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NKS-Norcmass reference material for analysis of Pu-isotopes and ^{237}Np by mass spectrometry

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Abstract

The aim of the reference material in the Norcmass-project was to produce a low-level (<<1mBq/g of ^{239}Pu) sample of sufficient amount to allow individual laboratories to perform several tests without risk of using up the material. Although there are several reference materials available (eg IAEA) few have ^{239}Pu/^{240}Pu data and almost none have ^{237}Np/^{239}Pu-data. Those who have (eg IAEA-384) have very high concentrations and are not useful for testing analytical methods designed for low-level measurements where a large sample mass may be required. The reference material consist of the top 10cm of 2mm sieved soil pooled together from 12 different Danish locations collected during 2003. The Soil was blended and sieved through 0.6 and finally through a 0.4 mm sieve. A total amount of 17 kg soil was produced. Several aliquots of the material was subject to analysis by alpha spectrometry and ICP-MS. The material contain $^{239+240}$Pu at a concentration of 0.24 ± 0.01 mBq/g and a ^{240}Pu/^{239}Pu atom ratio of 0.19 ± 0.006. The ratio ^{237}Np/^{239}Pu was determined to 0.32 ± 0.01.

Key words

Norcmass, ICP-MS, Mass spectrometry

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NKS-B Norcmass reference material for analysis of Pu-isotopes and ^{237}Np by mass spectrometry

Purpose

Although there are several reference materials available (eg IAEA) few have ^{239}Pu/^{240}Pu data and almost none have ^{237}Np/^{239}Pu-data. Those who have (eg IAEA-384) have very high concentrations and are not useful for testing analytical methods designed for low-level measurements. They are also often of different composition (eg IAEA-384 being a coral sample) than ordinary soils and are usually distributed in small amounts preventing testing at the 10-50g analytical scale. The aim of the reference material in the Norcmass-project was to produce a low-level (<<1mBq/g of ^{239}Pu) sample of sufficient amount to allow individual laboratories to perform several tests without risk of using up the material.

The main disadvantage with the current reference material is the very few laboratories capable of providing data on the sample.

Origin and preparation

The top 10cm of 2mm sieved soil from 12 different Danish locations collected during 2003 were pooled at Risoe Research Centre, Denmark. The Soil was further sieved through 0.6 and finally through a 0.4 mm sieve and coarsely mixed by hand. Following a single homogenization of all soil for 30 minutes in a large volume mixer a total of 17 kg soil remained. A second batch of 8.5 kg soil with the same origin was prepared simultaneously but was mixed separately and therfore not added to the larger soilsample. It is however expected that this smaller soilsample have an almost identical composition as the larger one.

Analysis

A total of 512.9g of the sieved and mixed reference soil was ashed in a large glass tray at 550 ºC for 12h. The weight of ashed soil was recorded and a total of 47.3g ash subsampled for Pu-analysis by alpha spectrometry. The remaining sample was leached in 500 ml *aqua regia* over night, filtered through GF/A glass fiber filters and the leached ash thoroughly washed repeatedly with 1M HCl until a total volume of 1.5 litre. After precipitation using ammonia, amphoteric elements were removed by 6M NaOH and the final $Fe(OH)_3$ precipitate washed two times with weak ammonia. Plutonium was separated from the soil by a two-column ion exchange method

The so far purified sample was diluted to a total of 32.98g in 1M HNO_3. From this 0.488g was taken (SampleR1) for U-analysis and two 10g samples (10.030g and 10.008g) was transferred to plastic bottles and sent to two of the other participating laboratories together with 1.2kg of the original reference soil. The remaining 12.45g

of solution was finally purified by a TTA-extraction procedure and the final solution diluted to 5ml with 1 M HNO_3. From this 0.5ml (Sample R2) was taken for U-Pu analysis. The remaining 4.5ml was diluted to 10ml (Sample R3) by deionized water (ELGA-water) and used for the Pu-isotopic measurement. This final sample thus represents a total of 72.77g ashed soil or 78.46g dry soil.

Mass-spectrometric analysis

At Risoe a PlasmaTrace2 (PT2) HR-ICP-MS with an ultrasonic nebuliser was used. Analysis was performed for uranium and plutonium in the three samples R1-R3. Tuning of the instrument before analysis was performed using a 0.5 ppb uranium solution.

Instrument settings	R1	R2	R3
Sample uptake rate [ml min^{-1}]	0.45	0.45	0.45
Cool gas flow [l min^{-1}]	13	13	13
Auxiliary gas flow [l min^{-1}]	1.4	1.4	1.4
Nebuliser gas flow [l min^{-1}]	1.03	1.03	1.03
Nebuliser heater temperature [ºC]	140	140	140
Nebuliser condenser temperature [ºC]	3	3	3
Detector	Multiplier	Multiplier	Multiplier
Dwell time:^{238}U [ms]	2	2	2
Dwell time:^{239}Pu [ms]	50	50	50
Dwell time:^{240}Pu [ms]	50	50	50
Points per peak	20	20	20
Peak width	2	2	2
Scans	1	1	1
Sweeps	75	75	15
Resolution	350	350	350

The reference soil sample (R3) in a 10 ml volume was continously pumped into the USN and 15 separate measurements of ^{238}U, ^{239}Pu and ^{240}Pu was performed in the peak jumping mode.

Results

The total peak counts for each isotope in sample R3 is given in Table 2 below

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Run No.	^{238}U	^{239}Pu	^{240}Pu	Atom $^{240}Pu/^{239}Pu$
1	1223	5000	911	0.18220
2	1180	5310	990	0.18644
3	1143	5368	923	0.17194
4	1082	5196	955	0.18380
5	1135	5111	964	0.18861
6	1058	5185	957	0.18457
7	1069	5140	979	0.19047
8	1117	5174	938	0.18129
9	980	4937	975	0.19749
10	1081	5004	967	0.19325
11	1031	5013	959	0.19130
12	991	5080	968	0.19055
13	1012	4985	894	0.17934
14	958	5179	966	0.18652
15	1020	4899	948	0.19351
Atom ratio:				**0.1868±0.0065** (1 std.dev)

Table 2: Raw data counts for each isotope measured.

The analysis of sample R1 showed that the levels of uranium already was sufficiently low to make the plutonium analysis without having any large corrections to the mass 239 due to tailing and UH^+. Sample R2 showed that after the TTA-extraction the uranium was removed to the extent where the dominating source of uranium is the chemicals themselves. This was concluded from nearly identical uranium amounts found in the R2-sample and the 8M HNO_3 used for backextraction from TTA.The fraction of counts in mass 239 due to the presence of uranium was measured to be 3.2 10^{-5} which means that the correction to mass 239 in this case was less than one count.

Due to the low count rates no dead-time corrections was applied to any of the isotopes. A standard U-solution (U112a) was used to monitor mass-fractionation. This was found to be insignificant and no corrections have been applied to the raw data.

Alpha-spectrometric measurements

The four subsamples of ashed material used for alpha spectrometry were separated for plutonium on a single ion exchange column. The samples were counted for 15 days on PIPS-detectors.

Sample	Mass of dry soil	$^{239+240}$Pu [mBq/g]	^{238}Pu/$^{239+240}$Pu
K1	12.38	0.237±0.009	0.032±0.007
K2	9.60	0.249±0.012	0.037±0.009
K3	18.67	0.220±0.007	0.031±0.005
K4	10.41	0.247±0.011	0.032±0.007
Average		**0.238±0.0135**	**0.033±0.0027**

Unfortunately there is an inverse correlation between Pu-activity and sample mass, which indicates incomplete isotopic exchange between tracer and analyte.

The samples were measured before equilibrium had been attained between ^{228}Th and ^{224}Ra so even if the very small ^{238}Pu peak was visibly separated from the tiny ^{228}Th peak the ^{238}Pu/$^{239+240}$Pu values should be treated with some care.

Measurements of ^{237}Np

The same soil as was used for the Pu reference material was also used for the ^{237}Np analysis. Eight subsamples of 10g each were analysed for ^{237}Np and Pu-isotopes using ^{242}Pu as tracer for both elements. The results are given in table 4 below.

Sample	Atom ^{240}Pu/^{239}Pu	Atom ^{237}Np/^{239}Pu	$^{239+240}$Pu via ICP-MS	$^{239+240}$Pu via alpha spectrometry
Soil-1	0.1908	0.283	0.240	0.251
Soil-2	0.1818	0.362	0.246	0.239
Soil-3	0.1969	0.329	0.239	0.238
Soil-4	0.1965	0.318	0.238	0.235
Soil-5	0.1895	0.294	0.227	0.231
Soil-6	0.1887	0.304	0.239	0.238
Soil-7	0.1928	0.316	0.240	0.246
Soil-8	0.1790	0.371	0.240	0.233
Atom ratio:	0.1895 ± 0.023	0.322 ± 0.01	0.238 ± 0.018	0.238 ± 0.087

Determination of $^{240}Pu/^{239}Pu$ in NORCMASS reference soil using ICP-SFMS at laboratory #1

The reference soil was prepared at Risö and sent to FOI together with a Pu-extract prepared from approximately 100 g of soil.

Sample preparation

Soil:
About 100g of the soil-sample was ashed at 650°C for 12h. After ashing, two different approaches were used for treatment of the soil prior to Pu-separation; lithium-borate fusion and acid leaching. For the fusion, 8 g of the ashed sample was mixed with a lithium-borate flux at a sample:flux ratio of 3:1 in a carbon crucible. The mixture was melted for 15 min at 1050°C and the melt was dissolved in 1.4M HNO_3. Silica was removed by precipitation with PEG2000, the actinides co-precipitated with calciumoxalate and Pu was separated using a 2ml TEVA column. Pu was eluted from the resin using 5 ml 0.1% HEDPA which was used for ICP-MS analysis. For the acid leaching, 40g of the ashed soil was mixed with 8M HNO_3 for 4 h. The sample was filtered and the leaching repeated once. The leachates were combined, evaporated and redissolved in 3M HNO_3. Pu was separated in the same way as the fused sample.

Extract:
The extract from Risö was further purified using a 1 ml TEVA column. Pu was eluted from the resin using 5 ml 0.1% HEDPA which was used for ICP-MS analysis.

Determination of Pu using ICP-SFMS

The instrument used is an Element2 (ThermoElectron) ICP-sector field MS equipped with a "Twister" cyclonic spray chamber and a conical nebuliser. Dead-time, mass-discrimination and UH^+ formation was monitored using IRMM184 (ref mtrl containing U of natural composition) in 0.1% HEDPA. The raw-data from the analysis of the samples were subsequently corrected for dead-time and UH formation. No significant effect of mass-discrimination was found and hence no correction was made for this.

Table 5 Instrument and data acquisition settings for the ICP-SFMS determinations

Instrument settings	
Argon flow rates	
Cooling gas	14 l min^{-1}
Auxiliary gas	1 l min^{-1}
Nebuliser gas	~0.95 l min^{-1}
RF power	1300W
Sample cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.8 mm orifice diameter
Sample uptake	~0.2 ml min^{-1}
Data acquisition settings	
Resolution (m/Δm)	300
Detection mode	Pulse counting
Data acquisition mode	E-scan
Quantitative determination of Am and Pu	
Isotopes	$^{238}U^+$, $^{239}Pu^+$, $^{240}Pu^+$, $^{241}Pu^+$, $^{242}Pu^+$ and $^{244}Pu^+$
Sample time	10 ms for $^{239}Pu^+$, $^{240}Pu^+$ and $^{241}Pu^+$, 3 ms for the other ions
Mass window	5%
Samples per peak	100
Number of scans	1500
Settling time	1 ms (default minimum)
Magnet mass	238.050 u
Monitoring of dead-time, mass discrimination and UH^+ formation	
Isotopes and polyatomic ions	$^{235}U^+$, $^{238}U^+$ and $^{238}U^1H^+$
Sample time	3 ms for $^{238}U^+$, 5 ms for $^{235}U^+$ and 10 ms for $^{238}U^1H^+$
Mass window	5%
Samples per peak	100
Number of scans	1500
Settling time	1 ms (default minimum)
Magnet mass	235.043 u

Results

The results of the analyses are shown in table 6. The uncertainties of the results were calculated according to ISO/GUM using the software GUM Workbench®. All reported uncertainties are expanded uncertainties with a coverage factor of two (k = 2). The $^{240}Pu/^{239}Pu$ ratio for the soil-samples prepared using LiB-fusion and acid-leaching corresponds well with each-other. It can also be noticed that the uncertainty of the result from the LiB-fusion is only slightly higher than the one obtained for the leached sample, although the net intensity is over 12 times lover for the fused sample. This is due to a relatively high amount of U remaining in the Pu-fraction from the acid-leached sample, which leads to a quite large correction of the ^{239}Pu signal for $^{238}U^1H^+$. The contribution from this correction to the combined uncertainty of the

ratio is about 50%, while the corresponding contribution from the UH correction for the fused sample is only 0.5%.

The determined $^{240}Pu/^{239}Pu$ atomic ratio for the extract prepared at Risö is lower than the ratios obtained for the two aliquots of the soil sample. The uncertainty of this result is also lower than the uncertainties for the other results primarily due to a larger net intensity of the Pu-isotopes. Both the results from the soil prepared at FOI are significantly different from the result for the Risö-extract at the 95% confidence level. The reason for this bias is not clear. A source of uncertainty in determination of $^{240}Pu/^{239}Pu$ is the correction for contribution from $^{238}U^{1}H$, sand since the level of ^{238}U was high in the leached sample this could be an explanation for a biased result. However, since the result for the fused sample where the level of ^{238}U was low corresponds well with the result for the leached sample this is not a likely explanation. Further analysis need to be made before the discrepancy can be explained.

Table 6 Results of Pu-determination in NORCMASS reference soil

Sample	I_net_239Pu (cps)	I_net_240Pu (cps)	N_^{240}Pu/N_^{239}Pu	Uc (k=2)	Uc (%)
Fused soil	55.1	11.8	0.215	0.021	9.8
Acid leached soil	680	146	0.215	0.015	7.0
Risö extract	2286	428	0.187	0.004	2.0

Results obtained from laboratory #2 are without details and only final results are presented (Table 7 below). The ‘Norc soil’ data are from preparations of soil samples in the lab#2 laboratory while ‘Norc extract’ data refer to the pre-separated aqueous solution sent out.

	^{240}Pu/^{239}Pu ratio	**% stdv**	**Stdv**
Norc soil 1	0,11	12	0,016
Norc soil 2	0,12	13	0,02
Norc extract	0,193	2	0,004

Table 7.

Summary of determinations of $^{240}Pu/^{239}Pu$ atom ratio in Normass reference soil

(Leached soil solution prepared and pre-separated at Risoe)

	$^{240}Pu/^{239}Pu$
Lab #1	0.187 ± 0.004
Lab #2	0.193 ± 0.004
Lab #3	0.187 ± 0.006
Kelley et.al. 'Roskilde soil' (Sci.Tot. Env. 237/238, 1999, 483-500)	0.1904 ± 0.0012

Table 8

Determinations from 'Norcmass' soil

(data for reference soil prepared in the individual laboratories)

	$^{240}Pu/^{239}Pu$
Lab #1	0.215 ± 0.021
Lab #2	0.11 ± 0.02
Lab #3	0.189 ± 0.0062

Table 9

Comments to the results

The pre-separated soil solution prepared at Risoe before sending out to the two other laboratories contained Pu from approximately 100g soil. This is more than the individual laboratories used in their own leaching/dissolution of the soil and therefore the Pu-signal intensity in this sample was higher. Furthermore, the solution was pre-purified at Risø and the final sample might therefore be expected to be cleaner than

the individual soil leach/dissolution samples performed. The difference in results between the solution and raw soil samples is therefore due to both sample size (signal intensity) and sample purity. Only one of the laboratories managed to perform the ^{237}Np analysis so no comparison can be done on this subject.

Even if the reference material was expected to be homogenous it should be kept in mind that that is was pooled from several Danish locations and there may thus be a risk, even though small, that ^{240}Pu/^{239}Pu ratio as well as the ^{237}Np/^{239}Pu ratio varies in the sample due to either incomplete mixing or due to the presence of individual fall-out particles.

Variation in the fall-out ratios are well known and for the Nordic countries published values are given in the table below.

	^{240}Pu/^{239}Pu	^{237}Np/^{239}Pu
Reykjavik	0.1801 ± 0.0006	0.474 ± 0.01
Bergen	0.1738 ± 0.0006	0.391 ± 0.009
Oslo	0.1790 ± 0.0007	0.447 ± 0.009
Roskilde	0.1904 ± 0.0012	0.531 ± 0.013

Table 10.
Expected variation in fallout ratio ^{239}Pu/^{240}Pu & ^{237}Np/^{239}Pu in the Scandinavian countries. From Kelley et.al. (Sci.Tot. Env. 237/238, 1999, 483-500)

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