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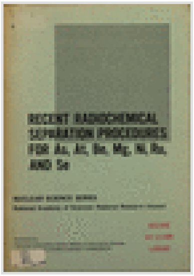

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Recent Radiochemical Separation Procedures for As, At, Be, Mg, Ni, Ru, and Se

Edited by K. V. Marsh

Radiochemistry Division
Lawrence Livermore Laboratory
Livermore, California

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Foreword

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences—National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the radiochemical purity of reagents, the place of radiochemistry in college and university programs, and radiochemistry in environmental science.

This series of monographs has grown out of the need for compilations of radiochemical information, procedures, and techniques. The Subcommittee has endeavored to present a series that will be of maximum use to the working scientist. Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique.

Experts in the particular radiochemical technique have written the monographs. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to radiochemists but also to research workers in other fields such as physics, biochemistry, or medicine who wish to use radiochemical techniques to solve specific problems.

Gregory R. Choppin, *Chairman*
Subcommittee on Radiochemistry

RADIOCHEMISTRY OF ARSENIC

(ADDENDUM TO MONOGRAPH NAS-NS-3002)

J. G. Cuninghame

Atomic Energy Research Establishment
Harwell, Didcot, Berks.

Procedure 1

Procedure by : L. Tomlinson and M. H. Hurdus; J. Inorg. Nuc. Chem. 30, 1649, 1968.

Type of procedure : Fast separation with carrier

Target material : Fissile material

Radioactivity production method : Fission

Purification method : Evolution of AsH_3

Approx. chemical yield : 20%

Time taken for purification : 5.4s.

Decontamination : Sn > 3 x 10^4; 1 1.5 x 10^5; Br > 9.5 x 10^4; Se and Te "contamination low."

1. Fill solution container with 5-ml solution made up as follows: 2.9 ml 41% v/v H_2SO_4; 0.5 ml 3.5N HCl containing 189 mg ^{235}U; 1.0 ml 3N HCl containing 1-mg Sb (III), 1 mg As (III) 50-μg Ge (IV) and 45 μg Sn (IV); aqueous solutions containing 40 μg Se as SeO_3 $(II)^-$, 20-μg as TeO_3 $(II)^-$, 2 mg thiourea, 0.2 mg KI, 0.2 mg KBr. Connect this via a loop to a silica reaction vessel heated to 100°C and containing 0.5g Zn powder with He gas flowing over it. Place the whole apparatus inside an operating reactor.

2. With reactor at power, blow the contents of the solution container into the reaction vessel by means of a high pressure of He.

3. Transport Sb, As and Ge hydrides to a silica tube furnace outside the reactor by means of a fast He flow. As and Sb deposit on the walls.

4. Count the Sb/As *in situ*.

5. After counting dissolve the Sb/As deposit with a hot mixture of 1.5 ml 8N H_2SO_4 and 0.1 ml conc HNO_3 and estimate chemical yield.

Procedure 2

Procedure by : T. E. Ward, D. L. Swindle and P. K. Kuroda; Radiochim. Act. 14, 70, 1970.[†]

Type of procedure : With carrier

Target material : ^{232}Th or ^{238}U nitrates

Radioactivity production method : Fission

Purification method : As extraction into CCl_4 from $\geq$ 10N HCl

Approx. chemical yield : 30%

Time taken for purification : 50 m

Decontamination : $\sim 3 \times 10^7$ from all activities

1. Dissolve target (2-10g) in water and add 15 mg each As(III) and Ge(IV) carriers. Add 0.25g $KBrO_3$ to oxidize the As to +5, then 0.5g $K_2S_2O_5$ to reduce it back to As(III).

2. Make solution $\geq$ 10N in HCl and extract the As into 30 ml CCl_4 by stirring for 5 min. Wash organic phase 2 min. with conc HCl. Back extract As into 10 ml water stirring 5 min.

3. Make aqueous phase 3-5N in HCl and precipitate elementary As by addition of 2g $NaH_2PO_2 \cdot H_2O$ and heating on a water-bath at 95° for 5 min.

4. Filter, dry at 105°C and weigh.

[†] We acknowledge the permission of the publisher of Radiochim. Acta to reprint part of this material.

Procedure 3

Procedure by : M. Inarida, A. Shimamura; Radiochem. Radioanal. Lett. 2, 87, 1969.

Type of procedure : Carrier free

Target material : Se

Radioactivity production method : Deuteron bombardment of Se

Purification method : Diethyldithiocarbamate/T.B.P. extraction.

Approx. chemical yield : 95%

Decontamination : As of "sufficiently high radiochemical purity" produced

1. Dissolve 50-mg Se target in 5 ml conc HNO_3 and evaporate to dryness on a water bath.

2. Repeat dissolution and evaporation to dryness (Se reduces to Se(IV), As oxidizes to As (V).

3. Dissolve residue in 35 ml 0.1M HCl add 5 ml 20% sodium diethyldithiocarbamate and shake with 10 ml tributyl phosphate to extract Se.

4. Repeat the extraction twice more.

5. Shake the aqueous phase 1 min with ether to remove traces of T.B.P.

6. Evaporate aqueous phase to dryness on a water bath with conc NHO_3 and $HClO_4$ to decompose carbamate.

Procedure 4

Procedure by : H. Hamaguchi, N. Onuma, Y. Hirao, H. Yokoyama, S. Bando, M. Furakawa; Geochim, Cosmochim. Acta 33, 507, 1969

Type of procedure : Neutron activation analysis

Target material : Chondrite meteorites

Purification method : Anion exchange + Sb_2S_3 precipitation

Approx. chemical yield : 20-30%

1. Add irradiated sample (0.2 - 1.5g) to a Ni crucible containing ∿10 mg each of As, Sb, and Sn (as solid salts), and then fuse with Na_2O_2.
2. Digest fusion cake with minimum amount of water and wash crucible contents into beaker with 30 ml conc HCl.
3. Pass H_2S into the solution while diluting gradually with 300 ml water to effect successive precipitation of As, Sb, and Sn.
4. Dissolve mixed sulphides in aqua regia, evaporate to dryness and dissolve to 20 drops of 4N HCl + ∿300 mg $NH_2OH.HCl$. Evaporate to dryness to reduce Sb(V) to Sb(III).
5. Dissolve residue in 20 drops 0.5M NH_4CNS-2N HCl solution and put on anion exchange column 1 cm x 7 cm containing 3 g Dowex 1X8 (200-400 mesh) CNS^- form resin. Elute As with 15 ml 0 .5M NH_4CNS - 0.5N HCl.
6. Wash column with 10 ml 0.005M NH_4CNS - 0.5N HCl solution and discard effluent. Elute Sb with 1N H_2SO_4 and collect 60 ml eluant.
7. Elute Sn with 30 ml 0.5M NaCl - 0.5N NaOH.
8. Add 10 ml conc HCl to As fraction and pass in H_2S.
9. Dissolve precipitate in aqua regia and evaporate to dryness. Dissolve residue in 10 ml 9N HCl and add crystalline $SnCl_2$ to precipitate elementary As.

Procedure 5

Procedure by : S. Ohno and M. Yatazawa; Radioisotopes (Tokyo) 19, 565, 1970.

Type of procedure : Neutron activation analysis

Target material : Soil

Purification method : As_2S_3 + quinoline molybdate precipitation

Approx. chemical yield : 80%

1. Transfer an irradiated sample, accurately weighed and dried, of about 0.1 g soil into a Ni crucible containing 5 mg each of Cu, As, and Sb carriers as solid salts. Cover with ~1 g each of NaOH and Na_2O_2 and fuse.

2. Dissolve fusion cake in 2N HCl and filter. Add thioacetamide to filtrate and filter sulphide.

3. Dissolve precipitate in a few ml conc HCl and dilute to about 50 ml in a 200-ml flask. Add 1 g $KClO_3$ and 5 ml conc HCl. Heat to boiling and add 20 ml 10% citric acid solution and stir well. Pour 10 ml quinoline molybdate solution* into it. Remove from hot plate and stir.

4. Filter and wash 3 times with 1:10 HCl and then with water until acid-free. Measure ^{76}As by gamma-ray spectrometry against a standard prepared similarly.

5. Sb can be recovered from the filtrate by sulphide precipitation.

---

*Dissolve 50 g sodium molybdate in 100 ml water and pour it into about 90 ml conc HCl and add 1 drop 30% H_2O_2, then add 5 ml of quinoline dissolved in 120 ml 1:1 HCl. Boil 1 min and set aside 1 day. Filter into a polyethylene bottle.

Procedure 6

Procedure by : J. J. Kroon and H. A. Das; Reactor-Centrum Nederland unpublished report RCN 124, 1970.

Type of procedure : Neutron activation analysis

Target material : Biological material

Purification method : Anion exchange + As precipitation

Time taken for purification : "Faster than procedures in literature"

1. Place up to 50 mg of irradiated sample in a 100 ml beaker and add 5 ml conc H_2SO_4 + 10λ As carrier (22 mg As/ml). Heat to destroy sample. When effervescence stops and conc HNO_3 dropwise until solution becomes clear.

2. Evaporate to dryness. If residue black, repeat destruction step. Dissolve in ∿15 ml 8N HCl and add sufficient H_2O_2 to make the concentration in the solution 0.2%. Add 2 ml carrier solution.

3. Add 4-5 g HAP* (sodium specific cation exchanger) and slurry the suspension. Allow to stand 15 min.

4. Centrifuge HAP and wash with 10-20 ml 8N HCl (0.2% H_2O_2). combine supernatant and wash liquid in a 100-ml beaker.

5. Pass solution through a 6 x 130 mm Dowex 1 X8 (100-200 mesh) ion exchange column; flow-rate ∿1 ml min^{-1}. Collect elute in 100-ml beaker. Wash resin in 5 ml 8N HCl (0.2% H_2O_2) and combine eluates.

6. Add 2 g $NH_4H_2PO_2$ and heat on steam bath until precipitate coagulates.

7. Filter elemental As on weighed filter paper and wash with 10 ml 0.01N HCl and 10 ml acetone. Dry at 60°C 1 hr.

---

*Hydrated Antimony Pentoxide

Standardization of Arsenic Isotopes

The only arsenic isotopes which are likely to be in common use and have sufficiently long half-lives to make standardization worthwhile are:

^{73}As	half life		76 days
^{74}As	"	"	17.5 days
^{76}As	"	"	26.5 hrs
^{77}As	"	"	39 hrs

Unfortunately, the two longest lived decay partly by electron capture and this makes standardization a complicated procedure involving X-ray counting. It therefore seems best to ignore these isotopes and to use as standards the two others, both of which are β^- emitters. ^{76}As has a prominent gamma ray of energy 0.559 MeV produced in 35% of all disintegrations and is therefore a suitable nuclide for $\beta\gamma$ coincidence counting. ^{77}As has no prominent gamma rays, the most abundant (0.24 MeV) having an intensity of only 2.5%; it is therefore best to standardize this nuclide either by $4\pi\beta$ counting or by liquid scintillation counting.

Preparation of ^{76}As and ^{77}As for Standardization

^{76}As is quite easy to prepare by the (n,γ) reaction in a reactor. Irradiate a suitable amount of the purest possible arsenic (1 mg irradiated for 1 hr at a flux of 10^{12} n/cm^2/sec will give $\sim 5 \times 10^7$ dis/min or ^{76}As). Dissolve in the minimum amount of conc HNO$_3$ + HCl and evaporate to dryness. Take up in 1N HCl and dilute as required. It is advisable to check the purity by following a decay curve on a portion of the product but, provided there were no significant impurities in the arsenic, a single component ^{76}As curve should be obtained.

^{77}As is best prepared from fresh fission products. Irradiate a suitable amount of natural uranium in a reactor (1 mg irradiated for 1 hr at a flux of 10^{12} n/cm^2/sec will give $\sim 2 \times 10^3$ dis/min of ^{77}As). Add the minimum amount of arsenic carrier (say 2 mg) and purify by one of the procedures given in the original monograph or this supplement for freshly irradiated fissile material. Test for purity by plotting a decay curve; the most likely contaminant is ^{76}As produced from arsenic impurity in the uranium.

Standardization Procedure

The suggested procedure for these two isotopes is as follows:

1. Obtain a supply of the isotope as described above.
2. Put it into a suitable size* volumetric flask and make up to the mark. Note that trivalent arsenic is volatile from concentrated HCl or HBr and so it is advisable to include about 1 ml of 30% H$_2$O$_2$ in the flask if either of these acids are present. This will insure that the arsenic is oxidized to As^V when step 3 is carried out. Alternatively,

the arsenic can be held in a neutral water solution (e.g., backwashed from a chloroform extraction - see supplemental Procedure 2) or made up as sodium arsenite.

3. Micropipette or weigh a small aliquot (not greater than 100 μl) on to the VYNS film and dry it carefully under an infrared lamp**.

4. Count the source and so obtain its absolute disintegration rate, thus standardizing the remaining material in the flask.

---

[*] The principle which determines volumes and quantities of materials throughout these standardization is that a maximum of ∿1 μg of inactive material should be present on a source to be used for $4\pi\beta$ counting. For the other methods of standardization the amount is not so critical, but it is good practive to keep it low.

[**] If the liquid scintillation method is being used, this step will consist merely of adding the aliquot to the scintillator and mixing.

RADIOCHEMISTRY OF ASTATINE

(ADDENDUM TO MONOGRAPH NAS-NS-3012)

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INTRODUCTION

Since the publication of the astatine monograph, Soviet chemists have done a considerable amount of work on the intermediate positive oxidation state (or states) of At.[1] Both cationic and anionic species have been reported, and their properties have been used in an interesting new separation method (see Procedure 5). The Soviet workers have also recently succeeded in characterizing seven-valent astatine-perastatate.[2]

A number of astatine analogues of organic iodine compounds have been prepared during the past decade; these have been characterized primarily by chromatographic techniques.[1]

Mass spectrometric studies have confirmed the existence of the interhalogen compounds AtI, AtBr, and AtCl.[3] These studies have also shown that in the absence of any deliberately added "swamping" reagent, the astatine is usually tied up in the form of one or more organic astatine compounds that result from reaction with adventitious organic impurities. This last fact is something that astatine radiochemists have often suspected but have rarely, if ever, been able to pin down.

RADIOCHEMICAL PROCEDURES

Procedure 1

Quantitative Separation of Astatine from Bismuth or Lead Bombarded with High-Energy Protons[4]

The target is dissolved in a minimum of concentrated HNO_3, and the solution is diluted with a large excess of 10% HCl. If a lead target was used, the precipitated lead chloride is removed. A 10% aliquot is adjusted to 30-40 ml by the addition of dilute HCl, and 0.25 ml of a 2% solution of tellurium in HNO_3 is added. Half molar $SnCl_2$ solution is introduced to precipitate the tellurium and astatine (along with polonium), and the precipitate is centrifuged. The addition of tellurium and $SnCl_2$ to the supernatant solution is carried out twice more to effect quantitative coprecipitation of the astatine.* The precipitates are combined and washed four times with 25-30 ml portions of dilute HCl to remove traces of bismuth, which might otherwise precipitate from base and adsorb astatine. The combined precipitate is dissolved in a few drops of concentrated HNO_3, and the solution is diluted with water to 10-15 ml and made alkaline with 20% NaOH. Sodium stannite is then added to precipitate tellurium, which under these conditions carries the polonium but not the astatine. A second portion of tellurium is added and precipitated with sodium stannite.* After removal of the precipitate, the solution is acidified, 2-3 mg of tellurium are added, and the Te is precipitated by the addition of 0.5 <u>M</u> $SnCl_2$. Two more 2-3 mg portions of tellurium are similarly added and precipitated.* The combined precipitates, which contain the astatine, may be washed with water and alcohol, transferred to stainless steel counting plates, and dried on a water bath.

---

*The authors do not indicate whether it is necessary to add more reducing agent to effect the second and third successive precipitations of Te.

Procedure 2

Preparation of Pure Astatine from Bismuth or Lead Bombarded with High Energy Protons[4]

A washed precipitate of astatine on tellurium is obtained as described in the first part of Procedure 1. The entire solution may be used instead of an aliquot. The precipitate is dissolved in 2 ml of concentrated H_2SO_4 containing two drops of concentrated HNO_3. The solution is diluted with 80-100 ml of water, and 2g of $FeSO_4$ are added. The astatine is now distilled from this solution into a vessel containing an NaOH solution. Distillation is continued until only 10 ml remain in the distilling flask. Five mg of tellurium are added to the distillate, and the tellurium (plus polonium) is precipitated by addition of sodium stannite solution. After removal of the precipitate, a radiochemically pure solution of astatine remains.

Procedure 3

Purification of Astatine Formed in Spallation of Thorium by High-Energy Protons[5,6]

The metallic thorium target is dissolved in 0.7 ml of concentrated HCl containing a trace of HF, and the solution is diluted with 2 ml of water containing ca. 5 mg of tellurium in the form of telluric acid. To this are added 2 ml of a 10% solution of $SnCl_2$ in aqueous HCl. The mixture is digested for 10 min on a water bath, after which it is centrifuged. The precipitate contains the astatine, along with polonium and such fission produces as gold and As(III).

The precipitate is washed and redissolved in a minimum of concentrated HNO_3. The solution is diluted to 3 ml with concentrated nitric acid and is heated to 100°. To it is added an equal volume of concentrated HCl saturated with hydrazine hydrochloride and with SO_2. The tellurium precipitate carries the astatine, but not the polonium.

The precipitate is dissolved in a drop of concentrated nitric acid, and the solution is made alkaline by the addition of 6 $\underline{M}$ NaOH. Two ml of 5% sodium stannite solution are added to reprecipitate the tellurium, which carries a variety of fission products with it but leaves the astatine in solution.

The precipitate is removed, and NaF is added to the solution to prevent the formation of collodial tin species during subsequent acidification. Such colloidal material can strongly adsorb the astatine. The solution is now acidified with nitric acid to give a final acid concentration of 0.3-0.5 $\underline{M}$.

A thin silver plate of about 20 cm^2 surface area is pretreated with 0.3 $\underline{M}$ HNO_3. It is then suspended in the astatine solution and rotated rapidly for an hour to collect the astatine as an adherent deposit of low volatility. The plate is dissolved in concentrated nitric acid and the silver is precipitated as the chloride, carrying with it the last traces of radioiodine. This precipitation should be carried out in the dark to avoid formation of metallic silver, which can adsorb the astatine. The purified astatine may then be collected on a second rotating silver plate. The overall yield of the procedure is 40-50%, and the radiochemical purity of the astatine exceeds 99.9%.

Procedure 4

Separation of Astatine formed by Proton Bombardment of Lead, Bismuth or Thorium[7]

Bismuth or thorium targets (ca. 1 g) are dissolved in 5 ml of concentrated HNO_3 by heating in a flask equipped with a reflux condenser. Forty ml of 8 M HCl saturated with Cl_2 are added to the solution. One gram lead targets are dissolved similarly in 5 ml of 6 M HNO_3, after which 20 ml of 4 M HCl are added, the solution is cooled, and the $PbCl_2$ precipitate is removed by filtration through a sintered glass filter. To the filtrate are added 20 ml of concentrated HCl saturated with Cl_2.

The following steps apply to solutions obtained from all three target materials. The astatine is extracted from the $HCl-Cl_2$ solution into 60 ml of diisopropyl ether, and the ether phase is washed with two 15 ml portions of 8 M HCl. The astatine is backextracted into 40 ml of 0.1 M sodium stannite in 2 M NaOH.

To the alkaline astatine solution are added 10-15 mg of sodium tellurite, 4-5 mg of $LaCl_3$, and 1-2 mg of sodium chloroaurate. The solution is filtered through sintered glass, and the filtrate is once more treated with tellurite and filtered. After the second filtration, the filtrate is acdified with 20 ml of concentrated HCl containing 0.2 mg of Te per ml. The mixture is stirred vigorously to coagulate the precipitate, and two more 5 mg portions of tellurium are added. The mixture is centrifuged, and the astatine-containing Te precipitate is washed with 6 M HCl and redissolved in several drops of concentrated HNO_3.

To the resulting solution are added 20 ml of 6 M HCl, followed by $SnCl_2$ to reprecipitate the tellurium and astatine. After coagulation of the precipitate, another 5 mg portion of tellurium is added. The combined precipitate is separated by centrifugation, washed with concentrated HCl, and dissolved in 5 ml of 8 M HCl through which Cl_2 is being bubbled.

The astatine is now extracted away from the tellurium by 6 ml of diisopropyl ether, the ether is washed with two 2 ml portions of 8 M HCl, and the astatine is backextracted into two 5 ml portions of water. The product is a solution of radiochemically pure astatine in ca. 0.01 M HCl containing a trace of diisopropyl ether.

When the target material is lead, the very low yield of astatine necessitates a further purification by distillation. Ten ml of 1 M $FeSO_4$ in 2 M H_2SO_4 are added to the aqueous astatine backextracted from the ether, and the astatine is distilled into an 0.5 M NaOH solution. Distillation is continued until crystals begin to appear in the distilling flask.

Procedure 5

Purification of Astatine formed by Spallation of Thorium with High-Energy Protons[8-10]

The target, about 2-3 g of metallic Th, is dissolved in 25 ml of concentrated HCl containing one drop of concentrated HF, and through which chlorine is being bubbled at a rate of 200-300 ml/min. To the solution are added 70 ml of water containing 10 mg of Te as H_2TeCl_6. The tellurium and astatine are precipitated by the addition of 5 ml of 1 m $SnCl_2$. The precipitate is separated by filtration through sintered glass and washed with three 30 ml portions of 3 M HCl containing 10^{-3} M $SnCl_2$.

The precipitate is redissolved in 0.5-1 ml of 8 M HCl through which chlorine is being bubbled at a rate of 10-20 ml/min. The solution is then introduced onto a column of Dowex 50 x 8 cation exchange resin, 200-400 mesh, in the hydrogen form. The column should be 2 mm in diameter and 100 mm long and should have been pretreated with 10-20 ml of 8 M HCl saturated with Cl_2.* The sample is passed through the column at a rate of 1-2 drops per minute, and is followed by 1-2 ml of 8 M HCl saturated with Cl_2, which completely washes the tellurium from the column, along with at least 99% of any polonium that was present. Some 3-10% of the astatine may be washed through with the tellurium.

Ninety percent or more of the astatine left on the column is now removed by elution with 1 ml of saturated chlorine water at a rate of 3-4 drops per minute. To the eluate are added 2 ml of 3 M HNO_3 containing 0.005 M $H_2Cr_2O_7$, after which 0.5 M $AgNO_3$ is added dropwise until all the chloride is precipitated. The least possible excess of Ag^+ should be used.

The silver chloride precipitate is removed by filtration through sintered glass, and a platinum foil 0.1 mm thick and of about 2 cm^2 cross-section is placed in the filtrate. This foil should have been pretreated by boiling for 2-3 hr in 13 M HNO_3-0.01 M dichromate, washing with water, and heating to yellow-white heat in a gas-oxygen flame. The astatine solution, with the platinum in it, is heated to 90°C and is stirred vigorously for 40 minutes. More than 85% of the astatine is adsorbed on the platinum, which is removed from the solution and washed with three portions of 6 M HNO_3 containing 0.005 M dichromate.

To remove the astatine, the platinum foil is made the anode of an electrolytic cell in 1 M HNO_3.** At an anodic current density of 4 ma/cm^2 some 95% of the adsorbed astatine is desorbed in 10 minutes to give a pure astatine solution in nitric acid. The overall chemical yield is 50-60%, and the decontamination factor from radiochemical impurities is at least 10^5.

---

[*] The resin that the authors used to prepare this column was first washed successively with (1) 8 M HCl saturated with Cl_2, (2) water, (3) 6 M HNO_3 + 0.1 M Ce(IV) (4) 6 M HNO_3, and (5) water. It was then dried at 60-70°C.

[**] Although the authors do not mention it, presumably a platinum wire of foil may be used as the cathode.

Procedure 6

Isolation of Astatine from Bismuth Oxide Targets (Modification of Procedure 7, NAS-NS-3012)[11]

The Bi_2O_3 target is dissolved in dilute perchloric acid containing a little iodine, and the bismuth is precipitated as the phosphate. The astatine is extracted with three successive portions of chloroform or carbon tetrachloride, each organic phase being equal in volume to the initial aqueous phase.* The astatine and iodine may be backextracted from the organic phase with a small volume of aqueous NaOH, or with a solution of a strong reducing agent such as SO_2 or Sn(II).**

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*This extraction frees the astatine from the last traces of polonium. The multiple extractions are suggested by the editor to insure nearly quantitative extraction of the astatine.

**The author suggests a reducing backextractant, but gas should do just as well, while avoiding the introduction of additional chemical contaminants.

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RADIOCHEMISTRY OF BERYLLIUM
(ADDENDUM TO MONOGRAPH NAS-NS-3013)

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INTRODUCTION

Since the beryllium monograph was written, a great many radiochemical separations of ^{7}Be or ^{10}Be from diverse materials have been reported. In most cases the procedures which were followed are based on the standard separation techniques discussed in the monograph. Those who may wish to separate beryllium and other radionuclides from targets bombarded by high energy protons may refer to the flow diagram of the radiochemical procedure followed by Rayudu[1] (C, O, Mg, Si, Fe, Ni targets) or to the procedures outlined by Furukawa et al.[2] (Aℓ target) and Ligonniere et al.[3] (Aℓ, V, Ta, and Au targets). The group associated with the Tata Institute have been interested in a variety of radionuclides in precipitation.[4-7] Their methods are based on ion exchange for collecting beryllium (see also the discussion below), followed by a TTA extraction into benzene from EDTA solution to separate beryllium from other cations.

Two radiochemical techniques which were not discussed before, and which merit attention, involve special ion exchange procedures. One is the use of insoluble hydroxide-dispersed cation exchange resins, described by Merrill et al.[8] In this procedure cations which are hydrolyzed at higher pH are collected on Dowex 50 x 8 resin beads which have been saturated with $Fe(OH)_3$ or $MnO_2 \cdot xH_2O$. The resin is prepared by first saturating it with Fe(III) or Mn(II) ions. After rinsing with distilled water, NH_4OH (or $NH_4OH + H_2O_2$ in the case of Mn(II)) is passed through the column to precipitate the corresponding hydrous oxides within the resin beads. Trace amounts of beryllium in sea water are absorbed very effectively by such columns. It should also be well suited to removing ^{7}Be of ^{10}Be from rainwater, although the extra time involved in preparing the hydrous oxide resin may not be warranted since ordinary Dowex 50 or IRA-400 resin are quite satisfactory for absorbing beryllium from rainwater.[4-6]

Beryllium is eluted from the hydrous oxide column with acid; if 0.12 M oxalic acid is used to elute the Fe(III) resin column, Fe(III) is selectively removed leaving Be^{+2} absorbed. Beryllium can then be eluted separately with acid.

This type of resin column can also be used to decontaminate beryllium solutions of non-amphoteric cations. A 10% NaOH solution containing beryllium will pass through the column while the other cations are absorbed.

The second ion exchange procedure involves a resin which is highly selective for beryllium, polydiallylphosphate. The recipe for preparing the resin is given by Kennedy et al.[9,10]; no commercial supplier of this resin is known to the writer. The sodium form of the resin absorbs beryllium from solutions containing Na_2 EDTA at pH4 while a variety of divalent and trivalent cations pass through.[10] After washing the column, beryllium is readily eluted with 0.5M

NH_4F, which forms the fluoberyllate anion. An example of the use of this procedure in a radiochemical separation is given below.

Procedure 1

Separation of Beryllium From Soil

Source: P. Moller and K. Wagener, "Dating Soil Layers by ^{10}Be," in Radioactive Dating and Methods of Low-Level Counting, Proceedings series #152, IAEA, Vienna, 1967, pp. 177-188.

Because of the small amount of ^{10}Be present in soil, large amounts, up to 10 kg, of soil must be processed. The following procedure is reported to yield pure $Be(OH)_2$ containing no other radionuclides.

1. Digest the fine-grained material for 24 hr with conc HCl in 10-liter plastic barrels. After decanting the solution, treat the residue again with conc HCl for 24 hr. Filter the solution and wash the residue with water. Depending on the amount of sample material, 5- to 20-liters of solution is obtained from the digestion step.

2. Evaporate the solution to the beginning of crystallization. Add conc HNO_3 to destroy organic matter. Redissolve any precipitate with conc HCl.

3. Extract Fe(III) from the strongly acid solution with methylisobutylketone.

4. Evaporate the aqueous residue to the beginning of crystallization. With rapid stirring add Sr carrier followed by strong H_2SO_4 to the boiling solution. Cool and filter the precipitated sulfates.

5. Dilute the filtrate with an equal volume of water. Add conc NH_4OH and sufficient EDTA to prevent precipitation (Note 1) until the pH is 6.5-7. Extract for 20 min with acetylacetone (AA) in chloroform (1% AA by volume) in the proportion of 100 ml AA solution per liter of aqueous phase. Repeat the extraction twice more, combining the chloroform phases.

6. Evaporate the combined chloroform phases to dryness in the presence of conc HNO_3. Treat the residue several times with conc HNO_3 to destroy organic matter (Note 2).

7. Dissolve the residue in dilute HCl. Bring the pH to 6.5 by addition of NH_4OH and sufficient EDTA to prevent precipitation. Heat for several minutes, then transfer the solution to a diallylphosphate column (1 cm x 10 cm) which has been prepared with 0.15M NH_4-EDTA at pH 7 and then saturated with NH_4^+ ion. (Note 3)

8. Wash the column twice with 25 ml 0.15M EDTA solution. Elute beryllium with 100 ml 1M MH_4F, collecting the effluent in a platinum crucible.

9. Evaporate the eluate in a glovebox or hood, heating the crucible to sublime NH_4F. Treat the residue with strong H_2SO_4; heat to drive off HF. Add 1 drop phenol red indicator followed by sufficient alcoholic NH_4OH as is necessary to change the indicator to violet.

10. Filter the precipitate through a membrane filter. Prepare the sample for counting.

11. After the sample is counted, decompose filter and beryllium precipitate with conc HNO_3. After evaporating the HNO_3 take the residue up in dilute HCl and make up to 50 ml in a volumetric flask. After taking a known aliquot for quantitative beryllium analysis (Note 4), reprocess the remainder by steps 7-10 as a check on the constancy of specific activity.

NOTES

1. Depending on the type of soil, up to several kg of EDTA may be necessary.

2. The residue at this point is mainly $Be(NO_3)_2$.

3. See Ref. 9 for the details of the preparation of this ion exchange resin.[11]

4. The recommended procedure is a photometric method using 8-hydroxyquinaldine.

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Standardization of a ^{7}Be Source

The fact that the gamma ray of ^{7}Be (0.480 MeV) has an energy close to that of positron annihilation radiation (0.511 MeV), makes the determination of the absolute disintegration rate of a given ^{7}Be source very easy. One can buy from commercial sources the positron emitter ^{22}Na of known disintegration rate, accurately determined by coincidence counting of the two annihilation quanta. If the ^{7}Be source is mounted so as to have geometry and self-absorption characteristics similar to the ^{22}Na source, the two can be directly compared. Assuming a single-channel analyzer is used, the slight difference in energy will require a corresponding displacement of the base level setting of one relative to the other. Note also that there are two 0.511 MeV-quanta per ^{22}Na disintegration so the disintegration rate of the ^{22}Na source is effectively twice as large when used for the purpose of this standardization.

If a well-type scintillation detector is used, there is some loss of counts in the 0.511-MeV channel due to summing from capture of both annihilation quanta, but this will be a second-order effect unless the crystal is of large dimensions. In that case, the comparison is best made with ^{7}Be source and ^{22}Na standard placed outside the well of the scintillator; the 180° angular correlation between the annihilation quanta precludes the possibility of both being captured in this geometrical configuration.

RADIOCHEMISTRY OF MAGNESIUM
(ADDENDUM TO MONOGRAPH NAS-NS-3024)

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INTRODUCTION

There is not much that is new to report by way of radiochemical separations of magnesium. Since the time the monograph was written, ^{28}Mg has been detected in rainwater; one procedure for isolating this radionuclide along with ^{24}Na is given below.[1]

Husain and Kuroda[2] have sketched a different procedure for separating ^{28}Mg from rainwater as follows: Mg is first scavenged from the rainwater with $Fe(OH)_3$ precipitated at pH 11, after which the Fe(III) is removed by precipitation at pH 7. After reprecipitating Mg with NaOH, Sr and Ba are removed by precipitation with fuming nitric acid. La and other rare earths are removed by precipitation of La oxalate. A H_2S scavenging of Pb and Bi removes insoluble sulfides. After passing through an anion exchange column, Mg is precipitated for counting with ammonium phosphate. The yield is 40 to 50%.

A solvent extraction procedure for Mg has been described by Krozyreva et al.[3] for isolating ^{28}Mg from the n-irradiated Li-Mg alloy used to produce the radioisotope. The procedure is as follows: the aqueous solution of the Li-Mg target is adjusted to pH 9 and extracted with a mixture which is 1M in 8-hydroxy-quinoline (oxine) and 0.4M in a primary aliphatic amine, the solvent being 2/3 chloroform and 1/3 ethanol by volume. After the organic phase is washed twice with 0.005N NH_4OH, Mg is back extracted with 1N HCl. The aqueous extract is then neutralized with excess ZnO, after which the oxine and amine are removed by extraction with chloroform. Finally, Zn is extracted with tributylphosphate from 2N HCl.

Those interested in isolating Mg from accelerator targets may wish to consult the outlined procedure used by Crespo et al.[4] to isolate ^{24}Na and ^{28}Mg from irradiated targets of Cu, Ag, Au and U. The procedure is based on 8-hydroxy-quinoline precipitation of Mg, followed by $Fe(OH)_3$ and acid sulfide scavengings. The alkaline earth elements are removed by oxalate and sulfate precipitations.

Procedure 1

Separation of ^{23}Mg and other radionuclides from rainwater.

Source: Reference 1

The separation is based on a schematic flow diagram which is not always specific as to amounts of reagents to be used. Carriers of Mg, Na, and Ca are presumably added at the beginning of the procedure. Ca. 200 ℓ of rainwater is used for ^{28}Mg analysis.

1. Pass the rainwater through Dowex - 50 resin. Elute with 6M HCl. Evaporate to dryness, fume with H_2SO_4. Dilute with water and filter off the precipitate of $CaSO_4$.

2. To the filtrate ad Pb^{++}, Bi^{+3}, and Cu^{++} carriers. Pass in H_2S. Filter and discard the precipitated sulfides.

3. Add Fe^{+3} and Zn^{+2} carriers. Make the solution basic with $NH_4OH + NH_4Cl$. Pass in H_2S. Filter and discard the precipitated sulfides.

4. Boil off H_2S, adjust pH to 6 and pass through Dowex-50 column. Elute with 500 ml of 0.5N HCl, rejecting the first 100 ml. Evaporate the rest, which contains ^{24}Na.

5. Elute with 300 ml of 1N HCl, rejecting the first 50 ml. To the remaining eluate add NaOH to precipitate $Mg(OH)_2$. Filter.

6. Dissolve the $Mg(OH)_2$ precipitate in acetic acid. Add PO_4^{-3} carrier, followed by Fe^{+3} to precipitate PO_4^{+3}. Filter.

7. Add $NH_4OH + NH_4Cl$ to the filtrate. Filter and discard the precipitate.

8. Acidify the filtrate with acetic acid. Add Pb^{+2} carrier followed by sodium dithiocarbamate. Filter and discard the precipitate.

9. Add citric acid to the filtrate followed by $(NH_4)_2HPO_4$ and NH_4OH. Filter the precipitate. Ignite to $Mg_2P_2O_7$.

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RADIOCHEMISTRY OF NICKEL

(ADDENDUM TO MONOGRAPH NAS-NS-3051)

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Procedure 1

Source: C. W. Thomas, unpublished laboratory procedures. (Battelle-Northwest, 329 Bldg., 300 Area, Richland, Washington 99352)

Sample Type: Water containing mixed activation products and fission products.

Advantages: Rapid separation of ^{65}Ni.

Yield: Approx. 100%[*]

1. To the hot (80°C) sample add 10 mg each of Cr, Ni, Mn, Zn, Co, and Cu carriers. Add 15 ml of ammonium citrate solution (40 gm/150 ml H_2O) and 10 gm of ammonium chloride (NOTE 1).
2. Add dimethylglyoxime solution (2 gm/10 ml ethanol) and let cool in a water bath to 25°C.
3. Filter through a Whatman #42 filter and wash the precipitate with 100 ml H_2O. Discard the filtrate.
4. Dissolve the precipitate in 20 ml 8<u>N</u> HNO_3, saving the filtrate.
5. Evaporate the filtrate nearly to dryness on a hot plate.
6. Dilute to approx. 500 ml with H_2O. Repeat steps 1 through 4, omitting the addition of more Ni carrier.
7. Dilute the filtrate to an appropriate volume with H_2O and count with a gamma-ray scintillation spectrometer (NOTE 2).

NOTE 1. The carriers and reagents are added to the quart sample container prior to collection of the sample.

NOTE 2. Using a 9" NaI(Tl) well crystal, the measurement is completed on the 1.481-MeV gamma-ray and coincidence sum peak.

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[*] Editors note: Although the chemical yield is reported to be approx. 100%, it would be best for each experimenter to determine it a few times for himself in his own laboratory. Any of the methods given in the original monograph should be satisfactory. An alternative method would be instrumental analysis for Ni on a suitable aliquot of the final solution.

Procedure 2

Source: J. J. Pinajian, J. Inorg. Nucl. Chem., 31, 1241 (1969).

Sample Type: ^{66}Ni preparations (50-mg targets of 98.56% enriched ^{64}Ni irradiated in a neutron flux of 2.45 x 10^{15} n/cm^2/sec for 48, 72 or 96 hours, and cooled 1.5 days).

Procedure:

1. Dissolve the target in conc HNO_3, add 10 mg Ag carrier and evaporate the solution to incipient dryness.

2. Take up the residue in H_2O and make slightly alkaline with 14.8M NH_4OH.

3. Precipitate AgCl by the addition of HCl and filter through a medium porosity sintered glass frit.

4. To the filtrate add 5 ml 36N H_2SO_4 and evaporate to strong fumes of SO_3.

5. Cool and dilute with approx. 100 ml H_2O. Neutralize the solution with 14.8M NH_4OH and add 25 ml in excess.

6. Electroplate the ^{66}Ni onto a platinum screen at 2 amps for 1.5 hr, using an ice bath and magnetic stirrer. Add 25 ml 14.8M NH_4OH and continue the electroplating another half hour to complete the recovery (NOTE 1).

7. Rinse the platinum screen in dilute NH_4OH and dissolve the ^{66}Ni in hot 6M HCl. Finally, make the solution 9M in HCl and pass through a BioRad AG-1 (100-200 mesh) column (NOTE 2).

8. Evaporate the column eluate to incipient dryness and treat with conc HNO_3 to destroy organic matter.

9. Treat the solution with 12M HCl to convert Ni to the chloride. Take up the activity in approx. 15 ml 0.1M HCl (NOTE 3).

NOTE 1. This step separates the ^{66}Ni from ^{24}Na activity.

NOTE 2. This step removes Co activities.

NOTE 3. Yields were measured using the 1.039-MeV gamma-ray, emitted through decay of the 5.1 minute ^{66}Cu daughter, counted with a 3" x 3" NaI(Tl) crystal.

Procedure 3

Source: V. Serment, A. Abu-Samra and A. H. Emmons, Nucl. Appl. Tech., 9, 662 (1970).*

Sample Type: Ni powder (3 mg of 97.92% enriched ^{64}Ni irradiated 200 hr in a thermal neutron flux of 1.69 x 10^{14} n/cm^2/sec, using 0.1% cobalt wire as a flux monitor, and cooled 4 days).

Advantages: Permits the separation of Ni isotopes from Cu, Mo, and Zn contaminants prior to measurement of ^{66}Ni for determination of the thermal neutron capture cross section of ^{65}Ni.

Yield: 75.5%

Procedure:

1. Transfer the Ni powder to a 40-ml centrifuge tube and add 20.1 mg Ni carrier, 50 mg each of Cu and Zn carrier, 2 ml conc HNO_3 and 2 ml conc HCl. Warm on a water bath until the Ni powder is dissolved.

2. Add 10 ml 2N HCl and rapidly bubble H_2S through the solution. Centrifuge and discard the precipitate.

3. Add 50-mg Cu carrier to the supernate and repeat the precipitation with H_2S. Centrifuge and discard the precipitate.

4. Repeat step 3.

5. Add 50-mg Co carrier to the supernate and make the solution basic with 6M NH_4OH. Saturate the solution with H_2S.

6. Centrifuge and discard the supernate. Dissolve the precipitate in conc HNO_3.

7. Add 1 ml H_2O_2 and 5 ml 2N NaOH and warm on a water bath to precipitate Co and Ni hydroxides. Centrifuge and wash the precipitate.

8. Dissolve the precipitate in 1 ml 6N HCl. Add 10 mg tartaric acid, adjust the pH to 8, add 10 ml 1% dimethylglyoxime solution and warm to 80°C on a water bath. Add a few ml of 1N NH_4OH to complete the precipitation of nickel dimethylglyoxime. Centrifuge and discard the supernate.

9. Dissolve the precipitate in 1 ml 6N HCl. Add Co carrier and repeat the precipitation of nickel with dimethylglyoxime.

10. Repeat step 9.

11. Wash the precipitate with 50 ml H_2O, dry at 115°C for 3 hr, and weigh to determine yield.

12. Count the ^{66}Ni in a 3" x 3" NaI(Tl) well crystal, using the 1.039-MeV gamma-ray associated with the decay of the 5.1-minute ^{66}Cu daughter.

*We acknowledge permission of the publisher of Nucl. Appl. Tech. to reprint part of this procedure.

Procedure 4

Source: C. E. Gleit and J. Dumot, Int. J. Appl. Rad. Isotopes, 12, 66 (1961).*

Sample Type: ^{63}Ni-containing solutions.

Procedure:

1. To an acidified solution containing nickel (II) add sufficient NaOH to precipitate $Ni(OH)_2$.
2. Wash the precipitate once with 10 ml H_2O and then twice with 10-ml volumes of ethanol.
3. Add 1 ml n-caproic acid to dissolve the precipitate.
4. Add 2 ml absolute ethanol and 20 ml of scintillator solution (NOTE 1).
5. Count in a liquid scintillation spectrometer (NOTE 2).

NOTE 1. Four grams PPO and 0.10 gm POPOP dissolved in 1 liter of scintillation grade toluene.

NOTE 2. The counting efficiency is influenced by the concentrations of n-caproic acid and nickel (II), and a calibration curve must therefore be prepared. Results are better at 0°C and up to 0.05 ml H_2O may be tolerated. For samples containing 10 ml Ni, the counting efficiency is about 28.5%.

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*We acknowledge permission of the publisher of Int. J. Appl. Rad. Isotopes to reprint part of this procedure.

Procedure 5

Source: J. C. Smith and B. Hadley, J. Nutr., 95, 541 (1968).

Sample Type: Rat tissues, blood and urine.

Advantages: All sample preparation is done in the counting vials.

Yield: 100%

Procedure:

1. Place up to 70 mg fresh tissue or 200 mg blood or urine in liquid scintillation counting vials. Add 0.2 ml 70% $HClO_4$ and 0.4 ml 30% H_2O_2.
2. Tightly cap the vials and heat at 70°C in a drying oven until the solutions clear.
3. Cool and add 6 ml ethyleneglycol monoethyl ether (Cellosolve). Add 10 ml toluene phosphor solution (NOTE 1) and equilibrate the samples 2 hr before counting.
4. Count the vials in a liquid scintillation spectrometer (NOTE 2).
5. Prepare a quenching curve using 1 μCi ^{63}Ni plus increasing quantities of bromcresol green indicator.

NOTE 1. Six-g PPO/liter of toluene.

NOTE 2. The authors used a Beckman liquid scintillation counter with adjustable iso-set module. The lower window was closed and upper window reading 3.5. The gain was adjusted to give an external standard counting ratio of 1.300 for the least quenched sample. Counting efficiency was 42% for the least quenched sample.

Procedure 6

Source: T. M. Beasley and E. E. Held, Science, 164, 1161 (1969).

Sample Type: Soil, clam kidney, crater sediment, chaetognaths, squid, lichen, and composite shellfish (marine and terrestrial biota, soil and sediment).

Advantages: ^{63}Ni is separated from other radioisotopes with high decontamination factors.

Procedure:

1. Add 6 mg of stable Ni to the sample and wet-ash with HNO_3 and $HClO_4$. After dissolution is complete, evaporate to fumes of $HClO_4$. Precipitate Ni with heptoxime according to the procedure of Vöter and Banks (NOTE 1).

2. Filter and dissolve the precipitate in 8M HNO_3. Wet-ash with $HClO_4$ to destroy organic material.

3. Reprecipitate Ni with heptoxime.

4. Repeat step 2.

5. Dilute the solution with water and add sufficient NaOH to precipitate Ni $(OH)_2$.

6. Dissolve the precipitate in 6N HCl.

7. Extract the solution with 10 ml 10% Alamine-336 in xylene solution. Centrifuge to separate phases.

8. Decant the organic phase and reprecipitated Ni with NaOH.

9. Dissolve the precipitate in 0.5 ml 6N acetic acid and add 2 ml Biosolv and 15 ml of scintillator solution (NOTE 2).

10. Count in a liquid scintillation spectrometer (NOTE 3).

11. Determine the yield by wet-ashing the scintillation solution and reprecipitation of Ni with heptoxime. Dry the precipitate 1 hr at 110-120°C and weigh. The factor for Ni is 0.1590.

NOTE 1. R. C. Voter and C. V. Banks, Anal. Chem., 21, 1320 (1949). The solution is boiled with HClO to fumes, cooled and diluted with 4 volumes of H_2O. SiO_2 is filtered if present. The precipitate is washed with 1% HCl, then H_2O. Then 18 ml citric acid solution (1 gm/3 ml solution) are added for each gram of sample, plus 3 ml in excess. If Pb is present add 5 ml ammonium acetate solution (1 gm/5 ml solution) and 10 ml sodium sulfite solution (1 gm/10 ml solution). The solution is diluted to 200 ml, adjusted to pH 3.5 with NH_4OH, warmed to 50°C and 20 ml ammonium thiocyanate solution (1 gm/2 ml solution) are added. Copper is filtered if present. One adds slowly 15 ml saturated heptoxime solution for each 10-mg Ni plus 5 ml in excess. The solution is heated to 80°C for 10 min. then cooled in tap water for 30 min. The precipitate is filtered, washed with cold H_2O, dried at 110-120°C for 1 hr and weighed.

NOTE 2. Five grams PPO plus 0.5-gm POPOP in 1 liter of toluene.

NOTE 3. Counting to 10,000 total counts or 500 minutes, the detection limit at an average overall efficiency of 59% was 1.4 ± 1.0 dpm at the 95% confidence level.

Procedure 7

Source: T. M. Beasley, Health Phys., 17, 743 (1969).

Sample Type: Solutions containing Ni radionuclides.

Procedure:

1. Separate Ni from $HClO_4$ solutions of pH 4.0 containing citrate, acetate, sulfite and thiocyanate by precipitation with heptoxime according to the procedure of Voter and Banks (NOTE 1 of previous procedure). For biological material, add 7 mg Ni carrier before wet-ashing and add 1 mg each of Cr, Co, Mn, Pb, Zn, Zr, Y, and Ag carriers.

2. Filter and dissolve the precipitate in 8M HNO_3. Wet-ash to destroy organic material.

3. Reprecipitate Ni with heptoxime.

4. Repeat step 2.

5. Dilute the solution with water and add sufficient NaOH to precipitate $Ni(OH)_2$.

6. ^{63}Ni is determined as in the previous procedure.

   If ^{59}Ni is to be determined, dissolve the precipitate in H_2SO_4 and electrodeposit Ni from ammoniacal solution onto Cu planchets. Measure the 6.9-keV X-ray.

   If ^{65}Ni is to be determined dissolve the precipitate in an appropriate volume of acid for gamma-ray scintillation counting.

7. For environmental samples, determine the yield by wet-ashing the scintillation solution and reprecipitating the nickel with heptoxime. Dry the precipitate 1 hour at 110-120°C and weigh.

Reagents

Heptoxime: Dissolve 2.4 gm in 500 ml distilled H_2O.

Liquid Scintillation Cocktail: Dissolve 5 gm PPO, 0.5 gm POPOP and 110 gm biosolv in 1 liter of scintillation-grade toluene.

Carriers: Dissolve the appropriate nitrate or chloride salt in dilute acid.

Procedure 8

Source: B. R. Harvey and G. A. Sutton, Int. J. Appl. Rad. Isotopes, 21, 519, (1970).*

Sample Type: Radioactive waste solutions from nuclear power stations.

Advantages: High decontamination factor for ^{63}Ni from other isotopes. Detects ^{63}Ni with high efficiency.

Procedure:

1. If the solution is strongly acid or more than 10 ml in volume, evaporate to dryness under an infrared lamp.
2. Dissolve the residue in distilled water, and transfer quantitatively to a 22-ml Packard polyethylene liquid-scintillation counting vial with distilled water.
3. Add NaOH (10%) to adjust the pH of the solution to as near neutral as possible, then add dilute acetic acid dropwise to obtain a pH of 6 or 7.
4. Add 0.2-gm NH_4CNS, followed by 1 drop of 10% Teepol (or similar wetting agent) and 3 drops of pyridine.
5. Shake gently and let stand 10 min before centrifuging.
6. Centrifuge until the precipitate is well compacted and is not disturbed when the supernate is removed by a glass spitzer.
7. Wash the precipitate with 5 ml of an aqueous solution containing 1% pyridine and 1% NH_4CNS. Centrifuge and discard the supernate.
8. Repeat the washing with a further 5 ml of wash solution; centrifuge and remove the supernate as completely as possible.
9. Fill the vial with 22-ml NE240 liquid scintillant (Nuclear Enterprises Ltd.) which has previously been bubbled with O_2-free nitrogen for 10 min.
10. Cool the sample, preferably overnight, in the refrigeration compartment of the liquid scintillation spectrometer before counting.

NOTE: Cooling the sample and storage in the dark prior to counting reduces the background count and eliminates luminescent effects which cause falsely elevated counting rates immediately following the preparation of the sample.

Materials Required:

1. Ni carrier solution - 1 mg Ni/ml as $NiCl_2$.
2. NH_4CNS (anal. reag. grade).
3. Pyridine (anal. reag. grade).
4. Wetting Agent (Teepol or equiv.) - 10% aqueous solution.
5. Acetic Acid - 30% aqueous solution.

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[*] We acknowledge permission of the publisher of Int. J. Appl. Rad. Isotopes to reprint part of this procedure.

Procedure 9

Source: A. H. Kahn, G. B. Saha and L. Yaffe, Can. J. Chem., 46, 3565 (1968).

Sample Type: ^{238}U and proton-induced fission products.

Procedure:

1. Dissolve the target in 2 ml HCl plus a few drops HNO_3 in the presence of 10 mg each of Ni, Zn, and Cu carriers and 15 mg Ga carrier.

2. Pass the solution through a Dowex 1 x 8 (100-200 mesh) column and elute Ni with conc HCl.

3. Reduce the acidity of the eluate to slightly acid by addition of NH_4OH. Scavenge with Mo, Cu, and Cd sulfides in slightly acidic medium.

4. Scavenge with $Fe(OH)_3$ and with Ba and Sr carbonates in excess ammonia.

5. Precipitate NiS.

6. Dissolve the precipitate in a small amount of acid, neutralize with ammonia, and precipitate nickel dimethylglyoxime.

7. Dissolve the precipitate in acid and perform the sulfide and hydroxide scavenges twice more (steps 3 and 4).

8. Precipitate nickel dimethylglyoxime, filter, dry and weigh.

9. After allowing the 5.1 min ^{66}Cu daughter to grow to equilibrium, count the sample on a low background beta proportional counter, using a 200 mg/cm^2 aluminum absorber to stop the low-energy beta particles.

Activation Analysis Methods for Ni in Various Materials

Introduction

Neutron activation analysis procedures for nickel frequently make use of the reactions ^{58}Ni (n,p) ^{58}Co and ^{64}Ni (n,γ) ^{65}Ni. Measuring the ^{58}Co ($t_{1/2}$ = 7.14 d) may be more convenient than measuring the ^{65}Ni ($t_{1/2}$ = 2.55 h) because no serious restrictions are placed on the time the irradiated sample must be counted. In the former case, one can also allow many short-lived, potentially interfering, radioisotopes to decay to negligible amounts before measuring the ^{58}Co. If only nickel is to be determined, it may be just as convenient to concern oneself with short irradiations and measure the ^{65}Ni, particularly if a rabbit facility and in-line counting instrumentation are available. But if other elements, such as iron and cobalt, are to be determined in the same sample, one long irradiation and several weeks' decay generally produce a sample in which many radioisotopes may be simultaneously counted. Many nickel-containing samples may be determined nondestructively, although dissolution or radiochemical separation of the desired radioisotope must sometimes be performed.

Typical applications are given in the source references below. Sources 1 through 5 contain information relative to determination of nickel by measurement of ^{65}Ni, and sources 4 through 18 contain information relative to determination of nickel by measurement of ^{58}Co.

Sources:

1. E. Ricci and T. H. Handley, Anal. Chem., 42, 378 (1970).

2. H. T. Millard, Jr., in Modern Trends in Activation Analysis, J. R. DeVoe, Ed., N.B.S. Spec. Pub. 312, Vol. 1, p. 395 (1969).

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8. V. Kliment, Chem. Zuesti, 20, 682 (1966); N.S.A., 20: 45584 (1966).

9. D. F. Schutz and K. K. Turekian, Geochim. Cosmochim. Acta, 29 259, (1965).

10. G. Harbottle, Archaeometry, 12, 23 (1970; N.S.A., 24; 38798 (1970).

11. J. Meyers, Archaeometry, 11, 67 (1969); N.S.A., 24: 27014 (1970).

12. J. W. Morgan et al., Nature, 224, 789 (1969).

13. J. W. Morgan and W. D. Ehmann, Anal. Lett., 2, 537 (1969).

14. W. D. Ehmann and D. M. McKown, Anal. Lett., 2, 49 (1969); also in Modern Trends in Activation Analysis, J. R. DeVoe, Ed., N.B.S. Spec. Pub. 312, Vol. 1, p. 308 (1969).

15. J. T. Wasson, Trans. Amer. Nucl. Soc., 13, 54 (1970).

16. W. H. Zoller and G. E. Gordon, Anal. Chem., 42, 257 (1970).

17. R. Davis et al., Anal. Chem., 42, 861 (1970).

18. J. Turkstra et al., Anal. Chem., 42, 835 (1970).

Sample Types:

1) (Rabbit system described for geology and biomedicine applications).

2) Cosmic spherules.

3) Terphenyls.

4) Crude oils, distillation factions, asphalts and related substances.

5) Petroleum, polyphenyls, aluminum.

6) Crude oils.

7) Selenium.

8) Ferrite computer memory.

9) Seawater.

10) Potsherds.

11) Ancient coins.

12) Allende Meteorite.

13) Chondritic meteorites.

14) Powdered meteorites.

15) Extraterrestrial materials.

16) Atmospheric pollutants.

17) Air pollution particles.

18) Ores, matte and lead assay beads.

Procedures:

Procedures vary markedly, depending on the specific types of samples to be analyzed. Sample preparation steps are extremely important, being frequently the steps that will determine the ultimate sensitivities. In many cases measurement of the ^{58}Co or ^{65}Ni can be made directly on the sample container following irradiation by comparison with standards similarly prepared. In other cases the activated sample must be manipulated to place it in some standard geometry. When radiochemiqal separation and purification of ^{58}Co or ^{65}Ni is necessary, sophistication of the procedure varies according to sample type. The counting systems available will have an important bearing in determining the degree of purification required. The reader is referred to the sources above for specific information on handling different types of samples, and for procedures used to separate and purify the desired activities.

Procedure 10

Source: I. I. Naumova, Radiokhimiya, 7, 502 (1965); N.S.A., 20, 14489 (1966).

Sample Type: Nickel-iron films.

Procedure:

Films of approximately 83% Ni, 17% Fe are analyzed by activation analysis. Approximately 10 μg samples of this allow and standards are sealed in aluminum vials and irradiated in a thermal neutron flux of 2×10^{13} n/cm^2/sec for approximately 1 month. The samples are processed one week after completion of the irradiation, with a sensitivity using ^{63}Ni of 1.4×10^{-8} g Ni. The samples are dissolved in 1:1 HNO_3 containing carrier and iron is precipitated with NH_4OH. Nickel is precipitated with dimethylglyoxime. After radiochemical purification, Ni is counted to a standard deviation of 1%. Analogous amounts are also determined following reaction with 14-MeV neutrons to produce ^{57}Ni via the reaction ^{58}Ni(n,2n)^{57}Ni.

Procedure 11

Source: Y. Oka et al., Nippon Kagaku Zasshi, 87, 147 (1966); N.S.A. 20: 18613 (1966).

Sample Type: Co and Ni in Fe matrices.

Procedure:

Nickel is determined by means of the photonuclear reactions $^{58}Ni(\gamma,n)^{57}Ni$ and $^{58}Ni(\gamma,p)^{57}Co$. The matrix Fe is used as an internal monitor of bremsstrahlung flux, which is approximately 9×10^6 R/min. The limit of detection is approximately 50 ppm Ni, and Mn and Cu cause appreciable interferences. Residual activities are 1.3 μCi ^{57}Ni per mg Ni and 0.015 μCi ^{57}Co per mg Ni.

Procedure 12

Source: P. Meijers and A. H. W. Aten, Jr., Radiochim. Acta, 11, 60 (1969).

Sample Type: Iron meteorites.

Procedure:

1. Prepare sources by placing iron meteorite particles between discs of standard Fe-Ni-Co alloy. Also prepare sources from discs of the pure metals.

2. Irradiate the sources in the bremsstrahlung produced by the bombardment of tantalum targets with 23-MeV electrons (NOTE 1).

3. Measure ^{57}Ni, using a NaI(Tl) detector to measure the 0.511-MeV annihilation radiation or to measure the characteristic gamma rays (NOTE 2).

NOTE 1. ^{57}Ni is produced by (γ,n) reaction on ^{58}Ni. ^{58}Co is also produced by (γ,pn) reaction on ^{60}Ni, and can be a disturbing factor which will require a correction that is determined from the irradiation of pure Ni.

NOTE 2. Measurement of ^{57}Ni is made about two days after completion of the irradiation in order to remove short-lived interferences through decay. ^{58}Co is measured about three weeks after completion of the irradiation.

Standardization of ^{63}Ni

Source: R. L. G. Keith and D. E. Watt, Nucl. Instr. and Methods, 42, 68 (1966).

Sample Type: ^{63}Ni 4π proportional sources.

Advantages: Uniform sources prepared having minimal self-absorption.

Procedure:

1. Cover a copper annulus with a Vyns film of superficial density 10-20 μg/cm^2.

2. Vacuum-deposit gold on one side of the film to $\geq$ 10 μg/cm^2, using a template under the film to define the source area.

3. Add one drop of insulin (20 units/ml) and 0.1 ml conductivity water to the center of the ungilded side and spread over the desired area. Remove the bulk of the solution with a fine glass capillary and water pump. Rinse the wetted area and remove the washings.

4. Add a known weight of ^{63}Ni solution to the wetted region and place the source in a bell jar (NOTE 1). Reduce the pressure to 1-mm Hg with an air ballast rotary pump (NOTE 2).

5. Vacuum-deposit gold over the source to $\geq$ 10 μg/cm^2 (NOTE 3).

6. Determine the superficial density of the Vyns and gold for each source using a spectrophotometer previously calibrated for these materials by chemical and physical methods (NOTE 4).

NOTE 1. Do not add the source to the gold as this tends to destroy conductivity of the layer.

NOTE 2. The solution freezes in 5 minutes and about 1 hour is required to evaporate 0.1-0.2 gm of solution.

NOTE 3. Breakages during gilding are minimized if the films are not too close to the hot filament or boat, and if occluded gasses have been removed from the gold by heating it *in vacuo* above the normal evaporating temperature for a short time before placing the films in the evaporator.

NOTE 4. For 10-20 μg/cm^2 film and 20-30 μg/cm^2 gold sources, corrections for 4π sources were 0.14% per μg/cm^2 for ^{63}Ni.

RADIOCHEMISTRY OF RUTHENIUM

(ADDENDUM OF MONOGRAPH NAS-NS-3029)

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INTRODUCTION

A search of the literature since 1961 has revealed only four procedures which are significantly different from those quoted in the original monograph. Otherwise, the more traditional techniques involving distillation, reduction with Mg or extraction of the tetroxide into chloroform or carbon tetrachloride continue to be the methods of choice.

Procedure 1

Source: R. R. Rickard, "Determination of Ruthenium in Aqueous Solutions", ORNL Master Analytical Manual, TID-7015, Sec. 2 (1964).

I. SCOPE

This method is applicable to the determination of ruthenium radioactivity in aqueous solutions except those that contain tartrates, glucosides, or reducing agents such as oxalate.

II. PRINCIPLE

Ruthenium in alkaline solution is easily oxidized to perruthenate, RuO_4^-, which is very soluble in pyridine.[1] The RuO_4 is extracted into pyridine from an alkaline hypochlorite solution and thus is effectively decontaminated from ^{233}Pa, ^{241}Am, ^{242}Cm, and mixed fission products.

The different oxidation states of ruthenium exhibit different colors, and this color difference is used to indicate the rate of oxidation of the lower-valent ruthenium to the orange hexavalent ruthenate, RuO_4^{2-} (which is insoluble in pyridine), and then to the yellow-brown pyridine-soluble perruthenate, RuO_4. Observation of these colors permits the analyst to select properly the digestion times. These digestion times may vary from sample to sample.

Following the extraction of ruthenium, an aliquot of the pyridine solution is gamma counted for either ^{103}Ru or ^{106}Ru, ^{106}Rh. Mixtures of the radioactivities from the two ruthenium nuclides are resolved by using a gamma scintillation spectrometer for the gamma measurements.

III. STATUS

The method is currently used for those ruthenium determinations that must be carried out in a glovebox. In addition, the method can be used as the ruthenium decontamination step of another radiochemical procedure.

The procedure is relatively simple. Less than 1% of cesium is extracted. It is not necessary to wash the organic phase; however, centrifugation removes unwanted aqueous droplets. The method is rapid and quantitative when reducing agents are not present in the sample.

The relative standard deviation of the method is 3 to 4%. Carrier-yield measurements are not necessary, and the time required to make duplicate determinations can be less than 30 min, depending on the selected digestion periods.

IV. REAGENTS

Use distilled water for the preparation of the reagents and when water is required in the procedure.

1. Oxidizing solution, 5M NaOH-5% NaClO. Prepare by dissolving 40 g of NaOH in 200 ml of a 5% solution of NaClO.

2. Pyridine, reagent-grade, equilibrated with 5M NaOH.

3. Ruthenium Carrier Solution, ∿10 mg of Ru per ml; prepare by dissolving 1.0 g of $RuCl_3$ in water and diluting the solution to 50 ml.

4. Sodium Hydroxide Solution, 5M NaOH. Prepare by dissolving 40 g of NaOH in water and diluting the solution to 200 ml.

5. Sodium Hypochlorite Solution, reagent-grade, ∿5% NaClO.

V. SAFETY

When not working in a glovebox, perform the extraction in a well-veltilated area to remove pyridine fumes.

VI. SAMPLING

Determine the size of the test portion of the sample from the gross radioactivity of the sample and the estimated percent that the ruthenium radioactivity contributes to the gross ratioactivity. A test portion that contains $\sim10^5$ dpm of ^{103}Ru or 10^6 dpm of ^{106}Ru is suitable, since a dilution of 10 may be incurred after the ruthenium is extracted into pyridine.

VII. PROCEDURE

1. Pipet a test portion (V_1) of the sample (see Section VI, Sampling) into a 50-ml, stoppered, graduated glass cylinder. Add about 1 mg of ruthenium carrier (2 to 3 drops of a ruthenium carrier solution).

2. To the solution in the cylinder, add 5 drops of conc HNO_3. Digest the solution at 50°C for 5 min. Cool the solution; then add to it sufficient 5M NaOH-5% NaClO to make it about 4M in NaOH.

3. Allow the solution to stand for sufficient time (∿10 min) to oxidize the ruthenium through the orange ruthenate (RuO_4^{2-}) state to the yellow-brown perruthenate (RuO_4^-). Add more 5% NaClO, if necessary.

4. Add 10 ml of equilibrated (with 5M NaOH) pyridine. Extract the ruthenium into the pyridine phase (∿1 min agitation); record the volume of the pyridine phase (V_2). Pipet 1.0 ml (V_3) of that phase into a glass culture tube for counting.

5. Measure the total gamma radioactivity of the separated ruthenium aliquot by counting it in a gamma scintillation counter, or measure the ratio of the 0.50-MeV gamma radiation to the 0.62- and 1.05-MeV gamma radiations on a gamma spectrometer to resolve mixtures of ^{103}Ru and ^{106}Ru-^{106}Rh.

Calculations

Let:

V_1 = test portion of original sample, ml.

V_2 = total volume of pyridine phase after the extraction, ml.

V_3 = aliquot of V_2 taken for gamma counting, ml, and

A = ruthenium radioactivity in V_3, cpm.

Then:

Ruthenium Radioactivity in Original Sample, cpm/ml =

$$\frac{AV_2}{V_1V_3}.$$

Procedure 2

Source: "Determination of Ruthenium-103 and Ruthenium-106 in Sand, Vegetation, Seaweed, Fish Flesh and Natural Waters, P.G. Report 308 (U), UKAEA, (1962).

The separation and purification methods described in this report are essentially the traditional ones of extraction of the RuO_4 into CCl_4, followed by precipitation of RuO_2 with methyl alcohol. The application of the method to samples of organic materials indicates that no significant losses of Ru occur during sample preparation.

"Samples of vegetation, seaweed and fish flesh are ashed [450-500°C]; samples of sand, etc. are dried and ground to a fine powder. After adding ruthenium carrier, the sample is fused with a mixture of potassium nitrate and potassium hydroxide [550-600°C]." After dissolution of the melt, the standard ruthenium oxidation, extraction, precipitation and counting are carried out. For natural water samples up to 1ℓ, the Ru is oxidized and extracted directly with no further preparation. Chemical yields are determined by measurement of the absorbancy of the solution at 430 nm.

Procedure 3

Source: F. M. Bathie and B. A. Burden, "A sequential Scheme for the Determination of Several Fall-out Nuclides in Water," Analyst, 93, (1102), 1 (1968).

This paper describes a method for the separation and measurement of Ru as well as nuclides of Mo, Te, Sb, and Sn in a single 10ℓ water sample. The Ru is separated from the entire sample by precipitation of the hydroxide with ethanol (after oxidation with sodium hypochlorite to ensure exchange). Since the precipitate often contains solids which were in suspension, a basic fusion is carried out, the melt dissolved and the Ru reprecipitated with alcohol. All other fractions are combined for recovery of the remaining elements. Ru is purified by the standard extraction and reduction techniques. Attempts were made to electroplate Ru from solutions of ruthenium nitrosyl chloride, but adherent and lustrous deposits could not be prepared over 1 mg/cm^2 thickness.

Procedure 4

Source: Y. Koda, "Determination of Radioruthenium Using a Polyethylene Film," J. Radioanal. Chem., 6, 345 (1970).

This procedure, although basically a distillation, is unique in that the separation, purification and mounting of the Ru is accomplished in a single step. A 100-ml conical flask is charged with the following mixture: 20 ml of 1N H_2SO_4, ∿0.1 mg of Ru^{4+}, ∿10 mg Ag^+, 0.1 g of KIO_4 and about 1 ml of the unknown solution of ^{106}Ru to be analyzed.[1] The mouth of the flask is covered with a specially cleaned polyethylene film, held in place with a rubber band about the neck of the flask. The flask is then heated to 80°C on a boiling water bath, whereupon ruthenium is oxidized to the tetroxide and steam-distilled. In two hours essentially all the tetroxide is condensed on the polyethylene film and firmly fixed by reaction with it. The film is then mounted in a convenient manner for counting.

The author has investigated the effects of various oxidants, reaction times, quantities of reagents (including the Ru carrier) and types of resin films. Cleanliness of the flask and film is especially important for good yields. Contamination ratios (cpm on the film/cpm in solution) were 2-3 x 10^{-2} for the nuclides ^{131}I and ^{36}Cl, 10^{-3} to 10^{-4} for ^{74}As and ^{99}Tc. Discussions of the steam distillation of RuO_4 and the mechanism of the reaction between RuO_4 and polyethylene are included.

Editor's note: This procedure works very well and is ideal for making thin and evenly distributed extended sources of ^{106}Ru.

REFERENCES

1. T. Kiba, A. Miura and Y. Sugioka, Bull. Chem. Soc. Japan, 36, 663 (1963).

The Preparation of Radioruthenium Standards

The two isotopes of ruthenium that are commonly used as tracers are ^{106}Ru and ^{103}Ru. Both can be purchased in "pure" form from Oak Ridge National Laboratory and perhaps other facilities. Also ^{106}Ru can be separated from relatively "old" fission product mixtures. By "old" is meant about two years after irradiation to give ^{103}Ru time to decay out of the fission product mixture.

Any of several procedures in the monograph can be used. The separated ^{106}Ru should be checked for gamma emitting impurities by gamma scanning, if possible, and a sample prepared for beta decay study. The dominant beta associated with the decay has a maximum energy (E_{max}) of 3.5 MeV, and gammas 0.513 and 0.624, all associated with the decay of ^{106}Rh, the 30-sec daughter of ^{106}Ru. The best value for the half-life of ^{106}Ru is 367 days.

If one wished to use ^{103}Ru with a small amount of ^{106}Ru, he could separate radioruthenium from mixed fission products in any convenient manner. The mixture should preferably have not had a very long irradiation (a few days) and also a relatively short cooling period. The presence of ^{106}Ru in this case might not be objectionable. Ruthenium-103 has a predominant gamma of 0.491 and can be distinguished from those gammas associated with ^{106}Ru.

Ruthenium-103 can be prepared by neutron activation. This should be done by using a target of ruthenium chloride, highly enriched with respect to ^{102}Ru. This is to give a product that will be low in ^{105}Ru and its daughter activity. A waiting period will be necessary in any case, if one wishes to use relatively pure ^{103}Ru tracer.

Contaminants that sometimes show up in irradiated ^{102}Ru targets are ^{192}Ir and ^{194}Ir. These can be eliminated by distilling or extracting ruthenium in the presence of some stable iridium used as a holdback carrier.

It is difficult to get ^{105}Ru in a pure form by any means. It and its daughters have innumerable gammas.

Standard solutions should be kept in glass (no plastics) in HCl.

RADIOCHEMISTRY OF SELENIUM
(ADDENDUM TO MONOGRAPH NAS-NS-3030 (REV.))

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I. INTRODUCTION

A great deal of interest has been shown in the biological significance of selenium in recent years. Attention has been shown in the physiological rather than the toxicological role of selenium. Selenium compounds in trace amounts may have important nutritional and metabolic functions.[1,2]

Considerable effort has been devoted to developing methods for the determination of microgram and submicrogram quantities of selenium. For the measurement of submicrogram amounts the outstanding methods at the present time are fluorometry and activation analysis. This addendum will only deal with the activation analysis methods or those methods of interest to the radiochemist.

Since the selenium monograph was revised and published in 1965, there have been many procedures published for the determination of selenium in all types of samples. Many of these procedures used the techniques described in the monograph and they will not be repeated here. However, many of these published procedures used these techniques in a variety of samples which might be of interest to those working with similar matrices. There were analyses done on animal tissue[3,4] blood and human tissues,[5,6] hair,[7,8,9] human dental enamel,[10] cigarette tobacco,[11] standard kale,[12] rocks and chondrites,[13,14] fish meal,[15] and other biological materials.[16,17,18]

One of the problems associated with instrumental neutron activation analysis is the activation of major and minor sample constituents which interfere in the analysis of selenium. Yule[19] experimentally determined the matrix sensitivities of over 65 elements in six matrix materials commonly encountered in activation analysis.

There have been a number of multiple separation schemes which analyze various samples for selenium as well as other elements.[6,20,21]

One of the most important advances in the analysis of selenium has been the improved instrumentation which includes the germanium (lithium drifted) detectors. This has enabled the analyst to do many more samples by non-destructive analysis.

II. BEHAVIOR OF SMALL AMOUNTS OF SELENIUM IN VARIOUS ANALYTICAL OPERATIONS[22]

There is little or no adsorption of traces of selenium(IV) on glass in either alkaline or acid solutions. Selenium traces may deposit on glass walls after the evaporation of a solution to dryness. These traces can be removed by treatment with a dilute base.

The volatility of small amounts of selenium upon concentration of solutions is a serious problem. The smaller microgram quantities of selenium show a greater percentage loss than those with relatively high concentrations. Tetravalent selenium is rather volatile even at water bath temperatures. It is also volatilized from strong hydrochloric acid solutions at room temperature. Acid selenite solutions also show considerable loss on concentration.

The addition of salt additives hinders the volatility of Se(IV), however, this is not a practical solution because large quantities of salts interfere in the selenium determination.

The loss upon evaporation on the water bath is reduced by the addition of oxidizing agents, however, at higher temperatures (∿300°C) a considerable amount of selenium is volatilized.

According to the experiments of Bock and Jacob,[22] the only way to concentrate selenium is from the following solutions:

1. Acid selenite solution in the presence of larger amounts of salts, and in the absence of halogen halide acids on the water bath.

2. Alkaline selenite or selenate solutions.

3. Acid selenite on the water bath.

Very small concentrations of selenates can be reduced by HBr, HI and $TiCl_3$ with heating. Numerous other reducing agents such as hydrazine sulfate, stannus chloride, ascorbic acid. formic acid, hydroxylamine hydrochloride, thiourea, and sodium thiosulfate are not efficient in reducing small quantities of selenium.

III. PRINCIPAL ANALYTICAL METHODS

Colorimetric

1,4-diphenylthiosemicarbazide reacts with selenium to form a yellow colored complex. The complex is extracted into chloroform and determined spectrophotometrically at 410 mμ.[23]

IV. SELENIUM SEPARATION REACTIONS

Separation by Solvent Extraction

1. Bismuthiol II (5-Mercapto-3-phenyl-1,3,4-thiadiazole-2-thione, potassium salt)[24,25]

Selenium(IV) can be extracted quantitatively from strong acid solutions (pH values below 3) into chloroform with this reagent. 100 mg Bismuthiol II in 50 ml of solution is used to extract milligram quantities of selenium into chloroform. The selenium can be completely re-extracted from the chloroform with dilute sodium hydroxide.

2. Di-n-butyldithiophosphoric Acid[26]

Tetravalent selenium can be extracted from acid, aqueous solutions containing di-n-butyldithiophosphoric acid into chloroform. This extraction is not very effective for traces of selenium.

3. Triphenyltin Hydroxide[22]

Selenium can be extracted as the triphenyltin compound into benzene. Selenium can be removed from the benzene phases with NaOH solutions.

V. COUNTING TECHNIQUES

The development of lithium drifted germanium detectors has made it possible to determine selenium in many matrices by instrumental activation analyses. Figures 1 through 5 give gamma ray spectra of the ^{73}Se, ^{75}Se, ^{77m}Se, ^{79m}Se, and ^{81m}Se radiosotopes as compiled by Adams and Dams.[27] These spectra were recorded with a 18 cm^3 sensitive volume coaxial germanium-lithium drifted detector.

The γ rays following the decay of the ^{81}Se isomers have been studied[28] by using Ge(Li) detectors and coincidence techniques.

A gamma-gamma coincidence arrangement for the activation analysis of trace amounts of selenium and iridium in minerals was developed[29] and the interferences due to the presence of other γ emitters can largely be prevented by adjustment of coincidence ranges.

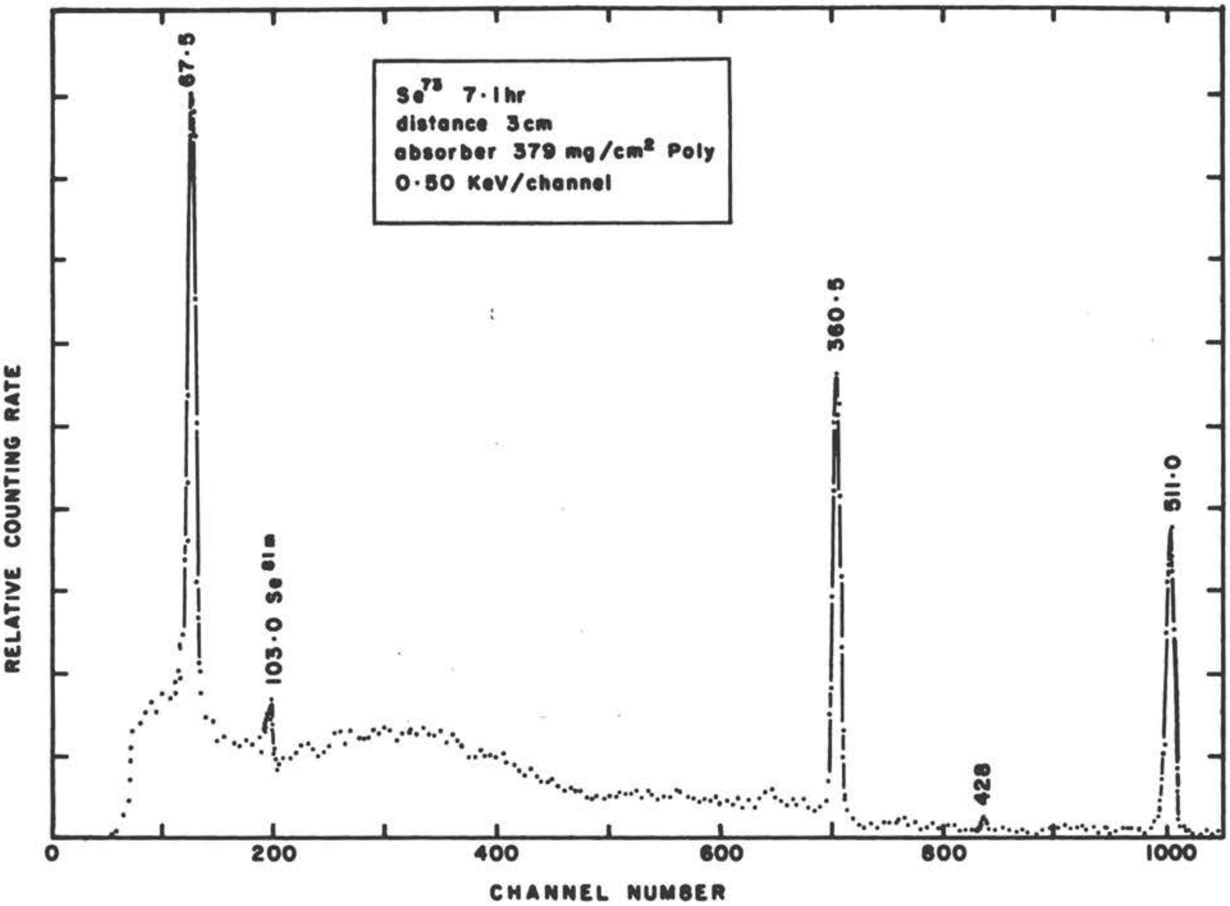

FIGURE 1. GAMMA RAY SPECTRUM OF ^{73}Se

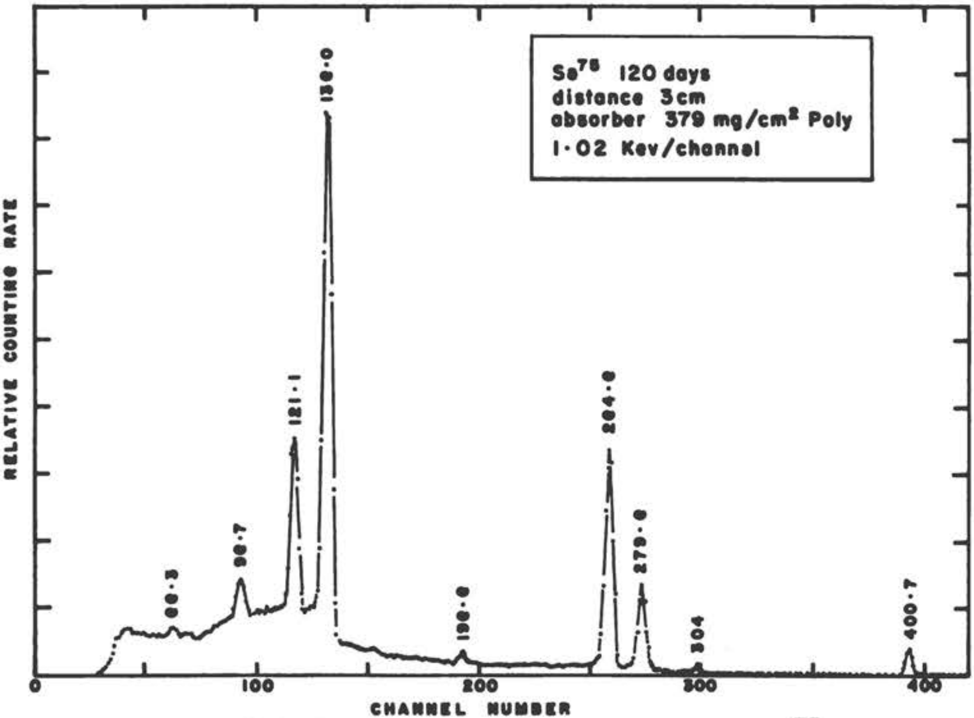

FIGURE 2. GAMMA RAY SPECTRUM OF ^{75}Se

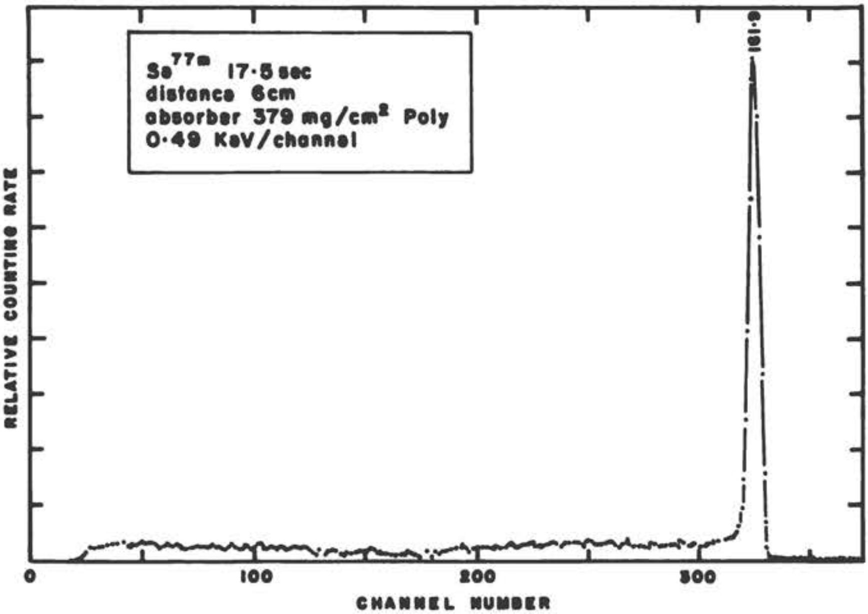

FIGURE 3. GAMMA RAY SPECTRUM OF ^{77m}Se

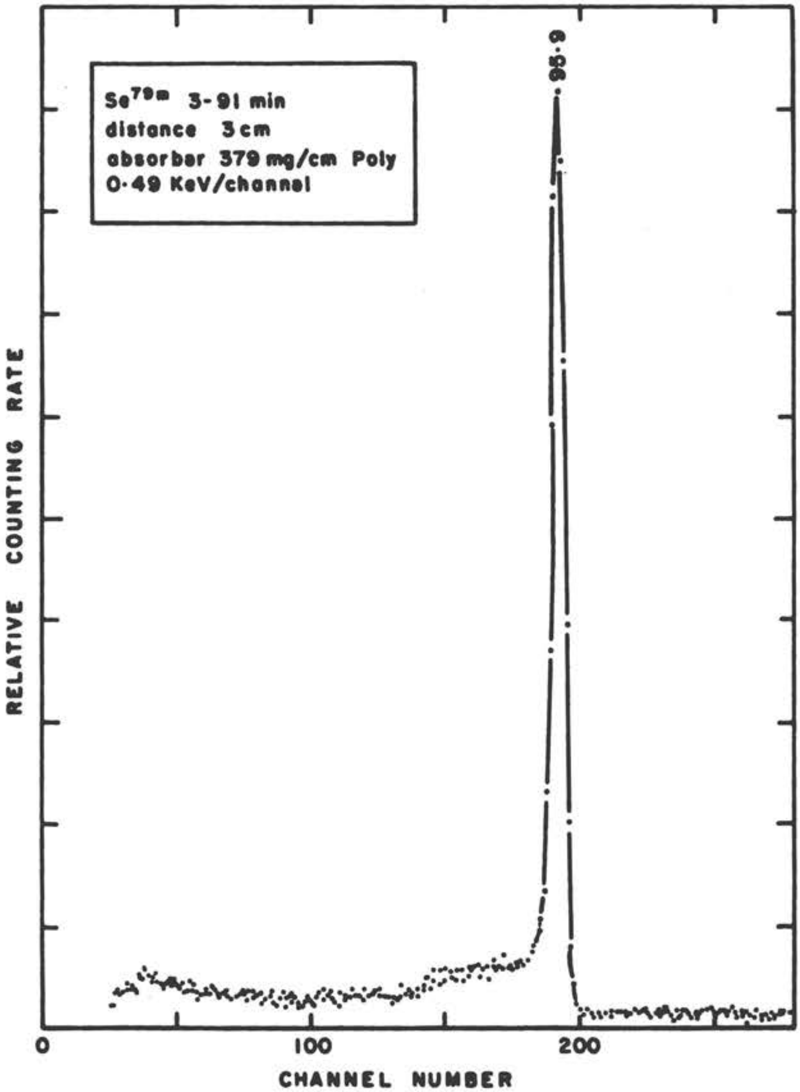

FIGURE 4. GAMMA RAY SPECTRUM OF ^{79m}Se

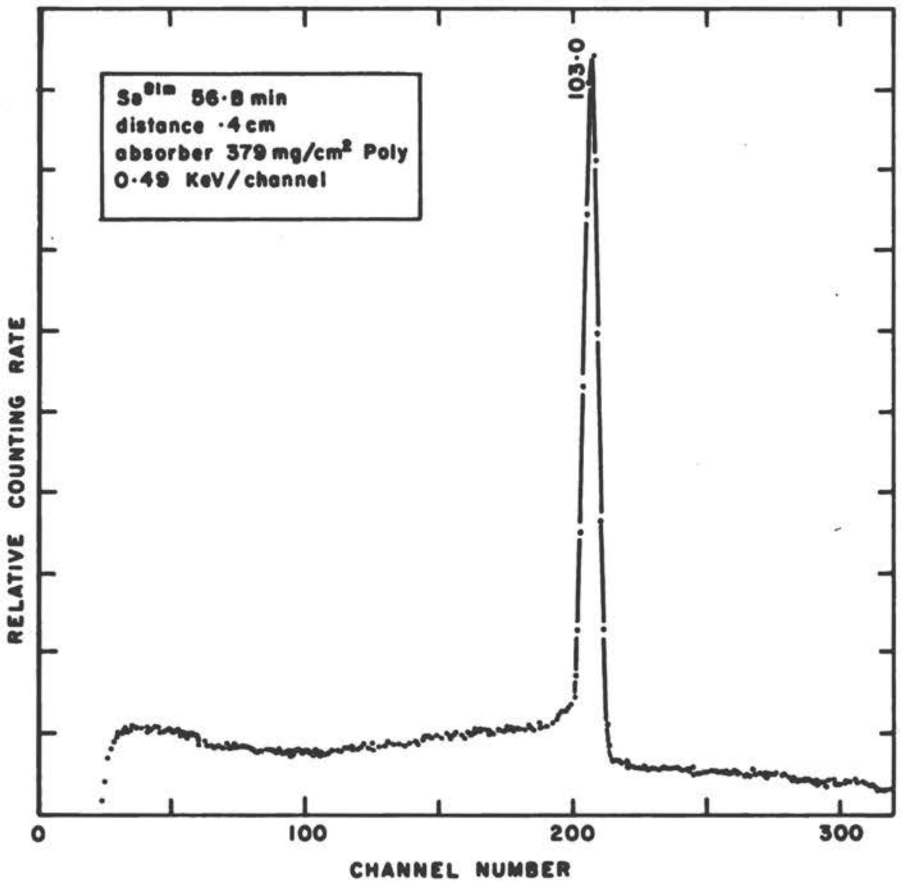

FIGURE 5. GAMMA RAY SPECTRUM OF ^{81m}Se

VI. SEPARATION PROCEDURES FOR SELENIUM

The following radiochemical procedures selected from the literature have some new technique or separation method which was not reported in the original monograph.

Activation Analysis Procedures

1. Standard Reference Materials: Orchard Leaves, Bovine Liver, Mercury in Coal[*]

Procedure used in:	Activation Analysis
Method:	Volatility
Nuclear bombardment:	$^{74}Se(n,\gamma)^{75}Se$
Procedure by:	Rook, H. L.[30]
Chemical yield of carrier:	Mercury carrier added, quantitative transfer
Separation time:	15 minutes
Degree of purification:	Excellent from other volatile components
Equipment required:	Neutron source, sample combustion apparatus and liquid nitrogen trap

Procedure:

a. Encapsulate 0.5 g samples and standard solutions in quartz tubes and irradiate for 2 to 6 hours at a thermal flux of approximately 6 x $10^{13}n/cm^2$.sec.

b. After a 5 day decay, wash the quartz tubes with 1:1 HNO_3, and cool the tubes in liquid nitrogen and cut open ~5 mm from top.

c. Weigh the samples into a ceramic combustion boat and add 2.5 mg of mercuric oxide carrier.

d. Insert the boat into the combustion chamber and pass a stream of oxygen (~30 cc/min) over the sample and then ignite the sample with an oxygen gas torch.

e. Allow the sample to burn and after combustion heat the ash to ~1000°C for five minutes. Heat the tube to drive all volatile components into the condenser.

f. After cooling, transfer the selenium and mercury carrier to a 4 oz. polyethylene bottle with 10 ml of concentrated nitric acid and 30 ml of distilled water. Adjust the total volume to 50 ml.

g. Count the sample using a 60 cc Ge(Li) detector and 2048 channel pulse height analyzer. Use the 260 keV gamma ray of ^{75}Se.

h. The standards are transferred to the similar container and counted and compared to the sample.

NOTE: The determination of Hg may be conducted simultaneously.

*We acknowledge permission of the American Chemical Society to reprint this procedure.

2. Biological Materials (Forage and Feces)

Procedure used in:	Activation Analysis
Method:	Preirradiation separation by solvent extraction
Nuclear bombardment:	^{76}Se$(n,\gamma)^{77m}$Se
Procedure by:	Ververis, et. al.[31]
Separation time:	15-24 hours
Degree of purification:	Satisfactory
Equipment required:	Neutron source and standard laboratory equipment

Procedure:

Preirradiation Separation

a. Dry samples in vacuo at 40°C and grind.

b. To a 5.0 g sample, add 5 g mg$(NO_3)_2$, 15 ml HNO_3 and 10 ml (30%) H_2O_2.

c. Place the mixture on a water bath for one hour at 40°C and then at 100°C for 10 hours.

d. Cool the material and add 1 ml of saturated urea solution.

e. Adjust the pH to 4 and add 8-mercaptoquinoline.

f. After 10 minutes, extract into 18 ml of $CHCl_3$.

g. Irradiate for 20 seconds in a reactor at 4×10^{12} n/cm^2.sec.

h. Compare the activity to standards.

3. Plasma and Serum Samples

Procedure used in:	Activation Analysis

Method: Separation by ion exchange and solvent extraction

Nuclear bombardment: $^{74}Se(n,\gamma)^{75}Se$

Procedure by: Maziere, B., Comar, D., and Kellershohn, C.[32]

Degree of purification: Radiochemically pure by gamma spectroscopy

Equipment required: Neutron source and standard laboratory equipment

Procedure:

a. Weigh samples of serum or plasma into quartz capsules and lyophilize.

b. After irradiation, break the capsules and digest the sample with a mixture of conc. HNO_3 and conc. H_2SO_4.

c. Pass the acid solution through a strong base anion exchange resin (DOWEX 2) to remove interfering ions.

d. Elute the selenium with 6 N HCl.

e. Add sodium diethyldithiocarbamate to complex the selenium and extract with CCl_4.

f. Compare to standards processed in the same manner.

4. On Stream Analyses of Selenium in Liquid Flow Systems

Procedure used: Activation Analysis

Method: Direct determination

Nuclear bombardment: $^{76}\mathrm{Se}(n,\gamma)^{77m}\mathrm{Se}$

Procedure by: Kliment, V., and Tolgyessy[33]

Degree of purification: In a flow rate of 800 ml/min, there is some interference from cobalt-60m

Equipment required: ^{239}Pu-Be neutron source, polyethylene piping, irradiation chamber, pumps and flow meter

Procedure:

a. The equipment consists of a reservoir of the solution, irradiation chamber, counting chamber, pump, flow meter, and the connecting tubing. A ^{239}Pu-Be neutron source is placed in the center of the irradiating chamber.

b. A solution of selenium and cobalt (11 mg Se/ml and 9 mg Co/ml) was flowed through the system at flow rates of 80-800 ml/min.

c. The volume of the counting chamber was 1000 ml and a NaI(Tl) detector 4.5 x 5 cm was used with a 400 channel analyzer.

5. Stainless Steel and Other Metals

Procedure used in:	Activation Analysis
Method:	Volatility or dry distillation
Nuclear bombardment:	$^{74}Se(n,\gamma)^{75}Se$ $^{82}Se(n,2n)^{81m}Se$
Procedure by:	Conrad and Kenna[34]
Chemical yield of carrier:	No carrier - quantitative transfer
Degree of purification:	Technetium interferes
Equipment required:	Counting system, LECO high frequency RF furnace (Model 523), and quartz collection tubes

Procedure:

a. Weigh a sample from 0.8 g to 1.5 g and place in polyethylene rabbits for irradiation.

b. Transfer irradiated sample to ceramic cup and place in furnace.

c. Place a quartz collection tube, packed with glass wool, in a downstream position and begin the burning cycle with a flow of oxygen.

d. After the burning cycle is complete, remove the quartz collection tube containing the volatilized selenium, cool and mount onto a small motor which will rotate the tube above the NaI(Tl) crystal.

e. A standard was then counted in an identical manner.

6. Standard Rocks, Meteorites, and Biological Samples

Procedure used in:	Activation Analysis
Method:	Substoichiometric determination - solvent extraction of Se(IV) with diaminobenzidine in ethyl acetate
Nuclear bombardment:	$^{74}Se(n,\gamma)^{75}Se$
Procedure by:	Nadkarni and Haldar[35]
Separation time:	2 samples/2 hr
Degree of purification:	Satisfactory, decontamination studies on 24 different isotopes show decontamination factors from 10^3 to 10^6
Equipment required:	Neutron source and standard laboratory equipment

Procedure:

a. Dissolve the accurately weighed irradiated material after adding 2 ml of 0.01 M H_2SeO_2 and about 5 mg each of other carriers.

b. The geological samples are dissolved in a HNO_3 + H_2SO_4 + HF mixture, the biological samples in a HNO_3 + $HClO_4$ mixture.

c. To the solution, add 2 ml of formic acid and adjust the pH to 2-3.

d. Add 0.8 ml of 0.01 M diaminobenzidine and heat on a water bath for 2-4 minutes.

e. Cool the solution and add 10 ml of 0.1 M Na_2EDTA and adjust the pH to 5.5-6.5.

f. Extract the solution with 10 ml of ethyl acetate.

g. Wash the organic phase with 20 ml water.

h. Take a 7 ml aliquot of the organic phase and place it in a planchet and dry under an infrared lamp.

i. The selenium standard is treated in an identical way.

Fission-Product Procedures

1.	Procedure used in:	Rapid separation of short-lived selenium fission or spallation products
	Type of bombardment:	Neutron source
	Procedure by:	Del Marmol and Tigchelt[36]
	Degree of purification:	Radiochemically pure by gamma ray spectroscopy
	Equipment required:	Special apparatus described

Procedure:

An apparatus is developed in which 30% H_2SO_4 solution containing uranium, fission products and 0.1 mg Se carrier (as SeO_3^{-2}) is poured over 20 mesh zinc. Gaseous hydrides containing selenium form and are removed by vacuum and then bubbled through a solution of 5 ml H_2O and 1 ml 1 M $NaHSO_3$ containing 1 mg Se carrier. At the end of the burst (4 sec), the solution is drawn by vacuum through a AgCl precipitate and recovered for further study.

2. Procedure used in: Separation of ^{83}Se from fission products

Type of bombardment: Neutron source - reactor

Procedure by: Tomlinson and Hurdus[37]

Degree of purification: Radiochemically pure by gamma spectroscopy

Equipment required: Special gas apparatus

Procedure:

Method is based on exchange of H_2Se gas and aqueous selenite solutions and gives a chemical yield of 65% in 10 seconds with no contamination.

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PREPARATION OF RADIOACTIVE STANDARDS

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General Discussion

Standardization implies that the number of atoms in a source is measured. Therefore, in the case of radioactive material, it is necessary to obtain from the observed data the disintegration rate, since this is related to the number of atoms through the fundamental equation of radioactivity

$$\frac{-dN}{dt} = \lambda N$$

In this equation, N is the number of atoms and λ is the disintegration constant. The experimental data will consist of the counting rate of some sort of radiation emitted by the source, e.g., of the β^+, β^-, γ radiations which are actually registered by the detector. This counting rate may or may not be equal to the disintegration rate and if it is not, there must be sufficient information to convert it to this rate.

This conversion calls for the precise determination of the decay scheme of the radionuclide involved and the geometry of the counter. If the chosen radiation cannot be counted with 100% geometry, then it is essential to know what the geometry factor is so that the necessary correction can be made. Even when this has been done, however, the disintegration rate is only known if every disintegration of the material gives rise to the radiation being measured. If this is not so as, for example, in most gamma-ray measurements, then it is essential to have an accurate knowledge of the decay scheme so as to deduce the disintegration rate.

Methods Used for Most Nuclides

The foregoing factors lead to the conclusion that, for most beta emitters, the only reasonably easy standardization methods are $4\pi\beta$ counting, $4\pi\beta\gamma$ coincidence counting, and liquid scintillation counting.

$4\pi\beta$ counting has the advantage of being simple to do but the disadvantage that the preparation of the source has to be extremely carefully carried out. A thin film (usually of a plastic material, V.Y.N.S., of thickness approximately 10 $\mu g/cm^2$ rendered conducting by a thin gold coating), is prepared for use as the source mount. The radioactive nuclide must be spread evenly over a suitable area of this film. Even spreading is assisted by first drying onto the film a small amount of some suitable spreading agent, such as insulin. Preparation and use of such films has been clearly described by Pate & Yaffe[1-4] (the application to ^{63}Ni is described in the last procedure for Ni in this volume), and a review of the whole subject of source mounting has been given by Yaffe.[5] Even with all precautions taken, 4πβ counting begins to become inaccurate (i.e., to have errors greater than $\sim\pm 3\%$, 1σ) below beta energies of about 0.5 MeV and one of the other methods should be used if possible for such beta particles.

The 4πβγ coincidence method is not seriously dependent on making a good thin source and it can therefore be used for softer beta emitters. It is, of course, no use for those nuclides which do not emit a suitable gamma ray.

The liquid scintillation method is not dependent on source thickness at all, since the material is dissolved in the scintillator, but it does require that the solution can be made. More energy must be absorbed for a particle to be detected than for the other methods and so the efficiency drops off with beta energy, making it difficult to make absolute measurements on the lower energy nuclides unless special techniques are used.

Information on all the above techniques can be found in Ref. 6-9.

A most useful tool for standardization of radionuclides which emit electromagnetic radiation of 100 keV or more, is a Ge(Li) diode, connected to a pulse-height analyzer. This system may be calibrated over an energy range of 100 keV to several MeV by counting various energy gamma rays from commercially available standardized sources. This calibration will automatically take into account the intrinsic efficiency of the detector plus the solid angle, scattering, the attenuation factors for radiation of a certain energy. After the efficiency vs. energy curve has been established, it is only necessary to mount the isotope of interest in the same manner as the standards, usually a small spot on a thin support, select one or more suitable gamma rays, and begin counting. The resulting counts per minute are converted to photons per minute by use of the efficiency curve and finally to disintegrations per minute from a knowledge of the decay scheme. A real advantage to this method is that the source need not be beta-pure or even monoisotopic. For example, a mixture of ^{141,143,144}Ce can be standardized for ^{144}Ce without having to wait for the decay of the 141 and 143 isotopes, or separation of the Pr daughters. For thin, point sources this technique can be extended well below 100 keV, with some problems from increased attenuation in this region. Much below 20 keV, background problems, bremsstrahlung from β± emitters and air attenuation make some of the 4πβ counting techniques more attractive.

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ROUTINE ANALYSIS OF RADIOACTIVE SAMPLES BY GAMMA-RAY SPECTROSCOPY

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At about the same time the original monographs in this series were being issued, a new detector material for gamma-ray spectroscopy had just appeared. This material was lithium-drifted germanium. Today these detectors are still smaller in volume, therefore less efficient than sodium iodide, but they are capable of resolving gamma-rays which differ in energy by only about 1-keV (see the selenium addendum for examples). This inherent good resolution makes possible the detection and identification of the gamma emitting nuclides present in complex mixtures. Whereas, in the past, it has been necessary to make extensive radiochemical separations to determine the nuclide concentrations in such a sample, the potential now exists for making good measurements with very little purification, or in many instances, with no separations at all, simply by analyzing a Ge(Li) spectrum. When coupled with a large data acquisition and analysis system the Ge(Li) spectrometer is a powerful tool and has come into widespread use.

Among the advantages of direct analysis of radioactive mixtures by Ge(Li) spectroscopy are: 1) freedom from chemical exchange problems, 2) absence of chemical manipulation problems which could lead to loss of samples, 3) convenience and speed, 4) accuracy potentially as good as standard radiochemical methods, and 5) applicability to the analysis of radionuclides which have undesirable chemical characteristics such as high volatility. Disadvantages and limitations include: 1) the detector must be kept at liquid nitrogen temperatures, even in storage, 2) the low sensitivity requires either fairly active samples (about 1 μC) or long counting times, 3) many gamma-ray interferences occur in complex mixtures, 4) lack of knowledge of decay schemes may reduce applicability in some cases, 5) analysis is best done with the aid of large computers.

A detailed description of the Ge(Li) diode spectroscopy system used at Lawrence Livermore Laboratory Radiochemistry Division will be found in report UCRL-51061, Vols, 1-4, by R. Gunnick and J. Niday. The following brief outline of the system will hopefully serve to acquaint the potential user of Ge(Li) spectroscopy with some of the useful equipment, techniques, and applications.

The system at Livermore presently obtains and reduces data on about 6000 spectra per year. In order to do this efficiently the samples are counted with automatic sample changers controlled by a PDP-8 computer, and the spectra are taken with 4096 channel pulse-height analyzers and automatically stored on magnetic tape.

The large number of data channels and the complexity of the spectra has necessitated the development of a computer program, GAMANAL, which reduces and interprets the spectral data. The analysis can be considered in two parts, consisting first in the reduction of the spectral data into entities such as photopeak energies and intensities, followed by the quantative interpretation of these values in the analytic sense of disintegration rates, atoms or grams of specific nuclides or materials.

After initial input of the spectral information, GAMANAL locates the photopeak positions corresponding to total gamma-ray energy absorption and determines the peak areas above the Compton continuum. From these quantities gamma-ray energies and photon emission rates are calculated using supplementary information regarding energy and efficiency calibrations. These data are then interpreted analytically using a previously prepared library tape which provides organized and cross-indexed data on half-lives, parent-daughter relationships, exact gamma-ray energies and branching intensities, and selected gamma-ray associative relationships. In interpreting the spectrum, the program uses this library information to find a set of likely components which qualitatively characterize the observed peaks. A matrix of linear equations is then formed with one column for each identified component and one row for each observed peak. The coefficient for each term in the matrix is the appropriate gamma-branching probability which is obtained from the library. The matrix set of equations is solved by the method of linear least-squares and the answers are expressed in disintegrations per minute for each nuclide found.

The techniques for counting samples and the methods of data reduction and interpretation can be refined to the point where "wet" chemistry is no longer required for obtaining certain radioisotope information. As one example of the technique, the following fission products can be determined simultaneously to within 2-5% in a week-old unseparated sample containing about 10^{13} fissions: ^{95,97}Zr, ^{99}Mo, ^{103,106}Ru, ^{131}I, ^{132}Te, ^{140}Ba, ^{141,143,144}Ce, ^{147}Nd. In addition, several neutron activation products in the same mixture can often be determined. These include ^{88}Y, ^{182}Ta, ^{233}Pa, ^{239}Np, ^{237}U. As another example, the isotopic and total analysis of plutonium solutions can be done.[1] Crucial to this analysis of ^{238,239,240,241}Pu and ^{241}Am is the computer analysis of the complex 100-keV region. Instrumental neutron activation analysis for the determination of several elements simultaneously in a single sample is another area in which the Ge diode has found application.[2]

Gamma-ray spectroscopy of unseparated samples with Ge(Li) diodes is now an established technique, one which competes favorably with more classical methods of radiochemical analysis. For routine analysis of the major components of samples containing microcurie and greater levels of activity, it is probably the method of choice, all else being equal. There will continue to be areas where Ge(Li) spectroscopy is not the answer. For samples in the picocurie to microcurie range, a trade off will exist between long counting times vs. chemical processing. Samples which emit only very soft or no electromagnetic radiation will still remain in the province of the "wet" radiochemist.

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2. Zoller, W. H. and Gordon, G. E., <u>Anal. Chem.</u>, <u>42</u>, pp. 257-265 (1970). Editor's Note: This paper has some excellent examples of Ge(Li) detector gamma-spectra.

NUCLEAR SCIENCE ABSTRACTS

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