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NUCLEAR SCIENCE SERIES

The Radiochemistry of Magnesium
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The Radiochemistry of Magnesium

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January 1961
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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The Radiochemistry of Magnesium*

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


* 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


III. ISOTOPES OF MAGNESIUM

The isotopes of magnesium which are known to exist 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 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 measurable, but there is no convenient way of synthesizing these nuclides at the present time, consequently their nuclear decay characteristics are unknown.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half Life</th>
<th>β Radiations</th>
<th>γ Radiations</th>
<th>Mode of Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{23}$</td>
<td>11.9 sec</td>
<td>2.95 Mev β$^+$</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Mg$^{24}$</td>
<td>stable-78.6%</td>
<td>1.75 Mev β$^-$</td>
<td>1.015 Mev</td>
<td>Mg$^{26}$ (n, γ)</td>
</tr>
<tr>
<td>Mg$^{25}$</td>
<td>stable-10.1%</td>
<td>1.59 Mev β$^-$</td>
<td>0.834 Mev</td>
<td>Mg$^{26}$ (d, p)</td>
</tr>
<tr>
<td>Mg$^{26}$</td>
<td>stable-11.3%</td>
<td>0.42 Mev β$^-$</td>
<td>1.34 Mev 70%</td>
<td>Li$^6$ + Mg$^{26}$ alloy</td>
</tr>
<tr>
<td>Mg$^{27}$</td>
<td>9.45 min</td>
<td>1.59 Mev β$^-$</td>
<td>0.40 MeV 30%</td>
<td>Mg$^{27}$ (α, 3p);</td>
</tr>
<tr>
<td>Mg$^{28}$</td>
<td>21.2 hr</td>
<td>0.42 Mev β$^-$</td>
<td>0.94 MeV 30%</td>
<td>Mg$^{27}$ (α, 3p);</td>
</tr>
<tr>
<td>Al$^{28}$</td>
<td>2.3 m</td>
<td>2.87 Mev β$^-$</td>
<td>0.034 MeV 100%</td>
<td>Mg$^{27}$ (α, 3p);</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>spallation</td>
</tr>
</tbody>
</table>

* daughter of Mg$^{28}$
The principle radioisotope of magnesium, from the point of view of a tracer, is Mg\textsuperscript{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\textsuperscript{28}. These include high energy spallation reactions\textsuperscript{3-11} on elements heavier than magnesium, bombardment of magnesium\textsuperscript{3} or aluminum\textsuperscript{12} targets with moderate-energy helium ions, and by the Mg\textsuperscript{26} (H\textsuperscript{3}, p) Mg\textsuperscript{28} reaction in a nuclear reactor,\textsuperscript{10,13} where the H\textsuperscript{3} projectiles come from the Li\textsuperscript{6} (n, H\textsuperscript{3}) He\textsuperscript{4} reaction.

Production of Mg\textsuperscript{28} by spallation reactions in high energy accelerators has the virtue that the Mg\textsuperscript{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\textsuperscript{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\textsuperscript{28} is presently made for tracer purposes almost exclusively in nuclear reactors.

Synthesis of Mg\textsuperscript{28} by neutron irradiation of a lithium-magnesium mixture means that the radioisotope is unavoidably diluted with magnesium. At the present time the sole commercial supplier of Mg\textsuperscript{28} in the United States, the Hot Laboratory Division of the Brookhaven National Laboratory, supplies Mg\textsuperscript{28} at a specific activity of 50 microcuries of equilibrium Mg\textsuperscript{28} - Al\textsuperscript{28} containing not more than 0.1 g of magnesium. The Mg\textsuperscript{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.\textsuperscript{14} Early in 1961 the Brookhaven Laboratory will begin supplying Mg\textsuperscript{28} which will have approximately a 20-fold higher specific activity. The use of magnesium enriched in Mg\textsuperscript{26} in the neutron-irradiated lithium-magnesium alloy will be responsible for the increased specific activity.

The radioisotope Mg\textsuperscript{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 \((n, \gamma)\) reaction on stable \(\text{Mg}^{26}\) means that this radioisotope is potentially useful in activation analysis for magnesium. The low cross section for absorption of a thermal neutron by \(\text{Mg}^{26}\), 0.026 barn, coupled with the low abundance of \(\text{Mg}^{26}\) 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 \(\text{Mg}^{28}\) was discovered in 1953, the 9.3 minute \(\text{Mg}^{27}\) was the longest-lived magnesium radioisotope which was known and this short a half-life makes \(\text{Mg}^{27}\) 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 \(\text{Mg}^{28}\) became available its use has been growing steadily and rapidly, mainly in the field of biological research. In a few instances it has been applied to studies of a chemical nature, 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 \(\text{Mg}^{28}\) 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, chloride, 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; MgNH₄PO₄ · 6H₂O, when precipitated by HPO₄⁻ 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.

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.

From the solubility product constant of Mg(OH)₂, \(3.4 \times 10^{-11}\), it is easy to show that Mg(OH)₂ will not be precipitated by an NH₄OH-NH₄⁺ buffer solution. However, addition of NaOH solution to a OH⁻ ion

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility in 100 ml H₂O</th>
<th>Other Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)₂</td>
<td>0.9 mg</td>
<td>acids, NH₄⁺ salts</td>
</tr>
<tr>
<td>MgF₂</td>
<td>7.6 mg</td>
<td>HNO₃, H₃BO₃ solution</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>10.6 mg</td>
<td>acids, aq. CO₂</td>
</tr>
<tr>
<td>Mg₂C₂O₄ · 2H₂O</td>
<td>70 mg</td>
<td>acids, (NH₄)₂C₂O₄ solution</td>
</tr>
<tr>
<td>Mg-oxinate · 2H₂O*</td>
<td>insoluble</td>
<td>acids</td>
</tr>
<tr>
<td>MgNH₄PO₄ · 6H₂O</td>
<td>6.5 mg</td>
<td>acids, insol. dil. NH₄OH</td>
</tr>
</tbody>
</table>

* oxine = 8-hydroxyquinoline
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. Insoluble hydroxides, such as Fe(OH)₃ are therefore good carriers for magnesium when precipitated from strongly basic solutions.

Precipitation of MgNH₄PO₄ · 6H₂O is a standard analytical method for magnesium. The precipitate is granular, and therefore easily filtered, and may be ignited to the pyrophosphate, Mg₅P₂O₇, for weighing. The precipitation is carried out by adding an excess of (NH₄)₂HPO₄ to the acidified solution containing magnesium. The solution is then made alkaline with NH₄OH, cooled, and allowed to stand, preferably for some hours, to permit formation of the precipitate. The precipitate, after filtration, is washed with dilute NH₄OH 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. 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. 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(C₉H₆ON)₂ · 2H₂O and is 6.98 percent Mg by weight.

Under rather special conditions magnesium oxalate can be precipitated as a densely crystalline precipitate of MgC₂O₄ · 2H₂O. The recommended procedure 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 is as follows: saturate with ammonium carbonate a mixture in the proportion by volume of 18 ml NH₄OH, 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, MgClO₄, 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.

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>
<thead>
<tr>
<th>Complexing Agent</th>
<th>Log K*</th>
<th>Ionic Strength</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA</td>
<td>8.69</td>
<td>0.1</td>
<td>a</td>
</tr>
<tr>
<td>oxalate</td>
<td>3.43</td>
<td>0</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>2.65</td>
<td>0.07</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>2.55</td>
<td>0.2</td>
<td>d</td>
</tr>
<tr>
<td>malonate</td>
<td>2.80</td>
<td>0</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>2.52</td>
<td>0.04</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>2.06</td>
<td>0.07</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>1.91</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>succinate</td>
<td>0.08</td>
<td>0.07</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>0.2</td>
<td>d</td>
</tr>
<tr>
<td>r-tartrate</td>
<td>1.36</td>
<td>0.2</td>
<td>d</td>
</tr>
<tr>
<td>sulfate</td>
<td>2.20</td>
<td>0</td>
<td>b</td>
</tr>
<tr>
<td>trimetaphosphate</td>
<td>3.34</td>
<td>0</td>
<td>f</td>
</tr>
<tr>
<td>ammoniatriacetic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acid</td>
<td>7.00</td>
<td>0</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>5.44</td>
<td>0.1</td>
<td>h</td>
</tr>
<tr>
<td>8-hydroxyquinoline</td>
<td>4.7</td>
<td>0</td>
<td>i</td>
</tr>
<tr>
<td>(oxine)</td>
<td>45.55 (1)</td>
<td>0</td>
<td>i</td>
</tr>
</tbody>
</table>

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

1) Solubility produce constant for $\text{Mg(oxinate)}_2$.


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

![INTERSTITIAL COLUMN VOLUMES](image)

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 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

![Image of 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.]

other members of the alkaline earths. Nelson and Kraus 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.

Kraus and coworkers 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 $\beta - \gamma$ emission (see Table I), and they may therefore be counted either by $\beta$ counting or by $\gamma$ counting. Mg$^{28}$ has the added feature that it decays to a 2.3 minute Al$^{28}$ daughter, which also decays by $\beta$ and $\gamma$ 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$^{28}$ was separated from Al$^{28}$ daughters.

For the counting of Mg$^{27}$ the short half-life suggests that $\gamma$ counting would be best. The reason is simply that $\gamma$ counting could be done with a liquid sample isolated as quickly as possible, whereas to $\beta$ count this species it would be necessary to prepare the magnesium in a dry, solid form. This would take additional time, and the sample would be weaker due to its radioactive decay.

A further consideration which suggests that Mg$^{27}$ be detected by $\gamma$ counting is the possibility of pulse height analysis of the detected $\gamma$ rays. Then becomes possible selectively to count a particular $\gamma$ ray component which is characteristic of Mg$^{27}$. This possibility is particularly attractive if Mg$^{27}$ is used in neutron activation analysis for magnesium. Here are numerous possibilities for radioactive contaminants of the isolated magnesium fraction. Gamma counting with pulse height analysis as an additional means of identifying the radioactive species being counted, a feature which $\beta$ counting does not have.

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

The rather energetic $\beta$ rays of both Mg$^{28}$ and Al$^{28}$ give assurance that in the $\beta$ counting of solid samples self-absorption and self-scattering of the sample combine to give an apparent specific activity of the sample which is independent of sample thickness$^4$ for samples thicker than about 4 mg/cm$^2$ up to thicknesses at least as thick as 20 mg/cm$^2$. 

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VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR MAGNESIUM

PROCEDURE 1
Separation of $^{28}$Mg from Tantalum Bombarded with 340 Mev Protons
Source - W. E. Nervik, UCRL-2542 (1954)

A procedure for isolating $^{28}$Mg, 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$_2$SO$_4$ 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$_4$OH. Centrifuge and discard the precipitate.

Step 4. Add 10 mg Cu carrier and pass in H$_2$S. 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$_4$OH and add excess (NH$_4$)$_2$HPO$_4$ to precipitate Mg. Centrifuge and wash the precipitate with dilute NH$_4$OH.

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
PROCEDURE 1 (Continued)

NH₄OH and precipitate Mg with excess (NH₄)₂HPO₄. Filter and wash the precipitate twice with dilute NH₄OH and twice with ethanol. Ignite the precipitate at 1300° F and weigh as Mg₂P₂O₇.

PROCEDURE 2

Separation of Mg²⁺ from Lead Bombarded with 0.6 to 3.0 Bev Protons


The following procedure, derived from an outline, will separate Mg²⁺ 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 lead target in 6 N HNO₃ 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.

Step 2. Add Cd and Mo carriers, neutralize excess acid and precipitate with H₂S. Centrifuge and discard the precipitated sulfides.

Step 3. Boil the solution to expel H₂S. Acidify with a few drops of concentrated HCl, add 1-2 mg FeIII carrier and make basic with NH₄OH. Centrifuge and discard the precipitate of Fe(OH)₃.

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

Step 5. 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.

Step 6. Adjust the acidity of the effluent from the column to 0.3 M (note 1). Add 10 mg Cu carrier and precipitate with H₂S. Centrifuge and discard the precipitate.

Step 7. Boil the solution to expel H₂S. Add 1-2 mg FeIII carrier and make the solution basic with NH₄OH. Centrifuge the precipitate.

Step 8. Evaporate the solution to dryness, add 2-3 ml of HNO₃ 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
PROCEDURE 2 (Continued)

in the proportion by volume of 18 parts NH$_4$OH, 75 parts of water and
95 parts 95% ethanol and saturating this mixture with (NH$_4$)$_2$CO$_3$.
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 Erlen-
meyer flask and evaporate the solution almost to dryness. Take up the
residue in water. Add 40 mg of Ca carrier, make the solution slightly
basic with NH$_4$OH and precipitate the Ca with (NH$_4$)$_2$C$_2$O$_4$. Centrifuge
and discard the precipitate.

Step 11. Add more NH$_4$OH and precipitate the Mg with (NH$_4$)$_2$HPO$_4$.
Filter the precipitate, wash with dilute NH$_4$OH and alcohol, dry and
count. Ignite to Mg$_2$P$_2$O$_7$ 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$_4$OH and precipitate with H$_2$S.
Centrifuge and discard the precipitate.

Step 2. Repeat the H$_2$S scavenging with Zn, Cu and Mn carriers twice
more. Filter the supernatant liquid from the last scavenging through a
fine porosity filter paper.
PROCEDURE 3 (Continued)

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

4. Dissolve the precipitated Mg(OH)₂ in dilute HCl. Reprecipitate Mg a second time with NaOH. Centrifuge the precipitated Mg and discard the aqueous phase. The precipitate of Mg(OH)₂ should now be free of radioactive contaminants. (Note 1).

NOTES

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

PROCEDURE 4

Production of Mg²⁸ Tracer Produced in Neutron-Irradiated Li-Mg Alloy by L.G. Stang, Jr., W.D. Tucker, A.J. Weiss, and H.O. Banks, Jr., Brookhaven National Laboratory Report BNL-3138, 1956.

The procedure, used for the production of Mg²⁸ tracer in the United States, is somewhat different from Procedure 3, which is the one used in 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 resultant precipitate of Mg(OH)₂. Discard the aqueous phase and wash the precipitate with ice water.

2. Dissolve the Mg(OH)₂ precipitate in concentrated HCl, add F₄⁺ carrier and boil to expel F⁻¹⁸.

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

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

5. Add excess NaOH to precipitate Mg(OH)₂. Chill the solution and centrifuge the precipitate. Discard the aqueous phase and wash the precipitate twice with ice water. The precipitate may now be dissolved in any acid for further use. (Note 1.)
PROCEDURE 4 (Continued)

NOTES

Note 4. 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 \( Fe^{III} \) 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.
PROCEDURE 5 (Continued)

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
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


Magnesium, along with zinc, manganese 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). Rinse the specimen tube with about 3 ml conductivity water ( > 8 x 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 x 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).
PROCEDURE 7 (Continued)

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$_2$O) 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 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 $\gamma$ ray of Mg$^{27}$ between 790 kev and 890 kev with a $\gamma$ 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.
REFERENCES


36. See, for example, Reference 33, Vols. III and IV.