residue: pyridine insoluble

This technique is carried out at room temperature under nitrogen, using high-quality solvent [pesticide or high-performance liquid chromatography (HPLC) grade]. The sample can be liquid, solid, or a mixture thereof, with less than 1% material boiling below 300°F. The reproducibility of the solvent-separation procedure on a total product liquid is exemplified by the following data:

	Mean (%)	Standard deviation[a] (%)
Oils	63.3	1.06
Asphaltenes	8.7	0.94
Preasphaltenes	9.7	1.23
Residue	18.2	0.31

---

[a] The result of five trials.

EQUIPMENT AND SOLVENTS REQUIRED:

Branson Model 350 Sonicator with 0.5-in. horn, or Heat Systems Model W375 Ultrasonic
Millipore 142-mm pressure filter with 1,500-mL capacity; No.'s XX42-142.35 and YY-30-142-35 with 142-mm filter, 5-mm LSWP 142-50
Glass, stainless-steel, or Teflon tubing can be used for solvent-transfer lines
Four round-bottomed distilling flasks (1 L)
Rotary evaporator RE 120, WWR No. 27582-406
Vacuum pump and trap
Nitrogen gas (0-20 psi adjustable), pressure-filter feed
Nitrogen gas (0-20 psi adjustable), rotovapor feed
Nitrogen liquid (1-2 L), freeze sample (Dewar)
Solvents: n-pentane, benzene, pyridine, methanol, or methylene chloride. Grade of solvent depends upon ultimate use of sample subfractions. Pesticide, distilled in glass, or HPLC grade are acceptable.
Fume hood, 150-200-cfm air-exchange rate
Cooling water or heat exchanger for rotary evaporator condenser
Balance to read weights to ±0.005 g or better with maximum load of 500 g
Glass Millipore, 47 mm, Model No. xx15047-00 with 5-mm No. LSWG-04700

SAFETY FEATURES:

Solvents must be used only under the fume hood. Workers must wear protective gloves and overalls for laboratory work. Hands can be mildly scrubbed with waterless hand cleaner, followed by a warm water wash. All normal safety precautions must be observed during the entire operation.

SAMPLE HANDLING FOR TOTAL PRODUCT LIQUIDS:

The sample selected for this procedure must represent the process unit output. Great care must be used to isolate about 5 g of gross product. Hot samples may be obtained in 8-oz glass jars.

The sample must be kept free of air (oxygen), heat, and light. Samples not ready for separation should be stored at 4°C under a blanket of nitrogen. Samples may be warmed to 65°C in the jars in an oven for 15 min and then sonicated for 15 min to induce good mixing just before a 5-g sample is procured for actual work-up.

PROCEDURE:

A. Prepare the laboratory equipment in the following order:

1. Weigh the jar containing the sample and the jar lid, record the weight, and sonicate the sample for 15 min. Mix the sample with a spatula and reweigh. Record any loss in weight as the weight of the light ends. Clean off spatula and sonicator horn by placing a tared 250-mL beaker with 200 mL of CH_2Cl_2 under the sonicator for 6 min. Evaporate CH_2Cl_2 by placing the beaker on a hot plate (at setting 2 or 3) for 1 hr. Record differences in beaker weight and subtract from weight of light ends.

2. Put Millipore filter in place after weighing the dry filter element. Ensure that all Teflon o-rings (and viton gasket) fit well, without leaks (test with n-pentane under 10 psi). No silicone gaskets or grease should be used in filter apparatus!

3. Prepare rotary evaporator bath temperature at 55-60°C for n-pentane; nitrogen flow rate should cause just a 0.25-0.5-in. dimple in the liquid in a 1-L flask.

4. Temperature of cooling liquid for rotary evaporator condenser should be less than 10°C.

B. Tare a 600-mL heavy-walled Pyrex beaker and then add about 5 g (±0.01 g) of the desired coal-derived sample. Obtain the sample as soon as possible after sonication, so that it is liquid. Slowly add about 100-150 mL of liquid nitrogen to the beaker to maintain a quiet solution. The total volume of liquid nitrogen used may exceed 300 mL.

C. With a Pyrex glass stirring rod (3/8-in. diameter), grind the frozen sample to a fine powder. This step requires 5-8 min. Fill the beaker with more liquid nitrogen to maintain a volume of at least 30 mL during grinding.

D. Allow the liquid nitrogen to evaporate to just above the solid mixture. Slowly add 100 mL of n-pentane; continue adding another 400 mL of pentane (to a total of 500 mL of pentane). Sonicate for 5 min at the 50% power level dial.

E. Prior to decanting, wipe outside of beaker to remove water condensate. Decant supernatant into filter unit, refill beaker with 500 mL of n-pentane, and sonicate again for 3-5 min. Allow decant liquid to filter into a 500-mL flask. To ensure complete recovery of oils, do not allow filter to dry from this time on.

F. Repeat step E five to eight times. If catch flask fills, transfer contents to rotary evaporator flask and begin to remove n-pentane under nitrogen at about 60°C. Transfer the solids from beaker onto the filter with small portions (25-50 mL) of pentane and wash sonicator probe and filter with pentane. Then wash sonicator again for 5-8 min with pure benzene. Set original sample aside for benzene extraction. (Do not discard beaker; hold for additional transfer of solvents to filter. This ensures removal of maximum amount of material and reduces loss.)

G. Filter the solids, adding nitrogen pressure (5-10 psi) if needed. (The solvents can be collected from the rotary evaporator unit during the continuous solvent removal steps.)

H. Continue solvent filtering using pentane (about 5-20 L), in a clean beaker, until the filtrate is a very light yellow. At the end of pentane extraction, switch collection flasks and add the benzene from the original sample beaker (step F).

I. The pentane solubles from steps G and H should be held on the rotary evaporator for 2 min after the last drop of pentane has condensed in the catch flask. Remove from the rotary evaporator, clean and dry the outside of the flask, and weigh. From the difference on tare, obtain the yield of oils as x grams. Store the oils in a refrigerator at 4°C.

J. Now extract benzene, similarly to steps G-I. Rotary evaporate in a new 500-mL, tared, round-bottomed flask under vacuum (15-20 in.) at 80°C to remove benzene. Keep adding 500-mL aliquots (totaling 5-20 L) until the filtrate is a very light yellow. Remove the flask containing benzene solubles from the rotary evaporator when two-thirds of the inner flask is evenly coated; freeze the solution in place.

Quickly transfer the flask to a vacuum line (1 mmHg) with a trap, and allow flask to stand unheated to freeze-dry (sublime) the benzene in about 2 hr. Calculate the yield of asphaltenes as x grams. [If weight recovery is greater than 100%, proton nuclear magnetic resonance (^{1}H NMR) may be used to detect either pentane (oils), benzene (asphaltenes), or pyridine (preasphaltenes). Use CD_2Cl_2 and a 10% sample size.]

K. After the last benzene extraction, start adding pyridine (total 5-20 L) and continue extracting as in steps G-I. Extract pyridine until the filtrate is light beige. Rotary evaporate the solvent to dryness at 100°C under 20 psi vacuum pressure. Clean rotary evaporator and condense by placing 300-500 mL of methylene chloride in a 1-L flask and rotary evaporating; discard as waste. Place 500 mL of methanol into the flask containing the pyridine solubles and shake. Pour onto a tared 47-mm Millipore glass filter (the filter may be weighed in an aluminum dish) and continue adding methanol, while shaking and scraping the flask until most of the preasphaltenes are on the filter. Wash with 100 mL of pentane to remove the methanol, which is vacuumed off. Allow filter to dry on hot plate before weighing. Reweigh rotary evaporator flask to check flask tare. Record yield of preasphaltenes as x grams.

L. Let the residue dry in place after washing with 500 mL of methanol, 500 mL of methylene chloride, and 500 mL of pentane. Dry the filter using N_2 pressure and weigh to obtain the yield of residues as x grams.

M.

Oils	A
Asphaltenes	B
Preasphaltenes	C
Residue	+ D
	Total recovered

Original mass of sample = MS

MS - total recovered = net loss or gain

If weight gain is observed, leave solvent in oils or asphaltenes and test with NMR. If weight loss is observed, oils have too much volatile matter.

Results should not be reported unless >97% material is recovered. Repeat the analysis.

Add net loss to mass of oils (A + net loss) and calculate material recovery.

	Recovered	Corrected	%
Report: Oils	A	A + net loss	
Asphaltenes	B	B	
Preasphaltenes	C	C	
Residue	+ D	D	
	Total recovered	MS	100%

Samples derived during the coal conversion process can now be compared with a high degree (±1%) of reliability, within 10-14 hr. After the classical separation has been made, the subfractions can undergo first-level chemical characterization.

Determination of Product Distribution by Soxhlet Extraction
(Wilsonville Procedure No. 34550-3)

SCOPE: This method is designed to characterize high-molecular-weight bituminous materials by separating them into three groups using solvents. Because results vary depending on conditions, the procedure is quite detailed and must be followed exactly. The method has been developed primarily to characterize coal extracts.

PRINCIPLE: Coal extracts are separated by solvent fractionation into the following high-molecular-weight fractions:

A. Benzene insolubles: that fraction of the SRC that is insoluble in benzene at its atmospheric boiling point.

B. Asphaltenes: the fraction of the benzene-soluble SRC that is insoluble at room temperature in a mixture of 100 parts of pentane and 9 parts of benzene, when the ratio of the liquid mixture to the weight of benzene solubles is 100.

C. Oil: the benzene-soluble, pentane-soluble fraction of the SRC.

EQUIPMENT:
Paper thimbles, 45 mm X 127 mm size, round-bottomed RA 98 type
Soxhlet extractor
Beaker A, a 600-mL Griffin beaker
Beaker B, a 100-mL Berzelius beaker
Beaker C, an 800-mL Griffin beaker
Buchner funnel, with fritted disc, medium porosity, 150-mL capacity
Wide mouth, 4-oz sample bottle

REAGENTS:
Benzene, reagent grade
Pentane, reagent grade
Celite #545, analytical filter aid
Tetrahydrofuran (THF)

PROCEDURE: A. <u>Separation of Benzene-Insoluble Fraction</u>

1. Grind an approximately 10-g sample to 100-200 mesh and place in a 1-oz bottle.

2. Fill an alundum thimble (45 x 127 mm) with 1-2 g of celite #545. Place in a drying oven at 105°C and leave overnight. In the same manner, dry a 24-cm filter paper that has been folded into quarters.

3. Remove thimble and filter paper from oven and place in desiccator to cool to room temperature. Then weigh the filter paper.

4. Within 30 sec:

   - Weigh the thimble that contains celite.
   - Add 1-1.5 g of sample; weigh again. This is critical because weight gains of 1-25 mg have been observed in less than 1 min.

5. Subtract weight of thimble and celite from weight of thimble, celite, and sample. This is the sample weight.

6. Mix celite and sample by stirring with a microspatula. <u>Caution</u>: thimbles are fragile. Rinse any material left on the spatula into thimble with benzene (use less than 2 mL).

7. Place thimble into soxhlet.

8. Put 3 boiling stones and about 250 mL of benzene into a 500-mL flask. Assemble soxhlet apparatus.

9. Set powerstat to /80-82°C and turn on heat. Check carefully for overflow of thimble and plugging of capillaries as soon as reflux starts. Recycle at about 5-min intervals. Achieve a constant drop, not flow.

10. After 3-4 hr of extraction, stop the apparatus; remove thimble and allow to drain in beaker. <u>Careful</u>! Remove any precipitate on outside of thimble by washing with benzene; transfer washings back into thimble.

11. Stir material in thimble with a microspatula. Replace thimble in soxhlet and continue extraction.

12. Stop the extraction (about 16 hr after initial 3-4 hr) after benzene comes through colorless.

13. Allow soxhlet to cool and then drain.

14. Remove thimble and air-dry in beaker.

15. Place thimble in drying oven at 105°C for at least 4 hr, or overnight.

16. Remove thimble and place in desiccator to cool to room temperature. Weigh and record weight. Subtract from the thimble/celite sample to obtain the weight of the benzene-insoluble fraction.

B. Separation of Benzene-Soluble, Pentane-Insoluble Asphaltene Fraction

1. Carefully transfer the contents of the 500-mL extraction flask into a Rotavapor evaporation flask. Rinse flask with benzene. Discard boiling stones.

2. Remove solvent to dryness in Rotavapor.

3. Redissolve residue with approximately 5 mL of tetrahydrofuran.

4. Pour residue into beaker filled with 900 mL of n-pentane; stir constantly with magnetic stirring bar.

5. Rinse flask with pentane and pour into the beaker. If necessary, use Teflon scraper to transfer all precipitate into the beaker. Do not exceed a total volume of 1,000 mL of n-pentane.

6. Stir for about 5 min; remove the stirring bar immediately and let the precipitate settle for about 10-15 min.

7. Place the dried, preweighed, 24-cm filter paper in a glass funnel and decant the supernatant through the filter. Then transfer the precipitate onto the filter, using additional pentane.

8. Wash the filter with pentane; do not allow paper to dry. This is very important; otherwise, hard-to-remove oils will coat the paper. Wash with about 1,000 mL of pentane, or until the filter paper is white where the asphaltenes do not coat it.

9. Let the filtrate drain from the filter; place the filter paper in a preweighed beaker and dry in the oven at 105°C overnight.

10. Remove filter paper from oven and allow to cool to room temperature in a desiccator.

11. Weigh and record. Subtract the weight of the filter paper to obtain the weight of asphaltenes.

C. Separation of Benzene-Soluble, Pentane-Soluble Oil Fraction

1. Remove the solvent from the filtrate in a Rotavapor until about 50 mL remains.

2. Transfer solvent into a preweighed beaker; rinse with a small amount of pentane.

3. Place beaker into drying oven at 105°C, let stand overnight, and then cool to room temperature in a desiccator.

4. Weigh and subtract the weight of the beaker to obtain the weight of the oils fraction.

D. Yield Calculations

To obtain the yields of the fractions, add the weights of oils, asphaltenes, and benzene insolubles (BI). Then divide this sum by the weight of the initial sample:

$$\text{Yield} = \frac{\text{wt of oils + wt of asph. + wt of BI}}{\text{wt of sample}}$$

The yield should be between 0.97 and 1.03. Then obtain the individual normalized weight-percent fractions:

$$\frac{\text{wt of oils}}{\text{wt of sample}} \times \frac{100}{\text{yield}} = \text{weight percent oils}$$

$$\frac{\text{wt of asph.}}{\text{wt of sample}} \times \frac{100}{\text{yield}} = \text{weight percent asphaltenes}$$

$$\frac{\text{wt of BI}}{\text{wt of sample}} \times \frac{100}{\text{yield}} = \text{weight percent benzene insolubles}$$

Beaker Extractions
(Kerr-McGee Procedure)

DEFINITIONS: Three fractions are defined as follows:

Oil:	Toluene and heptane soluble; determined as the difference between toluene-soluble and asphaltene content
Asphaltene:	Toluene soluble/heptane insoluble; determined directly as a heptane-insoluble residue
Preasphaltene:	Pyridine soluble/toluene insoluble; determined as the difference between the two solubilities

PROCEDURE:

A. For both pyridine and toluene solubility procedures, digest a 10-g sample for 30 min at the solvent boiling point using a 10:1 solvent-to-feed ratio.

B. Vacuum-filter the solutions hot through a Buchner funnel using Whatman No. 42 paper.

C. Rinse residues with the digestion solvent and then with heptane (toluene digestion) or toluene/heptane (pyridine digestion).

D. Determine the asphaltene content by evaporating the toluene-soluble filtrate to near-dryness on a steam bath, followed by heptane digestion and filtration.

E. Calculate solubilities as follows:

$$\% \text{ soluble (by wt)} = \frac{\text{sample net wt} - \text{residue net wt}}{\text{sample net wt}} \times 100$$

For those samples with significant ash content (i.e., >5%), also calculate solubilities as follows:

$$\% \text{ soluble (by ash)} = 100 - \frac{\% \text{ ash (original sample)}}{\% \text{ ash (digestion residue)}} \times 100$$

The two solubility values should agree within 1%; the reported value is then taken as the average of the two solubility calculations.

Determination of Percent Cresol Insolubles in SRC Products
(Wilsonville Procedure No. 34550-21)

I. SCOPE: This test is designed to measure the cresol-insoluble solids in SRC.

II. PRINCIPLE: The procedure is based on fractional solubility in organic solvents. Because the solvent was selected to give the maximum solubility of extract, the insoluble residue represents, primarily, unreacted coal or similar material in the product. Strict adherence to all specified conditions is essential because of the empirical nature of the test.

III. APPARATUS:
Beakers (300 mL)
Mechanical stirrer
Suction flask (100 mL)
Steam-jacketed Buchner funnel (15 cm)
Filter paper, no. 42 (15 cm)
Hot plate
Oven, 105 ± 5°C
Water aspirator
Wash bottle [for cresol (hot) methanol]
Analytical balance
Powder paper (glassine, 4-3/8 x 5-3/4, Eli Lilly Co.)

IV. REAGENTS:
Cresol
Acetone

V. SAFETY: SRC material should be treated as toxic chemicals. Gloves and a lab coat should be worn to protect hands and clothing. For specific handling precautions of SRC material, see the U.S. Department of Labor O.S.H.A. Material Safety Data Sheet located in the front section of the manual.

Cresol has a permissible exposure limit of 5 ppm (22 mg/m^3) and must be carefully handled in a well ventilated area.

VI. PROCEDURE:

A. Place 100 mL of cresol in a beaker and heat on a hot plate until vapors are visible.

B. Prepare sample to -20 mesh. Do not crush too finely.

C. Weigh 10-g sample on glassine paper.[a]

D. Add the sample, stirring constantly, to the hot cresol; stir the mixture for 0.5 hr. The sample can be weighed in a beaker and the hot cresol added to the sample while stirring.

---

[a] Sample size depends on the percent insolubles in the SRC. With a high percentage of insolubles present, a smaller sample can be used, and vice versa.

E. Weigh a No. 42 filter paper and prepare the steam-jacketed Buchner for filtering. Be sure the funnel is hot.

F. Filter the sample and wash several times with hot cresol or until the sample does not look tacky.[b]

G. Turn off the steam and let the funnel cool. Wash the insoluble material with acetone until the sample is free of cresol.

H. Dry the filter paper in the oven at 105°C for 30 min. Residue should be free of any cresol odor. Cool in a desiccator and weigh. Subtract weight of filter paper to obtain weight of insolubles.

VII. CALCULATION:

$$\frac{\text{Weight of insoluble material}}{\text{weight of sample}} \times 100 = \%\ \text{cresol insolubles}$$

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[b] Some samples filter very slowly. When this occurs, a new, smaller sample should be used, or the sample should be stirred and heated for a longer period of time.

GAS CHROMATOGRAPHY LABORATORY PROCEDURES

BOILING RANGE DISTRIBUTION OF PETROLEUM FRACTIONS BY GAS CHROMATOGRAPHY
(ASTM D 2887)

The procedure is applicable to SRC samples having a continuous boiling range greater than 100°F. This procedure can be used as a substitute for APCI procedure, "Gas Chromatographic Simulated Distillation For SRC Derived Products", when the amount of nonboiling residue in a sample due to ash, SRC or entrained coal is not to be quantified.

Safety

SRC liquids and related material should be treated as toxic materials. Gloves and a lab coat should be worn to protect hands and clothing.

For specific handling precautions for SRC liquids, see the appropriate ICRC Material Safety Data Sheets in the front of the manual.

Gas Chromatographic Simulated Distillation
for SRC-Derived Products
(APCI Procedure)

I. SCOPE

This method determines the boiling-point distribution of full-range SRC-derived materials. The method applies to SRC products and fractions containing material boiling between C_4 and 1,000°F, but is limited to samples having a continuous boiling range greater than 100°F. Furthermore, the method can be used with SRC solid, liquid, or homogeneous SRC blends and can quantitatively determine the amount of nonboiling residue in a sample.

II. PRINCIPLE

An encapsulated sample is inserted by a special sampler into a gas chromatographic column, which separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time axis from a calibration curve, which is obtained under the same conditions by running a mixture of standard hydrocarbons of known boiling points through 1,000°F. From these data, the boiling-point distribution may be obtained. In addition, the weight of residue left in the sample capsule is also measured. The residue weight defines the amount of sample boiling above 1,000°F.

III. APPARATUS

A. Gas Chromatograph: A Perkin-Elmer 3920 gas chromatograph, or equivalent, equipped with dual-flame ionization detector, subambient accessory, and linear temperature programmer (Perkin-Elmer Corporation, Norwalk, Conn.).

B. Autosampler: Perkin-Elmer AS-41 automated capsule injector (Perkin-Elmer Corporation, Norwalk, Conn.).

C. Strip Chart Recorder: Perkin-Elmer Model 023 or equivalent, single-pen recorder with 1-mV full-scale deflection (Perkin-Elmer Corporation, Norwalk, Conn.).

D. Integrator: Electronic integration system for determining the accumulated area under the chromatogram; a Hewlett-Packard 3352C lab data system meets requirements (Hewlett-Packard Corporation, Avondale, Pa.).

E. Column: Two 1/8 in. o.d. by 0.016 in. wall by 3 ft stainless steel columns packed with 3% Dexsil 300 on 80/100 mesh Chromosorb W, acid-washed (Supelco, Inc., Bellefonte, Pa.). Because a stable base line is essential to this method, matching dual columns are required to compensate for column bleed, which cannot be eliminated completely by conditioning alone.

F. Microbalance: A microbalance capable of measuring to 10^{-7}g is needed to weigh residue; a Perkin-Elmer AD-2 autobalance fulfills this requirement (Perkin-Elmer Corporation, Norwalk, Conn.).

IV. REAGENTS AND MATERIALS

A. Cylinder Gases: Helium is required for carrier gas and hydrogen and air are necessary for the flame detector (Air Products and Chemicals, Inc., Trexlertown, Pa.).

B. Liquid Nitrogen: Liquid nitrogen is used to cool samples to sub-ambient temperatures in the gas chromatograph (Air Products and Chemicals, Inc., Trexlertown, Pa.).

C. Calibration Mixture: A calibration blend of hydrocarbons (normal paraffins) of known boiling points that includes the boiling range of the sample is required (see Table 1). At least one compound in the calibration mixture must have a boiling point lower than the initial boiling point of the sample.

D. Capsules: Micro-sampling capsules are used with the AS-41 autosampler (Perkin-Elmer Corporation, Norwalk, Conn.).

E. Crimper: A capsule crimper is used to make the cold weld on the sample capsules used with the AS-41 autosampler.

F. Tungsten Carbide Tipped Pencil: Use to engrave identification numbers on the sample capsules.

V. PREPARATION OF APPARATUS

A. Column Preparation

The column must be conditioned at the maximum operating temperature to reduce base-line drift due to column bleed; use the following procedure:

1. Disconnect column from the detector.
2. Purge the column thoroughly at ambient temperature with carrier gas.
3. Turn off the carrier gas and allow the column to depressurize completely.
4. Raise the column temperature to the maximum operating temperature; hold at this temperature for at least 2 hr with no flow through the column.
5. Cool the columns to at least 100°C before turning on carrier gas again.

6. Program the column temperature up to the maximum several times with normal carrier gas flow. The column may now be connected to the detector and should be ready for use.

B. Column Resolution

To test column resolution, prepare a mixture of 1% C_{16} and 1% C_{18} n-paraffins in a suitable solvent such as hexane. Inject this mixture as a sample and obtain the chromatogram. Calculate resolution (R) from this chromatogram using the formula:

$$R = \frac{2(d_1 - d_2)}{Y_1 + Y_2} \qquad (1)$$

where d_1 = retention time of C_{18} (mm), d_2 = retention time of C_{16} (mm), Y_1 = width of C_{18} peak at the base line (mm), and Y_2 = width of C_{16} peak at the base line (mm). The resolution calculated from equation 1 must be at least three and not more than eight.

C. Chromatograph

Place chromatograph, autosampler, and data system into service according to manufacturers' instructions. Table 2 lists operating conditions for the chromatograph.

VI. PROCEDURE

A. Preparation of the Gas Chromatograph

1. Assemble the gas cylinders, necessary regulators, gas purifiers, liquid nitrogen delivery system, autosampler, gas chromatograph, recorder, and lab data system according to the manufacturers' directions.

2. Condition the columns as described in Section V.A.

3. Set the gas chromatograph operating conditions as outlined in Table 2.

4. Set the time between injections on the autosampler control module. To select the correct time, a heat cycle should be timed from start to finish, when the oven is cooled to its initial temperature. Set this time on the autosampler control to ensure that each injection occurs at precisely the same moment, so that identical oven temperatures are used in all calibration and sample analysis runs.

B. Sample Preparation

1. Sample Handling

Handle all samples in a fume hood and wear protective gloves at all times (see Section VIII).

2. Sample Storage

To protect the integrity of all samples, store them under a blanket of nitrogen in a refrigerator until analysis.

3. Loading Samples

Load samples into the sample capsules using a microliter syringe. Pull an appropriate amount of sample (0.2 to 1.0 μL) into the syringe and place syringe in the sample loader along with the cartridge containing the empty capsule. Lower the syringe into the capsule until the tip barely touches the capsule bottom (there is an adjustment screw for this); depress plunger to load the sample. Crimp and debur the capsule. If the sample is a solid, then simply place an appropriate amount in the capsule and crimp and debur the capsule. If the sample is too viscous to load with the syringe, place a small amount on the syringe tip and lower the syringe into the capsule to deposit the sample on the capsule bottom. Repeat this process as often as needed to load an appropriate amount of sample in the capsule. During this loading procedure, take care not to spill any sample on the sides of the capsule near the top because this portion is removed during deburring.

4. Weighing Capsules

First, adjust the microbalance to zero by placing equal weights on each pan. To ensure that the balance is properly adjusted, the zero reading should not drift for at least 30 sec. Since the capsules weigh more than 30 mg, determine the true mass of small weights and place them on the opposing pan. Periodically determine the true mass of these weights to ensure that they remain constant. After adjusting the balance and determining the true mass of the tare weights, weigh the sample capsules. Do not record weights until drift in the balance reading ceases for at least 30 sec.

C. Operation

1. Computer Method for Calibration

Prepare a computer method for the laboratory data system to collect information needed to calibrate the simulated distillation method. The calibration method merely calculates the retention time of each peak in the calibration run; a sample of this method is presented in Table 3. Consult the manuals for the Hewlett-Packard 3352C Lab Data System for a detailed explanation of the questions and responses for the computer dialogue. This method will yield a report consisting of the retention time and the area of each peak in the calibration mixture. Dump the data from this calibration run onto paper tape using the teletype (the reporting device of the data system). (Instructions for dumping data onto paper tape are included in the 3352C Lab Data Manuals.) The paper tape will contain the retention times and the raw area counts of each peak in the calibration mixture. The simulated distillation software requires that C_{12} be the largest peak in the calibration, and that all peaks before C_{12} must have an area at least 0.5% of the C_{12} area and all peaks after C_{12} be at least 0.05% of the C_{12} area. Any peaks not meeting these minimum requirements will be rejected. Therefore, the calibration blends should be prepared accordingly.

2. Computer Method for Simulated Distillation

Prepare a computer method for the laboratory data system to perform simulated distillation. The method collects area in 12-sec time slices, relates the times to the calibration curve of retention time vs. boiling point, and relates the area of each slice to the total sample area. From these data, a boiling-point distribution is calculated and reported. An example of a computer method for simulated distillation is shown in Table 4. Consult the manuals for the Hewlett-Packard 3352C Lab Data System for a detailed description of this computer dialogue.

3. Heat Cycle

Program the column temperature upward from initial to maximum temperature using the programming rate in Table 2. Cool the column to the starting temperature; at the exact time for each analysis, inject the next sample. Start column temperature programming immediately upon injection. Always start the injection cycle at the same time, preferably when the GC oven-ready light comes on. Such precautions ensure that each sample is run at conditions identical to those used for calibration. Using a gas chromatograph equipped with oven-ready sensing to activate the autosampler is preferable. If this is unavailable, inject the samples on a fixed-time basis, as described in Section VI.A.4.

4. Calibration

After preparing the calibration and simulated distillation methods and completing the heat cycle, start the calibration procedure. Load a sample capsule with the calibration blend and seal with a cold weld using the crimper. Place the capsule cartridge into the autosampler and start the injection cycle at the same point as the beginning of the heat cycle (when the GC oven-ready light comes on). Before injection, be sure that the calibration method has been called to the A/D converter connected to the gas chromatograph. At the completion of the calibration run, dump the data from the A/D converter onto paper tape (this procedure is described in the Lab Data System manuals). A sample chromatogram from a calibration run is presented in Figure 1.

Now clear the calibration method from the A/D converter and call up the simulated distillation method. Load the paper tape onto the system using the tape reader. Recalibrate the simulated distillation method by using the recalibrate command. If everything was done properly, the system response will be "DONE". If the response is "BAD CAL DATA", check the components of the calibration mixture for compliance with the minimum area requirements discussed in Section VI.B.2.

5. Sample Analyses

After successfully completing calibration (which should be done once a day), use the system to run sample analyses. Load the samples to be analyzed into sample capsules, place the full sample capsule cartridges in the autosampler, and start the first analysis when the oven-ready light comes on. Succeeding analyses will be injected automatically on a time basis, so the analyses can proceed unattended. Examples of a sample chromatogram and boiling-point distribution report are presented in Figure 2 and Table 5, respectively. Note that a constant base line at the end of each run is essential because the area-slice integration of the system software does not track the base-line. Therefore, all measures needed to avoid base-line drift must be taken into account, e.g., column bleed, detector temperature control, constancy of carrier gas flow, and leaks. Also, periodic blank runs should be made in the normal manner without injecting a sample to give an indication of the base-line stability. If an integration system that does perform base-line tracking is available, a constant base line is not as critical.

6. Residue Determination

If the amount of sample residue boiling above 1,000°F is desired, the sample capsules must be preweighed according to the procedure outlined in Section VI.B.4. For the best results, first place the capsules in a muffle furnace at 400°C for about 4 hr and then cool and store in a desiccator using a suitable desiccant such as drierite. This process removes any oils or moisture from the capsule surfaces that may have been deposited during their manufacture. After the capsules have been cleaned and cooled, remove the number desired from the desiccator and etch identifying numbers on the capsule sides using a tungsten carbide tipped pencil. Etch the markings near the bottom, closed end of the capsule, since subsequent crimping and deburring processes will remove a portion of the open-ended top of the capsule. After numbering, weigh the empty capsules using the microbalance. Record this tare weight and load the capsules into their appropriately numbered positions in the sample capsule cartridges. Next, load the capsules with sample as described in Section VI.B.3 and crimp only--do not deburr. Weigh the crimped capsules, record the weights, and return capsules to their proper positions in the cartridge. Now debur the capsules, and then reweigh and record weights. Place capsules in the autosampler and perform analyses. At the completion of GC analyses, remove the capsule collector tray on the autosampler and weigh spent capsules. Using the identification marks on the capsules, record this final weight determination for each sample.

VII. CALCULATIONS

A. Calibration

The computer system performs the following calculations to obtain a calibration curve:

1. The retention time of each component of the calibration mixture is recorded.

2. The boiling point of each component is stored in the computer memory as part of the simulated distillation software. These boiling-point values are listed in Table 1.

3. A calibration curve of retention time vs. boiling point is derived from the above data. This relationship is stored and used by the data system for all subsequent runs. A typical calibration curve is shown in Figure 3.

B. Boiling-Point Distribution

This calculation is also performed by the computer system, as follows:

1. The cumulative area under the chromatogram at each 12-sec interval is recorded.

2. At the end of the run, which is 25.5 min under the operating conditions outlined in Table 2, the total cumulative area counts are recorded.

3. The initial boiling point is defined as the point at which the cumulative area count is 0.5% of the total area.

4. The final boiling point is defined as the point at which the cumulative area count is 99.5% of the total area.

5. The cumulative area at each interval between the initial and final boiling points is divided by the total cumulative area counts. This yields the percent of sample recovered at each interval.

6. The percent recovered at each interval and the boiling temperature assigned to that interval from the calibration curve are tabulated and reported in 1% increments.

C. <u>Residue Determination</u>

1. The sample weight in each capsule is calculated as:

   sample wt = (sample wt + capsule wt) - capsule wt

2. The capsule weight after deburring is calculated as:

   deburred capsule wt = (deburred capsule wt + sample wt) - sample wt

3. The residue weight is calculated as:

residue wt = capsule wt (after injection) - deburred capsule wt

4. The percent residue is calculated as:

$$\% \text{ residue} = \frac{\text{residue wt}}{\text{sample wt}} \times 100$$

VIII. SAFETY

Because this method was developed primarily for analyzing SRC-derived materials, certain minimum safety practices should be followed:

Sample Handling

1. Handle all samples inside a good fume hood to avoid the inhalation of vapors.

2. Wear protective gloves whenever handling any SRC materials.

3. Wash hands with soap and warm water immediately after handling any SRC materials, even though protective gloves are worn.

4. If skin accidentally contacts SRC material, immediately and thoroughly scrub the area with soap and warm water.

XI. QUALITY ASSURANCE

A. Scope

The following are minimum procedures necessary to maintain encapsulated simulated distillation instrumentation (the Perkin-Elmer 3920 gas chromatograph and the AS-41 automatic sampler) in proper operating condition.

B. Calibration

1. System Calibration

Calibrate the simulated distillation method daily using the calibration standard described in Table 1. Follow procedures described in Sections VI.B.2-VI.B.4.

2. Column Evaluation

Check the column performance weekly by analyzing the resolution mixture described in Section V.B. Replace the columns if they do not meet the resolution requirements outlined in that section.

C. Maintenance

The minimum maintenance procedures needed to keep the simulated distillation equipment operating properly are listed below:

1. Check gas supplies daily and replace as necessary.
2. Check helium flow rates weekly.
3. Change gas purifiers when spent.
4. Clean the FID detector at every column change (approximately every 10 to 12 weeks).
5. Replace "O"-rings in the injector at every column change (10-12-week interval).
6. Inspect and clean the sample probe inside the injector (using a caustic solution) at every column change if necessary (10-12-week interval).

7. Clean and lubricate (with Apiezon grease) the autosampler every 2 weeks.

8. Check the injector's cooling-water level every week.

9. Clean and lubricate the teletype every 90 days.

10. Check the forepump oil level on the vacuum pump for the liquid nitrogen delivery system monthly, and replace quarterly. Use Welch Duo-Seal oil. Also check the belt monthly and replace as needed.

11. Inspect the oil diffusion pump for the liquid nitrogen delivery system and change the oil every 6 months according to the manufacturer's directions. Use Dow Corning 704 diffusion pump fluid.

XII. PRECISION AND REPRODUCIBILITY

Because initial investigation of the GCSD injection system revealed that injecting empty capsules resulted in weight losses of 0.02-0.18 mg, the precision of the microbalance was tested. A 1-mg tare weight was weighed 20 times over 10 days (see Table 6). The balance precision was ±0.0006 mg. The apparent weight loss of the empty capsule could then be reduced to 0.0020-0.0170 mg by zeroing the balance under load and using corrected values for the tare weights.

To study the precision of the capsule injection technique for determining nonvolatiles, three samples containing 6 to 74% residue were each analyzed 13 to 15 times. Results in Table 7 show that reproducibility of the residue measurement is about 1.6-2.1 wt %, absolute.

Reproducibility of the boiling point distribution was studied by analyzing an SRC sample from APCI's coal process development unit 19 times. Table 8 lists the reproducibility of the boiling temperature at every 10% off and Table 9 shows reproducibility for various cut points from the same analyses. A similar SRC sample was also analyzed five times over a year and a half (see Table 10 for results).

Also investigated was the method's ability to yield reproducible mass balance data. Results from analyses of an SRC light oil and a process solvent are shown in Table 11. The same samples were also blended in light-oil-to-process-solvent ratios of 3:1, 1:1, and 1:3. Results from analyzing these blended samples were compared to predicted values based on analyses of the components (Table 12). Results show that the method can give reliable material balance data.

Table 1

Calibration Blend

n-Paraffin component	Boiling point (°F)	n-Paraffin component	Boiling point (°F)
C_3	-44	C_{15}	519
C_4	31	C_{16}	548
C_5	97	C_{17}	576
C_6	156	C_{18}	602
C_7	209	C_{20}	651
C_8	258	C_{24}	736
C_9	303	C_{28}	809
C_{10}	345	C_{32}	874
C_{11}	385	C_{36}	928
C_{12}	421	C_{40}	977
C_{14}	488		

Table 2

Operating Conditions for Gas Chromatograph

Column dimensions	36 in. × 1/8 in. o.d., stainless steel, dual
Packing	3% Dexsil 300 on 80/100 mesh Chromosorb W, acid-washed
Initial temperature	-30°C
Final temperature	380°C
Programming rate	16°C/min
Carrier	Helium, purified by catalytic dryer and oxysorb
Carrier flow	50 cm^3/min (80 psig)
Injector temperature	250°C
Detector temperature	350°C
Detector	Dual differential flame ionization detectors
Injection	AS-41 capsule injection
Sample size	0.5-1.0 μL

Table 3

Calibration Method for Data System

```
CAL

1.   CHAN, PROC, RPRT, RDVC
     3, ZERO, SH, T1

2.   SAMP, UNTS, TITLE
     RECAL, AREA %, CAL

3.   #PKS, RTM, PRG
     50, 25.50, YES

4.   MIN AR, MV/M, DLY, DVT, DIL-FTR%
     4000, 0.30, 0.00, 0.00, 100.00

7.   # EVENTS
       0
```

Table 4

Simulated Distillation Method for Data System

1. CHAN, PROC, RPRT, RDVC
   3, SNRM, LO, T1

2. RTM, DATE
   25.50, 11/11/81

3. DEG F, FID, C3 and C4
   YES, NO, YES

Table 5

Boiling-Point Distribution by ASTM D2887

% off	°F	% off	°F	% off	°F	% off	°F
IBP	411						
1	422	26	622	51	737	76	857
2	442	27	627	52	740	77	862
3	456	28	631	53	745	78	868
4	467	29	636	54	750	79	874
5	480	30	642	55	754	80	879
6	491	31	647	56	759	81	886
7	501	32	652	57	763	82	892
8	510	33	656	58	768	83	898
9	517	34	659	59	773	84	904
10	524	35	665	60	777	85	911
11	533	36	670	61	781	86	918
12	540	37	675	62	787	87	925
13	545	38	678	63	791	88	932
14	550	39	682	64	796	89	939
15	558	40	688	65	800	90	947
16	565	41	692	66	805	91	955
17	573	42	697	67	811	92	963
18	577	43	701	68	815	93	973
19	581	44	705	69	821	94	983
20	589	45	710	70	826	95	993
21	596	46	714	71	830	96	1,005
22	601	47	716	72	835	97	1,017
23	605	48	722	73	841	98	1,032
24	610	49	727	74	846	99	1,049
25	616	50	732	75	851	100	1,060

Table 6

Microbalance Precision

[Weight Observed on 1-mg Tare Weight over 10-Day Period (mg)]

0.9802	0.9815
0.9796	0.9815
0.9807	0.9801
0.9809	0.9804
0.9810	0.9806
0.9809	0.9803
0.9808	0.9803
0.9817	0.9804
0.9801	0.9798
0.9798	0.9798

Mean +/- Standard Deviation: 0.9801 +/- 0.0006 mg

Table 7

Precision Study of Residue Determination

(Figures Are Weight Percent Residue)

1961CB	1963CB	1964CB
7.72	34.16	72.73
9.55	36.27	73.65
8.46	34.32	72.42
8.43	32.71	71.67
6.91	34.98	74.66
6.34	35.36	71.01
4.47	33.11	73.09
6.62	32.47	72.04
5.42	33.24	76.86
5.16	34.46	71.03
4.89	35.93	76.73
6.89	37.28	75.34
4.51	35.59	76.44
5.88	36.84	
5.38	39.21	
Mean +/- Standard Deviation:		
6.44 +/- 1.56	35.10 +/- 1.86	73.67 +/- 2.13

Table 8

Reproducibility of Boiling Point Distribution

% Off	Temperature, F
IBP	366.8 +/- 13.4
5	416.3 +/- 1.2
10	434.5 +/- 11.6
20	468.1 +/- 2.2
30	509.4 +/- 8.0
40	537.5 +/- 2.8
50	573.3 +/- 8.2
60	627.2 +/- 1.9
70	652.3 +/- 3.9
80	703.8 +/- 2.3
90	738.5 +/- 2.6
95	795.7 +/- 3.9
FBP	956.8 +/- 6.1

Table 9

Reproducibility of Boiling Ranges

Cut	%Off
IBP-550	43.6 +/- 1.2
550-650	26.0 +/- 0.5
650-750	21.8 +/- 0.5
750-850	5.7 +/- 0.2
850-FBP	2.8 +/- 0.1

Table 10

Reproducibility of Boiling Point Distribution over Time

Analysis Date:	12/80	1/81	3/81	6/81	7/82	Avg.+/- Std. Dev.
% Off	Temp., F					
IBP	348	353	355	352	340	349.6 +/- 5.9
5	416	422	417	418	413	417.2 +/- 3.3
10	422	432	423	424	421	424.4 +/- 4.4
20	464	474	467	467	462	466.8 +/- 4.5
30	498	504	494	496	492	496.8 +/- 4.6
40	532	539	531	532	529	532.6 +/- 3.8
50	561	570	560	561	558	562.0 +/- 4.6
60	615	626	617	619	615	618.4 +/- 4.6
70	626	638	633	632	629	631.6 +/- 4.5
80	687	697	693	686	686	689.8 +/- 5.0
90	719	727	732	716	722	723.2 +/- 6.4
95	766	771	780	760	773	770.0 +/- 7.5
FBP	943	968	938	920	930	939.8 +/- 18.0

Table 11

Boiling Point Cut Points of SRC Light Oil and Process Solvent

Light Oil

Cut points	% Off 1	% Off 2	% Off 3	Avg. +/- Std. Dev.
IBP - 450	97.7	97.5	97.9	97.7 +/- 0.2
450 - 550	2.3	2.5	2.1	2.3 +/- 0.2

Process Solvent

Cut Points	% Off 1	% Off 2	% Off 3	% Off 4	Avg. +/- Std. Dev.
IBP - 450	7.4	6.8	6.8	6.8	6.9 +/- 0.3
450 - 550	32.8	33.8	33.6	33.8	33.5 +/- 0.5
550 - 650	28.1	29.6	30.1	29.2	29.2 +/- 0.8
650 - 750	20.5	19.4	19.4	19.3	19.6 +/- 0.6
750 - 850	8.1	7.6	7.5	7.7	7.7 +/- 0.3
850 - FBP	3.1	2.8	2.6	3.2	2.9 +/- 0.3

Table 12

Mass Balances from Boiling Point Distributions

Ratio of Light Oil to Process Solvent :	Cut Points	Predicted Values (% Off)	Actual Values (avg. of 4) (% Off)
3.35/1	IBP-450	76.8	77.0
	450-550	9.5	9.5
	550-650	6.7	6.9
	650-750	4.5	4.2
	750-850	1.8	2.0
	850-FBP	0.7	0.4
1.01/1	IBP-450	52.5	51.4
	450-550	17.8	17.4
	550-650	14.5	15.5
	650-750	9.8	10.0
	750-850	3.8	4.0
	850-FBP	1.4	1.6
1/2.95	IBP-450	29.9	30.5
	450-550	25.6	24.8
	550-650	21.8	22.4
	650-750	14.6	14.1
	750-850	5.8	5.7
	850-FBP	2.2	2.4

Figure 1
Chromatogram of Calibration Blend

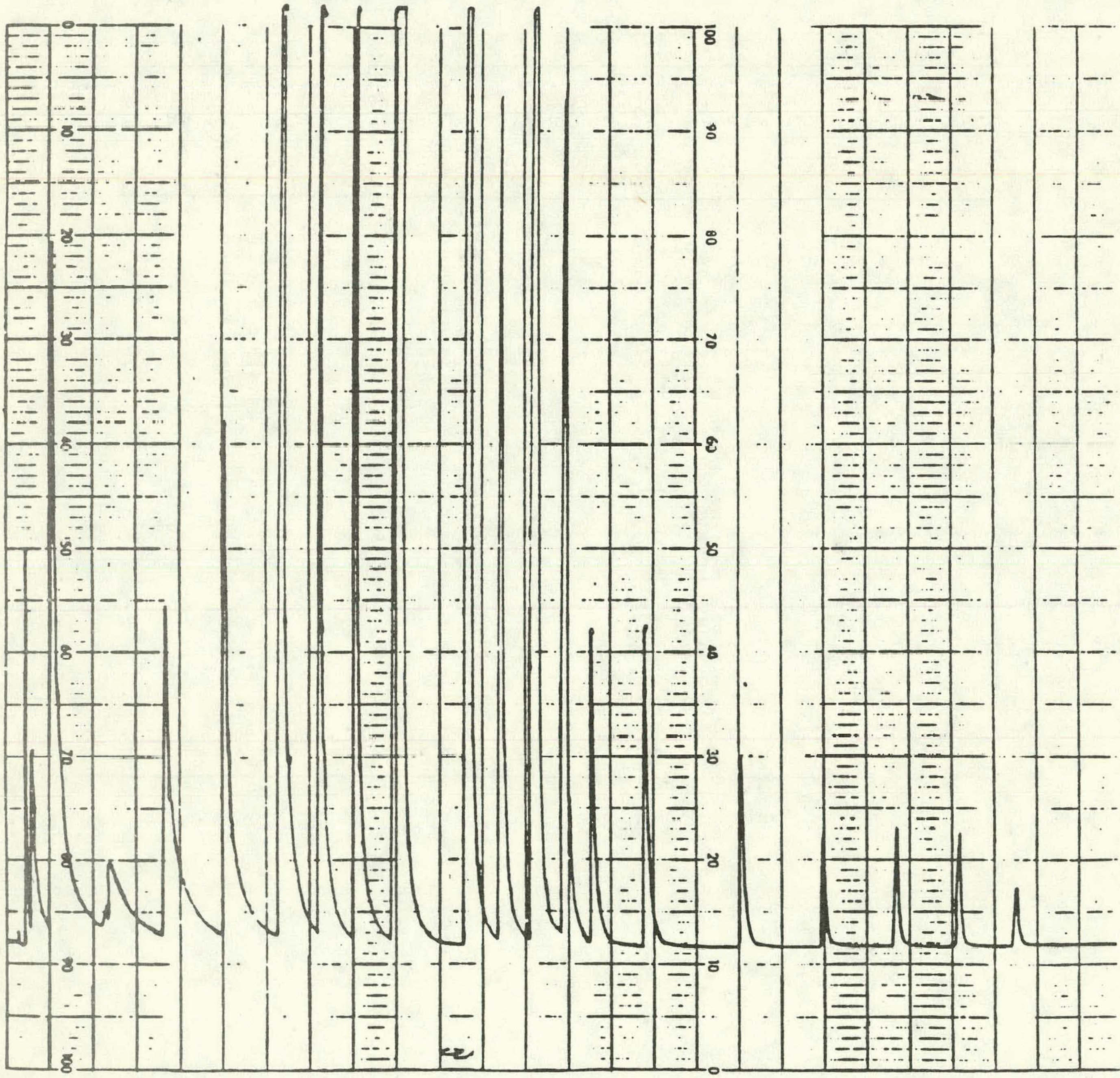


Figure 2
Sample Chromatogram

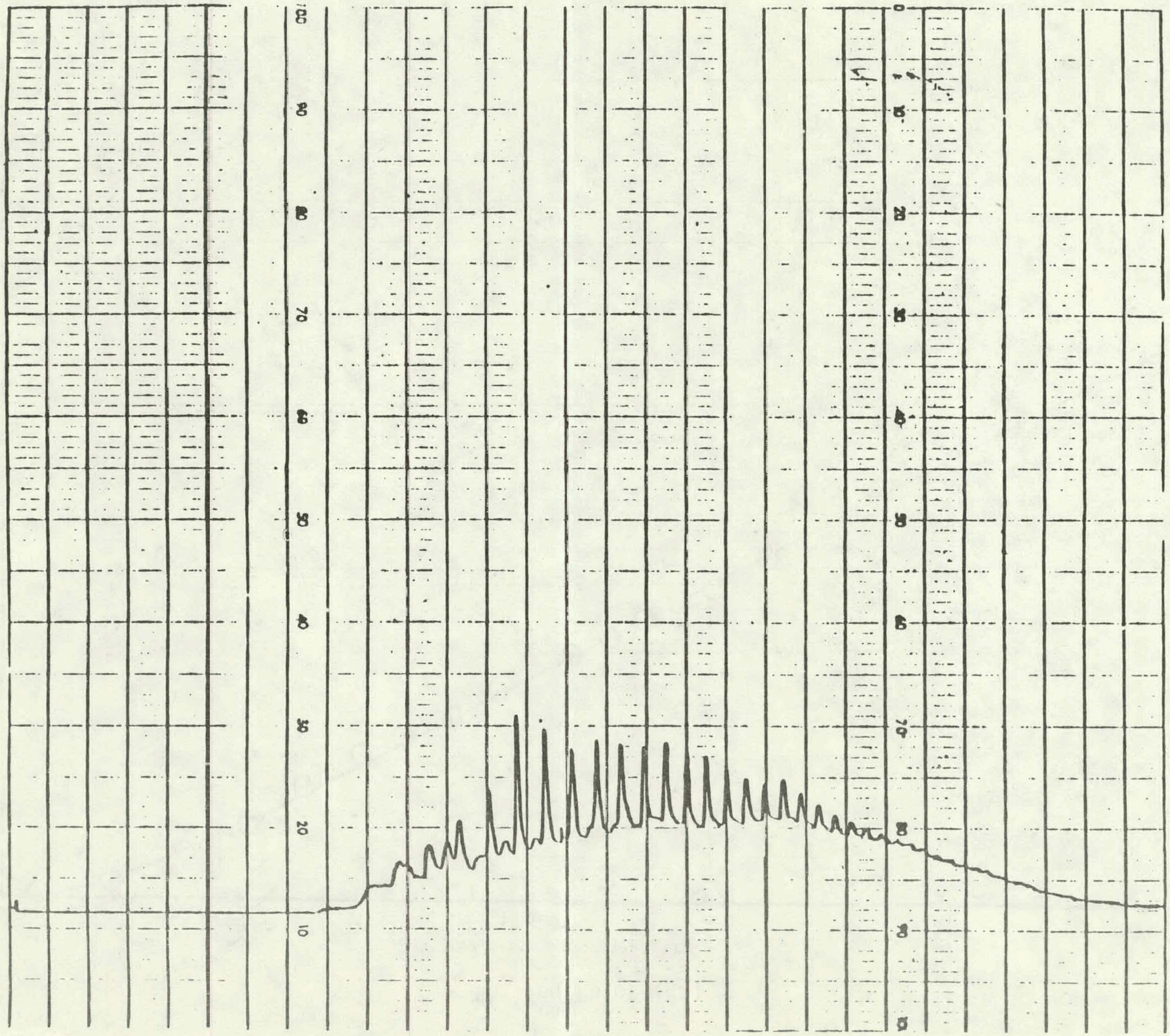
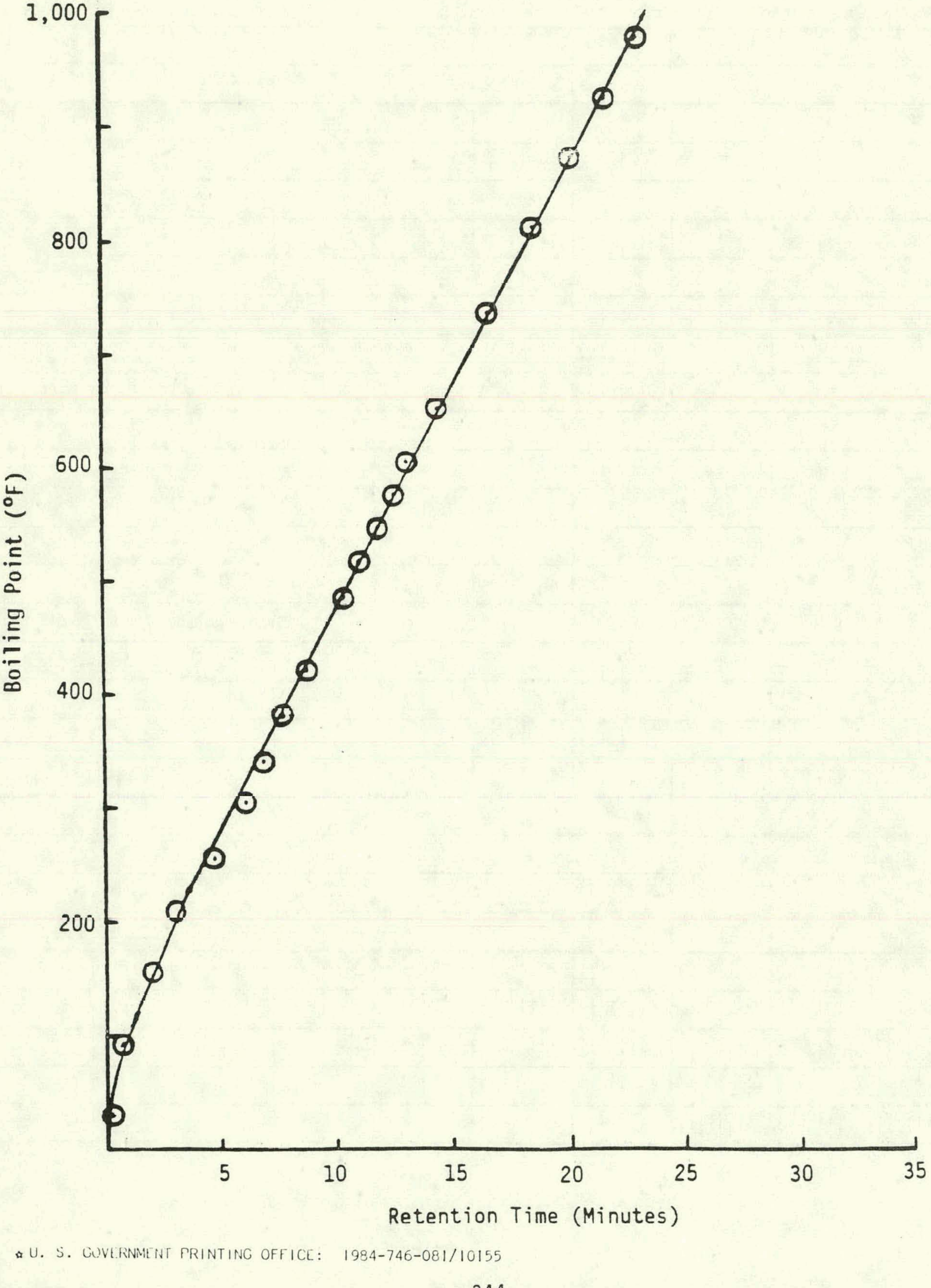


Figure 3
Calibration Curve



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