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Competitive & Sustainable Growth (Growth) Programme
A non-destructive Pulse Neutron Multiple Detector Tool for use in
environmental, hydrocarbon and mineral exploration work

(NuPulse)

EU Contract: EVK1-CT-2000-00046

WP1: Evaluation of Technologies

REPORT

TECHNOLOGIES FOR THE DETECTION OF
METALLIC & NON-METALLIC ELEMENTS
AND HYDROCARBONS

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Athens, October 2002

CONTENTS

	Page
1. Introduction	3
2. Technologies for the detection of metallic elements	4
2.1. Nuclear methods	4
2.1.1. Passive nuclear methods	5
2.1.1.1. Gamma ray spectrometry	5
2.1.2. Active nuclear methods	6
2.1.2.1. Gamma-gamma	6
2.1.2.2. Spectral gamma-gamma / density	6
2.1.2.3. Neutron activation techniques	6
2.1.2.4. Pulsed-neutron generator	7
3. Technologies for the detection of metallic & non-metallic elements and hydrocarbons	8
3.1. Atomic-absorption spectrometry	8
3.2. Optical emission spectroscopy	9
3.2.1. Flame emission spectroscopy	9
3.2.2. Semi-quantitative DC-arc spectroscopy	10
3.2.3. Direct-reading DC-arc spectroscopy	10
3.2.4. Inductively-coupled plasma spectroscopy	11
3.2.5. Inductively-coupled plasma and mass spectrometry	13
3.2.6. Optical spectroscopy	13
3.2.6.1. Infrared spectrophotometry	14
Identification of organic compounds	14
3.2.6.2. Ultraviolet-visible spectrophotometry	15
3.3. X-ray fluorescence spectroscopy	15
3.3.1. Portable XRF	17
3.4. Mass spectrometry	17
3.4.1. Portable Mass spectrometer / Gas chromatograph	18
3.5. Nuclear magnetic resonance	19
3.5.1. Liquid-state NMR	19
3.5.2. Solid-state NMR	19
3.6. Laser-based techniques	20
3.7. Chromatography	21
3.7.1. Ion-exchange chromatography	21
3.7.2. Gas chromatography	22
3.7.3. Liquid chromatography	23
3.7.4. Supercritical-fluid chromatography	23
References	23

1. INTRODUCTION

Knowledge of the chemical composition of a substance, whether naturally occurring or artificial, is of primordial importance in many fields, including:

- mineral exploration,
- environmental contamination investigations,
- process control, and
- quality assurance in industrial production.

Several well-established instrumental analytical techniques exist for the analysis of organic and inorganic materials. These conventional techniques usually involve several steps, starting with the taking of a sample of the substance to be analysed, then bringing the sample to the laboratory, preparing it for the actual analysis and possibly removing any interfering substances. Only then can the actual sample composition be determined, after which it may be necessary to dispose, in an appropriate manner, any residues left over.

The cost of such multi-step analytical operations are often very high, and increase enormously the cost of exploration and environmental investigations. Hence, explorationists are looking for effective *in-situ* techniques for the analysis of natural materials for both mineral exploration and contaminated land investigations.

Geochemical methods in mineral exploration and environmental contamination investigations rely on the systematic collection, preparation and analysis of different types of samples (soil, stream, sediment, floodplain sediment, surface & groundwater and plants), and the determination of element concentrations by different analytical methods and instruments (Fig. 1).

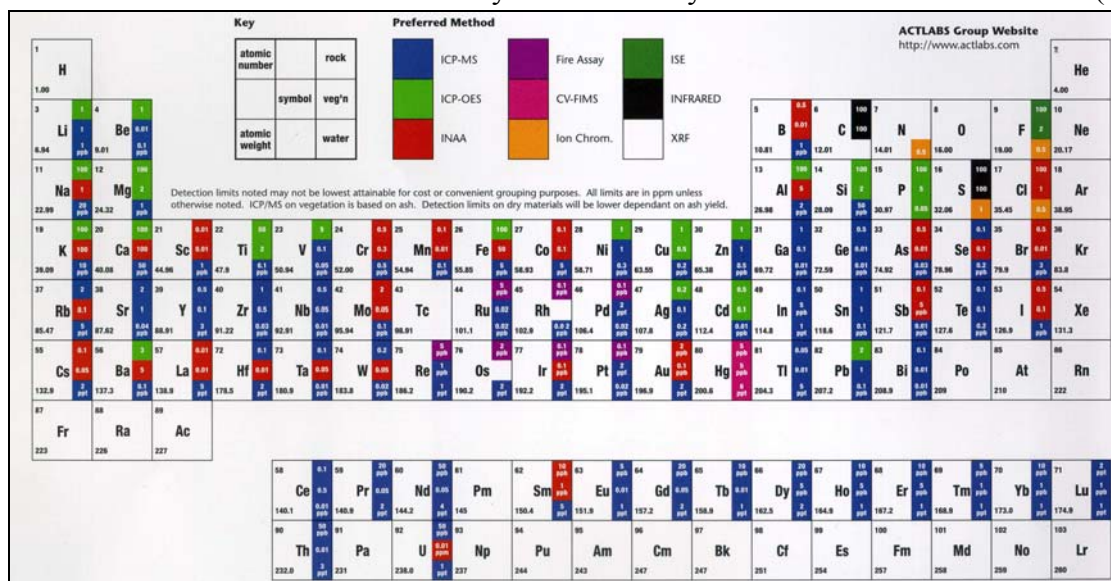


Fig. 1. Periodic table of elements with preferred methods of analysis (from Actlabs, Ancaster, Ontario, Canada, 2001 Fee Schedule catalogue).

Geophysics in mineral exploration has the function of both directly detecting ore deposits, because of some detectable physical characteristics, and of assisting in the interpretation of geology. Geophysical methods are generally indirect methods. They provide information related to the distribution in the earth of one or more physical properties, and the relationship between these physical properties, and any type of mineral deposit being targeted is usually an indirect one and often of low validity.

Regarding portable analytical instruments for the *in-situ* analysis of materials, there are colorimetric and spectrophotometric methods for the analysis of water samples (Figs. 1 & 2), but the selection for the analysis of inorganic and organic determinands in rock, soil and sediments is

nowadays not great, *e.g.*, scintillometers (total count or threshold), XRF (Fig. 3), mass-spectrometer/gas chromatograph (Fig. 4). Merck has recently developed a mobile on-site analyser for the testing of soil and waste water (Fig. 5).

A concise review of the different geochemical/geophysical analytical instrumental techniques that are available for the analysis of solid natural materials is given below. It is stressed that depending upon the intended use of the analytical data, one type of instrument may be more advantageous than another. Hence, the final decision on the analytical instrument to be used, depends on the applied geochemist, whose decision is made after considering the advantages and disadvantages of using a certain instrument, and the cost of analysis.



Fig. 1. Field analysis of stream water for Cu by colorimetry using visual comparison with a universal colour chart (from British Geological Survey flyer, Analytical Geochemistry Group, Capability Profile).



Fig. 2. An Ocean Optics Inc. Palm-Spec™ Spectrometer linked to a Compaq palm-size computer.



Fig. 3. Portable XRF scanner by EDAX, Kennewick, WA, USA.



Fig. 4. Portable Mass spectrometer by KORE Technology, Cambridge, U.K.



Fig. 5. Mobile Analyser for on-site testing of soil and water samples by Merck-KgaA, Darmstadt, Germany.

The Merck mobile analyser is designed for accurate on-site testing of soil and water samples. The Reflectoquant system comprises the Rqflex reflectometer, Reflectoquant test strips and barcode, which is used to load the test parameters for each batch of test strips loaded into the Rqflex meter. More than thirty different tests, ranging from ammonium to sulphite, are currently available, and five different test methods can be loaded into the memory at a time.

2. TECHNOLOGIES FOR THE DETECTION OF METALLIC ELEMENTS

2.1. Nuclear methods

All elements having an atomic number greater than 83 are radioactive. They decay towards stable end products by emitting alpha and/or beta particles (the latter often accompanied by

gamma radiation with characteristic energy) or by electron capture.

Nuclear methods provide information on the chemical composition of soil, stream sediment, floodplain sediment, rocks and ore, and are subdivided into *passive* and *active* methods.

Passive nuclear methods are based on the measurement of natural radioactivity emitted from naturally occurring radioactive elements (K, U, Th) in rocks (Rybach, 1974). *Active nuclear methods* involve the use of artificial sources of radiation (Fite et al., 1974). To perform analysis of non-radioactive elements by nuclear methods the nuclei must be transformed to a new radioactive isotope, or the atoms must be raised to some excited state. This is usually accomplished by bombarding the target with particles, such as X- or gamma-rays or neutrons. The resulting activity measured is then a function of the concentration of the element.

2.1. Passive nuclear methods

2.1.1. Gamma ray spectrometry

Scintillometers measuring the total count gamma rays cannot distinguish the source of the natural radioactivity, but after calibration are able to produce quantitative uranium ore measurements (Fig. 6). Gamma-ray spectral measurements can detect variations in the natural radioactivity originating from the trace elements U and Th, as well as changes in the concentration of K. A gamma-ray spectrometer besides the total counts, also measures the energy of each gamma ray detected, which are characteristic for K, U and Th, thus making possible the estimation of individual concentrations of the three radioelements (threshold scintillometers).

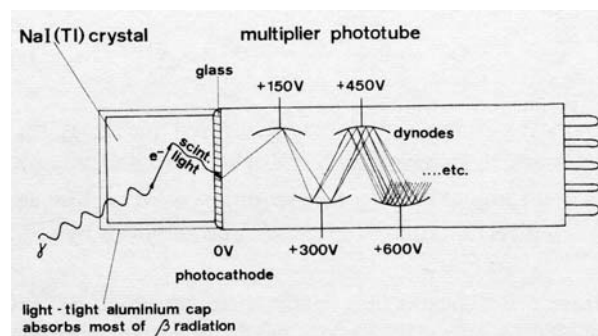


Fig. 6. Schematic diagram of scintillation detector for gamma counting (NaI is hygroscopic and must be hermetically sealed) [From Rybach, 1974, Fig. 5, p.282].

Besides the widespread application to uranium exploration, it has been established that spectrometric estimates of potassium, uranium and thorium concentrations, and derived ratios, may be applied to base metal deposit alteration studies. The main source of the natural gamma radiation is potassium, because alteration is characterised by the development of sericite, which results to an increase in the element potassium.

It has also been realised the potential for spectrometry to indirectly detect non-radioactive elements, such as Nb and Mo, associated with the U and Th radioelements, and the importance of using characteristic ratios to fingerprint geological and geochemical environments.

A gamma ray sensor is a scintillation detector, which is often a sodium iodide or cesium iodide detector. The detectors are usually of dimensions 76 mm x 76 mm for surface measurements, whereas in gamma-ray spectral logging the detectors are often 25 mm x 76 mm or smaller. The volume sampled is of 10-30 cm in radius surrounding the borehole detector, depending on the rock density.

Quantitative K, U & Th measurements may be used to derive quantitative ore estimates of

other elements indirectly related to them. Such examples are determination of the aluminum content of ore, associated with kaolinitic material within the ore matrix, assay of phosphorus deposits associated with uranium and tin/tungsten deposits, which are also associated with radioactive elements.

In borehole logging the natural gamma-ray spectral log may be combined with other logs to provide quantitative assay data.

2.1.2. Active nuclear methods

Active nuclear methods involve the use of an artificially made source of radiation, which may be in the form of a radioactive source or an electronic source, such as an X-ray tube or neutron generator. The obvious advantage of the latter sources is that they can be switched off when not in use.

2.1.2.1. Gamma-gamma

The gamma-gamma log, known as density log, is a measurement of the density of the rock surrounding the borehole. This measurement involves the gross count of gamma rays and the gamma-ray energies are not measured. The *in-situ* knowledge of the density is important in determining the specific gravity and estimates of ore tonnage and reserve computations.

The gamma-ray sources commonly used are Cobalt-60 and Cesium-137, and the detector measures the density of electrons, which cause the backscattering of the gamma rays in the rock. In mono-elemental ore bodies, a relation between the measured apparent density, and ore can be derived. In the case of complex ore bodies a combination of natural gamma ray, density and magnetic susceptibility is used in order to characterise the ore.

2.1.2.2. Spectral gamma-gamma / density

Spectral gamma-gamma/density instruments (SGG/density) measure the energy spectrum of the backscattered gamma rays over an energy range from 0.03 to 1.0 MeV. The density information is derived from the count rate in an energy window from about 0.2 MeV to 0.5 MeV.

Information about the elemental composition of the rock is obtained from the shape of the backscattered spectrum, based on the ratio of the count rates in two energy windows, one at high energy and one at low energy, referred to as the SGG ratio.

Changes in the density of the rock being measured are reflected as an increase or decrease in the count rates on both windows. In the case there is an increase in the content of high Z (atomic number) elements in the rock, the associated increase in photoelectric absorption causes a decrease in the low energy window with little effect on the high energy window. Since the low energy window is affected by both density and Z, where the high energy window is mainly affected by density, the SGG ratio is used to obtain information on changes in Z. The ratio increases when the probe passes through zones containing high Z materials, and the SGG ratio log is considered as a heavy element indicator. It can be calibrated to produce assays such as Pb assays. There is also a potential with the SGG technique to discriminate between economic (Pb, Zn), and non-economic sulphides (pyrite).

2.1.2.3. Neutron activation techniques

Neutron activation techniques utilise neutron sources to measure the qualitative and quantitative elementary composition of materials, including the naturally occurring (Fite et al., 1974). Most

of the sources employ an (α , n) reaction to produce neutrons in which an alpha-particle source (Radium) bombards the element Beryllium, which then emits neutron (Radium-Beryllium and Americium-Beryllium neutron sources). The neutrons are generated electronically with a neutron tube or neutron generator.

Neutron activation analytical techniques are used in the laboratory, and in the field, especially in boreholes, and the output is called a neutron log.

The neutrons when first emitted are considered as 'fast' neutrons, and after interacting with rock, and neutrons loose energy are called 'epithermal' neutrons and at a lower energy are 'thermal' neutrons. The neutrons produce gamma-rays, due to inelastic scattering, and their energies are measured with a gamma-ray spectrometer. From their characteristic energies additional information can be obtained about the atom with which the neutron interacted.

Neutrons emitted by the source are slowed down and scattered by collisions with atomic nuclei. The maximum energy loss in a collision happens when the target nucleus has a mass similar to the neutron, and the hydrogen atom is the most effective in slowing down the neutrons to thermal neutrons after which they are soon captured.

When a neutron is captured, the excited nucleus of the target emits a gamma-ray, called 'prompt' or 'capture' gamma-ray ($n-\gamma$).

The detector response is related to the hydrogen content of the rock, in the form of water in the pores, and is a measure of porosity. An ordinary gamma-ray log is usually run in combination with the ($n-\gamma$) log in order to subtract the background gamma radiation from the neutron induced radiation.

By combining a spectrometer to the ($n-\gamma$) log, and measuring the energies of the prompt gamma rays, it is possible to determine elemental compositions in ores (prompt gamma neutron activation analysis; PGNA).

A second type of gamma rays is also utilised by measuring their energy, called activation gamma rays. These are emitted by the decaying unstable isotope, produced in the capture of neutrons, called delayed gamma neutron activation analysis (DGNA). Gamma rays are emitted after a short time, which is the half-life of the particular isotope involved, and they have energies characteristic of the emitting element.

A third type of gamma rays exists. These are produced during the slowing down of the neutrons by inelastic scattering ($n, n\gamma$; PINAA). During inelastic scattering the nucleus of the atom involved in the collision gets excited, and a gamma ray with a characteristic energy is emitted. These gamma rays are emitted early in the life of the neutron, which requires timed measurement. This can be implemented with a pulsed-neutron source, which can be shut off intermittently.

2.1.2.4. Pulsed-neutron generator

The use of a neutron generator enables the measurements of all above types of gamma rays, at specific times after the pulse of neutrons is switched off. The gamma-rays from inelastic scattering are measured during the first 50 microseconds, then several neutron counting measurements are made to determine the shape of the decay curve of the neutrons. Similarly, the capture gamma rays are measured, which die away with a half-life dependent on the hydrogen content of the rock, and finally the half-life of the activation gamma-rays is determined by making several successive measurements of gamma-ray counts at specific energies.

The repetitive activation has been made possible with the development of pulsed neutron generators. In this case the activity of a very short-lived activation product can be measured at the appropriate time after each of several neutron pulses, yielding a much higher count rate than

if only one measurement was made. Due to the high pulse rate many measurements are made over a short distance in the hole, and continuous activation borehole logging is achieved by measuring very short-lived activities.

3. TECHNOLOGIES FOR THE DETECTION OF METALLIC & NON-METALLIC ELEMENTS AND HYDROCARBONS

Elemental analysis covers both qualitative and quantitative determination of all elements in the periodic table in concentrations from 100% down to ultra-trace levels, which may be as low as 1 ng/kg. In principle, all material types, both organic and inorganic can be analysed. The vast majority of elements in the periodic table are handled by spectroscopic techniques, *e.g.*,

- atomic absorption (AAS),
- X-ray fluorescence (XRF),
- inductively-coupled plasma (ICP), *etc.*

XRF is an ideal technique for accurate determination of major and minor (0.001–0.01 %) elements, heavier than Ca, in solid materials. AAS and ICP instruments are suited for the analysis of solid materials, aqueous and organic liquids at very low concentrations. In particular, ICP coupled to mass spectrometry (ICP-MS) offers ultra-low levels of detection. Elements not covered by XRF, AAS and ICP include hydrogen, carbon, nitrogen, oxygen, fluorine and chlorine. Chemical elemental analysis methods or neutron activation are used to cover this range of the periodic table. In addition, infra-red/ultraviolet spectrometry, ion exchange and gas chromatography are used as complementary instrumental tools.

3.1. Atomic-absorption spectrometry

Atomic-absorption spectrometry (AAS, Fig. 7) measures the absorption of radiation by atomic vapour, produced from the sample solution, at a wavelength that is characteristic of the element being determined (Elwell and Gidley, 1966; Angino and Billings, 1972; Butler and Kokot, 1974; Fletcher, 1983). The prepared sample solution is aspirated into a flame, which is irradiated by light from a hollow cathode lamp, the cathode of which is made of, or contains, the element being determined, and emits light of a wavelength characteristic of this element. Light is absorbed by the atoms of this element present in the flame; the degree of absorption is related to the concentration of the element and is measured photometrically. The instrument is calibrated by aspirating standard solutions treated similarly. Once the sample is in solution it is a matter of only a few seconds to determine the concentration of a particular element.

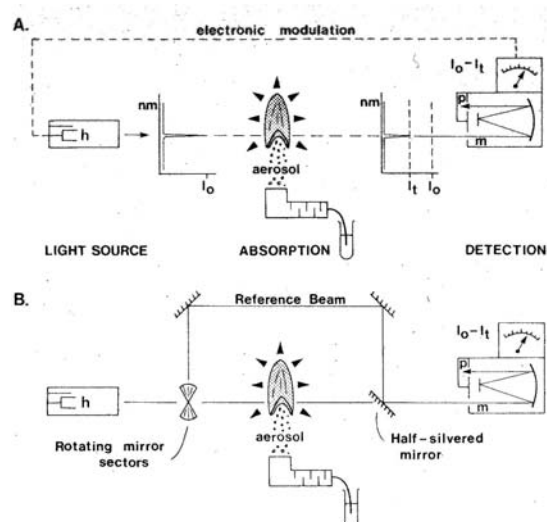


Fig. 7. Schematic diagram of AAS: (A) single-beam and (B) double-beam instrument. Notation: h = hollow cathode light source; m = monochromator, and p = photomultiplier. I_0 is the intensity of the signal from the light source, and I_t its intensity after absorption by analyte atoms in the flame (from Fletcher, 1983, Fig. 6.3, p.114).

The first AAS units were single beam instruments, and could not make background corrections, hence they were not sensitive enough. At the present time AAS units are double-beam, computerised with automatic sample changers, and after calibration with standard solutions and optimum sample treatment, very low detection limits are achieved. Modern computer controlled atomic absorption instruments with automatic sample changers coupled with:

1. graphite furnace are able to achieve very low detection limits;
2. hydride generation system can analyse elements forming gaseous hydrides. It has been applied to analysis of geochemical samples, including waters, for As, Sb, Se, Sn, and Te, and may also be applicable to estimation of Ge and Bi [all elements difficult to determine by conventional flame methods], and
3. mercury cold vapour system to determine mercury.

Atomic-absorption instruments may be considered as the ones that have given the biggest boost in the mineral exploration effort from the 1960's onward.

3.2. Optical emission spectroscopy

Optical emission spectroscopy includes the fields of flame-, arc-, spark- and plasma induced emission phenomena in the UV, visible, and near IR regions of the electromagnetic spectrum. As a technique, it furnishes the applied geochemist with both qualitative and quantitative information on the elemental composition of matter through simultaneous multi-element determinations. Detection limits in the low-ppm, low-ppb and ppt ranges are quite common, depending on the instrument used.

Optical emission spectroscopy techniques, because of their rapid, virtually simultaneous multi-element analysis offered great advantages to the mineral exploration effort. Hence, despite greater capital cost and complexity of equipment, compared to single element methods, there has been a continuing interest in emission techniques, based on sample excitation in DC-arc and, more recently, to inductively coupled plasma (ICP) and inductively coupled plasma/mass spectrometer (ICP-MS).

The desirable properties for spectroscopic sources according to Greenfield et al. (1975) are:

1. the ability to excite the lines of large number of elements;
2. high sensitivity;
3. good stability;
4. freedom from interferences;
5. reproducibility in the introduction of samples, and
6. convenience of operation.

The DC-arc is not an ideal source with respect to (3), (4) and (5) conditions. The inductively coupled plasma (ICP) has received considerable attention, and is proving to be a far better alternative source for multi-element determinations, with further very low to extremely low detection limits in the inductively-coupled plasma mass spectrometer (ICP-MS).

3.2.1. Flame emission spectroscopy

In flame emission spectroscopy the sample in solution is sprayed into a flame and the emission intensity of a suitable line of a particular element is measured with a monochromator and photomultiplier (Fletcher, 1983). The technique is largely limited to elements that are readily excited – notably the alkalis and alkali-earths. Chemical and ionisation interferences are similar to those for AAS.

3.2.2. Semi-quantitative DC-arc spectroscopy

The semi-quantitative DC-arc spectrometer consists of an excitation source, usually a DC-arc, and its power supply (Fletcher, 1983); the spectrograph itself, with either a prism or diffraction grating; and a camera to record spectral intensities on a photographic plate or film. Essential ancillary equipment is a darkroom for film processing, and some means of measuring or comparing the line intensities recorded on the films.

The method is semi-quantitative. It is, therefore, emphasised that, for comparison with standard films to be valid, consistent attention must be given to ensure that excitation and operating conditions remain constant over long periods of time. Hence, in order to monitor systematic errors resulting from equipment drift, changes in film batches or deterioration of old stock, operator proficiency, *etc.*, it is important to include at least one of a series of standard control samples on each film. The other problem is the small quantity of material analysed. So, it is particularly important to achieve a uniform distribution of the trace elements throughout the matrix of the control standards.

3.2.3. Direct-reading DC-arc spectroscopy

In the direct-reading DC-arc spectrometer the photographic plate is replaced by photomultipliers, mounted around the focal curve of the instrument so that, after dispersion, each of the selected analytical lines falls on a photomultiplier (Fig. 8) (Cruft and Giles, 1967; Tennant and Sewell, 1969; Scott et al., 1969; Foster, 1970; Langheinrich and Blair Roberts, 1974; Timperley, 1974; De Pablo Galan, 1975; Ahrens and Taylor, 1961; Fletcher, 1983). Output from the photomultiplier, which is dependent on incident light intensity and, hence, on element concentration, is fed to a voltmeter or other electronic readout system. Element concentrations determined by direct-reading spectrometers, with perhaps as many as 60 analytical channels, must be calculated automatically, and most direct readers are, therefore, interfaced to small dedicated computers. These are programmed to correct background, matrix effects and spectral interferences, thus improving precision and accuracy of the data.

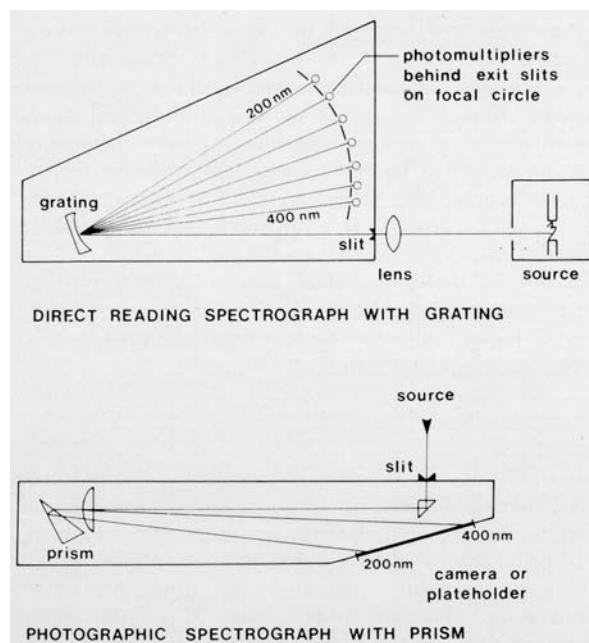


Fig. 8. Schematic diagrams of direct-reading and photographic spectrographs (from Fletcher, 1984, Fig. 7.1, p.142).

Direct-reading spectrometers must be standardised to begin with. This is done by firing synthetic or natural standards of known major and trace element composition. Calibration curves, either of line intensity versus concentration or intensity ratio to an internal standard versus concentration, are then stored in the computer.

Careful choice of analytical lines, and use of spectroscopic buffers, together with calculation of corrections for matrix and spectral interferences, can overcome these problems sufficiently to provide more reliable results, with a faster analytical throughput than with semiquantitative photographic methods.

Because of the various corrections that must be made (background, matrix effects and spectral interferences) the precision and accuracy of direct-reading spectrometers is not comparable to that obtained with AAS.

3.2.4. Inductively-coupled plasma spectroscopy

Inductively coupled plasma (ICP) techniques are used for quantitative multi-element determinations in various aqueous and organic matrices. Solids can be analysed after employing an appropriate dissolution technique. ICP is the method of choice for homogeneous liquid samples, which may or may not be diluted before analysis. In general, very limited quantities (a few millilitres) are sufficient for a full elemental analysis, and detection limits down to the ng/l range are achievable in both aqueous and organic solvents. Analysis can be quantitative, semi-quantitative or qualitative. Inductively coupled plasma-atomic emission spectrometry offers, therefore, a wide elemental coverage, and flexibility combined with simultaneous detection.

The advantages of ICP technology are:-

- determinations can be made of bulk and trace elements in a large variety of products, both in organic and aqueous phases;
- trace elements in polymers following dissolution may be determined;
- determination of elements in homogeneous catalysis systems (*e.g.*, sulphur, hydrogen, fluorine) may be made;

- ❑ determination of mercury, including chemical speciation, and
- ❑ determination of molecular mass distributions of organometallic species in oil and oil products using size exclusion chromatography (SEC) coupled to ICP-MS.

Plasmas are masses of gas sufficiently ionised in order to have a significant effect on their properties (Fletcher, 1983). Most important for their use as emission sources, large quantities of electrical energy can be pumped into them giving temperatures much higher than those attainable in flames or arcs (Figs. 9 & 10). An ICP argon plasma can reach temperatures of 8000 K. In contrast to DC-arc spectroscopy the sample is introduced into the plasma in solution. The technique, therefore, has all the advantages and disadvantages associated with dissolution of geochemical samples. There is an extensive literature on ICP technology going back to the 1960's (Greenfield et al., 1964; Fassel and Kniseley 1974a, b; Fassel, 1978; Boumans, 1979).

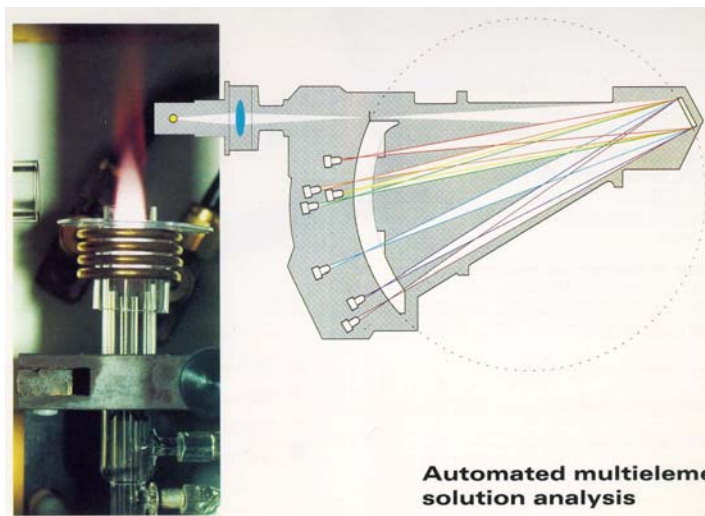
Principal variables controlled by the analyst are:

1. the argon and aerosol flow rate;
2. the generator power fed to the plasma, and
3. the height in the tail flame at which the emission is viewed.

Generally the objective is to establish optimum compromise conditions for determination of as many elements as possible, rather than to optimise for a single element.

In practical terms the longer residence times and higher temperatures should ensure complete volatilisation of the solute and dissociation of molecular species, thereby increasing sensitivity and eliminating band spectra and interferences caused by formation of refractory compounds

(A)



(B)

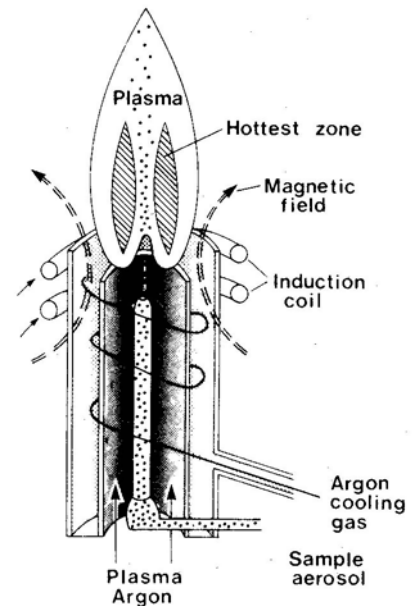


Fig. 9. The inductively coupled plasma. (A) from British Geological Survey flyer - "Analytical Geochemistry Group – Rapid Multi-element Analysis by ICP-AES"; (B) from Fletcher, 1983, Fig. 7.7, p. 159.

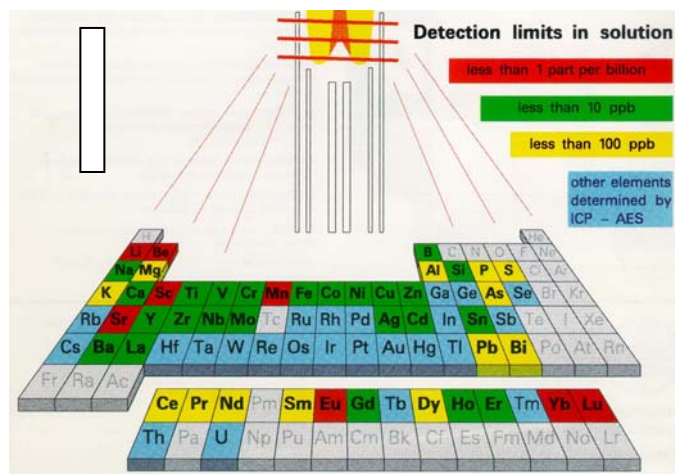


Fig. 10. Periodic table showing the possible detection limits achieved by an ICP-AES (from British Geological Survey flyer - “Analytical Geochemistry Group – Rapid Multi-element Analysis by ICP-AES”).

Ionisation interferences also appear to be less than with other sources, presumably due to the high electron densities. As a further advantage, the combination of increased sensitivity and, at high analyte concentrations, lower self-absorption gives the plasma a linear working range extending over five orders of magnitude compared to three for flames. It is, therefore, possible to determine both trace and major elements on the same solution without dilution.

In the absence of significant chemical and ionisation interferences the most serious analytical problems, particularly near an element’s detection limit, have been associated with spectral interferences from overlapping and coincident emission lines or from background. These are best avoided by careful selection of emission lines. If this is not possible, appropriate correction factors can be computed by measuring the signal produced in the analyte channel by a known concentration of interferent.

Correction of background is particularly important if low signal to background intensities are to be measured. Under these circumstances small changes in background emission can severely degrade analytical performance.

ICP instruments had two variations; the earliest model was an atomic emission spectroscope (AES), and the present day model is an optical emission spectroscope (OES).

Modern ICP instruments, depending on the dissolution technique of samples, have detection limits in solution of less than 100 ppb for most elements. Automated computer controlled systems, with automatic sample changers, have a great sample throughput, because more than 45 elements can be determined simultaneously, and with a good sensitivity (very low detection limit).

3.2.5. Inductively-coupled plasma and mass spectrometry

The inductively-coupled plasma and mass spectrometer (ICP-MS) is a combined instrument, and uses the advantages of both plasma emission and mass spectrometry to achieve very low detection limits (ppb/ppt range). Quantitative and semi-quantitative analysis, covering a wide mass range, with isotopic information is also available. ICP-MS is excellent for the heavier elements, *e.g.*, strontium, lead and cadmium, for which parts per trillion detection limits can be achieved.

3.2.6. Optical spectroscopy

Optical spectroscopy can be used to obtain qualitative and quantitative information about the

chemical and physical composition of a wide variety of materials. Solids, liquids and gases can be analysed, both in the laboratory and in the field. The information is obtained by analysing the non-destructive interaction of electromagnetic radiation (light), from far infrared up to ultraviolet, with molecules and crystals. By applying statistical techniques (multivariate analysis), it is often possible to predict product performance properties directly from the spectra, which can result in considerable time and cost savings.

The following spectroscopic techniques are available:

1. Fourier transform infrared (FTIR) spectroscopy in the far, mid and near infrared region (50 to $10,000\text{ cm}^{-1}$);
2. Raman microspectroscopy;
3. Electronic absorption spectroscopy (UV-vis, 190 to 800 nm), and
4. Fluorescence spectroscopy (UV-vis)

A wide range of accessories is available to handle the varied range of samples, and make use of the relatively high sensitivity of optical spectroscopy.

Examples are:

- Infrared microscopes to analyse sub-nanogramme quantities. The microscopes can also be equipped with an ATR (attenuated total reflection) objective for surface probing ($1\text{-}2\text{ }\mu\text{m}$ deep) and the analysis of small objects or areas $>10\text{ }\mu\text{m}$ across;
- GC-IR interface capable of analysing 100 picogramme of material;
- High-pressure or high-vacuum cells for *in-situ* studies of catalysts/processes (pressures from $10\text{-}6$ to 50 bar , temperatures up to 800°C);
- Polymer stretcher for structure performance studies (Carilon, polymer blends);
- Diffuse reflectance accessories for UV-vis and infrared spectroscopy. For hassle free measurements of powders;
- Near infrared fibre optics for in- and online sampling, and
- Variable-path-length gas cells (up to 7 m) for analysing trace amounts.

Optical spectroscopy can be used:

- to characterise complex mixtures, *e.g.*, filter deposits, deposits on engine cylinders and residues in tanks;
- to characterise inclusions in polymers films and other materials;
- to determine low concentrations (down to 10 ppm wt) of oxygenates in waxes and additives in oil samples;
- to determine the microstructure and tacticity of polymers (*e.g.*, propylene and elastomers (Kraton));
- to characterise catalysts (*e.g.*, acidity of zeolites or amorphous silica-aluminas), and
- to make rapid prediction of product properties with near infrared (hydroxide value, water content and EO/PO ratio in polyols, octane and cetane number of transportation fuels, product properties of cat-cracked feeds).

3.2.6.1. Infrared spectrophotometry

Absorbed infrared radiation causes rotational changes in molecules, and also causes vibrational changes (Britannica, 2002). The vibrational energy levels within a molecule correspond to the

ways in which the individual atoms or groups of atoms vibrate relative to the remainder of the molecule. Because vibrational energy levels are dependent on the types of atoms and functional groups, infrared absorption spectrophotometry is primarily used for organic qualitative analysis. It can be used for quantitative analysis, however, by monitoring the amount of absorbed radiation at a given energy corresponding to one of the peaks in the spectrum of the molecule.

Identification of organic compounds

In organic compounds, atoms are said to be bonded to each other through a σ -bond when the two bonded atoms are held together by mutual attraction for the shared electron pair that lies between them (Britannica, 2002). The two atoms do not remain static at a fixed distance from one another, however. They are free to vibrate back and forth about an average separation distance known as the average bond length. These movements are termed stretching vibrations. In addition, the bond axis (defined as the line directly joining two bonded atoms) of one bond may rock back and forth within the plane it shares with another bond or bend back and forth outside that plane. These movements are called bending vibrations. Both stretching and bending vibrations represent different energy levels of a molecule. These energy differences match the energies of wavelengths in the infrared region of the electromagnetic spectrum, *i.e.*, those ranging from 2.5 to 15 micrometres (mm; $1 \text{ mm} = 10^{-6} \text{ m}$).

An infrared spectrophotometer is an instrument that passes infrared light through an organic molecule and produces a spectrum that contains a plot of the amount of light transmitted on the vertical axis against the wavelength of infrared radiation on the horizontal axis. In infrared spectra the absorption peaks point downward because the vertical axis is the percent transmittance of the radiation through the sample. Absorption of radiation lowers the percent transmittance value. Since all bonds in an organic molecule interact with infrared radiation, IR spectra provide a great deal of structural data.

The stretching vibrations of strong carbon-hydrogen bonds cause the absorptions around 3.4 mm, with the sharp peak at 3.2 mm due to the hydrogen atom on the carbon-carbon double bond. The many bending vibrations of carbon-hydrogen bonds cause the complicated absorption pattern ranging from about 7 to 25 mm. This area of IR spectra is called the fingerprint region, because the absorption pattern is highly complex but unique to each organic structure. The stretching vibrations for both the carbon-carbon and carbon-oxygen double bonds are easily identified at 6.1 and 5.8 mm, respectively. Most of the functional groups discussed earlier have characteristic IR absorptions like those for carbon-oxygen and carbon-carbon double bonds. Infrared spectroscopy is, therefore, extremely useful for determining the types of functional groups present in organic molecules.

3.2.6.2. Ultraviolet-visible spectrophotometry

Absorption in the ultraviolet-visible region of the spectrum causes electrons in the outermost occupied orbital of an atom or molecule to be moved to a higher (*i.e.*, farther from the nucleus) unoccupied orbital (Britannica, 2002). Ultraviolet-visible absorptiometry is principally used for quantitative analysis of atoms or molecules. It is a useful method in this respect because the height of the absorption peaks in the ultraviolet-visible region of the spectra of many organic and inorganic compounds is large in comparison to the peak heights observed in other spectral regions. Small analyte concentrations can be more easily measured when the peaks are high.

Some ions and molecules do not absorb strongly in the ultraviolet-visible spectral region. Methods have been developed to apply ultraviolet-visible absorptiometry to those substances. Normally a chemical reagent is added that reacts with the analyte to form a reaction product that

strongly absorbs. The absorption of the product of the chemical reaction is measured, and related to the concentration of the non-absorbing analyte. When a non-absorbing metallic ion is assayed, the added reagent generally is a complexing agent. For example, 1,10-phenanthroline is added to solutions that are assayed for iron(II). The complex that forms between the iron and the reagent is red, and is suitable for determining even very small amounts of iron. When a chemical reagent is used in a spectrophotometric assay, the procedure is called a spectrochemical analysis.

Spectrophotometric titrations are another example of spectrochemical analyses. The titrant (reagent) is placed in a buret and is added stepwise to the assayed substance. After each addition, the absorption of the solution in the reaction vessel is measured. A titration curve is prepared by plotting the amount of absorption as a function of the volume of added reagent. The shape of the titration curve depends on the absorbances of the titrant, analyte, and reaction product; from the shape of the curve, it is possible to determine the end point. The end-point volume is used with the concentration of the reagent and the initial volume of the sample solution to calculate the concentration of the analyte.

3.3. X-ray fluorescence spectroscopy

The X-ray fluorescence method is a quantitative analytical technique for the determination of concentrations of elements in natural and artificial samples (Fig. 11). It is used in the laboratory and field, and as a drill hole probe. The theoretical background to X-ray fluorescence spectrometry is given by Liebhafsky et al. (1960) and Adler (1966).

An isotopic source of gamma rays is used to irradiate the sample, which in turn emits X-rays (10-100 keV) with energies characteristic of the elements in the sample. The energy is a function of the atomic number. The intensity of the emitted energy radiation is measured at an angle that is characteristics of the element being measured, and the XRF instrument is calibrated by treating known amounts of that element in a manner adopted for the sample. Certain important elements, such as Cu and Zn yield low energy X-rays. These are difficult to detect, particularly through borehole fluids, and this restricts the application of the method to surface exposures or samples. Provided the samples to be analysed are homogeneous, XRF yields very reproducible and accurate elemental concentrations. Detection limits with XRF are generally inferior to those of AAS, ES, ICP or ICP-MS. Nevertheless, XRF is capable of determining

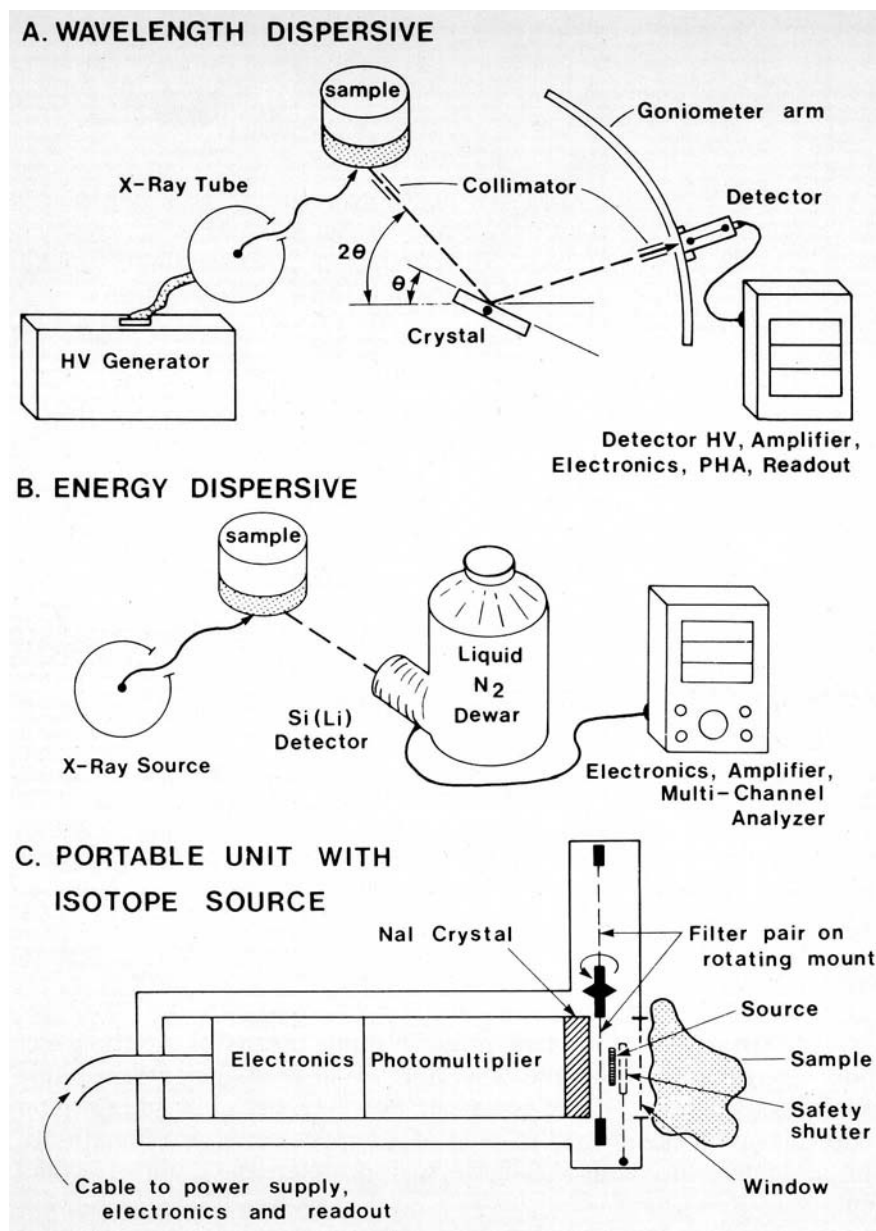


Fig. 11. Schematic diagrams of XRF spectrometers. A: Wavelength dispersive; B: Energy dispersive; C: A portable instrument with an isotope source and filters (from Fletcher, 1983, Fig. 8.4, p.174).

concentrations at least as low as 10 ppm for most elements heavier than Ca, but the sensitivity depends on the X-ray absorption by the sample matrix. In favourable cases (*e.g.*, polymers), detection limits may be as low as 0.1 mg/kg. X-ray fluorescence is particularly well suited to the rapid determination of major elements and the more abundant trace elements, and to the analysis of heavy mineral separates (Fletcher, 1983).

The XRF application to trace analysis is described by Luke (1968), who gives procedures for separating a large number of elements. However, these procedures are not all readily applicable to geological materials, and the most suitable methods are given by Stanton (1976) and Fletcher (1983). Detection limits for elements with low atomic number, notably Na, Mg, Al and Si, are severely curtailed by the Auger effect. However, XRF techniques are able to detect many of the trace elements of interest in exploration and environmental contamination samples. Because of the wide compositional variations in geochemical samples, and differential excitation of different components of individual samples, as a result of textural and mineralogical effects, it

is only possible to obtain reliable results if sample preparation is designed to minimise textural variations, and if corrections are made for mass absorption differences between samples and standards (Fletcher, 1983).

Liquid samples may be analysed by XRF using specially designed disposable sample cups equipped with a thin Mylar® film.

XRF is widely applied for the analysis of major and minor elements in virtually all materials. Of interest to the petrochemical industry and research and development are:

- analysis of major elements in materials used for heterogeneous catalysis;
- determination of palladium, platinum and calcium in Carilon®;
- determination of sulphur, nickel and vanadium in oil and oil products;
- analysis of deposits and corrosion products, and
- refractory materials, metals and slags.

Wavelength dispersive X-ray fluorescence spectrometry offers, therefore, qualitative and quantitative analysis of solid and liquid samples without pre-treatment. It is faster, but less sensitive, than ICP techniques.

3.3.1. Portable XRF

Portable XRF instruments are used nowadays in the field, and yield satisfactory quantitative results, provided the instrument is calibrated correctly (Fig. 3 & 11c). Manufacturers normally recommend that the calibration be carried out with samples collected from the study area, and the determinand concentrations analysed in a laboratory.

3.4. Mass spectrometry

Mass spectrometry is an analytical technique by which chemical substances are identified by the sorting of gaseous ions in electric and magnetic fields according to their mass-to-charge ratios (Britannica, 2002). The instruments used in such studies are called mass spectrometers and mass spectrographs, and they operate on the principle that moving ions may be deflected by electric and magnetic fields (Fig. 12). The two instruments differ only in the way in which the sorted charged particles are detected. In the mass spectrometer they are detected electrically, and in the mass spectrograph by photographic or other non-electrical means; the term mass spectroscopy is used to include both kinds of devices. Since electrical detectors are nowadays most commonly used, the field is typically referred to as mass spectrometry.

Mass spectroscopes consist of five basic parts:

- a high vacuum system;
- a sample handling system, through which the sample to be investigated can be introduced;
- an ion source, in which a beam of charged particles, characteristic of the sample can be produced;
- an analyser, in which the beam can be separated into its components, and
- a detector or receiver by means of which the separated ion beams can be observed or collected.

Many investigations have been conducted with the help of mass spectrometry. These include:

- determination of elemental composition, based on accurate mass measurement;
- identification of the isotopes of the chemical elements and determination of their precise masses and relative abundances;

- dating of geologic samples;

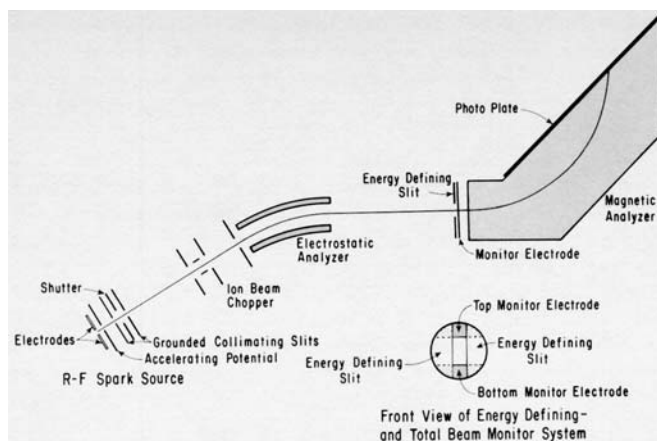


Fig. 12. Diagram of a Mattauch-Herzog double-focusing mass spectrograph (from Weber and Deines, 1974, Fig. 4, p.372).

- analysis of inorganic and organic chemicals (polymers), especially for small amounts of impurities or additives;
- analysis of organometallic complexes, such as those used in homogeneous catalysis;
- structural formula determination of complex organic substances, *e.g.*, characterisation of complex hydrocarbon (C_nH_{2n+z}) mixtures in terms of *n*- and *z*-numbers;
- strengths of chemical bonds and energies necessary to produce particular ions;
- identification of products of ion decomposition;
- identification of volatile components emanating from, for example, polymers, and
- analysis of unknown materials, such as lunar samples, for their chemical and isotopic constituents.

3.4.1. Portable Mass spectrometer/Gas chromatograph

Field portable mass spectrometers and GC/MS systems for on-site analysis are becoming slowly available (Fig. 4). The mass spectrometers used are generally quadrupole MS devices (White et al., 1998). The pumping systems tend to be either mains powered (requiring an electric generator for portable operation) or require a base station for rough pumping and maintaining the vacuum.

Some MS instruments are, however, completely portable, *i.e.*, they are battery-powered and the whole mass spectrometer for gas analysis is entirely contained in a single case. The key feature to the portability of these instruments is their high sensitivity of the Converging Annular Time-of-flight (CAT) mass spectrometer, which requires only extremely small quantities of sample gases, meaning that low-powered, zero maintenance vacuum pumps can be used. Using electron impact ionisation, the system generates spectra that correspond to those extensive and well-established mass spectral databases. The instrument's membrane inlet concentrator allows a wide range of gases to be identified and measured from the low ppb range up to percent levels. There is no need for a separate vacuum base station as the CAT vacuum system is kept permanently sealed, and is entirely self-contained within the instrument's case. The vacuum is maintained by an ion pump and a non-evaporable getter, which deals with all gases. The battery can run the ion pump for approximately two-and-a-half days. The analytical data are displayed on a notebook-PC. Hence, the instrument is very robust for on-site analysis.

3.5. Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) selective absorption of very high-frequency radio waves by certain atomic nuclei that are subjected to an appropriately strong stationary magnetic field (Britannica, 2002). Nuclei in which at least one proton or one neutron is unpaired act like tiny magnets, and a strong magnetic field exerts a force that causes them to precess in somewhat the same way that the axes of spinning tops trace out cone-shaped surfaces while they precess in the Earth's gravitational field. When the natural frequency of the precessing nuclear magnets corresponds to the frequency of a weak external radio wave striking the material, energy is absorbed from the radio wave. This selective absorption, called resonance, may be produced either by tuning the natural frequency of the nuclear magnets to that of a weak radio wave of fixed frequency or by tuning the frequency of the weak radio wave to that of the nuclear magnets (determined by the strong constant external magnetic field).

Nuclear magnetic resonance is used to measure nuclear magnetic moments, the characteristic magnetic behaviour of specific nuclei. Because these values are significantly modified by the immediate chemical environment, however, NMR measurements provide information about the molecular structure of various liquids and solids.

3.5.1. Liquid-state NMR

High-resolution, liquid-state NMR is a diagnostic tool to obtain qualitative and quantitative molecular structure information. In a high-resolution NMR spectrum, the peak positions provide knowledge on the chemical environment of the nuclei, whereas the integrated peak intensities are directly proportional to the number of nuclei that contribute to the peak. It is possible:

- to discriminate between primary, secondary, tertiary, and quaternary carbon atoms,
- to probe carbon-carbon and carbon-proton connectivities, and
- to monitor chemical exchange.

NMR can be applied in the:

- characterisation of oil products, *e.g.*, aromaticity, naphthenic content;
- structural analysis of reaction products, *e.g.*, detergents, hydroformylation and Fischer-Tropsch products;
- catalyst deactivation and catalyst structural analysis;
- determination of end groups and molecular weight of polymers;
- microstructure (tacticity) determination of polymers, *e.g.*, polyolefins, polyols, and
- copolymer studies, *e.g.* monomer distribution, EO/PO ratio in polyols.

3.5.2. Solid-state NMR

Solid-state NMR is a very versatile technique to study bulk chemical and physical properties of solid samples qualitatively and quantitatively.

The different applications of solid-state NMR are:

- to investigate the chemical composition of samples that can or may not be dissolved (*e.g.*, zeolites, cross-linked polymers, deposits, coke);
- to obtain information about the typical properties of a solid, that go beyond chemical composition (*e.g.*, morphology, crystallinity, amorphous phases, phase domains, anisotropy, bond geometry, order, exchange, mobility, diffusion, ageing);
- to study solid-liquid or solid-gas systems (*e.g.*, adsorbed molecules on zeolites,

- gels, colloidal systems), and
- to perform *in-situ* studies of heterogeneous systems (e.g., chemical reactions, phase changes, shearing).

3.6. Laser-based techniques

Laser-based techniques greatly simplify the whole analytical procedure by eliminating the pre-analytical steps, and also avoid the necessity of post-analytical disposal of residues. Such techniques are:

- laser-induced breakdown spectrometry (LIBS) (Hilb-Kortenbruck et al., 2001),
- laser absorption spectroscopy (LAS),
- laser-induced fluorescence (LIF), and
- coherent anti-Stokes Raman spectroscopy (CARS) (Demtroder, 1999).

These techniques all share the two fundamental properties (Fig. 13):

- of laser radiation, which give them their power, namely the ability to tune the wavelength of the laser to the particular atomic or molecular transitions, thus giving high selectivity, and
- the high spectral intensity of laser radiation, which gives the high sensitivity of the techniques, and renders them capable of measuring trace amounts.

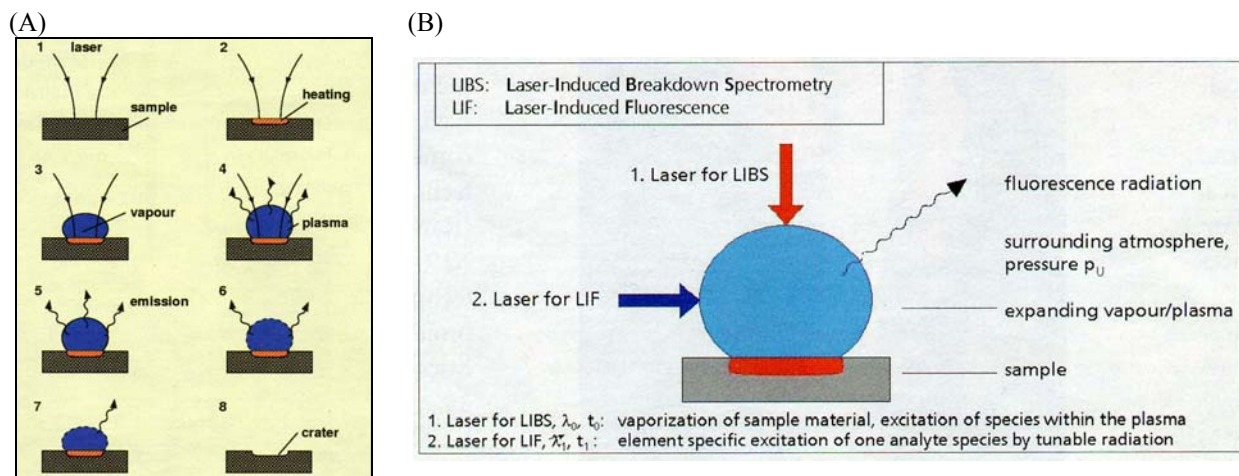


Fig. 13. Laser-induced breakdown spectrometry systems (LIBS). (A) Schematic representation of the principles of LIBS. (B) Schematic representation of the principles of LIBS-LIF. A second laser pulse from a tuneable UV laser source is used to excite analyte atoms plasma produced by the LIBS (from Hilbk-Korenbruck et al., 2001, Fig. 1, p. 12 & Fig. 2, p.13).

In most LIBS measuring systems, the laser radiation (and sometimes the measuring radiation as well) is guided by rigid optical paths, which can limit the applicability of the technique, particularly as a portable field measurement system. To address this issue, flexible measuring probes for LIBS are under development, using fibre optics to guide both the laser radiation and the radiation to be measured.

LIBS-LIF is used for the simultaneous determination of several heavy metals in soil (Hilbk-Kortenbruck, 2001). Typical limits of detection that can be achieved with this technique are in the range of 10-100 ppm. While this range may be sufficient for mineral exploration purposes,

in environmental investigations in order to decide whether most of the heavy metals meet the regulatory limits for unpolluted soil, sensitivities of 1 µg/g or better are needed to determine if the critical elements Cd, Hg, and Tl are below their legal limit. It has been shown, however, that the limits of detection, which were determined experimentally already fall below the regulatory limits for unpolluted soil. Hence, for critical elements with regulatory limits below 1 µg/g, the LIBS can be used, although this technique currently requires more sophisticated apparatus.

3.7. Chromatography

Chromatography is method for separating chemical substances that makes use of the relative rates at which they are adsorbed from a moving stream of gas or liquid on a stationary substance, which is usually a finely divided solid, a sheet of filter material, or a thin film of a liquid on the surface of a solid (Britannica, 2002). It is a versatile method that can separate very complex mixtures even in the absence of detailed previous knowledge of the number, nature, or relative amounts of the individual substances present.

Chromatography depends for its separating ability on differential retardation or retention caused by unequal adsorption of the different components carried along by a stream of inert liquid or gas. The method is widely used for the separation of chemical compounds of biological origin (for example, amino acid fragments of proteins), and of complex mixtures of petroleum and volatile aromatic mixtures, such as perfumes and flavours (which can contain hundreds of different components).

Chromatography is carried out by passing a gas or liquid (the mobile phase) containing the unknown mixture over or through an adsorbing material (the stationary phase) of high surface area. The components of the mixture will be separated by the stationary phase and can be identified individually. Further analysis can be carried out by subjecting the separated components to mass spectrometry.

Chromatography was originally used for the separation of coloured compounds (hence the name), notably by the Russian botanist Mikhail Tsvet (or Tswett), who investigated mixtures of plant pigments by adding solutions of these mixtures to the top of a column of powdered alumina and washing the column with an organic solvent. The pigments then separated into series of discrete coloured bands in the column. Each component thus isolated can be recovered either by extruding the solid column and physically separating the different bands or by using carefully chosen solvents to wash them off the column separately, a technique known as elution. Tsvet's method was neglected for many years, but since the 1930s it has been extensively used for identifying many biologically important materials, especially after it was adapted to use filter paper as the support. With suitable apparatus, mixtures applied to the paper can be separated in two dimensions; paper chromatography has been widely used to study colourless amino acids, steroids, carbohydrates, and other complex materials of natural origin. The components on the eluted paper appear as coloured spots when sprayed with suitable developing fluids.

3.7.1. Ion-exchange chromatography

Ion-exchange chromatography is a versatile method of separation and concentration, which is applicable to many kinds of analysis:

- inorganic,
- organic, and
- biochemical.

The experimental technique is simple, and in most cases fairly rapid. In the great majority of inorganic applications, all that is needed is a tube about 25 cm long and 1 cm i.d., constricted

at one end, with a glass wool plug or sintered disc to support a column of exchanger some 15 cm high (Walton, 1974) (Fig. 14). Obviously, the column can be scaled up or down according to sample size.

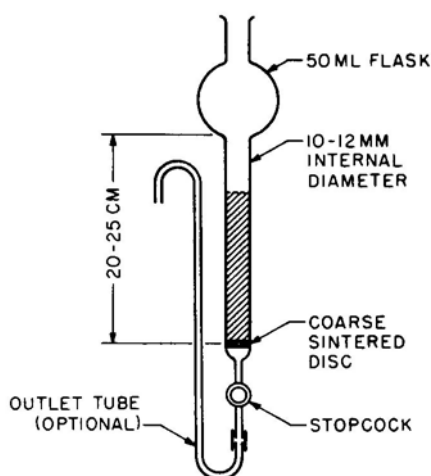


Fig. 14. Ion-exchange column for analytical use (from Walton, 1974, Fig. 1, p.74).

Ion-exchange chromatography is run in two basic modes, isocratic and gradient elution of many anions and the ammonium ion; and in ion-exclusion mode for the determination of organic acids. Analysis is generally quantitative.

Types of sample materials analysed include: soils, oils, fuels, deposits, solids, filters and bio-sludges. Some of the specialised determinations are:

- catalyst remnants in polymers;
- quantitative analysis of materials used in heterogeneous catalysis;
- trace metal (*e.g.*, mercury) contamination in hydrocarbon feedstocks, and
- accurate determination of hydrogen, carbon, nitrogen and sulphur in hydro-treated gas oils.

3.7.2. Gas chromatography

Gas chromatography (GC) employs a gaseous mobile phase, which is carried out in either a packed or capillary column configuration. In a packed column a solid support, contained in a metal or glass tube, serves as the stationary phase or is coated with a liquid stationary phase. Capillary columns are small-diameter tubes whose walls are coated with the stationary phase. Mixtures injected into the inlet of the column are driven by compressed gas (usually hydrogen or helium), and the components appear in well-separated zones. Several methods of detection of the eluted components are employed, notably devices that compare the thermal conductivity of the separated gas with that of a reference gas stream. Alternatively, in the flame ionization detector, the separated gas stream is mixed with hydrogen and burned; the resulting ions are detected by their ionization potential. This method is widely used for detection of microgram quantities of hydrocarbons.

Gas chromatography is used to separate volatile components in complex mixtures. The technique is very well developed and widely applied in the petrochemical industry as a process- and product-control technique. Hyphenated GC techniques allow direct determination of volatile components in non-volatile matrices. There is also a wide choice of detection techniques coupled to GC, ranging from element specific detectors (*e.g.*, for nitrogen and sulphur), and multi-element detectors (*e.g.*, the atomic emission detector, AED) to full mass spectrometric analysis.

Gas chromatography can be used:

- to determine volatile polyaromatics in bitumen;
- to characterise additives in SBR rubbers;
- in element-specific, high-temperature GC to determine boiling point distributions of sulphur- and nitrogen-containing compounds;
- to determine group type separations (paraffins, olefins, aromatics and naphthenics), and
- to determine chloroethers in effluents using AED.

3.7.3. Liquid chromatography

Liquid chromatography is performed either in a column or on a plane (Britannica, 2002). The most widely used columnar liquid technique is high-performance liquid chromatography, in which a pump forces the liquid mobile phase through a high-efficiency, tightly packed column at high pressure. Detection is accomplished by measuring some property of the sample components, such as absorbance or fluorescence.

Liquid chromatography (LC) is used to separate chemical components in liquid mixtures. Liquid chromatography is most useful if the sample is non-volatile (if the sample is volatile, see gas chromatography). Using appropriate chromatography columns, eluents and detectors, a wide variety of compounds in solution can be separated and analysed. Special methods of LC include size exclusion chromatography (SEC) (which allows the separation of polymers based on molecular size), and ion exchange chromatography (which permits separation of small anions and cations). Liquid chromatography is used:

- to determine the (absolute) molecular mass distribution of polymer molecules;
- to identify and quantify additives in polymers;
- to identify groups of hydrocarbons (*e.g.*, aromatics, olefins, aliphatics);
- to determine polyaromatics in complex matrices (*e.g.*, bitumen);
- to determination common anions in aqueous solution (F^- , Cl^- , Br^- , NO_3^- , SO_4^{2-} , *etc.*).

3.7.4. Supercritical-fluid chromatography

The mobile phase is a supercritical fluid, a vapour phase that has reached a specific temperature beyond which it can no longer condense to a liquid regardless of how high the pressure is raised. This method is particularly useful in separating compounds that are thermally unstable, non-polar, or non-volatile.

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