

Sequential determination of ^{99}Tc and ^{126}Sn in radioactive concentrate

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Abstract: This paper describes a new sequential method using anion exchange resin, which is commercially available from Eichrom Technologies, Inc., for the determination of ^{99}Tc and ^{126}Sn in nuclear waste samples. For the determination of non-actinide radionuclides in radioactive wastes, several methods have been recently introduced. This method is suitable for the separation of radionuclides ^{99}Tc and ^{126}Sn from acidic solutions. Samples after digestion were directly loaded in $2 \text{ mol} \cdot \text{dm}^{-3}$ HCl acid on a cation exchange resin and then on an anion exchange. They were eluted with HNO_3 . After elution, the eluted fractions were measured either by gamma spectrometry on an HPGe detector or liquid scintillation counter with high chemical recoveries for a short period of time. Activity concentrations of ^{126}Sn were below minimum detectable activity (MDA) for each experiment. A new radioanalytical method for the sequential determination of ^{99}Tc and ^{126}Sn in radioactive concentrates has been developed and successfully applied. The main advantage of the method was the time required for the separation of radionuclides, which was only five hours, and single column separation for the determination of these radionuclides, which makes the method very effective and cheap.

Keywords: anion exchange; radioactive concentrate; sequential determination; Sn-126 separation; Tc-99 separation

Introduction

In the last 20 years, separation methods using liquid extraction have been successfully tested. Dirks et al. dealt with a new type of extraction resin in their work, a so-called TBP resin from Triskem International. They proposed a separation process for Sn using a column packed with 0.7 g of TBP resin. The sample was loaded on the column in $2 \text{ mol} \cdot \text{dm}^{-3}$ HCl and the column was washed with a further amount of $2 \text{ mol} \cdot \text{dm}^{-3}$ and $1 \text{ mol} \cdot \text{dm}^{-3}$ HCl. High purity tin was removed from the column with $0.1 \text{ mol} \cdot \text{dm}^{-3}$ HCl. The radiochemical yields were around 90 % (Dirks et al., 2014). Shengdong et al. 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 analysed solutions, made it possible to measure both mass concentration and nuclide activity with high precision and accuracy (Shengdong et al., 1993). Catlow et al. analysed ^{126}Sn in samples from Hanford spent nuclear fuel reprocessing chemical waste. The predominant radionuclides in this type of waste were fission products, ^{137}Cs and ^{90}Sr , which interfere at beta or gamma measurements of ^{126}Sn . Bio-Rad chloride form AG-1 or AG MP-1, from 100 to 200 mesh anion exchange resin and ^{113}Sn in 2 to $4 \text{ mol} \cdot \text{dm}^{-3}$ HCl were used and ^{126}Sn

was quantitatively eluted with $2 \text{ mol} \cdot \text{dm}^{-3}$ 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 % (Catlow et al., 2005). Temba et al. used for the separation and determination of difficult to measure radionuclide ^{99}Tc extraction chromatography and radiometric techniques. After the dissolution of the sample in concentrated HCl and in 30 % H_2O_2 , KReO_4 carrier was added to the solution. The whole solution was refluxed for two hours and finally filtered. The solution was first applied on an anion exchange column (Dowex IX8, Cl form, 100–200 mesh). Then, it was loaded onto a TEVA column. Technetium was eluted from the column using $8 \text{ mol} \cdot \text{dm}^{-3}$ HNO_3 . The sample was analysed using methods like LSC and ICP-AES. Efficacy of the measurement was 97.5 %, and chemical yields ranged from 70 to 90 % (Temba et al., 2015)

For determination of non-actinide radionuclides in radioactive wastes, a few methods have recently been introduced. Lee et al. systematised a simple and rapid separation procedure for the determination of ^{99}Tc , ^{90}Sr , ^{94}Nb , ^{55}Fe and $^{59,63}\text{Ni}$ in low and intermediate level radioactive wastes. The integrated procedure involves precipitation, an anion exchange and extraction chromatography for the separation and purification of individual radionuclide from sample matrix elements and from other radionuclides (Lee et al., 2011). Mellado et al. focused their work on determining radionuclides ^{55}Fe , ^{63}Ni , ^{99}Tc ,

^{137}Cs and $^{90}\text{Sr}/^{90}\text{Y}$ in radioactive waste by liquid scintillation chromatography. For measurement, standard samples were used. To a certain standard, a scintillation cocktail was added. The authors managed to reduce the separation steps and the total time of analysis, even when they selected five beta-emitting radionuclides and measurement with high-overlapping signals for analysis (Mellado et al., 2005).

^{99}Tc and ^{126}Sn are among a group of 19 limited radionuclides for long-term storage in the National Radioactive waste Repository at Mochovce in Slovak Republic. In this paper, a new method for sequential separation of ^{99}Tc and ^{126}Sn on a cation exchange resin and an anion exchange resin from samples of nuclear waste originating from the NPP Mochovce was proposed.

Materials and Methods

Cation exchanger H^+ form, 50 W \times 8, 100–200 mesh size and anion exchanger – chloride form, 1 \times 8, 100–200 mesh size were supplied by Eichrom Technologies, Inc. All other chemicals used were commonly available analytical grade acids and chemicals.

Influence of hydrochloric acid concentration on Sn separation

10 cm^3 of HCl acid of different concentrations (from 0.1 to 11.3 $\text{mol}\cdot\text{dm}^{-3}$) was traced with ^{113}Sn and 5 mg of a stable tin carrier was added. Afterwards, the solution was loaded onto 1 g of an anion exchange resin preconditioned with 10 cm^3 of HCl (the same concentration as the acid used for each sample). The column was washed twice with 10 cm^3 of HCl. ^{113}Sn was eluted from the column with 20 cm^3 of 2 $\text{mol}\cdot\text{dm}^{-3}$ HNO_3 . The eluted fraction was counted on a gamma detector at 391.6 keV energy line.

Optimisation of the separation method (anion exchange resin)

10 cm^3 of 0.5 $\text{mol}\cdot\text{dm}^{-3}$ HCl were traced with ^{113}Sn and $^{99\text{m}}\text{Tc}$. The model sample was loaded onto 1 g of a cation exchanger conditioned with 10 cm^3 1 $\text{mol}\cdot\text{dm}^{-3}$ HCl. The column was rinsed twice with 2 cm^3 of 1 $\text{mol}\cdot\text{dm}^{-3}$ HCl, eluates were collected in a vial and loaded onto 1 g of an anion exchange resin preconditioned with 2 $\text{mol}\cdot\text{dm}^{-3}$ HCl. The column was rinsed twice with 10 cm^3 of 2 $\text{mol}\cdot\text{dm}^{-3}$ HCl. ^{113}Sn was eluted with 20 cm^3 of 2 $\text{mol}\cdot\text{dm}^{-3}$ HNO_3 (Dulanská et al., 2015) and technetium was finally eluted with 20 cm^3 of 14.35 $\text{mol}\cdot\text{dm}^{-3}$ HNO_3 . Each fraction was counted on a gamma detector to check Sn and Tc behaviour on the column.

Sequential determination of ^{99}Tc and ^{126}Sn in radioactive concentrate

Approximately 7 Bq of ^{113}Sn tracer and 5 mg of stable tin carrier were added to 20 cm^3 of evaporator concentrate from the nuclear power plant Mochovce. The sample was neutralized with 11.3 $\text{mol}\cdot\text{dm}^{-3}$ HCl and acidity of the concentrate was adjusted to approximately 1–2 $\text{mol}\cdot\text{dm}^{-3}$. This solution was loaded onto 2 g of cation exchanger H^+ form, 100–200 mesh size (conditioned with 10 cm^3 of 1 $\text{mol}\cdot\text{dm}^{-3}$ HCl) to remove ^{60}Co and the rest of ^{137}Cs . The column was washed with 2 cm^3 of 1 $\text{mol}\cdot\text{dm}^{-3}$ HCl and effluents were collected in a vial, acidity was adjusted with concentrated HCl to 2 $\text{mol}\cdot\text{dm}^{-3}$ HCl and loaded onto 1 g of anion exchanger, conditioned with 2 $\text{mol}\cdot\text{dm}^{-3}$ HCl. The column was washed with 20 cm^3 of 2 $\text{mol}\cdot\text{dm}^{-3}$ HCl and Sn was eluted with 20 cm^3 of 2 $\text{mol}\cdot\text{dm}^{-3}$ HNO_3 and technetium was finally eluted with 20 cm^3 of 14.35 $\text{mol}\cdot\text{dm}^{-3}$ HNO_3 . The eluted fractions were counted on an HPGe gamma detector.

Measurement of ^{126}Sn

After elution of tin, samples were immediately counted using an HPGe detector (ORTEC, 20 % relative efficiency) at 391.6 keV line of ^{113}Sn for tin chemical recovery determination. Activity of ^{126}Sn was determined by measuring gamma activity of ^{126}Sn daughter isotope $^{126\text{m}}\text{Sb}$ in radioactive equilibrium at 666.3 and 695 keV lines.

Measurement of ^{99}Tc

Final fractions were heated near to dryness and dissolved in 5 cm^3 of 0.05 $\text{mol}\cdot\text{dm}^{-3}$ HNO_3 . Final fractions were measured on an HPGe detector for $^{99\text{m}}\text{Tc}$ recoveries at 140 keV line. The samples were left for one week to allow $^{99\text{m}}\text{Tc}$ decay and subsequently counted on TRI-CARB 3100 TR by adding 15 cm^3 of scintillation cocktail ULTIMA GOLD AB to determine ^{99}Tc activity.

Results and discussion

The main focus of our work was to develop a suitable sequential analytical separation procedure for the determination of ^{126}Sn and ^{99}Tc from radioactive waste.

Tetravalent tin is adsorbed on an anion exchange resin Sn^{4+} and forms a very stable anionic SnCl_4^{2-} complex at HCl concentration higher than 0.7 $\text{mol}\cdot\text{dm}^{-3}$. The recovery of ^{113}Sn was higher than 80 % at lower acid concentration in the region of 0.5 to 8 $\text{mol}\cdot\text{dm}^{-3}$ HCl and the higher the acid concentration became, the lower the recovery occurred. The results are shown in Fig. 1.

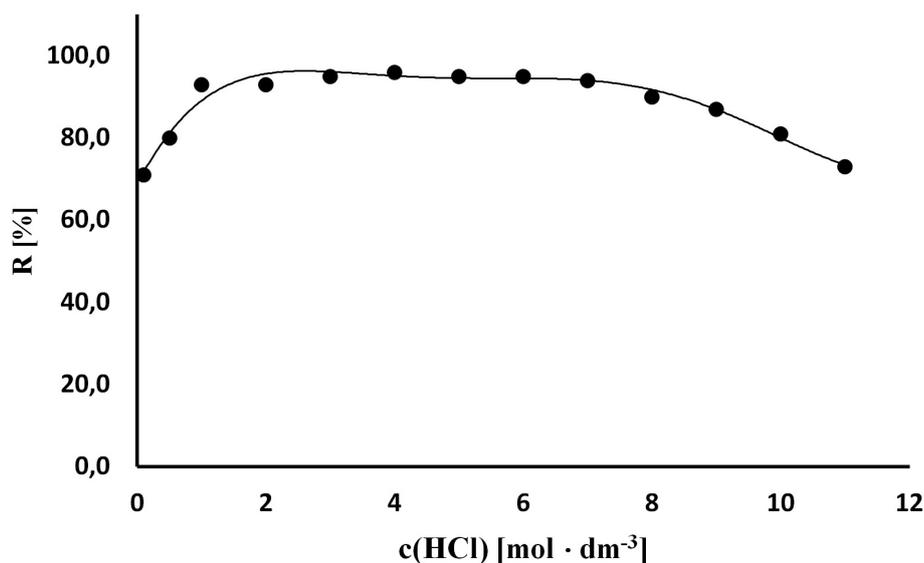


Fig. 1. Influence of HCl concentration on adsorption of ^{113}Sn .

Tab. 1. Activity concentrations of selected radionuclides in evaporator concentrate samples ($\text{Bq} \cdot \text{dm}^{-3}$ for concentrate).

Sample	^{99}Tc	$^{99\text{m}}\text{Tc}$	^{126}Sn	^{113}Sn
	A \pm U ($\text{Bq} \cdot \text{dm}^{-3}$)	R \pm U (%)	A \pm U ($\text{Bq} \cdot \text{dm}^{-3}$)	R \pm U (%)
1	4.08 ± 0.49	70 ± 8	< 9.1	74 ± 9
2	3.92 ± 0.47	82 ± 10	< 8.4	80 ± 9
3	5.99 ± 0.72	89 ± 11	< 3.2	83 ± 10
4	4.94 ± 0.59	88 ± 11	< 4.1	66 ± 8
5	3.17 ± 0.38	74 ± 9	< 9.2	76 ± 9

Note: U - expanded uncertainty, $U_{(A, R)} = k \cdot u_{(A, R)}$, $k = 2$, R - recovery.

Hydrochloric acid with a concentration of $2 \text{ mol} \cdot \text{dm}^{-3}$ was chosen as the complexing reagent for the separation of tin and technetium. Before the analysis by gamma spectrometric measurement, it was discovered that the radioactive concentrates were contaminated with ^{137}Cs and ^{60}Co . Therefore, before the separation of technetium and tin, a separation step using a cation exchange sorbent for elimination of ^{137}Cs and ^{60}Co was established. Sorption of tetravalent tin and technetium on an anion exchange from $2 \text{ mol} \cdot \text{dm}^{-3}$ of HCl and sequential elution of tin and technetium was tested. ^{113}Sn was eluted with 20 cm^3 of $2 \text{ mol} \cdot \text{dm}^{-3}$ HNO_3 . In those acid concentrations, the retention factor k' for TcO_4^- is around 500. Finally, technetium was eluted with 20 cm^3 of $12 \text{ mol} \cdot \text{dm}^{-3}$ HNO_3 . Activity concentrations of ^{126}Sn and ^{99}Tc determined by using an anion exchange resin are presented in Table 1.

It was found out that ^{113}Sn recovery was higher than 65 % and the highest recovery was obtained in the case of sample 1. Chemical yields for tin determination were in the range from 66 % to 83 %. On the

anion exchange resin technetium, recoveries were shown between 70 % and 89 %. Activity concentrations for ^{126}Sn were below minimum detectable activity (MDA). The advantages of this method were the simplicity of the sample preparation, cheap and quick single column separation of ^{99}Tc and ^{126}Sn radionuclides.

Conclusion

A new radioanalytical method for the sequential determination of ^{99}Tc and ^{126}Sn radioactive concentrate has been developed and successfully applied. Anion exchange resin was used to determine ^{126}Sn and ^{99}Tc activity concentrations in samples originating from Slovak NPP Mochovce and NPP A1 Jaslovské Bohunice in one column separation. The method was optimised by using model samples and tracer nuclides. The main advantage of the method was the time required for the separation of radionuclides, which was only five hours, and a single column used for the determination of these

radionuclides makes the method very effective and cheap.

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