ANALYTICAL METHODOLOGY IN THE SEARCH FOR METALLIC ORES

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Abstract

Atomic absorption and emission spectrography are the methods of analysis most widely used in geochemical exploration. Development of nonflame atomizers, particularly electrothermal devices and reduction cells for atom and metal-hydride generation, has expanded the application of atomic absorption spectrometry by pushing detection limits of many elements well into the parts per billion range and by reducing detection limits for others, such as As, Se, Te, and Sn, to levels useful in lithogeochemical surveys. The recent promotion of inductively-coupled plasma sources for excitation, as well as other variations, such as use of echelle gratings, has increased the number of available spectrographic methods for multielement surveys and has simplified the application of partial extraction techniques in emission spectrography.

Other methods that require mass spectrometers and gas chromatographs are being used to measure volatile indicator elements and compounds such as helium and sulphur gases. Analytical techniques, including those based on voltammetry, ion-selective electrodes, and the use of partial or selective extractions, are finding increased application as analytical tools and as aids in determining metal speciation better to understand geochemical processes of dispersion and concentration.

Current interest in uranium exploration has sparked a major effort to develop new analytical methods or improve existing ones for the determination of uranium and related radionuclides. Exploration geologists may now choose conventional fluorimetry, delayed neutron counting, X-ray fluorescence, laser-induced fluorescence, and nuclear-fission track techniques for the determination of uranium. The choice will depend on sensitivity required, sample media being analyzed, chemical species of the uranium to be determined, turnaround time required, and cost considerations. Two of the methods described, conventional fluorimetry and laser-induced fluorescence, can be adapted for use in the field.

While recent developments of new techniques and apparatus have greatly expanded the number of useful analytical techniques in exploration geochemistry, each has its own problems and limitations as well as its applications. A panacea for analytical problems does not yet exist, except perhaps in the person of the skilled analyst, whose ingenuity in developing and applying new methods augments diligent application of tried and true procedures.

Résumé

Pour l'exploration géochimique, les méthodes d'analyse les plus fréquemment employées sont la spectrophotométrie d'absorption atomique et la spectrographie d'émission. La mise au point de méthodes spectrophotométriques sans flamme, en particulier d'appareils électrothermiques et de cellules réductrices permettant d'obtenir des atomes et des hydrures métalliques, a élargi les applications de la spectrophotométrie d'absorption atomique, en poussant les limites de détection de nombreux éléments jusqu'à la gamme des parties par milliard, et en réduisant les limites de détection d'autres éléments, comme AS, Se, Te et Sn jusqu'à des niveaux utiles pour les levés lithogéochimiques. Récemment, la production de sources de plasma par couplage inductif comme sources d'excitation, ainsi que d'autres techniques telles que l'emploi de réseaux à échelettes, ont permis d'augmenter le nombre de méthodes spectrographiques possibles pour l'analyse d'éléments multiples, et de simplifier l'application des techniques d'extraction partielle en spectrographie d'émission.

D'autres méthodes, qui exigent l'emploi de spectromètres de masse et de chromatographes en phase gazeuse sont employées pour la mesure d'éléments et de composés indicateurs volatiles, comme l'hélium et les gaz soufrés. Les techniques analytiques, en particulier celles basées sur la voltamétrie, les électrodes sélectives, et les méthodes d'extraction partielle ou sélective sont de plus en plus fréquemment appliquées comme outils d'analyse et comme moyen de mieux déterminer les espèces métalliques; ceci permet de mieux comprendre les processus géochimiques de dispersion et de concentration.

L'intérêt actuel pour l'exploration des gîtes uranifères nous a fortement incités à mettre au point de nouvelles méthodes d'analyse, ou à améliorer les méthodes analytiques existantes, pour doser l'uranium et les radionuclides apparentés. Les géologues chargés de l'exploration peuvent maintenant choisir entre les méthodes courantes de fluorimétrie, d'activation neutronique retardée, de fluorescence X, de fluorescence induite par laser, ainsi que les techniques d'observation des trajectoires des particules en chambre de Wilson, pour doser l'uranium. Le choix dépendra du degré de sensibilité requis, du type d'échantillon à analyser, de l'espèce chimique constituée par l'uranium que l'on veut doser, du temps de récupération requis, et des considérations de coût. Deux des méthodes décrites, la fluorimétrie courante et la fluorescence induite par laser peuvent aussi être utilisées sur le terrain moyennant certaines modifications.

Bien que le récent développement de techniques et d'un appareillage tout nouveau ait grandement accru le nombre de techniques d'analyse que l'on peut utiliser en géochimie pour l'exploration des gîtes minéraux, chaque système présente ses propres inconvénients et ses limitations aussi bien que ses applications particulières. Il n'existe pas encore de solution universelle aux problèmes de nature analytique — la solution réside sans doute dans la façon dont procède l'analyste expérimenté, qui, s'il fait preuve d'imagination pour mettre au point et appliquer de nouvelles méthodes, accroît l'efficacité des modes opératoires éprouvés et applicables.

INTRODUCTION

All analytical methodology may be useful in the search for metallic ores, but often economics, short-term needs, and facilities are factors in choosing the procedures and techniques for identifying and quantifying constituents that provide clues to the presence of such ores. Analytical methodology based on chemical methods such as gravimetry and titrimetry, on instrumental methods including the various kinds of spectroscopy, and on other kinds of methodology such as pattern recognition techniques, may be useful.

As generally understood, however, analytical methodology in the search for metallic constituents has to do more with trace methods of analysis; and as for the term "trace", a comment by Hillebrand (1919, p. 32) concerning rock analysis is appropriate: "It may be said with regard to the use of the word 'trace' that the amount of a constituent thus indicated is supposed to be below the limit of quantitative determination in the amount of the sample taken for analysis. It should in general for analyses laying claim to completeness and accuracy, be supposed to indicate less than 0.02 or even 0.01 per cent." Commenting on trace analysis, Sandell (1959, p. 5) said, "The essential feature of a trace analysis is not the determination of a minute quantity of a substance, but the determination of such a quantity in the presence of an overwhelming quantity of other substances which may seriously affect the reaction of the trace constituent." With today's technology both of these statements require modification along the line of amounts determined. Many trace analytical methods are capable of detecting 10^{-12} g or less, e.g., spark source mass spectroscopy and an essential feature of several trace analytical methods is their ability to detect such small amounts with small samples — for example, fission track determination can be made of 1 μg uranium per litre (1 ppb) in a 0.1 to 1 mL water sample (Reimer, 1975).

With the possible exception of titrimetry, all methods of chemical analysis require some sort of instrumentation, and titrimetry is not an exception if one detects the end point of a chemical reaction with a colour or electrical potential change. Methods of chemical analysis for trace amounts of substances require some kind of instrumentation, even including those methods based on colorimetry wherein an instrument is used to measure the colour. Thus in day-to-day jargon the term "instrumental methods of chemical analysis" (Willard et al., 1974) is synonymous with trace methods of analysis.

Karasek (1975) has provided a list of instrumental methods of chemical analysis, and the methods included in Table 17.1 are taken from his work along with others listed by Sandell (1959). The detection limits are compared on the basis of grams of a substance studied and were obtained under optimum conditions. Actual limits often vary by a factor of 10 or more.

Detection limits may be measured not only in terms of mass but also in terms of the signal produced by a detector responding to the mass. Thus the detection limit may be a detectable signal twice that of the noise level. Ordinarily with time-based abscissas the analog signal traces out an area under the curve, but in the case of flameless atomic absorption spectroscopy or gas chromatography with large amplitude signals of short duration, peak heights are more easily measured than areas under the curve. Thus, in flameless atomic absorption spectroscopy the detection limit is conveniently defined as twice the standard deviation calculated from 10 or more replicate peak heights under a given set of conditions.

Detection limits are factors in the choice of methodology in the search for metallic ores, but they are not necessarily decisive factors, especially because they differ remarkably from metal to metal, and also because no one instrumental method of trace analysis is universally applicable, except perhaps for spark source mass spectrometry. The detection limit of zinc determined by atomic absorption spectroscopy is good; that determined by optical emission spectroscopy is poor, whereas the limit of silver by the latter is excellent.

In a bibliography of exploration geochemistry covering the period from 1965 through 1971, Hawkes (1972) listed eight different analytical techniques used to acquire the compositional data required in geochemical exploration as usually practiced in the United States and Canada. Of the eight techniques, procedures based on atomic absorption spectrometry and optical emission spectrography dominate and only scattered instances of the use of other techniques, such as neutron activation, occur in the literature. To be sure, colorimetric procedures were common; indeed, they provided

Table 17.1

Trace methods and detection limits

Method	Detection limits (g)
Electron impact mass spectrometry	10^{-12}
Spark source mass spectrometry	10^{-13}
Ion probe mass spectrometry	10^{-15}
Chemical ionization mass spectrometry	10^{-10}
Neutron activation analysis	10^{-12}
Isotopic dilution	10^{-9}-10^{-16}
Atomic emission spectroscopy	10^{-9}
Flame atomic absorption spectroscopy	10^{-9}
Flameless atomic absorption spectroscopy	10^{-12}
Molecular absorption	10^{-6}
X-ray fluorescence	10^{-7}
Anodic stripping voltammetry	10^{-8}
D.C. polarography	10^{-8}
Pulsed polarography	10^{-10}
Ion selective electrode	10^{-15}
Electron spectroscopy	10^{-10}
Auger spectroscopy	10^{-10}

Table 17.2

Detection limits, by flameless atomic absorption, in picograms
(n.d. indicates no data)

Element	Carbon rod analyzer	L'vov (1961) furnace 1% absolute	Massman (1968) furnace
Zn	1	0.03	0.04
Cd	2	.08	.25
Cu	20	.6	10.
Pb	20	2.0	10.
Ag	1	.1	n.d.
As	1000	n.d.	600

the basis for trace element measurements that triggered a mushroom-like development of geochemical techniques in mineral exploration. Colorimetric procedures are also responsible for geochemical exploration becoming a recognized tool in exploration. However, the widespread development and application of colorimetric procedures based on molecular absorption, in contrast to atomic absorption, occurred in the 1950s, and by the early 1960s the position of such procedures was being undermined by the rapidly developing atomic absorption procedures. Because of their innate sensitivity, apparent simplicity, and the availability of commercial instrumentation, the number of published procedures based on atomic absorption spectrophotometry grew very rapidly. It is not surprising that Hawkes (1976) in his bibliography of exploration geochemistry covering the period from 1972 through 1975 listed 12 different instrumental techniques including over 40 references to atomic absorption determinations.

During the 1960s the application of optical emission spectrographic procedures to exploration geochemistry did not exhibit the flamboyant growth of atomic absorption procedures but experienced a slow and steady growth as workers began to consider that single element analysis, good as it was, did not provide the volume of chemical data attainable with optical emission spectrography. This understanding, coupled with the common practice of assembling field spectrographic laboratories (as established by the U.S. Geological Survey in 1955 and promoted heavily during the 1960s), helped to ensure the extensive use of mobile spectrographic laboratories for attaining the volume of compositional data needed in purely reconnaissance surveys.

The promoters of mobile spectrographic laboratories envisioned the use of such laboratories in the orientation phase of a project to establish diagnostic elements which could then be measured by cheaper analytical methodology; however, several developments occurred to make such data more attractive. The cost of collecting samples increased in greater proportion than the cost of acquiring spectrographic facilities, and geologists and chemists alike learned that personnel could be trained fairly rapidly to make spectrographic analyses.

The idea of movable laboratories is not original with the U.S. Geological Survey. Possibly before World War II, Russian and Scandinavian scientists carted spectrographic equipment into the field to perform such analyses near their study areas. One may say that they had portable laboratories, but the idea of mobile laboratories, specially designed and dedicated vehicles for spectrographic and other kinds of laboratories, is a North American contribution. With the proliferation of time-shared computers and readily available terminals and

the faster transport of samples from areas of study to centrally based laboratories, the need for such mobile laboratories is hardly justifiable, especially from the economic side; but many geologists remain reluctant to part with a useful arrangement for private laboratory facilities during part of a field season.

One hardly needs to document the statement that to date most of the analytical methodology used in geochemical exploration has been based first on molecular absorption and then on atomic absorption phenomena, along with methods based on optical emission spectrography. Exceptions to such a statement are also evident, however, especially in the case of naturally occurring radioactive elements such as uranium, thorium, and potassium; but because of the widespread and predominant use of atomic absorption and spectrographic methods in geochemical exploration, we shall limit this discussion to certain innovations in the application of these techniques and the advantages realized therein. A casual glance at the number of presently available analytical methods shows levels of sophistication varying from the simple cold extractible copper test to neutron activation procedures (which require activation facilities and computer treatment of data), to spark-source mass spectrometric methods (which require not only a highly trained staff but rather elaborate instrumentation and data handling facilities). This very proliferation should warn exploration geochemists not to become infatuated by fads in methodology in the search for metallic ores.

The analytical methodology needs to be geared to the problem. If the problem is simply that of locating relatively large targets or favourable areas, then the cold extractible copper procedures (Canney and Hawkins, 1958; Holman, 1956) or the simple spot test for molybdenum minerals recently described by Griffitts et al. (1976) may suffice. The advantage of such methodology is that one can acquire the information on the spot at the sample location and change the sampling as needed. On the other hand, if the problem is one of lithogeochemistry then more sensitive methodology is in order. For example, small amounts of copper dispersed in some manner upward from a buried porphyry require sensitive methods for detection. Similarly, one may need elaborate instrumentation to detect small amounts of uranium or daughter products, for example, in uranium detection by fission track, laser-induced fluorometry, and radon measurements in groundwaters.

In the application of atomic absorption methods in the search for ore deposits, the flame absorption methods may be adequate for elements like copper, zinc etc. in soils and rocks; flameless absorption procedures may be essential when using natural waters as the sampling medium.

We shall here discuss several instrumental trace methods that have been found useful, some that are potentially useful, and others that appear to have limited usefulness in the search for metallic ores. Finally we shall include a discussion of several methods for determining uranium in geochemical exploration with supporting and illustrative data.

ANALYTICAL METHODOLOGY

Innovations in Atomic Absorption Spectroscopy

As a part of the more comprehensive technique of flameless atomic absorption spectroscopy, the various electrothermal devices for atomizing the sample and the

sample introduction of the hydrides of elements like arsenic, mercury, and antimony escorted by an inert carrier gas into a hydrogen flame, are innovations that deserve attention.

Graphite tubes or rods are the most commonly used electrothermal atomization devices, and their use is well established. Graphite furnaces were used by King (1908, 1932) to volatilize elements in spectral studies and later modified by L'vov (1961) for atomic absorption studies in which he achieved sensitivities of 10^{-8} to 10^{-11} g. In the system used by L'vov, a carbon rod with a dried sample was inserted into the hole of a heated atomization tube. The rod was heated and the dried sample volatilized into the confined space of the tube, where it remained in the path of a light beam during diffusion out of the ends of the tube. Working independently, Woodriff and Ramelow (1968) developed a similar furnace, with the advantage that it was used to atomize and maintain the atoms in a free state. In Woodriff and Ramelow's furnace the sample is completely enclosed except for the open ends of the tube, and the resulting uniform temperature helps to eliminate matrix effects. Later Massman (1968) devised a furnace having a hole in the tube wall through which the sample was added, after which the tube was heated to atomize the sample into the path of a line source, as in a conventional atomic absorption instrument.

The graphite rod (better known as the carbon rod) was another type of electrothermal atomizer developed, and West and Williams (1969) used it in atomic absorption and atomic fluorescence analysis. Amos et al. (1971) made a comparison of sensitivities of 11 different elements achieved with the carbon rod atomizer with the L'vov furnace and the Massman furnace. The comparison of six of these elements is shown in Table 17.2 and except as noted the values are in picograms.

The tantalum ribbon developed by Hwang et al. (1971) following the work of Donega and Burgess (1970) is a less commonly used electrothermal atomizer. However, it has several advantages, one of which is the small size of the ribbon and the resulting rapid heat dissipation. Air cooling is adequate, though time consuming. Sensitivities achieved with the ribbon are in the range of 10^{-9} to 10^{-12} g.

All of the electrothermal atomizing devices suffer from spectral interferences, chemical interferences, and background radiation. With certain elements, for example, lead, the graphite tube shows less spectral interference than the carbon rod (Amos et al., 1971), but one cannot generalize. Power requirements of the carbon tube are greater than those of the carbon rod, and hence cooling times between samples are longer. Long cooling times with carbon tubes and rods as well as the tantalum ribbon result in fewer determinations per day.

Maximum temperatures obtained by these devices differ somewhat, the tantalum ribbon being limited by the melting point ✓2996°-3000°C. The carbon rod can be heated to about the same temperature, but the life of the rod is limited to 20-40 determinations, and light scattering due to carbon particles is appreciable, causing increases in background absorption especially in visible region of the spectrum. Graphite furnace temperatures of 2800°C are also common.

Hydride generation of volatile elements like arsenic, selenium, antimony, bismuth, germanium, tin, tellurium, and lead (Pollack and West, 1973; Thompson and Thomerson, 1974) by reduction with sodium borohydride followed by atomization and combustion in a heated tube or in a hydrogen-argon or hydrogen-nitrogen flame is another innovation in atomic absorption spectroscopy that merits attention. The generated hydrides are swept along with a carrier gas such as argon or nitrogen, into a heated tube or hydrogen flame positioned in the light path of a hollow cathode or electrodeless discharge lamp. The chemical conversion of arsenic into arsine and its

introduction into an argon-hydrogen flame resulted in improved detection limits (Holak, 1969). Chu et al. (1972) eliminated the flame and swept the arsine into a heated absorption tube to achieve better sensitivity, which is possibly due to elimination of flame background and to longer residence times.

Goulden and Brooksbank (1974) automated the procedure for determining antimony, arsenic, and selenium but found that they needed to isolate the hydrides by means of a heated column from products of side reactions prior to combustion in an open-ended heated tube. Combustion of the isolated hydrides produced increases in sensitivity by two orders of magnitude over combustion of the hydrides in a conventional hydrogen-argon entrained air flames. Pierce et al. (1976) combined the heated column with the furnace of Chu et al. (1972) to develop an automated procedure for determining selenium and arsenic in surface waters that have detection limits respectively of 0.019 and 0.011 µg/L.

Hydride generation procedures appear to be relatively free from interferences, although one would expect that any element reducible by sodium borohydride and that forms a volatile hydride would interfere if present in large amounts. In a study of the determination of antimony and arsenic in geological materials, Aslin (1976) concluded that the hydride generation procedures were apparently free from interferences. Iron, cobalt, and copper did not interfere at the four levels studied. Nickel at the 1000 ppb level did interfere with the determination of arsenic, and both nickel and silver interfered with the determination of antimony.

Pierce et al. (1976) noted that copper concentrations in excess of 5 mg/L did compete with selenium and arsenic compounds during reduction, but that the competition could be inhibited by dilution. Also we have noted relatively high blanks in arsenic determinations caused by impurities in the sodium borohydride reagent. Improvements in the manufacture of this reagent are in progress, and despite a few drawbacks, hydride generation procedures provide reasonably reproducible methods for measuring elements like arsenic, selenium, and bismuth in geochemical exploration as well as in monitoring air and water quality in environmental studies.

Innovations in Optical Emission Spectrography

Optical emission spectroscopy has been a principal means of data acquisition in geochemical exploration from the beginning, when Russian scientists transported a spectrograph into the field to support field parties (Ratsbaum, 1939; Fersman, 1952) and Palmqvist and Brundin (1939) set up a stationary spectrographic laboratory to make about 400 determinations per day on ashed plant material. In North America the development of a truck-mounted spectrograph laboratory (Canney et al., 1957) triggered a widespread interest, and although the above authors suggested that spectrographic laboratories be used only in the reconnaissance part of an exploration program because of the cost, truck-mounted spectrographic laboratories soon became an essential part of the data acquisition process, at least in the United States. Data attainable by optical emission spectrography revealed some hitherto unknown mineral assemblages (Curtin et al., 1968).

Currently the optical emission spectrographic system used in geochemical exploration commonly uses d.c. arc excitation and original or replica gratings with photographic readout. The gratings are ruled with 15 000 lines per inch and provide a wavelength coverage from about 2050 to 4850Å in the second order. Ahrens (1950) and others found that d.c. arc excitation was best suited to geological materials especially when the terms semiquantitative and quantitative are carefully defined. Factors in favour of d.c. arc excitation are "simplicity, high concentrational sensitivity, adaptability

Table 17.3

Detection limits of elements

Element	Spectro-graphic d.c. arc (ppm)[1]	Flame AAS (ng/mL)[2]	Flameless AAS (ng/mL)[2]	ICP Excit (ng/mL)[3]
Zn	3(100)	2	0.006	2
Cd	10	1	.001	2
Cu	0.5	2	.01	1
Bi	20	40	.1	50
Pb	5	20	.06	8
Ag	0.5	2	.0025	4
Co	10	10	.04	3
Ni	5	10	.1	6
U	100	30 000	([4])	30
W	20	3000	([4])	2
Sb	20	100	.2	200
As	100	100	.1	40

[1]U.S. Geological Survey laboratories, written comm.

[2]Slavin et al. (1972).

[3]Fassel and Kniseley (1974a).

[4]No data.

and low cost" (Canney et al., 1957). Recently Timperley (1974) interfaced a dedicated minicomputer with a direct-reading spectrograph for use in data collection in rapid geochemical surveys.

Although a vast amount of semiquantitative spectrographic data has been acquired in geochemical exploration programs using the systems described, changes are inevitable and two such innovations are worth considering. These are plasma sources for excitation and echelle gratings, which have the property of concentrating the energy in the desired order. With regard to plasma sources for excitation most of our discussion will be about inductively coupled plasmas (ICP) which seem to have caught on almost as readily as atomic absorption spectroscopy. A recent quotation is as follows:

"This new technique will probably have a similar impact over the next decade as AAS did over the last" (Barringer Research 1975, written comm.).

Neither innovation is really new: plasmas have been around for several years (Greenfield et al., 1964; Wendt and Fassel, 1965); echelle grating construction was first described by Harrison (1949).

Inductively coupled plasmas are maintained by a high frequency, axial magnetic field in a laminar flow of argon at atmospheric pressures. The discharge does not contact any electrodes in contrast to capacitively coupled plasmas such as high-frequency torch or radio frequency discharges or d.c. plasma jets (Wendt and Fassel, 1965).

Spectrographic systems in common use require a finely powdered sample, often mixed with other materials, to achieve better presentation of sample to the d.c. arc or to simulate matrices whose burn characteristics are well defined. For example, iron oxide and silica may be added to plant ash so that the behaviour of the mixture in an arc resembles that of a granite or silicate rock. In contrast, inductive coupled plasmas take sample solutions with

attendant simplification of matrix. Obviously the solution has to be introduced into the plasma, and the process, involving atomization and nebulization, has been accomplished by ultrasonic generation of aerosols (Wendt and Fassel, 1965; Dickinson and Fassel, 1969) and later by pneumatic nebulization (Scott et al., 1974).

Fassel and associates have contributed much to aid in understanding the events taking place in the plasma excitation by developing a model for the plasma that enabled them to effectively optimize a number of experimental factors, such as:

1. desolvation of nebulized solutions prior to entry into plasma.

2. introduction of sample aerosol into the plasma.

3. sensitively tuned rf generator for optimum coupling of the output to the plasma.

When such factors were optimized, they were able to measure concentrations ranging from nanograms to fractional micrograms per mL which effectively extended the range in concentrations measured upward by two to four orders of magnitude. Thus the inductively coupled plasma excitation system has a wide dynamic range with obvious advantages.

The maximum temperature of an argon-supported plasma is of the order of 9000 to 10 000°K, and Fassel and Kniseley (1974b, p. 1158a), stated that "according to our preliminary measurements, the gas temperatures in the axial channel of the eddy current flow region is about 7000°K." They went on to say that this temperature is twice that achieved in the hottest combustion flame. They noted also that residence times of the sample in the plasma before reaching the observing point is about 2.5 ms. Fassel and Kniseley also provided a satisfactory explanation for the improved sensitivities (as compared with flame excitation) for many elements, especially those that form stable monoxide molecules with dissociation energies greater than about 7 electron volts.

A comparison of detection limits for 12 elements is given in Table 17.3.

In selecting these data we have leaned towards the conservative side; for example we choose a value of 6×10^{-12} g for the detection limit of zinc by flameless atomic absorption spectroscopy as compared with 2×10^{-14} g given by Dulka and Risby (1976). We conclude with Fassel and Kniseley (1974b) as follows:

(1) "Inductively coupled plasma excitation for some 30 elements is considerably more sensitive than d.c. arc excitation.

(2) Flame atomic absorption methods have greater sensitivity than d.c. arc excited spectrographic methods.

(3) Flameless atomic absorption methods are considerably more sensitive than flame methods.

(4) Flameless atomic absorption methods are more sensitive than spectrographic methods using either d.c. arc-excitation or inductively coupled plasma excitation."

Echelle gratings have been around for 25 or more years, but until recently attempts to take advantage of the echelle gratings whereby radiation of a given wavelength could be largely concentrated in one order were limited (Richardson, 1953) and of little success.

The echelle is a special kind of diffraction grating ruled with high precision. Its broad, flat grooves are ruled so that the width of each step is several times the height and the spacing between the steps is several times greater than the wavelength of the incident energy. The large number of

Table 17.4

Comparison of detection limits (ng/mL)
(n.d. indicates no data)

Element	Material	ASV diff. pulse	ASV linear scan	AA nonflame
zinc	seawater	0.04	0.04	0.008
cadmium	seawater	.005	.01	.01
lead	seawater	.01	.02	.5
tin	geological material	~1200[1]	n.d.	n.d.
silver	natural water rain and snow	n.d.	~400[1]	.0025[2]
mercury	natural water	n.d.	800[3]	n.d.

[1]Bond et al. (1970).

[2]Slavin et al. (1972).

[3]Perone and Kretlow (1965).

orders of the grating, as many as 90, may be separated by an order sorter which results in radiation of a given wavelength being concentrated in one order. A prism with dispersion at right angles to the grating is one kind of order sorter. Successful use of echelle gratings require that the orders be separated, and Danielsson and Lindblom (1972) have developed a spectrograph with a CaF_2 Littrow prism order sorter and an image tube with high sensitivity and resolution. Application of the image tube for spectral analysis required focusing a wide wavelength coverage on the relatively small photocathode, 20 mm in diameter, and easy electronic readoff. The echelle grating with an order sorter met their requirements, and they accordingly developed a stigmatic, coma-compensated echelle spectrographic system with high resolution and considerable dispersion (Danielsson et al., 1974).

In a commercially available d.c. plasma-echelle spectrometer system the temperature of the plasma reaches 6000-8000°K. For elements such as calcium, magnesium, boron, and copper, analytical results are similar to those obtained by atomic absorption spectrometry. Stray light is a problem in determining aluminum. The quartz chimney above the plasma causes interference, and substitution of Teflon for the quartz does not help. Molecular bands interfere with phosphorus determinations, but in general 30-40 samples can be analyzed for 18 elements in about one hour with a precision of slightly more than ±10 per cent.

Echelle gratings are not restricted to monochromators designed specifically for emission. They have also been used in monochromators designed for atomic absorption, and Keliher and Wohlers (1974) made a direct comparison between a line source (hollow cathode lamp) and a continuum source (150 W xenon lamp) using a high resolution echelle spectrometer. They found that the sensitivities obtained with the hollow cathode lamps were slightly superior to those obtained with the xenon lamps using the echelle spectrometer, and although the spectral bandwidth using the later continuum source and the echelle grating is wider than that of the absorbing line, the results were reasonably good.

The relatively poor detection limits of previous continuum systems were attributed to poor signal-to-noise ratios. Wavelength scanning is a viable technique for improving such ratios as long as the wavelength of the absorbing line is within the range of wavelengths scanned.

Veillon and Merchant (1973) described a piezoelectric scanning Fabry-Perot interferometer with a conventional grating monochromator to obtain an overall spectral bandwidth of 0.013Å. This was small enough to suggest the possibility of effectively scanning a wavelength interval of 0.01Å over the 0.1Å monochromator output and measuring the radiation within any 0.01Å interval. As long as the instrumental width of the interferometer is less than that of the absorbing line, the absorbance could be measured with maximum sensitivity and such measurement resulted in improved signal-to-noise ratio. Copper and silver sensitivities were similar to those obtained with line sources.

Thus echelle grating monochromators may find use in atomic absorption as well as in atomic emission methods, and provide the advantages of a single continuum source in place of the large number of line sources heretofore required in atomic absorption spectrometry. With such a development the cost of atomic absorption determinations can obviously be reduced.

Anodic Stripping Voltammetry

Like other instrumental techniques, anodic stripping voltammetry is not new, but recent developments in instrumentation have suggested applications of this method to the solution of several difficult analytical problems involving trace determination of elements like lead, bismuth, cadmium, thallium, tin, and silver.

The fundamental process involved in anodic stripping voltammetry (ASV) have been discussed by several authors, as illustrated by Copeland and Skogerboe (1974). Briefly two steps comprise an ASV measurement: First the analyte species is reduced and concomitantly plated out on an electrode, usually mercury or solid electrodes such as platinum, gold, or silver. Second, the reduced species is oxidized, stripped back into the electrolyte solution by systematically changing the potential in the direction to cause oxidation. Hanging-drop mercury electrodes are also used, but the spherical surface limits the amount of analyte that can be plated out. Alternatively thin-filmed mercury electrodes wherein the mercury is mounted as a film on a substrate such as graphite have been used; they have the advantage of a large surface-area-to-volume ratio, and they can be rotated or stirred during the plating and stripping. At the oxidation potential of each plated analyte species, the Faraday current produced by the oxidation is measured. The stripping current produced by the oxidation of one or more analyte species is proportional to the concentration of the respective species plated out on the electrode and ultimately to the concentration in the solution.

Different waveforms are used to strip the deposited analyte species from the electrode. The common choice is a linear ramp of the potential wherein the latter is scanned at a constant rate over a range covering the potential at which oxidation of the analyte species occurs. The scan rate is most important for achieving maximum stripping current. Infrequently a small sine wave potential is superimposed on the linear ramp, resulting in phase differences between stripping current and the ramping voltage, so that phase-sensitive detection can be used to separate the Faraday current from non-Faraday currents, all at the expense of more sophisticated instrumentation but with significant improvements in signal-to-background ratios. Relatively large amplitude pulses superimposed on the linear potential ramp for short periods are the basis of another stripping technique that provides a choice in measurement periods

during the stripping process to reduce non-Faraday currents. Moreover, as suggested by Osteryoung and Christie (1974), the pulsed stripping shows greater sensitivity than linear scan stripping because of better discrimination between Faraday current and the charging current. Pulsed stripping voltammetry also provides considerable signal enhancement due to the replating and reoxidation that takes place near the end of the pulse and during the next pulse, so that the same analyte species is seen repetitively as compared to a single run in linear scan stripping. The net result is a longer residence time using pulsed anodic stripping.

Among the advantages of anodic stripping voltammetric methods are the small size of sample needed due to innate sensitivity, the relatively inexpensive (although highly specialized) instrumentation, and the multielement possibilities, along with its essentially nondestructive aspects. The sensitivities given by Copeland and Skogerboe (1974) are shown in Table 17.4 except as noted. These sensitivities compare favourably with those obtained by flameless atomic absorption spectroscopy, and thus anodic stripping voltammetry may in some cases offer a viable alternative to atomic and molecular absorption techniques.

Selective Ion Electrodes

Selective ion electrodes have been in use since it was found that thin glass membranes could be used to seal off an insulating glass tube containing a dilute solution of hydrogen ion and that a potential would develop across the membrane which could be measured by reference to another solution of fixed concentration. Hence, the glass electrode quickly replaced the hydrogen electrode as well as other kinds such as the quinhydrone electrode to measure the pH of soils and other materials. Such measurements became standard practice in soil and agronomic studies.

In addition to hydrogen ion, the glass membrane electrodes were sensitive to sodium and more than 40 years ago Lengyel and Blum (1934) obtained a Nernstian response with sodium ion — a straight line plot of voltage against logarithm of sodium ion concentration. They predicted the development of glass electrodes that would be sensitive to different metals, but little progress was made until Schwabe and Dahms (1960), using tracer studies, established the fact that although the theory had been accepted for many years, the hydrogen ions did not really pass through the glass membrane to give an electrode potential, but rather, the charges are transported by an ion carrier wherein each charged carrier needs to move only a few atomic diameters before giving up its charge to another carrier. The behaviour of all electrodes was not readily explained by this simple mechanism, but the explanation was adequate to stimulate renewed interest in the development of electrode and associated measurement equipment.

In the meantime a new technology had developed to fabricate glasses of different composition that selectively responded to different cations. By 1958 the Beckman Company[1] was marketing "specific ion electrodes" for elements like sodium, potassium, and silver. The electrodes were far from being specific, hence the more acceptable term selective ion electrodes. The technology of developing selectively responsive glasses is covered by Rechnitz (1967).

As early as 1965 one of us proposed an analytical method for use in geochemical exploration, using the silver content of geological materials as the measurable parameter. Measurement was easily done in the field with simple equipment consisting of the Beckman sodium electrode and a small portable pH meter. The sensitivity of the electrode to silver ions increased with pH and at a pH of 11 to 12 (readily achieved with an organic base such as ethanolamine) as little as 20 µg of silver in 10 mL of solution could be measured. At that time most of our silver measurements were made by means of optical emission spectrography, and the procedure offered a viable alternative at considerable savings in time and costs.

In a theoretical treatment of membrane potentials Eisenman (1969) divided electrodes into three general classes: (a) solid ion exchangers (glass electrodes); (b) liquid ion exchangers; (c) neutral sequestering agents which act as molecular carriers of ions. And in a review paper Pungor and Troth (1970) summarized the electrical behaviour of various ion-selective membranes.

Of the general types, solid ion and liquid ion exchangers comprise most of the present-day practical electrodes, especially in the useful methodology in the search for metallic ores. More than 20 electrodes are available including metals like lead, copper, calcium, all halogens, and different anionic species such as nitrate, cyanide, thiocyanate, perchlorate, and even gases like ammonia and sulphur dioxide. And without doubt the fluoride electrode is not only the best available, but has experienced the widest application. It may be that its superiority accounts for the extensive use.

The fluoride electrode consists of a crystal of lanthanum fluoride doped with europium +2 and cemented in the end of a glass or polyvinyl chloride plastic tube containing a mixture of 0.1M sodium fluoride and 0.1M sodium chloride solutions connected to an outer lead through a silver-silver chloride electrode whose potential is fixed by the chloride ion. The fluoride ion governs the potential at the inner surface of the lanthanum fluoride crystal, and when the electrode is immersed in a fluoride solution, a potential difference occurs across the membrane. The magnitude of such potential is dependent on the ratio of the fluoride ion activities of the inner solution and the outer solution.

The fluoride electrode has been used to measure fluorine in the U.S.G.S. reference rocks (Ficklin, 1970; Ingram, 1970) and to measure fluorine in rocks associated with tin mineralization (Kesler et al., 1973). Farrell (1974) used Ficklin's method to measure fluorine in soils after partial and total extraction in the fluorine province of Derbyshire, England.

The full impact of the successful development of a practical fluoride electrode for measuring small amounts of fluorine can only be appreciated by those older practitioners of analytical chemistry who have struggled to observe the endpoint when a titrating fluoride solution with a thorium nitrate solution in presence of alizarin as indicator.

Friedrich et al. (1973) used the cupric electrode to measure copper ion concentrations in stream water samples from the Ramsback area of Germany. He concurred with Durst (1969) that the electrode was useful for copper concentrations down to 0.6 ppb and was "virtually interference free with respect to the usual divalent cations."

Selective ion electrodes sense activity, which may be a drawback except in dilute solution where activity and concentration are nearly equal. In concentrated solutions where activity and concentration differ markedly, the measurement requires some means of estimating the ionic strength so as to relate activity and concentration. From an analytical perspective one has to repeat ionic strength levels, and this can be achieved either by dilution or by the addition

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[1] The inclusion of brand or manufacturers' names in this report is for illustrative purposes only and does not imply endorsement by the U.S. Geological Survey.

of a high ionic strength solution to the analyte. The addition of a high ionic strength solution is more practical than dilution because of the innate sensitivity of the electrode. The former, called swamping, tends to nullify small variations due to different kinds of samples.

In a brochure on analytical methods Orion Research (1973) provided information on suitable ionic strength pH adjustor solutions for the different electrodes.

In summary the commercial availability of some 20 different electrodes, the relative cost of a suitable voltmeter, and the ease of making objective analytical determinations under rough conditions are plus factors in the use of ion electrodes in the search for metallic ores.

Miscellaneous Techniques

The following techniques are mentioned primarily to inform the reader of state-of-the-art methodology:

High-pressure liquid chromatography
Photoacoustic spectroscopy
Atomic fluorescence
Zeeman polarization effects.

Liquid chromatography is used to effect separations mostly in biological, clinical, and organic studies; and high pressure is simply a variation resulting in separations not easily accomplished otherwise. High-pressure liquid chromatography may have application in separation of metallic chelates which can then be detected and measured thus providing new methods of trace analysis for metallic constituents. At present, however, such applications are relatively rare and the number of metals measured by such a technique is probably less than a dozen.

Photoacoustic spectroscopy is an old phenomenon which was recently reviewed by Rosencwaig (1975). The solid photoacoustic absorption spectrum qualitatively resembles the solution absorption spectrum of certain materials. In practice, the sample is placed in a sealed, gas-filled cell containing a sensitive microphone for detection. When irradiated by high-intensity chopped monochromatic light, the light absorbed by the sample is changed to heat which raises the temperature of the boundary layer which then expands and contracts at the chopping rate. The microphone detects the alternate expansion and contraction and yields an electrical signal which can be treated in a conventional manner.

Atomic fluorescence is a form of flame spectroscopy wherein a solution of the sample is sprayed into a flame, and the ground state atoms are excited by radiation of the proper frequency from a continuum source in contrast to d.c. arcs, flames, plasmas, and so forth. The excited atoms are deactivated by emission of radiation of the same or lesser frequency. The emitted radiation is proportional to the concentration of excited species. Winefordner and Staab (1964) and Winefordner and Vickers (1964) have exploited this form of spectroscopy; they are responsible for demonstrating

the remarkable sensitivities of different elements as zinc, cadmium, and mercury. The state of development of this technique is illustrated by the work of Johnson et al. (1975), who described a procedure for determining 18 elements using a single source and a separated air acetylene flame, and 5 elements with a separated N_2O-acetylene flame in jet engine lubricating oils. They achieved detection limits comparable to those obtained by flame atomic absorption spectrometry and single element hollow cathode lamps. Although the general consensus is that atomic fluorescence determinations are somewhat difficult and costly, the possibilities of multielement determinations of metals in geological materials are attractive.

Although commercial instrumentation utilizing the polarization characteristics of Zeeman split lines to correct for background and other extraneous noise in flameless atomic absorption is available, the advances in the area are rapid enough to warrant delays in major expansions. For example, Hadeishi and McLaughlin (1975) reporting on use of the Zeeman effect in atomic absorption determination of mercury applied a magnetic field to the light source in the direction of propagation of the light beam and used the components of the Zeeman emission lines for absorbing and reference light respectively. During the same year Koizumi and Yasuda (1975) applied the magnetic field to the light source in a direction perpendicular to the propagation of the light beam and were able to determine elements other than mercury, such as lead, cadmium, and zinc (Koizumi and Yasuda, 1976). Later Koizumi et al. (1977) applied the magnetic field to the sample vapour perpendicular to the light beam with improved background correction and steadier baselines. They reported that this particular system was capable of measuring with high sensitivity practically all of the elements determined by conventional atomic absorption spectrometry.

Advantages of the proposed systems are that no sample preparation is necessary, both liquid and solids can be analyzed, and greater extremes in the conditions can be tolerated than in ordinary flameless atomic absorption spectroscopy.

GEOCHEMICAL METHODS OF ANALYSIS
FOR URANIUM

Exploration efforts directed towards discovery of new uranium deposits have never been greater than they are now. A measure of this level of effort is evidenced by the fact that in Canada over 60 per cent of all geochemical samples collected in 1976 and 1977 were or are being analyzed for uranium as the element of primary interest. Of the many different methods for measuring uranium, those most frequently used today in exploration geochemistry are listed in Table 17.5 in what is probably the order corresponding to their degree of usage globally in geochemical analyses for uranium.

Conventional Fluorometric Method

The conventional fluorometric method of uranium analysis is based on measurement of the fluorescence produced when uranium is fused into sodium fluoride or other alkali fluoride materials. The resulting fused bead will produce a brilliant fluorescence when it is illuminated with an ultraviolet light at 3550Å. This fluorescence output increases proportionally with increasing uranium concentration and can be measured by means of a suitable instrument such as the Jarrell Ash reflectance-type fluorometer. In practice, a measured aliquot of a sample solution containing uranium, either as a leachate of a solid sample or as a natural water, is placed in a platinum dish and evaporated to dryness. A suitable flux containing a fluoride

Table 17.5

Most commonly used methods for
geochemical analysis of uranium

1)— Conventional Fluorometric Method

2)— Delayed Neutron Activation Analysis

3)— X-ray Fluorescence Method

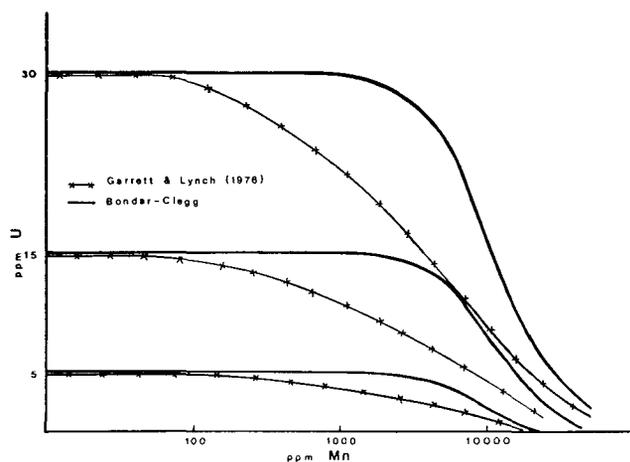4)— Fission Track Method

5)— Laser-Induced Fluorescence Method

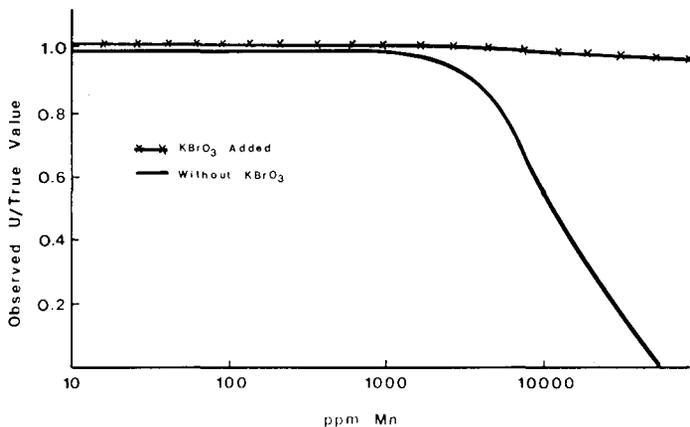**Figure 17.1.** Observed fluorometric uranium versus manganese.

Figure 17.3. Observed fluorometric uranium versus iron and manganese.

One often repeated criticism of the conventional fluorometric method is that both iron and manganese cause "quenching" or suppression of uranium fluorescence. Garrett and Lynch (1976) have shown in a series of control experiments, using manganese alone, that this problem can be severe in geochemical exploration. However it is not necessarily as serious a problem as is commonly believed and furthermore, it can be very easily eliminated.

Figure 17.1 shows observed fluorometric uranium values versus manganese as reported by Garrett and Lynch (1976) who used a high-carbonate flux; and as observed in a separate control experiment by Bondar-Clegg (unpub. data) who used a noncarbonate flux and a slightly different fluorometric procedure. Only the data for 5, 15 and 30 ppm uranium are shown. From these data, it can be seen that depending on the actual fluorometric procedure used, the suppression of uranium fluorescence may not become severe until concentrations approaching 5000 ppm Mn are encountered. Most stream or lake bottom sediments and soils contain less than this amount of manganese.

Figure 17.2. Effect of potassium bromate on fluorometric uranium versus manganese.

salt is then added to the dish and the sample is fused. After cooling, the uranium in the fused disc is measured fluorometrically.

A basically simple technique, the fluorometric method offers many advantages. It is relatively rapid and two analysts working together, can produce 300 analyses per work shift. The detection limits of 0.1 ppm for solid samples and 0.05 ppb for 25 mL samples of natural waters routinely attainable by the fluorometric method are adequate for almost all geochemical exploration requirements. Compared to other methods of uranium analysis it is inexpensive both on a cost per sample basis and in terms of the capital investment required to equip a uranium analysis facility. It can be adapted for use in the field. And finally, while capable of providing analytical data for total uranium, it also lends itself most readily to use in the partial or selective extraction procedures often used by geochemists to increase contrast between anomalous and background samples, or to obtain additional data on uranium fractionation in geochemical samples as an interpretive aid. Disadvantages of the method, simply stated, are that the routine fluorometric method of uranium analysis is not as precise at low uranium concentrations (0.1-2 ppm U) as are the X-ray fluorescence and delayed neutron activation methods when analyzing solid samples, and it is not quite as sensitive as the fission track method for the analysis of waters.
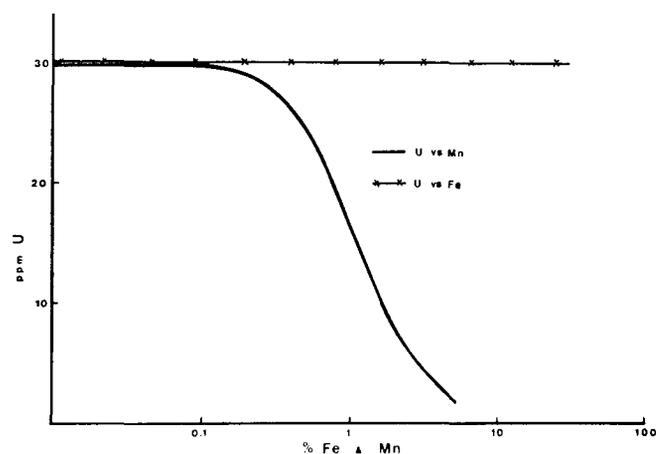
Ingles (1958) stated that in analyzing samples for uranium, those containing manganese as the principal interfering element can be treated by adding sodium chlorate or similar strong oxidant to precipitate out the interfering manganese.

Figure 17.2 shows the ratio of observed uranium concentration to the true value versus manganese added, with and without the addition of 0.15 gm potassium bromate. Only the data for 30 ppm uranium are shown, although the same results were obtained for other concentrations. The results show clearly that the quenching effect of manganese in concentrations up to 100 000 ppm Mn (10%) can be eliminated by simply adding 0.15 g potassium bromate to the test solution to precipitate the manganese as manganese dioxide. The supernatant liquid is then analyzed in the normal manner. The procedure is simple and does not increase the cost of analysis.

Separate tests, again using a noncarbonate flux, to test the effects of quenching by iron at concentrations up to 30 per cent Fe were also carried out.

The "quenching" effect of iron compared to manganese for increasing amounts of both elements is shown in Figure 17.3. Clearly, the "quenching" effect of iron is considerably less than for manganese and is not likely to be a problem in most geochemical samples.

The fluorometric method is simple and straightforward in theory, but delicate in practice. As such, it is very dependent upon the care of the individual analyst in performing the analysis if acceptable detection limits and precision levels are to be attained. Nonetheless it is very sensitive and can produce highly accurate results.

Delayed Neutron Activation Analysis

The delayed neutron activation method of analysis is based on the detection of delayed neutrons emitted in the decay of the fission products of uranium or other fissile material which is induced to fission by exposing samples to an intense neutron flux in a nuclear reactor. The number of delayed neutrons emitted following irradiation is proportional to the amount of fissile material present in the sample. Neutrons can be detected and selectively counted and the technique is highly specific for fissile material because, except for a number of short-lived light nuclides which have been shown to have negligible interfering effects, fission is the only nuclear reaction which produces nuclides that emit delayed neutrons.

The only naturally occurring fissile nuclides are ^{235}U, ^{238}U and ^{232}Th. ^{235}U is fissioned by slow or thermal neutrons whereas ^{238}U and ^{232}Th are fissioned by fast neutrons. Because the fast neutron flux component in a reactor is usually smaller than the thermal neutron flux component and because the fast neutron cross-section for ^{232}Th and ^{238}U is much lower than the thermal neutron cross-section for ^{235}U, slow thermal fission of ^{235}U greatly predominates. As a result, thorium interference is usually negligible for samples containing thorium in amounts equal to or less than the amount of uranium present. Except for samples which may have extremely high Th/U ratios the delayed neutron activation method can be considered specific for the determination of ^{235}U or uranium, assuming the normal isotopic abundance of ^{235}U in natural uranium. For samples with high Th/U ratios, a correction can be made for thorium interference by making two measurements: once by irradiating the sample in the normal manner with a mixed neutron flux to measure ^{235}U plus ^{238}U and ^{232}Th, and once with the thermal neutrons screened out so that only ^{238}U and ^{232}Th are measured. The ^{235}U content is then derived by difference.

The method as used by Atomic Energy Canada Ltd., Commercial Products Division (Boulanger et al., 1976) is as follows: samples are stacked in an automatic loader and transferred pneumatically to the Slowpoke reactor for irradiation up to a neutron flux of 1×10^{12} n cm^{-2} s^{-1}. After irradiation, the samples are cooled for 10 s and then transferred to a counting facility consisting of six BF_3 detector tubes embedded in paraffin. By comparing the delayed neutron count to that obtained from standards, the uranium content of the unknown samples is determined. After counting, the samples are ejected into a shielded storage container and held until safe to handle. AECL has determined that by using a 30/10/30 second irradiation/cool/ count sequence for geochemical analysis, the system is capable of providing a detection limit of 0.1 ppm with a precision of ±15 per cent at the 1 ppm level, ±10 per cent at 10 ppm U and ±2 per cent at the 100 ppm U level. Sensitivity for thorium is approximately 1 per cent of the sensitivity for uranium. Productivity is approximately 27 complete determinations per man/hour.

For the analysis of solid samples for total uranium, the delayed neutron activation method can be an accurate method which is fairly rapid, more sensitive than X-ray fluorescence, and more precise than fluorometry. Shortcomings of the method are, as a general statement, all cost related. The most obvious disadvantage of the delayed neutron counting method as compared to conventional fluorometry, XRF or laser-induced fluorometry is that one must have access to a nuclear reactor. Another most important shortcoming is that the method does not readily lend itself to measuring partial extractable and selectively extractable uranium in solid samples or to measuring uranium in natural waters. Both can be done but not very easily and not without preliminary separations and/or pre-concentration steps that in most cases are sufficiently complex and time-consuming to make the method slow, expensive, and therefore impractical for routine use in exploration geochemistry.

X-ray Fluorescence Spectrometry

Measurement of uranium by X-ray fluorescence spectrometry is based on measurement of the characteristic secondary X-ray spectra produced when a specimen is irradiated or bombarded with X-radiation of sufficient energy to produce electron transitions within uranium atoms in the sample. The intensity of this secondary radiation of characteristic wavelength is a measure of the amount of uranium present in the sample. Very sensitive detectors are used to measure this characteristic radiation and to distinguish these characteristic X-ray pulses from background radiation. By comparing the intensity of these secondary characteristic X-rays to those obtained from standards, the uranium content of unknown samples is determined.

Because variations in the major constituents of samples being analyzed may produce enhancement or absorption matrix effects which might lead to significant analytical error, a ratio method of calibration is often used. The analyte peak counts are ratioed to the background counts compensating for matrix variations and the ratios compared to calibration curves prepared from artificially prepared or certified natural uranium standard samples. The pressed pellet method commonly used for geochemical samples offers a detection limit of 1 ppm with a precision of ±10-15 per cent at the 10 ppm level. Productivity is approximately 27 determinations per man/hour. Only Rb and Sr, at concentrations in excess of several thousand ppm each, are likely to interfere. Since most rock types, soils, and sediments contain less than these amounts, these elements usually pose no difficulty.

The advantages and disadvantages of the X-ray fluorescence method are similar to those of the delayed neutron activation method. For the analysis of solid samples for total uranium, it can be an accurate method which is fairly rapid and precise. While not as sensitive as either the delayed neutron activation method or the fluorometric method it does nonetheless offer a detection limit of 1 ppm which is adequate for many geochemical applications and has a precision approaching that of the delayed neutron activation method. The disadvantages are that this method, like delayed neutron activation, does not readily lend itself to measuring partial and/or selectively extractable uranium in solid samples or to measuring uranium in natural waters at the low concentrations normally encountered in using these techniques. Again, it can be and has been done, but the time and expense associated with the procedures required to separate and/or concentrate the uranium sufficiently to provide adequate detection limits are simply not justified when other available methods are better suited for such purposes and less expensive on a cost/sample basis. Compared to other methods of uranium analysis, the capital investment required, if the cost of nuclear reactors is included, is higher than for any of the other methods under discussion. If reactor costs are excluded, it then becomes a comparatively inexpensive analytical system for high-precision and high-accuracy uranium measurement with the added bonus that it offers one of the best methods available

for the determination of thorium and can of course be used for measuring most elements with atomic number greater than fluorine.

Fission Track Method

The use of fission tracks in uranium analysis is now well known but not yet widely applied. When an atom such as ^{235}U is induced to fission by bombardment with thermal neutrons in a reactor, the atom splits into two more or less equally massive smaller atoms or "fission fragments." These move apart at high velocities producing "tracks" of radiation damage in surrounding matter. The material of the track differs from that of the unaltered solid around it in various ways being, for example, more soluble. This leads to the phenomenon of track etching: if a surface through which fission tracks pass is exposed to an appropriate solvent, the tracks dissolve out as pits to sizes visible in the optical microscope. In practice a sample containing uranium with a normal abundance of ^{235}U is placed in contact with a plastic sheet — usually Lexan — and irradiated. The sheet is then treated to render the fission tracks visible. The number of fission tracks appearing on the surface of the Lexan depends only on the concentration of uranium in the samples and the number of neutrons, or neutron dose, which passed through the samples. By comparing the number of tracks produced by unknown samples against those produced by standards of known uranium concentration during the same irradiation, the concentration of uranium can be calculated by simple proportionality. To date, by far the greatest utilization of the fission track method is in the measurement of low-level uranium concentration in natural water samples.

The procedure for analyzing waters as employed by Bondar-Clegg & Company Ltd. (unpub. data) is as follows: water samples are filtered to separate any suspended matter or sediment present and then acidified to 0.2 M HNO_3. Using a micropipette, 5 µL of sample are placed on Lexan discs and dried, and stacked in a Plexiglas capsule liner along with standards prepared in the same way. When the liner is full, it is placed in a polyethylene irradiation capsule and irradiated in the Slowpoke reactor of AECL to give a neutron dose of 1.6×10^{16} neutrons cm^{-2}. Up to 2400 samples can be

irradiated in one capsule. After irradiation, the discs are etched in 6 M NaOH and the tracks for both standards and unknowns are visually counted under a microscope. Calibration curves are constructed from the track counts for the standards irradiated along with the unknowns, and from these, the uranium content of the unknowns is determined.

The method gives a detection limit of 0.01 ppb. By increasing the neutron dose to 2×10^{17} neutrons cm^{-2}, the lowest measurable concentration of uranium is 0.003 ppb. At 10 times the detection limit (0.1 ppb) the theoretical precision of the method based on track counting statistics is ±15 per cent. The actual precision of the method under operating conditions has been studied by running many duplicate analyses. Figure 17.4 shows the results from two separate irradiations of duplicate analyses by the fission track method for a typical precision study.

Total and acid-extractable uranium in rocks and soils have been determined by the fission track method by Bondar-Clegg & Company Ltd. laboratories and good agreement with fluorometric data found. However, at this stage, because of its relative slowness compared to other methods, the fission track method does not offer any significant advantages to recommend its use for such analyses.

At its present state of development, the advantages offered by the fission track method can be summarized as follows: for the measurement of uranium in waters it is the most sensitive method available, with a precision comparable to that of the fluorometric method. It is unaffected by interfering elements. Assuming a reactor is available, the only significant cost involved is labour, as the capital equipment required is minimal. Additionally it requires samples of only a few millilitres, a significant advantage in reducing shipping charges when collecting many samples in remote regions. The principal disadvantage of the method is that with visual counting of tracks, the fission track method is slower and therefore more expensive on a cost/sample basis than conventional or laser-induced fluorescence methods. The reasons for this become obvious as indicated by Figure 17.5, which shows typical fission tracks as seen through a microscope from a sample containing 0.2 ppm U.

Various methods of instrumentally counting the etched fission tracks to speed the process have been investigated by a number of workers. One method of instrumentally counting the etched fission tracks is provided by the type of discharge counters utilized by Cross and Tommasino (1970) and is the approach taken by McCorkell and Yuan (1977). A prototype instrument, which is semiautomatic, has been built and operates as follows: the detector material bearing the tracks to be counted is a disc of Lexan whose thickness is less than the length of a fission track. Tracks therefore etch as holes through the detector. Detectors are pressed between two strips of aluminum-coated mylar, and a high voltage applied between these strips. Discharges take place through the etched tracks and these are counted on a scaler like those used for counting discharges in radiation detectors. The aluminum coating is removed from the mylar at the point of a discharge; therefore only one discharge takes place through each track and the number of discharges counted equals the number of tracks on the detector.

Early analyses of waters by the fission track method were checked quite closely and frequently by fluorometry and it was soon discovered that in some cases, puzzling discrepancies were found between uranium concentrations measured by fluorometry and those measured by fission track method. Investigation of these discrepancies has led to procedures for avoiding them but not to a complete explanation of the phenomenon. Two such cases involved analyses of river and lake waters collected from the Rabbit Lake area of northern Saskatchewan and the James Bay area
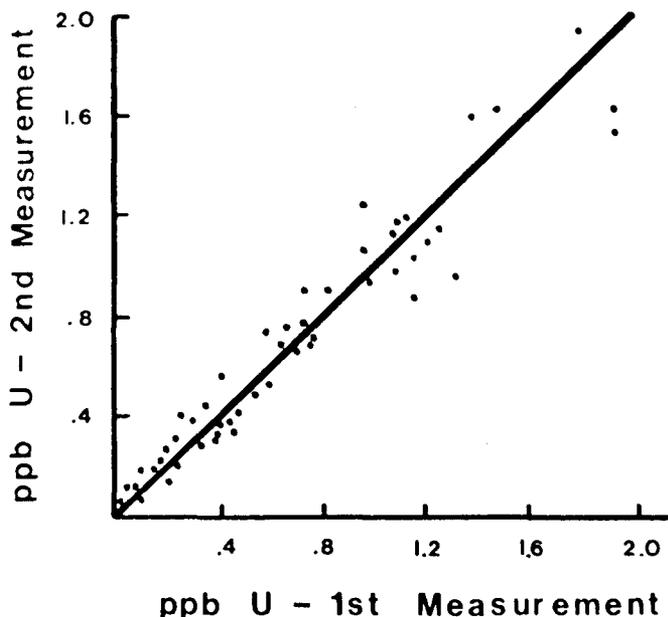

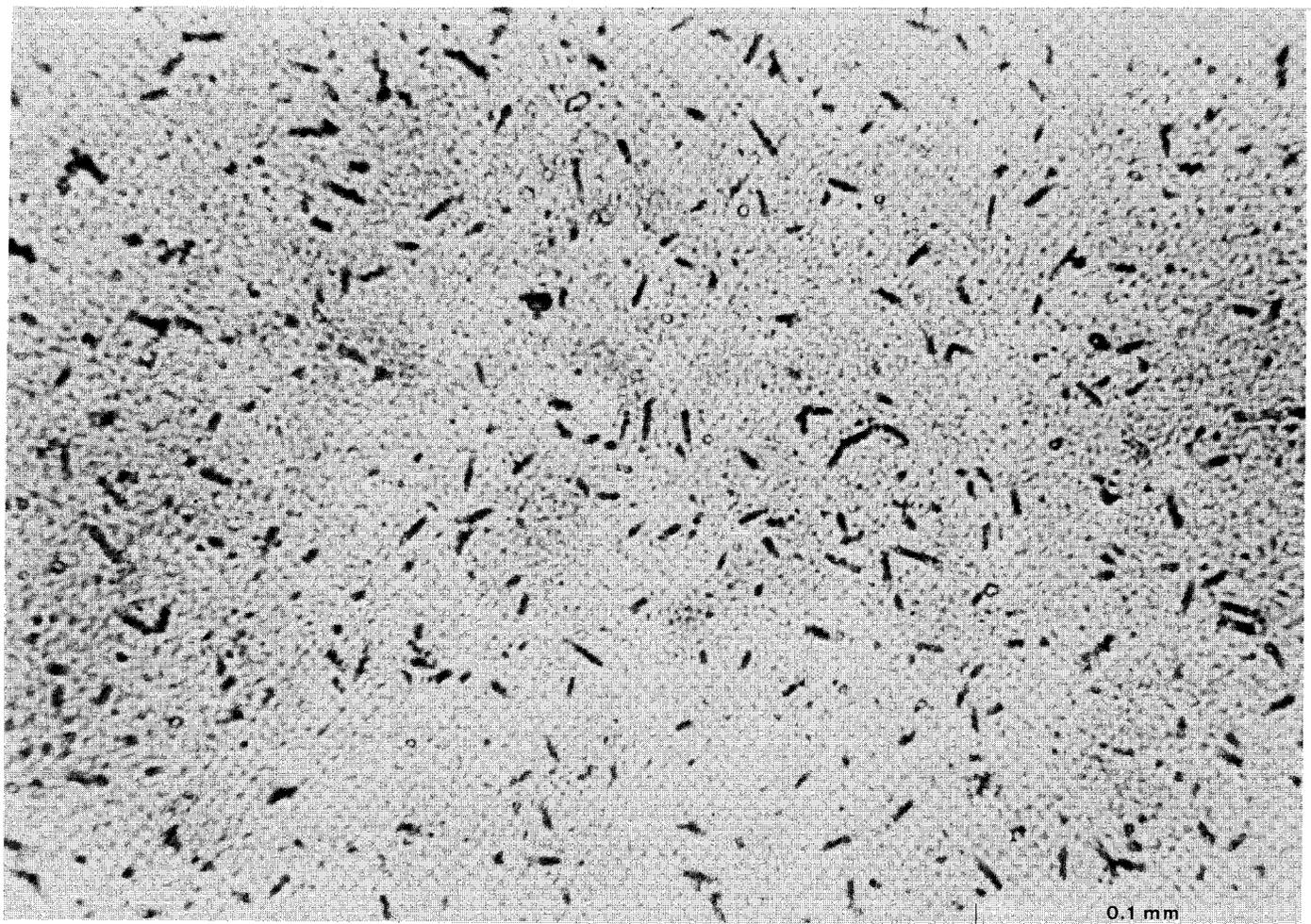**Figure 17.4.** *Precision of duplicate analyses, fission track method.*

Figure 17.5.   *Fission tracks. (GSC 203492-A).*

Table 17.6

Effect of filtration and acidification on some natural waters
fission track versus fluorometric method

Sample Source and Number		U — ppb			
		Before Acid + Filter		After Acid + Filter	
		Fluorometric	Fission Track	Fluorometric	Fission Track
Rabbit Lake Saskatchewan	1	0.08	ND	0.06	0.07
	2	0.14	0.02	0.15	0.11
	3	0.16	0.07	0.80	0.86
	4	0.27	0.07	0.28	0.23
	5	0.44	0.10	0.56	0.52
	6	4.8	6.7	3.5	3.9
James Bay Quebec	1	0.02	0.18	0.19	0.12
	2	0.07	ND	0.21	0.11
	3	0.35	0.09	0.45	0.34
	4	0.58	0.07	0.62	0.41
	5	0.70	0.03	0.19	0.20
	6	1.2	0.10	1.5	0.93

of northern Quebec. In both cases, analyses of the water samples as received in the laboratory by the fission track method gave results significantly lower than did fluorometric results. It was even more puzzling because the factor by which the fission track and fluorometric results differed varied so widely and because replicate fission track analyses agreed very well except, sometimes, when sediment was present in the samples.

As shown in Table 17.6, when these natural samples were filtered and acidified to 0.2 M HNO_3, the fission track method gave results which were in agreement with the fluorometric values. Moreover when known amounts of uranium were added to these samples, this uranium was correctly measured by the fission track method. Many sediment-free and suspended matter-free natural samples have shown good agreement between fission track and fluorometric results when not filtered and acidified, but no way to distinguish such samples before analysis has been found.

Another puzzling phenomenon observed was that some discrepancies were still found between fission track and fluorometric results for analyses of filtered and acidified artificially prepared standard solutions submitted along with the Rabbit Lake waters. The fission track results were low whereas the fluorometric results were in agreement with the intended concentrations. Known amounts of uranium added to the filtered and acidified standard solutions, however, gave the expected increase in uranium concentration by the fission track method when analyzed immediately.

A possible explanation for these phenomena is that in the unfiltered, unacidified samples, the uranium exists partly in the form of a suspended precipitate (probably a hydrated oxide with similar oxides of other elements and gelatinous organic matter). This may aggregate to varying degrees but being about the same density as the solutions and having almost no strength, it settles little and passes through filters. The 5 μL aliquot taken for fission track analysis may include none of these aggregates whereas the larger 25-50 mL samples taken for fluorometry may contain a representative portion of the aggregates. By acidifying after filtration, these aggregates are dissolved, thereby uniformly distributing uranium throughout the sample, making it representatively available in both the smaller 5 μL fission track aliquot and the larger aliquot used for fluorometry. Incomplete redissolving of these precipitates or aggregates may explain those cases where discrepancies still exist even after filtration and acidification as in the case of the artificially prepared standards just noted.

That some uranium in solution takes this postulated form was found by Reimer (1975). Pond water made 1 ppb in uranium and allowed to stand, produced track clusters on Lexan detectors that had been placed in the water and irradiated. These clusters extended over distances of 25-30 μm and did not appear to be radiating from a particle capable of passing through a 0.45 μm filter. However, the particle could not be removed by such a filter. It is probable that the particles are loose aggregates or gelatinous, and pass such filters by breaking up and reforming.

The explanation offered here to explain the discrepancies sometimes found between fission track and fluorometric methods of analysis is exceedingly ad hoc and needs further investigation. In such a comparison, when dealing at such low levels of concentration, one may not be comparing results by two different analytical methods so much as measuring uranium in different forms. The most important conclusion that can be drawn however, is that having now analyzed over 40 000 water samples for uranium by the fission track method, we can say that the fission track

technique is an extremely sensitive method of analysis which gives results in agreement with those determined fluorometrically if the water samples are filtered and acidified.

Laser-induced Fluorescence

One of the most recent developments in geochemical analysis of uranium is the laser-induced fluorescence method of analysis developed by Scintrex Ltd. It is used primarily for the determination of uranium in natural waters. Like the conventional fluorometric method of uranium analysis, it is based on measurement of the green radiation emitted by uranyl salts under ultraviolet excitation by a suitable photodetector. Basically, the laser-induced fluorescence method of uranium analysis differs from the conventional fluorometric method in two ways. First, instead of measuring uranyl fluorescence in a solid fused disc, it is measured directly in an aqueous sample to which a proprietary reagent trade-named "FLURAN" is added. This reagent increases the sensitivity of direct fluorescence measurements in dilute uranyl solutions to the point where direct analysis of <1 ppb uranium in solution is possible. "FLURAN" also serves to mask the effects of fluorescence quenching agents. The second difference is that a pulsed nitrogen laser is used as the ultraviolet light source. Organic matter normally found in natural waters produces a brilliant but short-lived fluorescence. By applying a short, intense pulse of ultraviolet radiation from a laser source, the fluorescence contributed by uranium is isolated from that produced by organic species in the sample by measuring only those photodetector signals produced after fluorescence of the organic species has decayed to zero.

The principal advantages of the laser-induced fluorescence method of uranium analysis are its operational simplicity and small size which permits its use in the field, thereby providing all those benefits resulting from immediate availability of analytical data to field crews while surveys are in progress. Requiring only small samples, it allows direct, in-field analyses of uranium in natural waters with a sensitivity similar to that of conventional fluorometry and
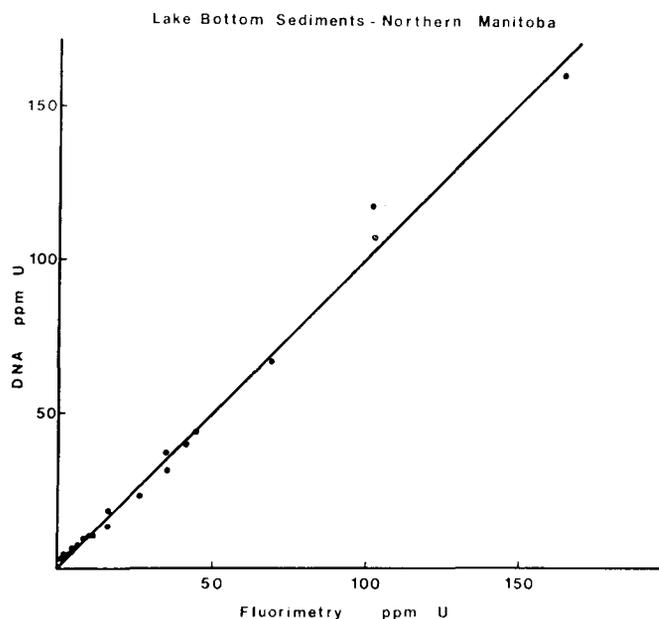

Figure 17.6. Delayed neutron activation versus fluorometry-lake bottom sediments. Fluorometric analyses by Bondar-Clegg; delayed neutron activation analyses by AECL.
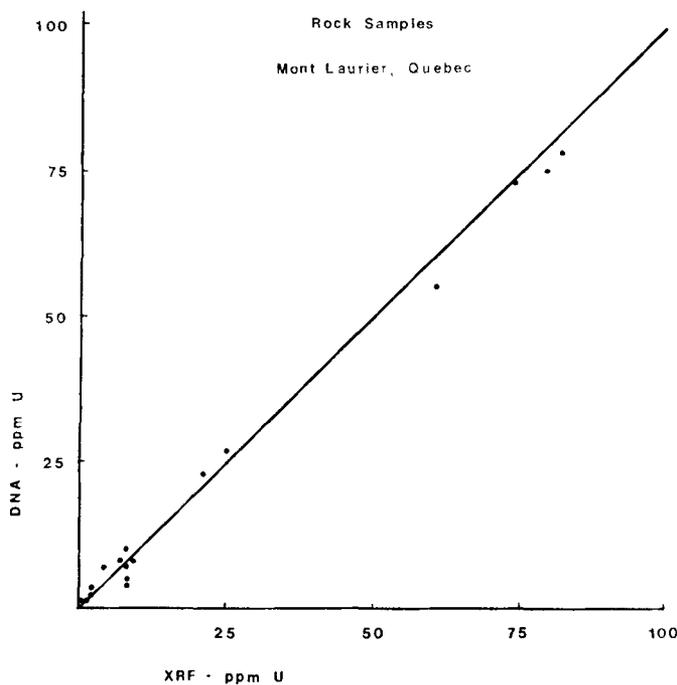
Figure 17.7. X-ray fluorescence versus delayed neutron activation. XRF analyses by Bondar-Clegg; delayed neutron activation analyses by AECL.

approaching that of the fission track method. With a moderate amount of additional laboratory apparatus, it can be used in the field to analyze solid samples for uranium as well. As with any newly introduced analytical method of instrumentation, the problems, limitations, or disadvantages do not become apparent until after the method or instrument has been available and in use for some time. Apart from some operational difficulties encountered in earlier designs of this instrument, now said to be corrected, the laser-induced fluorescence method of uranium analysis is still too new to enable any valid critical review of the method's deficiencies, if any.

Comparison of Various Methods of Uranium Analysis

How do the various methods of uranium analysis compare with one another in real situations? Figures 17.6 to 17.10 are scatter diagrams showing uranium concentrations in various types of samples as determined by different combinations of two analytical methods. The fluorometric, fission track and X-ray fluorescence analyses were performed by Bondar-Clegg and the delayed neutron activation analyses were performed by Atomic Energy Canada Ltd., Commercial Products Division. Laser-induced fluorescence data is from Scintrex Ltd. (Robbins, 1977).

Figure 17.6 shows HNO₃ extractable uranium by fluorometry versus total uranium by delayed neutron activation for a series of lake bottom sediments collected in northern Manitoba. Excellent correlation is shown over a concentration range of 1 to 160 ppm U with no evidence of quenching in the fluorometric method. At the lowest concentrations measured one can see that all data points fall very slightly on the DNA side of the line. This most certainly represents uranium tied up in silicates or some other resistate form that is not extracted by HNO₃. This component appears

to be constant at about 0.5 ppm over that which is measured by fluorometry and as such, is not distinguishable at higher concentrations.

Figure 17.7 shows randomly selected delayed neutron activation check analyses of earlier X-ray fluorescence data for rock samples from the Mont Laurier area of northwestern Quebec. Total uranium is measured by both methods and good correlation is shown over a concentration range of 1 to 111 ppm U.

In Figure 17.8, from Robbins (1977), laser-induced fluorescence versus fluorometric results for measurements of HNO₃ extractable uranium in rocks are shown. Good correlation over a concentration range of 1 to 3000 ppm is shown.

Figure 17.9 shows fission track results versus fluorometric results for water samples over a concentration range of 0.01 to 1.3 ppb U. The correlation shown is relatively good for this low concentration range.

Results for fluorometric versus laser-induced fluorescence measurements of uranium in waters over a concentration range of approximately 0.2 ppb to about 80 ppb are shown in Figure 17.10. Except for three samples below 1 ppb good agreement between the two methods is shown over a concentration range of 1-100 ppb.

Having made these comparisons, can we draw any conclusions? Except where the uranium concentration is less than 1 ppb, results of these comparison studies appear to suggest that any one of the analytical methods described here could be selected and would provide the exploration geochemist with suitable analytical data of adequate accuracy and precision. This is not always the case! Consider the following true case: one is looking for uranium deposits formed by secondary concentration of uranium minerals precipitated in a reducing environment from groundwater which has accumulated uranium from a basement source.
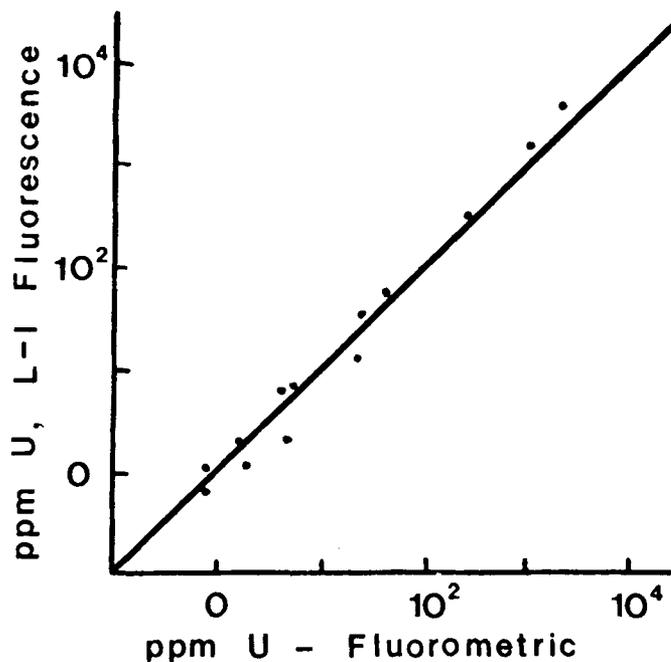

Figure 17.8. Laser-induced fluorescence versus fluorometric rock and ore samples.

Bedrock geochemistry and ground radiometric surveys are being used to test favourable sedimentary environments. Two anomalous areas are found. Both show anomalous radiometric eU values and both are geochemically anomalous in total uranium, as determined by X-ray fluorescence analysis of composited bedrock chip samples. If one anomaly conforms to the model and the other does not, how are they distinguished? In this case it was done by analytical differentiation.

Table 17.7 shows typical results of partial extractions carried out on bedrock samples previously analyzed for total U by X-ray fluorescence, in an attempt to determine those anomalies which did not conform. Comparative results from over a known occurrence, which is ore grade in outcrop and which corresponds to the model used, are shown for comparative purposes. Obviously Anomaly I supports the concept while Anomaly II does not. In this case the fluorometric method using a 2 per cent Na_2CO_3/5% H_2O_2 extraction, which can be considered almost selective in extracting uraninite/pitchblende from bedrock samples, was

most effective in detecting those anomalies of interest. Used in conjunction with a total U measurement the method was also effective distinguishing anomalies of interest from those that are not of interest. In this example, had only HNO_3 extractable uranium or Na_2CO_3/H_2O_2 extractable uranium been measured by fluorometry, the important anomaly would still have been detected. With only a total U measurement, the important anomaly would have been detected, but so were a number of others which subsequently proved of no interest. Proving that an anomaly is of no interest is often more costly than finding one that is. Considering the original concept, selection of an analytical method readily adaptable to measuring HNO_3 extractable, or in this case preferably Na_2CO_3/H_2O_2 extractable uranium in the first place, would have better achieved the objectives of the geochemical survey at lower cost. Note use of the word "readily" because all of the methods described here can be used to measure total uranium and all can be used to measure partially extractable uranium. Some methods just happen to do one or the other a lot easier than some other methods and at lower cost.

Table 17.7

Evaluation of anomalies using total uranium versus extractable uranium

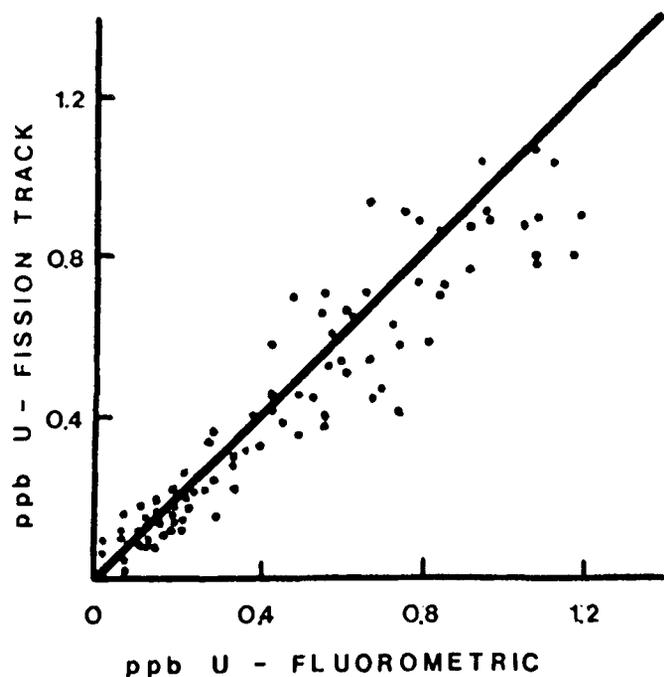|	Radiometric Results	Geochemical Results — ppm U		
		Total U — XRF	Fluorometric HNO_3 — Extractable	Fluorometric Na_2CO_3/H_2O_2 Extractable
Anomaly I	High eU	32	26	16
Anomaly II	High eU	32	4	0.2
Known Occurrence	Very High eU	144	94	45

Figure 17.9. Fluorometric versus fission track; water samples from Gatineau Park and James Bay areas, Quebec (McCorkell and Yuan, 1977).
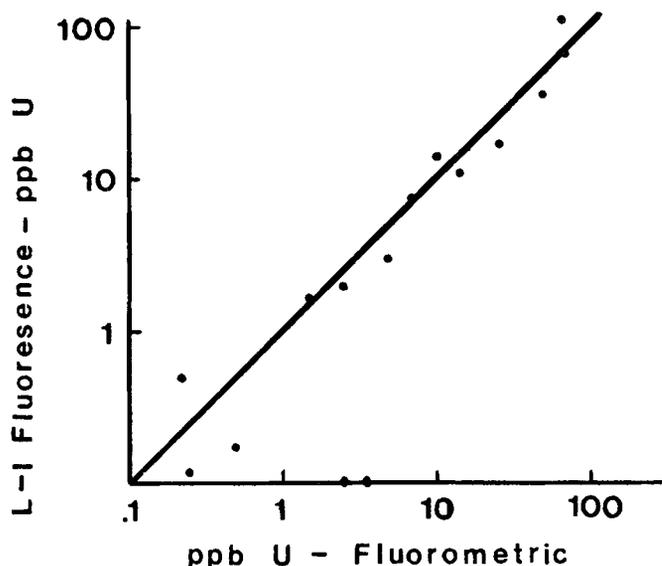

Figure 17.10. Laser-induced fluorescence versus fluorometric method; natural waters from eastern Canada (from Robbins, 1976).

How does one choose the method of geochemical analysis for uranium that best satisfies his needs? Any method selected must satisfy the following four requirements:

1. Must be capable of measuring the desired uranium fraction in a sample at the background concentrations encountered in samples collected.

2. Precision and accuracy must be adequate to recognize significant uranium concentration patterns and changes in these patterns.

3. Turnaround time for reporting results must be reasonable.

4. Cost must be acceptable.

All five methods described in this report can be summarized on the basis of criteria which should influence any such choice intended to satisfy the preceding four requirements. This summary, shown in Table 17.8, provides comparisons for nine criteria upon which a decision might be made to select or to establish an analytical method for geochemical uranium analysis.

Excluded from Table 17.8 are those methods described in the literature (low ppb measurement of U in waters by DNA or XRF for example) which depend on preconcentration of uranium by chelation/solvent extraction, ion-exchange, coprecipitation, or evaporation of large volumes of water, and so forth, to achieve useful detection limits. Such procedures of variable complexity are slow, and with each

extra step, additional chances of error are introduced, as are unavoidable losses. Given a choice, direct methods are almost always to be preferred if appropriate sensitivity can be achieved. All detection limits given in Table 17.8 are, with one exception, detection limits for direct measurement of uranium by the methods shown. The one exception is for uranium measurements in water by fluorometry. Since the specified detection limit of 0.05 ppb is readily attained by evaporative concentration of only 20 mL of water and because this can be done simply and rapidly with hundreds of samples at the same time, this one exception was made.

Table 17.8 is self-explanatory and the significant points can be summarized as follows:

(i)   Delayed neutron activation provides the best combination of precision and sensitivity for low levels of total uranium measurement, followed by X-ray fluorescence. The conventional fluorometric method is the method best suited for low-level U analyses requiring partial and/or selective uranium extraction procedures for solid samples.

(ii) There is little to choose between fluorometry, fission track and laser-induced fluorescence methods for uranium in natural waters unless extremely low detection limits are required, in which case the fission track method is preferred. The fluorometric method is generally faster than either fission track or laser-induced fluorescence analyses in waters.

Table 17.8

Comparison of five methods of uranium analysis

	Fluorometric	DNA	XRF	Fission Track	Laser-Induced Fluorescence

Detection Limit
   Solids (ppm)
   Waters (ppb)
	0.1
	0.05
		0.1
		—
			1.0
			--
				--
				0.01
					--
					0.05

Precision (@ 10 x det. limit)	±25%	±10-15%	±15%	±20-25%	±15%*
Productivity analyses/man/hour	20	27	27	13	13-25

Sample size req'd.
   Solids (gm)
   Waters (mls)
	0.25
	20
		1
		—
			5
			--
				—
				0.005
					0.05
					7

Dependence on analyst's care and skill	High	Low	Low	Moderate	Low
Simple differentiation of total/partial uranium	Yes	No	No	Yes	Yes
Adaptable for field use	Possible	No	No	No	Yes
Approx. capital cost of complete system	$5000	$40 000 + reactor	$140 000.	$1500 + reactor	$15 000

Analytical cost/sample**
   Solids
 	
   Waters
	$2.50-$3.50
	
	$2.00-$4.00
		$3.00-
		$15.00***
		—
			$2.25-
			$3.00
			--
				--
				
				$3.75
					Depends on users operating cost

*Detection limit for laser-induced fluorescence stated @ twenty x detection limit
**Approximate range of charges by North American commercial laboratories
***DNA cost/sample highly variable because of great variation in charges by various reactor facilities.

(iii) The conventional fluorometric technique is the most flexible analytical method for uranium in solid samples in that it can be easily used to analyze solid samples for total as well as partially extractable uranium unlike DNA or XRF. This capability has not yet been as well established for either the fission track method or the laser-induced fluorescence methods which are comparatively recent developments and whose limitations are therefore not yet fully understood.

(iv) For in-the-field measurements of uranium in natural waters, the laser-induced fluorescence method should be preferred because it has been designed as a truly portable analytical system for field use. Also, it is not as dependent on the operator's skill as is the fluorometric method which is highly dependent upon the care and skill of the analyst, a factor which may partially offset the laser-induced fluorescence system's capital cost. If the primary function of the field laboratory is to analyze soils, rocks or sediments, the fluorometric method is preferred.

(v) Capital cost required to establish an analytical system is usually, but not always, a direct function of the accuracy and precision of that analytical system. As seen in this report the most precise method is the neutron activation delayed counting method but this also requires the greatest capital expenditure to establish.

(vi) Cost of analyses per sample for any given method can be quite variable as shown in this comparison. To paraphrase G.E.F. Lundell, who originally made the following still valid points in 1933, at the 85th Meeting of the American Chemical Society, "Purchasers of analytical services usually get what they pay for and as a rule, are unwilling to pay very much. Since the buyer of analytical services is buying an intangible commodity, in fact an opinion, why pay five dollars when someone else is quoting fifty cents? A very good reason is that the correctness of the opinion cannot be checked except by buying other opinions, which is an expensive as well as a poor way to settle an argument."

This comparison is a summary of the general character-istics and capabilities of the five methods of uranium analyses described. One should not expect that all laboratories employing any of the methods described will, for example, attain the detection limits, precision or productivity figures shown here. Conversely, some laboratories may exceed these figures. This comparison does however, show what is attainable using any of the methods described and what an exploration geochemist should generally expect, as state-of-the-art for routine uranium analysis of geochemical samples.

Often, as we have shown by comparing one analytical method against another in a number of real situations, no obvious clear-cut preference emerges for one analytical method over another. Usually the quality or usefulness of analytical data will depend more on the analyst who performs the analysis than on the analytical method used, or as Carpenter (1972) so succinctly stated in describing the results of a trace element intercalibration study involving several different laboratories and several different analytical methods, "Equally disastrous results were achieved with a few thousand dollars worth of equipment as with devices costing millions of dollars."

SELECTED REFERENCES

Ahrens, L.H.
1950: Spectrochemical Analysis; Addison-Wesley Press Inc., Cambridge, 267 p.

Amos, M.D., Bennett, P.A., Brodie, K.G., Lung, P.W.K., and Matousek, J.P.
1971: Carbon rod atomizer in atomic absorption and fluorescence spectrometry and its clinical application; Anal. Chem., v. 43, p. 211-215.

Aslin, G.E.M.
1976: The determination of arsenic and antimony in Geological Materials by flameless atomic absorption spectrometry; J. Geochem. Explor., v. 6, p. 321-330.

Bond, A.M.
1970: Direct current, alternating current, rapid and inverse polarographic methods for determination of tin (IV); Anal. Chem., v. 42, p. 1165-1168.

Boulanger, A., Evans, D.J.R., and Raby, B.F.
1976: Uranium analysis by neutron activation delayed neutron counting; a paper presented at Canadian Mineral Analysts Conference, Thunder Bay, 1975.

Canney, F.C. and Hawkins, D.B.
1958: Cold acid extraction of copper from soils and sediments — a proposed field method; Econ. Geol., v. 53, p. 877-886.

Canney, F.C., Myers, A.T., and Ward, F.N.
1957: A truck-mounted spectrographic laboratory for use in geochemical exploration; Econ. Geol., v. 52, p. 289-306.

Carpenter, J.H.
1972: Problems in applications of analytical chemistry to oceanography; in Analytical Chemistry: Key to Progress on National Problems, National Bureau of Standards, Spec. Pub. 351, p. 393-419.

Chu, R.C., Barron, G.P., and Baumgarner, P.A.W.
1972: Arsenic determination at sub-microgram levels by arsine evolution and flameless atomic absorption spectrophotometric technique; Anal. Chem., v. 44, p. 1476-1479.

Copeland, T.R. and Skogerboe, R.K.
1974: Anodic stripping voltammetry; Anal. Chem., v. 46, p. 1257A-1268A.

Cross, W.G. and Tommasino, L.
1970: A rapid reading technique for nuclear particle damage tracks in thin foils; Rad. Eff., v. 5, p. 85-89.

Curtin, G.C., Lakin, H.W., Neuerburg, G.J., and Hubert, A.E.
1968: Utilization of humus-rich forest soil (mull) in geochemical exploration for gold; U.S. Geol. Surv., Circ. 562, 11 p.

Danielsson, A. and Lindblom, P.
1972: An echelle spectrograph for image tubes; Physica Scripta, v. 5, p. 227-231.

Danielsson, A., Lindblom, P., and Södermann, E.
1974: Image dissector echelle spectrometer system for spectrochemical analysis; Chemica Scripta, v. 6, p. 5-9.

Dickinson, G.W. and Fassel, V.A.
   1969:   Emission spectrometric detection of the elements
           at the nanogram per milliliter level using
           induction-coupled plasma excitation; Anal. Chem.,
           v. 41, p. 1021-1024.

Donega, H.M. and Burgess, T.E.
   1970:   Atomic absorption analysis by flameless atomiza-
           tion in a controlled atmosphere; Anal. Chem.,
           v. 42, p. 1521-1524.

Dulka, J.J. and Risby, T.H.
   1976:   Ultratrace metals in some environmental and
           biological systems; Anal. Chem., v. 48,
           p. 640A-653A.

Durst, R.A.
   1969:   Analytical technique and applications of ion-
           selective electrodes in Ion-Selective Electrodes;
           Durst, R.A., ed.: National Bureau of Standard's,
           Spec. Publ. 314, 452 p.

Eisenman, G.
   1969:   Theory of membrane electrode potentials: An
           examination of the parameters determining the
           selectivity of solid and liquid ion exchangers and
           of neutral ion-sequestering molecules; in Ion-
           Selective Electrodes, National Bureau of
           Standards, Spec. Publ. 314, p. 1-56.

Farrell, B.L.
   1974:   Fluorine, a direct indicator of fluorite mineraliza-
           tion in local and regional soil geochemical
           surveys; J. Geochem. Explor., v. 3, p. 227-244.

Fassel, V.A. and Kniseley, R.N.
   1974a: Inductively-coupled plasma-optical emission
           spectroscopy; Anal. Chem., v. 46, p. 1110A-1120A.

   1974b: Inductively-coupled plasmas; Anal. Chem., v. 46,
           p. 1155A-1164A.

Fersman, A.E.
   1952:   Geochemical and mineralogical methods of
           prospecting for mineral deposits; Chap. IV, Special
           Methods of Prospecting: U.S. Geol. Surv.
           Circ. 127, 37 p. (Transl. from Russian.)
           Originally published in 1939 as Geokhimicheskie i
           mineralogicheskie metody poiskov poleznykh
           isokopaemykh: I/d. Akad. Nauk, SSSR.

Ficklin, W.H.
   1970:   A rapid method for the determination of fluoride
           in rocks and soils, using an ion-selective
           electrode; U.S. Geol. Surv. Prof. Paper 700-C,
           p. C186-C188.

Garrett, R.G. and Lynch, J.J.
   1976:   A comparison of neutron activation delayed
           neutron counting versus fluorometric analysis in
           large-scale geochemical exploration for uranium;
           in Exploration for Uranium Deposits, IAEA,
           Vienna, p. 321-334.

Goulden, P.D. and Brooksbank, P.
   1974:   Automated atomic absorption determination of
           arsenic, antimony, and selenium in natural waters;
           Anal. Chem., v. 46, p. 1431-1436.

Greenfield, S., Jones, I.L., and Berry, C.T.
   1964:   High-pressure plasmas as spectroscopic emission
           sources; Analyst, v. 89, p. 713-720.

Griffitts, W.R., Ward, F.N., and Alminas, H.V.
   1976:   A simple spot test for molybdenum minerals;
           Econ. Geol., v. 71, p. 1595.

Hadeishi, T. and McLaughlin, R.D.
   1975:   Isotope Zeeman atomic absorption — a new
           approach to chemical analysis; Am. Lab., v. 7,
           p. 57-61.

Harrison, G.R.
   1949:   The production of diffraction gratings, II, The
           design of echelle gratings and spectrographs; J.
           Opt. Soc. America, v. 39, July 1949.

Hawkes, H.E.
   1972:   Exploration geochemistry bibliography, Jan. 1965-
           Dec. 1971; Assoc. Explor. Geochem., Spec. Vol.
           No. 1, 118 p.

   1976:   Exploration geochemistry bibliography, Jan. 1972-
           Dec. 1975; Assoc. Explor. Geochem., Spec. Vol.
           No. 5, 195 p.

Hillebrand, W.F.
   1919:   The analysis of silicate and carbonate rocks; U.S.
           Geol. Surv., Bull. 700, 285 p.

Holak, W.
   1969:   Gas-sampling technique for arsenic determination
           by atomic absorption spectrophotometry; Anal.
           Chem., v. 41, p. 1712-1713.

Holman, R.H.C.
   1956:   A method for determining readily-soluble copper
           in soil and alluvium — introducing white spirit as a
           solvent for dithizone; Inst. Min. Metall. Trans.,
           v. 66, p. 7-16.

Hwang, J.Y., Ullucci, P.A., and Smith, S.B., Jr.
   1971:   A simple flameless atomizer; Am. Lab., August,
           p. 41-43.

Ingles, J.C.
   1958:   A manual of analytical methods for the uranium
           laboratory, method U.1; in Mines Br., Mono.
           Ser. 866, Ottawa.

Ingram, B.L.
   1970:   Determination of fluoride in silicate rocks without
           separation of aluminum using a specific ion
           electrode; Anal. Chem., v. 42, p. 1825-1827.

Johnson, D.J., Plankey, F.W., and Winefordner, J.D.
   1975:   Multielement analysis via computer-controlled
           rapid-scan atomic fluorescence spectrometer with
           a continuum source; Anal. Chem., v. 47,
           p. 1739-1743.

Karasek, F.W.
   1975:   Detection limits in instrument analysis; Research
           and Development, July, p. 20-24.

Keliher, P.N. and Wohlers, C.C.
   1974:   High resolution atomic absorption spectrometry
           using an echelle grating monochromator; Anal.
           Chem., v. 46, p. 682-687.

Kesler, S.E., Van Loon, J.C., and Bateson, J.H.
   1973:   Analysis of fluoride in rocks and an application to
           exploration; J. Geochem. Explor., v. 2, p. 11-17.

King, A.S.
   1908:   The production of spectra by an electrical
           resistance furnace in hydrogen atmosphere;
           Astrophysical J., v. 27, p. 353-362.

   1932:   Lines of tungsten and rhenium appearing in the
           spectrum of the electric furnace; Astrophysical
           J., v. 75, p. 379-385.

Koizumi, H. and Yasuda, K.
   1975:   New Zeeman method for atomic absorption
           spectrophotometry; Anal. Chem., v. 47,
           p. 1679-1682.

Koizumi, H. and Yasuda, K. (cont'd.)
  1976: Determination of lead, cadmium and zinc using the Zeeman effect in atomic absorption spectrometry; Anal. Chem., v. 48, p. 1178-1182.

Koizumi, H., Yasuda, K., and Katagama, M.
  1977: Atomic absorption spectrophotometry based on the polarization characteristics of the Zeeman effect; Anal. Chem., v. 49, p. 1106-1112.

Lengyel, B.A. and Blum, E.
  1934: The behavior of the glass electrode in connection with its chemical composition; Trans. Faraday Soc., v. 30, p. 461-471.

L'vov, B.V.
  1961: The analytical use of atomic absorption spectra; Spectrochim. Acta, v. 17, p. 761-770.

Massman, H.
  1968: Comparison of atomic absorption and atomic fluorescence in graphite cuvettes; Spectrochim. Acta, v. 23B, p. 215-226.

McCorkell, R.H. and Yuan, D.Y.H.
  1977: Discharge counter for the determination of uranium in water by the fission track method; Rev. Sci. Instrum., v. 48, no. 8, p. 1005-1009.

Orion Research Inc.
  1973: Analytical methods guide; 5th Ed., 32 p.

Osteryoung, R.A. and Christie, J.H.
  1974: Theoretical treatment of pulsed voltammetric stripping at the thin film mercury electrode; Anal. Chem., v. 46, p. 351-355.

Palmqvist, S. and Brundin, N.H.
  1939: Svenska prospekterings aktiebologet, P.M., angaenda var. geokemiska prospecterings method, Lund. See Brundin, Nils, 1939, Method of locating metals and minerals in the ground, U.S. Pat. 2158980.

Perone, S.P. and Kretlow, W.J.
  1965: Anodic stripping voltammetry of mercury (II) at the graphite electrode; Anal. Chem., v. 37, p. 968-970.

Pierce, F.D., Lamoreaux, T.C., Brown, H.R., and Fraser, R.S.
  1976: An automated technique for the sub-microgram determination of selenium and arsenic in surface waters by atomic absorption spectroscopy; Appl. Spectroscopy, v. 30, p. 38-42.

Pollock, E.N. and West, S.J.
  1973: The generation and determination of covalent hydrides by atomic absorption; Atomic Absorption Newsletter, v. 12, p. 6-8.

Pungor, E. and Troth, K.
  1970: Ion-selective membrane electrodes; Analyst, v. 95, p. 625-648.

Ratsbaum, E.A.
  1939: Field spectroanalytical laboratory for supporting prospecting parties; Razvedka Nedr., No. 1, p. 38-41.

Rechnitz, G.A.
  1967: Ion-selective electrodes; Chem. Eng. News, p. 146-158.

Reimer, G.M.
  1975: Uranium determination in natural water by the fission-track technique; J. Geochem. Explor., v. 4, p. 425-431.

Richardson, D.
  1953: The use of echelles in spectroscopy; Spectrochim. Acta, v. 6, p. 61-65.

Robbins, J.
  1977: Direct analysis of uranium in natural waters; Scintrex Ltd., Toronto, Application Brief, 26 p.

Rosencwaig, A.
  1975: Photoacoustic spectroscopy, A new tool for investigations of solids; Anal. Chem., v. 47, p. 592A-604A.

Sandell, E.B.
  1959: Colorimetric determination of traces of metals; 3rd ed., Interscience Publ., New York, 1054 p.

Schwabe, K. and Dahms, H.
  1960: Investigation of the ion-exchange between a glass electrode and an alkaline solution through the use of radioisotopes; Naturwissenschaften, v. 47, p. 351-352.

Scott, R.H., Fassel, V.A., Kniseley, R.N., and Nixon, D.E.
  1974: Inductively-coupled plasma-optical emission analytical spectrometry; Anal. Chem., v. 46, p. 75-80.

Slavin, S., Barnett, W.B., and Kahn, H.L.
  1972: The determination of atomic absorption detection limits by direct measurements; Atomic Absorption Newsletter, v. 11, p. 37-41.

Thompson, K.C. and Thomerson, D.R.
  1974: Atomic-absorption studies on the determination of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium, and tin by utilizing the generation of covalent hydrides; Analyst, v. 99, p. 595-601.

Timperley, M.H.
  1974: Direct-reading d.c. arc spectrometry for rapid geochemical surveys; Spectrochim. Acta, v. 29B, p. 95-110.

Veillon, C. and Merchant, P., Jr.
  1973: High resolution atomic absorption spectrometry with a scanning Fabry-Perot interferometer; Appl. Spectroscopy, v. 27, p. 361-365.

Wendt, R.H. and Fassel, V.A.
  1965: Induction-coupled plasma excitation source; Anal. Chem., v. 37, p. 920-922.

West, T.S. and Williams, X.K.
  1969: Atomic absorption and fluorescence spectroscopy with a carbon filament atom reservoir, I, construction and operation of reservoir; Anal. Chem. Acta, v. 45, p. 27-41.

Willard, H.H., Merritt, L.L., Jr., and Dean, J.A.
  1974: Instrumental methods of analysis; 5th ed., D. Van Nostrand Co., New York, 860 p.

Winefordner, J.D. and Staab, R.A.
  1964: Determination of zinc, cadmium, and mercury by atomic fluorescence flame spectrometry; Anal. Chem., v. 36, p. 165-168.

Winefordner, J.D. and Vickers, T.J.
  1964: Atomic fluorescence spectrometry as a means of chemical analysis; Anal. Chem., v. 36, p. 161-165.

Woodriff, R. and Ramelow, G.
  1968: Atomic absorption spectroscopy with a high-temperature furnace; Spectrochim. Acta, v. 23B, p. 665-671.