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ANALYTICAL CAPABILITIES AND SERVICES OF LAWRENCE LIVERMORE LABORATORY'S GENERAL CHEMISTRY DIVISION

Ralph Gutmacher
Richard Crawford

March 9, 1978

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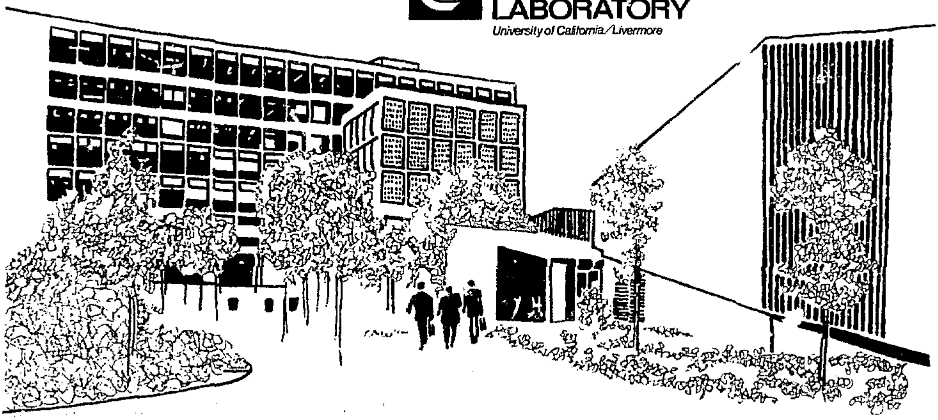

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MS. date: March 9, 1978

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PREFACE

This report is a reference guide to the diverse analytical capabilities and services available from Lawrence Livermore Laboratory's General Chemistry Division of the Chemistry and Materials Science Department. General Chemistry Division's mission is to develop and maintain state-of-the-art capabilities for chemical characterization of materials in support of all major Laboratory programs. Since the chemical compositions and impurities in the bulk and on the surface of materials often determine the essential physical, chemical, electrical, and nuclear properties of these materials, researchers and engineers would be well advised to obtain this information before beginning research. Readers are invited to discuss chemical analyses problems with listed staff members or with Robert Meisenheimer, head of the Analytical Measurement and Development Section.

Klaus Ernst, Head
General Chemistry Division

ANALYTICAL CAPABILITIES AND SERVICES OF LAWRENCE LIVERMORE LABORATORY'S GENERAL CHEMISTRY DIVISION

ABSTRACT

This comprehensive guide to the analytical capabilities of Lawrence Livermore Laboratory's General Chemistry Division describes each analytical method in terms of its principle, field of application, and qualitative and quantitative uses. Also described are the state and quantity of sample required for analysis, processing time, available instrumentation, and responsible personnel.

SERVICES

The three service functions and responsible section leaders of the General Chemistry Division are: Analytical Services under Robert G. Meisenheimer, Laboratory Automation under George W. Barton, and Weapons Materials Compatibility under Herman R. Leider. Several consultants are available in the Analytical Services section to aid with analytical problems, depending on the sample and method of analysis. These consultants and their areas of expertise are shown in Table 1.

Table 1. Analytical Services consultants.[a]

	Solid samples			
Material	Bulk analysis	Surface analysis	Liquids	Gases
Inorganic	J. E. Harrar (R. Lim)	R. G. Meisenheimer (J. W. Fischer)	J. E. Harrar (R. Lim)	R. W. Crawford (R. G. Meisenheimer)
Organic	R. W. Crawford (R. G. Meisenheimer)	R. G. Meisenheimer (J. W. Fischer)	R. W. Crawford (R. G. Meisenheimer)	R. W. Crawford (R. G. Meisenheimer)

[a] Special analytical problems or requests should be brought to the attention of R. G. Meisenheimer.

Spectroscopic Techniques

INFRARED SPECTROSCOPY

Molecular absorption of infrared energy results in the excitation of various modes of vibration. Each molecule has characteristic absorption frequencies particular to that molecule. The infrared spectrum is a plot of the energy transmitted by a sample versus its frequency. Absorption regions can be very sharp, particularly for gases, or very broad, as for some solids. A few vibrational modes for some organic molecules will be localized in functional groups. This localization produces characteristic group frequencies that can be used to identify parts of the compound being studied (e.g., hydroxyl, ether, carbonyl, and ester). The amount of infrared absorption is determined by the quantity of sample in the beam.

Field of Application

Infrared spectroscopy is applicable for molecular and functional analysis of all organic and some inorganic materials.

Uses

Qualitative

Infrared spectroscopy can be used for material identification of both mixtures and pure compounds, for functional group identification in organic compounds and isomers, and for polyatomic cation and anion identification in inorganic materials.

Quantitative

Accuracy. This technique is generally accurate to within ±5% of the amount of element present, although accuracy can be within ±1% in some cases. The accuracy produced by differential analysis can be as much as a factor of five better.

Sensitivity. Usually compounds can be determined at concentrations of a few percent. Special techniques can lower this to less than 0.1%.

Sample

State

Samples submitted for analysis may be liquids, solids, or gases.

Amount

Normally 10 to 100 mg of sample is required for analysis, but a few milligrams is sometimes sufficient.

Preparation

No particular preparation is required, except for removal of water.

Time Required

About 1 h is normally required to obtain a spectrum (Fig. 1), although faster scans or manual checks can be made. Analysis of complex unknowns may take a few days.

Instruments

The instruments available for infrared spectroscopy include a Perkin-Elmer Model 283 Infrared Spectrometer for the 4000–200 cm $^{-1}$ (2.5–50 μm) spectral region, and a RIIC FS-520 Far-Infrared Interferometer for the 400–10 cm $^{-1}$ (25–1000 μm) spectral region.

Location and Staff

Russ Sanborn is in charge of the infrared spectrometers, which are located in Room 1510 of Bldg. 222.

Examples

Examples of the use of infrared spectroscopy include:

- Identification of plastics and resins as polyethylene, Mylar, PVC, PVA, polystyrene, epoxy, etc.
- Identification of explosives and mock high explosives.
- Determination of residual hydrocarbons in Freon flushings of welded vessels.
- Analysis of surface contaminants such as silicone grease or pump oil.
- Analysis of surface coatings by attenuated total reflectance.
- Far-IR analysis of impurities in high-purity germanium.

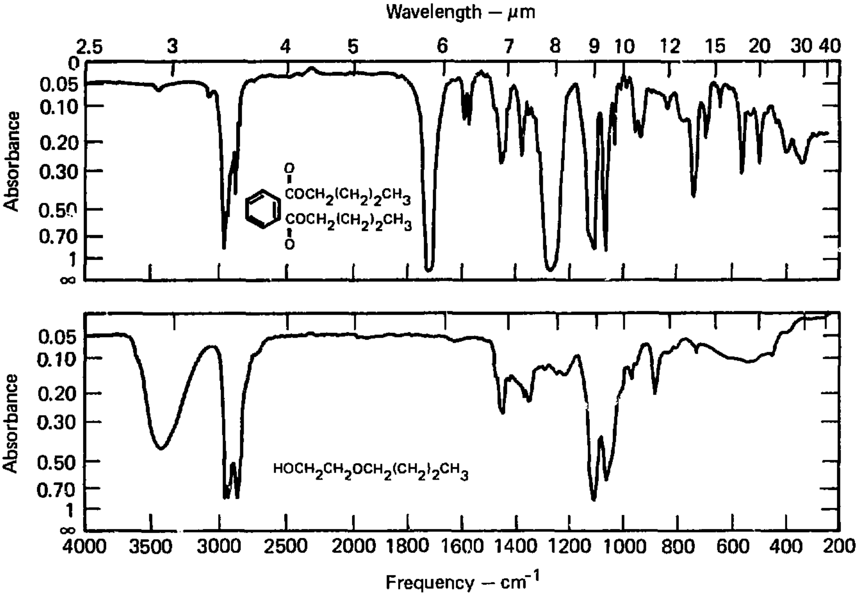


Figure 1. Infrared spectra of dibutyl phthallate (upper) and ethylene glycol monobutyl ether (lower).

VISIBLE AND ULTRAVIOLET SPECTROPHOTOMETRY

Certain bonding electrons are excited from their normal ground state when exposed to ultraviolet, visible, or near-infrared radiation. Samples in beams of such radiation absorb energy at wavelengths corresponding to the energy required for electronic transition. The probability of transition and the polarity of the excited state govern the amount of absorption. A spectrophotometer records absorption as a function of wavelength, and the resulting pattern is a summation of the absorbing species in the sample. The intensity of absorption is a function of the amount of absorbing substance in the sample.

Field of Application

Visible and ultraviolet spectrophotometry is applicable for qualitative and quantitative determination of molecular and ionic species that absorb light in the ultraviolet, visible, and near-infrared.

Uses

Qualitative

The absorption spectrum (Fig. 2) is useful in identifying many compounds. In some cases, the absorption spectrum of a mixture may be deconvoluted into its separate compounds.

Quantitative

Accuracy. Visible and ultraviolet spectrophotometry has a typical accuracy of 0.1 to 1%.

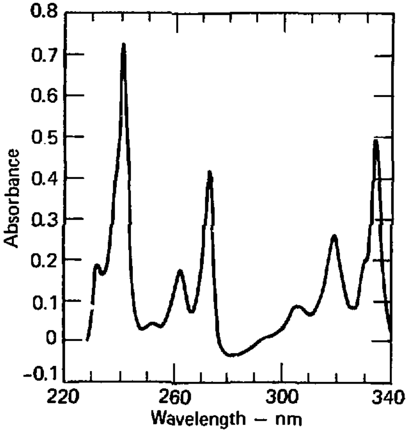


Figure 2. Ultraviolet absorption spectrum of $1 \times 10^{-5} M$ pyrene in hexane vs hexane, 1-cm-pathlength cell.

Sensitivity. The limit of detection depends on the molecular extinction coefficient. Detection of microgram quantities is sometimes possible.

Sample

State

Samples submitted for analysis may be liquids, gases, or solutions.

Amount

Convenient sample quantities range from 4 g to 10 mg.

Preparation

No particular preparation is required, although special procedures may be necessary after sample receipt to enhance the molecular extinction coefficient.

Time Required

The average time required for sample analysis depends on sample preparation, standardization procedures, desired accuracy, etc. This time ranges from 1 to 4 h; however, actual laboratory turnaround time is about 1 to 2 wk.

Instruments

A Cary Model 14 spectrophotometer is used for analysis.

Location and Staff

Spectrophotometric analysis is performed in Room 1511 of Bldg. 222. Roman Bystroff and Gilbert Haugen are responsible for operation of the spectrophotometer.

Examples

Spectrophotometry has been used for the determination of neodymium in neodymium-doped laser glasses.

ATOMIC ABSORPTION SPECTROSCOPY

A hollow cathode emits a line spectrum of the element to be determined. Samples are usually heated to a high temperature by burning in a flame, which breaks up chemical bonds between molecules, producing free ground-state atoms. Atoms in this condition can absorb energy at the resonance lines and attenuate these lines from the hollow cathode. A monochromator isolates a resonant wavelength and rejects all others, and a photodetector sees only the resonant line diminished in strength by sample absorption. Matrix interferences occur when the flame is unable to break up all chemical bonds in the sample, thus decreasing the efficiency of production of atoms of the element to be determined.

Field of Application

Atomic absorption spectroscopy is applicable for analyzing organic and inorganic materials to determine individual elements.

Uses

Qualitative

Atomic absorption spectroscopy has no known qualitative use.

Quantitative

Precision. Atomic absorption spectroscopy has a relative precision of 1 to 5% using flame techniques, or of 5 to 10% using flameless techniques.

Sensitivity. Flameless techniques can determine over 30 elements in solution at concentrations of 0.1 to 5 μg/ml.

Sample

State

Samples submitted for analysis may be liquids or solids.

Amount

About 1 to 5 g of solid sample is sufficient for several trace element determinations. For elements in greater than 0.1% concentration a minimum of 0.1 g is required. If the history of the solution is known, 5 to 10 ml of solution is adequate for quantitative analysis; if nothing is known about the sample, more solution will be required.

Preparation

No special sample preparation is required other than suitable packaging to avoid contamination.

Time Required

About 10 min of instrument time or 1 h overall time is required for determination depending on how hard the sample is to put into solution and the matrix it is in.

Instruments

The single-beam instrument used for atomic absorption spectroscopy is built around a 0.5-m Jarrell-Ash monochromator. Its components include a PAR Model 120 lock-in amplifier, a Fluke Model 4130, high voltage, dc power supply, an LLL current regulator, and a Techtron laminar-flow burner. The signal is fed into a Vidar V-to-F converter, and is processed by an Eclipse time-share computer (see Fig. 3). A Jarrell-Ash 810, double-beam spectrophotometer is available for routine work, and a graphite-tube furnace is on hand for ultratrace analyses. This sampling device is fitted to a Perkin-Elmer Model 305 BG spectrophotometer.

Location and Staff

William Sunderland and Miles Waggoner are in charge of the instruments, which are located in Room 1515 of Bldg. 222. Robert Lim is also available for consultation.

Examples

Anything that can be put into solution can be analyzed by atomic absorption for its metallic content. Atomic absorption spectroscopy has been used to analyze:

- Various alloys and plating solutions.
- Organic materials such as polymers and adhesives for trace metals and catalysts.
- Coal, oil shale, rocks, ores, and soils for inorganic constituents.
- Solutions from mineral extraction and natural waters.

```
                                  ATOMIC ABSORPTION ANALYSIS REPORT

DATE:   7 / 15 / 1977

ELEMENT AND SAMPLE SOURCE:  COPPER TYPED DATA

                                AVERAGE CONC.(PPM)     RELATIVE STANDARD   % RELATIVE STANDARD   AVERAGE % RECOVERY
SAMPLE NO. AND DESCRIPTION          OF 3 RUNS              DEVIATION            DEVIATION         SPIKE,STD, OR UNK.

  NO.   1   FIRST....               2522.57                  2.444                0.96              ----------
  NO.   2   SECOND...               503.175                  2.742                0.54              ----------
  NO.   3   THIRD....               75277.4                  3.076                0.40              ----------
  NO.   4   REAGBLNKK               2522.57                  2.444                0.96              ----------
  NO.   5   C&3......               752.775                  3.076                0.40               100.37
  NO.   6   SP12.....               752.775                  3.076                0.40                99.84
  NO.   7   OU1......               2522.57                  2.444                0.96               100.00
```

Figure 3. Computer printout of atomic absorption analysis report.

X-RAY FLUORESCENCE SPECTROMETRY

An outer shell electron will immediately fill the vacancy created by a K or L shell electron of an atom ejected by absorption of an x-ray photon. Energy appears as a photon with wavelength and energy characteristic of the originating atom. The originating atom is identified by detection of the photon and measurement of its wavelength in a wavelength-dispersive spectrometer or of its energy in an energy-dispersive system. The number of photons per unit time is proportional to the concentration of the element present. Correction must be made for photon absorption within the sample by any of the elements present.

Field of Application

X-ray fluorescence is applicable for quantitative and qualitative analysis of organic and inorganic materials. It is useful for elements with $Z \geqslant 13$. Trace analyses are routine for elements in low-Z matrices.

Uses

Qualitative

Energy-dispersive x-ray fluorescence can be used to rapidly identify and estimate the relative amount of each element in a sample.

Quantitative

Accuracy. The use of x-ray fluorescence for accurate determination is generally dependent on the standards made with a matrix identical to the samples being analyzed or on samples to which impurities may be added for standardization. Semitheoretical correction for matrix and interelement effects is also possible. Accuracy at low concentrations is equal to the detection limit. The accuracy for concentrations greater than 100 times this amount is about 1% of the amount of element present when good standardization is possible.

Sensitivity. The sensitivity or detectability of the as-received sample depends on the composition of the sample and the element to be determined. The best detectability for any element is in a low-Z matrix, and the elements in the middle of the periodic chart ($23 < Z < 53$) have the best detectability in any matrix.

Detectability normally falls between 1 to 60 ppm in low-Z matrices. Examples of detectability include 10 ppm sulfur in an organic matrix; 1 ppm zinc and 0.3 ppm molybdenum in B_4C; 30 ppm zinc and 100 ppm uranium in rocks; and 0.01% nickel in steel.

The elements of interest may be preconcentrated before analysis, which results in lower detectability. The impurities in water may be precipitated or collected on filter paper by ion exchange. Detectabilities obtainable with such an optimized sample range from 0.05 to 2.5 μg. Sample size determines the maximum weight or volumetric basis of detectability (e.g., 0.1 μg/100 ml ≈ 1 ppb).

Sample

State

Samples submitted for analysis may be liquids or solids.

Amount

A minimum of 1 g of powder, 5 ml of liquid, or a 2.5 cm^2 by 0.3 cm piece of solid is required for precise determination. A speck is sufficient for qualitative determination of major elements. Samples are not destroyed in analysis.

Preparation

Sample preparation is not generally required; however, powders should be ground to pass a 325 mesh screen (about 40 μm), and solid pieces should be polished for precise determination.

Time Required

Identification and approximate relative intensity ratios for common elements with $Z \geqslant 20$ can be determined in about 10 min. Quantitative and trace analyses require more time. From 4 to 8 h per sample is needed to determine all measurable elements semiquantitatively. Laboratory turnaround time is generally 1 to 2 wk.

Instruments

Three instruments are usually available for x-ray fluorescence spectrometry; two are energy-dispersive, the other is wavelength-dispersive.

One energy-dispersive spectrometer uses a Kevex lithium-drifted silicon detector and electronics and a Northern Scientific pulse-height analyzer. Spectral dispersion is accomplished electronically by pulse-height analysis. This instrument simultaneously analyzes about 20 elements and displays the spectrum. Spectra are accumulated digitally in the pulse-height analyzer, simplifying peak intensity measurements. These spectra may be photographed or recorded on an X–Y recorder.

The other energy-dispersive spectrometer utilizes an Ortec high-purity germanium detector and electronics and a Northern Scientific pulse-height analyzer. A 150-kV x-ray tube is used for excitation. This spectrometer is particularly useful for measuring elements with Z ⩾42 where excitation of K lines is difficult or impossible or where spectral overlap causes problems with other spectrometers, such as for rare earths in glasses or other materials.

The wavelength-dispersive x-ray spectrometer is a Norelco-Philips Universal Vacuum. Spectral dispersion is accomplished by Bragg reflections from crystals using a goniometer for angular measurements. Either a gas-flow proportional or scintillation detector may be used. The wavelength-dispersive spectrometer is used primarily when resolution is insufficient with the energy-dispersive spectrometers or for low-Z elements such as sulfur because of better sensitivity with the proportional counter.

Location and Staff

The x-ray fluorescence laboratory is located in *Room 1514 of Bldg. 222. Richard Ryon and Don* McKenzie are responsible for operation of the equipment.

Examples

X-ray fluorescence spectrometry has been used to:

- Analyze pure materials such as plastics, explosives, water, boron, coal, and biological tissues for trace elements.
- Identify alloys and determine the composition of rocks, minerals, and corrosion products.
- Detect sulfur in coal, oils, and explosives.
- Identify doping elements in laser glasses (being developed).
- Determine refractory elements such as tungsten, molybdenum, and uranium at trace levels.
- Determine the presence of all elements with Z ⩾13 (see Fig. 4).

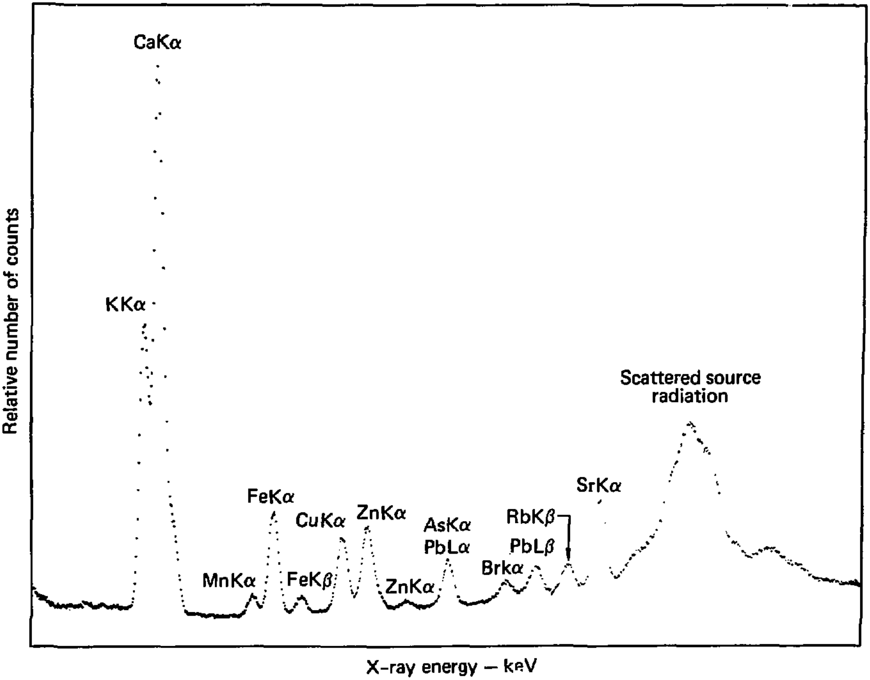


Figure 4. X-ray fluorescence spectrum of NBS orchard leaves.

MICROWAVE SPECTROSCOPY

Microwave spectroscopy is typical of other spectrometric techniques in that radiation is passed through a sample, and the amount of radiation absorbed is determined by a detector. It is, however, unique in at least two respects. Microwave spectroscopy takes advantage of discrete, molecular, rotational-resonant absorptions, rather than the vibrational absorptions used by other techniques. It also produces very sharp absorption lines because microwave radiation can be produced virtually monochromatic. These sharp absorptions give the technique a resolving power superior to any other, which enables it to specifically identify compounds sensitive to microwave absorption.

Field of Application

Microwave spectroscopy is applicable for qualitative and quantitative analysis of low molecular weight gases and liquids having moderately high dipole moments (methanol, vinyl chloride, sulfur dioxide, water, ammonia, acetonitrile, acetone, carbonyl sulfide, and others). It can also be used for determining molecular dipole and quadrupole moments and for gaseous free radical detection.

Uses

Qualitative

Microwave spectroscopy is used for positive and rapid identification of compounds in complex mixtures.

Quantitative

Accuracy. Microwave spectroscopy is accurate to within 1 to 20% of the amount of compound present, depending on the compound and the extent of calibration.

Sensitivity. This technique has a sensitivity of less than one to several hundred parts per million.

Sample

State

Samples submitted for analysis may be gases, liquids, or gas- and liquid-containing solids.

Amount

The amount of sample required for analysis ranges from 0.1 cc for liquids to 5 cc for gases.

Preparation

Sample preparation is usually unnecessary.

Time Required

Two or more hours are required for analysis, depending on the compound, mixture, sensitivity, and desired accuracy.

Instruments

Most of the microwave spectrometer is constructed from Hewlett-Packard components and accessories. A gas chromatograph is interfaced to the spectrometer, and the combination has proven a powerful qualitative and quantitative tool for a variety of applications.

Location and Staff

The microwave spectrometer is located in Room 1114 of Bldg. 222. Robert Morrison is responsible for spectrometer operation and consultation. Larry Hrubesh, who serves as backup for the spectrometer, is also available for consultation.

Examples

Microwave spectroscopy used in conjunction with gas chromatography is a powerful quantitative tool for accurately determining specific components in complex mixtures (e.g., methanol in a gasoline-water-methanol mixture). Figure 5 is a readout of an actual analysis. Note only the component of interest appears. Other typical applications include:

- Detection of carbonyl sulfide or sulfur dioxide in oil shale retort effluent.
- *Identification of phenols and amines from* coal-gasification experiments.
- Determination of isotopic ratios of hydrogen and deuterium in deuterated ammonia.
- Determination of water in a variety of substances.

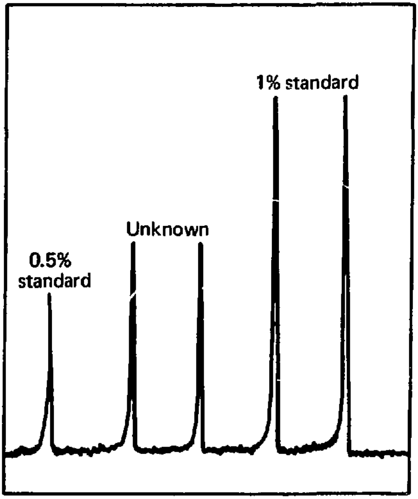


Figure 5. Chart recording of an analysis of methyl alcohol in gasoline by gas chromatography/microwave spectroscopy. Peaks for the 29636.933-GHz absorption of methyl alcohol are shown for sample and standard.

NUCLEAR MAGNETIC RESONANCE

Nuclear magnets align in specific orientations with respect to a steady magnetic field, H, when a sample with nuclei that have magnetic dipole moments is placed in the field. The energy difference between orientations is $\gamma hH/2\pi$, where γ is the magnetogyric ratio of the nucleus and h is Planck's constant. Nuclei are made to flip from one orientation to another by applying a weak magnetic field oscillating at resonance frequency $\nu = \gamma H/2\pi$. Nuclei at the resonance condition absorb energy from the field, and this energy is detected and plotted. Spectra are obtained by holding either ν or H constant and continuously varying the other parameter to reach the resonance condition, or by use of pulse techniques and Fourier transformations. A homogeneous field is needed for high-resolution, nuclear magnetic resonance because spectral line widths are of the order of 0.1 Hz when random molecular motions are very fast (true of fluids only). Partial shielding of the sample nucleus from the externally applied magnetic field is caused by electrons around the nucleus. Shielding variations from one part of a molecule to another cause shifts among spectral positions of the nuclear isotope. Magnetic nuclei in a molecule may be coupled by bonding electrons. This spin-spin coupling process gives characteristic splitting of chemically shifted absorption peaks, and patterns are determined by the number of coupled nuclei, the magnitude of coupling, and chemical shift differences. The area of a spectral line is proportional to the number of nuclei producing that line, and the magnitude of coupling reflects the type and orientation of chemical bonds separating coupled nuclei. This permits quantitative measurements to be made without a standard spectrum of the sample being examined.

Field of Application

Nuclear magnetic resonance is applicable for analysis of materials (usually organic) containing magnetic nuclei.

Uses

Qualitative

The nuclear magnetic resonance method is used to determine the molecular structure of pure and impure materials. With this method, it is possible to distinguish between different configurations or conformations of a molecule, to identify components in mixtures, to determine the direction and extent of chemical reactions, and to evaluate the purity of a compound without standards.

Quantitative

Accuracy. One can use the nuclear magnetic resonance technique to assay for specific components, functional groups, total hydrogen, deuterium, fluorine, etc. This technique can also be used to measure the rate of kinetic processes in a 1 to 10^5/s range and to determine the amount of element present to within 1 to 2%.

Sensitivity. The sensitivity of this analytical technique varies with the nucleus observed. It is most sensitive to protons (^1H) and fluorine (^{19}F) for which 1 mg in 0.5 ml of solution gives an adequate signal. As little as 10 μg may be observed with time averaging.

Sample

State of Sample

Liquid samples may be submitted for analysis. Temperatures may be varied from −150°C to 200°C.

Amount

About 0.1 to 0.5 gm of sample is needed for best observation. An adequate spectrum of the main component can be obtained with 1 mg, and smaller components can be observed with time averaging.

Preparation

Samples should be dissolved in solvents containing a minimum amount of the nucleus to be observed. Liquid samples are often run neat, and the method is nondestructive.

Time Required

The time required for analysis varies with the problem to be solved. A simple structure conformation can be done in about 1 h, whereas a ^{13}C structure may require averaging a few thousand transients. Complex structural analysis could take 1 to 2 wk. Since the instruments involved are not heavily used, some startup time may be required.

Instruments

The LLL Fast Fourier Transform (FFT) spectrometers used for analysis operate at a fixed field of

14,092 G. Frequency can be varied from 2 to 60 MHz in any increment desired, and existing nuclear magnetic probes can be used throughout this frequency range. The FFT spectrometer has fluorine and proton external lock capabilities as well as internal lock capabilities for a few nuclei (i.e., protons, fluorines, and deuterium). Fourier transformation occurs in a 16K minicomputer. The FFT can also be used in a continuous wave operational mode with an LLL ensemble averager. An LLL continuous wave spectrometer incorporates most features of the FFT except its time-domain (pulse) capabilities.

Location and Staff

The FFT nuclear magnetic resonance and continuous wave spectrometers are located in Room 1224 and 1220 of Bldg. 222. James Happe is responsible for analytical services.

Examples

The instruments employed in nuclear magnetic resonance can:

- Measure spin-lattice relaxation times of ^{31}P nuclei in protein-substrate complexes.
- Detect ^{13}C proton-decoupled spectra in sample tubes as large as 15 mm.
- Determine natural level ^{2}H signals to high precision for analytical needs.
- Determine the structure of a wide variety of samples.

TIME-RESOLVED PHOTOLUMINESCENT SPECTROSCOPY

The observed radiative lifetimes of molecules with similar spectral properties may vary appreciably depending on intramolecular and intermolecular environments. Light absorption takes place within about 10^{-15} s. Emissions from the lowest excited singlet state have radiative lifetimes of 10^{-9} to 10^{-6} s, while the lifetimes of those from the triplet state range from 10^{-3} to 10^{2} s. If two or more molecules with similar absorption and emission spectra have different radiative lifetimes, it may still be possible to measure the concentration of species in a complex mixture. The relative contribution of the various species to observed luminescence will change predictably when the time between excitation and observation is varied.

Field of Application

Time-resolved photoluminescent spectroscopy is applicable for determining the lifetimes of the excited and triplet states of many organic and inorganic compounds. It is also useful for qualitative and quantitative spectroscopic separation of mixtures in organic, inorganic, and biomedical matrices.

Uses

Qualitative

This technique can identify substances by observing differences in their fluorescent and/or phosphorescent lifetimes.

Quantitative

Accuracy. Instrumental and intrinsic molecular parameters affect accuracy; however, typical accuracies range from 10 to 1%.

Sensitivity. The sensitivity obtained with quinine sulfate in sulfuric acid is better than 1 ppb, and linearity is typically better than 1%. The intrinsic molecular parameters of the sample control the limit of detection.

Sample

State of Sample

Samples submitted for analysis may be solids, liquids, or solutions.

Amount

Convenient quantities for analysis range from 4 g to 10 mg.

Preparation

No particular sample preparation is required, although special procedures may be needed to enhance luminescence.

Time Required

The average time for sample analysis depends on sample preparation, standardization procedures, desired accuracy, etc. This time usually ranges from 1 to 4 h, and actual turnaround time in the laboratory is 1 to 2 wk.

Instruments

The nanosecond fluorescence spectrometer for time-resolved measurements is an Ortec 9200. A short-duration, optical light pulse excites the sample, and the spectrometer measures the decay time of the subsequent fluorescence. Single photon counting is used to measure the very low light levels associated with decay. The current pulse from the photomultiplier tube is amplified and fed to a discriminator. Analog-to-digital conversion and data storage are accomplished with a multichannel analyzer. Experimental data can be displayed in several formats or transferred to a computer for further processing. The sensitivity, stability, and accuracy of this system are orders of magnitude greater than those produced by analog techniques.

Location and Staff

The nanosecond fluorescence spectrometer is located in Room 1519-A of Bldg. 222. Gilbert Haugen is responsible for operation of this instrument.

Examples

This system measures single and multiple decay-time constants as short as 2 ns. Figure 6 shows an emission spectrum of quinine bisulfate in 0.05*M* H_2SO_4. The excitation wavelength was 300 nm, and band assignments were as follows:

(a) First-order scattering of excitation radiation.

(b) *Raman scattering by the solvent.*

(c) Fluorescence emission.

(d) Second-order scattering of excitation radiation.

(e) Second-order scattering by the solvent.

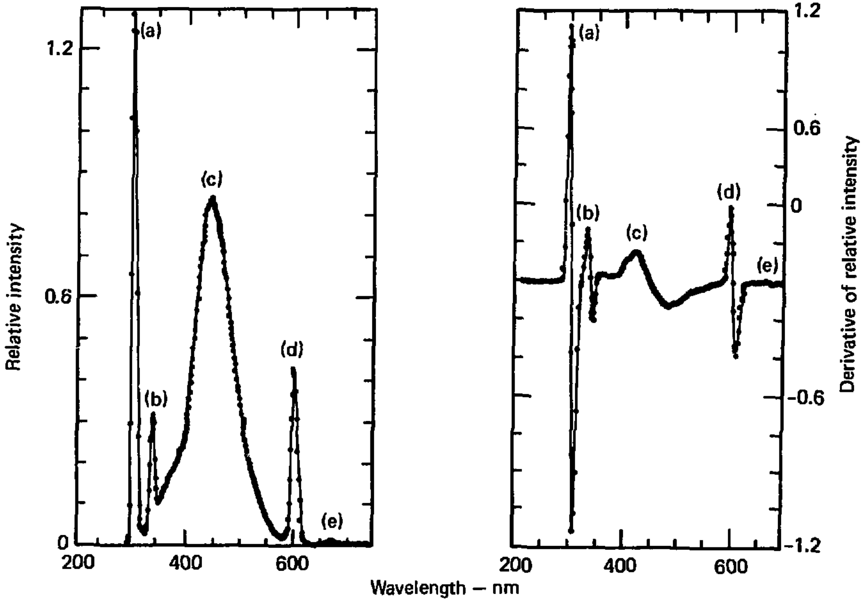


Figure 6. Emission spectrum of quinine bisulfate in 0.05*M* H_2SO_4.

ATOMIC-EMISSION SPECTROSCOPY

Each element in the vapor state emits a characteristic spectrum when suitably excited by an arc, spark, or other means. Radiation thus emitted passes into a spectrograph or spectrometer and is resolved into component wavelengths. These wavelengths are recorded photographically as a definite pattern of spectral lines or photoelectrically on a phototube array. The spectral lines are a unique property of the atoms and are unaffected by the initial physical state or chemical combination of the atoms. The position and intensity of these lines determine qualitatively and quantitatively the presence and amount of each element in a sample.

Field of Application

Atomic-emission spectroscopy is applicable for elemental analysis of organic and inorganic materials.

Uses

Qualitative

Emission-spectrochemical analysis will detect all elements except inert gases, halogens, hydrogen, carbon, nitrogen, oxygen, sulfur, selenium, and tellurium. Special techniques are required for detection of these elements.

Quantitative

Accuracy. Although routine procedures using a spectrograph are available, they are usually developed on request. Accuracy is generally within ±5% of the amount of element present.

Aqueous solutions may be analyzed with a spectrometer and an inductively coupled plasma (ICP) source. Accuracy is usually within ±2% of the amount of element present. This technique is limited to 17 common elements.

Sensitivity. Sensitivities to several parts per billion may be obtained with a spectrometer and ICP source.

Semiquantitative

Accuracy. The true value is usually within one-half to two times the reported value for elements in the 0.0001 to 0.5% by-weight range. Accuracy in by-weight determinations of 1 to 20% tends to decrease with increasing concentration.

Sensitivity. The limit of detection for most elements is in the 0.0001 to 0.01% by-weight range. Lower detection limits may be obtained by concentration or some other technique. Detection limits for the elements vary with the matrix and spectrochemical procedures used.

Sample

State

Samples submitted for analysis may be liquids or solids.

Amount

At least 5 mg of sample is required for analysis. Convenient quantities are 20 ml of liquid and 1 g of solid.

Preparation

No particular sample preparation is necessary.

Time Required

An average of 2 h per sample is needed for semiquantitative analysis, although 4 h may be required to analyze samples needing extensive preparation or having complex spectra. A quantitative analysis, exclusive of standardization procedures, requires at least 4 h with spectrographic techniques or 5 min with ICP-spectrometric techniques. Actual turnaround time in the laboratory is 1 to 2 wk.

Instruments

The instrument used for spectrographic analysis is a 3.4-m Jarrell-Ash, Ebert-mount spectrograph. The spectrometric instrument is a 0.75-m Jarrell-Ash Atomcomp. Other specialized instrumentation is available.

Location and Staff

Edgar Peck is responsible for the spectrometric section in Room 1520 of Bldg. 222. He is assisted by Bea Armstrong. William Morris, Ralph Gutmacher, and Earl Worden are available for consultation.

Examples

Examples of the use of atomic-emission spectroscopy include:

- Analysis of pure materials such as metals, plastics, compounds, water, and solutions for trace elements.
- Identification of alloys and unknown materials.
- Analysis of rocks, minerals, and corrosion products for approximate compositions.

Electrochemical Techniques

CONTROLLED-POTENTIAL COULOMETRY

The potential of an electrode can be controlled by a potentiostat at a level that precludes unwanted electrode reactions. Substances are exhaustively electrolyzed at this electrode, and those with oxidation-reduction or formal potentials near that of the ion being determined constitute interferences. As the electrode reaction proceeds in a normal electrolysis, electric current decreases exponentially until a background current is attained. Electrolysis is then terminated. A current-time integrator measures the amount of electricity required by the reaction. This allows calculation of the mass of the substance being determined from Faraday's Law (electrical calibration) or from calibrations of the instrument obtained by running standards (chemical calibration). Determinations based on electrical calibrations are absolute in that they are referred to the fundamental physical quantities of time and electric current. Coulometry is unique in this respect and thus is often used as a standard technique for analysis.

Field of Application

Controlled-potential coulometry is applicable for determining organic and inorganic substances when high accuracy and precision are required and use of a small sample is desirable. It is particularly useful for determinations of uranium, plutonium, coinage and platinum metals, and many transition elements. Indirect determinations of other substances are also possible.

Uses

Qualitative

Although coulometry may have a qualitative use, it is seldom utilized in that way.

Quantitative

Accuracy. This general technique of quantitative chemical analysis is similar in scope to oxidation-reduction titrimetry. It can also be used for sequential determination of several components in a mixture and for determination of the distribution of several oxidation states of a single element in a mixture. If there are no interferences, this technique is accurate to ±0.1% of the amount of element present in assay determinations.

Sensitivity. Not applicable.

Sample

State

Any material capable of solution in an electrically conducting solvent can be used for analysis.

Amount

From 1 to 10 mg of sample are ideal for each determination. The volume of solution should not exceed about 10 cm^3.

Preparation

Preparation can include any chemical scheme that makes a substance susceptible to electrolysis. Common dissolution methods are usually suitable for solid substances. Strongly complexing ligands that shift the oxidation-reduction potential of the substance must be avoided or removed.

Time Required

From 10 to 60 min of instrument time is needed for each determination once the solution has been prepared. The overall time varies from about 1 h to 2 d, depending on the dissolution and pretreatment steps required.

Instruments

The equipment for controlled-potential coulometry includes electrolysis cells (see Fig. 7), potentiostats, and integrators. A digital voltmeter measures and displays the voltage.

Location and Staff

Most controlled-potential coulometry facilities are located in Room 1524 of Bldg. 222. The facility for analysis of alpha-active materials such as plutonium and neptunium is in Bldg. 332. Jack Harrar is responsible for operation of the coulometry facilities. Les Rigdon and Fred Stephens are available for consultation, and Miles Waggoner is an experienced operator. John Walden is the contact for Bldg. 332.

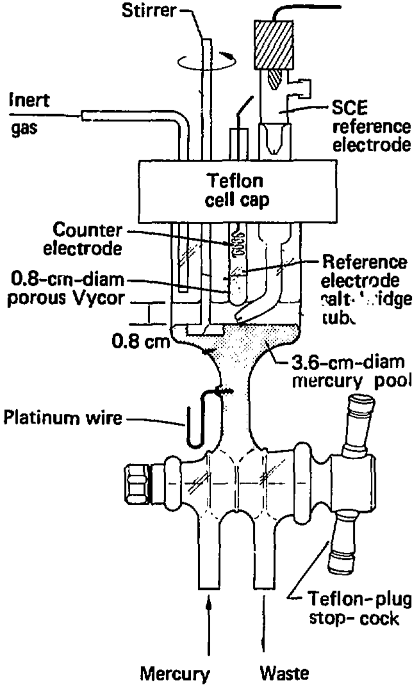


Figure 7. Mercury pool electrolysis cell.

Examples

Controlled-potential coulometry can determine:

- Gold, silver, palladium, and copper in electroplating solutions.
- Both uranium and copper in a mixture.
- Vanadium, manganese, iron, and titanium in alloys.
- Gold in thin films.
- Fe(III)/Fe(II) ratios.
- Nitrite ion and organic nitrates such as PETN.

ION-SELECTIVE, ELECTROMETRIC, AND COULOMETRIC TITRATIONS

Titration is defined by the International Union of Pure and Applied Chemists as "the process of determining a substance A by adding increments of substance B, with provision for some means of recognizing the point at which all of A has reacted, thus allowing the amount of A to be found from the known amount of B added up to this point (the end point), the reacting ratio of A and B being known." Substance B is added in a measured solution in all titrimetric techniques except coulometry. In coulometry, a controlled current effects an electrolysis and generates substance B *in situ*. A titration can be further classified according to the property of the solution sensed during titration (e.g., pH titration by glass electrode sensor or oxidation-reduction potentiometric (redox) titration).

Field of Application

Titrations are applicable for determining organic and inorganic substances in general solution-analytical schemes.

Uses

Qualitative

Titrations have no qualitative use except for indirect identification of functional groups on organic compounds.

Quantitative

Accuracy. This quantitative analytical technique can analyze only one component at a time. If no interferences are present, it can determine the amount of substance in the sample to within ±0.1 to 0.5%.

Sensitivity. Not applicable.

Sample

State

Any material capable of solution in an electrically conducting solvent can be used for analysis.

Amount

Ideally, 0.1 to 5 g of sample should be submitted for analysis; however, procedures can be scaled down with a corresponding loss of accuracy and precision.

Preparation

Common dissolution methods are usually suitable for solid samples. Solution samples can often be analyzed directly.

Instruments

The instruments and equipment needed for titration include pH and ion-activity meters, conductivity apparatus, constant-current sources, a PAR Model 174A polarograph, and various types of electrodes.

Location and Staff

The facilities for titration are located in Rooms 1314, 1515, 1523, 1524, and 1525 of Bldg. 222. R. Lim, W. Boyle, F. Stephens, W. Selig, and J. Harrar are the contacts for pH or oxidation-reduction titration. For ion-selective electrode titration, contact R. Lim, W. Boyle, F. Stephens, W. Selig, or J. Harrar. J. Harrar and F. Stephens can also be contacted for coulometric, amperometric, or conductometric titration.

Examples

Examples of the use of titration techniques include:

- pH determination of boron by mannitol, acid-base titration.
- Redox determination of uranium by Davies-Gray titration.
- Ion-selective determination of chloride in explosive mixtures.

ELECTROGRAVIMETRY

The substance determined is electrodeposited from an aliquot of sample solution onto an inert, working electrode that has been preweighed. Electrodeposition can be carried out at constant cell voltage, constant cell current, or controlled potential. When deposition is complete, the electrode is reweighed to obtain the quantity of substance deposited. The substance is then chemically stripped off the electrode.

Field of Application

Electrogravimetry is applicable for determining metals that can be plated onto solid electrodes. It is used when high accuracy, high precision, and independence of standards are desired.

Uses

Qualitative

Electrogravimetry has no qualitative use.

Quantitative

Accuracy. This quantitative technique can determine the amount of substance in a sample with better than 0.1% accuracy if no interferences are present.

Sensitivity. Not applicable.

Sample

State

Any material capable of solution in an electrically conducting solvent can be used for analysis.

Amount

Ideally, 0.1 to 1 g of sample should be submitted for analysis; however, procedures can be scaled down to about 10 mg with a corresponding loss of accuracy and precision.

Preparation

Common dissolution methods are usually suitable for solid samples. Solution samples can often be analyzed directly.

Time Required

Electrolysis may take from 1 h to 1-1/2 d, depending on the substance determined. The overall time required for analysis ranges from 1 h to several days, depending on the substance and the chemical pretreatment steps required.

Instruments

A regulated dc power supply of 20 V at 5 A and suitable electrolysis cells are required for electrogravimetry at constant voltage. Electrogravimetry measurements at constant potential require a 25-V potentiostat and suitable electrolysis cells.

Location and Staff

Electrogravimetry facilities are located in Rooms 1523 and 1524 of Bldg. 222. Jack Harrar is the principal contact. Fred Stephens and Miles Waggoner are also familiar with the technique and instrumentation.

Examples

Electrogravimetry has been used to assay copper in $CuSO_4$ solutions with a 0.002% bias and a relative standard deviation of 0.008%. About 150 mg of metal was plated for each determination.

POLAROGRAPHY

Many organic and inorganic species can accept or give up one or more electrons at a specific potential. When the potential of one of two electrodes placed in a solution containing such an ion is varied, the potential-vs-current curve that results is called a polarogram. An electrochemically inert salt such as potassium chloride must be present in the supporting electrolyte to provide a conducting path for the current. The magnitude of the polarographic wave in the polarogram is a function of the amount of electroactive species present.

Field of Application

Polarography is applicable for analysis of electrochemically reducible and/or oxidizable organic and inorganic ions.

Uses

Qualitative

Polarography is used to identify trace amounts of ionizable species in compounds and mixtures and to determine the number of electrons required for reduction or oxidation.

Quantitative

Accuracy. The concentration of analyte in a sample can be determined with ±10% accuracy in routine use. Accuracies of ±1 to 2% may be obtained with more time-consuming techniques.

Sensitivity. Detection is usually limited to about 1 ppm in solution depending on the ionic species. Lower sensitivities may be achieved with some sacrifice of accuracy.

Sample

State

Samples submitted for analysis may be solids, liquids, or gases that can be brought into solution, particularly aqueous solution.

Amount

Sample size depends on the type and amount of analyte in the sample. About 5 g of solid sample is convenient. The size of liquid samples will depend on the concentration of the species being investigated.

Preparation

Solid samples should be put into solution and diluted with the appropriate supporting electrolyte.

Time Required

Actual measurement time can vary from 10 to 45 min because of the polarographic technique used and sample preparation required. Analysis can take from 1 h to many hours, depending on the characteristics of the sample.

Instruments

A Princeton Applied Research polarograph (Model 174A) is used to analyze a variety of sample materials. An LLL-constructed differential polarograph is also available.

Location and Staff

The electroanalytical facilities are located in Room 1524 of Bldg. 222. Jack Harrar is responsible for this section, and Fred Stephens is available for consultation. Polarographic analysis of explosive materials is performed by Walt Selig and Glenn Crossman.

Examples

The need for trace-level detection of heavy metals in a variety of materials (e.g., biological fluids, food, and sea water) resulted in a polarographic technique known as differential pulse anodic stripping (DPAS). The sensitivity of this technique requires the analyst exercise extreme care in sample preparation and measurement to obtain meaningful results.

Ordinary differential pulse polarography is related to the DPAS technique. Figure 8 shows its application in an analysis for an explosive compound.

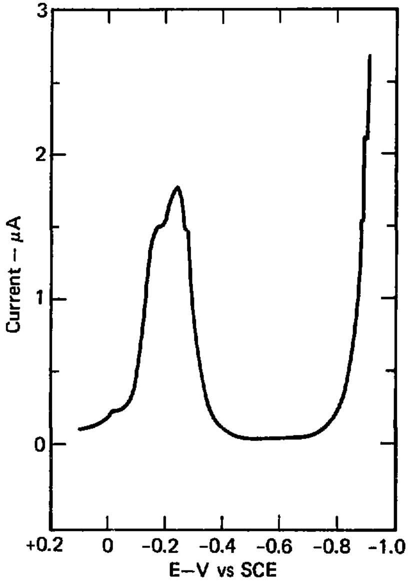


Figure 8. Differential pulse polarogram of saturated solution of TATB (1,3,5-triamino-2,4,6-trinitrobenzene) explosive in 66% H_2SO_4.

SOLUTION-CONDUCTANCE (RESISTANCE) MEASUREMENTS

Electrolytic conductivity is a measure of a solution's ability to carry electric current. This ability is expressed in units based on the specific conductance or resistance of a 1-cm cube of solution. It is measured by filling the space between two precalibrated electrodes and determining the resistance between them. Both dip, two-electrode cells and flow cells can be used. Note that the conductance technique is nonspecific, since any ionized species will contribute to conductance.

Field of Application

This technique is applicable for indicating the level of ionized material (without identification) in a solvent and of a specific substance if that substance is the only known contributor to conductance. It may also be used for continuous monitoring.

Uses

Qualitative

Nonspecific solution-conductance measurements have no qualitative use.

Quantitative

Accuracy. Solution conductance can be measured to within ±3% in a 0.05- to 10,000-μmho/cm range (18 MΩ to 100 Ω-cm resistance). Accuracy in terms of the concentration may be ±10%.

Sensitivity. Detection of dissolved, ionized material (chloride) in water is limited to 0.05 ppm.

Sample

State

Samples submitted for analysis may be solutions and pure solvents.

Amount

Samples may have 1 to 10,000 ppm dissolved solids.

Preparation

Measurements are usually made without pretreatment.

Time Required

The time required for measurement varies from 1 min with preconditioned electrodes to a maximum of 1 h.

Instruments

The instruments needed for analysis include Industrial Instruments Model RC16B1 conductivity bridges, a Leeds and Northrup Model 4958 conductivity monitor, and dip, flow, plastic, and glass cells with carbon and platinum electrodes.

Location and Staff

The instruments for solution-conductance measurements are located in Room 1524 of Bldg. 222. Jack Harrar is responsible for operation of the instruments, and Fred Stephens is available for consultation.

Examples

Solution-conductance measurement techniques have been used to:

- Check water purity.
- Measure leakage of ground water into field systems.
- Semiquantitatively monitor the concentration of single-solute solutions.

AUTOMATIC TITRATOR WITH ION-SELECTIVE ELECTRODES

Ion-selective electrodes are selective or specific to a particular ion. The sensing membrane, which can be of various materials or forms, ideally allows only the ion of interest to pass from solution at the outer membrane surface to an internal reference solution in contact with the inner membrane surface. When an ion-selective electrode is put in solution, ions flow across the membrane to that part of the solution containing the lowest concentration of mobile ions. The two main analytical techniques used are direct potentiometry, the measurement of signal based on the Nernstian logarithmic relationship between signal and ionic activity, which is capable of ±5% precision, and the more time-consuming and accurate potentiometric titration technique, which is capable of ±0.2% precision.

Field of Application

The automatic titrator is applicable for determining small quantities of ions in solution.

Uses

Qualitative

The automatic titrator is not used for qualitative analysis.

Quantitative

Accuracy. The accuracy of this method depends on the concentration of ions in a sample. Accuracy may range from 5% relative at the 50-μg level to 0.1% at the 5- to 10-mg level.

Sensitivity. Detection limits range from 20 to 30 μg.

Sample

State

Aqueous solutions are preferred, but solid samples will be accepted.

Amount

Samples should be submitted in at least milligram amounts.

Preparation

No pretreatment is required. Care should be taken to avoid contaminating the sample by excess handling, labeling, or packaging. A history and other analytical data of the sample would be helpful.

Time Required

Analysis can be completed in about 4 h if equipment is operational and sample preparation is not excessive.

Instruments

A Mettler Digital Buret, Model DV101, delivers titrant A data amplifier with switch-selectable gain and offset voltage adjusts the signal to the proper voltage for analog-to-digital converter input circuitry, and a simple control circuit enables the minicomputer to advance the buret. Visual display of the titration in progress is permitted by a CTR display. A plotter is used for recording titration curves. Programs available at the end of a titration allow one to interpret titration curves by calculating the endpoints with the second derivative method or by antilogarithmic linearization with the Gran method.

Location and Staff

Walt Selig is in charge of the titrator, which is located in Room 1314 of Bldg. 222.

Examples

One example of the use of an automatic titrator involved synthesizing benzotrifuran from trichlorotrinitrobenzene by reaction with sodium azide. Since it was important to know both the residual azide and chloride during this reaction, a method was developed to sequentially titrate for both in the same sample using a silver nitrate titrant and a chloride ion-selective electrode This very sensitive method was designed to require only small samples because of the potentially explosive nature of heavy metal azides.

Surface–Analysis Techniques

ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS

Materials to be analyzed are irradiated with x-ray photons, and photoelectrons ejected by irradiation are energy analyzed to determine their intensity as a function of their kinetic energy. Electron spectroscopy directly reproduces the electronic level structure from the innermost shells to the atomic surface. Elemental composition is determined by electron-binding energy spectra, and the chemical state is determined by the exact value of binding energy for a given energy level of a given atom.

Field of Application

Electron spectroscopy (ESCA) is applicable for determining atoms and their chemical states in the first 10 to 30 Å of a solid surface. It can be used for all elements in the periodic table, with the exception of H_2 and He.

Uses

Qualitative

This technique can determine the elements present in the first 3 to 10 atom layers of a sample surface. It can also be used to obtain the chemical state of these atoms.

Quantitative

Accuracy. The results on atom ratios are accurate to within ±10%.

Sensitivity. Detection limits for atoms on a surface vary from 10 to 100 ppm, depending on the element and the time taken for analysis.

Sample

State

Samples submitted for analysis may be powders or single-piece solids.

Amount

The amount of sample can vary from a few milligrams of powder to about a 1-cm^3 piece of solid.

Preparation

While no particular sample preparation is required, samples should be carefully handled so no foreign materials contact their surfaces.

Time Required

Required instrument time can vary from 5 to 10 min for chemical state determinations on a single high-concentration element to 10 to 24 h for determination of all elements in concentrations greater than about 100 ppm.

Instruments

A Hewlett-Packard 5950A spectrometer with a monochromatized A1K α x-ray source is used for analysis. In addition, a Hewlett-Packard 5952A data system and 2100A minicomputer are employed for both instrument control and data reduction.

Location and Staff

The ESCA spectrometer is located in Room 1106 of Bldg. 222. Robert Meisenheimer is the project leader, and J. W. Fischer is the major analyst.

Examples

The ESCA spectrometer has been used to examine a wide variety of materials, including metals and alloys, inorganic compounds, organic compounds, and biological tissues.

Figure 9 shows a typical spectrum of a uranium/zirconium/niobium alloy from 0- to 1000-eV binding energy. Electron spectroscopy was used in this example to determine the cause of corrosion on selected areas of the alloy.

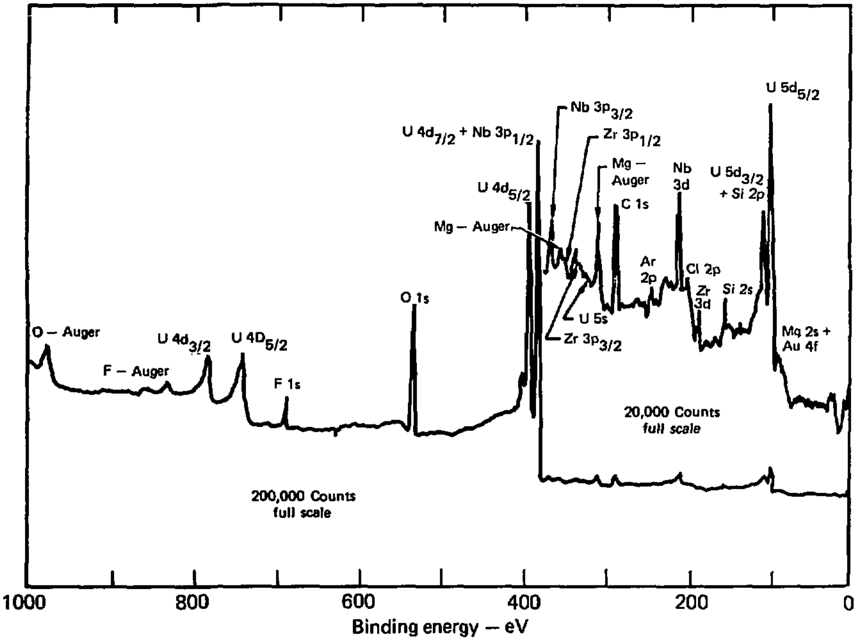


Figure 9. Electron spectroscopy spectrum of mulberry alloy.

SCANNING ELECTRON MICROSCOPE

A primary electron beam, obtained with an electron gun and a 15,000-V accelerating voltage, is focused on a specimen by an electromagnetic lens system. When the primary electron beam strikes the specimen surface, secondary electrons are produced. These secondary electrons are collected by a scintillator/photomultiplier system, and the resultant signal is displayed on a CRT. The primary beam of the scanning electron microscope is then scanned across the specimen surface in synchronization with scanning of the CRT display system.

Field of Application

The scanning electron microscope (SEM) provides magnified images of surface morphology with a high degree of three-dimensional character. Magnifications from 30 to 40,000 × are possible, and resolution is 300 Å.

Uses

Qualitative

The SEM can be used to determine the physical structure of material. The particle dimension, topography, and surface feature measurements achievable with the SEM's depth of focus are often superior to those possible with a light microscope. Figure 10 shows the structure of TATB at 2000 × magnification.

Quantitative

The SEM's magnification can be calibrated using standard samples. This allows highly accurate measurements of length to be made from photomicrographs.

Figure 10. Structure of TATB (200× magnification).

Sample

State

Solid samples may be submitted for analysis.

Amount

Sample sizes range from about 1 mg to a maximum that depends on the shape of the sample. A 1/4-in.-thick sample of 1/2-in. diam is convenient.

Preparation

Samples are usually examined in an as-submitted state; however, a conductive coating may be needed to prevent effects associated with sample charging.

Time Required

An average of 2 h is needed to provide an SEM micrograph.

Instruments

The model MSM-2 MINI-SEM used for analysis is manufactured by International Scientific Instruments, Incorporated, and is equipped with a polaroid camera for producing positive/negative photomicrographs. A Coates and Welter SEM with an x-ray fluorescence attachment for determining chemical elements is also available.

Location and Staff

The SEM is located in Room 1506 of Bldg. 222. R. G. Meisenheimer is the project leader. J. W. Fischer and D. W. McCoy are the major analysts.

Examples

The SEM has been used to:

- Examine glass fiber characteristics.
- Compare surfaces polished by different methods.
- Determine the crystalline nature of materials supplied by different vendors.

PHOTOELECTRON SPECTROSCOPY/ HIGH-RESOLUTION AUGER AND SCANNING AUGER MICROPROBE

The two techniques employed involve energy analysis of electrons emitted from a surface that has been bombarded with ultraviolet photons, x-ray photons, or electrons. Both techniques make use of the fact that emitted electrons have energies characteristic of particular energy level combinations in the solid and are, therefore, characteristic of atoms in the solid.

In photoelectron spectroscopy, an incident photon with sufficient energy ($h\nu$) will ionize an electronic shell. A photoelectron, bound to the solid with energy (E_B) will be ejected into the vacuum with kinetic energy (E_k). By conservation of energy,

$$E_k = h\nu - E_B.$$

The exciting source may be ultraviolet radiation or x-rays from aluminum or magnesium anodes. The spectrometer measures the number of electrons of a given kinetic energy emitted by a surface.

The Auger process, an alternative to x-ray emission, occurs after an atomic level has been ionized by incident photons or electrons. The hole in the inner shell is filled by an electron from a less tightly bound level, and a second electron escapes into the vacuum with the remaining energy. The energy of this Auger electron is roughly

$$E \sim E_{(\text{hole})} - E_{(\text{level 1})} - E_{(\text{level 2})}\ .$$

Thus, a $KL_1L_{2,3}$ Auger electron indicates an electron with measured energy (E) is released from the $L_{2,3}$ level after a hole is created in the K shell and an electron from the L_1 shell fills it. Auger electrons have energies characteristic of the atom levels from which they originate; therefore, energy analysis will identify the elements present.

Field of Application

The main application of the photoelectron (PES)/high-resolution Auger analyzer is for elemental identification of atoms and their oxidation state in the first 10 to 30 Å of a solid surface. All elements in the periodic table except helium and hydrogen may be identified by the PES and Auger techniques. The combination of the two techniques allows examination of the same portion of a sample without adjustment of its position. The PES and Auger techniques can be used to analyze spot sizes of ~1 and 0.1 mm diam, respectively.

The scanning auger microprobe (SAM) analyzer extends the analytical capabilities of the Auger technique because of the greatly reduced size of the electron beam used as a probe (3 to 5 μm). Scanning electron pictures of a surface can be produced, as well as maps of the distribution of a single element on the surface.

Profiles of surface composition by inert ion etching can be obtained with both Auger and SAM analyzers in either the PES or Auger mode.

The PES and Auger techniques complement one another because Auger is highly sensitive to low-Z elements, while PES is particularly sensitive to high-Z elements.

Uses

Qualitative

Both PES/Auger and SAM techniques allow elemental identification of elements in the first 3 to 10 atom layers of a surface. PES, and in some cases the Auger technique, will provide information on the oxidation state of detected elements.

Quantitative

Accuracy. Surface composition may be determined by both PES and Auger techniques. The use of photoionization cross sections in the PES technique permits determination of surface composition to within ±10%, and use of published elemental sensitivities in the Auger technique produces ±10% accuracy.

Sensitivity. The detection limits for elements on a surface, using both Auger and PES techniques, vary depending on the element, elemental sensitivity, and analysis time. The PES and Auger techniques have an ultimate sensitivity of 10^{-3} of a monolayer or about 10^{12} atoms/cm ^{2}.

Sample

State

Samples submitted for analysis may be solids and powders that are stable in vacuum (10^{-10} Torr) and not subject to decomposition under electron bombardment and x-ray or ultraviolet irradiation.

Amount

The amount of sample required for analysis may vary from a few milligrams to a relatively flat solid no more than 15 cm in diameter.

Preparation

Surfaces to be analyzed must not be contaminated by cutting oils, fingerprints, lubricants, etc. Samples should be wrapped in aluminum foil previously degreased with trichloroethylene or equivalent solvent and alcohol.

Time Required

About 4 h should be allowed for sample mounting and 16 h for attainment of a good vacuum ($\sim 10^{-9}$ Torr) in the analyzer chamber. Instrument time may vary from a few minutes for a single survey scan to several hours for determination of one or more elements in concentrations near 1000 ppm.

Instruments

The Physical Electronics ESCA-SAM system (Model 549) used for analysis utilizes either MgKα or AlKα x-ray sources. An ultraviolet source will soon be added. This spectrometer is linked with the Eclipse computer in Bldg. 222 for data storage.

Location and Staff

The surface analysis spectrometer is located in Room 1028B of Bldg. 222. C. Colmenares is the project leader, and R. L. Smith is the principal operator.

Examples

The surface analysis spectrometer has been used to study metals, alloys, organic compounds, ceramics, etc. Figures 11–14 show absorbed current micrographs and PES and Auger wide scans of a fractured stainless steel surface. The fracture is being examined to determine the cause of the metal failure.

Figure 11. Absorbed current micrograph of fracture area (100× magnification).

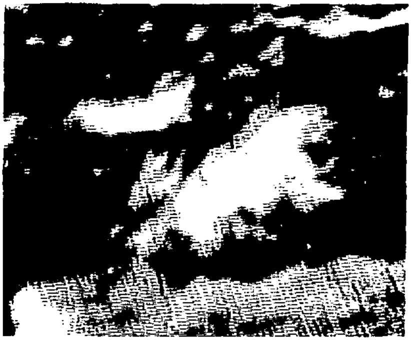


Figure 12. Absorbed current micrograph of fracture area (250× magnification). Center of large light area analyzed with SAM; entire area mapped for S, Cl, and Cr.

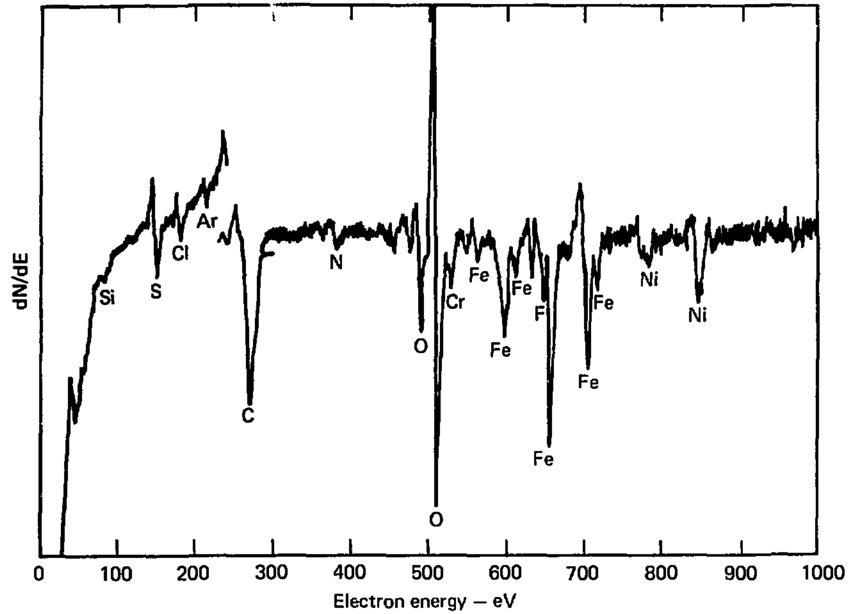


Figure 13. Auger analysis of fracture area shown in Figs. 11 and 12 performed with SAM analyzer.

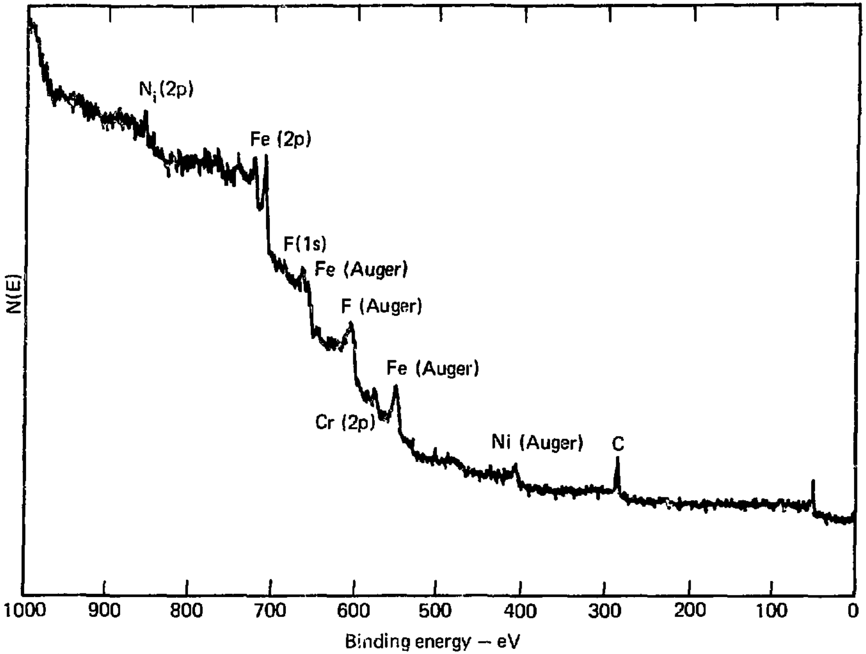


Figure 14. Low-resolution x-ray-excited photoelectron spectrum of fracture area shown in Fig. 12.

Chromatography Techniques

GAS CHROMATOGRAPHY

Gas or volatized liquid is injected into an inert carrier gas such as helium, argon, or nitrogen. The sample and carrier gas pass through long columns packed with a stationary phase on which separation occurs. Separation results from the absorption and desorption of various sample component vapors from the stationary phase. The amount of absorption varies due to the nature of individual components such as vapor pressure and the degree of polarity. Various detectors, such as flame ionization, thermal conductivity, and electron capture detectors, are used to monitor components eluting from the column.

Field of Application

Gas chromatography is applicable for analysis of liquids with boiling points below 400°C and gas mixtures.

Uses

Qualitative

Gas chromatography is not well suited to identifying unknowns, although some indication of identity can be obtained by comparison to standards.

Quantitative

Determinations with an accuracy of ±1% of the amount of substance present are possible with proper standards. It is also possible to detect impurities in ultrapure gases to a level of 10 ppb by volume.

Sample

State

Samples submitted for analysis should be liquids or gases.

Amount

The amount of liquid sample needed for analysis can vary from 0.5 cc for unknown mixtures to 0.1 cc for familiar ones. A minimum of 5 cc STP of gas is required, although larger samples with above atmospheric pressures are preferred for trace analysis.

Preparation

No particular sample preparation is required. Samples with subatmospheric pressures may be analyzed by evacuating and flushing the sample loop.

Time Required

Instrument calibration normally takes about 3 h since a minimum of three standards are run. Once calibration is completed, most gases can be analyzed in less than 1/2 h. Analysis of liquid samples may take less than 15 min to more than 4 h depending on the complexity of the mixture.

Overall time is equal to instrument time if columns and conditions are known and no sample preparation is required. If columns and conditions are not known and much sample preparation is needed, the development program required may take from several days to several months.

Instruments

Many instruments are needed for gas chromatography. These include Varian Aerograph Model 1532 trace gas analyzers with helium-ionization detectors for parts-per-billion analysis of ultrapure gases, automated trace gas analyzers with helium-ionization detectors for analysis of ultrapure hydrogen for cryogenics work in Nevada, automated and manual trace gas chromatographs for analysis of tritium impurities, and Varian 1520 and Hewlett-Packard 5840 instruments equipped with flame, flame photometric, and thermal conductivity detectors.

The Varian instruments are connected to a Spectra-Physics Autolab System IV integrator for data acquisition and computation.

A Hewlett-Packard 5830A chromatograph with a 18850AGC terminal and a Varian 2700 Dual Flame ionization chromatograph, being readied for oil shale retorting, are connected to a Hewlett-Packard 3380 integrator recorder.

Also available are a Chromolytics *SPEX MP-3* thermal chromatograph with an Infotronics CRS-100 digital integrator for oil and coal gasification, and two Varian Aerograph 2720 chromatographs connected to a Spectra-Physics Autolab System IV computing integrator for coal gasification.

Location and Staff

Virgil DuVal and Jack Clarkson, assisted by Ester Fultz and Jane Cupps, are responsible for operation of the various chromatographic instruments.

Most *instruments* are located in Rooms 1104 and 1110 of Bldg. 222. One trace-gas analyzer with helium-ionization detectors, currently in Bldg. 341, is tentatively scheduled for laser isotope separation. An automated trace gas chromatograph is located in Bldg. 331. Among the instruments on the mezzanine of Bldg. 243 are: the Hewlett-Packard 5830A and Varian 2700 Dual Flame ionization chromatographs, and the Hewlett-Packard 3380 integrator recorder. Two Varian Aerograph 2720 chromatographs, presently in Bldg. 243, will soon be deployed in the field at Hoe Creek, Wyoming. The Chromolytics SPEX MP-3 thermal chromatograph is in Room 1110 of Bldg. 222 but will soon be moved to Bldg. 241.

Examples

Gas chromatography is used to analyze:

- Ultrapure gases for trace impurities for laser, CTR, and weapons applications.
- *Liquids for composition* and purity, including FEFO for high explosives.
- Gas mixtures for coal-gasification experiments and oil shale retorts.

HIGH-PRESSURE LIQUID CHROMATOGRAPHY

Samples are injected into the front of 1/8-in.-diam by 10-in.-long columns of stainless steel that have been packed with small particles of solid material such as silica gel. Organic liquids or eluants are pumped through these columns to achieve separation. Eluant from the end of one or several columns is passed through detectors, and electronic devices produce graphic signals of the separated species. Detection is based on the refractive index difference between the eluant and sample components. Since the packing and eluant used determine achievable separation, they can be changed to produce adequate results.

Field of Application

High-pressure liquid chromatography (HPLC) is applicable for qualitative and quantitative analysis of components in mixtures of organic compounds. It is particularly useful for analysis of materials having low volatility or delicate thermal properties.

Uses

Qualitative

Variable wavelength, ultraviolet, differential refractive index, and infrared detectors allow qualitative judgments to be made on appropriate samples. Identification is based on comparative retention times with known standard materials.

Quantitative

Accuracy. This technique can determine the amount of substance present to within ±10%.

Sensitivity. Detection ranges from a high parts-per-million to high percentage limit.

Sample

State

Samples submitted for analysis should be solids or liquids suitably dissolved in chromatographic eluant.

Amount

The amount of sample for analysis may vary from a few milligrams to several grams.

Preparation

A 1-10% concentration of sample should be dissolved in appropriate solvent for general use, although some liquids can be injected directly.

Time Required

Calibration is required for all concentration measurements because of the selective nature of the detectors and their various response factors. About 1 to 2 h of instrument time is required for separation and analysis of known samples. Once the sample has been run and the instrument has been calibrated, calculation of the amount of species present usually takes 10 to 15 min. When conditions have not been predetermined, a day to several weeks may be needed for difficult separations.

Instruments

The high-pressure liquid chromatograph used for analysis is a Waters Model 202/401 with ultraviolet and differential refractive index detectors.

Location and Staff

The liquid chromatographic equipment is located in Room 1110 of Bldg. 222. Jack Clarkson, the principal chemist for this effort, is assisted by Virgil DuVal, Ester Fultz, and Jane Cupps.

Examples

High-pressure liquid chromatography has been used to analyze explosives, thermally unstable materials, polymers, and epoxy resins. Figure 15 shows typical chromatograms for several lots of TATB extracts, and Fig. 16 identifies several of the impurities found.

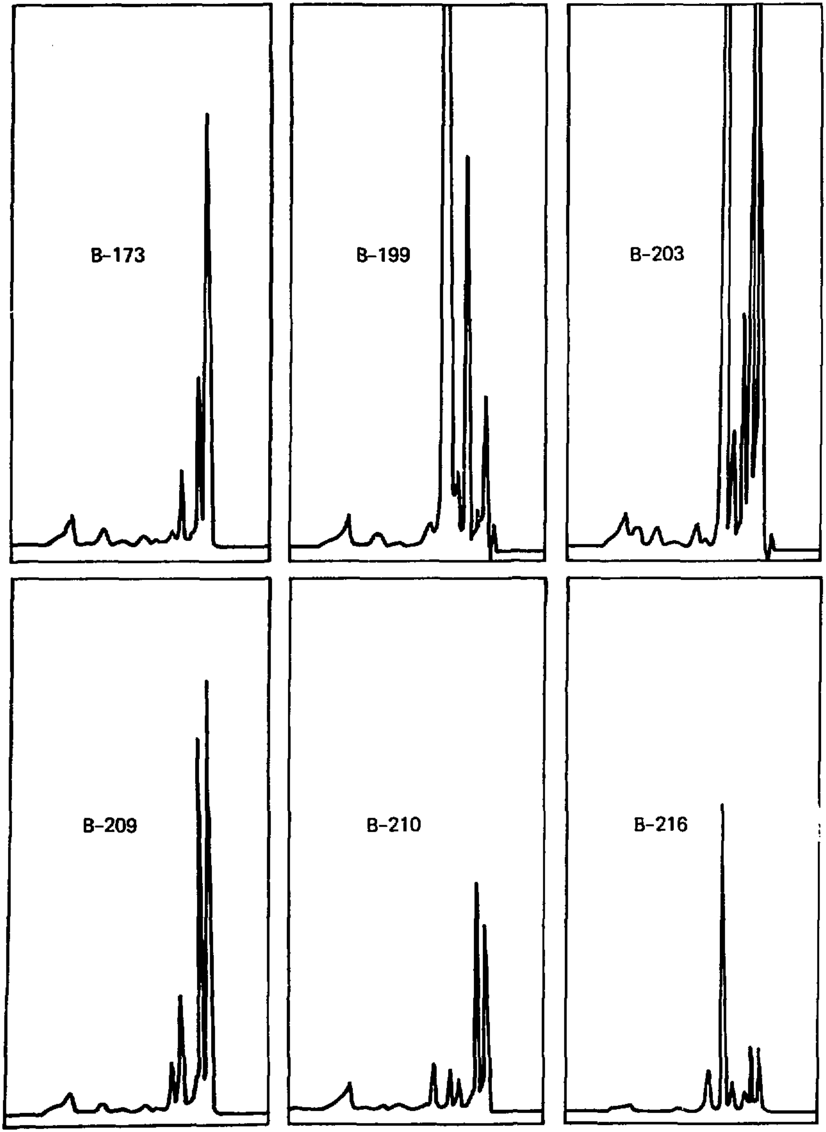


Figure 15. HPLC chromatograms of various lots of TATB extracts.

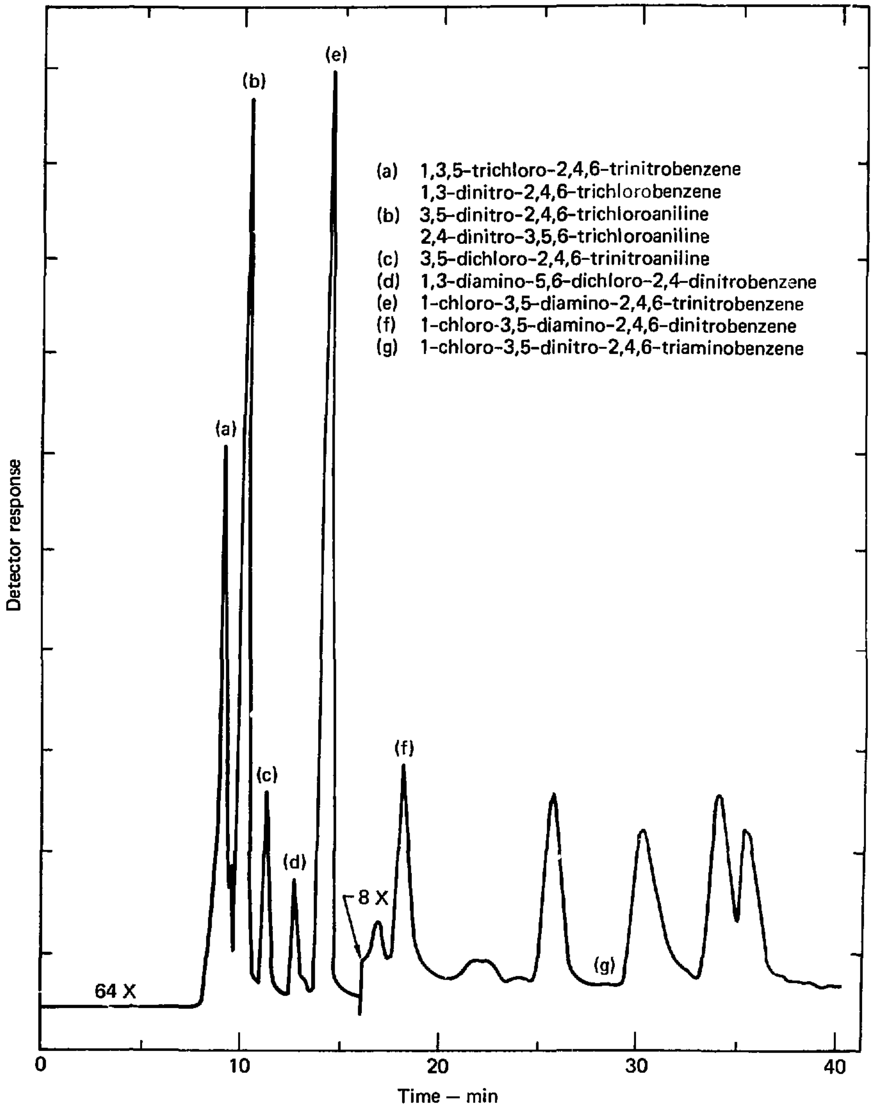


Figure 16. HPLC chromatography is used to characterize explosive sample extracts.

GEL-PERMEATION CHROMATOGRAPHY

Chromatographic eluant is passed through a column containing Styragel, a cross-linked polymer gel, at a 1-ml/min rate. This gel separates the molecules that diffuse into its pores on the basis of solution molecular size. Smaller molecules go into the pores, while the entry of larger molecules is determined by their size and the size of the pores in the selected column packing. Thus, larger molecules are eluted first; they are followed by smaller molecules until everything entering the column has been eluted. Detection is accomplished with a differential refractive index detector and appropriate electronic equipment and recorders.

Field of Application

Gel-permeation chromatography (GPC) is applicable for determining the molecular weight or size distribution of polymeric materials. It has recently been applied to size separation of 100- to 1000-mol-wt molecules in explosive formulations, epoxy resins, and prepolymers.

Uses

Qualitative

This technique is useful for separating noncomplex mixtures and for obtaining general molecular weight and size distribution. Specific identification of materials is difficult due to the lack of resolution. Fraction collection of separated materials can be used for identification by other techniques.

Quantitative

Accuracy. Gel-permeation chromatography provides number-average molecular weight and molecular weight distributions where adequate calibration standards exist. Polystyrene equivalent values can be given for systems where no standards exist.

Sensitivity. Quantification is accomplished by integrating peak areas and calibrating with known concentrations of standard materials. Detection ranges from tenths of a percent of a component to pure materials.

Sample

State

Samples submitted for analysis should be solids or liquids that can be completely dissolved in chromatographic eluant. Tetrahydrofuran (THF) is normally used as an eluant; however, other organic solvents can be used on very special occasions.

Sample

Amount

From 50 mg to several grams of sample may be needed for analysis. Larger amounts are required for fraction collection.

Preparation

Samples should be dissolved in chromatographic eluant for injection into the instrument. Calibration with standards is necessary.

Time Required

About 3 h is required to collect data and determine the values to be reported. When unusual materials are submitted, more time may be needed for instrument calibration.

Instruments

The principal instrument for analysis is a Waters Model 200 gel-permeation chromatograph equipped with Styragel high and low sets of separating columns. This chromatograph is connected to General Chemistry Division's Eclipse interactive computer system. The chromatograph has a fraction collection system and an automatic injection system that permits unattended sample injection. A Waters Model 202/401 liquid chromatograph with micro-Styragel columns is also available for research and development projects.

Location and Staff

The chromatographic analysis section is located in Rooms 1110 and 1104 of Bldg. 222. Jack Clarkson, the principal investigator, is assisted by Virgil DuVal, Ester Fultz, and Jane Cupps.

Examples

The two similar lots of nitrocellulose-containing explosive formulations shown in Fig. 17 illustrate one example of polymer analysis. The narrow peak going off scale is HMX explosive.

Figure 18 shows the differences of several epoxy resin materials. The peaks can be digitally integrated; peak areas of the components are reported.

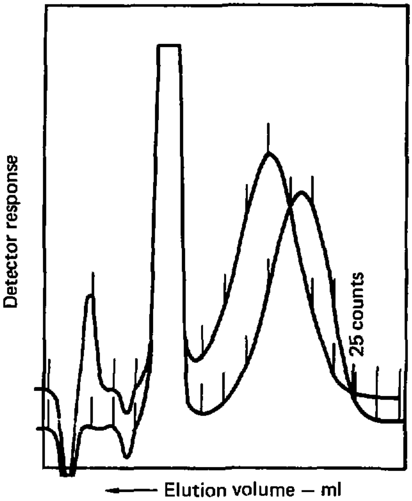


Figure 17. Polymer analysis with gel-permeation chromatography is used to compare two similar lots of nitrocellulose-containing explosives.

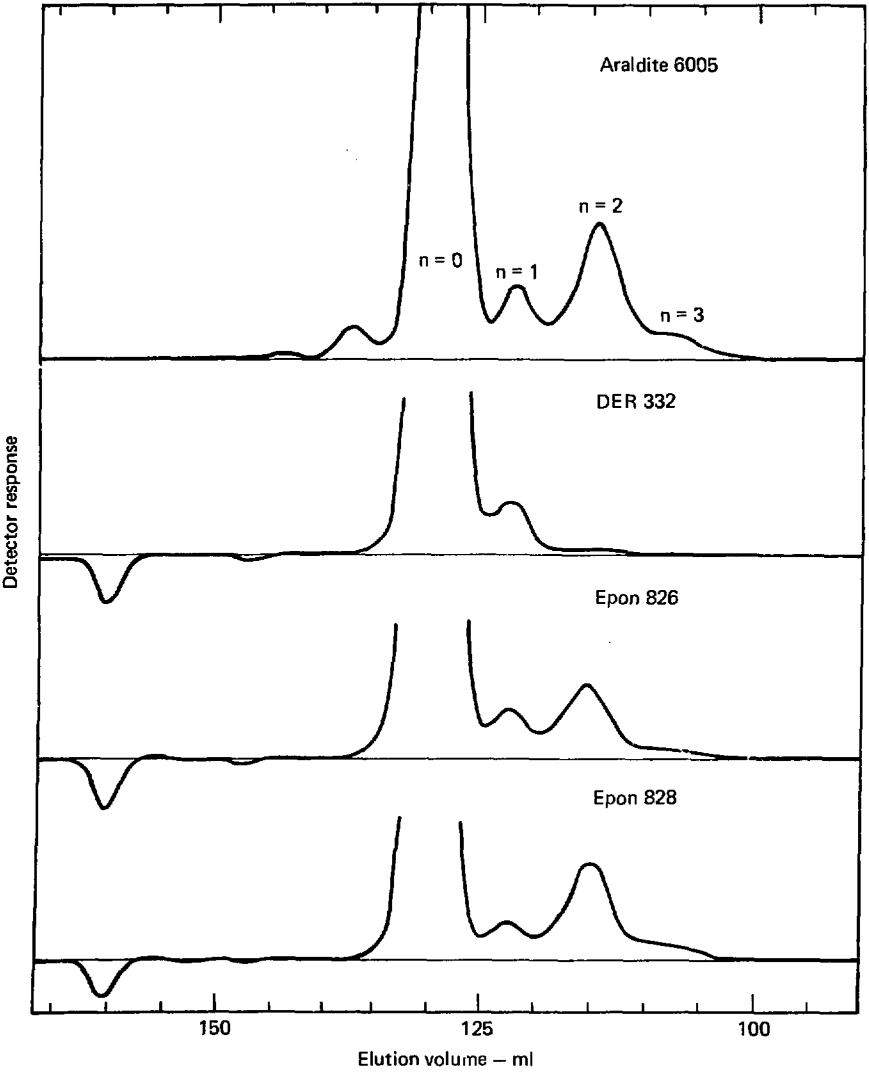


Figure 18. Gel-permeation chromatography used to analyze epoxy resins.

Mass–Spectrometry Techniques

GAS ANALYTICAL MASS SPECTROMETRY

A gas or liquid sample is expanded into a 3.5-l reservoir at about 6.7 Pa (50μ). The sample is then expanded through a molecular leak into the ion source of the mass spectrometer. The molecules are bombarded with electrons, causing ionization and bond rupture. The kind and amount of fragments obtained are characteristic of the molecule; thus, each compound has a unique cracking pattern or mass spectrum. When positive ions thus formed are accelerated into a magnetic field, they travel curved paths. The radii of these paths are proportional to the square root of the masses (molecular weights) of ions. Varying the magnetic field or accelerating voltage will cause the segregated ion beams containing ions of identical mass to be successively swept past a collector. Here the ions will discharge, producing currents proportional to the relative abundance of ions of each mass. These currents will then be successively recorded to form the mass spectrum.

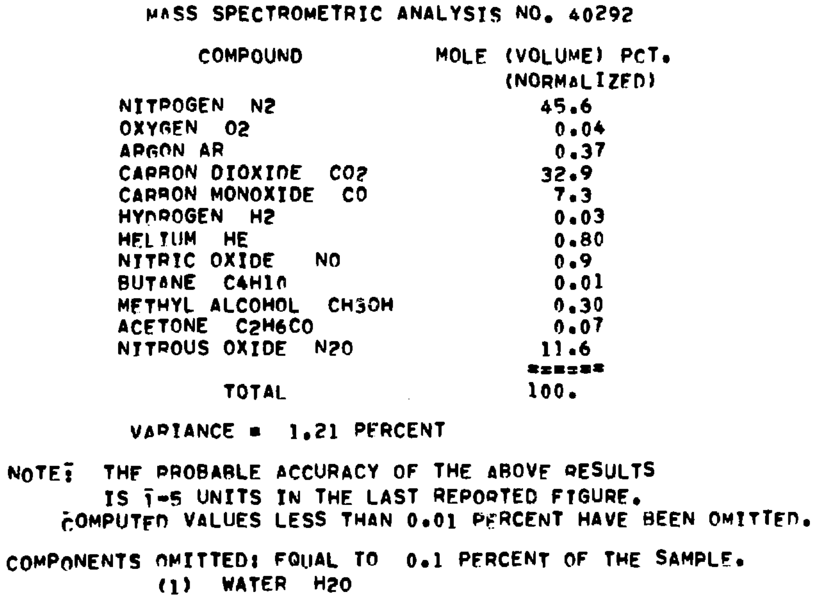
Field of Application

Gas analytical mass spectrometry is applicable for qualitative and quantitative analysis of all materials with vapor pressures of at least 6 Pa (50μ) at 50°C in a 0.01- to 100-vol% range. Isotopic ratios and molecular weights can also be obtained. Figure 19 shows a typical mass spectrometric analysis.

Uses

Qualitative

Gas analytical mass spectrometry can be used for positive, rapid identification of compounds. It can often distinguish between branched chain and position isomers, but seldom between geometric or stereoisomers. This technique can also be used for



```
            MASS SPECTROMETRIC ANALYSIS NO. 40292

                COMPOUND              MOLE (VOLUME) PCT.
                                           (NORMALIZED)
          NITROGEN  N2                       45.6
          OXYGEN  O2                          0.04
          ARGON AR                            0.37
          CARBON DIOXIDE  CO2                32.9
          CARBON MONOXIDE  CO                 7.3
          HYDROGEN  H2                        0.03
          HELIUM  HE                          0.80
          NITRIC OXIDE   NO                   0.9
          BUTANE  C4H10                       0.01
          METHYL ALCOHOL  CH3OH               0.30
          ACETONE  C2H6CO                     0.07
          NITROUS OXIDE  N2O                 11.6
                                             ======
                    TOTAL                    100.

           VARIANCE =  1.21 PERCENT

NOTE:  THE PROBABLE ACCURACY OF THE ABOVE RESULTS
       IS 1-5 UNITS IN THE LAST REPORTED FIGURE.
     COMPUTED VALUES LESS THAN 0.01 PERCENT HAVE BEEN OMITTED.

COMPONENTS OMITTED: EQUAL TO  0.1 PERCENT OF THE SAMPLE.
             (1)  WATER  H2O
```

Figure 19. Readout of typical mass-spectrometric analysis.

identification of pure compounds and simple mixtures and for distinguishing between position isomers without known standards. It can resolve 10 to 15 components in a complex mixture without separation when known standards are available, provide evidence of all volatile constituents in a sample from its mass spectrum, and determine molecular weight to the nearest mass unit.

Quantitative

This technique can determine the amount of compound present in a sample to within 0.5%; however, accuracies of 1 to 5% are considered routine.

Sample

State

Samples submitted for analysis may be liquids or gases.

Amount

At least 0.4 ml STP of gas is required for analysis; however, 5 to 10 ml of gas is preferred with pressures of 50 Pa to 100 kPa (400μ to 1 atm). A minimum of 0.5 ml of liquid is needed.

Preparation

Gases should be in vacuum-tight containers. Glass containers should have 18/9 ball joints, and metal containers with a 4-VCR female Cajon are preferred. Cryogenic separation of gas samples can often improve both qualitative and quantitative results.

Time Required

Samples are normally run on Tuesday, Wednesday, and Thursday. Results from routine gas analyses are usually available 2 d after the sample has been run. Results of simple mixtures can be obtained within 15 to 30 min after sample receipt in case of emergency.

Instruments

The original spectrometer, a Consolidated Electrodynamics Corporation Model 21-103C, was purchased by the Laboratory in 1954. The vacuum system, inlet, and almost all electronics have since been replaced, and the entire spectrometer has been computer automated. The 180° Dempster design analyzer has a 5-in. radius and is entirely in the magnetic field. This analyzer provides the high stability and reproducibility necessary for good quantitative work.

Location and Staff

The gas analytical mass spectrometer is located in Room 1223 of Bldg. 222. John Newton and Ray Bedford are responsible for routine operations. Richard Crawford is available for backup and consultation.

Examples

Examples of the use of gas analytical mass spectrometry include:

- Gross analysis of all gas samples taken from nuclear tests.
- Determination of the purity of separated fractions.
- Detection of small amounts of rare gases used as tracers after chemical separations.
- Examination of products formed from chemical compatibility tests.
- Analysis of gas composition changes for corrosion studies.
- Analysis of mixed gases used in lasers and purity checks on single gases.
- Analysis of samples from coal gasification experiments and oil shale outgassing.
- Analysis of isotopic ratios.
- H/D determinations at the naturally occurring level.

HIGH-RESOLUTION MASS SPECTROMETRY

The process for positive ion formation is identical to that used in the gas-analytical mass spectrometer. High mass resolution is achieved by accelerating ions through electrostatic and magnetic analyzers arranged according to Mattauch-Herzog geometry. The energy and velocity focusing and dispersion capabilities of the high-resolution mass spectrometer allow separation of ions that differ by as little as 1 amu in 30,000. Ions can be focused one at a time onto an electron multiplier by scanning the magnetic field or simultaneously recorded on a photoplate with a fixed magnetic field. Gas can be injected into the ionizing region by use of a vacuum manifold for gaseous compounds and a direct probe that can be cooled to -30°C or heated to 400°C for high boiling liquids and solids. A sophisticated, digital temperature control allows temperatures to be ramped so mixtures can be analyzed by the spectra of gases evolved at different temperatures.

Field of Application

The high-resolution mass spectrometer is applicable for qualitative and quantitative analysis of compounds with vapor pressures of at least 0.01 Pa (10^{-4} Torr) at 400°C in a 0.01- to 100-vol% range. It can also be used to determine isotopic ratios and molecular weights.

Uses

Qualitative

This spectrometer can perform all the qualitative determinations listed for the gas-analytical mass spectrometer. It is designed to identify compounds by determining their cracking patterns under electron impact and to measure the exact mass of ions to within ±0.005 amu.

Quantitative

Accuracy. The amount of compound in a mixture can be determined to within ±30%.

Sensitivity. Substances with vapor pressures in the 10^{-5}-Pa (10^{-7}-Torr) range are detectable.

Sample

State

Samples submitted for analysis may be gases, liquids, or solids.

Amount

At least 0.4 ml STP of gas is needed for analysis; however, 5- to 100-ml STP gas samples are preferred. About 100 μl of liquid sample is required. Smaller amounts can be used if the sample is dissolved in solvents. Solids of less than 1 mg are sufficient.

Preparation

Little sample preparation is required. Care should be taken to avoid contaminating samples by handling, inadequate packaging, or labeling.

Time Required

Instrument time can vary from 2 to 5 d, and interpretation can take from 1/2 to 2 d.

Instruments

A Nuclide Graf 3G spectrometer is used for analysis.

Location and Staff

The high-resolution mass spectrometer is located in Room 1228 of Bldg. 222. John Newton is responsible for operation, and Klaus Ernst is available for consultation.

Examples

The high-resolution mass spectrometer has been used to:

- Analyze explosives and explosive components.
- Look for trace quantities of impurities that cause the explosive to decompose.
- Identify mobile materials that may have migrated out of polymers and adhesives in the course of materials compatibility studies.

LIGHT-ISOTOPE MASS SPECTROMETRY

Gas samples are expanded into a 3.5-l reservoir at approximately 6.7 Pa (50μ). These samples are then expanded through a molecular leak into the ion source of the mass spectrometer. The molecules are bombarded with electrons, causing ionization and bond rupture. The kind and amount of fragments obtained are characteristic of the molecule, so every compound has a unique "cracking pattern" or mass spectrum. When the positive ions thus formed are accelerated into a magnetic field, they travel curved paths. The radii of these paths are proportional to the square root of the ion masses (molecular weights). Varying the magnetic field (accelerating voltage) will cause the segregated ion beams containing ions of identical mass to be successively swept past a collector. Here the ions will discharge, producing currents proportional to the relative abundance of ions of each mass. These currents are then successively recorded to form the mass spectrum.

Field of Application

Light-isotope mass spectrometry is applicable for quantitative and qualitative analysis of all materials with vapor pressures of at least 6 Pa (50μ) at 50°C in a 0.01- to 100-vol.% range. Isotopic ratios and molecular weights can also be determined.

Uses

Qualitative

The light-isotope mass spectrometer can be used for rapid, positive identification of compounds, of pure compounds or simple mixtures without known standards, and of 10 to 15 components of complex mixtures when known standards are available. It is generally considered superior to classic chemical means of compound identification. It can often distinguish between branched chain and position isomers, but not usually between geometric isomers or steroisomers. However, it is particularly useful when analyzing components in mixtures. Since all substances give a spectrum and the spectrum shows all constituents present in a sample, separate analyses are unnecessary. And, it can often determine molecular weight to the nearest mass unit.

Quantitative

Accuracy. Accuracies within 0.5% of the amount of component in a mixture are possible, although accuracies of 1 to 5% are considered routine.

Sensitivity. This spectrometer can detect 0.01% or less of component without concentration when interfering materials are absent. In some case, it is sensitive to as low as 2 ppm.

Sample

State

Gas samples are needed for analysis.

Amount

At least 0.4 ml STP is needed for analysis, but 5- to 10-ml-STP samples are preferred. Pressures may range from 50 Pa to 100 kPa ($400\,\mu$ to 1 atm).

Preparation

Gases should be in vacuum-tight containers. Metal containers with a 4-VCR female Cajon are preferred. Cryogenic separation of gas samples can often improve both qualitative and quantitative results.

Time Required

Samples are usually run on Tuesday, Wednesday, and Thursday. Results from routine gas samples are usually available 2 d after the sample has been run. In an emergency, results from simple mixtures can be obtained within 15 to 30 min of sample receipt.

Instruments

The original spectrometer, a Varian MAT, Model CH5, was purchased by the Laboratory in 1972.

Location and Staff

The light-isotope mass spectrometer is located in Room 131 of Bldg. 331. Ron Stump is responsible for routine operations, and Richard Crawford is available for backup and consultation.

Examples

Light-isotope mass spectrometry has been used to:

- Analyze all gas sample generated in Bldg. 331.
- Determine the purity of separated fractions.
- Examine the products formed in chemical compatibility tests.
- Analyze mixed gases used in lasers.
- Check the purity of single gases.
- Determine isotopic ratios.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Gas or liquid samples are injected into the gas chromatograph, and their various components are separated by a column. The carrier gas that contains the separated components is split into two streams upon elution from the column. One gas stream flows through the gas chromatograph detector, which determines the amount of each component in the mixture. Percentage composition is determined by comparing peak areas to those given by prepared standards run after sample analysis. The second gas stream passes the mass spectrometer inlet interface. A portion of the gas stream at this interface continually enters the mass spectrometer via the gas chromatography/mass spectrometry separator. This separator preferentially removes helium carrier gas to improve sensitivity. Rapid mass scanning each time a gas chromatograph peak appears will produce a mass spectrum for each separated component. These spectra are then used for component identification.

Field of Application

This technique is applicable for qualitative and quantitative analysis of almost all gas and liquid mixtures.

Uses

Qualitative

Gas chromatography/mass spectrometry can be used for positive identification of each component in a complex mixture. It is particularly useful for identifying the components in mixtures of similar organics or of many components and in mixtures containing one or more trace components.

Quantitative

Accuracy. The amount of each component in the mixture above trace levels can be determined to about 1%. Trace concentrations can be determined to about 5 to 50%.

Sensitivity. About 1 ng of each component is required for mass spectrometry identification. Smaller amounts can be determined with special techniques.

Sample

State

Samples submitted for analysis should be liquids or gases.

Amount

A few micrograms of liquid or about 0.5 cc STP of gas are required for analysis.

Preparation

Slightly pressurized gas samples are preferred, but containers allowing withdrawal via gas syringes are acceptable.

Time Required

Approximately 1 to 2 d of instrument time is required for routine qualitative analysis of uncomplicated samples.

Instruments

A Hewlett-Packard Model 9585A spectrometer and 5840A microprocessor controlled gas chromatograph are used for analysis. This spectrometer has a mass range of 10 to 1000 amu and a detection limit of about 50 pg. It is capable of operation in either an electron-impact or chemical-ionization mode. A Hewlett-Packard 21MXE computer controls all gas chromatograph/mass spectrometry operations and provides data reduction. This computer includes a library search routine that permits rapid identification of each compound in a sample.

Location and Staff

Samples will be accepted by C. J. Morris in Room 1215 of Bldg. 222.

Examples

Examples of the use of gas chromatography/mass spectrometry include:

- Determination of organic products formed from the curing of various epoxies and coatings.
- Identification of trace contaminants in liquid and gas samples.
- Identification of organic components from outgassing experiments.
- Analysis of organic gas mixtures.
- Qualitative and quantitative analysis of organic liquid or gaseous mixtures.

Volumetric- and Gravimetric-Analysis Techniques

VOLUMETRIC AND GRAVIMETRIC ANALYSIS

Substances resulting from quantitative chemical reactions can be measured in terms of volume, weight, and color intensity. Volumetric techniques usually employ a buret to measure the volume of a reactant that reacts with the element of interest. The point of complete chemical reaction can be located by potentiometric measurements, color changes, or other devices. Gravimetric measurements are obtained by weighing a known substance from a quantitative precipitation of the element of interest with an excess of pure reagent. Colorimetry or spectrophotometry is generally included in this solution-analytical methodology since it involves measurement of the optical absorbance of a quantitative reaction product between the element of interest and an excess of reagent. This technique give a measurable absorption of electromagnetic radiation between 250 to 800 nm. Comparison with standards provides quantitative information. All these methods are limited to the elemental composition of the sample, however, since the original structure is destroyed during dissolution.

Field of Application

Almost any substance that can be put in solution can be analyzed by these techniques.

Uses

Qualitative

Qualitative techniques are usually limited to visual observation of a chemical reaction such as that occurring in spot tests or to the general separation of elements into groups such as NH_4OH or H_2S precipitations.

Quantitative

Accuracy. The accuracy of quantitative measurements ranges from ±0.1 to 10%. An accuracy of ±0.2% can be obtained with standard methods, depending on the availability of suitable standards. The General Chemistry Division maintains a large collection of NBS standards and many elements in high purity form.

Sample

State

Samples for analysis should be solids, liquids, or gases.

Amount

The amount of sample required depends on the sample and analysis technique employed. Several grams are generally required because of the destructive nature of these techniques. High value materials may be recovered in an altered form.

Preparation

Sampling and preparation should be discussed with a chemist before samples are submitted for analysis. Care should be taken to avoid contaminating the sample.

Time Required

The time required for analysis varies depending on the complexity of the sample and the analytical technique employed. A simple liquid titration may take less than 1 h, while more than a month may be required to develop and test analytical techniques for dissolving and analyzing a refractory alloy.

Location and Staff

The analysis group consists of Bob Lim, Lew Gregory, Bill Sunderland, Miles Waggoner, Chuck Otto, and John Hill. Walt Boyle, Fred Stephens, and Les Rigdon are available for consultation.

Examples

Gravimetric and colorimetric analysis techniques have been used to determine the amount of beryllium in solution.

Gravimetric

The gravimetric technique requires that samples first be dissolved. The solution may then be diluted to volume, and aliquots may be taken for replicate determinations. The aliquot should contain about 100 mg of beryllium. Beryllium is precipitated as the hydroxide at pH 9.6 with ammonium hydroxide in the presence of ethylenediamine tetraacetic acid to keep other elements in solution. The precipitate is allowed to stand overnight, and then is filtered, washed, and ignited to BeO at 1100°C.

Colorimetric

Concentrations of beryllium in the 0.1- to 7-ppm range have been determined in solution by measuring the color developed with the dyestuff Fast Sulphon Black F. Potassium cyanide and ethylenediamine-tetraacetic acid are added to make the technique virtually specific for beryllium. The optical absorbance of the sample is compared with that given by standards.

Vacuum-Analytical Techniques

VACUUM FUSION

Measurements of nitrogen, oxygen, and hydrogen depend on the reduction of compounds containing these elements in a molten metal bath saturated with carbon. The volume of evolved gases is then measured, and the composition of the gaseous mixture is determined.

Field of Application

Vacuum fusion is applicable for quantitatively determining the total amount of nitrogen, oxygen, and hydrogen in metals.

Uses

Qualitative

Vacuum fusion has no qualitative use. No differentiation is made between the states in which interstitials (N_2, O_2, and H_2) exist in the sample.

Quantitative

Accuracy. Accuracy is usually within ±10% of the amount of element present in the sample.

Sensitivity. Detection is limited to 0.1 μg.

Sample

State

Solid samples should be submitted for analysis.

Amount

Samples should be submitted in an amount and form (e.g., wire, turnings, and strips) that will allow them to be cut into at least three pieces of about 100 mg each.

Preparation

Samples should be carefully handled to reduce surface oxidation. Many metals should be cut in an inert atmosphere; some of the most reactive metals must be handled in an inert-gas dry box. These samples should be placed in leak-tight metal chambers while still in the dry box.

Time Required

About 2 h is required for each analysis if many samples are run. Sample preparation can take from 15 min to several days.

Instruments

A computer-automated system designed and built at LLL is used for vacuum fusion. Samples are loaded in a turntable that is then evacuated and are subjected to a bath of molten metal (usually platinum) inductively heated to temperatures in the 2000°C range. Gases evolved from the samples are rapidly pumped into a calibrated volume, and gas pressures are measured with a capacitance-type diaphragm gauge. The gases are then analyzed by a small residual-gas analyzer that has been modified to act like a mass spectrometer. All actions are controlled and measured by the computer, and final results are printed out in parts per million by weight.

Location and Staff

The vacuum-fusion apparatus is located in Room 1219 of Bldg. 222. Don McCoy and Ron Stump are responsible for this equipment.

Examples

Vacuum-fusion techniques are often used with new metal alloys since the strength or brittleness of the alloys is strongly influenced by nitrogen, oxygen, and hydrogen. Some common materials analyzed with vacuum fusion include stainless steels, titanium alloys, uranium, and uranium alloys.

EVOLVED GAS ANALYSIS

Gases are evolved from or generated by materials in various states (i.e., from the decomposition of high explosives). Since evolved gas analysis depends on gas chromatography, physical chemistry, thermal decomposition, and high vacuum techniques, it also embodies their principles.

Field of Application

Evolved gas analysis is applicable for quantitative analysis of gas mixtures obtained from the thermal decomposition of materials such as high explosives, binders, plastics, adhesives, silicones, and perchlorates.

Uses

Qualitative

Analysis may include the use of gas chromatography, thereby allowing a qualitative idea of the gases generated by a sample to be quickly obtained. Although the gas chromatograph is presently configured for determining the gases generally evolved from high explosive decompositions, it may be used to identify routine samples without known standards. A mass spectrometer may be needed to identify unknowns. Some fractionation of a mixture of permanent and condensable gases is also possible by using a vacuum line with absorbent and cryogenic traps.

Quantitative

Accuracy. A gas chromatograph is often used for analysis of routine gas mixtures; it can determine the amount of gas present to within ±1%. If the gas is separated into fractions, a mass spectrometer is employed. Accuracies of ±1% to ±10% can be achieved with this spectrometer. Materials with high polarity or low vapor pressures are more difficult to quantify.

Versatility. A few tenths of a cubic centimeter to many liters of evolved gas may be examined.

Sample

State

Samples for analysis should be liquids, solids, or confined gases.

Amount

The amount of sample needed depends on the information required, the content of the species under study in the atmosphere, or on the extent of evolution on decomposition.

Time Required

The time required for analysis may range from 15 min to 4 y.

Instruments

The instruments required for analysis include a combination of: routine and specially designed glass or stainless steel vessels, oil and air baths, environmental chambers, vacuum lines, and the gas chromatograph in Bldg. 227.

Location and Staff

The facilities for evolved gas analysis are located in Rooms 1083 and 1094 of Bldg. 227. Some of the processes involved in analyzing up to 100 lb of high explosive can be done in Bldg. 827E-2 at Site 300. Al Pane is responsible for operations, and D. L. Seaton is available for consultation.

Examples

Routine chemical reactivity tests are, in principle, evolved gas analyses. Examples of data gained from this capability include:

- Identification of volatiles.
- Extent of oxidation.
- High explosive decomposition oxides of carbon and nitrogen.
- Evolution of hydrogen gas from heavy metals (corrosion by water).
- Identification of solvents entrapped by crystals.
- Extent of moisture absorption by desiccants.
- Outgassing of organic materials and silastics.

CARBON IN METALS

Determination of carbon in metals is based on the oxidation of all carbon to carbon dioxide and on the subsequent volumetric determination of the carbon dioxide formed.

Field of Application

The techniques employed are applicable for quantitatively determining the total amount of carbon in metals.

Uses

Qualitative

Determination of carbon in metals has no qualitative use.

Quantitative

Accuracy. Carbon in excess of 1 μg can be determined to within ±10%; amounts of less than 1 μg can be determined to within ±100%.

Sensitivity. Detection is limited to 1.0 μg.

Sample

State

Samples should be submitted in solid form.

Amount

At least three samples of 250 mg each are needed. Samples should be submitted in a form that can easily be cut into small pieces.

Preparation

It is critical that all surface contamination by carbon-containing compounds be eliminated. This includes fingerprints, cutting oil, solvents, plastic wrapping, paint, glue, marking pen, and marking pencil among others. Samples should be delivered in clean glass or metal containers.

Time Required

About 1 h of instrument time and 1 h of calculational time is needed for each sample. Sample preparation time is not included.

Instruments

The apparatus for carbon determination was designed and built at LLL. Metals are dropped into an inductively heated crucible with a stream of purified oxygen passing over it. The metals rapidly oxidize (burn) and carbon oxidizes to form carbon dioxide (CO_2). The oxygen stream containing trace CO_2 passes through a liquid nitrogen trap at a reduced pressure. The trapped CO_2 is subsequently heated, and the pressure is measured in a calibrated volume. The gas is then passed through a simple mass spectrometer to measure and correct for nitrogen oxides.

Location and Staff

Don McCoy and Ron Stump are responsible for the instruments, which are located in Room 1219 of Bldg. 222.

Examples

Carbon analysis has been used on a wide variety of pure metals and alloys. Some of the more common materials analyzed include uranium, stainless steel, copper, and gold.

Combustion Techniques

AUTOMATIC COMPUTER-CONTROLLED CARBON, HYDROGEN, AND NITROGEN ANALYZERS

Sample material in a platinum boat is placed in the combustion chamber of the Perkin-Elmer analyzer and burned. Gases generated by the combustion pass through combustion and reduction tubes, and carbon, hydrogen, and nitrogen are measured by detectors. In the LLL analyzer, the sample is oxidized by copper in a sealed, evacuated tube at about 900°C. The CO_2, H_2O, and N_2 gases that result are separated cryogenically, and the quantity of each is determined by PVT measurements. All control and data reduction functions are computer controlled.

Field of Application

Computer-controlled analyzers are applicable for determining carbon, hydrogen, nitrogen, oxygen, and sulfur in organic materials and for determination of greater than trace amounts in inorganic compounds.

Uses

Qualitative

These computer-controlled analyzers can be used to identify compounds and to determine the purity of synthesized products.

Quantitative

Accuracy. The Perkin-Elmer analyzer can determine the amount of element present in a 2-mg sample to within ±0.1%. The LLL analyzer is accurate to within ±1%.

Sensitivity. Detection is limited to 0.02% for a 2-mg sample.

Sample

State

Samples submitted for analysis may be nonvolatile and nonhygroscopic solids or liquids.

Amount

About 2 to 5 mg of sample is usually sufficient.

Preparation

No special sample preparation is required.

Time Required

After standardization, the Perkin-Elmer analyzer can analyze 10 samples in duplicate each day. The LLL analyzer can analyze six samples in duplicate in 2 d; this includes background and blank determination and standardization.

Instruments

Most samples will be analyzed with a Perkin-Elmer Model 240 Elemental Analyzer equipped with a Tektronix programmable calculator and an autobalance. Carbon, hydrogen, and nitrogen are normally determined; sulfur and oxygen can be determined by substituting appropriate combustion trains. Some samples will be analyzed with an analyzer designed and constructed at LLL.

Location and Staff

Lewis Gregory is responsible for operation of the Perkin-Elmer analyzer, which is located in Room 1519 of Bldg. 222. The LLL analyzer is located in Room 1219 of the same building, and Miles Waggoner is the analyst.

Examples

Carbon, hydrogen, and nitrogen determinations have been performed on shale oils, oil shales, and explosives.

DETERMINATION OF SULFUR

When a sulfur-containing compound is burned in a steam of oxygen, it generates sulfur dioxide and a small amount of sulfur trioxide. The oxygen then flows from the furnace to an absorber than contains a solution of hydrogen peroxide neutralized with sodium hydroxide. Here the sulfur dioxide is oxidized, and the sulfur trioxide is absorbed as sulfuric acid. The solution is later removed from the absorber, and the sulfuric acid is titrated with standard sodium hydroxide. The amount of sulfur in the sample is then calculated from the amount of sulfuric acid produced during combustion.

Field of Application

The combustion technique is applicable for determining sulfur in all types of inorganic materials and in a limited number of organic materials.

Uses

Qualitative

There is no qualitative use.

Quantitative

Accuracy. An accuracy of ±2% can be obtained with 50 to 100 μg of sulfur. As the sulfur content approaches the detection limit, accuracy is reduced by a factor of 10.

Sensitivity. The limit of detection for most materials is 5 μg.

Sample

State

Samples submitted for analysis should be solids in the form of drillings, turnings, or powders.

Amount

Up to 3 g of sample may be needed to obtain 50 to 500 μg of sulfur.

Preparation

If large samples are submitted, they will be drilled and the drillings will be used for analysis.

Time Required

The 20 min required to measure sulfur content includes 15 min for combustion and 5 min for titration. Analysis, which encompasses sampling, weighing, blanking, and standardization, may take 1 to 1-1/2 h.

Instruments

A Leco combustion furnace is used to burn samples. The absorption train was constructed at LLL.

Location and Staff

William Sunderland is responsible for sulfur analysis, which is performed in Room 1526 of Bldg. 222.

Examples

Sulfur has been determined in steels, ceramic tubes, coal ash, and geothermal scales.

Miscellaneous Techniques

ORGANIC ANALYSIS

Field of Application

Organic analysis is applicable for elemental, functional group, and compound determination in organic materials such as polymers.

Uses

Qualitative

Spot tests and infrared spectroscopy can be used to identify elements, functional groups, and compounds in organic materials.

Quantitative

Accuracy. A large number of standard, improved, and special techniques can be employed for elemental, functional group, and compound analysis. For this reason, no single figure can be given, although accuracies of ±0.3% can be achieved.

Sensitivity. Detection is limited by the technique employed.

Sample

State

Solids and liquids may be submitted for analysis.

Amount

The amount of sample required depends on the technique used for analysis. Larger amounts of amorphous materials will produce more meaningful results.

Preparation

No pretreatment of samples is required, although care should be exercised in handling to avoid contamination.

Location and Staff

Walt Selig is responsible for the organic analysis laboratories located in Rooms 1314 and 1318 of Bldg. 222. He is assisted by Glen Crossman.

Examples

Analyses are routinely run for acid and hydroxyl numbers, amine values, epoxy equivalence, percent isocyanate, ethylenic unsaturation, halogens, and viscosities. Amine values can be used for the fabrication of custom polymers. The number of amine groups must be precisely known so that the correct amount of cross-linking agent (isocyanate) can be added.

HIGH-EXPLOSIVE ANALYSIS

Field of Application

This analytical technique is applicable for analyzing the components in high explosives and related organic materials.

Uses

Qualitative

High-explosive analysis can be used to determine the percent of different components in a given sample mixture.

Quantitative

Accuracy. An accuracy of ±0.5% is acceptable for a production mixture of high explosives.

Sensitivity. The limit of detection is determined by specifications outlined for the high explosive. These specifications are sometimes written to the capabilities of the analysis.

Sample

State

Samples submitted for analysis may be solids, liquids, or powders.

Amount

Samples of 1 to 10 g are convenient for analysis. The quantity and transportation of all high explosives are controlled by the Hazards Control Department.

Preparation

No special sample preparation is required.

Time Required

The time required for analysis may vary from a few hours to many days.

Location and Staff

G. L. Crossman conducts routine analyses in Room 1318 of Bldg. 222.

THERMAL STABILITY AND CHEMICAL REACTIVITY TESTS

Chromatograms of gases evolved from tests of individual high explosives, binary mixtures of high explosives, or of a high explosive with another material are compared to chromatograms obtained from single components. The extent of reaction between components of a binary mixture may be determined by comparing results of the heat cycle with the mixture to those obtained from individual components.

Field of Application

These tests are applicable for determining the gases evolved from thermal decomposition of a high explosive or from the thermal reaction or combination of a high explosive with another material.

Uses

Qualitative

Thermal stability and chemical reactivity tests have no qualitative use.

Quantitative

Accuracy. The accuracy of these tests is determined by the chromatography, mass spectroscopy, or vacuum analytical techniques employed. These tests can be used to semiquantitatively identify and measure the relative volumes of $N_2 + O_2$, NO + CO, N_2O, and CO.

Sensitivity. Gas volumes of 0.001 cc can be detected and measured.

State

Samples submitted for analysis should be solids or low vapor pressure liquids.

Amount

At least 0.25 g of each material is required.

Preparation

No special preparation is required.

Time Required

A minimum of 24 h is required for analysis. Additional time will be required for full quantitative determination of all gases.

Instruments

A two-column chromatograph that can be operated in a series or parallel mode is employed. One column is used for analysis of heavy gases such as water and solvents; the other is used for light gases.

Location and Staff

The two-column chromatograph is located in Room 1096 of Bldg. 227. Albert Pane is responsible for routine operations. Hyman Golopol serves as backup, and Don Seaton is available for consultation.

Examples

Thermal stability and chemical reactivity tests have been used to evaluate the compatibility of new high-explosive systems and the stability of pure explosives. They can also be used to study the reactivity of high explosives, with organic materials, adhesives, cements, polymers, metals, inorganic compounds, and other materials.

Automation and Materials Compatibility

AUTOMATION OF LABORATORY PROCEDURES

Automation projects are scoped, potential costs/benefits determined, and functional and implementation designs prepared. Department of Energy and General Services Administration requirements must be satisfied before purchase orders for equipment are prepared. Placement of an order may be delayed for several months if competitive bidding is required, and delivery may take 3 to 8 mo. Software must be written, interface handware must be fabricated, and the system must be fully assembled and tested before use. The ultimate user is encouraged to participate in all steps of the process.

Field of Application

Automated procedures are applicable for routine analysis of large numbers of samples, repetitive measurements for high-precision analyses, extensive standardization for quality assurance, and continuous monitoring of processes.

Uses

Qualitative

The availability of instrumental methods will determine qualitative uses.

Quantitative

Accuracy. The ease of on-line, real-time calculation of nonlinear instrumental effects and the simplification of extensive standardization, duplication, and other calibration techniques should produce typical factor of 3 to 10 improvements over manual methods.

Sensitivity. Sensitivity is routinely increased by factors of 3 through use of the statistical independence of signal and noise in multiple measurements. Other techniques can produce even more dramatic improvements.

Sample

State of Sample

Automated techniques have been demonstrated with gases, liquids, and solids.

Amount

The amount of sample required with automated techniques is usually the same or smaller than that required with manual techniques. Automated techniques also enable statistically significant sampling of large batches.

Preparation

The preparation and measurement of samples can be automated.

Time Required

Instrument time can be optimized for maximum throughput at a predetermined accuracy, or accuracy can be optimized for a predetermined throughput. Automation can also drastically reduce the man hours required for instrumental logging and monitoring.

Instruments

The General Chemistry Division staff and supporting electronics engineers are skilled in the implementation of microcomputers, microprocessors, and special-function keyboards and electronics. Time-shared and stand-alone modes are utilized.

Location and Staff

The PDP-7, the world's first time-shared laboratory automation system, is located in Room 1223 of Bldg. 222. It is being replaced with a faster ECLIPSE C/300 employing BASIC language, which will operate a laboratory automation system and a primitive data-base management system. Questions may be directed to George Barton, Walter Boyle, Dick Crawford, Art Kray, or William F. Morris.

Examples

A number of instruments have been automated for use in General Chemistry as well as for other divisions and outside facilities. These outside facilities include Environmental Protection Agency water quality laboratories in Cincinnati and Chicago and another to be located at Annapolis. Examples of intradivisional automation can be found in the sections of this document dealing with automated titrators and automatic carbon, hydrogen, and nitrogen analyzers.

MATERIALS COMPATIBILITY

The Materials Compatibility Group studies the compatibility of various materials used in weapons systems and tries to predict the stability and lifetime of components. For details regarding the services offered by this group, please contact Herman Leider.