03 MAR 1993

TECHNICAL REPORTS SERIES No. 341

Analytical Techniques in Uranium Exploration and Ore Processing

INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1992

ANALYTICAL TECHNIQUES IN URANIUM EXPLORATION AND ORE PROCESSING

The following States are Members of the International Atomic Energy Agency:

AFGHANISTAN
ALBANIA
ALGERIA
ARGENTINA
AUSTRALIA
AUSTRIA
BANGLADESH
BELARUS
BELGIUM
BOLIVIA
BRAZIL
BULGARIA
CAMBODIA
CAMEROON
CANADA
CHILE
CHINA
COLOMBIA
COSTA RICA
COTE D'IVOIRE
CUBA
CYPRUS
CZECHOSLOVAKIA
DEMOCRATIC PEOPLE'S REPUBLIC OF KOREA
DENMARK
DOMINICAN REPUBLIC
ECUADOR
EGYPT
EL SALVADOR
ESTONIA
ETHIOPIA
FINLAND
FRANCE
GABON
GERMANY
GHANA
GREECE
GUATEMALA
HAITI
HOLY SEE
HUNGARY
ICELAND
INDIA
INDONESIA
IRAN, ISLAMIC REPUBLIC OF
IRAQ
IRELAND
ISRAEL
ITALY
JAMAICA
JAPAN
JORDAN
KENYA
KOREA, REPUBLIC OF
KUWAIT
LEBANON
LIBERIA
LIBYAN ARAB JAMAHIRIYA
LIECHTENSTEIN
LUXEMBOURG
MADAGASCAR
MALAYSIA
MALI
MAURITIUS
MEXICO
MONACO
MONGOLIA
MOROCCO
MYANMAR
NAMIBIA
NETHERLANDS
NEW ZEALAND
NICARAGUA
NIGER
NIGERIA
NORWAY
PAKISTAN
PANAMA
PARAGUAY
PERU
PHILIPPINES
POLAND
PORTUGAL
QATAR
ROMANIA
RUSSIAN FEDERATION
SAUDI ARABIA
SENEGAL
SIERRA LEONE
SINGAPORE
SLOVENIA
SOUTH AFRICA
SPAIN
SRI LANKA
SUDAN
SWEDEN
SWITZERLAND
SYRIAN ARAB REPUBLIC
THAILAND
TUNISIA
TURKEY
UGANDA
UKRAINE
UNITED ARAB EMIRATES
UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
UNITED REPUBLIC OF TANZANIA
UNITED STATES OF AMERICA
URUGUAY
VENEZUELA
VIET NAM
YUGOSLAVIA
ZAIRE
ZAMBIA
ZIMBABWE

The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world".

© IAEA, 1992

Permission to reproduce or translate the information contained in this publication may be obtained by writing to the International Atomic Energy Agency, Wagramerstrasse 5, P.O. Box 100, A-1400 Vienna, Austria.

Printed by the IAEA in Austria
December 1992

TECHNICAL REPORTS SERIES No. 341

ANALYTICAL TECHNIQUES IN URANIUM EXPLORATION AND ORE PROCESSING

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 1992

VIC Library Cataloguing in Publication Data

Analytical techniques in uranium exploration and ore processing. — Vienna :
International Atomic Energy Agency, 1992.
p. ; 24 cm. — (Technical reports series, ISSN 0074-1914 ; 341)
STI/DOC/10/341
ISBN 92-0-103792-9
Includes bibliographical references.

1. Uranium ores—Analysis. 2. Chemistry, Analytic—Technique. I. International Atomic Energy Agency. II. Series: Technical reports series (International Atomic Energy Agency) ; 341.

VICL 92-00048

FOREWORD

The Manual was prepared as part of a programme of the International Atomic Energy Agency to publish instruction manuals on a wide range of practical topics. Its purpose is to assist in the establishment of an analytical laboratory able to perform all the basic chemical and instrumental analyses commonly used in conjunction with uranium exploration and mining and ore processing activities, including the development of hydrometallurgical processes. It is intended for chemists with a general background in analytical chemistry, but with limited experience in the analytical chemistry of uranium and of related elements.

The Manual is divided in two parts. The first deals with the general aspects of laboratory design and operation and the second contains descriptions of 17 selected analytical methods that have generally been accepted in the international uranium industry. Other methods which may produce comparable results using more sophisticated, modern or efficient techniques have not been included, but are referred to in the general references. Also not included are those analytical methods which are widely used in the chemical industry and which may be found in readily available analytical chemistry manuals.

The Manual is based, in part, on techniques developed throughout the analytical community worldwide and, in particular, in the Grand Junction Laboratory of the United States Department of Energy (Grand Junction, Colorado) and at the Canada Centre for Mineral and Energy Technology (Ottawa, Ontario).

The Agency wishes to thank the Consultants who took part in the preparation of the Manual. They included R. Chessmore, United States Department of Energy, Grand Junction, Colorado, USA; J.L. Dalton, Canada Centre for Mineral and Energy Technology (CANMET), Energy Mines and Resources Canada, Ottawa, Ontario, Canada; and O. Suschny (retired), former head of the Analytical Chemistry Section of the IAEA Laboratory at Seibersdorf, Austria. Their valuable contributions, and those of their colleagues and associates, form the substance of the Manual. The Agency staff members responsible for the project were S. Ajuria and A.Y. Smith of the Division of Nuclear Fuel Cycle and Waste Management.

EDITORIAL NOTE

The Manual has been edited by the editorial staff of the IAEA to the extent considered necessary for the reader's assistance. The views expressed remain, however, the responsibility of the named contributors. In addition, the views are not necessarily those of the governments of the nominating Member States or of the nominating organizations.

The use of particular designations of countries or territories does not imply any judgement by the publisher, the IAEA, as to the legal status of such countries or territories, of their authorities and institutions or of the delimitation of their boundaries.

The mention of names of specific companies or products (whether or not indicated as registered) does not imply any intention to infringe proprietary rights, nor should it be construed as an endorsement or recommendation on the part of the IAEA.

The contributors are responsible for having obtained the necessary permission for the IAEA to reproduce, translate or use material from sources already protected by copyrights.

CONTENTS

PART I. GENERAL ASPECTS OF LABORATORY OPERATION

PART II. ANALYTICAL METHODS

INTRODUCTION

The role of the analytical chemistry laboratory is, simply stated, to provide analytical support both to uranium exploration and to uranium ore processing activities. While it is recognized that providing analytical support to either exploration or ore processing programmes requires skill and discipline, support for both increases the difficulties. The two activities might be submitting analytical input simultaneously, with varying demands and priorities. These workloads may often be in conflict, imposing stringent demands upon laboratory management. For this reason, it is imperative that there is continuous communication between exploration, mine/mill and analytical laboratory management in order to achieve the objectives of the organization, to locate and process the uranium ore, and to produce a uranium ore concentrate that is acceptable to a uranium ore refinery.

A practical and useful arrangement for establishing continuous communication between the three groups is to include laboratory management as part of exploration and mine/mill management. The requirements of each group are presented, thus providing an opportunity for formulating mutually agreed upon assignments and responsibilities. It is much better to have the analytical management working with the other two management groups than to have the former serving in a strictly service role. Experience has shown that input from analytical staff on the analytical workload can ultimately reduce costs and, at the same time, provide efficient and timely support with the specified accuracy and precision.

A significant aspect of the management agreements is to formulate the quality assurance/quality control (QA/QC) programme. The issues to be resolved by management include the definition and specification of accuracy and precision; the scope of the additional workload caused by the imposition of control samples; and the manner in which these samples are incorporated into the workload. Documentation of QA/QC procedures and results is also an important function. The three management teams should not operate independent and isolated control programmes, since this only increases the costs and disrupts the normal work flow, without any benefit. Agreed upon protocols should provide analytical results that meet all the requirements.

In addition to the major role of providing analytical results on samples that originate from exploration and/or production, analytical laboratory management has to deal with government regulatory agencies concerned with atomic energy, the transport of dangerous materials, the health of laboratory and possibly other workers in a uranium mine/mill complex, the environment, etc.

Analytical laboratory management has to ensure that the laboratory is operated in a safe, efficient and modern manner, and to demonstrate leadership in order that the staff is motivated to excel in its performance. Continuous on the job and formal training should play an important role in such management, including visits to operating mine and mill laboratories. Attendance at appropriate conferences, seminars and workshops, as well as membership in technical organizations, should also be encouraged.

The Manual is divided into two parts. Part I provides general discussions on uranium exploration, uranium ore processing, the analytical chemistry of uranium, establishment of a uranium analytical laboratory, sample preparation, calibration and quality control, and use of statistical methods in analytical chemistry. Part II describes 17 analytical methods of importance in the uranium industry. The first two are aimed at uranium exploration, while the others are essential to uranium ore processing. While the methods for uranium itself are covered quite extensively, those for other elements associated with uranium are not. Many of these are well known to analytical chemists and can readily be found in the literature. The aim throughout has been to present the methods in a clear and concise manner. References are provided after each method so that the reader can refer to original publications. Appendix 1 lists the techniques used for uranium determination and for those other than uranium, while the important question of laboratory safety is reviewed briefly in Appendix 2.

Part I

GENERAL ASPECTS OF LABORATORY OPERATION

Chapter 1

URANIUM EXPLORATION[1]

1-1. INTRODUCTION

The process of exploration for uranium deposits follows a number of steps or phases, with the overall objective of greatly increasing the chances of discovering an economic deposit at the least possible cost. Each phase has its clearly defined and understood objective; each has particular requirements as to the methods to be used and their cost-benefit; and each phase terminates with a decision to continue to the next phase at increasing cost or to terminate the project.

The phases of a modern exploration programme are: (1) area selection; (2) reconnaissance; (3) follow-up; and (4) detailed. During each phase, a process of selection and elimination is carried out with the aim of eliminating from further consideration those areas of little or no potential, while focusing attention on those areas of greatly increased potential. The regions selected during each phase become the areas of study during the succeeding phase. At the completion of the detailed phase, the prospects found become the subject of a completely different process, that of deposit development. The various exploration phases are discussed briefly in the following sections.

1-1.1. Area selection

Area selection is the beginning of any phased exploration programme. Starting with a region of perhaps 100 000 km^2, mainly desk studies are made in an attempt to define those parts of the region with the greatest uranium favourability. These studies are carried out by a senior, experienced uranium geologist. They entail compilation of all the available geological favourability information, photogeological studies and rapid field visits to examine the geology, radioactivity and general regional uranium distribution by means of uranium geochemical analyses of the samples collected. During these visits, the geologist has to examine the terrain and surficial environment in order to select those exploration methods most suitable for the programme. Regional data are normally compiled on maps of a 1:250 000 or 1:500 000 scale.

Depending on the size of the region studied, area selection may take 1–2 years, at a cost of perhaps US \$1–2/km^2. In the course of such studies, perhaps 70–80%

---

[1] Contributed by A.Y. Smith, Division of Nuclear Fuel Cycle and Waste Management, IAEA.

of the region is eliminated from further consideration, leaving one or more areas totalling perhaps 20 000–30 000 km^2 to be examined in the next, or reconnaissance, phase. National organizations carrying out the early phases of exploration may decide that the geological environment of the region is favourable for commodities other than uranium and select a larger proportion of the region for multi-commodity resource evaluation studies.

1–1.2. Reconnaissance phase

The objective of the reconnaissance phase is *to locate areas of interest* in the regions selected for exploration. Several exploration methods may be considered during the reconnaissance phase, and either used singly or in combination. Airborne radiometric surveys with a line spacing of up to 5 km are used frequently in this phase. In suitable environments, geochemical surveys may offer advantages in terms of simplicity and the increased amounts of data returned. In these cases, sample densities of one sample per 1–5 km^2 are common. Determination of radon in surface or subsurface waters or radon in soil–air has, on occasion, been used effectively. In reconnaissance surveys, however, radon methods would not be used alone but in combination with other geochemical and radiometric methods. Data from reconnaissance surveys are usually plotted at a scale of 1:100 000 to 1:250 000.

Usually, the reconnaissance programme eliminates more than 80% of the area surveyed. The costs for reconnaissance level surveys are generally of the order of US $15–50/km^2, depending on the difficulty of the terrain and the methods employed. The areas of interest or the *reconnaissance anomalies* outlined during the reconnaissance programme are the targets for study in the succeeding, follow-up phase.

1–1.3. Follow-up phase

The objective of the follow-up phase is *to locate exactly on the ground the extent of anomalies in the areas of interest.* This objective is achieved by resampling the areas of interest at a greatly increased sample density. Normally, densities of 10–20 samples/km^2 are used. It is customary to sample the same material as that used in the reconnaissance phase. However, where stream sediment or water was used, bank soils may also be sampled. Radioactivity measurements made at the same time provide valuable information at little extra cost. Radon measurements of waters or soil–air are frequently valuable and, if a sufficient number of springs can be found, the radon content of groundwaters should be measured. The occasion may be taken to improve geological mapping, but this should be done with the least possible delay in sampling. In most cases, the very high cost of good geological mapping precludes its extensive use at this stage. The results of the follow-up programme are reported at a scale of 1:25 000 or 1:10 000.

The follow-up programme may eliminate as much as 90% of an area of interest, outlining anomalies of a few to perhaps 10 km^2 in extent. Frequently, these may show strong directional trends, pointing to possible lithological or structural controls. The costs for follow-up surveys can be of the order of US $75–200/km^2. The follow-up anomalies outlined in this phase are the subjects of study during the succeeding, detailed phase.

1–1.4. Detailed phase

The objective of the detailed phase is *to distinguish between anomalies due to potentially economic mineralization and those due to uneconomic mineralization or other causes.* It is in this phase that direct indications of a mineral deposit are located and tested. A wide selection of exploration methods are used: radiometric prospecting, detailed geochemical surveys, detailed geological mapping, trenching, core and/or rotary drilling with radiometric logging, etc. Radon measurement of soil–air, along with soil sampling for uranium and/or radium determination, are used frequently. Bedrock sampling, including sampling and analysis of core or cuttings for uranium analysis, should also be considered.

It is clear that a high density of sampling and measurement is required in the detailed phase, perhaps as much as 2500/km^2. For this reason, it is difficult to put a cost figure on this phase. Several methods are employed in order to define and characterize the prospect more precisely. Each method has its own cost and benefit. Normally, the data developed during the detailed phase are compiled on maps at a scale of 1:500 or 1:1000.

The detailed phase, and the exploration programme in general, may be said to terminate with the achievement of ore grade intersections in surface trenches and/or in the subsurface drilling programme.

1–1.5. Deposit development

Proving of the deposit is duly the work of the development programme, and requires methods of mineralogy, structural geology, sampling, ore test work and ore reserve estimation that are different from, and much more costly than, those of the exploration programme. Extensive sampling of the surface trenches, drill core and/or cuttings, underground openings and water sources has to be done. Many of the samples are large bulk samples which have to be collected and prepared with care. Attention has to be paid to the correct procedures of sampling and subsampling so that the results obtained are of the correct economic significance.

Economic considerations play a large role throughout the development programme. At any point in the programme the results obtained may indicate that the deposit cannot be exploited economically. The validity of these conclusions depends on the quality of the work. It should not be forgotten that a deposit is only an *ore* deposit when the development programme has proved the existence of a concentration of ore minerals which can be mined, processed and sold at a profit. Errors made during the development programme can lead to financial disaster.

1-2. ANALYTICAL REQUIREMENTS FOR URANIUM EXPLORATION

During the course of uranium exploration several, rather different, analytical requirements are in evidence. These needs change as the programme progresses through the various phases outlined above. The laboratory called upon to support the analytical needs of an exploration programme should be aware of the particular requirements of each phase, of the number and type of samples to be expected and of the elements required. These matters require full discussion with the exploration geologist responsible for the execution of the project.

Most analyses carried out during the exploration programme, up to the later stages of the detailed phase, are of the geochemical type. A geochemical analysis is rapid, using a method capable of large throughput at low unit cost. In addition, geochemical methods should be capable of dealing with a wide range of element concentrations in a wide range of natural sample materials with varying and complex matrices, including soils, stream sediments, rocks, waters and biological materials. Most geochemical methods make use of partial rather than total sample attack because of the important geochemical information accumulated from the way in which an element is bound in a sample. Uranium, for example, is frequently determined after extraction of the sample with hot 4N HNO_3, because total dissolution of the sample liberates the uranium (held in the resistate phases) that has no bearing on the ore forming processes and may obscure evidence of the presence of those processes. The same applies to other ore elements. For this reason, instrumental methods such as delayed neutron counting, which determines the total concentration of uranium, may be less desirable. Therefore, geochemical methods are, for the most part, based on partial sample attack and rapid and simple determination methods.

Because of the use of partial dissolution of the sample, the concept of accuracy is seldom of relevance in geochemical analytical methods. Precision, on the other hand, is of great importance when the samples are to be analysed only once.

Steps should be taken to ensure that an acceptable level of precision is maintained. This is frequently done by introducing control samples into each batch. The assistance of the project geologist should be sought in establishing a satisfactory set of control samples. At the same time, the laboratory should be aware that the geologist may establish his own system of introducing blind controls into the sample batches he submits to the laboratory. The laboratory should not regard this antagonistically, but should understand and respect the geologist's need to provide results of adequate precision. Any deviation from satisfactory precision levels should be discussed with the laboratory and a solution sought. Basically, it is a question of the project geologist and the laboratory manager working co-operatively towards a common end — a successful exploration programme.

Many methods of geochemical analysis are available for a range of elements. It is difficult to specify the elements that may be of interest in a geochemical exploration programme. This depends on the geological environment and the mineral deposit potential of the region. A conservative list of elements applicable to many geological environments includes copper, lead, zinc, cobalt, nickel, mercury, manganese and, perhaps, arsenic and antimony. Of significance for the purpose of a uranium exploration programme is the determination of labile uranium by fluorimetry. The procedure given in Part II, Method 1, is simple, sensitive and, with care, provides an adequate level of precision. The solution prepared during the sample attack can be used for determining a range of other elements that may be of interest in geochemical survey programmes. It should be mentioned, however, that during exploration programmes uranium is its own best indicator. For the geochemical methods available for a range of elements, the reader is referred to Ref. [1].

Chapter 2

ANALYTICAL REQUIREMENTS IN URANIUM ORE PROCESSING AND PROCESS DEVELOPMENT[2]

2-1. INTRODUCTION

Analytical chemistry plays an essential role in the development of hydrometallurgical processes for the production of uranium concentrates, from initial laboratory studies, to bench scale studies and piloting, to the industrial operation of uranium mills. This chapter reviews the basic aspects of uranium extraction technology and outlines the analytical requirements, both for process development and the operation of a plant to produce uranium ore concentrates.

2-2. URANIUM EXTRACTION TECHNOLOGY

Extraction of uranium from its ores generally involves the following unit operations (Fig. I-1):

(1) *Size reduction:* The ore is crushed and ground to provide a suitable range of particle sizes required for effective leaching and to produce a material that can be slurried and pumped through the processing circuits

(2) *Leaching:* Uranium is leached from the ground ore using either acid or alkaline (carbonate) solutions with or without heating and with or without the addition of oxidants

(3) *Solid-liquid separation and washing:* The pregnant liquor is separated from the leached ore, which is then washed to remove any remaining dissolved uranium

(4) *Purification and concentration:* The pregnant liquor contains a low concentration of uranium (usually of the order of 1 g/L) and many impurities; it must, therefore, be concentrated and purified using either ion exchange resins or solvent extraction, or both

(5) *Precipitation and solid-liquid separation:* A uranium concentrate (yellow cake) is precipitated from the pregnant solution in one or two stages using a common base; the product is either filtered or dewatered by settling and centrifugation

---

[2] Contributed by S. Ajuria, Division of Nuclear Fuel Cycle and Waste Management, IAEA.

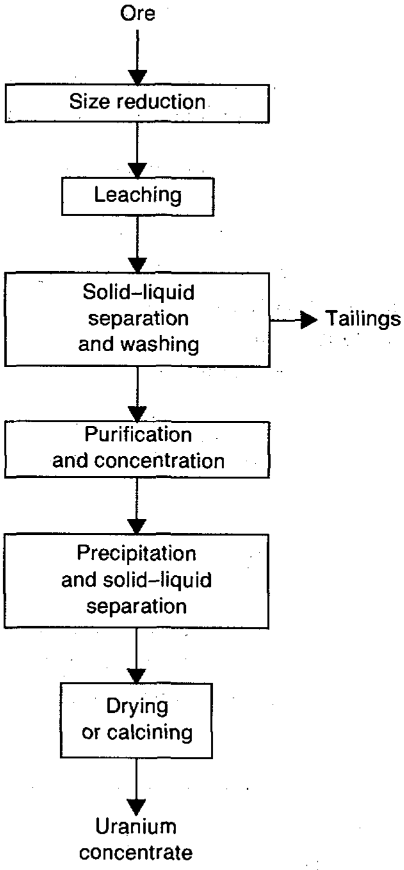

FIG. I-1. Generalized process for uranium extraction.

(6) *Drying or calcining:* The concentrate is dried or calcined and packed in steel drums lined with polyethylene

(7) *Tailings disposal:* The process should also include adequate provision for treating and impounding the tailings and for recovering and recycling some, or most, of the water used.

These unit operations are combined to constitute actual industrial processes.

Several recent articles [2, 3] and monographs [4–7] on uranium extraction technology are available and can be consulted. A detailed discussion of this topic is outside the scope of this Manual.

2-3. URANIUM EXTRACTION DEVELOPMENT PROJECTS

A project for a uranium ore processing plant, after a promising ore deposit has been discovered, can be considered to include the following main phases:

(1) *Pre-investment phase:* Order of magnitude studies; preliminary feasibility studies; preliminary evaluation and decision to continue; licensing (preliminary); final feasibility study; and final evaluation and investment decision.
(2) *Investment (implementation) phase:* Detailed engineering; procurement and construction; licensing (final); and startup and commissioning.
(3) *Operational phase:* Operation.
(4) *Post-operational phase:* Decommissioning.

These phases of development are not strictly sequential; they usually overlap (see Fig. I-2). The main phases are described in greater detail in the following sections.

2-3.1. Order of magnitude studies

On the basis of preliminary drilling, rough estimates of the ore body's grade and tonnage are prepared. One, or several, mining methods are tentatively selected and evaluated. Mineralogical examinations and preliminary laboratory tests are made

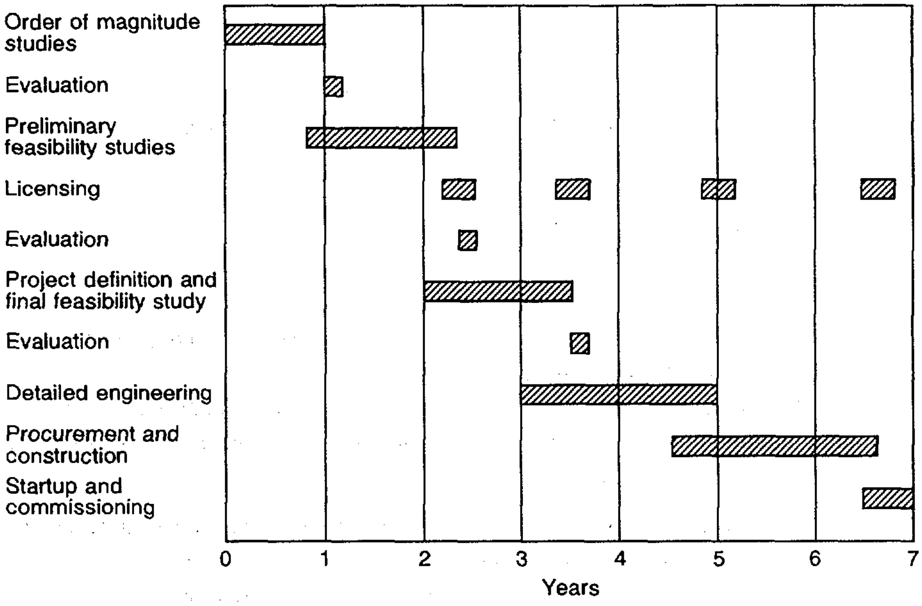

FIG. I-2. Project development phases.

using core samples, or any other samples that may be available. These tests are performed with the primary purpose of assessing the technical and economic feasibility of processing the ore. From the results of these tests, tentative process flow sheets are prepared. Order of magnitude estimates of the capital and operating costs are prepared, largely based on the published cost data and the costs of similar existing equipment and plants.

2-3.2. Preliminary feasibility studies

The ore body is extensively drilled to establish its type, morphology (in three dimensions), size (also in three dimensions) and degree of homogeneity. The mean ore grade and the ore reserves are calculated. The mining methods are proposed and evaluated. The mine's production rate and the expected mine life are estimated. Detailed mineralogical studies and bench scale metallurgical tests are performed using representative samples with the primary purpose of selecting and defining a suitable metallurgical process. The size of the plant is tentatively selected and complete flow sheets and material and energy balances are prepared. All this information is then used to prepare new estimates of the capital and operating costs, which are expected to be accurate to within ±20%.

2-3.3. Licensing

Licensing of uranium mines and mills is required in most countries and has become an important phase in the development of a project. In general terms, it is necessary to demonstrate that appropriate measures are being, or will be, taken to minimize the environmental impact of the mine and mill and to protect the health of the workers and the public within the limitations of currently available technology and reasonable costs.

2-3.4. Preliminary project evaluation

At this point, sufficient information should be available to make a preliminary economic evaluation of the project, i.e. to make an estimate of the costs and benefits associated with the project. The project should proceed only if a positive net benefit can be assured.

2-3.5. Final feasibility study

The suitable mining methods are developed and the mining equipment is selected. The process flow sheet is prepared from pilot plant studies. The overall objective of the pilot plant is to ensure that the decision to proceed with the full scale project is based on a proven process and on a reliable economic evaluation.

The definitive flow sheet, with the corresponding material and energy balances, is then prepared. A site for the plant and the tailings dam or dams is selected and a general study is made of the site and the infrastructure needed to support the mine and mill. Definitive estimates of the capital and operating costs, accurate to within ±10%, are prepared. The project can then be submitted for evaluation and approval.

2–3.6. Final evaluation and decision to invest

Final evaluation of the project can now be made, using generally accepted financial criteria, and the decision to invest can be taken.

2–3.7. Detailed engineering

On the basis of the conceptual and preliminary engineering designs previously prepared, the final engineering design of all the plant equipment and facilities can be completed. Orders can be placed for all the equipment and instrumentation required in the mine/mill complex and a contractor selected for the construction.

2–3.8. Startup and commissioning

All the equipment and the piping, electrical, materials handling and control systems are checked and any problems corrected. The plant is started, operating first at a reduced capacity and, finally, at full rate. Custody and control of the plant are transferred from the contractor to the operator.

2–4. ANALYTICAL REQUIREMENTS FOR PROCESS DEVELOPMENT AND PLANT OPERATION

Chemical and instrumental analyses are essential to guide the development of metallurgical processes, to monitor and control such processes during the industrial operation of a uranium mill and to ensure that the product meets the specifications. It is necessary to analyse the ores, process water, reagents, process solutions, including the aqueous phases (leach solutions, leach liquors, pregnant liquors, barren liquors) and the organic phases (barren organics, loaded organics, organics in raffinates), process solids (leach residues, precipitates, filter cakes, etc.), uranium concentrates, other by-products or co-products and tailings.

These analyses are needed during the various stages of developing a suitable hydrometallurgical process (both at the bench and the pilot plant scale) and during operation of an industrial plant on a continuing basis. Many of the analytical methods required are standard methods used widely in the chemical industry and can readily

TABLE I-I. TYPICAL SPECIFICATIONS FOR URANIUM CONCENTRATES
(Minimum U_3O_8 content, with a partial size of 65 wt%)

Maximum impurities permissible (expressed as weight per cent based on the U_3O_8 content)	
Na	7.5
H_2O	5.0
SO_4	3.5
K	3.0
Th	2.0
Fe	1.0
Ca	1.0
Si	1.0
CO_3^{--}	0.5
Mg	0.5
Zr	0.5
PO_4^{--}	0.35
Halogens (Cl, Br and I)	0.25
V_2O_5	0.23
Rare earths	0.2
P	0.15
Mo	0.15
As	0.1
B	0.1
Extractable organic matter	0.1
Insoluble uranium	0.1
Ti	0.05
^{226}Ra	740 Bq/g (20 000 pCi/g)
Particle size	6.35 mm (1/4 in.)

Note: Only natural uranium concentrates (non-irradiated material) containing 0.711 wt% of the iosotpe ^{235}U are acceptable.

be found in the literature. Other methods more specific to the uranium industry are described in detail in Part II of this Manual.

The frequency and precision of the analyses usually differ during the various stages of development, as do the preferred analytical methods (see Table I-I).

The analytical laboratory that provides support for a uranium project should be capable of performing all the analyses required, both routinely and occasionally. Those analyses that are required at infrequent intervals and are common in the chemical industry can be done by commercial laboratories, bearing in mind that contracting out analytical work requires its own quality control programme.

2–4.1. Ores

Analyses should be made of the ore that is being fed to the process (heads) and the barren solid residues (tails). Ore samples should be identified properly, indicating the nature of the ore, the place of origin, the analyses that have to be made and, if possible, an estimate of the result (or results) expected.

At the outset it is convenient to have an indication of the overall chemical composition of the ore sample. Any of several multielement techniques, such as emission spectroscopy, X ray fluorescence or inductively coupled plasma optical emission spectroscopy, can be used for this purpose. These techniques can provide, in a short time and at low cost, semi-quantitative determination of the elements that are present in the ore.

On the basis of preliminary analyses, further determinations of greater accuracy and precision are required for the elements of main interest.

2–4.2. Process water

Usually, the following analyses are done for the quality control of process water: the pH, conductivity, total hardness, alkalinity by direct titration, turbidity, total solids, dissolved solids and suspended solids, silica, total iron, ferrous iron, phosphate, dissolved oxygen and organic matter.

Frequent water analyses need not be made; once a month is sufficient, or when there is reason to believe that changes have occurred in the composition of the water being used.

2–4.3. Reagents

The reagents required for the production of uranium concentrates must meet certain specifications to ensure proper operation of the plant and the quality of the product. Usually, one can rely on the analyses provided by the manufacturer, but it may be necessary to analyse the reagents in case problems arise with the process. While it is convenient to make in-house analyses, such capability is not an essential requirement. In some cases, it may be more practical to have the analyses done by a commercial laboratory.

Some of the reagents commonly used in uranium ore processing are:

(1) *For leaching:* Sulphuric acid, sodium carbonate, sodium bicarbonate, manganese dioxide, Sodium chlorate, hydrogen peroxide and oxygen.
(2) *For solvent extraction:* Quaternary amines, kerosene and decyl alcohol.
(3) *For ion exchange:* Ion exchange resins and sodium chloride.
(4) *For precipitation:* Ammonium hydroxide, sodium hydroxide, magnesium hydroxide and hydrogen peroxide.
(5) *For neutralization of effluents:* Lime.

2–4.4. Process solutions

Analyses should be made of all the process solutions, both aqueous and organic, including:

(1) *Aqueous phases:* Leaching solutions, leaching liquors, pregnant liquors, washing solutions (for solvent extraction organic phases), raffinates, regenerating solutions (for ion exchange resins); eluates and barren liquors.
(2) *Organic phases* (if the process uses solvent extraction): Barren organics, loaded organics, organics in raffinates and mine/mill effluents.

These solutions should be analysed for uranium, manganese, ferrous and ferric iron, sulphate, chloride, fluoride, ammonia, carbonate, barium and other dissolved solids (such as zirconium, molybdenum and vanadium). The main physicochemical characteristics of the solutions, such as the pH, free acidity, oxidation reduction potential and quantity of suspended solids, should also be determined.

For the organic solutions used in solvent extraction, it is important to establish, and regularly monitor, their composition.

2–4.5. Process solids

Process solids should also be analysed. These include: leaching residues, uranium precipitates, filter cakes from solid–liquid separation after leaching, ion exchange resins (when required), solid phases from the solvent extraction operation, uranium concentrate filter cakes from solid–liquid separation after precipitation and dried or calcined uranium concentrates.

2–4.6. Uranium concentrates

The specifications for uranium concentrates are quite stringent. To ascertain whether the specifications are being met, the concentrates should be analysed for total uranium, and many other analytes, as shown in Table I-I. These analyses are of particular importance because they are used as the basis for accepting or rejecting a concentrate lot and for establishing the actual price to be paid for the uranium.

2–4.7. By-products or co-products

By-products or co-products (such as gold, silver, molybdenum, vanadium and copper) should also be analysed to ensure that they meet any applicable specifications. Care should be taken to ensure that the by-products are free of radionuclides.

2–4.8. Tailings

Analyses of tails are required for two main purposes: for process control (metallurgical accounting) and for environmental control, both of which require multielement analyses.

Chapter 3

ANALYTICAL CHEMISTRY OF URANIUM[3]

3-1. PROPERTIES OF URANIUM COMPOUNDS

The analytical chemistry of uranium [8] is unusually complicated but interesting. This is due to the particular and extreme position that uranium occupies in the Periodic Table of the elements. With an atomic number of $Z = 92$, it is the heaviest naturally occurring element. Like all elements beyond bismuth ($Z = 83$), it is radioactive and, moreover, fissionable. It has three natural isotopes, namely, ^{234}U, ^{235}U and ^{238}U, which have natural abundances of 0.0054, 0.71 and 99.28%, respectively (these may vary somewhat).

Chemically, according to older literature, uranium belongs to Group VI of the Periodic Table, following chromium, molybdenum and tungsten, and, in some respects, it behaves accordingly. In most reactions, however, the element proves to be a member of the actinide series, which comprises the elements from 90 to 103 in which the inner 5f electron shell is being filled and which in its properties parallels the rare earth (lanthanide) series. The gaseous uranium atom has an electron configuration of $5f^3 6d 7s^2$ (with the inner shells being complete, as for radon) and the 5f electrons are involved in the bonding.

Uranium metal is shiny, silvery, ductile and slightly paramagnetic. Its melting point is 1132°C and its boiling point close to 3820°C. Chemically, metallic uranium is highly reactive: when exposed to air it soon becomes coated with a black oxide film. Finely divided uranium metal is pyrophoric. Uranium dissolves in acids upon moderate heating and reacts with water at 100°C. Uranium halides may be formed by reaction with halogens at temperatures between 250°C and 650°C. Formation of carbides requires somewhat higher temperatures.

The prevalent state of uranium in solution is U(VI), which is the only stable state in contact with air; however, U(III) and U(IV) are also relatively stable. U(V), although known, disproportionates in solution to U(IV) + U(VI). The oxides and hydroxides of uranium are unstable. The stable oxidic form is U_3O_8, a mixed oxide into which all the other oxides are transformed upon heating. Such other oxides are UO, UO_2, U_2O_5 and UO_3. A peroxide, $UO_4.2H_2O_2$ (or $UO_2.2H_2O_2$), is also known.

The co-ordination number of uranium is 8; in the frequently encountered uranyl ion UO_2^{++}, two of these positions are occupied by oxygen atoms, leaving six

---

[3] Contributed by O. Suschny (retired), Analytical Chemistry Section, IAEA Laboratory at Seibersdorf.

positions available. With many anions, particularly nitrate and chloride, strong anionic complexes are formed that extract into organic solvents (alkyl ketones, esters and ethers). This property, which is practically confined to the hexavalent species, is very useful in the separation of uranium from other elements in solution. U(VI) chelates of oxime, dibenzoylmethane or acetylacetone are also useful for this purpose, while U(IV) can be extracted as chelate of cupferron or thenoyltrifluoroacetone.

Many uranium salts exhibit strong fluorescence on irradiation with ultraviolet light.

3-2. ANALYTICAL METHODS FOR URANIUM

The properties described above are the basis for a large number of the techniques used for the recognition, separation and determination of uranium. Rather broad classification and evaluation of these techniques are made here, leaving details to other sections of the Manual.

3-2.1. Radiometry

For analytical purposes, one of the most useful properties of uranium and its daughter products is their radioactivity. It is made use of directly in uranium prospection, which can be carried out initially by aerial gamma ray surveying, followed by carborne or footborne gamma radiation measurements. The method is also very useful in the laboratory: alpha, beta or gamma radiation can be measured. Care has to be taken, however, to distinguish uranium from other naturally occurring radioactive elements such as thorium or potassium. In gamma radiation measurements, this can be done by selecting gamma spectra according to their energy [9–11], e.g. the 2.62 MeV photopeak of ^{208}Tl, which is a decay product in the thorium series, is particularly useful in recognizing (and correcting for) any thorium contribution to the count. Even in the absence of thorium or significant amounts of potassium (whose contribution to the spectrum is normally small, in spite of the high abundance of the element, because of its long half-life (1.28×10^9 years) but low abundance (0.012%) of its only radioactive isotope ^{40}K), the quantity of uranium in a prospection sample cannot easily be evaluated. The most prominent gamma lines upon which such an evaluation is normally based are not due to the uranium itself but to its decay products. Moreover, some are rather complex, carrying contributions from more than one nuclide. If the uranium in the sample is in equilibrium with all its daughter products, it does not matter that evaluation of its concentration is based on measurement of the radiation from a daughter element. If, however, a disequilibrium exists (and this is frequently the case due to weathering, which causes separation in the nature of the chemically different species), such evaluation requires knowledge of the degree of disequilibrium which can be obtained by measuring the ratio of low energy over high energy gamma radiation. This ratio is higher for uranium and its immediate daughters than for later products of the series such as radium. Quantitative methods exist in which the ratio is measured, compared with that of the reference materials of uranium ore at different degrees of equilibrium, and used for direct determination of the uranium in the sample [12]. To achieve adequate sensitivity for the measurement of samples containing only small quantities of uranium, the method uses a well type sodium iodide detector and not a germanium detector. In the absence of large amounts of thorium and for samples in which the daughter products are within 30–200% of equilibrium with uranium, a sensitivity of 20 ppm can be achieved with a 76.2 m × 76.2 m (3 in × 3 in) detector in a reasonable counting time.

3-2.2. Neutron activation analysis

A useful, accurate and sensitive method used for uranium is neutron activation analysis [13]. It can be carried out with any source of thermalized neutrons, but usually requires access to a reactor, since other sources do not produce an adequate neutron flux. When an atom of ^{238}U captures a neutron, it is converted into ^{239}U which, in turn, decays by beta emission, with a half-life of 23.5 minutes, to ^{239}Np

$$^{238}\mathrm{U(n,\gamma)}^{239}\mathrm{U}(\beta,\ 23.5\ \mathrm{min})^{239}\mathrm{Np}$$

In addition, some of the atoms of ^{235}U, present at a concentration of 0.71% of the total uranium, undergo fission, thereby creating a large spectrum of radioactive fission products

$$^{235}\mathrm{U(n,f)}\ \text{fission products}$$

Uranium-239, ^{239}Np (with a half-life of 2.36 days, decaying by beta emission to ^{239}Pu) or any of the more abundant fission products can be used to determine the quantity of uranium in the sample. This quantity can be calculated from the activation formula, but is more often evaluated by simultaneous activation and subsequent measurement of a suitable uranium reference sample.

3-2.3. Delayed neutron counting

Of greater importance for prospection samples is an activation technique in which 'delayed neutrons' are counted. These arise in the thermal neutron fission of ^{235}U in which neutron rich intermediate fission nuclei are generated; these boil off groups of neutrons with characteristic half-lives. The only element in nature which behaves similarly is thorium (^{232}Th) which, however, is fissioned only by fast neutrons. In addition, ^{17}N formed from oxygen by fast neutrons decays by neutron emission. In delayed neutron counting [14], a sample weighing, say, 1 g is transferred to the irradiation position in the reactor by means of a pneumatic tube system ('rabbit'), irradiated and transferred back into position in front of a neutron counter, where it is counted after some delay (to distinguish it from neutrons formed with shorter half-lives). The entire procedure takes a few minutes per sample and has a sensitivity of less than 1 ppm of uranium.

3–2.4. X ray fluorescence analysis

X ray fluorescence analysis depends on the interaction of the electrons in atoms with the X rays. When an electron from an inner shell around the nucleus is knocked out of the atom by an X ray, the gap is immediately filled by an electron from an outer shell, creating a new gap which, in turn, is filled from a higher shell, and so on. Connected to this movement of electrical charges inside the atom is the emission of fluorescent radiation, which is characteristic for the element and the electron shell concerned. The original X radiation may come from an X ray tube or may be produced by an isotope. In a wavelength dispersive X ray spectrometer, an analysing crystal is used to separate the X ray emission from the sample. X ray emission includes the tube radiation scattered by the sample as well as all the characteristic radiation emitted by the elements in the sample. Energy dispersive spectrometers make use of high purity radiation detectors that are capable of energy resolution. Wavelength dispersive systems are usually expensive because of the high precision required by the mechanical parts of the goniometer, whereas energy dispersive systems can be made less expensive.

The advantages of the X ray fluorescence technique include its capability for a rapid throughput of samples (measurement may only take a few minutes) and its versatility, which can be used to determine other elements besides uranium. With modern apparatus, the sensitivity approaches that of radiometric methods. One difficulty with the technique is its sensitivity to the composition of the sample matrix. Elements other than uranium in the sample may absorb some of the primary and the fluorescent radiation, thus causing a lowering of the signal (less frequently, elements may increase that radiation, causing enhancement). Uranium itself, when present in higher concentrations, also interferes, leading to non-linearity of the calibration curve. To a large extent, these interferences can be corrected for by internal calibration using admixtures or by measuring directly the change in primary radiation. Another interference may arise from differences in the grain size of the sample and the standard. Such interference can be controlled by proper grinding and sieving and, in any event, is small with finely ground materials.

3-2.5. Fluorometry

Fluorometry is one of the most important methods for determining uranium at parts per million or lower concentrations [15]. It is one of the oldest methods used and many variations have been developed over the course of time. Most methods rely on fusion of the separated uranium fraction of a sample with a flux consisting of a mixture of carbonates and fluorides. The most common fluxes are: (1) sodium carbonate, potassium carbonate and sodium fluoride (9%), with a melting point of about 450°C, or (2) sodium fluoride and lithium fluoride (2%), with a melting point of about 800°C. The method of Centanni [16], further developed by Pakalns [15], uses flux (2) after leaching the uranium from the soil or rock samples with nitric, hydrofluoric and perchloric acid and extraction of the uranium into methylisobutyl ketone in the presence of Ca-EDTA (to separate from the quenchers). The method of Smith and Lynch [17] uses flux (1) and relies on dilution to diminish the influence of the quenchers. Veselsky and Ratsimandresy [18] have developed a rapid method in which a small quantity of sample (a few hundred micrograms) is fused directly with flux (2) and quenching corrected for by remelting with an internal standard. More recently, a laser fluorometer has been developed that allows the analyst to avoid fusion. However, the fluorescent agent is based on phosphate and is destroyed by acid [19]. While the results for neutral water samples appear to be immediately satisfactory, acid leachates of soil, rock or sediment samples require great care and additional treatment to reduce the acidity.

3-2.6. Spectrophotometry

A spectrophotometric method is used frequently for accurate determination of uranium at concentrations of the order of a few to several thousand parts per million. Many such methods have been developed, some of which, for example, use of hydrogen peroxide to produce uranyl peroxide (with a molar absorptivity of up to 2000) or measurement of the thiocyanate complex (with a molar absorptivity of close to 4000), are only of historical interest and are no longer used.

As many elements interfere with spectrophotometric measurement, it is usually necessary to separate the uranium from the other elements in the sample solution. The classical extraction method for this purpose relies on a tetrapropylammonium nitratemethylisobutyl ketone acid deficient aluminium nitrate extraction system (the aluminium nitrate acts as a salting out reagent). Other methods use trioctylphosphine oxide (TOPO) or tributyl phosphate (TBP). Sometimes, ethylacetate or diethylether are used. Separations may be assisted by complexing agents such as EDTA or DTPA to hold back certain interfering elements. Alternatively, ion exchange methods have been used to achieve separation. A relatively old method, reported in 1955 by Kraus and Nelson [20], relies on the formation of anionic complexes of U(VI) in 4-6M hydrochloric acid; these are retained on an anion exchanger (based on acid resistant polystyrene), while the important interfering elements (except iron III) are passed through the resin. Subsequently, uranium is eluted with dilute acid. About 10 years later, Korkisch and Hazan [21] used 0.5N hydrochloric acid in 90% methyl glycol to elute iron, while retaining U(VI). Stelow and van der Walt [22] reported use of a similar separation method, but they replaced the methyl glycol with acetone.

Numerous reagents have been used to form coloured compounds with uranium. An old method, but one with good sensitivity (and still used in many laboratories), used dibenzoyl methane (DBM) [23], usually with pyridine as the solvent and buffer. The absorptivity of the resulting U(VI) chelate is about 20 000, a factor of ten higher than peroxide absorptivity. DBM may be replaced by reagents yielding products of equivalent, or higher, molar absorptivity. The most important reagents are those of the arsenazo group, e.g. 3-(2-arsenophenylazo)-4, 5-dihydroxy-2, 7-naphtalenedisulphonic acid, 1-(2-pyridylazo)-2 naphtol (PAN), or neothrorone with absorptivities of about 35 000. Arsenazo and neothoron complexes of U(VI) are soluble in aqueous media and PAN complexes in organic solvents.

More modern and more sensitive reagents are arsenazo III for U(IV), with an absorptivity of about 100 000 [8], and chlorophosphoonazo II and bromo-PADAP [15], with molar absorptivities of 73 000 and 74 000, respectively. In using these reagents after some preconcentration steps, a sensitivity of less than 10 ppm can be achieved, which approaches the range of activation methods.

3-2.7. Gravimetry and volumetry

Gravimetry and volumetry are among the most accurate methods for determining uranium, but they can only be used at somewhat higher concentrations of the element and, as with spectrophotometry, they require prior isolation of the uranium from any elements which would interfere with determination. Most gravimetric methods end with U_3O_8, which is the only stable oxide weighing form of the element. Organic compounds or uranium and many inorganic salts can be converted into U_3O_8 upon prolonged heating. Uranium can be precipitated with carbonate free ammonia (in the presence of carbonate a soluble complex is formed), with hydrogen peroxide, oxalic acid, cupferron and 8-hydroxyquinoline, and with many other precipitants, However, none of these methods is specific for uranium and they are rarely used in its determination.

Of greater importance are volumetric methods [8] which, although rather old, are still used because of their relative speed and high accuracy. Various titrimetric methods are possible, such as oxidimetric titration of U(IV) to U(VI), reductometric titration of U(VI) to U(IV), complex titration with EDTA and precipitation titration with cupferron or ferrocyanide. The most frequently used of these methods is oxidimetric titration, using potassium dichromate as the titrant [24]. Because uranium, after dissolution and separation, is usually present as U(VI), it has to be reduced quantitatively to U(IV) before titration. This may be done with zinc amalgams

(90–99%), or with lead. If zinc amalgam is used (Jones reductor), the reduction proceeds partly to U(III), which has to be reoxidized to the tetravalent state before titration, e.g. by bubbling air through the solution. However, certain ions such as chromium, nickel, niobium and copper may catalyse oxidation back to the hexavalent state unless the conditions are controlled carefully. These difficulties are avoided when a lead reductor is used in place of the Jones reductor. Its lower ionization potential leads to a stoichiometric reduction of uranium to U(IV). Alternatively, electrolytic reduction, with electrometric indication of the end point, can be used. When reduction is complete, titration is started, using diphenylamine sulphonic acid or another suitable substance as the indicator, or by determining the end point potentiometrically (e.g. in automatic titrations). A reference method, developed in the United States of America, uses a weighed excess of solid potassium dichromate and back titration with a Fe(II) solution. Many variations of these procedures are possible and, under perfect conditions, a precision of 0.01% standard deviation can be achieved.

Titrants other than dichromate can be used, but they have little to recommend. Cerium (IV) is less specific because of its higher oxidation potential. Its one advantage is a sharper end point, using ferroin as the indicator, hence a lower blank; iron (III) has some advantage, namely, it avoids the need for separation of the iron from the uranium in the sample solution. Potassium permanganate has been used, but it involves the titration of hot solutions and is itself relatively unstable.

Of more practical interest as a precision method that avoids the need for separate standardization is coulometric titration. In this method, the titrant is electrolytically generated cerium (IV) or bromine, and the quantity of electrical current consumed in its production is measured.

Reduction methods are used less frequently, since they require strong reductants that are neither stable nor selective. One version that has found acceptance is direct coulometric reduction of U(VI) at a mercury cathode in 0.5M H_2SO_4.

Precipitation methods have no particular advantage, since they are not specific. For certain special purposes, cupferron, ferrocyanide or 8-hydroxyquinoline have been used, in some cases with back titration of the excess precipitant.

3–2.8. Other methods

Various other methods have been, and still are, used in uranium analysis. They include X ray absorption, polarography and emission spectroscopy. Of these, X ray absorption is useful mainly at concentrations well above 100 ppm. Emission spectroscopy normally has a similar limitation. However, better sensitivity can be achieved when an enhancing agent such as lead chloride is employed, or when the mineral sample is converted into a bead before arcing. In the latter case, sensitivity of a few parts per million is claimed, but accuracy at low concentrations is doubtful. Polarography with a dropping mercury electrode is very suitable for uranium, proceeding in steps from U(VI) through all the valencies down to U(III) and finally to zero valency as amalgam. Numerous media have been used, including inorganic media such as 0.5M H_2SO_4, 0.5M H_3PO_4 or 5M HCl, as well as organic media which increase the selectivity. The latter can also be increased by reduction or complexing methods, depending on the nature of the interfering ions. However, when many different ions are present, and particularly when uranium is the minor constituent, special techniques or preliminary separations have to be used. When uranium is the only analyte present it can be determined at parts per million levels.

3-3. SELECTION OF A SUITABLE METHOD

Various methods are used for analyses of uranium concentrates and geochemical samples and for monitoring health physics. Selection of the most appropriate method depends on many parameters: on the purpose of the analysis, the nature of the analyte, the concentration of the uranium, the presence and concentration of the other elements in the matrix, the methodology available, the accuracy required, etc.

Chapter 4

THE URANIUM ANALYTICAL LABORATORY[4]

4-1. INTRODUCTION

The responsibilities, organization and main operational procedures of the analytical laboratory are described, with a view to highlighting the general features of the design and layout and some of the main items of instrumentation that are needed. The laboratory has two principal functions: analysis of samples arising from uranium exploration surveys and from mining/milling operations.

4-2. LABORATORY ORGANIZATION

4-2.1. Laboratory responsibilities

The major responsibilities of the laboratory are as follows:

(1) Analysis of field samples from exploration projects. There may be a great number of samples from these projects, most of which require some form of sample preparation prior to analysis. Extensive sample storage facilities and record keeping systems are also required.

(2) Analysis of solid samples from the mining operation, which requires sample preparation and a rapid turn around time.

(3) Analysis of mill process samples such as powdered head samples and leach residues, aqueous and organic solutions and concentrates. With the exception of the concentrates, all these samples require a rapid turn around time.

(4) Analysis of uranium ore concentrates, which requires a high degree of accuracy in determining the uranium and the impurities.

(5) Analysis of environmental monitoring samples.

(6) Analysis of occupational health and safety samples such as urine.

(7) Issuance of appropriate analytical reports and maintenance of a report record system.

(8) Maintenance of a sample preparation and sample storage facility.

---

[4] Contributed by J.L. Dalton, Canada Centre for Mineral and Energy Technology (CANMET), Energy Mines and Resources Canada, Ottawa, Ontario, Canada.

4–2.2. Laboratory organization

To accomplish good organization, the laboratory needs several operating units, as shown graphically in Fig. I-3.

A convenient management method is to divide the work by the type of project, with several sections or operating units dealing with the different types of sample, as shown in the figure. This division is designed to prevent the cross-contamination of samples, which could occur if the same worker deals with both ore concentrates and exploration samples within a central facility during a shift. This division should also be physical, with different locations within the laboratory. It is suggested that there be several graduate chemists, or their equivalent, in a supervisory capacity within the organization, as shown on the organizational chart. These recommen-

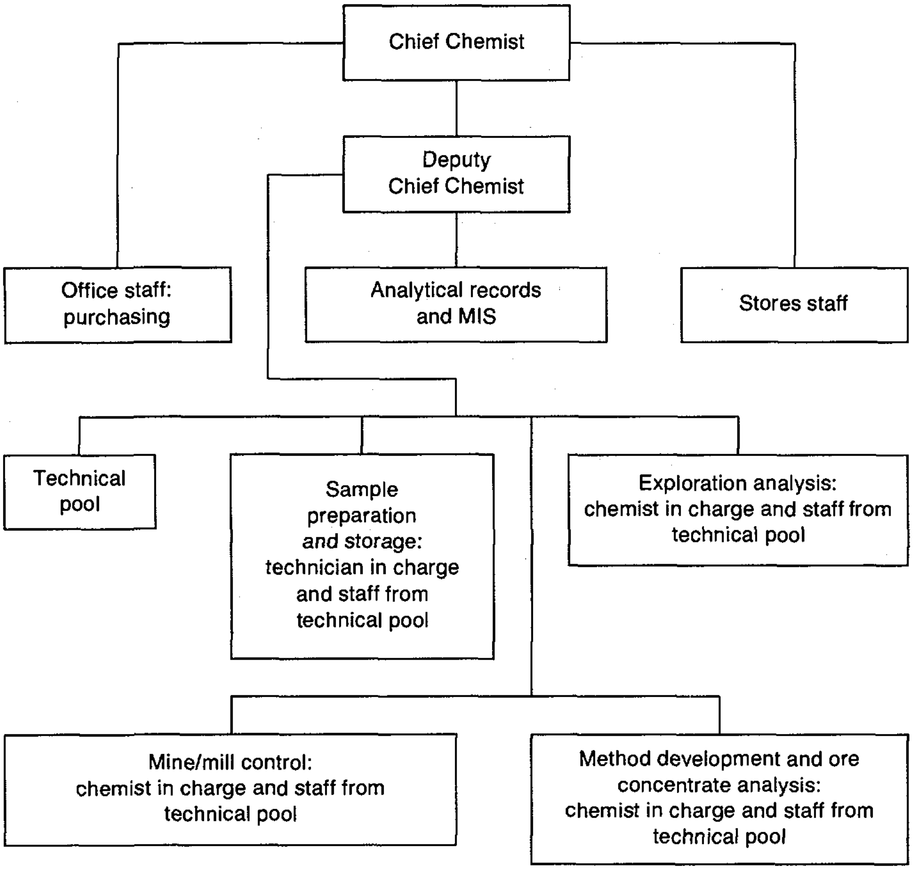

FIG. I-3. Organizational chart for a uranium analytical laboratory.

dations are based on the assumption that there is sufficient analytical work to support the four main operating units. If this is not the case, then an overlap is necessary, with less staff required than shown on the chart.

4–2.3. Personnel

The laboratory staff comprises senior staff: a Chief Chemist and a Deputy Chief Chemist; supervisory staff: working level graduate chemists and/or chemical technicians; working staff: about 20–30 people who have had some formal education in chemistry, preferably in analytical chemistry.

The Chief Chemist and the Deputy Chief Chemist should be university graduates in chemistry and possess a strong background in analytical chemistry, with several years of experience in the uranium industry. Both positions require good organizational and communication skills, self-motivation and the ability to work with people. The Chief Chemist should have received management training.

Several people report to the Chief Chemist, e.g. the Deputy Chief Chemist, the office staff, stores person/laboratory steward and the head of the environmental monitoring group. The office staff have to deal with correspondence, internal management documents such as purchase requisitions and payroll data, issuing of official reports and maintenance of an analytical records system. The responsibilities of the stores person/laboratory steward are to ensure the ready availability of chemicals, laboratory equipment and glassware. The steward may have to assist in sample recording and distribution and may also have to take some of the responsibility for maintaining cleanliness in the laboratory operations, depending on the workload of any one of the preceding three items.

The ready availability of instrumentation repair and service is an operational requirement of the analytical control laboratory so that rapid emergency repairs to the instrumentation used in critical functions can be effected. Control laboratories cannot afford to wait long periods for instrumentation to be repaired at the place of manufacture. If this service is not available through the mine/mill complex, then it is the responsibility of the Chief Chemist to ensure that staff or contract services are readily available to meet this requirement. A major responsibility of the stores staff is to ensure that instrumentation consumables and replacements are readily to hand. The delivery time for instrument parts is often months and therefore an immediately available stock is necessary.

It is anticipated that the uranium mining/milling operation will be subject to environmental constraints such as the regulations governing the escape of pollutants from the site and the health and safety of the workforce. Monitoring of effluents from the tailings ponds, which should include both collection and analysis of suitable samples, should be controlled by an experienced chemist who reports to the Chief Chemist. The head of this section is also involved in health and safety matters, such as analysis of mine and mill workers' urine for uranium.

The staff in charge of the four working groups report to the Deputy Chief Chemist, who is responsible for arranging the analytical work of the laboratory. As mentioned previously, difficulties may arise in having analytical work from both exploration parties and mine/mill control carried out in a central facility, if common instrumentation is shared between the two functions. The Deputy Chief Chemist has to schedule the work so that the objectives of both functions are met; any changes to schedules and priorities should only be carried out by this person. Another responsibility is rotation of the staff from the technical pool among the various groups; these assignments should be made every 6–12 months. It is recommended that all staff, including professionals, be rotated periodically so that personnel are available for all the laboratory functions. The Deputy Chief Chemist is also responsible for implementation of the laboratory quality control system developed by the management of the complex.

Quality control is a very important ongoing feature of the analytical laboratory's work. Policy, with respect to quality control on various analytical tasks, should be worked out to the mutual satisfaction of the laboratory management and the person requesting the analyses. Aspects that have to be settled are the turn around times and analytical tolerances. For example, in exploration programmes or mill control it may be much more important to have a rapid turn around time with ±10% relative error than a slow turn around time with ±3% relative error. Uranium ore concentrate, on the other hand, requires very precise and accurate analyses, because these provide the basis for the financial return to the organization.

Accuracy of analysis should be established by using certified reference materials (CRMs) and primary standards, and/or by participating in interlaboratory programmes on various representative samples. Once the representative samples have been analysed and it is known that the samples will not deteriorate with time, they can be used in a continuing quality control programme.

Quality control programmes should be used to monitor all the laboratory's analytical work. Depending on how critical the analytical work is to the project, quality control should vary between 5 and 20% of the workload. To meet environmental considerations, it may be necessary to have a standard for every four solutions when doing ^{226}Ra determinations. For uranium in exploration samples, five standards per 100 samples may be sufficient. The amount of quality control is dependent on the use of the data and the acceptable control limits established for that particular determination. Quality control policy varies a great deal from one operation to another, even within the same industry. It should be emphasized that quality control is an integral part of the laboratory's operation and cannot be overlooked. It assumes particular importance if the working staff changes constantly.

The health and safety aspects of the laboratory operation should be established and supervised by the Chief Chemist, since this person is ultimately responsible for the safe conduct of the work and the elimination of hazardous practices in the laboratory. Several factors should be taken into consideration, such as the proper operation of fume hoods with due regard to the safe use of perchloric acid, the proper storage of chemicals, the ready availability of personal safeguards, installation of emergency shower and eye wash fountains and access to radiation monitoring equipment. Health and safety matters should be reviewed periodically by the appropriate laboratory staff. Health and safety matters are dealt with further in Appendix 2. Since much of the mill process work is of a chemical nature, the Chief Chemist may also be asked to participate in the establishment and review of health and safety practices in the mill, for instance, analysis of the urine of the mill staff for uranium.

4–2.4. Operational procedures

The priorities and scheduling of analytical services should be mutually agreed upon before the laboratory commences operation. It is very important that the mine site objectives and goals are understood by the management of the analytical laboratory. There should also be periodic reviews of policy because goals may change with time. Implementation of established priorities and schedules will be largely the responsibility of the Deputy Chief Chemist. There could very well be an operational conflict between the analysis of a large number of field samples that require some form of sample preparation and the relatively small number of samples originating from the mine/mill control function. To resolve this potential conflict, it may be necessary to operate two separate functions in the laboratory, including expensive analytical instrumentation, in order to satisfy the objectives of each.

Samples arrive in the reception area where the appropriate information is entered into the Management Information System (MIS); sample numbers are assigned along with possible management information such as the level of priority, assignment to appropriate analytical programmes and any special considerations. It should be possible to expedite documentation by having standard forms. The information required includes, for example, the sample origin, management code, date and time and the required analytical work indicated by tick marks in the appropriate boxes. It is the submitter's responsibility to fill in the boxes of the form. Once documentation is complete, the sample is forwarded to sample preparation, if necessary, and to the relevant laboratory supervisor, or is included in established laboratory practice. The supervisor decides how and when the analytical work is to be carried out, depending on previously established management criteria. The Deputy Chief Chemist should be notified of the arrival of any unusual analytical work.

The style of reporting analytical results is a characteristic of the particular management style and the client's needs. If the laboratory has a computer based MIS, then all the results are entered into the system and are available on the client's terminal on demand; hardcopy printouts are to be available whenever desired. If the laboratory does not have a computer based system, the results from the mine/mill complex probably have to be submitted by telephone to the appropriate process control location. Hand written worksheets or report summary sheets are filed either in the laboratory office or with the appropriate supervisor. It is important to have records of all the analytical work done for possible future reference and also for the preparation of management reports. The survey work, and some of the mine/mill work, certainly require the preparation and issuance of an official report. These reports contain the number and description of the sample, a possible methodology reference and the analytical result.

The reporting of estimates of accuracy along with the analytical result is a contentious issue. Some analysts claim that control work is not necessary when the process and analytical method are known to be under control. In this case, accuracy in the analytical results is generally well known, and reporting of accuracy estimates with every result adds to the costs of the job without any apparent benefit. For survey work, however, with some elements it may very well be necessary to have an estimate of precision (see Chapter 2). The estimate of accuracy is generally reported as approximate figures following the analytical results. If possible, these figures should be obtained from the analysis of CRMs. For solution work, the accuracy estimates may be obtained by statistical analysis of the analytical data. It should be pointed out that replicate analysis of calibration solutions only provides estimates of precision, not accuracy. National Bureau of Standards (Washington, DC) (NBS) Special Publication 300 (see below) contains many articles on estimating the precision and accuracy from scientific and engineering measurements.

It is strongly recommended that senior analytical laboratory staff be provided with the opportunity of visiting other organizations doing similar work before designing and constructing the laboratory. If possible, the workload should also be defined before design.

The number of books and periodicals of use to the laboratory are too numerous to list; however, the following are considered essential:

(1) AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM), Philadelphia, Nuclear, Solar and Geothermal Energy, Volume 12.01, Nuclear Energy (1), current revision
(2) DONALDSON, E.M., Methods for the Analysis of Ores, Rocks and Related Materials, Monograph 881, 2nd edn, CANMET, Energy, Mines and Resources Canada, Ottawa, Ontario (1982)
(3) NATIONAL BUREAU OF STANDARDS, Washington, DC, Precision Measurements and Calibration, Special Publication 300, United States Department of Commerce, NBS, Stock No. 033-003-00072-8.

In addition, the following journals should be made available:

(a) Analytical Chemistry, American Chemical Society, Washington, DC
(b) Talanta, Pergamon Press, Oxford
(c) Analytica Chimica Acta, Elsevier, Amsterdam.

4-2.5. MIS

MIS is an important component of the laboratory. It can serve a variety of purposes, such as recording sample details and issuing sample numbers, documenting analytical progress and results, and printing analytical and management reports. MIS should also be able to handle routine office work such as purchasing records, personnel data and shift scheduling. Preservation of analytical records is also an important part of the MIS operation; they should be maintained for at least 2 years.

MIS plays an important role in the quality control operation of the laboratory. MIS software should be designed so that retrieval of actual sample data is accompanied by quality control data, which should be filed with the particular data batch. Absence of quality control data should be highlighted.

Operation of MIS is carried out by several people, none of whom is assigned to the system on a full time basis. Office personnel, laboratory steward(s) and the supervisory analytical staff should all be familiar with the system, albeit some more than others; the Deputy Chief Chemist and some of the supervisory staff should be thoroughly familiar with the system. Turnkey MIS systems can be purchased, but most operations are sufficiently unique to warrant the services of a programmer/analyst at the time of installation of the system. It is extremely important to have good documentation on the system prior to its acceptance. It is suggested that there be several terminals conveniently located throughout the work site, for example, in the laboratory office, the laboratory itself and in the mill/mine control rooms. In general, a terminal should be located wherever samples originate. However, only certain commands should be available on these terminals; these should be restricted to status and report functions. No system input, other than queries, should be allowed from most terminals.

A clerical records system has to be designed and implemented if a computer based MIS system is not available. A clerical system probably requires more permanent staff than a computer system. The clerical staff have to maintain the sample entry system, manually issuing laboratory numbers and recording such items as sample identification, level of priority, analytical work requested, a system to report the analytical results and compilation of management documents such as daily, weekly, monthly and yearly reports. Paperwork can be expedited greatly if well designed forms and/or laboratory worksheets are available.

4-2.6. Laboratory design and layout

The typical layout of an analytical chemical facility is shown in Fig. I-4. The facility is large enough to accommodate about 30 people, with a capacity of tens of thousands of determinations per month, assuming that the laboratory is equipped with modern instrumentation and that a substantial portion of the work is routine.

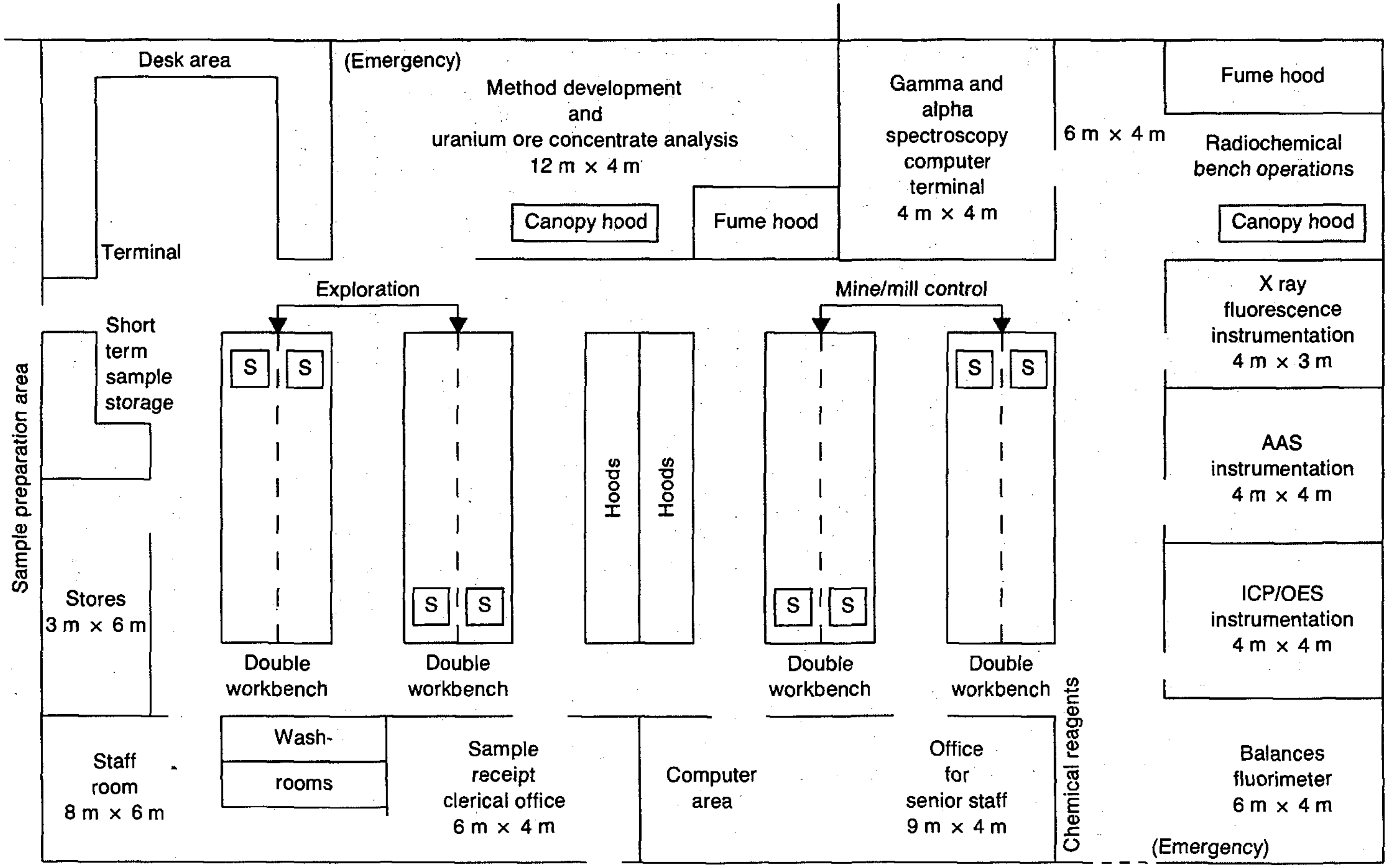

FIG. I-4. Typical layout of a uranium analytical laboratory.

The arrangement and dimensions shown in the figure are intended only as a guide. Sample preparation and sample storage facilities are described in Chapter 5.

The acid hoods should have adequate ventilation, hot plates, electrical, gas, purified and tap water services and lighting. It is recommended that all the hoods be capable of handling perchloric acid with wash down facilities. Each workbench should have adequate electrical, gas and water services. It is also convenient to have some pressurized air and vacuum outlets in the laboratory. The workbenches shown in Fig. I-4 are approximately 7 m long to accommodate two workers per aisle. Ideally, each worker should have access to about 3 m of double bench space. The benches should be equipped with shelves and drawers for storage of glassware, laboratory ware and sundry devices. The laboratory illustrated in Fig. I-4 should be able to accommodate ten bench workers in the central area.

Because of the possibility of contamination between samples, the workload is physically divided into three distinct areas. Both exploration and mine/mill control have their own sample preparation and workbench areas. Uranium ore concentrate analysis requires a special room. Glassware should be restricted to one work area.

Ideally, the whole laboratory should have a constant operating temperature. If this is not possible, then the three instrumentation rooms, the uranium ore concentrate analysis room and the radiochemistry room should have a constant operating temperature. Many instrumentation problems can be avoided by having a year round constant operating temperature. The accepted tolerance for constant operating temperature is ±2°C. The laboratory should also be fitted with isolation transformers, constant voltage units and filters to maintain a stable, well filtered electrical service.

The instrumentation rooms should be fitted with canopy hoods for the operation of atomic absorption and inductively coupled plasma optical emission spectrometers.

4–2.7. Main equipment

The following are considered to be the basic requirements for successful laboratory operation. The quantity, type and choice of instrumentation is left to the discretion of the Chief Chemist:

(1) The electricity supply in the laboratory should be established according to the instrumentation requirements. It is suggested that independent circuits be used as much as possible and that uninterruptable power supplies be available for radiochemical instrumentation and for the computer system.

(2) The laboratory water supply should be free of contaminants. This may be accomplished by a two stage process — a preliminary ion exchange batch system followed by Milli-Q secondary treatment (or the equivalent).

(3) The laboratory atmosphere should be at a constant temperature and humidity; 20°C and 30%, respectively, are suggested. In particular, computer areas need

to have a controlled atmosphere. The effect of fume hood operations on the air conditioning supply should be considered because of the withdrawal of air from the laboratory.

(4) Fume hoods should be capable of handling perchloric acid and be equipped with scrubbers; fume hoods should be reserved for organic chemical use and other fume hoods provided for general use.

(5) Modified fume hoods should be provided for use with fusion apparatus.

(6) Sufficient quantities and types of bottled gas should be provided, along with propane gas for burner use.

(7) Liquid nitrogen is required for high resolution gamma ray and energy dispersive X ray spectroscopy.

(8) Adequate storage facilities should be provided to handle acids, bases, organic and flammable chemicals.

(9) Balances and sturdy balance benches are required, along with burette stands and adjustable height laboratory stands.

(10) Drying ovens and muffle furnaces.

(11) Compressed air and vacuum supplies.

(12) Laboratory glassware, as follows: Beakers (Pyrex and Teflon), Erlenmeyer flasks, separatory flasks, volumetric flasks, watch glasses, stirring rods, specialized utensils (tweezers, spatulas), automatic pipettes and dispersers, Pyrex pipettes and burettes.

(13) Platinum fusion dishes.

(14) Platinum fluorometric dishes.

Chapter 5

SAMPLE PREPARATION[5]

5-1. INTRODUCTION

The function of the sample preparation facility is to prepare samples correctly for the analytical laboratory and to maintain their integrity. For the sample preparation laboratory to carry out its function, it is necessary that it be in direct contact with the analytical chemistry laboratory, or better, that it report to the manager of the analytical chemistry laboratory. The sample preparation laboratory should be designed to minimize cross-contamination from sample to sample. In addition, it should be laid out in a manner that facilitates the smooth flow of samples through the laboratory. Procedures for sample preparation and sample flow are necessary for the laboratory to function properly.

5-2. SAMPLE FLOW

MIS can be of great assistance in issuing the sample numbers, recording the sample history, listing the work required and printing the formal flow sheets for the laboratory as well as the report sheet when the work is finished. Thus, the first step in sample flow should take place at the MIS station. A management code should be established to prevent the submission of unauthorized analytical work. The presence of this code indicates management approval for the work requested; it should be sufficient justification to start the work.

The client, who is the manager of either the exploration or the mine/mill programmes, should be responsible for the proper completion of the Request for Analytical Services form.

If the sample does not require any sample preparation work, it is directed immediately to the analytical laboratory, for example, a pregnant liquor requiring only uranium determination. On the other hand, rock samples from the exploration programme require some sample preparation work. It should be possible to develop standard protocols for much of the analytical work. It is suggested that the protocol be established and adhered to as far as possible. This eliminates guesswork and tends to ensure that all the samples of a particular nature are treated in exactly the same manner.

A substitute clerical system has to be established if a computer based MIS is not available. A manual entry system can be quite labour intensive, although the end result could be the same as the computer based system.

---

[5] Contributed by R. Chessmore, United States Department of Energy, Grand Junction, Colorado, USA.

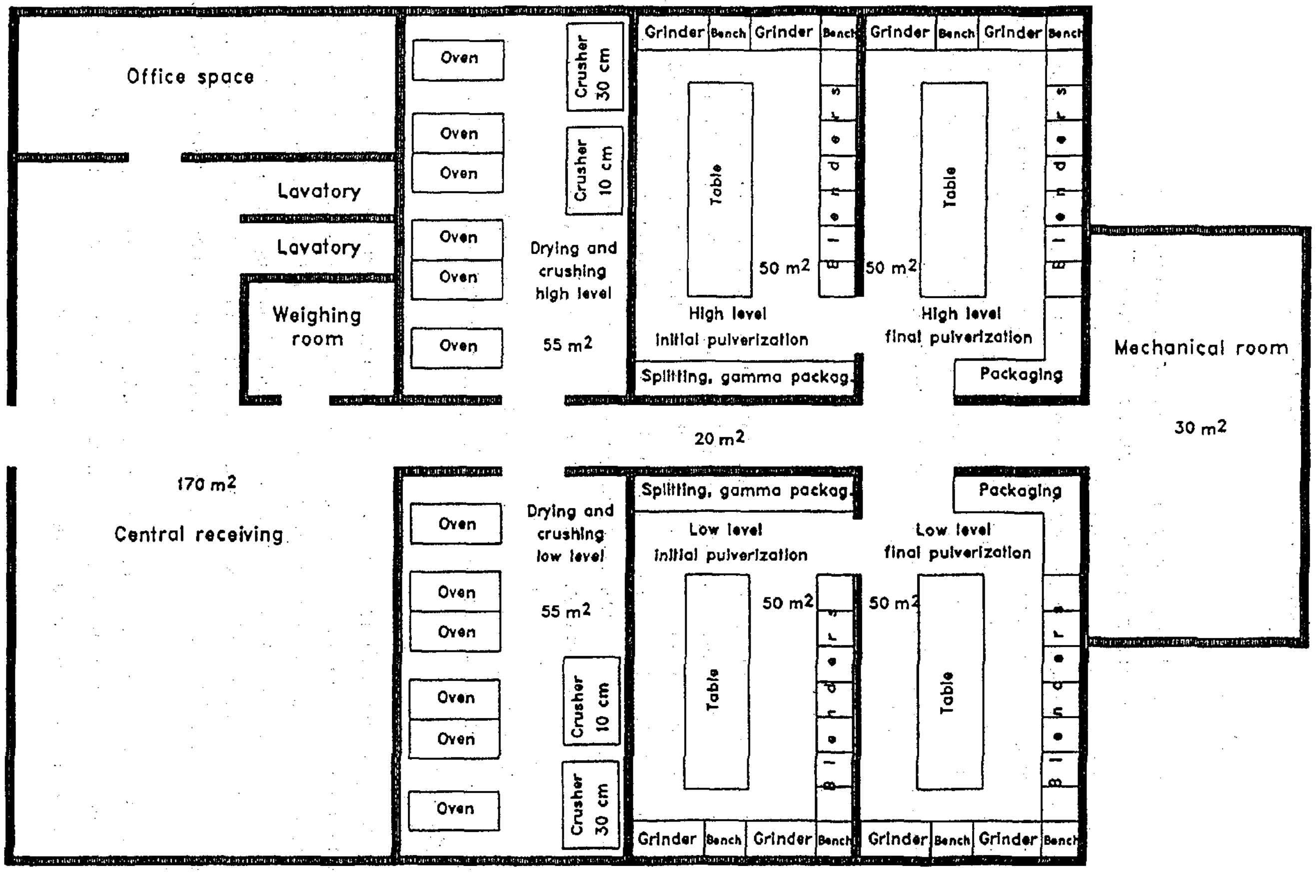

FIG. I-5. *Typical layout of a sample preparation laboratory.*

5-3. LABORATORY FACILITIES

The sample preparation laboratory should be laid out in such a manner as to facilitate the smooth flow of samples (Fig. I-5). The laboratory should include the following:

(1) *Central receiving area:* This should contain workbenches for the laying out of the samples, the separation of low and high grade ore samples, the completion of the sample identification form, and the filling in of the Request for Analytical Services and Sample Preparation forms.

(2) *Drying area:* There should be two such areas: one for geochemical and very low grade ore samples and the other for high grade ore samples. These areas house the drying ovens, which should be vented to the outside.

(3) *Crushing area:* There should be two such areas: one for geochemical and very low grade ore samples and the other for high grade ore samples. These rooms house the various sizes of jaw crusher, all of which should be housed in high velocity dust collection hoods attached to the central dust collection system.

(4) *Pulverizing and blending areas:* There should be two such areas: one for geochemical and very low grade ore samples, and the other for high grade ore samples. High and low areas should be laid out in the same manner. Each area should include equipment for initial pulverization (600 mm), sieving, blending and splitting, and for final pulverization to <75 mm, sieving, blending and packaging. These areas house the pulverizers, blenders, sieves, sample splitter, mortar and pestle and/or ball mill, and sample encapsulating equipment for packing samples for gamma ray spectrometry. All pulverizing, blending and sieving operations should be carried out under high velocity dust collection hoods connected to the central dust collection system. Packing of the sample for the analytical chemistry laboratory is also carried out in this area. *Note:* The unique sample identification number must be retained with the sample throughout the sample preparation process.

5-4. SAMPLE PREPARATION

5-4.1. Rock sample preparation[6]

The sample is crushed to approximately 0.64 cm using the jaw crushers and then dried at 110°C overnight. If the sample is too wet for crushing, it should first be dried in a drying pan, then crushed and redried. After drying at 110°C overnight,

---

[6] An alternative rock sample preparation scheme making use of ceramic ball mills for final pulverization has been described by Lavergne in Ref. [25].

the sample is pulverized to approximately 600 mm, and then blended in a V type blender for approximately 10 minutes. The resulting sample, referred to as the bulk sample, is now ready to be split for various other sample preparation procedures. If gamma ray spectrometry is to be performed, a split of the bulk sample is taken at this time using the sample splitter and is then placed in the gamma ray spectrometry container (200 g, or larger). If the sample weighs less than 200 g, it should be pulverized to <0.76 mm and blended. When placing the sample in the gamma ray spectrometry container, the sample should be packed well in the container and the container sealed (see the gamma ray spectrometry procedure described in Part II, Method 4). For analytical work other than gamma ray spectrometry, a finer particle size is generally required. Approximately 200 g of the bulk sample are taken using the sample splitter and pulverized to <0.76 mm, blended for 10 minutes and packed for the laboratory. Prepared samples should be placed in glass or plastic vials for transmission to the laboratory or storage. Samples in plastic or paper envelopes cannot be homogenized readily before weighing and will therefore be inhomogeneous, leading to erroneous results. The remaining bulk sample is packed and stored for future reference.

5–4.2. Stream sediment and soil sample preparation

The sample is first dried thoroughly at 110°C.[7] It is then disaggregated by mortar and pestle, taking care not to grind or crush the naturally occurring grains. The sample is sieved through a <0.180 mm sieve. The <0.180 mm fraction can be analysed or a portion pulverized to <0.075 mm, blended in a V blender for 10 minutes, and then packed in glass or plastic vials for the laboratory. The >0.180 mm fraction can either be stored or disposed of, depending on the requirements of the originator.

5–4.3. Vegetation sample preparation

Vegetation samples can be the most difficult samples to prepare. The sample should first be dried at 100°C overnight and the larger segments broken down into smaller segments. The sample is then pulverized using a knife type pulverizer. The particle size needed depends on the type of vegetation and the analytical procedure to be used. There is no need for blending unless the sample can be pulverized to approximately <0.600 mm.

---

[7] If it is intended to analyse the samples for mercury or other volatile elements, samples should not be dried at temperatures greater than about 30°C.

5-4.4. Liquid samples

In general, any sample preparation required for liquid samples is performed by the analytical chemistry laboratory.

5-4.5. Cleaning of equipment

All the sample preparation equipment should be cleaned before use and after each sample. The following procedures are recommended:

(1) *Drying pans:* These pans are first cleaned with compressed air and then washed in a detergent solution, rinsed in clean water and dried.
(2) *Jaw crusher:* This equipment is best cleaned with a wire brush and compressed air and generally does not have to be washed.
(3) *Pulverizers:* Cross-contamination of samples is greatest during pulverizing. The pulverizer should first be cleaned with compressed air and, if possible, a portion of the next sample to be pulverized should be run through the equipment and discarded. If insufficient sample material is available, a clean quartz sand can be used. The pulverizer should then be blown clean with compressed air. For high grade ore samples, the pulverizer plates should be washed and dried.
(4) *Mortar and pestle:* Wash and dry.
(5) *Sieves:* Compressed air blown through the sieve generally suffices. If the sieve openings become clogged, the sieve should be washed. A stiff bristle paint brush with short trimmed bristles can be used. Do not use a wire brush, since this damages the sieve.
(6) *Blenders:* These blenders are cleaned easily by first blowing through compressed air and then wiping them with a clean cloth. For high grade ore samples, the blender should be washed and dried.
(7) *Sample splitter:* Clean with compressed air.

5-5. EQUIPMENT AND USE

(1) *Stainless steel drying pans:* These pans should be prenumbered and tared, and are used to hold the sample during sample preparation. They should be large enough to hold a 2 kg sample.
(2) *Large drying ovens:* These ovens are used for 'loss on drying' analysis and drying samples before sample preparation; they should have a reliable temperature control.
(3) *Desiccator:* This is used for holding samples that absorb moisture from the air.
(4) *Jaw crushers:* Crushers of various sizes (10–30 cm) should be available for use; they are used to crush samples to approximately 0.64 cm.

(5) *Pulverizers:* The 203 mm disc/plate type pulverizer is reliable and efficient for grinding solid samples. This equipment grinds a sample to a very fine mesh size (45 mm) and is available with steel and ceramic plates. The choice of plates depends on which elemental analysis is to be performed. Steel plates can generally be used, except when iron or other metals associated with steel are of concern. Ceramic plates can be used, except where aluminium is of concern. They should be used for the preparation of all the geochemical samples.

(6) *Knife type pulverizer:* This is an efficient mill for pulverizing fibrous materials.

(7) *Mortar and pestle:* These are available in various sizes and materials and are used for small sample sizes (less than 200 g).

(8) *Standard testing sieves:* The full height (51 mm), 203 mm diameter sieve is available in various mesh openings (4750–45 mm). It is recommended that stainless steel sieves be used to minimize contamination. Brass sieves are softer and contaminate the sample with copper and zinc.

(9) *Blenders:* Stainless steel V type blenders vary from 0.5–10 L in size. They are easy to clean and are excellent for homogenizing a sample. Plexiglass (lucite) shells are available and are preferred for blending the geochemical samples.

(10) *Sample splitter:* The Jones Riffle type splitter splits out a representative sample aliquot from bulk samples. When using the splitter, the sample particle size should be uniform to prevent segregation during splitting.

(11) *Equipment cleaning supplies:* These include wire and bristle brushes of various size.

(12) *Sample containers:* These come in various sizes and types.

(13) *Analytical balances:* These are of various sizes.

(14) *Exhaust pans:* The exhaust system should be vented to a dust collection system and tied into hoods around the sample preparation equipment.

(15) *Air compressor:* The air supply should be sufficiently large to supply all the sample equipment needed for cleaning.

Chapter 6

CALIBRATION METHODS AND QUALITY CONTROL IN THE URANIUM ANALYTICAL LABORATORY[8]

The calibration methodology and quality control programmes that can be used in the analytical laboratory are described.

The ideal method of industrial calibration is to use calibration materials that are identical to the sample being analysed. The simplest way of preparing calibration materials is to collect several samples of each type of material of interest, and then to have these blended, homogenized and subsequently analysed by a reputable laboratory, or preferably by several laboratories. These materials can then be used for calibration purposes if they are reasonably stable. Care should be taken not to overlook any peculiarities in the ore deposit if analyses of the calibration material are to be carried out by the on-site laboratory. Most ore bodies have features that are sufficiently unique to warrant attention from the analyst with respect to the presence of possible interferences and the extent of acid solubility.

The form (or forms) in which an element is present in a particular ore deposit should be verified by dissolution tests that vary from the simple to the most stringent in order to determine which procedure is suitable for the control process and which for the exploration samples. For these two end uses, it may not be necessary to use the same type of dissolution procedure on a continuing day to day basis as that required by a theoretical scientific study. However, it is important to know the extent to which a given dissolution procedure dissolves different elements. For uranium, this may be as simple as comparing the results obtained directly on the solid material by the delayed neutron counting method with those obtained after various dissolution tests. These would probably vary from a cold or hot single acid leach (labile uranium) to a hot multiple acid leach, followed by appropriate fusion on any resultant acid insoluble residue (total uranium).

Internal standard and standard addition techniques are applicable in analytical work when the composition of the sample and the approximate analyte concentration are unknown, and where direct comparison with CRMs, pure compounds or single or multicomponent calibration solutions is impractical.

Calibration using an internal standard technique involves addition of a relatively large amount of the internal standard element to the sample and is best done with solutions. The choice of suitable element for an internal standard should take into consideration the compatibility with the matrix, the optimum concentration ena-

---

[8] Contributed by J.L. Dalton, CANMET, Energy Mines and Resources Canada, Ottawa, Ontario, Canada.

bling precise measurement and the chemical and physical properties of the internal standard element with respect to the properties of the analyte. Moreover, the intensity of the internal standard element should be affected by a matrix change in exactly the same manner as the analyte intensity. These changes are caused by the chemical and physical properties of the sample. The sample undergoing analysis should also be free, or contain very little, of the standard addition element.

Calibration by this method can be rapid and convenient, for example, determination of uranium in solution by X ray fluorescence (XRF) analysis using bromine as the internal standard. A small measured quantity of the internal standard solution (0.1 mL) is added to 5.0 mL of the solution, uranium and bromine XRF measurements are made and a uranium/bromine ratio is calculated from the net intensities. This ratio is then divided by that of the uranium standard solution to obtain the analytical result. If the internal standard calibration results are plotted, the ordinate is the ratio of the net analyte to the internal standard intensities and the abscissa is the concentration axis.

The choice of internal standard element is often restricted by the composition of the solution. The presence of certain elements may cause a precipitate to form on addition of the internal standard. For example, halogens cannot be used with solutions containing silver; alkaline earths form precipitates with sulphate; while phosphate and bismuth precipitate in the presence of hydrochloric acid. Examples of internal standard calibration are use of palladium and cobalt in optical emission spectrometry, and bromine, strontium and lead in X ray spectrometry. Use of internal standards in X ray spectrometry has been discussed by Bertin [26].

As mentioned previously, the internal standard method is best applied to solutions, but it can also be used to analyse powders, albeit with some care, by X ray spectrometry. The internal standard is mixed intimately with the sample in order to obtain a homogeneous mixture. If a shatter box or other robust device is used for mixing, there may be a grinding effect and a consequent change in the grain size distribution of the mixture with respect to the original sample. At a later stage, experience may show that the internal standard is not necessary for a particular analysis, but in order to continue using the existing calibration it is necessary to continue with all the sample preparation steps because the XRF intensities are a function of grain size distribution.

Internal standard calibration can be used conveniently when preparing fused glass discs for X ray spectrometry. For this work, the internal standard is simply added to the sample and the flux before fusion.

The standard addition method differs from the internal standard method in that the element being determined is the element that is added. Although standard addition is usually carried out on solutions, it can easily be applied in the preparation of fused glass discs, but this requires care if direct use of solids is involved. The same comments on grain size distribution mentioned previously in the discussion on the internal standard method apply to the standard addition method when it is used for

TABLE I-II. STANDARD ADDITION DATA

(Estimated value of sample solution = 0.1 mg/mL; standard solution = 1 mg/mL)

Solution No.	Volume of sample (mL)	Volume of water (mL)	Volume of standard (mL)	Analyte concentration		Instrument reading (units)[a]
				From sample (estimate) (mg/mL)	From standard (mg/mL)	
1	4.0	1.0	0.0	0.4	0.0	110-10 = 100
2	4.0	0.2	0.8	0.4	0.8	310-10 = 300
3	4.0	0.4	0.6	0.4	0.6	260-10 = 250
4	4.0	0.5	0.5	0.4	0.5	235-10 = 225
5	4.0	0.6	0.4	0.4	0.4	210-10 = 200

[a] 10 is the background contribution.

Extrapolation of the calibration plot gives an intercept of 0.4 mg. The sample contains 0.4 mg/4 mL of aliquot = 0.1 mg/mL = 100 ppm.

X ray spectrometric analysis. When the method is applied to sample solutions, usually three or four identical aliquots of the solution are taken and increasing volumes of a standard solution of suitable concentration are added. Typically, the final concentration of the analyte in the resulting solutions would be about 0.5, 1.5 and 2 times the concentration of the analyte in the sample solution. Care should be exercised in intensity measurement, because it is very important that the background measurement does not reflect the intensities of the added analyte. Small errors in background measurement may influence the slope of the calibration plot. Data from a hypothetical determination using the standard addition technique are given in Table I-II and plotted in Fig. I-6. The abscissa is plotted in terms of the analyte added. Consequently, the volumes of the standard analyte solution added and the final volumes of the solutions must be exact. When the standard analyte solution is added, it is important to maintain the same acid concentration in the resultant solutions as in the analyte solution.

In favourable cases, or after analysis of a relatively large number of samples, it may be observed that the slope of the calibration plot is constant, within analytical error. In these situations, it is not necessary to make additions; the slope can then be applied directly to the sample data to obtain the analyte concentrations. This is particularly useful for analysis of powders. However, it is advisable to check the slope periodically by the standard addition method.

For solution analysis, direct comparison between the sample and the standard is often carried out in measurement techniques such as atomic absorption and flame emission spectrometry, the various types of optical emission spectrometry and in X ray fluorescence analysis. Care should be taken to ensure that the sample and the standard are of a similar composition, including the acid type and strength, and that the concentration of analyte in the sample is within the range of the calibration standard. Extrapolation of the calibration curve can lead to serious error. Care should also be taken to ensure that any of the interferences present are detected and that corrective action is taken. Direct comparison is recommended in many of the methods described in the monograph by Donaldson [27].

CRMs are powdered ores, rocks, slags, metals and alloys that have been prepared, analysed and documented for use in analytical laboratories. They are invaluable in the laboratory for a variety of purposes, e.g. for calibration, quality control, preparation of in-house control materials and methodology comparisons. They provide a benchmark for analytical industry and should be used frequently.

Many organizations prepare and sell CRMs [28], most of which are government departments or institutions, although some are private companies. The geologi-

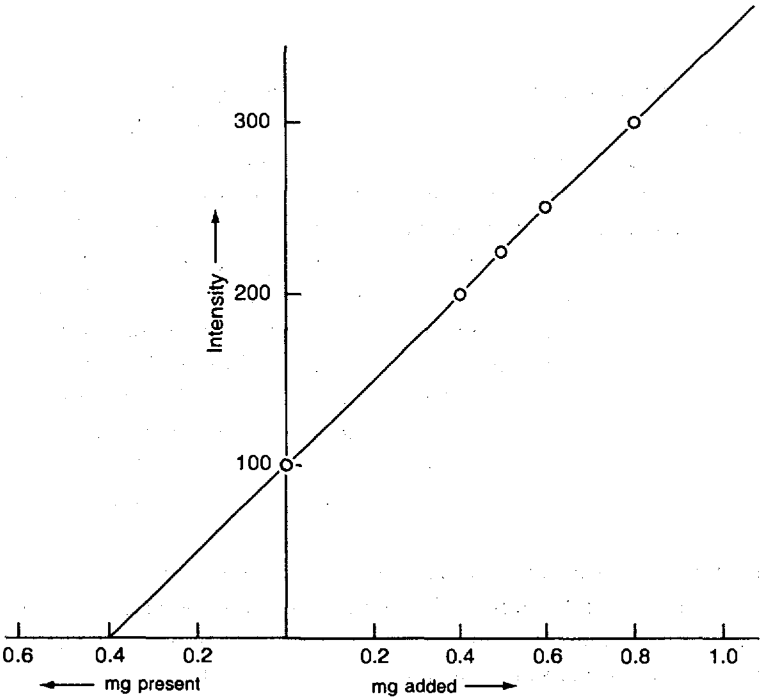

FIG. I-6. Plot of the standard addition data from Table I-II.

cal materials chosen for CRMs are representative of ores and rocks from around the world and may, in favourable cases, have similarities to the chemical composition of a particular ore deposit of interest to the laboratory. In certain cases, a CRM can be certified only for its uranium content, as with some materials from the International Atomic Energy Agency [29] and the Canadian Certified Reference Materials Project [30]. In other cases, several elements can be certified and additional analytical information is available on the remaining elements [30].

Preparation of certified material generally involves a large number of laboratories in order to reach consensus values. It is beneficial for a laboratory to participate in these programmes, because they provide an opportunity for comparing accuracy and precision; also, the laboratory's reputation can be enhanced by participation.

A sound QA/QC programme is essential for any organization that produces a product. Some organizations refuse to purchase a product unless the supplier's QA/QC programme is judged to be satisfactory. An important aspect of QA/QC is a process whereby standard solutions and/or reference materials are analysed concurrently with the sample in order to determine and document the accuracy of the various determinations. The reference solution or material should be subjected to exactly the same procedures and measurement steps as the sample in order to ensure that the whole method is checked. Without QC, the results obtained are directly dependent on the vagaries of the analyst, the laboratory services and the instruments. However, QC work often provokes considerable discussion because it is expensive, time consuming and increases the analytical workload, but it is the only way in which an analytical laboratory can realistically asssign accuracy statements to the analytical work produced during normal laboratory operation. For a given method, assignment of the same accuracy to a control laboratory as that estimated by a development laboratory can be quite misleading. The accuracy associated with the development laboratory methodology was probably accumulated over a lengthy period of time and special care taken during the manipulative and measurement operations. In the control laboratory, there are often pressing demands for rapid turn around and the laboratory has to contend with the idiosyncrasies of industrial shift work.

The supervisory staff of the analytical laboratory should bear in mind an important human consideration. The purpose of the QC programme is to monitor the performance of a whole method, not only the performance of the operator. Supervisory staff should not create the impression that the purpose of the programme is to harass the staff. When QC results indicate methodology problems, the whole method is suspect, not just the analyst. A QC programme can define when problems occur and which analytical results may be suspect. QC operation is particularly important when staff changes are frequent or when a periodic staff rotation system is practised in the laboratory.

The choice of materials for a QC programme is very important. They should be similar in composition and physical properties to the samples undergoing analysis. They must be stable for a relatively long time and be sufficiently well characterized to permit reasonable assessment of the accuracy and precision of the analytical work. For example, material containing a high concentration of iron would not be used as a QC sample for uranium determination by optical fluorometry, even though it contained an appropriate quantity of uranium, if a better, low iron material were available. Preparation of control materials can range from the simple and inexpensive to the complex and expensive. In the case of exploration and mine samples, the assistance of geological staff should be enlisted in obtaining the best, most suitable materials. A representative sample from a particular type of analysis, mill heads, for example, can be used as a control sample if one has a reasonably good supply and if it is stable for a reasonable length of time. Similarly, single or multielement calibration solutions can also be used, care being taken to match the acid strength and type between the standard and the sample. Such solutions can be prepared in the laboratory at relatively low cost. The disadvantage of their use is that these materials do not have any documentation outside the particular laboratory. If the results are circulated outside the organization, it is best to use control materials that have been analysed by a reputable laboratory. However, if the desire is to supply control documentation that has important ramifications, such as the sale of the product, then it is best to use internationally accepted CRMs, even though frequent use of these materials is expensive. In-house control materials can be used most of the time, but CRMs should be used in important cases and periodically to monitor the results obtained when using in-house materials.

The amount of control work necessary is a disputed issue. The control limits, i.e. the maximum deviation from the true value that can be tolerated by the appropriate industrial process, should be decided on by discussion between laboratory management and the end user of the results. These limits should be achievable in the laboratory and the associated cost of complying with the end user's requests should become an integral part of that particular production cost. Once control limits have been established, the amount of QC analysis should be decided on by the laboratory management. If the variability of the results obtained by the method approaches the established control limits, then the amount of control work may be large, e.g. making one sample in five, or 20%, a control sample. Conversely, if the control limits are well removed from that of the method variability, then the control work will only be a small fraction of the workload, say one control sample for every 20 analytical samples. However, there may be special circumstances where it is necessary to analyse a few samples at a time; for example, aqueous solutions from the barium chloride treatment pond requiring ^{226}Ra determination. In this case, it would be necessary to have a ^{226}Ra control solution and a reagent blank analysed concurrently with the few solutions. If the concentrations of the analytes in the solutions to be analysed are near the detection limit of the method, the concentrations in the control samples should be sufficiently higher than the detection limit to permit accurate measurement. Reagent blanks should be analysed as well in order to check the intercept value of the calibration curve and for possible contamination from laboratory glassware. The statistical aspects of experimental and industrial measurements are discussed in the NBS Handbook by Natrella [31] and the ASTM Manual [32].

There are several ways in which control samples can be introduced into the workload. The easiest is simply for the supervisor to give the control samples to the technical staff and to ask for one control sample analysis per certain number of samples. The disadvantage of this approach is that the staff may be more careful with this sample than with others, knowing that the supervisor will scrutinize the result. The advantage is that technical staff and the supervisor know immediately whether or not the results are acceptable. The technical staff may also be asked to chart control sample results on a continuing basis, thus providing some self-motivation to work carefully, since the chart will be a visual presentation of the work quality, especially if the plot shows the results of a single worker.

On the other hand, the control sample can be inserted into the workload by management, labelled as a management sample and the results reported directly to management. The supervisor may or may not be aware of the concentration(s) in the control sample, or even that the sample is a control sample. The advantage of this approach is that the control sample is truly an unknown. Again, the disadvantage is that the staff will be very careful with this sample. An alternative to this approach is to ask the end user of the analytical services to submit the control samples with the normal workload and to inform the laboratory management of the number assigned to the control sample. Management would have to refer to the end user's report to ascertain the accuracy of the analytical work on the control sample.

As mentioned previously, the purpose of the QC programme is to document the accuracy and precision of analytical work during normal operations. A necessary part of this programme involves suitable recording of the results of the control work. If a work sheet or notebook system for recording the analytical work is used in the laboratory, then the results obtained for the control sample are readily available, along with the corresponding sample results. If a computer based management system is used, however, some effort is required to ensure that the control sample data are entered into the database together with the relevant sample data, and that both sets of data can be retrieved at the same time.

Chapter 7

STATISTICAL TECHNIQUES FOR CHEMICAL ANALYSIS AND PROCESS CONTROL[9]

7-1. INTRODUCTION

Application of statistics to process industries is commonly associated with QC, which is necessary because the product of any process, be it a manufacturing, chemical or measurement process, is not, in general, consistent with the target value, even if all the variables have been controlled completely. The fluctuation in results that cannot be attributed to any known cause is usually called a 'random (statistical) fluctuation'. This fluctuation cannot be completely eliminated; however, it can be decreased to an acceptable level, but at a cost. It can occur at various stages of the process. To illustrate this point, consider a process for the conversion of uranium ore concentrate to UO_2 suitable for fuel fabrication. The objective is to produce UO_2 at a desired uranium concentration (purity), say, A% UO_2. Ideally, the process should produce powder containing exactly A% UO_2 batch after batch, day after day. In practice, however, this ideal condition never happens. The plant produces powder with a UO_2 content varying anywhere between (A − J)% and (A + M)%, with an average over a long period of time of perhaps (A − D)%. Thus, in the long run the plant misses its target by D% and fluctuates from day to day to the extent of (M + J)%. In statistical terms, the value of D is called the 'bias' of the process and the magnitude of M + J is called the range of the process variation, an expression of precision. The magnitudes of the bias and precision can only be estimated; they are not exact because of the existence of various errors during the measurement (analysis) of the powder. These measurement errors consist of both random and systematic errors. Furthermore, since, in general, it is not possible to analyse the whole stock of the powder, it is necessary to obtain a 'representative' sample for analysis. Thus, additional error due to sampling is introduced at this stage.

The purpose of the application of statistical methods to this process is to help analyse and, hopefully, control these errors. This chapter describes briefly what statistical methods can offer in achieving this objective. The International Organization for Standardization (ISO) Standards Handbook [33] contains useful material for supplementary reading.

---

[9] Contributed by R. Sutarno and J.L. Dalton, CANMET, Energy Mines and Resources Canada, Ottawa, Ontario, Canada.

7-2. FREQUENCY DISTRIBUTION

For the application of statistical methods, the process can be represented by the following basic model

$$x_i = L + B + e_i \qquad (1)$$

where x_i is the process result at any given time, L is the target value (accepted reference value), B is the bias of the process (systematic error) and e_i is the statistical (random) error.

For a given process at steady state, L and B are constant. Both e_i and x_i are random variables, assumed to follow a normal frequency distribution with the same variance and means of zero and (L + B), respectively. Thus

$$e_i = N[0, R]$$

$$x_i = N[L + B, R]$$

The assumption of normality used in most statistical methods is usually sufficient to represent a wide variety of processes for the following reasons: (a) according to the 'central limit' theorem, the distribution of a mean of a random variable tends to be more normal than the distribution of the variable itself; and (b) in general, one is concerned only with the tail of the distribution, so deviation from normality does not have a serious effect on the inference taken from the process results. In the case where distribution of the process results clearly deviates from normality, the data can often be transformed to make them closer to a normally distributed variable. For example, in the case of the distribution of concentration of respirable dust particles in uranium mines, a logarithmic transformation was found to be suitable.

7-3. ACCURACY

The accuracy of a process is a measure of how closely the process can meet the target consistently. In the case of a chemical process, the target value is definable by the operator, i.e. the quantity of the product with the predefined characteristics. In the case of chemical analysis, the ultimate target is the 'true value'. The problem here is that the true value is never known, although it may conceptually exist. For this reason, it is usually replaced by a reference value. Thus, in practice, the accuracy of the measurement process is defined as the measure of the closeness of the results of the measurement process to a reference value, such as the certified value given for a reference material.

Two components make up the accuracy of a process: precision and trueness.

7-3.1. Precision

Precision is a measure of the consistency of a process; it is not a measure of how closely the process can meet the target value. Unfortunately, the term precision is sometimes erroneously considered to be identical with the term 'accuracy'.

Quantitatively, precision is expressed in terms of the deviation from the mean. One of the most common measures of precision is the standard deviation

$$R = \left[\sum_{1}^{n} (x_i - \bar{x})^2/(n - 1)\right]^{1/2} \tag{2}$$

$$\bar{x} = \sum_{1}^{n} x_i/n \tag{3}$$

where x_i is an individual result, $\bar{x}$ is the mean of the results and n is the number of results. For a normally distributed variable, this measure of precision means that there is approximately a 68% chance (two out of three) that in the absence of bias the value of x_i will be within one standard deviation from its true value, i.e.

$$\Pr[\mu - \sigma \le x_i \le \mu + \sigma] = 0.68 \tag{4}$$

It is important to note that all the x_i must be obtained under the same well defined conditions. Usually, there is a qualifying subscript to define a particular σ. For example σ_r signifies the repeatability standard deviation, i.e., all the x_i are obtained under repeatability conditions. This quantity is not the same as σ_R, the reproducibility standard deviation, where all the x_i are obtained under reproducibility conditions (Eq. (2)). In many cases, precision is expressed in terms of a confidence interval with higher probability, usually 95% instead of 68%, by introducing a multiplying factor. Thus

$$\Pr[\mu - k\sigma \le x_i \le \mu + k\sigma] = 0.95 \tag{5}$$

where k is a factor for adjusting the probability level.

As mentioned previously, statistical fluctuation can be reduced, at a cost, to a desired level. For a chemical process, often this reduction is achieved by mixing batches of the product (powder). For a measurement process, normally this reduction is achieved by performing replications and averaging the results. The following relation is a very useful tool

$$\sigma_m = \sigma/\sqrt{n} \tag{6}$$

where σ_m is the standard deviation of the mean of n results. A further benefit of replication is that the distribution of the means is usually closer to 'normal' than the distribution of the individual results.

To avoid misunderstanding, a precision expression such as standard deviation should only be used to describe the precision of a variable from a well defined population. For example, a standard deviation of individual analytical results must be computed from Eq. (2) using individual results as the x_i. The standard deviation of the means of two results (paired results) must be computed using the same formula, replacing x_i with the means of two results. Other conditions such as the origin of the data should also be defined; thus, the standard deviation between laboratory (σ_R) should not be confused with the standard deviation within laboratory (σ_r), etc.

7-3.2. Trueness

The trueness of a process is a measure of how closely the process can, in the long run, meet its target value. In the measurement process, trueness is defined as 'the closeness of agreement between the average value obtained from a large series of observations and an accepted reference value' [34]. Quantitatively, the trueness is usually expressed in terms of bias, D

$$D = E[x_i] - L \qquad (7)$$

where $E[x_i]$ is the expected value of x_i and L is the reference value. Experimentally, the expected value of x_i is estimated by the long term mean of x_i

$$E[x_i] = \sum x_i/n \qquad (8)$$

7-4. SOURCE OF ERRORS

To assess the performance of a process, one must measure the predefined attribute of the process. It is inevitable that the decision made will be affected by the accuracy of the measurement process. In most cases, the overall measurement process involves a sampling process, preparing the sample into a suitable form/quantity for the measurement procedure, and the measurement procedure itself. Potentially, each of these processes introduces error. All these errors consist of two components: systematic/bias and random/statistical.

7-4.1. Sampling

A sample is a portion of the material (population) taken for the purpose of providing information on the population. The accuracy of the conclusion drawn from a sample depends on the variability of the material. For homogeneous materials, a sample taken from any portion of the population (batch) represents the population accurately; for heterogeneous materials, careful procedures should be followed in order to take a proper sample with a certain desired accuracy. For some materials, sampling error is an important component of overall measurement error.

Another factor to be considered in sampling is the objective, i.e. the information required on the population. Does one require only the average characteristic or the variability as well? What type of characteristics are required? Some characteristics have a tend to have a greater variation than others; in many cases, the particle size of the ores has a greater variation than the composition.

7-4.2. Sample preparation

In many cases, a sample taken directly from the population is unsuitable for the measurement procedure because of its quantity, size, form, etc. In this situation, it is necessary to use a sample preparation procedure and prepare the sample (by grinding, mixing, etc.) before the measurement procedure. The error introduced at this stage is usually referred to as the preparation error. As in the case of the sampling error, the preparation error consists of two components: systematic and random. The systematic component can be controlled by physical improvement in the equipment, while the random component can be controlled by the preparation of multiple samples.

7-4.3. Measurement error

This is the component of error generated by the measurement itself. In the case of chemical analysis, for example, this may originate from weighing, titration, instrumental error, etc. As indicated above, this error consists of both systematic and random components and depends on the nature of the measurement. This error could be smaller (chemical analysis of ores) or greater than the other components (an error in the tumbler test of iron ore is comparable in magnitude to that of the sampling error).

7-4.4. Overall measurement error

The overall measurement error is the total of the error components mentioned above. It is accepted that the variances (σ^2) of the above error components are additive. Thus

$$\sigma_{SDM} = (\sigma_S^2 + \sigma_D^2 + \sigma_M^2)^{1/2} \tag{9}$$

where σ_{SDM} is the overall measurement standard deviation, σ_s is the sampling standard deviation, σ_D is the preparation standard deviation and σ_M is the measurement standard deviation.

Note: The partition between the sampling and the sample preparation error is completely arbitrary; if desired, they can be combined into one error.

7-5. STATISTICAL INFERENCE

Before an experiment is conducted, the objectives must be defined clearly. For example, one can conduct an experiment to see if process B produces the same results as process A. To define this objective, one should first clearly define what is meant by the results of two processes being equal. Also, what degree of difference between the two processes will matter. In statistical terms, the results of the two processes are considered to be the same if they can be assumed to come from the same frequency distribution. The results of two processes are considered to be significant if they can be shown to come from two different distributions. The difference between the parameter under consideration (usually the mean or variance) of these two distributions must be greater than a certain value.

Before conducting the experiment, the experimenter must arrive at an hypothesis of the phenomena under consideration, i.e. is process A equal to process B? Alternatively, process A is not equal to process B. The former hypothesis is usually referred to as the null hypothesis (H_0) and the latter as the alternative hypothesis (H_1). The outcome of the experiment will help to decide which of these two hypotheses is true. Because of the inevitable statistical error, one can expect a wrong decision to be made occasionally. Although this error cannot be eliminated completely, one may be able to control the probability of committing it. There are two types of error:

(1) *Error type I:* This is an error committed when the experimenter rejects his null hypothesis when, in reality, it is true. The probability of committing this type of error, usually designated a, is called the significance level. In the above example, error type I is the error that is committed by the experimenter which concludes that the results of processes A and B are different when, in fact, they are not.

(2) *Error type II:* This is an error committed when the experimenter accepts his null hypothesis when, in reality, the hypothesis is false. The probability of committing this error, usually designated b, depends on the alternative hypothesis, H_1 (the difference in the two distributions that the experimenter considers significant according to his requirements); b can be calculated only if this alternative hypothesis is specified adequately. In the above example,

error type II is the error committed by the experimenter in concluding that the results of processes A and B are equal when, in fact, they differ by an amount greater than that given by the specified alternative hypothesis.

The values of both A (also known as the producer's risk) and B (consumer's risk) are important considerations in the design of an experiment.

An analyst frequently encounters the problem of deciding whether two methods are capable of producing the same analytical result as, for example, in replacing a manual method with an automated method. A statistically acceptable manner of calculating whether or not bias between the two methods exists is the use of the t distribution [35]. This distribution is used when a relatively small amount of statistical data is available, which is typically the case in analytical chemistry. The hypothesis under test is whether the populations (results) of the two independent methods are statistically equivalent.

7-6. CONTROL CHARTS

A control chart is a chart, with upper and/or lower control limits, on which the values of some statistical measures (such as the mean, range, etc.) for a series of samples or subgroups are plotted. The chart frequently shows a central line to assist detection of a trend of plotted values towards either control limit. Usually, a control chart is used as a graphic method to see if the process is operating satisfac-

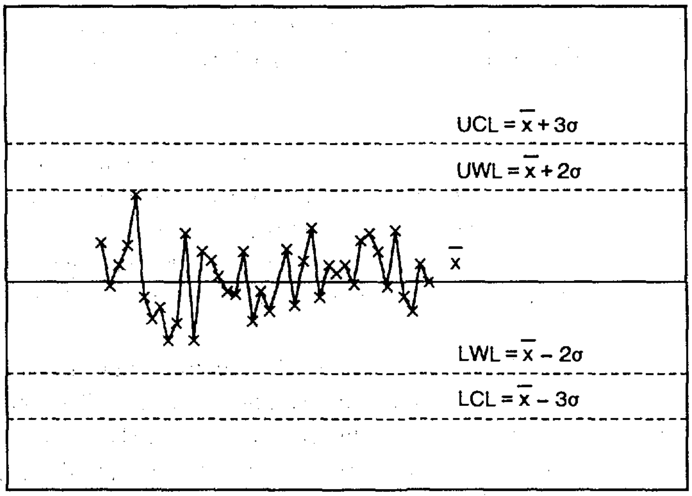

FIG. I-7. Mean chart showing the upper and lower warning and control limits.

torily, i.e. that the process variation is random in nature and that the process is in the state of 'statistical control'. A control chart is a 'life' chart; it should be updated periodically to see if there is a change in the process. The most popular and simplest control charts are Shewhart charts for the mean and the range of the process. The two charts are based on the assumption that the variables are distributed normally.

7-6.1. Mean chart

As its name implies, this chart is used to monitor the mean of the process, i.e. if the mean is constant or follows a trend. Figure I-7 shows an example of this chart. The vertical axis represents the process variable (results) and the horizontal axis represents time. It has a central line, which is the mean of the process. The chart usually has an upper warning limit (UWL), lower warning limit (LWL), upper control limit (UCL) and lower control limit (LCL). In theory, the operator should define these limits in accordance with his needs. Customarily, however, they are defined as follows: UWL and LWL are defined as the limits within which 95% of the process results will fall, and UCL and LCL are defined as the limits within which 99% of the process results will fall. Thus

Central line : $\bar{x}$
UWL : $\bar{x} + 2\sigma$ LWL : $\bar{x} - 2\sigma$
UCL : $\bar{x} + 3\sigma$ LCL : $\bar{x} - 3\sigma$
$\bar{x}$: $\Sigma x_i/n$ σ : $[\Sigma(x_i - \bar{x})^2/(n - 1)]^{1/2}$

It is important to note that the standard deviation σ is the 'total' standard deviation, which includes process, sampling, sample preparation and measurement (analysis) standard deviations.

7-7. RANGE CHART

As its name implies, the range chart monitors the range of a process variable and, therefore, the precision. The vertical axis of this chart represents the range of 'two' observations and the horizontal axis represents time. It is useful, for example, for monitoring the precision of chemical analyses. In many cases, the samples to be analysed are not identical, so the mean chart may not be suitable. In this case, the range chart is more suitable in order to ascertain if the analytical process is under (statistical) control. Figure I-8 shows an example of a range chart. It should be noted

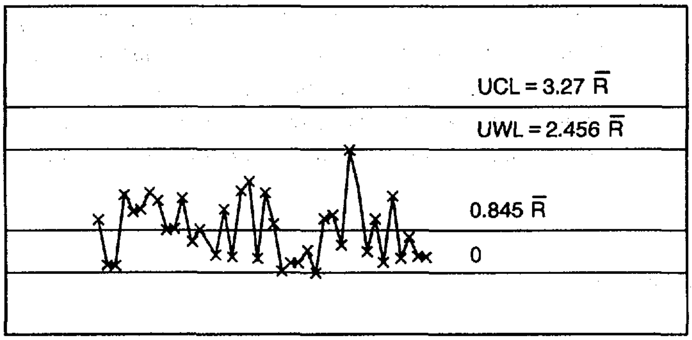

FIG. I-8. Range chart; the vertical axis is the range of two observations and the horizontal axis is the time.

that the distribution of the range is not symmetrical; the 50% level is $0.845\bar{R}$, the 95% limit is $2.45\bar{R}$ and the 99% limit is $3.27\bar{R}$. Thus

Central line : $0.845\bar{R}$
UWL : $2.456\bar{R}$
UCL : $3.27\bar{R}$
$\bar{R}$: Σ R/n
R : $|x_1 - x_2|$

7–7.1. Construction and update of control charts

Initially, the control chart can be constructed with a few determinations of the process results, for example, ten determinations. Once the initial chart has been started, the new data can then be added as they become available. It should be noted that, in adding points for the R chart, the condition for obtaining duplicate results should be consistent, i.e. if the duplication is carried out under a repeatability condition, it should always be carried out under the same conditions.

Since the main purpose of control charts is to see if the process is under control, i.e. to see if at any moment the process is out of control, it is imperative that it should be updated regularly. The frequency of update depends on the nature of the process. The mean can be updated periodically as new data become available, for example, by using the moving average method. The length of the period depends on the state of the process. A shorter period is necessary at the initial state and a longer period may be sufficient when the process has reached a steady state. The presence of a trend can be observed visually. Even though the availability of a personal computer currently simplifies the task of updating the control charts, the updating procedure should be chosen in such a way that the resulting control charts remain relatively simple. Updating the mean too frequently results in a more complicated looking central line. Process variation can be observed by both the magnitude of R and by the range chart. The limits of both the mean chart and the range chart should also be updated periodically. Visual observation or a statistical test (F ratio test) can be used to determine if these charts require updating.

7–7.2. Practical interpretation of control charts

The main use of control charts is to observe trends in both the precision and the mean. The probability that a process result will fall above the central line is about 50%. Thus, if for any reason these results fall above the central lines by significantly more than 50%, the operator will be able to detect the change. This change can also be detected by the movement of the moving average. The trend of the precision can be observed by the amplitude of the mean chart or by the movement of the mean range of the range chart. The probability that a result will fall above UCL or below LCL is less than 1% (0.05% on each side). Thus, if this phenomenon is observed, then a change in the process must have occurred. The probability that a process result will fall outside the warning limits (UWL and LWL) is less than 5%. If one result falls outside the limits this should be taken as a warning that a possible change may be justified. If two consecutive results fall on the same side of the warning limits, then there has certainly been a change in the process, and immediate corrective action is warranted.

REFERENCES

[1] ASSOCIATION OF EXPLORATION GEOCHEMISTS, "Analytical methods in geochemical prospecting", Handbook of Exploration Geochemistry, Vol. 1 (FLETCHER, W.K., Ed.), Elsevier, Amsterdam, 1981.

[2] SEIDEL, D.C., "Extracting uranium from its ores", Int. At. Energy Agency Bull. **23** 2 (1981) 24–28.

[3] GOW, W.A., "Recent advances in uranium ore processing", Advances in Uranium Ore Processing and Recovery from Non-Conventional Resources (Proc. Technical Committee Mtg Vienna, 1983), IAEA, Vienna (1985) 3–13.

[4] NUCLEAR ENERGY AGENCY OF THE OECD, Uranium Extraction Technology: Current Practice and New Developments in Ore Processing, OECD, Paris (1983).

[5] MERRITT, R.C., The Extractive Metallurgy of Uranium, United States Atomic Energy Commission, Washington, DC (1971) (Reprinted in 1979).

[6] INSTITUTION OF MINING AND METALLURGY, Geology, Mining and Extractive Processing of Uranium (JONES, M.J., Ed.), IMM, London (1977).

[7] INTERNATIONAL ATOMIC ENERGY AGENCY, Significance of Mineralogy in the Development of Flowsheets for Processing Uranium Ores, Technical Reports Series No. 196, IAEA, Vienna (1980).

[8] BOOMAN, G.L., REIN, J.E., Uranium, Vol. 9 of Part II of Treatise on Analytical Chemistry (KOLTHOFF, I.M., ELVING, P.J., Eds), Wiley, New York and London (1962).

[9] LEDERER, C.M., SHIRLEY, V.S., Table of Isotopes, 7th edn, Wiley, New York and Chichester (1978).

[10] The Radiochemical Manual, 2nd edn, The Radiochemical Centre, Amersham (1966).

[11] CROUTHAMEL, C.E., ADAMS, F., DAMS, R., Applied Gamma Ray Spectrometry, 2nd edn, Pergamon Press, Oxford and New York (1970) (Reprinted in 1975).

[12] SUSCHNY, O., Geochemical Analysis for Uranium, Rep. IAEA/RL/33, Seibersdorf Laboratory, IAEA, Vienna, 1975 (Internal report).

[13] Guide to Activation Analysis (LYON, W.S., Jr., Ed.), Van Nostrand, Princeton and Toronto (1964).

[14] AMIEL, S., Anal. Chem. **34** (1962) 1683.

[15] PAKALNS, P., "Fluorimetric determination of uranium", Analytical Chemistry of Uranium and Thorium (Proc. Symp. Lucas Heights, 1970), Australian Atomic Energy Commission, Sydney (1970).

[16] CENTANNI, F.A., ROSS, A.M., DE SESA, M.M., Fluorimetric determination of uranium, Anal. Chem. **28** (1956) 1651.

[17] SMITH, A.Y., LYNCH, L.L., PAKALNS, P., "Fluorimetric determination of uranium", Paper 69-40, Geological Survey of Canada, Ottawa, Ontario (1969).

[18] VESELSKY, J.C., RATSIMANDRESY, Y., An investigation of quenching effects in the direct fluorimetric determination of uranium in minerals, Anal. Chim. Acta **104** (1979) 345.

[19] ROBINS, J.C., Field technique for the measurement of uranium in natural waters, Can. Inst. Min. Metall. Bull. **797** (1978) 61–67

[20] KRAUS, K.A., NELSON, F., MOORE, G.E., J. Am. Chem. Soc. **77** (1955) 3972.

[21] KORKISCH, J., HAZAN, I., Ion exchange determination of uranium in ferrous alloys, Anal. Chem. **36** (1964) 2464–2466.

[22] STRELOW, F.W.E., VAN DER WALT, T.N., Quantitative separation of bismuth from lead, cadmium and other elements by anion exchange chromatography with hydrobromic acid–nitric acid elution, Anal. Chem. **306** (1981) 110.

[23] LYLE, S.J., TAMIZI, M., Anal. Chim. Acta **108** (1979) 437.

[24] DAVIES, W., GRAY, W., A rapid and specific titrimetric method for the precise determination of uranium using iron (II) sulphate as the reductant, Talanta **11** (1964) 1203–1211.

[25] LAVERGNE, P.J., Field and Laboratory Methods Used by the Geological Survey of Canada in Geochemical Surveys, No. 8, Preparation of Geological Materials for Chemical and Spectrographic Analysis, Paper 65-18, Geological Survey of Canada, Ottawa, Ontario (1965).

[26] BERTIN, E.P., Principles and Practice of X-Ray Spectrometric Analysis, 2nd edn, Plenum Press, New York (1975).

[27] DONALDSON, E.M., Methods for the Analysis of Ores, Rocks and Related Materials, Monograph 881, 2nd edn, CANMET, Energy, Mines and Resources Canada, Ottawa, Ontario (1982).

[28] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, Directory 1982, ISO, Geneva (1983).

[29] INTERNATIONAL ATOMIC ENERGY AGENCY, Analytical Quality Control Services, Seibersdorf Laboratory, IAEA, Vienna (Internal report).

[30] BOWMAN, W.S., Certified Reference Materials Project, Report CCRMP 91-1E, CANMET, Energy, Mines and Resources Canada, Ottawa, Ontario (1991).

[31] NATRELLA, M.G., Experimental Statistics, Handbook 91, United States Department of Commerce, National Bureau of Standards, Washington, DC (1963).

[32] AMERICAN SOCIETY FOR TESTING AND MATERIALS, Manual on Presentation of Data and Control Chart-Analysis, Manual 7, ASTM, Philadelphia, PA (1990).

[33] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, Statistical Methods, ISO Standards Handbook 3, 2nd edn, ISO, Geneva (1981).

[34] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, Precision of Test Methods: Determination of Repeatability and Reproductivity for a Standard Test Method by Interlaboratory Tests, 2nd edn, ISO-5725, ISO, Geneva (1986) 49 pp.

[35] DIXON, W.J., MASSEY, F.J., Introduction to Statistical Analysis, 4th edn, McGraw-Hill, New York (1983).

Part II

ANALYTICAL METHODS

Method 1

ANALYTICAL PROCEDURES FOR FLUOROMETRIC DETERMINATION OF LABILE URANIUM[1]

1-1. INTRODUCTION

This method is used commonly for the geochemical analysis of stream sediment, soil and rock samples for labile, or acid extractable, uranium. Samples are attacked with nitric acid or a mixture based on nitric acid. Between 10 and 100% of the uranium can be liberated by this treatment, depending on the proportion of uranium locked in the refractory minerals. This treatment is often preferred in geochemical exploration because the labile uranium is frequently more indicative of uranium mineralization than is total uranium.[2] The procedure is rapid, allowing for a throughput of 100–150 samples per day, which is necessary for geochemical exploration programmes of any size. The method is also suitable for water samples.

Several variations are possible using the fluorometric method. First, fusion can be carried out in small platinum dishes (0.70 mm diameter) using 0.60 g of the flux mixture. Second, in place of the flux mixture recommended, a mixture of sodium fluoride-lithium fluoride (NaF–LiF) is often employed. This mixture is fused at a temperature of 900°C. Finally, fusion is frequently done in the flame of a rotary burner rather than in a muffle furnace. These differences are described in Method 3.

1-2. PREPARATION OF EQUIPMENT AND REAGENTS

(1) *Platinum dishes:* The platinum dishes used in this procedure are of a special design and size to fit the fluorometer. They are prepared from discs of platinum metal (38 mm diameter) and formed with a steel dish forming tool. These dishes conveniently permit the evaporation of 2.5 mL of sample solution or water, and allow use of 3 g of flux; they should have numbers stamped on their undersides. Fifty are required for the analyses, while an additional eight are used for the standards.

---

[1] Contributed by A.Y. Smith, Division of Nuclear Fuel Cycle and Waste Management, IAEA.

[2] This method is modified from that published by Smith and Lynch [1] and is based on the use of the Galvanek–Morrison fluorometer manufactured by the Jarre-Ash Company. The method should be modified for use with other types of fluorometers.

(2) *Carbonate-fluoride flux:* Weigh 455 g of sodium carbonate, 455 g of potassium carbonate and 90 g of sodium fluoride. Place these compounds in a powder mixing mill and mix for 8 hours. This mixture is hygroscopic and must be kept in tightly sealed bottles away from moisture when not in use. A daily supply of flux is kept in a beaker and stored in a desiccator when not in use. It is convenient to prepare at least 1000 g of flux at one time.

(3) *4N nitric acid* (HNO_3): Add 125 mL of concentrated HNO_3 to 375 mL of deionized water and mix well.

(4) *50% hydrochloric acid:* Add 250 mL of concentrated hydrochloric acid to 250 mL of deionized water and mix well. This solution is used for cleaning the platinum dishes after each use.

(5) *Standard uranium solutions:* Weigh 210 mg of analytical reagent grade uranyl nitrate ($UO_2(NO_3)_2.6H_2O$) into a 100 mL volumetric flask.[3] Add approximately 25 mL of 4N HNO_3 and dissolve the uranyl nitrate. Dilute to the 100 mL mark with 4N HNO_3 and mix well. This solution contains 1000 μg/mL of uranium. From this solution prepare a standard solution containing 0.1 μg/mL of uranium by dilution as follows:

Standard used (μg/mL)	Aliquot taken (mL)	Diluted to (mL)	New standard (μg/mL)
1000	10	100[a]	100[b]
100	10	100[a]	10
10	10	100[a]	1[b]
1	10	100[a]	0.1[b]

[a] With 4N HNO_3.
[b] Prepare a fresh solution daily.

1-3. WEIGHING

(1) Prepare numbered and calibrated test tubes. Place 50 tubes in a test tube rack with 55 places, with five rows of 10 tubes at the right hand side of the rack. Leave one row of five holes empty on the left hand side of the rack.

(2) Weigh 0.50 g of *carefully mixed* sample into each numbered test tube calibrated at 10 mL. Tubes 15 and 30 should remain empty for reagent blank measurements. As each tube receives its weighed sample, place it one space to the left.

---

[3] Some methods recommend use of National Bureau of Standards material NBS 950A to prepare the standard solution, but this may be difficult to obtain in many parts of the world. The reagent recommended above is entirely satisfactory.

(3) The weighing of samples should be completed by 12:00 hours so as to be ready for leaching in the afternoon.

(4) Prepare all the analytical sheets and indicate the correspondence between the tube number and the sample number. Cover the tubes with analytical sheets to prevent dirt entering.

1-4. LEACHING

(1) At the end of the morning, turn on the water baths and adjust the water to a slow flow rate and the temperature control to 95°C.

(2) Using an automatic pipette, dispense 5.0 mL of the 4N HNO_3 into each sample tube. Care should be taken with samples high in carbonate to avoid frothing and loss of sample.

(3) Move each tube one hole to the right after it has received the acid. At the end of this procedure, all the tubes should be at the right hand side of the rack.

(4) Transfer the tubes (in five rows of ten) to the water bath. Leach for 1 hour. During the course of leaching, agitate each tube three times by removing the tubes one by one, shaking to mix the solution and returning the tube to its place. This ensures uniform attack on all the samples.

(5) After 1 hour, add 0.15 g of potassium bromate (K_2BrO_3) to each tube and shake to dissolve. Return the tubes to the water bath for an additional 10 minutes to precipitate the MnO_2 and to eliminate excess bromine. Remove each tube from the water bath, dilute to the 10 mL mark with demineralized water and mix well in the vortex mixer to homogenize. Allow the tubes to stand overnight. This is *Solution A.*

(6) *Solution B* is prepared the following morning (see below) by pipetting 2 mL of the sample solution (Solution A) into clean, numbered test tubes calibrated at 10 mL and diluting to the 10 mL mark with 4N HNO_3. Mix thoroughly with the mixer.

Note: The remainder of Solution A can be used to determine other elements, if required.

1-5. FUSION AND FLUOROMETRIC MEASUREMENT

(1) Pipette 1 mL of Solution B into a platinum dish and evaporate to dryness on a hot plate or under a heat lamp. Record the number of the platinum dish opposite the sample number on the analytical sheet.

(2) Bring the platinum dish to the point of dull red heat over a Meker burner. Allow to cool.

(3) Using a calibrated plastic scoop, dispense 3 g of carbonate-fluoride flux into the platinum dish.

(4) Fuse for 10 minutes in a muffle furnace at 650°C, timing from the moment the flux melts.

(5) Remove the platinum dishes from the furnace, allowing the flux to solidify in a level position, then place in a desiccator to cool for at least 20 minutes.

(6) Warm and adjust the fluorometer as described in the manufacturer's instruction manual.

(7) Remove the flux disc from the platinum dish and write lightly in pencil the number of the platinum dish on the back of the disc. Place the disc in the sample receptacle of the fluorometer and measure the fluorescence.

(8) By means of a standard graph prepared as indicated below, convert the fluorometer scale reading to micrograms of uranium.

(9) Calculate the uranium content of the sample by

$$\mu\text{g uranium} \times 200 = \text{uranium in ppm.}^{4}$$

(10) If the fluorometer scale reading is greater than 90, take a smaller aliquot of Solution B or make further dilutions, as necessary, and repeat the determination, taking into account the dilution factor.

1-6. DETERMINATION OF URANIUM IN WATER SAMPLES

(1) Pipette twice 2.5 mL aliquots of the water sample into a platinum dish, evaporate to dryness on a hot plate or under a heat lamp after each addition.

(2) Bring to the point of dull red heat over a Meker burner and allow to cool.

(3) Proceed from step (3) in Section 1-5.

(4) Calculate the uranium content in the sample by

$$\mu\text{g uranium} \times 200 = \text{uranium in } \mu\text{g/L or uranium in ppb.}^{5}$$

(5) If the fluorometer scale reading is greater than 90, take a smaller aliquot of sample and repeat the determination.

---

[4] The formula for calculating the uranium content of the sample is as follows:

$$\frac{a}{b} \times \frac{c}{d} \times \frac{e}{f} = \text{uranium (ppm)}$$

where a is the micrograms of uranium (from the standard curve), b is the weight of the sample, c is the volume of Solution A, d is the aliquot of Solution A taken, e is the volume of Solution B and f is the aliquot of Solution B taken for analysis.

[5] 1 ppb = 1 ng/g (one part in 10^9).

1-7. PREPARATION OF THE STANDARD GRAPH

(1) Carefully pipette 0.00, 0.05, 0.10, 0.20, 0.40, 0.60, 0.80 and 1.0 mL of the 0.10 g/mL uranium standard solution into platinum dishes stamped with letters A to H. Prepare two additional blanks.

(2) Evaporate to dryness on a hot plate or under a heat lamp.

(3) Add 3 g of carbonate–fluoride flux to each dish.

(4) Fuse for 10 minutes in a muffle furnace at 650°C, timing from the moment the flux melts.

(5) Remove the platinum dishes from the furnace. Allow the flux to solidify in a level position, then place in a desiccator to cool for at least 20 minutes.

(6) Tip the flux discs out of the platinum dishes and transfer with a soft pencil the letter of the dish to the back of each disc.

(7) Having adjusted the zero reading on the fluorometer according to the instruction manual, insert the 0.1 μg standard disc into the sample holder and adjust the instrument to read 100. Remove the standard disc and check that the zero setting has not changed.

(8) Proceed to read the standard discs, including the 0.0 μg standard. Re-read the 0.1 g disc after every few readings and adjust the instrument to correct for any drift that may have occurred.

(9) Prepare a plot of standard readings, with the instrument readings as ordinate against micrograms of uranium as abscissa. Draw a straight line between the background scale reading (0.00 μg disc) and the 0.1 μg disc scale reading as 100. Establish lines at 5% above and below the first line. Plot the values obtained for the standards. Reject those standards which do not fall within the 5% limits. If more than two standards fall outside the ±5% range, repeat the entire series of standards.[6]

(10) With careful standardization of the procedures and sufficient experience it should be possible to dispense with the preparation of a full set of standards each day. When all the points fall consistently within ±5% of the line, one intermediate standard plus blank and a 0.1 μg standard should suffice.

1-8. NOTES

(1) Care should be taken during fusion to ensure consistent and reliable results. The temperature within the muffle furnace should be uniform throughout. A variation in temperature between the dishes causes unreliable results.

---

[6] Alternatively, use the measurements to calculate a regression fit of the data. The results should be linear, with the correlation coefficient produced by the calculation having a value of 0.98. If not, repeat the measurement.

(2) Discs must be protected from humidity before reading. Exposure to moisture causes a decrease in the fluorometer reading. Store the sample discs in a desiccator until they are ready for reading.

(3) The standard curve should be a straight line. Its slope is governed by the reading obtained on the blank disc (0.00 μg uranium standard). Depending on the quality of the flux reagents, blank readings of between 3 and 10 are normal. If the blank disc gives a reading higher than 10, the batch of flux should be discarded and a new batch prepared.

(4) It is important to keep the fluorometer scrupulously clean. The sample slide should be cleaned regularly, removing all chips of flux, dust, lint, etc. that could lead to a high background reading.

(5) It is possible to eliminate day to day calculation of the uranium content of samples by preparing in advance tables of uranium content against the fluorometer reading. A separate table is required for each blank disc reading. If dilutions are required, these samples have to be calculated separately.

1-9. EQUIPMENT AND REAGENTS REQUIRED FOR THE ESTABLISHMENT OF A GEOCHEMICAL LABORATORY FOR FLUOROMETRIC URANIUM ANALYSIS

1-9.1. Equipment

Standard laboratory equipment	*Quantity*
Analytical balance	1
Balance, triple beam with attachment weight kit	1
Fume hood	1
Meker burner	5
Water baths 12 in × 26 in × 5 in (or dry baths) (see item (11) of Section 1-9.2)[7]	2
Demineralizer support	1
Cartridges, demineralizer (mixed)	6
Electric hot plate or heat lamp	2
Desiccator: 250 mm	2
Silica gel	2 kg
Crucible tongs (10 in. long, platinum tipped)	3
Test tube racks (60 tubes each)	10
Beakers (50 mL)	24
Beakers (100 mL)	24

---

[7] 1 in = 2.54×10^1 mm.

Standard laboratory equipment	*Quantity*
Beakers (250 mL)	24
Beakers (600 mL)	6
Beakers (1000 mL)	6
Cylinder graduated in 50 mL	5
Cylinder graduated in 100 mL	5
Cylinder graduated in 500 mL	3
Cylinder graduated in 1000 mL	3
Pipette (automatic) to deliver 2.0 mL	6
Pipette (automatic) to deliver 5.0 mL	6
Pipette (0.5 mL) graduated in 0.05 mL	12
Pipette (1 mL) graduated in 0.05 mL	12
Pipette (2 mL) graduated in 0.1 mL	12
Pipette (5 mL) graduated in 0.1 mL	12
Test tube, 18 mm × 150 mm, Pyrex	576
Volumetric flasks (50 mL)	2
Volumetric flasks (100 mL)	10
Volumetric flasks (250 mL)	2
Volumetric flasks (1000 mL)	2

1–9.2. Special equipment

(1) A Galvanek–Morrison solid state fluorometer basic console with a solid sample chamber for dual flux dishes and filters for uranium analysis
(2) Dish forming tool for 38 mm diameter dishes
(3) Platinum discs (38 mm diameter, 0.4 mm thick); 60 dishes are required
(4) Muffle furnace, double door, pyrometer controller
(5) Powder mixer (Rotomixer), 3 L capacity
(6) Spare plastic container for above
(7) Silica trays (size 118 mm × 175 mm); 12 are required
(8) Mini–shakers; two are required
(9) Infrared heating lamps with stands; two are required
(10) Infrared lamps (spare)
(11) Dry bath model 145 (220V); two are required
(12) Aluminium heating blocks for above; six are required.

1–9.3. Reagents (sufficient for 1 year of operation)

(1) Nitric acid, concentrated	360 L
(2) Hydrochloric acid, concentrated	160 L

(3) Potassium bisulphate, fused powder, reagent grade	60 kg
(4) Sodium carbonate, anhydrous, reagent grade	20 kg
(5) Potassium carbonate, anhydrous, reagent grade	20 kg
(6) Sodium fluoride, reagent grade	5 kg
(7) Uranyl nitrate, reagent grade	100 g
(8) Potassium bromate, reagent grade	3 kg

REFERENCE

[1] SMITH, A.Y., LYNCH, J.J., Field and Laboratory Methods Used by the Geological Survey of Canada in Geochemical Surveys, No. 11, Uranium in Soils, Stream Sediment and Water, Geological Survey of Canada, Ottawa, Ontario, Paper 69-40 (1969) 9.

Method 2

DETERMINATION OF URANIUM IN WATER USING A SCINTREX UA-3 URANIUM ANALYSER[8]

2-1. INTRODUCTION

A pulsed nitrogen laser is used to induce the luminescence of a uranium-phosphate complex. The luminescence is proportional to the concentration of uranium in solution. Since the uranyl luminescence is relatively long lived, interference by organic matter is eliminated by sampling the emitted light after most of the organic fluorescence has decayed [1, 2]. Quantitative results are obtained using the method of standard additions.[9]

2-2. INTERFERENCES

Samples containing large amounts of calcium or magnesium precipitate when the buffer is added and must be diluted before successful determinations can be made [3]. A high room temperature shortens the luminescence lifetime. Highly coloured samples contain too much organic matter for successful determinations and should be cleared by a suitable method (see *Note (1) of Section 2-7*). Other potential interferences are compensated for by using the method of standard additions.

2-3. PRECISION AND REPORTING LIMIT

The relative deviation of replicate measurements is approximately 10% at the 20 ppb level. The reporting limit is 1 ppb.

---

[8] Contributed by R. Chessmore, United States Department of Energy, Grand Junction, Colorado, USA.

[9] The UA-3 laser fluorometer manufactured by Scintrex Ltd of Toronto, Canada, has been succeeded by a multisample, computer based system. The LU-4 utilizes a 12 cuvette sample carousel for automated, computer controlled uranium determination. The software provides a variety of analytical sampling techniques, including use of a standard curve, and standard additions. It is estimated that the instrumentation is capable of producing between 40 and 100 determinations per hour, depending on the sample complexity, with a detection limit of 0.02 ppb of uranium.

2–4. REAGENTS

(1) Buffer solution (Fluran): Add 570 g of $Na_3PO_4.12H_2O$ and 33 g of $H_4P_2O_7.10H_2O$ to a graduated 3 L beaker. Add approximately 1.5 L of deionized water and about 40 mL of phosphoric acid (H_3PO_4). *Do not* exceed the 2 L volume mark. Heat gently to dissolve. Cool, dilute to 2 L with deionized water, and adjust the pH to 6.9 with H_3PO_4.
(2) HNO_3, concentrated.
(3) Hydrofluoric acid (HF), concentrated.
(4) Perchloric acid ($HClO_4$), concentrated.
(5) Sulphuric acid (H_2SO_4), concentrated.

2–5. METHODS

2–5.1. Instrument conditions

See Section 2–5.3.

2–5.2. Standards

(1) *Stock solution:* Digest 0.848 g of NBS 950A in 3 mL of H_2SO_4, 5 mL of HNO_3, 10 mL of $HClO_4$ and 1 mL of HF. Dilute to 1000 mL. This is the 1000 ppm uranium standard. Alternatively, a vendor supplied 1000 g/mL uranium standard can be used. Dilute 0.1 mL of the stock solution to 100 mL. This is 1 ppm and is used for standard additions.[10]
(2) *Calibration standards:* Dilute 1 mL of 1 ppm to 100 mL; this is 10 ppb. Dilute 0.5 mL of 1 ppm to 100 mL; this is 5 ppb. Dilute 0.1 mL of 1 ppm to 100 mL; this is 1 ppb.

2–5.3. Calibration method

The steps in the calibration method are as follows:

(1) Allow the instrument to warm up according to the instruction manual (record the laser intensity; a downward trend in the intensity reading is a clue that the laser is wearing out).
(2) Zero the meter using the ZERO control. The meter displays an integrated signal. It takes 4 seconds for the UA-3 to respond to a change in setting.
(3) Make sure the sample cuvette is clean, with no water spots or droplets. Add 5 mL of the 5 ppb standard to the cuvette.

---

[10] The 1000 μg/mL standard solution can be prepared as described in Method 1.

(4) Close the cell compartment and switch on the photomultiplier tube (PMT).

(5) Zero the instrument, this time using the BALANCE control.

(6) Turn off the PMT, open the cell compartment and add 1 mL of Fluran solution. Perform this addition forcefully with a syringe or automatic pipette to promote mixing. Close the cell compartment and turn on the PMT.

(7) Wait approximately 1 minute to ensure adequate mixing and observe the reading on the front panel meter. With the RANGE setting on high, a 0.5 ppb standard should cause a half-scale deflection to 0.5. The SENSITIVITY control is used to adjust the needle deflection.

(8) Repeat steps (3) to (7) with the 10 ppb standard. The SENSITIVITY setting should not need further adjustment.

(9) All the samples are checked by standard addition. The technique should also be checked during calibration. Once the 5 and 10 ppb standard checks are complete, repeat steps (3) to (6). The meter should read 5 without adjustment of the SENSITIVITY setting.

(10) Using an Eppendorf or similar micropipette, carefully add 10 μL of 1 ppm standard to the cuvette. Close the cell compartment, turn on the PMT and observe the reading after about 1 minute. The reading should be approximately 7.

(11) Repeat step (10) once again. The reading should now be approximately 9.

2-5.4. Measurement method

(1) Following calibration, pipette 5 mL of sample into the quartz cuvette. Turn on the PMT and zero the instrument using the BALANCE. Turn off the PMT.

(2) Add 1 mL of Fluran solution and wait 1 minute to permit mixing.

(3) Turn on the PMT and record the reading. Turn off the PMT.

(4) Add 10 μL of 1 ppm standard to the cuvette. Close the compartment, turn on the PMT and wait 1 minute before reading. Turn off the PMT.

(5) If the increase in the reading from steps (3) to (4) is approximately 2 ppb, there are no appreciable interferences, and the initial reading is correct. If the increase is smaller, repeat step (4).

(6) The incremental increases from steps (3) to (4) and then from steps (4) to (5) should be approximately the same. The actual result can then be calculated using the familiar additions graphic procedure [4].

2-6. CALCULATIONS

Calculate the uranium concentration in the sample as follows:

$$\text{Uranium } (\mu\text{g/L}) = \frac{AB}{(C - A)\,D}$$

where A is the sample intensity, B is the standard spike in micrograms, C is the sample + spike intensity and D is the sample volume in millilitres.

2-7. NOTES

(1) Highly coloured samples should not be digested with permanganate or peroxide, since they are severe interferences themselves. Digestion with potassium pyrosulphate or HNO_3 can be used. Samples can be taken to dryness and redissolved in dilute HNO_3.

(2) The overload light indicates that the sample contains more than twice as much uranium as the full scale calibration.

(3) The results are best if the samples are diluted to the 1–10 ppb range rather than extending the calibration curve.

REFERENCES

[1] CAMPEN, W., BACHMANN, K., Laser-induced fluorescence for the direct determination of small concentrations of uranium in water, Microchim. Acta **3/4** (1979) 159.

[2] ROBBINS, J.C., Field technique for the measurement of uranium in natural waters, Can. Min. Metall. Bull. **797** (1979) 61–67.

[3] KORTE, N.E., CHESSMORE, R., Interference Effects of Inorganic Ions in Natural Waters When Using the Scintrex UA-3 Uranium Analyzer, Open-File Report DOE-GJBX-109(80), United States Department of Energy, Washington, DC (June 1980).

[4] WILLARD, H.H., MERRITT, L.L., DEAN, J.A., Instrumental Methods of Analysis, 5th edn, Van Nostrand, New York (1974) 379–380.

Method 3

DETERMINATION OF URANIUM IN GEOLOGICAL MATERIALS BY FLUOROMETRY[11]

3-1. INTRODUCTION

Fluorometric determinations of uranium have traditionally been applied to solid samples containing low levels (<500 ppm) of uranium. Samples containing larger amounts of uranium are normally analysed by UV/VIS spectrophotometry or by XRF. The fluorometric method can also be applied to water samples.

The uranium in the sample is separated from potential interferences using an ethyl acetate extraction after digestion in a mixture of acids. An aliquot of the extract is fused with NaF–LiF flux and analysed by fluorometry. This method can be called a 'total' uranium method in that, unlike Method 1, the sample is totally dissolved by the mixture of acids. It is used appropriately where an accurate estimate of the abundance of the element is required [1].

3-2. INTERFERENCES

No interferences have been observed with the method (*see Note (1) of Section 3-7*).

3-3. PRECISION AND REPORTING LIMIT

Sample No.	Expected value (ppm U_3O_8)	Average value (ppm U_3O_8)	Relative deviation (%)	No. of determinations
BFE 30035	11	10.5	17	362
BFE 25581	84	83	8	248
BFE 22814	12	11	18	117
BFE 16809	176	172	11	104

The reporting limit is 1 ppm.

---

[11] Contributed by R. Chessmore, United States Department of Energy, Grand Junction, Colorado, USA.

3-4. REAGENTS

(1) HNO_3, concentrated.
(2) H_2SO_4, concentrated.
(3) $HClO_4$, concentrated.
(4) HF, concentrated.
(5) NaF–LiF: Mix 98% reagent grade NaF by weight, and 2% reagent grade LiF by weight. Blend for at least 48 hours prior to use.[12]
(6) Ethyl acetate ($CH_3COOC_2H_5$), 99 mol%, minimum reagent grade.
(7) Aluminium nitrate ($Al(NO_3)_3.9HO$), reagent grade: Prepare a saturated aqueous solution, approximately 900 g/L.
(8) Ammonium hydroxide (NH_4OH), concentrated.

3-5. METHODS

3-5.1. Instrument conditions

(1) *Jarrel-Ash fluorometer:* Turn on the instrument at least 20 minutes before use. Set the sensitivity at 6 or 7. Adjust the instrument to zero with the ZERO adjustment knob. Set the background at zero with the 0.01 scale switch.
(2) *Geoco rotary fusion burner*: Set for 1/2 minute at low temperature (450°C). Set for 3 minutes at high temperature (900°C). Set for 1/2 minute at low temperature for annealing.

3-5.2. Standards

Add 5.2 mL of HNO_3 for every 100 mL of dilution. Dissolve 1000 g of NBS 950A in 3 mL of H_2SO_4, 5 mL of HNO_3, 10 mL of $HClO_4$ and 1 mL of HF. Digest and dilute to 1000 mL with deionized water. This is a 1000 μg/mL U_3O_8 standard. Alternatively, a vendor supplied 1000 μg/mL uranium standard can be used.[13] (If the uranium standard is used, the calculation provides results in micrograms per gram of uranium, not U_3O_8.) To make a 5 μg/mL U_3O_8 standard, pipette 0.50 mL of the 1000 μg/mL stock standard into a clean 100 mL volumetric flask. Add 5.2 mL of HNO_3 and dilute to mark with deionized water. Using 100, 250, 500 and 1000 μL of this 5.0 μg/mL standard provides a working curve of 0.5, 1.25, 2.5 and 5.0 μg/mL standards, respectively. Prepare a series of standard solutions of the above concentrations by dilution of the 5.0 μg/mL standard.

---

[12] Alternatively, preformed pellets can be purchased from Analoids, United Kingdom.

[13] *Note:* In geochemical analysis, it is the practice to work in and report on concentrations as the element, while in general chemical practice the element is reported as the oxide. In preparing standard solutions it is important to respect this difference in practice.

3-5.3. Analytical method

For solid samples, begin at step (1). For water samples, omit steps (1) to (3) and pipette 2 mL of each water sample as in step (4).

(1) Weigh 0.5 g of sample into a 250 mL Pyrex beaker (carry a blank throughout the entire method).

(2) Add 10 mL of $HClO_4$, 10 mL of HNO_3 and 5 mL of HF to the beakers. Heat on a low setting until near dryness. Low readings may result if the samples are allowed to bake or char.

(3) Cool beakers, add 20 mL of deionized water and 2.5 mL of 1:1 HNO_3. Heat to effect the solution. Cool and transfer to 25 mL mixing cylinders. Dilute to 25 mL with deionized water.

(4) Pipette 2 mL of each sample and each of the 5.0, 2.5, 1.25 and 0.5 μg/mL U_3O_8 standards into a series of mixing vials.

(5) Add 15 mL of saturated aluminium nitrate to each vial.

(6) Add 1 mL of concentrated NH_4OH to each vial.

(7) Add 5 mL of $CH_3COOC_2H_5$ to each vial and cap. Shake for 1-2 minutes on an Eberbach shaker.

(8) Allow 5-10 minutes for the phases to separate (*see Note (1) of Section 3-7*). Pipette a 250 μL aliquot into a platinum fusion dish. Dry the dishes under an infrared lamp.

(9) When the dishes are dry, add a pellet of the NaF-LiF flux[14] (*see Note (2) of Section 3-7*).

(10) Place the dishes on the Geoco rotary fusion burner and fuse for 1/2 minute at low temperature (450°C), 3 minutes at high temperature (900°C) and 1/2 minute at low temprature for annealing. Cool.

(11) Read the pellets in the Jarrell-Ash fluorometer. The sensitivity should be set at 6 or 7, the instrument adjusted to zero with the ZERO adjustment, and the background set at zero with the 0.01 scale switch (*see Note (3) of Section 3-7*).

(12) Record the pellet readings, subtracting the reading of the blank from the readings of each pellet.

3-6. CALCULATIONS

A linear calibration curve is obtained from the standards using net fluorescence readings (reading after subtraction of the blank values). Generate a calibration factor based on this curve as follows

$$\text{Factor} = \frac{U_3O_8 \text{ standards } (\mu g)}{\text{Net standard readings}}$$

---

[14] A pellet maker apparatus is used to make the NaF-LiF pellets if preformed pellets are not available.

Calculate the U_3O_8 concentration in the solid sample as follows

$$U_3O_8\ (\mu g/g) = \frac{\text{Net sample reading}}{\text{Sample weight (g)}} \times \text{Factor} \times \frac{\text{Volume dilution of sample}}{\text{Aliquot of sample taken}}$$

Calculate the U_3O_8 concentration (or uranium, if the vendor supplied uranium standard was used) in the water samples as follows

$$U_3O_8\ (\mu g/mL) = \frac{\text{Net sample reading}}{\text{Sample volume (mL)}} \times \text{Factor}$$

3-7. NOTES

(1) $CH_3COOC_2H_5$ extraction eliminates the sample constituents that would quench the uranium fluorescence.

(2) Read a fusion blank for each disc before use. Repeat the process for discs when the pellet reading is too high (normally greater than 1 or 2, depending on the characteristics of the flux).

(3) A decline in sensitivity may be an indication that new UV lamps are needed. Replace approximately every 6 months.

(4) To calculate the results in terms of uranium, divide the U_3O_8 results by 1.1792.

REFERENCE

[1] CENTANNI, F.A., RUSS, A.H., DeSESA, MA., Fluorometric determination of uranium, Anal. Chem. **28** (1956) 1651–1657.

Method 4

DETERMINATION OF URANIUM, THORIUM AND POTASSIUM BY GAMMA RAY SPECTROMETRY[15]

4-1. INTRODUCTION

Gamma ray spectroscopy is used to determine the concentration of uranium, thorium and potassium in geological samples. This is done using a NaI(Tl) type gamma spectrometer system and a three window matrix calculation. The NaI(Tl) detector based system has proved historically to be a rugged, reliable and inexpensive system that can be used equally as well in the field as in the laboratory. The matrix calculation method gives excellent precision and accuracy and can be programmed in even very small computer systems. The premise of this calculation method is that three regions within the spectra can be defined to reflect the activity of uranium, thorium and potassium, respectively. To be useful in gamma ray analysis, the regions should be chosen after considering the gamma ray intensity and attenuation, the detector efficiency and resolution and the interferences.

If available, use of a Ge(Li) or hyperpure germanium detector with its high resolution can simplify greatly the interpretation of gamma ray spectra. The disadvantage of its use is the initial cost and the constant requirement of liquid nitrogen to cool the detector. Furthermore, high resolution detectors are much less sensitive than the NaI(Tl) type, resulting in longer counting times.

(1) *Compton background:* Compton scattering is the process whereby a single high energy gamma ray produces other gamma rays of lower energy by interaction with the sample or the detector. The counts measured in a region consist of the counts due to the specific gamma ray at the measured energy plus the Compton counts due to any gamma radiation of higher energies. The Compton continuum is a relatively smooth function, increasing with a decrease in energy. Low peak to Compton ratios generally require larger interference correction, resulting in higher analytical errors.

(2) *Detector efficiency:* The efficiency (photons detected/photons emitted) of an NaI(Tl) detector decreases as the photon energy increases. This decrease can exceed an order of magnitude of 300-3000 keV.

(3) *Gamma yield:* To be useful in gamma ray analysis, the gamma yield (photons emitted for every 100 disintegrations) should be high enough to produce good peak to Compton ratios at low activities.

---

[15] Contributed by R. Chessmore, United States Department of Energy, Grand Junction, Colorado, USA.

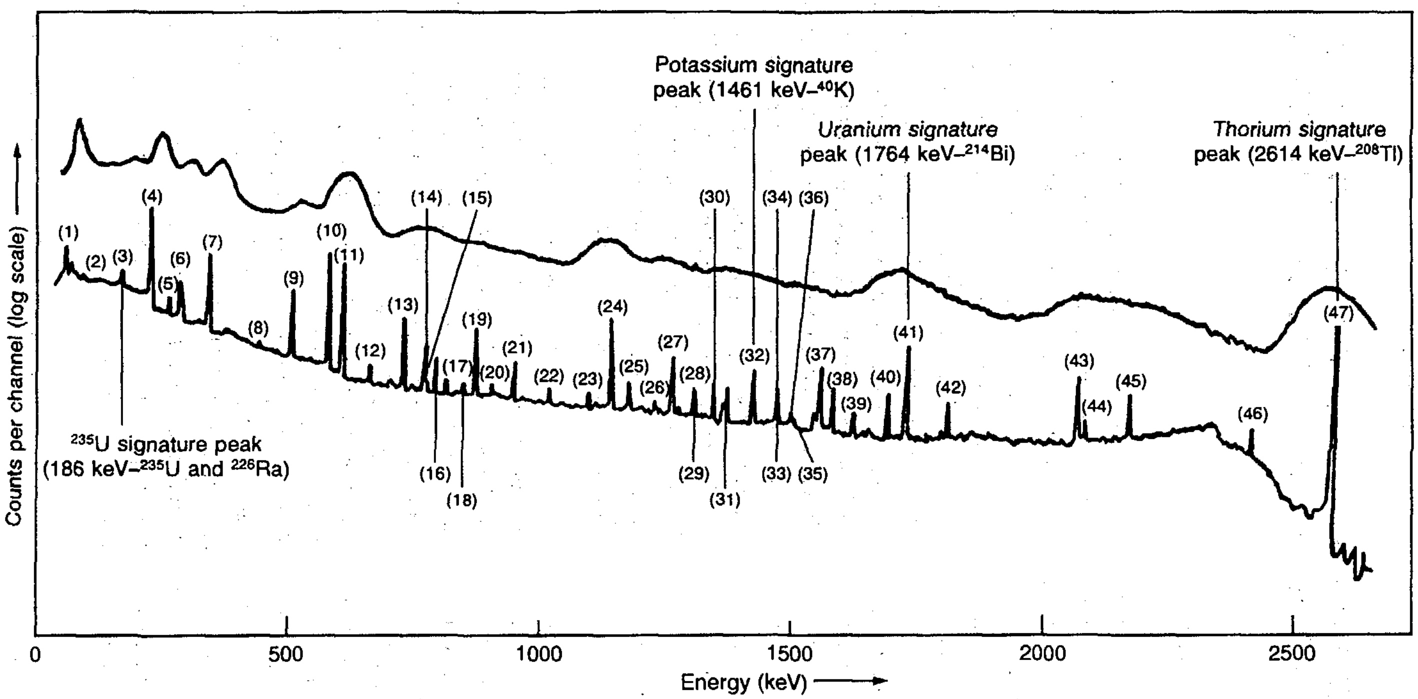

FIG. II-1. Comparison of NaI(Tl) and Ge(Li) detector resolution (refer to Table II-1 for peak identification).

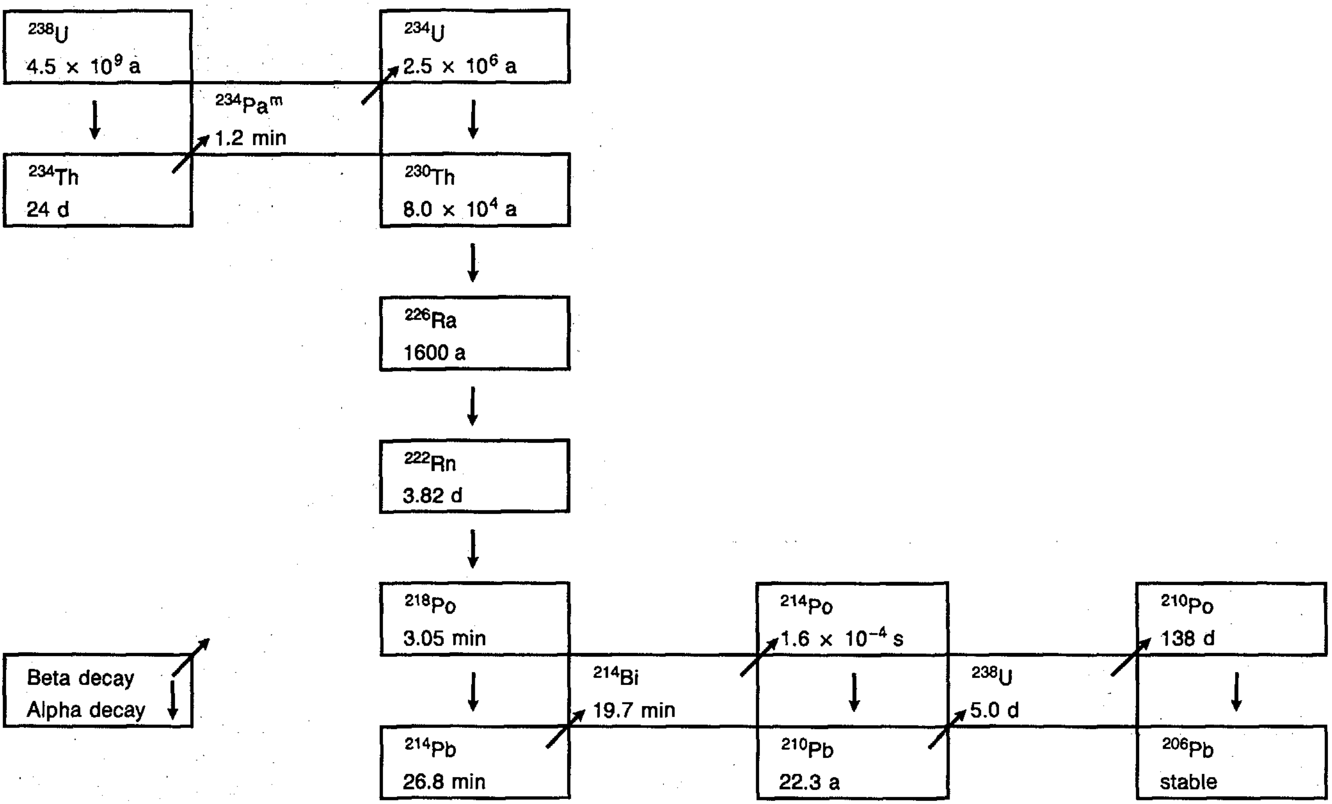

FIG. II-2. *Decay scheme of the uranium (^{238}U) series.*

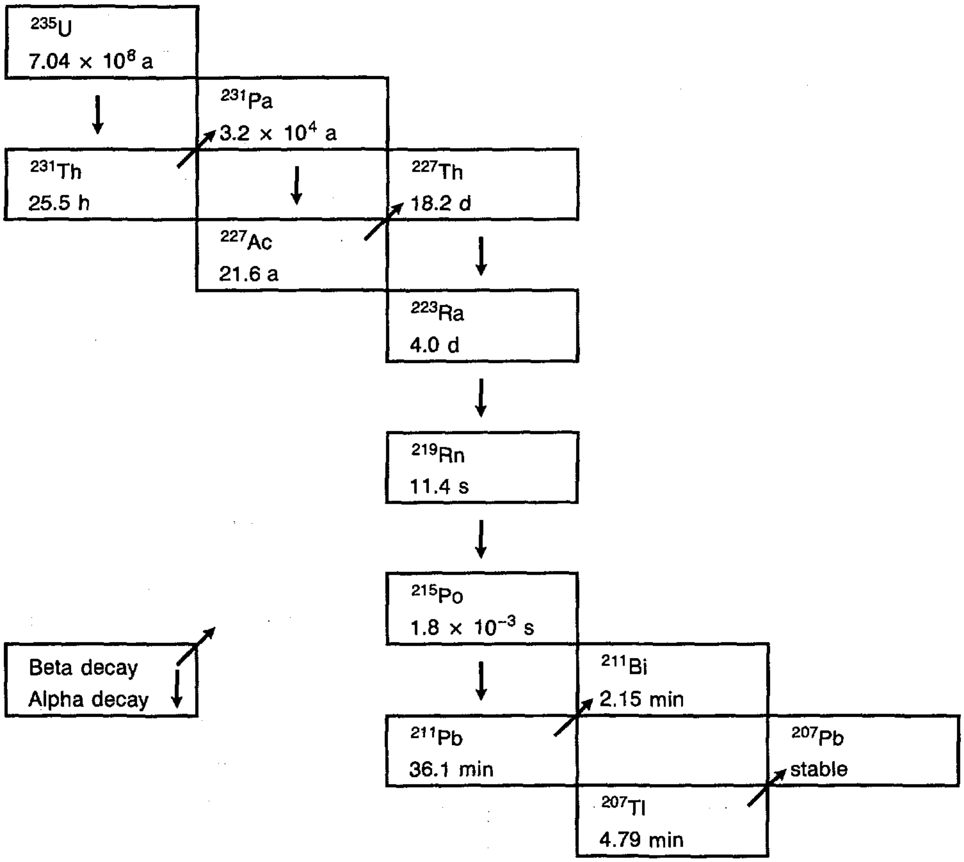

FIG. II-3. Decay scheme of the actinium (^{235}U) series.

(4) *Gamma ray resolution:* Figure II-1 shows a comparison of NaI(Tl) and Ge(Li) spectra. As can be seen from the figure, the poor peak resolution of the NaI(Tl) detector can produce gamma peaks that are actually a sum of several gamma peaks. Use of a gamma region containing several interfering gamma rays requires large corrections and, as with large Compton, results in large errors. Cross-interferences due to the poor peak resolution of the NaI(Tl) detector can be corrected using the matrix calculation.

(5) *Gamma ray attenuation:* One of the main difficulties in gamma ray analysis using low energy gamma rays is that the self-absorption of the radiation is relatively difficult to correct because the attenuation coefficient at low energy is highly dependent on the sample composition. Use of low energy gamma peaks requires either that the sample composition is known accurately, or that some other method is used to correct for self-absorption.

(6) *Equilibrium:* In analysis of the geological samples, it is common practice to assume secular equilibrium within the uranium and thorium chains. Although several long half-lived daughters occur within these chains, chemical mobility is generally very low. This assumption allows the measurement of any of the isotopes within the decay chain to represent the analysis of the parent.

Figures II-2 to II-4 show the decay chains of ^{238}U, ^{235}U and ^{232}Th, respectively, from the parent, through the daughters, to the stable lead isotopes. These chains show the intermediate decay products formed and the half-lives associated with these products for the three naturally occurring uranium and thorium chains. A sample of one of these nuclides is said to be in secular equilibrium when the activities of all the nuclides in the chain are equal. When secular equilibrium exists, measurement of the activity of any of the daughters of a nuclide gives the activity of the parent.

Figure II-1 shows a Ge(Li) spectrum with an equivalent NaI(Tl) spectrum and Table II-I identifies the Ge(Li) peaks shown in Fig. II-1. From a comparison of these data, the best NaI(Tl) energy windows for measurement can be selected.

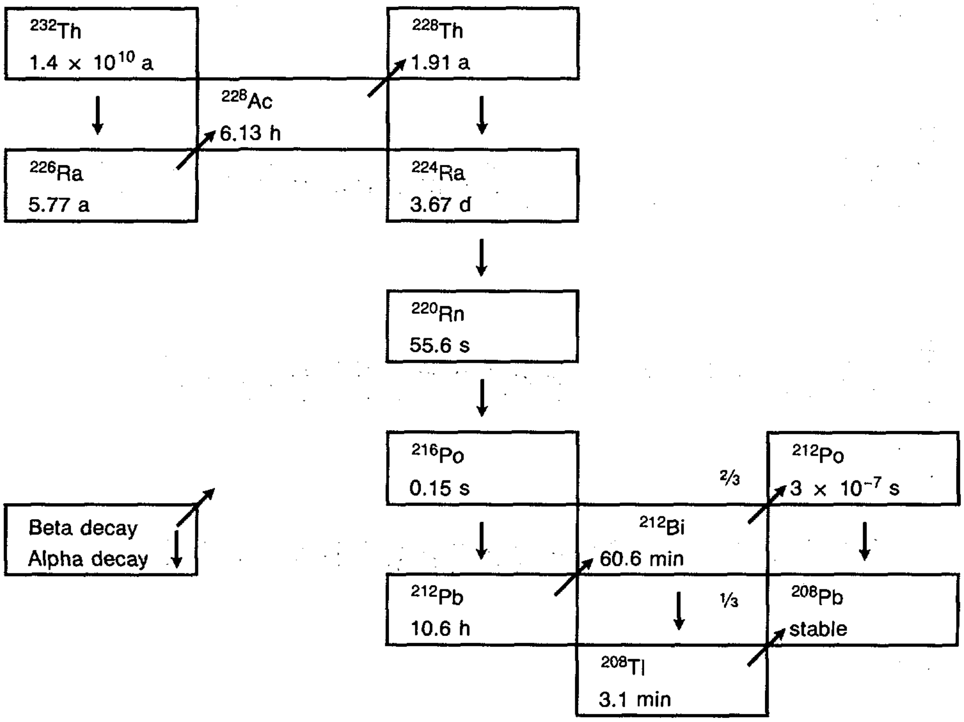

FIG. II-4. Decay scheme of the thorium (^{232}Th) series.

TABLE II-I. PEAK HEIGHT IDENTIFICATION FOR FIG. 1.

Data point	Energy (keV)	Source nuclide	Decay chain	Data point	Energy (keV)	Source nuclide	Decay chain
1	<100	X rays		23	1079	^{212}Bi	^{232}Th
2	144	^{235}U	^{235}U	24	1120	^{214}Bi	^{238}U
	186	^{235}U	^{235}U	25	1156	^{214}Bi	^{238}U
3	186	^{226}Ra	^{238}U	26	1208	^{214}Bi	^{238}U
	239	^{212}Pb	^{232}Th	27	1238	^{214}Bi	^{238}U
4	242	^{214}Bi	^{238}U	28	1254	(1765S.E)	^{238}U
	270	^{228}Ac	^{232}Th	29	1281	^{214}Bi	^{238}U
5	277	^{208}Tl	^{232}Th	30	1378	^{214}Bi	^{238}U
6	295	^{214}Pb	^{238}U	31	1408	^{214}Bi	^{238}U
7	352	^{214}Pb	^{238}U	32	1461	^{40}K	^{40}K
8	463	^{228}Ac	^{232}Th	33	1509	^{214}Bi	^{238}U
9	511	^{208}Tl	^{232}Th	34	1539	^{214}Bi	^{238}U
10	583	^{208}Tl	^{232}Th	35	1543	^{214}Bi	^{238}U
11	609	^{214}Bi	^{238}U	36	1588	^{228}Ac	^{232}Th
12	665	^{214}Bi	^{238}U	37	1592	(2614D.E)	^{232}Th
13	727	^{212}Bi	^{232}Th	38	1631	^{228}Ac	^{238}U
14	769	^{214}Bi	^{238}U	39	1661	^{214}Bi	^{238}U
15	772	^{228}Ac	^{232}Th	40	1730	^{214}Bi	^{238}U
16	795	^{228}Ac	^{238}U	41	1764	^{214}Bi	^{238}U
17	806	^{214}Bi	^{238}U	42	1848	^{214}Bi	^{238}U
18	836	^{228}Ac	^{232}Th	43	2103	(2614S.E)	^{232}Th
19	860	^{208}Tl	^{232}Th	44	2119	^{214}Bi	^{238}U
20	911	^{228}Ac	^{232}Th	45	2204	^{214}Bi	^{238}U
21	935	^{214}Bi	^{238}U	46	2448	^{214}Bi	^{238}U
22	1001	^{234}Pa^{m}	^{238}U	47	2614	^{208}Tl	^{232}Th

For analysis of potassium, the 1460 keV gamma ray from ^{40}K is used. The ^{40}K region is set from approximately 1400–1520 keV. This is the only region available for ^{40}K. Thorium-232 has several daughter peaks which could be used and ^{208}Tl has an intense line at 583 keV, but this line cannot be resolved from the ^{214}Bi gamma at 609 keV (see Figs II–2 to II–4). In addition, this energy area has a fairly large attenuation correction (approximately 30%). The only other higher energy line that has good peak to Compton ratios and minimal interferences is the 2614 keV gamma. The region set for ^{232}Th is 2550–2680 keV.

Two good regions exist for uranium analysis. The 1700–1820 keV window has a better peak to Compton ratio and is used normally; however, a 1056–1204 keV region can also be used.

4–2. INTERFERENCES

The results of these measurements have traditionally been reported as equivalent uranium (eU) and equivalent thorium (eTh) because the gamma rays measured are from daughter isotopes and equilibrium is assumed. As seen in the ^{238}U decay chain (Fig. II–2), the assumption of equilibrium requires little or no migration of the daughter ^{222}Rn. Since ^{222}Rn is an inert gas with a reasonably long half-life (3.82 days), this assumption cannot be considered valid for samples that have been crushed and blended. The radon loss occurring during sample preparation can be handled either by allowing the sample to equilibrate for about 3 weeks or by taking two measurements and mathematically correcting for the radon losses (see Section 4–6). In both cases, it is assumed that the radon is not free to migrate during the analysis period, i.e. the sample has been sealed in an air tight container. Some plastics allow radon migration through the container walls, and many of the screw type container lids are not air tight. Sample containers should be tested for their air tightness.

Potassium is normally reported as per cent potassium, assuming a natural occurring isotopic abundance of ^{40}K. Elevated ^{40}K activity gives incorrect potassium results but does not affect the eU and eTh values. A very high eTh concentration may produce elevated potassium values due to insufficient correction for the 1459 keV ^{208}Tl gamma.

4–3. PRECISION AND REPORTING LIMITS

The precision and the detection limit are functions of the sample size and the counting time. A precision of better than 10% at 10 ppm eU and a detection limit of < 1 ppm can be obtained for 500 g samples and 30–40 minute counting times.

4–4. EQUIPMENT

(1) NaI(Tl) detector; 4–6 in. crystal with an optically coupled PMT.
(2) High voltage power supply, adjustable from 0 to 2000 V.
(3) Detector preamplifier.
(4) A signal amplifier with both fine and coarse gain adjustment, a lower level discriminator and a preamplifier power supply. Fine and coarse gain adjustments should overlap and a coarse setting of 100X should be available. The recommended options include a baseline restorer, a pulse pile-up rejector and pole zero adjustment.
(5) A multi-channel analyser (MCA) with an analog–digital converter (ADC), having the following characteristics: (a) Storage for at least 1024 channels; (b) at least three user defined energy windows or regions of interest; total counts in the region displayed; (c) live time and actual time clocks. The recommended options include memory to store one to four spectra, a printer to the MCA interface, a net area function, data storage media and a channel off-set.
(6) Detector shielding: 4 in. lead and 1/8 in. copper.
(7) Electronics adjustments: General tests for the DC level, ground loops, baseline noise, pole zero and BLR threshold should be done at the initial set-up and whenever one of the equipment components is repaired or replaced [1].

4–5. METHODS

4–5.1. Energy calibration

The analysis regions are defined by the spectra of a ^{60}Co button source and two standards prepared in sample containers of the same configuration as those used for sample analysis. One standard mixture is prepared with about 0.1% thorium ore and K_2CO_3. The second standard is a 0.1% uranium mixture. The actual value may vary for the two standards, but the value should be known to within ±1% relative error.[16]

The gain should be set so that the range of interest (ROI) for the MCA is approximately 3000 keV. This is done using the gain adjust and placing the ^{60}Co 1333 keV peak maximum at Channel X:X = YM, where Y is 1333 keV/3000 keV and M is the number of channels in the MCA.

---

[16] The IAEA has available a set of radiometric reference materials called the RG set for the calibration of laboratory gamma ray spectrometers. This set, comprising RGU-1, RGTh-1 and RGK-1 in quantities of 500 g each, can be obtained from the Agency's Analytical Quality Control Service (AQCS) programme at a cost of US $150 per set.

Using the No. 1 standard, locate the peak maxima for the ^{40}K peak (1460 keV) and the ^{208}Tl peak (2614 keV). Set the ROIs at the actual peak maximum plus 65 keV. Adjust the ROIs visually to include the entire peak plus four to six channels on either side.

Use the No. 2 standard to set ^{214}Bi (1765 keV) for the uranium ROI.

4–5.2. Background correction

Any spectra collected will contain some counts due to the occurrence of the K-U-Th isotopes in the laboratory environment. Although shielding can reduce this problem greatly, complete elimination of environmental background is extremely difficult and expensive. Several methods for obtaining a background correction spectrum are presented. Normally, the counting time used to obtain background spectra should exceed the maximum count time used in analysing a sample by a factor of 10.

(1) *Empty container:* Analysis of an empty container gives the laboratory and the container background spectra. This method has a slightly high bias because routine samples shield the detector by an amount dependent on the depth and matrix of the sample. This effect is small, except when using large volume Marinelli beakers.

(a) Place an empty sample container on the detector and obtain a long count time spectrum; (b) record the counting time and the counts in the potassium, uranium and thorium ROIs.

(2) *Standard soil:* Analysis of a 'standard soil' gives a spectrum of a combination of the empty container plus an approximation of the naturally occurring background. Choice of the standard soil may include dunite, silica sand, or a material representative of the general background of the region. Measure as described in item (1) above.

(3) *Site background:* Analysis of site backgrounds requires that a background sample or set of samples is obtained from each area being evaluated. The obvious disadvantage is that each site requires a unique set of background subtractions. The advantages include ease of data interpretation of the samples from areas of high natural background. This method is not recommended for preliminary exploration, but it may prove very useful in site characterization once an anomalous area has been found. Once the site background sample is obtained, measure as described in item (1) above.

4–5.3. Standard count rates

Calibration factors and background subtractions are generally represented by count rates. Standard count rates are expressed with the background subtractions applied.

TABLE II-II. COUNT RATES OF CERTIFIED REFERENCE MATERIALS OF POTASSIUM, URANIUM AND THORIUM

Standard	Weight (g)	Count time (s)	K (%)	eU (ppm)	eTh (ppm)	Counts (K ROI)	Counts (eU ROI)	Counts (eTh ROI)
Background	0	20 000	0	0	0	19 468	10 291	4 532
Soil	537.8	20 000	0	0	0	31 529	12 391	5 540
K	541.1	1 500	56.58	0	0	27 037	486	321
K	641.8	1 500	14.145	0	0	8 839	483	337
K	666.5	1 500	28.29	0	0	16 558	503	298
eU	503.6	1 500	0	1 044	0	44 378	33 220	808
eU	504.5	1 500	0	508	0	22 303	16 400	561
eU	592.8	1 500	0	170	0	7 938	5 283	389
eTh	499.6	1 500	0	40.8	1 028	12 129	5 157	10 888
eTh	505.6	1 500	0	20.5	516	7 034	2 900	5 680
eTh	579.6	1 500	0	0	278	5 518	1 758	3 538

(1) *Response and monitor:* (a) Measure a set (three or more) of CRMs that contains different concentrations of one of the nuclides (Table II–II). (b) Plot a graph of the concentration versus the count rate and visually inspect the graph for linear response.

Note: A non-linear response indicates that electronics adjustment or replacement may be required. Non-linearity at higher concentrations indicates inadequate electronic dead time correction or spectral shift. Dead time corrections can be made mathematically, but the preferred method is either sample dilution using silica sand or two sample geometric configurations, a small volume for high concentrations and a large volume for low concentrations.

(c) Record the materials used, the count rates, the geometric configuration, the concentrations and the least square fit of the data.

Note: Test (a) is run every 1–2 months to monitor any long term instrument degradation.

(2) *Calibration factors:* The calibration factors are the concentration term and cross-interference terms used to solve the 3 × 3 matrix calculation. Three materials are used which have known concentrations of potassium, uranium and thorium. The preferred materials contain only one isotope in each. However, mixtures can be used if the concentrations of all three isotopes are well known. The uranium and thorium materials must be in secular equilibrium. (a) Collect and record the mass (weight × concentration) and the count rates for the background and standards in the potassium, uranium and thorium ROIs (Table II–II). (b) Using the calculations described below, calculate the standards matrix.

Note: As long as the quality control checks remain acceptable, the standard matrix can be considered valid.

4–5.4. Sample analysis

The sample is packed into and sealed in the same type of container as that used for the standards. It is very important to preserve sample geometry, since detector response is a function of the sample detector geometry. Care should be taken to ensure that the containers are full; those that are not full do not have exactly the same geometry as those that are full.

Once the sample has been prepared and sealed, a waiting period is required before analysis. A sample in which the radon is completely depleted will return to about 98% equilibrium within 21 days. Since most ores have an emanation factor of no more than a 40%, and generally less than 20%, most of the samples can be considered to have attained about 98% equilibrium within 14 days.

For rapid analysis, two measurements are required: the first is done 4 hours after sealing and the second 3–6 days later (Section 4–6.3).

(1) Record the sample identification code and the sample weight, and preset the count time. If rapid analysis is to be done, record the date and the time of the analysis.

(2) Acquire a spectrum and record the count rate in each analysis window and the actual analysis time.

(3) Using the standard matrix and background from item (2) of Section 4–5.3 and the calculations in Section 4–6.3, calculate the K, eU and eTh concentrations.

4–6. CALCULATIONS

4–6.1. Count rate

The count rate in each of the three spectral windows is related to the concentration of the radioelements in the standards by the equation set

$$R_{ij} \sum_{k} (A_{ik} C_{kj}) + B_i$$

where R_{ij} is the region count rate for the i-th region of the j-th standard, A_{ik} is the calibration coefficient (proportionality constant), C_{kj} is the nuclide concentration and B_i is the background count rate.

For a single measurement, the above equation set can be expressed in matrix form as

$$[R] = [A] [C] + [B]$$

where [R] is a 3 × 1 matrix of the observed count rates, [A] is a 3 × 3 matrix of the calibration coefficients, [C] is a 3 × 1 matrix of the nuclide concentrations and [B] is a 3 × 1 matrix of the background count rates. This equation is solved and the [A] matrix is inverted to arrive at the equation used to relate the observed count rates to the concentrations.

$$[C] = [A]\{[R] - [B]\}$$

Annex 1 gives a simple FORTRAN program for the determination of the $[A]^{-1}$ matrix. Included in the calculations is the matrix condition number. The optimum condition number is 1; condition numbers greatly different from 1 may produce erroneous results. The condition number is a function of both the [C] and [R] matrices. Optimization of the $[A]^{-1}$ matrix can be done by varying the concentrations of the standards [C] or the sample geometries [R]. Generally, it is more efficient to vary the concentrations of the standards. Normally, the best conditioned matrix is obtained with standards that have reasonably high concentrations of the nuclide of interest and zero amounts of the other two nuclides.

4–6.2. Sample calculations

The relationship used to calculate the concentrations of the three isotopes is expressed as

$$\begin{array}{ll} \mathrm{C_K} & \mathrm{R_K - B_K} \\ \mathrm{C_U} = \mathrm{A}^{-1} & \mathrm{R_U - B_U} \\ \mathrm{C_T} & \mathrm{R_T - B_T} \end{array}$$

The concentrations are calculated in the same units as those used in the standard [C] matrix. The actual calculations are

$$\mathrm{C_K = R_K\, A_{KK} + R_U\, A_{KU} + R_T\, A_{KT}}$$

$$\mathrm{C_U = R_K\, A_{UK} + R_U\, A_{UU} + R_T\, A_{UT}}$$

$$\mathrm{C_T = R_K\, A_{TU} + R_T\, A_{TU} + R_T\, A_{TT}}$$

where $\mathrm{R_T}$ is the background corrected count rate (counts/s) in the i-th nuclide ROI. The concentrations ($\mathrm{C_I}$) are the total activities or weights. To obtain the activity per unit weight, divide the [C] values by the sample weight.

4–6.3. Radium-radon disequilibrium correction

The disequilibrium correction calculation is used for samples that are not allowed to equilibrate for 21 days and requires two measurements. The general equation is expressed as

$$\mathrm{C_{Ra}(t) = C_{Ra}(t_1) + \frac{C_{Ra}(t_2) - C_{Ra}(t_1)}{1 - e^{-(\lambda t)}}}$$

where $\mathrm{C_{Ra}(t)}$ is the projected radium (eU) concentration at equilibrium, $\mathrm{C_{Ra}(t_1)}$ is the concentration at first measurement, $\mathrm{C_{Ra}(t_2)}$ is the concentration at second measurement, λ is 0.00756 $\mathrm{h^{-1}}$ and t is the elapsed time (in hours) between the measurements.

4-6.4. Errors of analysis

The major errors associated with analysis consist of the following.

4-6.4.1. Sample homogeneity

The analysis assumes homogeneous samples. In general, large mesh sizes can be used with large sample sizes. The major limiting factor is that, in grinding the samples, the radioactive portion is often associated with fine heavy particles. With proper mixing and minimal handling, this will not contribute significantly to the total error. A common method of determining and monitoring this error is by using duplicate analysis of 5–10% of the samples.

4-6.4.2. Calibration standards

The two major errors associated with the calibration standards is the certified uncertainty in the values and the time dependent handling errors. Handling error results from particle size separation with repeated handling, usually resulting in increases in the count rates due to the settling of heavier, finer radioactive particles. Control charts should be kept on the count rates of standards if the standards are used often. Standards should be ground to a fine particle size and packed under pressure (1/2–1 tonne).

4-6.4.3. Count rate errors

The four major influences in counting error are:

(1) *Gain drift in the electronics:* This includes: (a) changes in the system backgrounds; (b) disequilibrium in the decay series; (c) positioning; and (d) amplifier drift, which is normally associated with temperature fluctuation. The detector system should be maintained at a cool, constant temperature, and peak energy windows (ROIs) should be checked at least once a day. The Th/K standard is the daily calibration standard. Before analysing a set of samples (whenever a temperature change has occurred or whenever visual inspection indicates that a spectral shift has occurred), this standard should be used and the gain readjusted so that the potassium and thorium peaks are properly located.

(2) *Changes in the system backgrounds:* These can be minimized with proper shielding and proper handling of the sample containers.

(3) *Disequilibrium errors:* Most of these are caused by improperly sealed containers, resulting in ^{222}Rn losses. In addition to obvious sealing problems, some plastic containers allow radon migration through their walls. Before a

sample container is chosen, adequate tests should be made to verify that the container seal is satisfactory.

(4) *Positioning:* The calibration assumes constant sample geometry. This means that the samples must be positioned in exactly the same manner for all analyses. Positioning the jigs helps to maintain a constant presentation. All the samples should have the same volume. Samples of insufficient volume should be analysed using smaller containers with comparable calibrations.

4-6.4.4. Calculation errors

The propagation of errors associated with items (1) to (3) above using the matrix calculation is beyond the scope of this procedure. An error can be assigned to the reported values by calculating a relative function of the concentration from replicate analyses [2].

REFERENCES

[1] ZINMER, W.H., EG and G ORTEC Systems Application Studies, PSD No.12, EG and G Idaho, Inc., Idaho Falls, ID (1979).

[2] STROMSWOLD, D.C., KOSANKE, K.L., Calibration and error analysis for spectral radiation detectors, IEEE Trans. Nucl. Sci. **NS-25** (1978) 782–786.

BIBLIOGRAPHY

HANSEN, D.A., Geological Applications Manual for Portable Gamma Ray Spectrometers, United States Geological Survey, Denver, CO (1975).

KOSANKE, K.L., KOCH, C.D., WILSON, R.D., High Resolution Gamma Ray Spectroscopy Applied to Bulk Sample Analysis, United States Geological Survey, Denver, CO (1978).

MARUTZKY, S.J., STEELE, W.D., KEY, B.N., KOSANKE, K., Surface Gamma Ray Measurement Protocol, United States Geological Survey, Denver, CO (July 1984).

TEKTRONIX, INC., Tektronix Matrix Functions Instruction Manual, Beaverton, OR (1976).

Annex

PROGRAM NAIMATC

```
C********************************************************************
C
C1    PROGRAM: NAIMAT    COMPUTER: PDP-11-44    REVISION:  01
C2    SYSTEM: GAMMA NAI DETECTOR
C3    PURPOSE: CALCULATE K-EU-ETH MATRIX
C4    VARIABLES:
C5    PROGAMMER: G. DECHANT
C
C******************REVISION LIST*************************************
C
C     RV DATE      BY          REASON FOR CHANGE
C     -- ----      --          --------------------------------------
C     01 03/DD/86  GLD         INITIAL RELEASE
C
C********************************************************************
      DIMENSION AMAT(3,3),CON(3,3),WT(3),BKG(3),AA(3,3),AI(3,3)
C
C     USER DATA ENTRY
C
5000  FORMAT(F8.0)
10    CONTINUE
      TYPE 1000
1000  FORMAT(3X,' POTASSIUM (K) DATA SECTION',/,
     1' WEIGHT OF K STANDARD ',$)
      ACCEPT 5000,WTK
      TYPE 1010
1010  FORMAT(' CONCENTRATION OF K IN THE K STANDARD ',$)
      ACCEPT 5000,CC
      CON(1,1)=WTK*CC
      TYPE 1020
1020  FORMAT(' CONCENTRATION OF EU (RA-226) IN THE K STANDARD ',$)
      ACCEPT 5000,CC
      CON(1,2)=WTK*CC
      TYPE 1030
1030  FORMAT(' CONCENTRATION OF ETH (TH-228) IN THE K STANDARD ',$)
      ACCEPT 5000,CC
      CON(1,3)=WTK*CC
      TYPE 1040
1040  FORMAT(' COUNT TIME FOR THE K STANDARD ',$)
      ACCEPT 5000,TIME
      TYPE 1050
1050  FORMAT(' COUNTS IN THE K WINDOW (ROI) ',$)
      ACCEPT 5000,CTS
      AMAT(1,1)=CTS/TIME
      TYPE 1060
1060  FORMAT(' COUNTS IN THE EU WINDOW (ROI) ',$)
      ACCEPT 5000,CTS
      AMAT(1,2)=CTS/TIME
      TYPE 1070
1070  FORMAT(' COUNTS IN THE ETH WINDOW (ROI) ',$)
      ACCEPT 5000,CTS
      AMAT(1,3)=CTS/TIME
```

```
C
C
      TYPE 1100
1100  FORMAT (//,3X,' EU (RA-226) DATA SECTION ',/,
     1' WEIGHT OF EU STANDARD ',$)
      ACCEPT 5000, WTK
      TYPE 1110
1110  FORMAT(' CONCENTRATION OF K IN THE EU STANDARD ',$)
      ACCEPT 5000,CC
      CON(2,1)=WTK*CC
      TYPE 1120
1120  FORMAT(' CONCENTRATION OF EU (RA-226) IN THE EU STANDARD ',$)
      ACCEPT 5000,CC
      CON(2,2)=WTK*CC
      TYPE 1130
1130  FORMAT(' CONCENTRATION OF ETH (TH-228) IN THE ETH STANDARD ',$)
      ACCEPT 5000,CC
      CON(2,3)=WTK*CC
      TYPE 1140
1140  FORMAT(' COUNT TIME FOR THE EU STANDARD ',$)
      ACCEPT 5000,TIME
      TYPE 1050
      ACCEPT 5000,CTS
      AMAT(2,1)=CTS/TIME
      TYPE 1060
      ACCEPT 5000,CTS
      AMAT(2,2)=CTS/TIME
      TYPE 1070
      ACCEPT 5000,CTS
      AMAT(2,3)=CTS/TIME
C
C
      TYPE 1200
1200  FORMAT(//,3X,' ETH (TH-228) DATA SECTION',/,
     1' WEIGHT OF ETH STANDARD ',$)
      ACCEPT 5000,WTK
      TYPE 1210
1210  FORMAT(' CONCENTRATION OF K IN THE ETH STANDARD ',$)
      ACCEPT 5000,CC
      COM(3,1)=CC*WTK
      TYPE 1220
1220  FORMAT(' CONCENTRATION OF EU (RA-226) IN THE ETH STANDARD ',$)
      ACCEPT 5000,CC
      CON(3,2)=CC*WTK
      TYPE 1230
1230  FORMAT(' CONCENTRATION OF ETH (TH-228) IN THE ETH STANDARD ',$)
      ACCEPT 5000,CC
      CON(3,3)=CC*WTK
      TYPE 1240
1240  FORMAT(' COUNT TIME FOR THE ETH STANDARD ',$)
      ACCEPT 5000,TIME
      TYPE 1050
      ACCEPT 5000,CTS
      AMAT(3,1)=CTS/TIME
      TYPE 1060
      ACCEPT 5000,CTS
```

```
      AMAT(3,2)=CTS/TIME
      TYPE 1070
      ACCEPT 5000,CT
      AMAT(3,3)=CTS/TIME
C
C     BACKGROUND DATA SECTION
C
      TYPE 1300
1300  FORMAT(//,' BACKGROUND DATA SECTION ',/,
     1' COUNT TIME FOR BACKGROUND ',$)
      ACCEPT 5000,TIME
      TYPE 1050
      ACCEPT 5000,CTS
      BKG(1)=CTS/TIME
      TYPE 1060
      ACCEPT 5000,CTS
      BKG(2)=CTS/TIME
      TYPE 1070
      ACCEPT 5000,CTS
      BKG(3)=CTS/TIME
C
C     CORRECT COUNT RATES FOR BACKGROUND
C
      DO 20 I=1,3
      DO 20 J=1,3
      AMAT(I,J)=AMAT(I,J)-BKG(J)
20    CONTINUE
C
C     CALCULATE DETERMINATE
C
      DET=AMAT(1,1)*AMAT(2,2)*AMAT(3,3)
      DET=DET-AMAT(1,1)*AMAT(2,3)*AMAT(3,2)
      DET=DET+AMAT(1,2)*AMAT(2,3)*AMAT(3,1)
      DET=DET-AMAT(1,2)*AMAT(2,1)*AMAT(3,3)
      DET=DET+AMAT(1,3)*AMAT(2,1)*AMAT(3,2)
      DET=DET-AMAT(1,3)*AMAT(2,2)*AMAT(3,1)
C
C     INVERT MATRIX
C
      DO 50 I=1,3
      DO 50 J=1,3
      K=I+J
      DK=(-1)**K
      IF(I.EQ.1) LA=2
      IF(I.EQ.1) LB=3
      IF(I.EQ.2) LA=1
      IF(I.EQ.2) LB=3
      IF(I.EQ.3) LA=1
      IF(I.EQ.3) LB=2
      IF(J.EQ.1) NA=2
      IF(J.EQ.1) NB=3
      IF(J.EQ.2) NA=1
      IF(J.EQ.2) NB=3
      IF(J.EQ.3) NA=1
      IF(J.EQ.3) NB=2
      AA(I,J)=(DK/DET)*(AMAT(LA,NA)*AMAT(LB,NB)-
```

```
     1  AMAT(LA,NB)*AMAT(LB,NA))
50      CONTINUE
C
C       CHECK CONDITION OF MATRIX
C
        HCN=0.
        HAA=0.
        HAM=0.
        DO 80 I=1,3
        DO 80 J=1,3
        IF(HAA.LT.ABS(AA(I,J))) HAA=ABS(AA(I,J))
        IF(HAM.LT.ABS(AMAT(I,J))) HAM=ABS(AMAT(I,J))
        IF(HCN.LT.CON(I,J)) HCN=CON(I,J)
80      CONTINUE
        CMA=HAA*HAM
        TYPE 1400,CMA
C400    FORMAT(//,' CONDITION NUMBER = ',G13.6,//)
C
C       CALCULATE FINAL MATRIX
C
        DO 90 I=1,3
        DO 90 J=1,3
        AI(I,J)=0.
90      CONTINUE
        DO 100 I=1,3
        DO 100 J=1,3
        DO 100 K=1,3
        AI(I,J)=AI(I,J)+CON(I,K)*AA(K,J)
100     CONTINUE
        TYPE*,'      FINAL MATRIX'
        DO 110 I=1,3
110     TYPE 1420,(AI(I,J),J=1,3)
1420    FORMAT(1X,3G13.6)
        END
```

Method 5

URANIUM DETERMINATION BY THE FISSION TRACK METHOD[17]

5-1. INTRODUCTION

When a neutron enters the nucleus of an atom of ^{235}U the atom splits or 'fissions' into two more or less equally massive smaller atoms ('fission fragments') which move apart at high velocities. When a fission fragment passes through a solid it breaks down the crystal lattice or molecular structure of the material along its path, producing a 'fission track' [1]. The material of a fission track differs from that of the unaltered solid around it in a number of ways and is, for example, more soluble. Thus, fission tracks, which, when formed, are no more than 100 Å in diameter, can be enlarged to a size visible through an optical microscope by exposing the material to a solvent. The fission tracks dissolve more rapidly than the surrounding material and become holes of a size and shape which depend on the material, the length of exposure to the solvent, and other factors. This process is known as track etching.

Only ^{235}U will fission by the 'thermal' or 'slow' neutrons used in neutron irradiations in nuclear reactors. Since the fraction of ^{235}U in natural materials is a constant, if a sample containing uranium is placed in contact with a detector material initially free of fission tracks and of uranium, irradiated with neutrons in a nuclear reactor and the surface then etched, the number of fission tracks appearing in the detector material will depend only on the concentration of uranium in the sample material and the number of neutrons (the neutron 'fluence' or 'dose') that passed through them. The detector material used is usually a sheet of plastic with the trade name of LEXAN; sometimes, clear high grade muscovite mica is used. If a standard of known uranium concentration was irradiated at the same time, the concentration of uranium in the sample material similarly treated can be calculated by simple proportionality.

When solid samples are to be analysed it is usual to place LEXAN surfaces against them and to irradiate, etch and determine under a microscope the density of tracks (i.e. the number of tracks per square centimetre) in the LEXAN opposite the sample.

$$\frac{[\mathrm{U}]\ \text{sample}}{[\mathrm{U}]\ \text{standard}} = \frac{\rho\ \text{sample}}{\rho\ \text{standard}}$$

---

[17] Contributed by R. McCorkell, CANMET, Energy Mines and Resources Canada, Ottawa, Ontario, Canada.

5-2. METHODS

5-2.1. Background

The background of tracks due to uranium in the track detector material can be determined by irradiating and etching the surfaces that are placed against other track detectors. The background of LEXAN is usually negligible. When muscovite is used, the background is usually higher because of the natural uranium content in most muscovite. In addition, muscovite usually contains 'fossil' tracks before use, which may be removed by heating for 1 hour at 550°C–600°C.

5-2.2. Mounting samples

If the solid sample is homogeneous, a piece of suitable size may be mounted in an epoxy disk, ground and polished to produce a surface against which the track detector can be placed. Inhomogeneous samples such as rocks and soils are usually ground and pressed into pellets (such as are used in XRF) and the track detectors are placed against these [2, 3]. Standards that may be used repeatedly are prepared in the same way. Convenient standards for this method are now available from the National Bureau of Standards in Washington, DC (SRM 610-617 and 961a–964a).

5-2.3. Irradiation

Sample and standard disks covered with track detectors are stacked in an irradiation capsule and irradiated with a suitable neutron dose in a nuclear reactor. If the approximate uranium concentration in the samples is known, a suitable neutron dose, n, may be calculated from the formula

$$\sigma = (2)\ 10^{-5}\ n\ [U]$$

where σ is the 'induced' fission track density (which should be about 10^4–10^6 tracks per square centimetre), [U] is the weight fraction of uranium in the sample, and n is the neutron dose (neutron per square centimetre). Hence, if [U] is 1 ppm, a suitable neutron dose would be $(5)10^{15}$ n/cm^2 and, in a reactor with a neutron flux of 10^{13} n$\cdot$cm$^{-2}\cdot$s^{-1}, the irradiation should be for 8–9 minutes. If it is believed that the neutron flux varies from point to point within the capsule during irradiation, several standards may be placed in the capsule at different positions. Commercial aluminium foil is a convenient secondary standard for this purpose; disks of it, covered with LEXAN, may be placed throughout the capsule [4]. After irradiation, the track detectors or 'overlays' are removed and etched.

5-2.4. Etching

LEXAN is etched in 6M aqueous NaOH for about 24 hours. Muscovite is etched in 48% ('concentrated') HF for 15-60 minutes, both at room temperature.

5-2.5. Counting the tracks

Generally, the etched fission tracks are counted visually with the aid of a microscope. For most uranium measurements, this is entirely satisfactory. Magnifications of 150X-600X are used, and better grade student microscopes are adequate.

5-2.6. Instrumental counting

Many instruments for counting etched particle tracks have been developed. The most widely used instrument is the discharge counter [5, 6]. Fission tracks are recorded by a LEXAN film of such thickness (2-15 μm) that fission fragments pass through it. After etching, this film is placed between the two flat electrodes of the track counter. When a DC voltage of about 500 V is applied between these electrodes, discharges pass through the etched track holes. If one of the electrodes is a sheet of aluminized Mylar from which the discharges evaporate the aluminium, only one discharge passes through each track, and the number of discharges, recorded on a scaler, gives the number of tracks in the film.

Counting fission tracks by means of a discharge counter is fairly simple when the fission tracks are uniformly distributed over the track detector. This, of course, is the case when the sample and standard materials are homogeneous. If the uranium is inhomogeneously distributed throughout a sample, however (as when uranium rich grains occur in powdered rocks), track clustering may occur in the detector. Adjacent and overlapping tracks etch as single holes and the number of discharges through the detector no longer bears a direct relationship to the number of fission tracks.

The only other track counting instrument frequently referred to in the literature is the image analyser [7-10]. When the appearance of the etched tracks can be controlled sufficiently, they may be used in routine track counting.

5-2.7. Inhomogeneity

When inhomogeneity is a problem in the analysis of a solid, some means of homogenization must be found. The residues left by evaporating water droplets may be redistributed with sufficient homogeneity for fission track-discharge counter determination of their uranium content by placing drops of diluted collodion on the residue [6]. Such track clustering is less of a problem in visual track counting, partly because the eye can distinguish the tracks in clusters better than an instrument. In addition, a person counting tracks would recognize the clusters and would know which analyses had been affected by them and how serious the effect might be.

5-2.8. Sources of error

The formation of fission tracks is a random process and therefore the standard deviation in a count of T tracks should be $\sqrt{T}$, if there is no other source of variation and uncertainty in the determination. For this reason, as many tracks as possible should be counted in every measurement. Other sources of error and uncertainty vary with the nature of the samples, the procedure used, and other factors. One which needs comment is the error in recognizing fission tracks and distinguishing them from other features. In some materials, etched fission tracks may vary considerably in appearance. Other features which, to some extent, resemble tracks may be present so that different analysts may report different numbers for tracks in the same area. This will not introduce systematic error if two rules are followed:

(1) Each analyst determines the c to T or c to σ relationship from his own track counts on standards and uses this in converting his track counts for the samples to c.

(2) The analyst decides on criteria for distinguishing fission tracks from other features, which ensures that, although he may miss some real tracks, he will not count any other features. If he abides by these criteria, he will always count some fixed fraction of the fission tracks. As the ultimate determination is based on the ratio of σ or T for the sample to the standard, this factor cancels out.

The last rule assumes that the criteria or characteristics for distinguishing etched fission tracks from other features are the same for the samples as for the standards. This can be achieved when the tracks are being counted in overlays placed on the samples and standards, and not in the sample and standard materials themselves.

5-2.9. Analysis of liquids

The same technique may be used in the analysis of liquids [11-13], but it is usually more convenient to evaporate the measured drops of a liquid sample on the LEXAN surface, irradiate and etch, and to determine T, the total number of tracks arising from the residue of each drop. The following relationship applies [14, 15]:

$$c = TM/VGN_AI\sigma n\epsilon$$

Here, c is in units of mass per mass, M is the atomic weight of the element whose isotope fissions, V is the volume of the water drop in millilitres, G is the fraction of the fission events which produce tracks in the detector, N_A is Avogadro's number, I is the fraction of the atoms of the element which is the fissioning isotope, σ is the cross-section of this isotope in square centimetres for neutron induced fission, n is the neutron dose in neutrons/cm^2 and ϵ is the efficiency with which the fission tracks become countable on etching. Where the element whose isotope fissions is uranium and the track detector is LEXAN, $M = 238$, $G = 1$, $I = 0.0072$, $\sigma = 5.82 \times 10^{-22}$ cm^2 and $\epsilon = 1$. Using these values for the various terms, the equation becomes

$$c = 94.4T/nV$$

This method was employed for measuring trace uranium concentrations in natural waters using LEXAN polycarbonate plastic as the detector, drop sizes of 0.05 or 0.005 mL and visual counting of the etched tracks. The method is fast and inexpensive (3–6 minutes are required for track counting and as many as 1200 samples and standards can be irradiated in one capsule).

Problems sometimes arise, apparently because chemicals in the solutions or other types of radiation present during the neutron irradiation affect the ability of the LEXAN to record etchable fission tracks [15]. At present, these effects are poorly understood. They would probably not occur if mica were used for the track detector. However, even the best grade of muscovite contains much more uranium than LEXAN. In any case, the method requires constant checking and recalibration. This is easily carried out by including standard uranium solutions and 'spiked' samples among the solutions being analysed. In practice, the uranium concentrations are calculated from the c to T relationship found from these and not from the theoretically derived relationship shown above. A person planning to use this method for measuring uranium in natural water should test both the materials and the procedures with the standards before proceeding.

5–3. OTHER USES

LEXAN or muscovite overlays may also be used to map the uranium distribution in inhomogeneous solids, to locate the uranium bearing minerals in a petrographical thin section or to learn if uranium and its radioactive decay products (located by other types of 'autoradiography') have become separated [16].

REFERENCES

[1] FLEISCHER, R.L., PRICE, P.B., WALKER, R.M., Nuclear Tracks in Solids: Principles and Applications, University of California Press, Berkeley, CA (1970) 605 pp.

[2] FISHER, D.E., Homogenized fission track determination of uranium in whole rock geologic samples, Anal. Chem. **42** (1970) 414–416.

[3] STUCKLESS, J.S., MILLARD, H.J., Jr., BUNKER, C.M., NKOMO, I.J., ROSHALT, J.N., BUSH, C.A., HUFFMAN, C., Jr., KEIL, R.L., A comparison of some analytical techniques for determining uranium, thorium and potassium in granitic rocks, J. Res. US Geol. Surv. **5** (1977) 81-91.

[4] AUMENTO, F., Uranium content of mid-oceanic basalts, Earth Planet. Sci. Lett. **11** (1971) 90–94.

[5] CROSS, W.S., TOMMASINO, L., A rapid reading technique for nuclear particle damage tracks in thin foils, Radiat. Eff. **5** (1970) 85-89.

[6] McCORKELL, R.H., HUANG, Y.F., Discharge counter for the determination of uranium in water by the fission tracks method, Rev. Sci. Instrum. **48** (1977) 1005-1009.

[7] CARPENTER, B.S., Determination of trace concentration of boron and uranium in glass by the nuclear tracks technique, Anal. Chem. **44** (1972) 600–602.

[8] CARPENTER, B.S., Quantitative applications of the nuclear track technique, Microscope **20** (1972) 175–182.

[9] CARPENTER, B.S., Lithium determination by the nuclear track technique, J. Radioanal. Chem. **19** (1974) 233–234.

[10] CARPENTER, B.S., LAFLEUR, P.D., Nitrogen determination in biological materials by the nuclear track technique, Anal. Chem. **46** (1974) 1112–1113.

[11] BERZINA, J.S., POPENKO, D.P., SHIMELEVICH, Yu.S., Determination of trace amounts of uranium in petroleum by means of fission tracks, Geokhimiya **8** (1969) 1024–1027 (In Russian with English abstract; translation available, see Geochem. Int. **6** (1969) 847).

[12] HASHIMOTO, J., Determination of the uranium content in sea water by a fission track method with condensed aqueous solution, Anal. Chim. Acta **56** (1971) 347–354.

[13] REIMER, G.M., Uranium determination in natural water by the fission-track technique, J. Geochem. Expl. **4** (1975) 425–431.

[14] FLEISHER, R.L., LOVETT, D.B., Uranium and boron content of water by particle track etching, Geochim. Cosmochim. Acta **33** (1968) 1126–1128.

[15] McCORKELL, R.H., A fission track method for determination of uranium in natural waters for geochemical exploration, CIM Bull. **76** (1983) 89–92.

[16] DYCK, W., McCORKELL, R.H., A study of uranium rich reduction spheroids in sandstones from Pugwash Harbour, Nova Scotia, Can. J. Earth Sci. **20** (1983) 1738–1740.

Method 6

DETERMINATION OF URANIUM BY DELAYED NEUTRON COUNTING (DNC)[18]

6-1. INTRODUCTION

Uranium, from trace to major constituent levels, can be determined using neutron activation followed by neutron counting. The method is quick, fully instrumental, non-destructive and gives accurate and reproducible results for a wide variety of matrices and concentrations. It is also almost free of interferences.

6-2. PHYSICAL BACKGROUND TO THE METHOD

Soon after the phenomenon of fission was discovered, it was observed that some of the products of fission decayed with the apparent emission of a neutron, rather than the expected beta particle.

Fission products are almost all radioactive and, because they are neutron rich, will decay back to the line of stability by beta emission, usually taking two or three steps before this stability is achieved. In some steps, the binding energy of the 'last' neutron is less than that of the excited state in which a nucleus finds itself, and so direct neutron emission is allowed energetically. Such emissions compete with beta and gamma decay, and will thus take place in a fraction of the total decays of that particular nucleus. Since the energy involved in these kinds of decay is high (approximately 5-8 MeV), the life time of the excited nucleus is extremely short (approximately 10^{-10} s), and the delayed neutron emitter has an *apparent* half-life equal to that of the previous unstable nucleus. These neutrons are termed 'delayed' to distinguish them from those ('prompt') which are emitted spontaneously during the fission process. This previous nucleus is termed a 'delayed neutron precursor', and a number of them have been identified unambiguously, while some delayed neutron emissions are not, as yet, attributable to unique precursors. In any case, the half-lives of the precursors are also quite short, but easily measurable. They range from approximately 0.1 second to approximately 55 seconds, and so delayed neutrons are observable using conventional counting equipment.

Any process involving fission will give rise to delayed neutron emission, hence detection of delayed neutrons indicates the presence of fission products, which themselves can only have come from fissile elements. Only very heavy elements, essentially thorium and above, can undergo fission. Furthermore, of these, only thorium

---

[18] Contributed by A. Egan, Nordion International, Ottawa, Ontario, Canada.

and uranium are stable enough to exist in nature in significant quantities. So, generally, uranium provides the vast majority of observed delayed neutrons. Hence, the method has been applied almost exclusively for uranium analysis.

The process of fission occurs spontaneously in nature, but at a very slow rate. Free neutrons are capable of inducing fission and, effectively, of speeding up the process enormously. As far as the analytical method using delayed neutrons is concerned, the most important nuclide is ^{235}U. This occurs in nature as 0.7% of all the uranium, and has a half-life of 7×10^8 years. Its predominant mode of decay is alpha emission, but spontaneous fission does occur, with an apparent half-life of 2×10^{17} years. Clearly, this latter phenomenon is extremely rare by comparison. Uranium-235 has a certain affinity for capturing a free neutron, especially if this is moving slowly, with a kinetic energy equivalent to normal 'room' temperature (say 20°C), a 'thermal' neutron. This capture, measured by a parameter called the cross-section, results in a new isotope, ^{236}U, being formed in a highly excited state. In the majority of such cases, the excited ^{236}U nucleus undergoes fission and the whole process may be written

$$^{235}\mathrm{U} + \mathrm{n} \rightarrow {}^{236}\mathrm{U}^* \rightarrow \mathrm{x} + \mathrm{y} + \mathrm{e}\,(\mathrm{n})$$

where * denotes the excited state, x and y are the fission products, n is the neutron and e is a whole number, denoting the number of prompt neutrons released (the average e value is approximately 2.5).

Bombardment of ^{235}U by thermal neutrons induces fission, and some delayed neutrons will consequently be emitted. A vast number of neutrons exist in nuclear reactors. Indeed, neutrons may be considered as the working fluid of reactors, so irradiation of uranium bearing samples in a reactor will induce fission and, hence, the subsequent delayed neutron emissions. This is the basis of the DNC method for uranium analysis: irradiation of a sample in the neutron flux of a reactor (many of these neutrons are 'thermal'), followed by detection and counting of the delayed neutrons emitted. Since the half-lives involved are short, the delay between irradiation and counting should be minimal. Likewise, both irradiation and counting times need only be of the order of seconds, since the saturation activity is approached rapidly; equally rapidly, the relevant activity dies away. The method lends itself to a considerable degree of automation. In addition, data reduction is extremely simple.

6-3. TECHNICAL REQUIREMENTS

The equipment necessary is as follows: source of the neutrons, transfer system for moving the samples to the irradiation and counting areas, neutron detectors and associated counting equipment, a data processing facility and sample preparation and post-irradiation storage facilities.

(1) *Source of the neutrons:* Commonly, but not exclusively, a nuclear reactor is used to provide the bombarding neutrons. The fluxes available range from approximately 10^{11} to approximately 10^{14} $n \cdot cm^{-2} \cdot s^{-1}$, depending on the reactor. Depending on the position in the reactor, the proportion of thermal neutrons (compared with 'fast' neutrons) is also variable. The other sources of neutron flux are neutron generators and isotopic sources. A neutron generator is essentially a small particle accelerator that produces neutrons *subsequently* via a nuclear reaction. The most widely used scheme provides neutrons with an energy of 14 MeV. One form of isotopic source consists of two materials, one radioactive, the other an inactive target. The two components are intimately mixed. Particles emitted from the active component strike target nuclei and effect a neutron producing reaction. One commonly used combination is plutonium (active) and beryllium (target). The other form is a single transuranium element for which spontaneous fission is a significant decay mode; ^{252}Cf is the most widely employed. It is important to note that the neutron fluxes available in reactors are at least 3 or 4 orders of magnitude higher than those available with commercially produced neutron generators or isotopic sources.

(2) *Transfer system:* For reactors, the system is usually pneumatic, and moves the samples, suitably encapsulated, from a loading position into the reactor, out to the counting station and, finally, to a safe storage area. It lends itself to automation, and the timing of each move can be prescribed and controlled to approximately 0.1 second. Pneumatic systems can also be used with generators and sources in exactly the same way. Generators can be turned on and off electronically, so the sample need not move at all. Both generators and sources can be used in an on-line analytical mode. In this case, bulk amounts of sample material pass continuously through the neutron beam (on a conveyor belt), and delayed neutrons are counted downstream. A continuous readout of the uranium content thus becomes available.

(3) *Detectors and counting equipment:* A block diagram of the components of a suitable system is shown in Fig. II-5. After activation, the sample emits not only (fast) neutrons but also alpha particles and gamma rays. Neutron detectors (BF_3 or ^3He tubes) surround the sample and are embedded in paraffin wax (or some other moderating material) to thermalize the neutrons. The two types of detector are much more sensitive to slow than to fast neutrons. The shielding materials are chosen to absorb neutrons and gamma rays. The rest of the electronics consists of compatible standard modules. The only adjustments necessary concern the amplifier and the single channel analyser (SCA) in order to ensure that only signals due to neutrons, not gamma rays, are recorded by the scaler. If the system is automated, then the irradiation controller handles all the necessary pneumatic valve openings and closings, according to the programmed sequence.

(4) *Data processing facility:* In this facility, the system records the number of neutrons detected and counted by the system during the specified counting period. This

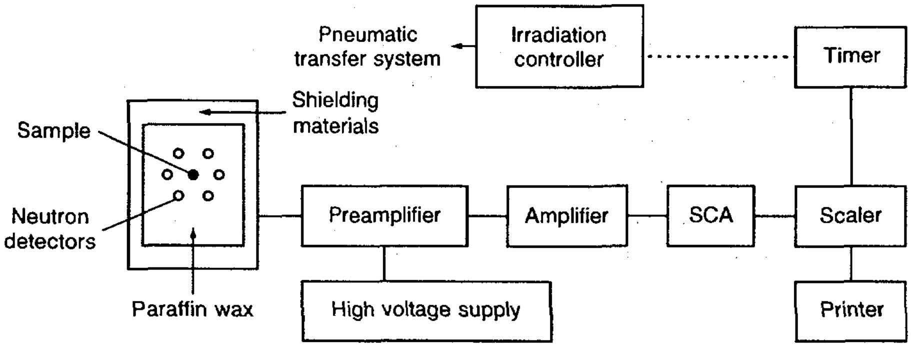

FIG. II-5. Components of a suitable system.

number is then compared with a calibration curve, or formula, generated using standards containing known concentrations of uranium, irradiated and counted under identical conditions. The sample mass can then be included to provide a value for the uranium concentration.

(5) *Sample and storage facilities:* In the sample preparation facility the sample sizes handled in off-line work are quite small (usually 1–10 g), therefore it is important that they are taken from a carefully homogenized material. For irradiation, the sample is weighed and sealed in a capsule made of some non-activatable material, e.g. polyethylene. After irradiation and counting, the samples still exhibit induced radioactivity and must be stored in a suitably shielded and ventilated area. Since the irradiation times are quite short, this induced activity decays rapidly and, generally, the samples can again be handled safely within 24 hours or so. They may be reanalysed by any method, since DNC is non-destructive.

6–4. INTERFERENCES

Four circumstances can give rise to interferences in the DNC method for uranium analysis:

(1) *The presence of a large amount of thorium:* Thorium, as naturally found, consists only of the isotope ^{232}Th, which has a very low cross-section for fission by slow neutrons and a higher one for fast neutron induced fission. However, depending on the distribution of neutron flux energy, large amounts of thorium contribute to the delayed neutron emission and, hence, mimic small amounts of uranium. Should it be necessary, a correction factor for thorium content can be deduced and applied.

(2) *Uranium-235 is not present at natural abundance levels:* Although ^{235}U comprises only 0.7% naturally occurring uranium, it accounts for almost all the delayed neutron emissions described above. This is because its cross-section for fission with slow neutrons is perhaps 10^6 times that of the other naturally occurring isotope of uranium, ^{238}U. Since the DNC system is calibrated using 'natural' uranium, the calibration factor presumes natural abundance levels. The DNC method *cannot* be used for 'enriched' or 'depleted' uranium unless only the ^{235}U content is required. Uranium salts, or any other material known to be depleted in ^{235}U, should not be used for calibration.

(3) *Other neutron emitting activation:* There are a few other neutron activation products that have neutron emission as one of their decay modes. One of these is ^{17}N, which has a half-life of about 4 seconds and neutron reaction from ^{17}O. Thus, this neutron emission mimics the presence of a very small amount of uranium. These interferences are generally extremely small, and rarely are corrections for them considered necessary.

(4) *Counting losses:* As in all counting systems there are events that are not recorded, usually because the system is still processing the previous event. This processing time is variously referred to as the 'system busy', or 'dead' time, and there are various ways of correcting for the counting losses associated with it. These methods can be computational or electronic. For DNC, a simple way of correcting for the losses is to generate a calibration curve (and/or associated equation) that includes standards containing amounts of uranium that are large enough to cause significant counting losses. Thus, the curve or equation includes the necessary correction.

6-5. SUMMARY

In summary, it can be stated that DNC, after neutron activation, is an accepted and reliable method for uranium analysis. It is instrumental, non-destructive and capable of automation; using reactor neutron fluxes, uranium at the below parts per million level can be determined at rates of approximately 60 samples per hour. The method is also viable for percentage concentrations of uranium, and samples can be any well homogenized solid or liquid. The method is normally free of significant interferences.

6-6. FURTHER READING

(1) *Physics of fission*

EVANS, R.D., The Atomic Nucleus, McGraw Hill, New York.

(2) *Neutron detection and counting systems*

KNOLL, G.F., Radiation Detection and Measurement, Wiley, New York.

(3) *Automated uranium analysis based on DNC*

ROSENBERG, R.J., PITKÄNEN, V. SORSA, A., An automatic uranium analyzer based on delayed neutron counting, J. Radioanal. Chem. **37** (1977) 169–179.

BOULANGER, A., EVANS, D.J.R., RABY, B.F., "Uranium analysis by neutron activation delayed neutron counting", Proc. 7th Annu. Mtg, Canadian Mineral Analysts, Thunder Bay, Ontario (1975).

SPENDER, M.R., "SLOWPOKE-2 based uranium analysis laboratory", Industrial Application of Radioisotopes and Radiation Technology (Proc. Symp. Grenoble, 1981), IAEA, Vienna (1982) 100–101.

(4) *Comparison with other methods*

GARRETT, R.G., LYNCH, J.J., "A comparison of neutron activation delayed neutron counting versus fluorometric analysis in large scale geochemical exploration for uranium", Exploration for Uranium Ore Deposits (Proc. Symp. Vienna, 1976), IAEA, Vienna (1976) 321–334.

Method 7

DETERMINATION OF URANIUM IN ORES, ROCKS AND MINERAL PROCESSING SOLUTIONS BY XRF ANALYSIS[19]

7-1. INTRODUCTION

Uranium has been determined by XRF analysis in geological materials [1–3], ores [4, 5], process solutions [6–8], uranium ore concentrates [9, 10] and nuclear reactor materials [11, 12]. As the last two references are not of direct interest to the readers of this Manual, they are not discussed here.

Wavelength dispersive spectrometry was used in Refs [2, 4, 7, 9, 10], while energy dispersive spectrometry was used in the remainder. In all but one case, the uranium Lα peak was measured. Reference [3] constructed special instrumentation to measure the Kα peak. The calibration techniques varied considerably. Reference [4] simply used a ratio of the net uranium count rate of the sample to that of a reference material, with a calibration range of 0.01–0.25 wt% U_3O_8. Reference [2] used a ratio of the uranium to the background count rates over a range of 0–100 μg/g. Dilution of powdered sample material with elemental sulphur was used in Ref. [1] to determine uranium and some 39 other elements at the trace level. Reference [4] used the method of standard additions directly on the solids, as well as dissolving the ore sample and analysing the solutions, using thallium as an internal standard, at a 0.2 wt% concentration. A ratio between the uranium Lα and the iodine Kα incoherent scatter count rates was used in Ref. [6] over a concentration range of 1–500 g/L.

Two preconcentration techniques, ion exchange and precipitation with collection on a silver membrane (Refs [7, 8], respectively), were used to determine the uranium at 25 μg/g. References [9, 10] determined the uranium in uranium concentrates by dissolving the solid material and analysing the solution. Calibration was accomplished with yttrium and strontium internal standards, respectively.

The methods described here use bromine as the internal standard for analysis of solutions and tube scattered radiation, to compensate for the variation in matrix, for analysis of solids [13].

For both aqueous and organic solutions, the detection limit is estimated to be 10 ppm, with an accuracy estimate of ±5% relative at 1.0 g/L. For solids the detection limit is estimated to be ±5% relative at 0.1 wt%.

---

[19] Contributed by J.L. Dalton, CANMET, Energy Mines and Resources Canada, Ottawa, Ontario, Canada.

7-2. ANALYSIS OF AQUEOUS SOLUTIONS USING BROMINE AS THE INTERNAL STANDARD

(1) *Instrumentation:* A Philips PW-1400 X ray spectrometer with a PW-1730 X ray generator, a digital equipment PDT-1140 programmable data terminal with PW-1400 software used for instrumentation control and data processing, a rhodium target X ray tube operated at 50 kV, 30 mA, fine collimation, a helium path, a lithium fluoride 220 analysing crystal, uranium Lα measured at 37.26° 2Θ with background measurement at 36.26° 2Θ using a scintillation detector, bromine Kα measured at 42.80° 2Θ with background measurements at 41.80° 2Θ and 43.80° 2Θ for both the scintillation detector and the flow counter.

(2) *Reagents: (a) Uranium stock solution:* Using NBS 950b pure uranium oxide [14], weigh 0.50 g and transfer to a 250 mL Pyrex beaker. Add about 25 mL of distilled water and 10 mL of concentrated nitric acid, and heat gently. After dissolution, transfer quantitatively to a 250 mL volumetric flask and dilute to the mark with water. Prepare several concentrations in the range of 0–2 g/L by appropriate dilution; 25 mL of each diluted concentration is adequate. (b) *Bromine internal standard solution:* 4 mL of concentrated 48% HBr is diluted to 100 mL with distilled water. Polypropylene X ray cells and rings suitable for use in the PW-1400 spectrometer and Mylar film, 1/4 mil (Spex Industries, Inc., Metuchen, NJ, USA).

(3) *Calibration:* Five millilitres of diluted uranium stock solution in the range of 0–2 g/L and 0.10 mL of the bromine internal standard solution are pipetted into an X ray cell, which is covered with Mylar film, and the ring is snapped into place. The cell is then placed in a Philips PW-1220 sample holder, which also has a Mylar window. This assembly is then placed in the PW-1400 sample holder. The measurement times for the uranium and bromine peaks and backgrounds are 10 and 6 seconds, respectively. The net uranium and bromine counts and the uranium/bromine intensity ratio are obtained and plotted against the concentration. Data from a typical calibration are shown in Table II–III. With these conditions, one sigma counting statistics for uranium is 0.7% at the 0.4 g/L concentration and 0.4% for the bromine intensity.

(4) *Procedure:* Dilute the solution sample to fit the calibration range if necessary. Five millilitres of sample is transferred to the X ray cell and 0.1 mL of internal standard is added; the cell is covered with Mylar film and the ring is snapped into place. Proceed with measurement and calculation as described in item (3) above. Calculate the uranium content by referring the uranium/bromine ratio of the sample to that of the standard solutions.

(5) *Comments:* Use of bromine as an internal standard compensates for most of the compositional changes in the sample solutions. However, if a certain element, or elements, is continually present in high concentrations, then it may be necessary

TABLE II-III. CALIBRATION DATA: DETERMINATION OF URANIUM IN AQUEOUS SOLUTIONS

Solution	Composition (g/L)			I_U (counts/s)	I_{Br} (counts/s)	I_U/I_B	U concentration (g/L)	
	Fe	S	Ca				Sought	Calculated from regression
Standard A[a]	—	—	—	5876	4498	1.3066	2.00	1.98
Standard B[a]	—	—	—	3176	4811	0.6602	1.00	1.01
Standard C[a]	—	—	—	1257	4830	0.2603	0.40	0.40
Standard D[a]	—	—	—	118	5201	0.0227	0.04	0.046
1	3.0	3.0	3.0	62	2614	0.0239	0.04	0.045
2	3.0	3.0	3.0	42	3891	0.0108	0.02	0.022
3	3.0	3.0	3.0	258	3829	0.0674	0.10	0.107
4	6.0	1.0	1.0	932	3406	0.2736	0.40	0.424
5	1.0	2.0	2.0	3005	4451	0.6752	1.00	1.03
6	0.5	2.0	2.0	2875	4340	0.6625	1.00	1.01
7	0.4	0.8	0.8	4739	4501	1.0529	1.60	1.59
8	5.0	—	—	2497	3705	0.6741	1.00	1.03
10	—	—	5.0	2735	4143	0.6602	1.00	1.01
11	—	2.0	—	3036	4569	0.6647	1.00	1.02
12	0.5	2.0	5.0	2938	4338	0.6773	1.00	1.01

[a] Solutions used for calibration.

to add that element(s) to the uranium calibration solutions. Bromine intensity responds well to acid changes, as shown in Fig. II-6. A significant silver content prevents the use of bromine, but this is not likely to occur. Strontium can be used as an internal standard for uranium determination. However, its use is often hindered by the presence of sulphate or phosphate in the process solutions. In most cases, spectral interference is not likely to occur, even with a high thorium and a low uranium concentration, for either the uranium or the bromine peak. Some care must be taken to ensure that backgrounds are not taken in the immediate vicinity of the thorium $L\alpha$ peak at 39.23° 2Θ or the bromine K_β peak at 38.24° 2Θ.

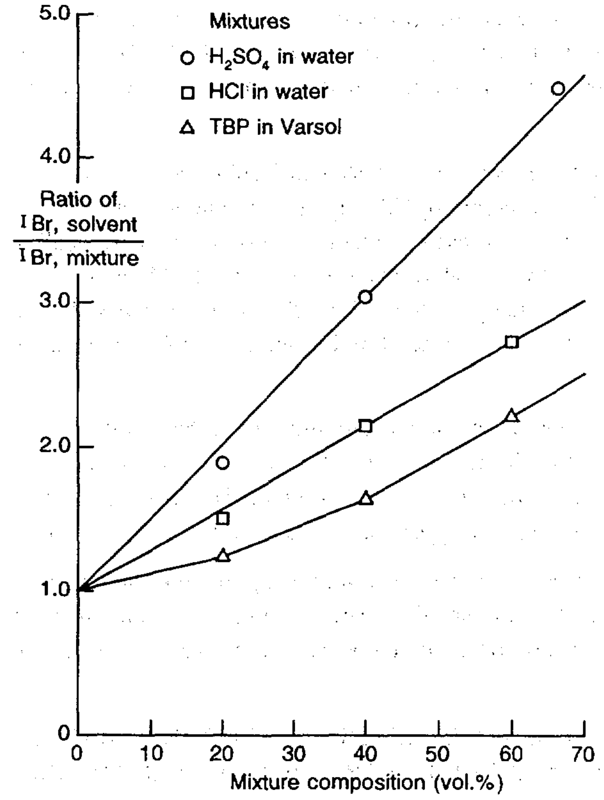

FIG. II-6. Effect of solution mixture on the bromine K_α intensity (TBP: tri-n-butyl phosphate).

7-3. ANALYSIS OF ORGANIC SOLUTIONS USING BROMINE AS THE INTERNAL STANDARD

The same instrumental parameters are used for organic solutions as for aqueous solutions, but the concentration range is reduced to 0–1 g/L of uranium. The concentration range is reduced because of the limited solubility of the uranium compound chosen for the standard. 2-bromohexanoic acid is used as the internal standard. The same volumes are used, i.e. 5.0 mL of solution and 0.1 mL of internal standard.

(1) *Reagents:* (a) *Uranium stock solution:* 0.17 g of reagent grade uranyl acetate is weighed and transferred to a 250 mL Pyrex beaker. Ten millilitres of methanol, 20 mL of versatic acid and approximately 30 mL of Varsol are added to the beaker.

Heat gently, with stirring until dissolution is complete. Transfer to a 100 mL volumetric flask and make up to the mark with Varsol. (b) *Bromine internal standard solution:* Dilute 5 mL of reagent grade 2-bromohexanoic acid to 100 mL with Varsol.

(2) *Calibration:* Prepare several standard solutions with concentrations in the range of 0–1 g/L of uranium by diluting appropriate quantities of the uranium stock solution. Place 5.0 mL of each standard solution in the X ray cell and add 0.1 mL of the bromine internal standard solution, cover with Mylar film and snap the ring into place. Use the same parameters for XRF measurement and subsequent calculations, as detailed in the calibration for aqueous solution analyses (item (3) in Section 7–2).

(3) *Procedure:* Dilute the organic solution to fit the calibration range of 0–1 g/L if necessary. Five millilitres of the solution is placed in the X ray cell, 0.10 mL of the organic bromine internal standard solution is added, the cell is covered with Mylar film and the ring is snapped into place. Proceed as described in item (2) above.

(4) *Comments:* As with aqueous solutions, the bromine intensity responds to changes in the matrix composition. The variation in bromine intensity as a function of the volume fraction of tributylphosphate in Varsol is shown in Fig. II-6.

7–4. ANALYSIS OF POWDERS USING SCATTERED RADIATION TO COMPENSATE FOR VARIATIONS IN THE MATRIX

XRF intensities are influenced significantly by the sample matrix [2]. Scattered radiation from the X ray tube may be used to compensate for both the physical and the chemical variations, since it is sensitive to changes in the average atomic number, density and grain size [15]. Calibration is achieved by plotting the ratio of the uranium net counts to the scatter net counts versus the uranium concentration.

An important variable that should, if possible, be controlled is that of grain size distribution. This variable may be controlled if all the powder samples are ground in the analytical laboratory using the same grinding apparatus under the same conditions. It has been reported that the grinding apparatus has its own characteristics and produces a characteristic grain size distribution [16]. Size distribution, in turn, has a direct influence on the X ray intensities [17, 18]. While scatter correction compensates for some changes in the grain size, control of this variable is recommended.

It is also recommended that separate calibrations are established for each type of sample, such as geological, mine, mill head and tailings, to minimize the matrix variations within a particular calibration. However, one of the problems with this practice is that it may be difficult to obtain a suitable calibration range with just one type of sample. This is the reason for referring to the scatter as a matrix variation correction, so that a single calibration can be used for more than one type of material.

TABLE II-IV. CALIBRATION DATA: DETERMINATION OF URANIUM IN POWDERED SAMPLES

Material	Source	I_U (counts/s)	I_{Rh} (counts/s)	I_U/I_{Rh}	Uranium (wt%)	
					Certified	Calculated from regression
DH-1[a]	Canada	1 803	2122	0.8487	0.177	0.175
UTS-1	Canada	33	2130	0.0153	0.0049	0.005
UTS-2	Canada	51	2750	0.0186	0.0056	0.006
UTS-3	Canada	655	2658	0.2464	0.0513	0.052
UTS-4	Canada	1 701	3029	0.5620	0.1010	0.117
BL-2A[a]	Canada	4 679	2251	2.0787	0.426	0.425
BL-3[a]	Canada	10 256	1940	5.2877	1.02	1.077
BL-4A[a]	Canada	1 580	2412	0.6550	0.1248	0.136
CUP-1	USA	1 295	1763	0.7344	0.128	0.152
EJ-177	China	406	2168	0.1875	0.0285	0.031
EJ-178	China	1 418	3112	0.4555	0.0788	0.095
EJ-179	China	1 079	2932	0.3680	0.0682	0.077
EJ-180	China	2 356	2802	0.8409	0.194	0.173
EJ-181	China	9 115	2308	3.9495	0.703	0.805
EJ-182	China	997	1790	0.5573	0.0986	0.115
EJ-183	China	164	510	0.0167	0.0536	0.066
DH-1A[a]	Canada	2 539	2216	1.1459	0.2629	0.235
DL-1	Canada	52	3280	0.0159	0.0041	0.006
DL-1A[a]	Canada	164	3190	0.0513	0.0116	0.013

[a] Materials used for calibration.

Linear regression data

	I_U versus uranium (wt%)	I_U/I_{Rh} versus uranium (wt%)
Slope	10 795.3	5.261
Intercept	81.424	0.04126
Correlation coefficient	0.9865	0.9957

The calibration described later used material from two different Canadian ore deposits. These were used to determine the uranium in Canadian tailings, United States ore grade samples and Chinese geological materials. All the materials shown in Table II–IV are available from the Canadian Certified Reference Materials Project (CCRMP), except the Chinese materials [19].

(1) *Instrumentation:* (a) A suitable grinding apparatus such as a shatterbox (Spex Industries, Inc.); (b) A suitable pellet press such as the Herzog (Philips Electronics Ltd, Scarborough, ON, Canada); (c) A Philips PW-1400 X ray spectrometer.[20] The instrument parameters are the same as those for the analysis of solutions, except for the following differences: a rhodium target X ray tube operated at 50 kV 50 mA; a rhodium scatter peak measured at 26.28° 2Θ and backgrounds at 24.28° and 28.08° 2Θ with the scintillation detector; the measurement times for both the uranium peak and the rhodium scatter peaks are 10 seconds and the backgrounds are 6 seconds; preferably a helium path. (d) Aluminium sample cups suitable for use in the PW-1400 spectrometer (Spex Industries, Inc.).

(2) *Procedure:* The material should be ground in the grinding mill until the desired grain size distribution is obtained. The criteria should be that 100% of the powder passes through a 74 μm sieve (200 mesh). CCRMP reference materials are typically 100% minus 74 μm and some 70% less than the 37 μm size (400 mesh) [19]. The ground material is used either for the preparation of a pressed powder pellet or it is simply placed in the X ray cell. If a pressed powder pellet is used, the material is placed in the aluminium cup and tapped firmly several times after each addition. The cup is filled almost to the rim and then placed in the pellet press and pressed at a suitable pressure for approximately 100 seconds. The benefits of using a pressed powder pellet are a constant density and the possible use of a vacuum path. Some materials require the addition of a binding agent to obtain a smooth surface from the pressed pellet. If the polypropylene cell is used, enough material is placed in the cell to almost fill it. The cell is covered with Mylar film and the ring is snapped into place. The cell is then placed directly in the XRF sample holder. The XRF measurements are made with the parameters detailed in item (1) above. A ratio is calculated for the net uranium to the net scatter counts and this is plotted against the weight per cent uranium in the reference materials. Sample ratios are referred to this plot to obtain the uranium concentration. Data from a typical calibration are shown in Table II–IV. The last column lists the results calculated by the linear regression equation produced by data from the reference materials denoted with an asterisk. Perusal of this data suggests that the accuracy of the method is generally within ±10% of the certified value, but there are some exceptions. The

---

[20] Any X ray spectrometer with similar specifications can be used satisfactorily.

regression data show the advantage of using the scattered radiation to compensate for a variation in matrix. The correlation coefficient from the ratio data indicates less scatter than with using only the uranium count rate.

REFERENCES

[1] GIAUQUE, R.D., GARRETT, R.B, GODA, L.Y., Determination of forty elements in geochemical samples and coal fly ash by X-ray fluorescence spectrometry, Anal. Chem. **49** (1977) 1012–1017.

[2] JAMES, C.W., Parts per million determination of uranium and thorium in geologic samples by X-ray spectrometry, Anal. Chem. **49** (1977) 967–968.

[3] KUMPULAINEN, H., Uranium analysis by K X-rays from geological samples, J. Radioanal. Chem. **59** (1980) 635–640.

[4] Use of the PW-1250 for the Analysis of Uranium Ores, 79.177/FS11, Scientific and Analytical Equipment Department, NV Philips Gloeilampenfabricken, Eindhoven (1979).

[5] ZIMMERMAN, J.B., The Determination of Uranium in Ores from Denison and Beaverlodge Mines by X-ray Fluorescence Spectrometry, Rep. EMT 71-4, Extraction Metallurgy Division, CANMET, Energy, Mines and Resources Canada, Ottawa, ON (1971).

[6] SHENBERG, C., AMIEL, S., Analytical significance of peaks and peak ratios in X-ray fluorescence analysis using a high resolution semiconductor detector, Anal. Chem. **43** (1971) 1025–1030.

[7] JABLONSKI, B.B., LEGDEN, D.E., X-ray fluorescence determination of uranium as the barium diuronate precipitate, Anal. Chem. **51** (1979) 681–683.

[8] FELDSTEIN, H., GILATH, I., Determination of low uranium concentration in carbonate–bicarbonate solutions by X-ray fluorescence, J. Radioanal. Chem. **57** (1980) 47–52.

[9] JENSEN, C.L., BAUR, G.S., Determination of uranium in high-grade uranium concentrates by an X-ray emission spectrographic method, Appl. Spectrosc. **26** (1972) 57–59.

[10] DONAHUE, B., "The determination of uranium in high-grade chemical precipitates by X-ray spectrometry", Proc. 3rd Annu. Mtg, Canadian Mineral Analysts (1971).

[11] DRAGNEV, T.N., KARAMANOVA, J., DAMIANOV, B., Precise non-destructive X-ray fluorescence method for uranium and thorium concentration measurements, J. Radioanal. Chem. **52** (1979) 439–448.

[12] BERDIKOV, V.V., GRIGOREV, O.I., IOKLIN, B.S., X-ray fluorescence determination of uranium and neighbouring elements in solution, J. Radioanal. Chem. **68** (1982) 181–192.

[13] DALTON, J.L., CANMET, Energy, Mines and Resources Canada, Ottawa, ON, Unpublished results.

[14] Reference Material 950b, United States Department of Commerce, National Bureau of Standards, Washington, DC.

[15] ANDERMANN, G., KEMP. J.W., Scattered X-rays as internal standards in X-ray emission spectrometry, Anal. Chem. **30** (1958) 1306–1309.

[16] ALCOCK, A.R., Rapid X-ray analysis of geological samples', Geoanalysis '78 Symposium, CANMET, Energy, Mines and Resources Canada, Ottawa, ON (1978).

[17] CLAISSE, W., Overcoming the particle size effect in the internal standard method of X-ray fluorescence analysis, Spectrochim. Acta, Part B **25** (1970) 209–218.

[18] LUBECKI, A., HOLYNSKA, B., WASILEWSKA, M., Grain size effect in non-dispersive X-ray fluorescence analysis, Spectrochim. Acta, Part B **23** (1968) 465–470.

[19] YANG, Z., LIA, X., Seven standard ore samples of uranium, thorium and radium by the Bureau of Uranium Geology, Geostandards Newsl. **VII** (1983) 251–260.

Method 8

DETERMINATION OF URANIUM IN ORES AND OTHER SAMPLES BY UV/VIS SPECTROPHOTOMETRY[21]

8-1. INTRODUCTION

This method is based on the formation of a uranyl-dibenzoylmethane complex [1] and is normally applied to solid samples containing more than 500 ppm of uranium. Uranium is extracted with tributyl phosphate from a solution containing aluminium nitrate after mixed acid digestion. An aliquot of the extract is diluted with a solution of dibenzoylmethane and pyridine to form the desired complex for determination by spectrophotometry.

8-2. INTERFERENCES

Thorium interferes when it is ten or more times the concentration of uranium.

8-3. PRECISION

The precision of the method is generally within 3%; the reporting limit is 0.02%.

8-4. REAGENTS

(1) HNO_3, concentrated
(2) $HClO_4$, concentrated
(3) HF, concentrated
(4) Aluminium nitrate, reagent grade: Prepare a saturated aqueous solution, approximately 900 g/L
(5) Dibenzoylmethane (1,3-diphenyl-1,3-propandedione): Dissolve 10 g in 1 L of acetone

---

[21] Contributed by R. Chessmore, United States Department of Energy, Grand Junction, Colorado, USA.

(6) Iso-octane (2,2,4 trimethylpentene)
(7) Acetone, reagent grade
(8) Metacresol purple: Dissolve 0.05 g in 100 mL of deionized water containing two to three pellets of sodium hydroxide
(9) Pyridine, reagent grade
(10) Sodium sulphite solution: Dissolve 1 g of anhydrous sodium sulphite in 20 mL of deionized water (keep refrigerated)
(11) EDTA, tetrasodium salt dehydrate: Dissolve 41.6 g in deionized water and dilute to 250 mL
(12) Tri-n-butyl phosphate, iso-octane solvent extractant: One volume of tri-n-butyl phosphate combined with 10 volumes of iso-octane
(13) Mixed colour reagent: Add approximately 18 mL of dibenzoylmethane solution to 809 mL of acetone; add approximately 40 mL of pyridine; dilute this to 1 L with deionized water.

8–5. APPARATUS

(1) UV/VIS spectrophotometer (double beam)
(2) Eberbach reciprocating shaker
(3) 50 mL mixing cylinders
(4) Vials, screw cap 4, 4f/4 or with foil lined disposable caps.

8–6. METHODS

8–6.1. Instrument conditions

Consult instrument manual for instrument operating instructions. Instrument set-up: with a wavelength of 410 nm.

8–6.2. Standards

Add 5.2 mL of HNO_3 per every 100 mL dilution of the standards to keep the HNO_3 concentrations the same.

(1) *Stock solution:* Dissolve 0.5003 g of NBS standard 950A in 3 mL of H_2SO_4, 5 mL of HNO_3, 10 mL of $HClO_4$ and 1 mL of HF. Dilute to 500 mL. This is a 1000 μg/mL U_3O_8 standard solution. Alternatively, a vendor supplied 1000 μg/mL uranium standard can be used.

(2) *Working standard:* Pipette 5 mL of the 1000 μg/mL U_3O_8 stock solution into a 50 mL volumetric flask. Add 2.5 mL of HNO_3 and dilute to 50 mL with deionized water. This is a 100 μg/mL U_3O_8 working standard, which must be prepared fresh daily.

8-6.3. Analytical method

(1) Weigh 1 g of sample into a 250 mL beaker. Add 15 mL of HNO_3, 10 mL of $HClO_4$ and 5 mL of HF. Cover with a watch glass and digest to a moist salt (2–3 mL). Cool and add 2–3 mL of HNO_3 and 25 mL of deionized water. Heat to boiling and cool. A blank containing all the digestion acids should be carried throughout the entire method.

(2) Transfer the samples to 50 mL mixing cylinders. Dilute to the mark with deionized water and mix. Allow the insoluble matter to settle.

(3) Using glass pipettes, pipette 5 mL of each sample into a series of mixing vials. Pipette 2 mL of deionized water into a mixing vial and carry this undigested blank through. Pipette 1, 2 and 5 mL of the 100 μg/mL standard into three mixing vials.

(4) Mix after each of the following additions. To each of the vials add:

(a) Three drops of 5% sodium sulphite solution
(b) One drop of metacresol purple indicator
(c) 0.5 mL of EDTA solution
(d) 1:1 ammonium hydroxide or 1:1 HNO_3 dropwise to the yellow form of the indicator
(e) Two drops of glacial acetic acid
(f) 15 mL of aluminium nitrate saturated solution
(g) 5 mL of tri-n-butyl phosphate iso-octane mixture.

(5) Shake for 1 minute on the Eberbach shaker and allow 5–10 minutes for the phases to separate.

(6) Pipette 2 mL of the organic phase into a clean, dry vial and add 25 mL of the mixed colour reagent. Cap and mix the solutions. Allow 60 minutes for colour development.

(7) Read the samples as follows:

(a) Deionized water
(b) Blank containing 80% acetone
(c) Water blank: Adjust the absorbance reading to 0
(d) Standards: Read and record the absorbance
(e) Digested blank: Adjust the absorbence reading to 0
(f) Samples: Read and record the absorbance.

(8) Clean the cells as follows:

  (a) Deionized water
  (b) Blank containing 80% acetone
  (c) Deionized water
  (d) Turn instrument to standby.

8-7. CALCULATIONS

Construct a curve by plotting the absorbance of the standards versus the microgram of the standards. A linear calibration curve should be obtained. Calculate the U_3O_8 concentration in the sample as follows

$$\% \ U_3O_8 = \frac{\mu\text{g (from calibration curve)}}{\text{Sample weight (g)}} \times \frac{\text{Volume dilution (mL)}}{\text{Aliquot taken (mL)}} \times 10^{-4}$$

REFERENCE

[1] FRANCOIS, C., Anal. Chem. **30** 1 (1958).

Method 9

DETERMINATION OF URANIUM (U_3O_8) IN URANIUM MILL PRODUCTS AND ORES BY THE LEAD REDUCTION METHOD[22]

9-1. INTRODUCTION

This method comprises mixed acid digestion followed by hydrogen sulphide group separation in a $HClO_4$ solution and cupferron–chloroform extraction separation. The residual cupferron is removed by fuming down with $HClO_4$. A reduction in the uranium in a lead reductor followed by titration with standard ceric sulphate solution completes the procedure [1].

9-2. INTERFERENCES

See Section 9-8.

9-3. PRECISION

Under the recommended conditions, the method is accurate to about 0.2%.

9-4. REAGENTS

(1) $HClO_4$, 70–72%
(2) HNO_3, concentrated
(3) Hydrochloric acid, concentrated
(4) HF, 48%
(5) Sulphuric acid, concentrated
(6) Sodium bisulphite, meta
(7) Hydrogen peroxide, 15%
(8) Potassium permanganate solution, 2% aqueous solution
(9) Cupferron: Dissolve 7 g of cupferron in 100 mL of distilled water; keep refrigerated

---

[22] Contributed by R. Chessmore, United States Department of Energy, Grand Junction, Colorado, USA.

(10) Chloroform, US Pharmacopeia grade
(11) Lead metal; granulated test lead, 15–80 mesh
(12) Phosphoric acid, 85%
(13) Ferroin indicator solution, 0.001M aqueous solution
(14) Ceric sulphate standard solution: Transfer 100 g of ceric sulphate to a 2 L beaker and add 475 mL of concentrated sulphuric acid; heat gently and stir for 30 minutes, cool and add small portions of distilled water carefully until the solution is clear; cool and dilute to 18 L; the titre should be approximately 0.0015 g of U_3O_8 per millilitre of standard solution (*see Note (9) of Section 9–8*).
(15) Thioacetamide, 2% aqueous solution.

9–5. APPARATUS

The reductor is made of triple strength Pyrex glass. The column is 380 mm in length, with a 12–13 mm inside diameter. The bell is 75 mm in length, with a 50 mm inside diameter. The column is slightly flared at the column to bell weld to aid in the removal of the lead.

9–6. METHOD

9–6.1. Standards

The standard ceric sulphate solution may be standardized using NBS 950A, standard black uranium oxide.

(1) Weigh a 0.7000 g sample and transfer to a 500 mL Erlenmeyer flask
(2) Add 20 mL of $HClO_4$, a few glass beads and heat on low heat until the volume of the solution is approximately 5 mL; cool, transfer to a 500 mL volumetric flask, dilute to the mark at 20°C and pipette 50 mL of aliquots
(3) Add 20 mL of concentrated hydrochloric acid
(4) Reduce and titrate the aliquots in the same manner as for the sample.

9–6.2. Analytical method

(1) Weigh out 2.0 g of previously dried sample for low grade ores, or less for high grade ores, and transfer to a dry 250 mL Vycor beaker (*see Note (1) of Section 9–8*). Heat in the open beaker for 15–20 minutes at a dull red heat (*see Note (2) of Section 9–8*). Cool, add 10 mL of HNO_3, mix, add 1–2 mL of HF, cover, digest on low heat for a few minutes and then fume down to 3–5 mL.

(2) Cool and wash down the cover glass and the inside of the beaker with water, add 10 mL of $HClO_4$ and dilute to 100 mL, mix. Add 0.2 g of sodium metabisulphite and boil until all the soluble salts are in solution and the sulphur dioxide odour is absent from the vapours.

(3) While boiling gently, add 2 mL portions of 2% thioacetamide solution until the precipitation of the hydrogen sulphide group is complete. Two to four additions are usually sufficient. Boil for 2 minutes, filter through a 12.5 cm Watman 40 paper using a little paper pulp in the cone. Wash the filter well with water, catching the filtrate in a 500 mL Erlenmeyer flask.

(4) Add 10 mL of $HClO_4$. Boil for a few minutes and add 15% hydrogen peroxide dropwise until no further colour change is noted (do not add an excess). Continue boiling to the first fumes of $HClO_4$. Cool, add 30 mL of distilled water, pink with 2% permanganate solution, cool to 5°C and transfer to a cold 250 mL separatory funnel, washing out the flask three times with a little water. Mix the sample by swirling the separatory funnel. The final volume in the separatory funnel should not exceed 90 mL. To the separatory funnel add 85 mL of cold, freshly made 7% cupferron and shake the samples for about 15 seconds. If the samples are not clear, add another 25 mL of cupferron and shake for 15 seconds (*see Note (3) of Section 9-8*) (avoid a large excess of cupferron). At this point, the cupferrate precipitate should coagulate and the solution should be clear. Add 40–45 mL of cold chloroform and shake for 15 seconds. Allow the phases to separate, release the pressure in the separatory funnel by draining off a few millilitres of the chloroform layer so that the stopper can be removed without any splattering. Drain off the chloroform layer into a beaker containing a little water (addition of water to the beakers receiving the chloroform extracts prevents violent decomposition of these extracts). Add 25 mL more chloroform, shake for 15 seconds and drain off the chloroform layer. Add a few millilitres of cupferron with a dropping pipette (if the cupferron solution turns white as it is added, this indicates that the sample has sufficient cupferron; if it turns brown, additional cupferron is required). Add 15 mL more chloroform and shake for 15 seconds. Drain off the chloroform layer. Repeat this step two more times to make a total of five chloroform extractions (*see Note (6) of Section 9-8*). If the extraction of cupferrates does not appear to be complete, continue until the chloroform layer is nearly colourless. If the sample taken contains over 50 mg of U_3O_8 (or over 1% U_3O_8 in the ore), add an additional 10 mL of $HClO_4$ before cupferron precipitation and extraction. After extraction is finished, wash off the outside of the funnel stem carefully with chloroform and transfer the sample to a 500 mL Erlenmeyer flask, washing out the funnel three times with a little water.

(5) Add a few glass beads and evaporate to strong $HClO_4$ fumes (*see Note (7) of Section 9-8*). If chromium is present, as shown by a yellow to red colour, add 0.5 g portions of sodium chloride to the boiling $HClO_4$ solution and shake vigorously to

volatilize the chromium. Repeat until no more red fumes evolve. The last traces of chromium are best volatilized at the point where the salts have just begun to separate from the solution. Fume off the $HClO_4$ until the residual salts are only slightly moist, not dry. Do not bake. If manganese is present, as shown by a brown colour, add 10 mL of concentrated hydrochloric acid and boil until the brown colour has disappeared and all the chlorine has been expelled. Add 60 mL of water and 20 mL of concentrated hydrochloric acid, boil for 2 minutes and cool to room temperature. A clear solution should result (*see Note (8) of Section 9-8*).

(6) Pack a reductor tube with dry granulated lead metal, 15–80 mesh, placing a glass wool pad at the top and bottom of the lead column. Wash the lead in the reductor several times with dilute hydrochloric acid and then with water. Keep the reductor filled with water and allow no air to enter. Before running samples through the reductor, wash it several times with a solution of 3N hydrochloric acid to which has been added 0.1 g of ferric chloride per litre. Then wash the reductor several times with 1N hydrochloric acid. Run a blank consisting of 60 mL of water plus 20 mL of concentrated hydrochloric acid through the reductor, washing the flask and reductor with 80 mL of 1N hydrochloric acid, in small portions, making a volume of 160 mL in the receiving flask under the reductor. Add 1 mL of 0.001M ferroin indicator solution and 2 mL of 85% phosphoric acid, and titrate the blank solution with ceric sulphate solution.

(7) Run the sample solution through the reductor, washing the flask and reductor with 80 mL of 1N hydrochloric acid, in small portions. Add 1 mL of ferroin and one or two drops of 85% phosphoric acid, and titrate with standard ceric sulphate solution until the indicator colour starts to fade (*see Note (4) of Section 9-8*). Add 2 mL of 85% phosphoric acid and add ceric sulphate dropwise until the indicator colour returns, then titrate slowly until the indicator colour again starts to fade. Let the solution stand for at least 30 seconds and finish the titration by splitting the drops. Leave the reductor full of 1N hydrochloric acid if it is going to be used again within 2–3 hours, otherwise flush and fill the reductor with water for longer periods.

(8) The titration blank is determined indirectly by titrating a 1X aliquot and 2X aliquot. Twice the 1X aliquot titration less the 2X aliquot titration equals the titration blank (*see Note (5) of Section 9-8*).

9-7. CALCULATIONS

9-7.1. Calculation — standards

$$\frac{\text{g of } U_3O_8}{\text{mL of titration} - \text{reductor blank} - \text{titration blank}} = \begin{array}{l}\text{g of } U_3O_8 \text{ per mL of} \\ \text{standard ceric sul-} \\ \text{phate solution, titre}\end{array}$$

9-7.2. Calculation — samples

$$\frac{\text{mL of titration} - \text{reductor blank} - \text{titrator blank} - \text{titre} \times 100}{\text{g of sample}} = \%\ U_3O_8$$

9-8. NOTES

(1) Use of Vycor beakers during the pretreatment heating step is preferred because of their high resistance to thermal shock.

(2) The occurrence of asphaltic compounds in some of the uranium ores interferes in the titration, causing high results. Heating of the dry ore eliminates these organic compounds.

(3) Cupferron separation is the critical step in the method. To prevent low results, the $HClO_4$ concentration of the uranium solution in the separatory funnel, prior to the addition of the cupferron, should not fall below the minimum, as given in the method. Also, excessive shaking after cupferron additions may produce erratic results.

(4) The presence of large quantities of phosphate in the ore prevents a false end point being obtained in the titration, and may also cause the uranium phosphate to precipitate upon reduction of the uranium.

(5) For the 1X and 2X aliquots in the determination of the titration blank, a 10 mL and a 20 mL aliquot of the standard uranium solution can be taken.

(6) The additions of cupferron and chloroform are approximate measurements based on the samples normally analysed.

(7) As the sample evaporates, it usually becomes dark brown in colour as a result of excess cupferron. A point will be reached where the $HClO_4$ reacts with the cupferron, resulting in an effervescence which can rise up and out of the Erlenmeyer flask. It may be necessary to have the sample on the edge of the burner at this point. After the reaction, high heat can be re-employed to finish the evaporation down to the moist perchloric salts.

(8) After the samples are cooled, salts usually appear, but this should be ignored.

(9) If desired, the ceric sulphate solution can be prepared from G. Frederick Smith ceric sulphate reagent 25 by adding 350 mL of sulphuric acid to 10 L of water with mixing. Add 323 mL of G. Frederick Smith reagent 25. Dilute to 18 L with water and mix.

REFERENCE

[1] SILL, C.W, PETERSON, W.E, Anal. Chem. **24** (1952) 1175.

Method 10

ATOMIC EMISSION SPECTROSCOPY METHODS FOR MEASUREMENT OF IMPURITIES IN URANIUM[23]

10–1. INTRODUCTION

Atomic emission spectroscopy methods of analysis suffer limitations when samples with high uranium concentrations are analysed. These problems arise because the plethora of the uranium wavelengths emitted can result in spectral interferences. Chemical interferences can also occur, depending on the method of excitation. If inductively coupled plasma (ICP) excitation is used, the problem of chemical interference is virtually eliminated, but spectral interferences remain and, in fact, can be more severe. Spectral overlap can be minimized if a high resolution spectrometer is employed or if an ICP mass spectrometer is used. Alternatively, the spectral and chemical interference problems can be reduced by using a pretreatment procedure to separate the uranium from the analytes.

Two methods for the effective removal of uranium from the analytes are described: one is a solvent extraction method for use with solution samples, which are then measured with an ICP spectrometer; the other is for use with solid samples and employs a carrier distillation technique with DC arc excitation. A third method is also described for measuring impurities in the uranium process solutions without prior separation of the analytes using a high resolution spectrometer.

10–2. SPECTROGRAPHIC ANALYSIS OF U_3O_8 USING THE GALLIUM OXIDE CARRIER TECHNIQUE

10–2.1. Introduction

The following procedure is a slightly condensed version of the Standard Test Method for Spectrographic Analysis of Uranium Oxide (U_3O_8) by the Gallium Oxide Carrier Technique, which appears in the 1991 Annual Book of ASTM Standards, Volume 03.06, Analytical Atomic Spectroscopy; ASTM Designation: E 402-70 (reapproved 1989).

---

[23] Contributed by T.R. Churchill and R.E. Horton, CANMET, Energy Mines and Resources Canada, Ottawa, Ontario, Canada.

10-2.2. Summary of method

The sample as received is ignited to U_3O_8. It is important that the sample is in the same physical oxide form as the comparison standards. The sample is mixed with pure gallium sesquioxide (Ga_2O_3) in the ratio of 98 parts U_3O_8 to two parts Ga_2O_3. If densitometric determinations are desired, the Ga_2O_3 used in the mixture contains 1% chromium or 1% cobalt by weight. The chromium or cobalt is used as an internal standard element in spectrochemical analysis. The U_3O_8-Ga_2O_3 is placed in a special cupped electrode and excited in a DC arc. Varying amounts of impurities, either in vapour form or as solid particles, are carried up into the arc steam, along with the vaporized Ga_2O_3. The spectrum is recorded on a photographic plate and the spectral lines are either visually compared with standard plates or photometrically measured and compared with synthetic standards prepared according to standard spectrochemical procedures.

10-2.3. Equipment

For mixing the sample and carrier, either a highly polished agate mortar and pestle or a suitable small mechanical sample mixer can be used. A balance is required with a capacity of up to a few grams and capable of weighing accurately to the nearest 0.1 mg. The excitation source must be capable of providing a 14 A DC arc (short circuit) and the excitation stand should be of the conventional type, with adjustable water cooled electrode holders. The spectrograph must provide pre-exposure and exposure timers, have a wavelength coverage of 225–865 nm, a reciprocal linear dispersion of at least 0.5 nm/mm and sufficient resolving power to separate cadmium 228.802 nm from arsenic 228.12 nm. Photographic processing equipment for developing, fixing, washing and drying is required and must be capable of providing constant and reproducible solution temperatures. To examine the photographic plates, a comparator-microphotometer is required, as a comparator to provide sufficient magnification and facility to compare the spectral line densities of the sample and a reference standard plate or film, and as a microphotometer with a precision of 1.0%, or better, for transmittance values between 5 and 95%.

10-2.4. Reagents and materials

For the visual comparison analysis, use a 99.99% pure Ga_2O_3. For densitometric analysis, except for chromium, use a mixture of 98.54 parts of Ga_2O_3 and 1.47 parts of chromium sesquioxide (Cr_2O_3). This is equivalent to 1% chromium in this mix, or to 200 ppm in the final U_3O_8–Ga_2O_3 mixture. For densitometric analysis, except for cobalt, use a mixture of 98.53 parts of Ga_2O_3 and 1.47 parts of cobalt oxide (Co_2O_3). This is equivalent to 1% cobalt in this mix, or to 200 ppm in the final U_3O_8–Ga_2O_3 mixture. The anode, pedestal and counter electrodes should be of the S-1, S-2 and C-1 types, respectively. The graphite should be of the high purity type, with an average density of about 1.86 g/cm^3 and a specific electrical resistance of approximately 4.5×10^{-4} Ω·in.

10–2.5. Standards

Standards can be synthesized by adding the impurity elements to purified U_3O_8 and homogenizing. Impurities in a solid or powder form, preferably as oxides, may be blended with U_3O_8; impurities in solution may be added to U_3O_8 and the mixture dried, blended and reignited. Alternatively, the impurities and uranium can be combined in solution and reconverted to U_3O_8. The individual elements should grade in such a ratio as to facilitate visual comparisons; a ratio such as 10:5:2:1 covers the desired analytical range for each element. No single standard should have a total concentration of impurities that exceeds 2000 ppm. The bulk densities of the standards and the sample U_3O_8 should be as nearly identical as possible. Similar element responses should be obtained with U_3O_8 standards of similar bulk densities, regardless of the method used to make the standards. The sample and comparison standards should, if possible, have the same physical oxide form and oxide preparation. Wherever possible, an independent analytical method should be used to verify the established concentrations in the standards. The elements or compounds used to synthesize the U_3O_8 standards should be of the highest purity.

10–2.6. Preparation of samples

Combine 980 mg of the U_3O_8 sample and 20 mg of the proper Ga_2O_3 carrier by thoroughly grinding with an agate pestle in an agate mortar. Weigh quadruplicate 100 mg U_3O_8–Ga_2O_3 charges into anode electrodes held in a plastic electrode board. Gently tap the electrode board to settle the electrode charges. Compress the charges and introduce a centre vent hole into the charge with a venting tool.

10–2.7. Preparation of apparatus

Insert a 3.18 mm counter electrode into the upper holder. Mount a 3.18 mm pedestal electrode so that it extends 12.7 mm above the lower electrode holder. Position the anode electrode, with its charge, firmly on the pedestal. Adjust to an analytical gap of 4 mm, with its centre aligned with the optical axis of the spectrograph. The sample is electrically positive. Produce and record the spectra in accordance with the following conditions.

10–2.7.1. Electrical parameters

Voltage	250 V
Current	14 A (short circuit)

10–2.7.2. Exposure conditions

(1) General procedure for the following elements: silver, aluminium, arsenic, gold, boron, beryllium, bismuth, cadmium, cobalt, chromium, copper, iron, germanium, indium, magnesium, manganese, molyb-denum, nickel, phosphorus, lead, antimony, silicon, tin, thallium, vanadium and zinc

Spectral region	225–350 nm
Slit width	20 μm
Preburn period	5 s
Exposure period	35 s

A step sector may be used to increase the concentration ranges

Photographic emulsion, Eastman Kodak, type SA-1, or equivalent

(2) Barium, lithium and sodium

Spectral region	430–680 nm
Slit width	20 μm
Preburn period	0 s
Exposure period	40 s

Photographic emulsion, Eastman Kodak, type II-F

Filter, Corning No. 3850

(3) Caesium, potassium and rubidium

Spectral region	740–865 nm
Slit width	20 μm
Preburn period	0 s
Exposure period	40 s

Photographic emulsion, Eastman Kodak, type I-N

Filter, Corning No. 3480.

Make duplicate or quadruplicate exposures of each sample.

10–2.8. Photometry

10–2.8.1. Visual comparative analyses

Visually compare the density of the sample impurity spectral line with the corresponding line on a standard reference plate. Estimate the impurity concentration using the lines listed in Table II-V. It is highly improbable that many of the 32 impurities will appear simultaneously in the 100–200 ppm concentration range. However,

TABLE II-V. VISUAL SPECTRAL LINES (nm)

Ag	328.068	Cd	228.802	Li	670.784	Rb	780.023
Ag	338.289	Co	345.351	Mg	280.270	Sb	259.806
Al	309.271	Co	242.493	Mg	279.553	Sb	287.792
Al	308.216	Cr	283.563	Mn	279.827	Si	250.690
As	234.984	Cr	284.335	Mn	279.482	Si	288.158
As	278.022	Cs	852.110	Mo	313.259	Sn	317.502
Au	267.595	Cu	324.754	Mo	317.035	Sn	326.233
Au	242.795	Cu	327.396	Na	588.995	Tl	276.787
B	249.773	Fe	259.940	Na	330.232	V	318.540
B	249.678	Fe	278.810	Ni	305.082	V	318.398
Ba	493.408	Ge	265.118	Ni	300.249	Zn	334.502
Be	234.861	Ge	265.158	P	255.328	Zn	328.233
Be	313.042	In	325.609	P	255.493	Bi	306.772
In	303.936	Pb	283.307	Bi	289.798	K	766.491
Pb	280.200						

TABLE II-VI. ELEMENTS AND ANALYTICAL RANGES

Element	Concentration range (ppm)	Element	Concentration range (ppm)	Element	Concentration range (ppm)
Sb	1–200	As	10–200	Au	1–100
Be	1–200	Ba	10–200	In	1–100
Cr	1–200	Cs	10–200	Mn	1–100
Co	1–200	P	10–200	Rb	1–100
Pb	1–200	V	10–200	Sn	1–100
Ni	1–200	Zn	10–200	Mo	2–100
K	1–200	Li	0.5–100	Tl	5–100
Na	1–200	Mg	0.5–100	Ag	0.1–50
Al	5–200	Cu	0.5–100	Cd	0.1–10
Fe	5–200	Bi	1–100	B	0.2–10
Si	5–200	Ge	1–100		

TABLE II-VII. ANALYTICAL LINES USED FOR DENSITOMETRY (nm)

Element and wavelength		Internal standard element and wavelength				
B	249.773	None			None	
Cr	283.563	Co	304.400			
Fe	259.940	Co	304.400	*or*	Cr	276.259
Mg	280.270	Co	304.400	*or*	Cr	276.259
Mn	279.827	Co	304.400	*or*	Cr	276.259
Ni	305.082	Co	304.400	*or*	Cr	276.259

in most cases, the initial or alternate spectral lines designated will be free from spectral interference even when the other elements are near the maximum concentration, as indicated in Table II-VI. A notable exception is the cadmium 228.802 nm line, which is subject to interference from arsenic above the 30 ppm level. Unusually high concentrations of one or more elements in a sample require cautious checking for unexpected spectral interferences.

10-2.8.2. Densitometric analyses

Chromium and cobalt have been used beneficially as internal standards to determine four commonly encountered impurities. For the best precision, the analytical line pairs shown in Table II-VII should be measured with a microphotometer. An internal standard is not used for boron, but its reliability is improved by using the measured transmittances of the lines shown in the table.

10-2.9. Calibration

10-2.9.1. Densitometric method

Calibrate the emulsion using standard practices. Make quadruplicate exposures of at least four standards. Convert the per cent transmittances of the analytical lines and the internal standard lines to log the intensity ratios using the emulsion calibration curve. Prepare the analytical curves by plotting the log intensity ratio versus the log concentration for each element.

10-2.9.2. Visual method

Make a single exposure of each standard so that each exposure is adjacent to the preceding one, producing a graded pattern of element concentrations. Tag the spectral lines indicated in Table II-V. Using ink, write the parts per million concentrations of each element of the respective standards next to the chosen spectral lines.

10-2.9.3. Standardization densitometric method

With each group of samples, analyse two standard samples in quadruplicate. If the averages of the control values indicate a curve shift of 20%, or more, make one half of the correction needed.

10-2.9.4. Standardization visual method

With each group of samples, analyse two control samples in quadruplicate. If the averages of the control values exceed the established values by 25%, correct all the sample values proportionately.

TABLE II-VIII. SUMMARY OF CO-OPERATIVE TEST RESULTS FOR SPECTROCHEMICAL ANALYSIS OF U_3O_8 FOR IMPURITIES DETERMINED BY THE GALLIUM OXIDE CARRIER DC ARC TECHNIQUE: DENSITOMETRIC ANALYSES

Element	U-1		U-2		U-3	
	Average value (μg/g U)	Average coefficient of variation (%)	Average value (μg/g U)	Average coefficient of variation (%)	Average value (μg/g U)	Average coefficient of variation (%)
B	0.87	12.7	0.38	8.7	0.57	7.5
Cr	31	16.3	7	23.1	47	18.7
Fe	18	20.7	119	9.4	190	11
Mg	49	21.8	6	28.9	—	—
Mn	29	8.9	8	13	38	10.1
Ni	—	—	97	8.7	120	12.3

TABLE II-IX. SUMMARY OF CO-OPERATIVE TEST RESULTS FOR SPECTROCHEMICAL ANALYSIS OF U_3O_8 FOR IMPURITIES DETERMINED BY THE GALLIUM OXIDE CARRIER DC ARC TECHNIQUE: VISUAL COMPARATIVE ANALYSES

Element	U-1		U-2		U-3	
	Average value (μg/g U)	Average coefficient of variation (%)	Average value (μg/g U)	Average coefficient of variation (%)	Average value (μg/g U)	Average coefficient of variation (%)
Al	62	11.6	8	21.1	—	—
Bi	35	17.6	5	19.3	—	—
Cu	2	12.2	46	8.5	50	5.4
Mo	35	19.4	6	18.3	—	—
P	203	13.8	—	—	—	—
Si	—	—	193	9.0	267	6.7
Sn	27	19.9	2	33.8	—	—
V	70	14.6	20	16.1	—	—
Zn	—	—	133	13.6	—	—

10–2.10. Calculations

For the densitometric method, calculate the log intensity ratio for each analytical line pair from the emulsion calibration curve. Refer this ratio to the previously prepared analytical curve to obtain the per cent concentration.

10–2.11. Precision and accuracy

For the densitometric method, the average coefficient of variation is 14.5% for boron, chromium, iron, magnesium and nickel in the range of concentrations given in Table II-VI. Normally, a +100% to −50% indication of precision is assigned to visual analytical results. For certain elements with sharply differing gradations in spectral responses for adjacent standards, a standard deviation of 30% can be obtained. The accuracy of the method can approach the precision stated above, provided the appropriate standards are used. This method has been studied in a co-operative test. Summaries of test data from five laboratories are presented in Tables II-VIII and II-IX.

10-3. ANALYSIS OF IMPURITIES IN URANIUM BY ICP SPECTROSCOPY AFTER SOLVENT EXTRACTION: SEPARATION [1]

10-3.1. Introduction

The extraction method described here is a modified version of a method described by Walker and Vita [2] prior to analysis by atomic absorption. The method was applied in conjunction with ICP measurement by Maney et al. [3]. The sample of uranium is dissolved in concentrated acid, diluted to volume and the solution treated with TBP to separate the uranium from the impurities. The aqueous solution containing the impurities is analysed using an ICP spectrometer.

10-3.2. Equipment and reagents

Separatory flasks of 60–100 mL capacity are required for the extraction procedure. The acids and water used should be of the highest possible purity to optimize the extraction process. The organic reagents used are TBP and carbon tetrachloride,

TABLE II-X. INSTRUMENT SPECIFICATIONS

Instrument		Jarrell-Ash Model 975
Focal curve		0.75 m
Grating		2400 grooves/mm
Wavelength range		190-500 nm in air
Linear dispersion		0.54 nm/mm in first order
Gas flow:	coolant	18 L/min
	plasma	0 L/min
	nebulizer	0.7 L/min
Radio frequency power:		
	forward	1100 W
	reverse	10 W
Observation height		16 mm above the working coil
Integration time		2 × 7 s on line 1 × 7 s on background
Nebulizer		Cross-flow type
Solution uptake		1 mL/min

and both should be prewashed with 6N HNO_3, even if they are designated as purified materials. The instrument used for the analyses was a Jarrell-Ash Model 975 direct reading ICP spectrometer. The operating parameters and some specifications are listed in Table II-X. Any ICP instrument of either the simultaneous or the sequential type with comparable, or better, dispersion could be used. Use of a sequential instrument would, of course, result in a smaller sample throughout.

10-3.3. Sample preparation

Weigh a 1-2 g sample of uranium (as oxide or fluoride) into a 100 mL beaker and digest to fumes in 5 mL of concentrated HNO_3. Dissolve the residue in 20 mL of 6N HNO_3. Transfer the solution to a separatory flask and add 40 mL of TBP. Shake the contents for at least 2 minutes (take care to vent the flask occasionally) and then allow 15 minutes for good separation of the organic and aqueous layers.

Draw off the aqueous layer and save in a second separatory flask. Wash the organic layer with 10 mL of 6N HNO_3 and combine this wash with the first aqueous solution. The second wash should be done to re-extract any trace metals that may have been extracted along with the uranium. Add 10 mL of carbon tetrachloride to the combined aqueous solutions and shake the contents to remove any TBP drawn off with the aqueous layer.

Transfer the aqueous solution to a 100 mL beaker and heat to near dryness to eliminate the excess acid. Dissolve the residue in 5 mL of 0.2N HNO_3. For the best possible sensitivity, analyse 5 mL of the solution directly. It can preferably be diluted to a 25-50 mL volume in 0.2N HNO_3. The sample is now ready for ICP analysis.

10-3.4. Results and discussion

The recoveries for the various trace metals are shown in Table II-XI. The listed values are the percentages of the 5 ppm standard additions remaining after the uranium is extracted. These recoveries are usually reproducible to well within ±5%. After average extraction, only 0.01% of the uranium remains in the aqueous phase.

The detection limits in parts per million for elements in aqueous solutions, in the presence of both 1000 ppm of uranium and a uranium extracted solution, are presented in Table II-XII. These detection limits are defined as the concentration required to give a signal equal to twice the standard deviation of ten consecutive exposures of the various blanks. A distinct similarity is observed between the detection limits in water and the extracted uranium blank. The detection limits in the presence of 100 ppm of uranium are markedly degraded because of the greater noise level resulting from the high background.

Degradation of the calcium results by more than a factor of 30 can be explained by the number of uranium lines adjacent to the 317.9 nm calcium line. Cobalt, iron, manganese and vanadium are other elements whose detection limits suffer in the

TABLE II-XI. RECOVERIES (%)

Al	99	Mn	92
As	79	Mo	87
B	82	Ni	89
Ba	94	Pb	89
Cd	87	Rh	94
Co	92	Se	85
Cr	94	Sr	94
Cu	92	Ti	84
Fe	100	V	87
Li	91	Zn	87
Mg	97	U	0.01

TABLE II-XII. DETECTION LIMITS IN THE SOLUTIONS (μg/L)

Element	H_2O	1000 ppm U	100% U (extracted)
Ca	3	100	22
Co	1	15	2
Fe	1	20	6
Mg	0.1	1.5	4
Mn	0.5	6	0.6
Ni	8	14	4
Pb	15	25	20
Sr	0.2	0.8	0.2
Ti	1	5	2
V	2	25	3
Zn	1	1.5	1
Zr	2	15	5

TABLE II-XIII. DETECTION LIMITS IN THE ORIGINAL SAMPLE (μg/g)

Element	1000 ppm U	100% U (extracted)
Ca	100	0.11
Co	15	0.01
Fe	20	0.03
Mg	1.5	0.02
Mn	6	0.003
Ni	14	0.02
Pb	25	0.2
Sr	0.8	0.001
Ti	5	0.01
V	25	0.015
Zn	1.5	0.005
Zr	15	0.025

TABLE II-XIV. TYPICAL ANALYSIS OF HIGH PURITY U_3O_8 (μg/g)

Al	1.0	Mg	1.75
As	0.65	Mn	0.50
B	0.34	Mo	0.08
Ba	<0.01	Ni	0.93
Ca	7.0	Pb	0.39
Cd	0.07	Rh	<0.15
Co	0.02	Se	0.1
Cr	1.72	Sr	0.54
Cu	<0.01	Ti	0.19
Fe	7.5	V	<0.01
Li	<0.02	Zn	0.34

presence of high concentrations of uranium. The detection limits for these elements are worsened by more than a factor of 10 in the presence of a 1000 ppm uranium solution.

The detection limits for metals in the original undissolved sample are presented in Table II-XIII. To dissolve a 1 g uranium sample and obtain a 1000 ppm uranium concentration, a dilution factor of 1000 is required. Therefore, the lowest detectable amount in the original sample would be 1000 times higher than the detection limit of the solution. When extractions are performed, however, a large dilution factor is not required to mitigate uranium interference. In this example, where a 1 g sample was put in a final sample volume of 5 mL, the calculated detection limits for the original solid sample were only a factor of 5 worse. Extraction processes allow for an improvement in the detection limits by using larger sample sizes and smaller final volumes.

The concentrations found in a high purity uranium oxide sample are listed in Table II-XIV. In most cases, it is obvious that the ICP sensitivity is capable of determining the concentration of impurities when a 1–5 dilution is involved. In summary, the accuracy and sensitivity of ICP analysis combined with solvent extraction make it a useful technique for the analysis of uranium containing products.

10–4. MEASUREMENT OF IMPURITIES IN URANIUM PROCESS SOLUTIONS BY ICP SPECTROSCOPY

10–4.1. Introduction

Uranium process solutions are diluted sufficiently to reduce the concentration of any alkali ions which can cause enhancement or suppression effects. The impurities in the solutions are, therefore, measured directly using an ICP spectrometer. The results for nine elements are presented, but the method can be used to measure any elements for which a suitable wavelength (free of uranium or other line interferences) can be selected.

10–4.2. Equipment

The ICP spectrometer must be capable of providing a resolution of 0.006 nm, or better, as measured at a wavelength in the region of the iron triplet at 310 nm. The instrument must be of the sequential type, or have freedom of wavelength choice. The specifications and operating conditions for the instrument used to analyse the process solutions described here are listed in Table II-XV.

TABLE II-XV. SPECIFICATIONS AND OPERATING PARAMETERS

Instrument:		Jobin Yvon Model JY 38
Focal length		1 m
Grating		3600 grooves/mm
Wavelength range		170-500 nm (nitrogen purged)
Linear dispersion		266 nm/mm in first order
Resolution		0.006 nm (measured at 310 nm)
Gas flow:	auxiliary	0.2 L/min
	plasma	16 L/min
	nebulizer	0.8 L/min
Radio frequency power:		
	forward	1100 W (27.17 MHz)
	reflected	0 W
Integration time		0.5 s/measurement point
Nebulizer		Meinhard type
Solution uptake		1.5 L/min

TABLE II-XVI. WAVELENGTHS SELECTED

Element	Wavelength (nm)
Al	221.005
As	193.699
Ca	315.891
Fe	238.201
Mg	279.563
Mo	202.025
Ni	231.600
V	214.005
Zr	256.895

10–4.3. Procedure

The process solutions can be measured directly without dilution if the uranium concentration is of the order of 2–3 g/L and the salt concentration is 0.1M, or less. Solutions with higher concentrations must be diluted to avoid effects which can render the results completely unreliable.

Careful selection of a sensitive analytical wavelength for each element to be measured is crucial to the success of the measurements. For each sample, the region around the selected wavelengths for each element should be examined to ensure that there are no interfering lines. In addition, if the background on either side, or both sides, of the selected lines is high, then measurements should be made at these positions so that appropriate corrections can be applied. The wavelengths selected for the nine elements measured in the process solutions used to test this method are listed in Table II-XVI.

To provide suitable calibration data, and for subsequent standardization, a set of at least two standards for each element must be prepared. Each standard solution can contain some, or all, of the elements to be measured. The standard solutions can be prepared from high purity compounds, or from commercially prepared solutions. If the approximate composition of the matrix of the solutions to be analysed is known, then the standards should be prepared with a similar matrix. Any reagents used must be of the highest possible purity to obtain optimum detection limits. In addition, the reagents should be analysed to ensure that they are not contributing impurities and to provide data which will allow corrections to be made. The standards used for the analysis reported on here were prepared from commercially available standard solutions using purified HNO_3 to provide a 1% acid solution. If a suitable CRM is available, then a sample of this material should be analysed as a further verification of the accuracy of the results. During measurement of a set of samples, a standard should be included after at least five samples, or more often if the spectrometer system is subject to instrumental drift. In addition, the accuracy of wavelength selection should be checked periodically to ensure that the correct wavelength is being measured.

10–4.4. Results and discussion

Measurements for a batch of uranium process solutions are presented in Table II-XVII. The results for uranium were determined by XRF and indicate the approximate concentration. All the analytical wavelengths selected (Table II-VI) were sufficiently resolved from any adjacent wavelengths that no interelement corrections were necessary. The reagent blank (HNO_3) contained measurable amounts of molybdenum and iron, which necessitate a correction for these elements for maximum sensitivity. All the results are the average of three determinations and the per cent relative standard deviations were typically in the range of 0.5–2.5%, which

TABLE II-XVII. PROCESS SOLUTION RESULTS (μg/mL)

Sample	Al	As	Ca	Fe	Mg	Mo	Ni	V	Zr	U (g/L)
1	320	1.5	175	150	72.0	107	0.7	80.0	29.0	21.9
2	300	<0.4	175	100	57.0	30.1	0.7	60.0	3.0	22.0
3	275	<0.4	165	90.0	55.0	12.0	0.5	53.0	1.9	16.9
4	325	7.4	139	44.0	52.0	32.0	3.0	24.0	153	17.4
5	<0.5	10.0	3.5	0.5	0.4	24.0	0.2	1.6	11	19.6
6	<0.5	4.5	2.5	0.5	0.2	15.0	<0.1	3.0	5.8	12.8
7	<0.5	4.5	2.4	0.4	0.2	22.0	0.2	2.0	6.3	21.9
8	246	3.5	139	134	24	100	0.6	82.0	59.0	7.0
9	13.0	4.0	30	75.0	3.0	12.0	0.6	62.0	3.0	10.8

TABLE II-XVIII. TECHNIQUE COMPARISON (μg/mL)

Sample	Mo			Fe			As			V		
	XRF	ICP	AAS[a]	XRF	ICP	AAS[a]	XRF	ICP	AAS[a]	XRF	ICP	AAS[a]
9	31	26	32	99	80	89	29	4	5	116	56	66
10	<11	7	8	16	4	4	6	2	3	<36	13	15

[a] AAS = atomic absorption spectrophotometry.

indicates good short term measurement stability. The measurements were also repeated after an interval of a few days and all the results agreed within a 0.5–5% relative change with the initial set of measurements. A CRM was not available to verify the accuracy of the measurements. An approximate check on the accuracy was achieved by analysing for the elements molybdenum, iron, arsenic and vanadium by both the atomic absorption and XRF techniques. The results of these measurements on two samples are compared with the ICP results given in Table II-XVIII. While the results indicate that the ICP values for these four elements are probably accurate to within ±15% of the true value, there is no certainty of the absolute accuracy of the results. This serves to emphasize the necessity of a CRM to establish the accuracy of measurement.

The major disadvantage of the measurement of solutions without the prior separation of uranium is that optimum sensitivity cannot be achieved because of the high backgrounds of many of the elements. The sensitivity is adequate for many routine applications. The detection limits for the solutions measured in this investigation were approximately 0.1 μg/mL for the diluted (1:10) solutions, with the exception of arsenic, which was 0.5 μg/mL. The advantage of this method is that the reduced number of sample preparation steps can provide improved precision and higher sampling throughout.

REFERENCES

[1] AMERICAN SOCIETY FOR TESTING AND MATERIALS, Standard Test Methods for Chemical and Atomic Absorption Analysis of Uranium Ore Concentrate, 1991 Annual Book of ASTM Standards, Volume 12.01, Nuclear Energy (1), ASTM Designation: C1022-84 (reapproved 1990), ASTM, Philadelphia, PA (1991).

[2] WALKER, C.R., VITA, O.A., Determination of impurities in uranium compounds by atomic absorption, Anal. Chim. Acta **43** (1968) 27, 35.

[3] MANEY, J.P., LUCIANO, V., WARD, A.E., Analysis of Energy Resources by ICAP Spectroscopy. Part III. Uranium, Technical Application Note 3, Jarrell-Ash Co., Newtonville, MA.

Method 11

DETERMINATION OF MOLYBDENUM IN ORE SAMPLES AND URANIUM MILL PRODUCTS[24]

11-1. INTRODUCTION

The sample is digested in mixed acids and taken to sulphuric acid fumes. Vanadium and chromium are reduced with potassium bisulphite, the molybdenum precipitated with alpha-benzoin oxime. If the ore samples are being analysed, the precipitate is dissolved and the molybdenum is determined spectrophotometrically as the thiocyanate (*see Note (1) of Section 11-9*). If uranium mill products are being analysed, the alpha-benzoinoxime precipitate is ashed at 500°C-525°C and the molybdenum is weighed as molybdenum trioxide.

11-2. INTERFERENCES

See Section 11-9.

11-3. PRECISION

The precision of the method is generally about 4%, or less. The reporting limit is about 0.1 μg/g.

11-4. REAGENTS

(1) HNO_3, concentrated
(2) Sulphuric acid, concentrated
(3) $HClO_4$, 70-72%
(4) Potassium bisulphite, meta
(5) Bromine water, saturated solution
(6) HF, 48%
(7) Methanol
(8) Alpha-benzoin oxime solution, 2% wt/vol.: Dissolve 8 g of alpha-benzoin oxime in 400 mL of methanol; prepare fresh

---

[24] Contributed by R. Chessmore, United States Department of Energy, Grand Junction, Colorado, USA.

(9) Potassium thiocyanate, 10% wt/vol.: Dissolve 10 g of potassium thiocyanate in 100 mL of water
(10) Stannous chloride, 10% wt/vol.: Dissolve 10 g of stannous chloride in 21 mL of hydrochloric acid, heat to effect solution and dilute to 100 mL
(11) Ferrous ammonium sulphate, 1% wt/vol.: Dissolve 1 g of ferrous ammonium sulphate in 75 mL of water containing 1 mL of sulphuric acid and dilute to 100 mL
(12) Ethyl acetate, reagent grade, anhydrous
(13) Tartaric acid
(14) Ammonium hydroxide, with a specific gravity of 0.90.

11-5. APPARATUS

(1) UV/VIS beam spectrophotometer with matched cells
(2) Porcelain crucibles, Coors 37-H
(3) Muffle furnace.

11-6. INSTRUMENT CONDITIONS

Consult the instrument manual for operating instructions. Instrument set-up: wavelength of 470 nm.

11-7. METHOD

11-7.1. Standards (for ore samples)

(1) For the molybdenum stock solution, weigh 7.539 g of MoO_3 into a 250 mL beaker. Add 150 mL of 1 + 1 ammonium hydroxide and heat until in solution. Cool, transfer quantitatively to a 500 mL volumetric flask, dilute to mark and mix well. One millilitre of this solution contains 0.01 g of molybdenum. Prepare the following standards:

   (a) Pipette 5 mL of stock solution, dilute to 100 mL: contains 500 ppm
   (b) Pipette 2 mL of stock solution, dilute to 100 mL: contains 200 ppm
   (c) Pipette 1 mL of stock solution, dilute to 100 mL: contains 100 ppm
   (d) Pipette 10 mL of solution (a), dilute to 100 mL: contains 50 ppm
   (e) Pipette 10 mL of solution (b), dilute to 100 mL: contains 20 ppm
   (f) Pipette 10 mL of solution (d), dilute to 100 mL: contains 5 ppm.

(2) Pipette 1 mL of the (c), (d), (e) and (f) standards into individual 60 mL separatory funnels containing 14 mL of 1 + 3 hydrochloric acid and then carry through the method described in item (5) of Section 11-7.2.

11-7.2. Analytical method

(1) Weigh a 2.0 g sample and transfer to a 250 mL beaker, add 30 mL of 1 + 1 HNO_3, 20 mL of 1 + 1 sulphuric acid, 5 mL of $HClO_4$, 1-2 mL of HF and heat on low heat for 5 minutes, then heat to a strong reflux of sulphuric acid.

(2) Cool, dilute to 100 mL and add approximately 0.5 g of potassium bisulphite. Boil gently to dissolve the salts and continue boiling until all the sulphur dioxide is removed (about 10 minutes). Filter while hot through 12.5 cm Whatman 40 filter paper (use a little paper pulp in the cone), catching the filtrate in a 400 mL beaker. Wash the beaker and filter paper five times each with water. Dilute to 200 mL. Cool to about 5°C. Add, while stirring, 9 mL of the alpha-benzoin oxime solution. Add 2 mL of bromine water (*see Note (4) of Section 11-9*) and mix, then add 3 mL more of the alpha-benzoin oxime solution. Add some ashless paper pulp and let stand for 15 minutes at about 5°C. Filter through 12.5 cm Whatman 40 filter paper (*see Note (2) of Section 11-9*). Wash each filter paper and beaker six times with a cold wash solution prepared as follows: add 40 mL of 1 + 1 sulphuric acid to 2 L of water, cool to 5°C, add 50 mL of the alpha-benzoin oxime solution and mix. Normally, about 200 mL of wash solution is required for each sample.

(3) To analyse the uranium mill product samples, place the filter paper containing the precipitate in a porcelain crucible and transfer to a hot plate. Heat until the paper is charred (do not allow to flame). Ignite sample at 500°C-525°C in a muffle furnace for 2 hours. Cool and weigh the ash as molybdenum trioxide. Determine a filter paper blank using a blank filter paper.

(4) To analyse the ore samples, transfer the filter paper and precipitate to a 500 mL Erlenmeyer flask. Add 25 mL of water, 10 mL of HNO_3, 10 mL of $HClO_4$, 5 mL of 1 + 1 sulphuric acid and heat on a shaking hot plate to a 2 in. sulphuric acid reflux. Cool, add 5 mL of ammonium hydroxide dropwise and agitate to redissolve any tungsten. Add 20 mL of water, 12.5 mL of hydrochloric acid and 1 g of tartaric acid and heat for 15 minutes on a low heat hot plate. Cool, transfer the solution to a 50 mL volumetric flask and dilute to the mark with water.

(5) Pipette 15 mL of the solution into a 60 mL separatory funnel (*see Note (3) of Section 11-9*). A reagent blank consisting of 15 mL of 1 + 3 hydrochloric acid, in a 60 mL separatory funnel, is carried from this point. Add a few crystals of tartaric acid and dissolve. Add the following and mix after each addition: five drops of 1% ferrous ammonium sulphate, 1 mL of 10% potassium thiocyanate solution and 1 mL of 10% stannous chloride solution. Stopper and shake for 10 seconds. Pipette

20 mL of ethyl acetate to the separatory funnel and shake vigorously for 30 seconds. Allow the two layers to separate for 15 minutes, then drain the aqueous layer and discard.

(6) Transfer a portion of the ethyl acetate solution to the cells and determine the absorbance of the samples and the standards. The blank is used in the reference cell.

11–8. CALCULATIONS

11–8.1. Uranium mill products

$$\%\mathrm{Mo} = \frac{[(\text{Weight of } \mathrm{MoO_3}\ (\mathrm{g}) - \text{Weight of blank } (\mathrm{g}))] \times 0.6667 \times 100}{\text{Weight of sample } (\mathrm{g})}$$

11–8.2. Ore samples

The parts per million molybdenum standards versus the absorbance of the molybdenum standards are plotted on linear graph paper, a curve is drawn and the unknowns read from the curve

ppm Mo = ppm Mo (from the graph) × the dilution factor.

11–9. NOTES

(1) United States Geological Survey Professional Paper 391-A.

(2) The precipitate formed in the catch flask after washing the molybdenum precipitate can be ignored. This precipitate is excess alpha-benzoin oxime.

(3) For ore samples containing less than 25 ppm, it may be desirable to transfer the total sample into a 125 mL separatory funnel. Adjust the reagents to sample size, but maintain the 20 mL of ethyl acetate used. If the sample contains a high molyb-denum content, it may be necessary to dilute to a volume greater than 50 mL, maintaining the same hydrochloric acid ratio.

(4) A distinct colour change is usually evident. For ores, the colour change goes from clear to pale yellow; for uranium mill products, the colour changes from yellow green to a darker yellow green.

Method 12

DETERMINATION OF TITANIUM (TiO_2) BY UV/VIS SPECTROMETRY[25]

12-1. INTRODUCTION

Determination of titanium in silicate rocks is based on the yellow colour produced with the Tiron indicator and is normally applied to samples containing up to 3% TiO_2. For higher concentrations, a smaller aliquot should be taken.

12-2. INTERFERENCES

Ferric iron reacts with Tiron to produce a purple solution that can be decolorized by reduction with sodium dithionite.

12-3. PRECISION

The precision of this method is generally within 5%.

12-4. REAGENTS

(1) Tiron, dry reagent powder
(2) Buffer solution: Dissolve 40 g of ammonium acetate in water, add 15 mL of glacial acetic acid and dilute to 1 L with water
(3) Sodium dithionite (also called sodium hydrosulphite), dry reagent powder: Store in a desiccator
(4) Sulphuric acid (H_2SO_4), concentrated
(5) HF, 48%
(6) $HClO_4$-HNO_3 mixture: Mix one part concentrated $HClO_4$ and one part concentrated HNO_3
(7) HNO_3, concentrated
(8) Hydrazine sulphate solution, 0.2%: Weigh 0.2 g of hydrazine sulphate, dissolve in 50 mL of water and dilute to 100 mL; prepare fresh as needed and store in a refrigerator.

---

[25] Contributed by R. Chessmore, United States Department of Energy, Grand Junction, Colorado, USA.

12-5. APPARATUS

(1) Steam bath
(2) Teflon beakers, 100 mL
(3) Vycor beakers, 250 mL
(4) Blast burner
(5) UV/VIS spectrophotometer, double beam
(6) Platinum crucibles.

12-6. METHOD

12-6.1. Instrument condition

A wavelength of 430 nm; consult the individual spectrometer manuals for detailed operating instructions.

12-6.2. Standard

Standard TiO_2 solution: Weigh 0.1013 g of NBS standard sample 154a (titanium dioxide) and transfer to a platinum crucible. Add 2 g of sodium bisulphate and heat on a blast burner until the sample is fused. Cool and place the crucible in a beaker containing 125 mL of 1 + 1 H_2SO_4. Heat and stir until the melt is completely dissolved. Cool, transfer the solution quantitatively to a 250 mL volumetric flask, add 40 mL of 1 + 1 HNO_3, dilute to mark and mix well. The TiO_2 concentration is 0.02 mg/mL.

12-6.3. Analytical method

One Teflon beaker serves for the reagent blank; it contains all the reagents and is carried through the entire sample preparation.

(1) Weigh 0.500 g of each sample and standard into 100 mL Teflon beakers. Carefully add 3 mL of sulphuric acid, 1 mL of HNO_3 and 10 mL of HF (48%). Swirl to effect mixture and heat on a steam bath for 4 hours, or until no acid fumes are given off.
(2) Transfer the contents to a 250 mL Vycor beaker using a minimum of water and a policeman.
(3) Transfer the Vycor beaker to the shaker hot plate and heat until the SO_3 fumes start to evolve, then remove. Cool, add five drops of the $HClO_4$-HNO_3 mixture, return to the hot plate and heat to about 1 in. reflux of H_2SO_4.

(4) Cool, add a few glass beads, 150 mL of water, 5 mL of HNO_3 and 1 mL of hydrazine sulphate solution. Return the beakers to the hot plate and heat to boiling. If a brown precipitate persists after 5 minutes, add an additional 1 mL of the hydrazine sulphate solution. Continue to boil until all the residue is in solution, or until only a small amount remains. If an appreciable amount of residue remains, it should be removed and analysed by suitable methods.

(5) Cool the solution, transfer to a 250 mL volumetric flask, dilute to mark and mix well. Transfer to a polyethylene bottle and mark with an identification label.

(6) Pipette 5 mL of each standard solution and blank solution into 150 mL beakers. Add about 125 mg of Tiron powder using a measuring scoop. Pipette 50 mL of the buffer solution into each beaker and mix.

(7) Add 15 mg of sodium dithionite to the blank solution, mix gently by rotating the beaker two or three times, but not more, since excessive mixing will cause the sulphur to precipitate. After 1 minute, pour the blank solution into the absorption cell. Add 15 mg of sodium dithionite to each of the samples and standards, rotate as before, wait 1 minute and then determine the absorbance of the samples and standards.

12-7. CALCULATIONS

Prepare a calibration curve by plotting the absorbance of the standards versus the TiO_2 concentration in the standards. Convert the milligrams of TiO_2 in the aliquot to weight per cent TiO_2 in the solid sample.

Method 13

DETERMINATION OF VANADIUM IN URANIUM ORES AND URANIUM MILL PRODUCTS BY VOLUMETRIC TITRATION[26]

13-1. INTRODUCTION

This method is used for the high precision assay of vanadium ore and is normally applied to samples containing levels of vanadium greater than 1%. Vanadium is oxidized with potassium permanganate and the excess permanganate reduced with sodium nitrate. Urea is added to decompose the excess nitrite, and the vanadium is titrated with standard ferrous ammonium sulphate, using sodium diphenylamine sulphonate as an indicator.

13-2. INTERFERENCES

A 20%, or greater, concentration of titanium in the original sample interferes by precipitating titanium phosphate after the addition of phosphoric acid [1].

13-3. PRECISION

This method is used for the high precision assay of vanadium rich ore. A relative standard deviation of 1% for samples containing 1-2% V_2O_5 is achieved routinely.

13-4. REAGENTS

(1) H_2SO_4, concentrated
(2) H_2SO_4, 1:1: To 1000 mL of cooled deionized water, slowly add 1000 mL of concentrated H_2SO_4
(3) HNO_3, concentrated
(4) HClO4, concentrated
(5) HF, concentrated

---

[26] Contributed by R. Chessmore, United States Department of Energy, Grand Junction, Colorado, USA.

(6) Ferrous ammonium sulphate ($Fe(NH4)_2(SO_4)_2.6H_2O$), 12% wt/vol.: For 2 L, dissolve 240 g of ferrous ammonium sulphate in 2000 mL of water containing 100 mL of H_2SO_4

(7) Potassium permanganate ($KMnO_4$), 2% wt/vol.: Dissolve 2 g of potassium permanganate in 100 mL of deionized water; filter

(8) Sodium nitrite ($NaNO_2$), 1% wt/vol.: Dissolve 1 g of sodium nitrite in 100 mL of deionized water

(9) Urea (NH_2CONH_2), technical

(10) Phosphoric acid (H_3PO_4), concentrated

(11) Sodium diphenylamine sulphonate indicator ($C_6H_5NHC_6H_4SO_3Na$): Dissolve 0.274 g of sodium diphenylamine sulphonate in 100 mL of deionized water

(12) Standard ferrous ammonium sulphate ($Fe(Na_4)_2(SO_4)_2.6H_2O$): Dissolve 85 g of ferrous ammonium sulphate in a solution of 90 mL of H_2SO_4 and 90 mL of deionized water; dilute to 9 L with deionized water

(13) Potassium dichromate ($K_2Cr_2O_7$), primary standard.

13-5. METHODS

13-5.1. Instrument conditions

None.

13-5.2. Standards

The standardization of titrant is to be performed from step (3) before each use (*see Note (1) of Section 13-7*).

(1) Weigh 1.4 g of primary standard potassium dichromate and transfer quantitatively to a 1 L volumetric flask

(2) Dilute to the mark with deionized water and mix well

(3) Pipette 50 mL of this solution into a 600 mL beaker; add 230 mL of deionized water, 20 mL of 1:1 H_2SO_4 and 15 mL of H_3PO_4; cool

(4) Add about 75% of the required ferrous ammonium sulphate standard solution (45 mL)

(5) Add three drops of sodium diphenylamine sulphonate indicator

(6) Titrate until the indicator colour becomes pale green

(7) Assume a blank of 0.08 mL for the calculation (Section 13-6).

13-5.3. Analytical method

(1) Weigh a 1 g sample into a 250 mL beaker

(2) Add 20 mL of 1:1 H_2SO_4, 10 mL of HNO_3, 2 mL of $HClO_4$ and 3 mL of HF (for samples high in organic content, *see Note (2) of Section 13-7*)

(3) Cover with a watch glass; heat the beaker gently for a few minutes, then heat to a strong reflux of H_2SO_4

(4) Cool; wash down the cover glass and the sides of the beaker with water

(5) Dilute to 75 mL with water

(6) Add boiling chips and boil gently until all the soluble salts are in solution (the undissolved residue should be white)

(7) Filter through 11 cm Whatman 40 filter paper and wash the paper five times with water (filtration can be omitted if the solution is clear enough to see the end point easily) (*see Note (3) of Section 13-7*)

(8) Cool and dilute to 110 mL with water

(9) Add 3 mL of ferrous ammonium sulphate, 12% wt/vol. solution

(10) Add 2% potassium permanganate dropwise until the pink colour persists for at least 2 minutes; avoid a large excess

(11) Add 1% sodium nitrite solution dropwise with agitation until the pink colour disappears; add one drop more of 1% sodium nitrite; allow several seconds between drops as the reaction is slow

(12) Immediately after the addition of the last drop of sodium nitrite, add 5 g of urea with a scoop

(13) Stir until dissolved and let stand for 1 minute

(14) Add 15 mL of H_3PO_4 and exactly three drops of sodium diphenylamine sulphonate indicator solution; hold the dropper in the same position for a uniform drop size (*see Notes (4) and (5) of Section 13-7*)

(15) Titrate with the standard ferrous ammonium sulphate solution until the blue indicator colour is discharged; the end point is sharp to less than one drop

(16) Add a 0.10 mL blank to the titration for all titrations larger than 0.2 mL; if the titration is less then 0.2 mL, add a blank of one half of the titration.

13-6. CALCULATIONS

Calculate the titre for V_2O_5 as follows

$$\frac{\text{g of } V_2O_5}{\text{mL of titrant}} = \frac{1}{\text{mL of titrant} + 0.08 \text{ (for blank)}} \times \frac{\text{g of } K_2Cr_2O_7}{294.197 \text{ g/mol}}$$

$$\times \frac{50 \text{ mL}}{1000 \text{ mL}} \times \frac{6 \text{ mol of Fe}}{\text{mol of } K_2Cr_2O_7} \times \frac{1 \text{ mol of } V_2O_5}{2 \text{ mol of Fe}} \times \frac{181.88 \text{ g}}{\text{mol of } V_2O_5}$$

Calculate the concentration of V_2O_5 as follows

$$\% \ V_2O_5 = \frac{\text{mL of titrant + blank}}{\text{Sample weight (g)}} \times \text{Titre} \times 100$$

13-7. NOTES

(1) Ferrous ammonium sulphate solutions are oxidized by air and must be standardized before each use

(2) Samples with a high organic content may foam during digestion; transfer such samples to 250 mL beakers, add 10 mL of H_2SO_4, heat until the H_2SO_4 fumes and *cautiously* add $HClO_4$ dropwise until the organic material is removed; cool; add 10 mL of HNO_3, 2 mL of $HClO_4$ and 3 mL of HF; proceed as usual

(3) Normally, it is not necessary to filter the samples

(4) The H_3PO_4 addition is necessary to reduce the oxidation potential of the Fe^{+3}–Fe^{+2} system below that of the diphenylamine sulphonate

(5) The H_3PO_4 addition must not be performed until immediately before the titration, otherwise the solution may set to a gel.

REFERENCE

[1] SILL, C.W., Volumetric Determination of Vanadium, United States Bureau of Mines, Salt Lake City, UT, USA.

Method 14

AMMONIA DETERMINATION IN URANIUM PROCESS SOLUTIONS[27]

14-1. INTRODUCTION

This method is applicable to the determination of ammonia nitrogen in samples from uranium process circuits. The ammonia is released by steam distillation from a strong alkaline solution and is absorbed by a solution of boric acid. The ammonia is determined acidimetrically with standard hydrochloric acid, using methyl red as an indicator.

14-2. INTERFERENCES

Some organic compounds such as amines and amides may give ammonia in hot alkaline solutions or be volatilized and give rise to errors. Urea and cyanates will hydrolyse on distillations at a high pH.

14-3. RANGE

This method is suitable for samples containing about 0.1 mg/L, and higher, concentrations of ammonia.

14-4. EQUIPMENT

Automatic steam distillation systems are commercially available.[28]

14-5. REAGENTS

All the solutions are prepared from distilled water purified with a Milli-Q (Millipore) system.

---

[27] Contributed by D.J. Barkley, CANMET, Energy Mines and Resources Canada, Ottawa, Ontario, Canada.

[28] From: Brinkman Instruments Co., Rexdale, Ontario, Canada (Bucki-Brinkman model 320), and Tecator Inc., Boulder, Colorado, USA (Tecator model 1003).

(1) Ammonia standard solution, 0.50 mol/L: Dry reagent ammonium sulphate ($(NH_4)_2SO_4$) for 1 hour at 100°C; accurately weigh 1.607 g and dissolve in water; dilute to 1 L in a volumetric flask

(2) Boric acid solution, 3% wt/vol.: Dissolve 30 g of boric acid (H_3BO_3) in water and dilute to 1 L

(3) Hydrochloric acid, standard solution, 0.05: Dilute 100 mL of 1.0M HCl to 2 L; standardize in accordance with Section 14-7 and calculate the milligrams of ammonia equivalent to 1 mL of standard HCl solution

(4) Indicator solution, 1 g/L: Dissolve 0.1 g of methyl red in 100 mL of ethanol (95%)

(5) Sodium hydroxide solution, 25% wt/vol.: Dissolve 250 g of NaOH in water and dilute to 1 L.

14-6. CALIBRATION

Transfer a 5 mL sample of standard ammonium solution to a distillation tube and distil the ammonia according to Section 14-7. Titrate with 0.05 mol/L of HCl to the methyl red end point. Calculate the milligrams of ammonia equivalent to 1.00 mL of HCl.

14-7. PROCEDURE

Refer to the instruction manual for operation of the distillation apparatus. Distil at least two water samples before commencing with the samples. Transfer a sample containing not more than 1.5 mg of ammonia nitrogen to the distillation tube. Set the tube into the distillation apparatus. Add 50 mL of boric acid solution to the collection flask. Add water to the sample to adjust the volume in the distillation tube to about 70 mL, then add 30 mL of NaOH solution. Start steam distillation and collect about 100 mL of distillate. Titrate with the standardized HCl solution to the methyl red end point.

14-8. CALCULATION

Calculate the ammonia concentration in milligrams per litre of ammonia in the original sample as follows

$$\text{Ammonia nitrogen (mg/L)} = A \times E \times \frac{1000}{V}$$

where A is the milligrams of HCl, E is the milligrams of NH^{3+} per millilitre of HCl titrant and V is the sample volume

BIBLIOGRAPHY

HUNT, G.A., GUEST, R.J., INGLES, J.C., HITCHEN, A., BARKLEY, D.J., A Manual of Analytical Methods Used by the Canadian Mining Industry, CANMET, Energy, Mines and Resources Canada, Ottawa, ON (1974) 196.

YOUNG, R.S., Chemical Analysis of Extractive Metallurgy, Griffin, London (1971).

Method 15

ANALYSIS OF MILL PROCESS SOLUTIONS FOR THE FERROUS/FERRIC IRON RATIO, SILICON AND PHOSPHORUS BY VARIOUS ANALYTICAL TECHNIQUES[29]

15-1. INTRODUCTION

This section deals with the determination of ferrous and ferric iron, silicon and phosphorus in mill process solutions. For all three methods, extensive reference is made to CANMET Monograph 881 by E.M. Donaldson [1]. Users of this Manual will require a copy of this Monograph as a working document. It is an invaluable reference work for those engaged in the analysis of ores and mineral processing products, and includes more than one hundred methods using classical and various other instrumental techniques.

15-2. DETERMINATION OF FERROUS AND FERRIC IRON IN SOLUTION BY TITRATION WITH POTASSIUM DICHROMATE

15-2.1. Introduction

This method is based on that described in Ref. [1]. After the addition of sulphuric and phosphoric acids to an aliquot of the sample solution, ferrous iron is titrated with potassium dichromate using either sodium diphenylamine sulphonate as the internal indicator or potentiometrically to -480 mV [2]. The total iron is determined in a similar manner after reduction of the iron III present to iron II with stannous chloride. Ferric iron is determined by the difference. For details of the methods, the reader is referred to Ref. [1]. The following is an outline of the method.

15-2.2. Reagents

(1) Standard potassium dichromate solution, 0.1N (16.67×10^{-3}M): Dissolve 0.8070 g of pulverized reagent, dried at 105°C for 1-2 hours, in water and dilute the solution to 2 L.

---

[29] Contributed by J.L. Dalton and G.A. Hunt, CANMET, Energy Mines and Resources Canada, Ottawa, Ontario, Canada.

(2) Stannous chloride solution, 5% mass/vol.: Dissolve 12.5 g of stannous chloride dihydrate in 50 mL of hot, concentrated hydrochloric acid and dilute the solution to 250 mL with water. Add several pieces of tin metal and store the solution in a dark bottle.

(3) Ferrous ammonium sulphate solution, 0.1N (0.1M): Dissolve 3.9216 g of ferrous ammonium sulphate hexahydrate in 5% sulphuric acid and dilute the solution to 100 mL with the same acid solution.

(4) Sodium diphenylamine sulphonate (oxidized) indicator tablets, 0.001 g: If the tablets are not available, an oxidized solution of the indicator can be prepared as follows. Dissolve 0.27 g of sodium diphenylamine sulphonate in 100 mL of water, add 10 mL of 50% sulphuric acid and dilute the solution to 300 mL with water. Slowly add 25 mL of 0.1N potassium dichromate solution in small increments, then add 8 mL of 0.1N ferrous ammonium sulphate solution and allow the resulting green mixture to stand for 3–4 days, or until a portion of the supernatant solution no longer yields a colour with a solution containing 100 mL of 5% sulphuric acid and 2 mL of 0.1N potassium dichromate solution. Carefully siphon off the supernatant solution, then add 300 mL of water and 15 mL of concentrated sulphuric acid and siphon off the solution again after the precipitate has settled. Centrifuge the precipitate and wash it with 5% sulphuric acid. Shake the washed precipitate with 100 mL of water, then transfer the resulting suspension to a small brown glass bottle. Shake the mixture well before use.

(5) Mercuric chloride solution, saturated.

(6) Sulphuric acid (oxygen free), 50% vol./vol.: Prepare the solution with oxygen free water.

(7) Phosphoric acid (oxygen free), 50% vol./vol.: Prepare the solution with oxygen free water.

(8) Water (oxygen free), freshly boiled and cooled.

15-2.3. Standardization of the potassium dichromate solution

Transfer 0.2000 g of high purity iron metal to a 600 mL beaker, cover the beaker, add 20 mL of concentrated hydrochloric acid and heat the solution gently until the iron has dissolved. Remove the cover, wash down the sides of the beaker with a small amount of 10% hydrochloric acid and dilute the solution to about 30 mL with the same acid solution. Heat the solution to just below the boiling point, then, while stirring, reduce the iron by adding 5% stannous chloride solution dropwise, until the yellow colour of the ferric chloride disappears. Add one to three drops in excess and cool the solution to room temperature in a water bath. Add 10 mL of saturated mercuric chloride solution, mix the solution thoroughly and then allow it to stand for approximately 5 minutes. Dilute the solution to about 300 mL with cold, oxygen free water, then add 10 mL each of the 50% oxygen free sulphuric and phosphoric acids and one sodium diphenylamine sulphonate indicator tablet, or five drops of indicator solution, and titrate the resulting solution immediately with standard potassium dichromate solution to a violet-blue end point. Correct the result by subtracting the value obtained for the blank solution carried through the reduction procedure. Calculate the normality and the iron equivalent (mg/mL) of the potassium dichromate solution; 1 mL of 0.1N potassium dichromate solution = 5.585 mg of iron.

15-2.4. Procedure

For ferrous determination, transfer a suitable aliquot of the sample solution to a 600 mL beaker and dilute to about 300 mL with oxygen free water. Add 10 mL each of the sulphuric and phosphoric acids and one indicator tablet, or five drops of indicator solution. Titrate the solution to a violet-blue end point. For ferric determination, transfer an identical aliquot of the sample solution to a 600 mL beaker and add 10 mL of concentrated hydrochloric acid. Heat the solution to just below the boiling point and proceed with reduction and subsequent titration as described in Section 15-2.3. The difference between the two titrations is equivalent to the ferric ion content of the aliquot.

15-3. DETERMINATION OF SILICON IN SOLUTION AND ACID SOLUBLE POWDERED MATERIAL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

15-3.1. Introduction

The atomic absorption method described in Donaldson's Monograph [1] can be used to determine silicon in solutions.

15-3.2. Reagents

(1) *Standard silicon solution, 500 μg/mL:* Transfer 0.5345 g of pure silicon dioxide to a 30 mL zirconium crucible, add approximately 4 g of sodium peroxide from a 5 g weighed portion, mix thoroughly and cover the mixture with the remaining sodium peroxide. Cover the crucible and heat the mixture in a muffle furnace at approximately 640°C for about 30 minutes. Allow the melt to cool for about 5 minutes, then transfer the crucible and the cover to a covered 400 mL Teflon beaker containing 100 mL of water. When the subsequent reaction has ceased, add 36 mL of concentrated hydrochloric acid, then remove the crucible and the cover

after washing them thoroughly with water. Transfer the solution to a 500 mL polypropylene volumetric flask, dilute it to volume with water and mix thoroughly. Immediately transfer the solution to a plastic bottle if plastic volumetric flasks are not available. The sodium concentration of this solution is approximately 6000 μg/mL.

(2) *Sodium solution, 30 000 μg/mL:* Dissolve 76 g of sodium chloride in water and dilute the solution to 1 L. Store the solution in a plastic bottle.

15-3.3. Calibration solutions

To an appropriate number of 100 mL plastic volumetric flasks, add (by burette) suitable increments of the standard 500 μg/mL silicon solution to cover the range 10-300 μg/mL. Add sufficient concentrated hydrochloric acid so that 5 mL are present and a sufficient volume (30 000 μg/mL) of sodium solution so that the resultant sodium concentration is approximately 6000 μg/mL. Add 5 mL of concentrated hydrochloric acid and 20 mL of 30 000 μg/mL sodium solution to a separate flask. This constitutes the zero calibration solution. Dilute each solution to volume with water.

15-3.4. Procedure

15-3.4.1. Refractory acid soluble material

Depending on the expected silicon content, decompose 0.5-2 g of the powdered sample by fusing it with 5 g of sodium peroxide; dissolve and treat the melt as described in the method for the preparation of the standard silicon solution (item (1) in Section 15-3.2). Transfer the solution to a 500 mL volumetric flask and dilute to volume with water. Measure the absorbance of the resulting solution at 251.6 nm in a slightly luminous nitrous oxide-acetylene flame. Determine the silicon content of the solution by relating the resulting value to those obtained concurrently for standard silicon solutions of slightly higher and lower concentrations and containing approximately the same amount of sodium. If dilution of the sample solution is required, transfer a suitable aliquot (up to 50 mL) to a 100 mL volumetric flask. Add sufficient concentrated hydrochloric acid so that 5 mL are present, then add sufficient 30 000 μg/mL sodium solution so that the resultant sodium concentration is approximately 600 μg/mL. Dilute the solution to volume with water and determine the silicon content of the aliquot as described above.

15-3.4.2. Mill process solutions

Transfer a suitable aliquot of the sample solution to a 100 mL plastic volumetric flask, add 5 mL of concentrated hydrochloric acid and 20 mL of

30 000 μg/mL sodium solution, dilute to volume with water and proceed with the determination of silicon as described above.

15–4. DETERMINATION OF PHOSPHORUS IN SOLUTIONS BY THE SPECTROPHOTOMETRIC PHOSPHOVANADOMOLYBDIC ACID METHOD

15–4.1. Introduction

Depending on the composition of the solutions, phosphorus in solutions can be determined either directly by the spectrophotometric phosphovanadomolybdic acid method [1] or after separation from interfering elements by extraction of the complex in n-amyl alcohol [2]. In the direct method, interferences from coloured ions are avoided by using an identical aliquot of the sample solution (not treated with ammonium vanadate and ammonium molybdate) as the reference solution [1].

15–4.2. Reagents

(1) Standard phosphorus solution, 0.2 mg/mL: Dissolve 0.4584 g of anhydrous disodium phosphate (Na_2HPO_4), dried at 105°C for 1–2 hours, in water and dilute the solution to 500 mL. Store in a plastic bottle. Prepare a 10 μg/mL solution by diluting 10 mL of this solution to 200 mL with water.

(2) Ammonium vanadate solution, 0.25% mass/vol.: Dissolve 2.5 g of ammonium metavanadate (NH_4VO_3) in about 500 mL of water and add 20 mL of concentrated HNO_3. Allow the solution to stand overnight, then filter, if necessary, and dilute to 1 L with water.

(3) Ammonium molybdate solution, 5% mass/vol.: Dissolve 50 g of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) in about 500 mL of warm water. Allow the solution to stand overnight, then filter, if necessary, dilute to 1 L with water and store in a plastic bottle.

(4) HNO_3, 50% vol./vol.

(5) $HClO_4$, 5% vol./vol.

15–4.3. Calibration curve

15–4.3.1. Without extraction

Add 5 mL of concentrated, colourless HNO_3 to each of eight 100 mL volumetric flasks; then add (by burette) to the last seven flasks 0.5, 1, 2, 4, 6, 8 and 10 mL, respectively, of the standard 0.2 mg/mL phosphorus solutions. The contents of the first flask constitute the blank. Dilute the contents of each flask to approximately 50 mL with water, then add 10 mL of 0.25% ammonium vanadate solution and mix thoroughly. Add 20 mL of 5% ammonium molybdate solution, dilute the resulting solutions to volume with water, mix thoroughly and stand at room temperature for approximately 30 minutes. Measure the absorbance of each phosphovanadomolybdic acid solution at 460 nm against the blank solution as the reference solution, using 20 mm cells. Plot the milligrams of phosphorus versus the absorbance.

15-4.3.2. After extraction

Add 7 mL of 50% HNO_3 and 5 mL of concentrated $HClO_4$ to each of the six 100 mL beakers, then add (by burette) to the last five beakers 2, 4, 6, 8 and 10 mL, respectively, of the standard 10 μg/mL phosphorus solution. The contents of the first beaker constitute the blank. Dilute each solution to about 40 mL with water, heat to about 80 °C, add 10 mL of 0.25% ammonium vanadate solution and cool the solutions to room temperature in a water bath. Transfer the resulting solutions to 125 mL separatory funnels and dilute to about 80 mL with water. Add (by pipette) 10 mL of peroxide free n-amyl alcohol to each funnel, stopper and shake for 1 minute. Allow 5 minutes for the layers to separate, then drain off and discard the aqueous layer. Wash the extract twice by shaking it for about 30 seconds each time with 5 mL of $HClO_4$. Drain the extracts into 15 mL centrifuge tubes and centrifuge for about 30 seconds. Measure the absorbance of each extract at 425 nm against the n-amyl alcohol as the reference solution, using 10 mm cells. Correct the absorbance of each extract by subtracting the blank extract. Plot the micrograms of phosphorus versus the absorbance.

15-4.4. Procedure

15-4.4.1. Interfering elements absent

Transfer two 10–40 mL aliquots of the sample solution, containing not more than 2 mg of phosphorus, to two 100 mL volumetric flasks. Transfer two identical portions of the blank solution to two more flasks, then add 5 mL of concentrated, colourless HNO_3 to each flask. Dilute each solution to approximately 50 mL with water. Then, omitting the addition of ammonium vanadate and ammonium molybdate solutions to one aliquot of each solution, proceed with the complex formation, as described above. Measure the absorbance of the blank solution and the sample solution against the corresponding solution (to which no ammonium vanadate and ammonium molybdate solutions were added) as the reference solution. Correct the absorbance value obtained for the sample solution by subtracting that obtained for the blank solution and determine the phosphorus content of the aliquot by reference to the appropriate calibration curve.

15-4.4.2. Interfering elements present

Transfer a suitable aliquot of the sample solution containing not more than 100 μg of phosphorus to a 100 mL beaker. Add 7 mL of 50% HNO_3 and 5 mL of concentrated $HClO_4$, then proceed with the complex formation, the extraction and the subsequent determination of phosphorus, as described above.

REFERENCES

[1] DONALDSON, E.M., Methods for the Analysis of Ores, Rocks and Related Materials, CANMET Monograph 881, 2nd edn, CANMET, Energy Mines and Resources Canada, Ottawa, ON (1982) 175 pp.

[2] HUNT, G.A., GUEST, R.J., INGLES, J.C., HITCHEN, A., BARKLEY, D.J., A Manual of Analytical Methods Used by the Canadian Mining Industry, Part 2, Extraction Metallurgy Division Report EMI74-14 (1974) 104–106.

Method 16

NITRATE AND SULPHATE DETERMINATIONS IN URANIUM PROCESS SOLUTIONS BY ION CHROMATOGRAPHY[30]

16-1. INTRODUCTION

The procedures described are applicable to samples from uranium process circuits containing sulphate and nitrate ions. Two ion chromatographic (IC) separation techniques using conductivity detection are described: single column IC and suppressed IC.

A filtered aliquot of sample is injected on to an anion exchange column. The sample is pumped through the separation column by an ionic mobile phase, i.e. the eluent. Ions are separated on the basis of their affinity for the exchange sites on the column. In the single column technique, the separated anions to be measured are pumped directly into a conductivity detector. In suppressed IC, the ions, after leaving the separator column, pass through a membrane suppressor that contains cation exchange resin in the hydrogen form. This reduces the background conductivity of the eluent. The detection limits for suppressed IC are two to three times lower than for single column IC, but with the single column technique a choice of eluents is available. This allows the relative retention times to be changed and thereby reduces interference from extraneous anions.

Anions are identified on the basis of their retention times compared with known standards. Quantification is accomplished by measuring the peak height or area and comparing it to a calibration curve produced from known standards. These procedures allow determination of nitrate and sulphate in the parts per million range.

16-2. INTERFERENCE

If one of the sample components is present at very high levels, it may interfere by causing a very large peak on the chromatogram, which masks other peaks of interest. This type of interference is normally minimized by diluting the sample. If chloride and fluoride are not to be determined, then interference due to high levels of organic acids and alkali ions is not a problem.

---

[30] Contributed by D.J. Barkley, CANMET, Energy Mines and Resources Canada, Ottawa, Ontario, Canada.

16-3. EQUIPMENT

16-3.1. Chromatographic system

The system consists of a pump for delivering the eluent, an injector valve with a 50 or 100 μL sample loop, a conductivity detector, and a recorder or an integrator to measure the area under the chromatogram.[31]

16-3.2. Precolumn

A short length column of similar material to the separator column and placed before the separator column is recommended to protect the main column from being contaminated by particulates and the irreversibly adsorbing constituents.

16-3.3. Separator columns

A stryene-divinylbenzene based low capacity pellicular anion exchange column (Dionex PIN 35311) for suppressed IC and a hydrophyllic polymethacrytate gel anion exchange column (Waters IC Pak-A PN07355) for single column IC are required.

16-3.4. Suppressor column

A column or membrane is needed that is a high capacity cation exchanger and is capable of converting the eluent and separated anions to their respective acid forms.

16-4. REAGENTS

Reagent grade chemicals are used in all the preparations. All the solutions are prepared from distilled water purified with a Milli-Q system (Millipore).

16-4.1. Eluent (for suppressed IC)

Dissolve 1.0080 g of sodium bicarbonate (0.003M $NaHCO_3$) and 1.0176 g of sodium carbonate (0.0024M Na_2CO_3) in water and dilute to 1 L with water. Dilute

---

[31] A chromatographic system for suppressed IC is available from Dionix Corp., 1228 Titan Way, Sunnyvale, CA 94086, USA. A single column IC system is available from Waters, 34 Maple Street, Milford, MA 01757, USA.

250 ± 1 mL to 1 L, filter through a 0.45 nm filter, store the stock in the refrigerator and make up the eluent fresh each day.

16–4.2. Eluent (single column IC)

Gluconate–borate eluent–1.2M potassium gluconate, 1.3M boric acid: Dissolve 0.30 g of potassium gluconate, 0.50 g of sodium tetraborate ($Na_2B_4O_7.10\ H_2O$), 0.50 g of boric acid (H_3BO_3) and 5.0 g of glycerine in 500 mL of water. Transfer to a 1 L flask. Mix together 120 mL of acetonitrite and 30 mL of n-butyl alcohol. Add this mixture to the contents of the 1 L flask and dilute with water. Check that the pH is 8.4–8.5. Filter through a 0.45 nm filter.

16–4.3. Anion stock solutions

(1) Nitrate, 1 mL = 1.00 mg of NO_{3^-}: Dry about 2 g of sodium nitrate ($NaNO_3$) at 105°C for 24 hours; dissolve 1.3707 g of the dried salt in water and dilute to 1 L with water.
(2) Sulphate, 1 mL = 1.00 mg of $SO_4^=$: Dry sodium sulphate (Na_2SO_4) for 1 hour at 105°C and cool in a desiccator; dissolve 1.4790 g of the dried salt in water and dilute to 1 L with water.

16–4.4. Anion working standards

Prepare three working standard solutions to contain concentrations of anions as shown in Table II-XIX. Prepare a high range standard solution by transferring 10.0 mL of nitrate stock standard and 20.0 mL of sulphate stock standard to a 250 mL flask and dilute with the appropriate eluent. Prepare an intermediate range standard solution by diluting 10.0 mL of the high range standard solution to 100 mL with eluent. Prepare the low range standard solution by diluting 10.0 mL of the intermediate range standard solution to 100 mL with the eluent.

TABLE II-XIX. CONCENTRATION OF STANDARD SOLUTION FOR CALIBRATION

Anion	High standard (mg/L)	Intermediate standard (mg/L)	Low standard (mg/L)
NO_3^-	40	4	0.4
$SO_4^=$	80	8	0.8

16–5. CALIBRATION

16–5.1. Determination of retention times

The retention time for each anion is determined by injecting a standard solution containing only the anion of interest and noting the time required for a peak to appear on the chromatogram. Although retention times may vary from one column to another and are affected by the temperature and eluent flow rates, the elution order of the anions is always NO_3^-, followed by $SO_4^=$.

16–5.2. Preparation of calibration curves

Analyse the blank and each of the prepared working standards in accordance with Section 16–6. Prepare the calibration curves for each anion by plotting (on linear graph paper) the peak height of the peak area versus the concentration of the anion.

16–6. PROCEDURE

Equilibrate the system by pumping the eluent through the columns until a stable baseline is obtained, after about 30 minutes. The detector ranges are variable; normal operating ranges are from 3 to 100 μS/cm, full scale. The range setting required for analysis depends on the concentration of the anions in the sample and should be chosen accordingly. Load the sample loop by injecting about 1 mL of sample into the entry port using a 3 mL plastic syringe. Inject the sample on to the column and record the ion chromatogram. To identify peaks of interest in a complex sample, inject a sample, adding the anion of interest.

16–7. CALCULATIONS

Refer the peak height or area noted for the anions to the appropriate calibration curves to determine the anion concentration in μg/mL.

$$\text{Anion concentration mg/L} = A \times F$$

where A is micrograms per millilitre, read from the appropriate calibration curve, and F is the dilution factor.

BIBLIOGRAPHY

HADDAD, P.R., HECKENBERG, A.L., Determination of inorganic anions by high-performance liquid chromatography, J. Chromatogr. **300** (1984) 357.

MALSUSKITA, S., YOSHIMITSU, T., NOBAYUKI, B., HOSAKO, K., High-performance ion chromatography of anions, J. Chromatogr. **259** (1983) 459–464.

SMITH, F.C., CHANG, R.C., The Practise of Ion Chromatography, Wiley, Toronto (1983).

Method 17

DETERMINATION OF RADIUM-226 IN SOLID AND LIQUID SAMPLES BY ALPHA SPECTROMETRY[32]

17-1. INTRODUCTION

This method is intended for use where a higher degree of accuracy, precision or specificity is required than is available from the gross alpha counting methods; it can be applied to either solid or liquid samples. It is also intended for use where the quantity of sample is limited, so gamma ray spectrometry cannot be used. Radium is collected from liquid samples with lead sulphate, dissolved in an alkaline solution of diethylenetriaminepentaacetic acid (DTPA), and reprecipitated with barium under special conditions to minimize the self-absorption of the alpha particles, as proposed by Sill [1]. Solid samples are decomposed by fluoride and pyrosulphate fusions before lead sulphate precipitation. A ^{225}Ra internal standard is used to compensate for varying recoveries and counting efficiencies.

17-2. INTERFERENCES

Barium and strontium carry through the entire method and result in degraded spectra if present in amounts greater than 0.5 mg. The sample size should be chosen with this in mind. Calcium also interferes, if present in large quantities.

17-3. ACCURACY AND PRECISION

New Brunswick Laboratory (NBL) certified control samples were analysed to determine the accuracy of this method. The analytical data are presented below.

---

[32] Contributed by R. Chessmore, United Sates Department of Energy, Grand Junction, Colorado, USA.

Sample	Expected (pCi/g)[a]	Found (pCi/g)[a]
101A	3418	3382
102A	349	346
103A	170	170
104A	34.6	36
105A	3.5	3.1

[a] 1 Ci = 3.70×10^{10} Bq.

The precision and detection limits vary with counting time. Using a 24 hour count time results in a relative standard deviation of approximately 7% at the 0.5 pCi/L level for water samples of 1 L.

17-4. REAGENTS

All the reagent solutions except the seeding suspension must be filtered through a 0.45 μm membrane filter to remove the insoluble materials that would otherwise degrade the alpha spectrum.

(1) Lead nitrate, 30% solution: Dissolve 30 g of $Pb(NO_3)_2$ in 100 mL of water and filter
(2) Sulphuric acid (H_2SO_4), concentrated
(3) Hydrochloric acid (HCl), concentrated
(4) Citric acid ($H_3C_2H_5O_7.H_2O$), 1M: Dissolve 192 g in 1 L of water and filter
(5) Ammonium hydroxide (NH_4OH), concentrated
(6) Ammonium sulphate ($(NH_4)_2SO_4$), 30% solution: Dissolve 300 g in 1 L of water and filter
(7) Acetic acid (CH_3COOH), concentrated
(8) Ethanol, 80%: Mix 80 mL of ethanol with 20 mL of water
(9) Barium chloride, 0.75 mg Ba/mL: Dissolve 338 mg of $BaCl_2.2H_2O$ in 250 mL of water and filter
(10) Sodium sulphate, 40% solution: Dissolve 200 g of Na_2SO_4 in 500 mL of water and filter
(11) Lead sulphate wash: Dissolve 25 g of K_2SO_4 and 2 mL of H_2SO_4 in 250 mL of water and filter; dilute to 500 mL
(12) Alkaline DTPA, 0.1M: Dilute 50 mL of 1M DTPA to 400 mL with water; adjust the pH to 10.6 with HCl and dilute to 500 mL
(13) Sodium hydrogen sulphate, 70% solution: Dissolve 100 g of Na_2SO_4 in 200 mL of water and 50 mL of H_2SO_4 and filter

(14) HNO_3, concentrated
(15) Potassium fluoride (KF), anhydrous
(16) Seeding suspension: Place 11.3 mg of $BaCl_2.2H_2O$, 10 mL of 70% $NaHSO_4$, and 1 mL of $HClO_4$ into a 250 mL Erlenmeyer flask; evaporate to dryness and fuse over a blast burner; cool to room temperature and dissolve in 25 mL of 40% Na_2SO_4 and 25 mL of water.

17-5. APPARATUS

(1) Alpha spectrometer system
(2) Platinum dishes, 150 mL
(3) Hot plates
(4) Blast burner
(5) 47 mm, 0.45 μm pore membrane filters
(6) Ultrasonic bath
(7) 25 mm, 0.1 μm polycarbonate membrane filter.

17-6. METHODS

17-6.1. Instrument conditions

Operate the alpha spectrometer at a pressure of 300 μm to reduce the alpha recoil contamination [2]. Consult the individual alpha spectrometer manuals for the instrument operating instructions.

17-6.2. Standards

(1) *Radium-226:* Use certified ^{226}Ra solution containing 100 pCi/mL
(2) *Radium-225:* Extract 10 mL of ^{226}Th solution (0.5N HNO_3) containing 200 pCi/mL with 10 mL of 2% TOPO (tri-n-octylphosphine oxide) solution in cyclohexane; discard the organic phase.

17-6.3. Analytical methods

17-6.3.1. Sample preparation

17-6.3.1.1. Soil dissolution

(1) Weigh a 0.25 g sample into a 150 mL platinum dish; add 1 mL of HNO_3 and 20 pCi of ^{225}Ra; prepare a standard containing 25 pCi of ^{226}Ra and precisely the same amount of ^{225}Ra as used in the sample

(2) Take to near dryness on a hot plate; do not bake
(3) Add 3 g of potassium fluoride and fuse over a blast burner until a clear melt is obtained; cool to room temperature
(4) Add 4 mL of H_2SO_4 and cautiously warm until a vigorous reaction is complete
(5) Heat on the blast burner until most of the H_2SO_4 has evolved: add 2 g of Na_2SO_4 and continue heating until a clear fusion is obtained; cool to room temperature
(6) Dissolve in 35 mL of water and 1 mL of HCl; transfer to a beaker and boil for 5 minutes; cool to room temperature and proceed with the precipitation of the lead sulphate.

17-6.3.1.2. Water sample preparation

(1) To the sample aliquot (usually 1 L) add 5 mL of citric acid; prepare a standard containing 25 pCi of ^{226}Ra in 1 L of deionized water
(2) Add 20 pCi of ^{225}Ra to the sample and standard; stir for 30 minutes; add 1 mL of $(NH_4)_2SO_4$ and adjust the pH to 9.5 with NH_4OH; proceed with the precipitation of the lead sulphate.

17-6.3.2. Precipitation of the lead sulphate

(1) Add 1 mL of $Pb(NO_3)_2$ solution while stirring; for water samples, adjust the pH to 2.5 with H_2SO_4; stir for 15 minutes
(2) Collect the precipitate on a 47 mm, 0.45 μm pore size membrane filter; wash with the lead sulphate wash solution
(3) Dissolve the precipitate in 10 mL of alkaline DTPA (an ultrasonic bath is useful in this step); remove the membrane filter, washing with 5 mL of DTPA solution; proceed with barium sulphate precipitation.

17-6.3.3. Barium sulphate precipitation

(1) To water samples containing virtually no barium, add 100 μL of $BaCl_2.2H_2O$ solution
(2) Add 3 mL of 40% Na_2SO_4 and 250 μL of acetic acid
(3) *Immediately* add 200 μL of seeding suspension and swirl to mix; cool in the freezer for 15 minutes
(4) Filter through the 25 mm, 0.1 μm polycarbonate membrane filter; wash first with water then with 80% ethanol; dry and preserve for counting
(5) Allow at least 3 days for the growth of the ^{225}Ra daughters before counting; count until the desired level of precision is obtained, using the ^{226}Ra peak and the ^{217}At peak for quantification; consult the Alpha Spectrometer Operator's Manual for the instrument operating instructions.

17-7. CALCULATIONS

The apparent activity of the ^{225}Ra spike is first calculated using the ^{226}Ra standard spectra and the equation

$$^{225}\text{Ra (pCi)} = \frac{\text{Counts } ^{217}\text{At peak}}{\text{Counts } ^{226}\text{Ra peak}} \times \text{Activity of } ^{226}\text{Ra}$$

Using this 'apparent activity', the ^{226}Ra activity in the sample is obtained by the equation

$$^{226}\text{Ra (pCi)} = \frac{\text{Counts } ^{226}\text{Ra peak}}{\text{Counts } ^{217}\text{At peak}} \times \text{Apparent } ^{225}\text{Ra activity}$$

The sample activity is then divided by the sample weight or volume and reported in picocuries per gram or picocuries per litre.

REFERENCES

[1] SILL, C.W., Determination of radium-226 by high-resolution alpha spectrometry, Unpublished data.

[2] SILL, C.W., OLSON, D.G., Sources and prevention of recoil contamination of solid-state alpha detectors, Anal. Chem. **42** 13 (1970) 1596.

Appendix 1

TECHNIQUES USED FOR URANIUM DETERMINATION AND THOSE USED FOR DETERMINATIONS OTHER THAN URANIUM

Appendix 1

TABLE A-1.I. TECHNIQUES USED FOR URANIUM DETERMINATION

	Minimum cost[a] (US $)	Detection limit	Application and comments
Fluorimetry	25 000	0–1 ppm solid, 1 ppb water	General application to powders and solutions, moderate to poor accuracy and precision[b]
Laser fluorimetry	25 000	ppb	General use in the analysis of waters with uranium at ppb concentrations; also for leachates of rock or soil samples; rapid sample preparation and measurement
Gamma ray spectrometry	30 000	ppm	Assumes secular equilibrium; main application is in soil and rock analysis; specialist training required; report results in equivalent uranium; provides total uranium
X ray fluorescence	80 000	10 ppm	General use but limited to ore grade concentrations; high throughput with automated equipment; simple sample preparation; provides total uranium
Colourimetric	10 000	0.01%	Working range is 0.1% uranium in solid samples[b]
Volumetric	Very low	0.1%	Limited to ore grades and concentrates; not generally used in exploration; often used for checking fluorimetric results[b]
Delayed neutron counting[a]	500 000	ppb in water, ppm in solids	Largest application is in soil and rock analysis; terrestrial $^{238}U/^{235}U$ ratio is required; instrument parameters must be established to prevent thorium interference; high throughput with automated equipment; provides total uranium
Fission track counting[a]	15 000	ppb	General use in the analysis of natural waters; uranium concentrations at sub-ppb levels; specific training required, since the technique is not widely used; most sensitive technique

[a] Assumes that a nuclear reactor is available.

[b] Sample preparation can be time consuming because of the lengthy digestion periods, which do not require constant surveillance.

TABLE A-1.II. TECHNIQUES USED FOR DETERMINATIONS OTHER THAN URANIUM

	AAS	ICP	XRF	IC	Colourimetric	Neutron activation analysis	Gamma	Alpha	Ion spectrometry
Acquisition costs	30 000–100 000	30 000–150 000	80 000–200 000	50 000	10 000–20 000	30 000–80 000	30 000–80 000	30 000–80 000	30 000–60 000
Staff training requirements	Generalist	Generalist	Quasi-specialist	Generalist	Generalist	Specialist	Specialist	Specialist	Generalist
Throughput	High	Very high	Moderate	Low–moderate	Low–moderate	High	High	Low–moderate, person-time intensive	High
Usual detection limit	ppb–ppm analyte	ppm analyte	ppm low concentration	ppm analyte, specific	100 ppm analyte, specific	ppm	ppm%	ppm% variable	ppb variable
Special facilities required	A/C, combustion, less ventilation	A/C, argon	A/C, liquid nitrogen for EDX	A/C	A/C	Reactor rabbit system, neutron detector	Stabilized AC–DC, A/C, computer, data reduction, liquid nitrogen supply	Stabilized AC, vacuum A/C	Stabilized AC–DC
Flexibility (multi-element)	Very good	Very good	Very good	Limited, normal application for anions	Limited	Multi-element	Limited to gamma emitting nuclides	Limited to alpha emitting nuclides	
Accuracy	Good	Good	Moderate	Good	Very good	Good	Good	Very good	Very good
Precision	Good	Good	Very good	Good	Very good	Good	Good	Very good	Very good
Sample type	Liquid/solid[a]	Liquid/solid[a]	Liquid/solid[a]	Liquid	Liquid/solid[a]	Solid	Powder samples (geological)	Liquid/solid[a]	Liquid/solid[a]
Usual productivity[b]	High	High	High	Analyte and matrix dependent	Analyte dependent, 20–100 analytes/d	20/d	1 sample/45 min, with automated system	6–20 samples/d, nuclide dependent	High

[a] Requires sample dissolution.

[b] Productivity estimates are difficult to quantify because the productivity is analytes, sample matrix and operator dependent, and will also depend on multi-use of the equipment.

Appendix 2

LABORATORY SAFETY

Appendix 2

The laboratory testing of uranium ores involves several potential hazards that must be understood, borne in mind and guarded against. Two broad types of hazard can be considered: general hazards, which are common to most chemical laboratories, and radiological hazards.

A-2.1. GENERAL SAFETY PRECAUTIONS

All the safety precautions that apply to a chemical laboratory also apply to a metallurgical laboratory for ore testing. These precautions have been well documented [1-3]. Standard precautions should be observed for:

(1) Corrosive substances, such as sulphuric and other acids.
(2) Explosive and flammable chemicals, including the diluents and extractants used for solvent extraction.
(3) Dusts, especially ore dusts and uranium concentrate dusts.
(4) Chemical spills, including acids, leach solutions and other process pulps and liquids.
(5) Mechanical hazards, particularly when crushing, grinding and otherwise handling ores.
(6) Electric shock.
(7) Toxic or irritating chemicals; virtually all the chemicals used in the laboratory are toxic or irritating to some degree. Special care must be taken with liquids used in heavy media separations, extractants used in solvent extraction and ammonia used for the precipitation of concentrates.
(8) Pressurized vessels, such as autoclaves. It is extremely important to study carefully and follow the manufacturer's instructions when using this type of equipment.
(9) Burns.

Laboratory coats or overalls should be worn at all times. Appropriate safety equipment such as hard hats, face shields, safety goggles, gloves, respirators and hard toe boots should be used as required.

Uranium ore and uranium compounds are naturally radioactive and present some radiological hazards, as discussed in Section A-2.2.

A-2.2. RADIOLOGICAL SAFETY

The radiological hazards in a uranium metallurgical laboratory are small and can be controlled easily [4-6]. The main hazards are the possible inhalation or ingestion of uranium concentrate dust and uranium ore dust. External irradiation and inhalation of radon and radon daughters are also possible but minor hazards.

Substantial amounts of dust can be generated during sample preparation: crushing, grinding, splitting, screening, sieving and blending. Sample preparation rooms should be isolated from other areas and be equipped with dust control systems such as hoods, filters and collectors. Access to these rooms should be controlled. The personnel preparing the samples should be attired properly with overalls, boots, gloves, face mask and cap. Workers should also shower and change their clothing before leaving the controlled area. Incorporation of uranium concentrate dust is less likely because the amounts handled in the laboratory are usually small, seldom more than a few hundred grams. Nonetheless, dry concentrates should be handled with care, especially during screening, blending or performing any operation that can generate dust. These operations can be done under a hood or in a glove box. Appropriate attire should also be worn.

Radon and radon daughters are normally not a problem, provided the laboratory is well ventilated. The hazard of external irradiation is usually negligible, except perhaps when working with very high grade ores. It is advisable to check the level of radioactivity in the laboratory, especially in the sample storage room and in the area where the uranium concentrates are stored. If the levels of radioactivity are significant, the hazard can be controlled by limiting the permanence time in these areas, although such time is likely to be short.

Care should be taken to keep the laboratory clean at all times. Special care must be taken to clean up all uranium bearing pulp or liquid spills. Surfaces, such as benchtops and floors, should be monitored regularly for possible contamination.

Eating, drinking and smoking should not be permitted in any area of the laboratory.

A-2.3. SAFETY RULES

Safety rules, covering both general and radiological safety, should be prepared and enforced. A discussion of these rules is outside the scope of this Manual, but it is strongly recommended that specialized books on these subjects, such as those cited in the References, be consulted.

REFERENCES

[1] Handbook of Laboratory Safety, 2nd edn (STEERE, N.Y., Ed.), CRC Press, Boca Raton, FL (1971).

[2] Prudent Practices for Handling Hazardous Chemicals in Laboratories, National Research Council, Washington, DC.

[3] Hazards in the Chemical Laboratory, 3rd edn (BRETHERICK, I., Ed.), Royal Society of Chemistry, London (1981).

[4] INTERNATIONAL ATOMIC ENERGY AGENCY, Manual on Radiological Safety in Uranium and Thorium Mines and Mills, Safety Series No. 43, IAEA, Vienna (1976).

[5] INTERNATIONAL ATOMIC ENERGY AGENCY, Radiation Protection of Workers in the Mining and Milling of Radioactive Ores, 1983 Edition, Safety Series No. 26, IAEA, Vienna (1983).

[6] INTERNATIONAL ATOMIC ENERGY AGENCY, Radiological Health and Safety in Mining and Milling of Nuclear Materials (Proc. Symp. Vienna, 1963), IAEA, Vienna (1964).

HOW TO ORDER IAEA PUBLICATIONS

An exclusive sales agent for IAEA publications, to whom all orders and inquiries should be addressed, has been appointed for the following countries:

CANADA UNITED STATES OF AMERICA	UNIPUB, 4611-F Assembly Drive, Lanham, MD 20706-4391, USA

In the following countries IAEA publications may be purchased from the sales agents or booksellers listed or through major local booksellers. Payment can be made in local currency or with UNESCO coupons.

ARGENTINA	Comisión Nacional de Energía Atómica, Avenida del Libertador 8250, RA-1429 Buenos Aires
AUSTRALIA	Hunter Publications, 58 A Gipps Street, Collingwood, Victoria 3066
BELGIUM	Service Courrier UNESCO, 202, Avenue du Roi, B-1060 Brussels
CHILE	Comisión Chilena de Energía Nuclear, Venta de Publicaciones, Amunategui 95, Casilla 188-D, Santiago
CHINA	IAEA Publications in Chinese: China Nuclear Energy Industry Corporation, Translation Section, P.O. Box 2103, Beijing IAEA Publications other than in Chinese: China National Publications Import & Export Corporation, Deutsche Abteilung, P.O. Box 88, Beijing
CZECHOSLOVAKIA	S N T L, Spálená 51, CS-113 02 Prague 1 Alfa, Publishers, Hurbanovo námestie 3, CS-815 89 Bratislava
FRANCE	Office International de Documentation et Librairie, 48, rue Gay-Lussac, F-75240 Paris Cedex 05
HUNGARY	Kultura, Hungarian Foreign Trading Company, P.O. Box 149, H-1389 Budapest 62
INDIA	Oxford Book and Stationery Co., 17, Park Street, Calcutta-700 016 Oxford Book and Stationery Co., Scindia House, New Delhi-110 001
ISRAEL	YOZMOT Literature Ltd., P.O. Box 56055, IL-61560 Tel Aviv
ITALY	Libreria Scientifica Dott. Lucio di Biasio "AEIOU", Via Coronelli 6, I-20146 Milan
JAPAN	Maruzen Company, Ltd, P.O. Box 5050, 100-31 Tokyo International
PAKISTAN	Mirza Book Agency, 65, Shahrah Quaid-e-Azam, P.O. Box 729, Lahore 3
POLAND	Ars Polona, Foreign Trade Enterprise, Krakowskie Przedmieście 7, PL-00-068 Warsaw
ROMANIA	Ilexim, P.O. Box 136-137, Bucharest
RUSSIAN FEDERATION	Mezhdunarodnaya Kniga, Sovinkniga-EA, Dimitrova 39, SU-113 095 Moscow
SOUTH AFRICA	Van Schaik Bookstore (Pty) Ltd, P.O. Box 724, Pretoria 0001
SPAIN	Díaz de Santos, Lagasca 95, E-28006 Madrid Díaz de Santos, Balmes 417, E-08022 Barcelona
SWEDEN	AB Fritzes Kungl. Hovbokhandel, Fredsgatan 2, P.O. Box 16356, S-103 27 Stockholm
UNITED KINGDOM	HMSO, Publications Centre, Agency Section, 51 Nine Elms Lane, London SW8 5DR
YUGOSLAVIA	Jugoslovenska Knjiga, Terazije 27, P.O. Box 36, YU-11001 Belgrade

---

Orders from countries where sales agents have not yet been appointed and requests for information should be addressed directly to:

Division of Publications
International Atomic Energy Agency
Wagramerstrasse 5, P.O. Box 100, A-1400 Vienna, Austria

92-05133

ISBN 92-0-103792-9