

# Simultaneous determination of radioactive halogen isotopes and $^{99}\text{Tc}^*$ )

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The purpose of this study was to develop a simplified method for simultaneous determination of radiologically important halogen isotopes and  $^{99}\text{Tc}$  from different types of samples like environmental, biological and waste samples. Due to their long half-lives (longer than  $10^5$  years) they play important role in the nuclear cycle, especially in environmental monitoring and protection.

For a rapid response in the evaluation of  $^{129}\text{I}$ ,  $^{36}\text{Cl}$  and  $^{99}\text{Tc}$  contamination levels of these samples it is advantageous to combine the existing individual methods. According to the present procedure, iodine, chlorine and technetium are separated selectively from the same sample aliquot followed by the  $\beta$ -spectrometry of the purified fractions. Increased sensitivities can be achieved by neutron activation (NA) especially in the case of  $^{129}\text{I}$ .

Our work intends to solve the problem by combining the well-known hot acidic distillation method for iodine separation with the organic extraction process characteristic for technetium separation. The major objective of the work was to separate the disturbing halides from iodine. For this purpose a selective oxidant was applied.

For the sample destruction and fractionated distillation an air flow-through installation was used with hot concentrated sulphuric and nitric acids. The trap for iodine contained 3 M NaOH solution. After iodine separation the trap was exchanged for a new one containing the same solution for trapping chlorine or bromine with an addition of 0.01 M  $\text{KMnO}_4$  solution as an oxidative agent. As expected, the main part of technetium was contained in the acidic residue after distillation. Tc purification was performed by organic extraction with TBP and TEVA column.

## 1 Introduction

Long-lived radioactive halogen isotopes and  $^{99}\text{Tc}$  are produced in the nuclear fuel cycle as a result of neutron-induced fission and activation processes taking place in the core and the construction materials, respectively. Because of their extremely high mobility they can be released into the environment causing contamination. Due to the variety of different chemical species, the migration into and along the environment is a rather sophisticated process. Hence, determination of these isotopes from different types of samples like environmental, biological and waste samples is essential.

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The most significant isotopes are those with long half-life, i.e.  $^{129}\text{I}$  ( $T_{1/2} = 15,7$  mil. y),  $^{36}\text{Cl}$  ( $T_{1/2} = 301\,000$  y) and  $^{99}\text{Tc}$  ( $T_{1/2} = 213\,000$  y).

The actual methods for their determination are specific for individual nuclides; they require separate sample aliquots.

Our work aimed to solve the analytical problem by combining the well known hot acidic distillation method for iodine separation with the organic extraction process characteristic for technetium separation, thus obtaining a combined procedure for the simultaneous determination of the nuclides.

## 2 Background, literature survey

### 2.1 Sample pre-treatment

According to the literature, most of the procedures started with heat treatment at about 250-650°C [1-3]. Temperature ranges and ashing times varied depending on sample complexity. Y. Muramatsu et al. [4] applied this method for destruction of plant and soil samples. Others tried to take advantage of the volatility of technetium and halides by sublimation through a dry-leaching technique [5] or applying hot acidic distillation. In the procedure of Tagami and Uchida [2], technetium sublimating from soil ash at 950 degrees was absorbed in a trap containing  $\text{K}_2\text{CO}_3$ . A frequently applied technique is alkaline-fusion [6].

### 2.2 Determination of $^{99}\text{Tc}$

After destruction samples were optionally pre-concentrated either by solvent extraction followed by back-extraction in aqueous phase [2] or by precipitation in alkaline media [7,8]. Preferably, Tc was separated by extraction with TBP/ $\text{H}_2\text{SO}_4$  [1,9,10], TBP/alkane [11], cyclohexanone [12], ethyl-methyl-ketone [6]), by extraction chromatography using TEVA Spec column/8M  $\text{HNO}_3$  eluent [5,8]) or by anion exchange chromatography (Dowex-1/ $\text{NaClO}_4$  [11] or Bio-Rad AG 1\*8/2 M NaOH [3]).

Liquid scintillation counting (LSC) by mixing the eluted fraction or the anion exchange resin or the organic phase with the scintillation cocktail as well as neutron activation (NA) were the measurement techniques used. Bate [12] measured the produced  $^{100}\text{Tc}$  by  $\gamma$ -spectrometry.

### 2.3 Determination of radioactive halides

Our work was aimed to determine iodine and chlorine radionuclides among halides.  $^{129}\text{I}$  and  $^{36}\text{Cl}$  are most frequently detected by  $\gamma$  and X-ray spectrometry. Conventional methods involve mass-spectrometry (ICP-MS, MS). LSC and neutron activation analysis (NAA) are scarcely used.

#### – Analysis by mass-spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) provides a very sensitive method for iodine determination, but in many countries these facilities are not available. Conventional thermally induced mass-spectrometry is usually not sensitive for the detec-

tion of trace levels of  $^{129}\text{I}$ . Higher sensitivity can be reached by the detection of the accumulated daughter  $^{129}\text{Xe}$  of  $^{129}\text{I}$ , a method used by Hertelendi [8] after 4-6 months cooling.

– Neutron activation analysis (NAA)

The nuclear reaction  $^{129}\text{I}(n, \gamma)^{130}\text{I}$  is used in neutron activation. The activated samples are measured by  $\gamma$ -spectrometry [8,13]. Extremely high sensitivity can be reached when iodine is concentrated and purified in course of pre- and post-irradiation separation processes.

Iodine can be extracted in  $\text{CCl}_4$  and back-extracted, followed by irradiation of the residue. The chemical yield can be determined by applying tracers, e.g.  $^{125}\text{I}$  [4] or  $^{131}\text{I}$  [14]. In post-irradiation chemical processing, authors preferably use solvent extraction with  $\text{CCl}_4$  [15,16] or chloroform [17] or precipitation as metal halides [7,15,18]. The chemical yield can be determined by gravimetry [17,18].

– Direct measuring techniques

Gamma-spectrometry and LSC were also used for  $^{129}\text{I}$  determination but sensitivities are the lowest among all the mentioned methods. To achieve acceptable efficiencies chemical processing cannot be avoided.

### 3 Experimental

#### 3.1 Initial preparation: pre-irradiation purification

For sample destruction an air flow-through installation was used with hot acidic leaching. The separation scheme is shown in *Figure 1*.

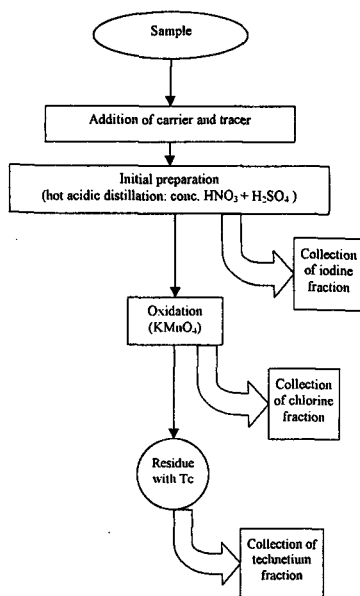


Fig. 1. Preliminary steps of sample destruction

The samples after the carrier or/and tracer addition were subject to hot acidic distillation (characteristic for  $^{129}\text{I}$ ) when the volatile iodine fraction was distilled from the original sample and organic components were destroyed. This step was realised by adding 150 mL  $\text{H}_2\text{SO}_4$  and 20 ml  $\text{HNO}_3$  in approximately 1-6 hours, depending on the complexity of the organic matrix. Iodine fraction was collected in a trap containing 3 M NaOH solution (approx. 60 mL). This solution was later used for the secondary purification of the iodine fraction.

After the separation of iodine the trap was replaced with a new one containing a solution with the same composition as before. An oxidation step with 0.01 M  $\text{KMnO}_4$  was used for the separation of the chlorine fraction [20].

The hot acidic residue was processed for the separation of the technetium fraction.

### 3.2 Secondary processing of iodine fraction

The distilled iodine fraction was extracted with  $\text{CCl}_4$  after oxidising it to  $\text{I}_2$  and back-extracted in aqueous solution by reduction with hydrazine.

Then the iodine fraction was carefully evaporated with LiOH without volatilisation. Samples were transferred into quartz ampoules and sealed.

After neutron activation the radioactive samples were subjected to post-irradiation treatment. The irradiated ampoules were opened carefully with a special tool without loss of iodine and residues were dissolved in 2 M NaOH. The alkaline fraction was newly extracted with  $\text{CCl}_4$  and the resulted organic fraction was analysed by  $\gamma$ -spectrometry.

The concentration of  $^{129}\text{I}$  was determined from 536 keV  $\gamma$ -peak of  $^{130}\text{I}$  produced by neutron capture, and the chemical yield was calculated from 388 keV  $\gamma$ -peak of  $^{126}\text{I}$  produced by  $^{127}\text{I}(\text{n}, 2\text{n})^{126}\text{I}$  reaction.

The scheme of secondary processing for iodine purification is presented in *Fig. 2*

### 3.3 Secondary processing of technetium fraction

The scheme of secondary processing for technetium is represented in *Fig. 3*.

First, the acidic distillation residue was diluted to 3 M acid concentration, extracted with TBP and back-extracted with 2 M NaOH solution. After neutralisation the aqueous solution was transferred to a TEVA Spec column and eluted with 8 M  $\text{HNO}_3$  solution. TEVA is the trade name of an extraction chromatographic material containing methyloctyldidecyl ammonium ion. The obtained acidic fraction was diluted with water and after addition of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  technetium was co-precipitated with 1 mL  $(\text{NH}_4)_2\text{S}$  as MnS + TcS mixture.

The filtered precipitate was counted both by  $\gamma$ -spectrometry to check the purity of the sample and liquid scintillation counter.

## 4 Results and discussion

The analytical procedure for the determination of  $^{129}\text{I}$  was tested by analysing a SRM (IAEA 375 soil) and comparing the method with another one developed at ATOMKI that is based on radiochemical separation of iodine followed by  $\gamma$ -spectrometry [21]. The comparison of data is presented in Table 1.

<b>Preliminary chemical processing</b>	
<ul style="list-style-type: none"> <li>• I<sub>2</sub> distillation, I<sup>-</sup> trapping in NaOH</li> <li>• Organic extraction with CCl<sub>4</sub></li> <li>• Iodine reduction with hydrazine and back-extraction in water</li> <li>• Iodide evaporation with LiOH <i>LiI LiOH</i> sealing in quartz ampoules</li> </ul>	$I^{-} + CCl_4 \xrightarrow{HNO_3, NaNO_2} I_2 / CCl_4$ $I_2 \xrightarrow{N_2H_5OH} I^{-}$
<b>Neutron activation analysis</b>	
<sup>129</sup> I (n, γ) <sup>130</sup> I, <sup>127</sup> I (n, 2n) <sup>126</sup> I $\phi \approx 10^{12} \text{ n/cm}^2 \text{ s}$ , $t_{ir} = 8 \text{ hour}$ , $t_c \approx 10 \text{ hour}$ $\phi \approx 10^{14} \text{ n/cm}^2 \text{ s}$ , $t_{ir} = 10 \text{ hour}$ , $t_c \approx 10 \text{ hour}$	
<b>Post irradiation processing</b>	
<ul style="list-style-type: none"> <li>• LiI dissolution</li> <li>• Iodine extraction with CCl<sub>4</sub></li> </ul>	$I^{-} \xrightarrow[NaNO_2]{HNO_3} I_2$
<b>γ-spectrometry</b>	
<sup>130</sup> I → <sup>129</sup> I <sup>126</sup> I → chemical yield calculation	

Fig. 2. Processing of iodine fraction

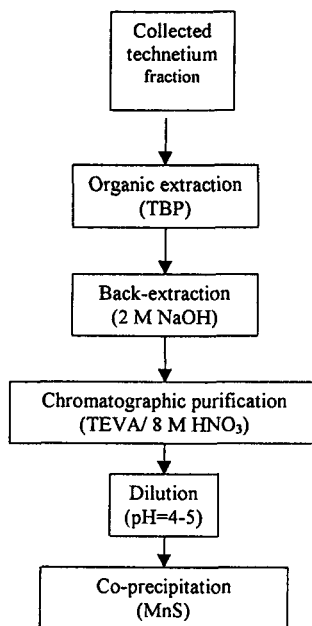


Fig. 3. Secondary processing of technetium fraction

Table 1. Intercomparison results of different type of samples and their provenience

Sample	INT-TUB		Intercomparison/reference data		
	Value [mBq/l] [mBq/kg]	Uncertainty [mBq/l] [mBq/kg]	Value [mBq/l] [mBq/kg]	Uncertainty [mBq/l] [mBq/kg]	Source
<b>Evaporation residue</b>					
ZS4	<b>64.3</b>	8.57	<b>71.9</b>	6.00	ATOMKI-gamma
ZS5	<b>13.92</b>	2.72	<b>29.3</b>	11.00	ATOMKI-gamma
<b>Ion exchange resin</b>					
ZSGY	<b>9630</b>	3032	<b>8780</b>	110	ATOMKI-gamma
ZSEEC	<b>17426</b> <b>11450</b>	1603	<b>&lt; 500000</b> <b>&lt; 9100000</b>		CEC intercomparison CEC intercomparison
<b>Environmental sample</b>					
IAEA 375	<b>3.24</b>	0.93	<b>1.70</b>	0.40	IAEA

Results obtained for  $^{129}\text{I}$  concentrations (at relatively high activity levels, i.e. in evaporation residue, ion exchange resins) agree with data obtained by the reference method (ATOMKI-gamma). The resin "ZSEEC" was used as reference material in an intercomparison exercise organised in the course of a European Commission Project CEC/PECO F 12W-0034-0109 on "Inventory and Characterisation of Important Radionuclides for Safety of Storage and Disposal" in 1995. No acceptable reference data were obtained for  $^{129}\text{I}$ , although reference values were established for several other radionuclides from the same matrix. Significant inhomogeneities are also expected in the resin what is revealed by our measurements. Slightly elevated environmental level of  $^{129}\text{I}$  was found in IAEA 375 soil. Our result is higher than the intercomparison data but the big uncertainty shows that the data is close to LD.

There is a lack of intercomparison exercises for  $^{99}\text{Tc}$  analysis, SRMs are not available thus there is no possibility to directly compare the obtained results. The technetium separation procedure was evaluated by measuring the chemical recoveries for each step of the procedure by model experiments that were performed with test samples spiked with  $^{99}\text{Tc}$ . The results obtained by these experiments can be seen in Table 2. The overall recovery was calculated by multiplying the intermediate chemical recovery values. This value was taken in consideration at calculation of the activity concentration.

The major part of technetium fraction is found in the distillation residue. It is not evaporated with halides during the boiling steps. The TEVA column is appropriate for

Table 2.  $^{99}\text{Tc}$  recoveries determined by model experiments with spiked samples

Separation step	Chemical recovery
Sample destruction	0.95
Extraction (TBP)	0.76
Back extraction (NaOH)	0.97
Chromatographic purification (TEVA Spec)	0.94
Co-precipitation (MnS) and LSC counting	0.78
Overall (Total)	$\Pi = 0.513$

Table 3. Measured activities in different types of samples during 2000-2001

Sample type	$^{129}\text{I}$ [mBq/l, mBq/kg]	Uncertainty	Yield of chemical process [-]
Evaporation residue			
ZS4	64.30	8.57	0.488
ZS5	13.92	2.72	0.253
ZS7	53.87	8.39	0.179
ZS8	101.28	12.80	0.427
Ion exchange resin			
ZSGY2	61747.34	4281.86	0.482
ZSCEC2	14361.47	1635.71	0.543
Environmental – Soil			
(IAEA 375)	3.24	0.93	0.609
Biological			
Thyroid	67.59	23.88	0.341

technetium purification. The convenient eluent is the 8 M  $\text{HNO}_3$  solution. The  $\gamma$ -spectra of MnS + TcS mixture evidenced the fact that the precipitate is contaminated with  $^{60}\text{Co}$  due to chemical similarities of cobalt and manganese as well as technetium. The decontamination factor for  $^{60}\text{Co}$  is in the range of  $10^4$ . In the LSC spectra, its contribution to the technetium region is calculated and corrected. The global yield of technetium measurement is estimated to be about 50%, which is considered to be good for a multistage method.

The developed method was applied for different types of samples and the results are shown in Table 3. The table contains data for evaporation residue, anion exchange resin used at NPP Paks (from 2000-2001), environmental sample (IAEA standard) and an animal thyroid as a biological sample. In the table the chemical yield of the global processing is also shown.

The activity concentrations measured for technetium in the used ion exchange resin together with the chemical yield for technetium are presented in Table 4.

## 5 Conclusions

Analysing the obtained results, the following conclusions could be drawn:

- The combined method for  $^{129}\text{I}$  and  $^{99}\text{Tc}$  is suitable for the simultaneous determination and separation of both nuclides from the same aliquot of sample. In the same time the chemical yield of the whole process is not reduced and the processing time is about 1-2 days.

Table 4. Activity concentration for technetium

Sample	$^{99}\text{Tc}$ [Bq/g]	Observation
MnS (red) CEC	12.9	e=51%, decont.fact.(Co)= 2.31E+4

- Intercomparison data (lack of data) show that measurement of these radionuclides is not easy and the evaluation of the method meets serious difficulties.
- Chemical recoveries for radioiodine were gradually increased during the years of method development due to the improved leaching, pre- and post-irradiation separation techniques and due to the adequate selection of reaction times. A major improvement was achieved by applying a mechanical tool to crash the ampoules in a closed system. Chemical recoveries for both nuclides were about 50%.
- It is evident that the method is adequate for determination of low levels of iodine (see environmental sample result). The detection limit for  $^{129}\text{I}$  by this method is between 2 and 100 mBq/L and mBq/kg, respectively. LD for  $^{99}\text{Tc}$  is about 0.1 Bq/g, in absence of  $^{60}\text{Co}$  contamination an LD of 0.05 Bq/g can be achieved.
- The sequential oxidation of halides from these samples did not lead to their separation; majority of chlorine is still located in the first trap (iodine fraction).
- Despite of the high decontamination factor, the LSC spectra of separated technetium showed the presence of  $^{60}\text{Co}$ . Applying NAA of  $^{99}\text{Tc}$  via  $^{100}\text{Tc}$  (instead of LSC) could eliminate the problem caused by  $^{60}\text{Co}$  interference and it would improve the sensitivity of the technique. This methodology is under development.

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