

Preparation and characterisation of a sorbent suitable for technetium separation from environmental matrices

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Abstract

An extraction chromatographic material based on Aliquat - 336 anchored on hydrophobised silica gel support as an ion exchanger, was prepared. Prepared material for column appeared to be suitable for separation of technetium - 99 from environmental matrices. The material properties, sorption characteristic and distribution coefficient of $^{99m}\text{TcO}_4^-$ in various medium was studied. The chemical yield of Tc during separation process was determined using ^{99m}Tc tracer and gamma measurement. Typical sorption recoveries of Tc for this sorbent from 0.1 M HNO_3 were more than 98 %. Typical desorption recoveries using 8 M HNO_3 were in the range 92 – 96 %. The commercial TEVA Spec resin from Eichrom Industries for comparison purpose was used as well. Prepared sorbent was conditioned with HNO_3 by washing with 25 ml of 0.1 M HNO_3 . The solution containing 35 kBq of $^{99m}\text{TcO}_4^-$ in 0.1M HNO_3 was passed through the column. Tc was eluted by 8 M HNO_3 . The activity of ^{99m}Tc in eluent collected in each 1 ml fraction was measured by well type NaI(Tl) detector. It was found that the prepared sorbent is suitable for separation of technetium from environmental matrices and radioactive waste.

Introduction

^{99}Tc is an artificial long live pure beta isotope ($T_{1/2} = 2.17 \times 10^5$ years). ^{99}Tc is produced with high yield during nuclear fission of ^{235}U (~6%) and has a radiological implication and environmental risk¹. In aqueous solutions, where no reducing agents are present, ^{99}Tc exists as a pertechnetate ion, TcO_4^- . Technetium in this form is very mobile in soils, ground and surface waters.²

Technetium behaves as a nutrient analogue and may be concentrated by plants and deposited on their outer membrane. In humans and animals the pertechnetate ion localizes in the gastrointestinal tract and thyroid gland.³

Several methods have been used to determine ^{99}Tc in the environment⁴. These methods mostly include concentration and purification step of the technetium on an ion exchange.

The most commercially ion exchanger used for separation and purification of pertechnetate is TEVA Spec resin, made by Eichrom Technologies.⁴

Sorption behaviour of technetium and other metal ions from nitric and hydrochloric acids using TEVA product is shown. Tc (as pertechnetate anion TcO_4^-) has higher distribution coefficient at lower acid concentration contrary to other metals.

The aim of this study was to prepare cheap and effective sorbent suitable for ^{99}Tc determination from environmental samples especially focused on technetium separation from soils⁵ and radioactive wastes.

Methods

The experimental studies were designed to provide all necessary data to estimate sorption capacity, competitive ion sorption, choice of suitable medium for technetium sorption and desorption processes, properties of prepared sorbent, as well as to determine influence of typical substances appeared after leaching technetium from soil on its distribution coefficient on sorbent.

The column used was the same as for TEVA Spec resin (100-150 mm in diameter, volume of 5 ml).

Sorbent preparation

The active component of the prepared sorbent is an aliphatic quaternary amine Aliquat-336 anchored on hydrophobised silica gel. Properties of this sorbent are similar to typical strong base anion exchange resins.

The column used in this study was constructed of plastic and was 1.5 cm in diameter and 15 cm in height (a total column volume - 5 mL).

60 g of silica gel were dried in the oven at 105⁰ C. The dried up silica gel were hydrophobised with adding twice of 100 ml of 3% solution of Lukoil – H / acetone and then dried up and heated for 20 minutes at 180⁰C in a laboratory drying oven. To the dry hydrophobised silica gel 100 ml of 40 % Aliquat -336/ benzene solution was added. After sorption of Aliquat -336 from solution to silica gel the rest of organic phase was decanted and sorbent was dried up to dryness at room temperature. The final weight of the prepared sorbent was 86 g.

There were prepared sorbents with different Aliquat -336 concentration in this study . The concentration of the mixture of Aliquat-336/ benzene was in the range of 10 % - 60%.

All concentrations in the range 10-60 % were used for experiments, but the most suitable concentration used for pertechnetate sorption experiments was 40 % Aliquat -336/benzene (described above) due to the highest distribution coefficient of sorbent for pertechnetate and not to be sticky.

Method summary for the sample of soils and radwastes

Approximately 35 kBq ^{99m}Tc and 2.5 Bq ⁹⁹Tc were added as a yield monitor to 10 g of soil or radwaste. Sample was wetted using 30 ml NH₄OH and evaporated to dryness. The sample was ashed for 8 hours by 550⁰C and then leached in 50 ml 8M HNO₃ on a hotplate at 125⁰C for 2 h. Centrifuged, filtered and neutralised with 25 ml NH₄OH until a reddish-brown precipitate was formed. Centrifuged, discard the precipitate and evaporate to dryness. Dissolved the sample in 20 ml of 0.1 M HNO₃. Then the chromatography column contained the prepared sorbent was washed with 20 ml deionised water and then with 20 ml 20 ml of 0.1 M HNO₃. The sample solution was loaded onto the sorbent and then eluated with 25 ml 8 M HNO₃. 1 ml from the eluate was taken for determination of the chemical recovery for gamma measurement of ^{99m}Tc. The rest was evaporate to dryness on a hotplate and dissolved in 5 ml of 0.1 M HNO₃ to determine ⁹⁹Tc concentration by scintillation counting.

Results and discussion

Study of the influence of various compounds for K_D values of $^{99m}\text{TcO}_4^-$ using prepared sorbent

To determine and estimate the influence of various ions presented in the soils, various compounds ($\text{Al}(\text{NO}_3)_3$, FeCl_3 , CaCl_2 , K_2SO_4 , MgCl_2 , NaCl) were added to the 0.1 M HNO_3 and the influence of these compounds on the sorption (K_D) of the $^{99m}\text{TcO}_4^-$ values was studied. Figure 1. shows the ionic influence at K_D values in 0.1 M HNO_3 .

The influence of H_2SO_4 , seen in the figure 2., on the sorption of ^{99m}Tc was also tested. To retain Tc onto the prepared sorbent was used 1 M H_2SO_4 and for stripping ^{99m}Tc was used 8M HNO_3 .

Fig. 1. Ionic influence at K_D values of $^{99m}\text{TcO}_4^-$ in 1M H_2SO_4 medium

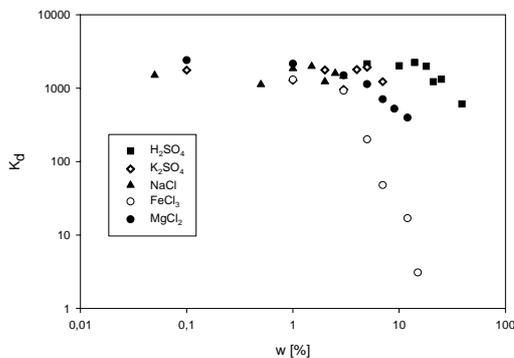
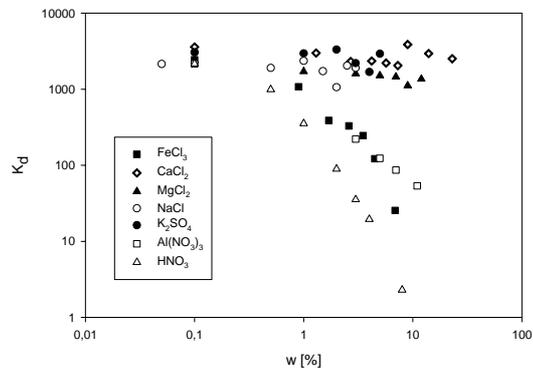


Fig. 2. Ionic influence at K_D values of $^{99m}\text{TcO}_4^-$ in 0.1 M HNO_3

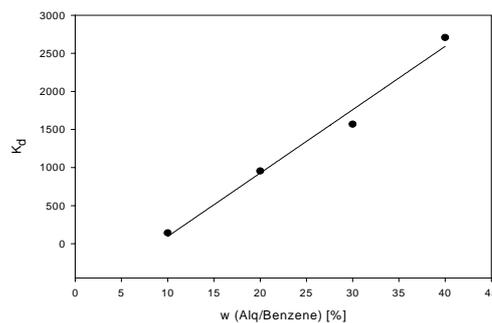


Ca^{2+} , Mg^{2+} , Na^+ ions in the form of chloride have no influence on the K_D of pertechnetate. Al^{3+} in the form of nitrate decrease K_D of pertechnetate because of NO_3^- anion and the effect was the same as HNO_3 with higher concentration. Fe^{3+} ion has an influence on K_D values of pertechnetate. With increasing FeCl_3 concentration a decrease of K_D pertechnetate was observed which may be caused due to loss of pertechnetate by reduction or by forming of $\text{Fe}(\text{OH})_3$ precipitate.

Prepared sorbents had different concentration of Aliquat – 336/ benzene added in the range from 10 –60 %. For determination of distribution coefficient K_D 50 mg of sorbent were taken to extraction tubes with 5 ml solution containing $^{99m}\text{TcO}_4^-$ in 0.1 M HNO_3 . One tube containing $^{99m}\text{TcO}_4^-$ only was used for determination of ^{99m}Tc counts. Tubes were shaken in rotation shaker for 40 minutes. 1 ml aliquot from each extraction tube was taken for gamma measurement using well-type $\text{NaI}(\text{TI})$ detector.

K_D value for $^{99m}\text{TcO}_4^-$ were higher for sorbent loaded with higher concentration of Aliquat – 336 and the dependence was linear as can be seen from Fig. 3. The sorbent with the concentration 60 % Aliquat – 336 / benzene was not suitable for separation process, because such prepared sorbent was sticky.

Fig. 3. K_D values of $^{99m}\text{TcO}_4^-$ for various concentration of prepared sorbent



Basic characteristics of prepared sorbent with commercial one from Eichrom TEVA are shown in Table 1. The prepared sorbent has similar properties as the TEVA Spec resin.

Table 1. Characteristic of TEVA Spec resin and prepared sorbent.

	TEVA	Prepared sorbent
Stationary phase	Aliquat-336	Aliquat-336
Support	acryl ester	modified silica gel
Available particle diameters	20-50 μm , 50-100 μm , 100-150 μm	54 -160 μm
Extractant loading	40 %	40 %
Bed density[g/ml]	0.35	0.726
V_m , ml/ml of bed	0.68	0.7
Experimentally measured capacity Cl ⁻ /ml	0.233 mmol Cl ⁻ /ml	0.33mmol

Chemical recoveries of $^{99m}\text{TcO}_4^-$ shown in table 2. were measured in 1 ml of solution after each separation step by well- type NaI(Tl) detector.

Table 2. Chemical recoveries of $^{99m}\text{TcO}_4^-$ after separation steps

Sample	ashing (%)	precipitation (%)	extraction chromatography (%)	total recovery (%)
Soils1	92.4	77.7	49.5	23.2
Soils2	97.2	78.6	54.2	25.1
Radwastes1	97	73.8	65.6	37.4
Radwastes2	98	79.4	76.6	52.4

CONCLUSION

Prepared sorbent is suitable for technetium separation from environmental samples prior to its beta measurement. Results from model matrices showed that this sorbent quantitative retained Tc from the 0.1 M HNO_3 sample and pertechnetate can be eluted from sorbent by 8M HNO_3 with high yield (more then 94%). The influence of Na^+ , Mg^{2+} , K^+ , Ca^{2+} ions on K_D values for $^{99m}\text{TcO}_4^-$ was not observed. Otherwise, with increasing concentration of FeCl_3 as well as $\text{Al}(\text{NO}_3)_3$ the K_D values of pertechnetate is decreasing.

The results of pertechnetate separation were found to be reproducible and prepared sorbent is cheap enough to be used in every laboratory.

A method was tested to determine technetium-99 in environmental matrices and radioactive waste, using ^{99m}Tc as a yield monitor. Chemical recoveries were typically in the range 23-52%.

References

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