

# Determination of $^{99}\text{Tc}$ in soil samples using molecular recognition technology product AnaLig<sup>®</sup> Tc-02 gel

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**Abstract** The purpose of this study was to test a method for  $^{99}\text{Tc}$  determination in soil samples from locality Bratislava Podunajske Biskupice by using solid phase extraction technique with a new sorbent AnaLig<sup>®</sup> Tc-02—molecular recognition technology product. The method is suitable for analyzing soil samples in a relatively short time and high recoveries. The use and effectiveness of AnaLig<sup>®</sup> Tc-02 were successfully tested by analysis of soil and spiked soil samples.

**Keywords**  $^{99}\text{Tc}$  · Soil · AnaLig<sup>®</sup> Tc-02

## Introduction

Technetium-99, pure beta emitter ( $E_{\text{max}} = 294 \text{ keV}$ ), with a half life  $T_{1/2} = 2.12 \times 10^5 \text{ years}$  is a product of the nuclear fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$  in relatively high yield  $\sim 6\%$ .

In trace level, it is found in the earth crust as a fission product of natural  $^{235}\text{U}$  and  $^{238}\text{U}$ , but into the environment was technetium released by testing of nuclear weapons, from nuclear fuel reprocessing plants and applying meta stable isotope  $^{99\text{m}}\text{Tc}$  in the nuclear medicine, where technetium is utilized on diagnostic purposes [1].

By a testing of nuclear weapons in the 50 and 60s of the past century raised the natural concentration of technetium in the environment from 1 to 5  $\text{mBq m}^{-3}$ , from processing

plants in the La Hague and Sellafield has been in the years 1982–1991 released 102 TBq, respectively, 40.2 TBq of  $^{99}\text{Tc}$  [2, 3].

In uranic ore uraninite, technetium arise from spontaneous fission of uranium isotopes in concentrations  $0.25\text{--}0.31 \text{ ng kg}^{-1}$ . Technetium has been detected in stars too, absorption spectrum of Tc(I) has been observed, though its presence in stars is object of various studies now [2, 3].

Determination of technetium-99 in the environmental and radioactive waste samples is very difficult task, which introduces a number of separation steps necessary for technetium separation from the others radionuclides. The activity of interfering radionuclides could be in some cases up to a few hundred thousands higher than is activity of technetium in the given sample. Interfering  $\alpha$ ,  $\beta$ ,  $\gamma$ -emitting radionuclides could have unfavorable interference on measuring of  $^{99}\text{Tc}$ . The matrixes of analyzed samples were often complicated and varied radionuclides composition. Radiometric determination of  $^{99}\text{Tc}$  concentration in such samples in considerably prevailing concentrations of interfering radionuclides is special strenuous. Taking into account the chemistry of technetium,  $^{99}\text{Tc}$  will be released into the environment mostly as pertechnetate. The volatile species  $\text{Tc}_2\text{O}_7$  and  $\text{HTcO}_4$  are produced during reprocessing, and the highly volatile  $\text{TcF}_6$  is produced during the fluorination of uranium for uranium isotopes separation.  $^{99}\text{Tc}$  is also found in airborne discharges and liquid waste and is present as an impurity in uranium oxide from irradiated fuels [4]. McMahon et al. [5] estimate that the release of  $^{99}\text{Tc}$  to the environment through liquid discharges from a small covert reprocessing facility could be on the order of  $10^{10} \text{ Bq}$  or  $\sim 16 \text{ g}$ . Its behavior in the environment attracted much attention during the last two decades due to the long physical half-life of  $^{99}\text{Tc}$  and the high solubility and mobility of  $\text{TcO}_4^-$ , in aquatic systems. Considerable effort has been

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made to understand the long-term biochemical behavior of  $^{99}\text{Tc}$ , its transfer in food chains and the mechanisms controlling its mobility in diverse environments. Analysis data of global fallout  $^{99}\text{Tc}$  in environmental samples should give useful information for predicting the nuclide behavior [6]. Because the concentration of  $^{99}\text{Tc}$  is relatively low, it is necessary to concentrate and separate it for determination. This is another of the reasons why  $^{99}\text{Tc}$  analysis in samples is difficult to analyze.

In the previous work we determined the activity concentration of  $^{99}\text{Tc}$  in evaporator concentrates using molecular recognition technology (MRT) product AnaLig<sup>®</sup> Tc-02 gel [7]. This paper describes using AnaLig<sup>®</sup> Tc-02 gel for analyzing of soil samples from locality Bratislava Podunajske Biskupice in Slovak Republik.

## Experimental

### Reagents and materials

Soil sample 1—soil from locality Bratislava Podunajske Biskupice in Slovakia, laboratory number 3,254.

Soil sample 2—soil from locality Bratislava Podunajske Biskupice in Slovakia, laboratory number 3,258.

AnaLig<sup>®</sup> Tc-02 gel (60–100 mesh) was supplied by IBC Advanced Technologies, Inc. All other chemicals used were commonly available analytical grade acids and chemicals [8].

### Samples preparation

Both soil samples were first dried at 105 °C to the constant weight, stones, and organic material such as plants, roots were taken out and samples were homogenized by milling to fine powder and stored in plastic bottles before analysis.

For all experiments we used the same quantities of soil and the same conditions were maintained.

To 10 g of soil sample was 40 ml of 2.5 M  $\text{HNO}_3$ ,  $^{99\text{m}}\text{Tc}$  tracer solution, 2 ml conc.  $\text{H}_2\text{O}_2$  and 0.5 g of NPL ABH 2003 (for spiked samples) added. Concentrated  $\text{H}_2\text{O}_2$  was added to assure the Tc was present in  $\text{TcO}_4^-$  form. The solution was gently heated for 2 h at ~90 °C. After cooling down pH of the solution was adjusted with concentrated  $\text{NH}_3$  to ~8–9. The sample was filtered (filter paper 12  $\mu\text{m}$  pore size) and filter washed with 1 M NaCl solution. Filtrate and washings were used for further analysis.

### AnaLig<sup>®</sup> Tc-02 separation procedure

AnaLig Tc02<sup>®</sup> gel (1 g) was packed into the 2 ml column and conditioned with 10 ml of 1 M NaCl [6]. Flow rates were set to 1–2 ml  $\text{min}^{-1}$ . The sample digest was loaded

onto AnaLig<sup>®</sup> Tc-02 column. Each column was washed  $2 \times 10$  ml of 1 M NaCl than 5 ml of 0.1 M NaCl solution. Technetium was finally eluted with 30 ml of hot 0.05 M  $\text{HNO}_3$  ~90 °C to achieve complete elution of  $^{99}\text{Tc}$ . Samples were heated near to dryness and dissolved in 5 ml of 0.01 M HCl.

### Measurement

Final fractions were measured on an HPGe detector for  $^{99\text{m}}\text{Tc}$  recoveries at 140 keV line. The samples were left for 1 week to allow  $^{99\text{m}}\text{Tc}$  decay and subsequently counted on TRI-CARB 2900 TR (Perkin Elmer) after adding 15 ml of scintillation cocktail ULTIMA GOLD AB to determine  $^{99}\text{Tc}$  activity. The optimized energy window 10–90 keV was chosen to minimize background counts and minimum detectable activity (MDA). The TRI CARB 2900 TR was calibrated using  $^{99}\text{Tc}$  standard from Czech Metrology Institute with certified activity of  $^{99}\text{Tc}$ . The typical counting efficiency was 75% and samples were counted  $2 \times 120$  min.

## Result and discussion

Soil samples were processed and analyzed as described above in the experimental part of this paper. The main focus of this work was to test the feasibility of using AnaLig<sup>®</sup> Tc-02 gel for analysis of  $^{99}\text{Tc}$  in soil samples. In our previous work, we used AnaLig<sup>®</sup> Tc-02 gel for determination of  $^{99}\text{Tc}$  in evaporator concentrate with good results and high chemical recoveries [7]. Evaporator concentrate is typical for its high content of salts—high ionic strength as the soil digest was too. Another aspect was quick separation and one column design of the experiment.

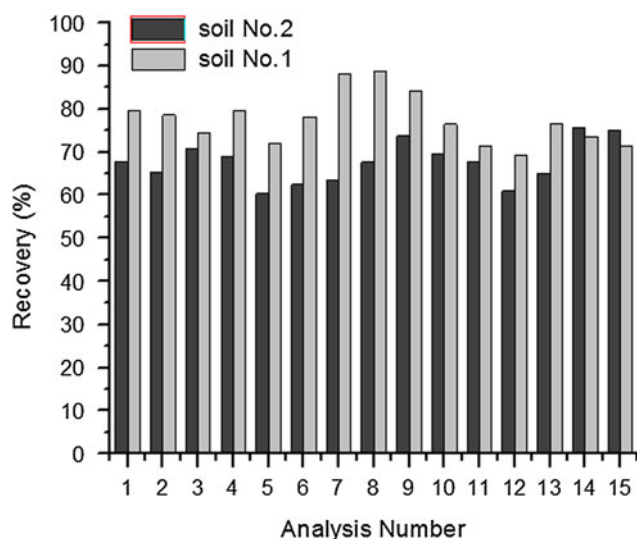
We tested the AnaLig<sup>®</sup> Tc-02 separation procedure first by using 0.1 M  $\text{HNO}_3$  for soil digestion and we obtained very low chemical recoveries (<30%). We checked the pH of digest and was ~7–8. Nitric acid was neutralized by soil and  $\text{TcO}_4^-$  probably reduced by organics, therefore not adsorbed on column and precipitated together with iron hydroxide by pH adjusting before loading onto AnaLig<sup>®</sup> Tc-02 column. After that we used 2.5 M  $\text{HNO}_3$  for digestion. The results for samples 1 and 2 are presented in Table 1.

Fortunately we have not measured positive  $^{99}\text{Tc}$  activities in our soil samples. All values were below MDA and calculated MDA for 10 g of soil sample and 120 min counting was 4.2 Bq  $\text{kg}^{-1}$  (Currie). Because the activity of  $^{99}\text{Tc}$  in soil was less than MDA we spiked both soils with known activity of  $^{99}\text{Tc}$  (0.5 g of NPL ABH 2003 3.56 Bq  $\text{g}^{-1}$ ) to check the effectiveness and usability of the method. We analyzed spiked samples as is described above. All results are in good agreement with reference

**Table 1** Recoveries of  $^{99\text{m}}\text{Tc}$  and activity concentrations in  $\text{Bq g}^{-1}$  for  $^{99}\text{Tc}$  and NPL-ABH 2003 obtained by method AnaLig<sup>®</sup> Tc-02

Soil sample (1)	AnaLig <sup>®</sup> Tc-02 Recovery (%)	AnaLig <sup>®</sup> Tc-02 A $\pm$ 2U ( $\text{Bq kg}^{-1}$ )	Soil sample (2)	AnaLig <sup>®</sup> Tc-02 Recovery (%)	AnaLig <sup>®</sup> Tc-02 A $\pm$ 2U ( $\text{Bq kg}^{-1}$ )
1	79.6	<4.0	1	67.8	<4.7
2	78.6	<4.1	2	65.3	<4.8
3	74.4	<4.2	3	70.9	<4.6
4	79.7	<3.9	4	69.0	<4.6
5	71.9	<4.3	5	60.3	<4.9
6	78.2	<4.2	6	62.4	<5.2
7	88.2	<3.7	7	63.5	<5.2
8	88.6	<3.7	8	67.7	<4.7
9	84.1	<3.8	9	73.7	<4.4
10	76.5	<4.3	10	69.6	<4.7
11	71.5	$3.6 \pm 0.4^*$	11	67.8	$3.6 \pm 0.4^*$
12	69.3	$3.7 \pm 0.4^*$	12	60.9	$3.6 \pm 0.4^*$
13	76.7	$3.6 \pm 0.4^*$	13	65.0	$3.6 \pm 0.4^*$
14	73.6	$3.6 \pm 0.4^*$	14	75.5	$3.5 \pm 0.4^*$
15	71.5	$3.8 \pm 0.4^*$	15	75.0	$3.7 \pm 0.4^*$
Average	77.5	$3.7 \pm 0.4^*$	Average	67.6	$3.6 \pm 0.4^*$

\* Spiked samples 0.5 g of NPL ABH 2003 ( $3.56 \text{ Bq g}^{-1}$ ), activity in  $\text{Bq g}^{-1}$

**Fig. 1** Chemical recoveries of  $^{99\text{m}}\text{Tc}$  in soil sample 1 and sample 2 using 1 g of AnaLig<sup>®</sup> Tc-02

values. Average chemical recoveries were higher than 75% for soil 1 and 65% for soil 2 Fig. 1.

The method was proven to be efficient and quick, with flow rates higher than  $1\text{--}2 \text{ ml min}^{-1}$ . The pure time of separation was app. 2 h.

## Conclusion

In summary, the technetium analysis method based on AnaLig<sup>®</sup> Tc-02 is also very effective and quick for determination of technetium in soil samples. The methods

performance was investigated by analysis of NPL ABH 2003 intercomparison sample. The chemical yields for this method were about 65–75% and separated Tc fractions were radiochemical pure enough for LSC measurements.

Solid samples were leached with dilute nitric acid. The leachates were passed through on AnaLig<sup>®</sup> Tc-02 column which is highly specific for technetium in the pertechnetate form.

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