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### Rapid Determination of Burn-Up of Nuclear Fuel—a Possible Approach

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RAPID DETERMINATION OF BURN-UP OF NUCLEAR FUEL- A POSSIBLE APPROACH

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ABSTRACT

High performance liquid chromatography (HPLC) has been used for the separation and estimation of light rare earths by making use of an anion exchanger or a dynamically modified reverse phase column as a cation exchanger. Both these methods were studied and relative performance was assessed from the point of view of their suitability for the determination of burn-up of nuclear fuels.

1. INTRODUCTION

The total number of fissions in a given amount of irradiated fuel is generally determined by measuring the number of atoms of a fission monitor, such as  $^{148}\text{Nd}$ , by isotope dilution mass spectrometry. Usually the fission product element is separated in pure form by the tedious and time consuming conventional ion exchange chromatography. The procedure takes several days. There is a need for a more rapid method.

The high performance liquid chromatography (HPLC) technique has been used, albeit rarely, for the separation of inorganic elements such as rare earths, transition metals and alkaline earths. Larsen (1) have separated neodymium from other lighter fission product rare earths in  $\text{CH}_3\text{OH}-\text{HNO}_3$  medium for the above purpose. Knight et al.(2) have developed dynamic ion exchange chromatography for the separation of individual rare earths from

their mixture by complexing with  $\alpha$ -hydroxyisobutyric acid ( $\alpha$ -HIBA) on a reverse phase column which was dynamically converted to a cation exchanger by using 1-octanesulfonic acid in the mobile phase. They have demonstrated that the fission product lanthanum in irradiated  $(\text{Th},\text{U})\text{O}_2$  can even be estimated by HPLC with necessary precision and accuracy. These studies indicate that considerable reduction in the burn-up measurement time might be possible for any type of fuel material by HPLC- even some of the mass spectrometric analyses can be avoided.

For the purpose of burn-up measurement by HPLC, neodymium is preferred over lanthanum because of the following reasons. (1) The elemental yield of neodymium is about three times that of lanthanum. Thus, the sensitivity is higher. (2) Six stable isotopes of neodymium ( $^{143}\text{Nd}$ ,  $^{146}\text{Nd}$ ,  $^{148}\text{Nd}$  &  $^{150}\text{Nd}$ ) are generated as compared to only one of La ( $^{139}\text{La}$ ). The effect of transmutation due to neutron capture (especially in high burn-up thermal reactor fuels) is much less in Nd as most of transmuted isotopes are also of Nd. Therefore, the burn-out correction is insignificant. (3) In the case of Nd, natural blank level can be checked periodically by monitoring  $^{142}\text{Nd}$  by mass spectrometry as this isotope is not produced in fission but has the maximum abundance in natural neodymium.

It is possible to estimate neodymium directly by HPLC if pre-separation of rare earths (from actinide elements) is carried out prior to injection onto the HPLC column. But there will be uncertainty in the chemical recovery during the preseparation stage. This can be avoided by making use of another rare earth element such as samarium, which is very similar in properties and whose elemental fission yield is less than one third that of neodymium, as an internal standard. The procedure would involve addition of a known amount of samarium to the irradiated fuel solution followed by group separation of rare earths and finally measurement of samarium to neodymium peak area ratio in the chromatogram. Thus, the concentration of neodymium can be calculated from the difference in ratio measured with or without the addition of samarium.

The success of the proposed HPLC based method would depend on (1) resolution, (2) reproducibility, (3) linearity of response and (4) constancy of the ratio of relative response factors of Nd and Sm over a range of concentration. Cation and anion exchange separation of rare earths by HPLC, following the published procedures mentioned above, were further studied from the point of view of these requirements. Investigations were carried out to examine the multi element analysis capability with improved sensitivity.

## 2. EXPERIMENTAL

### 2.1. Apparatus

This consisted of a solvent delivery pump (Micromeritics model 750), a variable wave length detector (Micromeritics model 787) with a 12  $\mu$ l flow cell and an integrator/plotter. For post-column reagent addition a peristaltic pump was used.

### 2.2. Separation based on anion exchange

The column (250 mm x 4.6 mm ID) was packed with a strong anion exchanger (Partisil 10 SAX) of 10  $\mu$ m particles. All chemicals used were of analytical grade.

The rare earths were obtained in oxide form from Indian Rare Earths Ltd. having a purity greater than 99.99% and of natural isotopic composition. The oxides of Sm(+3), Nd(+3), Pr(+3) and La(+3) were dissolved in concentrated nitric acid, evaporated to dryness and stock solutions were made in dilute nitric acid (1.5M). Ce(+3) was prepared by dissolving ceria in nitric acid and reducing Ce(+4) to Ce(+3) with hydrogen peroxide.

Elutrients of different compositions were made by mixing appropriate quantities of reagent grade methanol, deionized quartz distilled water and distilled nitric acid. The optimum composition arrived at was 0.7 v% 1M nitric acid in methanol.

The flow rate was maintained at 1 ml/min and the concentration of each ion was of the order of  $10^{-4}$  M. 20  $\mu$ l of the sample solution was injected through a Rheodyne 7125 injection valve. Metal ion elution was monitored by UV detection at 280nm. A typical chromatogram is shown in fig. 1.

It was observed that the optimum elutrient composition arrived at by us is much different from that of Larsen (1). This is possibly due to the difference in the resin from batch to batch. Use of a second column which was obtained along with the first one, possibly of the same batch, yielded results similar to those obtained with the first.

### 2.3. Separation based on dynamic ion exchange

The column (150 mm x 4.6 mm ID) used was of reverse phase C<sub>18</sub> bonded material, a Spherisorb-5-ODS-2. This was dynamically modified to act as a cation exchanger by reversible sorption of 1-octanesulfonate from the mobile phase onto the n-octadecyl groups bonded onto the silica support. The mobile phase also contained the complexing agent,  $\alpha$ - HIBA. The elements were detected by post column reaction (PCR) with pyridyl-azo-resorcinol (PAR) or arsenazo -III.

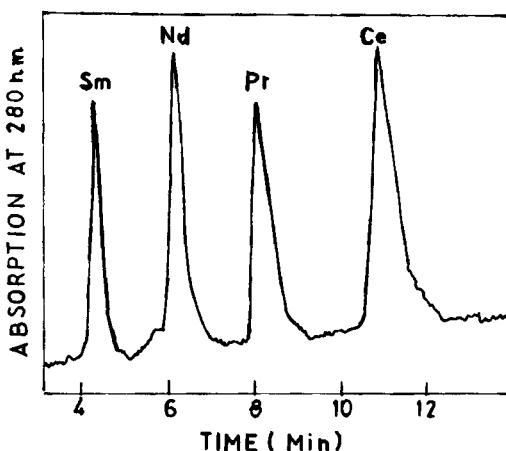


Fig. 1 Anion exchange separation of lighter rare earths on Partisil 10 SAX column. Eluent: 0.7 v% 1M nitric acid in methanol.

All the reagents,  $\alpha$ -HIBA, sodium salt of 1-octane sulphonic acid, PAR and arsenazo-III were of reagent grade and were used without further purification.

The concentrations of  $\alpha$ -HIBA and 1-octanesulphonic acid were varied from 0.075M to 0.25M and 0.001M to 0.1M respectively. The pH was maintained at 4.6. The flow rate was set at 1 ml/min. The derivatizing reagent was added using either a peristaltic pump or an LDC-Milton Roy mini pump. The mixing was done in a zero dead volume tee and the solution was then passed through a 3m(0.5mm ID) coiled stainless steel capillary tubing, which acted as a pulse dampener, prior to admitting it into the flow cell. The output of the detector was fed into a strip chart recorder/integrator and printer. The absorption was monitored at 535 nm when PAR ( $2 \times 10^{-4}$  M PAR in 2M ammonium hydroxide and 1M ammonium acetate) was used as the post column reagent and at 653 nm when arsenazo-III ( $1.5 \times 10^{-4}$  M) was used.

The optimum mobile phase composition arrived at was 0.178M  $\alpha$ -HIBA and  $5 \times 10^{-3}$  M 1-octanesulphonate, which was similar to that obtained by Cassidy et al.(3). A typical chromatogram obtained is shown in fig.2.

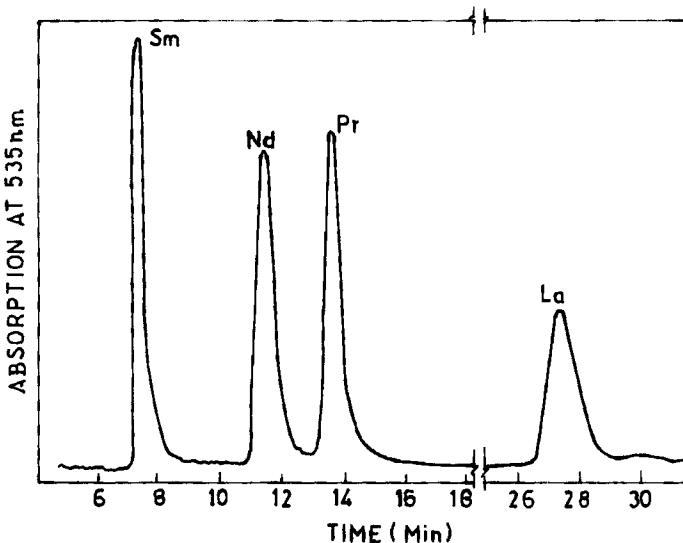


Fig. 2 Separation of lighter rare earths on Spherisorb-5-ODS-2 column dynamically modified with 1-octane sulfonate. Detection by post-column reaction with Pyridyl-azo-resorcinol.

#### 2.4. Post column reaction detection in anion exchange

To assess the relative sensitivities in post column detection, the representative effluent for both types of columns discussed above were mixed with different complexing agents and spectrophotometrically scanned from 700 nm to 250 nm. Lanthanum was taken as the reference for rare earth elements. The resulting absorption spectra are given in fig. 3.

It is evident from these absorption spectra that, among the various combinations attempted, maximum detection sensitivity can be achieved in the case of anion exchange separation by post column reaction with arsenazo-III. A chromatogram generated under these conditions is given in fig. 4. The aqueous arsenazo-III solution was added to the column eluents at the rate of 0.5 ml/min and the mixture was then passed through the UV detector. Absorption was monitored at 653 nm.

#### 3. RESULTS AND DISCUSSION

According to Cassidy et al.(2) the bonded phases showed poor column to column reproducibility with poor efficiencies and

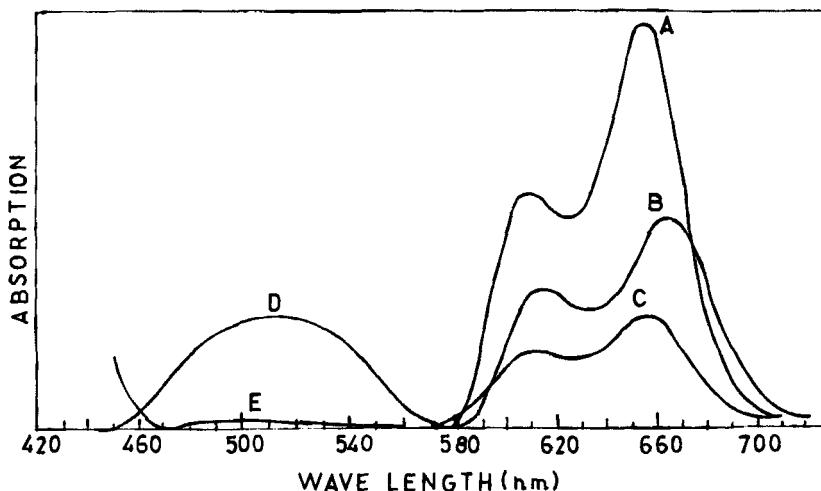


Fig. 3 Absorption spectra of complexes of lanthanum in different mobile phases:

- (A) in methanol-nitric acid with arsenazo-III (aq.)
- (B) in  $\alpha$ -HIBA + 1-octane sulfonate with arsenazo-III (aq.)
- (C) as in A but with arsenazo-III (0.1 M  $\text{HNO}_3$ )
- (D) in  $\alpha$ -HIBA + 1-octane sulfonate with PAR
- (E) in methanol-nitric acid with PAR

the column beds were unstable. But we found that even though the column did exhibit a lack of reproducibility from batch to batch, the columns belonging to the same batch gave consistent results. The reproducibility from sample to sample on the same column was found to be good. Even after three months of regular use the column bed was stable and well-behaved.

The post column detection system employed gave very good detection limits (in the nanogram levels) but was limited due to noise and pulsations caused during the delivery of post column reagent. With the peristaltic pump we could obtain a detection limits of 10 ng for lanthanides.

On introduction of PCR detection into the anion exchange method of separation of rare earths in methanol-nitric acid-water medium a drastic improvement in sensitivity could be achieved compared to direct detection at 280 nm. Earlier Cassidy et al.(2) had coupled PCR detection to dynamic anion exchange but reported that difficulties were encountered due to the large

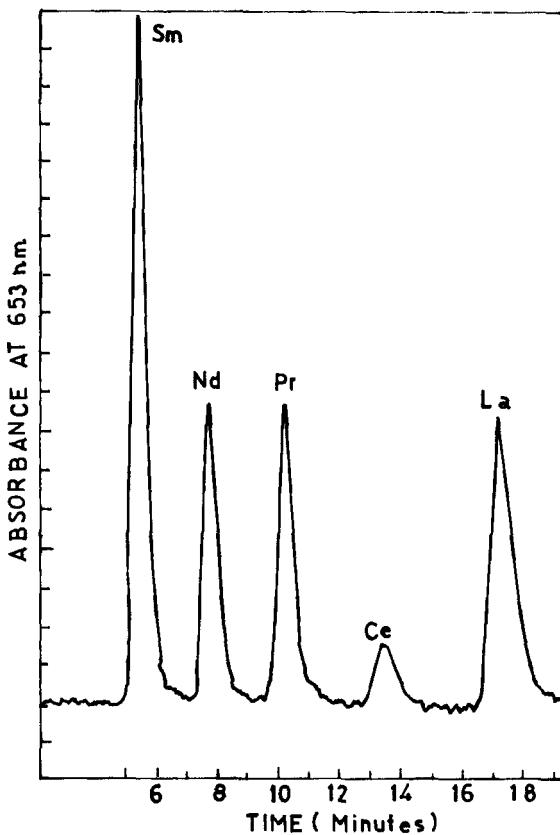


Fig. 4 Anion exchange separation of lighter rare earths with 0.7 v% of 1M nitric acid in methanol as the mobile phase. Detection by post-column reaction with arsenazo-III.

amounts of organic solvents present in the mobile phase. We did not observe any such effects with the bonded phase exchangers. The derivatizing agent PAR did not have any significant effect on the analytical sensitivity, but a considerable improvement in detection sensitivity was observed with arsenazo-III. It can also be seen from fig. 3 that for the same concentration of La present, the absorption is much higher in methanol-nitric acid-water than in aqueous  $\alpha$ -HIBA medium. Thus well resolved chromatograms with improved sensitivity could be obtained using the anion exchange column.

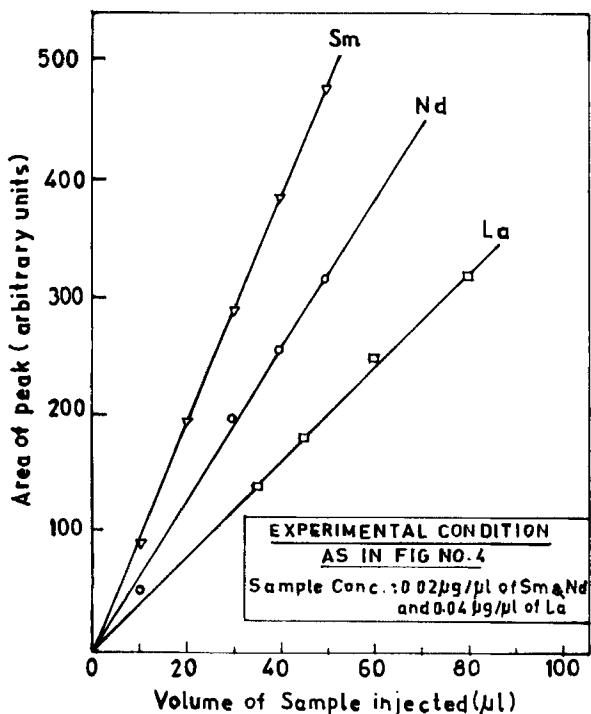


Fig. 5 Calibration plots of Sm, Nd and La by cation exchange in  $\alpha$ -HIBA + 1-octane sulfonate with PCR detection at 653 nm.

TABLE 1

Ratio of relative response factor	Amount injected			
	100ng	200ng	500ng	1000ng
Sm/Nd	1.47	1.48	1.49	1.48
Nd/La	1.60	1.60	1.60	1.59
Sm/La	2.35	2.35	2.40	2.39

As discussed in section 1, one of the requirements for successful application of the method based on the use of an internal standard is that the ratio of relative response factors of the two elements should remain constant over a range of concentrations. Experiments were carried out to check this constancy. Calibration plots (fig.5) of peak area vs amount injected were obtained for samarium, neodymium and lanthanum which were present in a mixture. Linearity of the plots demonstrates that quantitative estimation is possible by this technique.

Relative response factors as a function of injected amount can also be obtained from these plots. Ratio of relative response factors for three different pairs are given in table 1. For every pair the ratio remained almost constant over the examined range. Thus samarium can be used as internal standard for the estimation of neodymium.

#### 4. CONCLUSIONS

Rapid chemical separation of lighter rare earths is possible by HPLC. Both anion exchange and cation exchange procedures yield highly resolved and reproducible chromatograms necessary for quantitative analysis. It thus appears likely that this procedure could find applicability in measuring the burn-up of irradiated nuclear fuel by determining the content of fission product neodymium, using samarium as an internal standard. The procedure would be much more rapid than conventional techniques.

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