

Instrumental neutron activation in geoanalysis

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ABSTRACT

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Theoretical aspects of instrumental neutron activation analysis (INAA) are discussed. Various applications of INAA to exploration geochemistry are described demonstrating its capabilities and its limitations.

Cost, turnaround time, high sensitivity for certain elements, the non-destructive nature of analysis and its precision and accuracy have combined to make INAA an indispensable method for multielement determination on virtually all geological matrices. Humus, vegetation, heavy minerals, lake bottom sediments as well as rocks and soils comprise the major sample types analyzed by INAA. As many as 50 elements can be determined routinely and easily by INAA.

INTRODUCTION

Instrumental neutron activation analysis (INAA) is an analytical technique which is dependent on measuring primarily gamma radiation induced in the sample by irradiation with neutrons. The primary source of neutrons for irradiation is usually a nuclear reactor. Each element which is activated emits a "fingerprint" of gamma radiation which can be measured and quantified. Multielement analysis of practically any material from the smallest sample which can be weighed accurately to very large samples of up to 1 kg have been analyzed routinely by INAA. The method is highly selective and extremely sensitive for a wide range of elements.

INSTRUMENTATION

The process of activating samples is inherently simple. The samples are encapsulated and placed into or near the core of a neutron source. The pri-

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mary neutron source is usually a nuclear reactor and we will limit further discussion to reactor-induced NAA. The neutrons interact with the target nucleus, thereby converting the latter into a radioactive nucleus. Figure 1 illustrates a typical neutron capture reaction and the subsequent radiation which is emitted. The capture gamma-rays emitted (Fig. 1) usually have extremely short half lives on the order of ms and can be measured during irradiation utilizing a technique called prompt gamma activation analysis (PGAA). PGAA is described in detail by Chrien (1984) and by Lindstrom and Anderson (1985). For geological samples the main application of PGAA is in the determination of B and Gd. As the radioactive nucleus decays back to a stable state, decay gamma-rays are emitted. It is these decay gamma-rays which are measured and quantified by INAA. Each radioactive nuclide which is formed during irradiation decays with a specific half-life emitting gamma rays of characteristic energy. Measurements of the gamma radiation can be used to both identify and accurately quantify the nuclides present in the sample.

Subsequent to irradiation, the samples can be measured instrumentally simply by placing the sample on a high resolution germanium detector, or for better sensitivities, chemical separations, can be performed for reducing interferences, with subsequent measurement. The latter type of analysis termed radiochemical neutron activation analysis (RNAA) is discussed elsewhere in this volume (Parry, 1992).

Prior to the 1960's, sodium iodide (NaI) detectors were commonly used for measurement of gamma-rays; however the resolution of these detectors was and still is at least an order of magnitude poorer than the Ge(Li) detectors which followed in the 1960's. As a result, radiochemical separations were

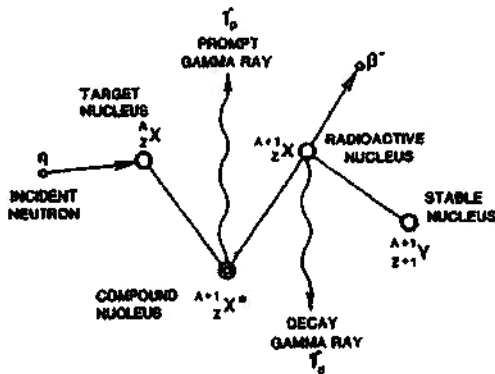


Fig. 1. Neutron interaction with target nucleus and subsequent radiation emitted (from Bode et al., 1990).

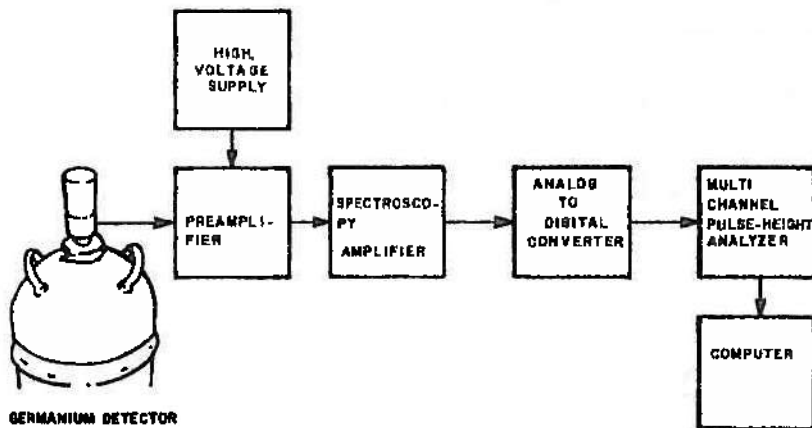


Fig. 2. Diagrammatic scheme for a germanium detector counting system (Bode et al., 1990).

quite popular and necessary in the 1950's and 1960's. The advent of high resolution solid state Ge(Li) detectors allowed INAA to develop and flourish. Over the last decade significant advances in the manufacture of high purity Ge detectors with very good resolution and also able to process high incident count rates have provided the necessary detection equipment for high quality, high volume INAA. Micro and minicomputers developed during the same period allowed for rapid on-line analysis of gamma spectra from the activated samples. A diagrammatic scheme of a typical Ge detector and associated electronics is shown in Fig. 2. Further details on the technical operation of activation equipment is available in Bode et al. (1990).

PRINCIPLES

The relatively high neutron flux, derived from the fissioning process of the U-235 contained in the reactor core, has associated neutron energies ranging up to 15 MeV with an average energy of 2MeV. As the neutrons move out from the core, elastic collisions with the reactor moderator (water or heavy water) thermalize the neutrons creating a broad energy distribution with three principal components: thermal, epithermal and fast neutrons.

For INAA, the thermal neutrons are the most important, and are defined as those neutrons having energies below 0.5 keV. This is the upper energy limit established by which neutrons will pass through a cadmium foil 1 mm thick ("cadmium threshold"). A typical 2 MW research reactor will have a thermal neutron flux of $2 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$. Epithermal neutrons are those which have been only partially moderated and their energies range from the

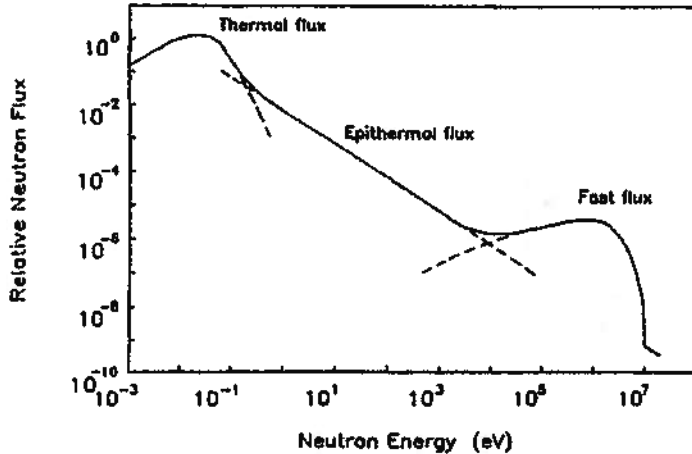


Fig. 3. Thermal neutrons make up the major proportion of flux from a nuclear reactor. Epithermal (epicadmium) neutrons are also used for activation of geological samples (Bode et al., 1990).

“cadmium threshold” to 1 MeV. The epithermal flux of a research reactor is about 2% of the thermal flux. Fast neutrons are rarely employed in INAA. The distribution of neutrons from a reactor described above is shown in Fig. 3.

The total reaction rate (R) for a target atom for the common (n,γ) reaction (neutron captured by nucleus, gamma-ray emitted on decay) for a neutron flux which consists of both thermal and epithermal neutrons is:

$$R = \text{thermal neutron flux} \times \text{average thermal cross section of nuclei} \\ + \text{epithermal neutron flux} \times \text{epithermal cross section of nuclei}$$

Cross section is defined as a measure of the ability of a nucleus to absorb neutrons and is measured in barns (10^{-24} cm^2). The thermal and epithermal cross sections are different for each target isotope. The higher the cross section generally the more sensitive the reaction. Some of the elements which have higher epithermal cross sections than thermal cross sections include Br, Rb, Sr, Mo, Ba, Ta, U and Au. If samples are irradiated behind a screen (e.g., cadmium) it is possible to screen out the thermal neutrons with energies below the “Cd-threshold” and irradiate primarily with epithermal neutrons. This type of analysis is known as epithermal neutron activations analysis (ENAA). Thermal activation analysis is the predominant procedure used by most INAA laboratories.

The activation analysis equation for a radioisotope with a half life of $t_{1/2}$ is:

$$A = (kNWF\phi/M) (\text{irradiation term}) (\text{decay term})$$

- A = measured activity of a radionuclide
 k = proportionality constant (includes detection efficiency)
 N = Avogadro's number (6.023×10^{23} atoms/mole)
 W = weight of an element (g)
 F = natural fractional isotopic abundance of target isotope
 M = atomic weight of the element
 σ = nuclear reaction cross section cm^2
 ϕ = reactor neutron flux ($\text{n cm}^{-2} \text{s}^{-1}$)
 irradiation term = $[1 - \exp(-\lambda T_i)]$
 decay term = $\exp(-\lambda T_D)$
 λ = decay constant ($\ln 2 / t_{1/2}$) of the radioisotope
 T_i = length of irradiation
 T_d = length of decay after irradiation

When the time of irradiation is much greater than the half life of a particular isotope saturation occurs causing the irradiation term above to approximate 1. When the irradiation time is much shorter than the half life the irradiation term can be reduced to T_i .

From the above equation it is obvious that improved sensitivity can be achieved by increasing sample weight, detection efficiency, irradiation time and neutron flux. There are some problems to be concerned with, however, such as overirradiation which may activate isotopes which are unwanted and can lead to higher overall backgrounds. The relative sensitivity of one element to another is a function of atomic weight, fractional isotopic abundance, neutron reaction cross section, the half-life and decay scheme for the radioisotope being measured. Multielement INAA is a compromise aimed at obtaining maximum information for a given set of conditions. Optimization of irradiation, decay and counting parameters can be easily done for any particular element.

Samples are usually irradiated with standards and/or neutron flux monitors. After irradiation the samples and standards are measured under identical geometrical conditions with the same detector. This allows the activation equation to be simplified as follows:

$$W_{\text{sample}} = (A_{\text{sample}} / A_{\text{standard}}) (W_{\text{standard}})$$

where W is the weight of the element sought and A is the decay corrected activity measured.

In some procedures flux monitors and standards are irradiated with samples. A stored calibration, based on multiple synthetic and international reference materials, for each element is referenced when the flux monitor is measured. Values can be computed based on the stored calibration. The standard co-irradiated is used solely as a check on accuracy. This procedure does not rely on a direct comparison of all elements in one or two co-irradiated refer-

ence materials. For long lived isotopes INAA is a multielement technique where as many as 36 elements are determined simultaneously. It is usually not possible to find one or two standards which will give adequate precision for all the elements determined. Further details on the theory of INAA are available in Amiel (1981), De Soete et al. (1972) and Kruger (1971).

ADVANTAGES OF INAA

The INAA technique benefits from having substantial freedom from systematic errors. The physical process of radioactive growth and decay are well understood and are rigorously exponential. The number of energetically possible nuclear reactions from a target nuclide is small and all possible reactions can be seen and easily evaluated on a table of nuclides (Erdtmann, 1976; Lederer and Shirley, 1978). The gamma-ray lines in energy space associated with a particular nuclide are easily resolved from one another with the high resolution of modern detectors. This facilitates simple peak integration with very few multiplet peaks in the gamma-ray spectrum. The fact that most nuclides emit multiple gamma-ray energies and these energies have strictly relative intensities to each other, allows for an easy evaluation and elimination of possible spectral interferences. It is important to recognize in reading older INAA literature that the type and quality of detector used is critical in evaluating reported interferences. For example, As interference reported on Au in older literature was a function of using a NaI detector. The main photopeak measured for As is 559.1 keV while Au is 411.8 keV. Modern detectors can easily resolve even the 411.1 keV Eu interference on the 411.8 keV Au peak. The INAA gamma spectrum also tends to be much simpler and less prone to interferences than the optical spectrum obtained from the inductively coupled plasma atomic emission (ICEP-AES) or X-ray spectra from X-ray fluorescence (XRF) analysis.

A major advantage of INAA is the fact that the sample does not have to be put into solution, particularly beneficial for some geological matrices where complete dissolution is difficult to effect. In addition, placing samples into solution is more laborious and complex than the simple weighing and encapsulation required by INAA. Refractory elements are very difficult to put into solution easily and will be discussed in more detail under the REE/REFRACTORY section. Even elements like Au can also be extremely difficult to put into solution completely. Hall et al. (1989) did a comparison of Au by the 4 major methods in use for the determination of Au at 15 major commercial and government laboratories in North America. Aqua regia digestion followed by MIBK (methyl isobutyl ketone) extraction was shown to yield low results (as low as 58%) compared to INAA. Fire assay followed by AA or ICP-AES finish were also shown to be low for certain samples (low by 26% in the case of porphyry Cu drill core). This was attributable to deleterious ele-

ments like Cu preventing efficient collection of Au in the Pb button. The results of the survey reported by Hall et al. (1989) illustrate the unique advantage INAA has by virtue of the direct determination on the solid material.

The absence of the dissolution step in INAA also provides relative freedom from analytical blanks or contamination usually associated with dissolution procedures. The sole risk of contamination in INAA is during sample preparation and weighing of the sample. Once the sample is encapsulated and irradiated, any amount of an element added to the sample will be undetectable by INAA as it is non-radioactive. The total concentration of an element is determined by INAA. Phase-specific concentrations may also be determined by INAA of both the untreated sample and the residue remaining after a specific, partial attack.

The recent advent of PC and minicomputer based multichannel analyzer systems combined with high resolution detectors have allowed the multielement characteristics of the INAA technique to be easily realized. Similarly, the widespread application of computers in the mineral exploration industry has also recently (over the last 3 to 4 years) resulted in requests for multi-rather than single-element analyses. As current trends in exploration are shifting away from Au towards base metals, the need for multielement analysis will increase.

The feature of radioactive decay of different isotopes with different half-lives has allowed the activation analyst to resolve peaks which may have overlapping gamma-rays. This is done strictly based on the half-life of the isotopes measured. An example of this would be the determination of Ti and Cr using Ti-51 ($t_{1/2} \approx 5.75$ min, principal gamma ray 320.1 keV) and Cr-51 ($t_{1/2} = 27.71$ days, sole gamma ray 320.1 keV). The exponential decay dictates that, after eight half-lives have elapsed, greater than 99.9% of the activity generated by that isotope will have decayed. Hence, 46 min after irradiation Ti-51 in the sample will have decayed almost completely while virtually all the Cr-51 activity generated in the sample would still be there. It is therefore simple to determine both Ti and Cr concentrations using the same gamma-ray energy but different decay times. Generally the short half-life isotopes are easily activated with short irradiations (s to min). Long lived isotopes generally require a much longer exposure to neutrons to activate them.

The variation in sensitivity in INAA for elements in the Periodic Table also provides both distinct advantages and disadvantages. This variation, categorized as high, medium and low sensitivity, is shown in Fig. 4. Certain elements such as Au have high sensitivities. However, this can sometimes present a problem in that high amounts of a sensitive element will create high amounts of radioactivity in the sample. Usually, at about 10,000 times the detection limit, this high amount of activity will require an increase in the sample to detector distance to prevent saturation of the detector preamplifier. In addition, the high count rate also adds to the Compton background, thus

RELATIVE SENSITIVITIES FOR ROCK MATRICES BY INAA																	
H																	
Li	Be	HIGH - H MEDIUM - M LOW - L										B	C	N	O	F	Ne
Na	Mg																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Ce	Sm	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Pr	Ba	Ac	(Pa)	(Th)													

Fig. 4. Periodic Table indicating the relative sensitivities of elements determined by INAA.

hindering detection of smaller photopeaks. For example, a net peak area of 1000 counts on a background of 1000 counts is statistically significant while a net peak area of the same 1000 counts on a background of 100,000 counts is not. This increase in background activity results in an increase in detection limits. The low sensitivity of INAA for elements like C, H, N, O facilitates the determination of ultra-low levels of many trace elements in vegetation because the matrix is not activated. Similarly, for rocks and sediments, Si, Fe and Ca have low sensitivities while Al, Mg, Mn, Ti, and K all have predominantly short lived isotopes. This makes rock-type matrices also ideal for INAA.

INAA is a complementary analytical technique. A different suite of elements is measured using INAA than with other techniques. One of the major suites of elements which are not easily determined by INAA include the major rock-forming elements which are more easily determined by XRF or ICP-AES. In addition the base metals such as Cu, Pb, Zn, Ni, and Cd are best determined by atomic absorption spectrometry (AAS), ICP-AES or DCP-AES.

Another advantage of the INAA technique is freedom from narrow working ranges prevalent with techniques such as AAS and, to a lesser degree, ICP-AES. The relationship between count rate and concentration is strictly linear from detection limit to major amounts of any particular element. For certain elements which are high neutron absorbers (e.g., Au or some REE elements), this may not be strictly true. Although INAA is generally regarded as a matrix independent technique, when dealing with high neutron absorbers it is pru-

dent to match the matrix of the standard to that of the sample. Most other analytical techniques also require matrix matching.

Unlike analytical techniques like XRF where particle size is very important, INAA is independent of particle size with some exceptions. Some INAA laboratories use low energy planar Ge detectors (LEPS) which provide measurement of high energy X-rays and low energy gamma-rays. The maximum efficiency of LEPS detectors is in the energy range 10–80 keV. Resolution in this energy range is also far superior to the standard co-axial Ge detectors which are commonly used in the 80 to 3200 keV range of most activation analysis. However, in the energy region efficiently measured by LEPS detectors, severe self absorption of low energy gamma-rays or X-rays can occur. Therefore, it becomes important in calibration to match particle size as well as matrix when doing low energy work. For samples which are not ground finely, self-shielding may also be a problem. For example, if Au is present as a large particle, neutrons will be absorbed by the outer layer of Au and may never activate the interior of the particle. This self-shielding effect is severe when irradiations are performed using the epithermal spectrum of neutrons but only minor when using thermal neutrons because of the higher effective absorption cross-section of Au for epithermal neutrons (1550 barns) compared to that for thermal neutrons (99 barns). Epithermal activation analysis is not recommended for Au because the results may be significantly low as a result of self-shielding. With thermal activation analysis, Au can be determined accurately even at very high levels of hundreds of ppm by INAA without showing self-shielding effects. Samples with high levels of REEs also present self-shielding problems and proper precautions such as diluting with SiO₂ should be taken if the total REE content exceeds 1%.

It is possible with INAA to quantitatively estimate the precision of analysis. This is possible because the random process of radioactive decay gives rise to Gaussian peaks which allows the calculation of precision based on counting statistics. Both accuracy and precision are possible well below 1% even for a decaying source.

INAA measurements are based on physical phenomena which take place in the nuclei of elements and therefore, results are totally independent of the chemical state of the elements. Au, for example, is reported to be bound as a carbonaceous complex in certain ore types. The INAA method will determine Au present in any chemical form.

LIMITATIONS OF INAA

A disadvantage of INAA is the necessity to make fission product corrections. When U is irradiated, U²³⁵ fissions to produce elements which are measured by INAA. Landsberger (1989) has compiled all the fission product corrections. When the U content in samples becomes large enough, the correction

becomes sufficiently large as to make reporting numbers impossible. Elements which must be corrected for fission products include Ba, La, Ce, Nd, Sm, Mo, Zr, Ru, Pd, and Te.

Another potential disadvantage of INAA is the need for a neutron source. A limited number of nuclear reactors are suitable for use in activation analysis and, as time progresses, the high cost of replacement will reduce availability. There are few new reactor research facilities being built to replace those shut down. Many existing reactors, however, will provide service irradiations to outside users on a small scale. Few reactor designs are suitable for irradiation and handling of larger volumes of samples (i.e. 1000s/day).

Some other problems with INAA which have been reported by Hall et al. (1989) include improper flux monitoring and maintaining consistent sample to detector geometry. This type of problem is not a disadvantage but merely a technical aspect which is easily addressed.

No single analytical technique is a panacea and INAA is no exception. For certain applications like "whole rock" analysis it is much simpler to use XRF or ICP-AES as the analytical techniques. Cu, Pb, Ag, Cd, Zn, are also more easily determined with better sensitivities by ICP-AES or AAS.

MAJOR APPLICATIONS

Au

INAA provides a cost effective and rapid means of analysis for several types of geochemical samples. Over the last several years the mineral industry has concentrated on Au exploration and more recently has chosen the route of multielement analysis. Methods have been developed for large volume, rapid, accurate and timely analyses by INAA for Au as part of multielement packages. Hoffman (1989) has described INAA procedures for rocks, soils, sediments (both stream and lake bottom), humus, vegetation and heavy minerals (from overburden drilling and stream sediment) which have become popular. Some methods of analysis for Au available by INAA on different matrices are shown in Table 1. Most major commercial laboratories in North America servicing the mineral industry provide INAA analyses on their own or through sub-contractors because of demand.

Rock, soils, stream sediments and lake bottom sediments

Au is known as an element which occurs very inhomogeneously distributed in geological matrices. To provide meaningful results, analytical methodology must take this fact into account and, as a result, relatively large sample sizes must be analyzed. Methods have been developed for the analysis of rocks, soils and sediments by INAA using large samples. One assay ton subsamples (ca. 30 g) are encapsulated, irradiated in a rotating facility for 30 min at a

thermal neutron flux of $5 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ and measured by gamma ray spectrometry approximately 7 days after irradiation, for "Au+34" other elements simultaneously.

Table 2 lists the elements for a stream sediment matrix, detection limits, half-life, principal gamma-ray energy or energies used and the isotope measured. Detection limits are a function of the sample matrix and will vary depending on the chemical composition. Table 3 shows a comparison of detection limits for various matrices. For most stream sediments and soils a detection limit of 2 ppb is possible for Au for 99% of samples measured. Rocks however tend to have high levels of inorganic material or contain higher levels of elements such as Na, Sc or REEs which cause an elevation in spectral background and hence a degradation in detection limits. This may be improved by increasing counting times (i.e. rock "research" package). The length of decay from irradiation to measurement for geological samples is usually directly a function of the amount of Na present. For samples low in Na (a few hundred to a few thousand ppm) the decay time can be shortened by a day or so. An alternative method of decreasing the decay time is to irradiate with epithermal neutrons. This will allow the decay time to be reduced from 6-7 days to 4-5 days; however, sensitivities will suffer for many elements but may be slightly improved for Au, As and W due to the shorter decay period. The self-shielding of Au becomes a major problem when using epithermal neutrons for irradiation unless the Au concentrations are very low and evenly dispersed throughout the sample. The problem is a function of Au particle size. Particles of 10s of microns will begin to show the self-shielding effect when using epithermal neutrons and result in low values (values as low as 50% have been noted). This problem can be avoided by using thermal neutrons for irradiation. The cross section for Au with thermal neutrons is 99 barns while the cross section is 1550 barns for epithermal neutrons. The larger the cross section, the more effective the element becomes as an absorber of neutrons. With epithermal neutrons, the 1550 barn cross section for Au causes the outer rim of the Au particle to absorb most of the neutrons while not allowing the neutrons to penetrate the interior of the particle to the same degree. The much lower thermal cross section does allow the penetration of neutrons and hence allows accurate determination of Au even at higher levels.

The cost for this type of analysis is comparable to other single element analytical techniques for Au. The cost on a per element basis becomes very cost effective when employed in a multielement mode. The multielement nature of analysis will also provide information on alteration, geological structures, pathfinder elements, geology, and other elements of economic significance. As with most multielement packages, certain elements may be present below detection limits (e.g., Hg), but for certain types of deposits (e.g., Nevada-Carlin type or epithermal type mineralization) Hg can be detected. Compet-

TABLE 1
Methods of analysis for Au

Sample material	Preparation required	Method No.	Method	Routine wt. of sample	Elements determined simultaneously*	Detection limits (Au)	Comments
Rock	Crushing & milling	1	Pb-FANA	30 g	No	1 ppb	detection limit a function of fire assay reagent blank which may yield occasional sporadic results used to determine background levels in rocks
	Crushing & milling	2	Pre-irrad. Pb-FANA	1 g	No	0.1 ppb	
	Crushing & milling	3	Direct irrad. INAA	30 g	Yes, Group 1	5 ppb	sample sizes can vary from (1 g to 500 g). Detection limits may vary due to sample composition used in evaluation PGE deposits
	Crushing & milling	4	Ni sulphide-FA-INAA	50 g	Yes; Rh, Pt, Pd, Os, Ru, Ir, Re	1 ppb	
	Crushing & milling	5	Pb-FA-ICP-ES or DCP-ES	30 g	Yes; Pd, Pt	2 ppb	used for routine PGE exploration
Soil	Drying & screening	1	Pb-FANA	30 g	No	1 ppb	amount of organics impt. to method & interpretation
	Drying & screening	3	Direct irrad. INAA	30 g	Yes, Group 1	2 ppb	
	Drying & screening	5	Pb-FA-ICP-ES or DCP-ES	20 g	Yes; Pd, Pt	2 ppb	useful for PGE exploration
Glacial till or planned concentrates	Heavy mineral separation	6	Direct irrad. INAA	<1 g to 60 g	Yes Group 1 or Group 2	5 ppb	epithermal irradiation results in low gold values due to selfshielding. The whole concentrate usually non-magnetic) should be analyzed

	Separate -250 mesh	7	Direct irradi. INAA	<1 g to 30 g	Yes, Group 1	2 ppb	lower detection limits to 0.1 ppb possible by using method 2
Humus (mull)	Drying, macerating, briquetting	8	Direct irradi. INAA	8 g to 30 g	Yes, Group 1	1 ppb	sample must be 90%+ organic. Detection limits affected by inorganic content
Vegetation	Drying, macerating, briquetting	9	Direct irradi. INAA	8 g to 30 g	Yes, Group 1	0.1 ppb	detection limit may be slightly elevated due to high levels of Na or Br in some species
	drying, ashing	10	Direct irradi. INAA	<1 g to 2 g	Yes, Group 1	5 ppb	ashing losses are possible, ashing is expensive but advantage of using larger sample. Ash yield 1-5%
Water	Concentrated on activated charcoal	11	Direct irradi. INAA	100 ml	Yes, Group 1	1-5 ppt	caution must be taken in collecting sample (Au is adsorbed onto polyethylene)
	evaporation	12	Direct irradi. INAA	100 ml	Yes, Group 1	1-5 ppt	evaporation in polyethylene liners
Lake bottom sediments	Drying & milling	13	Direct irradi. INAA	5-30 g	Yes, Group 1	1-5 ppb	detection limit a function of the inorganic content
	Drying & milling, briquetting	14	Direct irradi. INAA	8-30 g		1-5 ppb	can only be done if the organic content is high
	Drying & milling	15	Direct irradi. INAA	5-20 g		1 ppb	if organic content is very high the sample may have to be ashed (ashing losses may result)

*Group 1: Thermal activation elements: Au, Ag, As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, Hg, Ir, Mo, Na, Ni, Rb, Sb, Se, Sr, Ta, Th, U, W, Zn, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu. Group 2: Epithermal activation elements: As, Ba, Co, Cr, Fe, Mo, Sb, Se, Sr, Ta, Th, U, W, Zn, La, Ce.

TABLE 2

Analytical parameters for determining "Au + 34" package on lake bottom sediments by INAA

Element	Detection limit*	$T_{1/2}$	Principal energy used (keV)	Measured isotope
Ag	5 ppm	249.8 d	657.8, 884.7, 837.5	Ag-110M
As	0.5 ppm	26.3 h	559.1, 657.1, 1216.1	As-76
Au	2 ppb	2.7 d	411.8	Au-198
Ba	50 ppm	11.8 d	216, 373, 496	Ba-131
Br	1 ppm	35.3 h	554, 777, 619, 1044	Br-82
Ca	1 %	4.54 d	1297.1	Ca-47
Ce	3 ppm	32.5 d	145.4	Ce-141
Co	1 ppm	5.27 y	1173.2, 1332.4	Co-60
Cr	5 ppm	27.7 d	320.1	Cr-51
Cs	1 ppm	2.06 y	796, 604.7	Cs-134
Eu	0.2 ppm	13.33 y	121, 344, 964, 1408	Eu-152
Fe	0.01 %	44.5 d	1099.3	Fe-59
Hf	1 ppm	42.4 d	482	Hf-181
Hg	1 ppm	46.6 d	279.2	Hg-203
Ir	5 ppb	73.8 d	316.5, 468.1	Ir-192
La	0.1 ppm	40.3 h	329, 487, 816, 1596	La-140
Lu	0.05 ppm	6.71 d	208.4	Lu-177
Mo	5 ppm	65.94 h	140.5, 739.6	Tc-99M
Na	0.05 %	14.96 h	1368.6	Na-24
Nd	5 ppm	10.98 d	91, 531	Nd-147
Ni	50 ppm	70.8 d	810.8	Co-58
Rb	30 ppm	18.7 d	1076.6	Rb-86
Sb	0.1 ppm	2.7 d	564.2	Sb-122
Sc	0.1 ppm	83.8 d	889, 1120	Sc-46
Se	5 ppm	119.8 d	136, 264.7	Se-75
Sm	0.1 ppm	46.3	103.2	Sm-153
Sr	0.05 %	64.8 d	514	Sr-85
Ta	1 ppm	114.5 d	1121, 1221	Ta-182
Tb	0.5 ppm	72.3 d	298.6, 879	Tb-160
Tl	0.5 ppm	27.4 d	311.8	Po-233
U	0.5 ppm	2.36 d	106.1, 277.6, 228.2	Np-234
W	2 ppm	23.9 h	479, 686	W-187
Yb	0.2 ppm	4.2 d	282, 396	Yb-175
Zn	50 ppm	244 d	1115.6	Zn-65

*Upper limit: none.

ing analytical methods are primarily based upon aqua regia digestion followed by solvent extraction and determination by AAS or fire assay preconcentration followed by dissolution of the bead and determination of Au by AAS, ICP-AES, DCP-AES, or INAA (without dissolution of the bead). The AES competing methodologies are more labour intensive, involve multiple handling steps and require skilled personal to provide reliable results. Some of the problems associated with these types of analysis are documented by

TABLE 3

Typical detection limits for INAA analysis of soil, rock and heavy minerals

Element	Soil	Rock	Rock research	Heavy minerals
Ag	2 ppm	5 ppm	2 ppm	5 ppm
As	1 ppm	2 ppm	1 ppm	2 ppm
Au	2 ppb	5 ppb	1 ppb	5 ppb
Ba	100 ppm	100 ppm	20 ppm	200 ppm
Br	1 ppm	1 ppm	0.5 ppm	5 ppm
Ca	1 %	1 %	0.2 %	1 %
Co	1 ppm	5 ppm	0.1 ppm	5 ppm
Cr	5 ppm	10 ppm	0.5 ppm	10 ppm
Cs	1 ppm	2 ppm	0.2 ppm	2 ppm
Eu	0.2 ppm	0.2 ppm	0.05 ppm	0.2 ppm
Fe	0.01 %	0.02 %	0.005 %	0.02 %
Hf	1 ppm	1 ppm	0.2 ppm	1 ppm
Hg	1 ppm	1 ppm	1 ppm	5 ppm
Ir	5 ppb	5 ppb	1 ppb	50 ppb
Mo	2 ppm	5 ppm	2 ppm	20 ppm
Na	0.1 %	0.05 %	0.001 %	0.05 %
Ni	50 ppm	50 ppm	50 ppm	200 ppm
Rb	30 ppm	30 ppm	10 ppm	50 ppm
Sb	0.1 ppm	0.2 ppm	0.1 ppm	0.2 ppm
Sc	0.1 ppm	0.1 ppm	0.01 ppm	0.1 ppm
Se	3 ppm	5 ppm	0.5 ppm	20 ppm
Sn	0.01 %	0.01 %	0.01 %	-
Sr	0.05 %	0.05 %	0.01 %	0.2 %
Ta	1 ppm	1 ppm	0.3 ppm	1 ppm
Tb	0.5 ppm	0.5 ppm	0.1 ppm	0.5 ppm
U	0.5 ppm	0.5 ppm	0.1 ppm	0.5 ppm
W	3 ppm	4 ppm	1 ppm	4 ppm
Zn	50 ppm	50 ppm	10 ppm	200 ppm
La	1 ppm	1 ppm	0.1 ppm	1 ppm
Ce	3 ppm	3 ppm	1 ppm	3 ppm
Nd	5 ppm	5 ppm	1 ppm	10 ppm
Sm	0.1 ppm	0.1 ppm	0.01 ppm	0.1 ppm
Eu	0.2 ppm	0.2 ppm	0.05 ppm	0.2 ppm
Tb	0.5 ppm	0.5 ppm	0.1 ppm	2 ppm
Yb	0.2 ppm	0.2 ppm	0.05 ppm	0.2 ppm
Lu	0.05 ppm	0.05 ppm	0.01 ppm	0.05 ppm

Hall et al. (1989). Fire assay based methods are also more laborious, are prone to contamination from reagents and other samples and require a skilled fire assayer to properly flux the samples.

Biogeochemistry

Another major application of INAA for Au exploration has been in the field of biogeochemistry. Methods have been developed for the determination of Au and 35 elements in vegetation. The last decade has seen a rapid increase: first, in the use of humus; and in the last several years, the use of vegetation

TABLE 4

Detection limits routinely achievable by low cost INAA in humus, vegetation and vegetation ash

Element	Humus	Vegetation	Veg-Ash
Au	1 ppb	0.1 ppb	5 ppb
Ag	2 ppm	0.2 ppm	2 ppm
As	1 ppm	0.01 ppm	0.5 ppm
Ba	100 ppm	5 ppm	10 ppm
Br	1 ppm	0.01 ppm	1 ppm
Ca	0.1 %	0.01 %	0.2 %
Co	1 ppm	0.1 ppm	1 ppm
Cr	1 ppm	0.3 ppm	1 ppm
Cs	0.5 ppm	0.05 ppm	0.5 ppm
Fe	0.05 %	0.005 %	0.05 %
Hf	0.5 ppm	0.05 ppm	0.5 ppm
Hg	0.5 ppm	0.05 ppm	1 ppm
Ir	5 ppb	0.1 ppb	2 ppb
K	-	0.01 %	0.05 %
Mo	0.5 ppm	0.05 ppm	2 ppm
Na	100 ppm	1 ppm	10 ppm
Ni	10 ppm	2 ppm	50 ppm
Rb	20 ppm	1 ppm	5 ppm
Sb	0.1 ppm	0.005 ppm	0.1 ppm
Sc	0.1 ppm	0.01 ppm	0.1 ppm
Se	2 ppm	0.1 ppm	2 ppm
Sr	100 ppm	10 ppm	300 ppm
Ta	0.5 ppm	0.05 ppm	0.5 ppm
Th	0.5 ppm	0.1 ppm	0.1 ppm
U	0.1 ppm	0.01 ppm	0.1 ppm
W	1 ppm	0.05 ppm	1 ppm
Zn	20 ppm	2 ppm	20 ppm
La	0.1 ppm	0.01 ppm	0.1 ppm
Ce	1 ppm	0.1 ppm	3 ppm
Nd	3 ppm	0.3 ppm	5 ppm
Sm	0.1 ppm	0.001 ppm	0.1 ppm
Eu	0.2 ppm	0.05 ppm	0.01 ppm
Tb	0.2 ppm	0.01 ppm	0.5 ppm
Yb	0.1 ppm	0.005 ppm	0.05 ppm
Lu	0.1 ppm	0.001 ppm	0.05 ppm

has grown dramatically as a result of successful applications in boreal forest, desert and tropical terrains. There are two main method of analysis by INAA for biogeochemical samples. The prevalent method is based on the direct analysis of a large sample (up to 30 g) of compressed dry vegetation. The alternate method involves the analysis of ash from vegetation followed by INAA analysis of the ash. Detection limits are equivalent on a dry weight basis when compared for either of these INAA techniques.

Samples of dry macerated vegetation or humus up to 30 g in size can be

compressed into a wafer using a conventional XRF briquetting press. This method has been described by Hoffman and Brooker (1986) and Cohen et al. (1987). The samples can be stacked and irradiated with as many as 120 samples for a single irradiation. After a 5 to 7 day decay to allow Na to decay, as many as 36 elements can be measured simultaneously. The elements determined and detection limits for humus and vegetation and vegetation ash are listed in Table 4. This technique has major advantages in that it is rapid, low-cost and provides excellent quality of data and detection limits. The dry ashing of samples for the ash technique has been described by Dunn (1986) and results in loss of volatile elements which may include Au (Girling et al., 1979; Hoffman and Brooker, 1982).

A method for Au in humus which involves selective extraction of Au in humic acid has been described by Perry et al. (1991). The gold in the extract is collected on activated charcoal and analyzed by INAA. This method may reduce the false anomalies generated using humus sampling in glaciated terrain as a result of transported Au in the till.

Most competing analytical techniques for vegetation require either wet or dry ashing, followed by determination of Au by solvent extraction-graphite furnace AAS. Other elements are usually determined in ash by aqua regia digestion-ICP-AES, when elements such as Cu or Ag are required.

A competing technique for humus which involves fire assaying the humus directly has also been used. Trying to fire assay humus with high organic content can result in substantial Au losses. The fire assay blank problem also makes this a very undesirable procedure, and will usually result in many false, analytically created anomalies from fire assay reagents.

Heavy minerals

The analysis of heavy minerals obtained from glacial till or stream sediments usually requires that the entire sample be analyzed for Au exploration. This is primarily because Au will tend to occur as "nuggets" in the sample and to obtain meaningful results the Au content of the entire sample must be known. Pulverising the sample as a means of homogenizing it may result in loss of Au due to smearing on mills or, in many cases, the heavy mineral sample may weigh only a fraction of a gram and a large percentage may be lost on milling. The INAA technique involves the simple process of encapsulation of the entire sample, irradiation and INAA measurement. The sample can later be treated by other analytical methods for determination of some of the elements not determined well by INAA including Cu, Pb, Ni, Ag, Zn and Hg. It is very important in analyzing heavy minerals for Au that only thermal neutrons are used to avoid the previously discussed self-shielding problem of Au with epithermal neutrons. After the samples have been irradiated they can be handled only by laboratories with radioisotope licenses owing to the small but measurable remaining radioactivity.

An alternative method of analysis involves milling and fire assaying part of the concentrate. This method of analysis is not suggested because of the problems already described.

Platinum group elements

For certain elements a chemical separation prior to irradiation is necessary to obtain better sensitivities or eliminate interferences. This is the case for the PGEs. Hoffman et al. (1978) described a nickel sulphide fire assay preconcentration procedure which effectively collects all the PGEs and Au from large sample sizes (e.g., 50 g) and acts to separate the PGEs from their matrix. It is necessary to use a large sample size to overcome "nugget effects" for the PGEs. The fire assay-dissolution procedure is necessary to eliminate direct interference, of Ca on Pt, and of fission product production of Pd and Ru from any U. The general separation of the PGEs from the matrix also has the effect of creating a much lower background and hence detection limits in the sub-ppb to low ppb range.

Modifications to the original technique have been described by Borthwick and Naldrett (1984), who changed the nature of the flux for chromite-rich samples, and by Asif and Parry (1989) who have used a smaller sized bead for the collection. Advances in resolution of detectors and loss-free counting systems have allowed a lowering of detection limits to those shown in Table 5.

Parry (1992) has also described radiochemical procedures which have permitted sub-ppb detection of the PGEs.

Competing technology is limited to the nickel sulphide fire assay-ICP mass spectrometry (ICP-MS) procedures described by Date et al. (1987). Detection limits for Rh and Os are still inferior to those by the INAA procedure, but better for Pt, Pd and Ru. There are also potential losses of Os on dissolution. A low cost alternative (both nickel sulphide methods are expensive)

TABLE 5

Detection limits obtainable by NIS-INAA, NIS-ICP-MS and PbO-ICP.

Detection limit (ppb)	NIS-INAA	NIS-ICP-MS	Pb-ICP-AES
Ir	0.1	0.1	-
Os	1	3	-
Ru	5	1	-
Rh	0.1	1	-
Pd	2	1	2
Pt	5	1	5
Au	0.5	1	1

involves a standard Pb collection, followed by GFAAS, ICP-AES or DCP-AES determination of Pt, Pd and Au. Certain types of materials (oxidized or high chromite content) may return low results with the Pb collection. The other PGEs are either not collected quantitatively, cannot be dissolved quantitatively (Beamish and Van Loon, 1977), or are volatilized on fire assaying.

REEs/refractory elements

A major application in the field of geoscience research involves the determination of REEs and other elements like Sc, Hf, Ta, Th and U which are important in petrogenetic studies as well as in the study of rock-water interactions and various alteration types associated with ore deposits. Detection limits adequate for most of these elements in most rocks are listed in Table 3 as part of a 35 element INAA long lived isotope rock-research package. These limits are compromised somewhat by the nature of simultaneous analysis and can often be improved by an order of magnitude or more by increasing the count time or changing the delay times on measurement after irradiation depending on the half-life of the elements being sought. If further improvements are still required, radiochemical separations can be performed to improve detection limits (Parry, 1992).

The competing technology for determination of this group of elements is ICP-MS. Geological materials containing refractory minerals such as chromite, garnet, sphene and zircon are commonly regarded as difficult samples to put into solution easily. Hall and Plant (1990) recently described the determination of the REEs by ICP-MS and have compared this method to the analysis of the REEs by INAA. They found that the heavy REEs were tied up in phases which were not easily put into solution. The resulting REE chondrite plots by ICP-MS gave rise to an incorrect interpretation of the resultant pattern. Richardson et al. (1990) reported that they had found the same problem with REE determination by ICP-MS and required that all samples be analyzed by XRF as well for Zr to determine if the Zr values agreed by both analytical techniques. If ICP-MS results were lower they believed that the REE results would be suspect.

Short lived isotopes

A suite of short lived isotopes listed in Table 6 extend the range of elements being determined by INAA. The major factors influencing the level of detection for these elements is the amount of Al and Mn present in the sample. The high sensitivity of Al and Mn result in large amounts of induced radioactivity which may result in increased detection limits. The detection limits for short lived isotopes are generally more matrix dependent and hence more variable than for long lived isotopes.

TABLE 6

Short lived isotopes by INAA and typical detection limits for rocks.

Element	Detection limit	Element	Detection limit
Al	0.0001 %	Mg	0.05 %
Cl	100 ppm	Mn	0.1 ppm
Cu	50 ppm	Na	0.01 %
Dy	0.5 ppm	Ti	0.01 %
I	0.5 ppm	U	0.1 ppm
In	0.1 ppm	V	0.5 ppm

TABLE 7

Detection limits on liquid samples (water or petroleum) by INAA using short or long lived isotopes.

Element	Detection limit	Element	Detection limit
<i>Long lived isotopes</i>			
Ag	50 ppb	Re	0.5 ppb
As	5 ppb	Na	0.1 ppb
Au	0.01 ppb	Nd	10 ppb
Ba	0.5 ppm	Ni	1 ppm
Br	10 ppb	Rb	0.1 ppm
Ca	50 ppm	Sb	0.5 ppb
Ce	10 ppb	Sc	0.1 ppb
Co	50 ppb	Se	50 ppb
Cr	50 ppb	Sm	0.1 ppb
Cs	5 ppb	Sr	0.1 ppm
Eu	5 ppb	Ta	5 ppb
Fe	1 ppm	Tb	20 ppb
Hf	5 ppb	Th	1 ppb
Hg	50 ppb	U	0.5 ppb
Ir	0.1 ppb	W	1 ppb
Ga	10 ppb	Yb	1 ppb
K	1 ppm	Zn	0.1 ppm
La	0.5 ppb		
Lu	0.2 ppb		
Mo	10 ppb		
<i>Short lived isotopes</i>			
Al	5 ppb	I	5 ppb
Cl	0.1 ppm	In	1 ppb
Cu	0.5 ppm	Mg	1 ppm
Dy	1 ppb	Mn	2 ppb

Aqueous samples

Petroleum and water samples can also be analyzed by INAA. Table 7 lists all the elements determined and their detection limits. Preconcentration by evaporation can generally improve these limits by several orders of magnitude as can multiple irradiation and counting schemes. Again certain elements (e.g., Cu, Pb) are not listed because of lack of sensitivities. Upon irradiation, heat is generated and proper encapsulation to avoid leakage is important.

Uranium analysis

The determination of U by delayed neutron counting with an automated system capable of determining U down to 0.1 ppm in solids at a rate of 2400 samples/day has been described by Ernst and Hoffman (1982). Using longer irradiation and counting times and with increased samples sizes, it is possible to determine levels down to 0.01 ppm on any material. Water can be analyzed for U to 0.2 ppb by evaporation of 100 ml samples.

CONCLUSIONS

INAA provides a means of rapidly determining as many as 36 elements simultaneously on virtually all types of geological matrices including vegetation using the long lived isotopes. Elements such as B and Gd are determined by prompt gamma analysis. Uranium is determined rapidly by delayed neutron counting. Twelve additional elements not determined using any of the above procedures can be determined using their short lived isotopes. Despite being able to determine approximately 50 elements in many geological materials by INAA, certain elements such as those forming the major oxides and a base metal suite of Cu, Pb, Ni, Ag, Cd, and Zn are more easily determined by other analytical methods at low levels although all of these elements except Pb can be determined with good accuracy and precision at higher levels by INAA.

The cost of analysis by INAA is usually competitive or much lower than with other analytical techniques. While the capital cost of building a reactor for neutron activation only would probably be prohibitive, various reactor centres around the world help defray their operating costs by leasing time to commercial activation labs or by providing a limited INAA service themselves.

Improvements in detector resolution and efficiencies as well as speed of electronic components promises to continue the technological advances that have occurred within the last decade and have allowed for low cost, rapid, accurate INAA analyses. Advances in computer technology will continue to reduce the capital cost of multidetector computer systems.

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