

MASS SPECTROMETRIC DETERMINATION OF IMPURITIES IN REACTOR CORE GRAPHITE FOR RADIOACTIVE WASTE COMPOSITION MODELLING

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In this work concentrations of minor graphite impurities in virgin graphite of the Ignalina Nuclear Power Plant (Ignalina NPP) measured by high resolution inductively coupled plasma mass spectrometry (ICP-MS) are presented and applicability of the method for the evaluation of minor graphite impurities is discussed. It is shown that ICP-MS is a promising technique for determination of graphite impurities in 10 ppm – 10 ppt concentration range as a rapid and relatively cheap method. The most important nuclides for evaluation of short- and long-lived activation products in the Ignalina NPP graphite were measured with the accuracy sufficient for the radioactive waste classification. These results could be used for planning of dismantling and disposal of the Ignalina NPP graphite.

Keywords: reactor graphite impurities, ICP-MS, X-ray fluorescence, neutron activation analysis

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1. Introduction

The main source of radioactivity in equipment of a nuclear power plant is neutron activation products. The amount of activation products depends on the elemental composition of materials used for building a nuclear facility. In cores of channel and gas cooled reactors a huge amount of high purity graphite is used as a moderator. Being in an intensive neutron flux for a long irradiation period, minor graphite impurities such as Cs, Sr, Eu, U, Cd, U, and Th play the major role in generation of short- and long-lived radioactive nuclides [1].

Two RBMK–1500 reactors of the Ignalina Nuclear Power Plant (Ignalina NPP) are entering the preparatory stage of their dismantling as both units have been already shut down in 2004 and in 2009. The decommissioning of reactors will involve management and disposal of a big amount of operational waste and dismantling residues. A total amount of graphite (3843 tons) was used as a moderator and a reflector in both reactors [2], thus graphite substantially contributes to the total volume of radioactive waste.

Strategy of graphite waste management after the dismantlement of reactors strongly depends on inventory

and activity of short- and long-lived neutron activation products generated from graphite impurities during the reactor operation. Thus, the list of nuclides of the main interest is to be defined. However, only part of nuclides in minor places of interest could be measured in the graphite stack directly. Because of that, modelling of build up of activation products in the reactor and validation of calculated results with ones determined experimentally in a limited amount of accessible points is the only affordable way to evaluate the activity of short- and long-lived radioactive waste [3–6].

Although the reactor graphite is a relatively pure material, the concentration of the most part of impurities is at ppm level and below, there are still enough impurities able to produce numerous difficult-to-measure radionuclides by activation. Such minor impurities in virgin graphite could not be measured with common atomic emission spectrometers or by various X-ray fluorescence techniques. As there are tens of important elements which have to be measured for modelling short- and long-lived waste, not all of them could be measured by sensitive but expensive neutron activation analysis as well. Concentrations of minor impurities in different places of the same reactor graphite construction

could be in the wide range [7]. Therefore, it is necessary to make many measurements in order to adequately characterize the graphite waste from a reactor. Thus, application of a rapid and relatively cheap inductively coupled plasma mass spectrometry (ICP-MS) technique for measuring minor concentrations of elements in the graphite matrix could be promising. The aim of the study is to measure concentrations of important minor impurities in the reactor graphite stack by the mass spectrometric technique and to determine precision of the method.

2. Experiment

2.1. Preparation of samples

The sample was taken from a spare ring part of graphite sleeve of the RBMK–1500 reactor fuel channel.

For *X-ray fluorescence measurement*, 10 g of the sample was ground for 3 minutes with the mill made of stainless steel till homogeneous powder appeared. After that the sample powder was squeezed to the (3×1) cm cylinder shape tablet (glue was not used) and placed into the X-ray spectrophotometer.

For *ICP-MS measurements*, as graphite is a material difficult to dissolve completely even in a microwave oven, a piece of graphite ring was poured with 10 ml of 2% nitric acid (p. a. grade, “Stanchem”, Poland), closed with a parafilm tape and left for 72 hours. After that 5 ml of solution was taken and diluted up to 15 ml with distilled water (NANOpure Barnstead/ThermoLyne Co., USA). It is worth mentioning that there have been plenty of efforts to dissolve graphite completely by using HF acid, mixtures of H₂SO₄ and HClO₄ with V₂O₅, H₂SO₄ and HNO₃ with V₂O₅ (all chemicals were p. a. grade) using slight and moderate heating, but extremely significant sample contaminations reaching up to (50–70)% of the signal level were observed. Nevertheless, as graphite is a porous material, it was assumed that impurities should partly or even completely wash out from the graphite sample.

2.2. Instruments

X-ray fluorescence analysis was carried out with the wavelength dispersive X-ray fluorescence spectrophotometer S4 Pioneer (Bruker) using factory default measurement options.

ICP-MS measurements were performed with a double focusing high resolution sector field inductively

coupled plasma mass spectrometer Element 2 (Thermo Scientific). For the solution-based analysis Multi-Element standard solution VI CertiPUR (Merck, Darmstadt, Germany) at the concentration of 1 ng g⁻¹ was used for the optimization and calibration of the ICP-MS instrument. Optimized Element 2 ICP-MS operating conditions and data acquisition parameters are summarized in Table 1.

Table 1. Optimized Element 2 ICP-MS operating conditions and data acquisition parameters.

Operating conditions	
Forward power (W)	1100
Cooling gas flow rate (l min ⁻¹)	14.0
Auxiliary gas flow rate (l min ⁻¹)	0.75
Nebulizer gas flow rate (l min ⁻¹)	1.32
Solution uptake rate (ml min ⁻¹)	0.70 (peristaltic pump)
Nebulizer type	Conical U-type 1 ml min ⁻¹ (Glass expansion)
Spray chamber type	Cyclonic of 50 ml volume (Glass expansion)
Data acquisition	
Resolution (m/Δm, 10% valley)	4000 (medium)
Runs and passes	10×1
Mass window (%)	300
Samples per peak	15
Search window (%)	150
Integration window (%)	80
Sampling time (s)	0.01
Integration type	Average
Scan type	E-scan

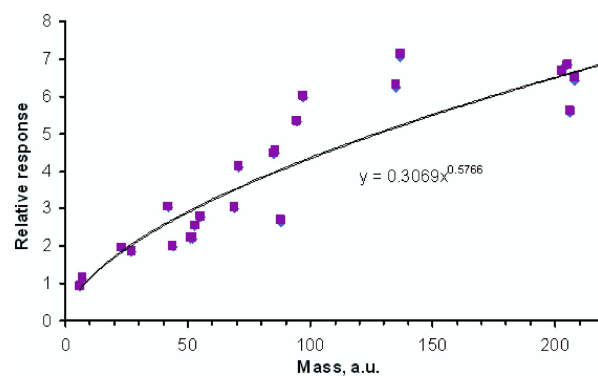


Fig. 1. Mass spectrometer Element 2 response dependence on atomic mass.

The instrument response curve, obtained from measurements of Merck VI standard solution at known concentrations of low ionization potential elements (Fig. 1) as in [8], was used for normalization of the signals of different elements. Corrections because of the difference of ionization potentials were introduced according to Saha equation if appropriate (at temperature of 7700 K and electron density of $3 \cdot 10^{15} \text{ cm}^{-3}$ as obtained from measurement).

As the extract from the graphite sample in the form of solution was the main test sample, standard solutions were of importance for analytical calibration of the instrument. However, for solutions only part of elements could be covered by acceptable standards. In addition, determination of percentage of the mass of elements dissolved from the graphite was another problem. Because of this, Fe was used as an internal standard, and the obtained concentration value from ICP-MS for this element was normalized to the value obtained by the X-ray fluorescence technique.

3. Results

The concentration of graphite impurities measured by the ICP-MS technique was compared with previously performed neutron activation measurements (measured by gamma spectrometry) [1]. The concentrations of elements are provided in Table 2.

The concentrations of 40 elements were measured by the ICP-MS technique. As seen from Table 2, almost all concentrations of elements determined by mass spectrometry are of the same order as the values measured by the neutron activation analysis technique. Such measurement precision is enough for the radioactive waste characterization. Concentrations of a few elements such as Na, K, Ti, V, Zn, Ga, Ge, Ag, and Ta measured by various methods showed too much different results.

Concentrations of Na and K observed in ICP-MS analysis were higher by one order than ones measured by the neutron activation analysis technique. These elements are very common in the environment, thus higher concentrations could be influenced by contamination of the sleeve by Na and K during its usual handling in the Ignalina NPP as this spare part was stored under ordinary conditions there.

It was found that Ti, V, Ga, Ge, and Ta concentration values were lower by one order (Ge by three orders) than ones measured by neutron activation analysis. This could happen because the elements did not

Table 2. Comparison of ICP-MS results with neutron activation analysis.

Element	ICP-MS		Neutron activation analysis [1, 9]	
	Concentration, g/g	Rel. unc. (%)	Concentration, g/g	Rel. unc. (%)
Li	3.9E-08	13.4	–	–
B	9.6E-06	1.8	–	–
Na	3.6E-05	4.2	4.6E-06	6.3
Mg	2.8E-06	12.5	7.0E-06	–
Al	1.1E-05	2.9	9.2E-06	1.3
Si	7.8E-05	7.1	–	–
P	1.9E-06	3.1	–	–
S	4.7E-05	2.2	–	–
Cl	1.6E-05	7.9	7.6E-06	2.3
K	2.2E-05	2.0	1.9E-06	12.0
Ca	7.5E-05	4.1	5.2E-05	4.3
Ti	3.8E-06	3.9	1.7E-05	2.7
V	1.9E-07	4.0	1.7E-05	1.3
Cr	4.7E-07	5.5	6.0E-07	1.7
Mn	5.9E-07	3.4	5.8E-07	1.7
Fe	4.1E-05	4.1	1.9E-05	5.3
Co	3.5E-08	11.3	1.9E-08	0.7
Ni	6.1E-07	4.4	3.9E-07	8.3
Cu	6.6E-07	3.4	–	–
Zn	2.7E-06	3.6	2.0E-08	–
Ga	4.3E-09	37.8	1.0E-08	–
Ge	2.1E-09	200.2	9.0E-06	–
Sr	1.1E-06	5.8	9.6E-07	5.7
Zr	7.3E-07	7.4	1.0E-06	7.0
Nb	6.0E-09	14.2	–	–
Mo	5.8E-08	26.6	1.7E-07	0.7
Ag	6.5E-08	14.1	3.0E-09	20.0
Cd	3.4E-08	26.1	1.5E-08	–
Sn	1.4E-07	12.6	1.5E-07	–
Cs	2.1E-09	33.6	1.6E-09	9.3
Ba	1.3E-06	1.4	2.0E-06	2.3
Eu	2.3E-09	50.0	2.6E-09	2.0
Ho	2.1E-09	38.1	9.4E-09	6.7
Hf	1.5E-08	24.4	5.8E-09	1.7
Ta	2.4E-10	104.2	1.9E-09	3.3
W	4.2E-08	11.8	4.7E-08	3.7
Pb	2.1E-06	8.2	–	–
Bi	1.7E-09	30.2	–	–
Th	3.4E-09	26.4	7.9E-09	1.7
U	5.4E-09	18.8	1.6E-08	2.7

wash out from the graphite matrix so well as other elements due to lower solubility. Besides, higher concentration of Zn was also observed in ICP-MS analysis. Higher concentration by two orders of magnitude could be influenced by contamination of a parafilm tape used as it contains a significant amount of Zn [10]. However, higher Ag concentration by one order than in neutron activation results shows that the neutron activation value having comparatively high RSD could be undervalued.

It seems that Cl, an important element for modelling long-lived graphite waste, can be successfully measured by the ICP-MS technique. Cl is an element difficult to be measured by the ICP-MS due to high contamination from the environment and chemicals used for the preparation of a sample. Nevertheless, in spite that the background/signal ratio was high (up to 47%) in comparison with other elements, the contamination influence was stable, and thus the Cl concentration can be included into the measurement results.

4. Conclusions

The most important elements for evaluation of short- and long-lived activation products in the Ignalina NPP graphite by simulation of activation were measured with the accuracy sufficient for the characterization of radioactive waste. The Fe concentration obtained by the X-ray fluorescence technique was used as an internal standard for normalization of the ICP-MS measurement results. Concentrations of the most elements measured by the ICP-MS show acceptable agreement with the concentrations determined by neutron activation method. In this work it has been shown that ICP-MS is a promising technique for determination of concentration of graphite minor impurities as a rapid and relatively cheap method.

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REAKTORIAUS AKTYVIOSIOS ZONOS GRAFITO PRIEMAIŠŲ, SVARBIŲ RADIOAKTYVIŲJŲ ATLIEKŲ SUĖTIES MODELIAVIMUI, NUSTATYMAS MASIŲ SPEKTROMETRIJOS METODUA. Puzas^a, V. Remeikis^a, Ž. Ežerinskis^b, P. Serapinas^b, A. Plukis^a, G. Duškesas^a^a Valstybinis mokslinių tyrimų institutas Fizinių ir technologijos mokslų centras, Vilnius, Lietuva^b Vilniaus universiteto Teorinės fizikos ir astronomijos institutas, Vilnius, Lietuva**Santrauka**

Reaktoriaus grafito atliekų tvarkymo problema yra aktuali Lietuvai, 2009 m. nutraukusiai grafitinių RBMK reaktorių eksploataciją, bei kitoms šalims, kuriose buvo ir yra eksploatuojami grafitiniai reaktoriai. Apšvitinto reaktoriaus grafito tvarkymo problema taip pat bus aktuali ateityje, nes kai kuriuose projektuojamuose IV kartos reaktoriuose neutronų lėtiklis irgi bus grafitas. Kadangi veikiančiame reaktoriuje neutronų spektras nėra vienalytis, todėl skirtingose vietose priemaišos aktyvuojamos taip pat nevienodai. Dėl to aktyvacijos produktų koncentracija įvairiose grafito konstrukcijų

vietose taip pat yra skirtinga. Praktinių galimybių išmatuoti reikiamą kiekį ėminių, kad būtų galima tinkamai apibūdinti atliekas, nėra, todėl tam yra pasitelkiamas modeliavimas, kurio kokybė esmingai priklauso nuo žinių apie priemaišų koncentraciją neapšvitintame grafite. Parodyta, kad grafito priemaišoms išmatuoti tinka induktyviai susietos plazmos masių spektrometrija (ICP-MS). Šiuo metodu galima teisingai nustatyti daugumos priemaišų koncentracijos eilę, ir to pakanka, kad modeliuojant galima būtų deramai apibūdinti apšvitinto grafito atliekas.