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ScienceDirect
Applied Radiation and Isotopes 65 (2007) 355–364
Applied Radiation and Isotopes
www.elsevier.com/locate/apradiso

A new determination of ^{79}Se half-life

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Received 10 July 2006; received in revised form 26 September 2006; accepted 29 September 2006

Abstract

A new value of ^{79}Se half-life was determined by the means of inductively coupled plasma mass spectrometry (ICP-MS) and liquid scintillation counting (LSC) on a sample source isolated from a nuclear reprocessing solution. The procedure used to extract Se from the complex sample solution consisted in liquid–liquid extraction and ion exchange chromatographic methods. The concentration of ^{79}Se was measured using ICP-MS coupled with electro-thermal vaporisation to eliminate potential isobaric interferences. The activity was measured using LSC after γ-ray spectrometry to check the contribution of residual radioactive contaminants. From these results, the half-life of ^{79}Se was found to be $3.77\ (19) \times 10^5$ *a*.

Keywords: ^{79}Se; Half-life; ICP-MS; LSC

1. Introduction

^{79}Se is a pure β-minus emitter that disintegrates directly to the ground state level of ^{79}Br. It is mainly produced in nuclear reactors by spontaneous fission of uranium 235. With a low fission yield of 0.04%, ^{79}Se can only be found at significant levels in spent nuclear fuel and in waste materials resulting from fuel reprocessing. Although its half-life is not well documented yet, ^{79}Se is considered as a long-lived radionuclide of importance for the management of nuclear waste disposal sites. In France for instance, ^{79}Se belongs to the list of critical nuclides to be declared by waste producers for the acceptance of low to intermediate level radioactive waste packages on the Centre de l'Aube disposal facility (ANDRA). In order to improve the estimation of ^{79}Se radiological impact on the environment, a review of the bibliography revealed that additional work was however needed to know the half-life of this nuclide with more accuracy.

First tentative evaluations of ^{79}Se half-life were done in the years 49–51 and a value of 6.5×10^4 *a* was accepted by the various tables and chart of isotopes (Glendenin, 1951; Parker et al., 1949). In 1993, due to inconsistencies in the measured and calculated fission yields of ^{79}Se for an irradiated fuel, the calculations of Parker were reviewed (Singh and Hermann, 1993) and a new value of 6.5×10^5 *a* (i.e. one order of magnitude more) was deduced. Hence, in 1995, a Chinese team carried out the first measurement of this half-life by the means of a radiochemical method, they obtained $4.8\ (4) \times 10^5$ *a* (Yu et al., 1995). However, and since this date, the same team published various results (He et al., 2000; He et al., 2002; Jiang et al., 2000; Jiang et al., 2002), the greatest being $1.1\ (2) \times 10^6$ *a* (1997), and the latest $2.80\ (36) \times 10^5$ *a* (2002) (Table 1).

In this work, a new measurement of ^{79}Se half-life was undertaken on a different sample source and using different analytical tools with respect to the other studies. ^{79}Se was extracted from a fission product solution collected during nuclear fuel reprocessing, according to a procedure already experimented in a previous work (Comte et al., 2003). It was isolated from the sample matrix and from the other radionuclides by the means of selective chemical

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doi:10.1016/j.apradiso.2006.09.009

Table 1
^{79}Se half-life, published values

	References	T (a)
Historical values		
1949	Parker et al.	$\leqslant 6.5 \times 10^4$
1951	Glendenin	$\geqslant 7 \times 10^6$
Revised value		
1993	Singh and Hermann	$\leqslant 6.5 \times 10^5$
Measured values		
1995	Yu et al.	$4.8\ (4) \times 10^5$
1997	Jiang et al.	$1.1\ (2) \times 10^6$
2000	He et al.	$1.24\ (19) \times 10^5$
2002	Jiang et al.	$2.95\ (38) \times 10^5$
2002	He et al.	$2.80\ (36) \times 10^5$
This work		$3.77\ (19) \times 10^5$

separation methods using liquid–liquid extraction and ion exchange chromatography. The concentration of ^{79}Se was measured using inductively coupled plasma–mass spectrometry with electro-thermal vaporisation (ETV-ICP/MS) and the activity was measured using liquid scintillation counting (LSC). However, ^{79}Se is not an easy nuclide to measure and the absence of reference material constituted an additional difficulty for both techniques to achieve high selectivity, precision and accuracy. All these procedures are discussed in details and then the derived ^{79}Se half-life value is presented.

2. Sampling and chemical separation

The sample solution was collected in the nuclear fuel reprocessing plant of Cogema La Hague (France). The original solution coming from spent fuel dissolution was very complex, with uranium concentration around $200\,\mathrm{g\,L^{-1}}$, a large panel of fission products, some actinides and very high activity levels from $\beta-\gamma$ emitters ($\sim 10^{13}\,\mathrm{Bq\,L^{-1}}$). The isolation of selenium from such a matrix needed a very selective separation procedure to be carried out and heavy biological protections to be used with respect to irradiation.

At first, uranium was eliminated from the sample solution using liquid–liquid extraction with tributylphosphate (TBP) in 3 M nitric acid, following the PUREX process. A known amount of natural Se (5 mg) was added at this stage to act as a carrier with respect to traces of ^{79}Se present in the sample. Then, the solution was split in two sub-samples in order to duplicate the separation procedure. Each solution was diluted with deionised water to adjust nitric acid molarity to 0.3 M, and an aliquot of 4 mL was introduced on a chromatographic column filled with mixed beds of cationic and anionic resins. In these conditions, it was shown that most of the elements present in the fission products solution could be retained onto the resin whereas Se, in its neutral molecular form as H_2SeO_3, passed through the column (Dewberry et al., 2000; Comte et al., 2003). The fraction collected for Se was eluted with 14 mL HNO_3 0.3 M at a flow rate of $1\,\mathrm{mL\,min^{-1}}$. γ-spectrometry performed on this solution indicated substantial levels of activity in ^{125}Sb and ^{106}Ru/Rh ($\sim 10^4$–10^5 Bq) which however allowed us to transfer the solution outside the hot cell. After preliminary analyses and regulatory radiological controls, the two aliquots were sent to the CEA laboratory in Cadarache for ICP/MS measurements and for further purification prior to LSC measurements at LNHB in Saclay.

As it will be discussed in the next section, ICP-MS analyses could be carried out directly on the solutions recovered after chromatographic separation. In contrast, a complementary separation stage was required for LSC measurements in order to decrease activity from $\beta-\gamma$ contaminants. This was done by solvent extraction with $CHCl_3$ in the presence of KI following the work of Shabana and Ruf (1978) and our own experience about the determination of ^{79}Se in used resin samples from nuclear power plants. After addition of 5 mg of KI, 5 mL of the sample solution were mixed with 5 mL of $CHCl_3$ and shaken for 30 min. The organic phase was washed first by 5 mL of a solution with $0.5\,\mathrm{g\,L^{-1}}$ KI and second by 5 mL of deionised water. Finally, selenium was back-extracted by 5 mL of a solution composed of HNO_3 7 M and H_2O_2 6%. With residual $\beta-\gamma$ activity in the range of a few Bq, this procedure made it possible to undertake LSC measurement in good conditions.

3. Measurement of ^{79}Se concentration

The potential of ICP-MS for the measurement of long-lived radionuclides has been discussed in several papers, more especially for the determination of α (actinides) and pure β emitters in used nuclear fuel or radioactive waste (e.g. Bienvenu et al., 1998; J.S. Becker, 2002; Epov et al., 2003). In the case of ^{79}Se, the intrinsic performances of ICP-MS are however rather limited when compared to those achievable for other long-lived nuclides because of the high ionisation potential of selenium (9.75 eV) and the occurrence of Ar polyatomic species in the mass range of Se isotopes. The potential interferences to take into account for ^{79}Se measurement are listed in Table 2. They may arise from elements present in the sample solution (mainly Br, K, Cu, Gd) and/or in the plasma gas (Ar). Unfortunately, no instrumental system presently available

Table 2
Potential interferences for the determination of ^{79}Se by ICP/MS

	Atomic mass
$^{79}Se^+$	78.91849
$^{79}Br^+$	78.91834
$^{39}K^{40}Ar^+$	78.92609
$^{38}Ar^{40}Ar^1H^+$	78.93294
$^{63}Cu^{16}O^+$	78.92451
$^{158}Gd^{2+}$	78.96204