DETERMINATION OF DIFFICULT-TO-MEASURE ISOTOPES IN LOW- AND INTERMEDIATE-LEVEL LIQUID RADIOACTIVE WASTES

Arpad BIHARI, Laszlo PALCSU, Mihaly MOLNAR, Mihaly VERES, Nora VAJDA, Zsuzsa MOLNAR

1 Institute for Nuclear Research, Bem ter 18/c, Debrecen, 4026 Hungary
2 Isotoptech Co. Ltd. Piac utca 53 II/9, Debrecen, 4025 Hungary
3 RadAnal Ltd. Konkoly-Thege M. ut 29-33, Budapest, 1121 Hungary
*Corresponding author: palcsu.laszlo@atomki.mta.hu

ABSTRACT

The low- and intermediate-level (L/ILW) liquid wastes produced by the Paks Nuclear Power Plant (NPP) contain routinely measureable gamma-emitting (e.g. $^{54}$Mn, $^{60}$Co, $^{110m}$Ag, $^{137}$Cs) as well as many so-called “difficult-to-measure” (DTM) isotopes. These latter have the following properties: i) their specific activity is usually low; ii) they are either pure alpha/beta emitters or possess gamma-rays of very low intensity/energy; iii) compared to the short- and middle-lived (half-life is in the range of less than one year to some 10 years), they are usually rather long-lived (half-life ranges from 5730 y [$^{14}$C] to 15.7 million years [$^{129}$I]). Conclusively, they can only be measured following careful (and usually difficult/complex) radiochemical separation. At the radiochemistry laboratory of the Institute for Nuclear Research, Hungarian Academy of Sciences the $^3$H, $^{14}$C, $^{36}$Cl, $^{99}$Tc, $^{108m}$Ag and $^{129}$I content of the evaporator concentrate samples are routinely determined (using beta- and gamma-spectrometry). Method development is also in progress for the separation and measurement of $^{79}$Se and $^{107}$Pd (using ICP-MS technique). Separation techniques, incl. vacuum-distillation, acidic digestion, organic extraction, ion exchange, etc. are presented, with emphasis on the possible difficulties. Additionally to the above mentioned isotopes, contents of $^{90}$Sr, $^{239,240}$Pu, $^{238}$Pu, $^{241}$Am, $^{242}$Cm, $^{238}$U, $^{235}$U, $^{234}$U, $^{59}$Ni, $^{63}$Ni, $^{55}$Fe, $^{93m}$Nb and $^{94}$Nb isotopes are routinely measured from evaporator concentrates at the radiochemistry laboratory of RadAnal Ltd. New analytical methods for determination of $^{125}$Sb, $^{93}$Zr, $^{237}$Np isotopes are under development. For measurement of these isotopes, alpha-, beta-, XR- and gamma-spectrometry is used, while in case of $^{93}$Zr and $^{237}$Np ICP-MS technique is applied.

Introduction

Determination of the physical, chemical and radiological properties of wastes intended for disposal in any radwaste repository represents one of the major goals for every country dealing with nuclear facilities. In most disposal facilities the long lived $\alpha$- and $\beta$-emitting radionuclides have the most restrictive inventory limits, because they do not decay appreciably in the lifetime of the facility. These isotopes are called difficult-to-measure (DTM) isotopes, because their activity concentrations (AC) are usually several order of magnitude lower than the „bulk” (mostly $^{60}$Co + $^{137}$Cs), due to

- Low formation probability (fission or activation);
- Low „escape” probability (from an intact fuel rod);
- Low specific activity (as a result of long half-life).
Furthermore, they are either pure alpha/beta emitters or have only very low energy and intensity X-ray or $\gamma$-ray lines. As a result, the determination of their AC requires a radiochemical separation of various complexity.

The basic concepts of radiochemical separations are the following:

*Addition of carrier compound if it’s not readily present in the sample:* preferably the non-radioactive form of the element in question are used as carrier, but for elements with no stable isotopes one must use a substitute carrier, like rhenium for technetium.

*Addition of radiotracer for chemical yield measurement:* especially in case of alpha-emitting isotopes different alpha-emitting isotope of the same element are used, like $^{232}$U, $^{236}$Pu, $^{243}$Am for the measurement of the chemical yield of the separation. In most cases, the non-radioactive carrier compound can also be used for (gravimetric) yield measurements.

*Acidic destruction of the matrix:* depending on the sample matrix and the chemical behavior of the element in question, HCl, HNO$_3$, H$_2$SO$_4$, HF, *aqua regia* are used in various concentrations and mixtures to destroy the complexing agents (like EDTA, oxalates, citrates) and make the element in question available for further operations.

*Precipitation formation:* the formation of various non-soluble oxides, sulfides, oxalates, etc. of the element in question is usually a versatile tool of the removal of the “bulk” by the filtration of the precipitation.

*Ion exchange and extraction chromatography:* for the mass-removal of several impurities (cationic or anionic compounds) and/or the selective concentration of one or more elements (especially for uranium and trans-uranium isotopes).

In the followings, a short description will be provided on the radiochemical separation of several isotopes determined from evaporator concentrate (high-salinity, highly alkaline solution with density around 1.2 g/cm$^3$) samples of Paks NPP, Hungary. While these methods have been developed for liquid waste samples, they can be applied with minor modifications for spent ion-exchange resins, sludge, etc. as well.
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Tritium (^3H, half-life: 12.32 y) separation

Using a low-pressure, cold distillation, one can extract the water (and together with it the tritium) content of 1-2 ml evaporator concentrate sample without any other radio-impurities.

For this purpose, a two-fingered, vacuum-evacuable glass vial is used, with the sample injected in one of the fingers. Freezing the sample using liquid nitrogen, the vial is evacuated to 10^-3 mbar and the water is distilled into the other finger using liquid nitrogen as coolant.

The resulting water is checked for impurities with a HPGe gamma-detector and re-distilled if necessary before LSC counting (using Ultima Gold LLT as scintillation cocktail).

Radiocarbon (^14C, half-life: 5730 y) separation

Since the evaporator concentrate samples contain organic and inorganic carbon compounds in macroscopic concentrations, one can use an acidic destruction for the release of the carbon (incl. ^14C) content as CO₂ and trap it in an appropriate substance free of any other radio-impurities.

Using 100 ml cc. H₂SO₄ and mild heating (100-150 °C), 100 ml evaporator concentrate sample is digested in constant nitrogen stream in a semi-closed system. CO₂ is trapped in ca. 450 ml 0.3M Ba(OH)₂ solution, forming BaCO₃ precipitation. After the sample is digested (no more BaCO₃ forms), the resulting BaCO₃ precipitation is digested in a similar system using cc. HCl. In this case the trapping solution is 3M NaOH (ca. 450 ml similarly). The end of the process is indicated by the complete disappearance of the BaCO₃ precipitation.

Radiocarbon activity of the NaOH-based Na₂¹⁴CO₃ is determined with LSC counting, using Hionic-Fluor as scintillation cocktail.

Separation of radiohalogenides ^36Cl (half-life: 301 ky) and ^129I (half-life: 15.7 My) [1]

Radiohalogenides can be volatilised using cc. H₂SO₄ and trapped in appropriate substances such as carbon-tetrachloride (CCl₄) and water free of any other radio-impurities.

1000 ml evaporator concentrate sample is spiked with KI and NaCl carriers and evaporated to near dryness. In constant nitrogen stream in a semi-closed system, the residual is digested using 600-800 ml using cc. H₂SO₄ (added in small amounts to avoid uncontrollable reactions), coupled with a slow raise in temperature up to 200 °C. Vapours are trapped in 100 ml CCl₄, cooled with ice and covered with 50 ml deionised water. Elemental iodine (I₂) is trapped in CCl₄ (indicated by a bright pink colour), while other (more oxidised) iodine forms are trapped in the water, along with HCl vapours.

After the digestion is complete, the organic and inorganic phase of the trap is separated. The inorganic phase is mixed with a fresh batch of carbon-tetrachloride, and the more oxidised (IO₃⁻ and IO₄^{2-}) iodine forms are reduced to elemental form using NaHSO₃. Adding the new organic phase to the
original one, iodine is back extracted to water after reducing to iodide. Silver nitrate solution is added to form AgI precipitation, which is filtered onto a glass-microfiber plate. Chemical yield is determined gravimetrically and the $^{129}$I activity of the precipitate is measured by a thin-windowed HPGe detector (X-ray lines).

The pH of the remaining inorganic phase is set to 10-12 using 1M NaOH solution and is evaporated till solubility limit. Chemical yield is determined using ICP-MS (for $^{35}$Cl) and the $^{36}$Cl activity of the solution is determined with LSC counting, using InstaGel as scintillation cocktail.

**Separation of iron ($^{55}$Fe, half-life: 2.73 y) and nickel ($^{59}$Ni, half-life: 75 ky; $^{63}$Ni, half-life: 100 y) isotopes**

For the separation of iron and nickel radioisotopes, extraction chromatography using supported methyl-isobutyl-ketone (MiBK) and supported di-methylglyoxime (DMG) is utilised to gain samples for X-ray and LSC counting.

100 ml evaporator concentrate sample is spiked with Fe and Ni carriers and evaporated using cc. HNO$_3$ and cc. HCl sequentially. The residue is dissolved in 6M HCl and passed through a MiBK column. The effluent after evaporation is neutralised using NH$_4$OH and used later for nickel separation.

The MiBK column is cleansed with 6M HCl and iron is eluted using 0.1M HCl. The yield is determined using atomic adsorption spectrometry (AAS) and then the solution is evaporated on plate for X-ray spectrometry of $^{55}$Fe.

The nickel phase is passed through a DMG column which is subsequently cleansed using ammonium-citrate. Nickel can be eluted with 6M HCl. The yield is determined using atomic adsorption spectrometry (AAS), the activity of $^{59}$Ni and $^{63}$Ni is determined by X-ray spectrometry and LSC counting, respectively.

**Separation of niobium ($^{93m}$Nb, half-life: 16.1 y; $^{94}$Nb, half-life: 21 ky) and antimony ($^{125}$Sb, half-life: 2.76 y) isotopes [2]**

For the separation of niobium and antimony radioisotopes, a multi-stepped acidic destruction (HF-HCl-HNO$_3$-HF) and ion exchange chromatography using a strongly basic anion exchange resin is utilised to gain samples for X-ray and $\gamma$-ray spectrometry.

10 ml evaporator concentrate sample is spiked with Nb and Sb carriers and radiotracers ($^{65}$Nb, $^{124}$Sb). The mixture is evaporated using several small aliquots of cc. HF, cc. HCl, cc. HNO$_3$ and cc. HF again sequentially. The residue is taken up with 1:1 HF and filtered to remove non-dissolvable parts.

The filtrate is passed through a Bio-Rad AG1-X8 anion exchange resin column pre-treated with 6M HF. The column is cleansed using several small aliquots of 6M HF and cc. HF before niobium is
eluted with 7M HNO₃. Antimony remains on the resin with 100% yield and without any radio-impurities.

From the niobium phase, niobium-oxide precipitation is formed, which is filtered on a plate and measured with X-ray and γ-ray spectrometry. Antimony isotopes are measured directly from the resin with γ-ray spectrometry.

**Separation of ^{99}\text{Tc} (half-life: 221 \text{ ky}) and ^{108m}\text{Ag} (half-life: 418 \text{ y}) [3]**

This method is based on that isotopes of manganese and silver, as well as of the member of platinum group are practically not soluble in the strongly basic, highly alkaline liquid phase of these samples, while technetium is in the form of water-soluble TcO₄⁻. That is, by the filtration of the samples, ^{108m}\text{Ag} (along with ^{110m}\text{Ag} and some radio-impurities) remains in the solid phase with ≥95% yield, while technetium does not attach to the solid parts.

200 ml evaporator concentrate sample is spiked with AgNO₃ as carrier, KReO₄ as substitute carrier and ^{99m}\text{Tc} as tracer. The sample is filtered with Millipore™ Millex®-GV 0.22 µm syringe filter. After the addition of CaO and 25% NH₄OH, the liquid phase is evaporated to complete dryness. The residue is taken up with 1:2 HCl, the insoluble parts are filtered out. In H₂S stream TcO₄⁻ and ReO₄⁻ are reduced into Tc₂S₇ and Re₂S₇ (dark coloured precipitation), respectively, while the vast majority of radiocesium and radiocobalt remains in the liquid phase and can be removed by filtration. The precipitation is dissolved in 15% H₂O₂, the insoluble parts are filtered out. The filtrate is purified with Bio-Rad AG50W-X8 cation exchange resin and activated ALUMINA extraction chromatography. The technetium content of the effluent is concentrated on Eichrom® TEVA Spec Tc-selective resin (supported methyl-octyl-di-decyl ammonium nitrate).

The resin is measured with γ-ray spectrometry for chemical yield and then mixed with InstaGel scintillation cocktail. (LSC counting after the decay of ^{99m}\text{Tc}.) The syringe-filter is measured directly with γ-ray spectrometry.

**Separation of uranium (^{238}\text{U}, half-life: 4.47 \text{ Gy}; ^{235}\text{U}, half-life: 704 \text{ My}; ^{234}\text{U}, half-life: 246 \text{ ky}), transuranium (^{239}\text{Pu}, half-life: 24.4 \text{ ky}; ^{240}\text{Pu}, half-life: 6.6 \text{ ky}; ^{238}\text{Pu}, half-life: 86.4 \text{ y}; ^{241}\text{Am}, half-life: 432 \text{ y}; ^{244}\text{Cm}, half-life: 17.9 \text{ y}; ^{242}\text{Cm}, half-life: 163 \text{ d}) and strontium (^{90}\text{Sr}, half-life: 28.9 \text{ y}) isotopes [4]**

This method utilises ferrous hydroxide and Ca-oxalate co-precipitation, extraction chromatography using supported di-pentylpentyl phosphonate (UTEVA), supported N,N-octylphenyl-di-i-butylcarbamoylmethyl phosphine oxide, supported octylphenyl-N,N-diisobutyl carbamoylphosphine oxide with TBP (TRU) and supported bis-(t-butylcyclohexano)-crown(18,6)ether
(SR.SPEC), as well as NdF₃ micro co-precipitation, to gain samples for alpha-spectrometry and LSC counting.

100 ml evaporator concentrate is spiked with $^{232}$U, $^{242}$Pu and $^{243}$Am as tracer and Sr as carrier. The sample is evaporated with cc. HNO₃ and cc. HCl, the residue is taken up with 1-4M HNO₃, the insoluble parts are removed by filtration.

Actinides are pre-concentrated and co-precipitated using Fe(OH)$_₂$, from the filtrate Sr is co-precipitated with Ca(COO)$_₂$.

Fe(OH)$_₂$ precipitate is dissolved in 8M HNO₃. The solution is passed through an UTEVA column. Plutonium is stripped with 9M HCl – 0.1M NH₄I, while uranium is eluted with 0.1M HCl.

To the effluent of the UTEVA CaCl$_₂$·2H$_₂$O and oxalic acid is added and the pH is adjusted to 5 with 25% NH$_₄$OH. The sample is filtered. The oxalate precipitate is destroyed by evaporation with several small aliquots of cc. HNO₃. The residue is taken up in 2M HNO₃ and loaded on a conditioned TRU column. The column is cleansed with 2M HNO₃ and 9M HCl. Americium and curium is eluted with 4M HCl.

Thin α-sources of each separated element is prepared by micro co-precipitation with NdF₃. Chemical yields are determined by the alpha-spectrometry measurements of the tracers.

Ca(COO)$_₂$ precipitate is destroyed by repeated small aliquots of cc. HNO₃, evaporated to dryness. The residue is taken up with 3M HNO₃ and loaded on a conditioned SR.SPEC column. The column is cleansed with 3M HNO₃, strontium is stripped with distilled water.

Sr oxalate source is prepared after the addition of oxalic acid and adjusting the pH to 9 with 25% NH$_₄$OH. Chemical yield is determined gravimetrically. The precipitate is dissolved with 2 ml 1M HNO₃ and mixed with InstaGel scintillation cocktail, followed by repeated LSC countings.

**Conclusions**

Radiochemical separation methods for a large number of DTM isotopes are being developed since the mid 1990s based on the evaporator concentrate samples of Paks NPP. Whenever possible, combined methods (for the determination of multiple isotopes from the same aliquot) have been developed for the reduction of unnecessary human radiation exposure, as well as of secondary nuclear waste. The methods listed in the previous sections are more or less “final”, with average chemical yields as high as 55-95%, depending on the sample matrix. However, separation techniques for $^{79}$Se/$^{107}$Pd and $^{93}$Zr/$^{237}$Np are presently under development. The detection of these isotopes will utilise the ICP-MS technique, instead of one of the radiation counting methods.
References


