
SEPARATION OF LANTHANUM FROM NUCLEAR FUEL SOLUTIONS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

This paper presents the separation of uranium, praseodymium and lanthanum from nuclear fuel solutions by high performance liquid chromatography (HPLC). The aim of this study is to establish a minimum concentration of lanthanum which can be analyzed by high performance liquid chromatography, and also to study the effect of uranium concentration on the separation of praseodymium and lanthanum.

Optimum gradient mode was established for mixture standard stock solutions with uranium in a concentration of 1 mg/ml, praseodymium and lanthanum in a concentration range of 1-5 µg/ml from each element. These conditions were applied for the separation of lanthanum from a nuclear fuel solution in which praseodymium and lanthanum were added in a concentration of 3 µg/ml from each element. The elution behavior of lanthanum as a function of the pH and the concentration of the mobile phase, using a mixture of 1-octanesulfonic acid sodium salt with α -hydroxyisobutyric acid is presented.

Key words: high performance liquid chromatography, uranium, praseodymium, lanthanum, burn-up monitor

Introduction

The main objective of the post-irradiation examination of nuclear fuels is to improve the knowledge of the inventories of actinides, lanthanides and fission products in spent fuel elements. Therefore analysis of lanthanum in nuclear fuels is of great importance also for the calculation of burnup. Among lanthanides, lanthanum is widely used as burn-up monitor of nuclear fuel. Selection of suitable separation procedure is complicated because of the multiple constituents of the fuel solutions. The application of high performance liquid chromatography (HPLC) for the separations of lanthanides from fuel solutions has been reported by several authors. Most of the reported papers used α -hydroxyisobutyric acid as eluent for the separations of lanthanides.

The aim of this study is to develop a separation procedure for uranium, praseodymium and lanthanum by studying the optimum physico-chemical conditions.

α - Hydroxyisobutyric acid was chosen as eluent because it provides efficient separation of uranium, praseodymium and lanthanum with the usual decrease in retention as the ionic radius of the element decreases. The influence of different parameters such as pH of the eluent and the concentration of the mobile phase, using a mixture of 1-octanesulfonic acid sodium salt with α -hydroxyisobutyric acid is presented. The experimental conditions were established using a mixture of uranium, praseodymium and lanthanum of known concentration. The application of this method to fuel solutions analysis is also discussed [1].

In this paper is also presented the burn-up calculated by Thermal Ionisation Mass Spectrometry for the pure fraction of uranium which was isolated from the diluted dissolver solution of the fuel element.

Separation procedure

The HPLC system consists of a binary eluent pump, an autosampler, a C_{18} separation column, a post-column mixture unit, a UV-VIS detector and a computer for the data acquisition and also for the remote control of the certain components of the system. The main components of the HPLC system are presented in the figure 1.

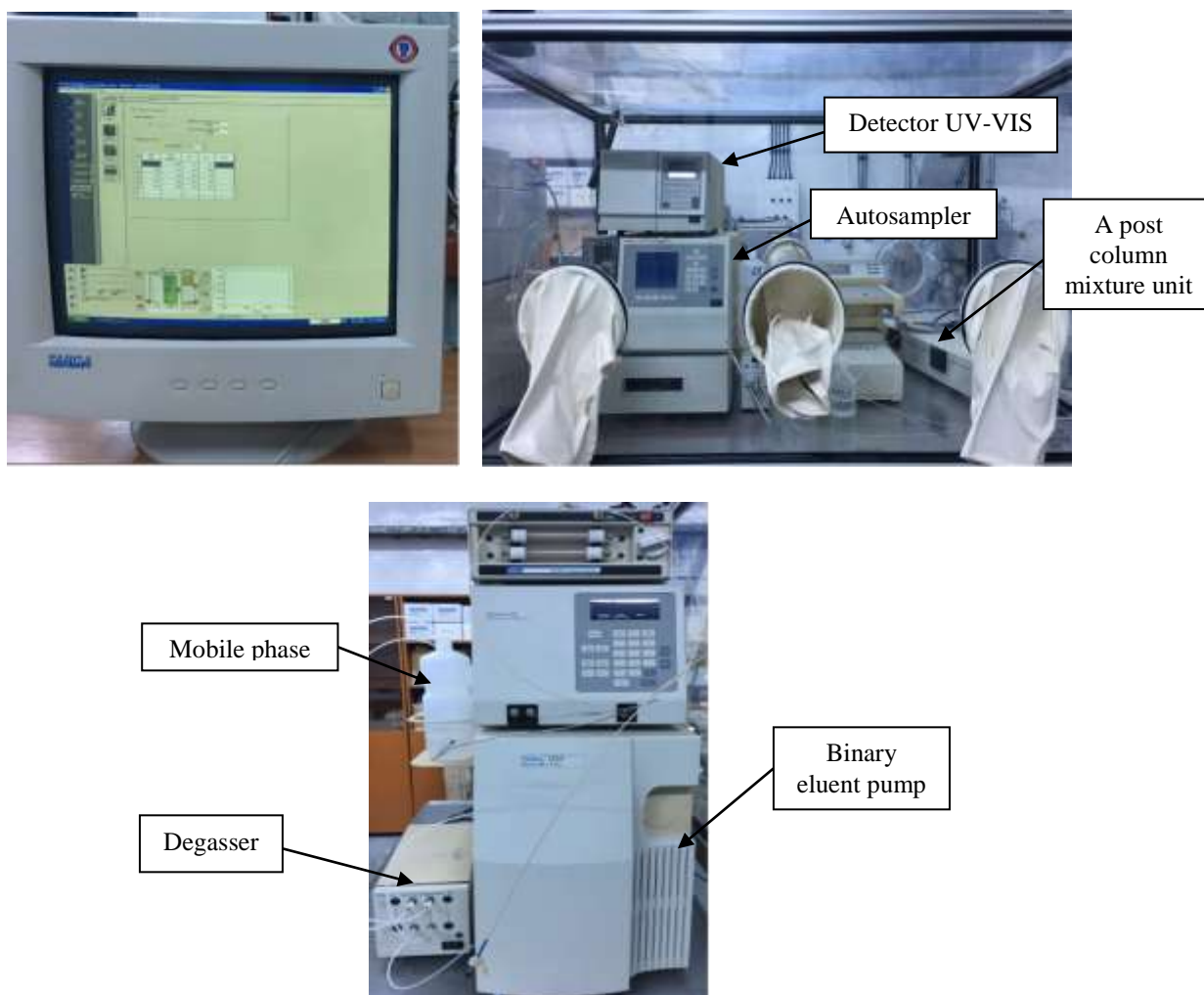


Fig. 1 The Waters High Performance Liquid Chromatography System (HPLC)

The selectivity, low amount of sample needed and simultaneous analysis of several elements in a relative short time are some advantages of this technique. However, chemical dissolution of the sample is required, as well as the previous separation of lanthanides from most of the major nuclear fuel components to prevent overloading and precipitation of interfering elements in the column.

The Waters Symmetry C_{18} column of 150 mm length and 4.6 mm internal diameter is packed with silicagel of particle size 5 μm and was used as stationary phase. Solutions were injected into the column using an autosampler. The eluted species were monitored after post-column reaction with a

metallochromic reagent. Arsenazo (III) was used as the post-column metallochromic reagent (PCR). The arsenazo complexes of uranium, praseodymium and lanthanum were monitored at 658 nm. The signal from the detector was processed by Breeze software package. The important advantage of the HPLC is the speed of the sample analysis. The complete separation and analysis of uranium, praseodymium and lanthanum needs about 30 min per sample.

The procedure used in the hot cells comprised:

- Sample cutting (the sample, usually considered to be representative, amounts to one fuel pellet). A burn-up sample was cut from the fuel element.
- Fuel dissolution (typically in 50 ml of a mixture solution with 8 M nitric acid and 0.1 M hydrofluoric acid heated up to about 200 °C in a steel vessel for 2 hours).
- Dilution of the liquid sample. The further dilution step was carried out with 8 M nitric acid up to a concentration of about 1 mg/ml uranium.

The pure fraction of uranium required for Thermal Ionisation Mass Spectrometry was isolated from the diluted dissolver solution of the fuel element. The separation procedure needed at least two days. The isotopic composition of the separated uranium was used to calculate the burn-up of the fuel element [3].

In liquid chromatography the interactions such as solute-mobile phase, solute-stationary phase and mobile phase-stationary phase need to be optimized to achieve satisfactory separation [1]. Changes in mobile phase composition are recommended to obtain the separation of lanthanum from uranium and praseodymium on the dynamically modified reversed phase Waters Symmetry C₁₈ column. In gradient elution the mobile phase composition was changed so that an increase in strength caused a decrease in retention.

In aqueous solutions, praseodymium and lanthanum were present as strongly hydrated trivalent cations. Because their ionic properties are very similar, they cannot be separated easily by cation exchange. The selectivity of the separation can be increased with the use of appropriate chelating agents such as α -hydroxyisobutyric acid (HIBA). Praseodymium and lanthanum form complexes with HIBA which lower the affinity of the element for the cation exchange resin. Therefore praseodymium formed the most stable complexes with HIBA and eluted first from the separation column.

Uranium was present as uranyl cation UO_2^{2+} in aqueous solutions, and formed complexes which were not retained on a cation exchange resin, and therefore uranium eluted first from aqueous solutions with uranium, praseodymium and lanthanum. The sequence of separation was the following: uranium eluted first which was followed by praseodymium and lanthanum.

Figure 2 shows the retention time of uranium, praseodymium and lanthanum as a function of the changes that occurred in the mobile phase composition. The results are from a run at room temperature when the separation characteristics were good. The retention time increases for praseodymium at pH 3.8. Uranium eluted with heavier lanthanides (praseodymium) at pH of 3.8 showing a good separation from the two lanthanides.

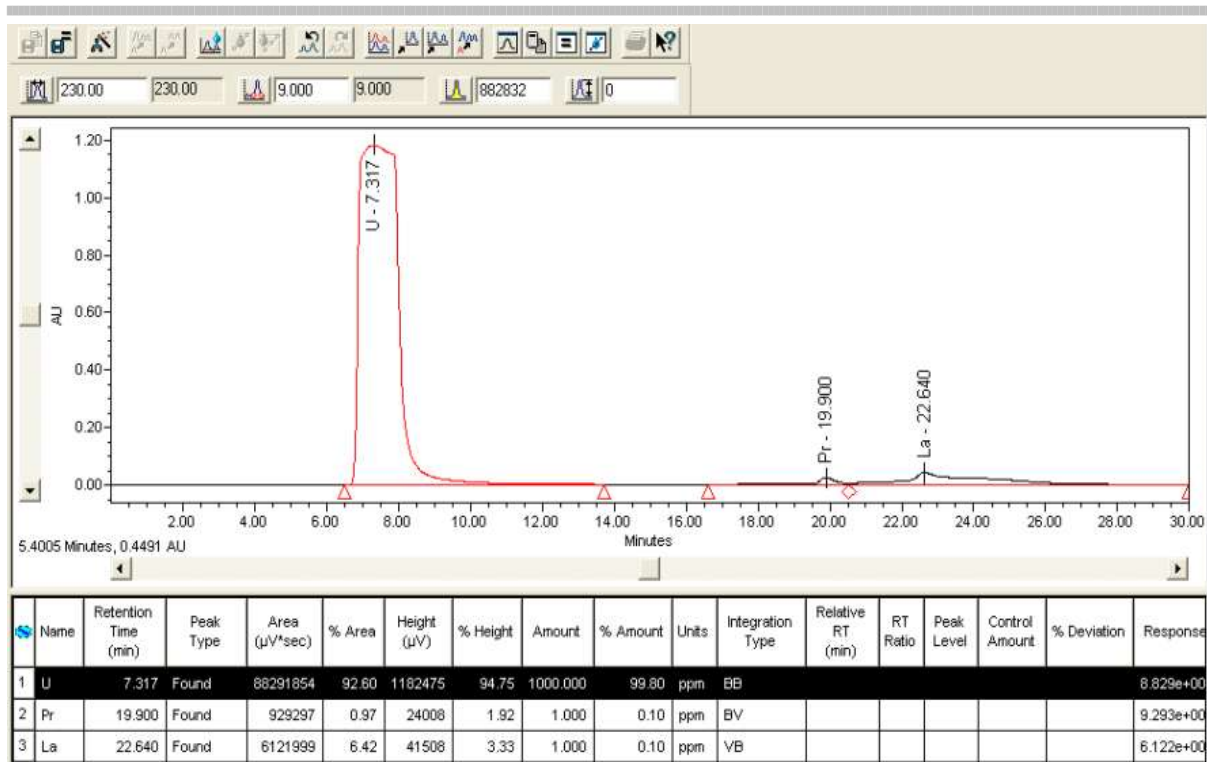


Fig. 2 Separation of praseodymium and lanthanum in a gradient mode from a mixture standard stock solution with uranium of 1 mg/ml, praseodymium of 1 µg/ml and lanthanum of 1 µg/ml

Before analysing the nuclear fuel sample a test method was started with standard stock solutions of uranium, praseodymium and lanthanum, to investigate the best measurement parameters for accurate analysis. The stock solutions of uranium, praseodymium and lanthanum were prepared by dissolving a known quantity of uranyl nitrate hexahydrate in 8 M nitric acid and by adding a known aliquot of each standard solution with praseodymium and lanthanum in a concentration of 1, 3 and 5 µg/ml [2].

Optimum gradient mode was established for mixture standard stock solutions with uranium in a concentration of 1 mg/ml, praseodymium and lanthanum in a concentration range of 1, 3 and 5 µg/ml from each element. These conditions were applied for the separation of lanthanum from nuclear fuel solutions in which praseodymium and lanthanum were added in a concentration of 3 µg/ml from each element. The elution behavior of lanthanum as a function of the pH and the concentration of the mobile phase, using a mixture of 1-octanesulfonic acid sodium salt with α-hydroxyisobutyric acid is presented.

For the separation of lanthanum from nuclear fuel solutions to study the effect of uranium concentration is an important aspect since uranium is the main component of the nuclear fuel. The effect of uranium concentration on the mutual separation of praseodymium and lanthanum was investigated in solutions with uranium in the concentration of 1 mg/ml. This effect was determined based on the retention time of the elution profile as a function of uranium concentration.

The separation profiles of uranium, praseodymium and lanthanum obtained at pH of 3.8 and room temperature are shown in figure 3. The profiles demonstrate clear mutual separation of the praseodymium and lanthanum which were added in diluted nuclear fuel solutions.

Uranium was eluted at 7.29 minute of retention time, praseodymium at 19.8 minutes and lanthanum at 22.6 minutes. In this study uranium separate clearly from praseodymium and lanthanum [1].

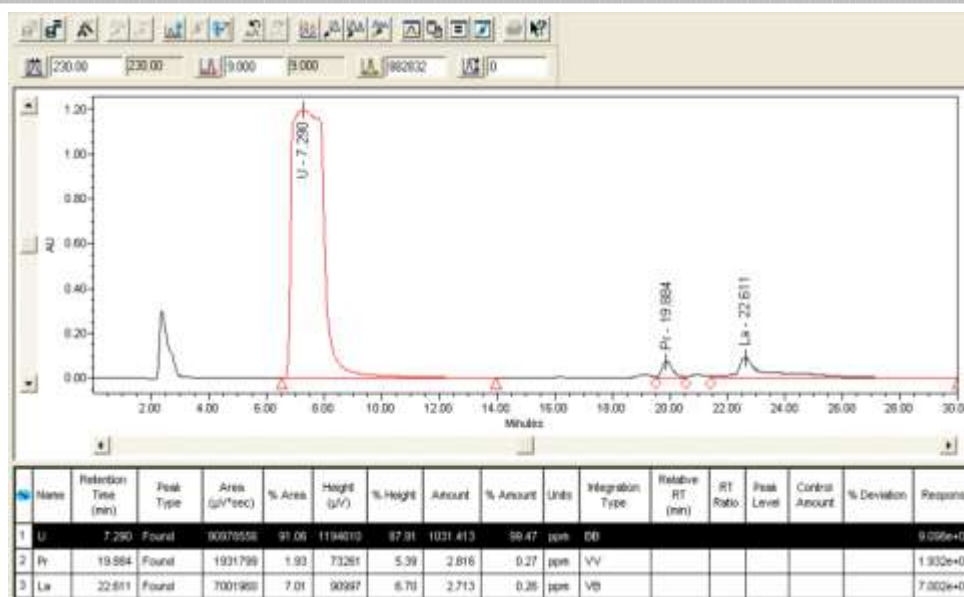


Fig. 3 Separation of praseodymium and lanthanum in a gradient mode from a nuclear fuel solution with praseodymium of 3 µg/ml and lanthanum of 3 µg/ml

In table 1 are presented the concentration of uranium in the nuclear fuel sample, which was measured based on his peak area, the retention time of uranium and the three standard solutions used to find the best measurement parameters for accurate analysis (pH and concentration of α -hydroxyisobutyric acid). Uranium was separated from praseodymium and lanthanum on a dynamically modified reversed phase Waters Symmetry C₁₈ column using a mixture of 1-octanesulfonic acid sodium salt with α -hydroxyisobutyric acid.

Table 1 Analytical result for the separation of uranium from a diluted nuclear fuel solution

Standard / Sample	Peak	Amount of U added (µg/ml)	Retention Time (min)	Area	% Area	Amount of U measured (µg/ml)
Std.1	Uranium	1000	7.317	88291854	92.60	
Std.3	Uranium	1000	7.302	88252792	90.68	
Std.5	Uranium	1000	7.286	88078443	88.34	
Sample 1	Uranium		7.290	90978556	91.06	1031.413

In table 2 are presented the concentration of praseodymium in the nuclear fuel sample, which was measured based on his peak area, the retention time of praseodymium and the three standard solutions used to find the best measurement parameters (pH and concentration of α -hydroxyisobutyric acid). The recovery yield of praseodymium was better than 91% on a dynamically modified reversed phase Waters Symmetry C₁₈ column using a mixture of 1-octanesulfonic acid sodium salt with α -hydroxyisobutyric acid.

Table 2 Analytical result for the separation of praseodymium from a diluted nuclear fuel solution

Standard / Sample	Peak	Amount of Pr added (µg/ml)	Retention Time (min)	Area	% Area	Yield η %	Amount of Pr measured (µg/ml)
Std.1	Praseodymium	1	19.900	929297	0.97		
Std.3	Praseodymium	3.067	19.887	1995305	2.05		
Std.5	Praseodymium	5.067	19.878	3264063	3.27		
Sample 1	Praseodymium	3.067	19.884	1931799	1.93	91.82	2.816

In table 3 are presented the concentration of lanthanum in the nuclear fuel sample, which was measured based on his peak area, the retention time of lanthanum and three standard solutions used to find the best measurement parameters (pH and concentration of α -hydroxyisobutyric acid). The recovery yield of lanthanum was better than 88% on a dynamically modified reversed phase Waters Symmetry C₁₈ column using a mixture of 1-octanesulfonic acid sodium salt with α -hydroxyisobutyric acid.

Table 3 Analytical result for the separation of lanthanum from a diluted nuclear fuel solution

Standard / Sample	Peak	Amount of La added (µg/ml)	Retention Time (min)	Area	% Area	Yield η %	Amount of La measured (µg/ml)
Std.1	Lanthanum	1	22.640	6121999	6.42		
Std.3	Lanthanum	3.067	22.612	7072402	7.27		
Std.5	Lanthanum	5.067	22.600	8356975	8.38		
Sample 1	Lanthanum	3.067	22.611	7001960	7.01	88.46	2.713

The HPLC technique can provide only an elemental rather than an isotopic yield. The concentrations of uranium, praseodymium and lanthanum were determined in the diluted dissolver solution using a calibration plot.

Conclusions

An HPLC method is presented for the separation and determination of uranium, praseodymium and lanthanum from nuclear fuel solutions. Individual separation of uranium, praseodymium and lanthanum is a challenging task because of:

- 1) The presence of complex matrix like irradiated fuel and
- 2) The lanthanides having similar physical and chemical properties.

The HPLC method gives a detection limit for lanthanum in nuclear fuel solutions after de separation on the dynamically modified reversed phase Waters Symmetry C₁₈ column as low as 1 µg/ml.

The individual lanthanides were separated by high performance liquid chromatography (HPLC) using a mixture of 1-octanesulfonic acid sodium salt with α -hydroxyisobutyric acid. The HPLC technique can provide only an elemental rather than an isotopic yield. The concentrations of uranium, praseodymium and lanthanum were determined by standard addition method in the diluted dissolver solution using a calibration plot. The recovery yield of praseodymium was better than 91% while the recovery yield of lanthanum was better than 88%.

The fuel burn-up is usually determined by measuring the content of the isotope ^{139}La that accumulates through the fission process. In order to calculate the burn-up is necessary to consider all the fissile isotopes present in the fuel composition. The isotopic composition of uranium was determined by Thermal Ionisation Mass Spectrometry and the fuel burn-up estimated was $GA = 4086 \text{ MWday/t U}$.

The isotope of lanthanum ^{139}La has proven to be ideal burn-up monitor due to his chemical and neutron-physical properties. On the other hand, the amount of this isotope can only be determined by the analysis of dissolved nuclear fuel samples, which means using time consuming chemistry methods.

References

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