Proceedings of the
International Symposium on

ACTINIDE/ LANTHANIDE SEPARATIONS

Editors:
G R Choppin
J D Navratil
W W Schulz

Proceedings of the International Symposium on

ACTINIDE/ LANTHANIDE SEPARATIONS

Honolulu, Hawaii, USA
16-22 December 1984

World Scientific

Published by

World Scientific Publishing Co Pte Ltd.
P. O. Box 128, Farrer Road, Singapore 9128
242, Cherry Street, Philadelphia PA 19106-1906, USA

Library of Congress Cataloging-in-Publication Data

International Symposium on Actinide/Lanthanide
Separations (1984: Honolulu, Hawaii)
Proceedings of the International Symposium on Actinide/Lanthanide Separations
Honolulu, Hawaii, USA, 16-22 December 1984.

1. Actinide elements — Congresses. 2. Rare earth metals — Congresses.
3. Separation (Technology) — Congresses. I. Choppin, G. R.
II. Navratil, James D., 1941- . III. Schulz, Wallace W. IV. Title.
QD172.A3156 1984 546.4 85-20329
ISBN 9971-978-68-7

Copyright © 1985 by World Scientific Publishing Co Pte Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

Printed in Singapore by Singapore National Printers (Pte) Ltd.

PREFACE

The papers in this volume are based on presentations at the Symposium on Actinide-Lanthanide Separations which was part of the scientific program of the International Chemical Congress of Pacific Basin Societies. The Congress was held in Honolulu, Hawaii, in December 1984. This symposium stressed the developments in actinide separation methods since the last such symposium in 1978 and also includes some papers on new developments in lanthanide separation science. The papers in this volume further provide broad insight into the state of separation science of these f-elements as the papers describe studies from Japan, Canada, USSR, France and the major U. S. laboratories.

The volume is opened with papers covering actinide-lanthanide group separations. These are followed by a group of papers reporting the use of new and highly promising extractants for actinides. Several papers report on topics such as automatic separations, separation by oxidation state and separation of the early actinides. The last one-third of the papers are concerned with plutonium and/or americium recovery from a variety of media using principally pyrochemical techniques.

The papers in this volume represent the state-of-the-art methodology in f-element separations in 1985. We hope chemists and engineers involved in research and in the technology of these elements find much value in these reports.

June, 1985

G. R. Choppin
J. D. Navratil
W. W. Schulz

CONTENTS

Preface v

1. High Performance Separations of Lanthanides and Actinides on Dynamic Ion Exchanges 1
R. M. Cassidy, C. H. Knight, B. M. Recoskie, S. Elchuk, F. C. Miller, and L. W. Green

2. Actinide-Lanthanide Group Separation Using Sulfur and Nitrogen Donor Extractants 19
C. Musikas

3. Preliminary Separation of the Lanthanide Group Using DHDECMP 31
J. Kwinta, P. David, and G. Metzger

4. TRU Decontamination of High-Level Purex Waste by Solvent Extraction using a Mixed Octyl(Phenyl)-N, N-Diisobutyl-Carbamoylmethylphosphine Oxide/TBP/NPH (Truex) Solvent 43
E. P. Horwitz, D. G. Kalina, H. Diamond, L. Kaplan, G. F. Vandegrift, R. A. Leonard, M. J. Steindler, and W. W. Schulz

5. Uranium and Neodymium Extraction by Neutral Organophosphorus Extractants in an Aliphatic Diluent: The Truex Process 7
R. G. Hubert, and D. W. Tedder

6. Extraction of Thorium, Americium, and Curium from the Mixed Acid Solutions of Nitrate and Perchlorate by Bifunctional Organophosphorus Extractant
T. Mitsugashira, M. Maki, and S. Suzuki

7. The Extraction of Uranium (VI), Yttrium (III) and Lanthanum (III) from Hydrochloric Acid Solutions by Acid Organophosphorus Compounds 11
T. Sato

此为试读,需要完整PDF请访问: www.ertongbook.com

8. A Process for the Recovery of Americium from Analytical Wastes 126
P. Brossard, J. Kwinta, and Y. Schwander

9. Automatic Chemical Separation Apparatus for Uranium and Trans-uranium Elements 140
F. Hirayama, M. Takashi, Y. Yuasa, and A. Tani

10. Extraction of Complexes of Actinides with Water-Soluble Organic Reagents in Two-Phase Aqueous Systems of Salt-Poly(Ethylene Glycol)-Water 164
B. F. Myasoedov, N. P. Molochnikova, V. M. Shkinev, T. I. Zvarova B. Ya. Spivakov, and Yu. A. Zolotov

11. Separation of Actinides in Aqueous Solution by Oxidation State 176
G. R. Choppin

12. Gram-Scale Separation of Curium from Americium Using Ammonium α-Hydroxyisobutyrate in High-Pressure Cation Columns 194
J. E. Bigelow, D. E. Benker, F. R. Chattin, L. J. King, J. B. Knauer, R. G. Ross, R. G. Stacy, and J. T. Wiggins

13. Sequential Determination of Radium-226, Radium-228, Actinium-227 and Thorium Isotopes 212
D. B. Martin

14. Plutonium Separations Chemistry and Technology 226
C. E. Baldwin, and J. D. Navratil

15. Plutonium Metal Preparation and Purification at Los Alamos – 1984 238
D. C. Christensen, J. D. Williams, J. A. McNeese, and K. W. Fife

16. Actinide Recovery from Pyrochemical Residues 267
L. R. Avens, D. G. Clifton, and A. R. Vigil

17. Aqueous Recovery of Plutonium from Pyrochemical Processing Residues 294
L. W. Gray, and J. H. Gray

18. Plutonium and Americium Separation from Molten Salt Extraction Waste Salts 313
K. W. Fife, D. C. Christensen, and J. D. Williams

19. Content and Removal of TRU Elements from Aqueous Zirconium Cladding Waste 326
K. M. Hodgson, D. L. Herting, W. W. Schulz, L. A. Bray, and J. L. Swanson

20. Plutonium Metal and Alloy Preparation by Molten Chloride Reduction 348
J. G. Reavis

HIGH PERFORMANCE SEPARATIONS OF LANTHANIDES AND ACTINIDES ON DYNAMIC ION EXCHANGES

R.M. Cassidy, C.H. Knight, B.M. Recoskie, S. Elchuk, F.C. Miller and L.W. Green

General Chemistry Branch, Chemistry and Materials Division, Chalk River Nuclear Laboratories, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada, K0J 1J0

ABSTRACT

High-performance dynamic ion exchange has been used for the analysis of metal ions in nuclear fuels, and for the collection of pure fractions for further characterization. For the determination of burnup, the liquid chromatograph was used to determine the fission monitor ^{139}La in dissolved fuel solutions. Comparisons with mass-spectrometric techniques for ThO_2 fuels gave agreement to within 0.1%. Similar procedures were also used to determine small concentrations ($< 0.2\ \mu g \cdot g^{-1}$) of lanthanides in unirradiated fuels.

The application of dynamic exchangers for the collection of pure metal ion fractions was examined, and the factors influencing memory effects and peak purity were determined by both ^{140}La tracer studies, and isotope dilution mass spectrometry. Memory effects could be reduced to .006 to .03%, and for the separation of equal amounts of Sm and Ce in a dissolved rock solution the Sm contamination in the Ce fraction (Sm elutes before Nd) was ~ 4 parts in 10^4, and the Ce contamination in the Sm fraction was too low to obtain a reliable estimate.

1. INTRODUCTION

Chromatographic separations, ion exchange in particular, have played a fundamental role in the development of atomic energy. The analytical chemistry of the actinides and lanthanides is still dependent on chemical separations, and many of the ion separations, and many of the ion exchange procedures used are similar to those published in the 1940's and 1950's. Compared to techniques used in the modern high-performance liquid chromatography (HPLC) of organic species, such classical ion-exchange techniques are vastly inferior due to poorer resolution and longer separation times. Campbell[1] was

the first to recognize the potential of modern liquid-chromatographic techniques for lanthanide separations, and used small-particle resins for the preparative separation of the lanthanides; Campbell[2] has also published work on actinide separations. Both ion-exchange resins and silica based bonded-phase exchangers have been applied to analytical separation problems in nuclear chemistry[3,4], but our experience has shown that these types of exchangers do not give true high-performance separations of metal ions. The resins have poor rigidity and slow mass transfer, while the silica packings suffer from poor column reproducibility and stability, and exhibit tailing peaks, possibly due to mixed retention mechanisms. Our recent studies on inorganic anion separations[5,6] have shown that dynamic ion exchangers, which are formed by the sorption of hydrophobic ions onto hydrophobic surfaces, offer a versatile approach for inorganic HPLC ion-exchange.

For the past two years our research has focused on the development of dynamic ion exchangers for rapid analytical separations of actinides and lanthanides. Although our studies have been restricted to analytical applications, the potential of such exchangers for larger scale separations will become apparent from the results presented here. This paper will give an overview of the results obtained in these studies, and briefly discuss the present status of our programs in the following areas: burnup analysis of nuclear fuels; determination of lanthanides in unirradiated fuels; actinide separations; and fraction collection for other analyses such as isotope-dilution mass spectrometry and α-spectrometric analyses for waste management studies.

2. EXPERIMENTAL

A schematic of the "hot-cell" and glove-box facility is shown in Fig. 1. Dissolutions of active samples, dilutions, and weighings were done in the "hot cells", and aliquots (~ 1 mL) of the diluted

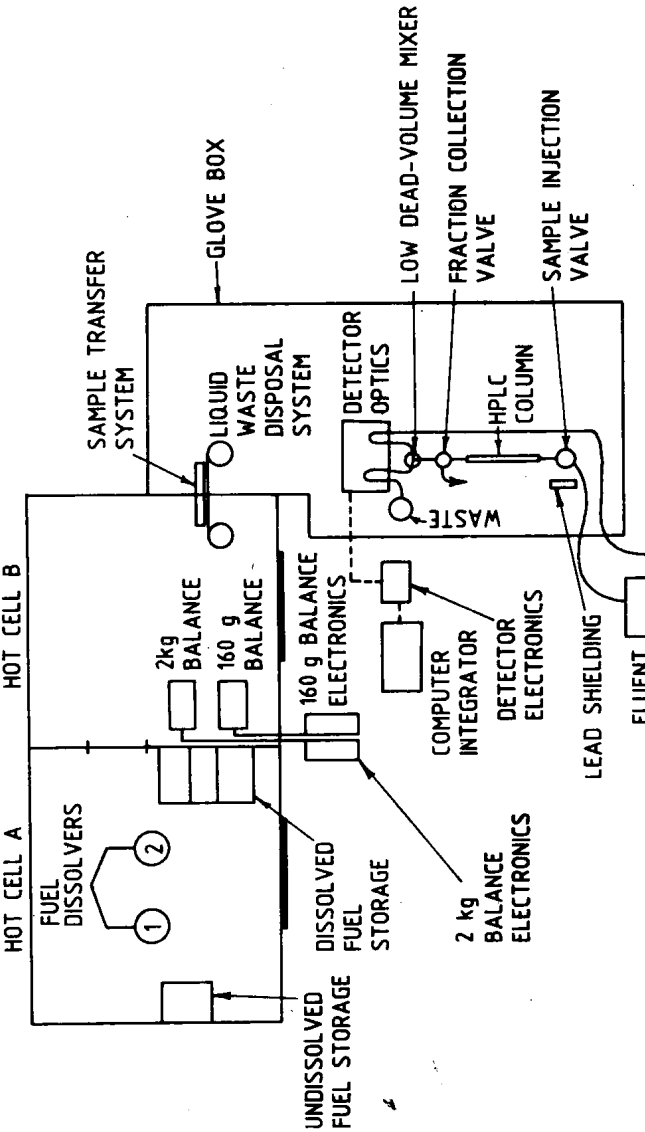

Figure 1. Schematic diagram of containment facility used for HPLC analyses of radioactive samples.

samples were then transferred to the glove-box. A typical irradiated then transferred to the glove-box. A typical irradiated fuel solution contained ~ 1 $mg \cdot mL^{-1}$ of the fuel sample in the diluted fuel solution used for HPLC analysis; all dilutions were done by weight, and the HPLC mobile phase was used for the dilutions.

Samples were injected via a Rheodyne HPLC injection valve (Model 7125, Rheodyne, Berkley, CA), and separated on a 5 μm Supelcosil LC-18 column (4.6 x 150 mm, Supelco Inc., Bellafonte, PA); for some studies a totally organic reversed phase, PRP-1 (Hamilton Co., Reno, Nevada), was used. For sample characterization by mass spectrometric or other techniques, fractions were collected via a low dead-volume Rheodyne valve (Model 7030). Eluted metal ions were monitored at 658 nm with a Waters 440 detector (Waters Scientific, Milford, MA) after a postcolumn reaction with 3,6-bis[(o-arsenophenyl)azo]-4,5-dihydroxy-2,7-napthalenedisulfonic acid (Arsenazo III). The post-column reagent (1.5×10^{-4} $mol \cdot L^{-1}$ and 0.1 $mol \cdot L^{-1}$ in nitric acid) was added to the eluate at ~ 0.5 $mL \cdot min^{-1}$ via a low dead-volume mixer[4]. A similar "inactive" HPLC system was used for nonradioactive samples.

The mobile phases were aqueous solutions containing 10^{-3} to 10^{-1} $mol \cdot L^{-1}$ of n-octylsulfonate and 0.03 to 0.3 $mol \cdot L^{-1}$ of a complexing reagent such as α-hydroxyisobutyric acid; the pH of the mobile phase was adjusted (normally to pH 3 to 4) with ammonium hydroxide.

For burnup measurements the concentration of ^{139}La in the fuel was determined in triplicate by direct injection of diluted fuel solutions; quantitative values were obtained by comparison of ^{139}La peak areas with peakarea calibration curves obtained for mock fuel standards. The heavy element content was estimated from the weight of the fuel sample; this procedure is valid for fuels having relatively low burnup (< 10 atom percent)[7].

此为试读,需要完整PDF请访问: www.ertongbook.com

3. RESULTS AND DISCUSSION

3.1 Principles of Dynamic Ion Exchangers

The techniques used for the dynamic ion-exchange separation of metal ions are similar to those used in "ion-pair" chromatographic separations of organics. The ion-exchange surface is established as shown in Fig. 2, which illustrates the reversible sorption of n-octylsulfonate onto a n-octadecyl phase bonded to a porous silica support. This sorption will produce a negatively charged surface with its associated cation counter-ion region in the mobile phase, and ion exchange of cations can occur in this counter layer. Two important features of dynamic exchangers are their high column efficiency and easily varied ion-exchange capacity. The high column efficiency is likely a result of the excellent mass transfer characteristics of a "well-defined" charged surface. The ion-exchange capacity depends on the surface concentration of the sorbed modifier and this concentration can be quickly changed (few minutes) over a wide range. Variations in ion exchange capacity can have important effects on column selectivity and this feature is not available with conventional ion exchange resins. The ion-exchange capacity can be changed by a number of techniques, but the simplest is to change the mobile-phase concentration or the hydrophobicity (increase molecular size) of the modifier added to the mobile phase. These exchangers can also be used in a "permanently" sorbed mode where the modifier is not present in the mobile phase[5,6].

3.2 Burnup Analysis

The analytical technique normally chosen for the determination of burnup (atom percent fission) in nuclear fuels has been isotope-dilutionmass spectrometry, because of its accuracy and its ability to determine individual isotopes. However, the overall procedure is time-consuming and the total cost per analysis can be high. Recently

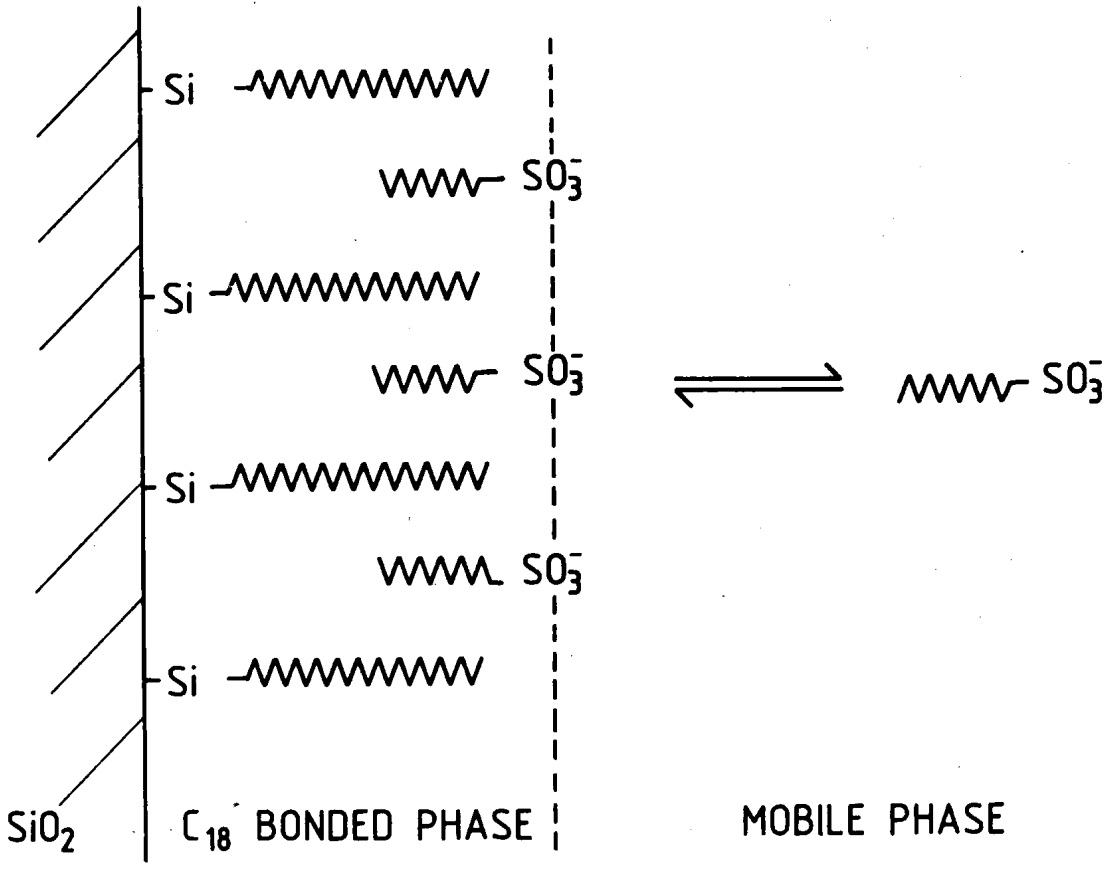

Figure 2. Preparation of dynamic ion exchanger for metal ion separations.

we developed a method for the determination of the number of fissions in $(Th,U)O_2$ fuels based on the HPLC determination of the fission monitor ^{139}La in dilute solutions of irradiated fuel[7]. This study showed that the relative standard deviation for a single determination calculated from the pooled HPLC results for 13 fuel solutions analyzed over a one month period was 0.96%, and the agreement between HPLC burnup results and those obtained by mass spectrometric procedures (^{145}Nd + ^{146}Nd fission monitor) was within 0.1%. Similar HPLC techniques are presently being investigated for the determination of the number of fissions and burnup in UO_2 and $(U,Pu)O_2$ fuels. Lanthanum is essentially monoisotopic (^{139}La) in the fuel, but unlike $(Th,U)O_2$ fuels, the fission yields for ^{139}La from the major fissioning isotopes are not similar; 6.38 ± 0.06% for ^{235}U, 5.62 ± 0.2% for ^{239}Pu, and 5.95 ± 0.4% for ^{241}Pu. Consequently an average fission yield is estimated from computer simulations for the fuel; the uncertainty introduced by this estimation should be less than the uncertainty associated with the individual fission yields.

A chromatogram obtained from the determination of La in an irradiated UO_2 fuel is shown in Fig. 3. This chromatogram shows that each determination takes only ~ 5 min, and that peak resolution is more than adequate without any preliminary sample treatment (other than dissolution and dilution). Consequently samples can be quickly analysed in triplicate, and the results in Table I show that the reproducibility for an analysis is < 1%; this is similar to results obtained for $(Th,U)O_2$ fuels. Preliminary comparisons with mass-spectrometric burnup measurements have shown agreement to within 3%. This is considered acceptable for most of our requirements; however we are attempting to determine the source of this small bias and are presently examining fission yield accuracy and contamination as potential sources of error[8]. Similar techniques have also been used for a limited number of burnup determinations for U-Al metal fuel; although controlled comparisons have not been made with other techniques, no apparent problems have been observed.

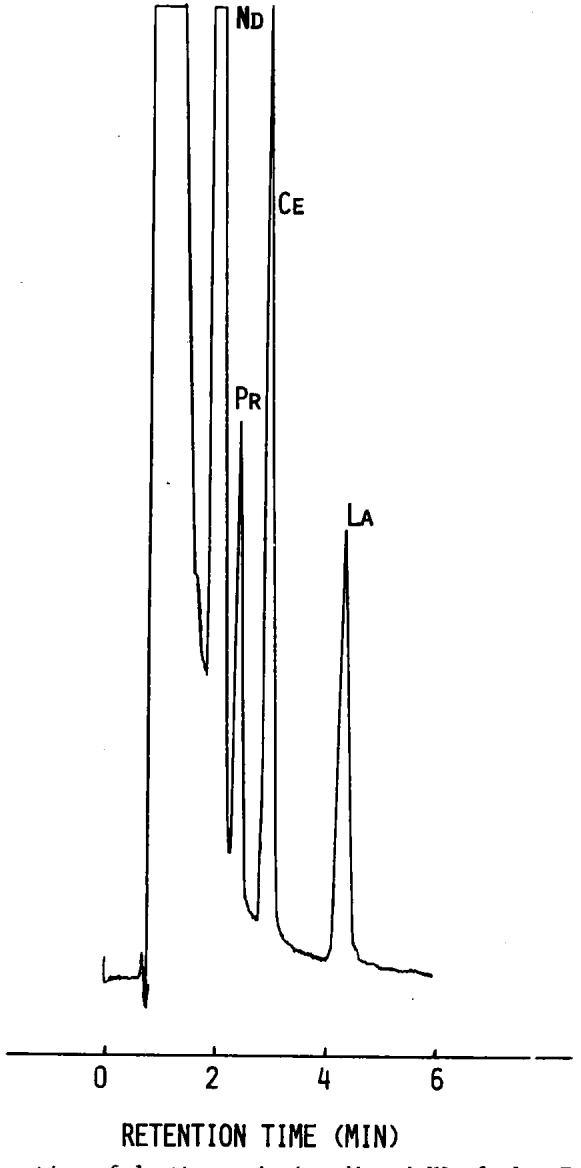

Figure 3. Separation of lanthanum in irradiated UO_2 fuel. Experimental conditions: Supelco LC18 column; eluent, 0.3 mol·L^{-1} α-hydroxyisobutyric acid, 5 x 10^{-3} mol·L^{-1} 1-octanesulfonate, pH 3.8, 2.0 mL·min^{-1}; sample, 100 µL of diluted fuel solution containing ~ 300 µg U (burnup ~ 1 atom percent); detection at 658 nm after postcolumn reaction with Arsenazo III.

Table I. Precision of Chromatographic Burnup Analysis of UO_2 Fuel

Sample†	Atom % Burnup
1	2.93
2	2.94
3	2.95
4	2.94
5	2.91
6*	2.92
7*	2.91
8 Standard	2.92
9 Addition	2.91
$\bar{X} = 2.926$, $\sigma = 0.015$ (0.5%)	

† Each sample was diluted separately from the original dissolved fuel solution.
* Samples done at different date with separate calibrations.

HPLC techniques for burnup measurements are particularly attractive due to their simplicity and speed, with little or no sacrifice in overall accuracy. Table II shows a comparison of the HPLC and mass spectrometric methods currently used at the Chalk River Nuclear Laboratories (CRNL). The interpretation of such a comparison will depend somewhat on the instrumentation and procedures used, but Table II should be realistic for most situations because conservative estimates were used for the HPLC technique. The data in Table II show that the relative time and cost advantages of the HPLC procedure can be as large as 10 fold.

3.3 Analysis of Lanthanides in New Fuels

Lanthanides with large cross sections for neutron capture (Dy,Gd, Eu, Sm) must not be present in new fuels above levels of ~ 0.2 $\mu g \cdot g^{-1}$. Quality-control analysis for these elements is difficult by spectrographic techniques, and results are unreliable at these low levels. Emission spectrometry in an inductively-coupled plasma (ICP) gives better results, but is sensitive to spectral interferences from the small amounts of the heavy elements not removed during sample preparation; this is particularly true for fuels

containing thorium. For new radioactive fuels, such as $(Th,Pu)O_2$ and $(Th,^{233}U)O_2$, sample containment is necessary, and this is not available in our laboratories for ICP analysis. Because of these problems HPLC is being investigated for this analysis.

Table II. Comparison of Methods to Determine Number of Fissions in Eight Samples of Nuclear Fuel

	La-HPLC	Conventional Nd-MS	CRNL Nd-MS
Dissolution and Spiking	---------- Constant Time Requirements ----------		
Separation from Actinides	0 h	16 h	0 h
Separation from Lanthanides	0 h	16 h	4 h*
Instrumental Analysis	6 h	24-36 h	24-36 h
Labour Costs at $50/h	$300.00	$3 200.00	$1 700.00
Equipment Costs	$30 000.00	$200 000.00	$200 000.00
Analyst Exposure	< 6 mR	~ 30 mR	~ 18 mR

*These separations are done by HPLC.

Fig. 4 shows the separation of Dy, Gd, Eu, and Sm that had been added to ThO_2 at the 0.1 $\mu g \cdot g^{-1}$ level; the bulk of the Th was removed by tributylphosphate extraction prior to injection of the sample. The unspiked ThO_2 showed peaks for Nd and La, but Dy, Gd, Eu and Sm were present at levels of < 2 $ng \cdot g^{-1}$ of ThO_2. Although this HPLC method is sufficient for ensuring compliance of new fuels with lanthanide specification limits, recoveries of the trace lanthanides during Th extraction were low (~ 75%), and faster and more efficient techniques are being studied for the removal of the bulk of the Th in the sample prior to injection into the HPLC.

此为试读,需要完整PDF请访问: www.ertongbook.com