High resolution ICP-OES analysis of neptunium-237 in samples from pyrochemical treatment of spent nuclear fuel

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A B S T R A C T

A straightforward and reliable ICP-OES procedure for ^{237}Np analysis of samples potentially originating from spent nuclear fuel has been developed. In contrast to most other analytical techniques employed for the determination of ^{237}Np in radioactive samples, ^{237}Np was analyzed without prior separation from the residual elements present in the analyte solution. External calibration of the ICP-OES response was accomplished using a certified ^{237}Np stock solution that was additionally characterized in-house using ICP-MS as well as γ-spectrometry. Thirteen prominent ^{237}Np emission wavelengths were tested for their suitability in terms of sensitivity, peak shape, occurrence of spectral interferences and stability of spectral background. The investigated ^{237}Np emission wavelengths revealed complex ICP-OES spectra with either broad peaks having widths of up to 30 pm or splitting of the ^{237}Np signal into multiple peaks, i.e. multiplets. Compared to previous ICP-OES investigations, ^{237}Np detection limits (LOD) were lowered by at least one order of magnitude in the current study. The most intensive ^{237}Np emission line at $\lambda = 382.92$ nm providing the lowest LOD of 3.1 μg kg^{-1}, however, was of limited practical use because severe spectral interference from Nd (a representative fission product with a significant content in spent fuel) at $\lambda = 382.914$ nm overlapped with the ^{237}Np signal. Additional detailed interference studies helped identify potential complications during ^{237}Np analysis caused by concomitant elements (Nd, Pu, Th, U) in the analyte solution. Ultimately, emission signals at $\lambda = 410.84$ nm, $\lambda = 429.09$ nm, and $\lambda = 456.04$ nm were used to analyze selected salt and deposit samples from pyrochemical separation experiments. ICP-OES Np results were cross-validated using sector field ICP-MS, largely confirming each other, and thus underpinning the validity of the developed ICP-OES procedure. The successful use of two independent analytical techniques for all analyses helped to prove the quality of the achieved results.

1. Introduction

Neptunium (Np), a transuranium element, is formed in noticeable quantities in the fuel by neutron capture of ^{238}U in nuclear power plants and subsequently accumulates in waste repositories [1–4]. On average ~10 kg ^{237}Np are produced in each conventional pressurized water reactor each year from the interaction of neutrons with predominantly ^{235}U and ^{238}U in the nuclear reactor [4].

Among all Np isotopes, ^{237}Np has by far the longest half-life ($t_{1/2} = 2.14 \times 10^6$ year) and as such, continuously contributes to the dose inventory via decay of its daughter products, e.g. ^{233}Pa (protactinium) [1–4]. Therefore the determination of ^{237}Np in spent fuel is required for the long-term assessment of nuclear waste repositories.

Within the context of separation concepts (e.g. pyrochemical treatment), partitioning and transmutation concepts [5,6] are under development worldwide for minimizing the amount and radiotoxicity of both spent nuclear fuel and radioactive waste. These strategies are based on multi-recycling of all actinides and their subsequent neutron irradiation to form short-lived isotopes in dedicated advanced nuclear reactors. For this reason, techniques for recovery of the minor actinides Np, americium (Am), and curium (Cm) together with uranium and plutonium are being investigated [7]. Pyrochemical techniques represent a promising alternative to aqueous processes for a group-selective recovery of all actinides from the considered new types of fuels [8]. The most developed pyrochemical separation process is based on electrorefining of metallic fuel dissolved in molten LiCl–KCl eutectic mixtures using different inert or reactive cathodes, originally proposed by Argonne National Laboratory, USA [9].

Besides others, neutron activation analysis and α-spectrometry have been commonly employed for the determination of ^{237}Np in both environmental and nuclear samples over the last few decades [4]. More recently, ICP-MS is increasingly used for this purpose [4,10–12]. All these analytical methods, however, rely on an efficient separation of

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Np from the other actinides which are normally present in the sample. If not well separated, potential interferences might largely hamper the reliable determination of [237]Np in both environmental and nuclear samples. In ICP-MS, for example, the huge—and therefore broad—[238]U signal will always overlap with the minor [237]Np signal, if both elements are not separated from each other prior to analysis. Separation procedures [4] based on liquid–liquid extraction, ion exchange or co-precipitation commonly employed for this purpose are not only laborious but also always imply an additional radiation dose to the laboratory personnel dealing with radioactive samples. Therefore, it would be most useful to have at hand a straightforward analytical procedure for the reliable determination of [237]Np in nuclear samples that do not require the separation of the element from other transuranium elements.

ICP-OES may provide the potential to overcome this analytical difficulty. In contrast to ICP-MS, not separation of masses (m/z), but emission of light at different wavelengths is the basic principle for ICP-OES analysis. As such, ICP-OES signals obtained at selected Np emission wavelengths must not necessarily overlap with spectral interferences originating from other elements present in the analyte solution. Although several Np emission wavelengths have been tested for their corresponding detection limits, detailed interference studies are not yet available in the scientific literature [13,14]. This information, however, is urgently needed to investigate the possibility of analyzing Np in real samples without separating the element from the matrix. Pant and co-workers [15] investigated the influence of U, Pu, and Fe on the ICP-OES signal at $\lambda = 382.920$ nm only, indicating an overestimation of Np results if U/Np and Pu/Np ratios exceed values of 25 and 50, respectively. For other potential Np wavelengths, however, no such information is available at all.

The main focus of this study was the identification of sensitive, spectroscopically non-disturbed emission lines of Np and to lower detection limits (LOD) compared to previous ICP-OES studies. To this end, an outdated Np standard was characterized extensively for its concentration with γ-spectrometry using [233]Pa as well as [237]Np. Complementary sector field ICP-MS analysis was employed to cross-validate the γ-spectrometry data. With this information at hand, selected nuclear samples from pyrochemical separation experiments were analyzed with ICP-OES results compared to in-house sector field ICP-MS data. This comparison supports quality assurance of analytical results in a scientific area where matrix-matched, certified reference materials are rarely available.

2. Experimental

2.1. Instrumentation

All ICP-OES measurements were carried out with a commercial high resolution ICP-OES instrument (Ultima2, HORIBA Jobin Yvon, Longjumeau, France). The sample introduction system of the employed spectrometer has been installed in a glove box to allow the analysis of radioactive samples. This complex modification of the original instrumental design was necessary to protect the operator from α and β radiation originating from the radioactive sample solutions. The employed glove box was always operated in under pressure (controlled permanently by manometers and sensors) to prevent any possible outside contamination in case of a potential leakage of the glove box. Exhaust gases from the ICP were passed through several absolute filters with the gas streams monitored by radiation detectors guaranteeing radioactive emissions to be well below legal limits.

To further improve the stability and intensity of the ICP-OES signals, a high efficiency sample introduction system (Apex E, Elemental Scientific, Inc., Omaha, NE, USA) was employed. Detailed operating and data acquisition parameters of the sequentially operating ICP-OES are summarized in Table 1.

A high-purity Ge-detector in 2π-geometry (GEM40P-PLUS, S/N 41-TP11698A, Ortec EG&G, USA) was employed for γ-spectrometry measurements [16]. Both the [233]Pa and the [237]Np γ-emission intensities of two aliquots of the [237]Np working standard solution were assessed

Table 1
Operating conditions of the ICP-OES instrument for neptunium measurements.

Plasma parameters	
Radio frequency	40.68 MHz
Forward power	1000 W
Reflected power	<1 W
Argon gas flow rates	
Plasma gas	12 L min^{-1}
Nebulizer gas	2.5 L min^{-1}
Sheath gas	0.2 L min^{-1}
Acquisition parameters	
Sample introduction	Apex E, ESI, USA
Nebuliser	PolyPro ST, polypropylene, ESI
Sample uptake	0.30 ml/min, pumped
Gain	3
Wavelength	Various, see text for details
Entrance slit	20 μm
Exit slit	15 μm
Measurement	Peak top, background
Integration time	8 s per measurement point
Number of replicates	3

over a period of 1–5 days to determine the Np concentration of this standard solution.

Comparative sector field ICP-MS analyses (Element 2, Thermo Fisher Scientific, Bremen, Germany) were carried out using external calibration and applying routine instrumental operating procedures.

2.2. Reagents

High purity water (18.2 MΩ cm) from a MilliQ (Merck Millipore) water purification system and sub-boiled nitric acid were used for the preparation of all solutions. Because of their radioactive nature, all Np standard solutions as well as samples from the pyrochemical treatment had to be prepared in glove boxes.

For quantification purposes external calibration solutions of [237]Np (nominal 0; 200; 350; 500; 700; 850; 1000 μg kg^{-1}) were prepared in 0.14 M nitric acid by dilution of a Np stock standard solution (CETAMA, CEA Valrho Marcoule, France).

The interference study involved single element ICP stock solutions of U and Th (both 1000 mg L^{-1} each, Specpure®, Alfa Aesar, Karlsruhe, Germany). The used Pu solution (10 mg L^{-1}) consisted of predominantly [239]Pu (~77%) and was characterized isotopically in-house using thermal ionization mass spectrometry (TIMS).

Regarding the experiments related to pyrochemical treatment, the eutectic mixture of LiCl–KCl (59:41 mol%, Aldrich, 99.99% purity, packed under Ar) was used as received. The electrochemical cell for electrolysis consisted of a cathode including an Al plate (Alfa Aesar, 99.99%) and a chlorine gas producing anode prepared from a graphite rod in a quartz tube with a frit (porosity 0) welded to the bottom part of the tube to prevent penetration of chlorine gas into the melt. An Ag/LiCl–KCl–AgCl (1 wt.% AgCl) reference electrode prepared in a Pyrex glass tube was used to monitor the potential of the cathode. For each experiment, approximately 40 g of the melt was processed in an Al_2O_3 crucible [17].

2.3. Samples from pyrochemical separation

The analyzed samples originate from a pyrochemical process for homogeneous recovery of all actinides from metallic fuels [17] studied at the European Commission–Joint Research Centre–Institute for Transuranium Elements (EC-JRC-ITU). The process is based on electrorefining in a molten LiCl–KCl eutectic mixture using solid reactive aluminium cathodes. The fuel is dissolved anodically in the molten salt. The actinides (An) are all-together selectively recovered from the resulting mixture on an Al cathode as solid actinide–aluminium (An–Al) alloys. These alloys are subsequently treated by chlorination to remove Al as volatile chloride.

The investigated samples were obtained through electrolysis of a LiCl–KCl–PuCl$_3$–NpCl$_3$–NdCl$_3$ salt with initial concentrations of Pu, Np