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Chemical Measurement Capabilities at Lawrence Livermore National Laboratory

Compiled and Edited
by
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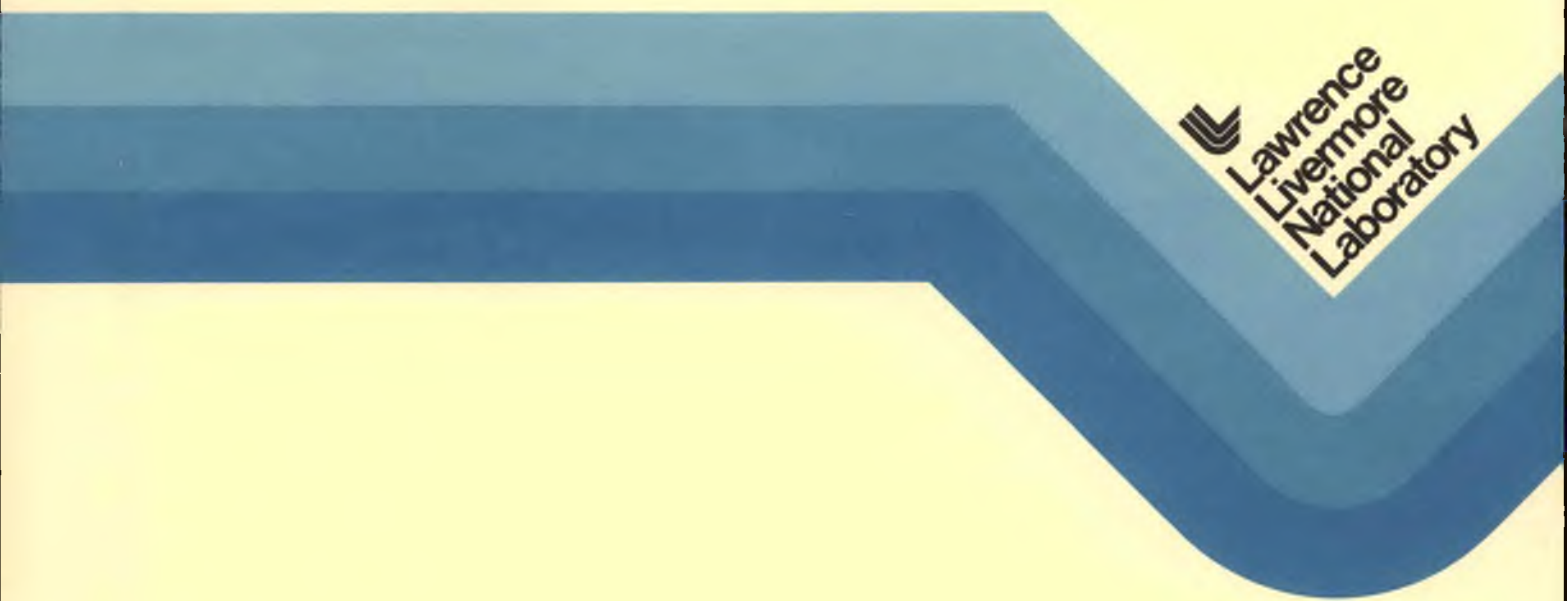
April 1992



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Contents

INTRODUCTION

This document is an attempt to summarize the available analytical chemistry and materials characterization techniques available at the Lawrence Livermore National Laboratory (LLNL). The specific emphasis of the techniques described is aimed at the variety of samples for which intelligence information is sought and/or applications where sample size would be very limited and duplicate samples are usually not obtainable. The current instrumentation available, the types of samples presently being analyzed and a description of the various methods have been provided. Although excluded from this compilation, a number of other techniques such as those of classical analysis and those employed to measure major constituents are also available.

LLNL has made an effort during the last three years to develop a forensic science approach to sample analysis. Many of these capabilities are presently utilized, to some degree, for ongoing analysis of unusual samples provided by various sponsor agencies. The analytical techniques utilized, although coordinated through the Special Projects Program, take advantage of the full range of capabilities available at LLNL. It is important to state that this document represents input from several organizations at LLNL, all working together to provide the maximum level of available expertise. These include: (1) The Condensed Matter and Analytical Sciences Division of the Materials Science Directorate, (2) The Nuclear Chemistry Division of the Defense Sciences Directorate, (3) The Center for Accelerator Mass Spectrometry of the Physics Directorate, (4) The Biomedical Sciences Division of the Environmental Sciences and Biomedical Directorate, and (5) The Applied Technology Division of the Special Projects Program Directorate. The methods described in this report are available to sponsor agencies for analytical services. Additionally, specialized methods can be modified and/or developed for other applications.

New capabilities are being added monthly and research and development activities are ongoing in the area of chemical analysis. We are constantly attempting to develop higher sensitivity methods while maintaining increased selectivity. We have the capabilities to handle most types of samples. Examples include solids, liquids, gases, wipes, clothing samples, body fluids, explosives, ceramic materials, soils, petroleum fuels, radiochemical mixtures, and reactive chemical mixtures.

I. INORGANIC ANALYSIS TECHNIQUES
(Chemistry and Materials Science Department)

DC-Arc Optical Emission Spectrography (DC-OES)

General Use

Primarily as an element survey technique to determine elements at trace, minor, and major levels in solid samples. The method can be used to determine more than 65 elements listed in the periodic chart. Because visual comparisons of spectra are made, DC-OES is by choice a qualitative or semi-quantitative (±20-50%) method intended to provide comprehensive information on trace elements or overall sample composition in a relatively short time.

Examples of Applications

- Determination of trace elements in metals, chemical compounds, plastics, aqueous and organic solutions.
- Identification of the elemental composition of alloys and unknown materials such as corrosion deposits.
- Determination of the approximate composition of geological materials such as rocks and minerals; corrosion products, etc.

Samples

Form: Solid or liquid.

Preparation: Solid samples as powder or fine turnings or chips in the case of metals are mixed with graphite and transferred to a graphite crater electrode. Liquid samples are evaporated to dryness. In most cases where only minor or trace elements are present, $Ga(NO_3)_3$ is added to collect the elements as the solution is evaporated. The residual salt is converted to Ga_2O_3, mixed with graphite, and transferred to an electrode. Organic samples are usually decomposed (wet-ashed) followed by collection of the trace elements in Ga_2O_3.

Limitations

Detection limits are usually in the ppm range and vary depending on the sample matrix, the complexity of the matrix spectrum, and whether pre-concentration procedures are used (e.g., solution evaporation or sample decomposition). Elements that cannot be determined include the halogens, noble gases, hydrogen, carbon, nitrogen, oxygen, sulfur, selenium, and tellurium. Specific compounds cannot be identified, nor can elemental oxidation states.

Estimated Analysis Time

Usually 2 hours per sample is required for semiquantitative determinations, although longer times (6-8 hours) may be needed for samples requiring extensive preparation, or spectral comparison where complex spectra are involved.

Principle of Technique

The material to be analyzed is placed in a graphite cup electrode and burned in a direct current arc. The elements constituting the material are vaporized into the arc plasma and the emitted light is directed by a lens system into an optical spectrograph where it is dispersed into a spectrum and photographed. Each element emits its own characteristic spectrum which varies in complexity depending on atomic structure. For example, sodium emits only a few lines, while uranium emits a very complex spectrum. The overall complexity of a sample spectrum, therefore, is a function of the elements present and their concentration. In making a visual determination, the optimum characteristic line(s) are chosen and the concentration is determined by comparison of the line intensity with its counterpart in a series of matrix-matched standards.

Capabilities of Related Techniques

Inductively-coupled plasma emission spectrometry (ICP-ES, see p. 6), atomic absorption spectrometry (see p. 8), and DC Plasma Emission Spectrometry (DCP-ES, see p. 7) are methods of choice for more accurate quantitative determinations, but solutions are required for analysis (solid samples must be dissolved). At least 10 mL of solution are usually required, but greater than 25 mL are preferred. The limits of detection are in the ppm range.

Inductively-coupled plasma mass spectrometry (ICP-MS, see p. 14) is similar in

application to ICP-ES, with limits of detection in the ppt and ppb range, and yields isotopic information.

X-ray fluorescence spectrometry (XRF, see p. 9) is also a method of choice for semiquantitative determinations and is applicable to solids. The method is nondestructive and the sample matrix is flexible. The detection levels are in the ppm range except for the low atomic number elements.

Instrumentation
- Jarrell-Ash 3.4 m Ebert Spectrograph
- Jarrell-Ash Model JA2100 Microphotometer

Inductively-Coupled-Plasma Atomic Emission Spectroscopy (ICP-ES)

General Use

Quantitative determinations of elements at sample concentration levels ranging from major constituent to parts-per-million.

"Simultaneous" determination of up to 44 elements in a single solution sample.

Examples of Applications
- Determination of leachable elements in geological systems.
- Determination of dopants in optical materials.
- Measurement of metals in groundwaters and hazardous waste samples.
- Determination of alloy compositions.

Samples

Form: Liquids, usually aqueous solutions, can be analyzed as received or after dilution.

Size: For liquid samples, 5 mL required for multichannel instrument, and about 1 mL/ element for the scanning instrument. Minimum amount of analyte that must be present is on the order of 1-100 µg. Smaller quantities may be accommodated for some elements.

Preparation: Solids must be dissolved in a suitable medium, usually an aqueous, acid solution.

Limitations
- Accuracy and precision of technique is 1 - 10%, depending on how well the background matrix is matched.
- Solid materials must be dissolved in an aqueous solution.
- Spectral interferences among elements in sample may limit applicability in certain situations.
- Does not yield information on chemical speciation.

Estimated Analysis Time

Including instrument startup time, analysis of a single sample generally requires 2 hours.

Quantitative determinations require 3-4 hours for preparation of samples and standards. Additional time may be required for sample dissolution and matrix separation.

Principle of Technique

Samples are introduced, generally as a nebulized solution, into an argon-supported, radio-frequency plasma discharge. The energetic conditions associated with the high temperature plasma are sufficient to evaporate and atomize both solvent and solute.

The thermal conditions within the plasma are sufficient to electronically excite the atoms of the analyte species (ions, atoms, etc.), and the subsequent radiative decay of these states produces photons characteristic of the elements present. This light is focused, dispersed by means of a monochromator and detected photoelectrically. Multiple photomultiplier tubes located at preset wavelengths of the spectral lines are used in the multichannel instrument. The intensities of the lines are proportional to the concentrations of the elements in the sample.

Capabilities of Related Techniques

Direct-Current Plasma Emission Spectrometry (DCP-ES, see p. 7) is closely related, differing somewhat in the optics and type of plasma employed. It is also a multielement technique with "simultaneous" detection, and has a higher spectral line resolution, but its limits of detection are generally higher than those of ICP-ES.

Inductively-Coupled Plasma Mass Spectrometry (ICP-MS, see p. 14) is also a multielement technique, has lower limits of detection for many elements, gives isotopic information, and has different interelement interference effects.

DC-Arc Optical Emission Spectrography (see p. 5) and X-ray florescence spectrometry

(see p. 9) may be applicable and can be used to analyze solids directly without dissolution.

Atomic Absorption Spectrometry (AAS, see p. 8) may be more accurate and precise in determinations of the alkali and alkaline-earth elements.

Instrumentation

- ARL (Applied Research Laboratories) Model 3560 Multichannel Spectrometer (43 channel, simultaneous measurement)
- Jobin-Yvon Model 38 Sequential Scanning Spectrometer

Direct-Current Plasma Optical Emission Spectrometry (DCP-ES)

General Use

Quantitative determinations of elements at sample concentration levels from major constituent to parts-per-billion.

"Simultaneous" determination of up to 20 elements in a single solution sample.

Examples of Applications

- Determination of impurity metals in plutonium and plutonium alloys.
- Measurement of regulatory toxic metals in hazardous waste samples.
- Semiquantitative elemental surveys using the photographic plate option.

Samples

Form: Liquids, usually aqueous solutions, can be analyzed as received or after dilution.

Size: 20 mL of solution is required for routine analysis. Solid quantity depends on analyte and concentration.

Preparation: Solids must be dissolved in a suitable medium, usually an acidic, aqueous solution.

Limitations

- Accuracy and precision of technique is 1 - 10%, depending on how well the background matrix is matched.
- Solid materials must be dissolved in an aqueous solution.
- Elements that can be determined are predefined by the group of metals in the instrument multichannel operating mode.
- Does not yield information on chemical speciation.

Estimated Analysis Time

Including instrument start-up time, analysis of a single solution sample requires 2 hours. Additional time is required for solid sample dissolution and matrix separation, if required. For environmental regulatory work, several standard solutions and blanks must be run before and after sample analysis. With this rigorous protocol, typical throughput is 10 samples/day.

Principle of Technique

The solution to be analyzed is aspirated into a spray chamber where 1 to 5 μm diameter droplets are entrained in an argon gas flow and larger droplets collide with the chamber walls and are drained away. The argon aerosol is then swept into the DC plasma that is created by a continuous arc between two graphite anodes and a tungsten cathode. The sample is desolvated, atomized, and excited by the 4000-6000°K plasma. The light from the plasma is focuses onto the entrance of an echelle spectrometer that disperses light in two dimensions using an echelle grating and a quartz prism cross dispersor. The echelle grating diffracts light with high dispersion in orders 28 to 118 while the prism refracts light with low dispersion to separate the overlapping orders. The intensities from selected emission lines are measured by a bank of photomultipliers placed at the most intense wavelengths for the 20 elements of interest. The intensities are converted to concentration by ratioing against the intensities from calibration solutions. The bank of 20 photomultiplier tubes are fixed for a certain group of elements and cannot be repositioned for other elements.

The DCP-OES instrument is occasionally operated in a qualitative mode by visually comparing the echelle spectrum with a template showing the location of the major lines of all elements excited in the DCP. In this qualitative mode the spectral image is diverted by a folding mirror out to a Polaroid film camera. By overlaying the template on the Polaroid image, one can qualitatively map out the elements that are present in a sample at high concentrations.

Capabilities of Related Techniques

Inductively-Coupled Plasma Emission Spectrometry (ICP-ES, see p. 6) is closely related, differing in the optics and the type of

plasma employed. ICP-ES generally has lower limits of detection because of a longer residence time of the analyte in the plasma, a higher plasma temperature, and a more stable plasma. DCP-ES on the other hand, has a higher spectral line resolution (because of the echelle spectrometer), thus may be less subject to interferences, especially by elements that have many spectral lines such as iron and uranium.

Inductively-Coupled Plasma Mass Spectrometry (ICP-MS, see p. 14) is also a multielement technique, has lower limits of detection for many elements, gives isotopic information, and has different interelement interference effects which can be utilized to complement or confirm.

DC-Arc Optical Emission Spectrography (DC-OES) (see p. 5) and X-ray florescence spectrometry (see p. 9) may be applicable and can be used to analyze solids directly without dissolution.

Atomic Absorption Spectrometry (AAS) (see p. 8) may be more accurate and precise in determinations of the alkali and alkaline-earth elements.

Instrumentation

- Spectrametrics Spectraspan IIIB DC-Plasma Spectrometer

Atomic Absorption Spectrometry (AAS)

General Use

Quantitative determinations of elements at the major constituent, fractions of a percent, and part-per-million levels. Flameless techniques can be still more sensitive.

Analysis of solutions when a relative precision and accuracy of 1-2% is desired, and only one or few elements are to be measured in the sample.

Examples of Applications

- Determination of alkali metal and alkaline earth elements in environmental soil and water samples.
- Determination of mandated metals and metalloids in hazardous waste samples.

Samples

Form: Liquids, usually aqueous solutions, can be analyzed as received or after dilution.

Size: Generally, 3-5 mL solution is required for routine analysis. The minimum amount of analyte that must be present varies by element but is generally on the order of 1-200 µg. Smaller quantities of analyte (down to a few nanograms) and much higher sensitivity can be obtained for some elements using flameless (furnace) techniques.

Preparation: Solids must be dissolved in a suitable medium, usually an acidic, aqueous solution.

Limitations

- Individual sources of emission light in the instrument are generally required for each element measured.
- Atomic absorption is inherently a single-element (not scanning) technology.
- Solid materials must be dissolved in an aqueous solution.

Estimated Analysis Time

Including instrument start-up time, analysis of a single solution sample generally requires 2 hours.

Quantitative determinations usually require 3-4 hours for preparation of samples and standards.

Principle of Technique

Samples are introduced, typically as a nebulized solution, into a flame where the solvent and solute are evaporated and dissociated into a collection of free atoms. A beam of light, generally from a hollow cathode lamp fabricated from the element of interest, is passed through the resultant reservoir of atoms. The intensity of the light beam at a wavelength characteristic of the analyte is compared in the presence and the absence of the analyte in the flame. The absorption of light is then related to the concentration of analyte atoms in the atom reservoir, and thus the original solution by the Beer-Lambert law. Quantitative analysis is performed by comparison of the results for the analyte solutions with those for a series of standard solutions of the element determined.

Capabilities of Related Techniques

Plasma Optical Emission Spectrometry techniques (see pp. 6 and 7) are multielement techniques, i.e., several elements can be determined efficiently at the same time. For certain elements they may also be more

sensitive than AAS, but precision may not be as high as AAS.

Inductively-Coupled-Plasma Mass Spectrometry (see p. 14) is also a multielement technique of generally higher sensitivity, is capable of yielding isotopic information, and its interelement interference effects are different.

Solution chemistry techniques may be applicable to certain samples, and are capable of higher accuracy and precision.

DC-Arc optical emission spectrometry (see p. 5) and *X-ray fluorescence spectrometry* (see p. 9) may be applicable, and can be used to analyze solids directly without dissolution. However, for single elements these techniques are generally not as accurate and precise.

Instrumentation

- Perkin-Elmer Model 5000 Flame AAS Spectrometer
- Perkin-Elmer Zeeman Model 4100ZL Graphite Furnace System

X-Ray Fluorescence Spectrometry (XRF)

General Use

Qualitative. XRF can be used to rapidly and non-destructively identify elements with atomic number Z greater than, or equal to aluminum, within a sample.

Limits of detection range from a few tenths of a percent to about 50 ppm, depending on the element and counting conditions.

Especially applicable to measuring high-Z elements in a low-Z matrix.

Semiquantitative. XRF can be used for semiquantitative analysis by using semi-theoretical calculations to correct for self-absorption and enhancement of the observed peaks. This can be done without standards or can use only a few standards.

Uncertainty in the semiquantitative results are generally on the order of 20-50% of the reported value. Limits of detection are similar to qualitative work.

Quantitative. Quantitative analysis with XRF involves comparison of a sample with a suite of standards of similar matrix. The standards and samples can be either analyzed "as received," or subjected to preparation techniques to improve the reliability of the measurement.

Accuracy is generally better than 1% with preparation and good standardization.

Limits of detection range from about 0.5% for boron, to less than 1 ppm for some elements in a good (low-Z) matrix. Higher Z matrices can reduce the sensitivities considerably. Very small samples with only a few components can often be quantified for these components in the 10-100 ng range.

Examples of Applications

- Determination of trace elements in equipment components.
- Qualitative analysis of surface swipes to identify materials from explosives testing.
- Quantitative determination of major elements in soil and oil shales.
- Qualitative analysis of unknowns for waste disposal.
- Quantitative analysis of laser targets for Inertial Confinement Fusion program and L-Division.
- Determination of trace elements in shale oil.
- Quantitation of fluorine-containing compounds on cloth.
- Measurement of impurities in materials used in the nuclear test program.

Samples

Form and Size: Samples may be analyzed as liquids, powders, or solids. For quantitative analysis, a minimum of about 1 gram of powder, 10 mL of liquid, or a 1 inch square of solid is required. Qualitative analysis can be performed on as little as a 50-100 mg, although larger amounts are preferred.

Preparation: Frequently no preparation is required for a simple qualitative analysis. For quantitative analysis, solid samples are often fused with lithium salts and cast into plates for analysis. Some samples can be pelletized in a press to yield a suitable sample, and occasional samples can be quantitated with virtually no preparation. Liquids are generally analyzed "as received".

Limitations

- XRF cannot be used for the analysis of H, He, or Be. The detection limits for the other light elements are poor.
- XRF does not provide any information on the chemical speciation or oxidation state

of the elements detected (e.g., it cannot distinguish Fe^{2+} from Fe^{3+}).

Estimated Analysis Time

2-4 hours for complete qualitative analysis. Approximately 3-8 hours for a semiquantitative measurement. Quantitative analysis time varies depending on preparation of the samples and standards.

Principle of Technique

In XRF, a sample is placed in a collimated flux of high-energy photons produced by an X-ray tube. As these photons pass through the sample, some are absorbed by the inner-shell electrons of the sample's constituents. If the photon energy is great enough, the inner-shell electron can be ejected from the atom, leaving a vacancy. An outer-shell electron will quickly fill this lower level according to atomic selection rules. In making this transition to a lower energy level, the excess energy can be emitted as an X-ray. Since the atomic energy levels are quantized and depend on the atomic number of the atom, the emitted X-rays form a pattern that is characteristic of each element. The energies of the observed X-rays identifies the element, and their intensities can, with some corrections for self-absorption or enhancement, determine the quantity of each material present.

Capabilities of Related Techniques

DC Arc Optical Emission Spectroscopy (see p. 5) is useful for lower-Z elements that XRF cannot detect. Sensitivities in ppb range. Also applicable to solid samples.

These various plasma and flame spectrometry techniques (see pp. 6, 7, 8, 14) are quantitative, but require solution samples. Limits of detection for lighter elements may be more favorable than XRF.

Instrumentation

- Kevex Analyst 770/8000 Energy-Dispersive System Spectrometer System
- Siemens Model SRS 303 Wave-length Dispersive Spectrometer System

Ultraviolet/Visible Spectrophotometry

General Use

- Qualitative measurement of light absorption of solutions in the range of 200 to 800 nm.
- Quantitative measurements of substances via colorimetric reactions.
- On-line process monitoring using flow spectrophotometry.
- Qualitative analysis of organic compounds.
- Measurement of speciation and oxidation states of elements in solution.

Examples of Applications

- Measurement of absorbance vs. wavelength of dye solutions.
- Determination of neodymium in laser glasses after dissolution in acid mixtures.
- Determination of monomeric silica in geothermal brine.
- Monitoring of alkalinity, sulfate, and chloride in scrubber solutions.
- Measurement of nitrogen dioxide in nitric acid process streams.

Samples

Form: Liquid

Size: 1 mL minimum at approximately millimolar concentrations.

Preparation: Solids require dissolution, and may require reaction with a color-forming reagent.

Limitations

- Substance measured must absorb light in the 200 to 800 nm range.
- Precision usually about 0.5 to 2% of concentration measured.
- Limits of detection with colorimetric reagents can be as low as 0.01 ppm.
- Multicomponent samples usually require separations.

Estimated Analysis Time

- 15 minutes to 1 hour per sample if no preparation required.
- Higher throughput possible with automated flow spectrophotometry.

Principle of Technique

Static Spectrophotometry - the fraction of light absorbed by the liquid or compound of interest is measured at specific wavelengths.

Flow Spectrophotometry - the same basic principle except that solutions containing analyte are mixed with color-forming reagents and then passed through a spectrophotometer flow cell to record the absorbances. Continuous monitoring or automatic, sequential analyses of individual solutions is possible with this technique.

Capabilities of Related Techniques

For determinations of low-levels of metals and some nonmetals, *atomic absorption spectrometry* (see p. 8) or the *plasma spectrometry techniques* (see pp. 6, 7, 14) are generally more convenient, except when continuous monitoring is needed. These techniques do not yield speciation information.

Molecular fluorescence spectroscopy can be much more selective and sensitive, but this technique is not currently available on a routine basis.

Instrumentation

- Hewlett-Packard Model 8450A Diode-Array Spectrophotometer
- Technicon Auto Analyzer systems

Infrared Spectroscopy

General Uses

- Fourier Transform Infrared Spectroscopy (FTIR) is used for structure determination and identification of organic and inorganic compounds.
- Infrared spectroscopy is particularly useful for determining functional groups in a molecule.

Examples of Applications

- Identification of plastics, resins, polymers, rubbers, explosives, mock explosives, surface coatings or contaminants such as plastics, grease or pump oil.
- Identification of solids (not applicable to mixtures).
- Quantitative determination of residual hydrocarbons in Freon flushings of welded vessels.

Samples

Form : Almost any solid, liquid or gas.

Size : Minimum :

(1) Solid : 10 mg, or less if soluble in an organic solvent. Flat surfaces 1 cm^2.

(2) Liquids : 50 mL if neat; less if soluble in an organic solvent.

(3) Gases : 10 mL.

Preparation: Minimal or none for qualitative analysis; for quantitative analysis, standards need to be mixed and evaluated.

Limitations

- Infrared spectroscopy is not recommended for mixtures of compounds, although it can be used for the analysis of well-characterized mixtures of less than 10 components. The compound of interest must be in a matrix that is transparent in the spectral region of interest.
- Aqueous samples are difficult because of the absorptivity of the O-H vibration in the mid-infrared region, and because water dissolves most windows used for sample support.
- Compounds can be determined at concentrations of a few percent; however, special techniques can lower this to less than 0.1%.

Estimated Analysis Time

About 1-2 hours are normally required to prepare the sample, obtain a spectrum and interpret the results; quantitation requires more time for preparing and analyzing standards.

Principle of Technique

The FTIR spectrometer consists of a broad-band infrared source, an interferometer, and a detector. Light from the source is directed into the interferometer, where a beamsplitter transmits 50% of the light to a fixed mirror and reflects 50% of the light to a moving mirror. The light then recombines at the beamsplitter, is directed through the sample and impinges on the detector. The resulting signal is then output to a computer for processing. The frequencies of the light absorbed is characteristic of the vibrational modes of the molecules present in the sample and these in turn depend on the functional groups, the molecular structure and its conformation. The FTIR instrument differs from a dispersive instrument in the replacement of the grating with an interferometer and in the

signal processing necessary to obtain a spectrum. The interferogram consists of a power versus time spectrum. Because the detector measures only total light, the value at each time is the sum of the energy from all wavelengths. The Fourier transform maps this time domain onto the wavelength domain. The result is a plot of frequency versus transmittance or absorbance. From this plot, molecular structure can be determined, and in many cases make positive identification of the particular compound can be made.

Additional FTIR Analysis Methods

Infrared Microscopy : A nondestructive technique applicable to solid matrices with transparent, nonhomogeneous portions. Can be used for identifying fibers, coatings, particles, and contaminants on metallic and dielectric substrates; and composition of each layer of laminated polymers.

Attenuated Total Reflectance: A nondestructive technique that is good for analyzing the surface of a solid, i.e., coatings, or it can be used to analyze a nontransparent solid, semisolid or liquid. This technique can be used for the identification of residues on surfaces, adhesives, oils, greases or pastes, plastic films, paper and paper coatings, paints and finishes, fibers and fabrics, foams and coated wires.

Diffuse Reflectance Spectroscopy: Good for characterizing adsorbates on oxide or supported metal catalysts. Also useful for identification of powders; requires minimal sample preparation.

Gas Chromatography/Infrared: Used for structure identification of organic mixtures. The gas chromatograph separates components, which are introduced to the infrared detector as they elute, thereby producing IR spectra for each compound. This allows for the positive identification of many compounds. Submicrogram quantities of mixtures of compounds can be identified using GC/FTIR. Components of the mixture must be soluble in a suitable solvent and volatile at temperatures below 250 to 300∞C.

Capabilities of Related Techniques

Raman Spectroscopy (see p. 12) may yield similar qualitative and quantitative information, and is applicable to aqueous solutions.

Near Infrared Spectroscopy (which typically employs different instrumentation) can be used to measure water and hydroxyl-containing compounds in organic solvents.

Nuclear Magnetic Resonance Spectroscopy (NMR, see p. 37) may yield more detailed structural information and is applicable to different types of compounds.

Instrumentation

- BioRad FTS-40 Fourier Transform Infrared equipped with UMA 300 Microscope for FTIR-microscope work. Also equipped with a Hewlett-Packard 5890 Series II Gas Chromatograph for FTIR-GC work.
- *Software* includes SP 3200 data system on a 380 mb hard disk drive. The Sadtler libraries on disk include the Basic Monomers and Polymers, Gases and Vapors, Polymer Additives, the Starter4 Library, and the EPA library. In addition, there are bound volumes of the Sadtler standard library and selected portions of the commercial library.
- *Accessories* include a Diamond Cell, Attenuated Total Reflectance, Diffuse Reflectance, Specular Reflectance and 4X Beam Condensor accessories.

Raman Spectroscopy

General Uses

- Qualitative characterization of solids, liquids, and solutions; Raman spectra may reveal structural information about molecules.
- Complements information derived from infrared spectroscopy, but is applicable to aqueous solutions.
- Quantitative measurement of major molecular constituents in samples.

Examples of Applications

- Determination of speciation of molecules and ions in aqueous solution.
- Qualitative identification of organic and inorganic compounds.
- Studies of structure and conformation of organic compounds.
- Structural and impurity analysis of polymers.

Samples

Form: Solid, liquid, or solution

Size: Liquids - 0.1 mL minimum Solids (powders) - 50 mg minimum for capillary cell.

Preparation: Samples can be analyzed as received or after particle-size reduction.

Limitations

- Requires concentrations greater than 1 to 5%.
- Sample fluorescence or absorption (near 488 nm) may prohibit Raman characterization.
- Accuracy and precision in quantitative analysis is about 5%.

Estimated Analysis Time

1 to 8 hours per sample. Additional time may be required to interpret spectra.

Principle of Technique

Samples are illuminated with a 15 mW, 488 nm laser beam. Using a double monochromator, a spectrum is obtained of the scattered, wavelength-shifted photons at a 90° angle to the laser beam. The wavelengths of the Raman-scattered light (in the range of about 200 to 5000 cm^{-1}) are characteristic of the internal vibrations of the molecules and are related to the same energy levels as in infrared spectroscopy.

Capabilities of Related Techniques

Infrared Spectroscopy (see p. 11) yields similar qualitative and quantitative information, but is not applicable to aqueous solutions.

Ultraviolet and Visible Spectroscopy (see p. 10) may also be used for compound identification and for quantitative analysis.

Nuclear Magnetic Resonance Spectroscopy (see p. 37) may yield more detailed structural information about particular compounds, especially those containing protons.

Instrumentation

- Spex Model 1488 Analytical Raman System, including Model D1B Computer Controller (488 nm laser)

Ion Chromatography

General Uses

Quantitative and qualitative determinations of inorganic and organic anions in aqueous solutions at concentrations above 0.01 mg/L.

Determinations of cations also possible, but not usually performed at LLNL.

Examples of Applications

- Measurement of fluoride ion in hazardous waste.
- Simultaneous determination of fluoride, chloride, sulfate, sulfite, nitrate, nitrite, and phosphate in groundwater.
- Measurement of acetate and propionate in experimental solutions.
- Measurement of anions from combustion of explosives.
- Characterization of high-purity water.
- Determination of anions on contaminated surfaces.

Samples

Form: Aqueous solutions.

Size: Minimum 1 mL.

Preparation: Aqueous solutions can usually be analyzed as received or after dilution. Complex solutions such as sea waters may require a prior separation to remove interfering constituents.

Limitations

- Species must be ionized in solution, preferably anionic.
- Only free, not bound anions are measured.
- Separation of analyte from matrix usually required if solution is high ionic strength, e.g., brines and sea water.
- Precision usually about 0.5 to 2% of concentration measured.
- Special techniques required for anions of very weak acids such as sulfide and cyanide.

Estimated Analysis Time

15 minutes to 1 hour per sample if aqueous solutions.

Development may be required for some organic acid anions and if separations are needed.

Principle of Technique

Sample is injected into a pumped, solution-carrier stream that passes through an ion-exchange column. Ions are separated and sequentially measured by means of a conductivity or amperometric detector.

Capabilities of Related Techniques

- Ion-selective electrode measurements or potentiometric titrations are possible for many anions, and may be better for high ionic strength solutions, and for cyanide and sulfide ions.
- Carbonate species better measured by aqueous carbon (TIC, TOC) analyzer (see p. 20).
- Silicate more easily measured as silicon by plasma or atomic absorption spectroscopy.

Instrumentation

- Dionex Model 2110i Ion Chromatography System, including 2-channel detection with conductivity or pulsed-amperometric detectors, gradient pump, and two Model 728 Micromeritic Autosamplers.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

General Uses

- Quantitative determinations of elements at sample concentration levels ranging from major constituent to parts-per-trillion.
- Qualitative multielement identification of elements (approximately 70 accessible) and elemental impurities, especially in solutions. ICP-MS is a scanning technique.
- Determination of isotopic composition of elemental constituents.

Examples of Applications

- Quantitative analysis of lanthanide dopants in optical materials.
- Qualitative identification, and quantitative determination of trace impurities in optical materials.
- Determination of naturally occurring metals in environmental soil and water samples.
- Isotopic and impurity measurements in AVLIS-enriched materials, i.e., uranium.
- Trace level determinations of metals in biological fluids.

Samples

Form: Liquids, usually aqueous solutions, can be analyzed as received or after dilution.

Size: Generally, 5 mL of solution is required for routine analysis. The minimum amount of analyte that must be present varies by element but is usually on the order of 500 pg.

Preparation: Solids must be dissolved in a suitable medium usually an acidic, aqueous solution.

Limitations

- Because of its high sensitivity, major constituent analysis requires several stages of serial dilution.
- Solid materials must be dissolved in an aqueous solution.
- No direct chemical speciation or structural information is obtained.
- Coincidental isotopic overlap in the mass spectrum can limit applicability of technique; however, this is usually not a problem for elements having isotopic masses greater than 80 amu.
- High salt or organic rich solutions may cause interference and require additional separations prior to injection.

Estimated Analysis Time

- Including instrument start-up time, analysis of a single solution sample generally requires 2 hours.
- Quantitative determinations usually require 3-4 hours for preparation of samples and standards.
- Qualitative analysis and data interpretation varies from 30 minutes to several days depending on sample matrix and mass spectral complexity.

Principle of Technique

Samples are introduced, generally as a nebulized solution, into an argon-supported, radio-frequency plasma discharge. The energetic conditions associated with the high temperature plasma are sufficient to evaporate and atomize both solvent and solute. A fraction of these atomic species undergo ionization within the discharge. A fraction of the plasma is extracted into a quadrupole mass filter by means of a pair of sampling orifices, together with several stages of differential pumping

which establish the required vacuum gradient between the ambient pressure used for operation of the plasma discharge and the high vacuum conditions required for mass filter operation. Within the vacuum system ions are focused into a beam by a set of ion lenses, separated on the basis of mass-to-charge ratio by means of a quadrupole mass filter, and detected by an electron multiplier operating in a pulse-counting mode.

Data Treatment

Qualitative Analysis: The presence of a given element is established by the presence of isotopes of a specific mass-to-charge ratio. In most cases unequivocal elemental assignment is possible because of the presence of several isotopes at specific masses with known isotopic ratios.

Quantitative Analysis: The concentration of an element is generally measured by comparison with a set of standard solutions of known concentration. Using internal standard techniques, measurement with a relative precision and accuracy of 1% is typical.

Isotopic Measurements: Isotopic ratios, typically accurate to 0.1-0.5%, may be measured using ICP-MS. This requires characterization of mass discrimination effects within the spectrometer for the particular element in question, using materials of known isotopic composition. Additional correction for detector system deadtime is also generally required.

Capabilities of Related Techniques

Plasma Optical Emission Spectrometry techniques (see pp. 6 and 7) are comparable multielement techniques, but are generally less sensitive than ICP-MS. For certain elements (e.g., transition elements, alkali, and alkaline earths) they may be more suitable because interference effects are different.

Atomic Absorption Spectrometry (see p. 8) may have higher accuracy and precision, but also is not as sensitive as ICP-MS.

Solution chemistry techniques may be applicable to certain samples, and are capable of higher accuracy and precision.

DC-Arc Optical Emission Spectrometry (see p. 5) and *X-ray Fluorescence Spectrometry* (see p. 9) may be applicable, but are not as sensitive as ICP-MS. They may be used to analyze solids directly without dissolution.

Instrumentation

- VG Isotopes Plasmaquad ICP Mass Spectrometers (four instruments at LLNL)

II. ULTRA-TRACE ORGANIC ANALYSIS TECHNIQUES
(J Division and Chemistry and Materials Science Department)

A variety of organic samples can be characterized for ultra-trace levels of organics and/or biochemical compounds. We can microscopically inspect the samples for trace particles and isolated ultratrace compounds from a variety of materials. Various techniques are available and utilized to identify unknown samples.

Many compounds and materials can be analyzed by following appropriate sample workup procedures. Some examples of the classes of compounds are highlighted below:

- Organic and organo-metallic chemicals of all types
- Explosives and explosive residue
- Chemical weapon agents
- Chemical agent precursor and degradation compounds
- Biochemical compounds of all types
- Industrial chemicals (lubricants, volatiles, solvents, plasticizers, vulcanization reagents, etc.)
- Drugs and drug precursor compounds

Sample Preparation

Solvent Extraction. Many of the samples are either dissolved or extracted off the surface of an object with a suitable solvent. The extract is then concentrated and a small portion of the solvent utilized for very sensitive analyses.

Organic Compounds. Samples are extracted with a very volatile, highly pure organic solvent which is easily evaporated to a concentrated form. The concentrated extract is then analyzed by many of the instrumental methods of analysis suitable for organic compounds.

Biochemical Compounds. Samples are washed with a suitable buffer solution. The biochemicals are isolated and analyzed immediately. Some select samples are passes through affinity columns to concentrated the target compounds prior to analysis.

Sample Derivatization. Often compounds are not amenable to the particular high sensitivity method of analysis. The chemicals may be too large or too polar, possess low volatility, be thermally unstable, or a stereo isomer which can only be analyzed following derivatization. However, following the chemical alteration (derivatization) of the target compounds, the new substance is most readily analyzed with a variety of analytical techniques.

Many types of derivatization are possible at our facility. The techniques which are often utilized include the following:

- Trimethylsilyl (TMS) derivatization
- Methylation and esterification (diazomethane, methanolic HC1, boron trifluoride/methanol)
- Acetone/HC1 derivatization of sugars
- DMSO/NaH-Methyl iodine methylation
- Catalytic (platinum, palladium, or nickel) hydrogenation
- Osmium tetroxide (hydroxlylation and identification of double bonds positions)

Mass Spectrometry Methods

Mass spectrometry by far yields the most chemical information about a sample than any other analytical technique. Chemical concentrations can be in the micrograms to femtogram concentrations. Typically a sample is introduced into the ion source of the instrument where molecular and fragment ions are generated. These ions are separated from the neutral fragments, manipulated through electrostatic and/or magnetic fields to be uniformly recorded. The intensity and ratios of the fragments allow for the identification, quantification, and characterization of most all types of chemical species.

The sample is ionized by a variety of techniques. The following are utilized in our laboratory for the analysis of all types of samples.

Principle of Technique

Electron Impact. In this technique, the target chemical is bombarded with an electron beam. The electrons impart energy, break bonds, and form stable and unstable fragment ions. The unstable fragment ions further break down and rearrange to other daughter ions. Many fragments are generated for each

molecule being analyzed. The fragments are often associated with the chemical structure of the chemical being analyzed. The measurement of all fragment ions and their relative ratios is performed and displayed as a mass spectrum.

Chemical Ionization. In this technique, a relatively high pressure reagent gas is bombarded with an electron beam in an enclosed chamber. The ionized reagent gas then transfers its charge to the target chemical during the initial analysis. This process generates few fragment ions of the target chemical due to the gentle nature of the ionization process. The most important aspect of chemical ionization is that often the molecular ion or molecular ion region of the mass spectrum is more abundant, and the molecular weight of a compound can be confirmed.

Field Desorption. Samples that will not derivatize, or will never volatilize into the ion source of a mass spectrometer (utilizing GC-MS or probe distillation) can be analyzed with field desorption. The technique utilizes very high voltages to draw off electrons from the target compounds placed on a special molecular filament. This process generates an ionized molecular ion and important fragment ions which are repelled of the surface of the ionization filament. Because high voltages and high velocity ions are formed, few fragment ions are generated. Therefore, the molecular weights of unknowns compounds can be determined. Field desorption is particularly important for the following types of compounds and mixtures which cannot be analyzed by standard methods:

- Toxins
- Venoms
- Zwitter ionic compounds (amino acids and polypeptides)
- Unstable organo-metallics
- Explosives

Fast Atom Bombardment (FAB). Chemicals that cannot be derivatized, sublimed into an ion source, or analyzed by other analytical techniques, can be introduced into the analyzer of a mass spectrometer utilizing FAB. The target compound is suspended in a drop of a polar reagent such as glycerol. The sample is then introduced into the path of a high velocity ionized atom such as argon. Upon impact with the surface of glycerol a charge exchange occurs and the target compounds are ionized and drawn into the ion source of the mass spectrometer. This analytical approach is relatively gentle and suitable for the following types of compounds:

- Toxins
- Venoms
- Zwitter ionic compounds (amino acids and polypeptides)
- Unstable organo-metallics
- Explosives
- Inorganic salts

Sample Introduction and/or Separation Methods. There are a number of methods to introduce a sample into the ion source of a mass spectrometer. Each analytical approach differs depending upon the type of compounds, purity of the sample, and type of data which is needed. The following are some of the methods which are utilized in our laboratory for sample analysis.

Computer Guided Gas Chromatography -Mass Spectrometry. The sophistication of GC-MS allows many types of compounds to be characterized. The following chemicals can be identified when the molecular weights are below 1,000 atomic mass units:

- Most all types of organic compounds
- Certain types of organo-metallic compounds
- All gases
- All organic solvents
- CW precursor compounds
- Precursors utilized in the manufacture of explosives
- Derivatized explosives
- Derivatized amino acids and polypeptides
- Industrial organic compounds and petroleum products

Typically the sample is either dissolved in a suitable volatile organic solvent or injected as a gas directly into the gas chromatographic column.

Probe Distillation. In specific situations, the sample can simply heated in a small crucible and sublimed into the ion source of the mass spectrometer. The probe distillation approach allows for maximum sensitivity for both underivatized and derivatized target compounds. However, if the sample is a

complex mixture, the associated impurities may mask the target compound during the probe distillation experiments. Samples that are amenable to this type of sample introduction are highlighted below:

- Pure crystalline material
- Ultratrace amounts of pure compounds in a mineral matrix
- Polymers that release monomers suitable for an identification of the parent polymer
- Single particles which may be explosives

Pyrolysis GC-MS Analysis. Samples that are very complex and those materials that are not soluble in any solvents can be pyrolyzed directly onto the gas chromatography column. This then allows complex mixtures to be analyzed and to separated major impurities away from the target compounds. The types of samples that are amenable to this type of analysis are highlighted below:

- Hair samples (containing drugs, precursors, and residues)
- Paint
- Unknown polymers
- Kerogen
- Dried blood or other body fluids (drug identification)
- Minerals containing trace organic compounds
- Minerals containing trace gases

Liquid Samples and Thermospray Interface. Certain samples in which the analyte is dissolved in aqueous solutions can be analyzed by mass spectrometry directly. An interface that will ionize all dissolved components as they are heated and sprayed past the ionization source of the mass spectrometer is available in our laboratory. This type of sample introduction allows very water soluble compounds to be analyzed without isolation, derivatization, and concentration. The following compounds are amenable to thermospray mass spectral analysis:

- CW precursors
- explosive hydrolysis products
- toxins
- venoms
- body fluids
- inorganics in water samples

Electrophoresis Mass Spectrometry. Capillary zone electrophoresis separates polar compounds by their selective migration through a suitable buffer while under the influence of a strong electrostatic field. We have an electrophoresis-mass spectrometry interface (EP-MS) that will selectively analyze electrophoretic components in real time. The interface is suitable to be added to our existing mass spectrometers and is important for the analysis of the following compounds:

- explosive
- amino acids and polypeptides
- toxins
- venoms
- polar and thermally unstable chemicals

Moving Belt Mass Spectrometry Interface. Chemicals in water or other solutions can be introduced into the ion source of the mass spectrometry utilizing a moving belt interface which carries the chemicals into the ion source. A differential vacuum pumping interface allows the solvent to be removed and the residue of the chemicals are then analyzed free of the solvent system. The following are all amenable to be analyzed with the moving interface:

- explosives
- organic compounds in solvents
- CW precursors in aqueous solutions
- residues of explosives in aqueous solutions
- chemical reactions in solvents systems

Instrumentation and Limitations

Hewlett-Packard 5985 GC-MS Systems (Four instruments). General purpose quadrupole instruments are available which allow for the characterization of routine samples. The instruments will analyze derivatized and underivatized compounds. The sensitivity limits are typically at the low parts-per-billion level (ppb).

The limitations of this instrumental method of analysis are highlighted below:

- Only organic and organo-metallic compounds which can be volatilized into the ion source of the instrument
- Molecular weights below 1,000
- Volatile compounds generated either by probe distillation or when analyzed by gas chromatography-mass spectrometer

- Analysis time: typically 30 minutes (1 hour for data display and interpretation)

Hewlett-Packard 5988 GC-MS Instrument. The HP-5988 instrument is a quadrupole computer guided GC-MS system. It incorporates a robotically controlled sample introduction capability which insures accurate quantitation when unknowns are compared to standards. The instrument incorporates the latest library search capabilities and currently allows each GC-MS run to be off-loaded for study on personal computers.

The limitations of this instrumental method of analysis are similar to the HP-5985 instrument. Analysis times are slightly longer due to the routine procedures followed by the robotically controlled sample introduction apparatus.

The advantages of the HP-5988 system are that the sample analysis can be programmed into the computer and all aspects of sample introduction are carried out robotically.

Finnigan-MAT-311 High Resolution GC-MS Instrument. *Formula Determinations.* This gas chromatograph, magnetic sector-mass spectrometry instrument is a high resolution mass spectrometer (resolution ca. 50,000) with accuracy obtained to 4 fractional significant figures (e.g., 28.0124 mass units). This level of mass accuracy allows for the assignments of elemental formula from each mass spectral fragment ion. In particular, computer calculations of molecular ions to high resolution allows one to obtain the molecular formula. This is particularly important for the identification of unknown or new compounds which have not previously been characterized.

Field Desorption of Polar Compounds. Another advantage of the Finnigan MAT-311 instrument is that it possesses field desorption capabilities.

Higher Molecular Weight Determinations. With modifications of the acceleration voltage, this instrument can record fragment ions up to 1,800 mass units.

Finnigan GC-Ion Trap Mass Spectrometer *Higher Sensitivity.* This ion trap mass spectrometer is very sensitive. Routinely it can be used to detect picogram amounts of organic substances. Under selected operating parameters the ion trap mass spectrometer can be used to detect femtogram amounts of target compounds in complex mixtures.

MS-MS-MS-etc... One of the advantages of the ion trap hardware and software is that this instrumental method of analysis can selectively isolate and trap unique fragment ions. This capability yields very specific selectivity for the identification of unique compounds in complex mixtures. This, in turn, yields greater confidence in the determination of the target compound in complex mixtures.

Pyrolysis GC-MS. The ion trap mass spectrometer is also set up to thermally desorb chemicals from complex sample matrices. This is very important for the identification of chemicals in the vegetation, hair, or explosive residues.

Thermal Energy Analyzer (TEA). The ion trap mass spectrometer is also configured for TEA analysis. This added feature allows for the screening of nitrogen compounds. TEA will point to compounds which contain nitrogen and simplify the data interpretation.

Finnigan MS-MS (TQS) Instrument with Thermospray Interface. (Two instruments) This gas chromatography and high performance liquid chromatography-triple quadrupole (tandem) mass spectrometer is one of the most sensitive and versatile of all our instruments. The basic capabilities of the instrument are all similar to other mass spectrometer. However, additional advantages and advanced applications are available with this new technology. High-lighted below are the additional attributed features of the TQS mass spectrometer.

Tandem Mass Spectrometer (3 quadrupoles, not in line) Three quadrupoles in a single mass spectrometer allow for the utilization of ion-molecule reaction in the middle quadrupole region. The three quadrupole are all off axis and less random gas ions do not strike the electron multiplier. Less background noise is detected and high sensitivity (0.01 ng) detection limits can be achieved. The specific ion-gas molecule reactions can be utilized to highlight specific chemicals in complex mixtures.

The TQS instrument is suitable for all types of samples (solids, liquids, and gases) which can be introduced under a variety of experimental conditions. The instrument is ideally suited for the detection (without

isolation or derivatization) of ultratrace levels of organic compounds in aqueous solutions.

Portable GC-MS Instruments. Utilizing HP 5971B mass analyzer and associated hardware, we have re-configured our own gas chromatograph and associated hardware into a portable suitcase GC-MS instrument. Weighing a total of 70 pounds, the new instrument package is suitable for on site GC-MS measurements of target compounds in complex mixtures.

Measurement of Carbon Compounds in Water

General Use
- Measurement of total organic carbon (TOC) and purgeable organic carbon (POC).
- Determination of carbonate, bicarbonate, and carbon dioxide in water via measurement of total inorganic carbon (TIC).

Examples of Applications
- Measurement of TOC for water pollution abatement studies.
- Characterization of high-purity water.
- Characterization of ground waters in geochemical studies.
- Measurement of carbonate/bicarbonate in solutions from HE detonation calorimetry.

Samples

Form: Aqueous solutions

Size: 0.34 to 10 mL pumped; down to 5 mL with syringe injection

Preparation: Samples can be analyzed as received or after dilution.

Limitations

Analysis range is:
- TOC - 4 ppb to 10,000 ppm carbon
- TIC - 1 ppb to 10,000 ppm carbon

Precision:
- TOC - 2% or 2 ppb C, whichever is greater
- TIC - 1% or 0.5 ppb C, whichever is greater

Estimated Analysis Time

TIC/TOC - 8 min. per sample

Principle of Technique

TIC and TOC are measured in sequence by means of an automated instrument. TIC is determined by measurement of the carbon dioxide released when the sample is acidified. Carbonate and bicarbonate are converted to carbon dioxide, which, together with any carbon dioxide originally in the sample, is carried into an infrared analyzer for measurement. TOC is determined by measurement of the carbon dioxide released by chemical oxidation of the organic carbon in the sample. POC is determined by the addition of a furnace and purgeables trap to the analysis train.

Capabilities of Related Techniques

Carbonate species in aqueous solution can also be measured by titration, acid CO_2 evolution, or by means of an ion-selective electrode. These techniques may be more accurate, but require much larger samples, and are subject to more interferences.

Instrumentation
- OI Corporation Model 700 TOC Analyzer
- OI Corporation Model 524PS Purging and Sealing Unit

III. BIOLOGICAL ANALYSIS TECHNIQUES (J Division and Biomedical Research Division)

A variety of biological techniques are available in our laboratory for the characterization of samples. These assay methods utilize a variety of modern techniques which focus on large molecular weight compounds including DNA, RNA, proteins, and chemicals within the cell.

Electrophoresis

This technique relies on the selective migration of charged compounds through a buffered gel under the influence of a high electric potential. The compounds that are very amenable to electrophoretic techniques include the following types of compounds:

- venoms
- toxins
- proteins (including immunoglobulins, protamines, etc.)
- DNA, RNA, and associated nucleic acids and bases
- chemically and radio-labeled bio-chemicals
- adducts from CW and BW exposures

Typically all unknown compounds are compared to standard analyzed simultaneously on the same electrophoretic gel.

Immunoassays

When target compounds are chemically bound to proteins from one animal and then injected into another organism, antibodies are produced to the target compound. We have utilized this approach for the sensitive analysis of a specific target compounds. The assay can be made more sensitive and specific when the antibody is labeled with either a radioactive tag or colorful dye pigment. When another additional antibody with affinity to the original target compound antibody is bound to a surface, unique chemical assay methods are available. We have exploited these types of chemical procedures for specific and sensitive assays with complicated samples.

Specific DNA Sequence Identification and Polymerase Chain Reaction

When specific organisms are to be identified, specific DNA sequences can be utilized to positively confirm the presence of the whole organism or fragmented portions of DNA indicative of the organisms. The analysis relies heavily on the new concepts of the polymerase-chain-reaction (PCR). The assay technique actually synthesizes small portions of single stranded, suspect DNA fragments and compares the specific DNA base sequence to a standard. Only when the original sequence is presence will the assay positively identify the target compounds. The assay is most sensitive when radiolabeled or fluorescent tags are added.

The PCR method is ideally suited for the identification of:

- pathogenic and common organisms from DNA samples
- samples derived from living systems
- male or female cell lines
- blood types
- human or animal cell lines

Microscopic Identification of Cellular Components

Through the use of special chemical staining techniques, cellular components can be stained to highlight specific components in cell lines. From these techniques the identification of attenuated organisms can be made. This is very important for the identification of specific pathogenic organisms which have been killed or are suspended in solvents or collection solutions. The use of filtered or fluorescent lighting will also aid in highlighting specific organisms.

Microscopic examination of materials is well suited for the following:

- particles collected from swipes and filters
- cells from living organisms
- spent culture media
- contaminated glassware and apparatus

- air samples and associated filters
- tubing utilized in culture media
- water supplies
- soil samples

Assays for Genotoxicity

Bacterial Mutagenesis

Ames/Salmonella Assay. Chemicals used in the laboratory or present in the environment may not be acutely toxic to handlers but may, nonetheless, present a health risk from long-term low-level exposure. Such health risk often involves damage to the genetic material of the cell potentially leading to mutation, cancer, and/or birth defects. A rapid, sensitive, inexpensive, and high throughput test for genotoxicity is the Ames/Salmonella Assay which tests a substances ability to cause mutations. The analysis is carried out by exposing special Salmonella bacterial strains to a variety of concentrations of the suspect substance, incubating the bacteria on agar that is growth limiting in the concentration of histidine, and assessing the ensuing substance concentration-mutation response relationship. The mutation response is measured by the growth of discrete bacterial colonies on the agar. Only bacteria that mutate are able to grow into colonies because the mutation allows the bacteria to manufacture its own histidine and thus does not require it in the agar media. The slope of a positive dose-response curve indicates the substance's mutagenic potency and sensitivity for mutagens, which can, depending on mutagenic potency, be at the ng level. We routinely conduct the Ames/Salmonella Assay as a means for testing for the presence of mutagenic agents in our laboratories and in research projects being conducted at LLNL. Two dedicated laboratories are available for conducting this analysis. Several hundred samples can be assayed at a time with an assay turnaround of 3 days. This assay is a standard assay used in safety testing chemicals and drugs for mutagenic/carcinogenic potential.

DNA Adduct Analysis

The initiating event in chemical mutagenesis and carcinogenesis is believed to be the covalent binding of a chemical agent to any of the four deoxynucleotide bases that make up DNA – the DNA adduct. A DNA adduct, then, is an indicator of a chemical's ability to be genotoxic as well as being a biological substance that can be used to identify a specific chemical exposure since each adduct is chemically identifiable with the appropriate chemical analysis. DNA adducts also may be stable in the DNA for days to years following the exposure. DNA Adduct analysis is carried out by a variety of methods including immunoassays, chromatography following isotopic labeling, mass spectrometry or any combination of these methods. We actively use these methods in research programs aimed at understanding mechanisms of carcinogenesis and mutagenesis and have developed a highly sensitive DNA adduct analysis capability. The most sensitive analytical technique for DNA adducts is the ^{32}P-postlabeling assay which is capable of detecting adducts at the fmole to amole levels in 1 - 50 µg sized DNA samples. The ^{32}P-postlabeling assay is routinely carried out in our laboratory and is very useful for measuring DNA adducts in humans and animals exposed to complex unknowns.

IV. GENERAL ORGANIC ANALYSIS TECHNIQUES
(Chemistry and Materials Science Department)

Gas & Liquid Analysis by Gas Chromatography

General Use

Qualitative and quantitative analysis of inorganic and organic gases or liquids with boiling points below 500°C. Both polar and nonpolar species can be analyzed.

Examples of Applications

- Analysis of high purity gases for contaminants.
- Specific compounds in liquid or gaseous mixtures can be quantified.
- Fingerprints and simulated distillations of retort oils can be determined using established procedures.
- Environmental screening for non-halogenated volatiles in water, as well as screening for gasoline/diesel oil in extracted soil or water samples.
- Measurement of percent composition and purity of liquid explosives.

Samples

Form: Liquids or gases.

Size: For liquids the amount needed can vary from 0.5 mL for unknown mixtures to 0.1 mL for "familiar" ones. A minimum of 5 mL STP of gas is required, although larger samples with above atmospheric pressures are preferred for trace analysis. Typically a quantity of several liters of gas at STP is desirable.

Preparation: Most samples can be analyzed as received; some may be subjected to a prior extraction.

Limitations

- *Inorganic gases*: Limits of detection in the low ppm range.
- *Organic gases:* Part-per-billion limits of detection for specific species. However, it may be difficult to identify components in complex mixtures. Mixtures containing corrosive gases cannot be analyzed due to reaction with columns and components.

Estimated Analysis Time

Instrument calibration may require several hours since a minimum of three standards are run. Once calibration is completed, most gases can be analyzed in less than 30 minutes. Analysis of liquid samples may require from less than 15 minutes to more than 4 hours, depending on the complexity of the mixture. Overall time is approximately the same as 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 required, the development of a new method is required.

Principle of Technique

Gas or volatilized liquid is injected through an injection port into a flowing stream of inert carrier gas such as helium, argon, or nitrogen. The sample and carrier gas pass through columns which contain a stationary phase. The sample components are separated through sorption or gas-liquid partitioning. The separated components are flushed sequentially from the column and through a detector; thermal conductivity, flame ionization, and electron capture detectors are the most common types. The elapsed time from injection to detection is the retention time for individual species. Identification of the individual components and quantification are achieved by comparing the retention times and peak areas of the sample with those of reference standards.

Capabilities of Related Techniques

Other variations of chromatography such as *High Pressure Liquid Chromatography* (HPLC see p. 24) may be useful for some liquids and solids.

Supercritical fluid extraction and chromatography (SFE/SFC), using carbon dioxide and nitrous oxide and flame ionization detection or ultraviolet detection may also be used. SFE/SFC can be used on solid materials and viscous liquids.

Gas Chromatography-Mass Spectrometry (see p. 17), GC-MS-MS, Gas Chromatography-Infrared Spectroscopy (see p. 12), or NMR (see p. 37) may yield better identification of some components in unknown samples.

Water in gases can be measured at the ppm level by means of a flowing-gas moisture analyzer.

Instrumentation

Instrument	Manufacturer	Model	Detector*	Attachments	Typical Applications
Gas Chromatograph	Antek	3002	He ID	Helium Ionization Detector GC	Trace Gas Analysis
Gas Chromatograph	Hewlett-Packard	5840	FID	Gas Sample Valve	Retort Gases, Hydrocarbons
Gas Chromatograph	Hewlett-Packard	5840	FID, TC	Gas Sample Valve	Refinery Gas Analysis
Gas Chromatograph	Hewlett-Packard	5840	FID, TC	Gas Sample Valve	Refinery Gas Analysis
Gas Chromatograph	Hewlett-Packard	5880	FID	Automatic Sample Injector	Shale Oil
Gas Chromatograph	Hewlett-Packard	5880	FID	Automatic Sample Injector, Headspace Analyzer	Shale Oil Simulated Distillation
Gas Chromatograph	Hewlett-Packard	5890	ECD	—	Freon Analysis
Gas Chromatograph	Hewlett-Packard	5890	MSD, ECD	Mass Sensitive Detector, Gas Sample Valve	Species Identification
Gas Chromatograph	Hewlett-Packard	5890	TC, FID	Gas Sample Valve	Pulse GC
Gas Chromatograph	Hewlett-Packard	5890	TC, FID	Gas Sample Valve	Retort Gases, Hydrocarbons
Gas Chromatograph	Hewlett-Packard	5890	AED	Automatic Sample Injector, Work Station, Element Specific Detector	Shale Oil, Environmental

*ID=Ionization Detector, FID=Flame Ionization Detector, TC=Thermocouple Detector, MSD=Mass Sensitive Detector, ECD=Electron Capture Detector, AED=Atomic Emission Detector

High Pressure Liquid Chromatography (HPLC)

General Use

Qualitative and quantitative analysis of components in mixtures of organic materials. High Pressure Liquid Chromatography (HPLC) is particularly useful for analysis of materials having low volatility or delicate thermal properties.

Examples of Applications

- Analysis of explosives, thermally unstable materials, polymers, and epoxy resins.
- Determination of trace amounts of explosives in soil or water at the ppm-ppb range.

Sample

Form: Liquids or solids.

Size: The amount of sample for analysis may vary from a few milligrams to several hundred grams used for soil extractions.

Preparation: Most samples can be analyzed as received; some may be subjected to a prior extraction.

Limitations

Solids must be freely soluble in the carrier solvent/eluent, and liquids must be miscible with the eluent. Typical eluents are methanol, tetrahydrofuran, and acetonitrile for reverse phase HPLC. Hexane, dichloromethane, chloroform etc are used for regular phase HPLC.

It is difficult to make unambiguous identification of a particular component, especially at trace levels. On-line ultraviolet spectroscopic measurements are possible during analysis for major components, and can be compared with reference standard spectrums for identification. Subsequent analysis by infrared spectroscopy or mass spectroscopy may be necessary in some cases. Not all materials are possible candidates for HPLC analysis due to solubility and detection problems.

Estimated Analysis Time

Calibration is required for all concentration measurement because of the selective nature of the detectors (UV or refractive index RI) and the response factors for the species measured. Instrument time can vary from 30 minutes to 1-2 hours for separation of known samples.

Once a sample has been analyzed and a method developed, analysis time is usually 1-2 hours per sample. When conditions have not been predetermined or no method has been previously published for materials submitted for analysis, method development is required.

Principle of Technique

Samples are injected through an injection port into a flowing liquid eluent and onto the front of a HPLC column. The column is packed with materials such as silica gel, alumina, reverse-phase materials such as C-18, C-8 bonded packings, etc. The eluent (in reverse-phase HPLC) is usually water with some amount of methanol, acetonitrile, or tetrahydrofuran, and is pumped through the column. Separation is achieved by the interaction of the sample species with the column packing and the eluent. As the eluent and sample species pass through the detector, a signal is produced indicating the samples species, separated into its various components. Detection is usually based on ultraviolet response at the particular wavelength specific for the component of interest. Since the packing and eluent used to determine the separation are specific for the separation of interest, HPLC is not a screening technique. The species of interest must be known, and reference materials used to obtain the desired separations. Qualitative and quantitative analysis can then be achieved.

Capabilities of Related Techniques

Ultraviolet spectrophotometric analysis (see p. 10) can be used to determine detector response of specific reference materials.

Gas chromatographic analysis (see p. 23) may be possible for materials with thermally stable properties.

The various techniques in which gas chromatography or HPLC are coupled to mass spectrometry (see pp. 16 - 19) may be used for further identification or detection of unknown species.

Instrumentation

Instrument	Manufacturer	Model	Detector*	Attachments	Typical Applications
Liquid Chromatograph	Hewlett-Packard	1090	UV	Diode Array Det., Work Station	Explosives, Environmental
Liquid Chromatograph	Hewlett-Packard	1084B	UV, RI	Auto Sampling, Work Station	Explosives, Environmental, Curing Agents
Super-Critical Fluid Chromatograph	Suprex	MPS/2 25	FID, UV	Extraction, PC Link	Shale Oil, Environmental

*FID=Flame Ionization Detector, UV=Ultraviolet Detector, RI=Refractive Index Detector

V. ISOTOPIC, ION BEAM AND RADIOCHEMICAL ANALYSIS TECHNIQUES

(Physics Department and Nuclear Chemistry Division)

Accelerator Mass Spectrometry (AMS)

General Uses

Accelerator mass spectrometry (AMS) is used to detect extremely low concentrations (10^{-10}-10^{-16}) of cosmogenic isotopes such as ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, ^{41}Ca, ^{129}I, etc. relative to stable isotope or other elemental abundances. Because these isotopes have short half lives (<20 My) relative to geological time scales, they are very rare and make valuable chronometers or tracers. Several of these isotopes are produced in nuclear testing or are released as a consequence of some steps in the nuclear fuel cycle. AMS offers a general increase of sensitivity of 10^3-10^6 relative to scintillation counting, a reduction in required sample size of 10^3, and analysis time independent of isotopic half-life. AMS has been extensively applied to radiocarbon dating and to geoscience areas such as the carbon cycle, paleoclimatology, and hydrology. In combination with conventional radiochemical counting techniques and noble gas measurements, it may offer unique insights into device or fuel cycle tests, activities, or origins. As isotopes with long lives are accessible, AMS can be used for unique retrospective measurements. The ^{36}Cl content of building materials from Hiroshima and Nagasaki is currently being determined by AMS at LLNL in a reconstruction of the thermal neutron dosimetry of those events.

Samples

All materials for AMS analysis must be reduced to a solid form that is both compatible with and efficient in the operation of the cesium sputtering source used to produce the initial negative ion beam. Because the process starts with negative ions, noble gas isotopes cannot be measured. Specific organic and/or physical chemical pre-treatment processes may be required depending on the original sample matrix. Materials may come as gas, liquid, solid, or particulates on filters. Carbon containing samples are converted to graphite, beryllium to BeO, aluminum to Al_2O_3, etc. Sample sizes can be as low as 50 μg for carbon and are typically 0.5-2 mg for other materials. All molecular or chemical information must be determined before the sample is delivered for AMS characterization. For new isotopes or new matrices, a development sequence is usually required to determine sensitivity, efficiency, and accuracy of the techniques.

Estimated Analysis Time

Measurement time is dependent upon isotope and concentration. Actual time on the accelerator can range from 60 sec or less ("Modern" carbon, $^{14}C/^{12}C$ ratio of $1/10^{12}$) to as long as hours for samples containing low concentrations (i.e. 10^{-15}). In general, chemical preprocessing time of a day or so dominates the actual measurement cycle. LLNL has developed both parallel chemical processing techniques and the highest throughput spectrometer available. In the last year, over 5000 research samples have been measured.

Principle of Technique

A focused Cs beam strikes the solid sample packed into a 1 mm hole in a small aluminum slug that serves as the sample holder and ion source cathode. The ion source contains a cassette holding 60 such slugs, loaded with a mixture of unknowns, calibration standards, and background standards. These may be exchanged by remote control during operation of the source. The negative ion beam formed is accelerated to 35 KeV and then multiplexed over the mass species of interest into a tandem Van de Graaff accelerator. Initial formation of negative ions avoids production of some isobars (e.g. ^{14}N for ^{14}C); acceleration to 4-8 MeV and then stripping the injected beam from negative to positive destroys all molecular isobars of the desired ion (e.g. $^{12}CH_2^-$, $^{12}CD^-$, $^{13}CH^-$ for $^{14}C^-$). After final acceleration to 20-80 MeV depending on isotope of interest, the energetic rare and abundant isotope beams (e.g., $^{14}C^{4+}$, $^{13}C^{4+}$) are separated in a magnetic field. The abundant beam is integrated in a Faraday cup; the particles in the rare beam have further measurements of magnetic rigidity, velocity, energy and rate of energy loss. The resulting uniquely identified ions are counted and

compared to the measured abundant isotope charge. This absolute ratio, corrected for background and normalized to standards to correct for small isotopic fractionation effects, gives the fraction of the rare isotope in the sample.

LLNL can currently measure the isotopes ^{7}Be, ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, and ^{41}Ca. Capability to measure ^{3}H and ^{129}I is under test at present. Development of other nuclei such as fission fragments, U and Pu isotopes is planned.

Capabilities of Related Techniques

AMS is not generally applicable to all isotope measurements. Accuracy is lower than in conventional mass spectrometry of stable isotopes (1-3% as compared to 0.1% or better). For tritium, its sensitivity is not comparable to that of ^{3}He counting. For some heavy isotopes such as U or Pu, inductively coupled plasma mass spectrometry may have higher sensitivity.

Instrumentation

- HVEC Model FN tandem, upgraded to 10 MV operation
- High current 60-sample ion source
- Large aperture spectrometer: 5 cm dipoles, 10 cm quadrupoles
- Supporting sample preparation labs for hot and cold carbon samples, beryllium, chlorine, calcium, iodine and tritium

Ion Micro Analysis

General Uses

Ion microanalysis, as implemented at the Center for Accelerator Mass Spectrometry, in collaboration with Sandia Livermore, uses energetic beams of ions (both light and heavy) to probe the structure of materials. Using different techniques as outlined below, information can be obtained on density variations in materials, elemental composition, surface contamination and, in some cases, depth profiles. The techniques used are as follows:

Ion Microtomography (IMT)

Beams of energetic protons (≤20 MeV) are collimated and focused to beam spot sizes down to 2 μm. The beam is "rastered" in the x and y direction over the sample of interest. In addition, the sample is rotated through a small angle q. At each (x, y, q) point the energy loss of the protons is measured. Using known stopping powers, 3-D tomographic density images can be reconstructed from the data. This extremely powerful technique has been used to look for defects, asymmetries, etc. in a variety of samples ranging from ICF targets, microcircuits, and X-ray laser materials to artificial heart valves and biological samples. Heavy Ion Microtomography is in principle possible but has not been extensively developed at LLNL. This could provide greater sensitivity for thin samples. 2-D images by Scanning Transmission Ion Microscopy (STIM) are done in the same way as IMT except the q motion is eliminated.

Particle-Induced X-ray Emission (PIXE)

This technique employs proton beams of ~3 MeV or more energetic heavy-ion beams (i.e., ~20 MeV C) to probe the elemental composition of materials. Trace element analysis can be carried out at the μg/gr level. At present only elements above phosphorous can be detected. Two dimensional elemental images with a spatial resolution of 10-15 μm can be obtained. Elements from calcium to uranium have been investigated in samples analyzed to date.

The greater X-ray production cross sections for heavy-ions could lead to greater sensitivities for the PIXE technique. Developmental work using Li and C beams have shown X-ray production greater by a factor of 5-10. Carbon beams have been focused to ~25 x 25 μm. Use of heavy ions will require some further development for smaller beam spot sizes.

Rutherford Backscattering (RBS)

Rutherford Backscattering uses beams of protons and heavier ions to determine features such as surface contamination and alloy composition. The cross sections for the backscattered particle (at the appropriate bombarding energy) are determined by coulomb scattering, which allows the accurate determination of composition.. RBS has been used at LLNL with beams of protons to obtain quantitative information on sample composition and thickness of ICF films, for example. Oxygen beams have been used for the investigation of diffusion involving uranium.

Nuclear Reaction Analysis (NRA)

Nuclear reaction analysis uses a nuclear reaction between a target and beam for

materials analysis. As such it is element (isotope) and beam particle specific. An example is the $^{16}O(d,p)^{17}O$ reaction for oxygen analysis. Comparison to known cross sections can provide quantitative information on oxygen content in this case for suitable sample sizes. NRA has been used with the $^{3}He(d,p)^{4}He$ reaction to look at tritium concentrations (^{3}He is the decay product of tritium) in aged tritium bearing samples. Proton-Induced Gamma Ray Emission (PIGE) is another NRA technique which is under consideration for use at LLNL. Some development will be required, however.

Estimated Analysis Time

The specific measurement time for sample analysis is dependent on the technique/ sample/and amount of data required. Times can be from less than a few minutes for a PIXE single spectrum to several hours for a 3-D tomogram. This assumes that all samples are in a suitable form for the particular technique.

Samples

Sample size is, of course, dependent on the specific technique being used. For 2-D STIM using 3 MeV protons the raster size is ~ 6 x 6 mm in x and y. For this case, the sample thickness should be typically ≤400 μm. For IMT this would mean the largest dimension should be ≤400 μm. This insures adequate energy for the transmitted proton to be detected.

For 2-D PIXE using 3 MeV protons the raster size is ~10 x 10 mm. Either thick or thin samples can be used (beam stops in sample or passes through sample). If needed, the sample can be put on thin Mylar (~2.5 μm) which can in turn be mounted on a frame. Standard frames can be supplied

Instrumentation

- HVEC Model FN tandem (10 MV)
- Direct Extraction (Hydrogen) and Cs-sputter (other ions) Ion Source
- PIXE Beamline, Ion Microtomography Beamline, each with microbeam-forming lens.

Noble Gas Analysis Capabilities

Facilities

- Gas separation, processing and analysis laboratory for low, intermediate, and high radiation level samples.
- Small (cc) to large (stere) sized samples can be accommodated.
- Counting systems for alpha, beta and gamma emitting gaseous radionuclides.
- Mass spectrometric facilities for gas composition (including trace noble gases) and isotope ratio determinations.

Techniques/Procedures

- Separation and chemical purification of gas sample constituents by elution chromatography.
- Radiometric determination of tritium (HTO, HT, CH_3T etc.), carbon-14 (CO, CO_2, CH_4, etc.), argon-37 & 39, krypton-76, 77, 79, 85m, 85, 87 & 88, xenon-122, 123, 125, 129m, 131m, 133m, 133, 135, 137 & 138, and radon-222.
- Mass spectrometric determination of sample composition including major constituents and noble gas concentrations, and isotopic ratios in hydrogen, nitrogen, carbon, and all noble gases.

Because of their chemical properties, the noble gases are especially easy to measure at extreme sensitivities. We measure He through Xe. A typical large sample is 10^{10} atoms, a small sample is 10,000 atoms. The typical calibration sample of ^{3}He is 5×10^{7} atoms.

Utilizing Hydrogen Mass Spectrometry we can also measure D/H in samples with moderate sensitivity and precision. This capability has been used for nuclear test program applications of "residual tritium" measurements by supplying D based bomb-fractions.

Equipment

- Separation and processing systems:
  - 2 low + 3 intermediate + 1 high level
  - 3 gas handling and transfer facilities
- Counting systems:
  - 8 tube internal proportional
  - low background
  - 5 26-position thin window beta proportional

- 1 26-position single window gamma
- 6 16-position gamma ray spectrometers
- 1 liquid scintillation spectrometer

- Mass Spectrometer systems:
  - 1 automated magnetic sector, 1-150 amu
  - 1 quadrupole
  - 4 automated noble gas isotope ratio
  - 1 hydrogen isotope ratio
- Field equipment:
  - 2 quadrupole mass spectrometers
  - 2 gamma ray spectrometers
  - 4 sample pumping systems

Radiation Counting Capabilities for Heavy Elements

Definitions

- Low Level = 0 - 200 dpm (0 - 100 picocurie)
- Medium Level = 200 - 40,000 dpm (100 picocurie - 20 nanocurie)
- High Level = 40,000 - 2 x 10^9 dpm (20 nc - 1 millicurie)
- Very High Level = 2 x 10^9 - 2 x 10^{14} dpm (1 mc - 100 curies)

Facilities

- 6 chemistry labs (two fume hoods each) : low - high radiation levels
- 3 chemistry labs (two fume hoods each) : low - high radiation levels
- 2 counting labs: low - high radiation levels
- 2 counting labs: low - very high radiation levels
- LBL Bldg. 88 cyclotron ion irradiation cave 3, 4: low - very high radiation levels
- 4 remote manipulator caves with water shielding: very high neutron, alpha or gamma levels

Auxiliary Equipment

- Ozone generator
- Automated ion-exchange and extraction chromatography apparatus

Techniques/Procedures

- Chemical separations for uranium through lawrencium
- Preparation of "massless" samples for alpha and fission counting
- Preparation of very high level actinide samples (cyclotron targets, etc.)

Radiation Detection Equipment

	Radiation Level			
Technique	Low	Medium	High	Very High
Alpha Counting				
—Scalers	2	7	1	
—PHA	8	6	(---------1---------)	
Beta Counting				
—Scalers		5		
Gamma Counting				
—PHA		2		
Fission Counting				
—Scalers	4			

	Radiation Level			
	Low	Medium	High	Very High
Neutron Counting				
—Scalers	(---------1---------)			

Radioactive Sample Preparation

—Volatilizers		1	1
—Vacuum Sublimation		(----------1----------)	
—Electroplating	(---------2---------)		Several

Gamma-Ray Cross-Section Measurements

Techniques
- Neutron activation
- Charged-particle activation
- Proton-induced X-ray analysis

Measurement Codes
- GAMMANL - a general purpose analysis code for interpreting gamma ray spectra
- GRPANL - a user-interactive code for deconvolting gamma and alpha spectra
- Several actinide analysis codes

Facilities

10MV tandem accelerator and sophisticated computation facilities

Equipment
- 5 automated Ge detector systems for general purpose measurements
- 5 automated 26-position Ge counting systems for small sample counting
- 3 well-type Ge detectors, one with a Compton suppression (or coincidence-mode) NaI "hat"
- 3 portable gamma-spec systems (one "hardened") for field or off-site determinations
- Several stand-alone Ge detector systems (small and large)
- Several Si, beta, and NaI counters
- Suite of gamma detectors
- BGO Compton-suppressed gamma detectors
- Superconducting solenoidal electron transporter
- Electron detectors
- Multiparameter Microvax-based data acquisition system

Additional Radiochemical and Isotopic Analytical Capabilities

Techniques/procedures
- Low - and intermediate-level analysis of environmental samples for HTO, gamma-emitters, Tc, Pu, U, and potentially any radionuclides
- Determination of concentrations, speciation and chemistry of actinides; tracer studies (field and lab)

These methods are used especially for environmental samples, including isotope tracer studies for oceanographic and hydrologic applications. Past emphasis has been more for precision in isotope ratio rather than sensitivity. For thermal ionization mass spectrometry, typical sample sizes are micrograms for precisions of 1 in 10^4 - 10^5 for elements such as Nd and Sr. For uranium, we usually analyze about 100 ng. For Pu and Am we analyze sample sizes of about 100 pg.

Facilities
- Low-level (controlled use/limited access) and intermediate-level chemistry/radiochemistry and sample processing laboratories and counting facilities.
- Includes multiple-sample freeze-dry, distillation, vacuum distillation, electrolytic enrichment and acid dissolution (including perchloric) systems. Controlled atmosphere work/storage space.
- Cleanroom for elemental separations. The "blank" levels are comparable to the best cleanrooms.

Equipment
- Counting equipment – liquid scintillation spectrometers (4 llv, 2 general)
- Gas proportional counters (2 low background H-3), alpha spectrometers (12 llv, general)
- Gamma spectrometers (4 std llv, 2 low background/hi efficiency, 1 compton suppressed)
- Drying, ashing and vacuum ovens
- Combustion systems (dry, wet and bomb)
- Sample grinding and packaging equipment
- Surface area and porosity equipment
- Ultrafiltration (4, ranging from lab to pilot plant in capacity) and filtration gear
- Photoacoustic spectrometry (trace element concentrations and speciation)
- Systems for both static and dynamic tracer leaching and/or sorption experiments.
- Thermal ionization mass spectrometers

VI. NONDESTRUCTIVE PARTICLE ANALYSIS TECHNIQUES
(Chemistry and Materials Science Department)

Scanning Electron Microscopy

General Uses

The scanning electron microscope (SEM) is used primarily to observe the topography of solid surfaces. Because it combines high resolution with large depth of field, it is extremely useful for viewing rough or irregular surfaces. Specific applications include fractography, failure analysis, and electronic device examination. The addition of an energy dispersive X-ray (EDX) system permits simultaneous chemical and visual analysis of the sample. Specific features such as microparticles or inclusions may be analyzed individually, or the spatial distribution (map) of a given element can be displayed to allow direct correlation with visible features. Useful magnifications as high as 60,000X are attainable in the secondary mode (10,000X using back-scattered mode). Chemical analysis by EDX is normally limited to elements having an atomic number greater than ten. SEMs equipped with digital beam control can count and size particles or inclusions yielding information on size, shape, area, and composition.

Samples

Samples must be solid and may have any form. For two of the instruments, samples cannot exceed 30 mm in any dimension. The third SEM has a large stage capable of accommodating specimens up to 8 inches in diameter and up to 1 1/2 inches tall. Powder or particulate samples should be dispersed on a suitable substrate. Nonconductive samples may require a thin coating of conductive material, such as carbon or gold, to be satisfactorily imaged; such coatings are usually applied by sputtering or vapor deposition. The third SEM can examine some materials without coating, but only at a low beam voltage. All samples must be stable in a high-vacuum environment.

Estimated Analysis Time

Some samples can be viewed in a matter of minutes; however, several hours may be needed if extensive preparation or chemical analysis is required.

Principle/Technique

A focused electron beam interacts with atoms in the sample surface, causing electrons to be emitted. These electrons may be ejected from atoms lying within 50 nm of the surface (secondary electrons) or backscattered from depths as great as 500 nm. The intensities of the electron signals depend on local surface topography and elemental composition. An image of the surface is generated by displaying the spatially magnified secondary or backscattered electron yield on a cathode ray tube. Secondary electron imaging is suitable for high resolution of rough surfaces, whereas backscattered electron imaging is suitable for resolution of smoother surfaces, where differences in composition can be observed. The primary electron beam also causes X-ray emission from the atoms in the sample. The X-rays are analyzed by a solid state (EDX) detector which discriminates photon energies. Since each element has a unique set of energy levels, photon energies can be used to identify the elements present.

Related Techniques

Although it does not have as great a range of magnification or depth of field as the SEM, the light microscope can provide a great deal of information quickly and easily. Scanning Auger electron spectroscopy provides chemical information for light elements ($Z<11$) and is more specific to surfaces (2 nm depth) than the energy dispersive X-ray system (EDX) on the SEM. Transmission electron microscopy (TEM) permits higher resolution along with the capability of imaging internal structure (defects, interfaces, and crystallography). However, sample preparation can be more difficult and sample geometry is restricted. Electron probe microanalysis (EPMA) is capable of more precise quantitative analysis of a larger number of elements than the EDX, but requires flat samples that have been carefully prepared.

Instrumentation

- JEOL 35CF SEM with energy dispersive spectrometer
- Amray 1800 SEM (two instruments)

Electron Microprobe Analysis

Bulk chemical analysis provides unambiguous information about homogeneous materials. However, engineering materials, such as multiphase alloys, composites, commercial ceramic bodies, and diffusion bonded assemblies, are often heterogeneous in nature. The electron probe microanalyzer (EPMA) uses a focused beam of electrons to determine the elemental composition of features as small as 1 micrometer. The beam can be scanned over the specimen to produce both an image of the surface (from secondary or backscattered electrons) and a map of the spatial distribution of any element except hydrogen, helium, and lithium. Image resolution is limited to about 10 nanometers, and the threshold concentration for detection is approximately 0.1 weight percent. It should be noted that some materials, such as organics or hydrides, may be subject to decomposition by the electron beam. Moreover, characteristic X-rays escape from greater depths than the electrons used to produce the image, a fact which must be considered when interpreting EPMA data. EPMAs are equipped with digital beam control to count, size, and determine the composition of particles, second phase precipitates, and inclusions.

Sample

Almost any solid can be analyzed, but specimens are restricted to maximum dimensions of 80 x 80 x 20 mm and must be stable in a vacuum. Quantitative analysis requires a flat, polished surface and the use of appropriate standards. Metallographic preparation followed by thorough cleaning is usually required, and nonconductive materials may require coating to minimize charging.

Estimated Analysis Time

Normally, several hours are required to prepare a sample and conduct a qualitative or semiquantitative analysis. Full quantitative analysis demands careful preparation of samples and standards, and may require several working days.

Principle/Technique

An electron beam is focused onto the specimen surface, generating secondary electrons, backscattered electrons, back-scattered electrons, and characteristic X-rays. The electrons can be detected and used to produce a visual image of the sample, as in the scanning electron microscope. X-ray intensities are measured as a function of energy by both solid state (EDX) and wavelength dispersive detectors (WDX). The latter are used for quantitative analyses and for light element ($Z<11$) detection.

Related Techniques

In principle, the scanning electron microscope (SEM, see p. 31) equipped with any energy dispersive analyzer (EDX) and the electron probe microanalyzer (EPMA) are very similar. The EPMA however, is designed to yield analyses which are quantitative; moreover, the wavelength dispersive spectrometer (WDX) gives the microanalyzer light element capability ($5 \leq Z \leq 10$) that the SEM's EDX does not have. Auger electron spectroscopy (see below) is the most surface-specific technique of microanalysis and is most sensitive to light elements, but it also lacks the quantitative precision of the electron probe microanalyzer.

Instrumentation

- Kevex 8000 EDS

XPS Photoelectron Spectroscopy/ Auger High-resolution Auger and Scanning Auger Microprobe

General Uses

The main application of the photoelectron spectroscopy (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 diameter, 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.

Examples of Application

The surface analysis spectrometer has been used to study metals, alloys, organic compounds, ceramics, etc. The main advantage of this technique is its effectiveness in identifying compounds. Such materials as boron carbide, boron nitride, uranyl compounds, etc. have been easily identified.

Principle/Technique

The two techniques utilized together involve energy analysis of electrons emitted form 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 (hv) 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,

$$E_k = hv - E_B.$$

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

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

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.

Data Treatment

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. 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 $\pm$ 10% accuracy, and use of published elemental sensitivities in the Auger technique produces $\pm$ 10% accuracy.

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.

Samples

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.

Estimated Analysis Time

About 4 h should be allowed for sample mounting and 16 h for attainment of a good vacuum (~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.

Instrumentation

The Physical Electronics ESCA-SAM system (Model 549) used for analysis utilizes either MgKa or AlKa X-ray sources. An ultraviolet source will soon be added. This spectrometer is linked with an Eclipse computer for data storage.

Scanning Tunneling Microscopy and Atomic Force Microscopy

General Uses

Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) have scan ranges from the Å to the 100 μm scale, and hence can resolve the structure of surfaces with atomic resolution and determine the morphology of μm-size objects adsorbed on surfaces with high precision. They can operate in vacuum and in all fluids of low electrical conductivity over a temperature range from 0 - 1000K. STM requires that the object under analysis conduct electrons well enough that the resistance across the object to the conducting substrate is smaller than the resistance of the tunneling gap (~Mega-ohm). AFM on the other hand does not require that the object or the substrate be electrically conducting.

Applications

We have used these techniques to determine e.g., atomic surface structure, epitaxy of atoms and molecules on surfaces, morphology and volume of inorganic, organic and biological particles and changes thereof induced by changes in environment, surface morphology of laser fusion implosion spheres, of diamond-machined surfaces, of diffraction gratings. In-situ determination of changes in surface morphology induced by environment, e.g. corrosion, combustion, laser damage, sputter-damage etc.

The instruments can also be used to change (indent, erode, chemically react etc.) surfaces on the nanometer scale.

Samples

Form: Electrically conducting or non-conducting solids and/or particulates as received.

Size. Samples can be of any size, from Å on up. Samples in size between 1 Å and 1 cm are analyzed on sample-holders held inside one of these instruments. Samples range in size from 1 cm upward (there is no size limit) are analyzed by placing the scanning probe (weight ~ 1 lb) onto the surface. The instrumentation can be brought to the sample of interest.

Estimated Analysis Time

Sample preparation is minimal, and a surface scan takes minutes. Consequently *routine* analysis of surface morphology is quick.

Principle of Technique

An atomically sharp "probe" is attached to the end of a piezoelectric crystal which can be controlled with Å precision in x, y, and z. The probe "senses" the proximity of the surface and a feedback mechanism guides the probe to stay in constant proximity to the surface as it is scanned in the x and y directions. In the scanning tunneling microscope the "sensing" is done by monitoring the deflection of a micro-cantilever that occurs as the last atom of an atomically sharp tip mounted at the end of the cantilever "touches" the surface.

Related Techniques

Stylus profilometry (surface height profile along a line with Å resolution in height, and indeterminate resolution in x and y directions).

Scanning electron microscopy(see p. 31). Restricted in sample size, vacuum required, and sample must be (made) electrically conductive. It is difficult to measure surface morphology at nanometer-level because of beam-induced contamination.

Instrumentation

- Digital Instruments Nanoscope II, Nanoscope III with many attachments, operating in air or any fluid.
- Data: digital record of z as f(x,y), displayed in false-color "images".
- Fourier analysis of surface morphology, surface "roughness" analysis, "bearing" analysis, along any line on the surface or over any subset of the surface area can be performed.
- McAllister instrument for operation in ultra high vacuum.

Transmission Electron Microscopy (TEM)

The following paragraphs describe transmission electron microscopy studies that are ongoing at LLNL. These examples demonstrate the wide range of characterization capabilities and include such analytical tools as microdiffraction and energy dispersive X-ray spectroscopy, as well as high resolution electron microscopy and surface replication techniques.

Conventional Transmission Electron Microscopy and Diffraction

General microstructural information can be obtained from materials by thinning to electron transparency and viewing the structures as images having diffraction or Z contrast differences. Reciprocal space information can then be obtained using diffraction techniques.

Applications

- observation of general microstructure
- analysis of crystal orientations
- identification of second phase materials
- dark field analysis of dislocations and precipitates

High-Resolution and Cross-Sectional Capabilities

Method involves the direct imaging of columns of atoms in crystalline materials; thus, it is possible to determine atomic and electronic structures of oriented periodic specimens up to a resolution of 1.6 Å.

Applications

- atomic relationships of interfaces
- coherency between bulk structures and bounding surfaces, e.g. precipitates
- superlattice characterization
- identification of atomic core structure in dislocations and shear planes
- investigation of phase-contrast theory for interpretation of microcrystallites and nonperiodic specimens

Microdiffraction Capabilities

Using a focused electron beam to isolate nanometer-sized areas, the TEM can analyze across very limited interfaces to obtain diffraction information. Minimum probe size is ~ 100 Å.

Applications

- microdiffraction of micro-phase regions
- dark field imaging of microstructures
- crystal structure determination of ultra fine regions
- differentiation between crystal defects having similar contrast effects: twins, precipitates, long-range ordered structures, double diffraction
- orientation relationships between microstructures and matrix
- Burger's vector determination

Surface Replication Capabilities

Technique allows imaging of non-traditional TEM samples such as those that are non-conductive or are fluid:

- polymers
- biological tissue
- suspensions and emulsions
- Indirect imaging of the surface features is possible by evaporation with Pt and C on the specimen and washing away the sample itself to emphasize topological features.

Applications

- determination of shape, size, structure, and distribution of particles in liquid
- imaging of surface features and possible internal structure of macromolecules
- identification of brittle fracture faces
- study of long range order in polymers
- resolution of details to 10 Å

Analytical Capabilities

Quantitative chemical information can be obtained from very small areas in the sample by utilizing the scanning TEM portion of the instrument where the resolution limit is ~30Å. Elements with Z greater than 6 are detectable to 0.5% using a minimum probe size of 200Å. Energy resolution is 150 eV.

Applications

- microanalysis of precipitates
- identification of grain boundary phases
- detection of segregants at defects
- elemental mapping of phases
- quantitative determination of chemical content

Specimen Preparation

The following equipment is available to cut, grind, polish and ion mill material to thicknesses as small as 1000Å:

- diamond saws (small sample cutting)
- microtomes (thin slicing of non-metallic materials)
- diamond corers (small diameter coring)
- spark cutters (coring of metallic specimens)
- slurry corers (coring of non-metallic specimens)
- grinding, fine polishing (down to 1μm finish)
- dimplers (indentation over area of interest)
- ion mills (sputtering of final surface area)
- electropolishers (nonmechanical thinning)

Instrumentation

- JEOL Model 200CX Transmission Electron Microscope
- Kevex Model 8000EDS Energy Dispersive Spectrometer system

Electron Spectroscopy for Chemical Analysis

General Use

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.

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. The results on atom ratios are accurate to within ±10%. Detection limits for atoms on a surface vary from 10 to 100 ppm, depending on the element and the time taken for analysis.

Examples of Applications

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

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 contract their surfaces.

Estimated Analysis Time

Required instrument time can vary from 5 to 10 minutes 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.

Principle of Technique

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 electronics 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.

Instrumentation

- A Hewlett-Packard 5950A spectrometer with a monochromatized AlKα X-ray source is used for analysis.
- Hewlett-Packard 5952A data system and 2100A minicomputer are employed for both instrument control and data reduction.

VII. OTHER TECHNIQUES
(Chemistry and Materials Science Department)

Nuclear Magnetic Resonance Spectroscopy

General Use

Nuclear magnetic resonance spectroscopy (NMR) is applicable for analysis of compounds that contain magnetic nuclei. Compounds typically examined are those that contain the isotopes ^{1}H, ^{2}H, ^{13}C, ^{19}F, ^{27}Al, ^{29}Si, and ^{31}P. Structural, qualitative, and quantitative information can be obtained for both organic and inorganic compounds.

Examples of Applications

- Identification and structure determination of a variety of organic compounds.
- Analysis of solid organic material such as high explosives or rocks from the Nevada Test Site for water content.
- Measurement of coordination type and concentration of silicon atoms in aerogels.
- Determination of Si and Al coordination numbers in zeolites.
- Measurement of phosphorous in metabolites and DNA fragments.

Samples

Form: Liquids, solids, or gases. Nuclear magnetic resonance is a nondestructive technique.

Size: 1 mg quantities are preferred for liquid-state proton (^{1}H) NMR but as little as 10 mg can be used. 10-100 mg quantities are preferred for liquid state ^{13}C NMR. Solid-state NMR quantities vary from 20-200 mg. In every case, analysis time can be exchanged for sample quantity.

Preparation: Samples are dissolved in deuterated solvents for high resolution liquid-state NMR. Solid samples are ground to uniform particle size for magic-angle spinning experiments. Water can be determined in rocks without extensive sample preparation.

Limitations

Limits of detection vary with the nuclei being examined. Protons are the most sensitive nuclei (with the exception of tritium), with the sensitivity for fluorine and phosphorous also being high. Natural level ^{13}C NMR is also routinely performed. We have detected as little as 5×10^{-9} g of hydrogen in 10 mg of sample.

Estimated Analysis Time

An average of 15 minutes is required to obtain a proton spectrum for 1-3 mg of material in 0.5 mL. An average time of 30-60 minutes is required for a natural level ^{13}C spectrum of 100 mg in 0.5 mL. Detailed structural analysis and quantitation requires more time. Dilute solution or solid-state NMR may require overnight data accumulation. The maximum time for data accumulation is usually a weekend.

Principle of Technique

For measurement by NMR techniques, the molecule must contain magnetic nuclei. For example, ^{13}C and ^{17}O can be detected by NMR, but the naturally abundant ^{12}C and ^{16}O nuclei cannot. The sample is placed in the coil of a radio frequency tuned circuit in a magnet field of strength H. The resonant coil must be tuned to the frequency

$$\nu = \omega/2\pi$$

where $\omega = \gamma H$ and g is a constant for each magnetic nucleus (42.57 MHz/tesla for protons). The sample is dissolved in an appropriate, usually deuterated, solvent for high-resolution liquid-state NMR, or is examined as a fine powder for magic-angle spinning studies. Broad line NMR can be performed on samples as received. A radio frequency (rf) pulse of the appropriate frequency is applied to the tuned circuit and the response is monitored in a rf receiver. The response is an exponentially decaying sine wave which is Fourier transformed to yield a spectrum of signal amplitude vs. frequency. Samples are characterized by spectra from which chemical shifts, J-coupling splittings, line widths and shapes, and individual relaxation parameters are obtained.

Capabilities of Related Techniques:

IR, Raman, and UV-VIS spectroscopy (see pp. 10-13) are more sensitive techniques and

give some structural information, but cannot yield the detailed structural or quantitative information derived from NMR.

X-ray diffraction spectrometry (see below) gives related crystal structure information.

Gas chromatography-mass spectrometry (see p. 16) is useful for the identification of complex mixtures and is a more sensitive technique.

Instrumentation

- Bruker Model MSL-300 NMR Spectrometer (300 MHz, for liquids and solids)
- Chemagnetics Model CMX-300 (300 MHz, for solids)

X-Ray Diffractometry

General Use

- Identification of specific compounds and phases on the basis of crystal structures.
- Characterization of solid phase transformations and mixtures of phases.
- Measurement of crystal lattice parameters.
- Measurement of average crystallite sizes.
- Measurement of residual stresses in materials.
- Identification of fiber texture.
- Characterization of multilayered structures.
- Thin film analysis of epitaxial growth.

Examples of Applications

- Identification and semiquantitative estimation of concentrations of phases present in samples.
- Analysis of single crystals for orientation, unit cell size and location of atoms.
- Studies of phase transformations as functions of temperature and pressure.
- Identification of fiber texture in swage and forge worked materials.
- Measurement of residual stresses in annealed materials.
- Examination of surface contamination or thin films of one material on another.

Specific Capabilities

The table on the next page summarizes the characteristics of the equipment and the capabilities in X-ray diffractometry.

Principle of Technique

When a randomly oriented aggregate of small crystal fragments (such as a powder), or a single crystal, is irradiated with a monochromatic beam of X-rays, the various planes of atoms diffract the X-ray beam at angles determined by the spacing between the planes. The diffracted beams are recorded on a film placed concentrically around the sample, or the radiation is detected by a scanning counter, and their position (d-spacing) recorded as a function of scattering angle. Each crystalline phase present in the sample supplies its own unique contribution to the total diffraction pattern. Unknown compounds and phases can be identified by their characteristic patterns. In mixtures, the relative intensities of the patterns can be used to estimate the concentrations of the phases present, and the breadths of the peaks in the pattern are characteristic of the average crystallite size.

X-Ray Diffractometry Capabilities

	Diffractometry	Pole Figure	Glancing Angle	Debye-Scherrer	Guinier	Read	Gandolfi	Laue
Sample Form	Solid or Powder	Solid	Solid	Powder	Powder	ThinFilm Coatings	Single Crystal	Single crystal
Material Size	0.1 mg to inches	1/8" to 1" diameter about 1/8" thick	1/8" to 1" diameter about 1/8" thick	0.1 to 2 mg	2 mg	Less than 2"	50 μm to 2 mm	200 μm to many cm
Preparation	Some may be required	Some may be required	Some may be required	Some may be required	Minimum	Minimum	Small crystals hard to mount	Minimum
Data Collection Time	2 hrs. to 12 hrs.	1/2 hrs. to 3 hrs.	3 hrs. to 12 hrs.	5 hrs. to 8 hrs.	1 hrs. to 2 hrs.	2 hrs. to 8 hrs.	5 hrs. to 12 hrs.	5 min. to 30 min.
Data Reduction Time	1/2 hr. to 1 hr.	1/2 hr. to 1 hr.	1/2 hr. to 1 hr.	1/2 hr. to 2 hrs.	1/2 hr. to 2 hrs.	1/2 hr. to 2 hrs.	1/2 hr. to 2 hrs.	1/2 hr. to 2 hrs.
Limitations	More or less none. Can detect only planes parallel to surface	Size of sample	$2\emptyset < 80°$	Some material not suited to film method	None applicable	Film may be hard to read	None applicable	Film may be hard to read
Output Media	Computer graphics w/ Hardcopy	Computer graphics w/ Hardcopy	Computer graphics w/ Hardcopy	Film	Film	Film	Film	Film
Unique Features	Qualitative, Semiquanti-tative & Quantitative Analysis	Texture in oriented solids	Thin Films, Epitaxy and Surface Contamination	Primarily qualitative	Precision lattice measurements	Texture in oriented solids	Powder pattern from single crystal	Crystallographic orientation

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GLOSSARY

Analyte	The substance or element measured in a chemical analysis.
Bulk Analysis	Analysis of a substantial fraction of all of sample of material, not just its surface.
Major Constituent	Major component of sample; >10 wt%.
Matrix	Background or major constituents of the sample other than the analyte.
Minor Constituent	Minor component of sample; 0.1 to 10 wt%.
Qualitative Analysis	Identification of constituents.
Quantitative Analysis	Measurement of concentrations of constituents.
Semiquantitative Analysis	Measurement of approximate concentrations of constituents.
Surface Analysis	Qualitative or quantitative analysis of surface of sample to a depth of approximately 10 nm or less.
Trace	Concentration or analysis of a constituent at less than approximately 1000 ppm.

ABBREVIATIONS

AAS .....Atomic Absorption Spectrometry

AC.....Alternating Current

AFM.....Atomic Force Microscopy

AMS.....Accelerator Mass Spectrometer

APHA .....Alpha Pulse Height Analysis

AVLIS.....Atomic Vapor Laser Isotope Separation

C&MS .....Chemistry and Materials Science Department

CHN .....Carbon, Hydrogen, and Nitrogen

DC.....Direct Current

DC-ES .....DC-Plasma Emission Spectroscopy

DC-OES.....DC Arc Optical Emission Spectroscopy

EDS, EDX .....Energy-Dispersive X-ray Spectrometer

EPMA.....Electron Probe Micro Analyzer

FTIR.....Fourier Transform Infrared

GC.....Gas Chromatography

GC-MS.....Gas Chromatography/Mass Spectrometry

GC-MS-MS .....Gas Chromatography/Mass Spectrometry/Mass Spectrometry

HPLC .....High Pressure Liquid Chromatography

IC.....Ion Chromatography

ICF.....Inertial Confinement Fusion

ICP-ES.....Inductively-Coupled Plasma Emission Spectroscopy

ICP-MS.....Inductively-Coupled Plasma Mass Spectrometry

IMT .....Ion Microtomography

IR.....Infrared

ISE .....Ion-Selective Electrode

LLNL.....Lawrence Livermore National Laboratory

MS.....Mass Spectrometry

NMR .....Nuclear Magnetic Resonance Spectroscopy

NRA.....Nuclear Reaction Analysis

PES.....Photoelectron Spectroscopy

PIGE.....Proton-Induced Gamma-Ray Emission

PIXE.....Particle Induced X-Ray Emission

POC.....Purgeable Organic Carbon (in Water)

RI.....Refractive Index

RBS.....Rutherford Backscattering

SAM.....Scanning Auger Microprobe

SEM.....Scanning Electron Microscopy

STIM .....Scanning Transmission Ion Microscopy

STLC.....Soluble Threshold Limit Concentration (TEST)

STM.....Scanning Tunneling Microscopy

TEM.....Transmission Electron Microscopy

TIC.....Total Inorganic Carbon (in Water)

TOC.....Total Organic Carbon (in Water)

UV .....Ultraviolet

WDS .....Wavelength-Dispersive Spectrometer

XRD .....X-Ray Diffraction or Diffractometry

XRF.....X-Ray Fluorescence Spectrometry

Z .....Elemental atomic number