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DIRECTORY OF ANALYTICAL METHODS

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GLOSSARY OF COMMON ACRONYMS

		Page
AA	atomic absorption spectroscopy	8
EMP	electron microprobe analysis	48
ES	emission spectroscopy	2
FT-IR	Fourier transform infrared spectroscopy	36
GC	gas chromatography	26
GC/MS	gas chromatography/mass spectroscopy	30
HPLC	high performance liquid chromatography	32
IA	image analysis	44
ICP	inductively coupled plasma	6
IC	ion chromatography	20
IR	infrared spectroscopy (dispersive or Fourier)	34/36
ISS	ion scattering spectroscopy	58
LECO	Laboratory Equipment Company	22
MET	optical metallography	42
NA	neutron activation analysis	12
RBS	Rutherford backscattering spectroscopy	64
SAM	scanning Auger electron microscopy	54
SEM	scanning electron microscopy	46
SIMS	secondary ion mass spectroscopy	60
STEM	scanning transmission electron microscopy	50
TEM	transmission electron microscopy	50
XRD	x-ray diffraction	52
XRF	x-ray fluorescence analysis	10
XPS	x-ray photoelectron spectroscopy	56

PRIMARY USES OF CHARACTERIZATION METHODS IN DEPARTMENT 1820*

TECHNIQUE	elemental	molecular/compound	qualitative	semi-quantitative	quantitative	structure	morphology/topography	macro/bulk	micro	surface	major	minor	trace	solids	liquids	gas	organic	inorganic	mass/isotope	reference page
Emission Spectroscopy	X		X	X	X			X			X	X	X	X				X		2
ICP/Atomic Emission	X		X	X	X			X		*	X	X	X	X	X			X		6
Atomic Absorption	X				X			X			X	X	X	X	X			X		8
X-Ray Fluorescence	X		X	X	X			X			X	X		X	X			X		10
Neutron Activation	X		X	X	X			X				X	X	X	X		X	X		12
Gamma-Ray Spectroscopy	X		X	X	X			X			X	X	X	X	X	X	X	X	X	14
Classical Wet Chemistry	X		X	X	X			X		*	X	X	X	X	X		X	X		16
Electroanalytical	X				X			X			X	X	X	X	X			X		18
Ion Chromatography	X		X	X	X			X			X	X	X	X	X	*	X	X		20
LECO Elemental Analysis	X				X			X			X	X	X	X				X		22
Organic and Elemental Functional Group Analysis	X	X	X	X	X			X			X	X		X	X		X			24
Gas Chromatography	X	X	X	X	X			X			X	X	X	*	X	X	X	X		26
Gas Mass Spectrometry	X	X	X	X	X			X			X	X	X	*	*	X	X	X	X	28
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Dispersive IR		X	X	X	X			X		*	X	X	X	X	X	X	X	X		34
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Optical Metallography							X	X	X	*				X			X	X		42
Microstructural Image Analysis							X	X	X	*				X			X	X		44
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Electron Microprobe	X		X	X	X		X		X		X	X	*	X			*	X		48
TEM	X	X	X	X	*	X	X		X		X	X	*	X			*	X		50
XRD	X	X	X	X	*	X		X			X	X		X			*	X		52
SAM	X		X	X					X	X	X	X		X				X		54
XPS	X	X	X	X	*					X	X	X		X			X	X		56
ISS	X		X	X					X	X	X	X	*	X			X	X	X	58
SIMS	X	X	X						X	X	X	X	*	X			X	X	X	60
Ion Microscopy	X	X	X	X					X	X	X	X	X	X			X	X	X	62
RBS	X		X	X	X					X	X	X	X	X				X	X	64

*Many of these techniques can be modified to perform special analyses other than those indicated. This table is intended as a quick reference.

INTRODUCTION

The Materials Characterization Department, 1820, performs chemical and physical analyses in support of programs throughout the Laboratories. The department has a wide variety of techniques and instruments staffed by experienced personnel available for these analyses, and we strive to maintain near state-of-the-art technology by continued updates. We have prepared this Directory of Analytical Methods in order to acquaint you with our capabilities and to help you identify 1820 personnel who can assist with your analytical needs.

The descriptions of the various capabilities are requester-oriented and have been limited in length and detail. Emphasis has been placed on applications and limitations with notations of estimated analysis time and alternative or related techniques. A short, simplified discussion of underlying principles is also presented along with references if more detail is desired.

The contents of this document have been organized in the order: bulk analysis, microanalysis, surface analysis. This arrangement follows fairly closely the numerical order of the divisions (1821, 1822, 1823), although some deviations exist.

As the design on the cover suggests, many of our techniques are interrelated and frequently yield more than one type of information. A cross-referenced index is provided to help you identify methods which may be applied to solve your specific problems.

We urge you to contact our personnel as far in advance as possible so that we may do our best to ensure that the appropriate analyses are performed in an acceptable time period. We may also be able to provide guidance in the design of experimental matrices and sampling methods, which are frequently critical to obtaining valid analytical results.

Technique - EMISSION SPECTROSCOPY

General Uses

- Qualitative, semiquantitative, or quantitative analysis for up to 72 elements.
- Determination of major (>10%). minor (1-10%), and trace (<1%) elements.

Examples of Applications

- Alloy analysis for metallic elements as well as C, P, and S.
- Analysis for low Z elements such as Li, Be, B.
- Residue or contaminant analysis.

Samples

- Form: solid or liquid.
- Size: depends on method and information sought.
- Materials: alloys, ceramics, semiconductors, organics, geologic specimens.
- Preparation: depends on method used (see below).

Limitations

- Cannot detect noble gases, halogens, N, O, H.
- Detection limits, ppm to ppb.
- Quantitative analysis requires standards for calibration.

Estimated Analysis Time

- Qualitative: 10 minutes to 4 hours.
- Semiquantitative: ≤ 8 hours.
- Quantitative: depends on method (see below).

Comparisons of Available Methods

- Emission Spectrographic Analysis: fast (≈ 4 hrs); qualitative, quantitative, or semiquantitative; can detect ppm; sample must be ground to 200 mesh or ashed and mixed with conducting graphite.
- Direct Reading Spectrometer: very rapid (≈ 5 min) after standardization; requires standards; quantitative analysis presently limited to Fe-, Aℓ-, Ti-, and Cu-base alloys; requires flat surface, 10 mm in diameter and 0.1-mm-thick; accommodates Fe, Ni, and Ti samples up to 12"x18"x24"; precision within ± 1% for most elements.
- Laser Microprobe System: very fast (10 min to 1 hr); qualitative or semiquantitative, surface or small spot analysis (≥ 50 μm dia by 25 μm deep); no sample preparation.

Capabilities of Related Techniques

- X-Ray Fluorescence: fast; requires standards for quantitative analysis; not as sensitive for most elements; can detect halogens and sulfur; not useful for Z ≤ 9.
- Atomic Absorption Spectroscopy: usually slower; cannot do qualitative analysis; analyzes for 1 or 2 elements at a time.
- Inductively Coupled Plasma System: slower; quantitative analysis of over 70 elements; ppb detection limits; requires dissolution of sample.

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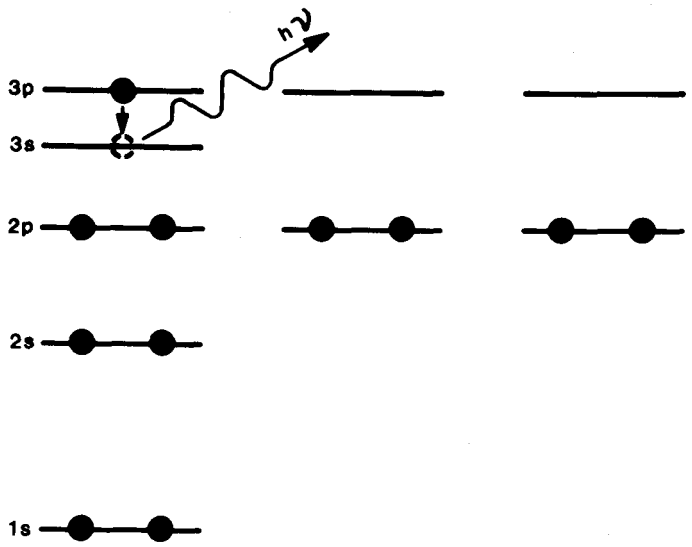
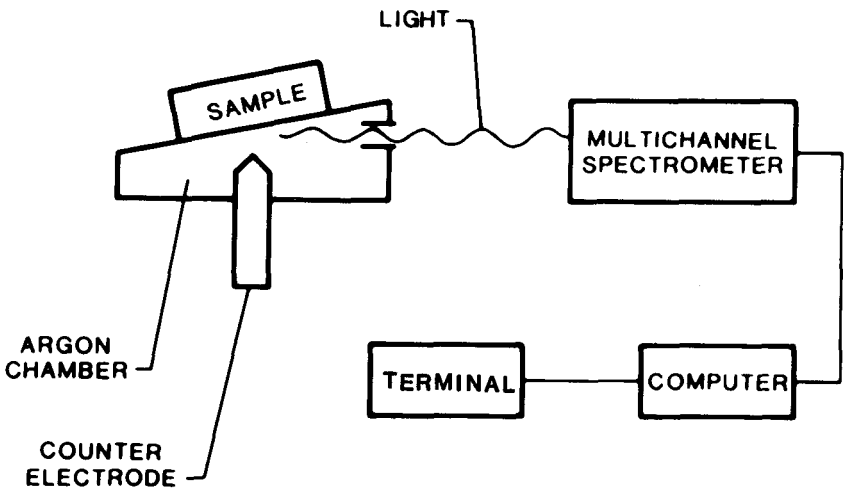
Principles

When the substance to be analyzed is supplied with sufficient energy to cause the constituent atoms to be raised to upper electronic states, the atoms can relax to the ground state by emitting characteristic radiation. By monitoring the frequencies and intensities of the radiation, the composition of the substance can be obtained. Several methods of excitation and detection are available, making emission spectroscopy a very versatile technique.

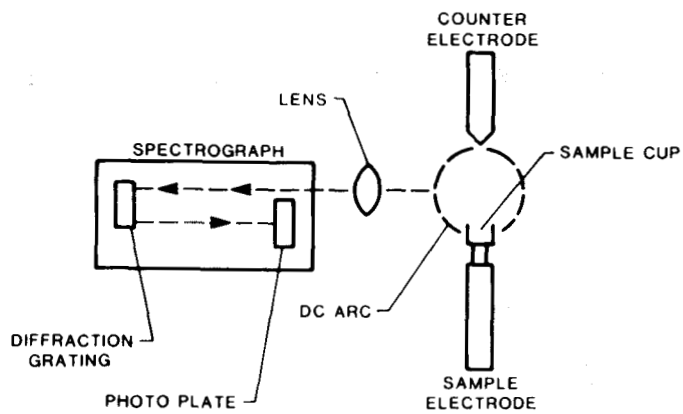


EXCITED Na ATOM RELAXING TO GROUND STATE

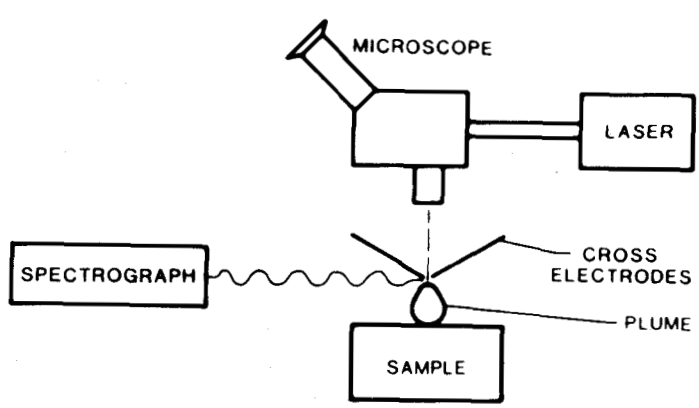
Direct Reading Spectrometer: A flat specimen of an alloy is placed over a small opening in an argon chamber. A high voltage unidirectional spark discharge is produced between the alloy and a tungsten counter electrode. Light emissions produced by the discharge are analyzed by a multichannel spectrometer. The resultant signals are processed by a computer, and the concentrations of the various elements are determined by comparison with known alloys.



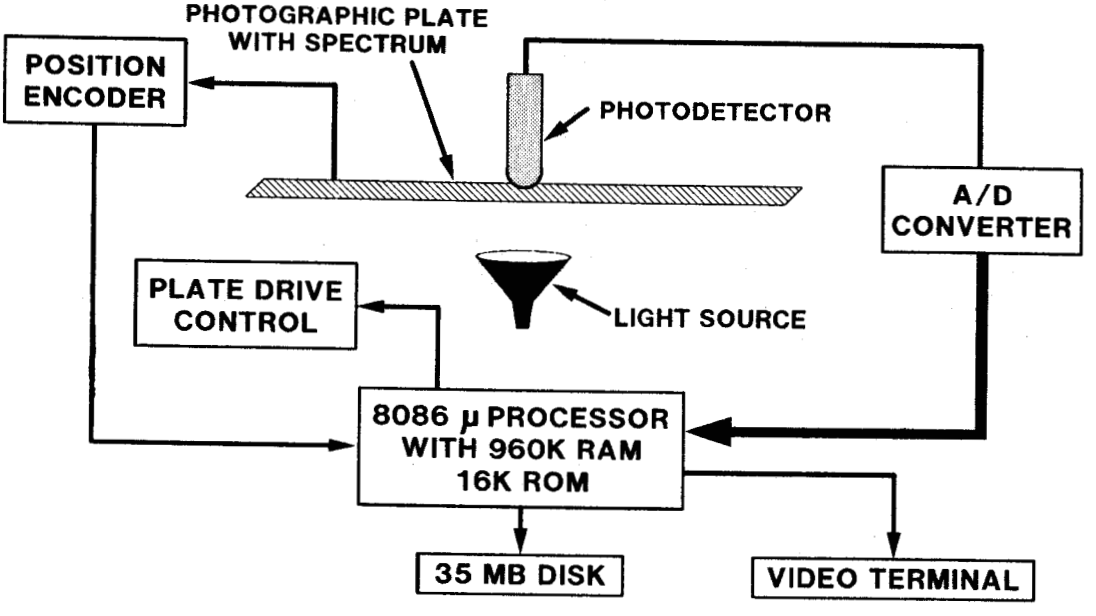
Emission Spectrograph: A sample is mixed with graphite and loaded into a cupped graphite electrode. A 20 amp dc arc is drawn between the sample electrode and a graphite counter electrode. The high temperature (3600°C) of the arc causes the sample to boil out of the cup and into the arc gap where the atoms are excited and emit their characteristic spectra. Light from the gap is passed through a lens system and into a spectrograph. A diffraction grating disperses the light into a spectrum which is recorded on photographic plates. Qualitative analyses are made by examining the spectrum for the presence of lines produced by the elements in the sample. Semiquantitative and quantitative analyses are performed by comparing intensities of the sample spectrum with the spectra from a series of standards.



Laser Microprobe System: A sample is placed under a microscope and a small area is vaporized by a laser burst. The resultant plume triggers a discharge between two "cross electrodes" positioned just above the sample. The discharge excites the atoms in the plume and produces an emission spectrum which is characteristic of the sample material. The spectrum is recorded on photographic plates or polaroid film and evaluated visually by comparison with standards.



Densitometer: A photographically recorded spectrum provides information on the identity and concentrations of the elements in a sample. The densitometer measures the density of the recorded spectrum and calculates the wavelengths of unknown spectral lines. The elements are identified from the MIT Wavelength Tables. Spectrographic analyses are performed by comparing the intensities of selected spectral lines in the sample spectrum with spectra from a series of standards. Emulsion and standard calibration curves improve the accuracy and precision for quantitative analyses.



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Technique - INDUCTIVELY COUPLED PLASMA (ICP) ATOMIC EMISSION SPECTROMETRY

General Uses

- Quantitative and qualitative analysis for over 70 elements with detection limits less than 1 ppm.
- Determination of major (>10%), minor (>1%) and trace (>10^{-6}%) elements.
- Simultaneous multielement analyses.

Examples of Applications

- Trace impurities in alloys, reagents, solvents.
- Si and P in thin films for microelectronics.
- Water analysis.
- Determination of elements which form refractory oxides or carbides, e.g., Ti, U, V, Zr.
- Analysis of glasses, metals, alloys.

Samples

- Form: solids and solutions.
- Size: ranges from ≈ 100-500 mg (solids) or ≈ 10-50 mL (solutions), depending on the materials and the elements to be determined.
- Preparation: solutions can be analyzed as received or diluted to optimum concentration; solids must be dissolved.

Limitations

- Detection limits: ppm to ppb.
- Cannot analyze directly for noble gases, halogens, H, or O.
- Certain elements, e.g., K, Li, Na may be analyzed more effectively by AA.

Estimated Analysis Time

- Dissolution requires up to 16 hours.
- Analysis takes 2-8 hours.

Capabilities of Related Techniques

- Atomic Absorption Spectroscopy: good sensitivity for elements that are poor on ICP; furnace mode often more sensitive; analyzes for 1 or 2 elements at a time.
- Emission Spectrographic Analysis: faster; used for solid samples; less quantitative and with higher detection limits.

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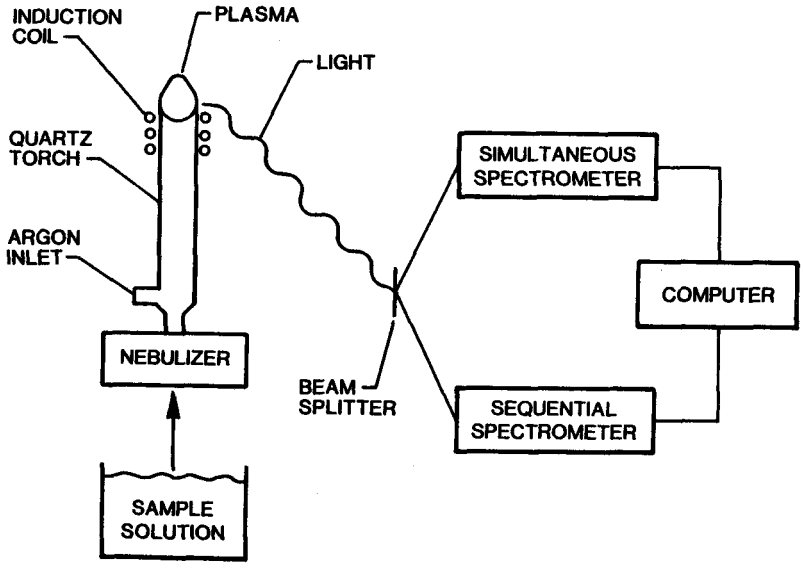
Principle

A high temperature (9000 K) plasma "flame" is produced by inductively coupling radio frequency power into a stream of argon gas. Sample materials are dissolved and introduced into the plasma by a nebulizer where the respective elements emit their characteristic radiation. The diffraction gratings in each spectrometer disperse the light into wavelengths characteristic of each element, and the intensity is measured using photomultiplier tubes. About 30 elements can be determined on the simultaneous spectrometer, and the remainder on the sequential spectrometer which determines one element at a time. The analyte concentration is calculated by comparison with a series of known standards. Refer to Emission Spectroscopy for more details on the principle involved in Inductively Coupled Plasma Atomic Emission Spectroscopy.



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2. R. M. Barnes, Applications of Plasma Emission Spectroscopy, Heyden, Philadelphia, PA (1979).

Technique - ATOMIC ABSORPTION SPECTROSCOPY (AA)

General Uses

- Quantitative elemental analysis of a wide variety of materials which can be dissolved.
- Useful for determination of major (>10%), minor (>1%), and trace ($>10^{-6}$%) elements.
- Most elements on the periodic chart can be quantitatively determined.

Examples of Applications

- Ground waters.
- Trace impurities in alloys, reagents, solvents.
- Salt cores.
- Glasses and ceramics.
- Thin films for microelectronics.

Samples

- Form: solids and solutions, gases if concentrated in liquid or solids.
- Size: flame mode, solids must be 200 mg, solutions must be ≈ 25 mL; graphite furnace techniques can be used on smaller samples.
- Preparation: solutions can be analyzed as received or diluted to optimum concentration; best suited for analyzing solutions in the μg/mL range and greater.

Limitations

- Not suitable for qualitative analysis because each element is determined separately.
- Most effective when approximate composition of sample is known.
- Dissolution is required for solid samples.
- Detection limits ≈ ppm for flame mode, ppb for graphite furnace.
- Chemical or matrix interferences may exist and limit usefulness.
- Cannot analyze directly for H, C, N, O, S, F, Cℓ, Br, I, the noble gases, and a few other elements.

Estimated Analysis Time

- Dissolution requires up to 16 hours.
- Analysis takes ≈ 1-8 hours when in solution.

Capabilities of Related Techniques

- Inductively Coupled Plasma: good sensitivity for elements that are poor on flame AA; can be used for simultaneous multielement analyses.
- Spectrographic Analysis: faster; used for solid samples; useful for qualitative analysis; less quantitative and with higher detection limits.

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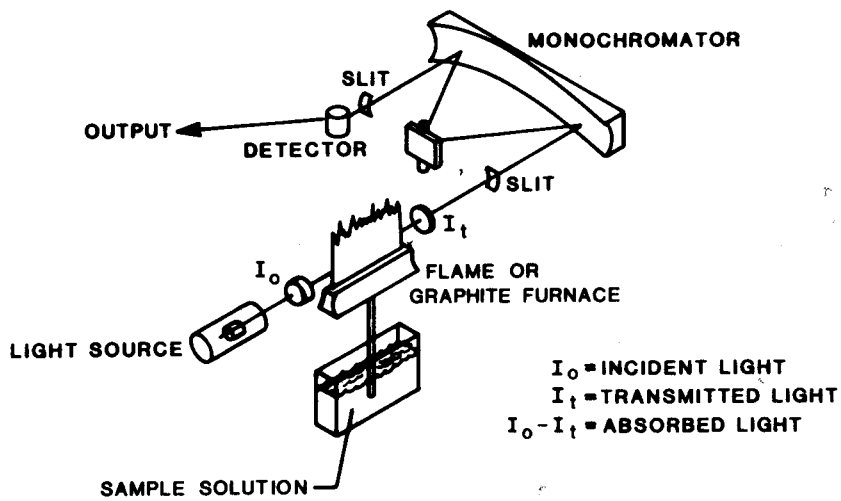
Principle

A light beam with a wavelength characteristic of the analyte element is directed through the sample which is in the form of an atomic vapor. The atomic vapor is formed by aspirating the sample in a flame or by pipetting the sample into a graphite tube which is quickly heated. A fraction of light proportional to the concentration of the element is absorbed by the atoms in the vapor state. The transmitted light is measured against a blank and a series of standards of known concentration from which the analyte concentration is calculated.



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2. C. W. Fuller, Electrothermal Atomization for Atomic Absorption Spectrometry, Analytical Sciences Monographs, The Chemical Society, London (1977).

Technique - **X-RAY FLUORESCENCE ANALYSIS (XRF)**

General Uses
- Bulk qualitative and quantitative elemental analysis of solids and liquids.

Examples of Applications
- Quantitative determination of the composition of materials such as metals and alloys, ceramics, glasses, geologic materials.
- Qualitative analysis to expedite more tedious quantitative methods (x-ray diffraction, atomic absorption, etc.)

Samples
- Form: solids (metals, ceramics, glasses, geologic materials), or liquids.
- Size: powder, 1 gram; bulk, 0.01 to 0.05 m diameter x < 0.05 m high (sampling depth $\approx 10^{-4}$ to 10^{-5} m).
- Preparation: frequently none; some materials must be ground to produce a flat surface; others must be pulverized, pelletized, or dissolved in a tetraborate glass.

Limitations
- Cannot analyze for elements with atomic number < 9.
- Threshold sensitivity: ≈ 0.1%.

Estimated Analysis Time
- ≈ 15 minutes per specimen (if standards are available).

Capabilities of Related Techniques
- Inductively Coupled Plasma and Atomic Absorption Spectroscopy: better sensitivity for all elements, especially those with Z < 11; can do some combinations of elements which cannot be done by XRF because of interferences.
- Emission Spectroscopy: can do semiquantitative analysis of many trace elements at concentrations below XRF threshold.

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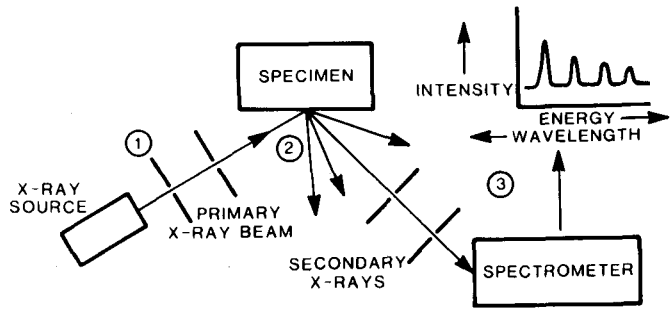
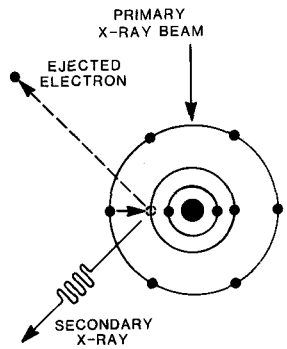
Principle



Region 1: A beam of primary x-rays is generated and directed toward the specimen.

Region 2: The primary x-ray beam penetrates the specimen to a depth of 10^{-4} to 10^{-5} m. and causes ejection of inner shell electrons from the atoms in this region. Outer shell electrons drop down to fill the lower energy electron vacancies. This results in the production of secondary x-rays whose energies are defined by the energy differences between the acceptor and donor electron shells. Since each element has its own unique set of electron energy levels, it also has its own characteristic "fingerprint" of secondary x-ray energies.



Region 3: The secondary x-rays are analyzed by either an electronic energy dispersive spectrometer or a crystal wavelength dispersive spectrometer to obtain a plot of intensity vs energy (or wavelength). Qualitative identification of the elements present in the specimen is performed by comparing the x-ray energies (or wavelengths) from the specimen with the known characteristic energies (or wavelengths) of the elements. Quantitative determination of the percentage of each element in the specimen is obtained by comparing the intensities of the various elemental "fingerprints" from the specimen with those from standard samples of known composition. When appropriate standards are not available, the intensity data can be reduced using a fundamental parameters program to give a less precise semiquantitative analysis of the percentage of each element in the specimen.

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2. E. P. Bertin, Principles and Practice of X-Ray Spectrometric Analysis, Plenum, New York (1975).

Technique - NEUTRON ACTIVATION ANALYSIS

General Uses

- Minor and trace element analysis of a wide variety of sample types.
- Nondestructive analysis for 15 to 30 elements in a sample.
- Mapping distributions of some elements.

Examples of Applications

- Oxygen and silicon in metals, alloys, polymers, ceramics and other materials.
- Analysis for trace elements in semiconductors.
- Rare earth and other trace elements in geological materials.
- Trace and minor elements in metals.
- Mapping U, B, Li distributions in materials using particle tracks.

Samples

- Form: solids or liquids (gases if contained in quartz or aluminum).
- Size: typically 0.1 to 0.5 g but can use larger or smaller.
- Materials: metals, ceramics, minerals, semiconductors, inorganics, organics.
- Preparation: handle or process sample as little as possible.

Limitations

- Detection limits and sensitivities often controlled by interfering activities produced by major elements in the sample matrix: sensitivities can often be enhanced by radiochemical separation procedures.
- Samples may retain some radioactivity.
- Precision typically about 5% relative.
- Analysis time sometimes limited by isotope half-lives.
- Some elements (H, C) cannot be detected because of poor nuclear properties.
- Mapping technique for U, B, Li, requires a flat, polished surface.

Estimated Analysis Time

- For neutron generator irradiations: up to 20 samples can be analyzed per day.
- For reactor irradiations: 2-30 days depending on sample composition and reactor scheduling.

Capabilities of Related Techniques

- Atomic Absorption, Inductively Coupled Plasma, Wet Chemistry: comparable sensitivity in many cases; normally faster analysis but are destructive, susceptible to contamination, and multielement analyses are more difficult.
- Emission Spectroscopy: comparable sensitivity but not quantitative.
- X-Ray Fluorescence: useful for major and minor elements, but sensitivity not high enough for trace; limited to $Z \geq 9$.

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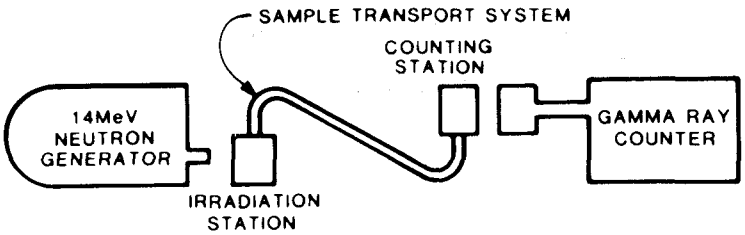
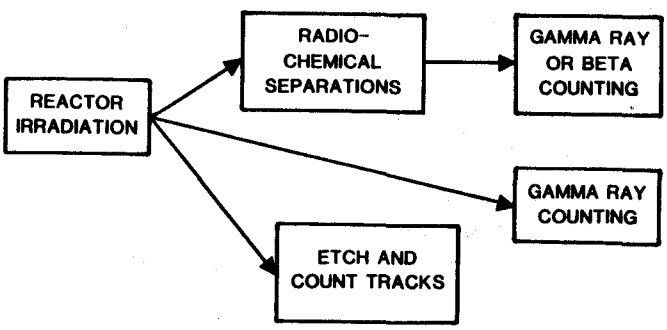
Principles

14 Mev Neutron Activation Analysis: Samples and standards are irradiated with neutrons from a 14 MeV neutron generator. Some elements in the sample are transmuted to radioactive isotopes, generally by (n,p) or (n,α) reactions. Gamma rays from the radioactive products are detected and counted. The energies of the gamma rays are characteristic of the target elements in the sample, and the intensities of the gamma rays are proportional to elemental concentrations in the sample.



REACTIONS FOR OXYGEN ANALYSIS: $n + {}^{16}O_8 \rightarrow {}^{16}N_7 + p$ ${}^{16}N_7 \xrightarrow[7.15s]{t_{1/2}} {}^{16}O_8 + \beta^+$ GAMMA RAYS

Thermal Neutron Activation Analysis: Samples and standards are irradiated with neutrons in a reactor causing most elements in the sample to become radioactive. Gamma rays emitted by the radioactive products are sorted by energy and counted. The gamma ray energies are characteristic of the elements in the sample, and the intensities of the gamma rays are proportional to concentration. For mapping techniques, a particle track detector is placed against the sample during the irradiation to capture fission fragments or α-particles.



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2. D. DeSoete, et al., Neutron Activation Analysis, John Wiley, NY (1972).

3. S. S Nargolwalla and E. P. Przybylowicz, Activation Analysis with Neutron Generators, John Wiley, NY (1973).

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Technique - **GAMMA-RAY SPECTROSCOPY FOR RADIOISOTOPE IDENTIFICATION AND FOR RADIOTRACER STUDIES**

General Uses
- Nondestructive identification of radioactive materials.
- Monitoring progress of radiotracer experiments.

Examples of Applications
- Distinguishing between depleted and natural uranium.
- Identification of radioactive species in radioisotope thermoelectric generator heat sources.
- Determination of amount of ^{24}Na tracer collected on filters during a tracer experiment.
- Leaching studies using radioactive tracers.

Samples
- Form: solid, liquid, or gas.
- Size: any size usable; < 100 g samples are most convenient.
- Material: any material that emits gamma rays or decays to a material that emits gamma rays; may be a pure element, alloy, or compound; or may be contained in or on a nonradioactive matrix.
- Preparation: sample should be sealed in polyethylene, glass, or some other container to prevent contamination of laboratory with radioactivity.

Limitations
- Radioactive isotope must emit gamma rays of suitable energy and intensity to be detected.
- One strongly radioactive isotope in a sample might mask presence of other isotopes.
- Samples must be handled as radioactive materials.

Estimated Analysis Time
- 1 to 48 hours of counting time.
- 1 to 2 days to complete data reduction.

Capabilities of Related Techniques
- Wet Chemistry, Atomic Absorption, X-Ray Fluorescence, etc., can identify elements present but cannot distinguish a radioactive isotope of an element from stable or other radioactive isotopes of the same element.
- Mass Spectroscopy can identify isotopes but is destructive, requires sample preparation, and is usually not set up to handle radioactivity.

Contacts - Division 1821, Bldg. 805, Room 310
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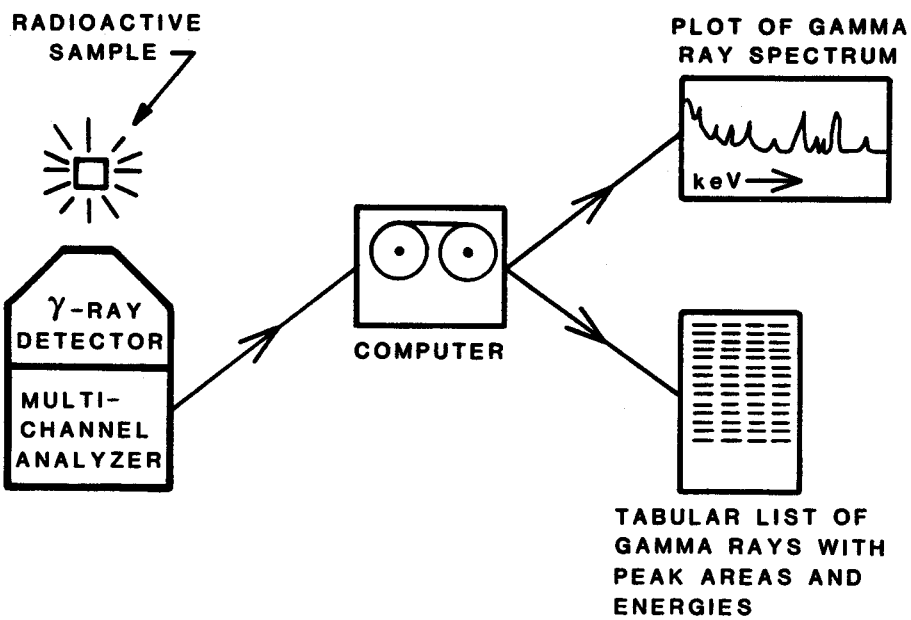
Principles

Identification of Radioactive Materials: The sample is placed near a Ge(Li) gamma-ray detector and counted for up to 48 hours. Output for the detector is processed by a 4096 channel multichannel analyzer to produce a gamma-ray spectrum. The energies of the gamma-ray peaks in the spectrum are characteristic of the radioactive isotopes present in the sample. The intensity of a gamma-ray peak is proportional to the amount of the radioactive isotope present.

Radioactive Tracer Experiments: Samples containing the radioactive tracer are counted on a Ge(Li) or NaI(Tl) gamma-ray detector. The intensity of the radiation in the sample is proportional to the amount of radioactive tracer in the sample.



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Technique - CLASSICAL WET ANALYTICAL CHEMISTRY

General Uses

- Quantitative analysis of samples which cannot be analyzed by instrumental methods.
- Analysis of materials used as standards by instrumental analytical techniques.

Examples of Applications

- Alloys.
- $LiC\ell/KC\ell/CaCrO_4/SiO_2$ for thermal batteries.
- Geological waters and minerals.
- Thick film inks.
- Plating bath analysis

Samples

- Form: liquid or solid, organic or inorganic.
- Size: varies from 1-50 grams depending on the element and its concentration.

Limitations

- Labor intensive.
- Method development or a literature survey may be required before analyses can be done.
- Not applicable to hydrogen or inert gases.
- Usually requires considerable sample.

Estimated Analysis Time

- 1/2 to 6 days depending on the element analyzed and the number of separations required in the process of analysis.

Capabilities of Related Techniques

- Atomic Absorption: preferred for alkali metals; not as accurate on major components.
- Electron Microprobe: more useful for microanalysis; not sensitive to low Z elements.
- Emission Spectrograph: more useful for qualitative and semiquantitative analysis.
- Ion Chromatograph: much faster; useful for many anions and limited number of cations.

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Pam Proctor	4-6450
Mike Gonzales	4-6450

Principle

A chemical analysis of an unknown material involves the identification of its component parts by qualitative chemistry and the determination of the proportions in which these components are present by quantitative chemical procedures. A typical quantitative procedure consists of dissolution of a weighed sample, use of chemical techniques to provide necessary separations and purification, and measurement of the element in question by gravimetric, volumetric, electrochemical, or spectrophotometric procedures.

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Technique - ELECTROANALYTICAL CHEMISTRY

General Uses

- Quantitative analysis of anions, cations, and organic compounds in solution.
- Ultratrace analysis for some heavy metals (Pb, Sb, Cd).
- Identification of oxidation state of elements in solution.

Examples of Applications

- Alloy analysis.
- Precious metal assay: Au, Ag, and others.
- Water analysis for heavy metals and organics.
- Analysis of brines for heavy metals.
- Trace Cr(III) in $CaCrO_4$.
- Plating bath analysis.

Samples

- Size: sample must contain at least 10 μg of the species of interest.
- Materials: must be soluble in a solvent with a dielectric constant greater than $\approx$ 25; e.g., water, ethanol, acetonitrile..

Limitations

- Limited qualitative analytical capability.
- Requires sample dissolution.
- Impractical for Group IA and Group IIA elements.

Estimated Analysis Time

- Sample preparation 1/2-4 hours. Actual analysis time <10 minutes.
- Methods development may be necessary.

Capabilities of Related Techniques

- Atomic Absorption Spectrometry: comparable sensitivity and accuracy for trace analysis; more tolerant of matrix effects but does not provide information on oxidation states.
- Wet Chemical Techniques: generally more accurate, but do not offer the sensitivity of electroanalytical techniques.

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Principle

When a current or potential is applied to a pair of electrodes in a solution, the electrodes respond in a manner which can provide quantitative information on the species in the solution. The application of a potential across these electrodes causes a current to flow which can be related to the analyte concentration. On the other hand, when a current is forced to flow between the pair of electrodes, the resulting potential between them can be used for the quantitative analysis of electro-active ions or molecules in the solution.

Electroanalytical chemistry is dominated by seven special techniques which offer a wide range in sensitivity and accuracy.

- Amperometry: used primarily to enhance the sensitivity and accuracy of classical titrimetric techniques. A sensitivity of 1 mg with a 0.1% accuracy is possible.

- Anodic Stripping Voltammetry: extremely sensitive method best suited for the analysis of heavy metal ions. A detection limit of 10^{-8} M is often achieved.

- Cathodic Stripping Voltammetry: designed for the quantitative analysis of anions at trace levels. The method is restricted to those anions which form insoluble mercury salts.

- Conductimetry: a quick and simple technique for measuring the total electrolyte concentration of a solution. The accuracy is rarely better than 5% but, when this technique is used for endpoint detection in volumetric analysis, the determination of numerous anions and cations with an accuracy of 0.5% is possible.

- Coulometry: not well suited for trace analysis, but perhaps the most accurate instrumental technique available. This is an excellent method for precious metal assay.

- Polarography: a very versatile technique for trace analysis with some qualitative information. Simultaneous analysis of several species in the 10^{-3} to 10^{-6} M range with an accuracy of 3% can be provided.

- Potentiometry: a simple and specific method for the analysis of ions. Although a detection limit of 10^{-9} M can be achieved, the accuracy is generally not better than ± 20%.

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Technique - ION CHROMATOGRAPHY (IC)

General Uses

- Qualitative and quantitative analyses of a wide range of inorganic and organic anions and certain cations in aqueous solutions.

Examples of Applications

- Aqueous solutions such as leachates, brines, well waters, condensates.
- Organically bound halides and sulfur following Schoniger flask combustion and absorption techniques.
- Determination of anions on contaminated surfaces.
- Plating bath solution analysis.

Samples

- Form: solids or aqueous solutions.
- Size: minimum of 10 mg for solids; minimum of 1 mL for solutions; 0.5 μg can be detected on surfaces.
- Materials: inorganic and organic materials, geological samples, glasses, ceramics, leachates, explosives, alloys, and pyrotechnics.
- Preparation: aqueous solutions can be analyzed as received or after dilution; analysis of solids must follow a sample preparation and dissolution procedure.

Limitations

- Detection limits below part per million level for many ions; ppb under ideal conditions.
- Cations: limited to alkali and alkaline earths, ammonia, and low molecular weight amines.
- Must be ionic in solution.
- Must be water soluble.
- Limited work has been done in organic solvents.

Estimated Analysis Time

- Requires 15 minutes to 1 hour per sample if already in aqueous solutions.
- Requires 1 hour per sample for organics.
- Times for other sample matrices are not well established.

Capabilities of Related Techniques

- Wet Chemistry: much slower and less sensitive when mixtures of ions are to be analyzed.
- Selective Ion Electrode: less sensitive and limited to one ion at a time.
- Atomic Absorption Spectroscopy: not capable of analyzing anions; more versatile for analysis of cations.

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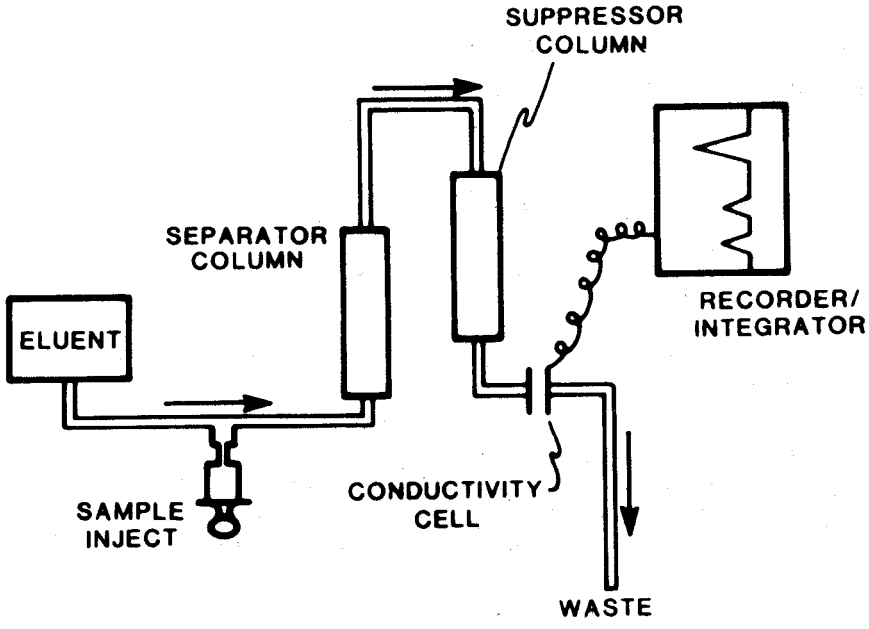
Principle

Solutions containing the ions of interest are injected into an eluent stream and passed through ion exchange columns in which the ions have different residence times according to their affinity for the ion exchange resins. The stream is passed through a second column which removes eluent ions. The ions of interest are detected by a conductivity or electrochemical cell and the subsequent signal is proportional to concentration.



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Technique - LECO ELEMENTAL ANALYSIS

General Uses

- Quantitative determination of carbon, sulfur, oxygen, nitrogen, and hydrogen in metals and alloys.

Examples of Applications

- Verification of alloy specifications.
- Determination of hydrogen in stress corrosion specimens.
- Determination of interstitial oxygen and nitrogen in alloys.

Samples

- Form: solids.
- Size: need at least 2 grams of sample.
- Materials: metals, alloys, slags, glasses, and ceramics.

Limitations

- Neither alkali metals nor organics can be analyzed.
- Method is destructive.
- Oxygen in metals must be carbon reducible.
- Hydrogen analysis being contracted to Rocky Flats; analysis requires ten days.
- Detection limits: carbon, 0.001%; sulfur, 0.005%; oxygen and nitrogen, 1 ppm.

Estimated Analysis Time

- Samples can be analyzed in duplicate in 5-10 minutes (except for hydrogen).
- Samples for hydrogen analyses are sent to Rocky Flats for analysis, and require about 2 weeks for results. Faster service is available for high priority analyses.

Capabilities of Related Techniques

- Neutron Activation: can be used to determine total oxygen and also sulfur in metals.
- No other practical methods exist for these types of analyses.

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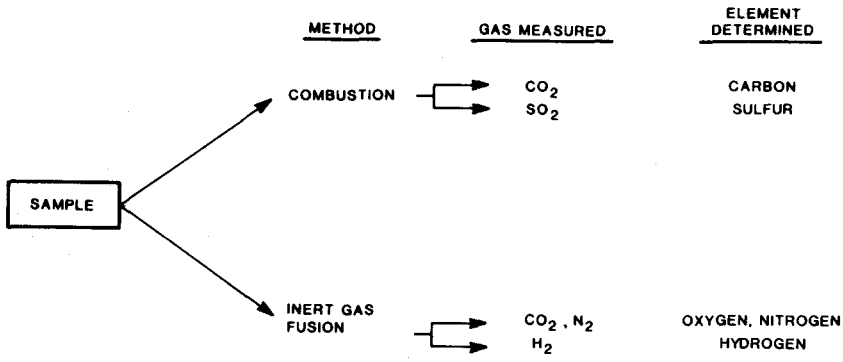
Principle

Element to be analyzed is removed from the sample either as the gas by the application of high heat, or is converted to a gas by combustion. Interferences are removed by passing the gases through special chemical absorption trains; then the gases are quantized by thermal conductivity (oxygen, nitrogen), infrared (carbon, sulfur), or by measuring gas volume (hydrogen).



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Technique - ORGANIC ELEMENTAL AND FUNCTIONAL GROUP ANALYSIS

General Uses

- Elemental composition and functional group determinations for characterization of organic and certain inorganic materials.
- Water contamination in organic materials.

Examples of Applications

- Equivalent weights of polymer components.
- Aging studies of organic materials.
- Identification of organic compounds.
- Analysis of proprietary materials.
- Hydrogen content in metallic hydrides.
- Purity of organic solvents and polymer resins.

Samples

- Form: solid or liquid.
- Size: for C, H, N, O, S by combustion, 2-100 milligram; for Kjeldahl N, 0.2-4 grams depending on N content; for functional group, 1-100 grams depending on sample; for halogens or sulfur by Schöniger flask, 100 mg; for Karl Fischer water, 0.1-100 grams depending on water content.

Limitations

- Samples requiring functional group analyses must be soluble in a suitable solvent for the analytical procedure. Some combinations of functional groups present interferences during the analysis.
- Samples for elemental analyses must be combustible in oxygen.
- Metallo-organic samples require special methods and special combustion tube packing.
- Fluorinated compounds require a specialized analytical train.
- Organic compounds containing silicon require a modified procedure.
- Some functional groups interfere in Karl Fischer water analyses.
- Samples for oxygen determinations must not contain Si, metals, or halogens.

Estimated Analysis Time

- C, H, N analysis by elemental analyzer, 4 hours.
- Kjeldahl nitrogen, 4 hours.
- Schöniger flask combustion for S and halogens, 1 day.
- Functional group, 1-8 hours depending on functional group.
- Karl Fischer water determination, 2 hours.

Capabilities of Related Techniques

- Infrared/Fourier Transform Infrared Spectroscopy: useful for identification of organic compounds; not as accurate for quantitative analysis.
- Gas Chromatography/Mass Spectroscopy: especially useful for identification of components in complex organic mixtures; only semiquantitative.

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Principles

Elemental Combustion Techniques: An organic sample is combusted in oxygen and the resulting combustion products (CO_2, H_2O, SO_2, and N_2) are purified by a special tube packing, then measured by gravimetric, volumetric, or electronic means. For oxygen, the sample is pyrolyzed over platinized carbon to form CO_2 which is detected as above. The quantities of these gases are compared to standards, and composition of the unknown is calculated.

Kjeldahl Nitrogen: A sample containing amine-type nitrogen is digested in a mixture of sulfuric acid, potassium sulfate, and copper sulfate, and the nitrogen converted to ammonium bisulfate. The ammonia contained in the solution is accurately measured following a neutralization and distillation procedure.

Schöniger Flask: A sample is combusted in an oxygen atmosphere inside a special glass flask, the combustion products are absorbed in an aqueous medium, and the element in question (S, Cℓ, Br, F and I) is determined by classical gravimetric, volumetric, or ion chromatographic procedures.

Functional Group Analysis: Analysis for a functional group depends on the use of a characteristic chemical reaction for the functional group in question. The reaction must be specific, rapid, and involve a reactant or product which can be easily measured. Functional groups often determined are: epoxide, hydroxyl, acid, base, amine, peroxide, isocyanate, and unsaturation.

Karl Fischer Water: Precise measurements of water content may be made on a wide variety of organic and inorganic samples. Karl Fischer reagent reacts rapidly and quantitatively with water which permits titrations with endpoints determined amperometrically. As little as 10 ppm water can be detected in 100 mL sample. A larger amount of water can be determined accurately on a smaller sample.

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3. A. Steyermark, Quantitative Organic Microanalysis, The Blakiston Co., Philadelphia, PA (1951).

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5. G. Ingran, Methods of Organic Elemental Microanalysis, Reinhold Publishing Corp., NY (1962)

Technique - GAS CHROMATOGRAPHY (GC)

General Uses

- Qualitative and quantitative analysis of inorganic and organic compounds and mixtures.
- Identification of sorbed gases and liquids in high molecular weight materials.
- Identification of bulk and trace quantities of polymeric and high molecular weight materials.

Examples of Applications

- Analysis of internal atmospheres of sealed components.
- Analysis of high-purity gases for contaminants.
- Quantification of specific compounds in liquid or gaseous mixtures.
- Gas analysis in inorganic and geologic materials.
- Identification of polymers, epoxies, textiles, adhesives, and other trace level contaminants by Curie-Point Dual Capillary Column GC.

Samples

- Form: gases, solids, and liquids.
- Size: dependent upon analysis, typically less than milligrams.
- Preparation: sampling techniques are essential for accurate analyses. Please contact the lab personnel for sampling advice and containers which are compatible with our instruments.

Limitations

- Inorganic gases: low ppm detection limits.
- Organics: ppb detection limits.
- Difficult to identify peaks in complex mixtures (refer to Gas Chromatography/Mass Spectroscopy).
- Components of interest must be volatile or pyrolyzable.

Estimated Analysis Time

- Requires one day installation and bakeout of proper separation column.
- Requires 1/2-1 hour per analysis; may require several analyses per sample.

Capabilities of Related Techniques

- Gas Chromatography/Mass Spectrometry: greater capability for compound identification; not quantitative.
- Infrared/Raman Spectroscopy: difficult to use on complex mixtures because of overlapping spectral features; less sensitive; limited quantitative capability; can be used on nonvolatile materials.
- High Performance Liquid Chromatography: used to separate and quantitate labile and high molecular weight compounds.

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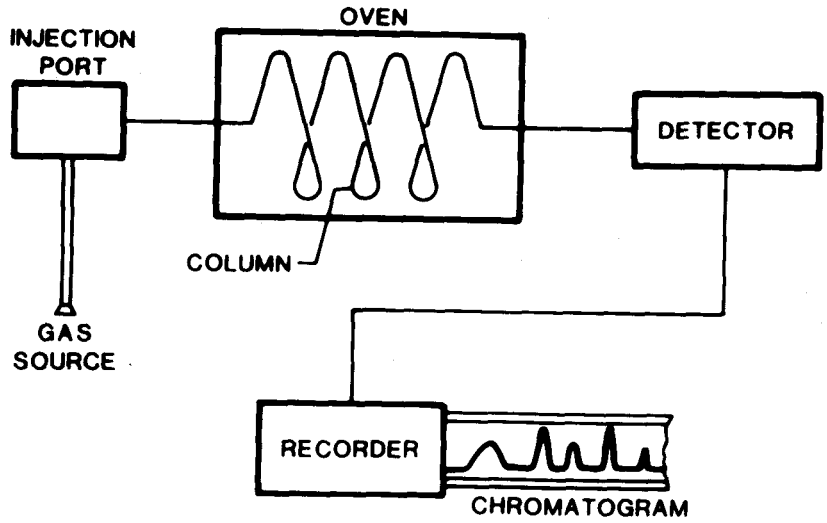
Principle

Chromatography is similar to extraction and to fractional distillation in that the components of a sample are distributed between two phases: the stationary packing and the mobile gas phase. The sample, which has been introduced into a column containing the stationary phase, is separated into its individual components through sorption and/or gas-liquid partitioning. The gas phase containing the sample components enters a detector (thermoconductivity, flame ionization, photoionization, or others). Identification is made by comparing the retention times of known compounds to those of the sample. Quantification is achieved by comparing peak areas of the sample to those of standards.



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Technique - **GAS MASS SPECTROMETRY (Mass Spec)**

General Uses

- Qualitative and quantitative analysis of inorganic and organic compounds and mixtures.

Examples of Applications

- Analysis of internal atmospheres of sealed components.
- Analysis of gas inclusions in ceramic or glass-to-metal seals.
- Quantitation of specific compounds in volatile liquids or gaseous mixtures.
- Analysis of gases in inorganic or geologic materials.
- Analysis of high-purity gases for contaminants.
- Gas isotope ratios.

Samples

- Form: primarily gases.
- Size: 0.001 atm-cc or larger.
- Preparation: sampling techniques are essential for accurate analyses. Please contact the lab personnel for sampling advice and containers which are compatible with our instruments.

Limitations

- Inorganic and organic gases: low ppmv detection limits.
- Difficult to identify components in complex organic mixtures (refer to gas chromatography/mass spectrometry).
- Components of interest must be volatile.

Estimated Analysis Time

- Requires 1/2 to 1 hour per analysis, not including sample preparation and calibration time.

Capabilities of Related Techniques

- Gas chromatography/Mass spectrometry: greater capability for compound identification in complex organic mixtures; not quantitative.
- Gas Chromatography: quantitative, but requires larger sample size.
- Infrared/Raman Spectroscopy: requires larger sample size; IR does not detect some inorganic gases.

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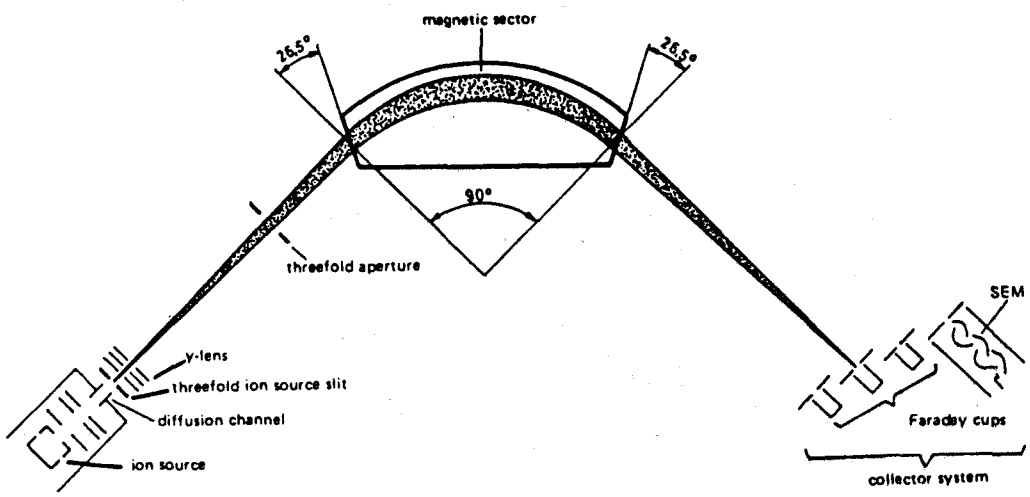
Principle

In a gas mass spectrometer a gas, or a vapor derived from a liquid or a solid is bombarded by a beam of electrons in an evacuated chamber called the ionization chamber. The positive ions formed are accelerated by an electric field into a magnetic field in the analyzer section. In the analyzer the action of the magnetic field at right angles to the electric field causes an ion of a given mass to charge ratio (m/z) to travel in a circular path, the radius of which is proportional to the square root of m/z. By varying either the voltage or the magnetic field, ions of different m/z ratios travel in the same path and pass through a narrow slit into the detector where the corresponding small electric current is amplified and is either measured or recorded. Quantitation of the gases being analyzed is obtained by the use of either pure gases or calibration standards.



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Technique - GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

General Uses

- Identification of components in complex organic mixtures.
- Qualitative and semiquantitative analysis of complex organic mixtures.
- Molecular weight determinations.

Examples of Applications

- Monitoring the cure and aging of polymers.
- Molecular weight determination to within 1 part in 10,000.
- Identification of unknown organic compounds.
- Identification of internal atmospheres and contaminants in sealed components.
- Volatile species produced by pyrolysis can be analyzed and related to nonvolatile parent species.
- Volatile species produced by laser desorption from solid substrates.

Samples

- Form: solids, liquids, and gases.
- Size: dependent upon analysis; typically micrograms to milligrams are used.
- Preparation: sampling techniques are essential for accurate analyses. Please contact the lab personnel for sampling advice and containers which are compatible with our instruments.

Limitations

- Individual compounds may be detected at picogram (10^{-12} g) levels.
- Single-ion monitoring provides femtogram (10^{-15} g) detection levels.
- Molecular weight must be less than 1200 AMU.
- Low vapor pressure materials may be difficult to vaporize and analyze.

Estimated Analysis Time

- Requires one day installation and bakeout of proper separation column.
- Requires 1/2-1 hour per analysis.

Capabilities of Related Techniques

- Infrared/Raman Spectroscopy: difficult to use on complex mixtures because of overlapping spectral features; less sensitive; limited quantitative capability; can be used on nonvolatile materials.
- Gas Chromatography: quantitative for mixtures.

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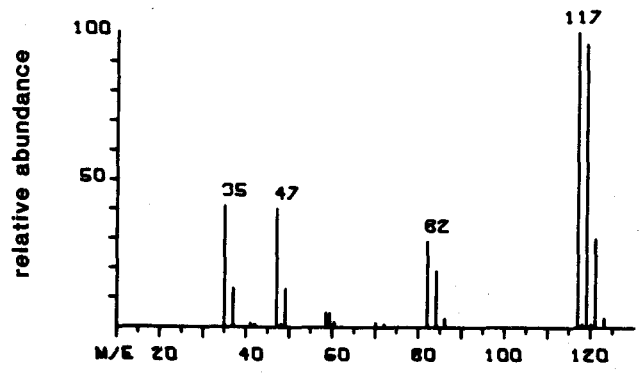
Principle

GC/MS employs the same separation scheme as that outlined under Gas Chromatography, except that the detector is a high resolution Fourier transform mass spectrometer. As the sample components enter the mass spectrometer, they are first ionized and then the ions are trapped in a strong magnetic field. An RF excitation is applied with a range of frequencies covering the range of masses of interest. An RF excitation frequency equal to the natural cyclotron frequency of ions of a given mass causes them to coalesce and diverge in a spiral orbit. The ions are detected by the current they induce in a pair of receiver plates. The signal is amplified, and Fourier transforms in a computer to give mass as a function of radio frequency. In addition to a gas chromatograph, samples can be introduced by means of a heated probe or by laser desorption. Organic compounds, when ionized, typically produce a molecular ion as well as numerous fragment ions; these are usually unique to the compound and are used for identification. An example is shown below. Due to the large amounts of data produced, a computer is used to collect and analyze the spectra. Searchable libraries (>100,000 compounds) are often used to aid in the identification of compounds.



$CC\ell_4$ (carbon tetrachloride)

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Technique - HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

General Uses
- Qualitative and quantitative analysis of organic mixtures.
- Analysis of organic and inorganic compounds for impurities.

Examples of Applications
- Analysis of solvents for low level organic contaminants.
- Verification of purity of organic materials.
- Monitoring the stability of polymers during aging tests.
- Preliminary separations for mass spectrometry analysis.

Samples
- Form: solids (dissolved in the carrier solvent) or liquids.
- Size: solids, mg; liquids, 0.1 mL; an injection volume of $\leq$ 100 μL is typical.

Limitations
- Detection limits can be sub-ng with a suitable detector.
- Solids must be freely soluble in the carrier solvent, and liquids must be miscible with it.
- Difficult to make an unambiguous identification of a particular peak (cf. Gas Chromatography/Mass Spectrometry).

Estimated Analysis Time
- Requires 1/2-1 hour for an analysis; multiple runs are usually made.
- May require 1/2 day to change column, solvents, or detectors for a particular analysis.

Capabilities of Related Techniques
- Gas Chromatography: very similar in many respects but restricted to volatile or pyrolyzable samples.
- Gas Chromatography/Mass Spectrometry: used for identification of components separated by HPLC.
- Ion Chromatography: a form of HPLC which uses an aqueous carrier solvent and provides for the separation of ionic species in aqueous solutions.
- Infrared Absorption: useful for one or few component mixtures where spectral overlap is not a problem.

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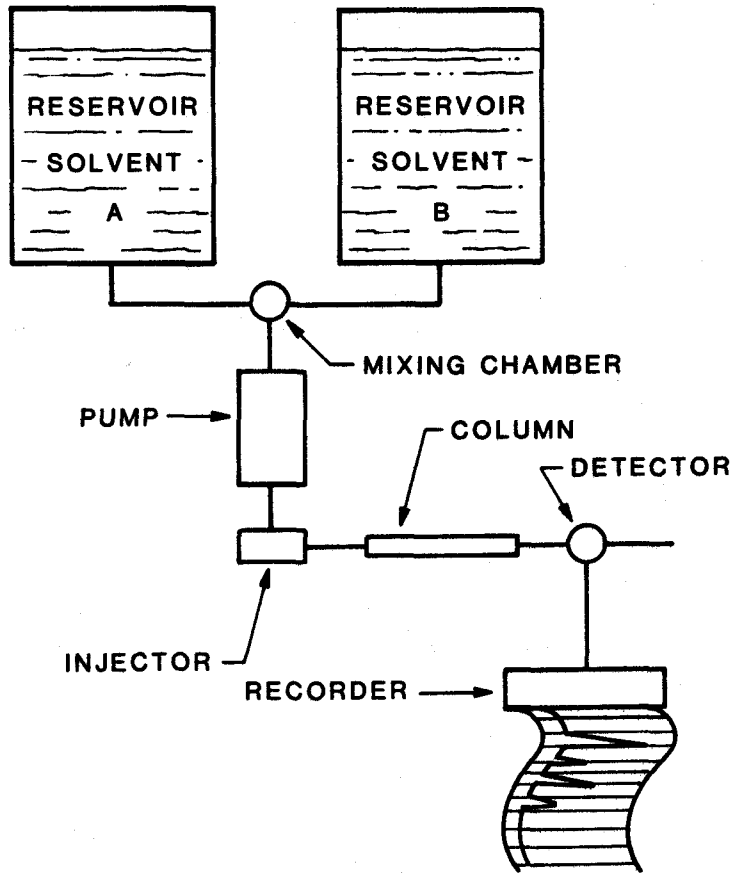
Principle

A mixture of organic materials is injected into a stream of carrier solvent at the top of a chromatographic column. As the mixture is carried through the column each component interacts with both the carrier solvent (mobile phase) and the column packing material (stationary phase). The time required for a component to move through the column depends upon its degree of interaction with each phase. A material which associates strongly with the mobile phase moves through the column quickly while a component which associates strongly with the stationary phase moves much more slowly. Each component is then carried by the liquid phase through a detector at the end of the column. The identity of a component is usually made by comparing and matching its retention time (the elapsed time between injection and detection) with the retention time of a known compound. The quantity of material is determined from the area of its peak on the chromatogram and known standards.



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Technique - **DISPERSIVE INFRARED SPECTROSCOPY (IR)**

General Uses
- Identification of organic chemical species in bulk materials.
- Identification of organic contamination (greases, etc.) that can be removed from component surfaces.
- Limited identification of inorganic materials.
- Measurement of the thickness of transparent thin films.

Examples of Applications
- Changes in structure of organic materials due to aging or curing.
- Measurements of impurities in silicon.

Samples
- Form: solids (5.0 mg min); liquids (3.0 mL min).
- Materials: polymers, adhesives and sealants, fats and waxes, surface active agents, lubricants, solvents, and textiles.
- Preparation: depending on optical thickness--as received, cast film, solution, KBr pellet, or nujol mull.

Limitations
- Difficulty in identifying individual constituents in complex mixtures, especially if absorption bands overlap.
- Analysis complicated by presence of impurities or inorganic materials (e.g., fillers); however, automated search routines have been implemented.
- Species which do not absorb infrared radiation cannot be detected.
- Quantitative analysis capability is limited.
- Spectral range 4000-200 cm^{-1} (2.5-50 μm).

Estimated Analysis Time
- Optical spectra require about 15 minutes.
- Sample preparation including pyrolysis or solvent extraction, if required, may take a few hours.
- Identification of unknown materials may require from a few minutes to several hours, depending upon the nature of the sample and resultant quality of the spectrum obtainable.

Capabilities of Related Techniques
- Fourier Transform Infrared: faster and more sensitive than dispersive infrared; instrumentation more complex and expensive.
- Raman: less sensitive than dispersive infrared; more capable of microscopic analysis; some species not Raman active.
- X-ray Photoelectron Spectroscopy: not structure sensitive as is infrared; much more surface sensitive.
- Gas Chromatography./Mass Spectroscopy: more sensitive; sample must be volatile or pyrolyzable; useful for complex organic species or mixtures.

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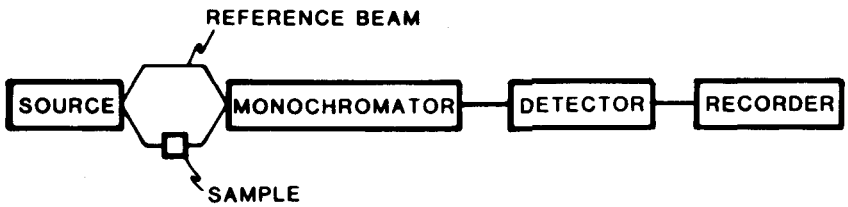
Diana Blair 4-6778

Principle

When a beam of infrared radiation is transmitted through a sample, the constituents preferentially absorb certain wavelengths of radiation resulting in transitions to excited vibrational states. For a given wavelength, λ, the absorbance, A, can be expressed as $A = \log_{10}(I_o/I) = \epsilon C \ell$: where I_o = the intensity of the incident light, I = intensity of the transmitted beam, C = concentration of the absorbing species, ℓ = path length, and ϵ = the extinction coefficient at λ, characteristic of the absorbing species. The variation of the absorbance as a function of wavelength comprises an infrared spectrum which is sufficiently unique as to permit identification of the components present.



Light from a source of infrared radiation is alternatively passed through the sample path and reference path, into the monochromator which scans through the entire wavelength range, and finally onto the thermocouple detector. The signal is amplified and recorded as either percent transmittance vs wavelength or absorbance vs wavelength.

References

1. N. Alpert, W. Keiser, and H. Szymanski, IR Theory and Practice of Infrared Spectroscopy, Plenum. NY (1970).

2. A. L. Smith, Applied Infrared Spectroscopy. John Wiley & Sons, NY (1979).

Technique - FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

General Uses

- Identification of organics and some inorganics.
- Identification of functional groups present in mixtures.
- Quantitative analysis of mixtures.

Examples of Applications

- Trace gas analysis.
- Time resolved spectroscopy of surface chemical reactions.
- High sensitivity analysis of light impurities including H in silicon.
- Quantitative analysis of glass.

Samples

- Form: solids, liquids, solutions, or gases.
- Size: >3 mm for maximum sensitivity, but spectrum is possible in some cases to 100 μm; gas cell path length 1 cm to 20 m.
- Preparation: depending on optical thickness--as received, cast film, solution, KBr pellet, or nujol mull.

Limitations

- Must be infrared active.
- 5000-400 cm^{-1} (2-25 μm) spectral range.
- No metals (except coatings or films on metals).
- Optical density ≤ 4 for qualitative, ≤ 1 for quantitative.
- Lateral resolution in microscopic mode ≈ 50 μm.

Estimated Analysis Time

- Five minutes to several hours depending on concentration of species being analyzed and sample transmission.
- May require nitrogen purge of spectrometer (1-15 minutes) depending on sample.

Capabilities of Related Techniques

- Dispersive Infrared: generally slower and less sensitive than Fourier transform infrared, but equipment is simpler and more reliable.
- Raman Spectroscopy: may be sensitive to species which are not detected using absorption spectroscopy.
- X-Ray Photoelectron Spectroscopy: not structure sensitive as is infrared; much more surface sensitive.

Contacts - Division 1823, Bldg. 806, Room 301/303

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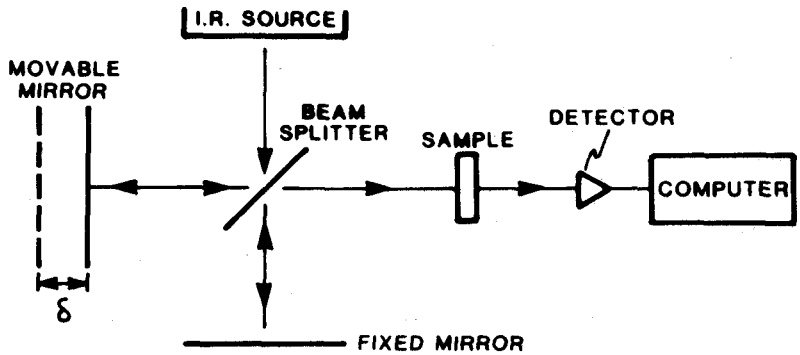
Alex Pimentel	4-8139

Principle

The principle is the same as that of Dispersive Infrared Spectroscopy; however, the technique of obtaining the sample absorbance as a function of infrared wavelength is quite different.



Light from an infrared source is incident on a beam splitter which reflects 50% of the light toward a movable mirror and transmits 50% of the light to the fixed mirror. After reflection from these mirrors, about 50% of the light from the fixed mirror is reflected from the beam splitter and combined with the light from the movable mirror which had been transmitted by the beam splitter. If the distances from the beam splitter to the fixed and to the movable mirrors are the same, the recombined light will constructively interfere at all frequencies. If the movable mirror is moved a distance, δ, farther from the beam splitter, light waves being reflected from the mirror must travel a distance 2δ farther than light waves reflected from the fixed mirror. Since the source emits light waves of many frequencies, some frequencies will still constructively interfere (for wavelengths where $n\lambda = 4\delta$; n = even). But, some wavelengths will destructively interfere ($n\lambda = 4\delta$; n = odd). Thus, the total light at the detector (with no sample in the beam) is a maximum where $\delta = 0$. If we measure the intensity of light at the detector as a function of δ, we obtain an interferogram. This data can be Fourier transformed in a digital computer to give the intensity as a function of frequency (intensity spectrum). If the intensity spectra with and without a sample in the beam are divided, the absorption (or transmission) of the sample is obtained. Because this method measures all frequencies of light at once, it is much faster (or much more sensitive for a given measurement time) than dispersive infrared.

References

1. P. R. Griffiths, Chemical Infrared Fourier Transform Spectroscopy, John Wiley & Sons New York (1975).

2. R. J. Bell, Introductory Fourier Transform Spectroscopy, Academic Press, NY (1972).

Technique - **FLOURESCENCE/RAMAN MICROANALYZER**

General Uses

- Identification of the molecular composition of chemical species by optical emission and scattering properties.
- Molecules on the surface or in the near surface layer of a solid can be identified by their characteristic vibrational frequencies.
- Maps of the location of various molecular species can be obtained.
- The crystal structure surrounding certain fluorescent ions can be characterized.
- Ultratrace levels of fluorescent organic/inorganic species can be detected and quantified.

Examples of Applications

- Determination of the molecular-level structure of glassy and crystalline materials.
- Identification of surface contaminants or corrosion products.
- Identification of microscopic chemical phases in/on geological and synthetic materials.
- Monitoring of chemical processes, e.g., on catalysts or at elevated temperatures.

Samples

- Form: primarily solids, but liquids and gases can be analyzed using Raman if contained in a suitable sample holder.
- Size: $\leq$ a few cm diameter and 1 cm thick.
- Materials: virtually anything Raman active, fluorescent or capable of being doped with fluorescent species.

Limitations

- Some species not Raman-active or fluorescent.
- Raman detects species with concentrations $\geq$ 1%.
- Optical penetration often limited to a few thousand Å.
- Incident laser beam may cause damage due to sample heating.
- Laterial resolution $\approx$ 1 μm.

Estimated Analysis Time

- 1 to 4 hours per sample.

Capabilities of Related Techniques

- Infrared and Fourier Transform Infrared Spectroscopies: more sensitive to bulk constituents and impurities; more extensive libraries of reference spectra available; some species not infrared active.
- X-Ray Photoelectron Spectroscopy: more surface sensitive but does not give an unambiguous identification in many cases.

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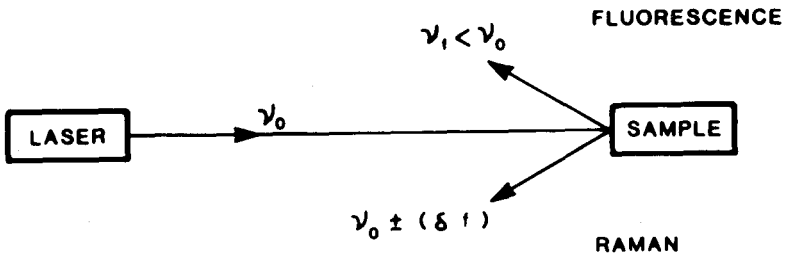
Principle

The most common interactions of visible and infrared light with matter are absorption and reflection. The incident light may also be inelastically scattered (Raman process) or absorbed and subsequently re-emitted at a lower frequency (fluorescence), ν_f. Raman scattering occurs when the incident beam interacts with molecular and/or lattice vibrations of the sample. As a result of these interactions, the frequency of the scattered light is shifted from that of the incident beam by an amount equal to the molecular and/or lattice vibrational frequency, δ_f. Fluorescence is characteristic of both the emitting atomic or molecular species and its immediate environment.



The light source for the Raman scattering or fluorescence experiment is a laser which can be focused to a small spot (diameter ≈ 1 μm) to examine microscopic features of a sample.

References

1. D. A. Long, Raman Spectroscopy, McGraw-Hill, New York (1977).

2. J. D. Winefordner, S. G. Schulman, and T. C. O'Haver, Luminescence Spectrometry in Analytical Chemistry, Vol. 38 of Chemical Analysis Series, Wiley-Interscience, New York (1972).

Technique - ULTRAVIOLET/VISIBLE SPECTROPHOTOMETRIC ANALYSIS

General Uses

- Quantitative analysis of cations, anions and neutral species which absorb in the UV/Vis spectral region (185-875 nm).
- Quantitative analysis of species which can be converted into complexes which absorb in the UV/Vis region.

Examples of Applications

- Explosives analysis and measurement of decomposition kinetics.
- P and B analysis on integrated circuit thin films.
- Cr(III) analysis in plating baths.
- Turbidimetric analysis of chloride in plating baths.
- Complex formation in the Li/SO_2 battery.
- Transmission of filters and glasses.

Samples

- Form: solids, liquids, or gases.
- Size: varies according to molar absorptivity--may be as low as 10^{-7} g.

Limitations

- Must have a distinct absorption band with no interferences or interferences which can be compensated for using multicomponent analysis software.
- Species with low molar absorptivities must be converted to a complex with strong absorption in either the visible or ultraviolet region.
- Not useful for noble gases.

Estimated Analysis Time

- Analysis less than 4 hours once an analytical method and calibration curve are developed.

Capabilities of Related Techniques

- Atomic Absorption/Inductively Coupled Plasma: not capable of chemical speciation, e.g., Cr(III) and Cr(VI).
- Wet Chemistry: generally more time-consuming.

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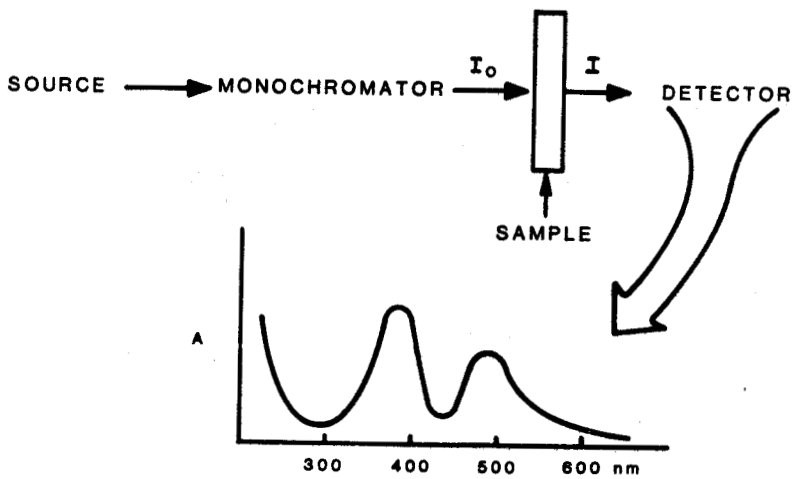
Principle

Ultraviolet (185-400 nm) and/or visible (400-875 nm) light is absorbed by ions or molecules in solution and causes changes in the electronic structure of the absorbing species. The wavelength of maximum absorption and the absorption intensity (molar absorptivity) are characteristic of the species in solution and their concentration. Many ions are weak absorbers but can be easily and quantitatively converted to complexes which are highly absorbing and exhibit a linear increase in absorbance with concentration (Beer's Law). Direct and indirect spectrophotometric analysis procedures have been developed for all elements except the noble gases.



$$A = \text{ABSORBANCE} = -\log_{10}\frac{I}{I_o} = abc$$

I_o = INTENSITY OF INCIDENT BEAM

I = INTENSITY OF TRANSMITTED BEAM

a = MOLAR ABSORPTIVITY (L/mol · cm)

b = CELL LENGTH (cm)

c = CONCENTRATION (mol/L)

References

1. E. B. Sandell and H. Onishi, Photometric Determination of Traces of Metals, John Wiley & Sons, NY (1978).

2. F. Dee Snell, Photometric and Fluorometric Methods of Analysis - Non Metals, John Wiley & Sons, NY (1981).

3. F. Dee Snell, Photometric and Fluorometric Methods of Analysis - Metals, Parts 1 and 2, John Wiley & Sons, NY (1978).

4. G. Guilbault, Practical Fluorescence, Marcel Dekker, Inc., NY (1973).

Technique - OPTICAL METALLOGRAPHY (MET)

General Uses

- Imaging of topographic or microstructural features on polished and etched surfaces of magnifications of 1 to 1500X.
- Characterization of grain structures and phase morphologies.

Examples of Applications

- Determination of fabrication and heat treatment history.
- Determination of braze and weld joint integrity.
- Failure analysis.
- Characterization of the effects of processing on microstructure and properties.

Samples

- Form: metals, ceramics, geologic materials.
- Size: dimensions ranging from 10^{-5} m to 10^{-1} m.
- Preparation: grinding and polishing to produce a flat scratch-free surface; chemical etching to reveal microstructural features of interest.

Limitations

- Resolution limit: $\approx 10^{-6}$ m.
- Limited depth of field (cannot focus on rough surfaces).
- Does not give direct chemical or crystallographic information about microstructural features.

Estimated Analysis Time

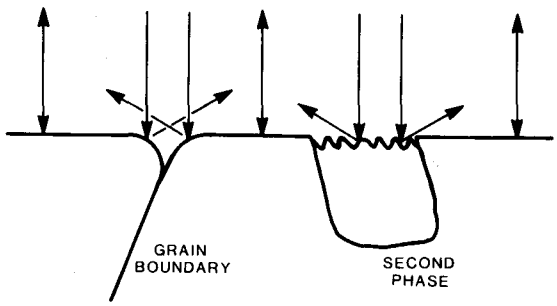
- 1/4 to several hours per speciman.

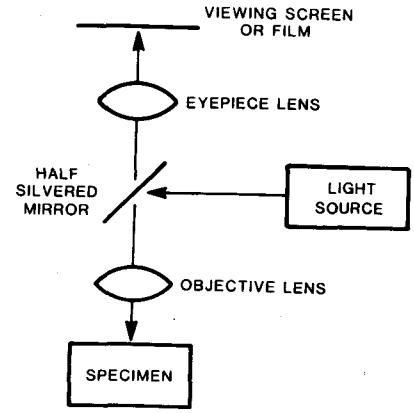
Capabilities of Related Techniques

- Scanning Electron Microscopy: provides better resolution (higher magnifications); greater depth of field (can image rough surfaces); qualitative elemental microanalysis.
- Electron Microprobe Analysis: provides quantitative elemental microanalysis.
- Transmission Electron Microscopy: provides much better resolution (much higher magnifications); semiquantitative elemental microanalysis; crystallographic information on microstructural features.

Contacts - Division 1822, Bldg. 805, Room 123
Mark McAllaster 4-7634
Alice Kilgo 4-7634

Principle





A specimen is polished to produce a scratch-free surface. This surface is then exposed to a chemical etchant which preferentially etches (roughens) selected microstructural features such as grain boundaries or second phase particles. The polished and etched surface is then positioned on a microscope perpendicular to the illuminating light beam. Areas of the surface that are unetched reflect the light back into the microscope, while etched areas scatter the light. The magnified image is projected onto a viewing screen or photographed. Unetched areas appear light; etched areas appear dark.

References

1. Metals Handbook, 8th edition, Vol. 8, "Metallography, Structures and Phase Diagrams," American Society for Metals, Metals Park, OH (1973).

2. G. F. VanderVoort, Metallography, Principles and Practice, McGraw-Hill, NY (1984).

Technique - MICROSTRUCTURAL IMAGE ANALYSIS

General Uses

- Quantification and correlation of the morphological and microchemical aspects of images obtained by optical metallography, scanning electron microscopy, and transmission electron microscopy.

Examples of Applications

- Quantitative determination of grain size, grain shape, grain boundary area per unit volume, etc., in single phase metals and ceramics.
- Quantitative determination of 2nd phase volume fractions, sizes, interfacial areas per unit volume, spacings, etc., in multiphase metals and ceramics.
- Quantitative determination of particle size and shape distributions in powders, including correlation of size and shape with practical chemistry.

Samples

- Instrument is interfaced with an optical microscope and a scanning electron microscope to permit direct analysis (without taking photographs). See optical metallography and scanning electron microscopy sections for specimen form, size, and preparation requirements.
- Instrument is also interfaced with epidiascope to permit quantification of features on photographs (from optical microscope, scanning electron microscope, transmission electron microscope, etc.). Photographs must have sufficient contrast.

Limitations

- Measures 2-dimensional geometric quantities; 3rd-dimensional parameters must be inferred.

Estimated Analysis Time

- 1/2 to several hours per specimen.

Capabilities of Related Techniques

- Electron Microprobe Analysis: gives quantitative elemental compositions, but no quantitative geometric characterization.

Contacts - Division 1822, Bldg. 805, Room 121-1
Bill Chambers 4-6163
Bill Sorenson 4-2774

Principle

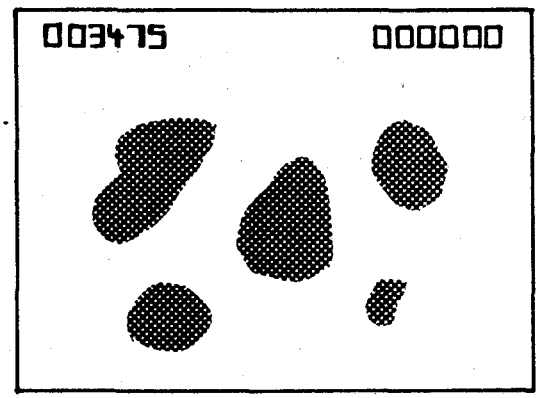


Image is displayed on cathode ray tube consisting of 500,000 picture points. Each picture point can assume 32 different gray levels. Volume fraction (area fraction) is determined by counting the fraction of these picture points in a specified gray level range. Individual features are defined as all of the adjacent picture points in a specified gray level range. The size of a feature is calculated from the number of perimeter picture points, etc. The chemistry of feature can be determined semiquantitativly from x-ray signal detected by EDS detector on the SEM. The analyst can also edit information on the CRT, i.e., delete features known to be artifacts, separate touching or overlapping features, fill in features which do not exhibit uniform contrast, etc. A dedicated minicomputer is available for data reduction, plotting of histograms, etc.

References

1. Stereology and Quantitative Metallography, ASTM, Philadelphia, PA, Chap. 4, (1972).

2. R. T. DeHoff, F. N. Rhines, Quantitative Microscopy, McGraw-Hill, New York (1968).

Technique - **SCANNING ELECTRON MICROSCOPY (SEM)**

General Uses

- Imaging of topographic or microstructural features on polished or rough surfaces at magnifications of 25 to 50,000X.
- Qualitative or semiquantitative elemental analysis of selected surface features as small as $\approx 10^{-6}$ m diameter.
- Imaging of p-n junctions and electrically active regions in microelectronic devices.

Examples of Applications

- Fracture surface analysis.
- Identification of surface contaminants and corrosion products.
- Characterization of microstructures in metal, ceramic, and geologic materials.
- Inspection of and characterization of defects in integrated circuits.

Samples

- Form: most solids (metals, ceramics, glasses, polymers, geologic materials, integrated circuits, chemical powders, etc.).
- Size: dimensions from 10^{-5} m to 10^{-1} m.
- Preparation: frequently none; sometimes must be polished; nonconductive samples must be coated with a very thin conductive layer.

Limitations

- Changing resolution limit:
  a. Secondary electron mode (topographic contrast): $\approx 10^{-8}$ m.
  b. Backscattered electron mode (atomic number contrast): $\approx 10^{-7}$ m.

- Elemental microanalysis:
  a. Minimum size of region analyzed $\approx 10^{-6}$ m diameter x $\approx 10^{-6}$ m deep.
  b. Threshold sensitivity for elemental detection $\approx 0.2\%$.
  c. Limited detection of elements with atomic number < 11.
  d. No detection of elements with atomic number < 6.

Estimated Analysis Time

- One to several hours per specimen.

Capabilities of Related Techniques

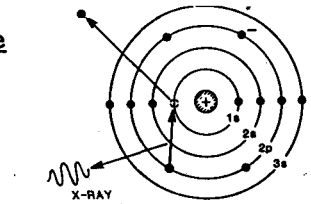
- Optical Metallography: etching reveals some features not revealed in SEM.
- Electron Microprobe: provides quantitative elemental analysis of equally small features.
- Transmission Electron Microscopy: provides images and elemental analyses of smaller features (higher magnifications possible); gives crystallographic data on microstructural features.
- Scanning Auger Microprobe Analysis: more surface sensitive (analyzes 20 Å-deep layer); more sensitive to lower atomic number elements ($3 < Z < 11$).

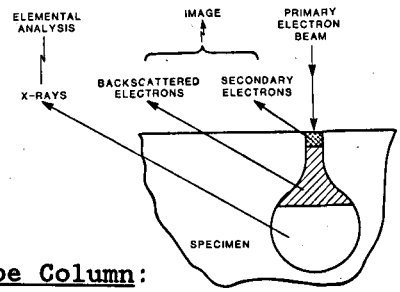
Contacts - Division 1822, Bldg. 805, Room 124

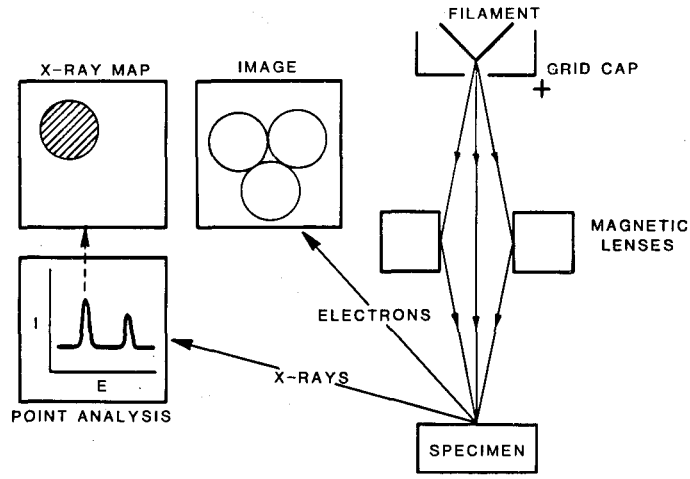
Dave Huskisson	4-7760	
Lori Maestas	4-7760	

Radioactive Materials:
Carol Fryer 4-3285
(Area V M0232/Room 1)

Principle







Microscope Column:
An electron beam is produced and focused to a point (as small as $3x10^{-9}$ m diameter) on the specimen surface. The electron beam penetrates the specimen to a depth of $\approx 10^{-6}$ m and fans out over a diameter of $= 10^{-6}$ m. It interacts with the atoms in this region, resulting in the generation of backscattered primary electrons, ejected secondary electrons, and x-rays.

Imaging:
The image is generated by rastering the primary electron beam over an area of the specimen surface and synchronously displaying on a cathode ray tube the spatially magnified secondary or backscattered electron output. This results in an image where bright and dark regions correspond to areas of high and low electron output. Secondary electrons escape from depths of only $\approx 3x10^{-8}$ m, and signal strength depends mostly on the angle between the primary beam and the surface, hence a secondary electron image gives a high resolution "picture" of specimen topography. Backscattered electrons escape from much greater depths, and signal strength depends mostly on atomic number, hence a backscattered electron image gives a lower resolution "picture" of microstructural features having different average atomic numbers.

Elemental Analysis:
X-rays are produced when outer shell electrons drop down to inner shell vacancies resulting from secondary electron production. The energies of these x-rays are defined by the energy differences between the acceptor and donor electron energy levels, hence. each element has its own characteristic "fingerprint" of x-ray energies. Thus, the elements present in a small region of the sample can be identified by stopping the beam there and analyzing the x-ray energies using an electronic energy dispersive detector (as in x-ray fluorescence). An x-ray map showing the distribution of any specified element can be obtained by rastering the beam and synchronously displaying on a CRT the spatially magnified output of x-rays of the appropriate energy.

Imaging of Electrically Active Regions and p-n Junctions
The intensity of the secondary electron signal varies as electrical potential is applied to the sample (or portions of the sample). This principle can be used to image electrically active regions in microelectronic devices. Current flow is also produced when the primary beam impinges on p-n junctions. Using the strength of this electron beam-induced current (EBIC) to modulate the intensity of the cathode ray tube results in an image of the p-n junctions in microelectronic devices.

References:
1. J. Goldstein, H. Yakowitz, Practical Scanning Electron Microscopy (1975).
2. B. L. Gabriel, SEM: A User's Manual for Materials Science, ASM (1985)

Technique - ELECTRON MICROPROBE ANALYSIS (EMP)

General Uses

- Imaging of polished surfaces at magnifications of 25 to 50,000X.
- Quantitative multielement analysis of selected surface features as small as $\approx 10^{-6}$ m diameter.
- Computer controlled sequential analyses across a sample surface in preselected spatial increments.

Examples of Applications

- Determination of elemental compositions of microconstituents in metal, ceramic, and geologic materials.
- Measurement of diffusion profiles.
- Studies of thermal battery mechanisms.
- Elemental analysis of very small samples.

Samples

- Form: most solids (metals, ceramics, geologic materials, chemical products).
- Size: dimensions ranging from 10^{-5} m to 10^{-1} m.
- Preparation: grinding and polishing to produce a flat scratch-free surface; nonconductive samples must be coated with a very thin conductive layer.

Limitations

- Imaging reaolution limit: $\approx 10^{-8}$ m.
- Elemental microanalysis:
  a. Minimum size of region analyzed $\approx 10^{-6}$ m diameter x $\approx 10^{-6}$ m deep.
  b. Threshold sensitivity for elemental detection $\approx$ 0.02%.
  c. Limited detection of elements with atomic number < 11.
  d. No detection of elements with atomic number < 4.

Estimated Analysis Time

- Several hours per sample.

Capabilities of Related Techniques

- Optical Metallography: faster, but does not give elemental microanalyses.
- Scanning Electron Microscopy: faster, but yields only qualitative or semiquantitative elemental microanalyses.
- Transmission Electron Microscopy: provides images and semiquantitative analyses of smaller features (higher magnifications possible); gives crystallographic data on microstructural features.
- Scanning Auger Microprobe Analysis: more surface specific (analyzes 20 Å-deep); more sensitive to low atomic weight elements ($3 < Z < 11$).

Contacts - Division 1822, Bldg. 805, Room 120
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Ellen Semarge 4-6174

Principle

Identical to scanning electron microscopy except that the electron microprobe analyzes the x-rays emitted from the sample using a wavelength dispersive crystal spectrometer. This is slower but more discriminating than the solid state energy dispersive analyzer used on the SEM. Comparison of the x-ray energies obtained from the specimen with the known characteristic x-ray energies of the elements enables qualitative identification of the elements present in the specimen. Quantitative determination of the percentages of each element in the specimen can be obtained by comparing the intensities of the individual element "fingerprints" from the sample with those from standards of known composition (same principle as x-ray fluorescence).

Reference

1. J. I. Goldstein and H. Yakowitz, Practical Scanning Electron Microscopy, Plenum, New York (1975).

Technique - **TRANSMISSION ELECTRON MICROSCOPY (TEM, STEM, AEM)**

General Uses

- Imaging of microstructural features at very high magnifications (to ≈ 1,000,000X).
- Qualitative or semiquantitative elemental analysis of microstructural features or regions as small as $3x10^{-8}$ m.
- Crystal structure and orientation determination of microstructural features as small as $3x10^{-8}$ m.
- Lattice imaging of crystals with interplanar spacings > $1.4x10^{-10}$ m.

Examples of Applications

- Very high magnification characterization of microstructures of metals, ceramics, and geologic materials (phase identification and distribution; elemental distribution, dislocation structures, twin and stacking fault structures, etc.).
- Identification of very small particles or amounts of inorganic phases, precipitates, and contaminants.

Samples

- Form: solids (metals, ceramics, geologic.materials, etc.).
- Size: ≈ 10^{-7} m thick x $3x10^{-3}$ m diameter.
- Preparation: bulk samples must be cut and electro-thinned or ion milled to permit transmission of electron beam; powdered samples are dispersed on a thin carbon substrate.

Limitations

- Sample preparation is tedious and time consuming.
- Imaging resolution limit: ≈ $1.4x10^{-10}$ m.
- Elemental microanalysis:
  a. Minimum size of region analyzed ≈ $3x10^{-8}$ m diameter.
  b. Threshold sensitivity ≈ 1%.
  c. No detection of elements with atomic number < 11.
- Microdiffraction:
  a. Minimum size of region analyzed ≈ $3x10^{-8}$ m diameter.
  b. Phase identification limited to phases tabulated in powder diffraction file (≈ 40,000 phases and compounds).
  c. Crystallographic orientation determination requires knowledge of crystal structure.

Estimated Analysis Time: 3 to 30 hours per specimen.

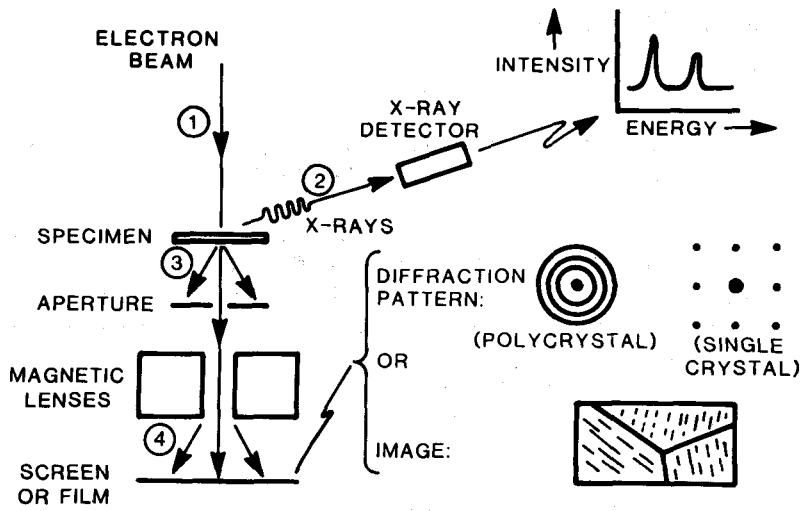
Capabilities of Related Techniques

- X-ray Diffraction: faster; gives bulk crystallographic information.
- Optical Metallography: faster; gives much lower magnification global overview of microstructure; gives no elemental or crystallographic information.
- Scanning Electron Microscopy: faster; gives lower magnification global overview of microstructure and topography; gives no crystallographic information.
- Electron Microprobe Analysis: faster; gives more quantitative elemental analysis, but with poorer spatial resolution gives no crystallographic information.

Contacts - Division 1822, Bldg. 805, Room 117

Tom Headley	4-4787	Marty Carr	6-1405
Chuck Hills	4-4787		

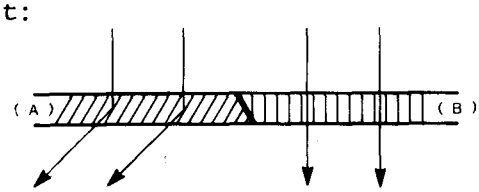
Principle



Region 1. A constant wavelength electron beam is focused onto a small area of the specimen surface.

Region 2. Elemental analysis by energy dispersive analysis of characteristic x-rays--identical to elemental analysis in the scanning electron microscope.

Region 3. Electron diffraction and image contrast: The electron beam is diffracted from crystals which are oriented to satisfy Bragg's law $\lambda = 2d \sin \theta$ (as in A). The electron beam is transmitted by crystals which are not oriented to satisfy Bragg's law (as in B).



Region 4. Imaging: Only the transmitted beam passes through the aperture and is magnified and projected onto the fluorescent screen or film. Portions of the specimen which transmitted the electron beam appear light on the screen and positive print; portions which diffracted the electron beam appear dark.

Electron diffraction: The electron diffraction pattern is displayed or photographed by removing the aperture and decreasing the power to the magnifying lenses. This enables the d-spacings of the crystal planes to be calculated, and the compounds or phases in the specimen to be identified (same principle as x-ray diffraction). It also enables the orientations of small single crystal portions of the specimen to be determined.

References

1. P B. Hirsch, et al., Electron Microscopy of Thin Crystals, Butterworths, London, (1965).

2. J. J. Hren, et al., Introduction to Analytical Electron Microscopy, Plenum, NY (1979).

Technique - X-RAY DIFFRACTION (XRD)

General Uses

- Identification of phases or compounds in unknown samples.
- Quantitative determination of the fractions of each phase in multiphase samples.
- Measurement of crystal defect density, crystal size, residual stresses, etc., from broadening and shifting of diffraction peaks.
- Determination of crystal structure and lattice parameters.
- Determination of orientations of single crystals and characterization of preferred orientations in polycrystals.
- Direct studies of phase diagrams, phase transformation kinetics, annealing kinetics, etc., using elevated temperature diffraction.

Examples of Applications

- Identification of chemical reaction products (thermal batteries, corroded components, etc.).
- Analysis of minerals present in geologic specimens, phases present in metals and ceramics.
- Investigation of nucleation and growth kinetics of crystal phases in glass ceramics, phase transformations in metals.
- Orientation of single crystal piezoelectric strain gages.

Samples

- Form: crystalline solids (metals, ceramics, geologic materials, corrosion products, etc.).
- Size: powder, 10^{-3} gram ($\approx 10^{-6}$ gram minimum in some cases); flat surface, 3×10^{-2} m square x 5×10^{-3} m thick (sampling depth, 10^{-5} to 10^{-4} m).
- Preparation: frequently none; sometimes must be pulverized or ground.

Limitations

- Sample must be crystalline.
- Phase must constitute > 2% of sample to be detected.
- For routine phase identification, phases must be tabulated in the powder diffraction file ($\approx$ 40,000 phases or compounds).

Estimated Analysis Time:

- One to several hours per specimen.

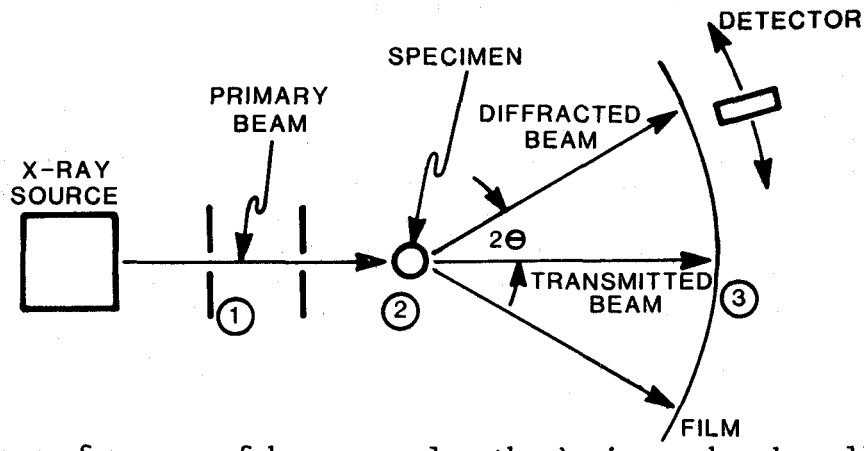
Capabilities of Related Techniques

- Infrared Spectroscopy: molecular identification of organic and some inorganic materials.
- X-Ray Fluorescence Spectroscopy: elemental analysis of bulk specimens with $Z \geq 9$.
- Transmision Electron Microscopy: identification of very small particles ($\geq 3 \times 10^{-8}$ m) by diffraction; combination of morphological characterization with elemental and phase or compound identification.

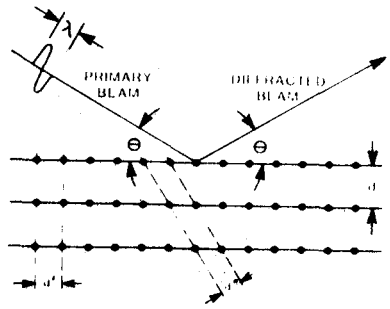
Contacts - Division 1822, Bldg. 805, Room 314

Mike Eatough	4-7761
Ralph Tissot	4-5671
Rick Lujan	4-5671

Principle

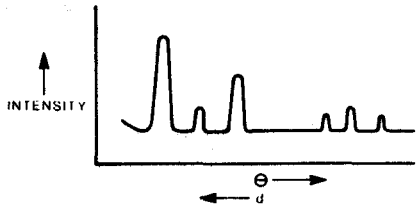


Region 1. A beam of x-rays of known wavelength, λ, is produced, collimated, and directed toward the specimen.



Region 2. The beam is diffracted from crystals in the specimen whenever the Bragg equation, $\lambda = 2d \sin \theta$, is satisfied. If the sample contains many randomly oriented crystals of the same compound, diffraction peaks corresponding to numerous crystal planes each with a characteristic d-spacing are obtained. Hence, each compound has its own characteristic "fingerprint" of d-spacings.

Region 3. The θ-anglea at which diffraction occurs are measured using either photographic film or a moving electronic detector. The d-spacings of the specimen are calculated using the Bragg equation. This d-spacing "fingerprint" of the specimen is compared with those of known compounds to identify the compound(s) in the specimen. When the specimen contains more than one compound, the specimen "fingerprint" consists of several superimposed individual ccmpound "fingerprints." The percentage of each phase present can be quantitatively determined by comparing the intensities of the individual compound "fingerprints" from the sample with those from standards of known composition.



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1. B. D Cullity, Elements of X-Ray Diffraction, Addison-Wesley, Reading MA (1956).

2. C. S. Barrett, T. B. Massalski, Structure of Metals, McGraw-Hill, New York (1966).

Technique - SCANNING AUGER ELECTRON MICROPROBE (SAM)

General Uses

- Qualitative and semiquantitative surface analyses. The elements on the surface and within 20 Å thereof can be detected and measured.
- Scanning electron micrographs (SEMs) and elemental distribution micrographs. Micrographs showing the distribution of the individual elements of interest within a given area can be obtained.
- Compositional depth profiles. The sample surface is bombarded by a 2-keV ion beam which removes successive atomic layers from the surface. Auger analysis of the fresh surface exposed during the erosion process enables concentration gradients to be obtained to depths of $\leq 0.5\ \mu m$.

Examples of Applications

- Elemental identification of surface contaminants.
- Analysis of compositions and morphologies of thin films.
- Investigation of interfacial phenomena.
- Identification of second phase inclusions or particulates.
- Analysis of oxidation and corrosion products.

Samples

- Form: solids, but not pure insulators.
- Size: ≤ 2.5 cm diameter and ≤ 1 cm thick; larger samples may be accommodated by special fixturing.
- Materials: metals, alloys, semiconductors, thin film samples on conducting substrates.
- Preparation: samples must be free of fingerprints, oils, and other high vapor pressure materials.

Limitations

- Detects elements with $Z \geq 3$.
- Practical detection limits ≥ 1 at.%.
- A conductive sample is required.
- Possible beam damage to certain types of samples.

Estimated Analysis Time

- Requires an hour vacuum pumpdown before analysis.
- Requires 1/2-4 hours per sample, depending on requested work.

Capabilities of Related Techniques

- Electron Microprobe: faster; more sensitive to higher Z elements; not as surface sensitive as Auger; sample to a depth of $\approx 2\text{-}3\ \mu m$.
- Ion Scattering: more surface sensitive; not element specific; less quantitative than Auger.
- X-Ray Fluorescence: faster; more sensitive to high Z elements than Auger, but x-ray fluorescence is a bulk technique.

Contacts - Division 1823, Bldg. 805, Room 118

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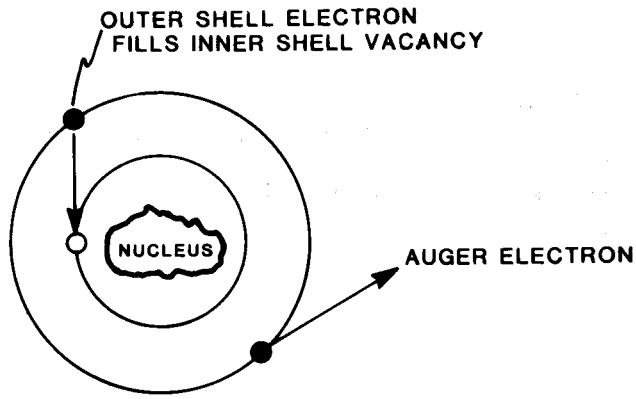
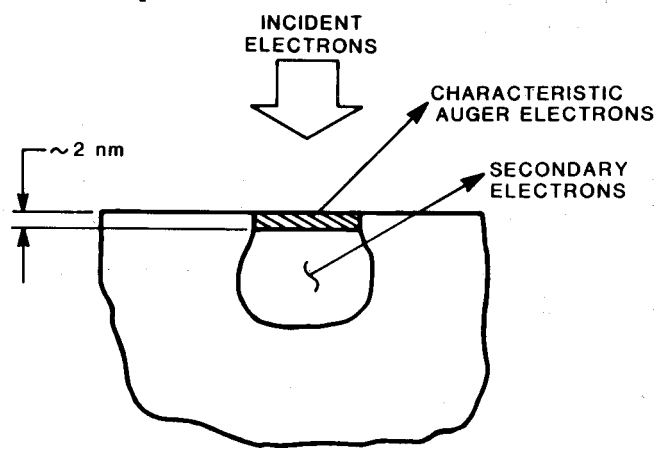
Bill Wallace	4-8749
Paul Mott	4-8749

Principle

When an electron or x-ray beam strikes a material, orbital electrons from the target atoms are ejected and the atoms are left in "excited" or higher energy states. If the ejected electron is from an inner shell, the excited atom can relax to lower energy by a process whereby an electron in an outer shell falls into the vacancy in the inner shell. When this occurs, excess energy is generated and is dissipated either by the ejection of another electron called an Auger electron or by the emission of an x-ray photon. The Auger electron has a kinetic energy characteristic of the host atom. Thus, detection and energy analysis of the Auger electrons lead to the identification of the target atoms. The process is shown schematically below.



The inner shell vacancies are normally created by a finely focused electron beam (500 Å to 5 μm) which can be scanned across the surface to generate elemental maps. A schematic of the experiment is shown below.



References

1. A. W. Czanderna, ed., Methods of Surface Analysis, Elsevier, Amsterdam (1975).

2. P. F. Kane and G. R. Larrabee, eds., Characterization of Solid Surfaces, Plenum, NY (1974).

Technique - **X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)**

General Uses
- Qualitative and quantitative analysis of solid surfaces.
- Characterize surface compositions of conducting, semiconducting and insulating solids.
- Identify some chemical states of atoms.
- Surface charging is used to identify insulating thin films on conductors.
- Limited depth profiles of insulating materials.

Examples of Applications
- Oxidation states of metal atoms in some metal oxide surface films.
- Identification of surface carbon as graphitic or carbide.

Samples
- Form: solid.
- Size: $\leq$ 2.5 cm x $\leq$ 1 cm thick.
- Materials: low vapor pressure ceramics, glasses, semiconductors, metals, alloys and polymers.
- Preparation: samples must be free of fingerprints and oils or other surface contamination.

Limitations
- $Z \geq 3$.
- Concentration $\geq$ 1 at.%.
- Analysis depth $\approx$ 3 nm.
- Minimum analysis area $\approx$ 5 mm diameter.
- Material vapor pressure must be low.

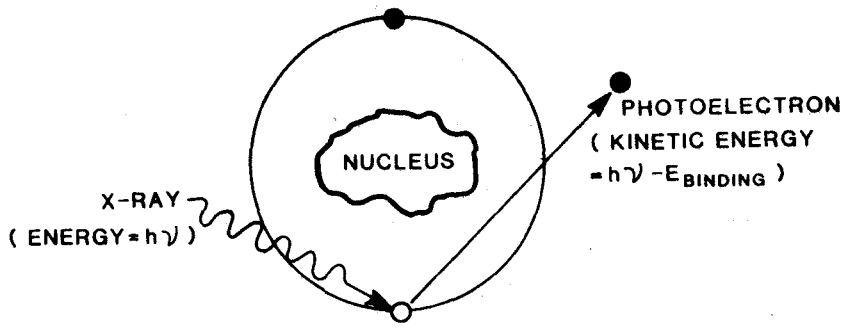
Estimated Analysis Time
- Elemental survey in $\approx$ 4 hours; more detailed chemical analysis takes longer depending on the complexity of the system.

Capabilities of Related Techniques
- Electron Microprobe: faster, not as surface sensitive; less chemical bonding information.
- Infrared (Dispersive and Fourier Transform): generally more structural information and more sensitive; some species undetectable; less surface sensitive.
- Auger: less chemical information; more sample damage; smaller excitation area so areal mapping is possible.

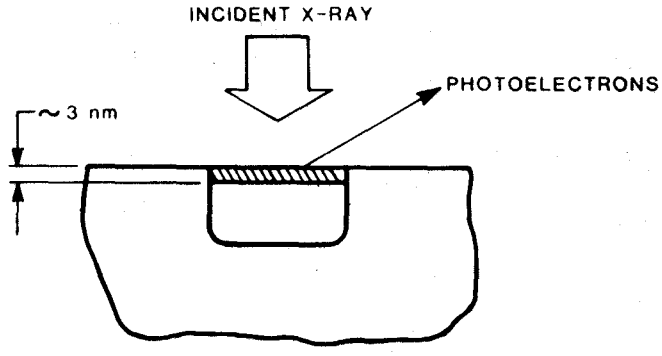
Contacts - Division 1823, Bldg. 805, Room 118
Alan Galuska 4-3187

Prinicple

When an x-ray strikes a material, electrons from the target atoms can be excited to higher energy states or completely ejected from the atoms. In this process, all of the energy of the x-ray is absorbed. Electrons which are ejected from the material by this process are called x-ray photoelectrons and their energy is equal to the x-ray energy ($h\nu$), where ν is the x-ray frequency, minus the binding energy of the electron in the shell from which it was ejected. Energy analysis of the photoelectrons can thus lead to an identification of the target atoms and, in many cases, to a determination of the oxidation states of those atoms which affect the binding energies. This process is shown schematically below.



An x-ray beam from an Aℓ or Mg anode is normally used to excite the photoelectrons from atoms within 3 nm of a solid surface. The photoelectron energies are usually analyzed using an electrostatic analyzer of cylindrical or hemispherical geometry.



References

1. A. W. Czanderna, ed., Methods of Surface Analysis, Elsevier, Amsterdam (1975).

2. P. F. Kane and G. R. Larrabee, eds., Characterization of Solid Surfaces, Plenum, NY (1974).

Technique - ION SCATTERING SPECTROSCOPY (ISS)

General Uses

- Qualitative and semiquantitative analysis of the outermost atomic layer of a solid sample.
- Compositional depth profiles over the first few hundred Å with monolayer depth resolution.
- Elemental mapping of the surface monolayer for simple systems.

Examples of Applications

- Surface segregation.
- Preferential sputtering.
- Composition of oxidation, corrosion, and contamination films.

Samples

- Form: solids.
- Size: greater than 1 x 1 mm; less than 150 x 150 mm; less than 25 mm thick.
- Materials: any vacuum-worthy material.
- Preparation: samples should be handled with care not to contaminate surface.

Limitations

- $Z \geq 2$.
- Concentration $\geq$ 0.01 at.% of a monolayer.
- Elemental interferences can occur.
- Beam diameter $\approx$ 10 μm to 2 mm.
- Quantitative analysis not available for all samples.
- Some sputtering occurs which causes sample damage.

Estimated Analysis Time

- Requires an overnight vacuum pumpdown before analysis.
- 1-4 hours per sample, depending on requested work.

Capabilities of Related Techniques

- Auger: less surface sensitive; gives elemental identification, not just the atomic mass.
- Rutherford Backscattering: more quantitative; less surface sensitive.

Contacts - Division 1823, Bldg. 805, Room 113
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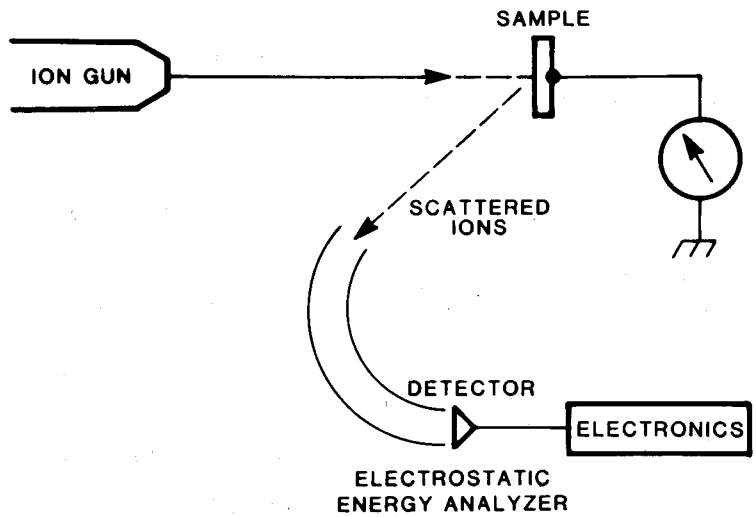
Wayne Buttry 6-1696

Principle

When a beam of low energy ions is directed on a surface, the ions can be elastically scattered from the target atoms. Energy analysis of the scattered ions provides data on the masses of the target atoms. Ions which penetrate the target beyond the first layer of atoms have a very high probability of being neutralized. Thus, if only ions are detected and analyzed, the information on target atom masses comes only from the first layer of atoms.



A focused beam of ions (generally He, Ne, or Ar at 0-5000 eV) is scattered from a sample. The scattered ions are energy analyzed. Ions which were neutralized during scattering are not detected.

References

1. A. W. Czanderna, ed., Methods of Surface Analysis, Elsevier, Amsterdam (1975).

2. I. H. Wilson and K. G. Stephens, eds., Low-Energy Ion Beams, Institute of Physics, London (1980).

Technique - **SECONDARY ION MASS SPECTROSCOPY (SIMS)**

General Uses
- Qualitative elemental and chemical analysis of the outermost 1 to 5 monolayers of a sample.
- Quantitative isotopic ratios in the same layer.
- Elemental depth distributions over the first few hundred Å.

Examples of Applications
- Identification of corrosion products.
- $^{235}U/^{238}U$ and $^{6}Li/^{7}Li$ ratios in unknown materials.
- Dopant profiles in semiconductor devices.

Samples
- Form: solids
- Size: greater than 1 x 1 mm; less than 150 x 150 mm; less than 25 mm thick.
- Materials: any vacuum-worthy material.
- Preparation: samples should be handled with care to avoid contamination.

Limitations
- Quantitative analysis not generally available.
- Beam diameter ≈ 10 μm to 2 mm.
- Elemental sensitivities can vary by 10^5 across the periodic table (1 part in 10 to 1 part in 10^6 for Division 1823 system).
- Elemental interferences can occur.
- Sputtering causes sample damage.

Estimated Analysis Time
- Requires an overnight pumpdown before analysis.
- 1-4 hours per sample depending on requested work.

Capabilities of Related Techniques
- Auger: more quantitative; less sensitive to most elements; gives little chemical information.
- Ion Scattering: more quantitative; more surface sensitive; gives no chemical information.
- Ion Microscopy: more quantitative; faster; 3-dimensional profiles.

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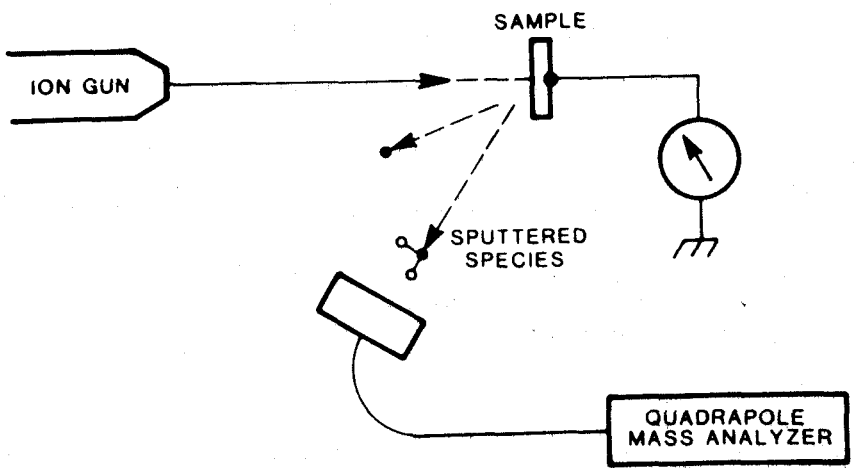
Principle

When a beam of ions is incident on a solid surface, atoms and molecular species can be sputtered from the surface. The sputtered species can be mass analyzed to determine the atomic composition and, in many cases, chemical information can be obtained from the molecular species. In addition, mass analysis also yields isotopic ratios.



References

1. A. W. Czanderna, ed., Methods of Surface Analysis, Elsevier, Amsterdam (1975).

2. T. L. Barr and L. E. Davis, eds., Applied Surface Analysis, ASTM, Philadelphia (1980).

Technique - ION MICROSCOPY

General Uses

- Qualitative and semiquantitative elemental and chemical analysis of the outermost 1 to 5 monolayers of a sample.
- Quantitative isotopic ratios from microvolumes with a mass resolution of 10,000.
- Elemental depth distributions from 10 to 2000 nm in depth with a depth resolution of approximately 10% of the depth.
- Elemental images with 200 to 1000 nm spatial resolution.
- 3-D elemental analysis.
- Trace (generally ppm detection limits or less) elemental analysis for most elements.

Examples of Applications

- Dopant and impurity measurement and distribution in Si and III-V semiconductor devices.
- Elemental examination of inclusions and particulates.
- Investigation of interfacial phenomena.
- Isotopic ratios in unknown materials.

Samples

- Form: solids.
- Size: greater than 1x1 mm; less than 25x25 mm; less than 15 mm thick.
- Materials: any vacuum-worthy material except bulk insulators.
- Preparation: samples should be handled with care to avoid contamination.

Limitations

- Quantification is possible only when standards are available or can be fabricated by techniques such as ion implantation.
- Elemental interferences can occur.
- Sputtering can cause sample damage.
- Elemental sensitivities can vary by orders of magnitude.
- Bulk insulators are difficult to analyze.

Estimated Analysis Time

- Requires approximately 30 min. pumpdown before analysis.
- 1-4 hours per sample depending on requested work.

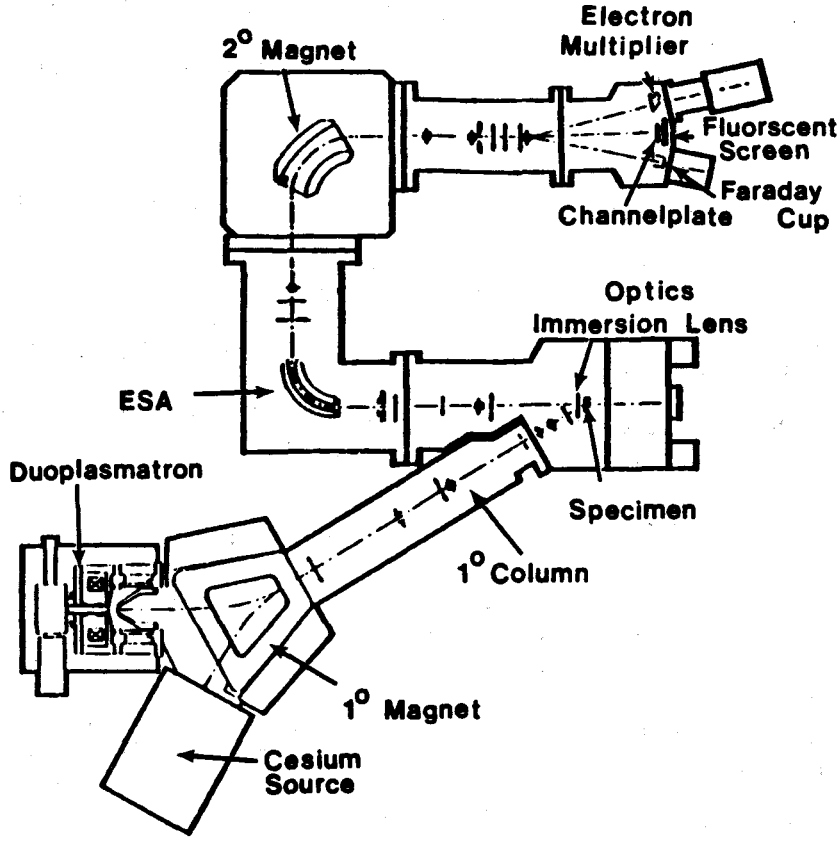
Capabilities of Related Techniques

- Auger: similar spatial resolution; more quantitative; less sensitive.
- X-Ray Photoelectron: superior chemical information; poor lateral resolution; more quantitative; less sensitive.
- Secondary ion: better for insulators, less sensitive, less lateral and mass resolution, no true 3-D capability.

Contacts - Division 1823, Bldg. 858 (Facility expected on-line after Mar. 1989).
Alan Galuska 4-3187
Fred Greulich 4-7760

Principle

When a beam of ions is incident on a solid surface, atoms, ions, and molecular species can be sputtered from the surface. The sputtered ions can be mass analyzed to determine the atomic composition, chemical information, and the distribution of the species of interest throughout the sample. Elemental depth distributions are obtained by monitoring the elements of interest as the ion beam sputters away the surface layers of the specimen. Ion images can be acquired by the stigmatic imaging of the secondary ions as they leave the sample surface or by scanning a focused primary ion beam across the sample surface. The use of a magnetic sector mass spectrometer yields isotopic analysis which can readily distinguish isotopes and molecular ions with nominally the same mass. As shown below, the primary ions are created in either the duoplasmatron or the cesium ion sources. These ions are mass filtered and then focused on the specimen surface. The secondary ions are extracted through the immersion lens optics, energy filtered in the electrostatic analyzer (ESA), and then mass filtered in the magnet. The selected ions are then either focused into an electron multiplier or a faraday cup for ion counting, or onto the channelplate/fluorescent screen for stigmatic ion imaging.



References

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2. C. A. Evans, Jr., Anal. chem. 47, 818A (1975).

Technique - **RUTHERFORD BACKSCATTERING ANALYSIS (RBS)**

General Uses

Measurement of thickness and compositional depth profile in thin film structures.

- Quantitative measurements of heavy surface or near surface impurities and constituents.
- Quantitative analysis of near surface layers in solids.

Examples of Applications

- Analysis of thin film metallization and passivation layers on microelectronics and solar cell devices. Quantification of surface concentrations to calibrate other analysis techniques.
- Investigation of interdiffusion reactions between thin films and substrates.

Samples

- Form: solids (1 mm x 1 mm to 25 mm x 25 mm); limited more by the sample holder than the technique.
- Material: any nonvolatile solid; powders require an appropriate sample holder.

Limitations

- Sensitivity proportional to $(Z_{target})^2$; thus, the technique is insensitive to low Z elements in high Z matrices.
- Measures target atom mass, not species.
- Poor mass resolution at high masses (> 150 amu).
- Requires lateral uniformity across sample due to large beam size (1 mm).
- Analysis depth ≈ 1.0 μm with 200 Å resolution at surface for $^4He^+$; 10.0 μm with 500 Å resolution at surface for protons.

Estimated Analysis Time

- Analysis requires 15 minutes to 1 hour per sample.

Capabilities of Related Techniques

- Auger: more surface sensitive; less quantitative; elemental identification; depth profiles require sample destruction; much better lateral resolution.
- Low Energy Ion Scattering: less quantitative; more surface sensitive; requires sample destruction to obtain depth profiles.
- Electron Microprobe: less surface sensitive; lower sensitivity to high Z elements; elemental identification; much better lateral resolution.

Contacts - Division 1823, Bldg. 805, Room 321

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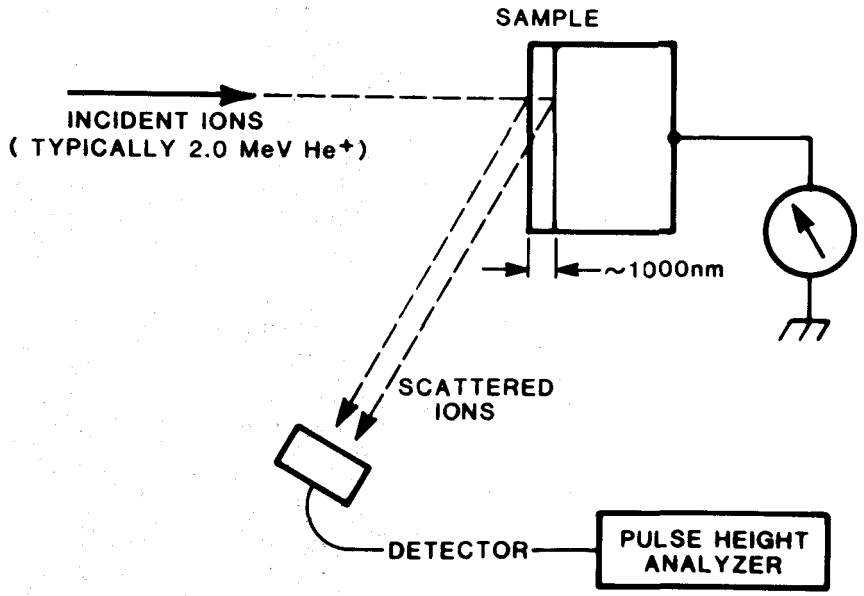
Paul Mott	4-8749

Principle

When an energetic ion enters a solid, it can be elastically scattered from the nuclei of the target material. The energy of the scattered ion is proportional to the incident energy. The proportionality constant is a function of the scattering angle, the incident ion mass, and the target nuclei mass. Thus, measurement of the energies of scattered ions provides data on the masses of the target nuclei. Most ions do not scatter at any given depth but penetrate the solid. As they pass target atoms they lose small amounts of energy to electronic excitations. Ions which are scattered after these energy losses enable a measurement of target depth.



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