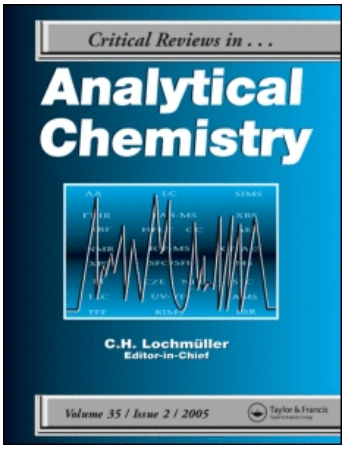

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Advances in Neutron Activation Analysis

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ADVANCES IN NEUTRON ACTIVATION ANALYSIS

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I. INTRODUCTION

A. Aims of the Review

The 50th anniversary of the description of neutron activation analysis (NAA) by Hevesy and Levi[1] was celebrated at the Seventh Modern Trends in Activation Analysis Conference (MTAA-7) held in Copenhagen, Denmark, in June 1986. NAA is now considered to be a mature field. The principles are well understood, and no dramatic improvements in either instrumentation or methodology that would revolutionize the method are expected. This is in contrast to other analytical techniques where significant advances and changes in instrumentation and scope of applications are seen within a relatively short time. However, the field of NAA remains vigorous as researchers continue to develop innovative applications of NAA using existing facilities, link NAA with the developing technologies in separation science to form a unique and powerful new group of "hyphenated techniques", refine sample handling and data processing procedures, and continually strive to improve the quality of the data generated by activation analysis procedures. An excellent brief review of developments that were presented at MTAA-7 has been provided by Heydorn.[2]

Other analytical techniques have become competitive with activation analysis in sensitivity, selectivity, and multielement capability. However, NAA still retains a special place in the analytical arsenal because its potential for blank-free, matrix-independent, multielement determinations makes it an excellent reference technique. Greenberg,[3] for example, has discussed the extensive use of NAA to certify standard reference materials at the U.S. National Bureau of Standards (now the National Institute of Standards and Technology).

The aim of this review is to present the reader who is a nonspecialist in NAA with a brief review of the basic principles and scope of application of the technique, and with an overview of some current trends in NAA that can be considered as advances in the field and as predictors of future work. Some of the methods discussed here were suggested many years ago, but are only now being implemented. Others are actually new methodologies that have not been previously explored. In selecting topics for this review, the authors drew heavily on the proceedings from the MTAA-7 and from a computerized literature search on "Radiochemical Analysis" from December 1985 through December 1987. A few references from early 1988 are also included. We have chosen to confine our review specifically to neutron activation techniques, since neutron production facilities are more accessible to most analysts. For reviews of charged particle activation analysis (CPAA), instrumental photon activation analysis (IPAA), isotope dilution analysis (IDA), ion beam-analysis methods (PIXE, PIGE, RBS), and radiotracer methods, we refer the reader to the references listed in Table 1a.[4-14]

A brief review of the general principles and applications of NAA is followed by a summary of recent advances in NAA methodologies. We then examine some novel applications of

Table 1a
SELECTED RECENT REVIEWS OF NUCLEAR METHODS OF ANALYSIS

Topic	Ref.
Charged particle activation analysis	4, 5
Instrumental photon activation analysis	6, 7
Ion beam analysis	8—11
Tracers	12, 13
Isotope dilution analysis	14

NAA, including proton track mapping, neutron depth profiling, neutron tomography, and *in vivo* neutron activation analysis.

B. Principles and Applications of Neutron Activation Analysis

The fundamentals of NAA have been reviewed in detail in many recent articles.[15-18] Only a brief summary is presented here. NAA is an analytical technique that can provide both qualitative and quantitative information regarding the elemental composition of a wide variety of samples. The sample is irradiated by neutrons, resulting in the formation of activated products. Typically, gamma rays, resulting either from transitions among activated nuclear energy states of the compound nucleus or from radioactivated decay products, are measured. The gamma-ray energies are characteristic of specific indicator radionuclides, and their intensities are proportional to the amounts of the various target nuclides in the sample.

There are two approaches to NAA:

1. Measurement of delayed particles or radiations from the decay of a radioactive product of a neutron-induced nuclear reaction
2. Immediate measurement of prompt gamma rays emitted by the (n,γ) reaction

The first approach is known as simple or delayed-gamma NAA and may be purely instrumental (INAA) or may involve radiochemical separations (RNAA). The second approach is known as prompt gamma neutron activation analysis (PGNAA) and requires the analyst to collect data at the site of the source of neutrons.

The number of target atoms in the sample may be calculated directly from the basic equation of activation analysis:

$$A = n \Phi \sigma(1 - e^{-\lambda t})(e^{-\lambda d}) \quad (1)$$

where A = absolute activity of the sample (disintegrations s^{-1}), n = number of atoms of the target nuclide, Φ = neutron flux density (n cm^{-2} s^{-1}), σ = cross section for reaction (cm^2), λ = decay constant for the product radionuclide (s^{-1}), t = time of irradiation (s), and d = time of decay before counting (s).

Although it is possible to use the above equation directly to obtain elemental concentrations (''absolute'' activation analysis), this is not done ordinarily. The reason is that significant uncertainties often exist for some of the parameters, for example, the cross section and the effective flux density. Therefore, in practice a comparator method is used, in which standards containing known amounts of the element of interest are irradiated simultaneously with the samples. Combination of the activation equations for sample and standard gives:

$$\frac{R_{std}}{R_{sam}} = \frac{W_{std}(e^{-\lambda t})_{std}}{W_{sam}(e^{-\lambda t})_{sam}} \quad (2)$$

where R = measured experimental counting rates of the indicator radionuclide in the standard (std) and sample (sam) and W = mass of the element of interest in the standard (std) and sample (sam). Use of this equation assumes that both samples and standards are exposed to the same neutron flux density and are counted with equivalent counting efficiencies. If either condition is not fulfilled, suitable corrections must be applied.

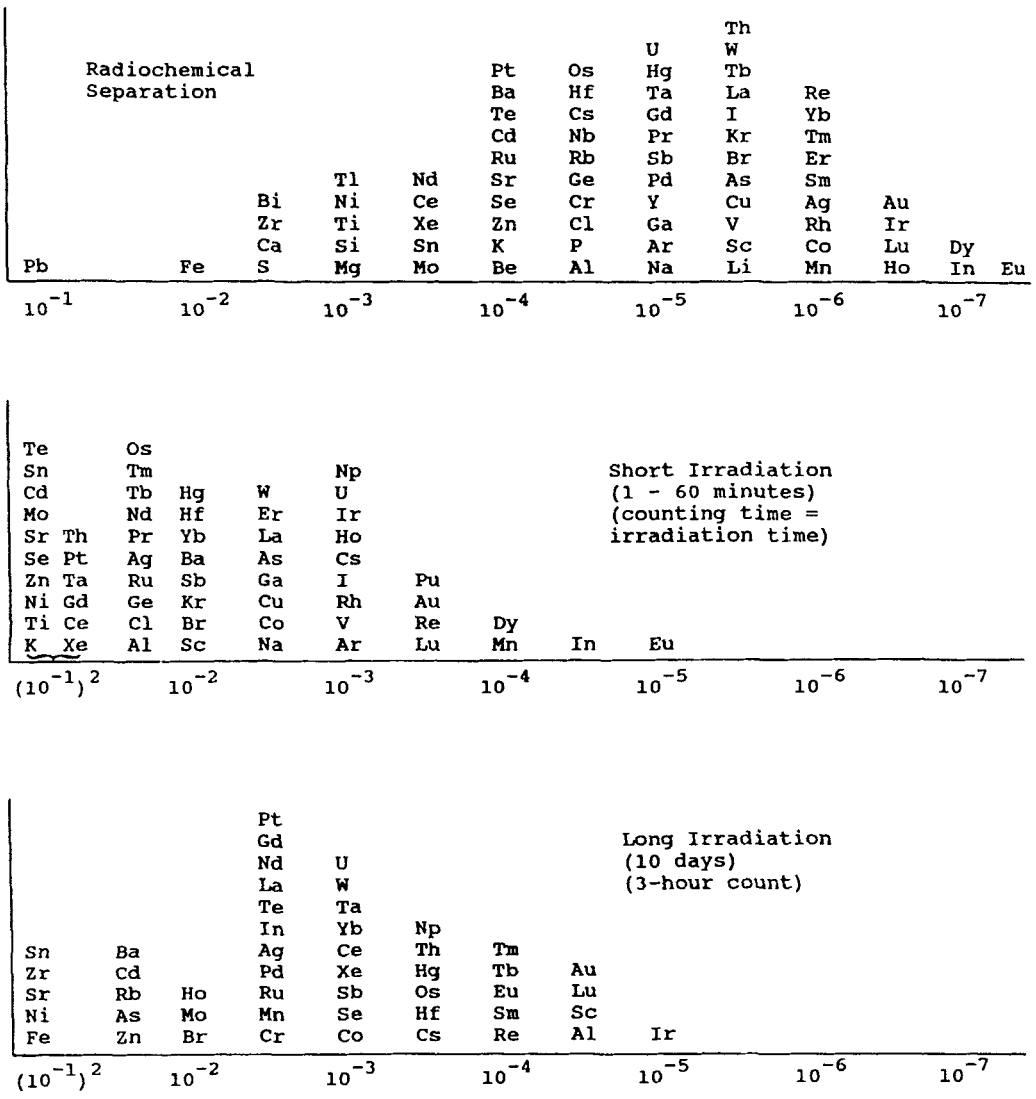
There are three types of neutron sources used traditionally for activation analysis: reactors, accelerators, and isotopic sources. The most common is the nuclear reactor, in which neutrons are produced by the fission of uranium. Accelerators that produce 14-MeV neutrons through the $^{3}H(d,n)^{4}He$ reaction are used for fast neutron activation analysis (FNAA). Perhaps the most convenient neutron sources are the isotopic sources. These low-intensity sources may be based on either the spontaneous fission of ^{252}Cf, Pu-Be or Am-Be mixtures that produce neutrons via the $^{9}Be(\alpha,n)^{12}C$ reaction, or ^{124}Sb-Be photoneutron sources that use the $^{9}Be(\gamma,n)2-^{4}He$ reaction.

The detectors most commonly used for NAA are intrinsic or high-purity germanium (HPGe) or lithium-drifted germanium (Ge[Li]) semiconductor detectors and sodium iodide (NaI[Tl]) scintillation detectors. These detectors are usually interfaced to computer controlled multichannel pulse-height analyzer systems for data collection and reduction. Several excellent books (see References 19 through 22) are available for the reader who wishes a more detailed presentation of the principles of NAA.

Many rather unique advantages of NAA have allowed this technique to become an important tool in a wide variety of disciplines. It is quite sensitive, with the capability of detecting many elements at the nanogram-per-gram level. Figure 1 lists ideal sensitivities of three NAA approaches for commonly determined elements. It is apparent that the lowest detection limits are for RNAA. NAA can also be a selective technique, because modification of experimental parameters such as irradiation and decay times and use of neutrons of varying energies can discriminate against unwanted elements. For most applications sample preparation is minimal, so laboratory contamination problems are lessened. NAA is nearly matrix-independent and has the potential to be an absolute method that would not require reference standards. NAA is essentially nondestructive for many samples and can provide simultaneous multielement determinations in the same sample. These advantages of NAA are widely exploited in its many applications.

The earliest application of NAA was the measurement of several rare earth metals in geological samples, and this is still a common application of NAA today. The sensitivity, selectivity, and multielemental capabilities of NAA are especially useful in the analysis of geological materials, where precise determinations of elemental concentration ratios are needed. These same three advantages have also provided the impetus for the application of NAA to determination of trace elements at very low levels in complex biological matrices. Industry has found increasing uses for NAA, especially for the elemental analysis of ultrapure semiconductor materials. Ehmann and Yates[23,24] have produced two recent, extensive reviews of advances in methodology and current analytical applications of INAA. A few representative current applications are presented in Table 1b.[25-52]

There are a number of difficulties associated with NAA. Laboratories must be equipped to handle radioactive material and possess the necessary detectors and analyzer equipment. An on-site reactor or other source of neutrons is not absolutely necessary, because many service reactor irradiation facilities, both commercial and through academic institutions, are available. Overnight air shipments make possible even the determination of relatively short-lived indicator radionuclides. A disadvantage of the method is that it does not provide information on the chemical form of the element, a factor that is of increased interest in



[1]Adapted from Reference 101.
[2]or poorer
Assumptions: thermal neutron flux of 8×10^{13} n cm^{-2} s^{-1}
epithermal neutron flux 4×10^{12} n cm^{-2} s^{-1}
detector has peak-to-Compton ratio of 25

FIGURE 1. Sensitivities of Neutron Activation Analysis.[1] Determination limits given in microgram per gram.

biomedical and environmental studies. Also, there are a number of elements that cannot be readily determined by NAA, including several of the lighter elements and some environmentally important elements such as lead. Finally, applications where a rapid turn-around time on a small number of samples is required, such as in diagnostic clinical analyses, may not be suitable for NAA, based on unit cost and/or processing time.

Table 1b
SELECTED APPLICATIONS OF NAA

Area	Ref.
NAA — archeology	25 (General); 26 (glass); 27 (ceramics); 28 (metal)
NAA — biology, medicine	29 (Nutrition); 30 (nerve); 31 (general); 32 (blood); 33 (bone); 34 (muscle)
NAA — environmental	35 (General); 36 (food); 37 (fish); 38 (general); 39 (metals); 40 (particles)
NAA — forensics	41,42 (General)
NAA — geology	43 (General); 44 (coal); 45 (meteorites); 46 (minerals); 47 (general); 48 (rocks)
NAA — industry	49 (Semiconductors); 50,51 (electronics materials); 52 (high-purity materials)

II. NEW METHODOLOGIES FOR NEUTRON ACTIVATION ANALYSIS

A. Neutron Sources

Characteristics of some common sources of neutrons for NAA are presented in Table 2.

The properties and applications of isotopic neutron sources for use in NAA have been summarized recently by Garg and Batra.[53] These sources have the advantages of simplicity of installation, low price, and freedom from many of the problems associated with the operation of a nuclear reactor. The low neutron flux produced by these sources limits their utility to the determination of high-abundance elements, or those with large cross-sections. The (α,n) sources are more commonly used than the photonuclear sources because they produce higher neutron fluxes, have a longer useful life, and produce less environmental gamma radiation. The ^{252}Cf fission source provides a higher neutron flux, but is also more expensive.

Accelerators commonly used for neutron production include sealed-tube generators of the Cockroft-Walton type, cyclotrons, and Van de Graaff accelerators. A handbook on the use of small accelerators as neutron sources has been published recently by Csikai.[54]

Two new developments in the use of reactors as neutron sources are discussed in more detail. The first is the construction of facilities equipped to produce neutrons with subthermal energies and the use of these "cold neutrons" to enhance the sensitivity of PGNAA. The second is the operation of certain reactors in a pulsed mode to achieve extremely high neutron-flux densities for brief periods of time.

1. Cold Neutrons for PGNAA

Use of cold neutrons for analytical applications has only recently become a reality as new facilities for this purpose are constructed. Cold neutrons have energies of about 0.005 eV. This low energy means that the neutrons have large deBroglie wavelengths, which result in larger capture cross-sections. The enhanced wave properties of the cold neutrons also lead to the possibility of guiding and even focusing beams of cold neutrons. Very low-energy neutrons have been used for some time by physicists to study the fundamental properties

Table 2
CHARACTERISTICS OF SOME NEUTRON SOURCES[a]

Reaction	Half-life	Neutron energy (MeV)	Neutron yield ($n\ s^{-1}\ Ci^{-1}$)
Photonuclear sources			
^{24}Na with ^{9}Be	15 h	0.2	1.4×10^{5}
with D_2O		0.8	2.9×10^{5}
^{88}Y with ^{9}Be	108 d	0.16	1×10^{5}
with D_2O		0.3	3×10^{3}
^{124}Sb with ^{9}Be	60 d	0.02	1.9×10^{5}
Alpha emitter (α,n) sources			
^{210}Po with ^{9}Be	138 d	4.3	2.5×10^{6}
with ^{10}B		4.3	5×10^{5}
^{226}Ra with ^{9}Be	1620 y	3.6	1.1×10^{7}
^{241}Am with ^{9}Be	458 y	4	2.2×10^{6}
with ^{10}B		4	5×10^{5}
^{242}Cm with ^{9}Be	163 d	4	4×10^{4}
Spontaneous fission sources			
^{252}Cf	2.65 y	2.3	$2.3 \times 10^{12}\ n\ s^{-1}\ g^{-1}$
Cockroft-Walton accelerators			
$^{3}He(d,n)^{4}He$	—	14	$10^{8} - 10^{11}\ n\ s^{-1}$
Cyclotron			
10 μA of 30 MeV deuterons on Be	—	Broad distribution	$2 \times 10^{11}\ n\ s^{-1}$
Nuclear reactor			
Fission	—	Distribution	$10^{12} - 10^{18}\ n\ cm^{-2}\ s^{-1}$

[a] Adapted from Garg, A. N. and Batra, R. J., *J. Radioanal. Nucl. Chem.*, 98, 167, 1986.

and interactions of the neutron.[55] Only recently have they been used as activating particles for analytical applications.

In PGNAA the prompt gamma rays that result from decay of nuclear states excited during neutron capture are used for analytical purposes. PGNAA is complementary to simple, delayed-gamma NAA, because it is often used for determination of major abundance elements in natural samples (e.g., H, N, S, Si, C, and P) for which NAA is relatively insensitive. PGNAA is also a satisfactory technique for determination of a few especially sensitive trace elements, such as B and Cd. Reviews of the principles and applications of PGNAA have been published recently by Lindstrom and Anderson,[56] Anderson et al.,[57] and Glascock.[58]

In their original work, Isenhour and Morrison[59,60] noted that PGNAA would be superior to delayed-gamma NAA for many elements in the intensity of gamma-ray emission if equal neutron fluxes could be attained. In practice, PGNAA has been used much less than NAA. The necessity for simultaneous irradiation and measurement creates a difficult experimental situation. Location of counting facilities in proximity to the reactor can cause problems with

very high gamma-ray and scattered neutron backgrounds. The presence of these backgrounds can result in poor detection limits due to low signal-to-noise ratios. Reduction of the background mandates a large amount of shielding for the detector system. The shielding itself then becomes an additional source of interferences as neutron-induced reactions take place with the shielding material, producing prompt capture gamma-ray emission. Other problems associated with PGNAA include low sample throughput, because only one sample at a time is irradiated, and the lower neutron fluxes in an external beam compared with internal reactor core irradiation positions.

The use of cold neutron beams for PGNAA can alleviate several of these problems. Because the neutron guide tubes permit the sample-detector facility to be located farther from the reactor, the background can be reduced considerably. In addition, cold neutron beams are relatively free of gamma rays and higher-energy neutrons that can induce interfering reactions.

Special facilities are required for the production and use of cold neutron beams. The cold source (such as liquid D_2) is placed in a region of high neutron flux density in the reactor, and a neutron guide tube is provided to extract beams of cold neutrons from this source. Inside the guide tubes, the cold neutrons undergo internal reflection with little loss, while the flux of higher-energy neutrons and gamma rays decreases as $1/r^2$ from the reactor core. Thus, a high-quality beam of low-energy neutrons can be guided to experimental areas well removed from the reactor (tens of meters). The combination of enhanced capture rate (due to the higher cross section for the cold neutron interactions) and improved experimental conditions should generally lead to an increase in PGAA sensitivity for the elements being determined.

Worldwide, there are only a few facilities now equipped for cold neutron activation analysis. The ELLA Neutron Guide Laboratory at the FRJ-2 (DIDO) reactor of the Nuclear Research Center Juelich was the location of the first experimental demonstration that the predicted advantages of cold neutron PGNAA could be realized in practice. Lindstrom et al.[61] obtained clean, low background neutron beams with a flux density of 8.4×10^8 n cm^{-2} s^{-1}, and cadmium ratios (Au) of 1.0×10^4, from the liquid hydrogen cold source. The facility has been used to analyze standard reference materials as well as a variety of "real" industrial, biological, and environmental specimens. The sensitivity for PGNAA (expressed as counts s^{-1} g^{-1}) was a factor of 4.5 times higher than that presently attainable at the University of Maryland-National Bureau of Standards thermal neutron PGNAA facility.

A limiting factor for the sensitivity of cold neutron PGNAA is the presence of large amounts of hydrogen in the samples. The capture cross-section of H for cold neutrons is high, and the capture gamma ray at 2223.2 keV contributes strongly to the Compton continuum. This results in decreased sensitivity for elements with analytical peaks at lower energies. This problem has yet to be fully explored.

Only one other application of cold neutrons for an analytical problem was found in the published literature. Fischer et al.[62] used a cold neutron beam at the high-flux reactor in Grenoble to scan Rembrandt paintings for pigment analysis. The autoradiographs obtained in this work demonstrated the potential of this technique for activation of objects that are larger than the extracted beam.

The U.S. National Bureau of Standards Research Reactor facility has recently installed a cold source, and construction of a new experimental hall dedicated to cold neutron research has begun.[63] The facility is expected to be operational by the early 1990s.

An even greater enhancement of sensitivity could result from an increase in the cold neutron flux by using neutron optics to focus the neutrons on smaller areas. Focusing a 10 $\times$ 10-cm beam of 10^9 n cm^{-2} s^{-1} to a 1 $\times$ 1-mm area could increase the flux to 10^{13} n cm^{-2} s^{-1}, a very respectable value. Further focusing of the neutron beam would suggest the potential development of a neutron probe analogous to electron probe instruments, but this is still in the future.

Interest in the use of cold neutrons will continue to grow as additional facilities become available. Much basic research on the potentials and limitations of cold neutron PGNAA remains to be done.

2. Pulsed Neutron Sources for Short-Lived Nuclide Analysis

Research reactors for NAA are routinely operated in a "steady-state" mode, where the neutron flux remains relatively constant. However, some reactors, such as the TRIGA, can be operated in a pulse mode, in which the expulsion of a control rod from the reactor results in a brief (10 to 50 ms) power transient of up to the 1000-MW. Intense neutron flux densities equivalent to 10^{16} or 10^{17} n cm^{-2} s^{-1} can be attained during this pulse. Yule and Guinn[64] first demonstrated the feasibility of using the pulse mode of operation to enhance the sensitivity of NAA. They characterized the pulse operation of a TRIGA Mark I reactor and experimentally investigated the predicted enhancements by pulse activation for 13 elements with half-lives of less than 1 min. They demonstrated that the activity produced by pulse irradiation as compared with a steady-state saturation irradiation was $(70 \pm 20)/t_{1/2}$, where $t_{1/2}$ is the half-life in seconds of the induced activity. Hence, the greatest advantage was found for shorter-lived nuclides, as would be expected. Since that time, only a few laboratories have pursued pulsed NAA. Most of the work reported has dealt with development of the technique and characterization of the reactor pulses, with analyses reported for only a limited number of materials.

Miller[65] has characterized the pulse mode of operation of the TRIGA reactor at University of California at Irvine. The time needed to reach peak pulse power depended on the pulse size, and ranged from 245 to 285 ms after firing of the control rods. The FWHM (on a plot of reactor power level vs. time) of the pulses varied with pulse size. A 1000-MW pulse exhibited a FWHM of 12 ms, while smaller pulses had a larger FWHM. The pulse shape was nearly Gaussian, but exhibited increased tailing at lower power. Reproducibility of the pulses was evaluated by measurement of the induced activity of ^{108}Ag and ^{139m}Ce. Normalized sample activity varied within $\pm 2\%$ for pulses of a given size, but was $\pm 5\%$ for pulses of varying size. Miller also evaluated the activity enhancements produced for 1000-MW pulses relative to saturation irradiation at 250 kW, and found an average of $(46 \pm 4)/t_{1/2}$. He noted that matrices high in Al and O inhibit the detection of short-lived species.

James and Oyedele[66] reported on pulse operation of the TRIGA reactor at Texas A&M University. The FWHM of 1000-MW pulses at this reactor was 12.8 ms. The linearity of the activation, evaluated using normalized sample activity, was found to be poorer than that reported by Miller, with reproducibility for a given pulse size varying as much as $\pm$ 3.7%. Both authors note that timing uncertainties may become important sources of variation. This is especially true for smaller pulses, since the tailing observed at lower pulse magnitudes is significantly increased.

The principal advantages of pulsed NAA are the increased sensitivities for elements with short-lived indicator radionuclides and the relatively rapid analysis time, when compared with conventional NAA. However, use of pulsed NAA implies sole use of the reactor facility by one user. The reactor can be pulsed only about every 15 min, so sample through put is low. Rapid transfer systems are required, and high activities may mean that special detection systems must be designed to handle high counting rates. Therefore, the cost of analysis is greatly increased, and the method will probably be limited to special problems.

In a study aimed at elucidating the use of pulse activation analysis on "real" samples, James[67] concluded that there were few elements for which determination by conventional NAA would not also have been possible. One element and matrix for which the determination was appreciably enhanced by pulsed NAA was Se in botanical materials. Detection limits for Se were 0.35 and 0.05 μg g^{-1} for steady-state and pulse activation, respectively. No chemical separations had to be performed for the pulse activation. James also noted that problems exist for analysis of matrices high in Al, O, and Cl.

Grass[68] reported on the use of pulse irradiation in a study of the activation analysis of short-lived nuclides. NBS SRM 1648, Urban Particulates, was analyzed by a 140-MW pulse activation. The results of analysis for ten elements showed that agreement between the experimental and NBS certified values was very good.

B. Chemical Procedures and Sample Handling

One of the advantages often cited for the use of NAA as a trace analysis technique is its potential freedom from chemical blanks. In many applications, samples can be analyzed without any significant chemical treatment. This advantage has been exploited particularly since the advent of semiconductor, high-resolution detectors. However, there now seems to be more recognition that purely instrumental NAA cannot meet all the analytical needs of today. Pre- or postirradiation chemical treatments are desirable, or necessary, for many matrices of current interest. The increased availability of high-purity reagents, clean-room facilities, and the advances made in separation chemistry have made preirradiation processing more effective and less susceptible to contamination problems. Trace element researchers are also more cognizant of the sources of contamination problems that occur for trace and ultratrace determinations.

Preirradiation chemical processing is used in "molecular NAA"[69] and "derivative neutron activation analysis" (DAA).[70] Postirradiation chemical processing includes the traditional field of RNAA.

1. Sample Handling for Trace Analysis

All analytical chemists are faced with the task of obtaining samples for analysis that are truly representative of the material to be analyzed. In some cases (few of which exist in the real world), this task is not too difficult. Materials that are homogeneous, contain high levels of the analyte, have compositions in a narrow, constant range, and are convenient to handle would require little in the way of special handling precautions. However, in the past 20 years there has been great interest in the trace element analysis of much more complex materials, such as biological tissues, that meet none of the criteria listed above. For these materials, close scrutiny of all the procedures involved in sample procurement, treatment, and analysis is mandatory, if valid analytical results are to be obtained. This is especially true when elements that are commonly present in the environment (e.g., Al, Cr, Mn, and Se) are being determined at trace (μg/g) and ultratrace (ng/g) levels.

In the past 10 years, the problems of quality assurance in biomedical trace element analysis have been recognized and widely discussed. An excellent general reference is the 1984 report of an International Atomic Energy Agency (IAEA) advisory group.[71] This report covers sample procurement, storage, preservation, and separations. It also discusses analytical problems that are unique to NAA, including calibration methods, reactor neutron fluxes, and gamma-ray spectrometry considerations.

There are many articles dealing with specific aspects of quality assurance. Parr[72] has discussed technical considerations for sampling and sample preparation of biomedical samples. Versieck[73] discusses problems of sample collection, manipulation, and analysis with particular attention to the analysis of Mn, Cu, and Zn in human blood samples. Stoeppler[74] summarizes the analytical steps, from collection through analysis, that should be taken to ensure quality in the experimental determinations of metals in biological samples. Cornelis[75] discusses sample handling procedures for ultratrace element determinations, including clean-room conditions, cleaning of laboratory ware, reagent quality, and good laboratory practices. Lux et al.[76] discuss the minimization of blank values from the implements used in sampling, including scalpel abrasion, sample homogenization implements, and external contamination of quartz vials. Iyengar and Kollmer[77] and Iyengar[78] have discussed the criteria for proper selection of biological tissue for a particular investigation. Statistical procedures for assessing the validity of analytical results have been developed by Heydorn.[79]

2. Preirradiation Chemistry

Reasons for preirradiation processing of samples include:

1. An interest in characterizing specific molecules to which trace elements are attached
2. A desire for information about the general speciation (organic-inorganic, oxidation state) of the element
3. The need to remove matrix elements that interfere with determination of the analyte
4. Use of a short half-life indicator radionuclide product of the analyte that precludes the possibility of postirradiation separation
5. The requirement for preconcentration for analysis of elements at ultratrace levels
6. The need to substitute a surrogate indicator element for the element of interest in order to enhance sensitivity

The increase in reports of preirradiation separations followed by NAA makes it appear that NAA will soon take its place among the already wide array of analytical "hyphenated techniques", in which two instruments or techniques work together to perform a task that could not be adequately undertaken by one alone. Braun et al.[80] have provided a useful review of many separation procedures used for preirradiation treatment.

a. Preconcentration and Group Separation

There are situations in which no analytical technique is able to detect directly the very low levels of an analyte in specific matrices. A wide variety of preconcentration schemes have been developed to overcome this difficulty.

Wu et al.[81] explored the feasibility of using hydride and mercury generation techniques to preconcentrate As, Hg, Sb, and Se in biological matrices prior to NAA. Samples were digested using a wet-oxidation procedure and placed in the hydride/Hg generation and collection system. The hydrides and elemental Hg collected were then determined by NAA. The authors note that there are interference effects in the generation process due to the presence of transition metals, oxidizing agents, and organic materials. The oxidation state of the element can also affect hydride production. Analyses of three National Bureau of Standards standard reference materials (NBS SRMs) showed good agreement between experimental and certified values for these elements at the microgram-per-gram level.

Huang et al.[82] used a preconcentration step to determine very low levels of Pt, Os, and Ru in ores and purified copper samples. A cation-chelating resin synthesized at Nankai University was used to perform group separation of the noble metals. Ore and copper samples were dissolved and passed through the chelating resin, which was subsequently ashed and irradiated for analysis. Analysis of the MOSNM ore sample (Managing Ore Sample of Noble Metals) verified the efficacy of this procedure.

Duke and Smith[83] reported a group separation procedure for low levels of rare earth elements (REE) in geological materials based on a cation-exchange separation. Yield determinations were done by mass spectrometry isotope dilution.

b. Molecular and Derivative Neutron Activation Analysis

"Molecular NAA", as used here, will include all types of procedures aimed at obtaining information about the specific molecules to which trace elements are attached, or about the chemical state (e.g., oxidation state, type of chemical combination) of the element itself.

Stone et al.[84] combined preirradiation electrophoresis with NAA to characterize trace elements in metalloproteins and to qualitatively detect the presence of proteins on a gel. In electrophoresis, protein bands are usually detected through staining procedures, or by autoradiography, if the proteins have been previously labeled with an appropriate tracer. Stone et al. irradiated entire gels (or sections of gels) and used the activity produced by all activable

elements in the protein bands to produce autoradiographs. They demonstrated that the autoradiography method was more sensitive for the P-containing protein phosvitin than was the traditional staining method with Coomassie Brilliant Blue.® An extension of this approach was to irradiate only certain bands of proteins that had been removed from the gels, and use INAA to determine the trace elements present. Bands for proteins known to be associated with zinc did show elevated Zn concentrations.

Frasch et al.[85] obtained quantitative information on protein content using a combination of silver staining and INAA. They incubated several proteins with a silver staining solution, separated the proteins by centrifugation, irradiated them, and counted for ^{108}Ag. For constant binding conditions, Frasch et al. found that the mole ratio of Ag to protein was constant, so determination of Ag by gamma-spectrometry could be used to obtain quantitative information on protein concentrations.

Snapka et al.[86] described an indirect-labeling technique in which proteins were separated by gel electrophoresis, bound to ligands containing highly activable elements (such as ^{55}Mn), and then irradiated.

Gallorini et al.[87] used temperature-controlled pyrolysis of solid biological samples to separate organic and inorganic As. The organic As was vaporized and trapped on an AG 50-X4 cation-exchange resin, while inorganic As was retained in the pyrolysis vessel. The column containing the organic As and the quartz boat with the residual inorganic As were irradiated and the concentrations of As determined. The method was applied to samples of commercial frozen shrimp, NBS SRM 1566 Oyster Tissue, and NBS SRM 1571 Orchard Leaves. The As results agreed well with NBS certified values for the SRMs.

Salbu[88] used size-fractionation techniques to investigate the physicochemical forms of trace elements in natural waters. Visking dialysis cells with a molecular weight cutoff of 10^4 were filled with deionized distilled water and submerged in the water sample. Diffusion of low molecular weight species into the dialysis membranes occurred. After equilibrium was established, the contents of the cells were transferred to irradiation vials and analyzed.

Blotcky et al.[89,90] used ion exchange separation to quantify the amounts of trimethylselenonium ion (TMSe) in urine. A single-step anion-exchange procedure was developed to separate TMSe and inorganic Se from each other and from organic Se compounds. Treated urine samples were passed through a Bio-Rad AG-2-X8 resin that effected a clean separation of TMSe from inorganic Se and from organic Se. Eluted fractions were irradiated separately for 20 s, and the ^{77m}Se activity assayed. Concentrations of TMSe and SeO_3^{2-} were calculated using the method of standard additions. The limit of detection for urine specimens from 13 normal subjects was 10 ng Se per milliliter.

Another type of preirradiation treatment is exemplified by derivative activation analysis (DAA). In DAA, an element of interest that is poorly determined by NAA is exchanged or complexed with a surrogate element that is easily determined by NAA. After the chemical processing, the sample is irradiated and the amount of the element of interest is inferred from the measured activity of the surrogate element. The principles of DAA have been discussed by Young.[91]

The few DAA procedures that have been developed have been summarized recently by Ehmann et al.[70] They include the determination of Mg by chelation with 5,7-dibromo-8-hydroxyquinoline and measurement of the ^{82}Br activity;[92] determination of Si by complexation with molybdosilic acid and measurement of the ^{101}Mo-^{101}Tc activity;[93] determination of P via formation of a phosphovanadomolybdate complex with measurement of the ^{52}V activity;[94] and determination of Ni by substitution of Au for Ni in a nickel-dithiozone complex.[70]

DAA can also give some speciation information. Ehmann et al.[70] determined the hydroxyl and carbonyl functionalities in coal using DAA procedures. Hydroxyl groups were converted to silyl ethers by reaction with hexamethyldisilazane and the increase in Si, as measured by

Table 3
PREIRRADIATION SEPARATION PROCEDURES

Method used	Material analyzed	Elements determined	Ref.
DDTC-extraction	Seaweed	Fe, Co, Ni, Cu, Zn	95
NiS fire assay	Geological	Pt group	96
Ion exchange	Rainwater	24 Elements	97
Sublimation/ filtration	Geological	Pt, Ir, Au, Ag, Re	98
Solvent extraction	Geological	Rare earths	99
Liquid chromatography	Geological	Noble metals	100

14-MeV FNAA, was used to infer the hydroxyl concentrations. Carbonyl groups were reacted with hydroxylamine to form oximes. Fourteen-MeV FNAA was used to determine the N in derivatized and oxime-decomposed coal, and the carbonyl content was calculated from the difference.

Table 3 lists some selected recent publications reporting preirradiation separation schemes.[95-100]

3. Postirradiation Separations

Postirradiation separations are generally preferable for trace element NAA determinations, since any extraneous addition of elements during processing would not contribute to the induced radioactivity of the sample. The use of RNAA waned following the introduction of high-resolution semiconductor detectors. However, the need for high sensitivity and accuracy in the analysis of complex matrices, such as biological tissues, has sparked renewed interest in performance of RNAA procedures.

The purpose of performing separation procedures after irradiation is the isolation of a single analyte element or group of elements from the sample so that greater sensitivity and selectivity is attained. Alternatively, the removal of specific interfering species may be the goal of the separation procedure.

In RNAA, the irradiated sample is dissolved, the element(s) of interest separated using techniques common to a variety of analytical approaches, and the fractions then assayed for the radioactivity of the analyte. Special considerations in RNAA center around precautions needed for handling radioactive materials and the very small amounts of active material that are actually present. This latter factor leads to the necessity of adding a chemical "carrier" to the solutions. The carrier, which is generally chemically identical to the analyte, provides a more easily manageable amount of material for the separations. It also provides the analyst with a way to determine the efficacy of the separation process. The chemical yield can be determined from a knowledge of the amount of carrier added and that recovered at the end of the separation.

There is copious literature on RNAA procedures that have been developed for application to a variety of sample types. Dissolution methods vary widely according to sample type. Ion exchange and solvent extraction are commonly used methods of separation, although many special schemes exist for specific elements and matrices. Some procedures are based on group separations, while others aim at one or only a few elements. Counting of separated fractions can be on HPGe or Ge(Li) detectors, but often the radiochemical purity of the fraction will permit use of the higher efficiency (but lower resolution) NaI(Tl) scintillation detectors. In some cases high-efficiency beta counting with a liquid scintillation counter may even be possible.

Table 4
SELECTED RECENT RNAA PROCEDURES FOR GEOLOGICAL, BIOLOGICAL, AND ENVIRONMENTAL SAMPLES

Element(s) determined	Sample type	Ref.
Rare earth elements	Geological	106-112
	Biological	113,114
Noble metals	Geological	115-120
Np, Pu, Am, Cm	Environmental	121
As	Biological	122
Cd	Biological	123-126
Cu	Biological	122, 123, 125-128
Hg	Biological	124, 125
Mn	Biological	123, 128
Mo	Biological	123
Se	Biological	125-127
Zn	Biological	122, 124-127

It is impossible in this review to discuss all aspects of RNAA and its applications. Therefore, a summary of the major types of matrices and of representative elements for which RNAA methods are most often used is presented. More extensive tables, giving information on element(s) determined, sample types, and procedures used, are given by Erdtmann and Petri.[101]

Geological samples are frequent targets for RNAA separations, especially for the determination of some REE and the noble metals. Both of these groups are reasonably difficult to determine at trace levels by other analytical methods. Laul[102] has reviewed the various separation procedures used with activation analysis of geological materials. Moebius[103] has discussed RNAA procedures for transuranium elements.

The determination of trace impurities in ultrapure and refractory materials can also be done by RNAA. As an example, many transition-metal impurities are often determined with thermal neutron RNAA. Krivan[104] has published a review of separation procedures for activation analysis of impurities in the refractory metals Hb, Mo, Ta, and W.

A third area for which large numbers of RNAA procedures have been developed is in the analysis of biological tissue. The elements As, Cd, Cu, Hg, Mo, Se, and Zn are frequent targets for these separations. Pietra et al.[105] have published a review of separation procedures for biomedical and environmental samples.

Table 4 presents a selected listing of some representative recent studies that have used RNAA.[106-128]

4. Activable Tracers

There are many situations in which radioactive tracers would be useful for a study but cannot be used for reasons such as the health and safety of a subject or the potential for environmental contamination. In these cases, activable tracers offer an attractive alternative. A stable isotope of the element of interest that is susceptible to determination by NAA is put into the system or subject to be studied. Samples are subsequently taken and can then be irradiated for analysis.

Zeisler and Young[129] demonstrated the use of the stable isotope ^{50}Cr as a tracer for blood volume measurements in pregnant women. The determination of ^{50}Cr at the low levels found in blood samples (<1 ng/ml) is a difficult problem for NAA, so highly thermalized fluxes and low background spectrometry were needed for the INAA procedures. The blood volume

measurement was done using the ratios of induced activity of ^{51}Cr to ^{59}Fe in three blood samples taken from each subject.

Infants are another group of subjects with whom radioactive tracers cannot generally be used. Whitley et al.[130] determined the bioavailability of Fe and Cu in infant food by addition of the stable isotopes ^{58}Fe and ^{63}Cu to the foods given to the infants. Fecal material was collected from the infants, and ^{59}Fe was determined by INAA, while ^{63}Cu was determined by an RNAA procedure.

C. Counting Systems

Instrumentation for NAA has not undergone revolutionary developments in recent years, but it is affected by many of the same trends seen for analytical instrumentation in general. These trends include increased use of more intelligent computer systems for control of all aspects of sample handling and data reduction, use of personal computer (PC)-based instruments, implementation of robotics (e.g., in chemical processing and sample transfer in counting), and automation of analysis procedures under computer control.

1. Detectors

The workhorses of the INAA laboratory are the NaI(Tl) scintillation detector, the Ge(Li) detector, and, more recently, intrinsic or high-purity-germanium (HPGe) semiconductor detectors. Among these detectors, one noticeable trend is the shift toward the use of the intrinsic germanium detectors that do not need continuous cooling. Intrinsic germanium detectors with high relative efficiency (40 to 60%) and high resolution (<2.0 keV) are now readily available and prices appear to be declining. The excellent peak-to-Compton ratio for these detectors makes the use of NaI(Tl) or bismuth germanate (BGO) Compton suppression systems less essential for NAA. These detectors are a boon to those working at the trace and ultratrace levels in complex matrices. Knoll[131] has reviewed some recent developments in gamma ray detectors, including advances in inorganic scintillation materials (such as BGO and barium fluoride, BaF_2), photodiodes as substitutes for photomultiplier tubes, passivated planar Si detectors, and cryogenic and superconducting detectors.

The BGO detectors with their high efficiency, good mechanical properties, and resistance to radiation damage would appear to have potential usefulness for *in vivo* NAA studies. They are also used in Compton suppression anticoincidence spectrometer systems. The good timing characteristics of the BaF_2 and CsF detectors are not usually of interest to activation analysts.

Photodiodes have the advantages of better energy resolution, lower power consumption, more compact size, and improved ruggedness as compared with photomultiplier tubes. Many X-ray CT scanners used for medical imaging have already adopted the photodiode detectors.

The passivated planar Si detectors are fabricated using ion implantation and photolithography. The resulting detectors have very low leakage currents and excellent operating characteristics. Aggarwal et al.[132] have evaluated these detectors in the measurement of naturally emitted alpha radiation from plutonium. Few NAA applications make use of charged-particle detection, however.

The cryogenic microcalorimeters measure the tiny temperature change induced by an incident particle in a very small sample of material (such as Si or diamond) maintained at temperatures of 1 K or less. Because the pulse produced does not consist of charge-carrier particles, the limits on energy resolution are theoretically many times better for the microcalorimeters than for normal pulse-mode detectors. Single microcalorimeter detectors are best for weakly penetrating radiations, such as low-energy X-rays. Some early work has already shown that X-ray energy spectra obtained with these detectors have five times better energy resolution than those obtained using Si(Li) detectors.

The superconducting grain detectors consist of materials, such as Sn and In, that change

from a superconducting to a normal state when the temperature is raised only slightly. In a very small particle of such material, incoming ionizing radiation can produce sufficient heat to cause this transition. Initial analytical applications of these detectors will probably be for detection of heavy charged particles or recoil nuclei.

No mention is found in the literature surveyed regarding the use of these three latter detectors in activation analysis, but potential for their application exists.

An unusual detection scheme for NAA was recently reported by Clarke et al.[133] They used mass spectrometry (MS) to detect the products of a neutron-irradiated sample. Lithium and B are present at very low levels in biological materials, and are not easily determined by conventional INAA, since neither produces a convenient indicator radionuclide. However, Li has a high cross-section for the $^{6}Li(n,^{3}He)^{4}He$ reaction, and B for the $^{10}B(n,^{4}He)^{7}Li$ reaction. Sample irradiations were done at the McMaster reactor and at the NBS reactor for periods of 3 to 10 h at thermal fluxes of 8×10^{12} and 3.3×10^{11} n cm^{-2} s^{-1}, respectively. The ^{3}He and ^{4}He produced in these reactions were detected by a mass spectrometer that had been specifically designed for isotopic analysis of small He samples. The procedure was used to measure Li and B levels in blood samples.

2. Data Acquisition Equipment

The power of the personal computer (PC) continues to increase, and it would now be a rare instrumental laboratory that did not have at least one. Several companies offer a range of systems for PC-based analyzers. A listing of 15 suppliers of PC/MCAs was given in a recent issue of *Physics Today*.[134] Some of the systems (such as the *Personal Computer Analyzer [PCA]* from the Nucleus, and the *ACE* system from ORTEC) use internal cards for the ADC and MCA functions, thus eliminating the need for external NIM modules. Other types of PC-based systems have external ADC/MCA modules that fit into standard NIM bins. Examples of the latter type include the ORTEC *ADCAM* system, Nuclear Data's *MicroMCA,* and Canberra's *System 100.* Prices of the basic units (not including the PC) typically range from $3000 to $5000, with options potentially doubling the price. These MCAs can run on a basic PC with dual floppy disk drives and at least 320K memory, but efficiency of operation is greatly enhanced through use of upgraded PC systems with additional memory, hard disk, and mouse. The internal card-based systems are less costly and are well suited for instructional applications. The three external bin systems are more costly, but have generally higher performance characteristics.

PC-based analyzer systems can provide the user with a relatively low-cost MCA that is also versatile, since the PC can be used separately. These systems will certainly be improved and can be coupled with more sophisticated software as demand for them increases.

Many laboratories have developed their own PC programs for INAA use. Nelson[135] reported one such program (CINA) that uses a PC microcomputer for INAA computations after data transfer from a conventional MCA. Many other examples of PC-software for INAA applications are given in Ehmann and Yates.[23,24]

3. Robotics and Automation

Use of robotics to automate repetitious or dangerous laboratory operations is growing very rapidly. Only a few reports have appeared in the literature on the use of robots in NAA systems. Yagi et al.[136] and Thompson et al.[137] both discussed the use of a robot as a sample changer to automate counting procedures. Stalnaker et al.[138] describe the use of a robotic system to prepare samples for Pu and Am determination. The robot performs dilution and extraction procedures on these radioactive materials. No doubt there are many other activation analysis laboratories where robots are used for these and other functions. Besides the usual advantages that robots have in any analytical laboratory (error reduction and increased productivity), the safety aspect is a primary advantage in radiochemistry laboratories, because robots can perform many hazardous operations.

Future developments in the use of robotics in NAA would probably include use of robots in more phases of the preirradiation sample handling, in RNAA, and also in the integration of robot technology with "expert-system" control.

In laboratories where very large numbers of samples must be processed, computer control of the entire analysis procedure is essential. Grossman and Baedecker[139] described a system used at the U.S. Geological Survey (USGS) to analyze over 3000 samples per year. At the Interuniversity Reactor Institute (IRI, The Netherlands), Bode et al.[140] have implemented a fully automated microprocessor-controlled facility to perform INAA on short-lived nuclides. As with robotics, no doubt there are many other laboratories that have adopted at least some degree of automated control of their operations.

4. Activation Analysis with Short-Lived Nuclides

In September 1987, the Second International Workshop on Activation Analysis with Short-Lived Nuclides was held in Vienna, Austria. Sessions dealt with transport and measurement systems, data processing, and applications in life sciences and geoscience. The proceedings of this workshop are to be published in 1988 in the *Journal of Trace and Microprobe Techniques*.

The analysis of short-lived nuclides (half-life $\leq$1 min) is practiced routinely at only about a dozen centers worldwide. Such analyses require special operating conditions that include very fast transport systems, data acquisition equipment that can handle high counting rates, and data-reduction procedures that can correctly process the accumulated data. An advantage of analysis with short-lived nuclides is the rapid sample turnover. The short-lived indicator nuclides are, in most cases, as sensitive as those used for conventional NAA. For elements like B and Pb, the short-lived radionuclides are the only ones available.

With the very high count rates that occur in the activation of short-lived nuclides, the usual live-time or pulse generator correction methods cannot be applied because the counting rate changes significantly during the counting period. This problem has been dealt with by Westphal[141] and Westphal and Kasa[142] by use of a virtual pulse generator correction method. This method does not use artifically injected signals, but uses a correlative test of amplifier baseline and MCA status to correct for counting losses.

Kennedy et al.[143] described a different approach for short-lived activation analysis, based on an IBM-PC, that used the analysis program to correct for counting losses. Zimmer[144] has described a specific gamma-spectroscopy system that can produce useful analytical spectra even at counting rates of 1 million 1-MeV photons per second.

Improvements in instrumentation systems used for high count rate gamma-spectroscopy have been discussed in detail by Westphal et al.[145] and Westphal.[146] Readily available commercial hardware to handle high count rate situations would encourage the expanded utilization of short-lived indicator radionuclides in INAA.

The actual performance of short-time activation analysis is fraught with potential experimental difficulties. Special transfer systems must be installed at the reactor facility. The rapid transfer process itself can cause problems due to the high acceleration and deceleration of the rabbit into and out of irradiation positions. As time of analysis decreases, the potential for errors introduced by timing uncertainties is increased. Loss-free counting techniques are very sensitive to electronic instability. Also, since loss-free counting introduces events into the peaks of interest that are not actually observed, the counting statistics can no longer be used directly as an *a priori* estimate of precision.

D. Data Processing

1. Processing of Counting Data

The tremendous amounts of data that can be generated by INAA with high-efficiency, high-resolution semiconductor detectors will require new approaches to data reduction. Better

algorithms for peak-fitting are needed, and greater reliance will be placed on computers to calculate detection limits and accurately estimate errors. Techniques that can extract pattern information from large data sets generated by multielemental NAA, such as factor analysis and cluster analysis, will become more familiar to analytical chemists and used increasingly.

Our reliance on "expert systems", "intelligent computers", and computerized data handling should not develop into blind use of these tools. Quality assurance must remain at the forefront of all analytical procedures, and programs for determinations of peak areas and calculation of elemental concentrations must be continually evaluated and improved. Computerized peak-fitting routines have been checked for precision and accuracy by several workers. Christensen and Heydorn[147] evaluated several commercial computer peak-fitting programs (Nuclear Data, ORTEC, SAMPO80, and a modified Covell method) for their ability to correctly resolve partially overlapping peaks, specifically the 843.8 and 846.6 keV ^{27}Mg-^{56}Mn doublet. They concluded that the Nuclear Data and SAMPO80 programs are best for doublet detection, but the ORTEC GELIGAM and SAMPO80 gave the most reliable calculation of peak areas in statistical control. Koskelo[148] evaluated the relative merits of parabolic, linear, and step functions for background determinations under a photopeak as used in the Canberra APOGEE package. He concludes that all these methods of background determination can be brought into statistical control in stable measuring conditions, but the parabolic background appears to be the least desirable for representing the data.

Factor analysis and cluster analysis are statistical procedures that can be used to extract information from very large and complex sets of data. In cluster analysis, the observations are sorted into groups so that the degree of association among members of one group is high, while that among the different groups is low. In factor analysis, the aim is to account for the correlations among the observations in terms of a small number of hypothetical variables or factors. Op de Beeck[149] has provided an excellent explanation of clustering techniques.

Cluster analysis techniques have been used for some time in the INAA of archeological objects because trace element patterns of these objects can give information on the place and, indirectly, the time of their origin. Hopke et al.[150] described several multivariate statistical methods used in the study of Turkish potsherds. Both supervised and unsupervised pattern recognition techniques were used in the analysis. The unsupervised methods included both hierarchical and nonhierarchical approaches. This study concentrated on the description of the statistical methods used rather than on the significance of the archeological results.

Unlike many archeological studies, where the object to be classified has a single identity or origin, environmental pollutants normally consist of components from a variety of sources. Therefore, a different approach, factor analysis, is commonly applied to these environmental materials. DeBruin et al.[151] describe an elaborated factor analysis approach, called Target Transformation Factor Analysis, used to identify sources of heavy metal air pollution.

2. Advance Prediction Computer Programs (APCPs)

The APCPs enable an analyst to calculate, without experimental measurements, the gamma-ray spectrum expected from a sample, given basic information about the likely elemental composition, neutron flux, irradiation, decay, and counting times, sample mass, and maximum allowable gamma-ray counting rate at the start of the counting period. Use of such programs can eliminate much lengthy and tedious laboratory work and can be especially useful for remote users of reactor facilities. They would also be useful for analyses of industrial materials where matrix compositions are often well-defined and where evaluation of on-line analyses within compositional limits is required. Details of an APCP have been described in several publications from the group at the University of California at Irvine.[152-155] One version of the APCP, written in BASIC-PLUS, includes the (n,γ) products from both thermal and epithermal NAA. Another version, written in FORTRAN-IV, also

includes fast neutron irradiation products, both from fission spectrum and 14-MeV neutrons. These programs have been tested extensively and the predictions are found to agree well with observed spectra.

The APCPs continue to undergo improvements and expansion for new irradiation conditions. Most recently, they have been developed for activation by high-intensity reactor pulses and for purely epithermal fluxes. Programs are in preparation for PGNAA, for X-rays emitted after NAA (using LEPS detectors), and for cyclic INAA.[156]

Burgess[157] has explored the use of interactive computer graphics to obtain optimum operating conditions for INAA. The adjustable experimental parameters of NAA and the analytical response to various values of these parameters (as determined by an APCP) are graphically displayed. The response surfaces thus generated can be observed and optimum conditions selected for a given problem.

3. Comparator Standards

An important advantage of INAA is its capacity for simultaneous multielement determinations. This feature has assumed increasing importance in biomedical research, environmental studies, and geological analyses, where symbiotic or antagonistic interelemental relationships are of interest. Prior to the widespread availability of high-quality multielemental reference standards, a primary standard was prepared and irradiated for each element to be determined by INAA. This method of standard preparation is still recognized as the ideal approach to INAA.[158] However, there are several practical drawbacks to this approach for multielement studies. These include the time needed for individual standard preparation, possible errors during preparation, the large number of standards and resulting irradiation unit space needed if many elements are to be determined, and the lack of ability to determine elements whose indicator radionuclides are found unexpectedly in the samples. Therefore, it was desirable to devise new approaches to simplify the practice of multielement INAA. Alternative approaches include the use of standard reference materials, single comparator methods (including the k_0 method), and synthetic multielement standards.

a. Standard Reference Materials (SRMs)

SRMs such as those available through the U.S. National Bureau of Standards and the IAEA in Vienna continue to be used as primary standards in many INAA studies. These reference materials are usually carefully homogenized natural materials. Becker[158] noted that 60% of the multielement studies reported in the *Journal of Radioanalytical and Nuclear Chemistry* for 1984 and 1985 used SRMs as their primary standard. The use of SRMs in this manner has been frequently and severely criticized,[71,159] since uncertainties in the certified values may be quite large for certain elements. In addition, many analysts use quantities of the SRM below the recommended size on which homogeneity tests have been based. This problem is minimized by some analysts by pooling the results of multiple small standards in a given irradiation unit. Finally, routine use of SRMs as primary standards can rapidly deplete the supplies of these laboriously prepared and expensive materials.

Use of SRMs as primary standards is somewhat more acceptable in comparison studies, where absolute values are of less importance than knowledge of relative differences between groups. The SRMs are also useful in laboratories where natural matrices similar to those available as SRMs are routinely processed and where preparation of a true primary standard in a suitable matrix would be difficult. In laboratories where many different types of matrices are analyzed, there is often no appropriate SRM available. Since SRMs are expensive, difficult to prepare, and available in limited amounts, their use is certainly not desirable in situations where very large numbers of samples are routinely processed. However, it seems likely that use of SRMs as primary standards will persist for some time.

b. Single Comparator Methods

The idea of using a single comparator for multielemental NAA instead of many individually prepared comparators is an attractive one because it would alleviate many of the difficulties cited above for preparation of multiple standards. Girardi et al.[160] were the first to critically evaluate this method for reactor neutron activation. From the basic equation of activation analysis (Equation 1), the mass of an element in an irradiated sample is

$$w = \frac{A_p M}{\Theta \Phi_r \sigma S D \gamma N \epsilon} \tag{3}$$

where w = mass of the element of interest, A_p = photopeak counting rate (N_p/t_m), N_p = peak area corrected for pulse losses, t_m = counting time, M = atomic weight of the element, Θ = isotopic abundance of target isotope, Φ_r = reactor neutron flux, σ = effective activation cross section for the neutron energy spectrum used, S = saturation factor ($1 - e^{-\lambda t}$), D = decay factor ($e^{-\lambda d}$), d = decay time, λ = decay constant, γ = absolute abundance of measured gamma ray, ϵ = full-energy peak efficiency of detector for measured gamma ray, and N = Avogadro number. The neutron flux (Φ) can be monitored by irradiation of a suitable monitor element and determined using the activation equation with known values of the parameters:

$$\Phi_r = \frac{A_p^* M^*}{w^* \Theta^* \sigma^* S^* D^* \gamma^* \epsilon^* N} \tag{4}$$

where the * refers to the monitor element. Substitution of Equation 4 into Equation 3 and rearranging gives

$$w = \left[\frac{M \gamma^* \epsilon^* \Theta^* \sigma^*}{M^* \gamma \epsilon \Theta \sigma}\right]\left[\frac{A_p S^* D^* w^*}{A_p^* S D}\right] \tag{5}$$

$$w = [k]\left[\frac{A_p S^* D^* w^*}{A_p^* S D}\right] \tag{6}$$

The quantity in the first set of brackets in Equation 5, defined as k, contains nuclear constants that could be evaluated from the literature, thus making this simply a variation of the absolute method. However, a different approach would be to determine k experimentally, by irradiation of a standard and a comparator, and calculate k from Equation 6:

$$k = \frac{A_p^* S D w}{A_p S^* D^* w^*} \tag{7}$$

Once the value of k has been determined, the amount of analyte in an unknown sample may be found by irradiating the sample together with a comparator and using Equation 6 to calculate the mass of the analyte element. A problem with the k factor defined in this way is that it is useful only for stable, well-thermalized irradiation conditions and fixed counting geometries. This, of course, limits the versatility of the method.

In order to make the k factors more versatile, De Corte et al.[161] introduced the concept of conversion of the k factors determined in one irradiation channel to k values for another channel with respect to the effective activation cross-sections. Using the relationships that

$$\Phi_r = \Phi_{th} + \Phi_e \tag{8}$$

and

$$\sigma = \sigma_{th}(\Phi_{th}/\Phi_r) + I_o(\Phi_e/\Phi_r) \tag{9}$$

and assuming that $\Phi = \Phi^*$, De Corte et al. defined the k factor as:

$$k = \frac{A_{sp}}{A^*_{sp}} = \frac{M^* \gamma \epsilon_p \Theta}{M \gamma^* \epsilon^*_p \Theta^*} \cdot \frac{\sigma_{th}(\Phi_{th}/\Phi_e) + I_o}{\sigma^*_{th}(\Phi_{th}/\Phi_e) + I^*_o} \tag{10}$$

where $A_{sp} = A_p/SDw$, Φ_{th} = thermal (subcadmium) neutron flux, Φ_e = epithermal neutron flux, σ_{th} = thermal neutron cross-section, and I_o = infinitely dilute resonance integral.

The k factor as defined here is the reciprocal of Equation 6, with a different expression for the cross section. De Corte et al.[161] showed that it would be possible to convert k factors determined in a reference channel to those in the analysis channel by determining the thermal-to-epithermal flux ratios, and they suggested a triple-comparator method for this purpose. This was an improvement upon the earlier methods, but still specific for a given reactor facility and counting arrangement.

Kim and Born[162] suggested a simplification for determining k factors by eliminating experimental determination of k and using only literature values for the nuclear data. The only experimental work needed would be the determination of the thermal-to-epithermal flux ratio and the efficiency of the detector. Kim[163] tabulated the physical constants needed for this monostandard method. Zaghloul et al.[164] recently reported analyses of 24 elements in Egyptian rock samples using this approach.

However, many authors feel that the tabulated nuclear data are not reliable enough to give the 3 to 5% accuracy level generally desired for analysis.[165] Therefore, Simonits et al.[165] proposed a new generalized k factor (k_o) that would couple the simplicity of "almost absolute" methods with acceptable accuracy. In contrast to the k factors defined above, which were valid only for a well-defined set of irradiation and counting conditions, the k_o factor would be generally applicable to all laboratories.

The theory and principles of the k_o method have been detailed in several papers.[166-169] The concept is similar to earlier approaches already discussed. The new k_o factor is defined as:

$$k_o = \left[\frac{M^*}{M} \cdot \frac{\Theta}{\Theta^*} \cdot \frac{\gamma}{\gamma^*} \cdot \frac{\sigma}{\sigma^*}\right] = \left[\frac{A_{sp}}{A^*_{sp}} \cdot \frac{(\Phi_{th}/\Phi_e) + (I_o/\sigma_o)^*}{(\Phi_{th}/\Phi_e) + (I_o/\sigma_o)} \cdot \frac{\epsilon^*_p}{\epsilon_p}\right] \tag{11}$$

The important difference in the definition of the k factor as given in Equation 11 is that now the factor contains only well-defined, invariable nuclear constants (M, Θ, γ, ϵ) and no terms that relate to the experimental conditions. Therefore, the k_o factors should be constants that are valid for any laboratory.

A value for k_o could be evaluated from available nuclear data, but this brings back all the problems associated with uncertainties in these data that exist in the absolute method. Therefore, the experimental determination of k_o factors, by use of the relationship in the second set of brackets in Equation 11, is preferable. Those quantities are all readily measurable in an activation analysis laboratory. Simonits et al.[166] note, however, that the k_o factors as defined in Equation 11 are valid only for cases where the epithermal neutron density distribution follows a 1/E shape, the nuclides have 1/v cross-sections up to 1 to 2 eV neutron energy, there are negligible burn-up effects or neutron or gamma absorption in the samples and standards, system dead time and pileup losses are negligible or corrected for, and the samples are point sources.

The actual determination of the k_o factors is not trivial. Careful attention must be given to possible sources of error in preparation of comparators and standards (to avoid neutron and gamma absorption and problems with nonstoichiometry), in measuring activity (dead time, pile up, etc.), in determination of detector efficiencies, and in determination of the thermal-to-epithermal flux ratio.[166] A project involving the Activation Analysis Laboratory of the Central Research Institute for Physics (KFKI, Budapest), and the Institute for Nuclear Sciences (INW, Ghent) was established to determine accurate k_o values and develop procedures for future corrections and refinements of the measured quantities. In 1980 this group presented tabulated k_o values and pertinent nuclear data for 32 nuclides,[166] in 1984 they reported on 72 nuclides,[168] and in 1987 on 94 nuclides.[170] These k_o factors were determined using a gold comparator. The 1980 and 1984 publications include extensive tabulations of the experimentally determined $k_{o,Au}$ factors and of pertinent nuclear data.

Many modifications have been made in the k_o factors to account for situations in which the requirements cited above are not met.[166,170] The k_o factors can also be adapted to more complicated decay schemes and to epithermal neutron activation analysis.[167]

A user-oriented outline of the k_o methods has been published recently.[170] The basic equation used for calculation of the concentration (P) of an element in a sample is

$$p(\mu g/g) = \frac{A_{sp}}{A^*_{sp}} \cdot \frac{1}{k_o} \cdot \frac{f + Q^*_o(\alpha)}{f + Q_o(\alpha)} \cdot \frac{\epsilon^*_p}{\epsilon_p} \qquad (12)$$

where $f = \Phi_{th}/\Phi_e$, $Q_o = I_o/\sigma_o$, and α = deviation of epithermal neutron flux from ideality.

To use the k_o method, the analyst must determine a reference peak efficiency curve for the detector to obtain values of ϵ_p. The value of f (the thermal-to-epithermal flux ratio) must be determined, along with α, the deviation of the epithermal flux from ideality. For a stable flux, these values can be determined one time using the Cd-ratio method for f, and a "Cd-covered multimonitor" method for α.[171] Determination of these values simultaneously with sample irradiation is also possible through irradiation of a 0.1% Au-Al wire and a thin Zr foil. The Au also serves as a comparator element. Best values for Q_o are obtained from the literature. Values for $k_{o,Au}$ are available from the tables cited previously. The activities of the samples must be determined after irradiation, and accurate values for the times of irradiation, decay, and counting must also be known. Computer programs that perform the necessary calculations have been developed.[170]

De Corte et al.[170] have provided extensive discussions of the parameters influencing accuracy and applicability of the k_o method, including the k_o values themselves, determination of Q_o values, corrections for non-1/E epithermal neutron flux distribution, geometry problems, primary interferences, and nonconstancy of the neutron flux during irradiation. They estimate the overall contribution of the application of the k_o method to the uncertainty of the analytical result to be approximately 4%.

c. Synthetic Multielement Standards

Another approach to the standardization problem is the preparation of synthetic multielement standards containing known concentrations of the elements of interest. The availability of such primary standard materials containing appropriate and accurately known amounts of the elements of interest for a given application would be very convenient for the analyst.

There have been only a few reports of such synthetic standards. The U.S. National Bureau of Standards has produced four multielement glass standards (SRMs 610, 612, 614, 616), with varying levels of trace elements. Rouchaud et al.[172] prepared multielement standards using both metallic and organic polymer matrices. The organic polymer seemed to give the more promising results. It is radiation resistant, can easily be dissolved after irradiation, and is sufficiently homogeneous to reduce the standard deviations to ±3%, or less, in comparisons between expected and observed values.

The Eastman Kodak Company now has available three NAA SRMs made of a gelatin matrix doped with trace elements. There is one short irradiation standard (containing Al, Mg, Ti, V, Cl, Mn, I, Rh, and Ir), and two long irradiation standards (containing Na, Au, Hg, Zn, Te, Sb, K, As, Se, Cu, Cr, Co, and U).

E. Current Applications of Traditional Techniques

1. Epithermal Neutron Activation Analysis (ENAA)

There have been relatively few recent advances in the area of ENAA. In this method, samples are placed into Cd metal or B-containing containers for irradiation. The Cd or B absorbs most of the thermal neutrons, while allowing neutrons of higher energies to pass through and activate the sample. Cadmium will absorb essentially all neutrons with energies less than 0.04 eV. Boron shows no sharp cutoff energy, but the cross-section exhibits a 1/v dependence that reaches a low value at approximately 280 eV. The advantage of ENAA is that the activities of indicator radionuclides for those elements with high resonance integrals (i.e., high cross-sections for epithermal activation) are enhanced compared to the activities of indicator radionuclides for elements normally activated principally by thermal neutrons. However, both activity levels are decreased significantly with respect to those in conventional INAA. ENAA is especially useful in geological and biological samples where activities produced by thermal neutron irradiation of Na, K, Cl, Al, and Mn can dominate the spectrum and mask the presence of other elements. General aspects of ENAA have been discussed recently by Alfassi.[173]

The advantage of ENAA over thermal NAA is usually expressed in terms of an advantage factor. The definition proposed by Brune[174] is widely used, but recently Tian and Ehmann[175] and Tian[176] proposed a new generalized advantage factor that not only includes improvements in counting statistics and detection limits, but also allows for the possibility of changes in counting geometry for samples irradiated by ENAA and thermal NAA. In ENAA, placement of the samples closer to the detector is usually possible, due to the lower gross activity levels.

Other recent work in ENAA has considered the advantages and disadvantages of Cd metal filters vs. those constructed of boron compounds. Although Cd is an excellent filter for thermal neutrons, with a ^{113}Cd cross-section of 1.99×10^4 b, there are some disadvantages associated with its use. Activity levels due to Cd radioisotopes are high following irradiation, and a long decay time is needed before the filter can be reused. Because of the high Cd activity, the determination of short-lived nuclides may be hindered by the precautions needed in opening the irradiation vessel. Cadmium is also known to be a toxic element, so care must be taken in fabrication and handling of the cans.

Several workers have investigated the possibility of using other high cross section materials as filters for ENAA. Ehmann et al.[177] found boron carbide filters to be a viable alternative to Cd for ENAA of geological samples. The containers are somewhat difficult to fabricate because the material is hard and brittle. However, they are corrosion resistant and can be used repeatedly with less decay time than Cd. Boron nitride containers were used by Glascock et al.[178] for ENAA of short-lived radionuclides. Substantial levels of ^{14}C can build up, however, due to the $^{14}N(n,p)^{14}C$ reaction.

More recently, Chisela et al.[179] have examined the use of both boron carbide and boron nitride filters for ENAA and discussed practical aspects of optimization of their design and construction. They determined 18 elements in NBS SRM 1566 Oyster Tissue and lyophilized human milk using BN and sintered B_4C filters for short (<20 min) and intermediate (1 h) irradiations, and a packing of powdered B_4C for longer irradiations (>24 h). They found ENAA to be effective for the rapid instrumental determination of ^{56}Mn, ^{76}As, ^{80}Br, ^{82}Br, and ^{128}I and for intermediate decay-time measurement of ^{76}As, ^{82}Br, ^{60}Co, ^{56}Mn, ^{87m}Sr, and ^{69m}Zn. ENAA was as effective as thermal NAA for ^{110m}Ag, ^{82}Br, ^{60}Co, ^{59}Fe, ^{99}Mo-^{99}Tc,

Table 5
RECENT APPLICATIONS OF TRADITIONAL ENAA AND FNAA TECHNIQUES

Technique	Material analyzed	Elements determined	Ref.
ENAA	Geological	17 Elements	186
	Geological	Rare earths and 17 others	187
	Coal	20 Elements	188
	Coal	U and Th	189
	Biological	11 Elements	190
FNAA	Coal	Major elements	203
	Air dust	Several elements	204
	Glasses and vitroceramics	Al	205
	Geological	Nb, Zr, Ti	206
	Coal	Major elements	207
	Fertilizers and plant samples	N, P, K, S	208
	Cyclic activation	22 Elements	209
	Monazite	Rare earths	210
	Geological	Oxygen	211
	Coal	Oxygen	212

Ni(^{58}Co), ^{86}Rb, ^{75}Se, and ^{65}Zn, and the measurements could be completed in a shorter time. Okada et al.[180] also investigated the effects of Cd, B, and Cd and B filters for ENAA of biological and geological samples. They concluded that sensitivities for In, I, Sn, Au, Sm, Yb, Ag and Se were improved using Cd filters, and that sensitivities for Ba, As, Mo, Br, Sn, Zr, Rb, and Ni were improved with B or B and Cd filters.

Williamson et al.[181] described a new ENAA irradiation facility at the University of Virginia Reactor that features a permanently fixed Cd shield. They characterized the reactor parameters and demonstrated its usefulness for analysis of I, Si, Ni, Zr, U, and Th. Holzbecher et al.[182] described the Cd-shielded irradiation facility at the SLOWPOKE reactor at Dalhousie University. A technique for reducing interferences in ENAA based on the existence of non-overlapping resonance peaks has been discussed by Tokay et al.[183]

There are relatively few new applications of ENAA in the current literature. Stroube et al.[184] used ENAA to determine the I content of foods. Iodine is difficult to determine accurately by thermal NAA and conventional analytical methods. Kennedy and Touhouche[185] used a B_4C filter to perform pseudocyclic ENAA of geological materials for Er, using the ^{167m}Er indicator nuclide. The detection limit was 0.5 μg/g. Other recent applications are listed in Table 5.[186-190]

2. Cyclic and Cumulative Activation Analysis

In cyclic activation analysis, the sensitivity and precision of activation analysis for short-lived radionuclides is enhanced by repeated activation of the sample and subsequent summing of the gamma-ray spectra produced in each irradiation. Spyrou[191] and Spyrou et al.[192] have published reviews of the general principles and usefulness of cyclic activation analysis. Cumulative activation analysis has a similar goal, but in this case many replicate aliquots of a larger sample are sequentially activated and the resulting gamma-ray spectra summed.

Jayawickreme and Chatt[193] used a combination of differential centrifugation and cyclic and conventional INAA to determine 23 elements in subcellular fractions of bovine kidney.

Concentrations of Ag, Rb, and Se were measured by cyclic activation, using an irradiation time of 20 s, a decay time of 10 s, counting time of 20 s, and 10 cycles. Al-Mugrabi and Spyrou[194] demonstrated that U could be determined through cyclic activation with detection of fission products. Papadopoulos[195] also reported a procedure for U determination that combines cyclic activation with intermediate sample storage and special data processing. McDowell et al.[196] determined Se in food items using cyclic activation for the ^{77m}Se nuclide. A detection limit of 3 to 5 ng/g was achieved with precisions of ± 1 to 5% and an accuracy of ± 7%. Cumulative NAA was applied to the determination of ^{197m}Au at milligram-per-kilogram concentrations in rock samples by Parry.[197] Use of this approach alleviated the problems of high ^{198}Au activity in large rock samples.

3. Fast Neutron Activation Analysis (FNAA)

FNAA is based primarily on (n,p), (n,n'), (n,2n), and (n,α) threshold reactions. Because fluxes of fast neutrons, whether from a reactor or from accelerators, are lower than those for reactor thermal neutrons, and because the cross-sections for fast neutron reactions are smaller than those for thermal neutron induced reactions, FNAA is used mainly for lighter elements not amenable to thermal NAA and for elements present at major and minor levels.

Fast neutron sources include Cockroft-Walton generators using the d(t,n)^{4}He reaction, Van de Graaff accelerators, cyclotrons, and the fast component of the neutron spectrum from reactors or isotopic sources. Schmidt[198] reported on a 14-MeV neutron generator tube based on the d-t reaction and constructed of glass, ceramic, and metal. The tube is compact, is sealed, and produces a yield of 6.5×10^{12} n s^{-1}. Cecil and Nieschmidt[199] have discussed the production of 3-MeV neutrons from a d-d, rather than a d-t, generator. A d-d generator would not experience the target deterioration that occurs in d-t tubes, since the target d would be continually replenished by the beam. However, H, t, and ^{3}He will build up, contaminating the 3-MeV neutrons with 14-MeV neutrons. Cecil and Nieschmidt have discussed the potential errors that could occur from such contamination.

Pepelnik[200] has published a comprehensive study of the sensitivity of 14-MeV FNAA. The KORONA irradiation facility at the GKSS Research Center Geesthact was used for the study. The analytical sensitivities for 78 elements were determined, using 770 reactions. Pepelnik also presents extensive tables listing relevant nuclear data for the 78 elements studied. Interference reactions were also considered.

A classic example of the application of reactor spectrum neutrons is the determination of Ni via the ^{58}Ni(n,p)^{58}Co reaction. This is perhaps the most sensitive NAA approach for Ni analysis. Tian and Ehmann[175] report this reaction has a generalized advantage factor of approximately 7×10^3 through use of thermal neutron filters rather than conventional thermal NAA for the determination of Ni.

An unusual application of 14-MeV NAA reported by Jayanthakumar and Bhoraskar[201] involved the determination of the thickness of Si films deposited on a glass plate. Both bare glass and Si-coated plates were irradiated with 14-MeV neutrons for 300 s. The gamma activity was measured using a NaI(Tl) detector. Barium, present in the glass, was used as an internal monitor to correct for the contribution of Si in the glass plate to the activity. Comparison of the results obtained using a weight method to determine the Si thickness and the NAA method showed agreement within ± 5%. FNAA continues to find widespread application in well-logging procedures.[202] Table 5 provides a list of selected recent FNAA applications.[203-212]

III. UNIQUE APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS

NAA has been used traditionally to determine bulk trace element levels in many different kinds of samples. Several investigators have developed applications of neutron activation

that provide information not usually thought to be obtainable by NAA. Activation of nitrogen-containing samples has provided information on the homogeneity of N in several materials. Highly thermalized neutron beams are used to profile the distribution of certain elements in surfaces. Tomographic procedures that use neutron beams as probes for activable elements in samples can provide two- and three-dimensional information about location of these elements in the samples. Determination of the total body burden of some key elements is routinely performed by *in vivo* NAA.

A. Proton Track Mapping

Analytical determinations of N are still most often done using classical chemical techniques. 14-MeV NAA has provided an alternative, nondestructive method for measuring major levels of N in a variety of matrices.[213] Another reaction that may also be used for N analysis is the $^{14}N(n,p)^{14}C$ reaction, which occurs with thermal neutrons and results in emission of protons with energies of 0.534 MeV. The protons resulting from the reaction can be detected using proton track techniques. Yegnasubramanian and Mitchell[214] showed that the proton track technique was reliable for determination of bulk levels of N in silicon nitride samples by comparing the track results to those obtained by 14-MeV NAA. They also discussed a different use of the proton track technique, that is, to characterize the microscale homogeneity of nitrogen in samples, and demonstrated the feasibility of this approach for N in silicon nitride.

Mitchell et al.[215] have also applied this technique to characterize N distribution in polymer materials. The polymers were sandwiched between sheets of cellulose nitrate (CN-85), which served as the proton detector, and irradiated with a ^{252}Cf neutron source at Oak Ridge Associated Universities. Detector films were processed and the proton track densities measured. The relatively poor agreement of the N bulk levels determined by proton track and by 14-MeV NAA pointed out the limitations of the CN-85 as a detector material. The large background resulting from the N in the CN-85 made data interpretation difficult. Mitchell et al. also prepared plots of N distribution in the polymer materials from image analysis of the proton track densities.

B. Neutron Depth Profiling (NDP)

The impetus for the initial development of NDP was the problem of determining B impurity concentrations in semiconductors, where B is used as a p-type dopant. The standard analytical techniques were not adequate for the task of determining B concentrations of tens of micrograms per gram. Ziegler et al.[216] were the first to use thermal neutrons to characterize the depth profile of B in a Si wafer.

The principles of NDP are straightforward. A beam of thermal neutrons is allowed to impinge on the sample material. In some light nuclides, these low-energy neutrons can induce the isotropic emission of charged particles (protons or alpha particles) and a recoil nucleus. Each of the particles has a specific energy defined by the Q value for the reaction. As the charged particles travel through the overlying material, they lose energy. The energy of the particle after leaving the target is determined, and the difference between the measured energy and the known original energy can be related to the depth of the origin of the particle in the sample.

To carry out NDP, a highly thermalized neutron beam relatively free of gamma rays is needed. The collimated beam illuminates the sample, which is kept under vacuum so that the emitted particles do not lose more energy passing through the space between the sample and the detector. The detector is generally a surface barrier detector that is connected to a multichannel analyzer. This allows the entire energy spectrum (and thus depth information) to be collected simultaneously. The NDP system at the U.S. National Bureau of Standards has been described in detail by Downing et al.[217] The resulting energy spectra are related to the depth profile by

Table 6
ELEMENTS DETERMINED BY NEUTRON DEPTH PROFILING[a]

Element	Reaction	Energy of emitted particles (keV)		Detection limit (atoms cm^{-2})
He	$^{3}He(n,p)^{3}H$	572	191	3.1×10^{13}
Li	$^{6}Li(n,\alpha)^{3}H$	2055	2727	1.8×10^{14}
Be	$^{7}Be(n,p)^{7}Li$	143	207	3.5×10^{12}
B	$^{10}B(n,\alpha)^{7}Li$	1472	840	4.3×10^{13}
N	$^{14}N(n,p)^{14}C$	584	42	9.1×10^{16}
O	$^{17}O(n,\alpha)^{14}C$	1413	404	7.1×10^{17}
Na	$^{22}Na(n,p)^{22}Ne$	2247	103	4.7×10^{12}
S	$^{33}S(n,\alpha)^{30}Si$	3081	411	1.2×10^{18}
Cl	$^{35}Cl(n,p)^{35}S$	598	17	3.4×10^{17}
K	$^{40}K(n,p)^{40}Ar$	2231	56	3.8×10^{16}
Ni	$^{59}Ni(n,\alpha)^{56}Fe$	4757	340	1.4×10^{16}

[a] Adapted from Downing, R. G., Fleming, R. F., Langland, J. K., and Vincent, D. H., *Nucl. Instrum. Methods Phys. Res.*, 218, 47, 1983.

$$x = \int_{E(x)}^{E_o} dE/S(E) \tag{13}$$

where x = path length traveled by the particle, E_o = initial energy of the particle, E(x) = energy of the emerging particle, and S(E) = stopping power of the material. Detailed information about the methods used for spectral deconvolution has been given by Biersak and Haggmark[218] and Maki et al.[219]

NDP can be used to determine the elements listed in Table 6. The detection limits presented were calculated assuming 0.1 counts per second detected and an acceptance solid angle of 0.1%. The depths of the material analyzed depend upon the range of the monitored charged particle in the matrix. Depth profiles of 1 to 10 μm are common for most materials, and spatial resolutions of 10 to 50 nm are typical.

There are many advantages and disadvantages associated with the use of NDP for surface analysis when compared with more conventional approaches, such as secondary ion mass spectrometry (SIMS). In contrast to SIMS, NDP is essentially a nondestructive technique, since the low-energy neutrons interact very little with the sample as a whole and long-lived activities are negligible. Measurements can be made in practically all solid materials, and the technique can profile across boundaries. There are few interferences, and the chemical or electrical state of the target atoms does not influence the determination. NDP is, however, an isotopic technique so the isotopic abundances of the sample must be known to obtain total concentrations. The sensitivity of NDP is not as good as SIMS, but NDP can determine absolute concentrations, which cannot be done with SIMS. The resolution attainable by NDP is also poorer than that seen with SIMS.

There are now more than ten nuclear facilities in the world that have used NDP to investigate a wide variety of materials. As noted previously, the most common application has been the analysis of Si semiconductor material for dopants, especially B. Downing et al.[220] surveyed more than 50 specific applications of NDP in this area. Applications of NDP to element profiling in other types of materials have also been summarized by Downing et al.[221]

The use of cold neutron sources for NDP (see Section II.A.1) should further improve the sensitivity of the method. In addition, the increased signal intensity will enable workers to use different detector geometries to enhance resolution. Improvements in charged particle detectors and in the algorithms used for spectral deconvolution should also help improve the currently attainable resolution and detection limit values.

C. Neutron Activation Tomography

The mathematical procedures for reconstructing an unknown image from many individual projections of a probe through an object were first discovered over 60 years ago. Since then, tomographic techniques employing X-rays in transmission mode and gamma rays in both transmission and emission modes have been used extensively to form images of body structures. These tomographic techniques have been combined with NAA to provide a unique method for two- and three-dimensional mapping of activable elements present in an object.

1. Two-Dimensional Neutron Tomography

The principles of neutron tomography have been discussed recently by Spyrou.[222] The object of interest is irradiated by neutrons, and either the prompt, or the delayed, gamma rays from the irradiation can then be monitored by a suitable detector. The detector (or the object) is translated and rotated through 360° and counts taken at regular intervals. The data are then computer processed to reconstruct an image of the object.

Pierce et al.[223] first reported on the use of neutron tomography for examining the distribution of activity in irradiated samples. They irradiated a solid cylinder in which was embedded a gold wire and monitored the 411.8-keV gamma ray from ^{198}Au. They demonstrated that information on the position of the wire inside the cylinder could be obtained.

Spyrou[222] used a delayed-gamma experimental approach to determine the distribution of Na via ^{24}Na activity in a section of human tibia. The bone was irradiated for 1 h at the Reactor Centre at Silwood Park at a thermal flux density of 2×10^{12} n cm^{-2} s^{-1}. NaI(Tl) and Ge(Li) detectors collimated to 1 mm were used to monitor the 1368 and 2753 keV gamma rays from ^{24}Na. Profile scans were taken every 8° at 1 mm step intervals, and reconstructed images of the bone formed. Although the actual spatial resolution was greater than 1 mm due to inadequate shielding and collimation, Spyrou concluded that the method could be useful for determination of elemental distributions in both biological and industrial materials. Spyrou et al.[224] also reported use of prompt gamma rays for neutron tomography. Two test objects, one Pb and one Al, containing three Cd pellets separated by 2 and 5 mm, were irradiated at the Institute Laue-Langevin in France, using a neutron beam of 1.8×10^{12} n cm^{-2} s^{-1}. The 559-keV prompt-gamma photopeak from ^{114}Cd was recorded using a high-resolution HPGe detector at 90° to the object. The three pellets were well resolved by the system, which had a spatial resolution of 0.4 mm.

Davies et al.[225] demonstrated the feasibility of using tomographic techniques to examine the distribution of elements in an irradiated nuclear fuel pin. They designed a phantom using ^{182}Ta as a photon source and showed that it was possible to resolve the six sources placed within the phantom.

Another application of neutron activation tomography was reported by Spyrou et al.[226] who used the technique to examine the diffusion of elements into wood samples. A piece of pine was immersed in a preservative solution containing B, F, Cr, As, and Na compounds and then stored to allow time for diffusion. The sample was irradiated and tomographic scanning measurements made for As and Na. The profiles obtained provided information about the distribution of these two elements across a plane of the sample.

Two sources of error associated with emission tomography are attenuation of photons in the object and the contribution of scattered photons to the photopeak of interest. The amount of scattered radiation reaching the detector can be reduced by making the collimating aperture

smaller, but this results in longer scan times needed for analysis. However, some mathematical corrections for the problem can be made.[225] The photon attenuation problem varies in severity with different sample matrices and is difficult to correct for in cases where it is a significant factor.

A point of emphasis in the studies cited above (especially Pierce et al.[223]) is that the equipment used was relatively inexpensive compared with that usually associated with tomographic techniques.

Future work in two-dimensional neutron tomography will examine the use of multienergetic sources and explore improvements in experimental apparatus.

2. Three-Dimensional Neutron Tomography

Pierce et al.[227] reported on the generation of three-dimensional images using neutron tomographic techniques. A Perspex phantom with various cavities drilled in it was used as a test object. The shapes were filled with ^{51}Cr solution and scanned not only with rotational and translational motion, but also with vertical displacement. The resulting images produced a good three-dimensional representation of the activity distribution in the phantom.

D. *In Vivo* Neutron Activation Analysis (IVNAA)

The application of NAA for determination of trace elements in biological tissues that have been removed from an organism is very familiar to anyone interested in biomedical analysis. However, the application of NAA to *in vivo* studies is not as well known. Anderson et al.[228] first suggested the possibility of applying NAA to determine whole-body elemental levels in a living organism. Since that time, *in vivo* NAA has become an established technique in nuclear medicine, although it is performed at relatively few centers worldwide. Several recent reviews of the principles and applications of this technique have been published.[229-232]

The general principles of IVNAA are the same as those for *in vitro* NAA. The entire body of the subject, or only a segment, is irradiated with neutrons, generally from an isotopic neutron source (Pu-Be, Am-Be, or ^{252}Cf), or an accelerator. The neutrons, with initial energies in the range of 2 to 14 MeV, may be moderated with external moderators before reaching the subject, and further moderation occurs within the body through neutron collisions with hydrogen. Table 7 lists some of the characteristics of the neutron sources used for IVNAA. Higher-energy neutrons are preferred partly because of their greater penetration into the body. Both delayed and prompt gammas have been used for analysis. Since many of the analytical peaks produced in the delayed-gamma procedures have very high energies, high-resolution detectors are not needed, and the high-efficiency NaI(Tl) detectors are often used. For prompt-gamma work, high-resolution Ge(Li) or HPGe detectors are normally needed to resolve the analytical peaks in the complex spectra produced.

The elements most commonly determined by IVNAA and their detection characteristics are listed in Table 8. Of these, Ca, N, and Cd have received the most attention. Oxygen and H are easily measured, and Na, Cl, and P can be measured simultaneously with Ca if desired. Chettle and Fremlin[229] have listed several other elements that may be more widely exploited with IVNAA in the future.

The practice of IVNAA results in problems that would occur in the activation analysis of any relatively large, irregular, bulky object. There will be variations in neutron flux and energy as the neutrons pass through the body of the subject. Primary and secondary interference reactions due to the occurrence of threshold reactions can also complicate the analyses.

IVNAA has found application in basic physiological studies, in clinical diagnosis of disease, and in the monitoring of therapeutic interventions for disease. An extensive review of the applications of IVNAA can be found in Cohn.[233] Hence, only a few references for the three most commonly determined elements are noted.

Table 7
NEUTRON SOURCES USED IN IVNAA[229,230]

Source and reaction	Neutron output (n/s)	Neutron energy (MeV)	Irradiation time (min)	Elements measured
Cyclotron:				
$^{7}Li(p,n)^{7}Be$	8×10^{10}	0.1—8 peak: 3.5	5—10	Ca, Na, N, Cd
Cyclotron:				
$^{9}Be(d,n)^{10}B$	5×10^{11}	4—12 peak: 8	1.3	Ca, Na, P
Cockroft-Walton: $^{3}(d,n)^{4}He$	3×10^{10}	14	5	Ca, Na, P, Cl, N
Isotopic:				
$^{238}Pu/Be$ $^{9}Be(\alpha,n)^{12}C$	1.4×10^{9}	2—8 mean: 4.5	5	Ca, Na, P, Cl
$^{241}Am/Be$ $^{9}Be(\alpha,n)^{12}C$	2×10^{4}	2—8 mean: 4.5	33	H
^{252}Cf: spontaneous fission		1—10 mean: 2		

Table 8
ELEMENTS COMMONLY DETERMINED BY IVNAA[a]

Element	Reaction(s)	Gamma ray detected
Ca	$^{48}Ca(n,\gamma)^{49}Ca$	Delayed: 3.10 MeV; prompt: many
N	$^{14}N(n,2n)^{13}N$	Delayed: 0.511 MeV
	$^{14}N(n,\gamma)^{15}N$	Prompt: 10.8 MeV
Cd	$^{113}Cd(n,\gamma)^{114}Cd$	Prompt: 0.559 MeV
O	$^{16}O(n,p)^{16}N$	Delayed: 6.1 MeV
H	$^{1}H(n,\gamma)^{2}H$	Prompt: 2.223 MeV
Na	$^{23}Na(n,\gamma)^{24}Na$	Delayed: 2.75 MeV 1.369 MeV
Cl	$^{37}Cl(n,\gamma)^{38}Cl$	Delayed: 2.168 MeV; Prompt: many
P	$^{31}P(n,\alpha)^{28}Al$	Delayed: 1.78 MeV
	$^{31}P(n,\gamma)^{32}P$	Prompt: 0.08 MeV

[a] Adapted from Chettle, D. R. and Fremlin, J. H., *Phys. Med. Biol.*, 29, 1011, 1984; Cohn, S. H., *Textbook of Nuclear Medicine, Volume 1: Basic Science*, Lea & Febiger, New York, 1984, chap. 17.

The measurement of total body calcium (TBCa) can provide information on the skeletal mass of an individual, since more than 99% of the body Ca is present in bone. The technique is useful for studies of many bone diseases, such as osteoporosis, and for assessing the efficacy of treatments for these diseases. Extensive studies on the TBCa of normal individuals have been done by Cohn et al.[234] Aloia et al.[235,236] used TBCa measurements to assess the effects of two different therapy programs in increasing the bone mass in postmenopausal patients. Harrison et al.[237] used IVNAA to diagnose and monitor treatment for osteoporosis.

Partial body Ca measurements, involving either peripheral bones or the trunk, are also performed when there is a reason to concentrate on only one part of the body. An example of this is in renal osteodystrophy, in which bone mass is lost from the hand, but not from

the central skeleton. Krishnan et al.[238] have described an IVNAA facility designed especially for small animals or portions of the human body, which uses two ^{252}Cf sources. They discuss the influences of sample volume and position on the induced Ca activity.

The $^{48}Ca(n,\gamma)^{49}Ca$ reaction is used most often for IVNAA Ca studies, although a few investigators have used the $^{40}Ca(n,\alpha)^{37}Ar$ reaction with subsequent detection of the exhaled ^{37}Ar. A variety of neutron sources have been used for Ca measurements. Typically the subject is irradiated for about 5 min, moved to a counting center, and counting takes place for about 20 min.

Measurements of total body nitrogen (TBN) can serve as indices of body protein content, nutritional state, and muscle mass. Cohn et al.[239] have used IVNAA to determine TBN in normal and cancer patients. Larsson et al.[240] have reported on the use of a ^{252}Cf source for IVNAA nitrogen determinations. McNeill et al.[241] used prompt-gamma IVNAA to determine N in three groups of subjects: normal, those with liver disease, and those undergoing peritoneal dialysis.

There are two methods commonly used for N measurement in IVNAA. The prompt-gamma method is the simpler of the two with respect to both operation and data interpretation, but the delayed-gamma method has the capability of simultaneous determination of several other elements (e.g., Na, Cl, and P). Irradiation sources are often 14-MeV generators, and irradiation times of 5 to 10 min are often used.

An example of an IVNAA study where an element is determined in a specific organ is the measurement of the toxic element Cd in kidney and liver. Scott and Chettle[242] have examined general aspects of Cd determination by IVNAA in liver and kidney. Franklin et al.[243] have studied some of the factors that affect the sensitivity and accuracy of the analysis, including organ depth and mass. Chang et al.[244] described the use of a mobile educational reactor for determination of Cd in organs. Spyrou[245] has suggested the use of a cyclic activation procedure to determine Cd and Se in the liver.

Cadmium is measured using the 559-keV prompt-gamma resulting from the (n,γ) reaction on ^{113}Cd. Isotopic neutron sources have been used most often. Irradiation times of 10 min, with counting times of 10 to 20 min, are typical. A high-resolution detector is necessary for the Cd analysis.

Future work in IVNAA will explore the possibility of determining other elements, such as C by inelastic scattering, and O by the (n,p) reaction. The multielement capability of the prompt-gamma methods will also be further exploited, and filtered neutron sources from nuclear reactors may also be useful for some single-organ measurements.

IV. SUMMARY

In a biennial Fundamental Review entitled "Nuclear and Radiochemical Analysis" in *Analytical Chemistry*, Ehmann and Yates[23,24] discuss advances in methodology and selected applications of all major nuclear methods of analysis. They found that approximately 1000 papers are published each year in the area of nuclear analytical chemistry. Most are abstracted in *Chemical Abstracts* under the key phrase "radiochemical analysis". Among the trace element analysis techniques, those based on neutron activation are clearly most prevalent. Thermal neutron reactor irradiation followed by counting of delayed gamma rays, with or without pre- or post-irradiation chemistry, is still the most popular neutron activation method, but prompt gamma neutron activation analysis (PGNAA) is probably the fastest growing area. The development of cold neutron sources coupled to neutron guide tubes will enhance the sensitivity of PGNAA, and we expect to see many new applications of PGNAA in the near future.

In this review we have not attempted to repeat the work of Ehmann and Yates[23,24] in documenting most of the recent individual NAA publications, nor have we attempted an in-

depth delineation of the principles of activation analysis. The recent treatise edited by Elving[19] eminently serves the latter purpose. Instead, our objective was to inform the analyst who is not a specialist in nuclear methods of the most recent advances in the powerful technique of neutron activation analysis. We also have attempted to identify areas that will probably experience the greatest growth in applications. Finally, we tried to present the information in a readable and concise manner. We hope the reader finds our product useful.

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