

## Atom counting of long-lived radionuclides using neutron activation analysis

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### Introduction

It is obvious from equation (1) that measurement of long-lived radionuclides can be carried out by both decay counting (radiometric method) and atom counting

$$A = \lambda N \quad (1)$$

where  $A$  is the activity,  $N$  is the number of atoms, and  $\lambda$  is the decay constant related to the half-life  $T_{1/2}$  by equation  $\lambda = \ln 2/T_{1/2}$ . Despite the advances in radiometric technologies, atom counting has recently received much more attention for measurement of long-lived radionuclides. Recently, mass spectrometry techniques, namely ICP-MS and AMS, proved to be superior for determination of long-lived radionuclides, when compared to radiometric counting (Povinec et al., 2018). Another possibility is neutron activation analysis (NAA) provided that a long-lived radionuclide has favorable nuclear characteristics, i.e., the nuclide has a large neutron capture cross section for formation of a product nuclide (or its daughter) with good measurement properties, such as a short half-life and suitable gamma-ray spectrometric characteristics (Byrne and Benedik, 1999). The activity,  $A$ , after the irradiation time,  $t_i$ , decay time,  $t_d$ , and counting time,  $t_c$ , is given by equation (2)

$$A = N(\Phi_{th}\sigma_{th} + \Phi_{epi}I_0)SDC \quad (2)$$

where  $N$  is the number of atoms,  $\Phi_{th}$  is the thermal neutron fluence rate,  $\Phi_{epi}$  is the epithermal neutron fluence rate,  $\sigma_{th}$  is the thermal neutron cross section,  $I_0$  is the resonance integral cross section,  $S$  is the saturation factor ( $S = (1 - e^{-\lambda t_i})$ ),  $D$  is the decay factor ( $D = e^{-\lambda t_d}$ ), and  $C$  is the counting factor ( $C = (1 - e^{-\lambda t_c})/\lambda t_c$ ).

The above authors calculated advantage factors (AFs) of long-lived alpha-emitters as a ratio of signals obtained in NAA and decay counting, whereas AFs for other long-lived radionuclides were calculated by another author for different NAA and radiometric conditions (Hou, 2008). Table 1 shows differences in both sets of values. It should be pointed out here that the AFs only indicate a potential for NAA relative to radiometry. Important factors to consider in practice are the counting efficiency and background of both measurement modes.

Since we have favorable conditions for NAA using a LVR-15 reactor at Řež, we explored the determination of <sup>99</sup>Tc, <sup>129</sup>I, <sup>232</sup>Th, <sup>238</sup>U in environmental and other samples by NAA as reported in this work.

Table 1. AFs for NAA of some long-lived radionuclides

Nuclide pair	$T_{1/2}$ of target (y)	AF <sup>a</sup>	AF <sup>b</sup>
<sup>99</sup> Tc/ <sup>100</sup> Tc	$2.1 \times 10^5$	-	$2.1 \times 10^4$
<sup>129</sup> I/ <sup>130</sup> I	$1.57 \times 10^7$	-	$1.3 \times 10^6$
<sup>135</sup> Cs/ <sup>136</sup> Cs	$2.06 \times 10^6$	-	$3.86 \times 10^3$
<sup>230</sup> Th/ <sup>231</sup> Th	$7.54 \times 10^4$	27	$8.6 \times 10^3$
<sup>232</sup> Th/ <sup>233</sup> Pa	$1.40 \times 10^{10}$	$4.0 \times 10^5$	$2.5 \times 10^6$
<sup>231</sup> Pa/ <sup>232</sup> Pa	$8.27 \times 10^4$	106	$1.2 \times 10^4$
<sup>238</sup> U/ <sup>239</sup> U	$4.46 \times 10^9$	$7.0 \times 10^6$	$3.4 \times 10^8$
<sup>238</sup> U/ <sup>239</sup> Np	$4.46 \times 10^9$	$8.0 \times 10^5$	$3.4 \times 10^8$
<sup>237</sup> Np/ <sup>238</sup> Np	$2.14 \times 10^6$	640	$3.6 \times 10^5$
<sup>242</sup> Pu/ <sup>243</sup> Pu	$3.75 \times 10^5$	-	$3.6 \times 10^4$

<sup>a</sup> – Byrne and Benedik 1999, <sup>b</sup> – Hou 2008

### Technetium-99 ( $T_{1/2} = 2.1 \times 10^5$ y)

The <sup>99</sup>Tc determination by NAA is based on parameters given in Table 2.

Table 2. Nuclear parameters for <sup>99</sup>Tc determination

Nuclear reaction	$\sigma$ (barn)	$I_0$ (barn)	$T_{1/2}$ of product	Main $\gamma$ -line (keV); int. (%)
<sup>99</sup> Tc(n, $\gamma$ ) <sup>100</sup> Tc	20	30	15.8 s	539.5; 6.6

We employed both instrumental NAA (INAA) and epithermal NAA (ENAA) with irradiation and counting parameters given in Table 3 together with the resulting limits of detection (LOD).

Table 3. Irradiation and counting parameters

INAA	ENAA
$\Phi_{th} = 3 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$	$\Phi_{epi} = 1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$
$t_i = 15 \text{ s}$	$t_i = 20 \text{ s}$
$t_d = 12\text{--}17 \text{ s}$	$t_d = 16\text{--}21 \text{ s}$
$t_c = 30 \text{ s}$	$t_c = 30 \text{ s}$
LOD=200 mBq	LOD=50–70 mBq

Irradiations were carried out using a pneumatic transfer system with a transport time of 3.5 s, however, due to manual repacking and sample transfer to a coaxial HPGe detector with relative efficiency of 21 % and FWHM resolution of 1.75 keV (both for the 1332.5 keV photons of <sup>60</sup>Co) the decay time,  $t_d$ , was somewhat longer compared to the transport time. In ENAA, thermal neutrons were shielded off with the aid of a Cd box with wall thickness of 1 mm. The LODs achieved in both NAA modes were insufficient for the Tc determination in environmental samples, such as algae *Fucus serratus* from the vicinity of La Hague reprocessing plant and Novo-Shepelyci soil from the vicinity of the crashed Chernobyl nuclear power plant (NPP). In these samples, the Tc

concentration was determined by liquid scintillation counting (LSC) after pre-separation with TOGDA-PAN resin and extraction using methyl ethyl ketone (Fikrlé, 2011, cf. Table 4). The accuracy of the <sup>99</sup>Tc determination by LSC measurement was proved by analysis of NIST SRM 4359 Seaweed Radionuclide Standard. Our values agree with the NIST noncertified value (median 38 mBq g<sup>-1</sup>, range 17–48 mBq g<sup>-1</sup>).

Table 4. Concentrations of <sup>99</sup>Tc determined by LSC

Sample	Tc (mBq g <sup>-1</sup> )
Fucus serratus 1	26.8 ± 5.4
Fucus serratus 2	22.7 ± 5.1
Soil Novo-Shepelyci	14.1 ± 2.6
NIST SRM 4359 Seaweed	20.2 ± 7.6; 29.6 ± 7.4

Although pre-irradiation separation may improve LOD of <sup>99</sup>Tc determination by NAA (Hou, 2008), there are other methods, namely resonance ionization mass spectrometry (RIMS), thermal ionization mass spectrometry (TIMS), ICP-MS and accelerator mass spectrometry (AMS), which provide much more favourable LOD of <sup>99</sup>Tc (Hou and Roos, 2008).

**Iodine-129 (T<sub>1/2</sub> = 1.57 × 10<sup>7</sup> y)**

The <sup>129</sup>I determination by NAA is based on parameters given in Table 5.

Table 5. Nuclear parameters for <sup>129</sup>I determination

Nuclear reaction	σ (barn)	I <sub>0</sub> (barn)	T <sub>1/2</sub> of product	Main γ-line (keV); int. (%)
<sup>129</sup> Tc(n, γ) <sup>130</sup> I	27±3	36±4	12.36 h	536.1; 15.7

There are several nuclear interferences in the <sup>129</sup>I determination by NAA, which should be accounted for (Hou, 2008).

We employed NAA with both pre-irradiation and post-irradiation separation, so-called radiochemical NAA (RNAA) with irradiation and counting parameters as follows: Φ<sub>th</sub> = 4 × 10<sup>13</sup> cm<sup>-2</sup> s<sup>-1</sup>, t<sub>i</sub> = 4–10 h, t<sub>d</sub> = 10–15 h, t<sub>c</sub> = 2–4 h. First we used the NAA procedures for large-scale studies of <sup>129</sup>I concentration and the <sup>129</sup>I/<sup>127</sup>I ratio in samples from the Baltic Sea (Hou et al. 2002), thyroid and urine samples from Ukraine and Denmark (Hou et al., 2003a), and in Chernobyl contaminated soil (Hou et al., 2003b). In these studies, we employed NAA with both pre-irradiation and post-irradiation separation (RNAA) described in the above publications. Later we measured both <sup>129</sup>I and the <sup>129</sup>I/<sup>127</sup>I ratio in biomonitors from the vicinity of Temelín NPP. The samples comprised thyroids of cattle grazing in the NPP vicinity, moss *Pleurozium Schreberi* and three river sediments collected in the catchment of the NPP, upstream and downstream of the NPP water outlets. The thyroid samples, highly sensitive biomonitors of radio-iodine pollution, were collected prior to the start of NPP operation and after several years of its functioning to investigate whether releases of <sup>129</sup>I occur into the environment during normal operation of the NPP. In this work, we developed pre-irradiation separation based on sample combustion followed by trapping of the released iodine in a LiOH solution and

RNAA procedure consisting of extraction of elementary iodine in CHCl<sub>3</sub>. LOD of <sup>129</sup>I of our procedure was in the range of 8 – 10 mBq kg<sup>-1</sup> (Krausová et al., 2013). Results for the <sup>129</sup>I/<sup>127</sup>I ratio in the bovine thyroids are schematically depicted in Figure 1 and compared with world-wide values of animal thyroids.

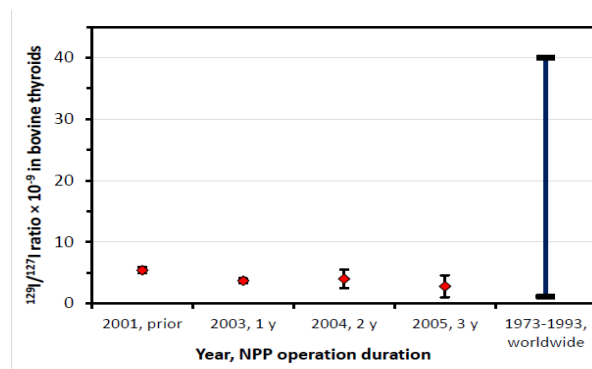


Figure 1. <sup>129</sup>I/<sup>127</sup>I ratios in bovine thyroids from the vicinity of Temelín NPP and their comparison with world-wide values.

Figure 1 shows no local contamination with <sup>129</sup>I due to the Temelín NPP releases. A similar conclusion can be derived from results of the <sup>129</sup>I and <sup>129</sup>I/<sup>127</sup>I ratio determination in moss and sediment samples, other biomonitors of <sup>129</sup>I pollution (cf. Table 6).

Table 6. <sup>129</sup>I levels and <sup>129</sup>I/<sup>127</sup>I ratio in biomonitors

Sample	Year of sampling (N)	<sup>129</sup> I (mBq kg <sup>-1</sup> )	<sup>129</sup> I/ <sup>127</sup> I x 10 <sup>-9</sup>
Moss <i>P. Schreberi</i>	2004 (5)	23 ± 16	2.3 ± 1.9
Sediment upstream NPP	2004 (4)	< 10	-
Sediment NPP catchment area	2004 (7)	< 8	-
Sediment downstream NPP	2004 (4)	< 10	-

Quality control of the study was pursued by analysis of reference algae sample *F. Serratus*, and good agreement was obtained with published results (Krausová et al., 2013). Our LOD values for the <sup>129</sup>I/<sup>127</sup>I ratio were better than those of other methods, except for AMS (cf. Table 7). However, ICP-MS and AMS techniques recently further improved their LOD values for <sup>129</sup>I (and other long-lived radionuclides), as was reported at this symposium.

Table 7. LOD for <sup>129</sup>I achieved by different methods (Rosenberg, 1993)

Method	Number of atoms	<sup>129</sup> I/ <sup>127</sup> I ratio
LSC	3.5 × 10 <sup>13</sup>	> 10 <sup>-6</sup>
γ-spectrometry	10 <sup>13</sup>	> 10 <sup>-6</sup>
ICP-MS	3 × 10 <sup>11</sup>	> 10 <sup>-8</sup>
TIMS	10 <sup>7</sup>	-
NAA	10 <sup>7</sup>	10 <sup>-12</sup> – 10 <sup>-13</sup>
AMS	2 × 10 <sup>6</sup>	10 <sup>-13</sup>

**Thorium–232 ( $T_{1/2} = 1.40 \times 10^{10}$  y)**

The  $^{232}\text{Th}$  determination by NAA is based on parameters given in Table 8.

Table 8. Nuclear parameters for  $^{232}\text{Th}$  determination

Nuclear reaction	$\sigma$ (barn)	$I_0$ (barn)	$T_{1/2}$ of product	Main $\gamma$ -line (keV); int. (%)
$^{232}\text{Th}(n, \gamma)^{233}\text{Th} \rightarrow ^{233}\text{Pa}$	$7.3 \pm 0.1$	$84 \pm 4$	27.0 d	311.9; 38.5

In underground nuclear physics experiments focused on investigations of rare nuclear processes and decays, radiopurity of construction parts of the detectors and all materials used is crucial for background reduction. For SuperNEMO experiment, which aims at detection of neutrinoless double beta decay of  $^{82}\text{Se}$  (Arnold et al., 2010), we measured levels of  $^{232}\text{Th}$  in the  $^{82}\text{Se}$  source material (with  $\sim 80\%$  enrichment) and in Cu, a part of the detection system, by RNAA using the following irradiation and counting conditions:  $\Phi_{\text{th}} = 4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ ,  $t_i = 20 \text{ h}$ ,  $t_d = 10\text{--}15 \text{ d}$ ,  $t_c = 4\text{--}8 \text{ h}$ . Counting was carried out with a coaxial HPGe detector (rel. efficiency 77 %, FWHM resolution 1.85 keV, both for the 1332.5 keV photons of  $^{60}\text{Co}$ ). Two types of RNAA procedures were employed. First (denoted A in Figure 2) was based on  $^{233}\text{Pa}$  extraction with 5% TOPO in toluene from 7 M  $\text{HNO}_3$  according to Byrne and Benedik (1999). It turned out that one of the enriched  $^{82}\text{Se}$  samples was contaminated with Te, which produced  $^{131}\text{I}$  upon neutron irradiation by the reaction  $^{130}\text{Te}(n, \gamma)^{131}\text{Te}$  ( $T_{1/2} = 1.26 \text{ d}$ )  $\rightarrow$   $^{131}\text{I}$  ( $T_{1/2} = 8.04 \text{ d}$ ) and significantly increased background in the measured  $\gamma$ -ray spectra (cf. Figure 2) Therefore, second RNAA procedure (denoted B) was designed, which was based on  $^{233}\text{Pa}$  separation from 7 M  $\text{HNO}_3$  with Triskem TRU resin (Kučera et al., 2017). Using RNAA-B procedure, LODs for  $^{232}\text{Th}$  in Cu and  $^{82}\text{Se}$  of 0.08  $\mu\text{Bq}$  and 1  $\mu\text{Bq}$ , respectively, were achieved (Kučera et al. 2017). It can be seen from a comparison of LODs for the  $^{233}\text{Pa}$  determination in Cu with different methods in Table 9 that RNAA provided the third lowest LOD, after AMS and ICP-MS.

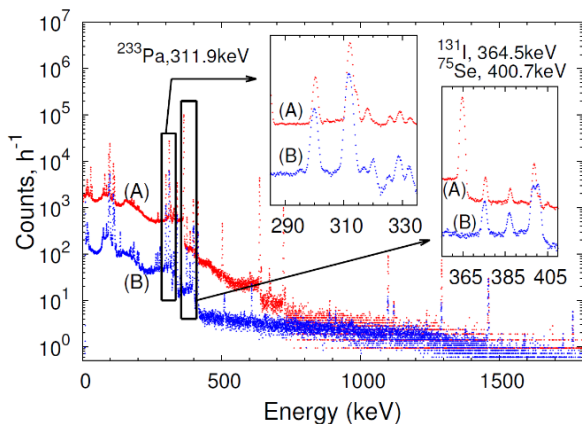


Figure 2. Comparison of  $\gamma$ -ray spectra in RNAA determination of  $^{233}\text{Pa}$  in  $^{82}\text{Se}$ . (A) – TOPO extraction method, (B) – TRU resin method.

Table 9. Comparison of LODs for  $^{233}\text{Pa}$  determination in Cu with different methods (Povinec, 2017)

Method	LOD ( $\mu\text{Bq}$ )
$\alpha$ -ray spectrometry	100
Underground $\gamma$ -ray spectrometry	2400
BiPo-3 detector	1.4
ICP-MS	0.003
AMS	0.0003
RNAA	0.08

**Uranium–238 ( $T_{1/2} = 4.5 \times 10^9$  y)**

The  $^{238}\text{U}$  determination by NAA can be based on parameters given in Table 10.

Table 10. Nuclear parameters for  $^{238}\text{U}$  determination

Nuclear reaction	$\sigma$ (barn)	$I_0$ (barn)	$T_{1/2}$ of product	Main $\gamma$ -line (keV); int. (%)
$^{238}\text{U}(n, \gamma)^{239}\text{U}$	$2.7 \pm 0.7$	$280 \pm 10$	23.5 min	74.7; 53.2
$^{238}\text{U}(n, \gamma)^{239}\text{U} \rightarrow ^{239}\text{Np}$	$2.7 \pm 0.7$	$280 \pm 10$	2.36 d	106.1; 25.3

For SuperNEMO experiment we also measured levels of  $^{238}\text{U}$  in the enriched  $^{82}\text{Se}$  and in Cu by RNAA. Of the two possibilities given in Table 10, the use of  $^{239}\text{U}$  measurement was chosen, because this option has a higher potential for obtaining a better AF, it is faster and easier to perform. We employed the following irradiation and counting parameters:  $\Phi_{\text{th}} = 2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ ,  $t_i = 3 \text{ min}$ ,  $t_d = 20\text{--}30 \text{ min}$ ,  $t_c = 3000\text{--}5400 \text{ s}$ . Three versions of RNAA were used based on  $^{239}\text{U}$  extraction with 50 % tributyl phosphate (TBP) in toluene from 7 M  $\text{HNO}_3$ . In the first version (denoted A in Figure 3), the organic phase was double scrubbed with 7 M  $\text{HNO}_3$  in the presence of Se or Cu hold-back carrier before counting with a well-type HPGe detector (active volume of 150  $\text{cm}^3$ , FWHM resolution 2.1 keV for the 1332.5 keV photons of  $^{60}\text{Co}$ ). A high  $^{83}\text{Br}$  activity was present in the organic fraction separated from the irradiated  $^{82}\text{Se}$  sample, which was created by the reaction  $^{82}\text{Se}(n, \gamma)^{83}\text{Se}$  ( $T_{1/2} = 22.3 \text{ min}$ )  $\rightarrow$   $^{83}\text{Br}$  ( $T_{1/2} = 2.4 \text{ h}$ ,  $E_\gamma = 529.6 \text{ keV}$ ) and significantly increased background in the measured  $\gamma$ -ray spectra (cf. Figure 3). After stripping of  $^{239}\text{U}$  with saturated solution of  $\text{Na}_2\text{CO}_3$ , the interfering activity of  $^{83}\text{Br}$  (spectrum B in Figure 3) decreased. A further decrease was obtained by precipitation of the formed  $^{83}\text{Se}$  as  $\text{Ag}_2\text{SeO}_3$  and precipitation of  $^{83}\text{Br}$  as  $\text{AgBr}$  prior to extraction of  $^{239}\text{U}$  by TBP with  $^{239}\text{U}$  stripping from the organic phase with saturated solution of  $\text{Na}_2\text{CO}_3$  as the last separation step (spectrum C in Figure 3).

Using RNAA-C procedure, LODs for  $^{238}\text{U}$  in Cu and  $^{82}\text{Se}$  of 0.2  $\mu\text{Bq}$  and 0.6  $\mu\text{Bq}$ , respectively, were achieved (Kučera et al. 2017). A comparison of LODs for the  $^{238}\text{U}$  determination in Cu with different methods (cf. Table 11) yields a similar picture as for the  $^{232}\text{Th}$  determination (cf. Table 10): RNAA provides the third lowest LOD, after AMS and ICP-MS.

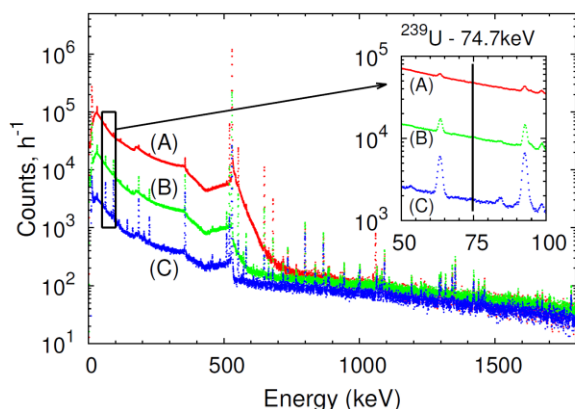


Figure 3. Comparison of  $\gamma$ -ray spectra in RNAA determination of  $^{239}\text{U}$  in  $^{82}\text{Se}$ . (A) – scrubbed TBP phase, (B) – stripped aqueous phase, (C) – stripped aqueous phase preceded by removal of  $^{83}\text{Se}$  and  $^{83}\text{Br}$ .

Table 11. Comparison of LODs for  $^{238}\text{U}$  determination in Cu with different methods (Povinec, 2017)

Method	LOD ( $\mu\text{Bq}$ )
$\alpha$ -ray spectrometry	100
Underground $\gamma$ -ray spectrometry	2000
BiPo-3 detector	1.6
ICP-MS	0.010
AMS	0.0001
RNAA	0.2

### Conclusions

Although the LODs of long-lived radionuclides by NAA have recently been surpassed by those achieved by ICP-MS and AMS, NAA as a primary method of measurement will keep its importance for quality control purposes. In most cases, no pre-irradiation chemistry is required (no risk of contamination of analyzed samples) and advanced post-irradiation chemistry (RNAA) has still a potential for further improvements of LOD values.

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