

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Separation and Purification of Magnesium, Lead, and Neodymium from Dissolver Solution of Irradiated Fuel

K. L. Ramakumar^a; S. K. Aggarwal^a; V. D. Kavimandan^a; V. A. Raman^a; P. S. Khodade^a; H. C. Jain^a; C. K. Mathews^b

^a RADIOCHEMISTRY DIVISION, BHABHA ATOMIC RESEARCH CENTRE TROMBAY, BOMBAY, INDIA ^b RADIOCHEMISTRY LABORATORIES REACTOR RESEARCH CENTRE KALPAKKAM, TAMIL NADU, INDIA

To cite this Article Ramakumar, K. L. , Aggarwal, S. K. , Kavimandan, V. D. , Raman, V. A. , Khodade, P. S. , Jain, H. C. and Mathews, C. K.(1980) 'Separation and Purification of Magnesium, Lead, and Neodymium from Dissolver Solution of Irradiated Fuel', Separation Science and Technology, 15: 7, 1471 — 1481

To link to this Article: DOI: 10.1080/01496398008056098

URL: <http://dx.doi.org/10.1080/01496398008056098>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Separation and Purification of Magnesium, Lead, and Neodymium from Dissolver Solution of Irradiated Fuel

K. L. RAMAKUMAR, S. K. AGGARWAL,
V. D. KAVIMANDAN, V. A. RAMAN,
P. S. KHODADE, and H. C. JAIN

RADIOCHEMISTRY DIVISION
BHABHA ATOMIC RESEARCH CENTRE
TROMBAY, BOMBAY 400085, INDIA

C. K. MATHEWS

RADIOCHEMISTRY LABORATORIES
REACTOR RESEARCH CENTRE
KALPAKKAM, TAMIL NADU, INDIA

Abstract

Magnesium and lead have been identified as tracers for the input accountability of plutonium in reprocessing plants whereas fission product ^{148}Nd is used as a burn-up monitor. Ion exchange procedures developed for the separation and purification of Mg, Pb, and Nd from the dissolver solution of irradiated fuel for their mass spectrometric analyses are presented. Distribution ratio curves of Pb, Ce, Nd, and Sm in $\text{CH}_3\text{OH-HNO}_3\text{-H}_2\text{O}$ medium used in the development of the separation and purification procedure are also shown.

INTRODUCTION

The input accountability of plutonium at reprocessing plants and burn-up determination of the irradiated fuel are two important measurements in the nuclear fuel cycle which one would like to carry out with the highest precision and accuracy. Isotope dilution mass spectrometry is the only technique which meets these needs. Magnesium and lead have been found as the useful tracers in tracer techniques (MAGTRAP,

LEADTRAP) for the input accountability of Pu in reprocessing plants (1–3), while fission product ^{148}Nd has been universally recognized as a burn-up monitor (4). The input accountability of Pu is based on the addition of a known amount of $\text{Mg}(\text{NO}_3)_2$ or $\text{Pb}(\text{NO}_3)_2$ tracer solution to the solution in the input accountability tank and the determination of Pu-to-tracer ratio in a small sample. The determination of burn-up using ^{148}Nd involves the measurement of the relative concentrations of U, Pu, and Nd in the dissolver solution of irradiated fuel using triple spike isotope dilution mass spectrometry (5). For these measurements it is necessary to deal with the dissolver solution which is highly radioactive. It is, therefore, desirable to handle small samples with a view to reducing radiation exposure and radioactive contamination hazards. Further, Mg or Pb added and ^{148}Nd formed are present in ppm levels. Moreover, ^{142}Ce and ^{148}Sm present in the dissolver solution cause isobaric interference at ^{142}Nd (used as a spike) and ^{148}Nd , respectively, during the mass spectrometric analysis of Nd. Thus it is essential to separate and purify Mg, Pb, and Nd from the bulk of other materials prior to their mass spectrometric analyses.

The dissolver solution contains U as the major constituent, Pu (U/Pu about 100 to 1000, depending upon burn-up), and various fission products; viz., alkali metals, alkaline earths, rare earths, etc. The tracer added for the input accountability and the various fission products can be separated from bulk of U and Pu by following the anion exchange procedure (6) using Dowex (Dow Chemical Co., USA) 1×8 resin (200–400 mesh) in 7.5 M HNO_3 as these are not absorbed on the resin. Studies were therefore carried out for the separation of Mg, Pb, and Nd from the fission products.

Ion-exchange methods in aqueous media cannot be employed for the separation and purification of these elements individually (7). However, a large number of anion-exchange techniques exploiting mixed organic-aqueous media have been reported in the literature (8–12) for the separation and purification of various elements. The method generally used for the separation and purification of Nd for burn-up measurements (13) involves two stages on Dowex 1×8 resin. In the first stage, Nd along with other rare earths is separated from alkali metals and alkaline earths, while in the second stage Nd is purified from other rare earths. Mg, if present, gets eluted along with alkali metals and alkaline earths and needs further purification, while Pb and Nd are eluted together in both stages. Moreover, the two-column separation and purification of Nd is lengthy and time consuming. To overcome these problems, (a) distribution ratios of Pb and Nd were determined on Dowex 1×8 resin (200–400 mesh) in different $\text{CH}_3\text{OH}-\text{HNO}_3-\text{H}_2\text{O}$ compositions to optimize the conditions for their separation, and (b) the distribution ratios of Nd, Sm, and Ce were determined in varying $\text{CH}_3\text{OH}-\text{HNO}_3-\text{H}_2\text{O}$ compositions on Bio-rad AG 1×2 resin (Bio-rad Laboratories, Richmond, California, USA).

This paper presents details of the investigations carried out for the separation and purification of Mg, Pb, and Nd from dissolver solution.

EXPERIMENTAL

Reagents

The H_2O , HNO_3 , and CH_3OH used were distilled in quartzware. Dowex 1×8 resin (200–400 mesh) was purified (14) by taking the resin in a glass column and washing with distilled water, 1 *M* NaOH followed by distilled water, CH_3OH , distilled water, 3 *M* HNO_3 , and finally with distilled water. It was dried at 90°C for 12 hr and stored in a desiccator. Bio-rad AG 1×2 resin (200–400 mesh) was treated in a similar way. Ethylene diaminetetraacetic acid disodium salt (EDTA) was also purified before use (15). A saturated solution of the reagent was prepared in H_2O . CH_3OH was added slowly till the impurities were precipitated out. It was filtered, and to the filtrate an equal volume of CH_3OH was added. The resulting precipitate was filtered through a Buchner funnel, washed with acetone, and then with ether. It was dried overnight in air and then in an oven at 80°C for 24 hr. Solutions of $\text{Mg}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ were prepared by dissolving Analar grade magnesium nitrate and lead nitrate in dilute HNO_3 . Solutions of Ce, Nd, and Sm were prepared by dissolving high purity oxides of these elements in dilute HNO_3 . The final concentration of each element was about 1 mg/mL of the solution. ^{141}Ce , ^{147}Nd , and ^{153}Sm tracers were prepared by neutron irradiation of high purity oxides of these elements.

Determination of Distribution Ratios

The distribution ratios were determined by the batch equilibration method. One milliliter of the metal ion solution was taken in the equilibration tube and evaporated to dryness under an infrared lamp. Five milliliters of the CH_3OH – HNO_3 – H_2O mixture of known composition was added to obtain a clear solution. A known weight of the resin (about 100 mg) was added to the equilibration tube. The tubes were stoppered, sealed, and shaken in a mechanical shaker for a sufficiently long time (4 to 10 hr) to attain equilibrium.

In the case of Pb, the distribution ratio (D_M) was calculated by

$$D_M = \frac{\text{amount of Pb/g of the resin}}{\text{amount of Pb/mL of the solution}}$$

Lead was determined by direct titration with EDTA at pH 6 using xylenol orange as the indicator (15).

In the case of Ce, Nd, and Sm, the distribution ratios were calculated with

$$D_M = \frac{A_0 - A_f}{A_f} \frac{V}{W}$$

where A_0 is the initial activity of the tracer in the solution before equilibration, A_f is the activity in the solution after equilibration, V is the volume of the CH_3OH – HNO_3 – H_2O mixture, and W is the weight of the resin.

A_0 and A_f were determined radiometrically by counting gamma activities due to ^{141}Ce (145 keV), ^{147}Nd (91 keV), and ^{153}Sm (103 keV) using NaI (Tl) detector with a single channel analyzer in the differential mode.

In the solvent mixture, CH_3OH concentration was varied from 20 to 90% whereas the HNO_3 concentration was changed from 0.2 to 6 M .

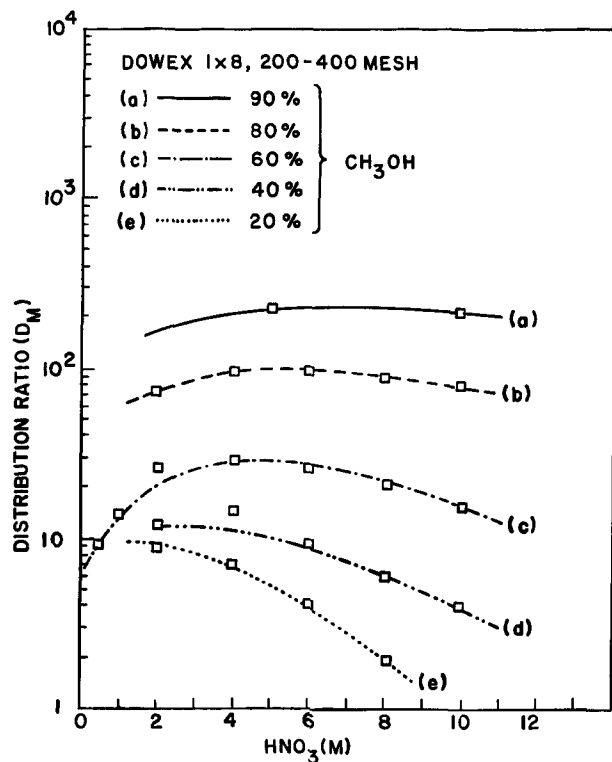


FIG. 1. Variation of distribution ratio of Pb with varying composition of HNO_3 and CH_3OH .

The distribution ratios were determined on Dowex 1×8 resin as well as on Bio-rad AG 1×2 resin.

RESULTS AND DISCUSSION

Separation of Pb and Nd from Dissolver Solution

The variation of D_M values for Pb and Nd with different compositions of CH_3OH – HNO_3 – H_2O is given in Figs. 1 and 2. It is seen that the D_M value for Pb and Nd increases as the percentage of CH_3OH is increased in the solvent composition. Further, the D_M value for Nd is less than that of Pb up to 70% CH_3OH . This trend is reversed at higher concentrations of CH_3OH , and the D_M value of Nd becomes much higher compared to that of Pb at low acidity. For a given concentration of CH_3OH , the D_M value of Pb increases, reaches a maximum, and then starts decreasing as HNO_3 concentration is increased, whereas in the case of Nd the D_M

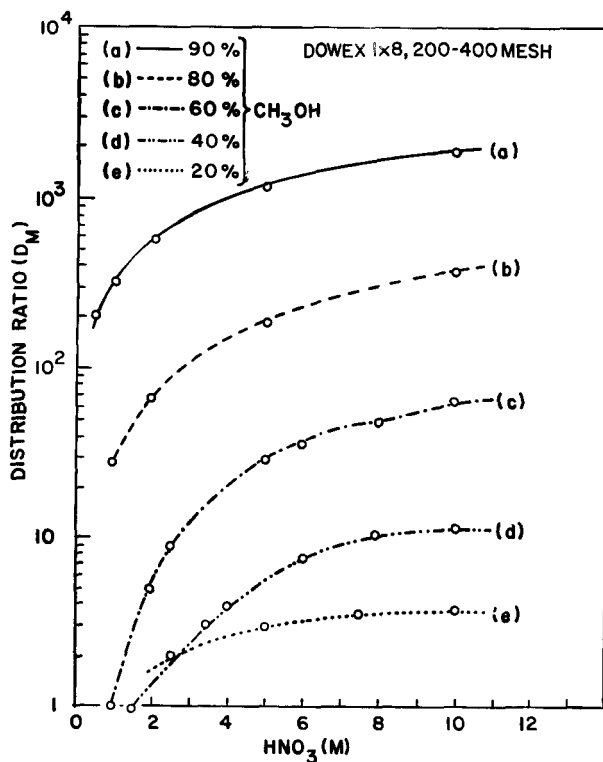


FIG. 2. Variation of distribution ratio of Nd with varying composition of HNO_3 and CH_3OH .

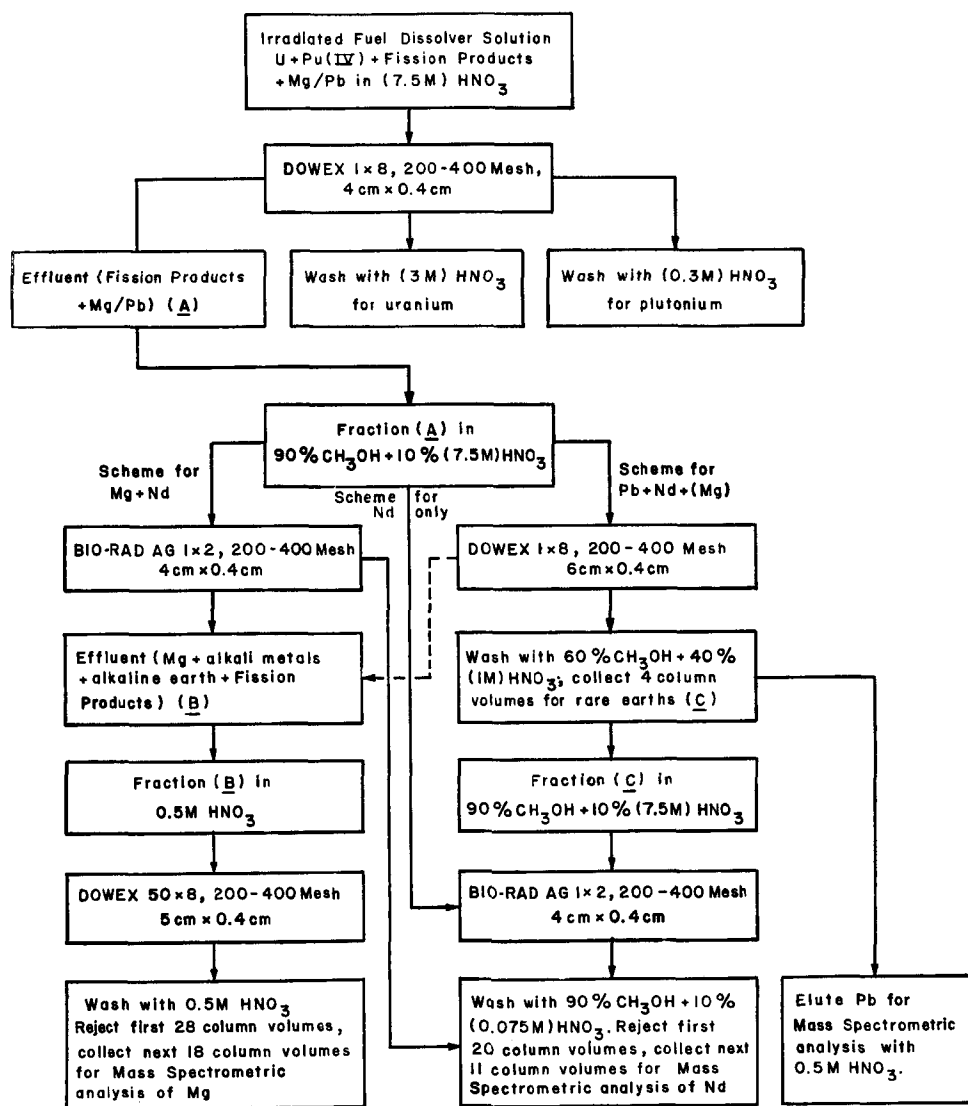


FIG. 3. Separation and purification scheme for magnesium, lead, and neodymium from irradiated fuel dissolver solution for mass spectrometric analysis.

value goes on increasing with an increase in HNO_3 concentration. Moreover, in both cases the change in the CH_3OH concentration has a pronounced effect on the D_M value as compared to that obtained by changing the HNO_3 concentration.

As the distribution ratios for Pb and Nd are maximum at a solvent composition of 0% CH_3OH + 10% (10 M) HNO_3 , this was selected as the loading medium for achieving maximum adsorption of Pb and Nd on Dowex 1 \times 8 resin (200–400 mesh). For the separation of Pb and Nd, the solvent composition 60% CH_3OH + 40% (1 M) HNO_3 was ideal as the separation factor between Pb and Nd (separation factor = ratio of distribution ratios) is maximum. Further, the D_M value for Nd being negligible at this solvent composition, it can be eluted in small volume.

The scheme for the separation of Pb and Nd from dissolver solution using Dowex 1 \times 8 resin is given in Fig. 3, and a typical elution curve obtained using this scheme is given in Fig. 4.

Purification of Nd

Nd obtained by using the above procedure is eluted along with other

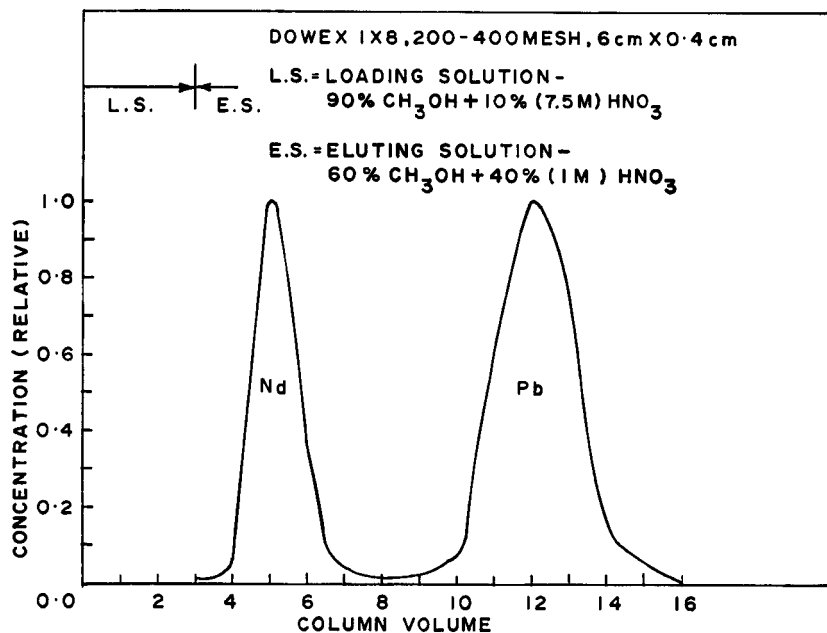


FIG. 4. Elution curve for the separation of Pb and Nd. Column volume refers to the length of the resin.

rare earths and needs further purification before carrying out the mass spectrometric analysis. This is essential for eliminating the isobaric interference from Ce and Sm at mass numbers 142 and 148, respectively. Though a method was previously available (13) for the purification of Nd from other rare earths using Dowex 1 \times 8 resin, employing 90% CH₃OH + 10% (7.5 M) HNO₃ as the loading solution, 90% CH₃OH + 10% (0.15 M) HNO₃ as the washing solution, and 90% CH₃OH + 10% (0.03 M) HNO₃ as the eluting solution, the procedure was lengthy and time consuming. It was therefore considered worthwhile to study in detail the procedure (16) using Bio-rad AG 1 \times 2 resin.

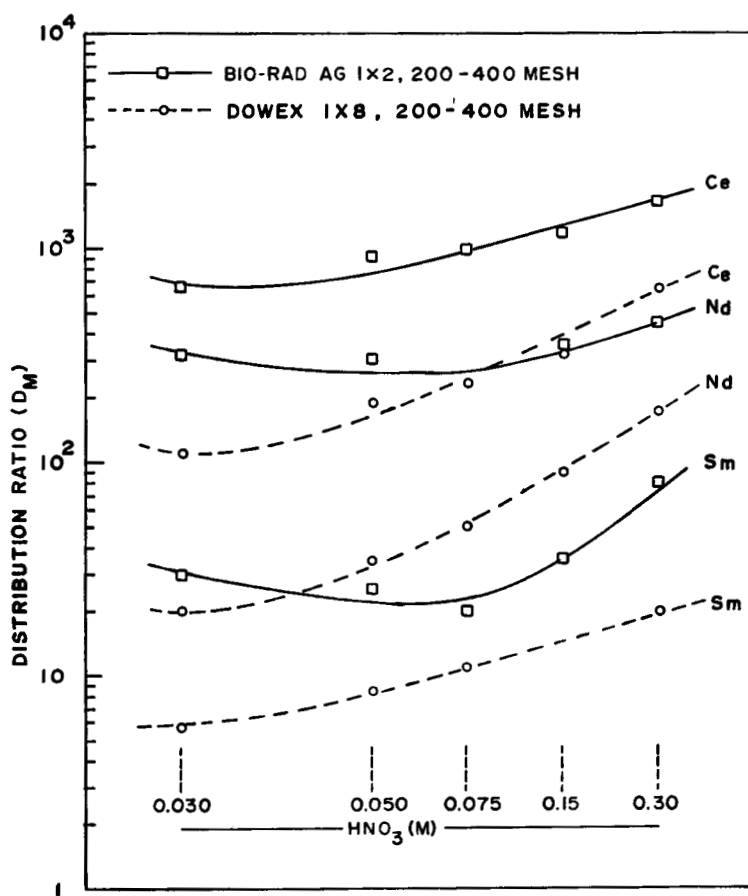


FIG. 5. Variation of distribution ratios of Ce, Nd, and Sm in varying concentration of HNO₃. Solvent composition: 90% CH₃OH + 10% HNO₃.

The distribution ratios of Ce, Nd, and Sm were determined on Bio-rad AG 1 \times 2 resin as well as on Dowex 1 \times 8 resin using a solvent composition of 90% CH₃OH and 10% HNO₃ of varying concentration. This solvent composition with 90% CH₃OH was selected because D_M values for Nd were maximum (as seen from Fig. 2).

The variation of D_M values for Ce, Nd, and Sm with different concentrations of HNO₃ and 90% CH₃OH is given in Fig. 5. It is seen that D_M values for Ce, Nd, and Sm decrease uniformly with changing acid concentration on Dowex 1 \times 8 resin. In the case of Bio-rad AG 1 \times 2 resin, the D_M values for Sm and Nd remain more or less unaltered at an acid concentration below 0.15 M HNO₃ whereas those for Ce continue to decrease. It was therefore concluded that Bio-rad AG 1 \times 2 resin will be more efficient than to Dowex 1 \times 8 resin in separating Nd from Ce and Sm. The optimum solvent composition of 90% CH₃OH + 10% (0.075 M) HNO₃ was selected for eluting Nd free from Ce and Sm. The use of lower acidity elutes Nd faster, but some Ce is eluted along with Nd, which causes isobaric interference in the mass spectrometric analysis.

The scheme for the purification of Nd from other rare earths, and in particular from Ce and Sm, using Bio-rad AG 1 \times 2 resin is shown in Fig. 3, and a typical elution curve obtained using this scheme is given in Fig. 6.

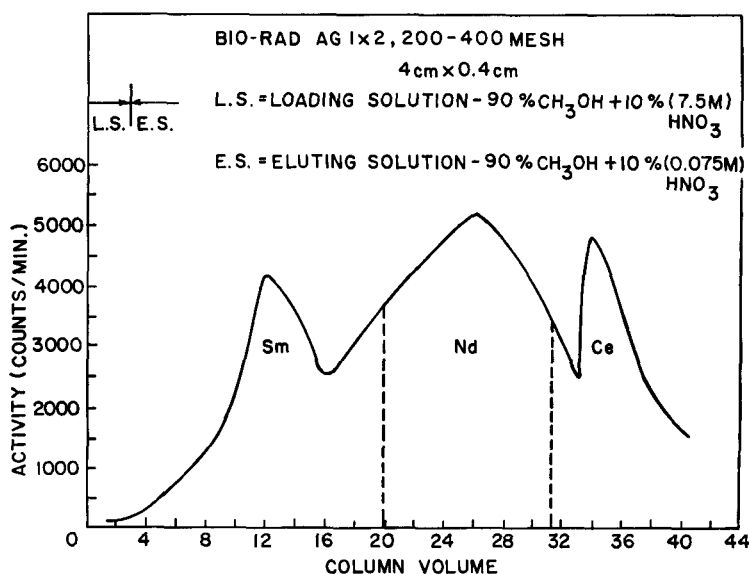


FIG. 6. Elution curve for the purification of Nd. Column volume refers to the length of the resin.

It is worth noting that in case Pb is not required, the single-stage procedure using Bio-rad AG 1×2 resin can be directly used for the separation and purification of Nd from fission products and other rare earths. This eliminates the two-stage, lengthy, and time-consuming procedure using Dowex 1×8 resin.

Separation of Mg and Nd from Dissolver Solution

As mentioned earlier, Mg and Nd are eluted together along with alkali metals, alkaline earths, and other rare earths on Dowex 1×8 resin in 7.5 M HNO_3 medium. Nd can be separated and purified from Mg and other rare earths by using the single-stage procedure shown in Fig. 3. The Mg fraction, however, needs further purification as it contains alkali metals and alkaline earths. This was achieved by using a cation-exchange resin Dowex 50×8 in 0.5 M HNO_3 . The scheme for the separation and purification of Mg and Nd from the dissolver solution is given in Fig. 3. A typical elution curve obtained for the purification of Mg is given in Fig. 7. The procedures developed have been successfully used for the input accountability of plutonium in reprocessing plants and for the burn-up determination.

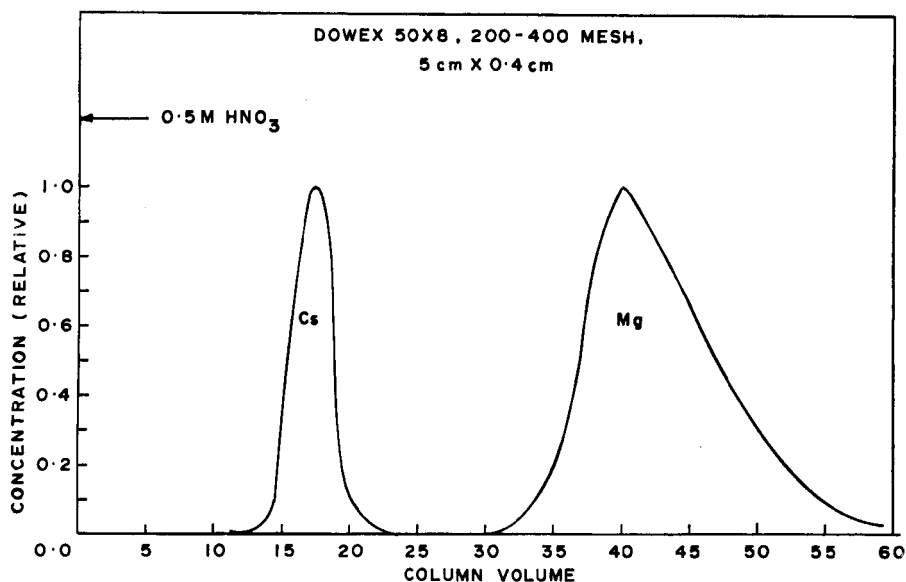


FIG. 7. Elution curve for the purification of Mg. Column volume refers to the length of the resin.

Acknowledgment

The authors are thankful to Dr. M. V. Ramaniah, Director, Radiological Group, for his keen interest in this work.

REFERENCES

1. C. K. Mathews, H. C. Jain, V. D. Kavimandan, and S. K. Aggarwal, in *Proceedings of the IAEA Symposium on Safeguarding Nuclear Materials*, Vienna, October 1975, Vol. II, p. 485, International Atomic Energy Agency, 1976.
2. S. K. Aggarwal, V. D. Kavimandan, S. N. Acharya, H. C. Jain, and C. K. Mathews, BARC-904 (1976).
3. C. K. Mathews, H. C. Jain, V. D. Kavimandan, and S. K. Aggarwal, *Nucl. Technol.*, 42, 297 (1979).
4. A. J. Fudge, in *Proceedings of the IAEA Panel Meeting on Reactor Burn-up Physics*, Vienna, July 1971, p. 239, International Atomic Energy Agency, 1973.
5. B. Saha, R. Bagyalakshmi, G. Periaswami, V. D. Kavimandan, S. A. Chitambar, H. C. Jain, and C. K. Mathews, BARC-891 (1976).
6. S. A. Chitambar, V. D. Kavimandan, B. Saha, S. K. Aggarwal, G. Periaswami, K. Bagyalakshmi, P. M. Shah, P. A. Ramasubramanian, A. I. Almaula, H. C. Jain, C. K. Mathews, and M. V. Ramaniah, BARC-865 (1976).
7. K. A. Kraus and F. Nelson, in *International Conference on Peaceful Uses of Atomic Energy*, Geneva, United Nations, Vol. 7, p. 113, 1956.
8. J. P. Faris and J. W. Warton, *Anal. Chem.*, 34, 1077 (1962).
9. R. G. Greene and J. S. Fritz, IS-1153 (1965).
10. Y. Marcus, in *Ion Exchange and Solvent Extraction*, Vol. 4 (J. A. Marinsky and Y. Marcus, eds.), Dekker, New York, 1973.
11. J. Korkisch, in *Progress in Nuclear Energy*, Series IX, Vol. 6 (H. A. Elian and D. C. Stewart, eds.), Pergamon, Oxford, 1966.
12. J. P. Faris and R. F. Buchanan, *Ibid.*, 1966.
13. ASTM Standards, Part 45, Method E-321-75, p. 878, American Society for Testing and Materials, Philadelphia, 1977.
14. J. I. Kim, *J. Inorg. Nucl. Chem.*, 37, 239 (1975).
15. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longmans, Green, London, 1961.
16. R. H. Abernathy, G. M. Matlack, and J. E. Rein, in *Proceedings of the IAEA Symposium on Analytical Methods in Nuclear Fuel Cycle*, Vienna, 1972, p. 531, International Atomic Energy Agency, 1972.

Received by editor November 21, 1979