



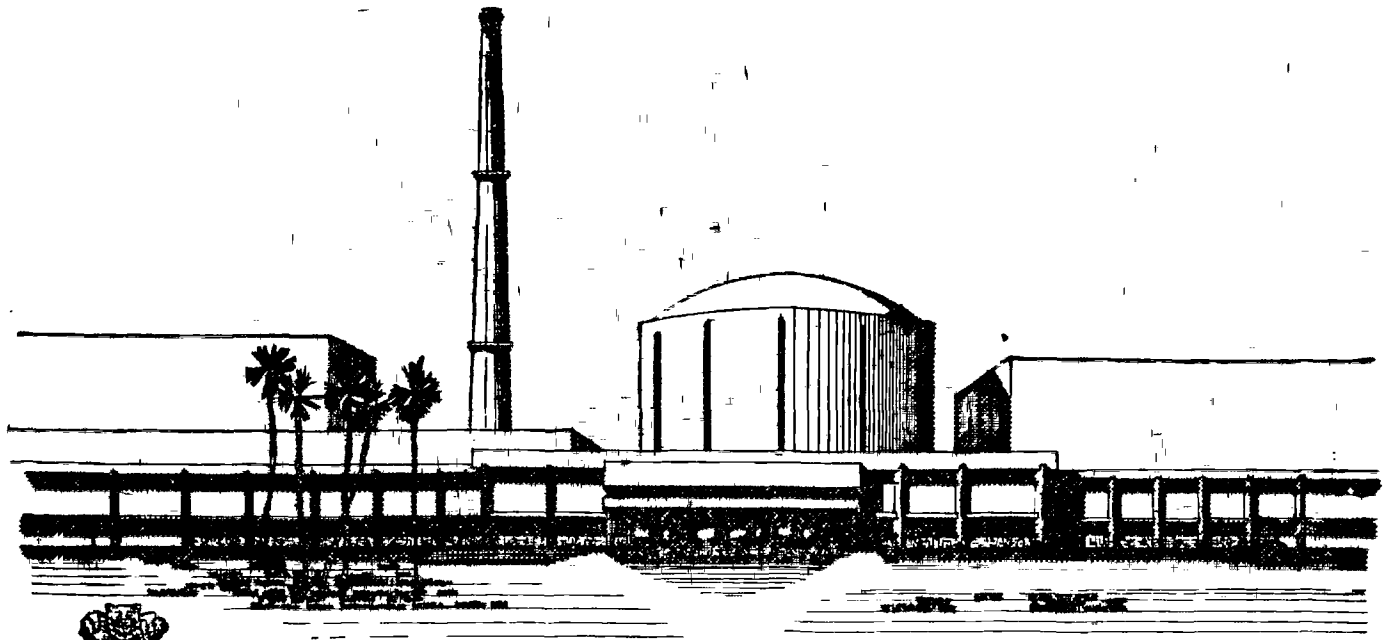
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Development of High Performance Liquid Chromatography for Rapid Determination of Burn-up of nuclear fuels

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ABSTRACT

Burn-up is an important parameter during evaluation of the performance of any nuclear fuel. Among the various techniques available, the preferred one for its determination is based on accurate measurement of a suitable fission product monitor and the residual heavy elements. Since isotopes of rare earth elements are generally used as burn-up monitors, conditions were standardized for rapid separation (within 15 minutes) of light rare earths using high performance liquid chromatography based on either anion exchange (Partisil 10 SAX) in methanol-nitric acid medium or by cation exchange on a reverse phase column (Spherisorb 5-ODS-2 or Supelcosil LC-18) dynamically modified with 1-octane sulfonate or camphor-10-sulfonic acid (β). Both these methods were assessed for separation of individual fission product rare earths from their mixtures. A new approach has been examined in detail for rapid assay of neodymium, which appears promising for faster and accurate measurement of burn-up.

Development of High Performance Liquid Chromatography for Rapid Determination of Burn-up of Nuclear fuels

M. Joseph¹, D. Karunasagar² and B. Saha³

1. Introduction

Among the important quantities requiring accurate measurement on irradiated nuclear fuel, after test irradiations during any fuel development campaign or even after normal irradiation in a reactor for checks on fuel performance, burn-up is a key parameter. The term burn-up is used in nuclear fuel technology to express the degree of fuel consumption by the fission process. Though it is defined in many ways such as megawatt-days of thermal energy produced per metric ton of fuel, fissions per cubic centimeter of fuel etc., the most common way is to express it in atom percent fission as, being more fundamental, it relates directly to the number of events of interest.

$$\text{Atom \% fission} = \frac{\text{number of fissions}}{\text{initial number of heavy atoms (> 225)}} \times 100 \quad \dots \quad (1)$$

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Total number of fissions as well as fission rates can be calculated from burn-up data.

The thermal energy produced by any fuel is determined by the total number of fissions.

This is necessary to evaluate the overall performance. Fission rates are used to determine fuel performance characteristics such as power levels, fuel and cladding temperatures and fuel-cladding gap conductance.

2. Techniques for determination of burn-up

Burn-up is determined most accurately by destructive chemical methods.

However, for relative measurements, such as its variation along the axial direction in a fuel pin, a non-destructive technique like gamma-ray spectrometry can be used.

The chemical technique makes use of either of the following approaches:

- through measurement of a suitable fission product monitor and the residual heavy atom contents of a dissolved fuel specimen and calculation of burn-up from these data, making use of the fission yield of the selected fission product isotope or
- through measurement of U and Pu isotopic contents in dissolved specimens of both the irradiated and unirradiated fuel and evaluating the burn-up from the changes, making use of appropriate nuclear cross-section data.

The first technique, namely the fission product monitor residual heavy atom method, has the advantage that it is applicable to samples of all fuel composition re-

ardless of burn-up level and it eliminates the need for analysis of unirradiated fuel specimen.

The other technique is applicable only when the burn-up is high and when an archive sample (unirradiated specimen) is available for analysis. Another marked disadvantage is that these analyses have to be done on the unirradiated and irradiated samples of equivalent weight, which is difficult to meet especially for FBR fuels as the high temperature operation and high burn-up brings about considerable changes due to several factors such as fuel slumping, fuel-cladding chemical interactions, restructuring and inhomogenous porosity.

The discussion hence forth is only with respect to the fission product monitor residual heavy atom technique as it is best suited for the fast reactor programme.

2.1. Fission Product Monitor - Residual Heavy Atom Technique

In this method the fuel sample is dissolved and the fission product monitor and the heavy atoms are determined. Burn-up can then be calculated using the following equation:

$$\text{Burn-up (at\% fission)} = 100 \times \frac{A/Y}{H + A/Y} \quad (2)$$

where

A - Number of atoms of fission product monitor

Y - fractional fission yield of the monitor and

H - Total number of residual heavy atoms.

The success of this method hinges on the ability to accurately determine the fission product monitor and heavy atoms as well as on the availability of accurate data on fission yield.

2.2. Selection of the fission product monitor

The desirable properties of the fission product monitor nuclide are :

- 1) stable or very long lived with short lived precursors.
- 2) chemical stability in the fuel matrix and in the dissolved fuel solution,
- 3) amenability for accurate and precise measurement,
- 4) significant fission yield with accurately known data,
- 5) production only through fission with negligible effect of burn-in or burn-out of the monitor by other side nuclear reactions.

For thermal reactors, ^{148}Nd has always been chosen because it possesses the desirable chemical properties, both in fuel and in solution. Its fission yield is practically same for ^{235}U and ^{239}Pu thermal fission and it can be accurately measured.

But for fast reactor fuels, the selection is not straight forward because of the following:

- 1) more widely varying fuel compositions,
- 2) varying sources of fission, especially in fuel development studies and
- 3) variation in the fission yields with neutron energy.

Many laboratories continue to use ^{148}Nd for fast reactor fuels though it is not the ideal monitor. However for FBTR fuel ^{148}Nd is a good fission monitor. For proposed fuel composition of PFBR some other isotope of Nd, either singly (like ^{143}Nd) or in combination can be used as fission monitor. Yields for Nd isotopes are given in table I [1, 2] for the fissionable isotopes of U and Pu.

Development of thorium based fuels for pressurized heavy water reactors (PHWR's) [3] are currently gaining importance. Though the sum of ^{145}Nd and ^{146}Nd has been used, it involves errors because of substantial differences on their fission yields from ^{233}U and ^{235}U [4]. For such fuels La has been used successfully; its determination being done by both thermal ionization mass spectrometry [5] and by high performance liquid chromatography [6].

2.3. Conventional method

Irrespective of the chosen fission product monitor, the most accurate technique to determine the concentration of the monitor isotope remains to be the isotope dilution

mass spectrometry (IDMS). It currently gives errors of $\approx 0.5\%$ on the measurement of fission product monitor nuclide, and $\approx 0.2\%$ for uranium and plutonium, achievable on a semi-routine basis by highly qualified individuals. The propagated uncertainty associated with the measurements is less than 1% relative. Measurement involve dissolution of irradiated fuel in a shielded facility followed by laborious and time consuming chemical separations. Separations are generally carried out in several steps by repeated extraction and ion exchange chromatography [7-9]. The steps involved in separation are shown in fig.1. At least two days are required just for chemical separation.

High Performance Liquid Chromatography (HPLC) offers a faster alternative. It can substantially reduce the separation time. Its easy adaptability to remote operation offers the added advantage that the operator is exposed to less dosage [10,11].

As noted earlier, isotopes of Nd are the best fission monitors. Their determination by IDMS requires that Nd be separated from spent fuel and must be obtained free from Ce and Sm since the isotopes ^{142}Ce , ^{144}Ce , ^{148}Sm and ^{150}Sm interfere with corresponding isotopes of Nd. The work carried out on the separation of light rare earths using anion exchange or dynamic cation exchange chromatographic techniques and a new approach for quantitative estimation of Nd using Sm as an internal standard are discussed in this report.

2.4. Proposed Method

Cassidy et al [10] showed that La^{139} , when used as the monitor isotope, can provide sufficiently accurate burn-up data, using HPLC for its assay for thorium based fuels where the major fissionable isotopes are U^{233} and U^{235} . However, when plutonium contributes significantly to total fission in thermal or fast neutron environment, the fission yield for La^{139} is different for different fissionable isotopes [12] (Table II). Isotopes of Nd are generally better choice for fuels containing plutonium. Also for the purpose of assay by HPLC, neodymium is preferred over La for the following reasons :

- i) The elemental yield of neodymium is about three times that of lanthanum. Thus, the sensitivity is higher.
- ii) Six stable isotopes of neodymium ($^{143-146}\text{Nd}$, ^{148}Nd and ^{150}Nd) are generated as compared to only one of La (^{139}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 the transmuted isotopes are also of Nd. Therefore, the burn-out correction is insignificant.
- iii) In the case of neodymium, natural blank level can be checked periodically by monitoring ^{142}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 Nd directly by HPLC if pre-separation of rare earths

(from actinide elements) is carried out prior to injection on to the HPLC column. But there is uncertainty in the chemical recovery during the pre-separation stage. This can be avoided by making use of another rare earth element such as Sm as an internal standard. It is very similar in chemical properties and its elemental fission yield is less than one third that of neodymium. The procedure involves 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 obtained from the difference in the ratio measured with or without the addition of Sm. The isotopic composition can be obtained by a single run of the Nd fraction in a mass spectrometer, thus greatly reducing the number of mass spectrometric runs as otherwise would have been needed by the conventional method. The overall time reduction through HPLC based chemical separation and through less mass spectrometric measurements is substantial.

The success of the proposed HPLC based method would depend on factors like

- i) Resolution,
- ii) Reproducibility,
- iii) Linearity of Response and
- iv) Constancy of the ratio of relative response factors of Nd and Sm over a range of

concentration.

We are looking for only the ratio of peak areas of Sm and Nd. Hence, extra care is not needed in quantitative dilution of the dried sample with eluent and the amount of the diluted sample injected for filling the loop, which are the main sources of error in quantitative estimation by HPLC in absence of the internal standard.

3. Experimental

3.1. The HPLC System

The HPLC system used in this study was assembled from components procured commercially. The solvent delivery pump used was a Micromeritics model 750 with a pressure rating of 6000 psi. The pumps used in the post column detection system are peristaltic pump (Watson Morlous) and Milton Roy (LDC) mini pump. Micromeritics model 753 solvent mixer was used for mixing different components needed for gradient elution. A variable wave length detector (Micromeritics model 787) equipped with 12 μ l flow cell was made use of to monitor the elution of the rare earth complexes and the absorbance was recorded on a strip chart recorder. For quantitative analysis, the detector output was fed to an integrator (LDC Milton Roy CI-10) in order to get the peak area directly. The schematic diagram of the experimental set up is shown in fig.2.

3.2. Separation based on anion exchange method

The column (250mm X 46 mm ID) was packed with a strong anion exchanger (Partisil 10 SAX) with quaternary ammonium groups as active sites, covalently bonded to silica particles of 10 μm diameters.

All chemicals used were of analytical grade. The rare earths were obtained from Indian Rare Earths Ltd., having a purity greater than 99.99% and of natural isotopic composition. The oxides of Sm(III), Nd(III), Pr(III) and La(III) were dissolved in concentrated nitric acid, evaporated to dryness and stock solutions were made up in dilute nitric acid (1.5 M). Ce(III) was prepared by dissolving ceria in nitric acid and reducing Ce(IV) to Ce(III) with H_2O_2 .

Prior to injection, the required amounts of metal ions were taken from stock solution, evaporated to dryness and redissolved in the desired elutriants. The Column was pre-conditioned for a sufficiently long time in order to get a steady base line.

Elutriants of different compositions were made by mixing appropriate quantities of reagent grade methanol, deionized quartz distilled water and distilled nitric acid. In this study, four rare earth elements namely Sm, Nd, Pr and Ce were chosen, on account of the fact that isotopes of neodymium are used as fission product monitors in the determination of burn-up. Consequently, the emphasis is on obtaining Nd which is

free from adjacent rare earths, particularly devoid of Sm and Ce which cause isobaric interference in the subsequent isotopic measurements.

In the sample, the concentration of each ion was of the order of 10^{-4} M. $20 \mu\text{l}$ of the sample solution was injected through the injection valve. The flow rate was maintained at 1 ml/min, which was considered optimum after some trials. The eluted nitrate complexes of the metal ions were monitored at 280 nm.

A detailed study of the effect of mobile phase composition on the retention behaviour of these rare earth nitrate complexes was carried out by changing the pH, volume percent of water and the nitrate ion concentration in the mobile phase [13]. The optimum composition was at 0.7 V% 1 M nitric acid in methanol and the chromatogram obtained under these conditions is shown in fig. 3. Two spurious peaks were observed between Sm and Nd when the sample solution was allowed to stand for more than 10 minutes before loading on to the column. The above peaks were not due to any rare earth complexes, as the eluate corresponding to these peaks not give colouration with arsenazo III. On re-evaporation of the sample to dryness and re-dissolving in fresh elutrient, those two extraneous peaks disappeared. Fig. 4 shows the spurious peaks in the chromatogram.

It was observed that the optimum elutrient composition, arrived at by us, is

much different from that of Larsen et al. [14]. 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.

3.3. Separation by dynamic cation exchange method

The column (150 X 4.6 mm ID) used was of reverse phase C_{18} bonded material, Spherisorb-5-ODS-2. The ion exchange surface was established by the reversible sorption of n-octylsulfonate or camphor-10-sulfonic acid (present in the mobile phase) onto an n-octadecyl phase bonded to a porous silica support (particle diameter of 5 μm). This sorption produced a negatively charged surface with its associated cation, counter-ion region in the mobile phase and the exchange of the cation can occur in this counter layer. This type of dynamic exchangers have high column efficiency and easily variable ion exchange capacity [15].

The chemicals used for the preparation of samples are as given in section 3.2. The elements were detected by a post column reaction (PCR) with pyridyl-azo-resorcinol (PAR) [E. Merck, West Germany] or 3,6-bis [(o-arsenophenyl)azo]-4,5-dihydroxy-2,7-naphthalene disulfonic acid (arsenazo III) [Tokyo Kesai, Japan]. The modifier used was either 1-octane sulfonate [BDH Chemicals, England] or Camphor-10-

sulfonic acid (β) [Fluka AG, Switzerland]. In addition to the modifier, the mobile phase also contained the complexing agent, α -hydroxy isobutyric acid (α -HIBA) [Tokyo Kesai, Japan]. All the reagents were used without further purification.

A number of experiments were carried out with various mobile phase compositions. When 1-octane sulfonate was used as the modifier, the concentrations of α -HIBA and the modifier were varied from 0.075 M to 0.35 M and 0.001 M to 0.1 M respectively. The pH was maintained at 4.6. In another set of experiments, a new modifier, camphor-10-sulphonic acid (β) was tried for the first time. It is about 15 times cheaper than the 1-octane sulfonate. The concentrations of α -HIBA and camphor-10-sulphonic acid were varied from 0.07 to 0.12 M and 0.005 to 0.02 M respectively. The pH of the solution was also varied from 3.5 to 5.5. The flow rate of the mobile phase was set at 1 ml/min and that of the complexing agent, PAR at 1 ml/min and arsenazo III at 0.5 ml/min. The derivatising reagent was added using either a peristaltic pump or a LDC Milton Roy mini pump. The mixing was done in a zero dead volume tee and the solution was then passed through a 3 meter (0.5 mm 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

(2×10^{-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 (1.5×10^{-4} M) was used.

When 1-octane sulfonate was used as the modifier, the optimum mobile phase composition arrived at was 0.175 M α -HIBA and 5×10^{-3} M 1-octanesulfonate, which was same as that obtained by Cassidy et al.[10]. A typical chromatogram is shown in fig.5.

With camphor-10-sulphonic acid as the modifier, the optimum mobile phase composition arrived at was 0.065 M α -HIBA and 0.05 M modifier. Using this modifier, complete separation of all the fourteen rare earths was obtained under gradient elution conditions as shown in fig. 6.

3.4. Post column reaction detection in anion exchange method

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 sepectrophotometrically scanned from 700 nm to 250 nm. Lanthanum was taken as the reference for the rare earths elements. The resulting absorption spectra are given in fig. 7.

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. 8. The aqueous arsenazo-III solution was added to the column effluent at the rate of 0.5 ml/min and the mixture was then passed through the UV detector. Absorption was monitored at 653 nm.

4. Results and discussion

4.1. On evaluation of Column performance

According to Knight et al. [6], the bonded phases showed poor column to column reproducibility with poor efficiencies and the column beds were unstable. But we found that, eventhough the columns 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.

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 Knight et al. [6] had coupled PCR detection to dynamic anion exchange method but reported that difficulties were encountered due to the large amounts of organic solvents present in the mobile phase. We did not observe any such effects with the bonded phase anion ex-

changers. 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. 7 that for the same concentration of lanthanum present, the absorption is much higher in methanol-nitric acid-water than in aqueous α -HIBA medium. Thus well resolved chromatograms with improved sensitivity could be obtained for the light rare earths using the anion exchange column.

The post column detection employed gave very good detection limits (in the nanogram levels) and was limited by noise and pulsations caused during the delivery of post column reagent. With the peristaltic pump we could obtain the detection limits of about 10 ngs for lanthanides.

4.2. On the proposed method

As discussed in section 2.4, one of the requirements for successful application of the method based on the use of an internal standard is that the ratio of the 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. 9) of peak area vs amount injected were obtained for Sm, Nd and La which were present in a mixture. Linearity of plots demonstrates that quantitative estimation is possible by this technique.

Relative response factor (RRF) as a function of injected amount can also be obtained from these plots. Ratios of relative response factors for three different pairs are given in table III. For every pair the ratio remained almost constant over the experimental range. Fig. 10 and 11 show plots of ratios of amounts of Sm to Nd vs the ratios of peak areas obtained. This confirms that the ratio of RRF is constant over a wide range of concentrations, for varying amounts of Sm to Nd.

In this proposed method, in the first stage, the rare earth group has to be separated from the host of other fission product elements, U and Pu. Generally this is carried out on a polymer based ion exchange resin (Dowex 1 X 8) using methanol-nitric acid mixture as the eluent [16]. The separated rare earth group will have U as an impurity. Hence for quantitative determination of Nd using Sm as an internal standard, complete separation of Eu (adjacent heavier rare earth to Sm), Sm, Nd and Pr (adjacent lighter rare earth to Nd) and U must be achieved. However it was found that in the anion exchange method (using Partisil 10 SAX), U peak overlaps either with Sm or Nd or both for the various compositions of mobile phase tried. Hence, for quantitative estimation of Nd by HPLC using Sm as a internal standard, the anion exchange method needs further investigation.

But with dynamically modified cation exchange method, the complete separation

of Eu, U, Sm, Nd and Pr was obtained within 12 minutes. Fig. 12 shows the chromatogram obtained for such a separation along with the experimental conditions. Under these conditions, a quantitative estimation of Nd was done using Sm as the internal standard (see table IV). The sample solution containing Eu, U, Sm, Nd and Pr was prepared to represent a typical irradiated fuel solution.

4.2.1 Determination of concentrations from chromatograms

The expression for determination of concentration of neodymium was arrived at in the following manner.

Initially the fission product sample has a neodymium to samarium atom ratio (sR) as decided by their respective fission yields.

$${}^sR = {}^sN_{Nd} / {}^sN_{Sm} \quad \dots (3)$$

where, sN represents the number of atoms in the sample.

Let a known number of atoms of the internal standard samarium (${}^T N_{Sm}$) be mixed with the sample, altering the Nd to Sm ratio to ${}^M R$ in the mixture.

$$\text{Then } {}^M R = {}^s N_{Nd} / [{}^s N_{Sm} + {}^T N_{Sm}] \quad \dots (4)$$

On elimination of ${}^s N_{Sm}$ from (3) and (4), one gets the following expression for the unknown number of neodymium atoms in the sample (${}^s N_{Nd}$),

$${}^s N_{Nd} = {}^T N_{Sm} [{}^s R \cdot {}^M R / ({}^s R - {}^M R)] \quad \dots (5)$$

The above equation has to be corrected for the relative response factor (RRF) as given in eqn. (6). This correction is needed in view of the fact that the response of the detector is not identical for Nd and Sm complexes.

$${}^{\text{Nd}}N_{\text{Nd}} = {}^{\text{Sm}}N_{\text{Sm}} [{}^{\text{Sm}}R_{\text{Sm}} / ({}^{\text{Nd}}R_{\text{Nd}})] * \text{RRF} \quad \dots (6)$$

where the RRF is defined as,

$$\text{RRF} = [C_{\text{Nd}}/C_{\text{Sm}}] * [A_{\text{Sm}}/A_{\text{Nd}}] \quad \dots (7)$$

(C_{Nd} is the concentration of Nd and A_{Nd} is the corresponding area of the chromatogram; C_{Sm} is the concentration of Sm and A_{Sm} is the corresponding area of the chromatogram and RRF is to be determined by a separate experiment as discussed in section 4.2).

The ratios mentioned above, in eqn. (6), can be derived from peak areas in the chromatograms. Data can be readily obtained in any concentration units from the knowledge of weights or volumes of the sample and the standard solutions mixed.

5. Conclusions

Methodologies have been developed for rapid and accurate determination of burn-up of reactor fuels based on a new approach for faster analysis of fission monitor in the dissolved fuel solution. Separation of light rare earths was achieved by HPLC within 15 minutes. Neodymium could be estimated with a good accuracy (<1%

error) using Sm as the internal standard. Results showed that the dynamic cation exchange method is better for separation over the one involving anion exchange, even though the sensitivity of detection is higher by the later method. In addition to faster chemical separation, the demand on mass spectrometer time is also considerably less for neodymium measurement. Thus the time involved for one burn up measurement can be reduced substantially. Moreover, in view of remote operability of the HPLC based appropriate separation cum analysis systems, the radiation exposure to the operating personnel can also be reduced considerably.

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Table I

Fast reactor fission yields for Neodymium isotopes [1,2] for different Fissioning nuclide.

Isotope	^{233}U	^{235}U	^{238}U	^{239}Pu	^{241}Pu
^{143}Nd	5.54	5.80	4.56	4.38	4.60
^{144}Nd	4.40	5.27	4.48	3.72	4.20
^{145}Nd	3.20	3.83	3.76	3.01	3.27
^{146}Nd	2.39	2.94	3.40	2.47	2.74
^{148}Nd	1.20	1.68	2.08	1.65	1.91
^{150}Nd	0.465	0.672	1.25	0.982	1.19

Table II

Fast and thermal fission yields for ^{139}La [12]

Isotope	Thermal	Fast
^{235}U	6.37	6.33
^{238}U	-	5.89
^{233}U	6.31	6.37*
^{239}Pu	5.68	5.50
^{241}Pu	5.86	6.33*
^{232}Th	-	7.06

* - Ref. [1,2]

Table III

Relative response factor with different injected amount

Ratio of relative response factor	Amount Injected			
	100 ngs	200 ngs	500 ngs	1000 ngs
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

Table IV

Quantitative estimation of Nd present in a mixture of U, Eu, Sm and Pr using Sm as the internal standard.

Sample No.	Conc. of Nd (ppm)
1	103.3
2	104.9
3	102.1
4	104.5
5	105.5
6	107.8

$$\bar{x} = 104.7$$

$$s = 1.2$$

$$\text{RSD} = 1.9\%$$

[Actual concentration of Nd in the sample is 103.86 ppm].

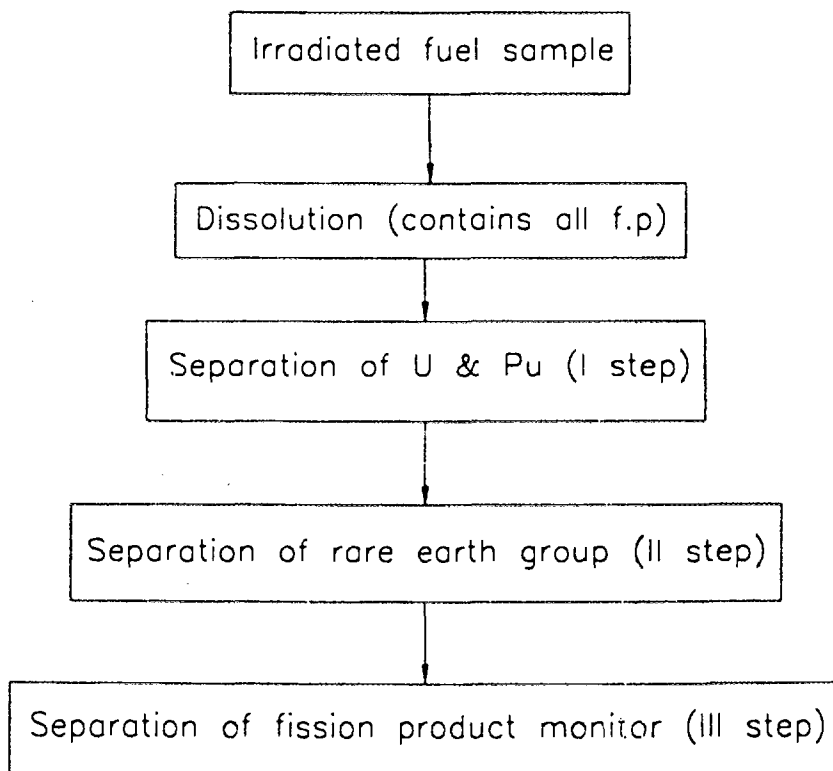


Fig. 1. Steps involved in the separation of a fission product monitor.

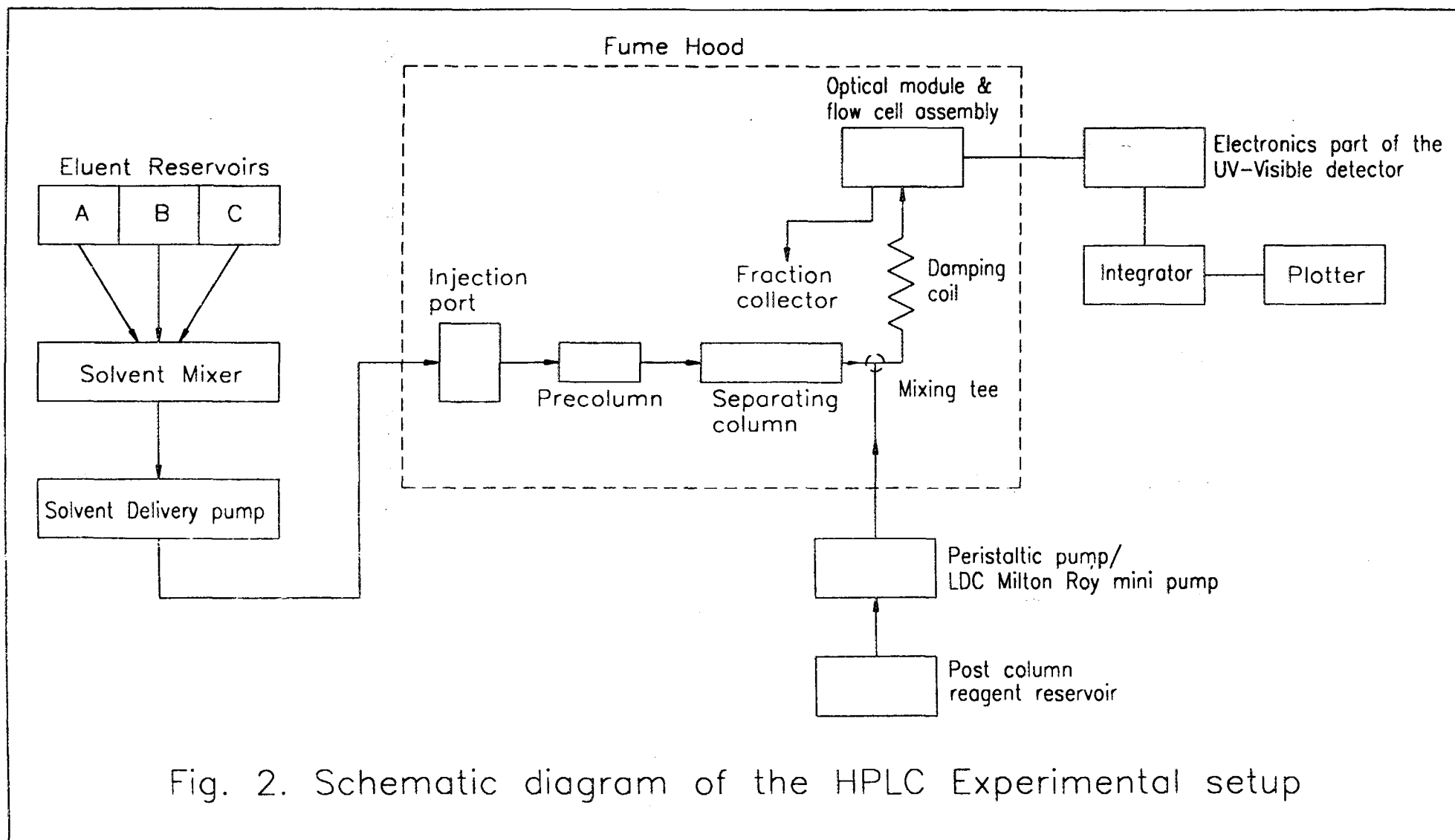


Fig. 2. Schematic diagram of the HPLC Experimental setup

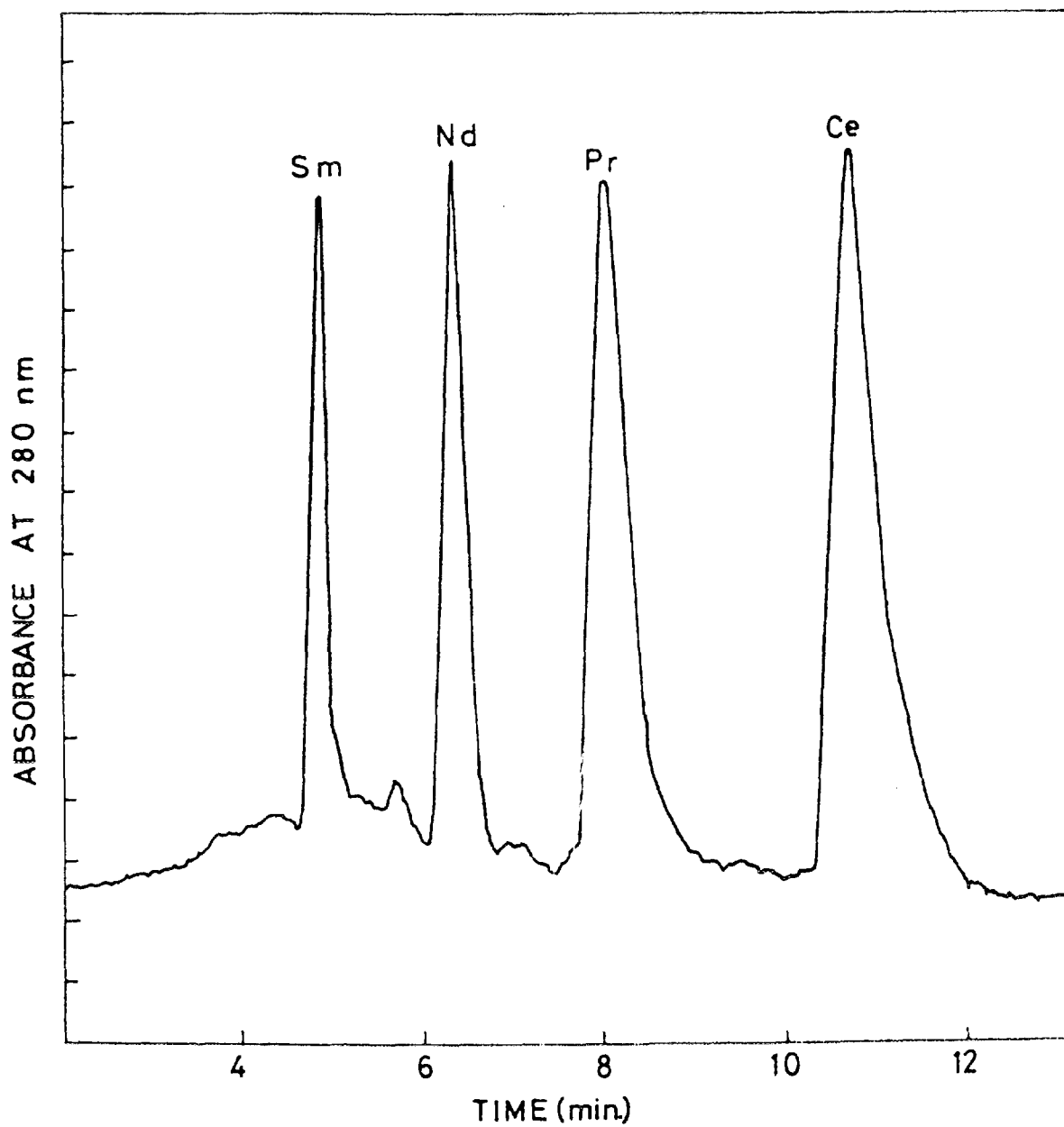


Fig.3 Chromatogram showing Anion exchange separation of lighter rare earths on Partisil 10 SAX column. Eluent: 0.7 v% 1M nitric acid in methanol.

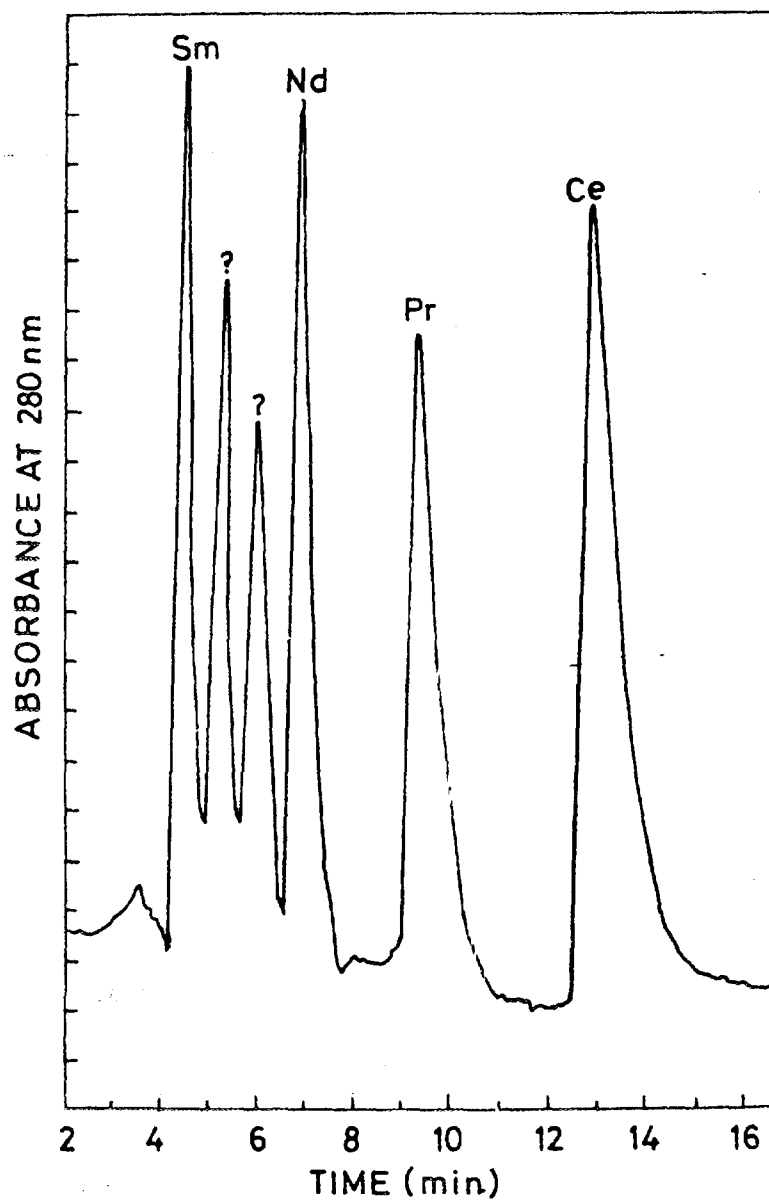


Fig.4 Chromatogram shows the occurrence of spurious peaks (Experimental conditions as in Fig.3).

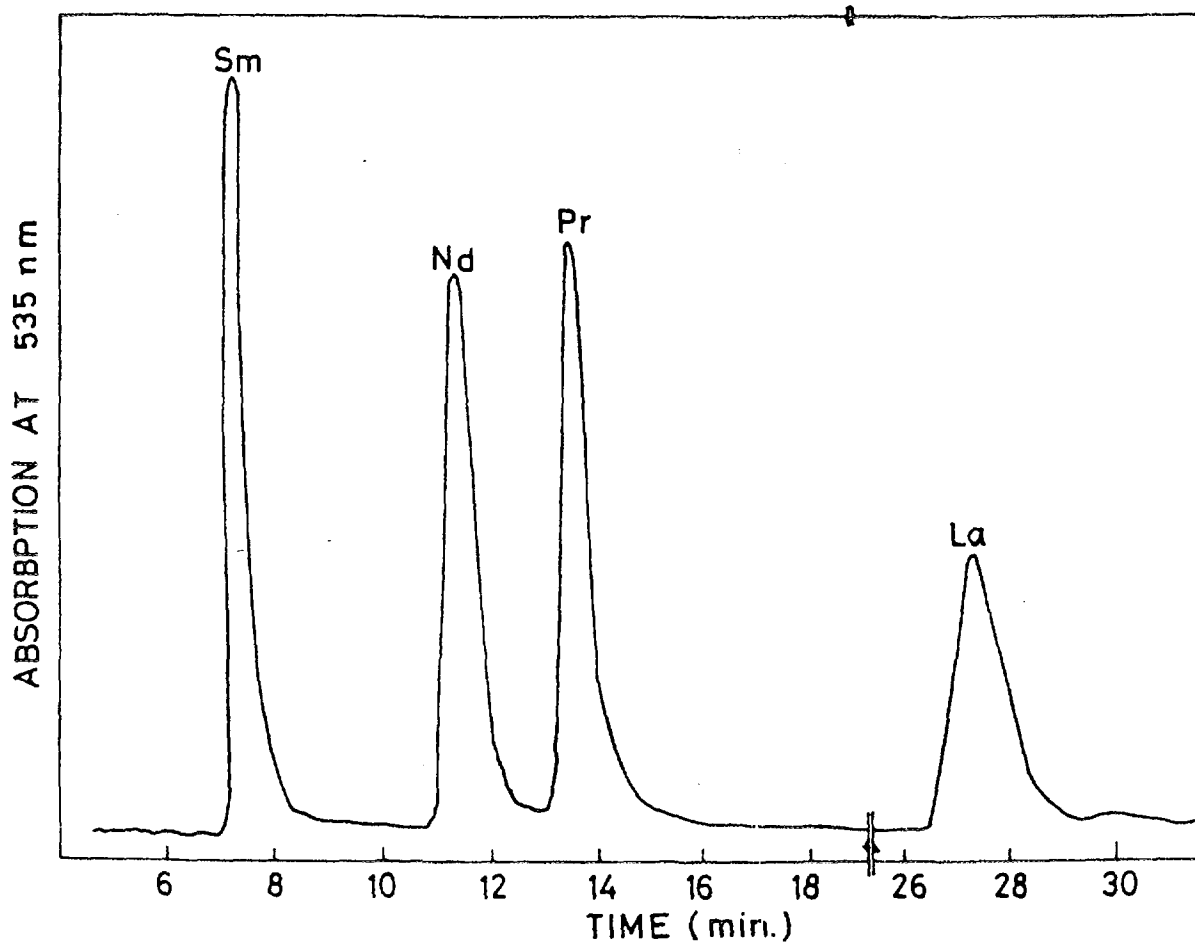


Fig.5 Separation of lighter rare earths on Sperisorb-5-ODS-2 column dynamically modified with 1-octane sulfonate. Detection by post column detection with PAR.

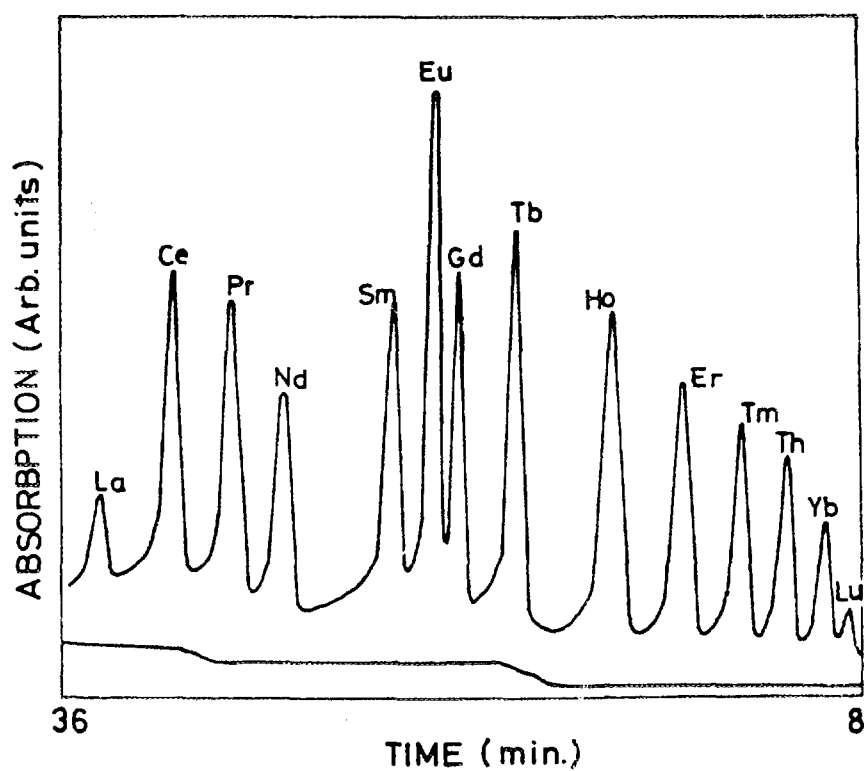


Fig.6 Separation of lanthanides on Supelco LC 18 column. Modifier: Camphor-10-sulfonic acid; Conc. of α -HIBA varied from 0.05 M to 0.2 M over a period of 35 min. pH=3.8; Detection at 653 nm using PCR with arsenazo-III

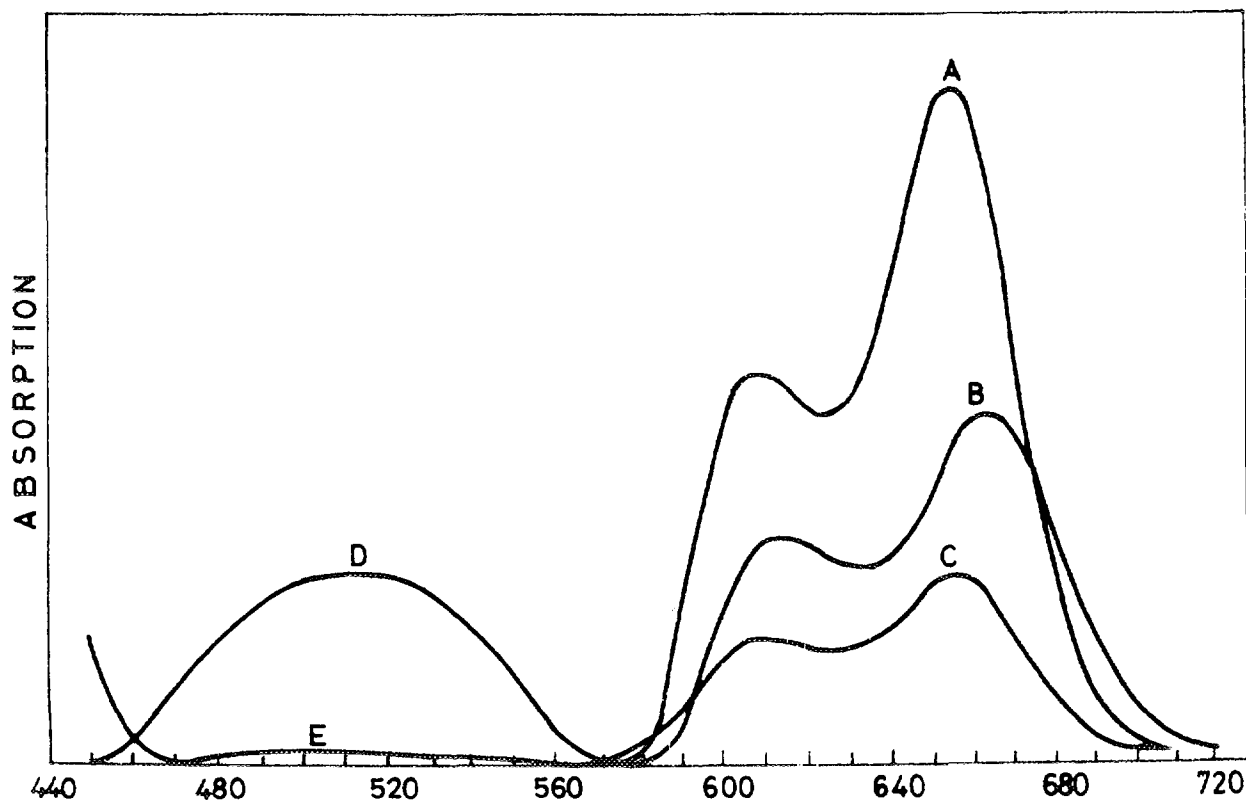


Fig.7 Absorption spectra of complexes of La in different mobile phases.

- (A) - in methanol + nitric acid with arsenazo-III(aq.)
- (B) - in α -HIBA + 1-octane sulfonate with arsenazo-III
- (C) - as in (A), but arsenazo-III (0.1 M HNO_3)
- (D) - in α -HIBA + 1-octane sulfonate with PAR
- (E) - in methanol + nitric acid with PAR

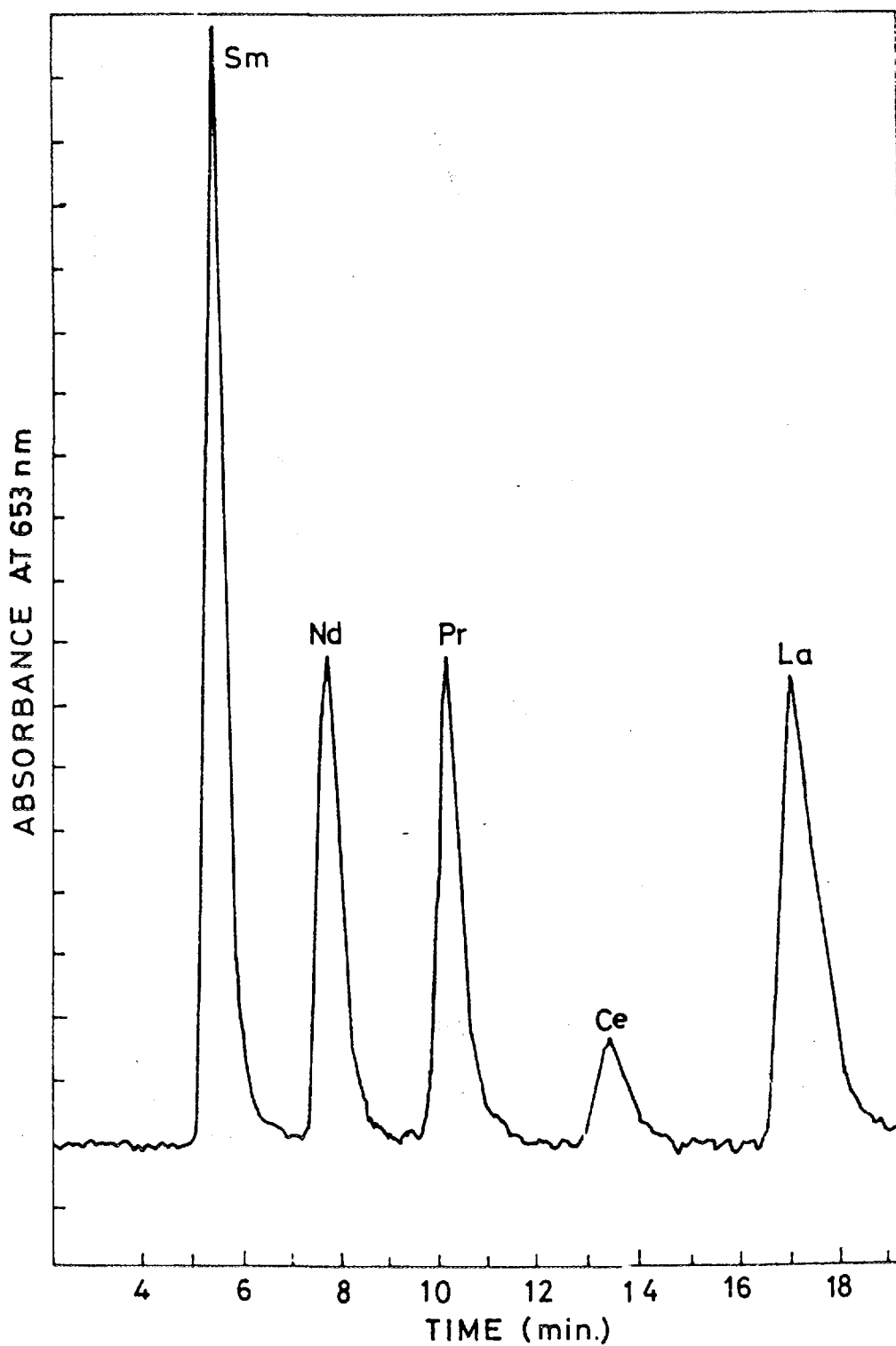


Fig.8 Anion exchange separation of lighter rare earths. Experimental conditions are as in Fig.3 except that the detection is by post column reaction (PCR) with arsenazo-III.

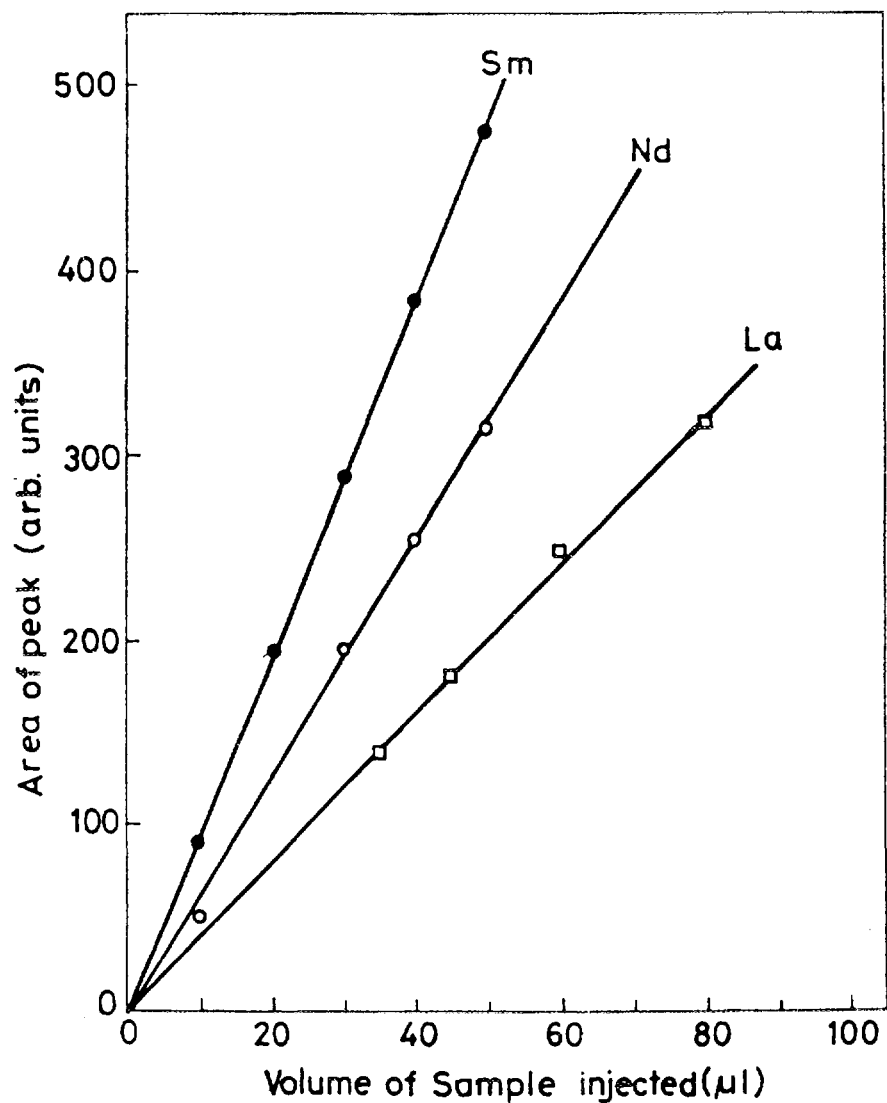


Fig.9 Calibration plots of Sm,Nd and La by cation exchange in α -HIBA & 1-octane sulfonate with PCR detection at 653 nm. Sample conc. $0.02 \mu\text{g}/\mu\text{l}$ of Sm & Nd and $0.04 \mu\text{g}/\mu\text{l}$ of La.

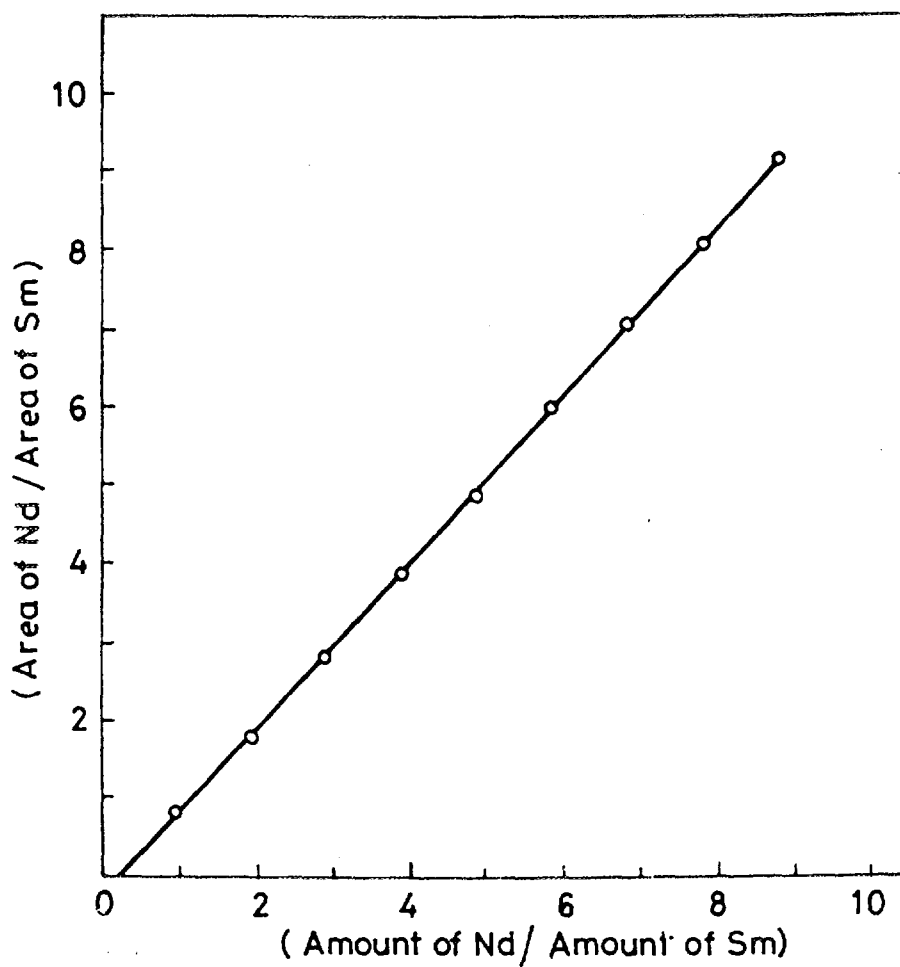


Fig.10 Plot of amounts of Nd/Sm against the ratio of their peak areas. (Sm is kept constant, 52 ng in the injected sample)

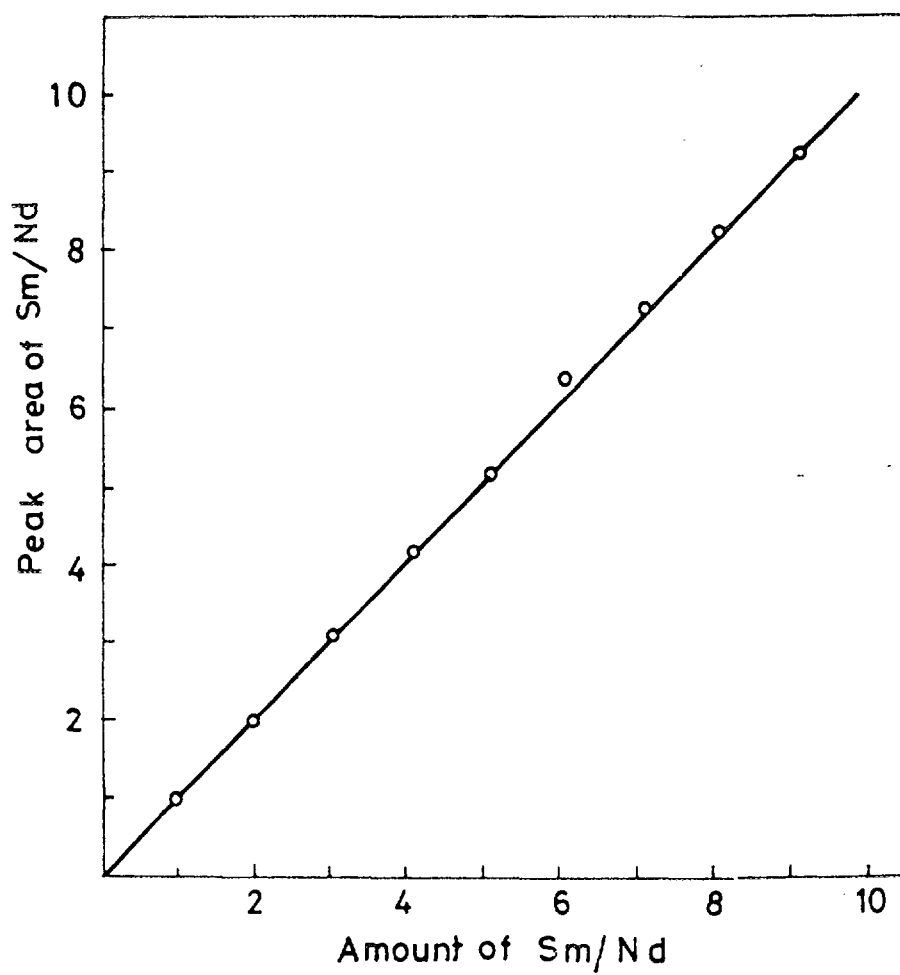


Fig.11 Plot of amounts of Sm/Nd against the ratio of their peak areas (Nd is kept constant, 51 ng in the injected sample)

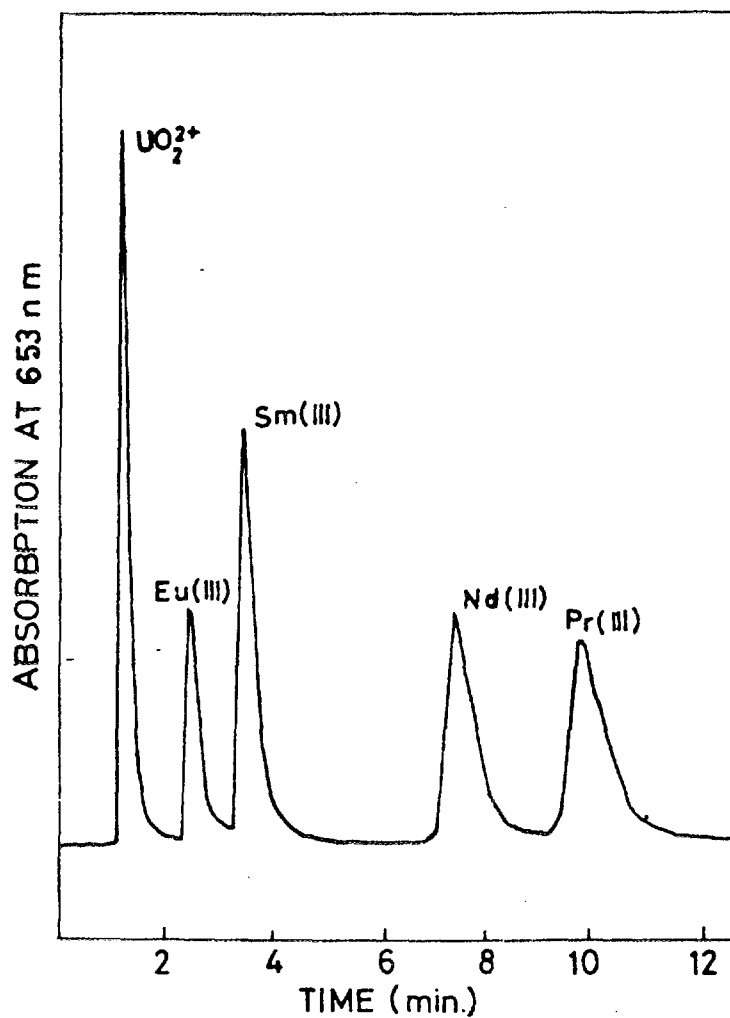


Fig. 12 Separation of UO_2^+ , Eu(III) , Sm(III) , Nd(III) & Pr(III) on cation exchange method using PCR detection with arsenazo-III. Column - Supelco LC_{18} ODS; Eluent: 0.175 M α -HIBA, 0.02 M 1-Octane sulfonate, 7.5v% methanol, pH = 4.2