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RADCHEM 2005 - Radiochemical analysis in emergency and routine situations

Edited by Rajdeep Sidhu
Institute for Energy Technology, Norway

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Abstract

The report describes the work performed under the NKS-B project Radchem during 2005. RadChem-2005 has been focused towards laboratory work, and each participant has worked with improvement of existing procedures or development of new procedures. In addition an intercomparison exercise on the determination of natural radionuclides in ground water has been performed. Other work performed in Radchem-2005 include:

- € Development of new procedures for the determination of Am and Cm in environmental samples
- € Development of a procedure for age determination of Pu
- € Rapid determination of Pu using ICP-MS
- € Determination of U, Pu and Am in emergency situations
- € Sequential determination of Sr, U, Pu, Am and Cm in urine
- € Ultra low level measurements using ICP-MS

Key words

radiochemistry, natural radionuclides, intercomparison, rapid techniques, ICP-MS, actinides

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RADCHEM 2005

Radiochemical analysis in emergency and routine situations

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RadChem 2005 – Activities performed under the NKS-B project RadChem in 2005

Rajdeep Sidhu, Elis Holm, Per Roos, Jukka Lehto, Tarja K. Ikäheimonen, Håkan Pettersson, Ulrika Nygren and Christina Greis

Background and introduction

An accurate determination of radionuclides from various sources in the environment is essential for assessment of the potential hazards and suitable countermeasures both in case of accidents, authorised release and routine surveillance. Reliable radiochemical separation and detection techniques are needed for accurate determination of alpha and beta emitters. Rapid analytical methods are needed in the case of an accident for early decision-making.

The objective of the first part of this project (RadChem-2004) was to compare and evaluate radiochemical procedures used at Nordic laboratories for the determination of strontium, uranium, plutonium, americium and curium.

A similar task was undertaken in 1985 in the framework of NKS (NKA): “The Sampling and Analysing Methods of Radionuclides used in The Nordic Countries for Environmental Samples”, Edited by Tarja K. Taipale [1]. Since then new separation methods and instrumentation has been introduced and is in use in most laboratories.

To gather detailed information on the procedures in use, a questionnaire regarding various aspects of radionuclide determination was developed and distributed to all (sixteen) relevant laboratories in the Nordic countries. The response and the procedures used by each laboratory were then discussed between those who answered the questionnaire. *A report summarising the findings and providing recommendation on suitable practice has been submitted to NKS.*

The second part of the project (RadChem-2005) is more practically orientated. Each participant has worked with improvement of existing procedures or development of new procedures. One participant has also arranged an intercomparison exercise on the determination of natural radionuclides in ground water.

Intercomparison on the determination of natural radionuclides in ground water

An intercomparison exercise on the determination of natural radionuclides in ground water has been arranged. Six laboratories participated in the determination of ^{210}Pb , ^{210}Po , U-isotopes, ^{222}Rn , ^{226}Ra and ^{228}Ra and the results show a very good consistency between the labs. The results for ^{222}Rn , ^{234}U and ^{226}Ra were in good agreement with each other within the two-sigma uncertainties. One ^{238}U result was a little bit lower than the others. The results for ^{210}Pb and ^{210}Po were not as good as the above mentioned. One reason for this could be the too small in-growth time of ^{210}Po after the first separation, which was due to the tight timetable. Depending of the initial ratio, the time between sampling and analysis will have an impact on the uncertainty in the results. Both radionuclides will have to be analyzed unless the Po/Pb ratio is very high or we are sure that they are in radioactive equilibrium. The reported uncertainties varied greatly. In future it will be necessary to observe if the uncertainty estimations are consistent with each other in all laboratories. The accuracy of the presented results

varied too. This issue should also be discussed. The intercomparison was considered very necessary and important. The results show that the general analytical capability for determination of natural radioactivity in drinking water in the Nordic laboratories is good. However, this kind of intercomparisons should be continued, and the results thoroughly discussed. *A report describing the test, the analytical methods used and the results has been published in the proceedings from the NKS-B Summary Seminar in Tartu October 2005.*

Determination of Am and Cm in environmental samples

Americium and curium determinations in environmental samples are often troublesome due to their low activities and interference from other elements and radionuclides. One lab has worked on a more secure procedure for their separation using extraction chromatographic resins (Deponix-, TRU- and TEVA-Resin). The results so far show that the yields and spectra are satisfactory when analysing water, soil and sediment samples, but the procedure requires modification for biota samples. This work continues in 2006.

Age determination of Pu

Age of a plutonium source containing ^{241}Pu can be determined by the determination of ingrown ^{241}Am . When using mass spectrometric techniques for activity determination this requires a good chemical separation between ^{241}Pu and ^{241}Am . One lab has developed a method using extraction chromatographic resins TEVA- TRU- and Ln-Resin for this purpose. Analysis of reference solutions and environmental samples show good agreement with reported values. *The full details of the procedure are published in the proceedings from the NKS-B Summary Seminar in Tartu October 2005.*

Rapid determination of Pu using ICP-MS

One participant is studying different aspects of plutonium determination with the aim of developing a rapid procedure for plutonium determination with ICP-MS:

- € Leaching of plutonium from different matrices with different acids using traditional hot plate leaching and microwave assisted leaching
- € Preconcentration using rare earth fluorides or $\text{Fe}(\text{OH})_3$
- € Use of different ion exchange resins
- € Use of different extractants (TIOA, TBP, TTA)
- € Use of extraction chromatography
- € Use of ICP-MS vs. alpha spectrometry

This work is part of a PhD-thesis, and the results will be published in international articles.

Determination of U, Pu and Am in emergency situations

Two participants have worked with simplification of U, Pu and Am determination in emergency situations. Proposed methods:

Americium and plutonium

- € Ashing, acid leaching and addition of tracers
- € Hydroxide precipitation using NH_3
- € Oxalate precipitation followed by gamma spectrometry of ^{241}Am and ^{243}Am or

- € Fluoride precipitation followed by gamma spectrometry of ^{241}Am and ^{243}Am
- € Destruction of the oxalates or fluorides and separation of Pu(IV) using TTA followed by activity determination using combinations of LSC, alpha spectrometry or ICP-MS.

Uranium

Extraction with TBP from 8 M HNO_3 , rinse with 1.2 M HCl and elution with water followed by alpha spectrometry or ICP-MS determination. Increased levels of uranium can also be confirmed by direct determination of ^{235}U using gamma spectrometry.

The background, and the full details of the procedure can be found on page 7.

Sequential determination of Sr, U, Pu, Am and Cm in urine

A procedure for the sequential determination of ^{90}Sr , U-isotopes, $^{238,239,240}\text{Pu}$, ^{241}Am and Cm-isotopes in urine samples has been developed. The analytes are first pre-concentrated using calcium phosphate co-precipitation and after destruction of the phosphates, they are separated from interferences and each other using three extraction chromatography columns stacked on each other (Sr-, UTEVA- and TRU-Resin). The procedure has been tested in PROCORAD urine intercomparison exercise with good results, and is used at one of the labs as a routine procedure. *The full details of the procedure can be found on page 15.*

Determination of americium, plutonium and uranium in emergency situations

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Americium

Americium is a trivalent actinide and a chemical analog to curium, and it has many chemical similarities to trivalent lanthanides. ²⁴¹Am (T_{1/2} = 432 years) is mainly produced by decay from ²⁴¹Pu (T_{1/2} = 14.35 years). The amount of ²⁴¹Pu produced increases with burn up time in a reactor and the activity ratio of ²⁴¹Pu/^{239,240}Pu can be 100 or higher. The ratio in the Chernobyl fallout was approximately 86. Fresh nuclear weapons fallout samples had a ratio of about 16 while weapons plutonium has a ratio of about 5. On a longer time scale this implies that americium concentrations in burned out fuel will exceed plutonium concentrations by a factor of 3, while the same ratios in nuclear weapons fallout and weapons plutonium will be 0.5 and 0.17, respectively. Small amounts of ²⁴³Am are also produced in a reactor. ²⁴³Am/²³⁹⁺²⁴⁰Pu activity ratio was about 0.01 in Chernobyl fallout. ²⁴³Am is foremost used as a radiochemical tracer for ²⁴¹Am and as a generator for the daughter ²³⁹Np, which is used as a radiochemical tracer for ²³⁷Np. Table 1 shows the decay properties of ²⁴¹Am and ²⁴³Am

Table 1. The main alpha and gamma energies of ²⁴¹Am and ²⁴³Am

Radionuclide	ζ-energies (MeV)	ζ-abundance	ν-energies (keV)	ν-abundance
²⁴¹ Am	5.442	0.13	59.5	0.359
	5.485	0.845	26.3	0.024
			17.7 (L _η)	0.057
			13.9 (L _ζ)	0.096
²⁴³ Am	5.275	0.87	74.6	0.68
	5.233	0.11	43.5	0.051
			17.7 (L _η)	0.043
			13.9 (L _ζ)	0.073

Even if both ²⁴¹Am and ²⁴³Am are considered as alpha emitters, Table 1 shows that it is possible to detect them through gamma spectrometry. This is not very often used as the concentrations of these normally are very low and alpha spectrometry provides much lower detection limit. The low gamma energies are also to a varying degree self absorbed in the sample. When the americium concentrations in the sample are high, the sample most often also contains many other gamma emitters that interfere in americium determination.

The radiochemical separation of americium for alpha spectrometry is time and cost demanding. A simple chemical separation that would separate most of the sample matrix and interfering radionuclides from americium could facilitate rapid americium determination through gamma spectrometry. ²⁴³Am can be used as tracer for ²⁴¹Am due

to its negligible concentration in most samples. If the sample contains ^{243}Am , two sub samples must be analyzed, one with the tracer and one without. The main gamma energies are 59.5 keV (^{241}Am) and 74.6 keV (^{243}Am). Sequential precipitations have been performed to test this procedure.

A ten-gram soil sample from the Chernobyl area was ashed, added ^{243}Am and treated with aqua regia. One-gram sample can be used if microwave oven assisted leaching is to be used. The resulting solution was then subjected to sequential precipitation.

- ∅ Hydroxide precipitation by adding ammonia to pH 10 and centrifugation to collect the precipitate. Iron and some heavy metals precipitate, while elements forming soluble complexes ammonia complexes stay in solution. All actinides (and lanthanides) co-precipitate. Cs, Sr, Ca and Ba do not precipitate, but our measurements showed that small amount of Cs did follow the precipitate.
- ∅ The precipitate was dissolved with HCl and a oxalate precipitation performed. A small amount of Ca and 10 gram oxalic acid was added and the pH raised to 2-3 with ammonia. Most of the iron forms soluble oxalate complexes and stays in solution. Tri- and tetravalent actinides co-precipitate, while hexavalent uranium stays in the solution. The oxalate was collected by centrifugation, ashed and ^{241}Am and ^{243}Am measured with Ge-detector.
- ∅ The sample was then dissolved in a small amount of HCl (final molarity < 4M) and the fluorides precipitated by the addition of a small amount (10-50 mg) of a lanthanide (La, Nd) and HF. This precipitate is difficult to dissolve and the sample is in this manner concentrated to a minimum. Tri- and tetravalent plutonium co-precipitates, while hexavalent Pu stays in the solution.

A large number of samples can be treated in a day. Gamma analysis tests with NaI detector will be performed to achieve further robustness and cost effectiveness. The NaI detector only needs to be a thin crystal, which will minimize interference from high-energy gammas and the need for thick lead shielding against background radiation. Tests will be performed to measure ^{241}Am in contaminated samples from Ranstad.

Plutonium

Most plutonium containing samples contain the Pu-isotopes ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu and even small amounts of ^{242}Pu . Normally the amounts of ^{242}Pu are very small and ^{242}Pu can be used as a radiochemical tracer for the other Pu-isotopes. The isotope composition is determined by the source term. The amount of ^{238}Pu and ^{240}Pu in comparison with ^{239}Pu increases from nuclear weapons plutonium to fresh fallout and burned out nuclear fuel. Table 2 shows the decay properties of some of the Pu-isotopes. As seen, ^{238}Pu , ^{239}Pu and ^{240}Pu cannot be distinguished from each other using gamma spectrometry. The gamma energies are low and are due to conversion of photons created when alpha decay does not lead to direct ground state. It is though possible to measure total plutonium by measuring the sum of the photons with energies 13.6 keV and 17.2 keV. The table also shows that ^{239}Pu and ^{240}Pu cannot be distinguished using alpha spectroscopy.

^{241}Pu is a so-called pure beta emitter (only 0.0025% ζ) with low energy. The best way of rapid determination of ^{241}Pu is with the use of liquid scintillation. Open GM gas flow detectors can also be used if the ^{241}Pu activity dominates the other Pu-isotopes, which

often is the case. If time is not a restraint ^{241}Pu can also be determined by measuring ^{241}Am after appropriate ingrowth of the latter (some months ingrowth period). If the sample planchet is recounted for ^{241}Am determination, it should be kept in mind that ^{238}Pu and ^{241}Pu have similar alpha energies. ^{241}Am can also be counted after separation from Pu-isotopes. We have performed a large number of ^{241}Pu determinations using this procedure. A radiochemical separation is needed for the determination of ^{239}Pu and ^{240}Pu . TTA extraction of plutonium, after precipitation procedures described for americium gives a fast and effective decontamination from uranium. ICP-MS is the detection method of choice for fast determination of ^{239}Pu and ^{240}Pu . A fraction of the plutonium solution can then be used for ^{241}Pu with liquid scintillation counting.

Tabell 2. The main alpha, beta and gamma energies of some Pu-isotopes

Radionuclide	ζ -energies (MeV)	ζ -abundance	ν -energies (keV)	ν -abundance
^{238}Pu	5.456	0.29	13.6 (L_ζ)	0.038
	5.499	0.71	17.2 (L_η)	0.039
^{239}Pu	5.11	0.12	13.6 (L_ζ)	0.016
	5.14	0.15	17.2 (L_η)	0.016
	5.16	0.73		
^{240}Pu	5.12	0.27	13.6 (L_ζ)	0.036
	5.17	0.73	17.2 (L_η)	0.037
	η -energy (keV max/average)	η -abundance		
^{241}Pu	20.8/5.2	1		

We recommend the following procedure for plutonium determination:

- ∄ ^{241}Am content in the oxalate or fluoride precipitate is first determined using gamma spectrometry, and then the precipitate is used for plutonium determination.
- ∄ The precipitate is dissolved in 1 M HNO_3 . The fluoride precipitate must first be dissolved in conc. HNO_3 and boric acid, and a hydroxide precipitation performed to remove fluorides (ammonia forms soluble complexes with fluorine).
- ∄ Pu is then held in the tetravalent state using NaNO_2 and extracted with 5% TTA-xylene. The organic phase is then washed with 1 M HNO_3 (preferably twice) and Pu eluted with 8M HNO_3 . Uranium and americium do not follow plutonium.

The solution can be used for alpha spectrometry (after electrodeposition or fluoride co-precipitation), liquid scintillation counting for measurement of $^{238+239+240}\text{Pu}$ and ^{241}Pu and mass spectrometry for measurement of ^{239}Pu and ^{240}Pu .

Uranium

The three uranium isotopes ^{238}U , ^{235}U and ^{234}U are found naturally in the environment. ^{238}U constitutes 99.27 mass percent of all uranium. The amount of natural uranium in nature varies from less than a nanogram per gram in biological material to some percent in uranium containing minerals. In most soils the uranium concentration is some ppm (microgram uranium per gram soil). The activity ratio $^{234}\text{U}/^{238}\text{U}$ in natural uranium varies due to alpha recoil and biogeochemical processes, while the ratio $^{235}\text{U}/^{238}\text{U}$ can be seen as constant (variations can be found, for example in fossil reactors).

Uranium can be extracted with e.g. TBP (tributylphosphate) from 8 M HNO_3 . The thorium fraction is then be washed with 1.2 M HCl before U is eluted with water. This is the preferred method for alpha spectrometry.

Table 3. The main alpha and gamma energies of some U-isotopes

Radionuclide	ζ -energies (MeV)	ζ -abundance	ν -energies (keV)	ν -abundance
^{234}U	4.722	0.28	13 (L_ζ)	0.034
	4.774	0.71	16.2 (L_η)	0.041
^{235}U	4.366	0.17	13.0 (L_ζ)	0.15
	4.397	0.55	16.0 (L_η)	0.14
	4.414	0.021	89.9 (K_ζ)	0.06
	4.502	0.017	93.3 (K_ζ)	0.11
	4.556	0.042	143.7	0.11
	4.596	0.05	163	0.051
			185.7	0.572
^{238}U	4.151	0.21	13 (L_ζ)	0.025
	4.198	0.79	16.2 (L_η)	0.03

ICP-MS

An alternative way of quick determination of actinides in large number of samples is by using ICP-MS. As most Nordic countries have several ICP-MS instruments available, they can be a valuable help provided the right organization in a emergency situation. The main advantage of using ICP-MS is the speed of the analysis, which is accomplished in a few minutes. The throughput is therefore very high (approx. 100 samples a day) especially as the instrument can be semi automated (sample change, calibration, instrument adjustment). Time-consuming sample preparations and chemical separations need prior to ICP-MS determination restricts the number of samples analysed per day. The lower the detections limit, the higher is the demand for an efficient radiochemical procedure.

A series of tests have been performed to evaluate the use of ICP-MS in emergency situations. The preliminary results are presented below.

Uranium and uranium isotopes

Unnatural sources of uranium can be found by either mapping total uranium concentrations or by studying the uranium isotope composition in the material. Since natural concentrations of uranium are relatively high, small unnatural increases are difficult to detect. The high concentration of uranium simplifies the analysis, as uranium determination normally can be performed without any chemical separations. Polyatomic interferences can disturb the determination of the low abundant ^{234}U and if present, ^{236}U .

The big advantage of using ICP-MS for uranium determination is that the technique allows the quantitative determination of ^{238}U levels down to sub picogram (nBq) and $^{235}\text{U}/^{238}\text{U}$ ratios with less than 1% RSD for nanogram (μBq) levels of natural uranium. The amount of sample treatment required is determined by the sample material. The solution introduced into the ICP should not have salt concentrations higher than about 1% to avoid clogging of the space between plasma and vacuum. This limits the amount of material to about 0.1-gram soil digest in 10 ml weak acidic solution.

A marked limitation of the ICP-MS instrument is its relatively bad mass separation and the coupled mass tailing. This relatively bad so-called abundance sensitivity puts limitations on how small amounts of an isotope with mass M that can be detected in presence of an isotope with mass M+1. Typical abundance sensitivity values for normal ICP-MS instruments is $5\text{-}10 \times 10^{-6}$ (5-50 ppm, meaning that for a million pulses in mass M, 5-50 occur in mass M+1). For uranium this is normally a problem when one wishes to detect small amounts of ^{236}U . The neighbouring ^{235}U isotopes contribution to ^{236}U must be corrected for. Even the contribution from ^{238}U (some ppm), two mass units higher than ^{235}U , must be corrected for. This has not been studied in this work as the contribution from ^{235}U and ^{238}U cannot be separated, and because the contribution from ^{238}U is smaller than the contribution from ^{235}U . An additional and similar contribution to ^{236}U comes from $^{235}\text{U}^1\text{H}^+$. Implying that the total “disturbance factor” for ^{236}U is about 10^{-5} or a bit smaller.

We have used a high resolution ICP-MS (HR-ICP-MS) for our uranium analysis. This instrument allows for a mass resolution of up to $M/\pm M = 10000$ (normal value about 300) which minimises the abundance sensitivity problem, but on the cost of transmission. The advantage of being able vary resolution is that it gives the opportunity to separate out other interfering polyatomic interferences (e.g. $^{204}\text{Pb}^{32}\text{S}$ and other combinations of elements normally present in most materials).

Plutonium and plutonium isotopes

The large differences in the analytical techniques for uranium and plutonium determination using ICP-MS are due to the large difference in the concentration of these in environmental samples. While the amount of uranium in soil samples is in the ppm level, the amount of plutonium is about ppt or lower. Problems with abundance sensitivity and $^{238}\text{U}^1\text{H}^+$ interference precludes direct determination of ^{239}Pu , and radiochemical separations are necessary prior to ICP-MS determination. The separation should primarily separate plutonium from the large amounts of uranium, but also from Pb, Hg, Bi and Tl as the isotopes of these elements form polyatomic interferences with

isotopes of Ar, Cl and S. Figure 1 shows a spectre recorded under “normal” instrument conditions for a plutonium determination. The sample just contains lead in concentrations typical for a 1-gram soil sample (2 ppm) and 5% HCl, and no plutonium. As seen, lead contamination causes serious interferences in plutonium determination.

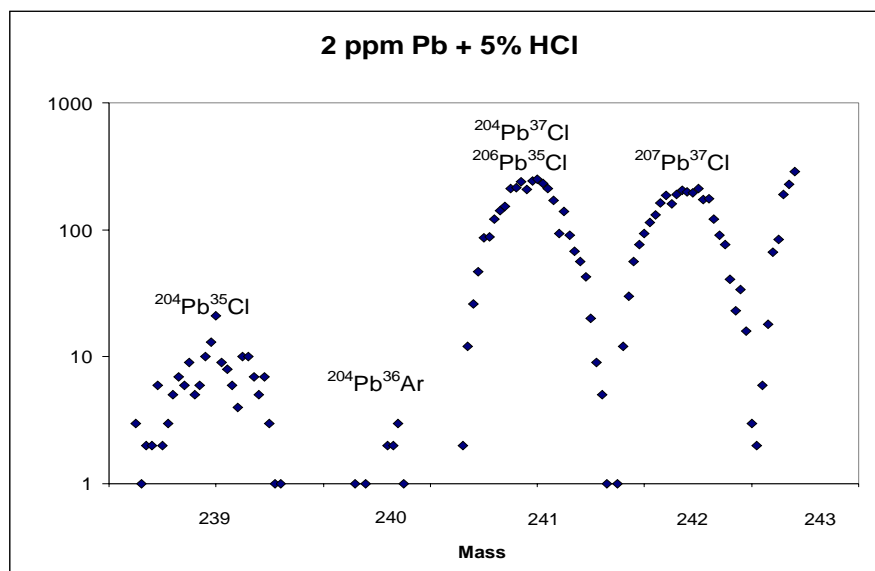


Figure 1. Mass spectrum of the area 239-243 m/z of a 2 ppb Pb + 5% HCl solution. Spectrum is recorded under same conditions as under normal Pu determination

The use of the same radiochemical procedure as used for alpha spectrometry has shown to be inefficient in removing uranium adequately. Using alpha spectrometry this contamination is not seen as ^{238}U has a very long half-life. The few tens of nanogram of remaining ^{238}U in the plutonium fraction increase the ^{239}Pu detection limit by ICP-MS to about 1 mBq, while the detection limit in a uranium free sample is about 1-10 μBq . The detection limit in a sample not subjected to any chemical separations is about 100 mBq, which does make ICP-MS to a excellent instrument for rapid plutonium determinations when plutonium levels are high.

We have also tested the possibility to instrumentally minimize the contribution from uranium to plutonium. This can be done through better resolution, elimination of water (to remove hydrogen to minimize the occurrence of UH^+ ions) and by optimising the sample injection depth in the plasma so that the ratio Pu/U becomes as high as possible without loss of too much plutonium intensity. Figure 2. shows an experiment where sample injection depth is varied by varying the gas flow (increased gas flow “presses” the plasma and thereby the sample injection depth forward.

Only a factor 4-5 discrimination of uranium relative to plutonium can be achieved when resolution is increased and by using a better nebuliser that gets rid of some of the water formed in the aerosols in the sample introduction unit. If an optimised sample injection depth in the plasma is used the uranium discrimination can be increased to about 10, giving a plutonium detection limit of about 10 mBq in a sample not subjected to any chemical separations.

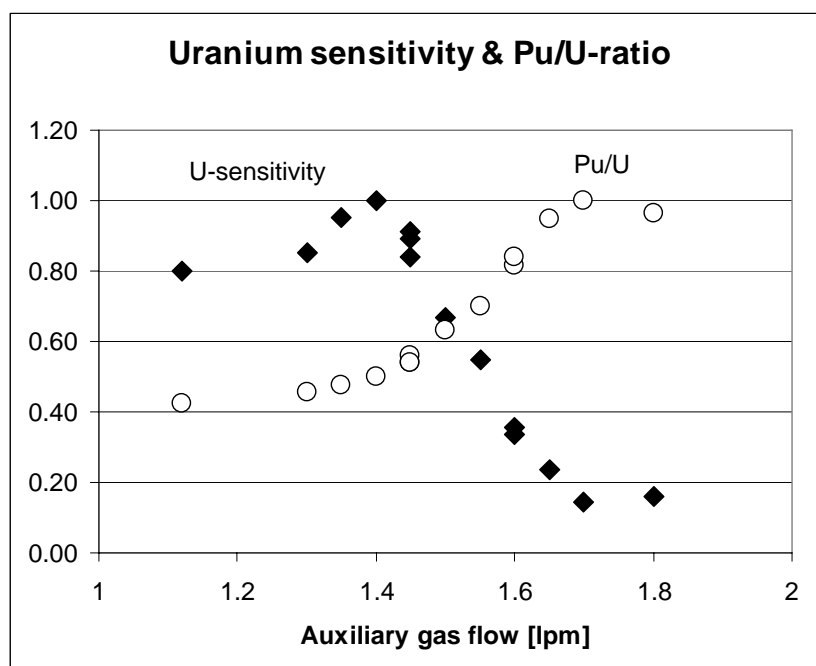


Figure 2. Signal strength for uranium and Pu/U ratio for varying sample introduction depths in the plasma (here by using different flow).

Americium

Only a few analysis of ^{241}Am has so far been done using ICP-MS. Interference from ^{241}Pu and the poly atomic interferences shown in Figure 1 must be avoided.

Combined actinide analysis

This is probably the most interesting analysis to perform in an emergency situation, as the composition of the contaminated material is unknown. In principle there are two ways to perform this analysis – either on a group-separated fraction containing the actinides, or on an unseparated sample. Group separation using an alcoholic medium on ion exchange resins is the most attractive as the method also eliminate elements as Pb, Tl, Hg and Bi that form polyatomic interferences. More tests of this method should be performed using complex matrix with varying elemental composition.

LA-ICP-MS

An often countered issue when analysis material where destructive sample treatment is required is whether refractory particles are dissolved or not. Using laser ablation ICP-MS this problem is avoided, and information about particle distribution is also gained.

Conclusion

Robust methods for the determination of U, Pu and Am have been developed. This is especially true for ^{241}Am that can be determined gamma spectrometrically after a simple separation. For rapid determination of plutonium isotopes in low concentrations mass spectrometric methods must be utilized. Total plutonium can be determined through low energy gamma spectrometry. The low energy gamma spectrometric determination does not provide isotope composition, which is essential in determining the source term. ^{235}U can easily be determined using gamma spectrometry. The information provided by this mean only shows increased levels of uranium, not the source term. Generally the mentioned actinides can relatively fast be determined sequentially with ICP-MS. The ICP-M is although a relatively advanced instrument that demands competent personnel, personnel able to handle the instrument that does not always work. The most time consuming step in the analytical procedure is the sample treatment, especially if large sample volumes must be handled to give representative sample gathering, ultimately being the most critical step in each radioanalytical determination.

Sequential extraction chromatographic separation of U, Pu, Am, Cm and Sr in urine samples

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Abstract

A method for the sequential determination of U, Pu, Am, Cm and Sr in urine samples is described. After pre-treatment of the samples, the analytes are collected using calcium phosphate co-precipitation and separated from interfering elements using actinide and strontium specific extraction chromatographic columns coupled together.

Introduction

Bioassay samples of radiation workers are routinely analyzed for appropriate radionuclides to monitor potential occupational intake and internal contamination. Generally this involves the analysis of urine samples. Normally a 24-hour urine sample is analyzed to calculate the body burden of different radionuclides.

When only actinides are to be analyzed in the urine sample, $\text{Fe}(\text{OH})_3$ co-precipitation can be used to pre-concentrate the actinides and to perform an initial separation from many other salts. $\text{Fe}(\text{OH})_3$ precipitation although does not carry strontium. Oxalate precipitations or phosphate precipitations are normally used when both actinides and strontium are to be pre-concentrated. For urine samples, calcium phosphate co-precipitation is the method of choice. Actinides are then purified using ion exchange chromatography, liquid extraction or extraction chromatography, while strontium is purified using fuming nitric acid precipitations or extraction chromatography. In many cases two different urine samples are used for strontium and actinide determination.

We wanted to develop an efficient procedure for the sequential determination of both actinides and strontium in the same urine sample. The commercially available Eichrom extraction chromatographic resins, TRU-, UTEVA- and Sr-Resin were chosen as potential candidates for the separation and purification procedure, as they all are able to concentrate the mentioned radionuclides from the same nitric acid solution.

Detailed procedure for the determination of U, Pu, Am, Cm and Sr in urine samples

1. Measure the volume of the 24-hour urine sample and transfer it to appropriate beaker.
2. Wash the sample container with 100 ml conc. HNO_3 per litre urine and transfer the solution to the beaker.
3. Add ^{232}U -, ^{242}Pu -, ^{243}Am - and ^{85}Sr -tracers, 2 mg Sr-carrier, 100 mg Ca-carrier and 3-4 drops of 1-octanol to avoid foaming during heating of the urine sample.

4. Heat the sample at about 90 °C for 2 hours. Use magnetic stirrer. Add additional 1-octanol if needed.
5. Turn off the heat and add 1-2 ml conc. phosphoric acid. Allow the urine to cool down a bit and add conc. NH₃ to pH 8 to precipitate calcium phosphate. Stir the sample for about half an hour.
6. Turn off the magnetic stirrer, take out the magnet and let the phosphates settle.
7. Decant off the supernatant to another beaker and transfer the precipitate to centrifugation tube.
8. Collect the precipitate by centrifugation at 2500 RPM for ten minutes, and transfer the supernatant to the beaker with rest of the supernatant.
9. Add the supernatant conc. HNO₃ to pH 2.
10. Add 1 mg Sr-carrier, 50 mg Ca-carrier, 1-2 ml conc. phosphoric acid and raise the pH to 8 using NH₃.
11. Allow the calcium phosphate precipitate to settle, decant off the supernatant and transfer the precipitate to the centrifugation tube with the previous precipitate.
12. Collect the precipitate by centrifugation and decant off the supernatant.
13. Transfer the precipitate to 100 ml beaker with conc. HNO₃.
14. Heat the solution to dryness and ash the precipitate at 450 °C.
15. Carefully add 10 ml conc. HNO₃ to the precipitate and heat the solution to near dryness.
16. Swell 0.75 gram UTEVA-Resin in 10 ml 3 M HNO₃ and make a column with an inner diameter of about 1 cm.
17. Swell 0.75 gram TRU-Resin in 10 ml 3 M HNO₃ and make a column with an inner diameter of about 1 cm.
18. Swell 0.75 gram Sr-Resin in 10 ml 3 M HNO₃ and make a column with an inner diameter of about 1 cm.
19. Attach UTEVA-column on top of TRU-column and TRU-column on top of Sr-column. Attach these to a vacuum box.
20. Dissolve the salts in 20 ml 3 M HNO₃ – 0,1 M sulphamic acid – 0,1 M ascorbic acid – 0,3 M Al(NO₃)₃. If the solution is unclear, filter it through 0.45µm membrane filter.
21. Pre-treat the columns with 20 ml 3 M HNO₃ and add the solution to the columns (Flow = 1-2 ml/min).

22. Rinse the columns with 10 ml 3 M HNO₃ and detach them from each other.
23. **UTEVA-column:** Wash the column with 5 ml 9 M HCl followed by 20 ml 5 M HCl – 0.05 M oxalic acid and elute uranium with 15 ml 0.01 M HCl directly into a 20 ml plastic scintillation vial. Add the uranium fraction 50 µg Ce(III), 1 ml 15% TiCl₃ and 2 ml 40% HF and allow the fluorides to develop for at least half an hour.
24. **TRU-column:** Wash the column with 10 ml 3 M HNO₃ – 0,1 M NaNO₂ followed by 2 ml 9 M HCl. Elute Am with 10 ml 4 M HCl directly into a 20 ml plastic scintillation vial. Wash the column with 10 ml 4 M HCl and elute Pu with 10 ml 4 M HCl added 200 µl 15% TiCl₃ directly into a 20 ml plastic scintillation vial. Add 50 µg Ce(III) and 2 ml 40% HF to the Am and Pu fractions and allow the fluorides to develop for at least half an hour.
25. Attach a 25 ml 0.1 µm polypropylene filter to the filtration equipment and condition it with 5 ml 80% ethanol followed by 5 ml H₂O.
26. Filter the U-, Am- and Pu-fractions through clean filters, wash the vials and the filters with 5 ml H₂O followed by 5 ml 96% ethanol. Flow: 1 drop per second.
27. Allow the filters to air dry for a few seconds and attach them to 25 mm metallic planchets using paper glue.
28. Perform alpha determination using alpha spectrometry.
29. **Sr-Resin:** Wash the column with 10 ml 8 M HNO₃ followed by 10 ml 3 M HNO₃ – 0.05 M oxalic acid. Note the time for ⁹⁰Y ingrowth. Elute Sr with 10 ml 0.05 M HNO₃ directly into a 20 ml plastic scintillation vial. Measure the ⁸⁵Sr yield using NaI detector and add 10 mg Y-carrier to the solution. Let the solution stand for about 14 days for ingrowth of ⁹⁰Y.
30. Transfer the solution to appropriate centrifugation tube, heat the solution on hot water bath and add conc. NH₃ to pH 8 to precipitate Y(OH)₃.
31. Centrifuge to collect the precipitate and transfer the supernatant to a clean bottle.
32. Dissolve the precipitate with 3-4 drops of conc. HCl, add 20 ml H₂O, heat the solution on water bath and precipitate the hydroxides once again using NH₃ to raise the pH to 8.
33. Centrifuge to collect the precipitate and transfer the supernatant to the bottle.
34. Dissolve the precipitate with 3-4 drops of conc. HCl, add 20 ml H₂O, 50 mg Sr-carrier and precipitate the hydroxides using NH₃ to raise the pH to 8.
35. Repeat point 33 and 34.

36. Dissolve the precipitate with 3-4 drops of conc. HCl, add 20 ml H₂O and 2 ml 2 M H₂SO₄. Stir and add 3-5 drops of 100 mg Sr/ml solution to precipitate SrSO₄.
37. Centrifuge to collect the precipitate and filter the solution through 0.45µm membrane filter. Discard the precipitate and the filter.
38. Heat the solution on hot water bath and add 1 ml hot saturated oxalic acid solution.
39. Adjust the pH to 2-3 with NH₃ and heat the solution for a while.
40. Cool the solution to room temperature and filter through 20 mm ashless paper filter to collect the oxalates.
41. Air-dry the filter and assemble it into appropriate filter holder for beta counting using gas flow proportional counter (we use RISØ GM-25-5).
42. Note the time and count the sample for ⁹⁰Y.
43. Transfer the counting data to spread sheet and compare the sample counting decay with theoretical ⁹⁰Y decay to ensure that the sample is free from contamination.
44. Let the ⁹⁰Y decay for 3-4 weeks and recount the planchet to determine the background.
45. Transfer the filter to porcelain crucible and ash the filter for 90 mins at 900 °C.
46. Dissolve the ash with 3 ml conc. HNO₃ and evaporate to dryness.
47. Dissolve the salts with 20 ml acetate buffer at pH 4.4, add 1 drop of xylene orange and titrate Y with 0.01 M EDTA to the yellow endpoint to.
48. Calculate the Y recovery by titrating at least three parallels of 10 mg Y.

Use this formula to calculate the amount of ^{90}Sr :

$$A = \frac{R_M}{Y_{eff} Sr_{eff} T_{eff}} \left(\frac{\zeta}{1 - e^{-\zeta t}} \right) \left(\frac{1}{1 - e^{-\zeta T}} \right)$$

A	= Activity of ^{90}Sr in the sample (Bq)
ζ	= ^{90}Y decay constant (s^{-1})
R_M	= Measured average (netto) count rate ^{90}Y (cps)
Δt	= Sample counting time (s)
t	= Time between ^{90}Y milking and counting start (s)
T	= ^{90}Y ingrowth time (s)
Y_{eff}	= Y-recovery
Sr_{eff}	= Sr-recovery
T_{eff}	= ^{90}Y counting efficiency

Results and conclusion

The procedure is in routine use at Institute for Energy Technology. The procedure was also used in the PROCORAD 2005 urine intercomparison exercise with success. Since only 500 ml urine was analysed in this exercise, calcium phosphate co-precipitation was only performed once. The chemical yields of all the analytes were typically 70-80%. When analysis 24-hour urine samples with a typical volume between 1.5 – 2.0 litres, the Sr-yield fell to about 50%, while the yield of the other analytes stayed between 70-80%. To achieve a higher Sr-yield calcium phosphate co-precipitation must be performed twice.

The Sr separation procedure described here is very time consuming. With the use of liquid scintillation counter, the Sr-determination can be performed much faster. Work is under progress to evaluate the use of Quantulus liquid scintillation counter for this purpose.

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Abstract	<p>The report describes the work performed under the NKS-B project Radchem during 2005. RadChem-2005 has been focused towards laboratory work, and each participant has worked with improvement of existing procedures or development of new procedures. In addition an intercomparison exercise on the determination of natural radionuclides in ground water has been performed. Other work performed in Radchem-2005 include:</p> <ul style="list-style-type: none">€ Development of new procedures for the determination of Am and Cm in environmental samples€ Development of a procedure for age determination of Pu€ Rapid determination of Pu using ICP-MS€ Determination of U, Pu and Am in emergency situations€ Sequential determination of Sr, U, Pu, Am and Cm in urine€ Ultra low level measurements using ICP-MS
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