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Development of ^{126}Sn separation method by means of anion exchange resin and gamma spectroscopy

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ABSTRACT

This paper describes a method employing anion exchange resin for determination of ^{126}Sn in radioactive waste. The method is suitable for the separation of ^{126}Sn isotope from hydrochloric and hydrofluoric acid solution. The separation is based on precipitation of tin with ammonium sulfide in 0.5 mol L^{-1} HCl, dissolution of the precipitate in concentrated HCl, loading in 2 mol L^{-1} HCl onto anion exchange resin column and elution with 2 mol L^{-1} HNO_3. ^{126}Sn was measured by gamma spectrometry.

1. Introduction

Long-lived radionuclides are of a major importance for the long term management of nuclear waste disposal sites. However, simple, rapid and efficient separation and extraction techniques of low abundance radionuclide as ^{126}Sn from various radioactive materials are still rare. Although ^{126}Sn as a fission product has relatively low yield of approximately 0.056% (Chain Fission Yields, 2015) by thermal neutrons, legislatures around the world demand declaration of this particular long-lived and potentially dangerous beta ($\beta_{max} = 252$ keV) and gamma (87.6, 86.94 or 64.3 keV) emitting radionuclide with a half-life of 2.35×10^5 years (Chart of nuclides, 2015).

In the last 20 years, separation methods using liquid extraction had been successfully tested. Shengdong et al. (1993) and Bienvenu et al. (2009) isolated ^{126}Sn by dissolution of fission product precipitates and applied liquid-liquid extraction with N-benzoyl-N-phenyl-hydroxylamine (BPHA) for tin extraction from nuclear fuel reprocessing waste. The abundance of ^{126}Sn atoms together with the absence of interfering species in the analyzed solutions made it possible to measure both mass concentration and nuclide activity with high precision and accuracy.

Catlow et al. (2005) analyzed ^{126}Sn in the samples from Hanford spent nuclear fuel reprocessing chemical waste. The predominant radionuclides in this type of waste were the fission products ^{137}Cs and ^{90}Sr, which interfere at beta or gamma measurements of ^{126}Sn. Acid digestion (HCl/HNO_3) and a fusion with potassium hydroxide followed by acid dissolution (HCl/HNO_3) of the melt were used for the preparation of samples for routine analyses. Bio-Rad chloride form AG-1 or AG MP-1, 100–200 mesh anion exchange resin and ^{113}Sn in 2–4 mol L^{-1} HCl were used. ^{126}Sn was quantitatively eluted with 2 mol L^{-1} HNO_3. The resulting solution was measured by either gamma-spectroscopy or mass spectrometry. The tracer recoveries based on ^{113}Sn were from 90% to 98%. Similar results were obtained for the acid leach sample preparation method.

Many authors around the world used combination of purification methods and mass spectrometry for ^{126}Sn determination. Asai et al. (2013) determined ^{126}Sn activity in a spent nuclear fuel solution by isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) for an inventory estimation in high-level radioactive waste. A well-characterized irradiated UO_2 fuel sample was used to evaluate the reliability of the methodology. Prior to the ICP-MS measurement tin was separated from ^{126}Te, which causes major isobaric interference in the determination of ^{126}Sn along with highly radioactive radionuclides, such as ^{90}Sr, ^{90}Y, ^{137}Cs and $^{137\,m}$ Ba by using an anion exchange column. The absence of Te counts at $m/z = 125$, 128, and 130 in the Sn-containing effluents (Sn fraction) indicates that Te was completely removed by the anion exchange column. After washing of the column Sn was eluted with 1 mol L^{-1} HNO_3 together with approximately 80% of the Cd and 0.03% of the U of the initial sample content. The measured concentration of ^{126}Sn in the spent nuclear fuel sample solution was 0.74 ± 0.14 ng g^{-1}, which corresponds to 23.0 ± 4.5 ng per gram of the irradiated UO_2 fuel.

Andris and Bena (2015) analyzed radioactive sludge sample from nuclear power plant by column extraction with TBP Resin. Tin was retained in 6 mol L^{-1} HCl and eluted with 0.1 mol L^{-1} HCl. A purification step to remove ^{137}Cs nuclide was introduced to improve the selectivity of the method.

In our recent paper (Dulanská et al., 2015) the behavior of ^{113}Sn on TEVA® Resin in HCl acid was tested and a method for ^{126}Sn determina-

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tion in nuclear waste based on the separation of tin on TEVA® Resin developed. Following this research, we focused on separation of tin from real radioactive waste samples on anion exchange resin supplied by Eichrom Technologies Inc.

2. Experimental

2.1. Reagents and materials

Anion exchange resin – chloride form, 1 × 8, 100–200 mesh size was supplied by Eichrom Technologies Inc. Eichrom's 2 mL columns with diameter of 0.8 cm were used for the column experiments. ^{113}Sn certified tracer solution was supplied by Czech Metrology Institute. All other chemicals used were commonly available analytical grade chemicals.

2.2. Overview of methods and sample preparation

2.2.1. Optimization of separation method

Tin^{4+} was separated on anion exchange resin as its chloride complex $SnCl_6^{2-}$ from hydrochloric acid media. For the method development and chemical yield determination, ^{113}Sn was used. 10 mL of 2 mol L^{-1} HCl was traced with ^{113}Sn (~ 70 Bq) and 5 mg of stable tin carrier was added to the sample. The sample was loaded onto 1 g of anion exchange resin preconditioned with 10 mL of 2 mol L^{-1} HCl. The column was washed with 10 mL of 2 mol L^{-1} HCl and ^{113}Sn was eluted from the column with different volumes of 2 mol mL^{-1} HNO_3 (from 5 to 30 mL). The eluted fractions were counted on HPGe gamma detector at ^{113}Sn 391.6 keV.

2.2.2. Influence of stable Sn on ^{113}Sn chemical recoveries

10 mL of 4 mol L^{-1} HCl was traced with ^{113}Sn and from 2 to 20 mg of tin carrier was added to the sample. This sample was loaded onto 1 g of anion exchange resin preconditioned with 10 mL of 4 mol L^{-1} HCl. The column was washed with 5 mL of 4 mol L^{-1} HCl and ^{113}Sn was eluted with 20 mL of 2 mol L^{-1} HNO_3. The eluted tin fractions were counted on a gamma detector at ^{113}Sn 391.6 keV energy line.

2.2.3. Influence of hydrochloric acid concentration on Sn separation

10 mL of HCl acid of different concentrations (from 0.1 to 11.3 mol L^{-1}) was traced with ^{113}Sn and 5 mg of stable tin carrier was added. Then, the solution was loaded onto 1 g of anion exchange resin preconditioned with 10 mL of HCl (the same concentration as the acid used for each sample). The column was washed twice with 10 mL of HCl. ^{113}Sn was eluted from the column with 20 mL of 2 mol L^{-1} HNO_3. The eluted fraction was counted on a gamma detector at 391.6 keV energy line.

2.2.4. Influence of hydrofluoric acid concentration on Sn separation

10 mL of HF acid of different concentrations (from 0.1 to 22 mol L^{-1}) was traced with ^{113}Sn and 5 mg of stable tin carrier was added. Then, the solution was loaded onto 1 g of anion exchange resin preconditioned with 10 mL of HF (the same concentration as the acid used for each sample). The column was washed twice with 10 mL of HF and ^{113}Sn eluted with 20 mL of 2 mol L^{-1} HNO_3. The eluted fraction was counted on a gamma detector at 391.6 keV energy line.

2.3. Tin separation methods for radioactive waste samples

2.3.1. Evaporator concentrate

Approximately 70 Bq of ^{113}Sn tracer and 5 mg of stable tin carrier were added to 20 mL of evaporator concentrate from the nuclear power plant Mochovce. The sample was neutralized with 11.3 mol L^{-1} HCl and acidity of concentrate was adjusted to approximately 0.5 mol L^{-1}. Tin was precipitated as SnS_2 by addition of 100–500 μL of 25% $(NH_4)_2S$ solution, centrifuged (10 min, 4000 rpm), washed with deionised water, dissolved in 5 mL of warm 11.3 mol L^{-1} HCl and diluted with deionised water to the final concentration of 0.5 mol L^{-1} HCl. This solution was loaded onto 2*g* of cation exchanger H^+ form, 100–200 mesh size (conditioned with 10 mL of 1 mol L^{-1} HCl) to remove ^{60}Co and the rest of ^{137}Cs. Sn isotopes were not adsorbed on cation exchanger as negative charged anion chloro-complexes. Column was washed with 2 × 2 mL of 0.5 mol L^{-1} HCl and effluents were collected in a vial, acidity was adjusted with concentrated HCl to 4 mol L^{-1} HCl and loaded onto 1g of anion exchanger, conditioned with 4 mol L^{-1} HCl. The column was washed with 4 × 5 mL of 4 mol L^{-1} HCl and Sn was eluted with 20 mL of 2 mol L^{-1} HNO_3. The eluted fractions were counted on HPGe gamma detector or treated for LSC and ICP MS measurements.

The approximate flow rates of loading and eluting solutions were 1 mL min^{-1} and standard Eichrome's 2 mL columns were used.

When LSC counting method for ^{126}Sn activity determination was used, ^{113}Sn tracer was not added and tin chemical recovery was determined by ICP OEC (from concentration of added stable tin carrier).

2.3.2. Radioactive sludge

Bq of ^{113}Sn tracer and 2 mg of stable tin carrier were added to 1 g of radioactive sludge from NPP V1 in Jaslovske Bohunice or Mochovce. A sample was digested in a mixture of 3 mL of 11.3 mol L^{-1} HCl, 3 mL of 22.1 mol L^{-1} HF and 3 mL of 14.4 mol L^{-1} HNO_3 on a hot plate at 120 °C. The digest solution was evaporated to dryness. Residue was dissolved in 10 mL of 2,5% H_3BO_3 −3 mol L^{-1} HNO_3, evaporated to dryness, dissolved again in 2 mL of 22.13 mol L^{-1} HF and evaporated to dryness. Final residue was dissolved in 10 mL of 0.5 mol L^{-1} HF or 0.5 mol L^{-1} HCl. This solution was loaded onto 2 g of cation exchanger H^+, 100–200 mesh size (conditioned with 10 mL of 0.5 mol L^{-1} HF or HCl), to remove ^{60}Co and the rest of ^{137}Cs. Tin isotopes were not adsorbed on cation exchanger as negative charged SnF_6^{2-} or $SnCl_6^{2-}$ complexes. Column was washed with 2 × 2 mL of 0.5 mol L^{-1} acid and effluents were collected in a vial, acidity was adjusted with concentrated HF or HCl acid to 4 mol L^{-1} and loaded onto 1 g of anion exchanger conditioned with 4 mol L^{-1} HF or HCl.. The column was washed with 4 × 5 mL of 4 mol L^{-1} HF or HCl and Sn was eluted with 20 mL of 2 mol L^{-1} HNO_3. The eluted fractions were counted on HPGe gamma detector.

The approximate flow rates of loading and eluting solutions were 1 mL min^{-1} and standard Eichrome's 2 mL columns were used.

2.3.3. Sample measurement

2.3.3.1. Gamma measurement. After elution of tin isotopes from the column, samples were directly counted using HPGe detector (ORTEC, 20% relative efficiency) at 391.7 (Chart of nuclides, 2015) keV line of ^{113}Sn for tin chemical recovery determination. Activity of ^{126}Sn was determined by measuring of gamma activity of ^{126}Sn daughter isotope ^{126m}Sb in radioactive equilibrium at 666.1 and 694.8 keV (Chart of nuclides, 2015) lines. The gamma detector was calibrated using a certified mixed gamma standard obtained from the Czech Metrology Institute.

2.3.3.2. LSC measurement. After elution of tin isotopes from the column, were samples evaporated to dryness, dissolved in 0.1 mol L^{-1} HCl, 15 mL of the scintillation cocktail ULTIMA GOLD AB was added and ^{126}Sn counted on TRI-CARB 2900 TR (Perkin Elmer) in optimized energy window (20–120 keV) and calibrated using ^{99}Tc standard (β_{max} = 293 keV) from Czech metrology Institute. ^{113}Sn tracer was not used for chemical yield determination; chemical yield was determined by ICP-OEC analysis of stable tin carrier.

2.3.3.3. ICP MS measurement. After elution of tin isotopes from the column, were samples evaporated to dryness, dissolved in 0.1 mol L^{-1} HCl and measured on Perkin-Elmer Sciex Elan 6000 instrument