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NUCLEAR SCIENCE SERIES

The Radiochemistry of Magnesium

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The Radiochemistry of Magnesium

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Subcommittee on Radiochemistry
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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 establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This volume which deals with the radiochemistry of magnesium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of magnesium which might be included in a revised version of the monograph.

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I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF MAGNESIUM

"Magnesium", pp 219-242, Vol. I of The Chemical Elements and Their Compounds", N. V. Sidgwick, Oxford University Press, London, 1950.

"Magnesium", pp 249-397, Vol. IV of "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", J. W. Mellor, Longmans, Green and Co., London, 1923.

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"Magnesium", pp 528-553, Vol. I of "Scott's Standard Methods of Chemical Analysis", N. H. Furman, editor, 5th Edition, D. Van Nostrand Co., Inc., New York, 1939.

L. W. Neidrach, A. M. Mitchell and C. J. Rodden, pp 359-363. "Analytical Chemistry of the Manhattan Project", C. J. Rodden, editor-in-chief, McGraw-Hill Book Co., Inc., New York, 1950.

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[*] This report was prepared at the request of the Subcommittee on Radiochemistry of the Committee on Nuclear Science of the National Research Council as a contribution to a proposed master file on the radiochemistry of the elements.

II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF MAGNESIUM

"Production and Availability of Magnesium-28", L. G. Stang, N. D. Tucker, A. J. Weiss, and H.O. Banks, Jr., Brookhaven National Laboratory Report BNL 3138, 1956.

"Production of Mg^{28} in the Pile and Cyclotron at Harwell", C. E. Melish and G.W. Crockford, Internat. J. Appl. Rad. and Isotopes 1, 299 (1957).

III. ISOTOPES OF MAGNESIUM

The isotopes of magnesium which are known to exist[1] are tabulated in Table I. They range over the rather narrow mass interval from mass number 23 to 28. The isotope of mass number 22 has been reported[2] to have a half-life of 0.13 second, but its existence is doubtful. Isotopes of mass numbers 29 and 30 might have long enough half lives to be measureable, but there is no convenient way of synthesizing these nuclides at the present time, consequently their nuclear decay characteristics are unknown.

TABLE I. ISOTOPES OF MAGNESIUM

Isotope	Half Life	β Radiations	γ Radiations	Mode of Preparation
Mg^{23}	11.9 sec	2.95 Mev β^+	none	
Mg^{24}	stable-78.6%			
Mg^{25}	stable-10.1%			
Mg^{26}	stable-11.3%			
Mg^{27}	9.45 min	1.75 Mev β^- 58%	1.015 Mev	Mg^{26} (n, γ)
		1.59 Mev β^- 42%	0.834 Mev	Mg^{26} (d, p)
Mg^{28}	21.2 hr	0.42 Mev β^- 100%	1.34 Mev 70% 0.40 30% 0.94 30% 0.031 100%	Li^6 + Mg^{26} alloy + thermal n; Al^{27} (α, 3p); spallation
Al^{28*}	2.3 m	2.87 Mev β^- 100%	1.78 Mev100%	

* daughter of Mg^{28}

The principle radioisotope of magnesium, from the point of view of a tracer, is Mg^{28}. Its half-life of 21.2 ± 0.1 hours is long enough for many purposes, but not really as long as one would like. For continued experimentation a given supply of tracer will have decayed to practically nothing in a week or two and a fresh supply must then be procured. The tracer is relatively expensive and this makes for costly experimentation.

There are several methods available for synthesizing Mg^{28}. These include high energy spallation reactions[3-11] on elements heavier than magnesium, bombardment of magnesium[3] or aluminum[12] targets with moderate-energy helium ions, and by the Mg^{26} (H^3, p) Mg^{28} reaction in a nuclear reactor,[10, 13] where the H^3 projectiles come from the Li^6 (n, H^3) He^4 reaction.

Production of Mg^{28} by spallation reactions in high energy accelerators has the virtue that the Mg^{28} can, theoretically at least, be obtained carrier-free. However there are a number of practical drawbacks: the low cross-sections for the spallation reactions leading to Mg^{28}, the formidable radiochemical procedures which would be necessary for a high degree of radiochemical purity, and the difficulty and cost of bombardments in high energy accelerators. Owing to these difficulties, Mg^{28} is presently made for tracer purposes almost exclusively in nuclear reactors.

Synthesis of Mg^{28} by neutron irradiation of a lithium-magnesium mixture means that the radioisotope is unavoidably diluted with magnesium. At the present time the sole sommercial supplier of Mg^{28} in the United States, the Hot Laboratory Division of the Brookhaven National Laboratory, supplies Mg^{28} at a specific activity of 50 microcuries of equilibrium Mg^{28} - Al^{28} containing not more than 0.1 g of magnesium. The Mg^{28} content at time of shipment is normally 50 - 100 microcuries to allow for radioactive decay during shipment. The price per 50 microcurie unit at the present time is $70, plus a handling charge of $30 per shipment.[14] Early in 1961 the Brookhaven Laboratory will begin supplying Mg^{28} which will have approximately a 20-fold higher specific activity. The use of magnesium enriched in Mg^{26} in the neutron-irradiated lithium-magnesium alloy will be responsible for the increased specific activity.

The radioisotope Mg^{27}, with a 9.45 minute half-life, is too short-lived to be of much practical use as a tracer. However, its formation by the (n, γ) reaction on stable Mg^{26} means that this radioisotope is potentially useful in activation analysis for magnesium.[15,16] The low cross section[17] for absorption of a thermal neutron by Mg^{26}, 0.026 barn, coupled with the low abundance of Mg^{26} and the need for speed in separating magnesium from the irradiated sample in a radiochemically pure form, are limitations on the usefulness of this technique.

IV. REVIEW OF THE CHEMISTRY OF MAGNESIUM OF INTEREST TO RADIOCHEMISTS

1. General Remarks

In the opinion of the author, magnesium does not have a well-developed radiochemistry. The reason for this is fairly clear: until the radioisotope Mg^{28} was discovered[3] in 1953, the 9.3 minute Mg^{27} was the longest-lived magnesium radioisotope which was known and this short a half-life makes Mg^{27} impractical as a tracer. During the time that radiochemical techniques were being developed for the other members of the alkaline earth family, because they possessed suitably long-lived radioisotopes, magnesium was largely neglected.

Since Mg^{28} became available its use has been growing steadily and rapidly, mainly in the field of biological research.[18-26] In a few instances it has been applied to studies of a chemical nature,[27-30] with notable success. Considering the ubiquitous nature of magnesium, in the crust of the earth, the oceans, as an important element in chlorophyll, hence of biological systems, and as a metal of commerce, one might imagine that there would be a great need for and interest in a long-lived tracer for so important an element. While the half-life of Mg^{28} is less than ideal, it is nevertheless a practical tracer for magnesium. It is to be hoped that its usefulness will continue to grow and that it will be applied to many more of these areas than has been the case until now.

2. Soluble Salts of Magnesium

The common salts of magnesium which are freely soluble in water include the acetate, benzoate, bromate, bromide, chlorate, perchlorate, chloride, chromate, citrate, ferrocyanide, iodate, iodide, lactate, permanganate, molybdate, nitrate, sulfate, sulfite and thiosulfate. In addition to these there are numerous other salts which are soluble in acidic solutions or in the presence of ammonium salts. Examples of these include the carbonate and the hydroxide in the presence of ammonium ion, and the arsenate and oxalate, which are soluble in acid or in the presence of a high concentration of ammonium salts. In general, magnesium has very few truly insoluble compounds, and even the moderately insoluble ones, such as the fluoride, which is soluble to the extent of 8 mg/100 ml of water, are too soluble for the purposes of radiochemical separation, considering the amounts of magnesium carrier which are usually used.

3. Insoluble Salts of Magnesium

There are five compounds of magnesium which are sufficiently insoluble under the conditions of their precipitation to make them useful in radiochemical separations of magnesium. These are the hydroxide, when precipitated by strong alkali; $MgNH_4PO_4 \cdot 6H_2O$, when precipitated by $HPO_4^{=}$ ion in the presence of ammonium salts; the chelate compound of magnesium with 8-hydroxyquinoline (oxine); the oxalate, when precipitated under rather special conditions; and the carbonate, when precipitated by alkali carbonate or by ammonium carbonate from ethanol solution.

TABLE II. SPARINGLY SOLUBLE COMPOUNDS OF MAGNESIUM

Compound	Solubility in 100 ml H_2O	Other Solvents
$Mg(OH)_2$ ✓	0.9 mg	acids, NH_4^+ salts
MgF_2	7.6 mg	HNO_3, H_3BO_3 solution
$MgCO_3$	10.6 mg	acids, aq. CO_2
$Mg_2C_2O_4 \cdot 2H_2O$	70 mg	acids, $(NH_4)_2C_2O_4$ solution
Mg-oxinate $\cdot$ $2H_2O$*	insoluble	acids
$MgNH_4PO_4 \cdot 6H_2O$	6.5 mg	acids, insol. dil. NH_4OH

* oxine = 8-hydroxyquinoline

In addition to these five magnesium forms relatively insoluble precipitates with the higher fatty acids, lauric, myristic, palmitic and stearic, for example, a fact which is made use of in the determination of magnesium (and calcium also) by titration with soap solutions[31].

From the solubility product constant of $Mg(OH)_2$, 3.4×10^{-11}, it is easy to show that $Mg(OH)_2$ will not be precipitated by an NH_4OH-NH_4^+ buffer solution. However, addition of NaOH solution to a OH^- ion concentration of only 0.001 M will suffice to precipitate macro amounts of magnesium essentially quantitatively. The formation of a radiocolloid by tracer magnesium in strong NaOH solution has been used in the separation of carrier-free magnesium[32]. Insoluble hydroxides, such as $Fe(OH)_3$ are therefore good carriers for magnesium when precipitated from strongly basic solutions.

Precipitation of $MgNH_4PO_4 \cdot 6H_2O$ is a standard analytical method for magnesium. The precipitate is granular, and therefore easily filtered, and may be ignited to the pyrophosphate, $Mg_2P_2O_7$, for weighing. The precipitation is carried out by adding an excess of $(NH_4)_2HPO_4$ to the acidified solution containing magnesium. The solution is then made alkaline with NH_4OH, cooled, and allowed to stand, preferably for some hours, to permit formation of the precipitate. The precipitate, after filtration, is washed with dilute NH_4OH to prevent hydrolysis, and subsequent dissolution, of the precipitate.

Precipitation of magnesium by 8-hydroxyquinoline has the virtues that the precipitation is essentially quantitative and under certain conditions may be precipitated in the presence of strontium and barium without the latter species coprecipitating to an appreciable extent[33]. Calcium coprecipitates with magnesium but can be dissolved from the precipitate with dilute acetic acid. A better method than this one for separating magnesium from the other alkaline earths is by cation exchange resins (see part 6).

The procedure for precipitation of magnesium with oxine from solutions containing no interfering ions is as follows[33]. The solution containing magnesium is made alkaline with ammonia and the solution is heated to 70-80° C. A 1% solution of oxine in 2 N acetic acid is added slowly until present in slight excess as shown by the yellow color of the solution. After digesting for 10 minutes the precipitate may be filtered, washed with water and dried at 105° C. The precipitate under these conditions has the formula $Mg(C_9H_6ON)_2 \cdot 2H_2O$ and is 6.98 percent Mg by weight.

Under rather special conditions magnesium oxalate can be precipitated as a densely crystalline precipitate of $MgC_2O_4 \cdot 2H_2O$. The recommended procedure[34] is to start with the magnesium dissolved in 15 ml of water in a 250 ml beaker. Add 75 ml of glacial acetic acid, and when solution is complete add 10 ml of glacial acetic acid containing 1 gram of ammonium acetate. Finally add 1.5 ml of ethyl oxalate and stir thoroughly. Cover the beaker with a watch glass, heat the solution to 100° C and keep it hot for 2-3 hours after precipitation of magnesium begins. As a precautionary measure, in case the proper temperature has not been maintained, add, 15 minutes before filtration, 5 ml of 85% acetic acid saturated with ammonium oxalate at room temperature. Filter the precipitate and wash with warm (70-80° C) 85% acetic acid. Dry at 105° C to constant weight.

Magnesium is not precipitated by ammonium carbonate from aqueous solutions containing ammonium salts, but does yield a precipitate with alkali carbonate. In the latter case the precipitate contains a mixture of magnesium carbonate hydrates and the double carbonate with the alkali metal. For gravimetric determination the carbonate is precipitated with ammonium carbonate from alcohol solution. The procedure[35] is as follows: saturate with ammonium carbonate a mixture in the proportion by volume of 18 ml NH_4OH, 75 ml water and 95 ml of 95% ethanol. To the magnesium dissolved in a volume of 50 ml add 50 ml of 95% ethanol and 50 ml of the prepared reagent. Stir for 5 minutes and let the mixture stand for 20 minutes. Filter and ignite the precipitate to MgO.

4. Formation of Complexes by Magnesium

The small size and double charge on the magnesium ion is conducive to complex formation. The formation of hydrates is a case in point. Most magnesium salts crystallize from aqueous solutions with several molecules of water of crystallization. One of the strongest drying agents known, $MgClO_4$, owes its dehydrating power to the strong tendency of magnesium to form hydrates.

Numerous chelating agents form complexes with magnesium. The salt of magnesium with 8-hydroxyquinoline has already been mentioned (part 3). Numerous other organic chelating agents have found use in the colorimetric determination of magnesium[36].

The formation constants for several magnesium complexes are tabulated in Table III.

5. Separation of Magnesium by Solvent Extraction

The anhydrous magnesium halides are readily soluble in a variety of oxygenated organic solvents (alcohols, ketones, ethers) owing to coordination of the magnesium to the oxygen of the solvent. These compounds are not stable in the presence of water, however, owing to the much stronger tendency of magnesium to form hydrated complexes, and solvent extraction of these species from aqueous solution is not possible.

The author was unable to uncover any solvent extraction procedures for magnesium.

6. Ion Exchange Behavior of Magnesium

TABLE III. FORMATION CONSTANTS FOR SOME MAGNESIUM COMPLEXES

Complexing Agent	Log K*	Ionic Strength	Reference
EDTA	8.69	0.1	a
oxalate	3.43	0	b
	2.65	0.07	c
	2.55	0.2	d
malonate	2.80	0	b
	2.52	0.04	e
	2.06	0.07	c
	1.91	0.2	
succinate	0.98	0.07	c
	1.20	0.2	d
r-tartrate	1.36	0.2	d
sulfate	2.20	0	b
trimetaphosphate	3.34	0	f
ammoniatriacetic acid	7.00	0	g
	5.41	0.1	h
8-hydroxyquinoline	4.7	0	i
(oxine)	−15.55 (1)	0	i

* Formation constant for $Mg^{++} + A^{-n} \rightleftarrows MgA^{-n+2}$

1) Solubility produce constant for $Mg(oxinate)_2$.

a. G. Schwarzenbach and H. Ackerman, Helv. Chim. Acta 31, 1029 (1948).

b. R.W. Money and C.W. Davies, Trans. Faraday Soc. 28, 609 (1932).

c. H.S. Simms, J. Phys. Chem. 32, 1121 (1928).

d. R.K. Cannon and A. Kibrick, J.A.C.S. 60, 2314 (1938).

e. D.I. Stock and C.W. Davies, J. Chem. Soc. 1949, 1371.

f. H.W. Jones, C.B. Monk and C.W. Davies, ibid., 1949, 2693.

g. G. Schwarzenbach, E. Kampitisch and R. Steiner, Helv. Chim. Acta 28, 828 (1945).

h. G. Schwarzenbach, H. Ackermann and P. Ruckstuhl, ibid. 32, 1175 (1949).

i. R. Nasanen, Acta Chem. Scand. 6, 352 (1952).

Magnesium is strongly absorbed from solutions of near-neutrality by cation exchange resins. The magnesium may be eluted from the resin by a complexing agent or by acid.

Milton and Grummitt studied the separation of the alkaline earth elements by means of Dowex-50 and the eluting agents ammonium lactate, ammonium citrate or hydrochloric acid. The use of ammonium lactate gave a somewhat cleaner separation of magnesium than was obtained using HCl. However, the ease of recovery of magnesium from the HCl effluent makes it the more desirable eluting agent. Their results using HCl are shown in Figure 1.[37]

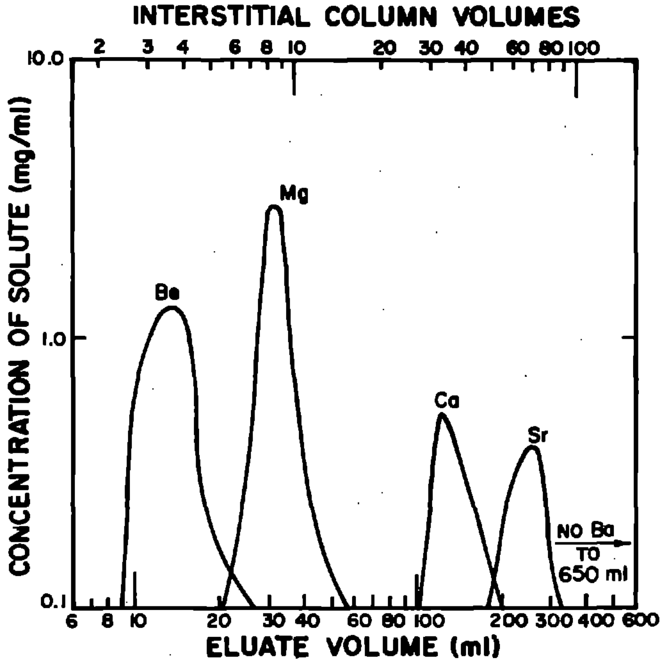

Figure 1. The separation of beryllium, magnesium, calcium, and strontium by cation exchange using 1.5 M HCl eluant. Dowex 50 column 1.1 x 8 cm, flow rate 1.0 ml/min, T = 60° C. Data of Milton and Grummitt, reference 37.

A similar study of the separation of magnesium from calcium using Dowex 50 and dilute HCl as the eluting agent has been reported by Campbell and Kenner.[38]

In the determination of the magnesium content of bone it is necessary to remove interfering ions derived from bone which are present along with the magnesium. Breibert, Lee, McCoord and Forbes[26] have described an ion exchange method for isolating magnesium from bone ash free of phosphorus, sodium and calcium. A typical elution curve for bone ash solution passed through a Dowex 50 column and eluted with 0.7 N HCl is shown in Figure 2.

Anion exchange has also been used to separate magnesium from the other members of the alkaline earths. Nelson and Kraus[39] have used Dowex 1 and ammonium citrate as the complexing agent to effect the separation. The separation of magnesium from beryllium is not perfectly clean, but magnesium is readily separated from the other members of the group.

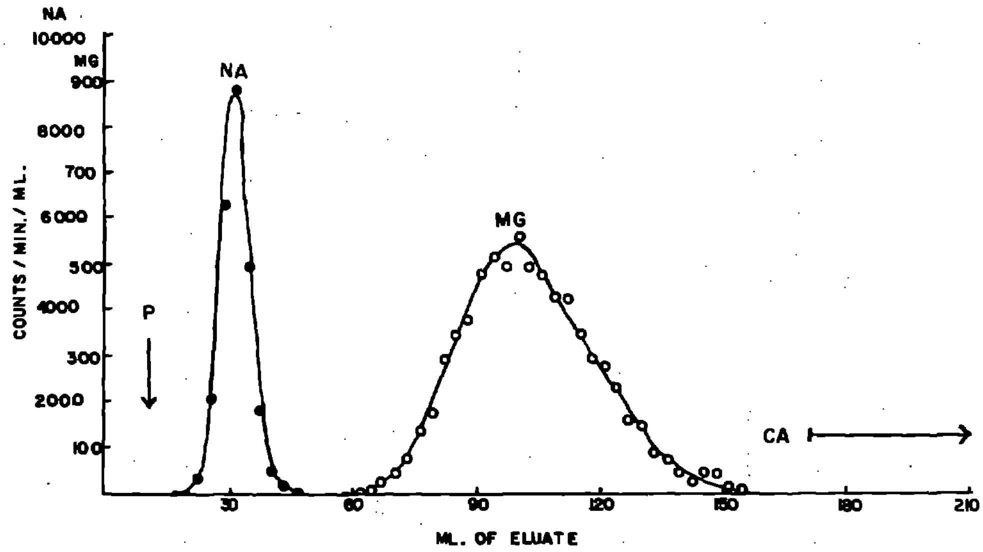

Figure 2. A study of the isolation of magnesium from bone ash solution using tracers for Mg and Na and Dowex 50 resin, 50-100 mesh, in a column 0.5 x 37 cm. An amount of bone ash solution, equivalent to 50-80 mg of dry bone ash, in dilute HCl was passed through the column. The absorbed ions were then eluted with 0.7 N HCl at a flow rate of about 0.7 ml/min. Data of reference 26.

Kraus and coworkers[40] have made extensive studies of the anion exchange behavior of the metals in chloride solutions. A large number of elements are absorbed from HCl solutions by Dowex 1 resin but magnesium is not absorbed from any of these solutions. This fact is useful in magnesium separations, for example where iron has been used as a carrier for magnesium in hydroxide precipitations it may later be removed by absorption on Dowex 1 from strong HCl solution allowing magnesium to pass through.

Examples of the application of ion exchange to the radiochemical separation of magnesium will be given in the compilation of procedures in part VII.

V. PROCEDURES FOR DISSOLVING THE SAMPLE

Since magnesium has only one oxidation state +2, and since most of its compounds are soluble in acid solution carrier-tracer exchange should be complete in acid solution. It is by no means obvious that carrier-tracer exchange would not occur in basic solution. However, there are very few materials which are completely soluble in basic solution. Traces of iron and other impurities which are insoluble and which would tend to occlude radiocolloids of magnesium tracer make carrier-tracer exchange of magnesium problematical under these conditions. Exchange is better carried out in acid solution.

In isolating magnesium from a given material with the aid of magnesium carrier, therefore, it is only necessary to add the carrier and render the material soluble in acid before beginning the separation. This may not always be a trivially easy problem, and several steps may be needed to accomplish it.

Obviously there are a great many materials from which it might conceivably be desired to isolate magnesium, and consequently detailed procedures for dissolving samples are not practical. However, for a few typical examples see Part VII.

VI. COUNTING PROCEDURES FOR MAGNESIUM

Both radioisotopes of magnesium, 9.45 m Mg^{27} and 21.2 h Mg^{28} decay by β - γ emission (see Table I), and they may therefore be counted either by β counting or by γ counting. Mg^{28} has the added feature that it decays to a 2.3 minute Al^{28} daughter, which also decays by β and γ emission. The short half-life of Al^{28} assures that parent and daughter be in secular equilibrium within a few minutes of the time that Mg^{28} eparated from Al^{28} daughters.

For the counting of Mg^{27} the short half-life suggests that γ counting ld be best. The reason is simply that γ counting could be done with uid sample isolated as quickly as possible, whereas to β count this ies it would be necessary to prepare the magnesium in a dry, solid n. This would take additional time, and the sample would be weaker ng to its radioactive decay.

A further consideration which suggests that Mg^{27} be detected by γ nting is the possibility of pulse height analysis of the detected γ rays. en becomes possible selectively to count a particular γ ray component ch is characteristic of Mg^{27}. This possibility is particularly attractive re Mg^{27} is used in neutron activation analysis for magnesium. Here re are numerous possibilities for radioactive contaminants of the lated magnesium fraction. Gamma counting with pulse height analysis es an additional means of identifying the radioactive species being nted, a feature which β counting does not have.

For the counting of Mg^{28} samples it is a matter of taste, or perhaps he equipment which is available. Beta counting of solid samples would perfectly adequate, although the simplicity of γ counting, from the point view of preparation of the counting sample and the relative insensitivity the method to the weight of material in the sample, makes the latter attractive method. Of course in γ counting of samples it may still necessary to determine the total quantity of magnesium present. is can either be done gravimetrically, or for routine assay one of the lorimetric methods for magnesium might prove more suitable.

The rather energetic β rays of both Mg^{28} and Al^{28} give assurance t in the β counting of solid samples self-absorption and self-scattering the sample combine to give an apparent specific activity of the sample ich is independent of sample thickness[41] for samples thicker than about mg/cm^2 up to thicknesses at least as thick as 20 mg/cm^2.

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR MAGNESIUM

PROCEDURE 1

Separation of Mg^{28} from Tantalum Bombarded with 340 Mev Protons

Source - W. E. Nervik, UCRL-2542 (1954)

A procedure for isolating Mg^{28}, formed as a spallation product, from a complex mixture of spallation and fission products. The procedure could be adapted without much modification to almost any medium-to-heavy element target bombarded with high energy particles.

Step 1. Dissolve the tantalum target in concentrated HF-HNO_3. Add 10 mg Mg carrier. Add CeIII carrier and centrifuge the precipitated rare-earth fluorides from the solution.

Step 2. Make the solution 18 N in H_2SO_4 and extract tantalum by shaking with di-isopropyl ketone.

Step 3. Evaporate the aqueous phase almost to dryness. Dissolve the residue in 30 ml water and add 3 mg FeIII carrier. Precipitate $Fe(OH)_3$ by making the solution basic with NH_4OH. Centrifuge and discard the precipitate.

Step 4. Add 10 mg Cu carrier and pass in H_3S. Centrifuge and discard the precipitated sulfides.

Step 5. Adjust the acidity of the solution to pH 4 with acetic acid, add 1 mg each Ca, Sr and Ba carriers, followed by 1 ml saturated oxalic acid solution. Centrifuge and discard the precipitated oxalates.

Step 6. Repeat step 5 twice more.

Step 7. Evaporate the solution almost to dryness, add concentrated HNO_3 and heat to destroy oxalate. Dilute with water, make the solution basic with NH_4OH and add excess $(NH_4)_2HPO_4$ to precipitate Mg. Centrifuge and wash the precipitate with dilute NH_4OH.

Step 8. Dissolve the precipitate in a minimum of concentrated HCl, dilute to about 0.1 M in HCl and pass through a 2 mm x 10 cm Dowex 50 column. Wash the column with water and discard the effluent.

Step 9. Strip the Mg absorbed on the column by passing 6 N HCl through the column. Repeat the procedure beginning with step 3.

Step 10. Evaporate the 6 N HCl effluent from the second column separation almost to dryness, dilute with water, make the solution basic with

NH_4OH and precipitate Mg with excess $(NH_4)_2HPO_4$. Filter and wash the precipitate twice with dilute NH_4OH and twice with ethanol. Ignite the precipitate at 1300° F and weigh as $Mg_2P_2O_7$.

PROCEDURE 2

Separation of Mg^{28} from Lead Bombarded with 0.6 to 3.0 Bev Protons

Source - R. L. Wolfgang, E.W. Baker, A.A. Caretto, S.B. Cumming, G. Friedlander and J. Hudis, Phys. Rev. <u>103</u>, 394 (1956).

The following procedure, derived from an outline, will separate Mg^{28} from a complex mixture of spallation and fission products. The procedure could be adapted without much modification to almost any medium-to-heavy-element target bombarded with high energy particles.

<u>Step 1.</u> Dissolve the lead target in 6 N HNO_3 and add 10 mg each of Mg and P carriers. Boil the solution 5 minutes and then add excess Zr to precipitate the phosphate. Centrifuge and discard the precipitate.

<u>Step 2.</u> Add Cd and Mo carriers, neutralize excess acid and precipitate with H_2S. Centrifuge and discard the precipitated sulfides.

<u>Step 3.</u> Boil the solution to expel H_2S. Acidify with a few drops concentrated HCl, add 1-2 mg FeIII carrier and make basic with NH_4OH. Centrifuge and discard the precipitate of $Fe(OH)_3$.

<u>Step 4.</u> Repeat the scavenging with 1-2 mg FeIII in ammoniacal solution twice more.

<u>Step 5.</u> Evaporate the solution to near dryness. Take up in 9 N HCl and pass the solution through a 0.5 x 10 cm column of Dowex 1 anion exchange resin. Rinse the column with 9 N HCl.

<u>Step 6.</u> Adjust the acidity of the effluent from the column to 0.3 M (note 1). Add 10 mg Cu carrier and precipitate with H_2S. Centrifuge and discard the precipitate.

<u>Step 7.</u> Boil the solution to expel H_2S. Add 1-2 mg FeIII carrier and make the solution basic with NH_4OH. Centrifuge the precipitate.

<u>Step 8.</u> Evaporate the solution to dryness, add 2-3 ml of HNO_3 and fume to dryness once more to remove ammonium salts. Dissolve the residue in 10 ml of water and add to the solution 10 ml of 95% ethanol. Precipitate the magnesium by adding 10 ml of a reagent made by combining

in the proportion by volume of 18 parts NH_4OH, 75 parts of water and 95 parts 95% ethanol and saturating this mixture with $(NH_4)_2CO_3$. Centrifuge the precipitate of $MgCO_3$.

Step 9. Dissolve the $MgCO_3$ in a minimum of concentrated HCl. Add 10 mg each Ba and Sr carriers. Evaporate the solution to 2-3 ml. Add 10 parts of fuming HNO_3 and chill in an ice bath. Centrifuge and discard the precipitated nitrates of Ba and Sr. Add more Ba and Sr carriers and again chill the mixture. Centrifuge and discard the precipitate.

Step 10. Transfer the fuming HNO_3 supernatant solution to an Erlenmeyer flask and evaporate the solution almost to dryness. Take up the residue in water. Add 10 mg of Ca carrier, make the solution slightly basic with NH_4OH and precipitate the Ca with $(NH_4)_2C_2O_4$. Centrifuge and discard the precipitate.

Step 11. Add more NH_4OH and precipitate the Mg with $(NH_4)_2HPO_4$. Filter the precipitate, wash with dilute NH_4OH and alcohol, dry and count. Ignite to $Mg_2P_2O_7$ for determination of chemical yield.

NOTES

Note 1. Methyl violet is a convenient indicator for adjusting the acidity of the solution.

PROCEDURE 3

Purification of Mg^{28} Tracer Produced in Neutron-Irradiated Li-Mg Alloy

Source - C.E. Melish and G.W. Crockford, Internat. J. Appl. Rad. and Isotopes 1, 299 (1957).

The principal impurities in neutron-irradiated Li-Mg alloy are Na^{24}, Zn^{65}, Cu^{64}, and Mn^{56}.

Step 1. Dissolve the Li-Mg alloy in dilute HCl. Add Zn, Cu and Mn carriers. Make the solution basic with NH_4OH and precipitate with H_2S. Centrifuge and discard the precipitate.

Step 2. Repeat the H_2S scavenging with Zn, Cu and Mn carriers twice more. Filter the supernatant liquid from the last scavenging through a fine porasity filter paper.

PROCEDURE 3 (Continued)

3. Make the solution strongly basic with NaOH. Centrifuge the ecipitate and discard the aqueous phase.

4. Dissolve the precipitated $Mg(OH)_2$ in dilute HCl. Reprecipitate e Mg a second time with NaOH. Centrifuge the precipitated Mg and scard the aqueous phase. The precipitate of $Mg(OH)_2$ should now free of radioactive contaminants. (Note 1).

NOTES

1. The radiochemical purity of the magnesium tracer at this point ill of course depend upon the chemical purity of the Li-Mg alloy which as used.

PROCEDURE 4

fication of Mg^{28} Tracer Produced in Neutron-Irradiated Li-Mg Alloy

ce - L.G. Stang, Jr., W.D. Tucker, A.J. Weiss, and H.O. Banks, Jr., Brookhaven National Laboratory Report BNL-3138, 1956.

procedure, used for the production of Mg^{28} tracer in the United s, is somewhat different from Procedure 3, which is the one used in t Britain. The procedure takes about 2 hours and the recovery is 95%.

1. Dissolve the foil of Li-Mg alloy in water and centrifuge the esultant precipitate of $Mg(OH)_2$. Discard the aqueous phase and wash e precipitate with ice water.

2. Dissolve the $Mg(OH)_2$ precipitate in concentrated HCl, add F rrier and boil to expel F^{18}.

3. Add NaCl to the solution and continue to evaporate the solution. dd equal volumes of concentrated HCl and ethanol, chill in an ice bath, d filter the precipitated NaCl.

4. Dilute the filtrate with water and add 2-3 mg FeIII carrier. ake the solution just basic to bromcresol green indicator with NaOH. entrifuge and discard the precipitate of $Fe(OH)_3$.

5. Add excess NaOH to precipitate $Mg(OH)_2$. Chill the solution and entrifuge the precipitate. Discard the aqueous phase and wash the recipitate twice with ice water. The precipitate may now be dissolved in any acid for further use. (Note 1.)

NOTES

Note 1. The material obtained by this procedure is said to contain a trace of H^3 impurity, derived from the $Li^6(n,H^3)He^4$ reaction on the lithium of the target, and very small amounts of F^{18} and Fe^{59}. The F^{18} impurity decays with a half-life of 112 minutes, Fe^{59} with a half-life of 45 days. Of course the chemical purity of the Li-Mg alloy is important in determining what other impurities might be present also.

PROCEDURE 5

Separation of Carrier-Free Mg^{28} from High Energy Proton-Bombarded KCl Targets

Source - C.E. Melish and G.W. Crockford, Internat. J. Appl. Rad. and Isotopes 1, 299 (1957).

Mg^{28} is produced as a spallation product along with F^{18}, Na^{24}, Si^{31}, P^{32}, S^{35}, K and Cl activities in bombardments of KCl targets with protons of energy in excess of 60 Mev.

Step 1. Dissolve the target in 10% HNO_3 and boil 5 minutes to oxidize Si, P and S activities. Add several grams of Na_2HPO_4 and a few mg of FeIII carrier. Make the solution alkaline with NH_4OH and centrifuge the precipitate. Discard the aqueous phase.

Step 2. Dissolve the $Fe(OH)_3$, which carries the Mg^{28} tracer, in dilute HCl. Reprecipitate the Fe and Mg^{28} tracer by making the solution strongly basic with NaOH. Centrifuge the precipitate and discard the aqueous phase.

Step 3. Dissolve the precipitate in 0.05 N HCl and pass the solution through a column of Zeocarb 225 cation exchange resin (note 1). Wash the column with several volumes of 0.05 N HCl. Finally strip the Fe and Mg^{28} tracer from the column with 6 N HCl. Evaporate this effluent to dryness.

Step 4. Take the residue up in 10 N HCl and pass the solution through a short column of DeAcidite FF anion exchange resin (note 2). Rinse the column with 10 N HCl. The effluent, which contains the Mg^{28} in a carrier-free form, may now be evaporated to dryness for recovery of the tracer.

NOTES

Note 1. Dowex 50 or equivalent American-made cation exchange resin may be substituted for this particular resin.

Note 2. Dowex 1 or equivalent American-made anion-exchange resin may be substituted for this particular resin.

PROCEDURE 6

Separation of Carrier-Free Mg^{28} from High Energy Proton-Bombarded NaCl Targets

Source - M. Lindner, Phys. Rev. 91, 642 (1953).

Mg^{28} tracer is separated carrier-free from other spallation products by a procedure which is somewhat similar to Procedure 5.

Step 1. Dissolve the NaCl target (note 1) in water. Add about 1 mg FeIII carrier and make the solution basic with NaOH. Centrifuge the precipitate, discarding the solution.

Step 2. Dissolve the precipitate of $Fe(OH)_3$ containing the Mg^{28} tracer in 6 N HCl. Add 1 mg phosphoric acid and an amount of Zr in slight excess of that required for complete precipitation of the phosphate. Centrifuge and discard the precipitate.

Step 3. Make the supernatant solution 10 N in HCl and then pass the solution through a short column of Dowex 2 anion exchange resin. Rinse the column with 10 N HCl.

Step 4. Evaporate the HCl effluent to dryness. Take up the residue in water and pass the solution through a short column of Dowex 50 cation exchange resin. Elute the Mg^{28} tracer with 0.5 N HCl.

Step 5. Evaporate to dryness that fraction of the HCl effluent which contains the Mg^{28} tracer.

NOTES

Note 1. The use of KCl target in place of NaCl yields about 10% more Mg^{28} owing to the formation of Mg^{28} by spallation of the potassium of the target (cf. Reference 10), but it also introduces more radioactive impurities. For the carrier-free separation of Mg^{28} from KCl target see Procedure 5.

PROCEDURE 7

Activation Analysis for Mg in Blood Cells and Blood Plasma

Source - R.A. Schmitt, D.A. Elehy and D. Goghor, General Atomic, (unpublished). Communicated by R.A. Schmitt.

Magnesium, along with zinc, manganses and copper, are determined in blood or blood plasma by neutron activation analysis. Only that portion of the procedure pertaining to magnesium is given.

Step 1. Irradiate about 3 ml of blood or about 3 ml of plasma and Mg standard. Transfer the specimen for irradiation into a 2 dram polyvial (about 7 ml capacity). Rince the specimen tube with about 3 ml conductivity water ($> 8 \times 10^6$ ohm resistivity) into the polyvial. Pipette 2 ml of Mg standard, containing approximately 2 mg of magnesium into a separate 2 dram polyvial. Bring volume of standard to volume of blood or plasma specimen. Place in reactor (Note 1), rotate specimen rack at 1 rpm and irradiate at a flux of about 2×10^{12} neutrons/cm^2· sec for 20 minutes. Remove sample promptly after irradiation.

Step 2. Transfer the Mg standard into an unirradiated 2 dram polyvial.

Step 3. Transfer the blood or plasma to a test tube containing Mg carrier, about 10 mg, and carriers for Cu, Zn and Mn. Swirl and stir the solution to homogeneity and complete "laking", then let stand for about 5 minutes to ensure complete carrier-tracer exchange.

Step 4. Add 15 drops concentrated HCl slowly to make about 2 N and to precipitate blood protein. Stir until all protein has precipitated. Centrifuge and decant the solution.

Step 5. Add about 3 ml 12 N NaOH to precipitate $Mg(OH)_2$. Centrifuge (Note 2).

Step 6. Dissolve the precipitate with 10 drops concentrated HCl. Dilute to about 10 ml. Make basic with 3 ml 12 N NaOH. Centrifuge and decant the solution.

Step 7. Dissolve the precipitate in 10 drops concentrated HCl. Dilute to 8 ml and add 10 drops 2 M NH_4Cl solution. Add 6 N NH_4OH until pH paper indicates neutrality and then 3 drops in excess. Heat the solution gently.

Step 8. Add 20 drops saturated $(NH_4)_2S$ solution. Swirl for 1 minute to precipitate MnS and CuS. Centrifuge. Decant the solution through a fine porosity filter paper (Note 3).

Step 9. To the filtrate add 2 ml of 12 N NaOH to precipitate $Mg(OH)_2$. Centrifuge and decant the solution.

Step 10. Dissolve the $Mg(OH)_2$ with 6 drops concentrated HCl. Dilute to about 10 ml. Add 10 drops Cu carrier (about 10 mg/ml), swirl and add about 5 ml Mannitol (20 g/100 ml H_2O) and 2 drops indicator. Make basic with 12 N NaOH and add 5 drops of 12 N NaOH in excess to precipitate $Mg(OH)_2$. Centrifuge and discard the solution.

Step 11. Repeat step 9.

Step 12. Dissolve the precipitate of $Mg(OH)_2$ in 6 drops concentrated HCl. Dilute to 4 ml. Filter through a fine porosity filter paper into a 2 dram vial. Bring volume to that of the irradiated Mg standard.

Step 13. Count the 843 kev γ ray of Mg^{27} between 790 kev and 890 kev with a γ ray spectrometer.

Step 14. After decay of Mg^{27}, determine the chemical yield by precipitation with 8 hydroxyquinoline after treating the solution with hot ammonium oxalate to remove Ca as calcium oxalate (Note 4).

NOTES

Note 1. The authors of this procedure use a TRIGA reactor operating at a power level of 250 kw. Separate standards for Cu, Mn and Zn would be irradiated also, if these elements are to be determined.

Note 2. If Zn is to be determined also, this solution is saved for later analysis for Zn.

Note 3. The precipitate may be analyzed separately later for Cu and Mn, if desired.

Note 4. See Section IV, Part 3 for the procedure for gravimetric determination of Mg as the oxinate.

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