IAEA-TECDOC-435

COMPARISON OF NUCLEAR ANALYTICAL METHODS WITH COMPETITIVE METHODS

PROCEEDINGS OF AN ADVISORY GROUP MEETING
ON COMPARISON OF NUCLEAR ANALYTICAL METHODS
WITH COMPETITIVE METHODS
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
AND HELD IN OAK RIDGE, 3–7 OCTOBER 1986

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FOREWORD

The use of nuclear analytical techniques, especially neutron activation analysis, already have a 50 year old history behind them. Nuclear methods provided means for reliable trace element analysis in a time when few other trace element analysis methods were available. Therefore the role of nuclear analytical techniques in developing science and technology, certainly have been important.

Today several sensitive and accurate, non-nuclear trace element analytical techniques are available and new methods are continuously developed. The Agency is supporting the development of nuclear analytical laboratories in its member states. In order to be able to advise the developing countries which methods to use in different applications, it is important to know the present status and development trends of nuclear analytical methods. Which are their benefits, drawbacks and recommended fields of application, compared with other, non-nuclear techniques.

In order to get an answer to these questions the Agency convened an Advisory Group Meeting in Oak Ridge, Tennessee, 3-7 October 1986. This volume is the outcome of the presentations and discussions of the meeting.

The Agency is grateful to all the experts who contributed papers and took part in the discussions, to the chairman Dr. H.H. Ross and to the Oak Ridge National Laboratory, which hosted the meeting in such an efficient and successful way.

EDITORIAL NOTE

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INTRODUCTION

An Advisory Group Meeting (AGM) was held on the 3rd, 4th, 6th, and 7th of October 1986 in Oak Ridge, Tennessee and was attended by scientists from over ten countries in Europe, Asia, and North America. The purpose of this AGM was to examine the role of nuclear methods of analysis vis-a-vis non-nuclear techniques. Our specific objectives were to evaluate critical parameters associated with various analytical methods, determine the range of application of the methods, suggest how critical analytical technology can be effectively transferred to developing nations, and most important, counsel the Agency on possible program initiatives that they might establish to encourage such technology transfer. Each of these objectives, of course, encompassed a variety of related questions. For example, problems related to analytical reference materials, personnel training, and an evaluation of strengths and deficiencies of key analytical methods were included subjects of discussion. It is clear that the range of topics considered by the AGM was very broad and yet very results oriented.

The format of the meeting consisted of essentially two parts: the formal presentations and comments, and the special sessions devoted to discussions. The schedule was kept very flexible to encourage an active exchange of ideas without having to worry about the "tyranny of the clock". Conclusions were first elaborated by four groups of individual session members led by a rapporteur and were later modified and/or expanded during a general meeting of the delegates. Finally, the explicit suggested directives to the Agency were prepared at a meeting of the session rapporteurs and the conference chairman.

This volume contains the texts of the formal presentations, the discussion that followed each, and the summary and conclusions of the AGM. It is also evident that much of what is said extends far beyond the interests of just the developing countries; chemical analysis is truly a global concern with global problems.

I would like to express my sincere appreciation to W. D. Shults and W. R. Laing of Oak Ridge National Laboratory and R. Rosenberg and V. Vasilyev of the IAEA for their significant contributions in helping plan and organize this meeting. Finally, I would like to thank all of the delegates to the AGM.

Their interesting presentations and their open and often spirited discussions are key factors in what I believe to be a most successful outcome.

Harley H. Ross, AGM Chairman
Oak Ridge National Laboratory

STATISTICAL EVALUATION OF RECORDED KNOWLEDGE IN NUCLEAR AND OTHER INSTRUMENTAL ANALYTICAL TECHNIQUES

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Abstract

The main points addressed in this study are the following. Statistical distribution patterns of published literature on instrumental analytical techniques 1981-1984. The structure of scientific literatures and heuristics for identifying active specialties and emerging hot spot research areas in instrumental analytical techniques. Growth and growth rates of the literature in some of the identified hot research areas. Quality and quantity in instrumental analytical research output.

There are basically two ways of assessing or evaluating the progres, trends, advances, growth, etc., of a given field or subfield of science:

1. Peer evaluation
2. Statistical evaluation of recorded knowledge /subject literature/

When the first of the abovementioned ways is used the paper, report, etc., communicating the results of the assessment begins usually with a sentence of the following type: "This paper /report/ provides my personal opinion on the status /the trends, progress, etc./ of ....., its present strengths, and its weaknesses. I also speculate on what the future will provide and indicate where the research opportunities appear to be."

Most of this type of assessment papers, written by well recognised individuals, are based on common shared insights, casual impressions and estimations, but they seem in general to lack a solid empirical base.

The evaluation used in this paper opted for the second abovementioned way i.e. it is using the statistical evaluation of the literature of analytical chemistry. The goal of the effort has been to chart comparatively of what was studied in the field of nuclear and other instrumental analytical techniques, to follow some of the trendlines of the main topics to see where this type of research has been in the past, currently is, and seems to be heading.

The reader interested in the details of this type of assessments is recommended to consult some previsous publications.[1-5]

In what follows we have collected a quite comprehensive amount of empirical data on the research and publication activity in the field of nuclear and other instrumental analytical techniques. The data are collated in tables and charts with very brief interpretation. That's because the reader is invited and encouraged to examine the tables and charts and see what additional comments, conclusions he/she can observe.

Table 1 shows the data on the distribution of uses of different instrumental analytical techniques in analytical research papers published during the 1981-1984 period. The database for this analysis was the 1981-1984 volumes of the Analytical Abstracts. A set of 15 elements has been selected /see the list of elements in Table 2/ and for each element the individual use of instrumental analytical techniques has been

Table 1

Frequency distribution of the uses of instrumental techniques in 1981-1984 research papers

World Total

Technique	No. of uses	%
atomic-absorption spectrophotometry	1648	24.1
spectrophotometry	1271	18.5
emission spectrometry	1005	14.7
neutron-activation analysis	585	8.5
x-ray fluorescence	452	6.6
thin-layer chromatography	149	2.2
high performance liquid chromatography	117	1.7
atomic-emission spectrometry	116	1.7
polarography	94	1.4
ionchromatography	81	1.2
differential pulse polarography	61	0.9
ionselective electrode	59	0.9
flow injection analysis	57	0.8
kinetic methods	56	0.8
fluorimetry	52	0.8
anodic stripping voltammetry	49	0.7
voltammetry	47	0.7
inductively coupled plasma	46	0.7
proton induced x-ray emission	45	0.7
atomic-fluorescence spectrometry	42	0.6
particle induced x-ray emission	40	0.6
coulometry	32	0.5
mass spectrometry	32	0.5
differential pulse cathodic stripping voltammetry	31	0.5
amperometry	29	0.4
stripping potentiometry	26	0.4
gas-chromatography	25	0.4
oscillopolarography	23	0.3
chemiluminescence	17	0.2
isotope dilution	17	0.2
Auger electron spectrometry	14	0.2
electron microprobe	12	0.2
liquid chromatography	12	0.2
conductometry	11	0.2
a. c. polarography	9	0.1
mol. emission cavity spectrometry	9	0.1
paper chromatography	9	0.1
photoacoustic spectrometry	8	0.1
proton activation	8	0.1
stripping(chrono)voltammetry	8	0.1
electron spin (or paramagnetic) resonance	7	0.1
f.a.n.e.s.	7	0.1
inverse voltammetry	7	0.1
pulse polarography	7	0.1
Miscellaneous	420	6.1
Total	6852	100.0

Table 2

Percentage distribution of the uses of merged [1] instrumental analytical techniques in 1981-1984 research papers

World total

Technique[2]	Element															Total
	Ag (%)	As (%)	Au (%)	Bi (%)	Co (%)	Cr (%)	Cu (%)	Fe (%)	Ga (%)	Hg (%)	Mn (%)	Mo (%)	Sb (%)	U (%)	V (%)	(%)
OPT	59.1	70.4	59.1	67.9	62.9	70.2	66.3	70.8	71.6	65.9	73.2	70.1	59.5	47.2	74.7	66.9
NUCL	14.1	15.1	25.9	3.3	13.6	14.0	8.2	13.5	11.9	12.9	16.2	12.6	21.6	29.1	11.1	13.8
ELEC	15.7	7.8	10.0	15.9	9.5	7.4	14.6	5.6	12.8	9.8	3.9	9.6	11.4	13.9	7.2	9.8
CHROM	3.5	4.2	2.7	9.3	10.0	5.8	6.8	5.2	1.8	9.1	4.1	4.8	3.4	6.8	3.6	5.8
MISC	7.7	2.5	2.3	3.7	4.1	2.6	4.1	4.9	1.8	2.3	2.6	3.0	4.2	2.9	3.4	3.7
	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

[1] For categorization into merged groups see Appendix 2

[2] OPT : optical, spectroscopical; NUCL : nuclear;
ELEC : electrochemical ; CHROM : chromatographic;
MISC : miscellaneous

counted in the subject index of each volume of the Analytical Abstracts. As such it has to be accentuated that the counting doesn't refer to the number of papers on instrumental techniques but to the number of uses of these techniques. That's why e.g. one paper can refer to the use of many instrumental techniques. The different instrumental analytical techniques taken into account were not selected i.e. defined by us. They were considered in the counting as they were defined and mentioned in the subject index classification system of the Analytical Abstracts database. The 6852 uses of different instrumental analytical techniques were distributed between a total of 143 distinct techniques /see list of techniques in appendix 1/. As visible, in table 1 we did collect only those 44 methods which had at least 7 uses in the research papers published in

the 1981-1984 period. The data show a very skewed distribution of the uses of different techniques.

A special type of cumulative-frequency graph known as the "Lorenz curve"[6] has been used effectively to portray distribution data, e.g. the distribution of wealth and income in relation to certain segments of the population, the productivity of farms in terms of cumulative proportions of farms, or the distribution of retail sales as related to various groupings of stores.

Figure 1 represents the Lorenz curve for the frequency distribution of instrumental analytical techniques.

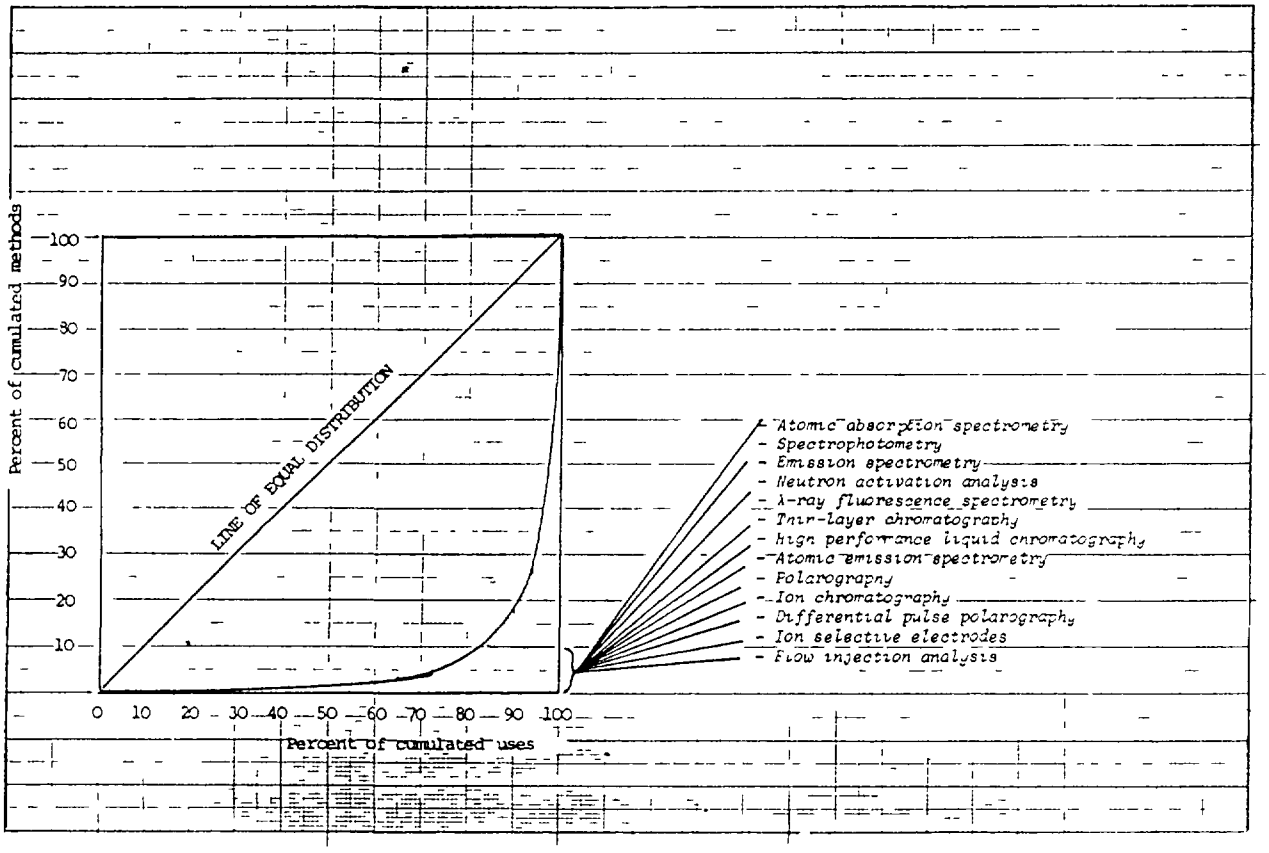


Fig. 1 Lorenz-type cumulative frequency distribution curve of the uses of instrumental analytical techniques in the 1981-1984 period

As shown, the distribution in uses of these methods is fairly "undemocratic" i.e. about 10 % of the methods account for approx. 85 % of the uses. Spectrometric methods are high in the ranking with atomic absorption spectrometry in strong first position but two nuclear analytical techniques /neutron activation analysis and XRF methods/ are also highly quoted.

Table 2 shows the distribution of the uses of instrumental analytical techniques according to the 15 elements taken into account. The data on the different techniques are merged here into 5 comprehensive groups. /Optical i.e. spectrometric, nuclear, electrochemical, chromatographic and miscellaneous; for merging into groups see appendix 2./

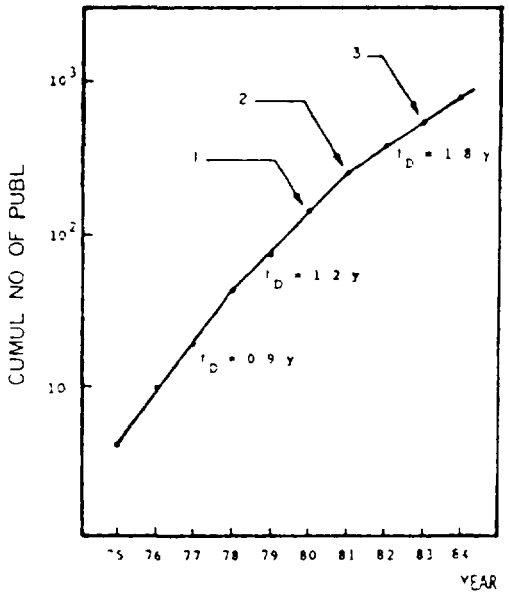


Figure 2 Cumulative growth of the world literature on flow injection analysis[10] /t_D: exponential doubling time, i.e. growth rate/[1,2,3]: dates of major conferences

As visible, nuclear analytical techniques are in strong second position after the spectroscopic ones.

It is interesting to compare the ranking data of table 2 to the results of two of our previous rankings of the different instrumental analytical techniques /Figure 2/.[3,4] We see nuclear analytical techniques ranked fourth in both of the previous investigations.

Tables 3-14 present the geographical distribution of the uses of the different instrumental analytical techniques /see appendix 3 for defining the different geographic regions/.

Table 3

Frequency distribution of the uses of instrumental techniques in 1983-1984 research papers

USA & Canada

Technique	No. of uses	%
atomic-absorption spectrophotometry	147	26.8
emission spectrometry	84	15.3
neutron-activation analysis	73	13.3
x-ray fluorescence	46	8.4
atomic-emission spectrometry	35	6.4
spectrophotometry	21	3.8
inductively coupled plasma	18	3.3
mass spectrometry	16	2.9
high performance liquid chromatography	12	2.2
ionchromatography	12	2.2
electron microprobe	9	1.6
flow injection analysis	8	1.5
differential pulse polarography	6	1.1
liquid chromatography	5	0.9
anodic stripping voltammetry	4	0.7
gas-chromatography	3	0.5
coulometry	3	0.5
differential pulse cathodic stripping voltammetry	3	0.5
ionselective electrode	2	0.4
isotope dilution	2	0.4
Auger electron spectrometry	2	0.4
thin-layer chromatography	2	0.4
atomic-fluorescence spectrometry	2	0.4
amperometry	1	0.2
polarography	1	0.2
fluorimetry	1	0.2
stripping(chrono)voltammetry	1	0.2
electron spin (or paramagnetic) resonance	1	0.2
Miscellaneous	29	5.3
Total	549	100.0

Table 4

Frequency distribution of the uses of instrumental techniques in 1983-1984 research papers

United Kingdom

Technique	No. of uses	%
atomic-absorption spectrophotometry	47	28.7
emission spectrometry	30	18.3
spectrophotometry	17	10.4
flow injection analysis	11	6.7
atomic-emission spectrometry	10	6.1
x-ray fluorescence	10	6.1
high performance liquid chromatography	9	5.5
inductively coupled plasma	9	5.5
ionchromatography	2	1.2
mass spectrometry	2	1.2
kinetic methods	1	0.6
fluorimetry	1	0.6
neutron-activation analysis	1	0.6
atomic-fluorescence spectrometry	1	0.6
particle induced x-ray emission	1	0.6
polarography	1	0.6
differential pulse cathodic stripping voltammetry	1	0.6
mol. emission cavity spectrometry	1	0.6
Miscellaneous	9	5.5
Total	164	100.0

Table 5

Frequency distribution of the uses of instrumental techniques in 1983-1984 research papers

Fed. Rep. Germany

Technique	No. of uses	%
atomic-absorption spectrophotometry	65	29.7
emission spectrometry	24	11.0
x-ray fluorescence	19	8.7
neutron-activation analysis	12	5.5
voltammetry	12	5.5
gas-chromatography	10	4.6
high performance liquid chromatography	9	4.1
spectrophotometry	7	3.2
particle induced x-ray emission	7	3.2
differential pulse polarography	7	3.2
Auger electron spectrometry	5	2.3
differential pulse cathodic stripping voltammetry	4	1.8
proton activation	4	1.8
ionselective electrode	3	1.4
mass spectrometry	3	1.4
amperometry	2	0.9
atomic-emission spectrometry	2	0.9
isotope dilution	2	0.9
anodic stripping voltammetry	2	0.9
thin-layer chromatography	2	0.9
inductively coupled plasma	1	0.5
kinetic methods	1	0.5
coulometry	1	0.5
polarography	1	0.5
photoacoustic spectrometry	1	0.5
ionchromatography	1	0.5
Miscellaneous	12	5.5
Total	219	100.0

Table 6

Frequency distribution of the uses of instrumental techniques in 1983–1984 research papers

France

Technique	No. of uses	%
emission spectrometry	9	22.0
atomic-absorption spectrophotometry	8	19.5
x-ray fluorescence	4	9.8
proton activation	3	7.3
neutron-activation analysis	2	4.9
spectrophotometry	2	4.9
differential pulse polarography	1	2.4
fluorimetry	1	2.4
anodic stripping voltammetry	1	2.4
inductively coupled plasma	1	2.4
particle induced x-ray emission	1	2.4
mass spectrometry	1	2.4
electron microprobe	1	2.4
atomic-emission spectrometry	1	2.4
Miscellaneous	5	12.2
Total	41	100.0

Table 7

Frequency distribution of the uses of instrumental techniques in 1983–1984 research papers

USSR

Technique	No. of uses	%
spectrophotometry	124	23.0
emission spectrometry	86	16.0
atomic-absorption spectrophotometry	73	13.5
x-ray fluorescence	40	7.4
neutron-activation analysis	38	7.1
ionselective electrode	12	2.2
polarography	11	2.0
ionchromatography	10	1.9
voltammetry	10	1.9
kinetic methods	7	1.3
thin-layer chromatography	7	1.3
atomic-fluorescence spectrometry	6	1.1
particle induced x-ray emission	6	1.1
amperometry	6	1.1
differential pulse cathodic stripping voltammetry	5	0.9
fluorimetry	5	0.9
anodic stripping voltammetry	4	0.7
coulometry	4	0.7
a. c. polarography	4	0.7
inverse voltammetry	4	0.7
chemiluminescence	3	0.6
mass spectrometry	3	0.6
paper chromatography	3	0.6
photoacoustic spectrometry	3	0.6
stripping(chrono)voltammetry	3	0.6
oscillopolarography	3	0.6
electron spin (or paramagnetic) resonance	2	0.4
high performance liquid chromatography	2	0.4
isotope dilution	1	0.2
liquid chromatography	1	0.2
inductively coupled plasma	1	0.2
stripping potentiometry	1	0.2
Miscellaneous	51	9.5
Total	539	100.0

Table 8

Frequency distribution of the uses of instrumental techniques in 1983–1984 research papers

Japan

Technique	No. of uses	%
atomic-absorption spectrophotometry	95	28.0
spectrophotometry	90	26.5
high performance liquid chromatography	22	6.5
x-ray fluorescence	13	3.8
neutron-activation analysis	10	2.9
emission spectrometry	9	2.7
atomic-emission spectrometry	9	2.7
flow injection analysis	7	2.1
ionselective electrode	6	1.8
ionchromatography	6	1.8
atomic-fluorescence spectrometry	4	1.2
particle induced x-ray emission	4	1.2
photoacoustic spectrometry	4	1.2
gas-chromatography	3	0.9
anodic stripping voltammetry	2	0.6
inductively coupled plasma	2	0.6
differential pulse polarography	2	0.6
polarography	2	0.6
mass spectrometry	2	0.6
thin-layer chromatography	2	0.6
chemiluminescence	2	0.6
fluorimetry	2	0.6
differential pulse cathodic stripping voltammetry	1	0.3
amperometry	1	0.3
stripping potentiometry	1	0.3
kinetic methods	1	0.3
coulometry	1	0.3
isotope dilution	1	0.3
Auger electron spectrometry	1	0.3
liquid chromatography	1	0.3
voltammetry	1	0.3
proton activation	1	0.3
Miscellaneous	31	9.1
Total	339	100.0

Table 9

Frequency distribution of the uses of instrumental techniques in 1983–1984 research papers

Asia

Technique	No. of uses	%
spectrophotometry	222	41.3
atomic-absorption spectrophotometry	63	11.7
thin-layer chromatography	18	3.3
emission spectrometry	17	3.2
x-ray fluorescence	16	3.0
amperometry	16	3.0
neutron-activation analysis	15	2.8
polarography	12	2.2
ionselective electrode	11	2.0
anodic stripping voltammetry	11	2.0
ionchromatography	11	2.0
atomic-emission spectrometry	10	1.9
inductively coupled plasma	9	1.7
oscillopolarography	7	1.3
differential pulse cathodic stripping voltammetry	5	0.9
fluorimetry	3	0.6
flow injection analysis	3	0.6
paper chromatography	2	0.4
kinetic methods	1	0.2
voltammetry	1	0.2
differential pulse polarography	1	0.2
coulometry	1	0.2
stripping(chrono)voltammetry	1	0.2
Miscellaneous	82	15.2
Total	538	100.0

Table 10

Frequency distribution of the uses of instrumental techniques in 1983–1984 research papers

Latin America

Technique	No. of uses	%
atomic-absorption spectrophotometry	10	30.3
spectrophotometry	8	24.2
neutron-activation analysis	2	6.1
x-ray fluorescence	2	6.1
differential pulse polarography	1	3.0
ionselective electrode	1	3.0
flow injection analysis	1	3.0
kinetic methods	1	3.0
pulse polarography	1	3.0
Miscellaneous	6	18.2
Total	33	100.0

Table 11

Frequency distribution of the uses of instrumental techniques in 1983–1984 research papers

Eastern Europe

Technique	No. of uses	%
atomic-absorption spectrophotometry	87	23.6
spectrophotometry	52	14.1
emission spectrometry	47	12.8
x-ray fluorescence	29	7.9
neutron-activation analysis	26	7.1
ionchromatography	17	4.6
anodic stripping voltammetry	17	4.6
thin-layer chromatography	11	3.0
polarography	11	3.0
ionselective electrode	5	1.4
voltammetry	5	1.4
a. c. polarography	5	1.4
stripping potentiometry	4	1.1
differential pulse polarography	4	1.1
atomic-emission spectrometry	3	0.8
conductometry	3	0.8
differential pulse cathodic stripping voltammetry	3	0.8
gas-chromatography	2	0.5
liquid chromatography	2	0.5
particle induced x-ray emission	2	0.5
coulometry	2	0.5
stripping(chrono)voltammetry	2	0.5
isotope dilution	1	0.3
amperometry	1	0.3
inductively coupled plasma	1	0.3
flow injection analysis	1	0.3
chemiluminescence	1	0.3
Miscellaneous	24	6.5
Total	368	100.0

Table 12

Frequency distribution of the uses of instrumental techniques in 1983-1984 research papers

North Africa & Near East

Technique	No. of uses	%
spectrophotometry	8	20.0
high performance liquid chromatography	5	12.5
atomic-absorption spectrophotometry	4	10.0
atomic-emission spectrometry	4	10.0
x-ray fluorescence	3	7.5
neutron-activation analysis	2	5.0
particle induced x-ray emission	2	5.0
liquid chromatography	2	5.0
ionchromatography	1	2.5
emission spectrometry	1	2.5
polarography	1	2.5
paper chromatography	1	2.5
Miscellaneous	6	15.0
Total	40	100.0

Table 13

Frequency distribution of the uses of instrumental techniques in 1983-1984 research papers

Rest of Africa

Technique	No. of uses	%
spectrophotometry	5	55.6
atomic-absorption spectrophotometry	3	33.3
Miscellaneous	1	11.1
Total	9	100.0

Table 14

Frequency distribution of the uses of instrumental techniques in 1983-1984 research papers

Rest of Developed Countries

Technique	No. of uses	%
atomic-absorption spectrophotometry	150	26.5
spectrophotometry	96	17.0
emission spectrometry	52	9.2
neutron-activation analysis	35	6.2
x-ray fluorescence	21	3.7
fluorimetry	17	3.0
particle induced x-ray emission	17	3.0
atomic-emission spectrometry	12	2.1
ionchromatography	11	1.9
differential pulse polarography	11	1.9
kinetic methods	9	1.6
differential pulse cathodic stripping voltammetry	9	1.6
anodic stripping voltammetry	8	1.4
high performance liquid chromatography	8	1.4
ionselective electrode	8	1.4
stripping potentiometry	8	1.4
gas-chromatography	7	1.2
polarography	5	0.9
thin-layer chromatography	5	0.9
mass spectrometry	5	0.9
inductively coupled plasma	4	0.7
voltammetry	3	0.5
conductometry	3	0.5
paper chromatography	3	0.5
coulometry	2	0.4
atomic-fluorescence spectrometry	2	0.4
chemiluminescence	2	0.4
electron microprobe	2	0.4
flow injection analysis	2	0.4
mol. emission cavity spectrometry	2	0.4
amperometry	2	0.4
liquid chromatography	1	0.2
isotope dilution	1	0.2
stripping(chrono)voltammetry	1	0.2
pulse polarography	1	0.2
Miscellaneous	41	7.2
Total	566	100.0

That science is a mosaic of specialties, and not a unified whole, either socially or intellectually, is a frequently made assumption. Most scientists have intuitive notions about the subdivisions of their fields, but no observer, however broadly trained, can gain overall perspective on the scientific mosaic. It is generally supposed that specialties are effectively organized as communication systems around certain key individuals and documents in science. Recently,

computer-based techniques have been devised to identify clusters of highly interactive primary journal papers. It is contended that these clusters represent the scientific specialties which currently exhibit high levels of research activity.

Early studies established the feasibility of examining specialties in terms of citation data.[7] Frequently cited papers are employed as basic units for analysis. This choice is based on evidence that the onset of rapid specialty growth is accompanied by the emergence of key papers which are quickly and frequently cited; co-citation is used as a measure of the association between pairs of frequently-cited papers. The strength of co-citation is defined as the number of times two papers have been cited together: it provides a natural and quantitative way to group or cluster the cited papers. Co-citation identifies relationships between papers which are regarded as important by authors in the specialty.

The strength of co-citation between two papers can be readily determined from the Science Citation Index®.[8] Each of the two papers is located in the index and their lists of citing papers are scanned. The number of identical citing items /i.e. newer papers citing both the earlier papers/ furnishes a quantitative measure of the strenght of co-citation between the two papers, or of the extent to which two items of earlier literature are cited together by the later literature. Therefore, co-citation is a relationship which is recognized and maintained by current researchers.

One way to think of a co-citation relationship is as a matrix of similarity coefficients. The more often two articles are cited together, the higher the probability that they are

seen by researchers in the field as similar to each other in intellectual focus. Such similarity matrices can be analyzed by a technique known as multidimensional scaling, an iterative procedure that can produce a plot of the set of highly cited papers in two dimensions such that the highly co-cited papers are placed near to each other and the little co-cited papers are placed farther apart. The relative distances between papers in the plane should then be an indication of the degree of their intellectual relatedness. To produce relatedness diagrams, each paper is treated as if it were a Gaussian hill whose height is the number of times it was cited /its visibility/ and whose width is arbitrarily set at a value convenient to produce attractive pictures. The Gaussians are added together and resulting plot of hills and valleys gives a sense of how much activity is going on in different parts of the "specialty space".

The abovementioned general approach has been used recently to test a co-citation based clustering approach for identifying emergent areas /clusters/ of growth in science. This study gave a list of growth topics or potential "hot spots" in science. Table 15 shows a selection of the "hot spots" enumerated in the abovementioned study which we considered to be of some relevance to the instrumental analytical techniques and general analytical chemistry field.

A quantitative illustration that most of these heuristically selected specialties are really "hot spots" is seen in Figure 2. As visible the growth of the research literature on flow injection analysis /FIA/[10] during the 1975-85 period has been exponential, with an average growth rate /doubling time, t_d/ of 1.3 years. There are however also other specialties in the

Table 15

Emerging Specialty "Hot Spot" Clusters[9]

/Analytical Chemistry and Instrumental Techniques/

- Chemically Modified Polymer Electrodes
- Pollution of Aquatic Environments
- Atomic Fluorescence Spectrometry
- Sulphur Compounds in the Atmosphere
- Field Desorption Mass Spectrometry
- Techniques of Photoacoustic Spectroscopy
- Mass Spectrometry
- Atmospheric Chemistry: Air Pollution
- Analytical Electrochemistry: Methodology and Application of Dynamic Techniques
- Continous-Flow Injection Analysis

instrumental analytical field which show similar fast growth rates. As example Figures 3 and 4 present the growth rates of ion chromatography[11] and of activation analysis.[1] We see on Figures 3 and 4 that the growth rates were of 1.3 and 2.2 years respectively which can be considered tremendously fast in all the abovementioned cases. As a comparison we see on Figure 4 the growth rate /t_d/ of the total literature on analytical chemistry of being 13.9 years /doubling time/. Do these exponential /fast/ growth rates really reflect growth of knowledge in the respective instrumental specialties? It would, provided two assumptions were correct: 1. all knowledge obtained by instrumental analytical researchers would be included in the literature, and 2. every paper would contain either an equal or known proportion of this knowledge. Obviously neither

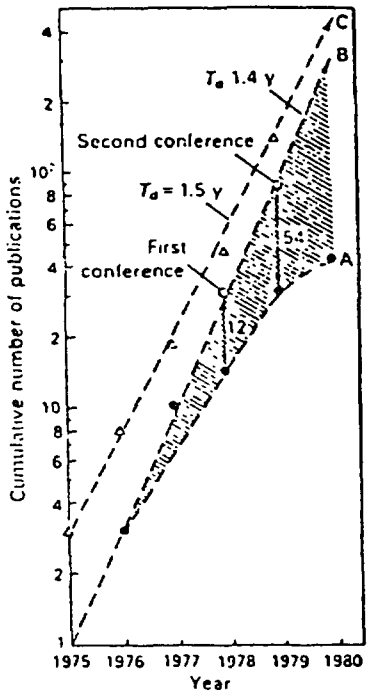


Figure 3 Cumulative growth of the world literature on ion chromatography.[11] Curve A: journal papers; Curve B: journal & conference papers; Curve C: cumulative growth of the number of authors /T_d: exponential doubling time, i.e. growth rate/

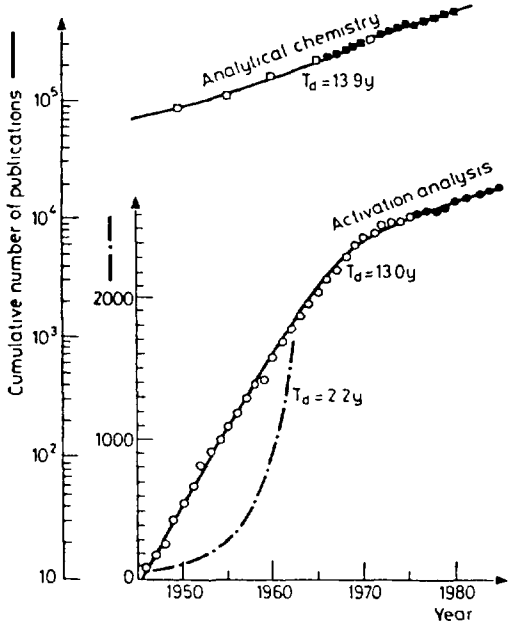


Figure 4 Cumulative growth of the world literature of activation analysis and analytical chemistry /T_d: exponential doubling time, i.e. growth rate/

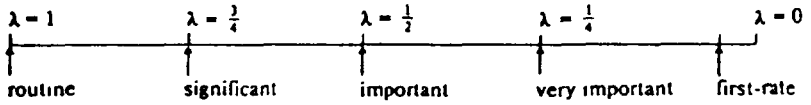
is true. Indeed, growth of knowledge in the instrumental analytical field /a rather abstract concept/ is different from growth of its literature. Moravcsik[12] distinguishes three relevant quantities when studying growth of science: scientific activity, scientific productivity and scientific progress. These he illustrates by analogy. A man desires to go from one place in a dense forrest to another one five miles away.

Activity corresponds to the amount of work done, for example, thrashing about in the undergrowth, blazing trails, exploring, etc. Productivity corresponds to the amount by which, as a result of all these activities, he advances toward his goal. Progress then is the ratio of productivity to the total task.

Scientific activity is concerned with the consumption of input resources and is related to factors such as number of scientists involved and research expenditures. Scientific productivity refers to the extent to which this consumption of resources creates a body of scientific results, which usually appear as published research papers. Scientific progress refers to the extent to which scientific activity - measured through scientific productivity - actually results in substantial contributions to scientific knowledge.

Rescher[13] defines a quantity, λ such that in a total population of papers /p/ at time t, p/t/ there will be $p\ /t/^{\lambda}$ papers at each λ level, as follows: $\lambda = 1$, at least routine; $\lambda = 0.75$, at least significant; $\lambda = 0.50$, at least important; $\lambda = 0.25$, at least very important /see also Figure 5/.

According to the abovementioned, the literature of λ quality grows with a doubling time of t_d/λ. With t_d for world analytical chemistry literature at about 13 years /see Figure 4



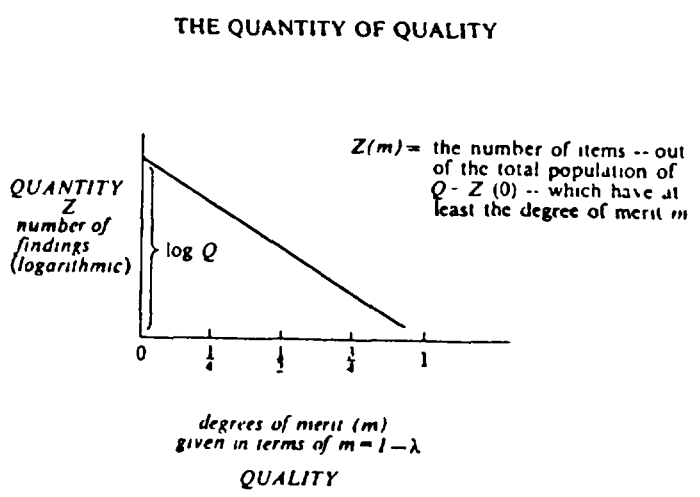


Figure 5 Graphical illustration of quantity-quality relationships in published science literature[13]

and Ref. 1/, the corresponding doubling times for the last three λ levels are 17.3, 26.0, and 52.0 years. The growth rates of the general analytical chemistry literature and those for the literature of flow injection analysis, ion chromatography and activation analysis at different quality levels are shown in table 16. From the above treatment one might conclude that papers containing significant advances in knowledge on general analytical chemistry and/or nuclear and other instrumental analytical techniques make up a tiny fraction of the total literature with a rather slower growth rate than that of the bulk of the literature. This poses a serious question. Does the bulk of publications on analytical chemistry, i.e. on nuclear and other instrumental analytical techniques serve a scientifically useful purpose? Admittedly these papers represent activity,

Table 16

The growth rates of the literature of analytical chemistry, flow injection analysis, ion chromatography and activation analysis at different quality levels

Quality level	Cumulative no. of findings of /at least/ this level	Doubling time /t_d/, years				
		Analytical Chemistry	Flow Injection Analysis	Ion Chromatography	Activation Analysis	
					1936-1972	1973-1985
Routine	$Q = p^{1.00}$	13.9	1.3	1.4	2.29	13.0
Significant	$Q = p^{0.75}$	17.3	1.7	1.8	2.9	17.3
Important	$Q = p^{0.50}$	26.0	2.6	2.8	4.4	26
Very important	$Q = p^{0.25}$	52.0	5.2	5.6	8.8	52

Table 17

Impact levels of papers published in the Journal of Radioanalytical Chemistry 1968-1974[14]

Year	Number of papers in the various quality groups, p^{λ}				Number of most cited papers, /papers with more than 50 citations/ C
	$\lambda = 1$[a]	$\lambda = 0.75$[b]	$\lambda = 0.5$[c]	$\lambda = 0.25$[d]	
1968	46	17.6	6.8	2.6	2
1969	136	39.8	11.6	3.4	3
1970	255	63.8	15.9	3.9	4
1972	472	101.2	21.7	4.6	5
1974	904	164.8	30.0	5.4	6

[a] at least routine,

[b] at least significant,

[c] at least important,

[d] at least very important.

but much of it may be misdirected in that confusion and communication channels get clogged. Perhaps it should be thought of as noise, always present but hopefully minimized.

Quality notions as "significant", "important", "very important" are quite hard to define. We tried to do a Rescher-type[13] categorization with the papers published in the Journal of Radioanalytical and Nuclear Chemistry in the

1968-1984 period taking citation impact /i.e. numbers of citations a paper received in the Science Citation Index/ as a criterion of "impact" instead of "importance"[14] Table 17 presents the results of a year-by-year categorization. As visible, the cumulative number of papers in the $\lambda = 0.25$ category /at least very important/ agrees quite well with the number of highly cited ones /$\lambda = 0.234 \pm 0.15$/. Table 18 shows the bibliographical list of the "at least very important papers" defined and found according to the procedure outlined in Table 18.

Table 18

Most-cited articles, 1968-1982, published in the Journal of Radioanalytical Chemistry arranged in alphabetic order by first author[14]

No.	1968-1982 citations*	Bibliographic data
1.	64 /4.9/	ADAMS, F., DAMS, R., A compilation of Precisely Determined Gamma-Transition Energies of Radionuclides Produced by Reactor Irradiation. J. Radioanal. Chem., 3 /1969/ 99.
2.	77 /9.6/	BOWEN, H.J.M., Problems in the Elementary Analysis of Standard Biological Material. J. Radioanal. Chem., 19 /1974/ 215.
3.	95 /9.5/	COOKSON, J.A., FERGUSON, A.T.G., PILLING, F.D., Proton Microbeams. Their Production and Use. J. Radioanal. Chem., 12 /1972/ 39.
4.	51 /3.6/	CROCKET, J.H., KEAYS, R.R., HSIEH, S., Determination of Some Precious Metals by Neutron Activation Analysis. J. Radioanal. Chem., 1 /1968/ 487.
5.	115 /8.2/	GIRARDI, F., SABBIONI, E., Selective Removal of Radio-Sodium From Neutron-Activated Materials by Retention on Hydrated Antimony Pentoxide. J. Radioanal. Chem., 1 /1968/ 169.
6.	73 /6.1/	GIRARDI, F., PIETRA, R., SABBIONI, E., Radio-chemical Separations by Retention on Ionic Precipitates. Adsorption Tests on 11 Materials. J. Radioanal. Chem., 5 /1970/ 141.

*Citation/year data are in parentheses.

Acknowledgment

The contribution of Drs. S. Zsindely and A. Schubert and Mrs. A. Tóth in the collection and systematization of data in tables 3-14 is gratefully acknowledged.

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2. T. Braun, E. Bujdosó, CRC Crit. Revs. Anal. Chem., 13 /1982/ 223.
3. T. Braun, Fresenius Z. Anal. Chem., 323 /1986/ 105.
4. T. Braun, Radioisotopes, 35 /1986/ 391.
5. T. Braun, W.S. Lyon, Fresenius Z. Anal. Chem., 319 /1984/ 74.
6. M.O. Lorenz, J. Assoc. Am. Stat. Assoc., New Series No. 70 /June 1905/ 209.
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11. T. Braun, Anal. Proc., 19 /1982/ 352.
12. M. Moravcsik, J. Res. Policy, 2 /1973/ 268.
13. N. Rescher, Scientific Progress, Univ. of Pittsburgh Press, Pittsburgh, 1978.
14. T. Braun, E. Bujdosó, W.S. Lyon, J. Radioanal. Nucl. Chem., 91 /1985/ 419.

Appendix 1

List of instrumental analytical techniques used in papers published in the 1981-1984 period

AACT	alpha activation
AAS	atomic-absorption spectrophotometry
ACPO	a. c. polarography
ACSV	a. c. stripping voltammetry
AES	atomic-emission spectrometry
AESP	Auger electron spectrometry
AFS	atomic-fluorescence spectrometry
AMP	amperometry
APIG	alpha-particle induced gamma-ray emission
ASNP	anodic stripping neopolarography
ASP	alpha-spectrometry
ASPC	alpha-spectrometry
ASTV	anodic stripping voltammetry
AUTR	autoradiography
BAA	bicyclic activation analysis
BEXE	beta-excited x-ray emission
CECH	cation-exchange chromatography
CFEN	continuous flow enthalpimetry
CFSS	coherent forward scattering
CHFA	charged particle activation
CLUM	chemiluminescence
COND	conductometry
COUL	coulometry
CPOT	chronopotentiometry
CVAM	chronovoltammetry
DACT	deuteron activation
DNC	delayed neutron counting
DPAS	differential pulse anodic stripping voltammetry
DPCS	differential pulse cathodic stripping voltammetry
DPP	differential pulse polarography
DSCA	differential scanning calorimetry
DTA	differential thermal analysis
ELMP	electron microprobe
EMSP	emission spectrometry
ESR	electron spin (or paramagnetic) resonance
FANE	f.a.n.e.s.
FDMS	field desorption mass spectrometry
FLIM	fluorimetry
FLIN	flow injection analysis
FSDP	fast scan differential pulse polarography
FSSP	forward scanning spectrometry
FTC	fission track counting
FTSP	flow through stripping potentiometry
GACT	gamma activation
GC	gas-chromatography
GEC	gel-chromatography
GLC	gas-liquid chromatography
GPLS	giant pulse laser spectrochemistry
GRA	gamma-ray attenuation
GSP	gamma spectrometry
HACT	heavy ion activation
HEAC	helium activation
HGMS	hydride generation mass spectrometry
HPLC	high performance liquid chromatography
ICHR	ionchromatography
ICP	inductively coupled plasma
ILUM	indirect luminescence method
INVV	inverse voltammetry
IOBB	ion-beam bombardement
IONF	ionflotation
IONM	ionmicroprobe
IRSP	intraresonance spectrometry
IRSP	intraresonance spectrometry

ISDI	isotope dilution
ISE	ionselective electrode
KIN	kinetic methods
LAPI	laser-atomic photoionisation
LCHR	liquid chromatography
LEIS	laser-enhanced-ionisation spectrometry
LEPS	low energy photon spectrometry
LIFL	laser induced fluorescence
LILU	laser induced luminescence
LMPM	laser microprobe mass analysis
LMSP	laser micro-spectrometry
LSCH	linear sweep chronoamperometry
LSPI	laser stepwise photoionisation
MAGN	magnetometry
MECS	mol. emission cavity spectrometry
MPE	magneto paper electrophoresis
MS	mass spectrometry
MTES	metastable-transfer emission spectrometry
NAA	neutron-activation analysis
NCGS	neutron capture gamma spectrometry
NCPG	neutron captured prompt gamma-ray analysis
NIAU	neutron induced autoradiography
NISC	neutron indirect scattering
NMP	nuclear microprobe
NMR	nuclear magnetic resonance
NTD	nuclear track detection
NTES	non thermal excitation spectrometry
NTIM	negative thermal-ionisation mass-spectrometry
OPOL	oscillopolarography
PACS	photoacoustic spectrometry
PACT	proton activation
PCH	paper chromatography
PESP	pulse excitation spectroscopy
PFDN	photo-fission delayed-neutron counting
PHAC	photonactivation
PHOT	photometry
PIXE	particle induced x-ray emission
PLES	plasma emission spectrometry
PLU	photoluminescence
POL	polarography
POT	potentiometry
PPOL	pulse polarography
PQCP	piezoelectric quarz crystal
PRAC	proton activation analysis
PRPS	proton induced prompt-photon spectrometry
PRXE	proton induced x-ray emission
PST	potentiometric stripping method
PVAM	pulse voltammetry
RADC	radiochemistry
RADM	radiometry
RIXE	resonance ionisation of Xe
RNC	radiative neutron capture
RRSP	resonance Raman spectrometry
RSSP	Raman scattering spectroscopy
SCHR	size exclusion chromatography
SCVA	stripping(chrono)voltammetry
SIMS	secondary-ion mass spectrometry
SLPI	stepwise laser photo-ionisation
SPCT	spectroscopy
SPFL	spectrofluorimetry
SPGR	spectrography
SPOT	stripping potentiometry
SPPH	spectrophotometry
SQWP	square wave polarography
SSCA	single sweep chronoamperometry
THCH	thermochemistry
THM	thermometry
TITR	titrimetry

TLC	thin-layer chromatography
TLSP	thermolense spectrophotometry
TMT	thermometric titrimetry
TNA	thermal neutron absorption
VAMM	voltammetry
XDIF	x-ray powder diffractometry
XESP	x-ray emission spectrometry
XMP	x-ray microprobe analysis
XPES	x-ray photoelectron spectrometry
XRF	x-ray fluorescence
XSEL	x+-selective electrode
XSPC	x-ray spectroscopy

Appendix 2

Merging of instrumental analytical techniques into groups
/see appendix 1 for abbreviations/

Optical methods

AAS	AES	AESP	AFS	CFSS	CLUM	ELMP	EMSP	ESP	FANE
FDMS	FLIM	FSSP	GFLS	HGMS	ICP	ILUM	IOBB	IONM	IPGP
IRSP	LAPI	LEIS	LEPS	LIFL	LILU	LMPM	LMSP	LSPI	MECS
MS	MTES	NMP	NTES	NTIM	PACS	PESP	PHOT	PLES	PLU
RPSP	PSSP	SIMS	SLPI	SPCT	SPFL	SPGP	SPPH	TLSP	XDIF
XESP	XMP	XPES	XSPC						

Nuclear methods

AACT	APIG	ASP	ASPC	AUTP	BAA	BEXE	CHPA	DACT	DNC
FTC	GACT	GPA	GSP	HACT	HEAC	ISDI	NAA	NCGS	NCPG
NAU	NISC	NMP	NTD	PACT	PPDN	PHAC	PIXE	PPAC	PPPS
PPXE	PADC	PADM	PNC	TNA	XPF				

Electrochemical methods

ACPD	ACSV	AMP	ASNP	ASTV	COND	COUL	CPOT	CVAM	DPAS
DPCS	DPP	FSDP	FTSP	INVV	ISE	LSCH	MPE	OPOL	POL
POT	PPOL	PST	PVAM	SCVA	SPOT	SQWP	SSCA	VAMM	XSEL

Chromatography

CECH	GC	GEC	GLC	HPLC	ICHP	LCHP	PCH	SCHP	TLC

Miscellaneous

CPEN	DSCA	DTA	FLIN	IONP	MIN	MAGN	POCR	PIXE	THCH
THM	TITP	TMT							

Appendix 3
Country groups

USA & Canada

Canada
USA

United Kingdom

United Kingdom

Fed.Rep.Germany

Fed.Rep.Germany

France

France

USSR

USSR

Japan

Japan

Asia

Hong Kong
India
P.R.China
Pakistan
Singapore
South Korea
Taiwan

Latin America

Argentina
Brazil
Chile
Cuba
Mexico
Venezuela

Eastern Europe

Bulgaria
Czechoslovakia
German Dem.Rep.
Hungary
Poland
Romania
Yugoslavia

North Africa & Near East

Algeria
Egypt
Iran
Iraq
Jordan
Libanon
Saudi Arabia
Tunisia
U.Arab Emirates

Rest of Africa

Ethiopia
Kenya
Mozambique
Nigeria
Sierra Leone

Rest of Developed Countries

Australia
Austria
Belgium
Denmark
Finland
Greece
Ireland
Israel
Italy
Netherland
New Zealand
Norway
Portugal
South Africa
Spain
Sweden
Switzerland
Turkey

DISCUSSION

C.J. Pickford. Why was lead omitted from the analysis: wasn't the division of techniques a little arbitrary?

T. Braun. The investigation was started with about 28 elements. A preliminary check-up indicated that the ranking doesn't change in case we reduce the list to 15 elements. The division of techniques we did base our rankings on was the devised and used by the Analytical Abstracts database.

W.D. Shults. Would it not be worthwhile to study the demography of instrumentation purchases in order to measure use of different methods in addition to publications (which reflect development of different methods)?

T. Braun. This was in fact done. Some of my talks (not shown in the oral presentation but included in the printed text) are collecting and displaying such types of data.

J. Tölgyessy. What is your opinion about the usefulness of nuclear analytical methods for the determination of organic species?

T. Braun. The recent study is dedicated exclusively to elemental analysis. The use and usefulness of nuclear analytical techniques (compared to other instrumental techniques) has been dealt with in one of our previous studies published in Radioisotopes (Japan) in July 1986.

H. Ross. Did you attempt to break down growth and usage as a function of speed, cost, sensitivity, accuracy and multielement analytical needs?

T. Braun. No.

USE OF SCIENTOMETRICS TO ASSESS NUCLEAR AND OTHER ANALYTICAL METHODS*

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Abstract

Scientometrics involves the use of quantitative methods to investigate science viewed as an information process. Scientometric studies can be useful in ascertaining which methods have been most employed for various analytical determinations as well as for predicting which methods will continue to be used in the immediate future and which appear to be losing favor with the analytical community. Published papers in the technical literature are the primary source materials for scientometric studies; statistical methods and computer techniques are the tools.

Recent studies have included growth and trends in prompt nuclear analysis impact of research published in a technical journal, and institutional and national representation, speakers and topics at several IAEA conferences, at modern trends in activation analysis conferences, and at other non-nuclear oriented conferences. Attempts have also been made to predict future growth of various topics and techniques.

INTRODUCTION

How does one go about choosing an analytical method for a particular determination? The naive answer is that he selects the best. Actually, best for many analysts is the method that they have available. Activation analysts advocate activation analysis; mass spectrometrists swear by mass spectrometry; atomic absorption people hold high the flame aloft. And so forth.

There have been, of course, comparisons of analytical techniques for different elements in certain matrices. TABLE I(1) shows typical data in such a comparison; the numbers are usually calculated on a best case scenario. Such tables are most useful for demonstration or comparisons. No one can really take them seriously except where differences are clearly large, or one method has an order of magnitude advantage. Different matrices require different methods. TABLES II & III(2) show

* Research sponsored by the Office of Energy Research, US Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

Table 1

ELEMENTAL SENSITIVITIES BY SEVERAL TECHNIQUES

Element	Sensitivity (nanograms/gram)			
	NAA[1]	AA[2]	ICP-AES[3]	SSMS[1]
Ag	0.1	2	0.7	0.2
Al	1	20	0.6	0.02
As	0.5	20	3	0.06
Au	0.05	10	-	0.02
B	-	2,000	1	0.01
Ba	10	10	0.1	0.2
Be	-	2	0.01	0.008
Bi	-	3	8	0.2
Ca	500	1	1.6	0.03
Cd	20	2	0.1	0.03
Ce	10	-	-	0.1
Cl	0.1	-	-	0.4
Co	0.9	10	2	0.05
Cr	200	3	0.4	0.05
Cu	0.2	1	0.06	0.06
F	0.1	-	-	0.05
Fe	40×10^3	10	0.5	0.05
Ga	0.4	100	5	0.09
Ge	2	200	10	0.2
Hg	2	200	20	0.06
K	40	1	1.0	0.03
Mg	50	1	1.5	0.03
Mn	0.005	2	0.02	0.05
Mo	30	600	2	0.3
Na	0.9	0.2	7	0.02
Nb	100	200	9	0.8
Ni	50	2	0.5	0.7
P	-	100×10^3	8	0.03
Pb	-	10	2	0.3
Pt	5	100	-	0.5
S	20×10^3	-	0.2	0.03
Sb	10	40	4	0.2
Sc	50	20	0.4	0.04
Se	50	100	2	0.1
Si	20×10^3	20	1	0.03
Sn	20	20	3	0.3
Sr	0.9	2	0.04	0.09
Te	9	50	4	0.3
Th	10	-	8	0.2
Ti	10	50	0.6	0.5
Tl	-	20	4	0.2
U	0.4	30×10^3	25	0.2
V	0.1	50	0.6	0.04
W	0.7	1×10^3	3	-
Y	1×10^3	100	0.1	-
Zn	20	1	0.2	0.1
Zr	200	1×10^3	0.7	0.1

(1) G.H. Morrison in Elemental Analysis of Biological Materials, IAEA Technical Reports Series 197, p. 222 (1980).

(2) G. F. Kirkbright, Ibid, p. 155.

(3) W. J. Haas, V. A. Fassel, Ibid, p. 170.

TABLE II. Comparison of INAA with IDSSMS for determination of Ba, Cr, and Sr, and with He Arc emission for determination of As

Procedure	N	$\bar{X}$ µg/g	σ	X_{min} µg/g	X_{max} µg/g	t	Significance Probabilities*
				Ba			
INAA	42	155.6	42.3	94	232	3.19	0.01
IDSSMS	42	132.3	46.0	40	220		
				Cr			
INAA	45	29.54	6.6	21	59	2.61	0.011
IDSSMS	45	24.91	10.6	7	48		
				Sr			
INAA	43	115.7	31.7	46	185	0.097	0.923
IDSSMS	45	114.9	37.6	44	230		
				As			
INAA	31	29.66	11.8	12.4	58	5.61	0.001
He Arc	31	36.24	13.3	16.2	65		

*Probability that the t value is due to chance alone. Values <.01 are taken as indicating a significant difference in the calculated means of the analytical results for a given element.

TABLE III. Comparison of AA and IDSSMS for determination of Cu, Zn, and Pb in coal

Procedure	N	$\bar{X}$ µg/g	σ	X_{min} µg/g	X_{max} µg/g	t	Significance Probabilities*
				Cu			
AA	23	21.77	1.73	17.3	25.0	1.18	0.25
IDSSMS	23	20.2	6.03	12	42		
				Zn			
AA	23	24.90	7.87	14.2	40	0.34	0.74
IDSSMS	23	24.09	8.46	10	40		
				Pb			
AA	23	13.22	4.67	8.2	30	1.33	0.19
IDSSMS	23	11.43	4.44	5.0	21		

*(See Table VI for explanation)

some actual experimental comparisons performed at ORNL for the determination of several elements in coal by several methods. Data such as these can be useful in deciding what method to use for specific problems, but time and effort is required to make these experiments.

From a philosophical or theoretical point of view it would be nice to know what methods are being most used for analysis, what trends are occurring, whether a new technique is catching on or whether an old technique is being replaced. Researchers would like to know which new methods are deemed most important by their peers; they would like to be 'where the action is'. Publishing papers on a subject in which no one is interested is more likely to lead to oblivion than to advancement.

Scientometrics is a term representing those quantitative methods that deal with science viewed as an information process. Scientometrics has been used to study information processes in a multitude of disciplines including physics, chemistry, analytical chemistry, biology, health physics and astronomy. Information flow in patents, in conferences, and in journals has been elucidated through scientometric techniques. Primary sources for these studies are the publication records from technical journals and books; statistical and mathematical techniques are the tools. An excellent general reference to the method and many of its applications is the monograph by Braun and Bujdoso (1).

The rest of this paper will be concerned with giving some examples of scientometric studies that relate to the problem of assessing different analytical methods. The thrust of the effort is to show how it is possible to predict which methods are more likely to be successful and in what direction analytical chemistry may be going. Obviously scientometric methods can never take the place of experiment for a particular application, but they can be used in policy making and in research planning, evaluation and prediction.

TOP ADVANCES IN ANALYTICAL CHEMISTRY, 1935-1985

A primary tool in scientometrics is the SCIENCE CITATION INDEX (SCI) published by ISI. In these volumes are collected all the citations to articles in past years in all the major technical journals. Thus, if one published an article in ANALYTICAL CHEMISTRY in 1984, and I referenced it in an article of mine in 1985, this citation would appear to your article in the SCI. It is apparent that the more heavily cited an article, the more impact it is having on the field. Thus, if one were to select the papers that had the greatest number of citations over a period of time, he would, in theory, have selected the most important advances in the field. Of course, another way to ascertain top advances would be to poll a number of influential experts in the field and ascertain what they considered were the best achievements.

Braun (4) did what was just described above: he used SCI to find the most cited papers in analytical chemistry while at the same time he sent a circular letter to 186 analytical chemistry gatekeepers. (A gatekeeper is one who exerts influence on a field as editor, reviewer, etc.) TABLE IV is a merged summary of the top advances as seen by the analytical chemists. From a list of most cited papers in SCI Braun deduced the methods used in these most cited papers; TABLE V gives his results. There is considerable agreement between the two sets of data which seems to lend support to the use of citation data for evaluating progress in a field. It is noteworthy that nuclear analysis ranks fourth among the top five in both compilations. That in itself should tell us something about the value of these techniques relative to others.

TABLE IV. Merged summary of top advances as seen by analytical chemists

Rank	Topic	Responses[a] (No.)
1.	Advances in spectroscopy and spectrometry	156
2.	Chromatography	127
3.	Advances in electroanalytical chemistry	79
4.	Nuclear analytical chemistry	77
5.	Continuous flow analysis	23
6.	Surface analytical chemistry	22
7.	Immunoanalytical chemistry	21
8.	Chemometrics	18
9.	Polydentate complexing ligands	14
10.	Organic reagents	6
	Thermoanalytical chemistry	6

[a] e.g. different advances in spectroscopy and spectrometry were mentioned a total of 156 times in the responses of the 69 respondents

TABLE V. Methods used in 133 "most-cited" analytical chemistry papers

Rank	Topic	% of total
1.	Spectroscopy and spectrometry	44.8
2.	Chromatography	36.8
3.	Immunoanalysis	13.8
4.	Nuclear analysis	3.4
5.	Electroanalysis	1.2

IMPACT OF RESEARCH PUBLISHED IN JOURNAL OF RADIOANALYTICAL CHEMISTRY.

Let us now turn to some specific radiochemical research and see what the top research papers in this field have been. Braun, Bujdoso and Lyon (5) used all the research papers published in the JOURNAL OF RADIOANALYTICAL CHEMISTRY (JRAC) in the years 1968-1981 as the data base. Total number of citations to these papers were obtained using the SCIENCE CITATION INDEX. Table VI lists the six most cited papers in alphabetical order by first author. This list of papers seems to provide a neat summary of the most active areas of research in nuclear analytical chemistry. Number one is the use of hydrated antimony pentoxide for removal of sodium in activation analysis. When this method was first reported, the authors (6) of the bi-yearly Nucleonics article in ANALYTICAL CHEMISTRY wrote, "The most exciting find in chemical separations, however, was the discovery that the radio-sodium interference, which has haunted biological analysis since the beginning of neutron activation, can be removed by a column of special grade hydrated antimony pentoxide." The other papers cover such topics of interest as radiochemical separations, gamma ray energies, proton microbeams, standard reference materials and precious metals. Probably most of us would agree that these were very important topics at the time, and for that matter are still important.

TABLE VI. Most cited articles 1968-1982 published in JRAC

No	1968–1982 citations*	Bibliographic data
1.	64 (4.9)	ADAMS, F., DAMS, R., A Compilation of Precisely Determined Gamma-Transition Energies of Radionuclides Produced by Reactor Irradiation *J. Radioanal. Chem., 3 (1969) 99*
2.	77 (9.6)	BOWEN, H. J. M., Problems in the Elementary Analysis of Standard Biological Material. *J. Radioanal. Chem., 19 (1974) 215*
3.	95 (9.5)	COOKSON, J. A., FERGUSON, A. T. G., PILLING, F. D., Proton Microbeams. Their Production and Use *J. Radioanal. Chem., 12 (1972) 39*
4.	51 (3.6)	CROCKET, J. H., KEAYS, R. R., HSIEH, S., Determination of Some Precious Metals by Neutron Activation Analysis *J. Radioanal. Chem., 1 (1968) 487*
5	115 (8.2)	GIRARDI, F., SABBIONI, E., Selective Removal of Radio-Sodium From Neutron-Activated Materials by Retention on Hydrated Antimony Pentoxide *J. Radioanal. Chem., 1 (1968) 169*
6.	73 (6.1)	GIRARDI, F., PIETRA, R., SABBIONI, E., Radiochemical Separations by Retention on Ionic Precipitates. Adsorption Tests on 11 Materials. *J. Radioanal. Chem., 5 (1970) 141*

*Citations/year data are in parentheses

USE OF CONFERENCE PAPERS TO DELINEATE TRENDS

Papers presented at conferences and national society meetings represent the cutting edge of science. Here is where advances are first reported to peers. The Modern Trends in Activation Analysis Conferences have been a primary vehicle for reporting in that field since 1961. Lyon (7) looked at papers and subjects included in five of these conferences between 1961 and 1976. He also attempted to predict the product mix of papers at the 1982 conference (8). The latter effort was only marginally successful. The data analysis of papers at the 5 conferences did show some interesting trends as seen in FIGURE 1. The rapid rise and fall of interest in neutron generators is easily seen, as is a similar rise of charged particle techniques. This paper also pointed out which countries and laboratories had a growing or declining interest in activation analysis, and suggested material science and industrial applications as the areas of most interest over the years. FIGURE 2 shows the percentage papers by category and is worth studying as a sort of historical record of scientific interest during the period.

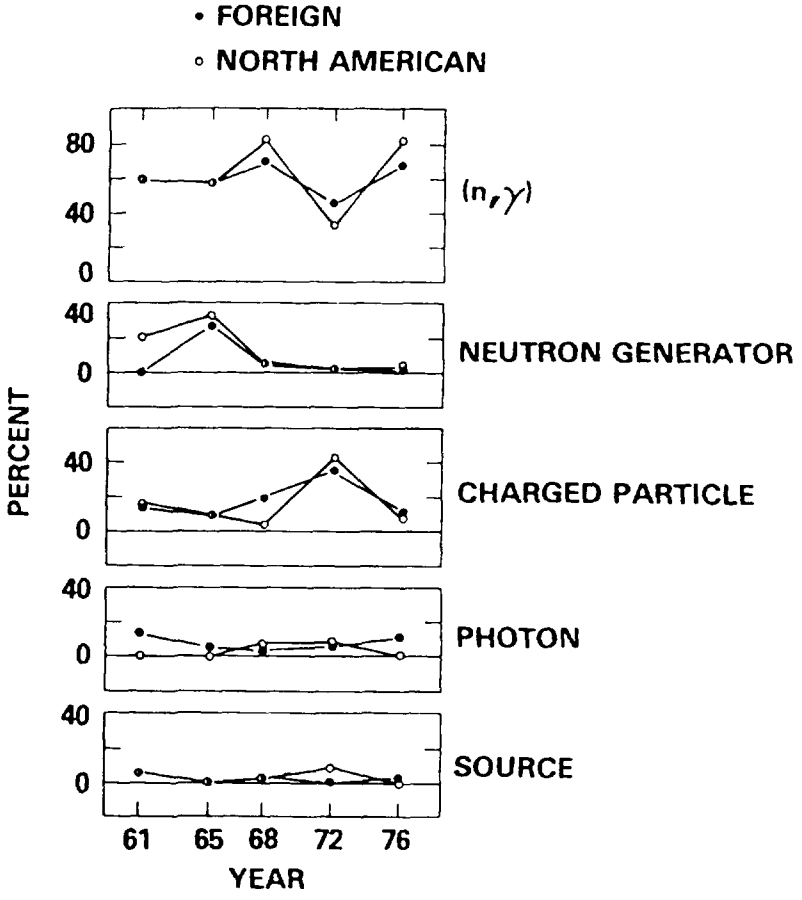

Figure 1. Paper Categorization by Technique

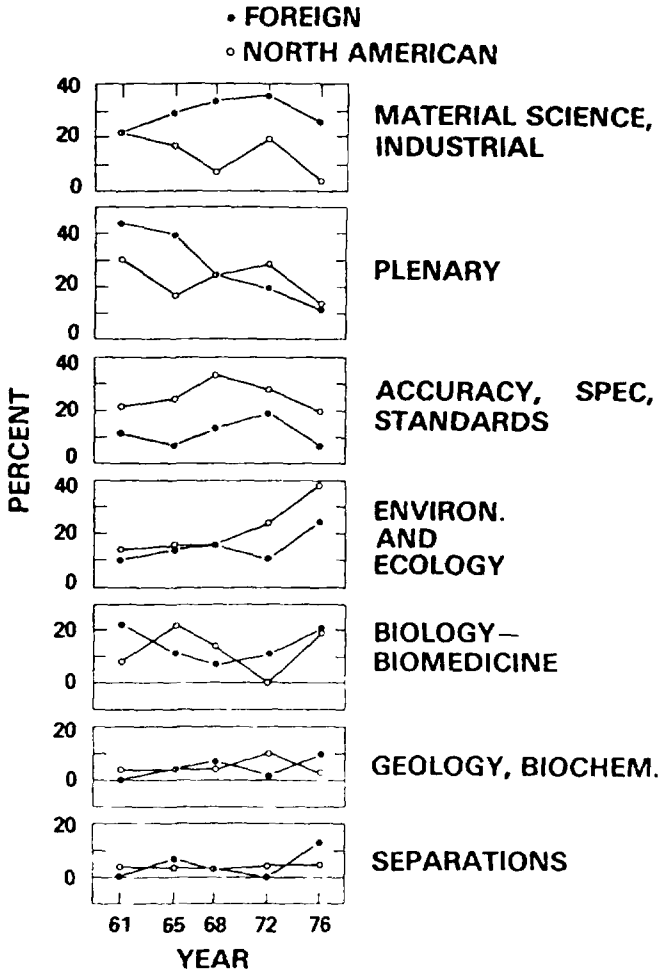

Figure 2. Paper Categorization by Subject

Other studies concerned with conference proceedings have been made by this author. The IAEA Nuclear Techniques in the Life Sciences conferences were studied and compared to other similiar meetings (9). The ultimate fate of papers presented at a national American Chemical Society meeting was ascertained through a literature survey (10). About half the papers presented orally were eventually published somewhere.

PROMPT NUCLEAR ANALYSIS: GROWTH AND TRENDS

Prompt nuclear analysis is defined in a review paper and two bibliographies as the use of prompt radiation accompanying a nuclear reaction to measure elemental or isotopic concentrations (11). Data from these were used in a study to assess growth and trends in the field by Bujdoso, Lyon and Noszlopi (12). Various methods were evaluated and a great wealth of data were generated using citation data from SCI. FIGURE 3 shows the growth of publications in this field over time, while FIGURE 4 shows distribution of papers on various types of nuclear reactions. From these two figures one sees an increasing interest in prompt methods as well as which nuclear reactions were in favor over the years. Backscattering seems ever popular. Oxygen, silicon,

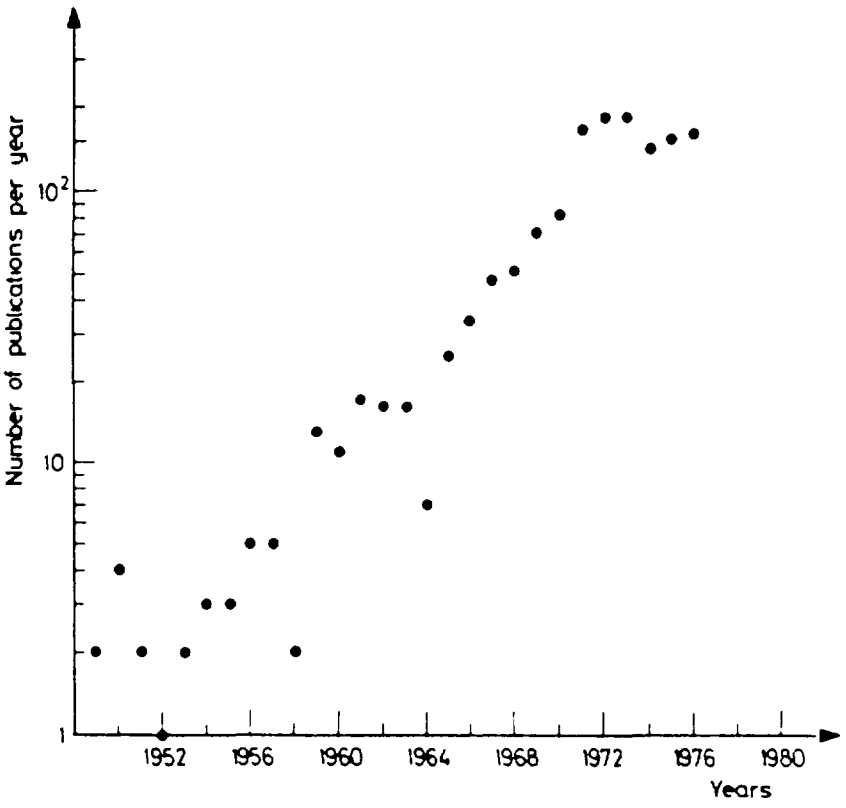

Figure 3. Publication Output in Prompt Nuclear Analysis

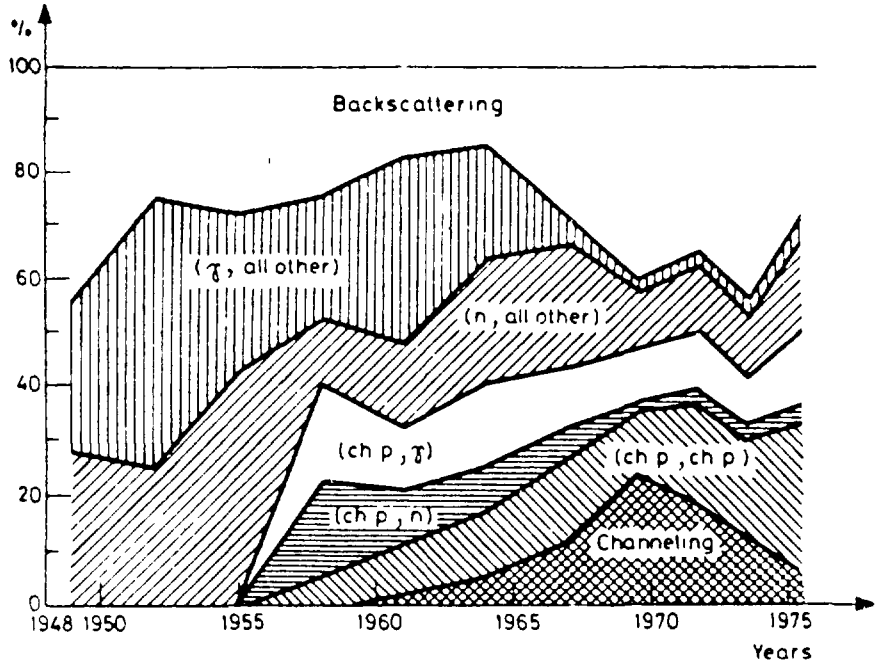

Figure 4. Distribution of Publications on Various Types of Nuclear Reactions

carbon, aluminum and nitrogen make up the first five most popular elements determined by prompt methods. Backscattering is larger than any other single charged particle technique, but makes up only about 1/3 to 2/3 of the total per element. TABLE VII shows the percent makeup of papers in analytical chemistry and prompt nuclear analysis by country. Three countries account for over 2/3 of the prompt papers. Little correlation is seen between the two groups. Careful study of the data in this paper will reward the researcher who may be thinking of entering the field; for example after three years of research, 68% of all publishing workers had left prompt nuclear analysis!

TABLE VII. Percent makeup by country of papers on prompt nuclear analysis and analytical chemistry

Country	Percentage of papers on	
	prompt nuclear analysis	total analytical chemistry*
USA	41.7	18.0
France	13	3.0
United Kingdom	10	5.4
Fed. Rep. Germany	4.8	5.7**
Soviet Union	4.6	25.5
Canada	3.5	
Sweden	2.9	
South Africa	2.8	
Belgium	2.4	
Australia	2.3	
Japan	2.1	8.8
Czechoslovakia	1.6	4.9
Italy	1.4	1.7
Poland	1.3	2.4
Denmark	1.2	
Finland	0.6	
Hungary	0.6	
Netherlands	0.5	1.0
India	0.4	3.7
Venezuela	0.3	
New Zealand	0.3	
Rest of the world	2.0	19.9

*Average of the years 1960–1970.[22]
**Includes both East and West Germany.

NUCLEAR AND OTHER TECHNIQUES FOR POLLUTANT ANALYSIS

Most of the work that this author has done has been concerned primarily with nuclear techniques, consequently the discussion so far has centered on them. Let us now, however, look at a recent comparison performed by Braun (12). He used articles in ANALYTICAL ABSTRACTS to ascertain techniques used

for pollutant analysis. He found that through 1984 chromatography accounted for 33% of papers published, spectrometry 31%, electroanalysis 19%, and nuclear 16%. These percentages agree rather well with the data shown in TABLE V.

Pursuing the comparison furthur, Braun tabulated the instrumental methods used in an IAEA (64 lab) round robin intercomparison of elements in environmental water samples. The result showed atomic absorption leading (53%). Neutron activation analysis was a distant second (22%), with other optical spectrometries (15%) and mass spectrometry (5%) filling out most of the remaining techniques.

Still another survey type approach to this question is to see which instruments are most available in different laboratories. This almost certainly removes nuclear techniques from the race. Allied to this type survey is that often published in trade magazines wherein labs are quizzed as to what instrumentation they plan to buy in the coming year.

During the past decade and a half, increasing emphasis has been placed on elemental speciation. Here nuclear techniques are at a severe disadvantage because any speciation done must be by a chemical separation. Braun has shown that between 1975 and 1985 publications involving speciation increased about threefold.

Finally it should be pointed out that the present trend in analytical instrumentation is toward sensors that can be placed directly in the environment and which make real time continuing measurements. In line gamma ray measurements have gone on for decades, but more sensitive and selective techniques are under development.

FUTURE AREAS FOR INVESTIGATION

The purpose of this paper has been to introduce the subject of scientometric study to the reader and to indicate how it has been used to evaluate progress in science. The field of analytical chemistry is ideally suited for such studies: there is an excellent literature composed of only a few top journals in which researchers publish, data on samples and methods are available from laboratories and government agencies, and new methods and instruments are constantly being added to the chemist's repertoire. On-line computer searches are easily and inexpensively performed. Results are often quite surprising and informative.

For those old-fashioned enough to want to work in the laboratory, the results of such studies will provide insight and direction as to where methods are needed and where the field is headed. The use of sensors has been mentioned as a fruitful area for study. Robotics is closely allied to sensors and is certainly an area of future growth. The analytical radiochemist is no longer the "new kid on the block;" there are many newer and often cheaper and better methods to perform elemental analyses. The challenge to the radiochemist is to find where his techniques can be best used ... and then improve them.

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COMMENTS ON THE ESTABLISHMENT OF A METHODOLOGY FOR THE METROLOGICAL CHARACTERIZATION OF ANALYTICAL METHODS

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Abstract

For the comparison of analytical methods, it is important to use a standardized set of statistical techniques for the evaluation of data and for the comparison of methods. There seems to be some confusion regarding the definitions and calculations for basic terms such as accuracy, precision, detection limits, etc. Currently, these concepts do not have commonly accepted definitions or methods of calculation.

It is proposed that we work toward the establishment of a common method of presenting such data, and a common method of its calculation. Only in this way will we be able to compare various analytical methods in a meaningful way.

In this paper, a proposal is made for a unified methedology for the metrological characterization of analytical methods.

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1. Introduction

One of the main characteristics of trace analysis is the need to identify and determine a large number of elements and chemical species, many at very low concentrations, and in samples of greatly differing composition. Because of the variety of analytes and sample types, a number of different techniques are needed, including nuclear analytical methods. A qualified analyst must be able to choose which method is best suited for a particular problem, and to do so effectively, a commonly used set of figures of merit should be available. Unfortunately, such a set of figures is not sufficiently developed at present. This represents a need which merits serious attention, especially for those interested in nuclear analytical methods.

As examples of figures of merit, we suggest considering concepts such as: sample and sample pretreatment requirements, total cost, total analysis time, accuracy, precision, the ability of a method to detect and/or quantify small amounts or concentrations, and sensitivity.

Some of these are difficult, or even impossible to quantify, such as sampling requirements. Others may be amenable to standardized evaluation processes, such as accuracy, precision,

and the ability to detect/quantify small amounts or low concentrations of analyte in samples of varying composition. Of these, we have chosen the last for discussion.

2. The IUPAC/ACS approach

The International Union of Pure and Applied Chemistry has provided the following definition [1]: "The limit of detection (LOD), expressed as a concentration or amount, is derived from the smallest measure that can be detected with reasonable certainty for a given analytical procedure." The American Chemical Society [2] gave a similar definition: "The limit of detection is the lowest concentration of an analyte that an analytical procedure can reliably detect." Before such concepts are useful, terms such as "reasonabale certainty" and "reliably" must be quantified.

The IUPAC and ACS have used similar approaches in quantification, which can be presented as follows: The limit of detection is a number that describes the lowest concentration or amount of analyte that can be determined as statistically different from an analytical blank with a certain degree of confidence. An actual measurement is usually made in terms of a signal (volts, number of counts, area under a spectrum) which must be related to a concentration or amount of analyte through some response function, such as a calibration curve. Thus we can write:

$S_T = S_X + S_B$, or $S_X = S_T - S_B$, where

S_T = total, or sample signal,

S_X = signal due to analyte, or net signal,

S_B = signal due to blank, or background.

The response function can be written as: $S_X = g(C_X)$, where C_X is a concentration or amount of analyte, and g represents some function. In the simplest linear case, we have:

$S_X = aC_X$; and $C_X = (S_T - S_B)/a$.

It is assumed that S_T, S_X, S_B will be randomly distributed according to some well-defined distribution function (eg. Normal, Poisson, Student-t, etc.).

Hence our ability to determine small amounts of chemical species depends on distinguishing small differences between S_T and S_B. But this in turn depends on fluctuations in S_T, S_B values; the more they fluctuate for repetitive measurements of a sample, the less able are we to distinguish them. A common measure of fluctuation is the standard deviation, defined as:

$s = \sqrt{\Sigma(S - \bar{S})^2/(n - 1)}$, where

$\bar{S}$ is the arithmetic average of n replicate measurements. If the random errors in S follow a normal distribution, a plot of frequency of observations vs signal size would appear as in Figure 1. Obviously, the ability to distinguish between analyte and blank depends on the difference: $(S_T - S_{\bar{B}})$. For instance, in the case of a normal distribution, if S_T is $3s_B$ larger than $S_{\bar{B}}$ (average of blank signals), there is a 0.13% probability that the signal is from a blank. This small probability is taken to fulfill the requirement of "reasonable certainty" or "reliably". More generally, we can write:

$S_D = S_{\bar{B}} + k_D s_B$; $k_D = 3$ for a normal distribution.

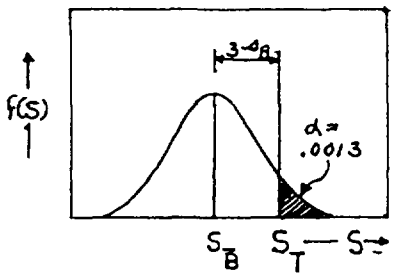

FIG.1. NORMAL DIST. OF ANAL. SIGNALS

Kaiser [3] has proposed a more conservative value: k = 6, and proposed the term: limit of guarantee. The ACS went on to define the limit of quantification as follows:

$S_Q = S_{\bar{B}} + k_Q s_B$; $k_Q = 10$ for a normal distribution.

If we assume a simple linear response function, these two signal limits translate into concentration amounts as:

$C_D = k_D s_B / a$

$C_Q = k_Q / a$.

A number of variations of this basic approach have been suggested [4], including:

1. Use of Student-t in place of k for cases where the number of replicate measurements is small. It should be noted that unlike the normal distribution, t values depend on the number of observations. It should be chosen to give the same confidence level as k (eg. 0.13% for LOD).

2. Use of Student-t and the standard deviation of the average blank signal, $s_{\bar{B}}$:

$s_{\bar{B}} = s_B/\sqrt{n_B}$: n_B = number of blank measurements.

In many cases, $3s_B > ts_{\bar{B}}(\alpha = 0.05)$, and hence the use of $s_{\bar{B}}$ can reduce C_D or C_Q by a significant amount. Therefore, it is important to state clearly which approach is being used.

3. Use of the pooled standard deviation, defined as:

$s_P = [s_T^2/n_T + s_B^2/n_B]^{\frac{1}{2}}$.

In this case, it is convenient to assume $s_T = s_B$, but this must be verified experimentally. If the assumption is valid, we may write:

$s_P = s_B[(n_T + n_B)/n_T n_B]^{\frac{1}{2}}$.

4. Use of the relative standard deviation, RSD, defined as:

$RSD = s_B/S_{\bar{B}}$, and

$S_D = k_D s_B$

$k_D = 1/RSD$.

The signal S_D in this case leads to the so-called concentration limit of detection. This RSD variation is related to the others, as can be seen from the equation for a simple linear response function:

$C_D = ks_B/a = k(s_B/S_{\bar{B}})(S_{\bar{B}}/a) = k(RSD)(S_{\bar{B}}/a)$.

Using the approach discussed above, the ACS has recommended the following terminology:

$S_X < 3s_B$: ND; analyte not detected

$3s_B < S_X < 10s_B$: Region of detection; signals measured and reported as amounts or concentrations with the LOD given in parenthesis

$S_X > 10s_B$: Region of quantitation.

3. Approach using the error in sensitivity (Graphical approach)

Winefordner and Long [4] and others have pointed out that the IUPAC/ACS models consider only the errors in blank measurements, whereas most practical cases are more complex. Many analytical methods require the use of a response function (calibration curve), which for the linear case will now be written:

$$S_X = mC_X + i.$$

This equation is best obtained by regression analysis of a good set of calibration data. The slope, m, is a measure of the sensitivity of the method, and i is the intercept, as shown in Figure 2. Apparently some workers assume m to be well defined, but in general it mayhave an uncertainty due to errors in the calibration points, or non-linearity. This error may be represented as:

$$m \pm ts_m,$$

where s_m is the standard deviation of the slope. Student-t is chosen to give the desired confidence level for a given number of observations (the number of points used to define the calibration curve). Figure 2 illustrates the effect of including errors in m when evaluating the LOD. Three concentration values can be found for a given value of S_X. The conservative LOD is C_R, which is based on the smallest sensitivity ($m - ts_m$). Analagous remarks can be made for LOQ values.

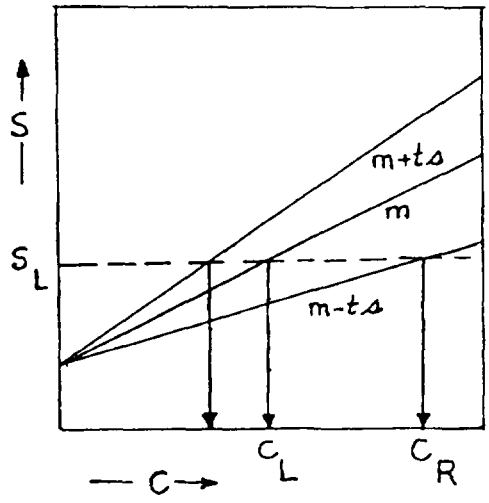

FIG.2. CALIBRATION CURVE

4. Propagation or erros approach

A closer look at Figure 2 indicates that perhaps errors in the intercept, i, should be included in LOD, LOQ values, and to do so, it is convenient to use propagation of error theory, which leads to the equations:

$$C_X = (S_X - i)/m$$

$$\sigma_c = [\sigma_{SX}^2 + \sigma_i^2 + (\frac{i - S_X}{m})^2 \sigma_m^2]^{1/2}/m.$$

This equation allows the evaluation of the standard deviation of a concentration/amount taken from a calibration curve.

For LOD calculations, S_X is the blank signal ($S_{\bar{B}}$), and $s_{SX} = s_B$. Further, in most cases, $S_{\bar{B}} = 0$. Substituting these equalities into the above equation gives:

$$s_C = [s_B^2 + s_i^2 + (i/m)^2 s_m^2]^{\frac{1}{2}}/m$$

$$C_D = k_D s_C, \text{ and } C_Q = k_Q s_C.$$

If there is no error in the slope or intercept, $s_m = s_i = 0$, and the equation above simplifies to the basic IUPAC/ACS model.

5. Approach using the relative standard deviation

More recently, Mocak and Beinrohr [5] have presented a method for calculation of terms similar to LOD, LOQ, which uses the appropriate relative standard deviations, RSD, and knowledge of their concentration/amount dependence. They begin by defining three different limits, as shown in Figure 3.

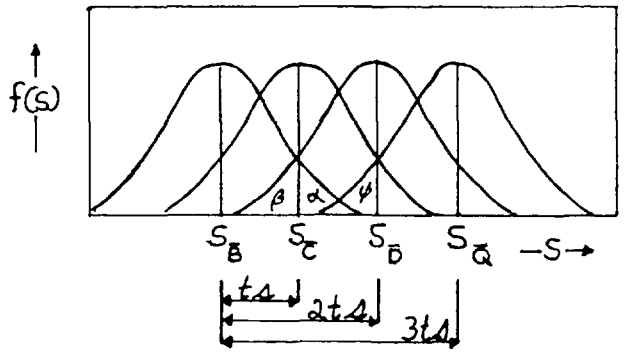

FIG.3. SIGNAL LIMITS

1. Decision limit. The signal corresponts to the upper (1-α) confidence interval for the distribution of blank signals. The Type I error is equal to α; ie. a signal is rejected as a blank, but it is really a blank at α% probability. For this case, we may write:

$$S_C - S_B = t_C s_{SC-SB} = \text{net signal}$$

$$s_{SC-SB} = [s_{SC}^2/n_C + s_{SB}^2/n_B]^{\frac{1}{2}} = \text{(Pooled stand. dev.)}$$

Assuming $s_{SC} = s_{SB} = s$, we may write:

$$s_{SC-SB} = s[(n_C + n_B)/n_C n_B]^{\frac{1}{2}}.$$

If we now assume a simple linear response function ($S = aC$), we have:

$$C_C = 1/a(S_{\bar{C}} - S_{\bar{B}})$$

$$s_C = 1/a(S_{SC-SB})$$

$$RSD_C = s_{CC}/C_C = [1/a(s_{SC-SB})]/[1/a(S_{\bar{C}} - S_{\bar{B}})]$$

$$= s_{SC-SB}/t^c(s_{SC-SB})$$

$$RSD_C(\%) = 100/t^c.$$

The one-sided Student-t depends on the degrees of freedom ($n_C + n_B - 2$) and on the confidence level, α.

Eg. $\nu = 6$; $\alpha = 0.05$; $t = 1.94$; $RSD_C = 100/1.94 = 51.1\%$

$\nu = 6$; $\alpha = 0.01$; $t = 3.14$; $RSD_C = 100/3.14 = 31.8\%$.

2. Detection limit. The signal, S_D is such that the (lower end) confidence interval for the group of S_D observations corresponds to the decision limit, $S_{\bar{C}}$. Commonly, $\beta = \alpha$. The Type II error is equal to β; ie. a signal is accepted as a blank even though it is not from a blank at $\beta\%$ probability. A derivation similar to that above leads to the expression:

$$RSD_D(\%) = 100/2t^D.$$

Eg. $\nu = 6$: $\alpha = 0.05$; $RSD_D = 100/2X1.94 = 25.5\%$.

3. Determination limit. The signal S_Q is such that the lower end of the confidence interval of observations of S_Q corresponds to the detection limit, S_D. Commonly, $\psi = \alpha \cong \beta$. According to the authors, a signal greater than S_Q "occurs in the region of signals detected with certainty." A derivation similar to that given for the decision limit gives:

$$RSD_Q(\%) = 100/3t^Q.$$

Eg. $\nu = 6$; $\alpha = 0.05$; $RSD_Q = 100/3X1.94 = 17.0\%$.

The authors used these limits to define concentration/amount regions as shown in Figure 4.

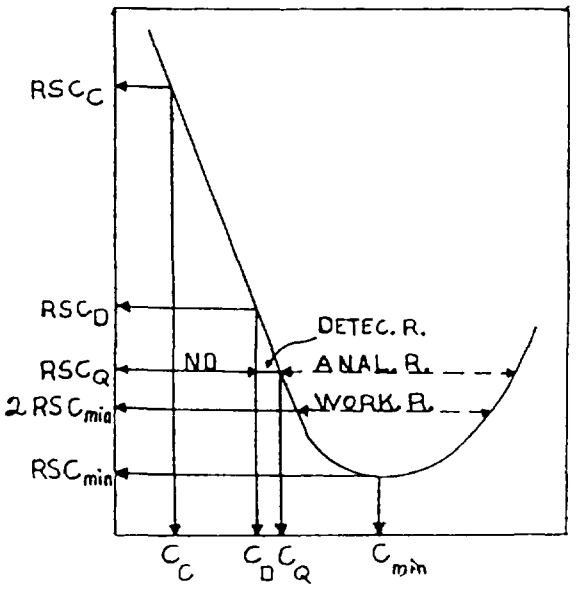

FIG.4. CONCENTRATION REGIONS

1. Analyte not detected. Region of concentration below the detection limit.
2. Range of detection. Presence of the analyte can be detected with a given confidence level. The lower border is the detection limit.
3. Analytical range. Results can be quantified with a given confidence level. The lower border is the determination limit, and the upper border has the same RSD_Q.
4. Working range. Range includes concentrations with RSD values less than a chosen value; eg. $2XRSD_{min}$.

To implement the method, one must determine the RSD of signal values over a range of concentrations/amounts. Once this is done, the RSD_C, RSD_D, RSD_Q and RSD_{min} values can be used to define the ranges mentioned.

The development , as presented here, depends on a simple linear response function. A more complex function would lead to other expressions for critical RSD values. As opposed to the IUPAC/ACS methods, the various limits depend strongly on the number of blank and sample measurements. This is because the RSD approach uses the Student-t rather than the normal distribution.

6. Comments

The basic IUPAC/ACS approach is simple and relatively easy to implement. However, it depends only on blank values, and refers to a single sample measurement. In good laboratory practice, replicate sample measurements should be made, and average signal values should be used. This would, in turn, lead to lower LOD, LOQ values than those predicted by the basic IUPAC/ACS approach.

In the modification with the pooled standard deviation, account is taken of replicate sample measurements, but the assumption $s_{SX} = s_B$ must be verified. If it is not true, the modification will be more complex.

The sensitivity error approach is valid only when the intercept is well defined, which is probably not the general case.

The propagation of error approach seems to be a powerful method, but sufficient replicates must be taken so that the normal distribution is valid. The Student-t distribution may be more appropriate.

The approach of Mocak and Beinrohr requires the greatest amount of data, but it seems capable of providing the greatest amount of information. Further studies are needed to assess the utility of their method.

It is not possible at present to give a definitive comparison of these approaches, and it is certainly premature to make any decision as to which, if any, is the best or most useful for the comparison of nuclear analytical techniques. Nevertheless, the ability to detect/quantify small amounts or low concentrations of analyte is of crucial impor-

tance in environmental studies. A well defined, concensus figure of merit for this concept would be of great benefit in discusing the applicability of nuclear techniques to environmental analysis, and help greatly to establish a rational basis for the comparison of nuclear analytical methods with competitive techniques.

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DISCUSSION

V. Krivan. In your talk you related blanks to determination methods. I would like to point out that the blanks, which without doubt determine the limits of detection and are in many instances also the dominating factor of the accuracy, are mainly introduced in the predetermination steps of the analytical procedure. Therefore, these should be first discussed in connection with blanks.

T. Braun. When it comes to the selection of a data base for verification of your statistical methodology, I don't think journal papers could be a good choice. It seems that there are quite comprehensive data bases available for such purposes. One of them could be the data collected by the IAEA Seibersdorf Laboratory during many years of intercomparison programmes.

R. Lindstrom. I doubt that a base of data exists (certainly not published) to test the usefulness of an approach such as you describe. One needs a large number of blank determinations by a stable procedure, and a body of calibration data for that procedure.

H. Ross. Conventional techniques for least squares fitting of data would tend to "wash out" uncertainties in the slope in the low concentration region. Do you see this as a problem in the determination of Sc?

E.H. Klehr. Yes, but at this point, I'm not sure how significant this valley is. We need to look at a carefully selected data base.

D.H. Smith. Can various definitions of limits of detection and quantification be evaluated by accessing and treating a large data base? I believe there must be many data bases at industrial labs (or EPA, etc.).

E.H. Klehr. Yes, I think so, and such work would be of great benefit. I urge that we consider not only the various limits of detection (quantitation, etc.), but various ways of analyzing precision as well.

PLUTONIUM ISOTOPIC MEASUREMENTS BY GAMMA-RAY SPECTROMETRY VERSUS MASS SPECTROMETRY

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Abstract

For several years Mound has actively contributed to the development of the measurement of plutonium isotopic composition by gamma-ray spectrometry. This development effort has been conducted primarily in support of calorimetry and safeguards measurements. As part of this effort, Mound has participated in a number of sample exchange programs. For the Metals Exchange Program, Mound has reported the results of isotopic measurements obtained by nondestructive (gamma-ray spectrometry) and destructive (mass spectrometry and alpha counting) means. Comparisons of the recent performance of nondestructive and destructive isotopics measurements at Mound will be presented. In addition, the instrumentation required for data acquisition and analysis of gamma-ray spectrometry measurements and their benefits will be presented.

DISCUSSION

D. Smith. In mass spectrometry, the 238 and 241 of Pu have interferents 238 and 241 Am; thus, mass spec analyses tend to be biased high. Mass spec analysis requires for less sample than gamma spectrometry (μg vs g), so the techniques are in many cases complementary.

R. Mayer. The authors agree that the techniques are often complementary. The advantages of gamma-ray analysis is primarily the ability to obtain an analysis in a short amount of time while not requiring that the sample be opened or prepared in any manner. This is a particular benefit in an area of interest, Safeguards. Mass spectrometry and alpha counting also have desirable features which gamma-ray analysis cannot provide, such as analysis combined with calorimetry to obtain a facility independent assay of material on site for a limited number of samples. Where problems arise, the item should be opened and sampled. The samples may then be analyzed by destructive means, at a later date, to verify the calorimetric assay (gamma-ray + calorimetry) value.

N. Ikeda. Is the gamma-ray spectrometric method applicable to the low-level Pu isotope measurements in environmental samples?

R.L. Mayer. First, we are not promoting the use of calorimetric (calorimetry and gamma-ray spectroscopy) for environmental samples. The point of this presentation was the comparison of gamma-ray and mass spectrometry results obtained at Mound through the Metals Exchange Programme.

In principal, the gamma technique, particularly the analysis program, could be applied to environmental samples. Of course, the specifics of detector specifications, count times, and sample size would have to be adjusted with the measurement goals in mind. Remember though that this is a measurement of relative isotopic composition. The atom ratios 238 Pu/239 Pu, 240 Pu/239 Pu, 241 Pu/239 Pu, and 241 Am/239 Pu are the quantities measured. To obtain a measure of the concentration of Pu in the sample, some alternative correction or comparison to standards is required. There are gamma-ray techniques for environmental measurements. It was not our intention to review these techniques.

URANIUM DETERMINATION BY FISSION TRACK COUNTING

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Abstract

To the analytical chemist, one of the most important aspects of nuclear tracks is the capability they give to quantitatively measure trace concentrations of alpha-emitting and fissile nuclides in matter. The procedure for determining ^{235}U is simple in principle. A sample is packaged in a clean dust-free atmosphere in contact with a track recorder and irradiated in a neutron flux for a suitable time. The recorder is etched to make the tracks optically visible and the ^{235}U concentration is estimated from the track density relative to the track density produced by a ^{235}U standard similarly treated. The detection limit for natural uranium is comparable to that of isotope dilution mass spectrometry and neutron activation analysis and has been reported to be below 40 picograms per gram. The method can be applied to nearly all solids, including powders, and very little sample preparation is necessary.

INTRODUCTION

Since the discovery in 1958 that the fission fragments of ^{235}U produce observable tracks in inorganic materials, study of the phenomena of nuclear tracks in solids has touched many divergent areas of science and contributed to growth in knowledge in both the area touched as well as of the science of track formation. Developments in basic nuclear particle physics, structure of crystalline and amorphous solids, geological and lunar dating of minerals, gas diffusion membranes, element mapping of fissile and alpha emitting nuclides, neutron flux monitoring, and analytical chemistry determinations are some of the well known examples where important achievements have occurred. The fascinating stories behind most of the developments in the field up to 1975 are related in the superb reference work "Nuclear Tracks in Solids" by Fleischer Price and Walker (1). Since 1977 the Journal of Nuclear Tracks and Radiation Measurements has been published to provide a focus for this area of research. Many of the current areas of research were described in 1983 at the 12th International Conference on Nuclear Tracks published in a special issue of the Nuclear Tracks Journal (2).

In a recent review of highly sensitive methods for the determination of uranium it was pointed out that only a few methods are capable of measuring the element in amounts of about

1 nanogram and/or concentrations in the range of nanograms per gram and below (3). Isotope dilution mass spectrometry (IDMS) will detect picogram quantities of natural uranium and is perhaps currently the most sensitive method (4). Measurements based on mass spectrometry have the advantage of being able to determine the individual isotopes of uranium. Resonance ionization spectroscopy (RIS) and resonance ionization mass spectrometry (RIMS) are currently not as sensitive as IDMS but show promise of comparable sensitivity with further development (3). Conventional fluorometric methods will detect about 0.1 nanogram of uranium, but measurements are not accurate unless the quantity of uranium is somewhat above 1 nanogram. Fluorometric methods based on laser excitation have extended the sensitivity considerably (5).

Nuclear methods used to determine uranium include alpha counting, neutron activation analysis (NAA), and fission track measurements. By counting for a 24-hour period the alpha particles from ^{238}U, 30 nanograms of natural uranium can be measured with an uncertainty of about 30 percent. Neutron activation analysis can be carried out on both ^{238}U, where either the induced ^{239}U or its daughter ^{239}Np are counted, and ^{235}U, where one or more fission products are counted. The combined effects of the large thermal neutron fission cross section of ^{235}U, the low isotopic abundance of ^{235}U, and the small yields of fission products, result in the NAA of natural uranium based on the activation of ^{238}U being about a factor of 10 more sensitive than NAA based on ^{235}U. The instrumental determination by NAA of about 6 picograms of uranium per gram of high-purity silicon using ^{239}Np counting was reported (6). Because the half-life of ^{239}U (23.5 m) is much shorter than that of ^{239}Np (2.35 d), it is practical to count a larger fraction of the parent than of the daughter and thus obtain a higher measurement sensitivity by counting ^{239}U. Although the potential sensitivity for determining natural uranium by NAA is higher with ^{238}U, it is frequently not possible to make use of this method (without chemical separations) because of interferences from other induced radionuclides. Interferences are much more likely with the low energy gamma rays of ^{239}U and ^{239}Np than with the high energy gamma rays emitted by some of the fission products of ^{235}U. For example, only a few radionuclides, such as ^{24}Na with its 2754 KeV photon, have gamma rays with sufficient energies to interfere with the measurement of the 1596 KeV gamma ray of the fission product ^{140}La. A common technique to measure weak sources of high energy gamma rays in the presence of strong sources of low energy gammas is to use a thin piece of lead to absorb the low energy gammas but transmit the high energy gammas. Thus instrumental NAA of uranium via the ^{235}U isotope is useful in situations where NAA with the ^{238}U isotope is not suitable due to interferences. The fact that the detection efficiency decreases with increasing gamma energy can be, however, another contributing cause for the lower measurement sensitivity of NAA of uranium via ^{235}U versus ^{238}U.

Although it is possible to determine uranium at the nanogram per gram level in certain matrices by the methods mentioned above with little or no chemical separations, in most analyses

chemical separation of the uranium or, in the case of NAA an activation product, is needed before the analysis can be completed. For example, the concentration of uranium in human urine can be determined by isotope dilution mass spectrometry at levels as low as 0.003 ug/L (3) but only after the uranium is isolated and placed on a filament for evaporation and ionization in the mass spectrometer.

Two nuclear methods, delayed neutron counting (7) and fission track analysis, do not require chemical separations to analyze for uranium. Delayed neutron counting (DNC) is an activation analysis method based on the fact that several fission products with half-lives ranging from below a second to nearly a minute emit neutrons following beta decay. The neutrons can be counted with efficiencies of 5 percent or better and lower limits of natural uranium in the range of 25 nanograms can be measured. With a minimum of care, determinations of ^{235}U can be effected instrumentally with no naturally occurring interferences. Fission track analysis is not a method of activation analysis, as is DNC, but is based on the fact that when fission of ^{235}U occurs near the surface of a sample some of the fission fragments escape and produce latent tracks in adjacent track recorders. The track density, the number of tracks per unit area, is proportional to the uranium concentration which can be measured in nearly all solids.

DETAILS OF THE FISSION TRACK METHOD

According to Fleischer et al (1), nuclear tracks will only form in insulators or semiconductors with electrical resistivities above 2000 Ohm-cm. Thus tracks will not form in silicon but will in silica. Tracks form by an incompletely understood mechanism that involves intense ionization in which the atomic structure of a microscopic region of the recorder is damaged. The damaged region can be observed with an electron microscope, but track densities are normally determined after the region is removed by chemical etching. Several methods, discussed below, can be used to determine track densities.

To determine uranium by the fission track method, a sample is packaged with a track recorder and the package is irradiated to a suitable neutron fluence (neutron flux x time). A standard containing a known amount of ^{235}U and a track recorder are either included with the package or prepared and irradiated separately to an equal or known fluence. A common method of packaging samples is to tightly wrap them in aluminum foil. The uranium concentration in the unknown is determined from the relative track densities and the concentration of uranium in the standard. Placing the recorder in intimate contact with the sample makes it possible to observe localized variations of uranium content over the surface of the sample, whereas allowing some distance between the sample and recorder causes the emitted fission fragments to spread out before they hit the recorder and produce a more uniform distribution of tracks (1). The more uniform the track distribution the easier it is to determine the average uranium concentration in the sample. The range of

fission fragments in air is about 4 cm, but irradiations have been made in evacuated quartz containers with the sample and recorder separated enough to give a uniform track density with highly inhomogeneous samples (1).

Because uranium is present as a parts-per-million contaminant in most atmospheric dusts, it is necessary to do all sample treatment and packaging in a dust-free environment such as a clean room with a laminar flow clean hood. Fleischer et al, indicated analyses can be made at 5 ppb, but that contamination problems generally limit the method to uranium concentrations of 50 ppb or higher. Riley, in an excellent application of the fission track method to uranium measurement in semiconductor packages, was able, by the use of clean hoods and "class 100" clean rooms, to measure concentrations as low as 1.5 ppb (8). The track density obtained by Riley on blank track recorders indicated that uranium concentrations as low as 0.04 ppb can be detected.

Although many materials can be used as nuclear track recorders (2), two of the most frequently used for analytical measurements employing nuclear reactor irradiations are mica and polycarbonate plastic, sold under the trade names Lexan (General Electric, USA), and Makrofol (Bayer AG, FRG). Mica track recorders are etched in hydrofluoric acid and the polycarbonate plastics are etched in NaOH or KOH solutions. Details of etching of most recorders are described by Fleischer et el. This type of polycarbonate is rather resistant to damage by the intense gamma radiation in nuclear reactors and can be irradiated in some facilities to neutron fluences of about 10^{17}. Care must be taken to keep the polycarbonate cool during irradiation or track fading will occur. Experience at ORNL with a pneumatic tube in the Oak Ridge Research Reactor with a thermal neutron flux of 5 $x10^{13}$ has shown that Lexan is marginally useful, but that it cannot be used at all in a pneumatic tube in the HFIR (6) where the flux is 5 X 10^{14}. The principal advantages of the plastic are its low cost and low uranium impurity. The reader is referred to Fleischer et al (1) and Enge (9) for details on the use of plastic track recorders. Mica is useful at much higher temperatures but suffers from the fact that samples of the highest purity contain about 5 ppb U. For measurements of very low levels of uranium, the very high purity fused synthetic silica used by Riley are recommended. Heraeus-Amersil of Sayreville, N. J. (USA) manufactures the silica and markets it under the trade name Supersil. The Supersil I grade of the fused silica is essentially bubble free and is used for nuclear track recorders. Flame polishing with a hydrogen-Oxygen torch of the fused silica surface helps to eleminate defects that may be misidentified as tracks by automated scanning systems. Tracks in the silica can be effectively etched at ambient temperature in two minutes in concentrated hydrochloric acid.

Methods used to determine track density include simple manual counting under a microscope, computer controlled image analyzers, spark counting, electrical conductivity, and light scattering techniques. These and other methods as well as techniques to enhance the appearance of tracks are discussed by

Fleischer et al. Usually in simple optical counting, only a limited fraction of the fields under the microscope are counted, although some workers have counted the total number of tracks on the recorder (10). Spark counting makes use of plastic track recorders whose thickness (~10 um) is less than the range of the particle that produces the tracks. The tracks are etched entirely through the recorder and sparks, that discharge through the tracks between electrodes placed on each side of the recorder are counted. Although the spark counting method is rapid and accurate, it is limited to track densities of several thousand tracks per cm^2 and in addition it would not be applicable to fission track measurements where reactor irradiation facilities prevent the use of plastic track recorders. Electrical conductivity methods also make use of thin plastic track recorders and measure conductivity through tracks that have been etched through the recorder. Optical scanners, as was used by Riley, are suitable for track density measurements in recorders such as fused silica.

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DISCUSSION

H. Ross. What other useful applications exist for track etch methods other than the analysis of uranium?

F. Dyer. There are many examples of the application of nuclear tracks in Fleischer, Price and Walker's book Nuclear Tracks in Solids. One interesting application is to measure very low nuclear cross sections.

R. Rosenberg. Do you expect to be able to analyze 7 ppb uranium in aluminium using delayed neutron counting without having serious problems by the high gamma-activity from the aluminium.

F. Dyer. We believe that we may be able to measure 3-5 ppb uranium in aluminium by DN counting because we have a lead shield between the sample and the BF_3 detector.

V. Krivan. The topic of this meeting is comparison of nuclear methods with other methods. In this connection I would like to emphasize that the instrumental and/or the radiochemical NAA is at present the only one analytical technique allowing an accurate determination of uranium and thorium at the 1 ppb-concentration level and below.

F.F. Dyer. The method of Resonance Ionization Mass Spectroscopy may soon be able to determine ppb and sub ppb levels of uranium in metals. At the present time it appears that fission track counting is the only method that will measure such low levels in all matrix materials. Conventional NAA will allow measurement of U at these levels in some material, e.g., but not many.

G. Revel. It is possible to obtain aluminium samples with a very low concentration in uranium: ($C_{Uranium} < 0{,}05.10^{-9}$ $g.g^{-1}$). This impurity is vey well removed by zone melting.

R.W. Bild. B, Li, N are other elements which can be determined by particle track techniques. The technique results in a map of elemental distributions as well as concentrations.

APPLICATIONS OF CERENKOV COUNTING: A USEFUL TECHNIQUE FOR ENVIRONMENTAL RADIO-ANALYSES*

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Abstract

Cerenkov radiation, produced by charged particles that exceed the velocity of light in a particular medium, has been used for some quantitative estimates of radionuclide concentrations. In general, such applications have been limited to a few special cases where the radionuclide in question has a high beta-particle energy. The major advantage of Cerenkov counting (the use of Cerenkov radiation for radio-analytical purposes), is in the simplicity of sample preparation, and a secondary advantage is in the ready availability of automated counting equipment for performing the counting procedures. Ordinary liquid scintillation spectrometers available in most laboratories that conduct analyses for weak beta emitters such as H-3 or C-14 may be used without modification for Cerenkov counting.

Sample preparation simply consists in measuring a 15-20 mL aliquot of a colorless solution of the radionuclide into a suitable vial, followed by counting with a liquid scintillation spectrometer adjusted for the feeble scintillations produced by the Cerenkov process. For 1-2 meV betas, the setting is similar to that used for H-3 in the typical liquid scintillation cocktail.

Deer harvested during managed hunts on the Oak Ridge Reservation have a potential bone burden of Sr-90 from ingestion of contaminated water or vegetation from formerly-used solid waste storage areas near Oak Ridge National Laboratory. The 1985 hunts produced 926 animals that were "screened" by use of a plastic-scintillator beta detector placed in close contact with an excised foreleg bone sample. This screening procedure resulted in the removal of 7 deer from the harvest due to the detection of Sr-90 in concentrations greater than 30 pCi/g. From the archived samples preserved in a frozen condition, Sr-90 concentrations were determined on a suite of 130 samples by use of a simple dissolution procedure on ashed bone followed by Cerenkov counting of the resultant solutions. The purpose of this study was to assess the accuracy of the screening procedure used in the field surveys and to compare the Cerenkov methodology with the contemporary radio-chemical method for Sr-90 in environmental samples.

Results showed that the Cerenkov technique provides a viable alternative to the more labor-intensive radiochemical procedure. In addition, the results indicate a possible 4% inaccuracy in the ability to detect Sr-90 at concentrations greater than 30 pCi/g by the simple use of a plastic scintillator detector during field screening procedures.

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DISCUSSION

W.S. Lyon. Did you try counting the dried bone samples prior to dissolution, etc. This would have taken a lot of time and trouble.

J.S. Eldridge. We did not try this technique because literature citations indicated a dependency on granularity. Thus, we would have had to spend effort in grinding the ash to a given mesh size. It would save time if the ash were counted directly.

COMPARISON OF ISOTOPE DILUTION ANALYSIS WITH OTHER ANALYTICAL TECHNIQUES

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Abstract

Isotope dilution analysis /IDA/ is the most useful of the indicator radioanalytical methods, especially for elemental analysis. New concepts of IDA, such as substoichiometric and sub-superequivalence IDA, have improved the sensitivity and expanded the applicability of the method for trace analysis. IDA has been used for the analysis of biological and geological materials, water, soils, semi-conductors, etc. In this paper, IDA is compared to other analytical methods, in terms of concentration range, limit of detection, selectivity, time and cost.

Isotope dilution analysis /IDA/ is the most often used indicator nuclear analytical method.

The basic principle of IDA is the conservation of activity upon dilution. If a radioactive material is diluted with its non-radioactive counterpart, the specific activity of the resulting dilution mixture is related to the original specific activity and the amount of material by means of a simple conservation equation. This equation can be rearranged in various ways, depending on the conditions of the experiments to solve for the unknown mass of analyte in the sample.

The basic method and its many variants, has been used for the determination of trace elements /especially metals/ in a wide variety of samples /metal, steal, alloys, rocks, minerals, water, soil, plastics, plants, biological materials, etc./ and also organic compounds /amino acids, steroids, vitamins, penicillins, insecticides, etc./ [1-6].

The method can be useful in the following general situations:

- a substance is to be determined in a mixture of similar materials, but a quantitative isolation is impossible,
- the analyte occurs at a low concentration, so that losses such as sorption onto vessel surfaces, etc., during the separation procedures are inevitable,
- the analysis must be performed quickly, e.g. because of decay or shifts in equilibria,
- the analyte is part of a large system, and only a part of it is available, e.g. water in a large living animal.

Variations of IDA

Classical IDA uses the comparison of the specific activity of a radioactive tracer before and after mixing with a non-radioactive compound which is to be determined /the analyte/. In other words, the radioactive tracer is "diluted" with its non-radioactive counterpart in the sample. The dilution causes a change in the specific activity of the added tracer, which can be measured and used to calculate the amount or concentration of the component of interest in the sample.

A number of variations of classical IDA have been developed including:

- Direct IDA, or Single IDA, where the non-radioactive sample is diluted with a radioactive tracer,
- Reverse IDA, where a radioactive substance is diluted with a stable one,
- Derivative IDA, where the analyte is originally non-radioactive, but is made radioactive by a stoichiometric reaction with a radioactive reagent,
- Double isotope dilution, where two radioactive isotopes of the same element are used,
- IDA after activation, where the radioactivity of the analyte is induced by an appropriate activation technique,
- Pseudo IDA, in which the diluting analyte is not the same element as the tracers, but has adequately similar chemical properties.

Classical IDA has been used for the determination at least thirteen elements, and for analysis of various sample matrices such as water, soil,

plants and animals. Separation procedures include precipitation, distillation, solvent extraction, coprecipitation, etc. Methods used for yield /mass/ determinations include gravimetry, colorimetry, fluorometry, flame photometry, etc.

The main disadvantage of the classical methods is the necessity of a second type of measurement, so that specific activities can be determined. This limits the sensitivity of the method.

However, in the basic equation, only the ratio of specific activities occurs. The means that if exactly the same amount /or an exact multiple/ of material can be isolated from sample and standard, the equations simplify drastically. This concept is the basis of the most often used method of IDA - substoichiometric IDA.

The principle of sub-superequivalence IDA consists in the preparation of two series of aliquots of the labelled sample; one series is isotopically diluted, the other is not. A constant amount of a suitable reagent is added to each aliquot and the product is separated and counted. The relative radioactivities of the isolated fractions are plotted versus the extent of isotope dilution and the intersection of this curve with a line corresponding to a special condition is used to calculate the result.

The method is similar to substoichiometric IDA in that only the activities of the portions isolated are measured but differs from it in that the condition of isolating equal amounts need not be fulfilled.

Sensitivity

The sensitivity of IDA is limited by the following factors:

1/ The smallest amount which can be determined or purified in direct IDA,
2/ The original specific activity in reverse IDA,
3/ Specific activity of the diluting radioactive tracer or of the radioactive reagent in derivative IDA,
4/ Equilibrium constants of extraction, hydrolysis, precipitation and similar separation reactions used in substoichiometric IDA,
5/ Blank values /reagent contamination/,
6/ Stability of reagents at low concentrations, sorption on surfaces, etc., in substoichiometric and sub-superequivalence IDA,

7/ Volumes of solutions used for substoichiometric IDA,
8/ Neutron, photon, or charged-particle flux in IDA after activation,
9/ Interferences.

The limit for the specific activity of the tracer is the case of carrier-free radionuclides, which is seldom possible in practice. In Table I hypothetical sensitivity ranges for the specific activity theoretically achievable are shown [9].

Factors 3 - 7 are typical for substoichiometric IDA, with 3 being the most important. It must be realized that this factor includes the counter efficiency and background. With automated procedures, the time available for counting may be the most important factor, and such procedures are generally less sensitive than manual methods.

TABLE I.

Sensitivity [g]	Radionuclides
10^{-8}–10^{-10}	^{42}K, ^{86}Rb, ^{99}Mo, ^{115}Cd, ^{114m}In, ^{181}Hf, ^{182}Ta, ^{187}W, ^{191}Os, ^{203}Hg, ^{204}Tl, ^{210}Bi
10^{-10}–10^{-12}	^{46}Sc, ^{59}Fe, ^{64}Cu, ^{72}Ga, ^{82}Br, ^{85}Kr, ^{109}Pd, ^{186}Re
10^{-12}–10^{-14}	^{24}Na, ^{58}Co, ^{125}Sb, ^{137}Cs
10^{-14}	^{32}P, ^{45}Ca, ^{77}As, ^{89}Sr, ^{90}Y, ^{95}Zr, ^{95}Nb, ^{103}Ru, ^{111}Ag, ^{131}I, ^{140}Ba, ^{141}Ce, ^{199}Au

The finite values of equilibrium constants explain why very low concentrations often cause difficulty in isolating precisely equal amounts of a species from two different systems. Large solubility products or small complex formation constants are good examples.

Blank values, rather than instrumental factors may limit the sensitivity of substoichiometric IDA. They can be reduced by careful purification of reagents.

Stary [8] evaluated the sensitivity of good substoichiometric IDA procedures as 10^{-9}-10^{-8} g, corresponding to the application of 10^{-7} M concentration of substoichiometric reagents. This sensitivity exceeds that of activation analysis in some cases.

An example of greater sensitivity of substoichiometric IDA as compared to activation analysis is the determination of palladium. Whereas in the given case the smallest amount of Pd determined was 10 ng, the substoichiometric method was shown to be capable of determining down to 3 ng. Moreover, the latter method is expected to be applicable to any type of matrix, whereas self-shielding effects were suspected to cause low results in activation analysis.

The detection limit of substoichiometric IDA is compared to other methods in Table II [10]. It can be seen that IDA is as good as, or better than other methods. In favourable cases, IDA has far superior detection limits /values are quoted to the nearest order of magnitude/. In Table III are presented some general characteristics of a variety of instrumental methods. In Figure 1 the applicability of IDA and other analytical methods are shown [2].

Accuracy and precision

By accuracy we mean the closeness of agreement between a true value and the mean result obtained by applying the same experimental procedure to the same sample a large number of times. Since "tru" values are never known with certitude, statements of accuracy are never absolute.

Precision is a statement of the closeness of agreement among results obtained by applying the same experimental procedure to the same sample several times. The smaller the random part of experimental errors, the more precise is the procedure. Some function of the standard deviation is commonly

TABLE II.

Detection limits of various analytical methods

	Method	Detection limit /g/	Volume of sample /ml/	Limit of conc. of analyte which mol. wght of 100 /mol L^{-1}/
Non-radioactive analytes				
Chemical	Classical methods	10^{-6}	10	10^{6}
	Special ultramicro procedures	10^{-12}	0.001	10^{-8}
Physical-chemical	Absorption spectrophotometry	10^{-8}	1	10^{-7}
	Emission spectroscopy	10^{-9}	0.01	10^{-7}
	Inversion polarography	10^{-10}	10	10^{-10}
	Mass spectrometry	10	0.01	10^{-9}
	Gas chromatography	10^{-13}	0.001	10^{-9}
	Atomic absorption spectrometry	10^{-13}	0.01	10^{-10}
Nuclear	Substoichiometric IDA	10^{-11}	1	10^{-10}
	Neutron activation analysis	10^{-13}	1	10^{-12}
Radioactive substances				
	Ionization and scintillation	10^{-19}	1	10^{-18}
	Micro radiography	10^{-22}	1	10^{-21}

TABLE III.

Comparison of some instrumental analytical methods

Method	Analyte	Conc.range[1]	Selectivity	Time[2]	Cost[3]
Classical polarography	Iden.and detn.of about 80 cations of heavy metals; many organic substances	10^{0}-10^{-4}	Good	Short	Low-medium
Inversion polarography	Detn.of about 40 heavy metals	10^{-4}-10^{-10}	Poor	Short	Medium
Atomic abs.spectrophotometry	Detn.of many heavy metals	10^{-2}-10^{-6}	Good	Short	Medium
Molecular abs. spectrometry /UV, Visible/	Detn.of practically all cations except alkali metals; a number of anions; some organic species	10^{0}-10^{-5}	Fair	Short	Medium
IR spectrometry	Idn.of functional groups and detn. of structure of org.substances	10^{0}-10^{-1}	Fair	Short	Medium
Emission spectroscopy	Idn.and detn.of almost all elements /multielement method/	10^{-1}-10^{-5}	Good	Short	Medium
Electron-microsonde	Iden.and detn.of elements with atomic no.>5; local surface analysis	10^{0}-10^{-3}	Good	Short	High
NMR Spectroscopy	Idn.; structural anal.;detn.of mainly organic species	10^{1}-10^{-1}	Poor	Short	High
Electron spin resonance spectrometry	Iden.and structural anal.of species which have an odd no.of electrons	10^{1}-10^{-1}	Poor	Short	High
Mass spectrometry	Iden.of org.species, structural ana.;rel. masses;iden.and detn of all isotopes	10^{1}-10^{-1}	Good	Medium	High

TABLE III. /contnd./

Method	Analyte	Conc.range[1]	Selectivity	Time[2]	Cost[3]
Neutron activation analysis	Multi-elemental iden.and detn.	10^{-1}-10^{-7}	Fair	Medium-long	High
Chromatography	Iden.and.detn.of many organic and inorg.species	10^{-1}-10^{-7}	Good	Short	Medium
X-Ray fluorescence with X-ray tubes	Multielement detn. of elements with at.no >15	10^{-1}-10^{-5}	Good	Short	High
X-Ray fluorescence with radionuclide excitation	Multielement detn. of elements with at.no. >11	10^{1}-10^{-4}	Good	Short	Low-medium
Classical IDA	Detn.of organic and inorganic species which can be labelled with appropriate radionuclide	10^{-1}-10^{-6}	Fair-Good	Medium	Low
IDA-substoichiometric and sub-superequivalence methods	Detn.of most elements when appropriate labelling nuclides are available	10^{1}-10^{-8}	Good	Medium	Low

[1]Percentage of analyte; sample weight 1 gram.

[2]Short: seconds to minutes; Medium: hours; Long - days

[3]Equipment cost, Low: < $ 10,000; Medium: $ 10,000-75,000; High: > $ 75,000

used to state precision values. In Figure 2 the precision of IDA and other analytical methods expressed as relative standard deviation s_r is shown and Figure 3 gives a comparison of the analysis time required for these methods. This information can be used for the comparison of analytical methods, and for help in choosing a solution to a specific problem.

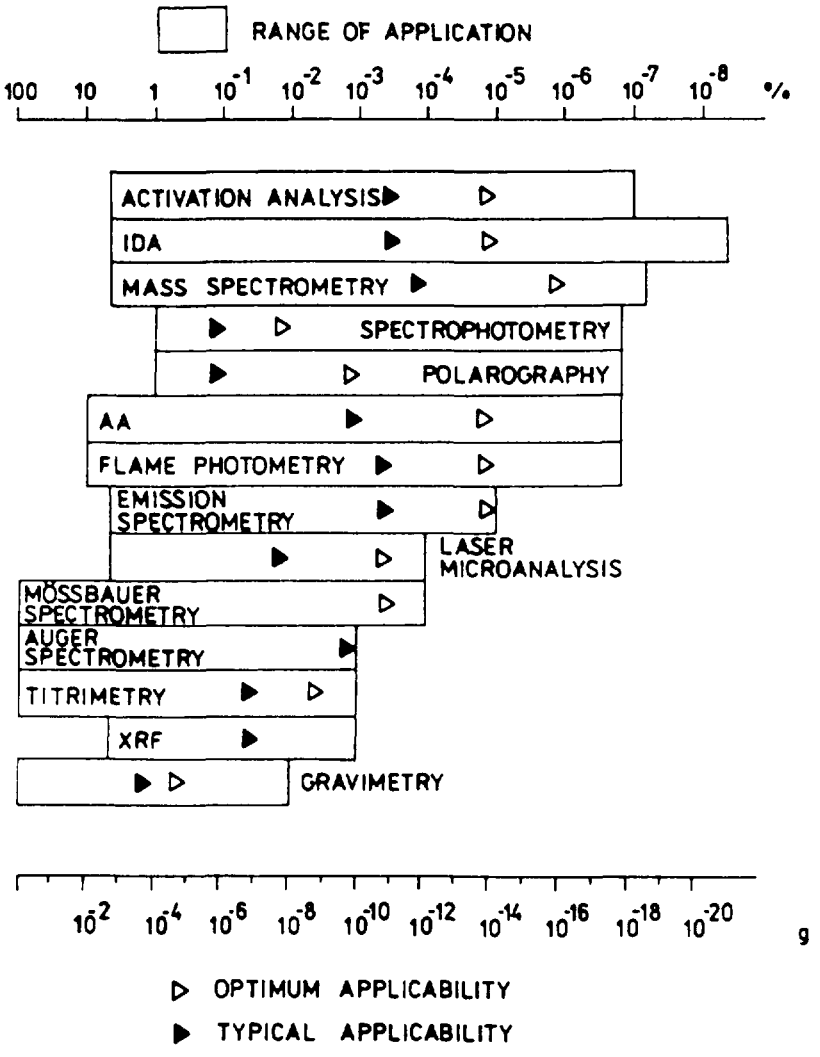

FIG.1. Range of application of some analytical methods.

Most authors claim that substoichiometric IDA is precise and accurate. This should be taken "cum grano salis" because this appraisement is valid for cases where a suitable reagent and proper conditions have been chosen, and skilled operators are employed. Even in such a typical and well elaborated procedure as the determination of mercury with Zn dithizonate, the average of six single determinations was $1.070 \pm 0.03 \mu g$ when $1.007 \mu g$ Hg was taken; that is, precision was within ~3% and accuracy not better than 6.3% [5].

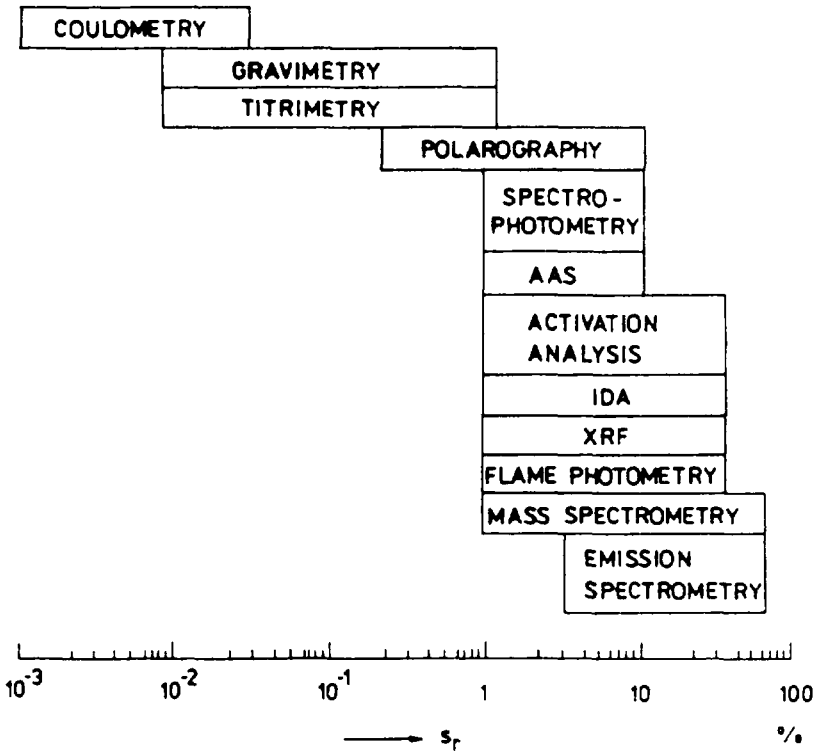

FIG.2. Precision of analytical methods expressed with the standard deviation s_r.

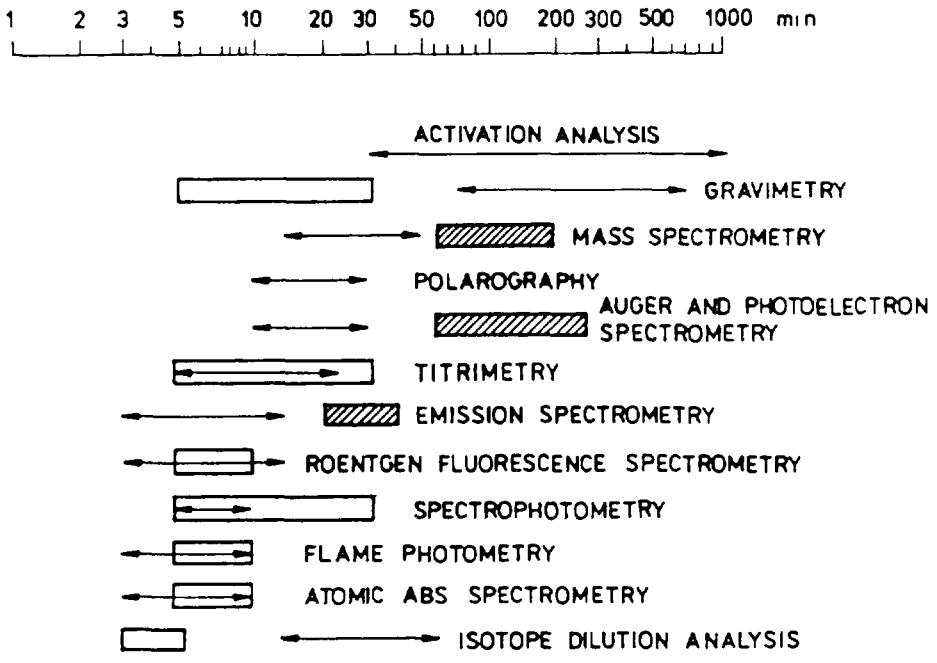

FIG.3. Analysis time for different analytical methods.

A positive example of a highly accurate substoichiometric determination is the analysis for iron using solvent extraction with substoichiometric amounts of oxine. Kudo and Suzuki [7] found in this way 548±9 ppm of Fe in spinach whereas the certified /NBS/ value was 550±20 ppm.

Although substoichiometric IDA is considered most useful at trace element levels, it can also be advantageously used for the precise determination of major component /such as total amount or iron in silicate rocks amounting to 3 - 13% of Fe_2O_3/. It may not be suited for routine analyses in this case but could be a useful supplement in cases where the results obtained by other methods are to be checked. In the above example, the substoichiometric reagent was EDTA and uncomplexed iron /^{59}Fe/ was retained on a cation-exchange column. The precision and accuracy are 1.5% or better.

Advantages, drawbacks and trends

The principal and decisive advantage of IDA is the possibility of using non-quantitative isolating procedures, so that in some instances IDA is the only analytical method of solving a problem. This possibility allows the analyst to perform an isolation quickly, to choose a purification method from a very wide selection of methods and to tolerate a partial decomposition of the substance analysed during the analysis.

As the analyte is radioactive, its path through the analytical scheme can be followed, to be sure of its identity and to check for adequate purity by its constant specific activity. Also, certain types of IDA are readily amenable to automation.

In IDA, there is no danger that the sought element can also be formed by a different nuclear reaction from another component of the irradiated sample /which may be a cause of false results in activation analysis/.

The substoichiometric principle has been used for the determination of more than 50 trace elements in pure substances, geochemical, biochemical and other materials, as well as in the analysis of radioactive substances, such as fission products with a detection limit of 10^{-4}-10^{-6}%, in special cases down to 10^{-8}%.

The trends expected in the future development of the method probably includes:

- efforts to find new highly sensitive, chemically stable and selective reagents,
- elaboration of new effective separation procedures /solvent extraction, chromatography etc./,
- finding possibilities of simultaneous determinations of several elements,
- automation of the process for routine analysis.

In sub-superequivalence IDA the systems studied are of the same type as those used in substoichiometric IDA. The main advantages of the sub-superequivalence method include:

- higher sensitivity in systems where stability constants limit the sensitivity of substoichiometric IDA,
- systems can be studied where changing complex composition makes isolation of equal amounts of material impossible,
- only one phase need be measured.

The development of this radioanalytical method will probably involve the use of other, presently non-described systems, applications of automated versions of procedures and applications to other samples /samples of environmental importance etc./.

Except for rare cases, IDA is not a multielement method, and it may not be practical to store radioactive isotopes of a large number of elements, or to prepare and keep a large assortment of labelled compounds which would be required for a multielement program. Moreover the availability of suitable nuclides and labelled compounds, particularly organic species, may be a problem.

As compared to activation analysis, the major drawback in IDA is the necessity of using reagents freed from traces of the substance to be determined and the very low concentration level at which the isolation must be performed. Therefore IDA is not advantageous for the analysis of traces in samples that require large amounts of concentrated reagents for their dissolution, because their purification may be difficult.

One trend in the development of IDA can be characterised by a quotation from Lyon: "There seems to be no lack of information being passed back and forth within the literature, but most of it continues to be rehashing, refurbishing or reevaluating of previously reported methods or techniques. We left our literature search with a feeling of "dejà vu" [11].

On the other hand, progress can be expected in some directions. A new possibility in IDA is the simple determination of the specific activity using Cherenkov photometry. If the compound of the radionuclide is coloured or can be converted into a coloured compound, it is possible to measure the activity and the concentration of the compound. Kulcsár et cl. [12] used, for the determination of the specific activity of ^{32}P, the yellow complex with molybdic and vanadic acids. The specific activity is determined from ^{32}P counting efficiency, activity and the phosphorus content of the sample using a liquid scintillation spectrometer.

For the use of IDA in organic chemistry and biochemistry the increasing assortment of commercially available labelled compounds and their decreasing price may be of great importance.

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DISCUSSION

G. Revel. I have two comments to make:

The first concerns the comparison between the different methods of analysis. Table given by Prof. J. Tölgyessy are very interesting because they situate the possibilities of these methods. However, it is important to consider that all methods do not oppose each other but are complementary. In practice, the choice of an analytical method depends on several factors: the nature of the sample and of the impurities, the concentration range required and also the future use of analytical results. For example, in material studies the chosen analytical method is not the same for a quality control and for a correlation between a property of the material and the concentration of one or several selected impurities.

My second comment concerns the limits of sensitivity. Now a large number of methods have very low detection limit, but in fact for concentrations lower than one p.p.m., it is often the blank values which limit the detection in real samples and not the potential sensitivity of the analytical method.

THE CONTRIBUTION OF RADIOTRACERS TO THE DEVELOPMENT OF TRACE ELEMENT ANALYSIS

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Abstract

This paper discusses applications of the radiotracers to methodological studies in trace element analysis. Owing some unique features, the radiotracer technique has proved to be an indispensable means for examining the individual steps of an analytical procedure and revealing the concomitant sources of systematic error. In most cases, the radiotracer technique is the optimum approach, and some problems cannot be solved by other means. The examples discussed in more detail were taken from the analytical chemistry of mercury, sulphur, lead and selenium. The radiotracer investigations aimed at improving the accuracy of analytical procedures.

1 INTRODUCTION

Reliable analytical data on trace element contents are of principal importance in many fields of science, medicine, and technology The analytical techniques for trace element analysis may be either direct instrumental or multistage techniques involving chemical processing of the sample prior to the measurement step The multistage techniques, in general, can be taken as a model for the methodology of trace element analysis Typically, an analytical process consists then of the following steps sampling, storage and pretreatment of the sample, decomposition, separation (preconcentration), and measurement

Each of these steps can be a source of systematic error In general, the most significant sources of error are contaminations and losses The blank not only determines the limit of detection, but with decreasing trace element concentration it becomes the predominating factor of accuracy Considerable losses of the trace element of interest can occur by adsorption and/or volatilization during the analytical process However, many other sources of error are also possible

The radiotracer technique has proved to be an excellent means for examining the individual steps of the analytical process and revealing the concomitant sources of systematic error [1-4] In many instances, it provides the best approach, and some problems cannot be solved by other means With the help of the radiotracers, many established analytical techniques were optimized and a large number of new powerful techniques was developed The radiotracers have greatly contributed also to the solution of many general problems of trace element analysis, such as determination of different analytically relevant constants, clearification of reaction mechanisms, electrode processes etc In addition, several important determination methods are based on the utilization of radioisotopes

In this paper, the potential of the radiotracer technique for studying the individual steps of trace analytical procedures and identifying the sources of systematic error is discussed and demonstrated by selected examples

2 CHARACTERISTIC FEATURES OF THE RADIOTRACER TECHNIQUE [5,6]

In the radiotracer technique, the component whose behavior during a given process is to be investigated, is labeled with a radioactive isotope This is usually achieved by adding a radiotracer containing a measurable amount of radioisotopes as atoms, ions or molecules to the test sample The basic assumptions in using radiotracers are

1 The rate of decay measured is proportional to the number of atoms left undecayed

2 The relative proportions of the radioisotopes and stable isotopes of an element are not changed by the processes under investigation

3 Radioactive radiation does not affect other properties of labeled matter

Assumption 1 is derived from the theory of radioactive decay and, within the counting errors, can be considered as fully true

In practice, three factors can determine how well assumption 2 is fulfilled the purity of the radiotracer, the quality of labeling and the extent of isotope effect Unsuspected radionuclidic and/or radiochemical impurities can behave otherwise than the radiotracer during the process studies and alter the isotopic proportions For perfect labeling, the radiotracer and the component of the test sample to be traced must be in the same chemical form In order to fulfill this requirement, in many instances special labeling techniques must be used such as in situ labeling by activation of the material to be examined or in vivo metabolization Incorrect labeling can be a reason for serious systematic errors of the radiotracer technique The isotope effect results from the fact that the behavior of different isotopes is not exactly the same because of their difference in mass This effect must be considered in the case of hydrogen, for other elements the error due to isotope effect is at or below 1%

Assumption 3 ist not exactly fulfilled, too In the case of substances with high specific activities, chemical changes of the radiotracer by radiation effects can give rise to considerable systematic error, and must therefore be considered

The main advantage of the radiotracer technique is the possibility of direct detecting the characteristic radiation in any stage of the analytical process with rapidity and simplicity Another important feature of the radiotracer technique is its high sensitivity Depending on the half-life of the radioisotope and the ability to determine its actual specific activity in carrier-free state, picogramm amounts and less of the component of interest can be traced through the analytical process The weights of some carrier-free radionuclides having an activity of 10 Bq, which, in general, can still be counted easily, are given as examples in Table I However, for different reasons, the real carrier-free concentrations are always higher than the theoretical Further, the radiotracer technique has a high degree of universality Radiotracers are available for almost all elements Only the elements He, Li, B, N, O, Ne and Al have exclusively very short-lived radioisotopes that are not suitable as radiotracers

Table I

Weight Amounts of Carrier-Free Radionuclides Corresponding to an Activity of 10 Bq

Radionuclide	$T_{1/2}$	Amounts by weight at 10 Bq (g)
^{14}C	5736 a	$5\ 2 \times 10^{11}$
^{60}Co	5 27 a	$2\ 4 \times 10^{-13}$
^{35}S	87 5 d	$5\ 8 \times 10^{-15}$
^{24}Na	15 03 h	$3\ 0 \times 10^{-17}$
^{27}Mg	9 46 m	$3\ 3 \times 10^{-19}$

3 SELECTED APPLICATIONS

The broad applications of radiotracers to investigations of analytical procedures include especially the following topics

- Presampling factors
- Sampling
  (efficiency, contamination)
- Sample homogeneity
- Sample storage
  (losses, contamination, chemical changes)
- Sample drying
  (losses, contamination)
- Sample decomposition
  (yields, chemical form, losses, contamination)
- Separation and preconcentration
  (separation factors, yields, distribution coefficients, kinetic studies, studies of mechanism of the separation processes)
- Determination stage
  (behavior of the element determined, influence of various parameters)

Some selected examples are discussed in more detail below

3.1 Pre-sampling behavior of mercury

The toxicity of mercury strongly depends on its chemical state which should be known before the analysis, as the species of concern may determine sampling , sample pretreatment and storage as well as other steps of the analytical process Basically, mercury occurs in the environment as elemental mercury vapor, and as inorganic and organic mercurials These different species must be differentiated with regard to their input, transport and mutual conversion

The radiotracer technique enabled to clarify the biological methylation of mercury by pure cultures of microorganisms and by mixed cultures of environmental systems such as lake water and sediments [7-9], fish intestinal tract [10] and other systems In several cases, however, methylmercury could not be detected in the system studied where it should have been present Experiments using ^{203}Hg provided an explanation for the absence of methylmercury it was demethylated to volatile elemental mercury [7] Further, it was found that some bacteria such as Escherichia coli, Skaphyloevecus aureus, several species of Pseudomonas, and some algae can reduce ionic inorganic mercury to elemental mercury For example [11], when soil was amended to 1µg Hg/g soil with mercury(II) nitrate labeled with ^{203}Hg, 20-45% of the ^{203}Hg-activity were lost from different soil types during the first 6 days The volatility rate decreased to a minimum after about 100 h Steam-sterilized soil lost only about 2% of the labeled mercury To ensure that the mercury loss was initiated biologically, the sterile soil was inoculated with the respective nonsterile soil after 160 h of incubation, and within 8 h, the inoculated soil started volatilizing mercury, reaching a maximum after 22 h

These examples show that the contents of the individual mercury compounds as well as of total mercury can be seriously affected by bacterial conversion processes Therefore, these processes must be considered in both the analytical procedure and the interpretation of results

3.2 Efficiency of sampling sulphuric acid from atmospheric aerosols

Collection of sulphuric acid aerosol in denuder tubes coated with sodium chloride has become a very important sampling concept This sampling technique was developed with the help of labeled $H_2{}^{35}SO_4$ [12] The labeled test aerosol was produced with a condensation-type generator The acid droplets react with the sodium chloride on the inner wall of the thermo-denuder

$$H_2{}^{35}SO_4 + NaCl \longrightarrow NaH^{35}SO_4 + HCl$$

The investigation of the efficiency of this sampling device as a function of temperature using sulphuric acid labeled with ^{35}S showed that more than 99% of the sulphuric acid was collected in the denuder at 413 K The effect of a number of salts on the collection of H_2SO_4 was examined in similar manner

3.3 Homogeneity of spruce needle samples

In sampling bulk material, the fundamental requirement is that the proportion of the component of interest is, within the limit of error, the same in sample as in the whole Usually, subsampling is carried out on the sample to obtain proportions required for a single analysis, for replicate analyses, or for analyses by different techniques In subsampling, the degree of homogeneity is of principal importance if precise and accurate results are to be obtained However, the homogeneity requirements can also depend on the determination method, as for different methods different sample portions are used for analysis

For example, for the analysis of spruce needles by INAA and AAS, sample portions of about 70 mg and 250 mg, respectively, are required Large variations of the element contents in needles of the same age were found for different branches of the same whorl, and even for different positions within one branch [13] Therefore, the preparation of a representative sample is of principal importance The radiotracer technique was used for examining the course of the homogenization process for subsampling examplary for the element manganese For this purpose, some whole needles were labeled in situ with ^{56}Mn by irradiation in nuclear reactor The irradiated needles were then mixed with unirradiated approximately 1 50 The needles were then homogenized by the brittle fracture technique with the

Mikro Dismembrator (Braun) The homogeneization standard deviation for seven aliquots of ~70 mg and ~250 mg was determined by counting the ^{56}Mn activity The results proved (Fig 1) that acceptable degree of homogeneity can be obtained for both sample portions during a homogenization time of at least 5 min

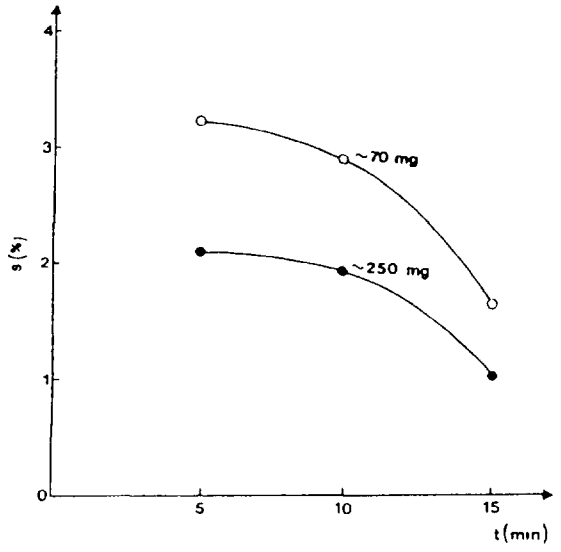

Fig 1
Dependence of the homogeneity standard deviation (n=7) on the homogenization time for two different sample portions (~70 mg and ~250 mg) of spruce needles homogenized by the brittle fracture technique using the Mikro-Dismembrator II

3.4 Investigation of preatomization behavior of lead in the graphite furnace

Valuable information can be obtained by the radiotracer technique also about the behavior of the elements in the graphite furnace during the individual steps of the temperature program Such studies often reveal sources of systematic error and facilitate the optimization of the determination procedure The potential of the radiotracer technique in this field is demonstrated by using lead as an example [14] The experiments were executed as follows an appropriate portion of a sample labeled with ^{203}Pb was introduced into the graphite tube, and the tube was counted Then the tube was placed into the furnace and the selected temperature program started After the step to be studied had been completed, the temperature program was stopped and the tube counted again The graphite furnace was placed in a closed Plexiglas chamber, which was connected to an exhaust of the radiochemical laboratory class B

The results for the thermal pretreatment are illustrated in Fig 2 It can be seen that the maximum tolerable pretreatment temperature is mainly dependent on the concentration of chloride in the sample, chloride promoted the loss of lead (Fig 2 a,b,c) Any significant improvement can be achieved by using the L'vov platform (2 d,e) The pretreatment temperature can be increased by addition of 1% hydrogen to argon (2 g,h) or by addition of ammonia to the sample solution (2 i), the stabilization is probably due to formation of volatile hydrogen chloride and ammonium chloride, respectively, that remove the chloride from the matrix before it can interfere with lead Using ammonium dihydrogen phosphat as matrix modifier, the pretreatment temperature can be increased by 200 - 400 °C (Fig 3 a,b) and the best stabilization of lead is achieved with ammonium dihydrogen phosphate as the modifier combined with using the L'vov platform (Fig 3 c,d)

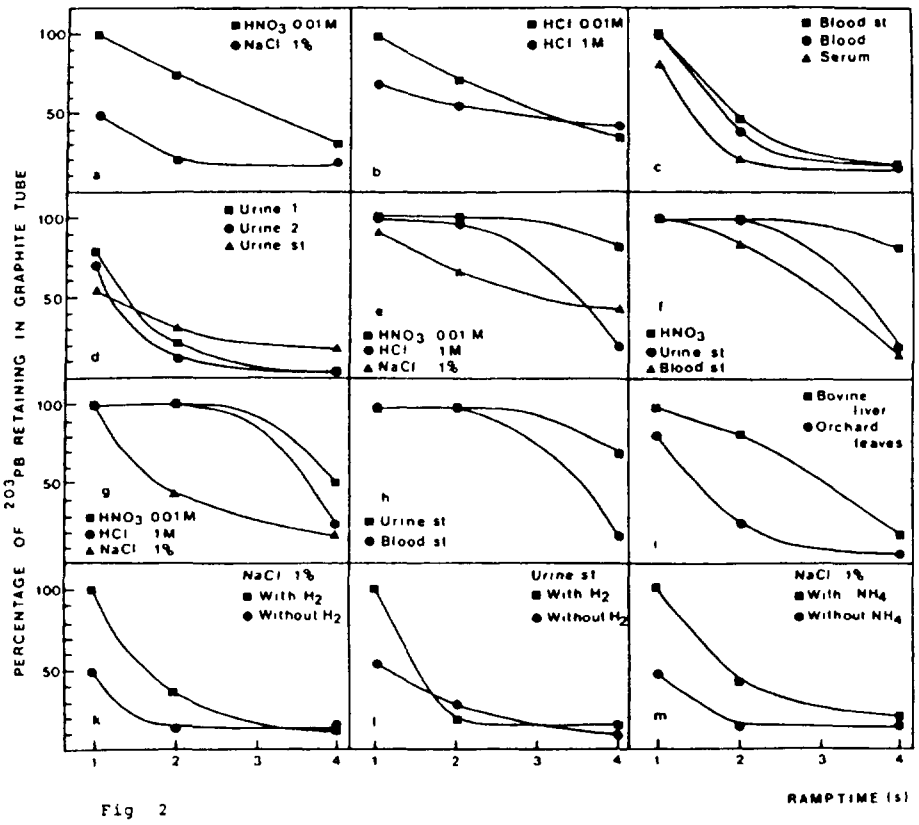

Fig 2
Influence of the ramp time in the heating step from charring to atomization temperature for various matrices· (a-d) graphite tube (e,f) L vov platform (g,h) graphite tube and addition of $NH_4H_2PO_4$ (i) graphite tube, solid samples (k,l) graphite tube and 1% hydrogen added to the flowing gas (m) graphite tube and addition of ammonia

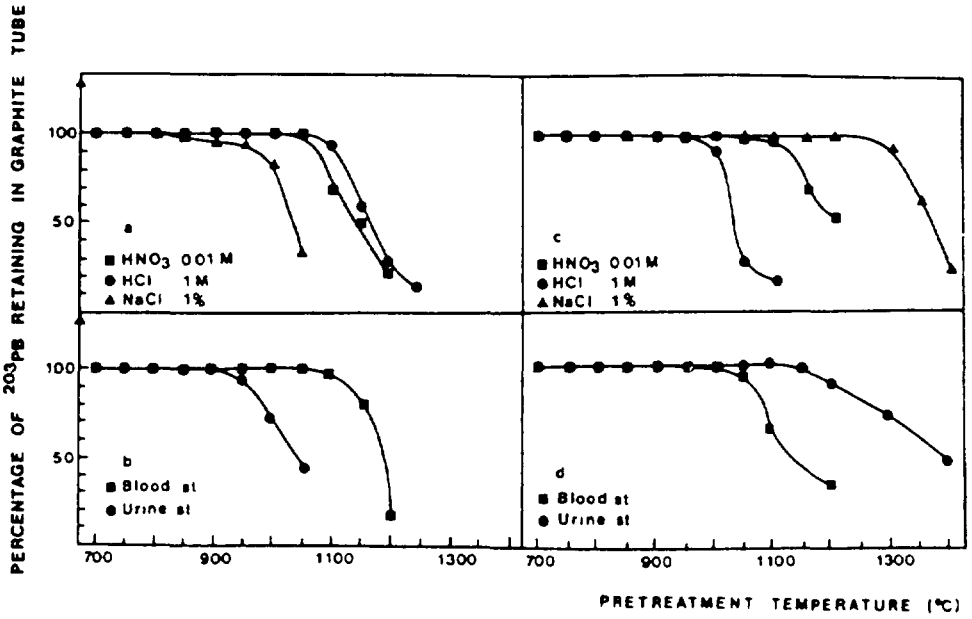

Fig. 3
Dependence of the losses of lead on the pretreatment temperature for various matrices to which $NH_4H_2PO_4$ was added (a,b) graphite tube, (c,d) L'vov platform

The heating phase from the pretreatment temperature to the atomization temperature can also give rise to systematic errors, especially when the absorbance is measured in peak heights During the heating phase, lead can evaporate as lead chloride which is not detected in the absorption measurement This heating phase cannot be studied at all by absorption measurements

For the gas stop mode, the losses of lead with and without addition of modifiers were investigated at different heating rates from a charring temperature of 500°C (without phosphate) or 700°C (with phosphate) to the atomization temperature of 2100°C using the gas-stop mode The results are illustrated in Fig 4 as the dependence of the Pb-203 activity remaining in the graphite tube on the ramp time Again, the losses of lead are strongly influenced by the chloride concentration of the matrix (Fig 4 a,b) The lower losses with 1 M HCl as compared with 1% NaCl solution can be explained by escape of HCl already during the drying and pretreatment step

A substantial reduction of lead losses could be achieved with the L'vov platform, these results are in good agreement with the theory of delayed heating on the L'vov platform Ammonium dihydrogen phosphate effectively stabilizes lead also during heating to the atomization temperature no lead was lost from any of the matrices after one second ramp time, but strongly matrix-dependent losses occurred at longer ramp times Significant stabilization can be achieved by addition of hydrogen to the sheath gas (Fig 4 k,l) or by addition of ammonia to the solution (Fig 4 m) Also in this case, use of the phosphate modifier and the L'vov platform leads to highest degree of stabilization of lead and minimizing the matric effects (Fig 5)

To investigate errors associated with the analysis of solid samples, radiotracer experiments were carried out with the NBS standard orchard leaves (SRM 1571) and bovine liver (SRM 1577) The different behavior of lead during the pretreatment and heating to the atomization temperature can be explained by the different phosphorus/lead ratios (10500 µg/g P, 0 35 µg/g Pb in bovine liver, 1980 µg/g P, 46 µg/g Pb in orchard leaves) High phosphorus/lead ratios stabilize lead in a similar manner as does addition of the matrix modifier ammonium dihydrogen phosphate Radiotracers could also provide information about the movement of lead within the graphite tube during the temperature program

3.5 Error-diagnostic investigation of selenium determination by hydride generation AAS

Losses of selenium up to 50% were reported in the determination of Se in wastewater and other environmental samples by hydride generation AAS involving treatment with H_2O_2 and HCl [15]

With Se-75 as the radiotracer, all the essential steps (mineralization by sulphuric acid and hydrogen peroxide, reduction of Se(VI) to Se(IV) by 5 M hydrochloric acid, hydride-generation, hydride transport) were systematically examined [16] None of these steps was responsible for the selenium losses Preliminary radiotracer measurements indicated that the recoveries of selenium in the hydride generation procedure could be influenced by the time elapsed between the reduction of Se(VI) to Se(IV) by hydrochloric acid and the generation of hydrogen selenide Additional more detailed experiments showed, that the Se 75 activity in the hydride-generation flask increased with increasing times between the Se(VI) to Se(IV) conversion and the hydride generation Eighty to 95% of the selenium remained in the hydride generator, when hydrogen selenide was generated one week after the Se(VI) to Se(IV) conversion We were able to prove that this increase of not reducible selenium with time is caused by a slow back oxidation of Se(IV) to Se(VI) by chlorine formed from hydrochloric acid and hydrogen peroxide The redox reaction between selenite and chlorine

$$H_2SeO_3 + Cl_2 + H_2O \rightleftharpoons H_2SeO_4 + 2\,HCl$$

is an equilibrium reaction Using standard heats of formation in 1 M aqueous solution an enthalpy value for this reaction, ΔH, of -144 9 kJ mol^{-1} is obtained at 25 °C The equilibrium, which favors selenic acid at room temperature, is shifted toward selenous acid at higher temperatures Radiotracer experiments showed that, in equilibrium, only 5% of the selenium are present as selenate at 100°C whereas 97% are in this form at room temperatures

Fig 6 shows the decrease of the selenium(IV) concentration with time past after the end of the reduction with hydrochloric acid Twenty minutes after the reduction 93% of the selenium was still in the tetravalent form After one week the selenium(IV) concentration had decreased to 6% A solution of selenite in 5 M

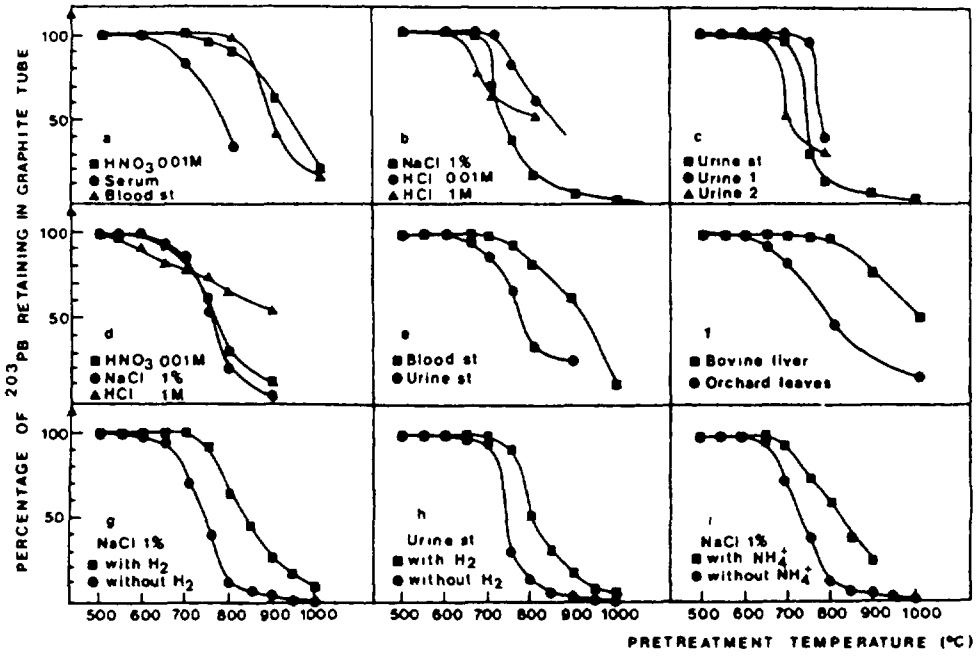

Fig. 4 Losses of lead from the graphite tube vs. pretreatment temperature for various matrices: (a-c) graphite tube; (d,e) L'vov platform; (f) graphite tube, solid samples; (g,h) graphite tube and 1% hydrogen in the flowing gas; (i) graphite tube and addition of ammonia.

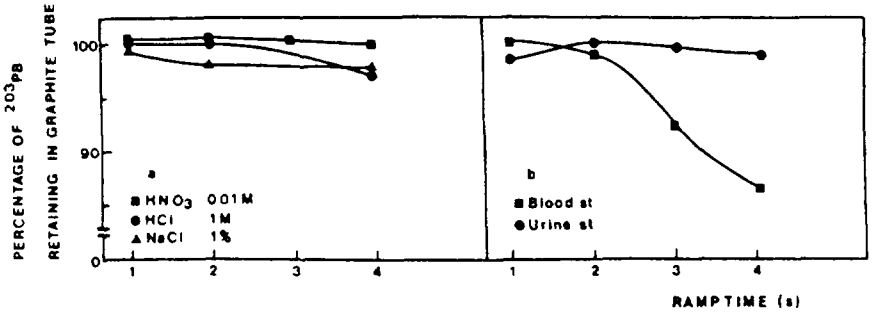

Fig. 5 Influence of the ramp time in the heating step from charring to atomization temperature for various matrices by using the L'vov platform and $NH_4H_2PO_4$ as the matrix modifier

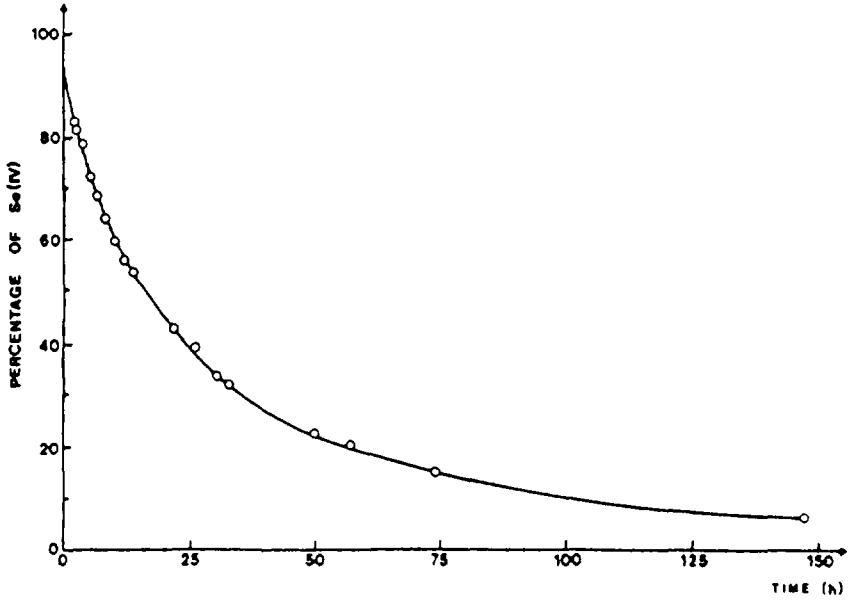

Fig. 6 Decrease of the Se(IV) concentration with time after the reduction of Se(VI) to Se(IV) with hydrochloric acid

hydrochloric acid, which had been saturated with chlorine at 25°C, contained only 3% Se(IV) ater 2 days Hydrogen peroxide in the absence of hydrochloric acid did not oxidize selenite to selenate

From these results it can be concluded that hydrogen peroxide oxidizes hydrochloric acid to chlorine at 25°, and chlorine, in turn, oxidizes selenite to selenate Selenate is not reduced by sodium borohydride and the amount of selenium hydride reaching the atomization tube decreases with time The oxidation of Se(IV) to Se(VI) can be prevented by flushing the chlorine formed during the reduction of selenate in boiling hydrochloric acid from the solution with a stream of nitrogen Recoveries of 98% independent of time up to three weeks between the reduction of selenate and the generation of hydrogen selenide were obtained for selenium in standard solutions and in wastewater samples, if chlorine was removed by flushing with nitrogen

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DISCUSSION

W.D. Shults. Your work on Cr(III) vs Cr(VI) is extremely important. Do you plan to publish it?

V. Krivan. Yes, it is in press in Analytical Chemistry.

APPLICATION OF THE ISOTOPE EXCHANGE METHOD OF ANALYSIS TO THE SPECIATIVE DETERMINATION OF PHOSPHORUS IN ENVIRONMENTAL SAMPLES

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Abstract

Speciative determination of phosphorus (PO_4^{3-}, PO_3^{3-} and total P) in natural water samples can be achieved by using the reverse isotope exchange method.

Five ml of a natural water sample is taken and dil. H_2SO_4 solution of ammonium molybdophosphate and a definite activity (a_0) of ^{32}P (in PO_4^{3-} form) are added. The solution is shaken with the 1,2-dichloroethane solution of tetraphenylarsonium molybdophosphate which contains a definite amount of P (W_1). After the quickly attainable exchange equilibrium between phosphate in the aqueous phase and tetraphenylarsonium molybdophosphate in the organic phase, the activity of the organic phase (a_2) is measured. The amounts of P (W_X) in the sample can be obtained by the equation of $W_X = (a_0/a_2 - 1)W_1$.

In this condition, only PO_4^{3-} exchanges, while PO_3^{3-} dose not. Therefore, PO_4^{3-} can be determined in the presence of PO_3^{3-} and unexchangable phosphorus.

When the sample water is treated with Br_2 water in advance, the amount of PO_4^{3-} + PO_3^{3-} can be obtained. When the sample is treated with H_2SO_4 and HNO_3, then the amount of total P can be obtained.

The method is compared with the conventional spectrophotometric method (the molybdenum-blue method). This method is

much simpler and rapider, and moreover, the speciative determination is possible.

---

1. Introduction

Among various methods of radioanalytical chemistry, the isotope exchange analytical method (IEA method) seems still rather unfamiliar, and the practical application of the method is still remained to be developed.

Langer [1] determined the amount of silver chloride precipitate by exchanging with radioactive silver ion. Since then, the isotope exchange methods for the determination of silver [2, 3], mercury [4], iodine [5], bismuth [6], antimony [7], arsenic [8], thallium [9], phosphorus [10,11], etc. were proposed.

The method used in these literatures is, according to my classification, the direct isotope exchange one, in which the inactive species is determined by exchanging with the radioactive reagent. In this case, therefore, it is necessary to prepare the radioactive reagent in advance. The author [5] proposed the reverse isotope exchange method, by which one can analyse the radioactive sample by exchanging with the inactive reagent. The reverse method is also applicable to the inactive sample when the sample is spiked and made radioactive with the carrier-free radioisotope of the species in question.

In this work, the application of the reverse isotope exchange method to the determination of phosphorus in the environmental water samples is shown comparing the results with those obtained by the conventional spectrophotometric method.

The method is further applied to the speciative determination of phosphite and total phosphorus in the environmental water.

2. General principle of the isotope exchange method of analysis

2.1 Direct isotope exchange method

To the sample solution which contains the inactive species AX to be determined, a definite amount of the radioactive species BX* (weight of X: W_1, activity: a_1) is added and mixed well. After the isotope exchange reaction

$$AX + BX^* \rightleftharpoons AX^* + BX$$

proceeds completely, AX and BX are separated from each other, and the activity (a_2) of the BX fraction is measured.

At the exchange equilibrium, the radioisotope of X distributes homogeneously among AX and BX and the specific activity becomes the same, so that the following equation holds good:

$$\frac{a_1}{W_X + W_1} = \frac{a_2}{W_1}$$

where W_X is the amount of X in AX species to be determined. W_X is readily obtained as follows:

$$W_X = \left(\frac{a_1}{a_2} - 1 \right) W_1 \qquad (1)$$

2.2 Reverse isotope exchange method

The reverse isotope exchange method is useful, when the sample to be determined is radioactive and its activity is measurable.

A definite amount of inactive BX (weight of X: W_1) is added to the sample solution of radioactive AX* (weight of X: W_X,

activity:a_0). After the isotope exchange reaction attains equilibrium, both species are separated from each other, and the activity (a_2) of the BX fraction is measured.

At the exchange equlibrium, the following equation holds:

$$\frac{a_0}{W_X + W_1} = \frac{a_2}{W_1}$$

Therefore,

$$W_X = \left(\frac{a_0}{a_2} - 1 \right) W \qquad (2).$$

The reverse method can be also applied to the inactive sample in place of the direct method. In this case, AX is made radioactive, in advance, by adding the radioactive AX species (activity: a_0) of the negligible weight. This method has an advantage to the direct one that tedious preparation of the radioactive reagent BX* can be eliminated.

3. Determination of phosphate ions

Determination of phosphorus in the environmental water is important from the standpoint of water pollution in addition to the geochemical and agricultural importance. The simple and rapid method of analysis for phosphorus is, therefore, very much desirable.

Perezhogin and Sidorova [12] pointed out that rapid isotope exchange takes place between phosphate (aqueous phase) and tetraphenylarsonium molybdophosphate (organic phase) in the presence of molybdate in the aqueous phase. Zeman and Kratzer [10] applied this isotope exchange reaction to the determination of phosphorus, and Vláčil [11] applied the method to the

determination of trace amounts of phosphorus in platinum alloys. In this paper, the direct exchange method proposed by Zeman and Kratzer is modified and made more simple and rapid by appling the reverse method, and the method is applied to the determination of phosphorus in some environmental water samples.

3.1 Experimental

3.1.1 Tetraphenylarsonium molybdophosphate solution (TPA-PMo solution)

10 ml of sulfuric acid (0.1M), 2 ml of ammonium molybdate (0.02M) and 33 ml of water were added to 2 ml of diammonium hydrogen phosphate solution (0.02M). The solution was then shaken in a separatory funnel with 30 ml of tetraphenylarsonium chloride solution (0.001M in 1,2-dichloroethane) for 3 min to extract phosphorus substoichiometrically in the form of tetraphenylarsonium molybdophosphate ($(TPA)_3PMo_{12}O_{40}$). The phosphorus concentration of this organic solution depends on the substoichiometric amounts of tetraphenylarsonium chloride used, and corresponds to about 10 μgP/ml. 20 ml of the organic phase was then diluted to 200 ml with 1,2-dichloroethane (TPA-PMo solution A).

The reagent solution of the lower phosphorus concentration was prepared by diluting 10 ml of the reagent solution A to 100 ml with 1,2-dichloroethane (TPA-PMo solution B).

Because of the partial solubility of 1,2-dichloroethane in water, all aqueous solutions used were preequilibrated by shaking with 1,2-dichloroethane.

3.1.2 Mock sample solution

Potassium dihydrogen phosphate dried at 110°C was dissolved in water and the solutions of several known phosphorus concentrations (0.01 ~ 10 μgP/ml) were prepared.

3.1.3 Activity measurement

The activity was measured most conveniently by counting bremsstrahlung from ^{32}P with a well-type NaI(Tl) scintillation counter.

3.1.4 Procedure

A 5 ml portion of a sample solution is taken and 2 ml of the sulfuric acid-ammonium molybdate solution (the mixture of the equal volume of 0.1M sulfuric acid and 0.02M ammonium molybdate solution) is added, and then spiked by adding 1 ml of the definite activity (a_0) of carrier-free ^{32}P solution (in the PO_4^{3-} form). The solution is then shaken with 2 ml of the TPA-PMo solution (the amount of P contained: W_1) for 1 min. The activity of the organic layer (a_2) is measured by pipetting a 1 ml aliquot and counting in a polyethylene counting tube.

The amount of phosphorus contained in 5 ml of the sample (W_X) can be readily calculated by Eq. (2).

In stead of calculating by Eq. (2), the phosphorus amount can be more conveniently obtained by use of a calibration curve, which is drawn by treating a series of standard samples containing various known amounts of phosphorus in the same way, and plotting $(a_0 - a_2)/a_2$ value vs. phosphorus amounts. It should give a streight line with a slope corresponding to W_1. In this calibration curve method, it is not necessary to know the exact value of W_1.

3.1.5 Spectrophotometric determination of phosphate by the Japan Industrial Standard (JIS) method [13]

A sample solution which contains 0.005 ~ 0.15 mg PO_4^{3-} in it is taken in a 50 ml volumetric flask and diluted to 40 ml with water and 5 ml of ammonium molybdate solution (1.5% in 3M H_2SO_4) is added. Then, 0.25 ml of tin(II) chloride solution (2% in 1.2M HCl) is added and the solution is diluted to the mark and shaken. After about 15 mins' standing, an aliquot of the solution is taken in an optical cell and the optical density of the blue coloration is measured at 700 nm with a spectrophotometer.

After the correction for blank, the phosphate amount in the sample solution can be obtained by using the calibration curve.

3.2 Result and discussion

Several mock sample solutions containing 0.1 ~ 50 μgP and 0.01 ~ 0.1 μgP of phosphate in each 5 ml were analysed by the procedure described in 3.1.4 using TPA-PMo solution A and B, respectively. The results are shown in Table I. By this

Table I Determination of phosphate by the reverse IEA method

PO_4^{3-} taken (μgP)	PO_4^{3-} found (μgP)	Error (%)
50.0	50.9, 48.2, 49.5	+1.8, -3.6, -1.0
20.0	19.3	-3.5
10.0	10.4	+4.0
5.0	5.0, 5.2, 5.1	0, +4, +2
2.0	2.0	0
1.0	1.0, 1.0, 1.0	0, 0, 0
0.50	0.51, 0.52, 0.50	+2, +4, 0
0.25	0.26, 0.24	+4, -4
0.20	0.19	-5
0.10	0.098	-2
0.050	0.048, 0.049	-4, -2
0.020	0.019	-5

Table II An example of water analysis by the IEA and spectrophotometric methods.

Sample	Concentration of phosphate (μgP/l)	
	by this method	by JIS method
Lake Kasumigaura (Ibaraki Pref.)	63	63
River Sakura (Ibaraki Pref.)	99	90

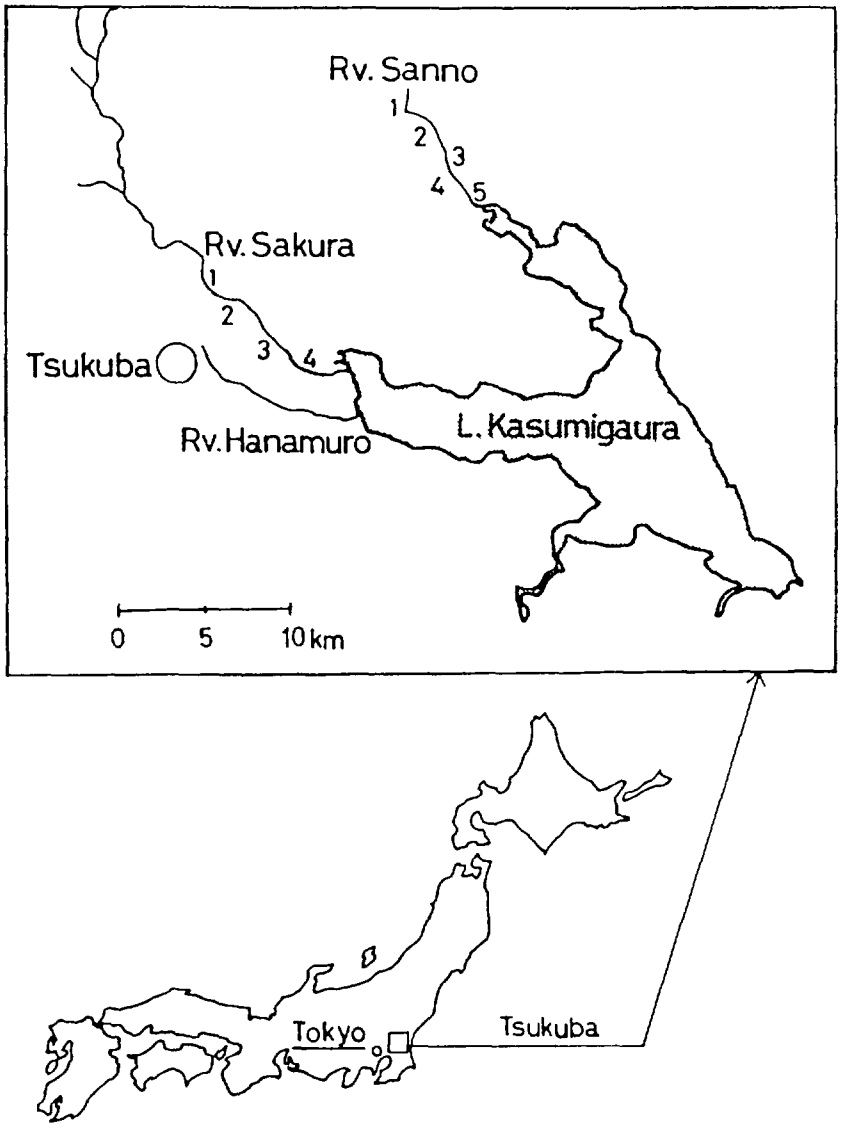

Fig. 1 Sampling sites

method 0.02 ~ 50 μgP (in 5 ml of a sample) of phosphate ions can be determined within ±5% error.

By the JIS spectrophotometric method, on the other hand, 2 ~ 50 μgP (in ~ 40 ml) of phosphate ions can be determined with 2 ~ 10% error [13].

In Table II, an example of the analyses of the lake and river water samples collected in the Tsukuba district (Fig. 1) by this IEA method and JIS spectrophotometric method is given, showing that this IEA method gives the results in fairly good concordance with those obtained by the conventional spectrophotometric method.

The IEA method has such advantages comparing with the conventional spectrophotometric method as follows:

(1) The IEA method reveals higher sensitivity and higher accuracy.

(2) The analytical operation is much simpler and rapider.

(3) As the isotope exchange equilibrium is attained quickly, the small variation in the experimental temperature, acidity of the solution or standing time does no harm. On the other hand, coloration of molybdenum blue is largely affected with these conditions, and rather unstable.

(4) In the spectrophotometric method based on molybdenum blue coloration, arsenic(V) and iron(III) are interfering ions and a large amounts of halogenides also interfere with coloration. In the IEA method, these ions do no harm. Although vanadium, zirconium, titanium and tin(II) interfere with the IEA method [10], the contents of these ions are negligible in environmental water samples.

(5) By the aid of an automatic sample changer, the activity measurements can be done automatically for a series of counting samples. So, the method is suitable for many-samples analyses.

4. Speciative determination of phosphorus

The IEA method can be applied to the speciative determination of phosphate, phosphite and total phosphorus in water samples according to the difference in the isotope exchange behaviros of each species.

As is shown on Fig. 2, phosphate ions exchange with TPA-PMo in the presence of ammonium molybdate in the acid region below pH 2, while phosphite ions do not. It is also confirmed that there occurs no isotope exchange reaction between phosphate and phosphite in this pH region. Therefore, when a water sample is analysed by the procedure written in 3.1.4, only phosphate can be determined even in the presence of phosphite ions. On the other hand, when the sample is pretreated with bromine to oxidise phosphite to phosphate, and then treated according to the above-mentioned procedure, the sum of phosphate and phosphite can be obtained.

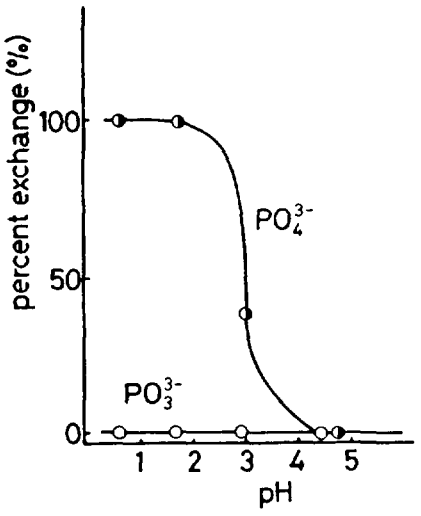

Fig. 2 Dependency if isotope exchange on pH

When the sample water is heated with the mixed acid solution of sulfuric acid and nitric acid, unexchangable phosphorus including organic phosphorus is decomposed to the form of exchangable phosphate, and thus total phosphorus can be determined.

4.1 Experimental

4.1.1 Procedure for the determination of phosphite

To 5 ml of a sample, several drops of saturated bromine water is added to oxidise phosphite to phosphate. The excess of bromine is eliminated by extracting with 1,2-dichloroethane. The solution is then analysed according to the procedure written in 3.1.4. The W_X value thus obtained corresponds to the sum of phosphate and phosphite originally present in the sample. Phosphite content can be readily obtained by substracting the phosphate amount which is determined with another 5 ml portion of the sample as described before.

4.1.2 Procedure for the determination of total phosphorus

To 5 ml of a sample, 5 ml of mixed solution of 9M sulfuric acid and 14M nitric acid (10:1 in volume) is added and gently boiled for 2 hr to decompose unexchangable phosphorus. After cooling, the solution is diluted with water to 100 ml. A 5 ml aliquot is taken and total phosphorus is determined according to the procedure written in 3.1.4.

4.2 Result and discussion

Several mock sample solutions which contains 0.05 ~ 50 μgP of phosphorous acid in each 5 ml were analysed. Results are shown in Table Ⅲ.

Table III Determination of phosphite by the IEA method

PO_3^{3-} taken (μgP)	PO_3^{3-} found (μgP)	Error (%)
50.0	50.8	+1.6
5.0	5.1	+2
1.0	1.0	0
0.50	0.52	+4
0.25	0.24	-4
0.050	0.048	-4

The mixture solutions of the definite amounts of phosphate and phosphite were analysed in the above-mentioned way, giving the results shown in Table IV. Phosphate and phosphite can be determined with in ±5% error.

Table IV Determination of phosphate and phosphite in their mixture

PO_4^{3-} taken (μgP)	PO_3^{3-} taken (μgP)	PO_4^{3-} found (μgP)	Error (%)	PO_3^{3-} found (μgP)	Error (%)
1.00	1.00	1.00	0	0.95	-5
		1.04	+4	0.97	-3
1.00	0.50	0.96	-4	0.48	-4
		0.99	-1	0.52	+4
1.00	0.25	0.95	-5	0.26	+4
		1.03	+3	0.25	0

The results of the so-called "addition test" with the actual river water samples are shown in Table V. In these tests, the water samples were first analysed, and then the known amounts of phosphate and phosphite were added to the water samples and analysed. It is revealed that the river water samples can be analysed within ±5% error suffering from no interference by the foreign ions.

Table V The results of the addition test

Sample	PO_4^{3-} contents PO_3^{3-} contents (μgP/5ml)	PO_4^{3-} added PO_3^{3-} added (μgP/5ml)	PO_4^{3-} found PO_3^{3-} found (μgP/5ml)	Error (%)
Rv. Sakura 1	0.22	0.10	0.33	+3
	0.00	0.10	0.10	0
Rv. Sakura 4	0.24	0.10	0.34	0
	0.00	0.10	0.10	0
Rv. Sanno 2	1.08	1.00	2.10	+1
	0.00	1.00	1.02	+2
Rv. Sanno 3	0.71	0.50	1.16	-4
	0.00	0.50	0.51	+2

An example of the speciative determination of phosphorus for phosphate, phosphite and total phosphorus in river water samples is given in Table VI. Phosphite was not detected in all samples tested. It is shown that the IEA method of speciative determination of phosphorus offers the useful tool to the environmental and geochemical problems.

Table VI Speciative determination of phosphorus in River Sanno (μgP/ml)

Sampling point	Total P	PO_4^{3-}	PO_3^{3-}
1	0.41 ± 0.01	0.01 ± 0.01	N.D.
2	0.59 ± 0.02	0.22 ± 0.01	N.D.
3	0.51 ± 0.01	0.14 ± 0.01	N.D.
4	0.88 ± 0.01	0.46 ± 0.02	N.D.
5	0.66 ± 0.01	0.02 ± 0.01	N.D.

5. Conclusion

It is shown that the IEA method can be applied to the speciative determination of phosphorus, and the method has many advantages comparing with the conventional spectrophotometric method as discussed in 3.2.

The reverse IEA principle proposed here makes the method much simpler by eliminating the preparation of radioacitve reagent which is necessary for the direct IEA method. Thus, it is preferable that the inactive sample is analysed by the reverse method rather than by the direct one.

The IEA method has many advantages which are listed as follows:

(1) Specificity or selectivity is high.

(2) The procedure is simple and rapid. In particular, when the heterogemeous (two-phases) exchange system is applied, the chemical separation of the exchanging components after the exchange equilibrium is unnecessary. Only necessary is the physical phase separation.

(3) The interfering foreign ions are generally few.

(4) The speciative determination is possible by using the difference in the isotopc exchange behaviors of each species.

(5) As there occurs no chemical reaction in the exchanging system, the chemically unchanged reagent once used could be used repeatedly after eliminating radioactivity by standing for radioactive decay or by shaking with excess of the counter species.

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DISCUSSION

J. Tölgyessy. What are the disadvantages of the isotope exchange methods?

N. Ikeda. The method is applicable to only a limited number of elements. It still remains to be developed in the future.

RESIN BEAD METHODOLOGY AS APPLIED TO FUEL BURN-UP AND FISSILE INVENTORIES*

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Abstract

A new technique has been developed that allows acquisition of samples from matrices difficult to access. While the examples given in this paper are from the nuclear field, the technique is readily modified to address other areas. The technique involves obtaining samples on resin beads; each bead then comprises a sample for mass spectrometric analysis. Through the application of isotope dilution, concentrations of the target elements can be obtained in addition to their isotopic compositions. Examples of application of this technique are given for U, Pu, and Nd.

1. INTRODUCTION

Operation of reactors generates situations in which it is very difficult to obtain an analytical sample due to the radioactivity of the matrix. Such situations arise, for example, in the nuclear fuel cycle, where it is important to obtain samples from all stages to establish a material balance for fissile components, and in evaluating reactor performance by determining burn-up. The conventional analytical approach involves time-consuming and costly elemental separations to obtain uranium and plutonium individually. Most of the chemistry involved must be carried out in a hot cell due to the intense radioactivity of the sample matrix. It is highly desirable, therefore, to develop a technique that both simplifies and expedites sample acquisition.

Two major areas benefit from such a technique: various safeguards programs that are charged with monitoring fissile components in the nuclear fuel cycle, and programs that monitor reactor performance. Safeguards programs must follow the course of uranium and plutonium through the fuel cycle from mining to reprocessing; it is at reprocessing plants that the new technique has had its greatest impact. Reactor operation is monitored by measuring the concentration of a fission product; we have used neodymium for this purpose. The sample matrix is fuel that has been burned in a reactor and is thus highly radioactive.

We have developed a technique involving adsorption of target elements on anion resin beads.[1] Each bead comprises a sample for isotopic analysis via mass spectrometry. Although any amount up to a microgram or two of analyte can be adsorbed on each bead, most of our work has been in the range of 1-3 nanograms. This quantity of material reduces radiation hazards and greatly simplifies shipping since the quantities involved do not require the costly shielding otherwise necessary.

* Research sponsored by the US Department of Energy, Office of Basic Energy Sciences and Office of Safeguards and Security, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

2. MASS SPECTROMETRY

Because the amount of sample is small, a highly sensitive mass spectrometer is required. At the time we were first working on developing the technique, specialized instruments were required, such as the ORNL multi-stage mass spectrometers.[2] These instruments are equipped with pulse-counting detection systems that count each ion individually; one nanogram of uranium is adequate sample for an analysis. They also have high abundance sensitivity to allow measurement of isotopic abundances in the part-per-million range. Another requirement is high sample throughput, since the areas to be monitored generate large numbers of samples. This is usually addressed by mounting a number of sample filaments on a carousel and mounting it in the ion source chamber of the mass spectrometer.[3] This provides the capability of analyzing each sample on the carousel without breaking vacuum; capacities of these carousels range from six to sixteen. An alternative approach is to use a sample insertion probe that allows introduction of the sample through a vacuum lock, but this system is extremely difficult to automate and its use has been limited.

Since the time of our original work (1974), commercial instruments have appeared on the market that have the sensitivity, both with regard to sample size and to abundance, to perform these analyses; they operate under computer control and have throughput superior to that of the specialized, custom-built instruments originally used. VG Isotopes and Finnigan MAT both market instruments with these properties.

3. DATA REDUCTION

The calculations required for analyses of the sort under consideration here demand automatic execution by a computer. Some of the operations are logically complex, and the speed of a computer is necessary to avoid having manpower tied up in routine manipulation of data. Extensive FORTRAN programs have been written to allow automatic processing of data and production of a report of results.[4] All the operations described below are incorporated in these programs.

3.1 Uranium and plutonium

Processing data from these two elements requires a correction to be applied to the 238 mass position to subtract the contribution of the contaminant element from the analyte element. Thus uranium and plutonium from resin beads are treated in pairs, one analysis for each element. Approximate values for the mass 238 position are obtained with no corrections applied. Then, using the 235/238 ratio from the uranium analysis as a basis, ^{238}U is subtracted from the plutonium data, and the plutonium data reprocessed to arrive at a composition for the final report. The corrected 238/239 ratio for plutonium is then used to correct ^{238}U position for plutonium; the uranium data are reprocessed and a final report generated using the corrected values.

3.2 Neodymium

Neodymium has interferences from cerium. Samarium also caused problems until a satisfactory separations scheme was developed; it is described below. Cerium contributes to the 142 and 144 mass positions of neodymium. Mass 142 is used to subtract the contrib-

ution of natural neodymium (a contaminant in this case) from the fission product isotopes. Mass 144 is used only if a total neodymium concentration is required. The program first processes the uncorrected neodymium data and then processes the cerium. After the cerium results are available, correction is applied for that element to the neodymium results obtained earlier, and the natural neodymium correction is applied. A report sheet of the corrected composition is produced, and burn-up calculations are performed according to a standard ASTM protocol.[5]

3.3 Isotope dilution

Isotope dilution is widely used in mass spectrometry to determine the concentration of the analyte element. A known amount of an isotopically enriched isotope is added to a known amount of the sample. Knowledge of the isotopic compositions of the spike, the unspiked sample, and the mixture of spike and sample, together with the weights of spike and sample, allow calculation of the concentration. The program thus requires access to the isotopic compositions of spike and sample when a mixture is being analyzed. When this requirement is added to that of analyzing mixed beads of uranium and plutonium, a program of some complexity is required. We most often use spikes of ^{233}U, ^{242}Pu, and ^{150}Nd.

3.4 Internal calibration

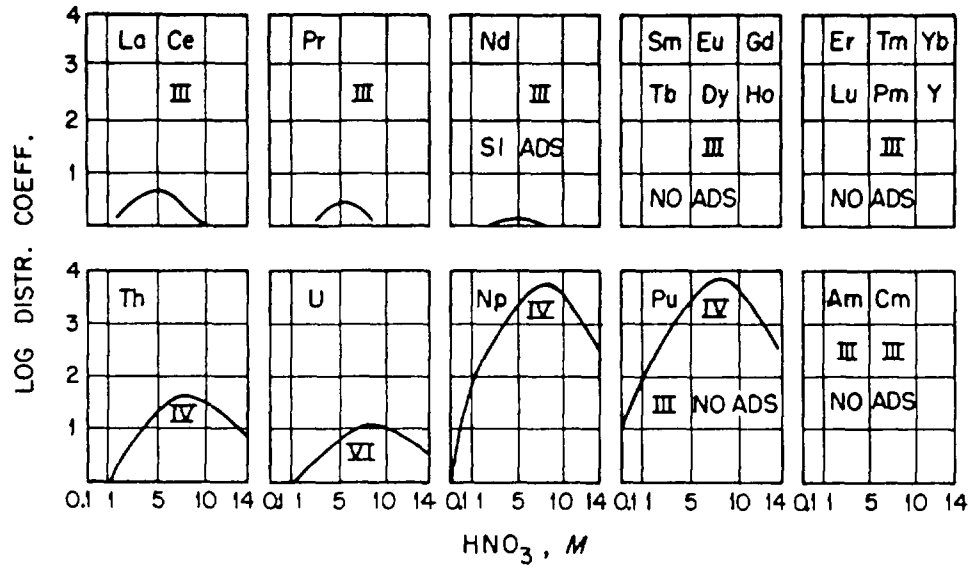
Using a double spike for internal calibration improves precision by a factor of five or more.[6] In this technique, a spike containing two enriched isotopes whose ratio is known to high degree of accuracy and precision is added to the sample. By comparing the measured value of this calibration ratio to the known, a bias can be calculated that is applicable to the analysis in question. An average bias is applied if internal calibration is not used; experience has shown that such an average does not usually reflect the conditions of the individual analysis. The resin bead technique is fully compatible with this technique; all that is necessary is to implement the necessary calculations in the software.

4. SAMPLE ACQUISITION

4.1 Uranium and plutonium

Spent reactor fuel is highly radioactive, being comprised of fission products, transuranium elements (including plutonium), and unburned uranium fuel. Because of the importance of safeguards programs and because of the number of samples that need to be analyzed, the resin bead technique has had its greatest impact in this area.

To obtain samples of uranium and plutonium from solutions, the fact that these elements form stable anions in nitric acid solution is exploited. Figure 1 shows the adsorption curves of various elements of interest from 8M nitric acid.[7] The elements that adsorb appreciably are U, Pu, Th, and Np. Most fission products and actinides higher than neptunium remain in solution. Neither neptunium nor thorium interferes with subsequent mass spectrometric analysis: neither has an isotope that overlaps one from uranium or plutonium, and neither is radioactive enough to cause problems on that score. Indeed, if a thorium-based fuel



IONIC METAL ADSORPTION BY STRONGLY BASIC ANION EXCHANGE RESIN (Dowex 1-X2)

FIG 1. Curves for adsorption from 8M HNO_3 of various elements on anion resin beads.

cycle is ever implemented, it will be advantageous to have that element already on the bead.

To obtain samples, an aliquot of sample solution is adjusted to 8M in nitric acid. A number of resin beads is introduced to the solution; the number will depend on the application. For operations at reprocessing plants, where large quantities of the analyte elements can be expected to be in the environment, we have modified our original technique to accommodate 1000 beads by sampling a solution containing 1 mg of uranium.[8] Even though it is difficult to envision a scenario where 1000 samples would be needed, this greatly reduces the effect of contamination. The solution-bead mixture is agitated on a vortex mixer for 10-20 minutes; this is long enough to allow adsorption of 1-3 nanograms each of uranium and plutonium on each bead. The beads are then separated from the solution. The level of activity on the beads is low enough that they can now be removed from the hot cell.

This work is expedited by use of specialized equipment we have had constructed to our specifications. Figure 2 is photograph of this equipment. The beads are caught on a filter inserted in the small funnel; this apparatus is removed from the hot cell and sealed at each end with plugs. It is then a convenient package in which to ship the samples. Because such small quantities of uranium and plutonium are involved, no special shielding is required. It is legal to ship such samples by mail as long as the number of beads is not too great; this results in great savings in safeguards programs where several thousand samples are analyzed annually.

4.2 Neodymium

Unlike uranium and plutonium, analysis of neodymium for reactor burn-up measurements is usually done at a laboratory near the site of the reactor. Other elements can be used for this purpose, the

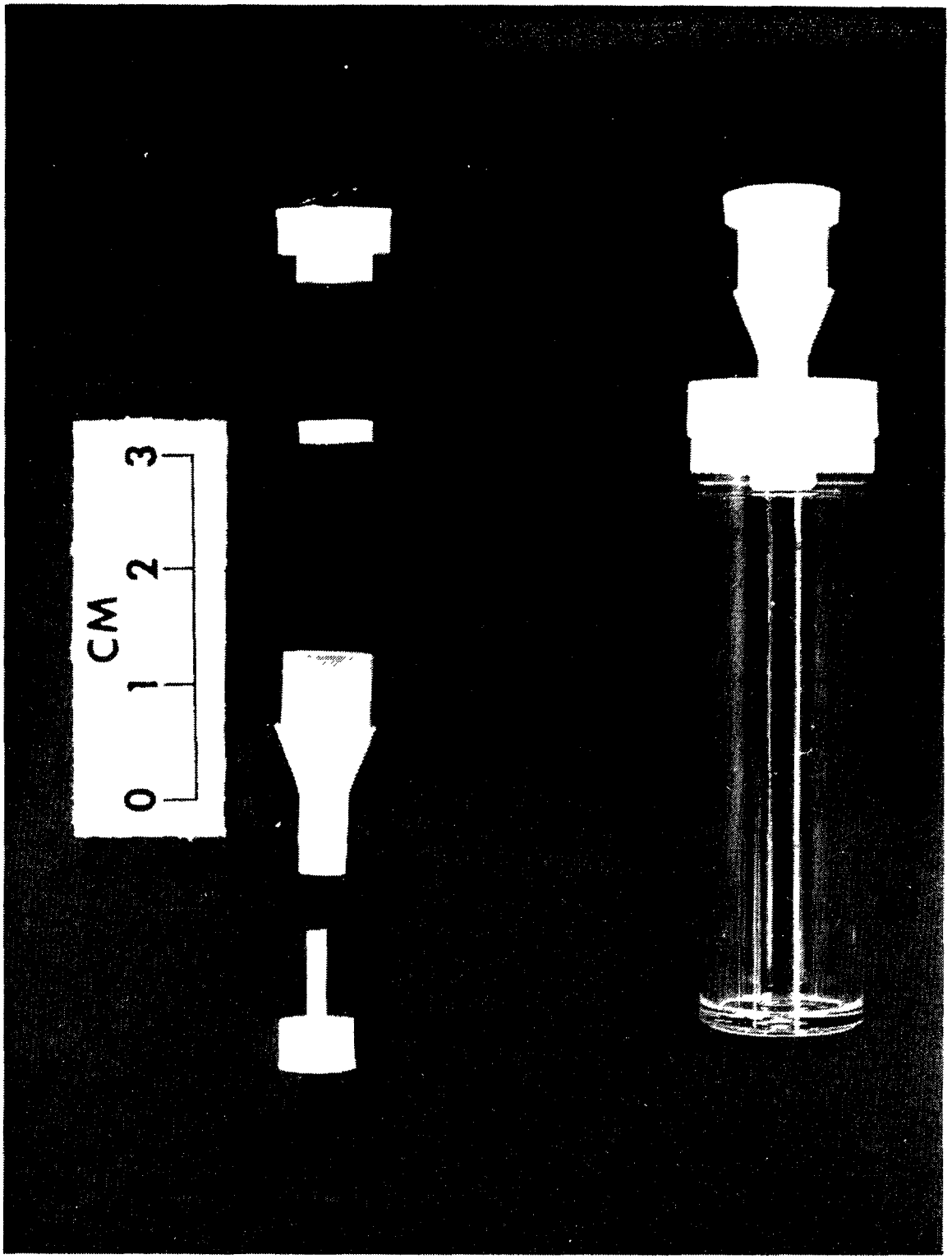


FIG. 2. Resin bead separations and shipping apparatus.

choice being dictated by the nature of the reactor; we have used zirconium to monitor burn-up in operation of the ORNL high temperature gas-cooled reactor.[9]

One of the major difficulties in using neodymium or any other rare earth element for this purpose is the presence of isobaric interferences; for neodymium, these arise from the presence of samarium and cerium in the sample: they, too, are fission products and are produced in the reactor simultaneously with neodymium. By extracting neodymium on anion resin beads by agitating them with a methanol-nitric acid medium (90% methanol, 10% 1:1 HNO_3-water), separation from fission products heavier than neodymium is achieved. This eliminates samarium from the sample; this is the most troublesome contaminant because its ionization characteristics are similar to neodymium. Cerium still remains and must be corrected for in the data-processing step; this requires measuring the isotopic composition of cerium at the conclusion of the neodymium measurements.

5 LOADING SAMPLES ON FILAMENTS

As mentioned previously, each resin bead constitutes a sample for mass spectrometric analysis. We have found the optimum bead size to be in the range of 150-250 μm. Beads of this size are difficult to see with the unaided eye, so we perform bead manipulations under microscopes. Single beads can be identified and picked up on sharp needles; these are made of tungsten or stainless steel to prevent chemical attack by nitric acid adhering to the bead. The bead is then transferred to a mass spectrometer filament; filaments are canoe-shaped, and touching the bead to the desired spot on the filament effects the transfer. The filament is then crimped to help hold the bead in place, although this is not strictly necessary.

6. ISOTOPIC ANALYSIS

6.1 Uranium and plutonium

We have developed a technique of analyzing plutonium and uranium sequentially from the same filament. This involves applying a correction to the 238 mass position for each element, which of course degrades somewhat the result for this isotope. Because 238 is the major isotope for uranium, this correction has little effect on the quality of the result for that isotope. The uranium correction is often significant for the ^{238}Pu, however, since this isotope is almost always a minor constituent of plutonium. If results of highest accuracy and precision are needed for ^{238}Pu, it is necessary to separate the two elements by washing the beads with water or dilute HNO_3 to remove the uranium. Mass 235 is monitored during plutonium analysis and mass 239 is monitored during uranium to provide reference isotopes to use in correcting the 238 mass position.

Since it ionizes at a lower temperature (1450-1550°C) than uranium, plutonium is analyzed first. Care must be exercised to avoid raising the temperature too fast; doing so apparently causes the bead to explode with some violence and often results in excessive loss of sample. With reasonable caution, however, this problem is eliminated: a rise in pressure signals the onset of bead disintegration, and carefully raising the temperature in small increments through this region is all that is needed to

assure sample integrity. To avoid excessive uranium contamination, the count rate for Pu^+ is kept in the neighborhood of 100,000 counts per second; temperatures above 1600°C are to be avoided.

One of the problems encountered in the isotopic analysis of plutonium is the accumulation of ^{241}Am from the decay of ^{241}Pu (half-life of 14.3 years). This causes no difficulty if the beads are fresh since complete separation of plutonium from americium is achieved in the sample-taking process. If, however, the beads are several months old, significant amounts of ^{241}Am will have accumulated. It is then necessary to burn off americium until a stable mass 241 signal is achieved. This is determined by monitoring the ratio of 241 to a convenient plutonium isotope. Since americium ionizes more readily than plutonium, this problem is usually dealt with fairly easily.

When enough data have been accumulated for plutonium, the remainder of this element is burned off by raising the filament temperature to about 1700°C. This usually takes about ten minutes, but can require longer if the bead was too heavily loaded with plutonium. Excessive burn-off times are to be avoided if possible; we have found that, since 238 is a minor constituent of plutonium and the major for uranium, data-taking for uranium can commence when the $^{239}Pu/^{238}U$ ratio reaches the range of 1-10; the value in this range to be used as a criterion is a function of the isotopic compositions of uranium and plutonium. Uranium data are accumulated at a count rate of about 300,000 counts per second on the major isotope.

If it is desirable, uranium can be separated from plutonium by washing the beads with dilute nitric acid; each element can be analyzed individually.

6.2 Neodymium

Because burn-up calculations require that natural neodymium be subtracted from the fission product component, an accurate measurement of ^{142}Nd must be made. Since cerium also has an isotope of this nominal mass, its relative abundance at this mass position must be determined so that the appropriate correction can be made.

The same precautions taken on initial heating for uranium and plutonium must be observed for neodymium analyses. A small signal from samarium at mass positions 148 and 150 is usually observed; this must be burned away before data accumulation for neodymium can be started. Neodymium runs at about 1500°C; like most rare earth elements, it is extremely well behaved under thermal ionization conditions. When enough data for neodymium have been collected, the temperature is raised to burn off the excess. Cerium is run at about 1700°C; a complete isotopic composition is not necessary since only the 142 and 144 positions are of concern; only masses 140, 142, and, if total neodymium is required, 144 are monitored. Mass 140 is monitored during neodymium analysis to provide a reference for cerium corrections.

6.3 Ionization from resin beads

Early in the development of this technique, we observed that performance characteristics during isotopic analysis were improved when samples were loaded on resin beads in comparison to samples loaded as solutions. An order of magnitude more sensitivity in collection efficiency was observed. To investigate this phenomenon, a secondary ion mass spectrometric analysis of resin beads was performed.[10] We found that, during analysis, uranium stayed in the carbon skeleton of the bead and did not migrate to any appreciable extent into the rhenium of the filament. The bead thus served as a point source of ions, enhancing the collection efficiency of the ion source, whose lensing action is designed to operate on a point source.

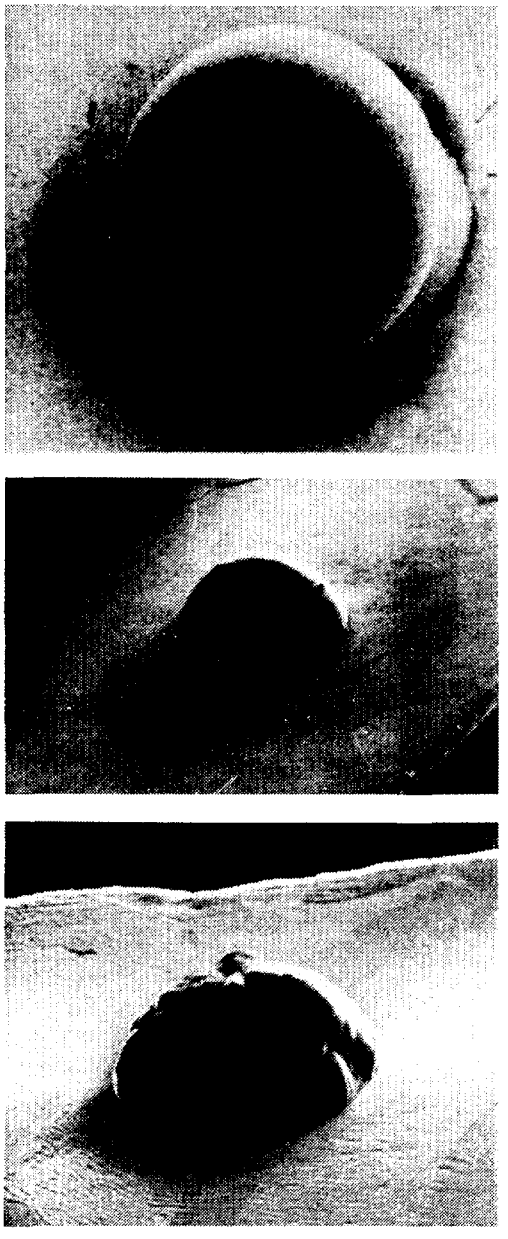


FIG. 3. Electron micrographs of resin beads before and after heating.

A rhenium-carbon mixture has a higher work function than pure polycrystalline rhenium.[11] Ionization occurs with about a factor of ten higher efficiency from such a surface. The interface between the bead and the rhenium filament forms a composite of this nature, and thus ionization will take place largely in this region. We found, in addition, that the carbon skeleton of the bead slowly dissolves into rhenium substrate; rhenium and carbon do not form a stoichiometric compound but are mutually soluble. Figure 3 contains three electron micrographs showing a pristine bead and two beads heated for 30 minutes at 1700°C. Dissolution of the beads from the side in contact with the rhenium is readily apparent; this was confirmed by elemental distributions determined by secondary ion mass spectrometry. Thus the carbon matrix serves as a reservoir of sample, delivering it to the ionization region as it dissolves in the rhenium. This allows for more controlled evaporation of the sample. An additional benefit is gained from the reducing nature of the carbon matrix. With solution loadings, loss of sample as oxide species (e. g., UO^+, UO_2^+) is an ever-present problem. Using resin beads virtually eliminates evaporation as oxides, contributing to enhanced ionization efficiency.

Ionization efficiency can be further enhanced by judicious overcoating of the sample. While colloidal graphite (aquadag) has the desired effect, greater benefit can be derived by overcoating with rhenium, either by electrolytic deposition[12] or by depositing it as a finely divided powder as a slurry in sucrose solution.[13]

7. RESULTS

A study of the comparative efficiency of plutonium ionization is summarized in Table I. As can be seen, efficiencies of about 1% can be realized, making possible acquisition of quality results from analysis of subnanogram samples. Because of the dangers of plutonium to human health, it is desirable to minimize the quantity of sample necessary for analysis. Table II presents results for all three elements under consideration here to give a unified example of the technique's performance.

TABLE I. Comparative Ionization Efficiency for Pure Pu Standards

Lab	Filament loading Technique	Amount Loaded, ng	% Efficiency
ORNL	Solution	1.0	0.01-0.05
ORNL	Resin bead	1.0	0.10-0.20
ORNL	RB/Re-C overcoat	1.0	0.5-1.5
ORNL	Sol/Re-C overcoat	1.0	0.02-0.05
LANL	Re electrodeposit	10.	0.014
LLNL	Solution	0.000125	0.05
KAPL	Solution	1.0	0.04

ORNL: Oak Ridge National Laboratory
LANL: Los Alamos National Laboratory
LLNL: Lawrence Livermore National Laboratory
KAPL: Knolls Atomic Power Laboratory

TABLE II. Isotopic Compositions from a Single Reactor Run (Atom %)

	Starting Fuel						
	234	235	236	238			
U	0.360	45.20	0.430	54.01			
	Spent Fuel						
	142	143	144	145	146	148	150
Nd	1.27	8.32	42.43	14.86	19.32	9.055	4.754
	238	239	240	241	242	244	
Pu	13.85	42.47	18.33	10.60	14.71	0.0023	
	234	235	236	238			
U	0.296	1.578	11.128	86.998			

TABLE III. Results of Joint IAEA-PNC-ORNL Resin Bead Experiment

Lab	Technique	Concentrations in µg/g Total U	Total Pu
PNC	Conventional	164.7	1.507
IAEA	Conventional	164.8	1.492
IAEA	Resin bead	164.7	1.498
ORNL	Resin bead	164.0	1.492

Lab	Technique	Isotopic Composition, weight % U 234	235	236	238
PNC	Conventional	0.0191	1.0942	0.3746	98.512
IAEA	Conventional	0.0211	1.0876	0.3718	98.519
IAEA	Resin bead	0.0201	1.0905	0.3699	98.519
ORNL	Resin bead	0.0201	1.0905	0.3722	98.511

Lab	Tech	Isotopic Composition, weight % Pu 238	239	240	241	242
PNC	Conv	1.458	60.178	22.623	11.515	4.227
IAEA	Conv	1.369	60.301	22.642	11.483	4.206
IAEA	Bead	1.375	60.171	22.599	11.624	4.231
ORNL	Bead	1.366	60.232	22.635	11.529	4.239

One of the requirements of a new technique is that it yield results at least as good as the one it is trying to replace. Table III summarizes results from an international experiment involving the International Atomic Energy Agency, the Power Reactor and Nuclear Fuel Development Corporation of Tokai, Japan, and ORNL.[14] Resin bead results are comparable to those obtained from solutions; IAEA and PNC interaction has continued with a series of similar experiments. A resin-bead sample round robin administered by the U. S. National Bureau of Standards[15] yielded results that were, on the average, better than those obtained for IDA-80, an international round robin using solution loadings.[16]

8. CONCLUSIONS

We have had more than ten years' experience now using resin bead sample loading. The benefits are so great, and the implementation so simple, that it is now the method of choice for introducing any sample into our pulse-counting mass spectrometers. If the analyte element is not amenable to separation by resin bead methodology, we introduce a cation resin bead to the filament to absorb the solution containing the analyte. In this way, we can exploit the benefits accruing from thermal ionization from resin beads without having to perform any separative chemistry with them. We know from experience that the operations involving the use microscopes tend to intimidate prospective users. Their use is, however, much less formidable than it appears: any technician can learn the necessary procedures in a few days, and, with experience, introducing samples to filaments on resin beads becomes quicker than as solutions, taking only a few seconds.

We have used the technique in many applications other than those described in this paper. These include support for the Three Mile Island incident[17] and determination of technetium in the environment.[18] A comparative study of the uptake of uranium, thorium, and plutonium by plants and animals has been published.[19] The three elements were analyzed sequentially from the same filament; thorium was analyzed after uranium.

The range of applications of the resin-bead/mass spectrometry combination covers a wide variety of elements and sample matrices. It provides a convenient shipping medium as well as a handy vehicle for introduction of samples into the mass spectrometer. Other major advantages of the technique are simplified sample preparation, both with regard to time and chemical operations; improved mass spectrometric performance due to enhanced ionization efficiency; reduction of contaminant species such as ^{241}Am due to the separative powers of the beads; reduction of loss of sample as volatile oxide species; and the ability to run both uranium and plutonium from the same filament. These are powerful arguments for widespread adoption of the technique.

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DISCUSSION

T. Braun. I would be interested in the type of resin beads you were using. Were they microreticular or macroreticular? I think swelling could have a certain role in the disintegration of the beads during the heating before the MS analysis.

D.H. Smith. They are macroreticular beads (125-250 micrometers in diameter). The size was chosen to make loading beads with U and Pu in quantities reproducibly variable from 1 nanogram to 1 microgram.

A SURVEY OF IMMUNOASSAY TECHNIQUES FOR BIOLOGICAL ANALYSIS

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Abstract

Immunoassay is a very specific, sensitive, and widely applicable analytical technique. Recent advances in genetic engineering have led to the development of monoclonal antibodies which further improves the specificity of immunoassays. Originally, radioisotopes were used to label the antigens and antibodies used in immunoassays. However, in the last decade, numerous types of immunoassays have been developed which utilize enzymes and fluorescent dyes as labels. Given the technical, safety, health, and disposal problems associated with using radioisotopes, immunoassays that utilize the enzyme and fluorescent labels are rapidly replacing those using radioisotope labels. These newer techniques are as sensitive, are easily automated, have stable reagents, and do not have a disposal problem.

In 1959, Berson and Yalow [1] reported the development of a revolutionary new type of assay which combined the specificity inherent in the antibody/antigen interaction and the excellent sensitivity obtainable from radioisotope measurements. Since that time, immunoassays have become one of the most important and widely used of all analytical techniques. A recent study by Frost and Sullivan [2] reported that in 1983 the U.S. market

for immunodiagnostic reagents and instruments exceeded $600 million and $105 million, respectively.

The success of immunoassay as an analytical procedure is due to the exquisite specificity and the high degree of affinity of the antigen/antibody interaction. Thus, the antibody, or the antisera in which it is contained, is the key reagent of an immunoassay. Initially, antibodies were obtained by injecting animals, usually goats or rabbits, with a quantity of purified or semipurified immunogen. After a given time interval, antibodies could be harvested by processing blood taken from the immunized animals. The resultant serum was then used directly in an assay or further purified by various precipitation, adsorption, or chromatographic techniques. Since antibodies are biological compounds, their variability, stability, and availability have been of concern, and a great deal of effort has been expended on ensuring and documenting the essential properties and characteristics of antibody reagents (i.e., affinity, avidity, specificity, stability, etc.).

In 1975, Kohler and Milstein [3] reported their development of a cell fusion technique that has revolutionized the immunodiagnostic industry. In this new technology, two different types of cells are fused to create a new type. The resulting cell, called a hybridoma, exhibits characteristics derived from both parent cells. For example, fusing fast-growing myeloma tumor cells with spleen cells derived from an animal that has been immunized with a specific antigen yields hybridomas that secrete antibodies against this antigen. Subsequent selection from the population of fused cells can isolate hybridomas that secrete a single type of antibody with

a unique set of biochemical characteristics and properties. Since the antibody is a specific immunoglobin from an immunoglobin gene of a single cell, it is called a "monoclonal antibody." In addition to antibody-producing capabilities, the hybrodomas acquire the growth characteristics of the myeloma parent and can be propagated by cell culture or other techniques to provide continuous quantities of the monoclonal antibody.

As immunochemical reagents, monoclonal antibodies have two significant advantages over conventional antibody reagents: (1) they have a unique and narrow antigenic specificity, and (2) they can be used to produce large quantities of essentially identical antibodies. Thus, it is possible to produce large quantities of monoclonal antibodies, maintaining both consistent yields and lot-to-lot quality.

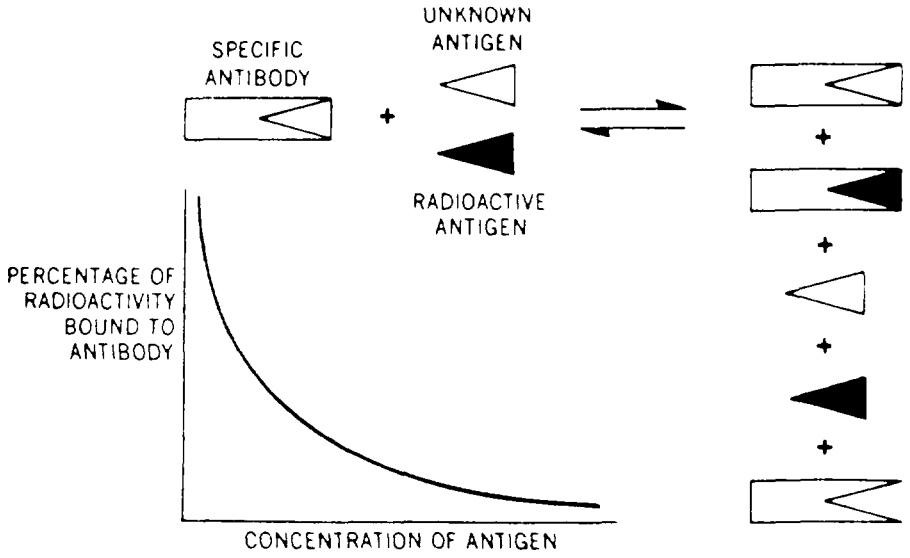

FIG. 1. **RADIOIMMUNOASSAY (COMPETITIVE PROTEIN BINDING)**

The theoretical basis of an immunoassay is illustrated in FIG. 1 and by the following formula:

$$Ag + Ag^* + Ab \rightleftarrows AgAb + Ag^*Ab \ , \qquad (1)$$

where

Ag = unlabeled antigen (i.e., analyte);

Ag* = labeled antigen;

Ab = antibody;

AgAb = unlabeled antigen/antibody complex; and

Ag*Ab = labeled antigen/antibody complex.

In the absence of unlabeled antigen (Ag), a quantity of labeled antigen (Ag*) will bind to the antibody (Ab) according to the law of mass action. In the presence of unlabeled antigen, the amount of antibody-bound labeled antigen (Ag*-Ab) will decrease because the unlabeled antigen competes with it for the binding sites on the antibody. The amount of unlabeled antigen displaced from the antibody is proportional to the amount of unlabeled antigen in the system. Using known quantities of unlabeled antigen, a calibration curve can be prepared and used to quantitate the amount of unknown antigen contained in a sample.

Various labels are used in immunoassays (TABLE I). Radioisotopes were the first labels used in immunoassays [1] since the capability then existed for measuring very low levels of radioactivity. Isotopes used include ^{125}I, ^{131}I, ^{3}H, and occasionally ^{14}C. As a consequence of combining the specifi-

TABLE I. Labels used in immunoassays (IA)

1. Radioisotope (RIA)
2. Enzymes (EIA)
3. Fluorescent dyes (FIA)
4. Chemiluminescent compounds
5. Stable free radicals

city of the antibody/antigen bonding with the sensitivity of radioactive measurements, radioimmunoassay (RIA) quickly became a very popular bioanalytical technique and widely used for determining hormones, vitamins, drugs, cancer antigens, enzymes, receptors, viruses, antibodies, polypeptides, and other proteins.

Unfortunately, RIA has several inherent problems — all associated with the use of a radioactive label. First, the specific activity of the labeled antigen will decay with time, and, consequently, the stability and reliability of the key analytical reagent in the process is continually changing. Thus, the shelf life of the reagent is short. Secondly, RIA-type assays have been traditionally difficult to automate because the technique requires a separation step of the free and bound portions of the labeled antigen before they are counted. Several attempts have been made to automate RIA methods, but, in general, these efforts have not been as successful as the development of automated equipment for routine chemical assays.

A third disadvantage of RIA is the safety and health concern associated with the use of radioactive compounds. Such use requires licensing and regulation of the laboratory by various state and federal agencies including the Nuclear Regulatory Commission, the Department of Transportation, and the Food and Drug Administration. In addition, both the laboratory and technologists should be continually monitored using a combination of area monitors and personal area monitors. It is also becoming a widespread laboratory practice to prohibit pregnant women from working in laboratory areas in which radioisotopes are used.

An additional disadvantage of RIA, which is rapidly becoming its MAJOR DISADVANTAGE, is the disposal of its radioactive waste. For many years, such waste was disposed of by a wide variety of means, including pouring down the drain. However, in recent years, disposal of radioactive waste has been strictly regulated, which has led laboratories to consider alternative analytical techniques.

In 1972, Rubenstein, Schneider, and Ullman [4] reported a new type of immunoassay in which the radioactive label was replaced by an enzyme. Such an assay is called an enzyme immunoassay (EIA) and is classified as a homogeneous assay because it does not require the separation of free and bound labels as does the RIA technique (i.e., a heterogeneous assay).

The theoretical basis of an EIA is illustrated by the following formulas:

$$\text{Ag} + \text{Ag-E} + \text{Ab} \rightleftarrows \text{AbAg} + \text{AbAg-E} \quad , \tag{2}$$

$$\text{AbAg-E} + \text{S} \rightleftarrows \text{AbAg-E} + \text{P} \quad , \tag{3}$$

where

Ag = unlabeled antigen,

Ag-E = enzyme labeled antigen,

AbAg = unlabeled antigen/antibody complex,

AbAg-E = enzyme labeled antigen/antibody complex,

S = enzyme substrate, and

P = product of enzyme-catalyzed reaction of the substrate.

In practice, an aliquot of specimen is added and mixed with aliquots of enzyme-labeled antigen, antibody, and the substrate appropriate for the enzyme. If there is no unlabeled

antigen in the specimen (i.e., the analyte being measured), the enzyme-labeled antigen and antibody react, forming a complex that blocks the active center of the enzyme and thus inhibiting any enzyme reaction. If the unlabeled antigen is present in the specimen, it will displace the enzyme-labeled antigen in proportion to its concentration. The displaced enzyme-labeled material is then free to bind with substrate, permitting the enzyme reaction to occur. The resultant enzyme activity can be related to the concentration of the unlabeled antigen by comparison with a calibration curve.

Sensitivity of an EIA can be increased by allowing the enzyme to react with the substrate for a longer period of time. Thus, the product increases in a stoichiometric manner, and the signal-to-noise ratio (and hence, the sensitivity of the assay) increase accordingly. Such assays are known by the acronym EMIT, which stands for Enzyme Multiplied Immuno Technique.

Another version of EIA is the enzyme-linked immunosorbent assay (ELISA), which is widely used to detect the presence of either antigens or antibodies in biological samples. This method utilizes enzyme-labeled immunoreactants (antigen or antibody) and a solid-phase binding support (e.g., coated test tubes, beads or wells of microtiter plates). In various types of assay modifications, the amount of immobilized enzyme activity is proportional to the concentration of the analyte being measured. Nano- and picogram quantities of analyte can be detected, making ELISA as sensitive as RIA.

Fluorescent labels are also becoming increasingly used in immunoassays. Fluorescent immunoassays (FIA) utilize fluorescent labeled antibodies or antigens to detect antigen-

antibody reactions. Measurement of the resultant fluorescence can be used to quantitate the concentration or titer of either the antigen or antibody. A variety of technical variations exist for FIA (TABLE II), with fluorescence polarization being one of the most useful [5].

TABLE II. Types of fluorescent immunoassays*

Fluorescence microscopy
Heterogeneous:
Solid-phase antigen assay
Solid-phase antibody assay
Homogeneous:
Antibody quenching
Fluorescence polarization
Internal reflection spectroscopy
Fluorescence excitation transfer
Fluorescence protection

*From *Dictionary and Encyclopedia of Laboratory Medicine and Technology*, J. L. Bennington, Ed., W. B. Saunders, New York (1984) 785.

Assays utilizing fluorescence polarization are based on the fact that light waves produced by standard excitation sources are oriented randomly. Also, light waves passed through certain crystalline substances (polarizers) become oriented in a single plane and are said to be plane-polarized. If a fluorophor is excited by polarized light, the size of the molecule will determine if the fluorophor emits polarized or depolarized light. If the fluorophor is large, the rotational relaxation time is long compared with the fluorescence decay time, and the emitted light will be plane-polarized, parallel

to the polarized excitation light. A small molecular fluorophor causes depolarization because its rotation relaxation is faster than the fluorescence decay time, and thus, its rotation may change between excitation and emission; light will therefore be emitted in many different directions (i.e., light will be depolarized). However, if such a small molecule is attached to a macromolecule, as in a fluorophor-labeled antigen-antibody complex, the small fluorophor will behave similarly to a large fluorophor and emit polarized light. This phenomenon can be used analytically, for example, in immunoassay methods for the quantitation of a number of therapeutic drugs, drugs of abuse, and other small molecules. The central principle of these methods is competition between the analyte in the sample and a known amount of fluorophor-labeled analyte for a limited number of binding sites on an antibody to the analyte. The amount of analyte present in the sample will, therefore, have a direct effect on the change in fluorescence polarization. For example, if the amount of analyte in the sample is small, more fluorophor-labeled analyte- (antigen-) antibody complex forms and the degree of depolarization is small. Conversely, if the analyte concentration in the sample is high, less fluorophor-labeled analyte- (antigen-) antibody complex forms, and depolarization is significant.

Immunoassays that use labels such as enzymes and fluorophores described above are known as nonisotopic immunoassays. These assays have comparable sensitivity with radioimmunoassay and have the additional advantages of having stable reagents and simple waste disposal of spent reagents. Also, these assays are amenable to automation, and instrumentation

exists for this purpose. For example, centrifugal analyzers [6] are commercially available that incorporate both enzyme and fluorescence immunoassays as part of their repertoire of automated chemistries. These machines are easy to operate, need only microliter volumes of both reagents and samples, allow for calibrators to be processed in real time with samples, and provide for on-line data acquisition and processing. In addition, special purpose instruments are available for automating fluorescence and fluorescence polarization immunoassays [5].

In summary, immunoassays are a very popular and widely used technique to measure a large variety of analytes in biological fluids. They offer excellent sensitivity and specificity and hence their wide applicability. A variety of labels are used with immunoassays; however, due to disposal problems with radioisotopes, radioisotopic-based assays are rapidly being replaced with nonisotopic labels such as enzymes and fluorophores.

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DISCUSSION

T. Braun. Do you think it would be possible to find a heptane forming a complex with some inorganic trace component and using the complex as a basis of an immunoassay for the determination of that inorganic trace component?

C. Burtis. It may be possible, but I do not personally know of any efforts to develop such an assay. I doubt that such an assay would be as sensitive as spectroscopic methods. In addition, an immunoassay would be a single element determination while spectroscopic methods can be multielement. I would also think that the spectroscopic methods would be methodologically simpler than an immunoassay.

H. Ross. Can immunoassay techniques be effectively extended to the analysis of materials not associated with clinical interest, i.e., organic pollutants at environmental levels?

C. Burtis. Yes. If an antibody can be prepared, an immunoassay can be developed. For example, many such assays have already been developed for polynuclear aromatics and their metabolites. Antobodies for smaller molecular weight compounds can be prepared by binding the compound to a larger molecular weight compound and then injecting the combined molecule into an animal which then produces an antibody.

R. Rosenberg. Does RIA have any future?

C. Burtis. In my opinion, RIA will have only small role in the clinical laboratory of the future. Since non-isotope labels (primarily enzyme and

fluorescence labels) are available and methods based on them can be easily automated on existing instrumentation. These types of assays will continue to displace and replace RIA techniques, however, for research purposes. I think RIA will continue to be used. As I mentioned in my talk, the major disadvantage with RIA today is the growing problem of disposing of the low-level wastes that are generated with its use.

THE ROLE OF INAA AS COMPARED TO CONVENTIONAL METHODS OF ANALYSIS FOR GEOLOGICAL SAMPLES IN CANADA

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Abstract

The instrumental neutron activation analytical technique (INAA) both competes with and compliments conventional commercial analytical methods like X-ray fluorescence emission spectrometry (XRF), direct coupled plasma emission spectrometry (DCP), inductively coupled plasma emission spectrometry (ICP), inductively coupled plasma-mass spectrometry (ICP-MS) and atomic absorption (A.A.).

The major advantages to the use of INAA in the geological field includes the fact that the analysis can be done non-destructively without encountering the many problems inherent in acid dissolution or fire assay techniques. The sensitivity for many elements are still unrivalled by commercially available analytical techniques for gold, platinum-group-elements, many of the rare earth elements and other elements. The multi-element nature of the analysis combined with ease of automation, data collection and spectral analysis procedures allows for rapid turnaround of samples at low cost. This technique competes very favourably with virtually all other analytical techniques.

The geological market being served by INAA includes university and government researchers as well as the mineral exploration industry. The needs of these groups varies considerably and will be discussed. The various applications of INAA to the geological community will also be discussed.

MINERAL EXPLORATION

The requirements of this sector for an analytical method includes providing high quality data with a fast turnaround time at low cost. The field exploration season in Canada begins in May and usually extends into October with some overburden and diamond drilling also occuring from December to April. As a result of the short field season the explorationist usually wishes and expects to receive analytical results within a few days and up to three weeks of submission of samples. The choice of analytical method is also frequently determined by the elements and sensitivities available for each different analytical technique, as well as cost. In the last few years, mineral exploration by the major

mining companies has been depressed as a result of low metal prices. The abundance of laboratories serving this sector as well as the more ubiquitous use of automated multielement analytical techniques has caused severe price competition with price per element now probably at 50% of prices five years ago. There are two qualities of analyses being sold by Canadian laboratories. These are classed as assay (accuracy and precision of better than ± 2-5%) and geochemical (accuracy and precision of ± 30%). The bulk of the samples being analyzed for this sector are of the geochemical variety. The lowest cost activation analysis packages typically will give better precision and accuracy than the required ± 30%.

The choice of analytical technique is determined to a large extent by the elements being sought. Exploration in Canada has for the last few years centered almost exclusively on gold with more minor exploration for platinum group elements (PGE), base metals and exotic elements. Prior to 1981 the bulk of the exploration was related to uranium.

In general there are certain elements or group of elements required by the mineral exploration sector which are determined accurately and at low cost by techniques other than INAA. These include the major rock forming oxides (Table I) and some trace elements which are determined primarily by X-ray flourescense (XRF), inductively coupled plasma (ICP) or direct coupled plasma (DCP) emission spectrometry techniques. For this type of analysis, INAA can't compete either in cost or precision for many of the elements. Another group of elements which are better determined by other than INAA

Table I Major and some trace element analysis by X-ray fluorescence

Major Oxides (Detection limit 0.01%)		Trace Elements (Detection limit of 10 ppm)
SiO_2	Fe_2O_3	Rb
Al_2O_3	MnO	Sr
CaO	Cr_2O_3	Y
MgO	P_2O_5	Zr
Na_2O	TiO_2	Ba
K_2O	Loss on ignition	Nb

techniques are what is termed a base metal suite which is shown in Table II. This suite includes some elements like Pb, Cu, Ni, Cd and Ag which are very difficult to determine by INAA in geological materials at the level required for geochemistry.

Table II Base metals are usually determined by ICP, DCP or atomic absorption techniques. A typical DCP package is shown below.

Element	Detection Limit	Element	Detection Limit
Cd	1 ppm	Mn	2 ppm
Co	1 ppm	Mo	1 ppm
Cu	0.5 ppm	Ni	1 ppm
Fe	2 ppm	Ag	0.5 ppm
Pb	2 ppm	Zn	0.5 ppm

This paper will be devoted to those elements which are done exceptionally well by INAA. Some of these elements are gold, platinum group elements, rare earth elements, as well as others.

Geochemical Methods for Gold and the Platinum Group Elements

Various methods exist for the analysis of gold and can be broken down into the following main categories:

a) Instrumental determination by a very sensitive analytical technique like instrumental neutron activation (INAA).
b) Fire Assay Collection (usually lead collection with silver added as a collector) followed by:
   i) gravimetric finish -(dissolving silver from the precious metal cupellation bead and weighing the minute gold (+PGE) flake). This is the classical technique.
   ii) instrumental finish by INAA, or dissolution of the cupellation bead followed by atomic absorption, flameless atomic absorption or DC plasma emmission spectrometric techniques.
c) Acid dissolution of the sample followed by solvent extraction of gold and an instrumental analysis of the organic solvent by atomic absorption or DC plasma. A subset of this technique, much less commonly used is direct cyanide extraction which can replace acid dissolution. Solvent extraction is an essential step. Direct analysis of an acid digest may give rise to spectrometric interferences and therefore erroneous gold values.

Table III Methods of analysis for gold at NAS

SAMPLE MATERIAL	PREPARATION REQUIRED	METHOD #	ANALYTICAL TECHNIQUE	ROUTINE WT OF SAMPLE	ELEMENTS DETERMINED SIMULTANEOUSLY*	DETECTION LIMITS (Au)	COMMENTS
Rock	Crushing & Milling	1	FANA	20g	No	1 ppb	detection limit a function of fire assay reagent blank
	Crushing & Milling	2	PREIRRAD FANA	1g	No	0.1 ppb	used to determine background levels in rocks
	Crushing & Milling	3	Direct Irrad INAA	30g	Yes, Group 1	5 ppb	sample sizes can vary from <1g to 500 g
	Crushing & Milling	4	Ni Sulphide FA INAA	50g	Yes, Rh,Pt,Pd,Os,Ru, Ir,Re	1 ppb	used in evaluating PGE deposits
	Crushing & Milling	5	FA DCP	20g	Yes, Pd,Pt	2 ppb	used for routine PGE exploration
Soil	Drying & Screening	1	FANA	20g	No	1 ppb	amount of organics impt to method & interpretation
	Drying & Screening	3	Direct Irrad INAA	30g	Yes, Group 1	5 ppb	
	Drying & Screening	5	FA DCP	20g	Yes, Pd,Pt	2 ppb	useful for PGE exploration
Glacial Till or Panned Concentrate	Heavy Mineral Separation	6	Direct Irrad INAA	1g to 60g	Yes, Group 1 or Group 2	5 ppb	if samples must be reused in timely fashion Group 2 elements only are possible The whole concentrate (usually non-magnetic) should be analyzed
	Seperate -250 mesh	7	Direct Irrad INAA	1g to 30g	Yes, Group 1	2 ppb	lower detection limits to 0.1 ppb possible by using method 2
Humus (Mull)	Drying,Macerating, Briquetting	8	Direct Irrad INAA	8g	Yes, Group 3	1 ppb	sample must be 90% + organic Detection limit affected by inorganics
Vegetation	Drying,Macerating, Briquetting	9	Direct Irrad INAA	8g	Yes, Group 3	0.1 ppb	detection limit may be slightly elevated due to high levels of Na or Br in some species
	Drying,Ashing	10	Direct Irrad INAA	<1g to 2g	Yes, Group 1	5 ppb	ashing losses are possible, ashing is expensive but advantage of using larger sample Ash yield 1-5%
Water	Concentrated on Activated Charcoal	11	Direct Irrad INAA	100 ml	Yes, Group 1	1-5 ppt	caution must be taken in collecting sample (Au is adsorbed onto polyethylene)
	Evaporation	12	Direct Irrad INAA	100 ml	Yes, Group 1	1-5 ppt	evaporation in polyethylene liners
Lake bottom Sediments	Drying & Milling	13	Direct Irrad INAA	5-30g	Yes, Group 1	1-5 ppb	detection limit a function of the inorganic content
	Drying & Milling, Briquetting	14	Direct Irrad INAA	8g		1-5 ppb	can only be done if the organic content is high
	Drying & Milling	15	FANA	5-20g		1 ppb	If organic content is very high the sample may have to be ashed (ashing losses may result)

Group 1 Thermal activation elements Ag,As,Ba,Ca,Co,Cr,Fe,Hf,Mo,Na,Ni,Sb,Sc,Se,Ta,Th,U,W,Zn,La,Ce,Sm,Eu,Yb,Lu

Group 2 Epithermal activation elements As,Ba,Co,Cr,Fe,Mo,Sb,Sc,Ta,Th,U,W,La

Group 3 Humus or Vegetation Ag,As,Ba,Br,Cr,Co,Fe,Mo,Se,Sb,Ta,Th,U,W,Zn

All of these techniques have advantages or disadvantages depending on the type of material being analyzed and the required geological information.

Analysis of Gold by INAA

A wide variety of techniques employing INAA are available depending on the type of material to be analyzed, and the type of information required. These techniques are summarized by method number (Table III) which will be referred to again. A description of the relative merits of each of the techniques is described, according to the type of sample media.

Rock and Soil

Various neutron activation analysis techniques, which yield gold detection limits from 0.1 ppb to 5 ppb, are listed as Methods 1 - 5. These include both fire assay (FANA) and direct irradiation based techniques. Sample aliquots range from less than 1 gram to 500 grams. The most popular procedure (Method #1) involves a lead fire assay collection on 20 gram aliquots followed by INAA of the fire assay bead. This technique has a detection limit of 1 ppb which is a function of the fire assay reagent blank. The main competing techniques would involve the same fire assay procedure but followed by acid dissolution and an analytical finish by DCP (DL 2 ppb) or flameless AA (DL 1 ppb).

In many instances a researcher may want to look at the differences for example, between an altered versus a fresh volcanic rock for background levels of gold. Method #2 would be applicable for this type of survey. The disadvantage to this technique is the relatively small sample which is analyzed as a result of the radiation hazard from larger samples. Gold contamination is not a problem as the sample is irradiated prior to fire assaying, and regardless of how much gold is introduced after irradiation only the radioactive gold will be measured. This technique is described by Bornhorst et al, [1].

Method #3 describes the INAA technique for the analysis of a 26 element package including gold. A 30 gram sample is routinely encapsulated, irradiated and after a suitable delay, measured. There is no chemical handling of the sample. This package allows one to obtain statistically meaningful gold values on relatively large sample sizes at the low ppb level as well as many other elements simultaneously, nondestructively, and at little additional cost to the gold analysis itself. A wealth of geochemical and geological information is obtained. Included in

this package are:

a)	Au to 5 ppb		This detection limit is suitable for most exploration surveys.
b)	As to	2 ppm	This group of elements can be useful as pathfinder elements which may occur in many types of gold deposits. Negative drill results may occur due to the inhomogenous distribution of gold. However, a mineralized zone may be followed using these elements if the mineralogy of the deposit is suitable.
	Sb to	0.2 ppm	
	W to	4 ppm	
	Ba to	100 ppm	
	Mo to	4 ppm	
	Ag to	5 ppm	
	Zn to	50 ppm	
	Se to	5 ppm	
c)	Ca to	1 %	These elements will reflect the degree of carbonitization or sericitization, respectively, when used in conjunction with other elements listed in this package.
	Na to	0.05 %	
d)	La to	1 ppm	These rare earth elements (REE) are considered relatively immobile during most alteration and metamorphic processes. Ratios such as La/Sm, La/Lu and Sm/Eu, combined with the absolute abundances, provide valuable information on rock type, degree of differentiation of the parent magma and potential for base metal deposits. A description of the use of the rare earths and other elements in this 26 element package are given by Campbell et al, [2].
	Ce to	3 ppm	
	Sm to	0.1 ppm	
	Eu to	0.2 ppm	
	Yb to	0.2 ppm	
	Lu to	0.1 ppm	
e)	Cr to	10 ppm	These elements will help identify rock type (ie, ultramafic bodies will be higher in Cr, Co and Ni) and might help locate potential platinum group element deposit host rocks.
	Co to	5 ppm	
	Ni to	200 ppm	
	Fe to	0.02 %	
f)	Ta to	1 ppm	Some of these elements are considered relatively immobile (even more so than the REE) and will help identify rock types. Commercial quantities of Ta and U may also be located. Correlation of rock units from drill hole to drill hole will also be aided by using these and the previous group of elements.
	U to	0.5 ppm	
	Th to	0.5 ppm	
	Sc to	0.1 ppm	
	Hf to	1 ppm	

Method 4 is a nickel sulphide fire assay procedure followed by INAA analysis of the residue formed on filtering the concentrated HCl solution which was formed on the dissolution of the nickel sulphide button. This method has been described by Hoffman et al, [3]. Although this method provides excellent data on the whole platinum group this method is relatively expensive as it requires two irradiations and three separate counts. A more cost effective method of geochemical exploration utilizes the lead fire assay collection followed by a DCP finish for Pt, Pd and Au and is listed as Method 5. In the event PGE mineralization is found it would then be advantageous to analyze for the whole platinum group.

Glacial till or heavy mineral concentrates

Overburden drilling is a preferred technique for gold exploration in glaciated areas. Heavy minerals are concentrated from the till and the non-magnetic fraction is usually analysed. Commonly, heavy mineral concentrates weigh from 1 to 25 grams with the occasional sample weighing as much as 60 grams. The gold "nugget" effect requires that the whole sample be analyzed for fear of missing the few particles in the sample that may be in the unanalyzed portion. In a 10 gram heavy mineral concentrate, a single 200 micron flake of gold would generate a 5000 ppb gold result which is considered highly anomalous. If this one flake was included in a sample split which was not analyzed the sample may not be recognized as anomalous. Fire assaying of the sample requires additional grinding, further enhancing the possiblity of losses. When the entire sample is used for fire assaying there is no material available for mineralogical examination or additional analytical testing.

The INAA technique (Method #6) is the answer to all these problems. The heavy mineral concentrate is encapsulated (no grinding required), irradiated and measured for as many as 26 elements including gold. However, with this technique, the problem of self shielding of gold arises. This effect is caused by the high nuclear cross section of gold. There is a depression of the gold value reported as a result of large gold particles absorbing all the neutrons on the outer layers of the particle. The effect has been calculated to cause an apparent decrease in gold content of 5% for a 200 micron diameter sphere and 9% for a 400 micron sphere. Any flattening of the particle which generally occurs in nature should reduce this factor. Reported values will still be considered highly anomalous due to the large grain sizes involved and this depression should not concern most explorationists.

Some exploration programs have used the clay size fraction of the till (-250 mesh) for gold exploration. Methods 1, 2 or 7 are applicable to this portion of the sample and the selection would depend on the required detection limits.

Vegetation and humus sampling

In areas of deep overburden the geologist or geochemist has frequently turned to analyzing soils in the search for gold deposits. In areas of transported overburden there is frequently no relationship between mineralized bedrock and overlying soil. Even in areas where soil may reflect buried mineralization, anomalies may be very erratic due to the "nugget" effect of gold. Arid to semi-arid climates frequently have very sparse vegetation cover, however many of the species present may be phreatophytes (ie, roots may reach depths in excess of 100 metres) as a result will sample much greater depths than a soil sample.

Unless a suitable precipitation mechanism exists, gold complexes will tend to remain in solution in the groundwater yielding no geochemical anomaly in soils or till adjacent to mineralization. Due to their extensive root systems, trees effectively sample large volumes of soil and groundwater. Many species may be cyanogenic or produce a very acidic root environment which has the ability to dissolve gold particles and then absorb gold into the vegetation.

Before the late 1970's, there was not a suitable economic and productive analytical technique which could detect gold contents in the low ppb range. Now, detection limits of 0.1 ppb gold can be achieved using direct irradiation INAA (Method #9). The vegetation is dried, macerated and 8 grams is compressed, and analyzed in a multielement mode by INAA. Further details and limitations are available from Cohen et al, [4] who conducted a biogeochemistry survey over the TeckInternational Corona and Noranda Golden Sceptre deposits in the Hemlo region of northwestern Ontario, Canada. This newly discovered mining camp will become one of the largest gold mining areas in North America.

Other researchers believe that ashing the sample and analyzing the ash (Method #10) will allow analysis on a much larger sample. Caution should be exercized as there may be extreme ashing losses and the chance of contamination increases with added handling. There will usually be a substantial ashing charge from commercial laboratories as well as a relatively slow turnaround time. The ash will generally be analyzed by INAA.

The analysis of humus continues to be a favourite method for gold exploration and is described under method 8. This technique is more fully described by Hoffman and Brooker, [5].

Water

The analysis of water for gold by INAA has been described by Hamilton et al, [6] and shows great promise. This technique developed in Australia has not received much attention yet from exploration geologists, at least in Canada. With this technique it is very important that a polyethelene liner and/or activated charcoal (Methods # 11 or 12) be used at the time of sample collection. This is important as the gold will absorb onto the sides of polyethelene or glass bottles.

Lake Bottom Sediments

This technique has been used in both regional and property scale surveys. The detailed property scale survey has been very useful in helping to evaluate geophysical conductors which are found under water. The survey is conducted by boring holes through lake ice and dredging up lake bottom samples using a G.S.C. type lake bottom sampler.

The samples obtained are difficult to analyze because they are usually a mix of organics and inorganics. INAA Methods # 13 to 15 can be used depending on the specific nature of the sample.

UNIVERSITY RESEARCH

The work performed for this sector usually requires the highest precision and accuracy. Cost and turnaround time are of lesser importance. Generally speaking university researchers are trying to obtain as much information as possible on a sample and usually require the best analytical method for each element.

NAS provides various multielement packages with up to 52 elements and options utilizing the following analytical techniques: INAA, Delayed Neutron Counting (DNC), Prompt Gamma Analysis, A.A., DCP, XRF and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Three different grades of analyses are available, however universities prefer to purchase the research grade shown in Table IV. This quality of analysis will allow plotting of chondrite normalized diagrams essential for helping to interpret genetic history of rocks.

Various options which are frequently requested include boron and gadolinium determinations by prompt gamma analysis, and uranium analysis by DNC.

Table IV Multielement multi-method package by INAA, DCP, AA and XRF (Total Metal).

Element	DETECTION LIMITS Basic	Exploration	Research	Element	DETECTION LIMITS Basic	Exploration	Research
Ag ppm	0.5	0 5	0 5	Mg %	-	0 01	0 01
Al %	-	0 01	0 01	Mn ppm	20	2	2
As ppm	5	2	1	Mo ppm	10	5	2
Au ppb	50	20	5	Na %	0 05	0 01	0 01
B ppm	-	10	10	Nb ppm	-	20	10
Ba ppm	1000	20	10	Ni ppm	5	1	1
Be ppm	-	10	1	P %	-	0 01	0 01
Bi ppm	-	0 5	0 1	Pb ppm	5	2	2
Br ppm	5	1	0 5	Rb ppm	100	20	10
Ca %	0 5	0 01	0 01	Sb ppm	1	0 2	0 1
Cd ppm	2	0 2	0 2	Se ppm	10	3	0 5
Co ppm	5	1	0 1	Si %	-	0 01	0 01
Cr ppm	10	2	0 5	Sr ppm	1000	20	10
Cs ppm	2	0 5	0 2	Ta ppm	2	1	0 5
Cu ppm	0 5	0 5	0 5	Ti ppm	-	100	10
Fe %	0 1	0 01	0 01	V ppm	-	10	2
Ge ppm	-	10	10	W ppm	10	3	1
Hf ppm	1	1	0 2	Y ppm	-	20	10
K %	-	0 01	0 01	Zn ppm	2	0 5	0 5
Li ppm	-	10	1	Zr ppm	-	20	10
Rare Earth and Actinide Elements							
Sc ppm	0 5	0 1	0 01	Tb ppm	-	-	0 1
La ppm	1	0 5	0 1	Yb ppm	0 5	0 2	0 05
Ce ppm	5	3	1	Lu ppm	0 2	0 05	0 01
Nd ppm	10	5	3	U ppm	5	0 5	0 1
Sm ppm	0 5	0 1	0 01	Th ppm	1	0 5	0 2
Eu ppm	0 5	0 2	0 05	Dy ppm	0 5	0 5	0 5

The entire platinum group element family is determined by nickel sulphide fire assay followed by INAA analysis of a residue produced during the processing of the sample. The detection limits achievable are shown in Table V.

Table V The platinum group elements, rhenium and gold are determined by a combination of nickel sulphide fire assay collection - acid dissolution and INAA analysis of the residue. The following detection limits are achievable on most materials.

Element	Detection Limit	Element	Detection Limit
Rh	1 ppb	Os	3 ppb
Pd	5 ppb	Ru	5 ppb
Pt	5 ppb	Re	5 ppb
Ir	0.1 ppb	Au	1 ppb

Competing techniques for the rare earth elements includes mass spectrometry, XRF, ICP and ICP-MS. Isotope dilution mass spectrometry provides an excellent quality of data however the method is slow and expensive. Spark source mass spectrometry is also sensitive however is also expensive. XRF analysis suffers mainly from limited sensitivity. ICP analyses for the rare earths suffers from the disadvantage of putting the sample into solution. This technique also frequently lacks sensitivity for some of the important rare earths like Eu. ICP-MS is new technology which links an ICP front end to a mass spectrometer. Preliminary experimentation shows much better sensitivities for most rare earths than the ICP technique however the sample must still be put into solution. Sensitivity for certain rare earths like Eu are still better by INAA.

The whole PGE family is commonly analyzed by a variety of techniques following the nickel sulphide collection. Most of these techniques for example, distillation for Os and Ru, suffer from being very costly, slow and with poor sensitivity. The ICP-MS technique shows promise particularly for Pt and Pd but is still largely experimental.

The main competitive technique for uranium analysis is flourimetry. Flourimetry suffers from being a much higher cost analytical technique than delayed neutron counting as well as having the requirement of putting the sample in solution.

Boron and gadolinium by prompt gamma analysis has the advantage of not having to put the sample into solution as well as having increased sensitivity compared to other techniques like DCP. This is important because the boron is usually tied up in very resistate minerals like tourmalines which do not readily dissolve.

GOVERNMENT GEOLOGICAL SURVEY APPLICATIONS

This market sectors' needs lie between that of the universities and the mineral exploration community. Generally, research related to mineral deposits or related to formulation of genetic models will require the best sensitivities similar to the needs of universities. The government geological surveys in Canada both federal and provincial also conduct regional geochemical reconnaisance programs. The aim of the latter type of program is to develop databases which will be of use to the mineral exploration community. This type of survey typically will consist of many hundreds or thousands of samples and are analyzed for selected specific elements. Usually the elements requested will be determined by the analytical technique which has been in use in

previous similar surveys regardless of whether it is the best technique. For most of these surveys uranium is usually determined by delayed neutron counting and heavy minerals are determined by INAA. One of the provincial surveys is also analyzing lake bottom sediments in a multielement mode by INAA, as they believe they can obtain the most information at the lowest cost with this technique.

Conclusions

INAA compliments other analytical techniques in that the elements it can provide cost effectively are frequently those elements which are difficult to analyze by competitive analytical techniques. The major multielement analytical techniques used most often by laboratories providing services to the geological community include INAA, ICP and DCP emission spectrometry and X-ray fluorescence spectrometry.

Certain groups of elements like the major rock forming oxides and base metal suites described are better determined by plasma or XRF techniques than by INAA. This primarily because of sensitivities and cost of analysis. Analysis by INAA, DNC or prompt gamma are preferred for gold, the platinum group elements, selected rare earth elements, uranium, boron and several elements which are usually included in multielement suites like Ta, Hf, Sc, Cr, Br, I, Cs, W, Re and In.

In a commercial sense INAA has proven to be as cost effective as other analytical techniques and provides usually a similar turnaround to potential competing techniques.

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DISCUSSION

R. Rosenberg. Which are the typical irradiation and measurement times used for NAA.

E.L. Hoffman. The typical irradiation time for long-lived isotopes would generally not exceed 1 hour for a 0.5 gram sample for geological rock material using a thermal neutron flux of 7×10^{12} $n.cm^{-2}S^{-1}$. Counting times would vary from 200 to 2000 seconds. Occasionally we may irradiate samples up to 10 hours for a specific reason.

DETERMINATION OF MINOR AND TRACE ELEMENTS IN DIETS USING NEUTRON ACTIVATION, INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION AND ATOMIC ABSORPTION SPECTROMETRY

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Abstract

The recognition of the role played by trace elements in human and animal health has stimulated interest in establishing their concentrations in a wide variety of biological materials. One of the current topics of interest in human environmental and nutrition research has to do with establishing recommended dietary allowances for essential as well as provisionally tolerable weekly intakes for toxic elements. The migration of trace elements in air, water and soil is reflected in the foodchain of man. The mineral and trace element contents of individual foodstuffs and especially human total diets are promising tools to detect possible health hazards in the environment.

In this connection there is a need to determine the concentrations of elements in foodstuffs, especially in total diet specimens. An important requirement in such work is the application of appropriate analytical quality control procedures based partially on the use of certified reference materials. Although several biological materials of environmental interest are now in common use no human diet is available that can be regarded for checking the accuracy and precision of analytical methods for the determination of trace and minor elements in these specimens.

To receive nutritional data with respect to minor and trace element content of total diets an Agency Co-ordinated Research Programme (CRP) was created joining 13 laboratories of the Member States all over the world. The Chemistry Unit of Agency's Laboratories at Seibersdorf serves the programme as a Reference Laboratory.

In this context, a co-operation with the National Bureau of Standards (NBS) and the Department of Agriculture of the United States (USDA), Human Research Centre Beltsville was established to produce freeze dried and powdered total diet materials which are assumed to serve as secondary standards for calibration purposes and to improve the accuracy of analytical trace element

results in such matrices. The Agency contributed a finish diet (H-9), the NBS a mixed American diet consisting of about 200 individual food items (US-Diet 1) and the USDA a typical American diet (TDD-1D).

The results of 21 (Al, Au, B, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, P, Rb, Se, Zn) elements determined in these diets using instrumental and radiochemical neutron activation analysis (INAA, RNAA), inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS) will be given and compared with respect to accuracy and precision as well as with the results obtained by the 2 other collaborating laboratories. Experiences in using Hydrated Manganese Dioxide (HMD) for the radiochemical determination of As, Cd, Cr and Se in total diet samples after separation from Na, K and P will be reported. The advantages and disadvantages of these analytical methods will be discussed.

DISCUSSION

W.D. Shults. What are the three reference diets which you mentioned? Are they comparable?

R. Schelenz. These diets have been produced in the frame of an IAEA Coordinated Research Programme (CRP) on "Human Daily Dietary Intakes of Nutritionally Important Trace Elements". These diets are comparable to such an extent that they represent typical diets related to their origin which not necessarily means that they are also comparable with respect to their minor and trace element content.

R. Rosenberg. The Se content of the Finnish diet should be lower than that of the U.S. diet. Isn't that true?

R. Schelenz. As a matter of fact the Se content of the two U.S. diets (TDD-1D, U.S. Diet 1) is two times higher than for the Finnish diet (H-G) as indicated in the tables. [The Se concentration of plant material reflects the respective soil Se concentration]. This is probably due to the fact that the average Se content of U.S. soils is significantly higher than found in soils originating from Finland because of concentration.

V. Krivan. I am surprised about the almost continuously higher values for iron by INAA. Possible primary interference nuclear reactions can easily be located, and so a systematic error analysis must relieve the source of this error. I should like also to ask if there are some approaches on the development which would allow to specify the valency state of elements in such a complex material as the different diets are representing.

R. Schelenz. (1) Possible interferences of nuclear reactions have been considered and don't give support to significant higher values. (2) To my knowledge only a few attempts have been made to approach this problem because a total diet composite sample represents a very complex matrix. Most of the analytical methods for trace element determinations in biological material used a wet digestion procedure. Therefore the probability of measuring speciation artefacts is increasing.

C.J. Pickford. Are total Co and Fe contents sufficient: surely organically bound values are more important toxicologically.

PRESENT AND FUTURE PROSPECTS FOR NEUTRON ACTIVATION ANALYSIS COMPARED TO OTHER METHODS AVAILABLE

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Abstract

The evolution of analysis by Neutron Activation during the last fifty years is briefly described. The reasons for its persistant success, in spite of more recent methods are examined. These reasons are based on the specific advantages of neutron irradiation : neutron penetration into the material, sensitive detection of 60 elements, selectivity and reliability. Furthermore the sensitivity is inversely proportional to the natural abundance of the element (for A > 80). However to benefit fully from the advantages of N.A.A., it is essential to study the potential sources of error inherent in each step of the analysis (sampling, preparation, calibration, irradiation, chemical separation, radioactive measurement, calculation and interpretation of the results). These risks are discussed and examples given. The principal areas in which the N.A.A. is being used more and more are ultra-traces analysis, studies on the multivarient correlation between elements and the validation of other methods. Based on present applications and the likely progress of this technique, its future prospects are discussed.

I - INTRODUCTION

The first results obtained by neutron activation analysis (NAA) through the work of HEVESY and LEVY, have been available for over 50 years (1). These authors used neutrons produced by a radium-beryllium source to determine dysprosium in Yttrium.

After the end of the second world war, the development of civil nuclear reactors allowed a large expansion for this analytical method. Analysts obtained a convenient access to the neutron beams that became more and more intense : 10^{9} n.cm^{-2}.s^{-1} then 10^{10} n.cm^{-2}.s^{-1} for the first experimental French Reactor "ZOE" in 1950, 5.10^{12} n.cm^{-2}.s^{-1} for the second "EL2" in 1952 and finally $3.5.10^{14}$ n.cm^{-2} for

the"OSIRIS" Reactor in 1966. The concomitant progress of electronic equipment has allowed a simplification of the chemical separation after irradiation and has therefore spread to fields other than chemistry.

When researchers only had Geiger counters, they had to separate each radioisotope before measurement, using the methods of classical mineral analysis now 30 years old (2). Scintillation detectors then allowed finer measurements of radiation and coincided with the development of column chromatography, which is well adapted to activation analysis. These new methods started with organic resin (3) and then mineral exchangers were added (4). The arrival of semiconductor detectors profoundly modified the conception of separation for activation analysis.

Many analyses are now carried out without any chemical separation and when this remains necessary, it is very selective and adapted to specific situations : only certain isotopes need to be isolated or eliminated before measurement (5).

Beginning in radiochemical laboratories, NAA has spread over 30 years into many areas such as : archeology, biology, environmental, geochemistry, solid physics ...

Many laboratories, now use this method of analysis intensively and have permanent access to one or several nuclear reactors. Some of them, such as the Pierre Süe Laboratory in France, use high power research reactors normally destined for other purposes. Others, such as the National Bureau of Standards in Washington, have their own reactor. In both cases, the reactor used is not specially destined for NAA.

II - THE ADVANTAGES OF NAA

The consistant success of NAA may surprise some. Since its discovery in 1936, many other analysis methods have been developed some of them extensively. These methods are often much simpler to apply and possibly cheaper than NAA. However, this method has specific advantages which explains why it remains unique for certain analyses.

NAA, like other methods is a sensitive, selective, multi-element system. Moreover it has the advantage of Nuclear Activation Methods, as it detects radioisotopes created by the irradiation of the atomic nuclei of the elements. This allows not only the by passing of chemical bonds and direct calibration, but also avoids most of the errors inherent in titration by classical methods.

Lastly, NAA has certain specific advantages over other methods of activation :

- High neutron penetration in the analysed material which simplifies calibration.

- The probability of the reactions and consequently the sensitivity of the detection, is all the more important as the element is naturally rare (for elements with an atomic weight : A > 80). The nucleus synthesis of our solar system explains this fact (fig. 1) (6).

- The simultaneous analysis of several samples is possible.

All these reasons explain why NAA is still the most frequently used activation method in the world.

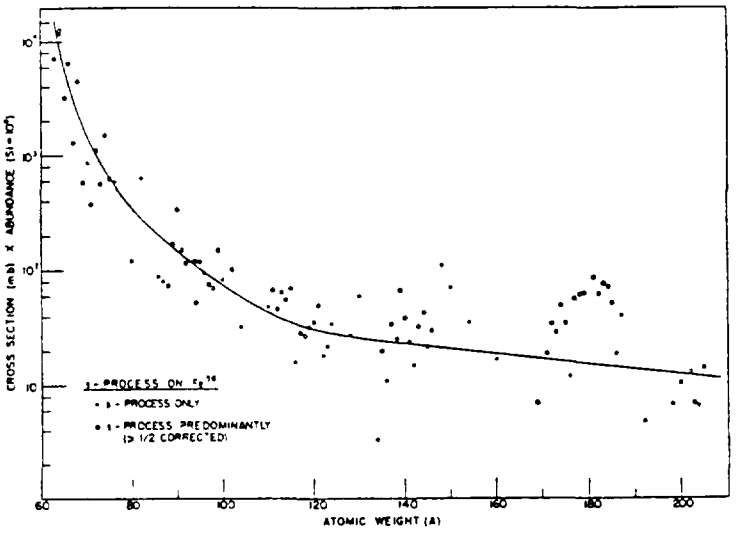

Figure 1 : Variation of the product of natural abundance of elements by their neutron cross section as a function of their atomic weight (6).

III - EXPERIMENTAL ERROR RISKS

As for other analytical methods, a large number of causes of errors exist for NAA. Errors can occur at each step of the analysis shown in fig. 2.

III.1. Preparation of samples and standards

For sampling the causes of error are the same as in classical analysis and the same precautions are needed. The impurities introduced during this step, are irradiated simultaneously with those of the sample and will alter their determination.

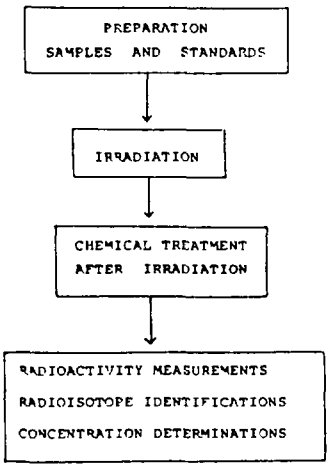

Figure 2 : Principe of Activation Analysis

The use of a clean room is sometimes essential to prepare the sample, especially for biological materials. For the latter, one of the principal causes of error cames from the container used for irradiation whether it is made of polypropylene (7) or of fused silica (8). These containers must be washed thoroughly before use. They must also be carefully sealed to avoid loss through vaporisation during irradiation as well as pollution due to the heating during the sealing (9).

The large range of neutrons in materials allows the analysis of samples of any shape and of a weight from one milligram to several grams. The mechanical operations and the possible resulting pollutions are thus reduced to a minimum. This is not the case for some other methods of analysis (e.g. spark mass spectrometry), which require a special shape for the sample.

Furthermore for solid samples, it is possible to avoid surface pollution by a cleaning of the surface after irradiation. However, the cleaning is not so easy and not so efficient as can be supposed. Therefore it is always advisable to irradiate solid samples with a clean surface.

The preparation of standards is not particulary difficult. As the irradiation concerns only the atomic nucleus, the chemical form of the impurity does not intervene during the measurement of radioactivity. It is often possible to use a direct standardization from the natural element itself. Generally, both samples and standards are irradiated together.

This possibility of carrying out a direct standardization absolutely independant of the chemical form, gives NAA a distinct advantage over other

analytical methods. It is superior to methods such as spectrometries of emission, of mass, of X-ray fluorescence achieved on solid samples, in which quantitative determinations cannot be obtained without standards of the same nature and composition as the samples to be analysed. This requires both time and money.

However in a reactor, samples and standards are never irradiated exactly in the same manner because of the microheterogeneity of the beam. This is the principal cause of inaccuracy in NAA and it introduces an error of a few per cent, whatever the level of concentration. Nevertheless, it is possible to reach an accuracy of one per cent or even less, using special configuration for irradiation (10).

III.2 Irradiation

The irradiation is the greatest drawback of the activation analysis methods. This is due both to the apparatus for irradiation to be used (reactors, cyclotrons, Van de Graaff, linear accelerators...) and to the error risks which occur.

In NAA apparatus required is particulary heavy especially to have intense beams to obtain sensitive determinations; but this apparatus can be used simultaneously for many other studies and the irradiations performed for NAA, do not increase the running cost of a reactor.

The error risks due to irradiation are known and so can be avoided in most cases (11).

- The Szilar-Chalmers effect and heating induced by irradiation are a hazard specially for fragile materials (e.g. biological samples).

- The absorption of neutrons in the sample can generally be neglected except for some materials with a strong cross section (B, Cd, Ag ...). In this case, the required corrections can be carried out (12).

- The recoil range, due to the nuclear reactions, concerns only a thickness of a few nanometers with thermal neutrons and is generally inferior to some micrometers with epithermal and fast neutrons (table II) (13).

- The abnormal diffusion under irradiation suggested by several authors (14) (15) (16), has been refuted in most cases (17) (18) (19).

- On the other hand, the production of the same radioisotope starting from two different elements, is to be taken into consideration for each analysis.

TABLE I : Detection limits neutron irradiation (indicative values in $ng.g^{-1}$ for a maximum time of irradiation of 72h in a flux of $10^{14} n.cm^{-2}.s^{-1}$)

	Ia	IIa	IIIa	IVa	Va	VIa	VIIa		VIII		Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	O
1	^{1}H																	^{2}He
2	^{3}Li	^{4}Be											^{5}B	^{6}C	^{7}N	^{8}O	^{9}F	^{10}Ne
3	^{11}Na 0.1	^{12}Mg 10											^{13}Al 1	^{14}Si 10	^{15}P 1	^{16}S 10	^{17}Cl 1	^{18}A 1
4	^{19}K 0.2	^{20}Ca 100	^{21}Sc 0.01	^{22}Ti 3	^{23}V 0.001	^{24}Cr 3	^{25}Mn 0.01	^{26}Fe 100	^{27}Co 0.01	^{28}Ni 10	^{29}Cu 0.01	^{30}Zn 10	^{31}Ga 0.05	^{32}Ge 10	^{33}As 0.01	^{34}Se 5	^{35}Br 0.01	^{36}Kr 0.5
5	^{37}Rb 0.1	^{38}Sr 10	^{39}Y 0.1	^{40}Zr 100	^{41}Nb 1	^{42}Mo 1	^{43}Tc* *	^{44}Ru 1	^{45}Rh 0.1	^{46}Pd 0.05	^{47}Ag 1	^{48}Cd 0.5	^{49}In 0.1	^{50}Sn 1	^{51}Sb 0.05	^{52}Te 10	^{53}I 0.01	^{54}Xe 10
6	^{55}Cs 0.1	^{56}Ba 1	57-71 T.R.	^{72}Hf 0.1	^{73}Ta 0.05	^{74}W 0.01	^{75}Re 0.01	^{76}Os 0.1	^{77}Ir 0.001	^{78}Pt 0.5	^{79}Au 0.0001	^{80}Hg 0.1	^{81}Tl 10	^{82}Pb 1000	^{83}Bi 10	^{84}Po* *	^{85}At* *	^{86}Rn* *
7	^{87}Fr* *	^{88}Ra* *	^{89}Ac*	^{90}Th 0.1	^{91}Pa*	^{92}U 0.01												
				^{57}La 0.01	^{58}Ce 0.1	^{59}Pr 0.01	^{60}Nd 0.5	^{61}Pm* *	^{62}Sm 0.005	^{63}Eu 0.01	^{64}Gd 0.1	^{65}Tb 0.1	^{66}Dy 0.001	^{67}Ho 0.2	^{68}Er 0.1	^{69}Tm 0.01	^{70}Yb 0.01	^{71}Lu 0.001
			T.R.															

* These elements only include natural radioisotopes with a higher specific activity with allows their detection without irradiation to concentration below one $ng.g^{-1}$.

TABLE II

RANGE IN SILICON OF $^{24}Na^{*}$ PRODUCED BY THE NUCLEAR REACTION : $^{27}Al(n,\alpha)^{24}Na^{*}$

NEUTRON ENERGY MeV	$^{24}Na^{*}$ RECOIL ENERGY (KeV)	$^{24}Na^{*}$ RANGE IN SILICON µm
4	125	0,2
5	293	0,47
6	461	0,75
7	629	1,02
8	797	1,3

For the $^{24}Na^{*}$ produced by the nuclear reaction $^{27}Al(n,\gamma)^{24}Na^{*}$, the range is only about 3 nm

The (n, τ) reactions are generally very selective. The interfering reactions due to epithermal and fast neutrons can only occur on elements which are close in atomic weight.

As an example, table III shows the blanks thus introduced in the determination of sodium in magnesium, aluminium and silicon. For the first two, the interference is well known and should not give inaccurate values but only a high detection limit.

TABLE III

NUCLEAR REACTOR PRODUCTION POSSIBILITIES FOR $^{24}Na^{*}$ USED FOR THE DETERMINATION OF SODIUM

ELEMENT	NUCLEAR REACTION	APPARENT CONTENT IN SODIUM AFTER AN IRRADIATION IN THE REACTOR	
		OSIRIS	ORPHEE
Na	$^{23}Na(n,\gamma)^{24}Na^{*}$	1	1
Mg	$^{24}Mg(n,p)^{24}Na^{*}$	3×10^{-4}	$2\ 10^{-6}$
Al	$^{27}Al(n,\alpha)^{24}Na^{*}$	$1,6 \times 10^{-4}$	1.10^{-6}
Si	$^{28}Si(n,p\alpha)^{24}Na^{*}$	$3\ 10^{-10}$	$< 1\ 10^{-10}$

For silicon, the (n, αp) reaction is less known. The threshold of this reaction is high (15MeV), few neutrons reach this energy in a reactor and the cross section is probably very small (22). However, when the apparent concentration of sodium in electronic grade silicon is found to be several 10^{-10} g, this reaction must be taken into consideration.

Uranium fission can also create the same radioisotopes as those used for the determination of some elements with an atomic number around 95 and 140. Table IV shows this risk which is well known for the determinations of rare earths in geological samples (23).

TABLE IV

INTERFERENCES OF URANIUM IN THE DETERMINATION OF SOME ELEMENTS BY NEUTRON ACTIVATION ANALYSIS

ELEMENT TESTED	RADIOISOTOPE USED	YIED FOR ^{235}U FISSION WITH THERMAL NEUTRONS	APPARENT WEIGHT (µg) OF THE ELEMENT PRODUCED BY 1 µg OF URANIUM	
			Calculated	Determined
Zr	$^{95}Zr^{*}$	6,4 %	10,5	9,2
Mo	$^{99}Mo^{*}$	6,1 %	3,3	2,8
La	$^{140}Ba^{*} \xrightarrow{\beta^-} La^{140}$	6,3 %	0,002	0,003
Ce	^{141}Ce	6 %	0,3	0,2

Values are calculated for an irradiation of 72 h in a flux of $1.10^{14} n_{th}\ cm^{-2}.s^{-1}$.

Determinations are performed after an irradiation of 72 h in the OSIRIS pool reactor.

III.3. Chemical treatment after irradiation

A chemical and eventually a mechanical treatment is generally carried out on the irradiated sample before the radioactivity measurements, except for the analyses using very short-lived radioisotopes.

For solid samples, this treatment usually includes the cleaning of the surface, which theorically allows to avoid surface contamination introduced during sampling, conservation and irradiation. Methods by activation have this a very great advantage over other methods. To obtain the best result it is however necessary to be particularly careful, specially for ultra-trace determinations (11).

Thanks to the progress of electronics and computers, it is now possible to determine a large number of elements in a wide range of concentrations without any chemical separation. This avoids difficulties and error risks, specially for materials that are difficult to dissolve (e.g. alumina) and for volatil elements that are difficult to determine without losses (e.g. mercury).

However in some cases, chemical separation prior to the measuring of radioactivity remains advisable and often indispensable to obtain the sensitivity required. The methods of separation used derived from classical methods with a preference for chromatography over columns and liquid-liquid extractions. In comparison with other methods, use of radioisotopes has two main advantages :

The suppression of blanks at the stage of analysis allows the use of a wide range of reactives, without the long and dreary task of ultimate purification and without compromising of the sensitivity obtained.

The use of inactive carriers minimizes the losses and allows their measurement for each separation.

An analyst using activation techniques should never make an incorrect radiochemical separation, because he can control the radioactivities at each step of the separation.

III.4. Radioactivity measurements

The performances of NAA have been much improved by technical progress in measurement systems. Is now common to determine up to forty elements in a concentration range under the p.p.m. and sometimes under the p.p.b., in one or several samples irradiated simultaneously.

The radioactivity measurements are very convenient to automatize. This automatization requires rigorous testing, but afterwards, it is possible to analyse a large number of similar samples with reduced labor costs.

The present evolution of the computer systems considerably reduces the cost of measurement apparatus. The association of a multichannel buffer with a microcomputer such as an IBM-PC, reduces the cost of the acquisition-treatment system by a factor 3 or 4 in comparison with the former systems, such as TRACOR 4000, ORTEC 7000 or NUCLEAR DATA Cosynus.

Moreover, the software used for the mathematical treatment of gamma spectrums with a personal microcomputer, are more accessible for the analyst than those written in assembly language. Thus

it is possible to have a better adaptation to the sample to be analysed and a better control for the results obtained.

The nuclear characteristics of the radioisotopes used in NAA (half-time, type of emission, gamma ray energies ...) are generally well known (24)(25). When samples and standards are irradiated simultaneously, incertitudes on the neutron flux and on the values of the cross-section do not intervene.

Consequently, the determination of the concentration is very easy: the radioactivity measured at the same time after irradiation is directly proportional to the number of atoms of the same element in samples and in standards.

However, some radioisotopes have very similar nuclear characteristics and can be confused. In fact, this error risk is exceptional when the measurements are correctly performed : both gamma-ray energies and half-life must be controlled. Nevertheless this risk cannot be entirely neglected.

TABLE V

DETERMINATION OF TITANIUM BY THE NUCLEAR REACTION $^{47}Ti(n,p)^{47}Sc^{*}$ AND OTHER INTERFERING NUCLEAR REACTIONS

ELEMENT	NUCLEAR REACTION	APPARENT CONCENTRATION PRODUCED BY THE ELEMENT	
		Calculated	Determined
Ti	$^{47}Ti(n,p)^{47}Sc^{*}$	1	1
V	$^{50}V(n,\alpha)^{47}Sc^{*}$	3×10^{-2}	5×10^{-2}
Ca	$^{46}Ca(n,\gamma)^{47*}Ca \xrightarrow{\beta^-} {}^{47}Sc^{*}$	2×10^{-1}	3×10^{-1} (sous Cd : 4×10^{-3})
Pt	$^{198}Pt(n,\gamma)^{199}Pt \xrightarrow{\beta^-} {}^{199}Au^{*}$	6.8×10^{2}	5×10^{2} (sous Cd : 4×10^{1})

Values are calculated for an irradiation of 72 h in a flux of $1.10^{14} n_{th}.cm^{-2}.s^{-1}$ and of $1.10^{13} n_{epi}.cm^{-2}.s^{-1}$

DETERMINATIONS ARE PERFORMED AFTER A 72 h IN THE OSIRIS POOL REACTOR

$^{47}Sc^{*}$ { T1/2 = 3,42 days ; E_γ = 159 KeV } $^{199}Au^{*}$ { T1/2 = 3,2 days ; E_γ = 158 KeV }

For example in the determination of titanium using the $^{47}Sc^{*}$, the $^{199}Au^{*}$ product by β decay of $^{199}Pt^{*}$ has quite the same τ ray energy and the same half-life as the $^{47}Sc^{*}$ (Table V). In this case it is necessary to use high resolution spectrometry measurements or a radiochemical separation after irradiation.

IV - DEVELOPMENT OF NAA AND PROSPECTS FOR THE FUTURE

A large number of papers presented in June 86 during the last meeting entitled : "7th Modern Trends in Activation Analysis" (26), show that not only NAA continues to be used throughout the world but also that its applications are developing in several domains and particularly in the three following.

1. Ultra-Traces analysis

In this case the suppression of pollution after irradiation and the showing of the losses during the chemical treatment, allow to reach theoretical limits in the analysis of real samples.

Table VI shows the results actually obtained in the analysis of high purity silicon. Generally the detection limits obtained on this material are better than those calculated previously in Table I. Several hundreds of silicon samples are analysed each year in the "Pierre Süe" Laboratory, at a very competitive costs in comparison with other methods, such as : S.I.M.S., I.C.P., S.M.S., ... which are much less sensitive in practice than NAA for the detection of most metallic impurities.

2. Correlation studies

Here, the multi-elementarity of the NAA allows to compare quantitatively the concentration of a large number of elements in a same sample and in a large range of concentration. This application is widespread in archeology, biology, geochemistry and environmental studies.

For example, in archeology the multielemental analysis of clay allows to trace the origins of pottery (27). In this case the instrumental NAA competes with X-ray fluorescence. The INAA allows the determination of a greater number of elements with greater accuracy than X-ray fluorescence, which is a complementary method to determine some elements (Si, Ca, Ti, Y, Zr, Nb, P and Pb) that are difficult to measure with the sensitivity required by NAA (28).

TABLE VI : Results obtained for high purity silicon by NAA (sample weighing : 1g irradiated for 72h in the OSIRIS reactor at C.E.N./SACLAY)

ELEMENT	NUCLIDE	HALF-LIFE	CONCENTRATION IN $ng.g^{-1}$ (10^{-9})	
			Detected	Detection Limit
Ag	^{110}Ag	250 d	$< 8\ 10^{-2}$	8.10^{-2}
As	^{76}As	26,3 h	$< 1.10^{-3}$	1.10^{-3}
Au	^{198}Au	2,7 d	$6,6.10^{-4}$	1.10^{-4}
Ba	^{131}Ba	11,8 d	< 1,5	1,5
Br	^{82}Br	35,3 h	$< 1.10^{-2}$	1.10^{-2}
Cd	^{115}Cd	44,6 d	$< 3\ 10^{-1}$	$3\ 10^{-1}$
Ce	^{141}Ce	32,5 d	$< 1.0^{-1}$	1.10^{-1}
Co	^{60}Co	5,27 y	$< 1.10^{-1}$	1.10^{-1}
Cr	^{51}Cr	27,7 d	$4,5.10^{-2}$	2.10^{-2}
Cs	^{134}Cs	2,06 y	$< 1.10^{-2}$	1.10^{-2}
Cu	^{64}Cu	12,7 h	$< 1.10^{-1}$	1.10^{-1}
Eu	^{152}Eu	13,4 y	$< 2.10^{-3}$	2.10^{-3}
Fe	^{59}Fe	44,5 d	< 4	4
Ga	^{72}Ga	14,1 h	$< 5.10^{2}$	$5\ 10^{-2}$
Hf	^{181}Hf	42,4 d	$< 5.10^{-3}$	$5\ 10^{-3}$
Hg	^{203}Hg	46,6 d	$< 7.10^{-1}$	7.10^{-1}
In	^{114m}In	49,5 d	$< 3\ 10^{-1}$	$3\ 10^{-1}$
Ir	^{192}Ir	74,0 d	$< 2.10^{-4}$	2.10^{-4}
K	^{42}K	12,4 h	$< 6\ 10^{1}$	6.10^{-1}
La	^{140}La	40,3 h	$< 7.10^{-4}$	$7\ 10^{-4}$
Lu	^{177}Lu	6,7 d	$< 6.10^{-4}$	$6\ 10^{-4}$
Mo	^{99}Mo	66,0 h	$< 1\ 10^{2}$	1.10^{2}
Na	^{24}Na	15,01 h	$< 3\ 10^{-1}$	$3\ 10^{-1}$
Ni	^{58}Co	71,3 d	< 3	3
Pt	^{199}Au	3,2 d	$< 5.10^{-3}$	$5\ 10^{-3}$
Ru	^{103}Ru	39,3 d	$< 1.10^{-1}$	$1\ 10^{-}$
Sb	^{122}Sb	60,2 d	$4\ 10^{2}$	$2\ 10^{2}$
Sc	^{46}Sc	83,8 d	$< 2.10^{-3}$	$2\ 10^{-3}$
Se	^{75}Se	119,8 d	$< 1\ 10^{1}$	$1\ 10^{-1}$
Sm	^{153}Sm	46,8 h	$< 4\ 10^{4}$	$4\ 10^{-4}$
Sr	^{89}Sr	50,6 d	< 4	4
Ta	^{182}Ta	115,4 d	$< 1.10^{-2}$	$1\ 10^{-2}$
Tb	^{160}Tb	72,1 d	$< 6.10^{-3}$	$6\ 10^{-3}$
Te	^{131}I	8,0 d	$< 2\ 10^{-1}$	$2\ 10^{-1}$
Ti	^{47}Sc	3,4 d	< 30	30
Th	^{233}Pa	27,0 d	$< 1,5.10^{-3}$	$1,5.10^{-3}$
U	^{239}Np	2,4 d	$< 2\ 10^{-2}$	$2\ 10^{-2}$
W	^{187}W	23,9 h	5.10^{-4}	$1\ 10^{-4}$
Yb	^{175}Yb	4,2 d	$< 1.10^{3}$	$1\ 10^{3}$
Zn	^{65}Zn	243,9 d	$< 2\ 10^{1}$	$2.10^{}$
Zr	^{95}Zr	64 d	< 2	2

The advantage of NAA in biology is to determine very low concentrations in very small samples (biopsies on babies and infants). Table VII summarizes these applications (29).

TABLE VII

Importance of elements in various areas of the Sciences of Life and their detection by NAA from (29)

(Indication of the detection level : 1 < 1.p.b. ; 2 = 1.10 p.p.b. ; 3 : 10-100 p.p.b. ; 4 > 100 p.p.b.)

Element	Importance in			Mode of analysis		Level of detection of the radiochemically isolated radioisotope
	Medicine	Nutrition	Environmental pollution	Instrumental	Radiochemical group separation	
Al	++	-	+	++	-	2
As	++	-	++	-	++	1
Be	-	-	++	-	-	-
Br	+	-	++	++	++	1
Ca	++	++	-	++	++	2
Cd	+	-	++	-	++	1
Cl	+	-	++	++	++	1
Co	++	++	-	++	++	1
Cr	++	++	-	+	++	1
Cu	++	++	-	+	++	1
F	++	++	++	+	-	4
Fe	++	++	-	++	++	3
Hg	+	-	++	+	++	1
J	++	++	-	+	++	1
K	++	++	-	++	++	1
Li	+	-	-	-	-	-
Mg	++	++	-	+	++	2
Mn	++	++	+	+	++	1
Mo	++	++	-	+	++	1
Na	++	++	-	++	++	1
Ni	++	++	+	-	++	2
P	++	++	+	-	-	1
Pb	+	-	++	-	-	-
Rb	+	+	-	+	++	2
Sb	+	-	++	++	++	1
Se	++	++	++	++	++	1
Si	+	++	+	-	++	2
Sn	++	++	+	-	+	3
Sr	+	-	+	+	++	2
Tl	-	-	++	-	-	1
V	++	+	+	+	++	1
Zn	++	++	+	++	++	2

The very high sensitivity of NAA in the determination of rare-earths is used in geology to modelize a large number of geochemical processes (30).

3. Standardization applications

The NAA is often used to certify standard samples. Moreover, radioisotopes produced by neutron activation can be used to show the pollution and loss risks in chemical separation of classical methods.

NAA, like other methods, cannot avoid all causes of errors. However, the radioisotopes allow to eliminate or at least to control most of these causes. In intercomparison runs to establish standards, the activation methods are those which generally achieve the values finally retained the most quickly.

Great organizations like the N.B.S. in the U.S. daily use NAA to certify their standards. The accuracy of this method proves to be superior to the

accuracy imposed by the dispersion between the results obtained by the other methods.

Development of NAA in differents fields

There are three principal fields in which the uses of NAA are spreading : biology, geology and environmental studies. Table VIII.

TABLE VIII

NUMBER OF PAPERS GIVEN DURING THE 7th MODERN TRENDS IN ACTIVATION ANALYSIS

BIOLOGY	42
GEOLOGY AND COSMOLOGY	36
ENVIRONMENTAL STUDIES	35
METALS AND SEMI-CONDUCTORS	14
ARCHEOLOGY	5
FORENSIC APPLICATIONS	2

In the future, applications in biology and environmental fields are likely to continue increasing. For these applications, the response time of the method is sometimes delayed, so the use of short-lived radioisotopes should be extended. In geology, the studies using rare earth determinations are widespread, but the studies of the elements of the platinum family could be developed. For metals and semi-conductors, NAA is used mostly for quality controls and for calibration of measurements of physical properties. After calibration, these measurements can be used for routine controls. As industry is more and more interested in high purity materials, there will be an increased demand for highly diversified standards. In other fields, such as archeology and criminal investigations, NAA is not wide spread, probably because potential users do not have sufficient training.

The main drawback to a greater and quicker developement of NAA is that access to nuclear reactors is difficult. As the latter are speading to new countries, NAA often develops in relation to theeconomic needs in these countries.

Another drawback is probably psychological. Many users consider that these techniques are very heavy, expensive and even dangerous. In fact, initial investments are high, but later the access to the method is easy and the cost of

NAA is no higher than the cost of other modern analytical methods which claim similar performances. The risks of irradiation and contaminations exist, but accidents are more than rare. On the one hand, radioanalysts are aware of the danger and are fully equipped for detection and protection. On the other hand, the level of radioactivity required for sensitive determination remains very low.

V - CONCLUSION

Although it is fifty years old, neutron activation analysis is still widely used and continues to develop all over the world. Up to now, no other new analytical methods have been able to replace it for some applications. The use of active isotopes, directly produced from nuclei of elements to be determined, gives it exceptionnal properties : sensitivity, selectivity, accuracy and the capacity to determine simultaneously a large number of elements in a large range of concentrations. The need to have access to a nuclear reactor constitutes its main drawback. As long as this access is further promoted and generalized, NAA applications will continue to develop.

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COMPARISON OF 14 MeV NEUTRON ACTIVATION ANALYSIS AND COMPETITIVE METHODS FOR DETERMINATION OF OXYGEN, NITROGEN, SILICON, FLUORINE AND OTHER ELEMENTS*

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Abstract

14 Mev neutron activation analysis (14 MeV NAA) makes use of small particle accelerators to produce 14 MeV neutrons from the D-T reaction. The neutrons produce radioactive isotopes in samples by the reactions (n,p), (n,2n) and (n,α). Gamma rays emitted are counted to determine the amount of the target element present. Major applications have been determination of total O, N or Si in solid and liquid matrices, but the technique can also be applied to determine concentrations of about 30 other elements including F, Cl, Al, P and Mg. Detection limits are a few micrograms in the best cases and milligrams for most others. The method has advantages of being nondestructive, fast and insensitive to sample inhomogeneities. It lends itself especially well to sequential analysis of the same sample by several techniques and to samples that are difficult to dissolve. Portable generators have been applied to industrial situations and to well logging. Major disadvantages are the necessity to house a radiation producing instrument, the cost of the equipment and the lack of useful neutron reactions for some important elements. Accuracy (typically ±1 to 10% relative) and precision (±1 to 5% relative) are comparable to competing techniques. For determination of low levels of O and N in most metals inert gas fusion is more rapid and sensitive; elemental analyzer is more sensitive for O and N in organics. Wet chemical methods rarely have any advantage over 14 MeV NAA for solid samples when concentrations are in the detection limit range of the 14 MeV NAA methods. Future developments in the field will come in the areas of simpler, more portable and higher neutron output generator designs.

INTRODUCTION

14 MeV neutron activation analysis (14 MeV NAA) became practical with the development of relatively inexpensive, low beam current, deuteron accelerators in the late 1950's and early 1960's. Outputs of 14 MeV neutrons were originally about 10^{10} s^{-1} but since then have increased several orders of magnitude.

* Work performed at Sandia National Laboratories and supported by the US Department of Energy under contract DE-AC04-76DP00789

The generators are well distributed in laboratories around the world, both in developed and developing countries. Applications have been primarily determination of bulk oxygen, silicon and nitrogen contents of a wide variety of solid and liquid samples. Applications to many other elements are possible and regularly reported. The intent of this paper is to review the technique, discuss its current applications and assess the future role and possible future developments of the method. This paper is not intended to provide a complete bibliography of all papers on the topic; more complete reference lists may be found in [1,2,3,4]. Competing analytical methods for each of the major 14 MeV NAA applications will be described and discussed with emphasis on the strengths and weaknesses of each method.

DESCRIPTION OF METHOD

Principles

14 MeV neutrons are a product of the deuterium-tritium (D-T) fusion reaction:

$$^{2}H + ^{3}H \longrightarrow ^{4}He + ^{1}n + 17.6\ MeV.$$

Approximately 14 MeV of the energy released is carried off by the neutron as kinetic energy. Small deuteron accelerators specifically designed for 14 MeV neutron production are generally used, though other types of particle accelerators, such as van de Graaff accelerators, can also be used. In either case a beam of deuterons is accelerated into a tritium loaded target. The sample to be irradiated is positioned close to the target while the generator is on and then moved (usually via a pneumatic transport system) to a gamma ray detector for counting. Excellent detailed discussions on the theory and practice of generator design and operation may be found in [2,3,5,6].

Equipment Required

Commercial generators are of two main designs. Open tube types typically accelerate a pure deuterium ion beam into a tritium loaded target. The neutron output decreases with target use, with targets usually being useful for just a few operating hours. Target replacement requires only a few minutes, but several hours of pumping may be required to restore the vacuum to the optimum level. A typical target loading is 0.8 to 1.6 Ci/cm^2 (3×10^{10} to 6×10^{10} Bq/cm^2) of tritium.

Sealed tube neutron generators have the entire ion source-accelerator-target assembly permanently sealed at the factory. A mixed beam of deuterium and tritium is accelerated onto the target, simultaneously producing neutrons and regenerating the tritium level in the target. Useful tube life is 100 or more hours, after which the entire sealed tube is returned to the manufacturer for replacement. With this type of generator the operator never handles an open tritium source.

The commercial generators typically operate with accelerating potentials in the 150 to 200 keV range and at 1 to 5 mA target currents. Neutron output is around 10^{11} s^{-1}.

Some van de Graaff and other particle accelerators that can be used with deuterons can also serve as 14 MeV neutron sources. Neutron output will depend on the target and beam currents and on individual design factors.

In addition to the generator, a room or cave with suitable personnel shielding for neutrons, gamma rays and other radiation produced by the operating generator is required. A pneumatic sample transport system is usually installed to carry samples between the generator and the counting station. The counting equipment is located in an adjacent room with the generator controls and the operator.

Counting equipment used for 14 MeV neutron activation is the typical sort found in radioisotope counting labs: NaI, Ge and Ge(Li) detectors with the appropriate shields, power supplies, amplifiers, multichannel analyzers and data reduction computers. 14 MeV NAA for oxygen requires only the NaI detectors; many other 14 MeV NAA applications work better with the higher resolution of modern, high efficiency Ge or Ge(Li) detectors.

Cost of Equipment

Setting up a complete 14 MeV neutron activation analysis facility with all new equipment can be expensive. Estimates of current prices, all in US$, are:

14 MeV neutron generator	$225,000
Pneumatic transport system	40,000
Detectors [NaI and Ge(Li) with shielding]	30,000
Electronics for counting equipment	10,000
Multichannel analyzer and computer	20,000
Total	$325,000

Costs for building or remodeling a lab to safely house and shield the generator are not included in the above. Expenses in setting up a 14 MeV NAA capability could be significantly less if there is existing counting equipment or even an existing particle accelerator which could be used.

Reactions with 14 MeV Neutrons

The most commonly used 14 MeV activation reactions are (n,p), (n,α) and (n,2n) reactions. Cross sections (σ) for these reactions are in the millibarn (mb) range, generally a factor of 100 to 1000 lower than those for capture (n,γ) reactions used for thermal neutron activation analysis. Capture reaction cross sections for 14 MeV neutrons are usually too small for the reactions to be useful. Some of the more commonly used 14 MeV neutron reactions are listed below (data from [7,8,9]). Potentially useful reactions with many other elements also occur ([2,7,10]).

$^{16}O(n,p)^{16}N$ $\quad t_{1/2}$ = 7.14 s $\quad \sigma$ = 39 mb

$^{14}N(n,2n)^{13}N$ $\quad t_{1/2}$ = 9.97 min $\quad \sigma$ = 7.0 mb

$^{28}Si(n,p)^{28}Al$ $t_{1/2}$ = 2.3 min σ = 230 mb

$^{19}F(n,2n)^{18}F$ $t_{1/2}$ = 109.8 min σ = 55 mb

Gamma rays produced by the reaction products are counted and used to calculate the concentration of element present.

When selecting a reaction for use, possible interferences must be considered. For example, the reaction

$^{19}F(n,\alpha)^{16}N$ $t_{1/2}$ = 7.14 s σ = 20 mb

produces the same product isotope as the reaction used to determine oxygen. Thus small amounts of oxygen cannot be determined in the presence of an excess of fluorine. Other interfering reactions can occur which produce a different isotope than the one of interest, but one that emits gamma rays of the same or nearly the same energy as the one of interest. In these cases the differing half-lives of the two isotopes can often be used to resolve the interference.

Advantages of Activation Analysis

The advantages of the 14 MeV activation analysis method are its nondestructive nature, speed, freedom from contamination and, for some element/matrix combinations, a lack of other good analytical methods. Samples to be analyzed by 14 Mev NAA need to be cut to fit the irradiation container being used, cleaned (where appropriate) and weighed (typically 0.1 to 10 g), but otherwise the method is nondestructive. This eliminates problems of sample dissolution, reagent contamination and loss of volatiles. There is no dilution of the samples due to dissolution; and a relatively large volume of the sample may be included in the analysis, making the results more representative of the total sample. The method also determines the total amount of the element present independent of chemical state. This can be an advantage, in that there is no problem about unexpected insoluble or unreactive phases, or a disadvantage, in that it is impossible to get chemical speciation data.

Because of the relatively low neutron fluences used in 14 MeV NAA and the low reaction cross sections, there is very little residual radioactivity left in the sample after a day or two of decay. The same sample may be easily used with other analytical techniques after 14 MeV NAA is completed. This feature is especially important for small, rare or inhomogeneous samples. One of the best examples for this was sequential analysis of some lunar material [11]. A sample was first analyzed by 14 MeV NAA for oxygen and silicon. The same sample was then irradiated in a reactor for analysis by thermal and epithermal instrumental neutron activation analysis (INAA) for an additional 20 to 30 elements. After completion of INAA the sample was re-irradiated for analysis for several additional elements by radiochemical neutron activation analysis. In all, concentrations of about 50 elements were quantitatively determined in the same <1 g sample.

Analysis by mass spectrometry, atomic absorption spectroscopy, optical petrography, electron microprobe, or other techniques could equally well have followed the 14 MeV work. This provided a large coherent set of data where inter-element trends could be examined independently of the homogeneity of the samples.

Disadvantages of 14 MeV Neutron Activation Analysis

The main disadvantage of 14 MeV NAA is the extra precautions needed to safely handle the radioactivity produced. The same types of administrative controls and personnel dosimetry required of workers in radioisotope laboratories are needed for a 14 MeV NAA lab [12]. In addition, personal dosimetry for neutron exposure should be provided.

When operating, the generator itself is a strong source of gamma radiation as well as neutrons. This requires that the generator be housed in a specially shielded room (cave) or underground pit. Depending on the specific generator output and the size of the area shielded, several meters of concrete or earth could be required. Boron- or lithium-loaded materials can be used in critical areas such as doors to obtain necessary shielding with less bulk. The design and construction of a room to house a 14 MeV neutron generator can cost a signifcant fraction of the cost of the generator itself. One advantage of a 14 MeV generator as a neutron source is that when the generator is off, neutron production stops completely and gamma radiation quickly falls to a very low level. This makes the equipment safe and easy to work around when it is not operating.

Generators with removable targets present some hazard of tritium contamination for equipment and personnel. Target changing needs to be done with the same care as is required in handling any radioactive sample in order to prevent this contamination. Large amounts of tritium may build up in the ion pump that maintains the high vacuum in the generator. Care needs to be used to contain this tritium if the generator is moved or decommissioned. Sealed tube generators have all tritium contained in the sealed section of the generator and thus have a much lower tritium contamination hazard. In all cases the generator room should be properly ventilated.

The samples analyzed become radioactive after irradiation, but because of the low neutron flux used and the low cross section for 14 MeV reactions, their maximum activity is very low compared to neutron-activated samples from a reactor irradiation. The primary 14 MeV produced isotopes also have short half-lives. Most samples will decay to close to background radioactivity levels after a day or two. Thus sample handling presents no significant problem.

Another disadvantage of 14 MeV NAA is that some important elements cannot be determined because of the lack of suitable fast neutron reactions. Some of these elements are H, C, Be, S and Bi.

MAJOR APPLICATIONS OF 14 MEV NEUTRON ACTIVATION ANALYSIS AND COMPARISON TO OTHER METHODS

The most common applications of 14 MeV neutron activation analysis have been determination of oxygen, nitrogen and silicon. These applications are discussed individually below. Some other applications are discussed in a later section of this paper.

Oxygen

The determination of oxygen concentrations has been by far the most popular application of 14 MeV NAA. The reaction used is:

$^{16}O(n,p)^{16}N$ $t_{1/2}$ = 7.14 s Gamma rays: 6.128 MeV (69.0%)
7.117 MeV (5.0%)

Escape peaks at: 6.606 MeV
6.095 MeV
5.617 MeV
5.106 MeV

The energies of these gamma rays are higher than essentially all other 14 MeV NAA produced gamma rays except those from $^{11}B(n,p)^{11}Be$. By setting a lower level discriminator (LLD) on the counting equipment to record only those gamma rays with energies above 4.5 to 5.0 MeV, interfering lower energy gamma rays are excluded, leaving only ^{16}N gamma rays to be counted. (An exception to this is discussed below.)

The major direct interference with the determination of oxygen concentration is fluorine which produces the same ^{16}N isotope by the reaction:

$$^{19}F(n,\alpha)^{16}N \quad \sigma = 20 \text{ mb.}$$

Thus oxygen cannot be determined in the presence of an excess of fluorine. A large excesss of boron can also interfere with the high energy gamma ray measurements, otherwise the oxygen concentration, if at or above the detection limit, may be determined in essentially any matrix.

In some samples the matrix element activates and produces an isotope that gives off an abundant gamma ray of relatively high energy, but still below the LLD setting. In the case of a Si-rich matrix (e.g., SiC, Si(Li) alloy) the reaction is $^{28}Si(n,p)^{28}Al$ with $t_{1/2}$ = 2.28 min and a gamma ray at 1.78 MeV. When a large amount of Si is present, the ^{28}Al activity is very high. Random triple coincidence of the 1.78 MeV gammas occur in the detector producing an apparent peak at 5.3 MeV, well above the LLD setting. This interference is usually significant only at high Si concentrations (>30 to 40%). Since the magnitude of the interference increases as the cube of the Si content, when the interference is present, it can be very severe [13,14,15].

The interference may be overcome by mathematical correction following repeated counts [15] or by using faster electronics. The efficiency of Ge(Li) detectors is too low at the high ^{16}N gamma ray energies to be of general use to resolve the gamma ray lines from the interfering activity.

The detection limit is about 10 μg for oxygen. For typical system designs and sample sizes, this corresponds to detection limits of 1 to 100 μg. At the lower levels it is necessary to replace air in the irradiation vials with an oxygen-free gas such as nitrogen, to use low oxygen sample carriers and to run blanks. Samples may be run at the rate of 12 to 15 per hour.

Some recent examples of the application of 14 MeV NAA to the determination of oxygen are:

1. Reagent chemicals [16].
2. Total oxygen [17,18] and organic oxygen in coal [19].
3. Coal conversion liquid [20].
4. Fe powders prepared by plasma jet [21].
5. Si_3N_4 and SiC films on Mo plates [22].
6. Mg powders and ingot [23].
7. Synthetic metal nitrides [24].
8. Rocks [25].
9. Nb alloys [26].

Competing Methods for the Determination of Oxygen

Several other techniques are used to determine oxygen in some materials. Each of these techniques is usually useful for a specific type of sample.

Inert gas fusion and vacuum fusion are two similar methods for determining oxygen, usually in metals. Inert gas fusion has become the more widely used of the two techniques and will be discussed further. Equipment manufactured by the LECO Corporation is typical of current inert gas fusion instruments. A sample is placed in a graphite crucible and heated to about 1700°C to melt the sample and free dissolved oxygen. The hot graphite crucible reduces oxygen-containing compounds and frees oxygen as CO or CO_2. All of the freed gases are swept away from the crucible and through a hot CuO column by a flow of He gas, converting the CO to CO_2 and driving the reduction reaction to completion. The CO_2 gas is purified by passing through additional columns to remove water, etc. and then to a detector (e.g., infrared) to quantify the amount of CO_2 produced. [27]

Inert gas fusion determination of oxygen works well for steels and many other metals. It is not suitable for very volatile metals (Na, Li, etc.) because of condensation of the metal vapor in cool parts of the gas train. Some metals also have melting points too high to allow easy analysis by this method. All forms of oxygen that can be converted to CO by hot graphite are detected. This includes oxides found in most common samples,

but may not be true for some oxides found in more exotic materials. Total analysis time is several minutes per sample (after sample cutting and surface cleaning). Sample size is typically about a gram and detection limits are less than 1 μg/g. Equipment costs are about US$ 55,000. Inert gas fusion is more sensitive, faster and about equally precise as 14 MeV NAA for oxygen determination in most metals. The inert gas fusion technique is destructive.

Elemental analyzers (manufactured by Perkin Elmer, LECO, Control Equipment Corp. and others) are used to analyze for oxygen, nitrogen, hydrogen and carbon in combustible materials, usually polymers and organics. Fluorine, phosphorus, silicon and many metals interfere with the analysis. In the oxygen method, the sample is pyrolyzed in helium over platinized carbon. Oxygen in the sample is converted to CO and then passed over hot CuO to convert CO to CO_2. After some purification steps, the CO_2 is detected and quantified using a thermal conductivity or other detector. The pyrolysis method works well for organics and can be applied to some other samples if care is taken to insure that all oxygen (or a known part of the oxygen) is freed. Sample size is about 3 mg which can lead to inaccuracies if samples are not homogeneous at this scale. Detection limits are about 0.5 to 1 wt %. After equipment calibration (which takes an hour or two), samples can be run at the rate of about 3 per hour. Equipment costs are approximately US$ 40,000. 14 MeV NAA is faster, better for inhomogeneous samples, about equally precise and sensitive as an elemental analyzer for determination of oxygen concentrations. The elemental analyzer is the better method for small (<0.1 g) samples but is destructive.

Several chemical methods for determining the amounts of oxygen-containing phases in metals are described in [28]. Most of these rely on dissolving the matrix metal but not the oxides. The oxides are collected and weighed or determined by some other chemical means. The oxides collected are very dependent on dissolution conditions and can be tailored to give information on oxygen speciation. The chemical methods are most useful where only a few samples need to be run, when access to faster techniques (14 MeV NAA, LECO, etc.) is not available or where the speciation information is important. Equipment required is that found in a typical chemistry lab plus a controlled atmosphere chamber or glove box. Analysis time per sample is generally several hours.

Nitrogen

Nitrogen is determined by 14 MeV NAA using the reaction:

$^{14}N(n,2n)^{13}N$ $t_{1/2}$ = 9.97 min. Gamma emission: none

Positron emitter:
0.511 MeV annihilation radiation (199.6%)

The relatively long half-life for ^{13}N requires (and permits) long irradiations (1 - 10 min) and counting times (2 - 20 min) compared to oxygen determinations. In order to resolve the 0.511

MeV annihilation gamma rays from other energies, a high resolution Ge(Li) or Ge detector is useful. NaI can be used in some cases when only ^{13}N is produced. Because many positron emitters can be produced by 14 MeV neutron irradiation, care must be taken to avoid interferences. Some possible interfering reactions are:

$^{109}Ag(n,2n)^{108}Ag$ $t_{1/2}$ = 2.42 min

$^{31}P(n,2n)^{30}P$ $t_{1/2}$ = 2.50 min

$^{79}Br(n,2n)^{78}Br$ $t_{1/2}$ = 6.50 min

$^{54}Fe(n,2n)^{53}Fe$ $t_{1/2}$ = 8.50 min

$^{63}Cu(n,2n)^{62}Cu$ $t_{1/2}$ = 9.80 min

$^{91}Mo(n,2n)^{90}Mo$ $t_{1/2}$ = 15.49 min

$^{121}Sb(n,2n)^{121}Sb$ $t_{1/2}$ = 15.90 min

Other reactions leading to 0.511 MeV annihilation radiation are tabulated in [2]. If interfering isotopes have significantly different (factor of 2 or 3 or more) half-lives than ^{13}N, the interferences may be resolved. For example, nitrogen may be determined in the presence of excess phosphorous by letting the samples decay for 20 to 25 minutes before counting the 0.511 MeV gammas. Essentially all ^{30}P will decay away in this time, leaving only the 10-minute ^{13}N activity. In other cases the interfering isotope may have gamma rays of other energies which may be used to calculate the contribution of the interfering isotope to the 0.511 MeV peak.

Samples containing hydrogen plus carbon and/or oxygen may exhibit an interference due to the proton recoil reactions $^{13}C(p,n)^{13}N$ and $^{16}O(p,\alpha)^{13}N$. Contributions from these reactions are generally low and corrections are possible [2].

Nitrogen detection limits for the usual 0.1 to 10 g sample sizes are about 0.1 wt%. Analysis times range from 5 to 10 samples per hour for straightforward applications to 1 to 2 per hour in more complicated cases where interference corrections are required.

One of the earlier applications of 14 MeV NAA for determination of nitrogen was determining the protein content of grain products [29]. The matrix elements (C,H,O) do not interfere making the application very straightforward. This method is rapid and precision is 0.3 to 0.5%. Determination of protein by

this method has also been reported in other food stuffs [30], plant samples [31,32] and Chinese medicines [33]. Other applications are the determination of nitrogen in Si_3N_4 and nitrided glasses [34], coal conversion liquids [35] and fertilizer [36].

Competing Techniques for the Determination of Nitrogen

Nitrogen may be determined in metals by inert gas fusion and vacuum fusion methods [27] similar to those described earlier for oxygen. LECO makes a combined nitrogen/oxygen analyzer that determines oxygen as described above. After the gas passes through the infrared detector for measurement of oxygen as CO_2, it is passed through absorber columns to remove H_2O and CO_2, then to a thermal conductivity detector to measure the remaining N_2. Detection limits are about 0.1 µg/g using sample sizes on the order of 1 gram. This is much more sensitive than the 14 MeV method and is probably the best method for nitrogen in appropriate metal samples.

The elemental analyzer described above for oxygen in organics is also applicable for nitrogen. Nitrogen contents as low as 0.05 to 0.1 wt.% may be determined on samples that typically weigh about 3 mg. Some inorganics can also be analyzed, but care must be used since many metals interfere with the analysis. Several samples per hour can be run. The method has comparable speed and precision and better sensitivity than 14 MeV NAA. The method is destructive, and the small mass of sample analyzed could present a problem if the sample is not homogeneous at the 3 mg level.

The classical chemical technique for the determination of nitrogen is the Kjeldahl method [37]. This basically consists of dissolving the sample in sulfuric acid, converting the nitrogen to ammonia. Excess sodium hydroxide is added and the ammonia distilled and collected in a known amount of acid. This solution is back-titrated to determine the amount of ammonia present. The method works for nitrogen compounds such as amines and amino acids but not for others such as nitrates and nitrites. Adaptations and variations of the Kjeldahl method have been developed for some of these latter sample types. One example is reduction of nitrate to ammonia with Devarda's alloy [38].

Many other chemical and instrumental (e.g., ion selective electrode and ion chromatography) methods have been reported in the literature. They generally are applicable to nitrogen in some, but not all, chemical forms; require the sample to be in solution and require several hours per sample to perform. Chemical methods use standard chemistry lab equipment that is relatively inexpensive. Accuracy and precision are comparable to 14 MeV NAA; detection limits are lower. The methods are destructive.

Nitrogen (and in some cases oxygen) may also be determined in some sample types by several mass spectroscopy techniques (e.g., glow discharge mass spectroscopy [39], laser mass spectroscopy [40]); ion chromatography [41] and, with some special sampling devices, inductively coupled plasma atomic emission

spectroscopy (ICP-AES) [42]. Application of these techniques is still limited. Some require conductive samples while others sample only a micro volume; all require expensive equipment (>US$ 100,000). None would be set up strictly for nitrogen or oxygen determinations.

Silicon

Silicon is determined by 14 MeV neutron activation analysis using the reaction:

$^{28}Si(n,p)^{28}Al \quad t_{1/2} = 2.25$ min

Gamma ray:
1.7788 MeV (100%)
Escape peaks:
1.2678 MeV
0.7568 MeV

Gamma ray counting is best done using a high resolution detector [Ge or Ge(Li)] to resolve the gamma rays of interest from the other gamma rays produced from most matrices. Interfering reactions are:

$^{27}Al(n,\gamma)^{28}Al$ and $^{31}P(n,\alpha)^{28}Al$.

The latter reaction has a cross section of 0.5 mb versus 250 mb for the reaction with ^{28}Si. Thus the aluminum interference is only a problem when aluminum is in great excess to silicon. Other gamma ray lines from other reactions with aluminum [e.g., (n,p) reaction to ^{27}Mg or (n,α) to ^{24}Na] may be used for interference correction. The cross section for the phosphorus interference is comparable to that for the reaction with silicon making this interference very serious. There are other gamma rays from other activation products of phosphorus that can be used to correct for the phosphorus interference. Detection limits for silicon by 14 MeV NAA are on the order of 100 µg, and reported precisions are typically ± a few percent relative.

Applications of 14 MeV NAA to determination of silicon have been most common with geological samples, especially in cases where the same sample will be analyzed by other techniques for other elements [11,40,43,44]. This was especially true for lunar samples and meteorites where samples are limited. The other advantage of doing all analyses on the same sample is that geological samples can be very inhomogeneous, especially for some trace elements that may concentrate in a few grains of a rare phase. Since data interpretation often requires comparing ratios of elements, it is important that all data be representative of the same sample. 14 MeV NAA has also been used to determine concentrations of Si in iron and steel [45], coal [18], bauxite [46], fly ash and slag [34], mine flue dust [47], wear metal silicon in lubricating oil [48] and biological samples [49]. It has also been used to measure the thickness of silicon films on glass plates [50].

Competing Techniques for the Determination Silicon

For many years the main competing techniques for Si determination were wet chemical methods such as gravimetric determina-

tion following acid dehydration, colorimetric or gravimetric determination using silico-12-molybdate or titrimetric or gravimetric determination of the $(SiF_6)^{-2}$ ion [2]. All of these are time consuming, destructive and subject to many interferences. Detection limits and precision are better than 14 MeV NAA; accuracy is comparable. Instrumental methods such as atomic absorption spectroscopy and ICP-AES are fast, accurate and more sensitive than 14 MeV NAA once the sample is in solution. X-ray fluorescence (XRF) is frequently applied to rock samples, though the samples generally are crushed and often fused. Access to proper standards is especially important for XRF. Electron microprobe is commonly used to determine the silicon content of small volumes of individual mineral grains. 14 MeV NAA would be quicker and easier to perform for bulk silicon determinations than any of the competing methods.

Some Other Applications of 14 MeV NAA

Fluorine may be determined by 14 MeV NAA using the reactions:

$$^{19}F(n,2n)^{18}F \qquad t_{1/2} = 112.0 \text{ min}$$

or:

$$^{19}F(n,p)^{19}O \qquad t_{1/2} = 27.1 \text{ s}$$

In addition the (n,α) reaction on ^{19}F produces the same ^{16}N isotope used for the determination of oxygen. In oxygen-free samples, this is an excellent reaction to use for fluorine determination. Detection limits of less than 100 micrograms of fluorine are possible. Since many fluorine compounds are difficult to dissolve and difficult to analyze by other methods, 14 MeV NAA can be a very useful tool. For example, the teflon content of a teflon-graphite composite was determined by 14 MeV NAA [34]. This sample would have been very difficult to dissolve for more conventional analysis. Some other applications of 14 MeV NAA for F are: bones [51], barite ores [52], and polymers [53]. X-ray fluorescence is capable of some analyses for fluorine if proper standards are available. Both ion chromatography and ion selective electrodes can be used to determine fluorine concentrations in some solutions. 14 MeV is perhaps unique in being a nondestructive instrumental method for determination of fluorine.

Other elements with good sensitivity by 14 MeV NAA include Mg, Al, P, Sc, V, Fe, Cu, Zn, Ga, Sb, Ba and Hg. Detection limits are in the range of 10 to 200 micrograms for each of these. Many other elements have easily detected and measured products when present in larger amounts. Some other applications from the recent literature include Sb and Cl in synthetic rubbers [54], S in coal [55]; Mg in cast iron [56], Si and Al in bauxite [46]; F and P in bones [51]; Pb in aquatic plants [57]; Cu, Si, Al, Mg and Mn in iron artifacts [58] and Cu and Ag in ancient coins [59,60].

THE FUTURE PLACE OF 14 MEV NEUTRON ACTIVATION ANALYSIS

14 MeV NAA should continue to be a method of choice for determination of oxygen or nitrogen in many samples. This is especially true for production or manufacturing situations where many analyses of a few types of materials are required. The nondestructive, minimal sample preparation features of the technique make it very rapid, especially compared to methods that require sample dissolution but also compared to instrumental methods that require vacuum, sample homogenization or surface preparation. 14 Mev NAA lends itself well to automated sample handling and data reduction. The one situation where 14 MeV NAA would be a second choice method is determination of oxygen and/or nitrogen in iron, steel and other metals where inert gas fusion is much more sensitive and comparably rapid.

Because of the cost of acquiring a 14 MeV neutron generator and setting up a lab to house it and use radioactive materials, most other applications of 14 MeV will probably be in facilities doing other types of work with radioactivity. These labs already have the administrative procedures for radioactive sample handling in place and have a personnel base already familiar with radiation handling, counting equipment and basic nuclear science. As with most instrumental analytical techniques, the basic principle of the method sounds simple, but application to a new type of sample requires skill and knowledge to avoid or manage possible interferences and other experimental pitfalls. Except for the repeated analysis for oxygen, nitrogen, or silicon in a production situation, there is probably no single analytical need to justify setting up a new 14 MeV neutron activation facility. The technique does continue to be a useful in research and educational laboratories where a large variety of sample types are analyzed. 14 MeV NAA is especially useful for hard to dissolve samples, composites and halogen-containing samples. The generator has the added use of being a neutron source (14 MeV or thermalized) for other nuclear physics or nuclear analytical applications (e.g., cross section determinations, radiation effects, shielding studies, neutron induced particle track production). The generator can also be used in a university setting as a major teaching tool. It can be used for isotope and tracer production, neutron activation analysis, neutron radiography and other uses, in a similar way to a teaching reactor, at a very small fraction of the cost of even the smallest reactor facility.

Several new developments are expanding the applications of 14 MeV NAA. The development of portable 14 MeV generators has allowed 14 MeV NAA to move into the field and into the plant. Generators and gamma detectors have been built into down hole probes for well logging and geochemical exploration [61,62]. Others have been built for medical applications and for monitoring flow and content in plant feed lines [63]. Several special high flux 14 MeV neutron generators capable of producing fluxes up to 2×10^{12} n cm^{-2} s^{-1} at sample irradiation positions have recently been built [64,65]. These permit determination of concentrations of up to 30 elements in a sample at the 1 μg/g level. Some new designs for 14 MeV generators are also being produced.

These include radial geometries, cyclotron sources and quadrapole generators [66]. These have capabilities for higher fluxes, smaller size and/or simpler operation than the traditional deuteron accelerators described earlier. Successful development of these could open new applications for 14 MeV NAA.

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DISCUSSION

E. Hoffman. What is the flux and cost of the portable neutron generator?

R.W. Bild. Portable generators I know of have been either prototype designs or well logging tools. I don't know a realistic cost for either type.

Neutron outputs are very dependent on design. Some pulse generators could put out about 10^{14} neutrons per pulse but might have a lifetime of less than 10 pulses. Other pulse generators produce orders of magnitude fewer neutrons but have lifetimes of thousands of pulses. Steady state generators could be made. Outputs of 10^{8} to 10^{10} neutrons per sec could probably be achieved. A practical portable generator for activation analysis has yet to be built.

R. Rosenberg. What kind of detection limit for fluorine in uranium would you predict?

R.W. Bild. I would expect the detection limit to be 100 to 200 micrograms. The uranium matrix should not be a particular problem in spite of the fissions that will be induced.

NUCLEAR ANALYTICAL METHODS AT NTT ELECTRICAL COMMUNICATIONS LABORATORIES

Substoichiometric Analysis and its Applications

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Abstract

This paper describes the nuclear analytical methods that are used at NTT Electrical Communications Laboratories. In particular, it focuses on the use of the activation method in substoichiometric analysis and its applications. The accuracy and precision of substoichiometric analysis are investigated by considering the effects on systematic and accidental errors caused in analytical procedures. It is shown that the total errors of substoichiometric analysis are dominated by statistical fluctuations in activity measurements. It is also shown that substoichiometric analysis is one of the most accurate analytical methods. This is useful in the characterization of electrical materials and devices and in the standardization of other analytical methods.

---

1. Introduction

Accurate and precise analytical methods are necessary in order to characterize and develop various new electrical materials and devices. Because of this, different types of nuclear analytical methods are being developed at NTT. Nuclear analytical methods are suitable for determining major and trace elements. Trace determinations of light and heavy elements have been confirmed by charged particle and neutron activation analysis. Major and minor elements have also been determined by radiometric and isotope dilution analysis.

Substoichiometric analysis is one of the most accurate nuclear analytical methods because contents can be determined by using only radioactivity measurements that use simple chemical separations. This can also be done without calibrating chemical yields.

Thus, substoichiometric analysis is a very useful method in obtaining relations between the chemical compositions and the properties of materials. In addition, substoichiometric analysis is also used in order to standardize other analytical methods.

This paper will describe various nuclear analytical methods. In particular it will focus on the accuracy of substoichiometric analysis. It will be shown that this is one of the most accurate analytical methods.

2. Nuclear Analytical Methods at NTT ECLS

Activation analysis, radiochemical analysis (RCA) and isotope dilution analysis (IDA) have been used for the determination of heavy and light elements in semiconductors, superconductors and optical fibers[1,2]. A summary of these analyses is shown in Figure 1. Trace amounts of heavy elements have been determined by neutron activation analysis using the nuclear reactors in the Japan Atomic Energy Research Institute. A small cyclotron has been used since 1984 for the trace determination of light elements by charged particle activation analysis[3]. RCA and IDA have been applied to the determination of major and minor elements. Radioisotopes have been produced by neutron irradiation and charged particle bombardment.

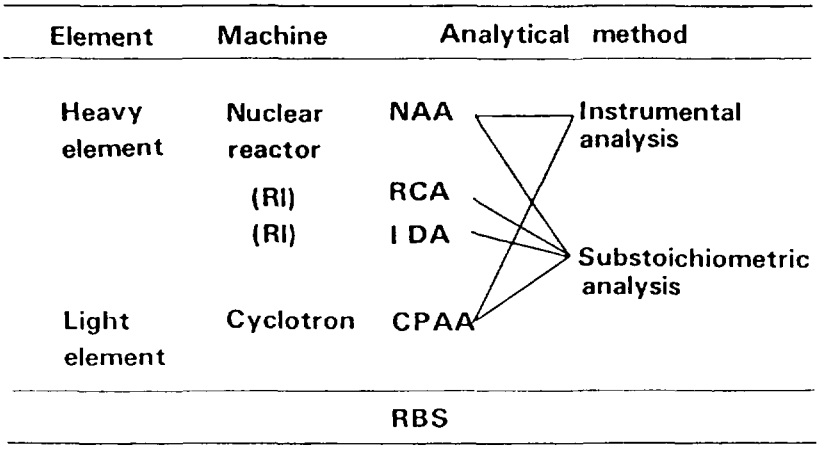


Fig.1 Nuclear analytical methods at NTT

In order to achieve simultaneous multi-element determination, instrumental analysis has been developed in both activation analyses. Substoichiometry has been introduced to all these analyses and substoichiometric analysis has been applied to about 33 elements.

3. Principles of Substoichiometric Analysis

Many types of substoichiometric analysis have already been developed. These include the direct method, the RI addition and the activation methods. In the direct method, a large excess and known amount (M) of carrier is added to the activated sample. A known amount (m) of element is separated substoichiometrically and its activity (ax) is measured. The activity Ax is obtained by Eq.1:

$$Ax = (M / m)ax \qquad (1)$$

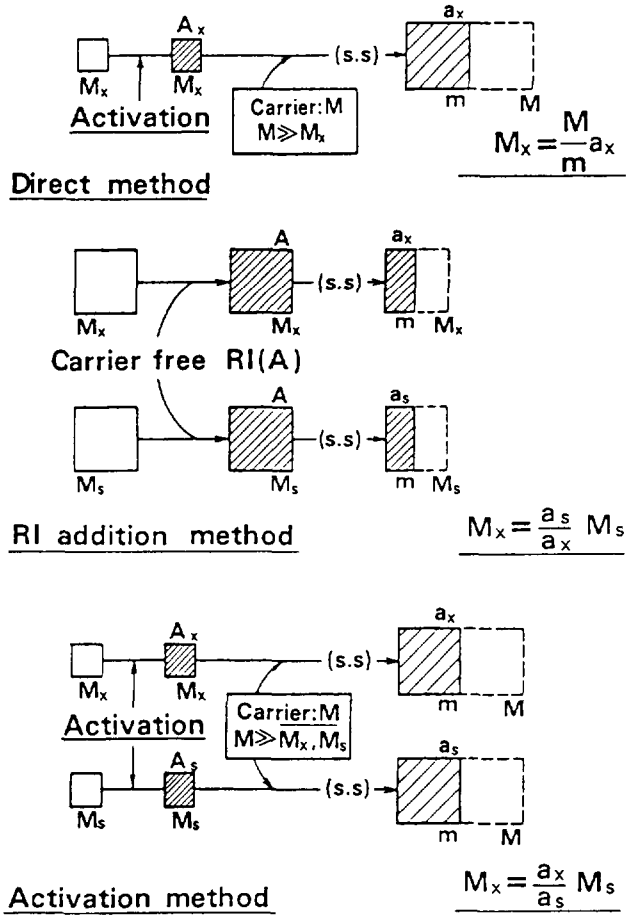
The direct method is useful for the determination of induced activity.

In the RI addition and the activation methods, a known amount of standard sample should be prepared. Test and standard samples (Contents; Mx, Ms) are labeled by adding carrier free

RI (Activity, A) in the RI addition method. Definite amounts (m) are separated substoichiometrically from both samples and their activities (ax, as) are measured. The content Mx is calculated by Eq.2:

$$Mx = (as / ax)Ms \quad (2)$$

These principles are shown in Figure 2.



$$M_x = \frac{M}{m} a_x$$

$$M_x = \frac{a_s}{a_x} M_s$$

$$M_x = \frac{a_x}{a_s} M_s$$

Fig.2 Substoichiometiric analysis

The principle of the activation method can be considered in more detail. Test and standard samples (Contents; Mx, Ms) are activated simultaneously under the same conditions. Then, the specific activity of the test sample (Ax / Mx) equals that of the standard sample (As / Ms). Large excess amounts (M) of carrier are added to both samples, followed by the pre-separation of objective element in order to remove the interfering activities and elements. The carrier amount M (Activities; Ax, As) varies by M' (Activity; Ax') in the test sample and by M" (Activity; As') in the standard sample. Content Mx is usually calculated by Eq.3:

$$Mx = (Ax'M" / As'M') Ms \quad (3)$$

M' and M" should be determined in this case.

In substoichiometric analysis, small and definite amounts (m) are separated from M' and M" and their activities (ax, as) are measured. Then, content Mx can be determined by Eq.4:

$$Mx = (ax / as)Ms \qquad (4)$$

It is clear from these equations that content can be determined by using only activity measurements. There is no needs for corrections of chemical yields in substoichiometric analysis. The principle of the activation method is shown in Figure 3.

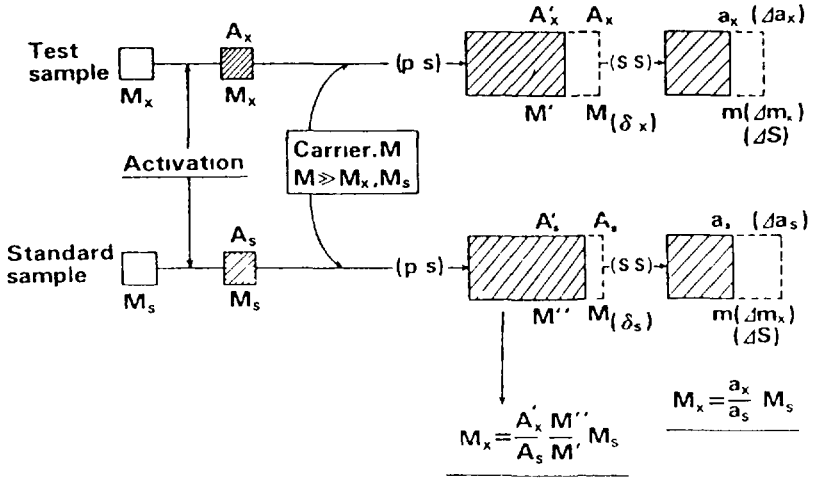


Fig.3 Errors in substoichiometric analysis (Activation method)

4. Errors in Substoichiometric Analysis

Three kinds of systematic errors and an accidental error are considered in the chemical procedures of substoichiometric analysis. These errors should be decreased to establish more accurate analytical methods.

If δx and δs contaminate the test and standard samples before substoichiometric separation, specific activity (Ax / M) of the test sample changes to (Ax / (M + δx)), and that of the standard sample (As / M) changes to (As / (M + δs)). This systematic error is caused by variations of specific activity with contamination.

There are two other kinds of systematic errors that affect the quantity (m) in substoichiometric separation. One is an error (Δ m) caused by co-existing elements. Their formation constants with the substoichiometric reagent are larger than those of the objective element. The other (Δ S) is caused by reactivity (or instability) of the reagent.

An accidental error is caused by statistical fluctuations in activity measurements.

5. Accuracy of Substoichiometric Analysis

The systematic errors caused by variations in specific activities and by interference of co-existing elements in the activation method can be treated in the same way. Systematic

error caused by variations in specific activity depends on the quantities of contamination (δs, δx) and their ratio (δs / δx). δs / δx is usually less than 1.0. The quantities of contamination can be decreased below 1 μg. 0.1 - 1 mg of carrier is usually added to the sample, therefore, the error will remain below 0.01. The error caused by interference of co-existing elements decreases because of pre-separation and becomes negligible. This is shown in Figure 4.

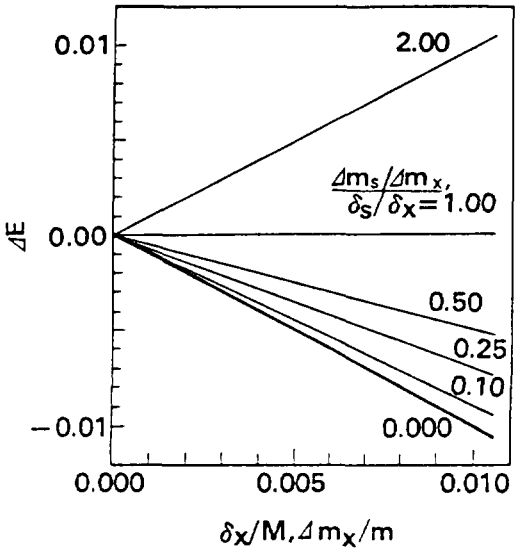


Fig.4 Errors in subtoichiometric analysis

These results indicate that it is necessary to add as large a carrier as possible and to treat both test and standard samples under the same conditions in order to establish more accurate activation method.

Reactivity (or instability) of the substoichiometric reagent causes systematic errors as shown in Figure 5. In this case the

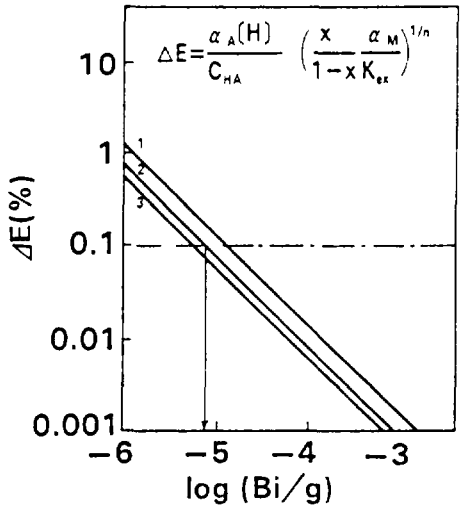


Fig.5 Error in reactivity of dithizone with bismuth

1) X=0.8, 2) X=0.5, 3) X=0.3

substoichiometric extraction of bismuth with dithizone is considered. The abscissa is bismuth weight. If the amount of bismuth is more than 10 μg, the error caused by reactivity of the reagent decreases below 0.1 %. This is because a reagent with a large extraction constant is used for the substoichiometric extraction. This type of error is also negligible.

The effect of accidental error in activity measurements are shown in Figure 6. When the total activity of bismuth is 10^4 counts and the extraction ratio (x) of bismuth is 0.5, accidental error reaches 1.4% .

These results indicate that it is easy to decrease systematic errors below 1 %. The activity of the separated part should be more than 10^4 counts in order to decrease total errors below 1%.

It is confirmed from these results that substoichiometric analysis is one of the most accurate methods.

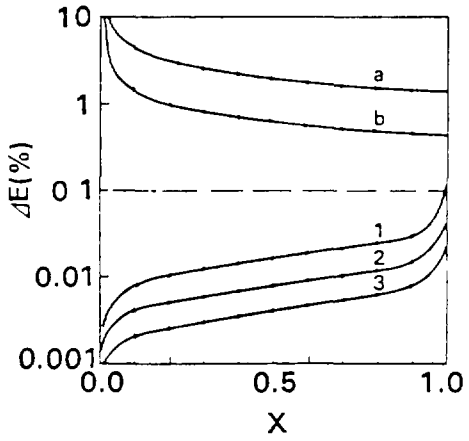


Fig.6 Error in activity measurement

a) 10^4counts 1) Bi 50μg
b) 10^5counts 2) 100μg
3) 200μg

6. Criterion of Substoichiometric Analysis

If substoichiometric separation for an element is established, the RI addition and the activation methods can be applied according to the content of the element. The activation method is used for trace determination and the RI addition method is used for determination of more than 10 μg of element. The sample weight also depends on the analytical method. This is shown in Figure 7. The criterion of substoichiometric analysis is shown in Figure 8. Generally, the RI addition method is useful for determination of major and minor components. The activation method is used for trace determination. However, the RI addition method is used in determining trace elements for large amounts of test samples. The activation method is adequate in determining major and minor elements for small test samples. Elements that can be separated substoichiometrically are shown in Figure 9. They make it possible to the substoichiometric analysis of 33 elements.

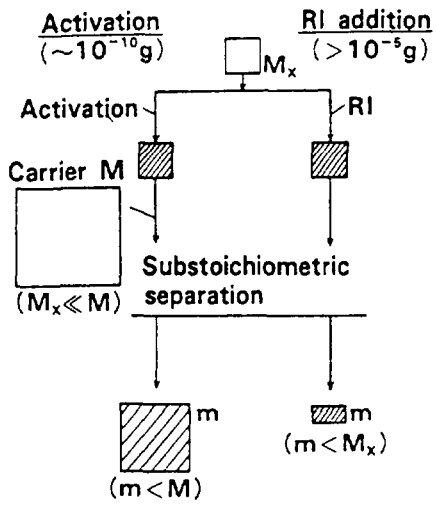


Fig.7 Substoichiometric analysis

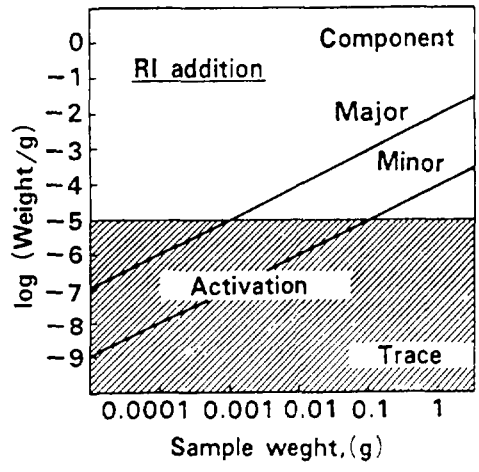


Fig.8 Criterion of analytical method

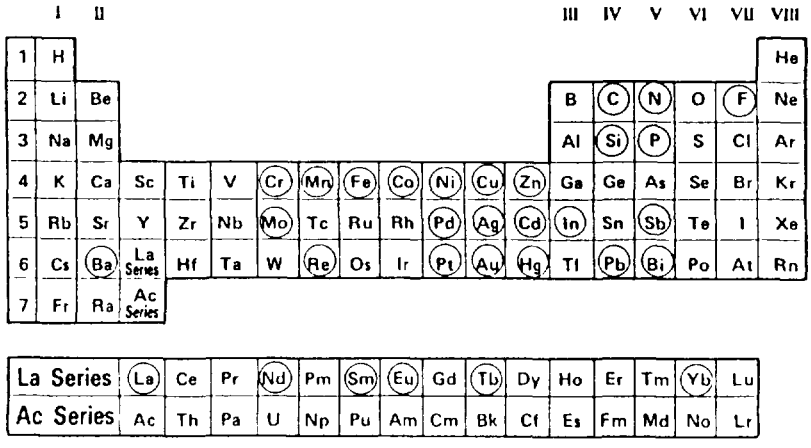


Fig.9 Substoichiometric separation of elements

7. Substoichiometric Analysis and other Analytical Methods

Substoichiometric analysis is used for calibration of other non-nuclear analytical methods. This is illustrated in the case of synchrotron radiation x-ray fluorescence analysis (SR-XRF) for determination of major components of a superconducting oxide $BaPb_{1-x}Bi_xO_3$ (BPB). This is a thin film crystal grown on SrTiO. Reference samples were prepared for the calibration of SR-XRF. The compositions of the reference samples were determined by the RI addition method within errors of 1%. In particular, this was done for lead and bismuth.

8. Conclusion

It is important to develop more accurate nuclear analytical methods. It was shown here that substoichiometric analysis is one of the most accurate analytical methods. This is important to characterize and develop new electrical materials and devices. This can also be applied to the standardization of other analytical methods.

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NUCLEAR ANALYTICAL METHODS IN STANDARDS CERTIFICATION

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Abstract

Nuclear methods of chemical analysis have played a prominent role in the accurate determination of the composition of Standard Reference Materials and other standards. The characteristic sensitivity, multielement capability, and freedom from chemical biases unique to nuclear methods assure them a continuing role in the standards laboratory.

I. The use of nuclear analytical methods for standards analysis

One of the few products (as distingished from services) of the U. S. National Bureau of Standards is a variety of Standard Reference Materials (SRMS), certified by the Bureau to possess certain physical properties or a specified chemical composition. Nuclear methods of analysis play a prominent role in the certification process [1,2]. Unless an unquestionably reliable "definitive" method of analysis can be used, concentrations in SRMs are certified by a combination of two or more analytical methods which are as different as possible in the sources of their characteristic errors. Nuclear methods, largely instrumental thermal neutron activation analysis with gamma-ray spectroscopy but also including some others, are of particular value in this work because of some of their distinguishing characteristics:

1. Substantial freedom from systematic errors. The physical processes involved in nuclear methods are well understood. Radioactive growth and decay are rigorously exponential. The number of energetically possible nuclear reactions from a given target nuclide is small, and for moderate irradiation energy all possible reactions can be enumerated by inspection of a table of nuclides. High-resolution gamma-ray spectroscopy affords qualitative identification of the nuclides present as well as their quantitation. The density of known gamma-ray lines in energy space is small compared with the resolution of modern detectors, and not many analytically important decay gamma rays remain to be discovered. The presence of possible interferences may often be readily tested when multiple lines of either component are emitted.

2. Complementarity to other methods. A different suite of elements is measurable by using nuclear rather than chemical reactions, and the detection limits are quantitatively different. Equally important, the kinds of errors to which nuclear methods are subject are due to different physical phenomena and are therefore likely to give a different bias in the results.

3. Freedom from analytical blank and other problems related to dissolution. Except for pre-irradiation handling and packaging, there is no reagent blank in the usual sense. Analytical methods which require that the analyte be in solution call for chemical laboratory skills far beyond simple weighing and packaging. With some matrices (rocks containing complex silicates like chromite or zircon; fatty animal tissues), it is not easy to assure complete dissolution without using extreme conditions or multistep chemistry.

4. Quantitatively known precision. The random process of radioactive decay gives an a priori estimate of the variation to be expected between samples. A simple t test [3] shows immediately whether counting statistics is the limiting factor in precision. The accuracy can be comparable to the precision at levels well below 1% [4,5,6], even for a decaying source.

5. Multielement capability. Gamma-ray spectroscopy is inherently a multinuclide analytical process, the components of which add linearly. Radioactive decay adds the dimension of time, which can often act as a perfect separations chemist to resolve otherwise interfering components such as Cr-51 and Ti-51.

6. Sensitivity. Neutron activation analysis in particular has been shown to be applicable to the analysis of many elements at sub-picogram amounts [7,8]. The option of chemical separation after irradiation is often available for the blank-free removal of interfering radioactivities. Macroscopic quantities of the sought-for and interfering elements may be freely added in order to ease the chemistry and to facilitate the measurement of chemical yield.

These characteristics of nuclear methods have been widely exploited, particularly in research into trace element analytical methodology. Fifty-six percent of all published analyses of NBS multielement SRMs have been performed by nuclear techniques, according to a recent survey [9]. Contemporary trace element geochemistry, from lunar sample and meteorite analysis [10] to mineral exploration, relies heavily on neutron activation analysis. Because of its freedom from blank, neutron activation is the most powerful technique available for the study of contamination in handling and sampling animal tissues [11].

II. Nuclear methods other than conventional activation analysis

Nuclear methods of analysis are older than the 50-year history of neutron activation, the first recorded tracer experiment following closely the discovery of radioactivity. Since then, natural and artificial radiotracers have been used in an enormous variety of applications, including engineering studies of metallic wear, distribution of solutes between solid and molten silicon, the movement of ocean currents and ground waters, and in countless studies of biochemical pathways [12]. Radiotracers can be a great aid in developing procedures to be applied with other analytical methods [13].

The analytical use of prompt nuclear radiation has expanded in recent years. Beams of neutrons from reactors have been used for the simultaneous determination of twenty or more elements by measurement of prompt gamma rays [14]. Pure beams of low-energy "cold" neutrons, now becoming available at several reactors, offer attractive possibilities for chemical analysis [15]. Rutherford backscattering and the newer technique of neutron depth profiling [16] are used to study the concentration of elements as a function of depth near surfaces.

III. SRMs as multielement standards

Although the oligomonitor method of activation analysis is being put on a firm theoretical and experimental basis, most analyses of high accuracy still employ a co-irradiated standard for each element to be determined. The use of standards has been recently discussed in two publications from this laboratory [1,17].

SRMs from NBS and Certified Reference Materials (CRMs) issued by other bodies are frequently used as multielement comparator standards [17], in addition to their recommended use as known materials to verify the correctness of a new or routine chemical procedure. In some ways CRMs are suitable for this use: they are conveniently available in many laboratories, and the analyst's confidence in their composition is backed by the reputation of a major institution.

Reference materials, are not ideally suited for use as comparators, however. These materials are expensive, and are never produced in a large enough supply to last for many years. Futhermore, CRMs made from geological materials or from plant or animal tissue invariably are made up of more than one solid phase and are thus necessarily heterogeneous at some level [18,19]. Ingamells and Switzer[19] give an extreme example: the expectation value of the number of grains of chromite, which carries at least half the chromium, in a 100-milligram analytical sample of the USGS standard granite G-1 is 0.5. Finally, the certified concentrations of at least some components of a multielement CRM are not as accurately known as the components of a synthetic standard solution that can be made in the analyst's own laboratory. With conventional analytical apparatus, weighing and pipetting can be accurate to 0.2% or better; by contrast, the average stated uncertainty

of seven major and minor elements in NBS SRM 1633a Fly Ash is 3.4%, and of seventeen trace elements 4.4%. Only four of twenty-one are certified to 1% or better. However, a CRM which is homogeneous may be accurately calibrated against primary standards by the user and used as a working standard thereafter [20].

A number of workers have addressed the need for a working multielement calibrant material which is homogeneous, similar in matrix composition to the samples to be analyzed, and of well-known composition. If a liquid or colloid is uniformly doped and then solidified into storable form, a standard can be prepared whose homogeneity is guaranteed merely by the mode of preparation. Many laboratories have used fine silica slurried with solution standards. Photographic grade gelatin [21], urea-formaldehyde polymer [22], and polyacrylamide gel [23] have been used as analogs of plant and animal tissue, while clay [24] and mineral glasses [25,26] have been made as geological materials. Synthetic multielement standards are now under active development in several laboratories.

IV. The future of nuclear methods

The well-publicized steep growth in the capability of computers and other electronic devices, along with steeply falling hardware costs, have worked to the economic advantage of nuclear methods, with the result that the instrumentation for activation analysis is comparable in cost to the newer atomic methods. A 4096-channel pulse height analyzer bought by our laboratory in 1974 cost $20,000; for this number of 1986 dollars one can buy an entire analytical system consisting of an 8192-channel analyzer, a substantial microcomputer, 30 Mbytes of disk, and software for data acquisition and spectral data analysis. The modern system is more linear, more reliable, more versatile, and performs much more work than its ancestor. Detectors are also more efficient, of higher resolution, more portable, and less fragile for a given number of currency units than was the case only a few years ago. Largely because of improved instrumentation, the number and quality of analytical measurements per analyst-week in our laboratory has increased noticeably in the past ten years.

Because the simple unit processes of instrumental neutron activation analysis are so easily automated, automatic sample changers have been familiar in radiochemical laboratories for decades. The multiplication of analyst and instrument time by the use of robots is only beginning to appear in more classical and complicated chemical applications.

Computer software for gamma-ray spectroscopy, and for the additional calculations involved in activation analysis, is becoming somewhat standardized since there are only a few commercial suppliers of specialized computer-based systems for data acquisition. The wide distribution of some of this software, among critical users with different requirements, has led to the elimination of weaknesses in the early algorithms. Some well-documented software created in users' laboratories (Sampo,[27] Hypermet [28]) can now be obtained from equipment manufacturers as well as directly from the authors. This quasi-standardization results in good

comparability of data obtained in different laboratories, and makes it likely that researchers will find familiar equipment and procedures when working as a visitor in another institution.

The most important limitation in the wide application of nuclear methods of chemical analysis in the near future and in the long run may be access to reactors and other sources of nuclear-active particles. A recent compilation listed 61 research and training reactors of 100 kW and above in operation in the United States alone [29], most of which are suitable for activation analysis and for producing radiotracers. Their number is not likely to increase soon, however. The decreasing necessity for new nuclear electric power plants implies that fewer nuclear engineers are being trained on fewer university reactors. Regulatory changes in response to concerns of public safety make operation of reactors more and more expensive; the additional capital expenses resulting from the recent requirement that research reactors convert to low-enriched fuel may well shut down some marginal facilities.

Despite these uncertainties, the immediate future of nuclear methods is secure: their special advantages are vital in special situations such as standards certification, and their routine use for many applications such as geochemical and biomedical trace analysis [30] is assured. In many ways, nuclear methods have set and will continue to set the standard for high-quality elemental analysis, especially at trace levels. Meinke's comment of twenty years ago is still valid: "No quarter will be given to radiochemical methods - and no quarter should be asked" [31].

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DISCUSSION

G. Revel. It is necessary to remain very prudent for the certification of very low concentrations. I know several cases where different methods preformed in different laboratories give for the same samples, the same results and the results were not true. In the case of the determination of oxygen in aluminium, during five years the concentrations considered like true varied from some p.p.m. to some p.p.b. and at each step, different methods give the same result at the same time.

My second comment concerns the blank value due to surface pollution for solid samples. Theoretically this blank is avoided in activation methods by the cleaning of the surface after irradiation. In fact in ultra-trace analyses, this cleaning is not so easy and not so efficient as can be supposed (irregular attack, redeposition, phenomena, etc.)

ANALYSIS OF DIFFICULT MATERIALS: COMPARISON OF NUCLEAR AND NON-NUCLEAR METHODS

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Abstract

In a laboratory analysing large numbers of dissimilar samples, of a routine and non-routine nature, the analytical procedures used for inorganic constituents must be chosen carefully. No single procedure is able to satisfy fully the analytical requirements for certain complex materials, and a combination of techniques must be used. The quality of data required must be weighed carefully against the performance characteristics of the individual techniques, and the economic resources which are available for the solution of the problem.

Some examples of this approach are given, drawn from the analysis of alloys, biological materials and fuel ashes.

Introduction

There is a tendency to compare analytical techniques in a competitive fashion. Comparative lists of detection limits are often published (1, 2) which emphasise the "one technique against the other" approach, as well as implying that the detection limits so listed are typical, can be achieved in any matrix, and are constant for any instrument or operator using that measurement principle. Performance data may also be compared in cases where separation or enrichment procedures have been used in one case, but not in the other. Manufacturers tend to promote this kind of competitive approach as part of the initial rush of enthusiasm and rapid sales growth which heralds the arrival of a new analytical technique. The recent introduction of the technique of inductively coupled plasma-mass spectrometry by Gray (3) and Houk (4) and its arrival in a commercial form illustrates this phenomenon only too well. Initial sales literature implied that the technique was simple to use i.e. "black box", without interferences of a spectral or matrix nature, and could replace many existing analytical instruments directly in routine operation, for example, in the monitoring of water quality. Reality has shown the technique to possess disadvantages (5) as well as advantages. However, it has several distinct, powerful attributes as a technique which guarantee its place in the analytical armoury (6).

At Harwell, a large number of routine and non routine samples are analysed by a selection of analytical techniques, in order to establish the compositional data required for research and monitoring programmes. The principal techniques used for compositional analysis of this kind include X-ray fluorescence (XRF), atomic absorption (AAS, flame and flameless), inductively coupled plasma-emission and mass spectrometries (ICP-ES and ICP-MS), neutron activation analysis (RNA and INAA) and ion chromatography (IC). Examination of the application of these techniques for the determination of constituents in difficult matrices such as alloys, fly ash and biological materials, illustrates the complementary nature of the procedures rather than the comparative one.

Choice of Analytical Technique

When a new problem is presented to the analyst, he must make a decision on the procedure to be employed. Assuming he has available a range of techniques, and that he must be cost conscious (both factors probably apply in most government and major industrial laboratories), the first question he will probably ask is: "what quality of data is required?" The chosen procedure will then probably be the cheapest one able to supply data to meet that quality requirement.

In Table 1 are listed the most frequently required levels of accuracy encountered in the Chemical Analysis Group at Harwell. It should be emphasised that accuracy can only be measured by the routine measurement, with samples, of SRM or CRM materials, of a similar nature to the samples, and preferably "blind" to the analyst. In the absence of suitable reference materials, a sub-set of samples may be analysed by an alternative procedure employing a fundamentally different measurement principle. Agreement should be within the limits required. An example of this approach is as follows:- A study (7) measuring the uptake and excretion of heavy metals in man required the measurement of lead in blood, and arsenic in urine. The former was measured by flameless AAS, using NBS SRM 955 as a control upon accuracy. One internal reference sample was repeated every five samples as a precision estimation procedure. Arsenic in

Table 1 Accuracy Requirements for Elemental Analysis

Can only be assessed by analysis of materials of known composition, eg. SRM, CRM (preferably blind).	
At major levels:-	1% relative accuracy required
At minor levels:-	1-5% relative accuracy required
At trace levels:-	5-25% relative accuracy required
At ultra-trace levels	Any answer will do!

urine was measured using ICP-ES. No reference material was available, and therefore 10% of the samples were analysed by RNA. Agreement was within 3%, which was deemed to be sufficiently good for the quality of analytical data required.

Having decided upon the quality of data needed in an analysis, choice of the procedure used will probably be decided by cost. It may be, of course, that only one procedure will be able to meet the requirements: this is often the case at trace and ultra-trace levels. The cost of an analysis in a commercially oriented laboratory such as our own is a composite of labour, instrumental and overhead costs: labour costs vary widely since the skill of staff required for some types of analysis, for example, Group I and II elements in water by flame AAS, is clearly much lower than that required for accurate work near to the detection limit by a technique such as ICP-ES or INAA. Instrumental costs vary widely, ranging from a few pounds for some techniques, up to £250.000 or so for mass spectrometers.

In general, in most laboratories in the UK today, labour costs are the most significant ones: this has tended to make rapid, instrumental techniques cheaper than labour-intensive procedures such as wet chemical methods. A qualitative indication of analytical costs in our laboratory is given in Table 2. The range of costs is approximately a factor of fifty.

Table 2 Relative Unit Cost of Analysis

Cost	Technique	Type of Determination
	RNA	Se in blood
	ICP-MS	Hf in Zr
	ICP-ES	Co in steel
	GF-AAS	Pb in blood
↑	INAA	Multielement eg. Flyash
	ICP-MS	Multielement waters
	XRF	
	ICP-ES	Multielement waters in simple matrices
	IC	
	Flame AAS	Single elements in water

Complementary Nature of Analytical Techniques

In practice, if multielement analysis of a difficult matrix is involved, one single procedure may well not solve the problem. A good example of this is found in the analysis of fly ash or pulverised fuel ash (pfa) (8). Vast amounts of these materials are disposed of every year in the UK.

Because of the risk of eventual contamination of water, the CEC has set stringent limits upon the maximum levels of certain elements that may be leached out of the waste disposal site: accurate analysis of the matrix is thus essential.

If we look at the relative sensitivities and costs of various methods for multielement analysis of fuel ashes for a range of toxic elements, it is apparent that ICP-ES is probably the most attractive procedure. However, some elements are difficult to dissolve by the normal procedures employed e.g. Ba and others may be lost during dissolution, e.g. Se, As. The sensitivity of ICP-ES is also insufficient for the ready determination of elements like U, Th, Sb, Se and Tl. In practice therefore, a combination of techniques will be used, with ICP-ES providing most elemental data, INAA being used for elements such as Sb, Se and Ba, and ICP-MS giving data for U, Th, Tl and the lanthanide elements. An added bonus is that two sets of data may be obtained for some elements, providing a valuable cross check upon accuracy. Data obtained in this way for As and Cr by both techniques for 200 pfa samples analysed over a period of six months, showed very close agreement between the two sets of data with a mean difference of ± 8% between data sets over the range 20 to 300 µg/g As or Cr.

The analysis of reactor grade steel samples (9) provides another good example of the complementary nature of procedures: the techniques used for multielement analysis of these materials are listed in Table 3. At major and minor element levels, XRF is the most cost-effective procedure for the determination of most of the desired metallic components necessary for alloy identification and specification testing. XRF is capable of reaching high levels of accuracy and precision if suitable standards are available, and is relatively economical since it is heavily automated.

Table 3 ANALYSIS OF REACTOR STEELS

ELEMENT	LEVEL %	TECHNIQUE
Ni, Cu, Mn etc	0.01 - 100	XRF
O, N, C, S	0.0005 -	LECO
Nb, Co	0.0001 - 0.01	ICP-ES
Eu, Ag	- 0.0005	NAA
C, O	- 0 0005	GPAA

Levels of O, N, C and S above 5 µg/g are determined by use of Leco CS144 and TC-136 elemental analyses. Again, the unit cost of analysis is extremely low, due to automated operation.

Elements such as Nb and Co which are important from the activation product point of view are present at levels below the limit of determination of XRF: ICP-ES is used therefore,

although considerably more costly than XRF when used in a single element, high resolution mode. Extremely low levels of Eu and Ag (less than 0.1 μg/g typically) which are also potential activation products, are measured by RNA. The high cost of this technique is justified in this case as it is the only procedure readily capable of reaching these levels of concentration. It is also, of course, blank-free which is an important pre-requisite at ultra-trace levels.

C and O are also measured at very low levels by Gamma-photon Activation Analysis. Again, although costly, this technique is able to reach very low levels of C and O, and can discriminate against blank and surface contamination effects, which limit other, non-activation, procedures.

Conclusions

Analytical procedures are complementary, and there is as yet no analytical panacea. The approach adopted in a busy analytical laboratory must therefore reflect this fact, and techniques must be chosen to match samples, rather than vice versa.

Rather than a competitive comparison between nuclear and non-nuclear methods being proposed therefore, it is important to recognise that both types of procedure have their merits, and each must be applied when most appropriate.

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DISCUSSION

R. Schelenz. Does the number of individual determinations also include multielement methods such as ICP-AES or INAA?

C.J. Pickford. In my slide I included both samples and determinations for this reason: the ratio between the two is about 6, which implies that the average sample is analyzed for this number of elements. Many are less, e.g., U, Th, Cs, Tc are measured individually in some leachates and water samples and many samples are analyzed by ICP for 45 elements.

TRACE ELEMENT ANALYSIS IN BIOLOGICAL MATERIALS: A COMPARISON OF NEUTRON ACTIVATION ANALYSIS WITH OTHER TECHNIQUES, ESPECIALLY ATOMIC SPECTROSCOPY

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Abstract

The analytical chemistry laboratory of GSF is concerned with trace element analysis mainly in connection with life sciences. It analyses annually 20.000 samples with an average of 20 elements per sample. Several different analytical techniques, including neutron activation analysis and non-nuclear methods are available. The paper discusses the advantages and disadvantages of the different analytical techniques as applied to biological and environmental samples.

Our laboratory in the GSF is concerned with trace element analytical chemistry since the end of 1966, especially in the life sciences.
Our main tasks now are:

1. A central analytical laboratory for trace elements in environmental samples, especially for Bavaria.
2. A central analytical laboratory for the whole research center (GSF).
3. Own research programmes in the bio-medical field.

The number of samples which will be analyzed per year is about 20.000 for 20 elements on an average.
The type of the samples varies from different body fluids like blood serum, amneotic fluid, breast milk and others up to soils, sediments and sludges. This variety describes also the variation in the concentration ranges of the different trace elements.

The element spectrum which is routinely investigated covers Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Sb, Se, Sn, Sr, Ti, V and Zn.

It is well known, that there does not exist an universal analytical technique which is able to detect this element spectrum in the very different concentration ranges. Therefore always different analytical methods are necessary to solve the given problems. In general, it is impossible to discuss the capacity of on analytical method without discussing the problem simultaneously. In the following I will see my statements always in relation to the problem to be solved. In our laboratory, we have the following different analytical methods available (the succession is not a judgement as to value, it is the chronological order of the application in our laboratory.

1. Neutron activation analysis (instrumental (INAA) and with radiochemical separation (RNAA))
2. Atomic Absorption Spectroscopy
   a) Flameless AAS, graphite furnace, Zeeman-background correction
   b) Flameless AAS, hydride system
   c) Flameless AAS, cold vapour
3. ICP- and DCP-emission spectroscopy
4. Voltammetry (DPASV)

Before I come back to the discussion of the different methods, I like to say some words to the elements in which we are interested now.
In the bio-medical field we are mainly interested in the known essential trace elements Fe, J, Cu, Mn, Zn, Co, Mo, Se, Cr, Sn, V, F, Si and Ni in all kinds of tissues and body fluids for clearing up the role and the function of trace elements in the organism.
In the environmental field specific attention must be called upon the known heavy metals like Pb, Cd, Hg, As, Tl and other more. From main interest is also the interaction of these elements with the essential one in the organism.

Therefore not only the pure pollution view is in the foreground, but also the biochemistry of these elements which have a toxic action in low concentration ranges. But the main point in the environmental field is to control the loading of our environment with different substances. Here, we have a lot of different matrices for analyzing purposes: soil, sediments, water, air, aquatic and terestial, plants, animals and also tissues and body fluids of man.

What is the capacity of these mentioned methods in these application fields:
ad 1) In general NAA does not work as a routine method for a great number of samples.

One of the main difficulty is concerned with the continous decrease in number of the nuclear reactors available for this technique. An other is the continuous increase in the safeguards for working with radioactive material and the permanent denunciation of radioactivity in the public opinion, so that it is a hard task to find somebody who is willing to work in a so called hot laboratory. On the other hand the laboratory equipment becomes more and more expensive due to these safety regulations, which also influences the "price" for the analysis. But these are more political problems and do not correspond in the different countries.

From the scientific point of view NAA is a powerful tool for trace element research work, also for testing other techniques and for the certification of standard reference materials. The greatest advantages are a complete independence from the matrix (chemical nature), the lack of blanc values, the absence of contamination problems during the analysis, the possibility to handle the sample without any pre-treatment and the possibility to detect a lot of elements simultaneously.

But these are theoretical advantages. In practice we must look for the problem and I come back to the elements, matrices and application fields, I have mentioned before. I

want to restrict me now to biological material. With INAA one can solve only a very small part of the analytical problems. Due to a normally high ^{24}Na and ^{32}P activity in these kinds of samples you must work either with very short irradiation times for detecting short living isotopes in the half live range of minutes or with a long irradiation time including a long decay time for detecting long living isotopes. In the first case one needs appropriate reactor facilities like a fast rabbit system combined with a suitable detecting system very near of the reactor itself. The other method with the long living isotopes is more or less independent on the distance between laboratory and reactor. With both of the INAA techniques one is restricted to the elements Se, Zn, Fe, Cr and Co (sometimes Cu and Mn; it depends on the concentration) in biological material. For the toxic heavy metals we have normally no chance due to very low concentrations. It is therefore only a small part of the interesting element spectra. Combining NAA with radiochemical separation after irradiation one can extremly extend the number of elements depending on the chemical and time expenditure. In our laboratory we are working with the radiochemical separation method developed by Samsahl and we can detect up to about 40 trace elements simultaneously from one sample of 100 mg weight. But it is a very time expensive method in the chemical procedure and in γ-spectroscopy and therefore one person can only process up to 10 samples per week, and this is much to less for routine analysis. And one needs a "hot" laboratory for handling the radioactive material with all the well known and expensive special equipments.

This is one of the main disadvantages of NAA (INAA and RNAA), that it is a very time and money expensive method. For diagnosis in the medical field or control in the environmental field, it is not possible to wait for the results for some weeks or months and even some days are to long in most of the medical applications (diagnosis or therapy control). Most of the interesting elements can be detected only by an high expenditure using radiochemical

separation methods and therefore the costs of the analysis become very high. Adding the normally high costs for irradiation in the reactor, only some special equipped research laboratory can do and pay the analysis for research application on a small number of samples but never for routine analysis.

NAA was for long period the most sensitive analytical technique and most of the research work detecting the essentiality and also the toxicity of the different trace elements was done by using NAA-techniques in the past. From this technique we have learned the importance of trace elements in many fields and outgoing from this the development of other analytical techniques was started and forced.

Today for routine analysis in the wide range of applications the atomic spectroscopy methods are well established. Here one must distinguish for practical work between atomic absorption (AAS) and atomic emission spectroscopy (AES). AAS was for long period after the development of the flameless techniques (graphite furnaces etc.) and by this the increase in the sensitivity the only competitor of the NAA-techniques. Due to the development of the different plasma excitations, atomic emission spectroscopy has become a new peak-time since about 1978 in practice.

In general, the most considerable disadvantage of all the atomic spectroscopy methods is the need of mineralization of the samples. There exist also some newer techniques for solid sample measurements but up to now they do not play an important role in routine analysis due to the well known main difficulties in calibration. They have their place for investigating homogeneity of samples, for instance in case of standard reference materials, but in normal analysis there does not exist such a well homogenized sample that a sample intake of 1 mg say enough about the whole sample.

For the problem of mineralization of a given sample a lot of different ashing procedures are available for the different matrices. They all have the well known advantages and disadvantages and one must always observe the element and the matrix in choosing an adequate technique. There is not time enough to speak about those. For biological material the pressure ashing technique with HNO_3 in teflon bombs (with or without additional quartz tubes) has become a nearly universal method. We have developed in our laboratory a special pressure ashing device which is very easy to handle and safe and we are ashing more than 10.000 samples per year by this technique.

AAS is for many interesting elements - essential and toxic - a very sensitive analytical technique. By flame AAS one can detect especially the matrix elements like Na, K, Ca, Mg and P, or the essential trace elements Cu, Fe and Zn. By the flameless technique using graphite furnace and Zeeman - instead of deuterium - background correction one can detect the heavy metals Pb and Cd, the most interesting essential trace element today Se and a lot of other interesting elements like for instance Cu, Mn, Cr, Ni, Al etc. Finally one can use the hydride system or cold vapor AAS for detecting elements like As, Se, Sn, Sb and Hg. One sees there is a wide spectrum of elements detectable, but the main disadvantage is that all the AAS-techniques are single-element- methods. You have to change the light-source for each element you want to measure and therefore the time consumption for analyzing for instance 20 elements in one sample is relatively high, but in every case lower than using NAA. An other serious disadvantage is the appearence of the different chemical matrix influences due to the relative low temperature available by the different excitation sources which can cause a lot of systematic errors. The use of adequate standard reference material (matrix and element concentration range should be very near to the unknown sample) is necessary to avoid these. A big step in the direction of accuracy of AAS-measurements was the introduction of Zeeman background correction because this

technique is much more specific than deuterium background correction and works sufficient over a wide range of disturbing influences.

With the newer fast data systems one can also observe each signal - the specific and the unspecific one -, therefore with some experiences one can obtain true results. In general the instruments are relatively cheep, there are no special demands on the laboratory equipment and they are easy to handle also by the technical staff.
The operating costs are depending on the technique; the most expensive one is graphite furnace AAS due to the high price for the graphite tubes and due to there low expectation of life.

In our laboratory AAS-techniques are used especially for the determination of lower concentrations of the elements Pb, Cd, Cr, Ni, Mn, Al, direct Se determination in blood serum (graphite furnace) and using the hydride system for the elements Hg, Se, As. Sn and Sb is in most of the bio-medical samples not detectable by this technique due to their low concentrations.

For our purposes we have 3 instruments combined with graphite furnace, Zeeman background correction and fast data systems and also 3 instruments combined with hydride systems. For the big amount of samples we have to analyze it is neccessary to have one technician for each instrument.

The other most common used atomic spectroscopy technique in our laboratory is AES using plasma excitation sources. We have ICP and DCP plasma. Their is no big difference between but in general one can say that the DCP plasma have due to the lower temperature (about 6000 K) compared to the ICP (about 8000 K) more chemical interferences but is not possible to go into details here. Due to the high excitation temperature in both of the plasma sources the emission line spectra are very complex and therefore the most important demand is for an efficient spectrometer with a high optical

resolution power. Otherwise one has to fight against a lot of physical interferences, especially line coincidences which may lead to a lot of systematic errors. In general you have to test the reliability of a result on at least a second emission line and/or using again adequate standard reference materials. One of the big advantages of this technique is the possibility of doing simultaneous multi-element- analysis. But beginners in this technique should always start with the sequential technique using a monochromator because only by this technique one can collect the experiences which are necessary for applying the simultaneous method. In most of the cases there exist some comparable (from the sensitivity point of view) emission lines of each element, but they are not comparable for getting true results in different matrices due to different interferences from other elements which are dependent on the different concentration ranges of the disturbing elements to the elements to be measured. By using a monochromator one can test all the circumstances and choose the most sufficient line for a given problem. By using the simultaneous technique one must believe the computer and with no experience the results are mostly wrong. An other very important point is the necessity of background correction because the background can be strongly influenced by different salt concentrations, by different density and viscosity of the samples, by different matrices etc. Therefore an adequate background correction is necessary in both techniques - sequential and simultaneous. For sufficient short and long time stability of the instruments a good and effective gas regulating system - at best using electronic mass flow regulators at least for the aerosol carrier gas - is necessary. Also a peristaltic pump in the nebulizing system should be installed for a reduced sample consumption especially for bio-medical samples in which one wishes to get a lot of informations out of a small sample amount mostly available.

Plasma emission spectroscopy is a very sufficient tool for trace element analytical chemistry in all kinds of sample

material. The sensitivity and specifity of the method allows the detection of a lot of interesting elements. But also here one must know the limits to avoid systematic errors. From the list of elements which we are routinely investigating in bio-medical and environmental samples (given at the beginning) ICP and DCP can detect: Al, B, Ca, Cu, Fe, K, Li, Mg, Mn, Na, P, S, Sr, Ti, and Zn. In some cases, especially in some environmental samples like soils, sediments, sludges etc. also the concentrations of Cd, Cr, Ni, Pb and V are detectable. Using also a hydride system you can in these samples also detect the elements Hg, As and Se, sometimes Sb and Sn. One can not say in general which elements can be analyzed and which not, because it depends always on the concentration and on the matrix. But this is valid for all the different analytical methods.

Sufficient done plasma emission spectroscopy needs a longer time of experience, at least one year for a scientist. The instruments are relatively expensive, especially combinations of sequential and simultaneous devices and the operating costs are also relatively high due to a high gas (argon) consumption. Time consumption for an analysis is relatively low. We have 3 sequential and one simultaneous instrument. In the simultaneous machine we have installed 16 channels for 16 different elements. The time for one analysis including three repetitions is about 4 minutes. The sample consumption is about 0.8 ml/min. Especially the new JY 38 Plus from Instruments SA, France is a very safe operating system and combined with an adequate sample changer, we can use also the night-hours for analysis without any supervision.

The new developments of ICP coupled mass spectrometer promise in my opinion to be succesful in future. Today the difficulties do not really allow the application in routine analysis.

A completely other analytical technique is Voltammetry. There exist a lot of different subtechniques within. We are

using DPASV (Differental Pulse Anodic Stripping Voltammetry) with the mercury-drop technique. This methode is the most sensitive one in this comparison for some elements especially Cd, Pb, Tl, Ni, Co, Cu and Zn. These are the elements which we analyze routinely by this method. The technique expects a great deal from the quality of the ashing prodecure because small amounts of organic material disturb the analysis of all the elements due to a high background signal or to a bad peak-form.

Therefore special ashing procedures for biological materials must be applied. The normal pressure ashing technique with HNO_3 is not sufficient enough. One must use additionally $HClO_4$ or acid combinations to have sufficient sample solutions for this method. From the theory, it is a multi-element method but one can use this advantage only when the concentrations of the different elements do not differ very much. Otherwise one must work sequentially. The same is valid f.i. for the determination of Ni and Co because one must have an other electrolyte. The technique can be used for the lower ppb-range or down to the upper ppt-range. These low concentrations require special laboratory equipment and special chemicals for very low blanc values. The instruments are relatively cheep in comparison to the atomic spectroscopy, but one analysis takes a relatively long time because all the measurements must be done by the standard addition method. But for the determination of Pb and Cd, sometimes also for Ni and Co in f.i. milk-powder, breast milk, blood serum, urine and other body fluids, it is often the only method of choice.

Going back to the beginning or better to the problem to find competitive methods for the NAA-techniques, one has to say that there does not exist any universal analytical method. This includes also NAA. I think each method is a competitor for an other method for a special given problem. The problem to be solved demands for on adequate technique. This includes all the questions about the element, the matrix, the quantity of sample material available for the analysis, the

application in practice (routine analyis or research; time consumption especially for diagnosis and therapy control) and other more. Only combinations of different analytical techniques can help in solving the various problems in trace element analytical chemistry in bio-medical and environmental field. No serious analyst should try to solve all the problems by one technique which he has in his laboratory by chance. This would be in most of the cases a violation of the method and should be avoided for internationally better and comparable results in trace element research and practical applications.

AAS and Plasma-AES promise to be an useful combination for a relatively wide application field. At the end again I want to point to the need and the application of well certified standard reference materials for all kinds of analytical techniques. It is the only way to reduce systematic errors and it can also help to develop new methods in these fields.

THE DEVELOPMENT OF ACTIVATION ANALYSIS IN CHINA

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Abstract

Since the first nuclear research reactor and accelerator was built in 1958 activation analysis methods have been developed and applied in China. Four national activation analysis symposiums have been held. More than 200 papers on activation analysis have been published. The paper gives a review of applications. A miniature research reactor, MNSR, designed for neutron activation analysis is described.

The activation analysis is an unigue method in analytical chemistry of trace elements and it forms an important part of nuclear analytical chemistry. This paper will draw an outline of the development of methodology and application of activation analysis in China. Since the first experimental nuclear reactor and accelerator were built in 1958, China has started research work of the activation analysis. In the 60's, the activation analysis was mainly used to analyse reactor materials, nuclear fuels and semiconductor materials in China.

Based on the use of semiconductor detector and computer technique in nuclear measurement and the success of radiochemical separation procedures much progress of activation analysis has been made in the 70's in China. The first symposium on activation analysis was held in 1978. The major part of the symposium proceeding[1] involves neutron activation analysis in pile. The use of neutron activation analysis with preconcentration and postirradiation radiochemical separatron for determination fourteen rare earth elements and noble metals Os, Ru, Ir, Au, Pt and Pd in Jinlin meteorite are deseribed by several investigators. In this symposium a number of papers presented the application of neutron activation analysis in different areas including the determination of biological, geological

and environmental materials. The development in methodology were also made in the fast neutron activation(FNAA) and the charged particle activation analysis(CPAA). Determination of 0.1ppm carbon and oxyen in silicon by using 3MeV deuteron and 29MeV α particle respectively from cyclotron was reported. Such results can not be reached by mass spectrometry and vacuum fusion or innert gas fusion methods.

During the period from 1978 to the mid 1985 the activation analysis in the world was becoming a mature techique. In the same time China has also made great progress in the development of activation analysis technique. For example, computer programs for comparative method of activation analysis have been studied and developed in several labs, and the automatic pneumatic transfer systems have already been set up in several research centers. Along with that the second and third national symposium on activation analysis were held in 1981 and 1984 respectively. In the meantime the national symposium on applications of activation analysis in enviornmental science and geology was also held in 1983. The applications of neutron activation analysis in the verious fields of science and technology have expanded rapidly in recent years in China. This can be seen in the following statistical figures of the publications[1-6] related to the activation analysis.

Field of Science and Technology	Number of Published works
Geology / Cosmology	58
Biology / Enviornmental Science	64
Methodology	41
Standard / SMR	19
Material Science	17
Archaeology / Forensic Medicine	7
Total	206

The publications which deal with applications of the instrumental neutron activation analysis (INAA) for multielemental determinations havs been multitudinous. For example, determination of 41 microelements by INAA has been reported[3]. A certain number of the investigators have focused their attention on analysing the rare earth elements in geological and biological samples by using INAA and it has been shown in their papers that eight to eleven rare earth elements can be analysed[3,4]. The methods which are based on postirradiation chemical separation or sample preconcentration neutron activation analysis(RNAA) still remain active in spite of the possibility of lossing integrity of sample. For instance, a freeze-drying preconcentration technique of water samples has been used in neutron activation analysis of different kinds of water samples[3,4]. The ultratrace noble elements such as 10^{-10}g of Ag, Au and Os in geological, cosmic and biological samples are successfully analysed by RNAA[4,5]. Besides, the determination of trace U,Th, Sm, La, Tb, Yb, Ta and Cs in geological and environmental samples by reactor epithermal neutron activation analysis methods[3] are described. This method reduces the interferences of Fe, Sc and other metals in matrix. The mono-standard and two-standard neutron activation analyses[3,4] are applied in determination of trace multielements in coal and fly-ash. On the basis of using a beam of thermal neutron extracted from a beam port of test reacter prompt γ neutron activation analysis technique has been studied in order to analyse composition of coal[6]. It also reported that the proton activation thin layer analysis has been adopted to study trace erosive wear of industrial machine and gun barrel[1,3].

During this period much emphasis has been put on improving the accuracy of analytical results. The preparation of new working standard as well as the preparation and certification of the standard reference materials (SMR) have been studied and discussed in some papers. A new mercury standard with sulfhydryl cotton matrix for NAA has been proposed[4] and its advantage is to obviate the loss of mercury in the course of preparation and irradiation. It is noted that a synthetic phenolic resin matrix standard which contains 17 elements was prepared and analysed and the stability, homogeneity and the uncertainty

of resulted values were described in the paper[4]. The national issued standard reference materials[3] include river sediment (81-01), coal fly-ashes (82 201) and peach leaves (82 301) and geochemical SRM GSD1-8. Among them SRM GSD1-8 have been analysed by 41 labs. The analytical methods include flame and flameless AAS, spectrophotometric, AES and ICPAES, XRF, polargraphic, NAA, gravimetric, volumetric, flame-photometric and mass spectrometric methods. Three labs of NAA have provided results for 36 elements which is 66.7% of all the elements with certified values. Furthermore, the elements including As, Ce, Cs, Dy, Eu, Gd, Hf, Ho, La, Lu, Nd, Rb, Sc, Sm, Ta, Tb, Tm and U ect. have been analysed by either NAA or other methods, and it has been proved that NAA is more efficient technique than any other method for these elements.

The miniature neutron source reactor (MNSR)[7] designed and constructed by the Institute of Atomic Energy was commissioned in the early 1984 in China and it will make the application of NAA even more popular. The neutron flux inside the irradiation tube of this MNSR is $1 \times 10^{12} n/cm^2.s$ and the corresponding thermal power is 27kw. This MNSR is equipped with two pneumatic transfer systems, one timer ranging from 1' to 999'59", one capsul cutting and transfer station as well as multi-function SPAN computer programs. It can be shown that the MNSR is a safe and simple toolin nuclear analytical chemistry and it is particularly suitable for neutron activation analysis using short-lived radionuclides. During the last two years more than 10,000 samples from various fields have been analysed by using MNSR and 64 kinds of elements have been quantatively measured with sensitivities of hundreds of ppm up to ppb.

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DISCUSSION

R. Rosenberg. What is the position of NAA compared with other techniques in China?

T. Xin-hua. NAA is a unique trace and ultratrace multielement analytical technique. In China more than 13 labs have worked with NAA to solve a great number of topics in various fields of science and technology, such as geology, biology, environmental science, SMR certification, superpure material, archaeology, etc. For example, 10,000 samples have been analyzed in MNSR from various fields in the last two years. So in view of the importance and the ability in resolving analytical subjects NAA stands in the same position as ICPAES. In some special cases it is even better than ICPAES, for example it can be used as a nondestructive method. But the radiation sources are limited and the total price of NAA are still higher than the nonnuclear analytical techniques. Now NAA is not so widely and frequently used as the AAS, ICPAES, spectophotometric and electrochemical methods in China.

NEUTRON ACTIVATION ANALYSIS OF GEOLOGICAL SAMPLES IN FREE COMPETITION — A CASE HISTORY FROM FINLAND

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Abstract

At the Reactor Laboratory neutron activation analysis (NAA) of geological samples is performed on an analytical service basis. The expenses of this activity is expected to be covered by the income. Methods and automatic analyzers have been developed for the low cost analysis of large numbers of samples. During the period 1973-79 20,000-30,000 uranium determinations were made annually. During the period 1982-85 more than 10.000 samples were analyzed annually for gold and 23 other elements. The performance and cost of NAA compared with competitive methods are discussed.

1. INTRODUCTION

When analytical techniques are compared with each other a number of performance criteria are usually applied. Those applicable to all techniques are sensitivity, accuracy, cost and capacity, the latter usually being related to the cost. Other aspects to take into account are special features of some techniques. Availability, for reactor neutron activation analysis, sampling area and depth, for surface analysis methods and so forth. An appraisal may easily be subjective. There are several reasons for this. The person doing it may be in favour of one method because a specific instrument happens to be available to him. The reason may also be that one of the criteria is more important to the person doing the comparison than the other ones. Related to this is the fact that some criteria are more scientific and interesting to evaluate. Such are accuracy and sensitivity. Capacity and cost being less interesting to a scientist. The persons for whom those criteria are important work in laboratories doing routine work in service for geologists, steel producers and so on. They usually do not produce so many scientific papers.

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Another approach to the comparison would be to go out on the open market. Sell the services with a price covering all the costs and see how it comes out. One could say that this is an objective comparison. The people who need the results can choose between different techniques. In principle the analytical technique which combines all criteria in the most favourable way will be the most successful one. In practice there is not one method which covers all analytical problems in the best way. But the technique most suitable for a specific problem will be found.

At the Reactor Laboratory of the Technical Research Centre of Finland, reactor neutron activate analysis has been practised almost since the start of the reactor in 1962. Through all this time part of the work was done on analytical service basis. The analysis of 40 elements was more or less actively marketted. The work was strongly sponsored by the government. In 1974 started the effort to commercialize the neutron analysis activity. In this paper the means and outcome of this project will be described and discussed.

2. GENERAL CONSIDERATIONS

Geological research and mineral exploration has a long tradition in Finland. Basic research is performed by the Geological Survey of Finland and a number of universities. Direct mineral exploration is performed by the Geological Survey and a few mining companies. The universities possess modest analytical laboratories and very limited funds for buying analytical service. It is quite common for them to have joint projects with the mining companies. In this cases the samples can be analysed by the laboratories of the mining companies for no cost to the university. The Geological Survey and the mining companies have excellent analytical laboratories with modern, usually automated instrumentation.

To sell analysis to this community is not easy.

In 1974 the activation analysis group comprised four professionals and four technicians. Excellent electronical and mechanical workshops were available. The irradiation were performed with the Triga MK II reactor of the institute. Samples could be irradiated in the rotary specimen rack, in the central thimble or using two pneumatic transfer systems.

Until 1974 the work had been performed on a small scale for universities and research institutes. All the work was done with care and the results were accurate and the sensitivity as good as can be attained by optimal timing and radiochemical separations when needed. The unit cost was far too high for anybody to buy so the work had to be strongly sponsored. It was realized that accuracy and sensitivity could not easily be improved anymore. What was needed was a decrease in cost combined with an increase in the number of samples. The decrease in cost was attainable through rationalization of the work mainly through automation. The increase in the number of samples again required more efficient marketing.

So in 1974 two different projects were started. One to build an automatic uranium analyzer and another one to build an automatic gamma spectrometer. In the same time a realistic price list was worked out and the marketing was increased. The folowing face started in 1981 and still continues. The NAA was completely commercialized and the automation of the laboratory strongly increased.

3. ANALYSIS OF URANIUM BY NEUTRON ACTIVATION AND DELAYED NEUTRON COUNTING

The uranium analysis project was started in the time when the exploration for uranium was intensified in Finland. In the end of 1973 a manual uranium analyzer was taken into use. Because of the low cost of the analysis it was not difficult to get customers. The mining companies sent control samples for analysis and the results proved that the work could be done at the Research Laboratory. With the low prices it was not worthwhile for the mining companies to build own analysis capacity. The only problem was the capacity. With the manual analyzer the annual number of samples which could be analyzed was 8000. So in the beginning of 1974 it was decided to build an automatic analyser.

The project started during 1974. The analyzer was taken into use in August 1975.

The operating principles of the analyzer can be seen in FIG. 1. The device comprises a sample changer, a pneumatic transfer system, a measurement station with detectors and auxiliary electronics, a microcomputer, a weighing system and a container for the storage of the analyzed samples. [1].

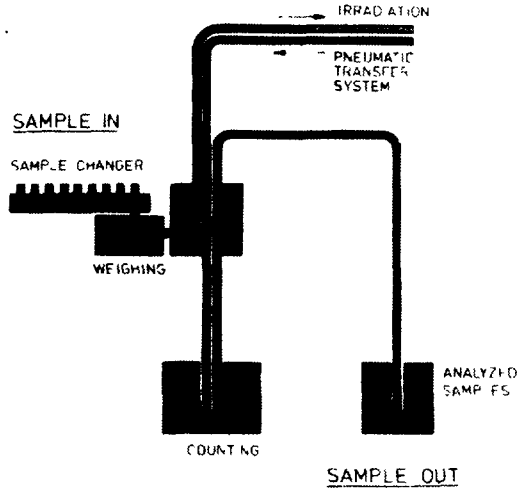

FIG. 1. Principles of the automatic uranium analyzer.

The measurement station comprises a moderator of polyethylene in which 12 ^{3}He detectors are imbedded in a circular configuration around the sample position. The moderator is surrounded by a sheet of cadmium and borated paraffin.

The system works in the following way. The samples are loaded into the sample changer. The first sample is a blank, the next a standard and the following samples with blanks and controls according to need. The analyzer irradiates and measures the samples automatically and shoots them into the waste container. The samples are also weighed automatically. The computer calculates the elemental concentrations and prints the results on paper and paper tape.

An efficient capacity of 400 samples per working day can be reached. The detection limit is 0.1 ppm. The system uses rabbits of polyethylene. These are transported in boxes of styrox holding 90 rabbits each. They are sent to the customers who insert the samples into the rabbits, mark them with the appropriate code numbers and send them back. The results are sent as paper listings or paper tape.

During 1976 to 1979 the annual number of samples analyzed varied between 20,000 and 30,000. Then geochemical exploration for uranium decreased strongly, the annual number of samples being 4,000 in 1985. During the best year the income from uranium analysis was about 75% of the total income from analytical service by activation analysis, but it still covered only about

half of the budget of the activation analysis group. The uranium analysis itself made a considerable profit because only 1.2 man years were needed for the work. This time includes service of the analyzers.

4. INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

4.1 Analysis by using thermal neutrons

INAA of 31 elements [2] was performed on a service basis. Table I shows the elements and the obtained detection limits. All the work was made manually, the spectra were recorded on paper tape and the results calculated by a separate computer. The number of samples analyzed annually was about 3000 in small series. As a consequence the unit price was high. In order to improve the situation it was decided to apply automation. In 1975 a sample changer was built [3]. Thus the measurements could be performed automatically. Manual work was saved and the capacity of the analyzed increased because also the nights and week-ends could be efficiently utilized for measurements. The spectra were recorded on magnetic tape and a separate computer was used for calculations. The price of the service could be decreased somewhat but still the cost was not competitive. For institutions with their own laboratories there is always a high threshold for sending samples outside for analysis. Mainly lanthanoids and some other elements, not easily analyzed by other techniques were determined in small quantity.

Table I. Detection limits of 31 elements in rocks determined by instrumental neutron activation analysis.

Element	Detection limit (ppm)	Element	Detection limit (ppm)
Na	90	Ba	160
Al	300	La	0.5
K	3000	Ce	2
Ca	10^5	Nd	5
Sc	0.06	Sm	0.06
Cr	5	Eu	0.05
Ti	6000	Gd	4
V	30	Tb	0.05
Mn	10	Dy	0.3
Fe	350	Yb	0.07
Ni	15	Lu	0.2
Co	0.3	Hf	0.6
Rb	20	Ta	0.02
Zr	200	Th	0.4
Sb	0.2	U	0.5
Cs	0.4		

4.2 Analysis by using epithermal neutrons

In the beginning of the 1981 there was an increasing demand for the analysis of gold in geochemical samples. Geochemical exploration of gold requires a low limit of detection so that all anomalies can be found. It also requires a low unit cost of the analysis because large numbers of samples have to be analyzed. The laboratories of the mining companies could not satisfy the needs of the geologists so there was a market for outside service. It was decided that the Reactor Laboratory should try to utilize the situation.

Two problems had to be solved. How to do the analysis in order to reach the low detection limits required and how to organize the work in order to reach a high enough capacity and low enough a cost.

The detection limit 10 ppb, obtainable with thermal NAA is not low enough to enable the detection of all anomalies. In order to increase the attraction of the service a number of other elements should be analyzed simultaneously with gold. In Finland a very important one is molybdenum which cannot be analyzed with thermal NAA. These two aspects compelled the use of epithermal NAA. Nobody had previously reported the use of ENAA in such a large scale and therefore it was a challenge.

First the method for the irradiation of the samples in cadmium had to be developed. After testing some different approaches the following was arrived at. Twenty containers of aluminium, ⌀ 30mm x 200mm lined with 1mm of cadmium and 0.2mm of aluminium, are kept in the rotating specimen rack of the reactor. The containers are kept in the reactor all the time. They are only lifted up when samples are inserted and removed. Because of the special shielding system the dose obtained by the handler is negligible. 640 0.5g samples can be irradiated simultaneously.

The samples are weighed into capsules of polyethylene which are wrapped into a thin foil of aluminium. The bundles are inserted into the irradiation containers together with standards. They are irradiated for one week (35h), let decay for four days and measured for 20 min per sample. Thus the measurement of one series of 160 samples takes 2.5 days using a sample changer. Table II shows the elements detected and their detection limits in rocks [4].

Table II. Detection limits for 25 elements in rocks determined by instrumental epithermal neutron activation analysis of till. Samples are measured four days after irradiation.

Element	Detection limit (ppm)	Element	Detection limit (ppm)
Na	250	Sb	0.1
Sc	0.5	Cs	0.6
Cr	40	Ba	80
Fe	2500	La	1.5
Co	2.5	Sm	0.05
Ni	40	Eu	2
Zn	100	Lu	0.05
As	1	Ta	0.5
Br	0.6	W	2
Rb	15	Au	0.003
Mo	1.5	Th	0.4
Ag	3	U	0.3
Sn	100		

Usually the samples are weighed by the customers into capsules provided by the Reactor Laboratory. The capsules are transported and stored in boxes of styrox. The boxes hold 100 capsules. On arrival to the Laboratory the samples are subject to the Laboratory's book-keeping system and included in the routine flow of samples. Then the samples are irradiated, let decay and measured with one of the five automatic gamma spectrometers of the NAA group(s).

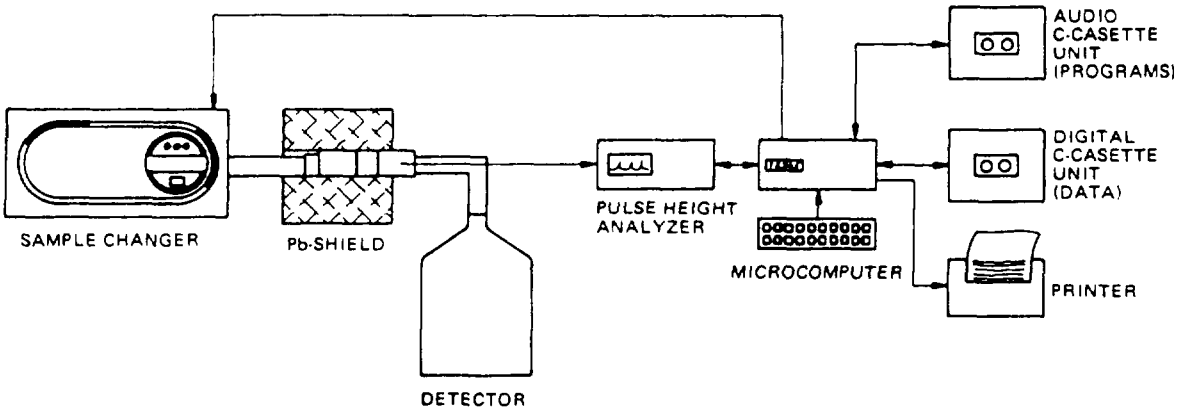

FIG. 2. Principles of the automatic γ-spectrometer.

FIG. 2 shows the structure of the spectrometer. It comprises

- sample changer
- detector with auxiliary electronics
- multichannel analyzer
- microcomputer
- input/output devices

Sample changers for 66, 80 and 120 samples have been built. 0.5 - 5 ml capsules can be used.

Four Ge-detectors with 10-25% relative efficiency and one low-energy photon detector with dimensions of 5 x ⌀ 10 mm and an energy resolution of 600 eV at 122 keV are used.

The central board of AIM 65 by Rockwell is used as basis for the computer. Memory extensions, the power unit, the case, interfaces and the programs are made at the Reactor Laboratory. The I/O devices are an Epson MX-80 printer, an MFE 2500 digital cassette terminal and a philips NE2235 audio recorder.

The system functions as follows. The samples with standards first are loaded in the sample changer. The data containing measurement parameters and sample codes and weights are loaded from a cassette into the computer memory. Then the system automatically measures the samples and calculated the results giving as output elemental concentrations.

The elemental concentrations are printed on paper and also on a digital cassette. This can be used for the transfer of data to another computer for data processing. If the user does not have a cassette terminal, the data is transferred from the cassette to a floppy disc or computer compatible magnetic tape using other computers in the institute.

The number of samples analyzed annually by ENAA has been more than 10,000 for several years.

5. DISCUSSION

The basic starting point is that a geologist has samples he want to be analyzed and then some money. Now the first point is to find a laboratory with a technique to do the work. To analyze the specific elements he is interested in. The requirements are the following:

The technique has to be accurate enough for the results to be useful and sensitive enough for the elements to be detected.

There are some differences in the accuracy of anaytical techniques but when up to date instrumentation is available, these differences are not significant. Much more important is the skill of the persons doing the work.

In Finland the laboratories are of high quality and there are not significant differences in accuracy between the laboratories.

The sensitivity is important. NAA in general is a very sensitive technique when chemical separations can be applied. But that is too expensive. INAA on the other hand is not especially sensitive for most elements. Some techniques are sensitive for other elements and some others for other ones. As a consequence the technique is chosen according to the problem at hand. For instance there are few techniques capable of detecting lanthanoids in their background concentrations. Therefore INAA is mainly used. The same stands for some of the platinum group metals. For most other elements at least a few different techniques are possible. Another thing is that some techniques are sensitive to concentration but they require a large sample. In INAA the sample size can be varied considerably without losing in sensitivity. To be able to analyze 40 elements from one 10 mg sample is important sometimes. Likewise it is sometimes important that the method is non destructive. In geology these features are needed so seldom that it is not a basis for an economical success of the technique.

Sometimes the multielement capability is mentioned as one of the advantages of INAA. Now there exist a number of other techniques possessing the same feature. And then this is really a feature which only affects the cost of the analysis. A single element method which is capable of ten single element determinations in a certain time is as good as a method which is capable of one ten element determination in the same time.

One of the real drawbacks of NAA is that it can be used only in a few places because a research reactor is needed. But when analytical service is discussed this does not apply because the customer always have to send their samples somewhere when they use outside laboratories.

The capacity is usually not a problem in itself. It is basically always a matter of cost. According to our calculations the irradiation capacity in the Reactor Laboratory using 35h irradiations, would be 90.000 samples per annum if the reactor were run in three shifts. Gamma spectrometers can be purchased according to need. The same effect could be arrived at with the current running schedule by decreasing the irradiation time and increase, the measurement time corresponding.

Table III gives examples of the cost of analytical service in Finland. It can be seen that single element (U) or difficult multielement (REE) NAA is expensive but so is single element analysis using other techniques (Au). Routine multielement analysis using NAA is competitive in price with any other technique.

Table III. Cost of analytical sevice of geological samples in Finland. Data from price lists of different companies.
DNAA: neutron activation analysis and delayed neutron counting
INAA: instrumental reactor neutron activation analysis.
ENAA: instrumental epithermal neutron activation analysis
XRF: wave dispersive X-ray fluorescence analysis.
AA: atomic absorption spectrophotometry. ICP -inductively coupled plasma emission spectrography. FAA - furnace atomic absorption spectrophotometry.

Method	cost of first sample $	cost of additional sample $	batch of 100 samples, cost per sample $	Elements determined	cost per element in batch of 100 samples $
DNAA	163	3.2	4.8	U	4.8
ENAA	124	16	17.1	24 elements	0.74
INAA	194	49	50.5	10 REE-elements	5.0
XRF	34	34	34	28 elements	1.2
AA/ICP	10.6	10.6	10.6	11 elements	0.96
FAA	10	10	10	Au	10

The NAA services most sold are DNAA of uranium, ENAA of 24 elements and the analysis of 10 lanthanoids. These three cases will be discussed in the following.

When the geochemical exploration of uranium started in Finland it immediately got considerable funding for field work. A number of samples were collected by the mining companies but they did not have a technique ready for low-cost sensitive uranium analysis. For XRF the detection limit is 10 ppm while a detection limit of 1 ppm or better was needed. The Reactor Laboratory was immediately ready to receive samples. Therefore the samples were sent to the Reactor Laboratory, instead of building up own capacity, which would have taken time. Probably the work could have been done in the laboratories of the mining companies by fluorescence, for a lower, or at least comparable cost. This was never done, but the number of analyzed samples decreased, because of a decrease in exploration for uranium in the country.

The situation was more or less the same when the geochemical exploration for gold started in a larger scale. The Reactor Laboratory could analyze gold with a detection limit of 3 ppb which was barely enough for geochemical exploration. Several geologists complained that a detection limit of 1 ppb would be needed. The capacity could be rapidly increased to thousands of samples annually. Therefore most of the mining companies and the Geological Survey sent these samples to the Research Laboratory. The cost per sample was quite high but a number of additional elements were obtained. Many of these elements were not really needed and the Geological Survey and some of the mining companies developed FAA techniques for the analysis of gold in their own laboratories. A detection limit below 1 ppb could be obtained. The Reactor Laboratory still gets all the samples from some companies, and the samples which exceed the capacity of the laboratories, from the Geological Survey and some other laboratories.

In Finland there still does not exist a competitive method for the analysis of lanthanoids. Therefore all the samples are sent to the Reactor Laboratory. Because this work is mainly related to basic research the number of samples is low, below 1000 annually. Therefore its economical significance for the Reactor Laboratory is only marginal.

During 1982-85 the annual number of analyzed samples was about 20.000 corresponding to 300.000 element determinations. The average annual income from analytical service was US$220.000. This covered the cost of the activity including development work. Now the trend is decreasing.

The present situation can be summarised as follows: Research groups not possessing their own laboratories still send their samples for NAA because the technique is better than other ones for uranium and lanthanoids. The ENAA analysis gives a better picture of the concentration of economically significant trace elements than any other single technique. But they also send the same samples for XRF and ICP-analysis. By combining these three techniques, a geochemical sample can be almost completely characterised as to its chemical composition.

Well equipped laboratories, on the other hand, have a number of different techniques available to them. For each element, there exist at least one non activation analysis technique which is at least as good as INAA. Therefore the Geological Survey and the big mining companies try to analyze their own samples, when they have capacity enough. In a time when the

laboratories were fully occupied with work, the introduction of new capacity and methods could be difficult and outside contractors were used. But now the mineral exploration is decreasing and the instruments and personnel has to be utilized even for work which could be more economically performed outside.

In order to survive the activation analysis has to be further developed. The selection of elements has to be increased to include new ones which cannot be easily analysed by other techniques and the cost has to be decreased. Currently a new completely automatic activation analyzer for short lived nuclides is being constructed. A central computer is also being connected with the automatic gamma spectrometers in order to obtain a centralized data handling, storage and reporting system. All this is done to further decrease the cost of the analysis but also to increase the number of different elements to be analyzed.

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DISCUSSION

F.F. Dyer. What is the counting efficiency of your He-3 neutron counting?

R. Rosenberg. It has not been measured but we get 100 counts per microgram U using our standard procedure.

SUMMARY AND CONCLUSIONS

Formal presentations at the AGM consisted of four main sessions:

1. Research Trends, Present and Future
2. Measurement systems
3. Tracers, and
4. Activation techniques.

This summary will address first the principal ideas developed at each of the above sessions. Information is drawn from comments at the end of each presentation, from the discussion that was held between individual session participants only, and from an open forum of all AGM delegates. As might be expected, several important observations cut across the thematic boundaries of a single session. When this occurred, the item is discussed where it seems most appropriate.

The development of analytical measurements science, in a country involves education and coordination. Such activities run the gamut from basic research on one extreme through applied research (task solving), development, production, and training. As nuclear and non-nuclear analytical technology reaches new levels of sophistication, it becomes increasingly more difficult to match critical measurement problems with the most appropriate analytical methodology. This is especially true in the developing nations where facilities, equipment, and trained manpower may be limited. Thus, complex issues must be resolved before decisions can be made. What are the country's special needs? Are these needs located in a university, industrial, or government laboratory environment? How sophisticated is the local scientific infra-structure? It is with these kinds of questions that a country must plan and operate its programs.

While nuclear techniques are clearly being challenged by other analytical methods, virtually all participants agree that they still play an important role in the arsenal of analytical chemical science. In many instances this role is seen as complimentary rather than competitive. For example, it was noted that nuclear methods, when used, were primarily associated with research studies rather than extensive, routine applications. Nuclear techniques can often provide advantages that simply cannot be realized

with competing procedures. Superior accuracy for trace element analysis or freedom from certain matrix effects are notable examples. On a fundamental level, however, the choice of a specific measurement method still depends on the special characteristics of the sample combined with the analytical criteria of the required results. Unfortunately, many of these basic criteria (e.g. sensitivity, limit of detection, elements of cost) are often confusing, especially when applied to different analytical methods.

A relatively new discipline, scientometrics, was discussed. The full potential of scientometrics is only now being recognized. Scientometrics can be used to indicate significant trends in research and may be able to differentiate between quality and quantity in publications and information flow. It may also suggest the way that analytical samples are effectively linked with appropriate analytical methods. But scientometric methods must still be combined with other rating techniques such as peer review and expert adjudication to achieve a valid, broadly-based evaluation. Regardless of the tactics used, all such appraisals are best carried out using rigorous definitions for the figures of merit and the economics of the techniques being considered. Only if this is done can inter-method comparisons be made successfully. As noted above, however, existing definitions are often poorly developed and frequently cannot serve as an effective basis of method selection. Clearly, the creation of precise criteria for analytical methods appraisal is needed. Chemometrics, another advanced concept, may offer new and different insights for the study of analytical methods research.

A significant trend in the evolution of analytical measurement systems is the use of micro computers (PC's) as the major component of instrument control. Previously, small computers were used primarily for data collection and reduction and were often dedicated to a specific measurement application. Now, however, many special plug-in "boards" are being manufactured for personal computers that allow the unit to be configured into many different instruments via software control. In effect, the computer becomes the instrument. Some commercially available boards already provide functions for a multi-channel analyzer, an optical spectrum analyzer, digital and analog oscilloscopes, and multi-purpose input/output control. Thus, a personal computer, using selected software, can be quickly re-configured into virtually any type of analytical instrumentation that might be needed. One decisive advantage to the use of such boards is greatly reduced cost, especially in multipurpose applications. In the very near future, it is

probable that PC instruments will form the backbone of many measurement devices that are now supplied commercially as hard-wired units.

Tracer techniques represent a very useful area of nuclear analytical chemistry. Isotope dilution analysis, with the aid of both active and stable isotopes, and immunoassay techniques are perhaps the most important. Isotope dilution analysis can be used with biological and geological materials, water, soils, semiconductors, etc. Often the detection limits equal or exceed that of other techniques while selectivity is fair to excellent. The principal and decisive advantage of isotope dilution is the possibility of using non-quantitative isolating procedures so that in some instances, it is the only analytical method that can be used to solve the problem.

Owing to simplicity, sensitivity, and selectivity, immunoassay methods are becoming a major approach to the solution of many analytical problems. These techniques, though usually associated with clinical applications, are finding new uses outside this area. In the near future, the extension of immunoassays is expected in nephrology and in the field of prophylaxis and control of cancer treatment.

Until now, the reactions of isotope exchange have been used primarily for research studies of chemical system dynamics. Reaction mechanisms, kinetics, complex formation, and ionic and molecular mobility have all been addressed. Exchange methods are also used for radiochemical isolation of materials and for the determination of micro quantities of elements. Mass spectrometry is another versatile and powerful technique capable of being employed for both organic and inorganic problems in a variety of contexts. Although the formal presentation emphasized safeguards applications, it is equally useful in the environmental, nutritional, and materials science areas. It is, however, equipment intensive and requires very capable technicians.

Future development of tracer techniques include the design of new and more effective reagents for isotope dilution and immunoassay, development of novel separation procedures, fashioning of techniques for the simultaneous determination of two or more analytes, and automation of the processes for routine analyses. Radiotracer techniques are extremely useful in both the developed and developing countries because of their simplicity, low instrumentation costs, and relatively short analysis time. Also, the

precision and accuracy of these methods compares favorably with other analytical techniques.

Activation analysis is a major nuclear technique that has significant advantages and recognized limitations. Accuracy, matrix independence, little or no sample preparation, multi- element capability, sensitivity, and reliability are key benefits. A critical constraint to broader application, however, is the necessity for access to a reactor; these facilities are often sparsely distributed or non-existent in many countries. Another disadvantage of the technique is that a variety of radioactive materials are generated; this leads to the associated problems of waste handling and disposal as well as other concerns of public health.

The cost of activation methods is widely perceived to be higher than competing methods. For large-scale analytical projects this need not be true, especially if the measurement procedure is properly scaled to the precision required in the use of the data. Commercial activation analysis software has been available for less than a decade, and even now, an integrated package for irradiation, counting, and data reduction is not readily available. Costs for equipment are dropping, however. For the price of a simple multichannel pulse-height analyzer of a few years ago, we can now obtain one with better performance and interfaced to a computer for data handling (see above). The price/performance ratio of germanium detectors is also going down.

Modern methods of instrumental analysis frequently require major support functions such as liquid nitrogen, specialty gases, air conditioning, and technical and maintenance staff. Activation analysis is no exception and, for this reason, it may be best to concentrate new, sophisticated analytical installations at national nuclear centers or other locations where this support structure is already well developed. Modern activation analysis equipment can be added to an existing reactor for a comparatively modest cost. This may be justified if the demand for analysis is high. Other approaches, such as the use of neutron generators, particle accelerators, and photon sources can be employed when special analytical requirements exist.

As noted above, the selection of an analytical method is strongly influenced by the type of sample being studied and the characteristics of the required results. Powerful optical techniques like ICP-ES can often be employed where activation methods were once used. Such methods are clearly

indicated when no reactor neutron source is available. However, activation analysis is still perceived as holding a commanding position when sensitive, reliable, and multi-element response is needed. Thus, for some applications, travel to a reactor activation facility may be both appropriate and cost effective when one is not locally accessible.

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