

## Complex Method of Determining the Specific Activity of $^{129}\text{I}$ , $^{99}\text{Tc}$ and $^{63}\text{Ni}$ in Natural Groundwaters

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**Abstract.** During 2014 as a stage of Bulgarian National Strategy for management of spent nuclear fuel and nuclear wastes until 2030, close to NPP “Kozloduy” on “Radiana” site, it was held groundbreaking ceremony for building of National Repository for Disposal of Radioactive Waste. The sitting has to be performed in four stages: “development of a conception for disposal and sitting plan”; “data collection and analysis of the regions”; “characterization of the site”; and “confirmation of the site”. According to first stage we develop a sequential procedure for determination of  $^{129}\text{I}$ ,  $^{99}\text{Tc}$  and  $^{63}\text{Ni}$  in groundwater sample matrix. It includes usage of ion-chromatography resins for separation and concentration of target radionuclides. The measurements of sample aliquots were performed by using of two different measurement techniques – liquid scintillation counting and ICP-MS. The provided analysis was fast and reliable according to evaluated data.

**Keywords:** radionuclides, nickel, technetium, iodine, ICP-MS

### 1 Introduction

In 2014, as part of the National strategy for management of spent nuclear fuel and radioactive waste by 2030, site “Radiana” (Figure 1), near the NPP “Kozloduy”, was made the first sod for construction of National Radioactive Waste Repository (NRWR. As part of the initial stage, should be made an environmental impact assessment (EIA) and its preparation is required prior determination of radionuclides  $^{129}\text{I}$ ,  $^{99}\text{Tc}$  and  $^{63}\text{Ni}$  in samples from underground natural water taken from the site “Radiana” south of NPP “Kozloduy”. For this purpose in Laboratory “Radioanalyt-

ical methods” to INRNE BAS were delivered water samples from drilling wells of groundwater from the site.

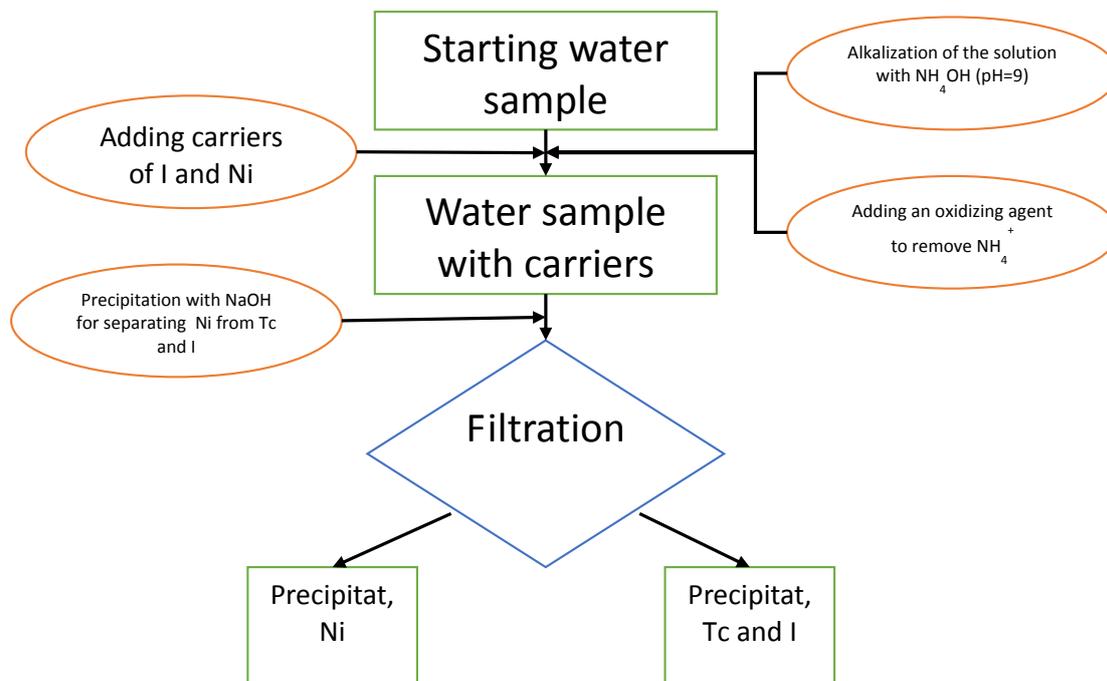
For the realization of the task - analysis of target radionuclides - was developed complex process relying on global experience in performing of such analyzes.

### 2 Summary of the Method

To an aliquot of the sample was added a stable isotopes of Ni (as nitrate) and I (from a solution of KI). Samples were basified with  $\text{NH}_4\text{OH}$  to about  $\text{pH} = 9$  – is preferred aqueous ammonia then NaOH alkalization because in that



Figure 1. Scheme of the location of the site “Radiana” and the future “NRWR”.

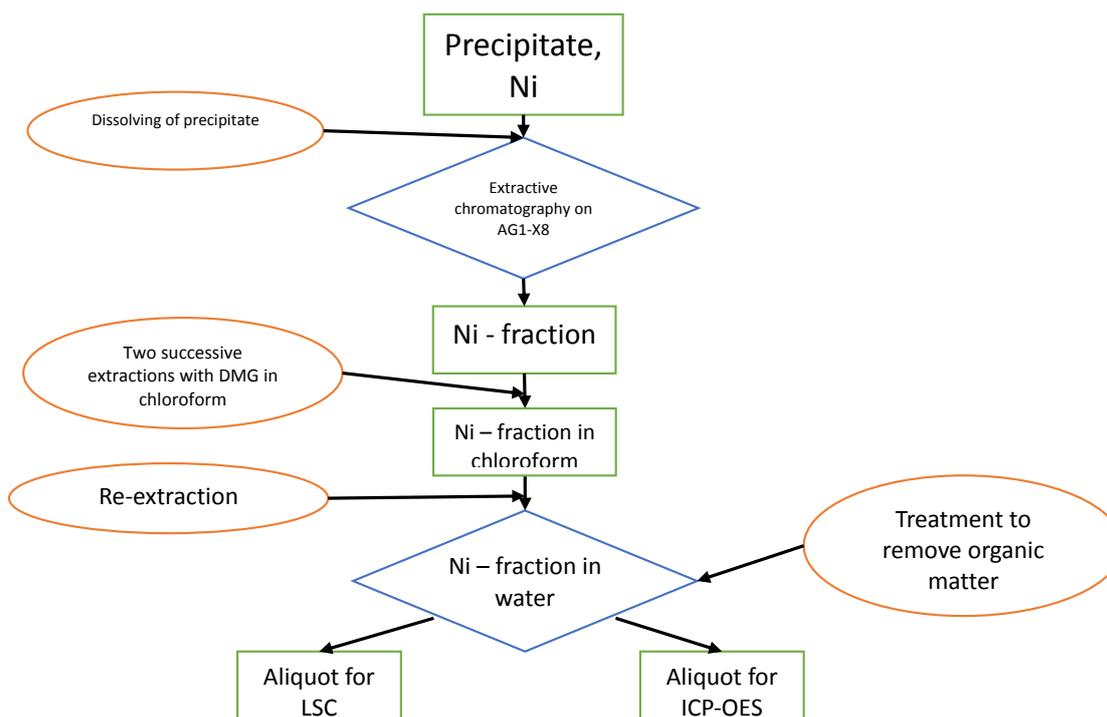


Scheme 1. First stage of preparation and separation of nickel from technetium and iodine.

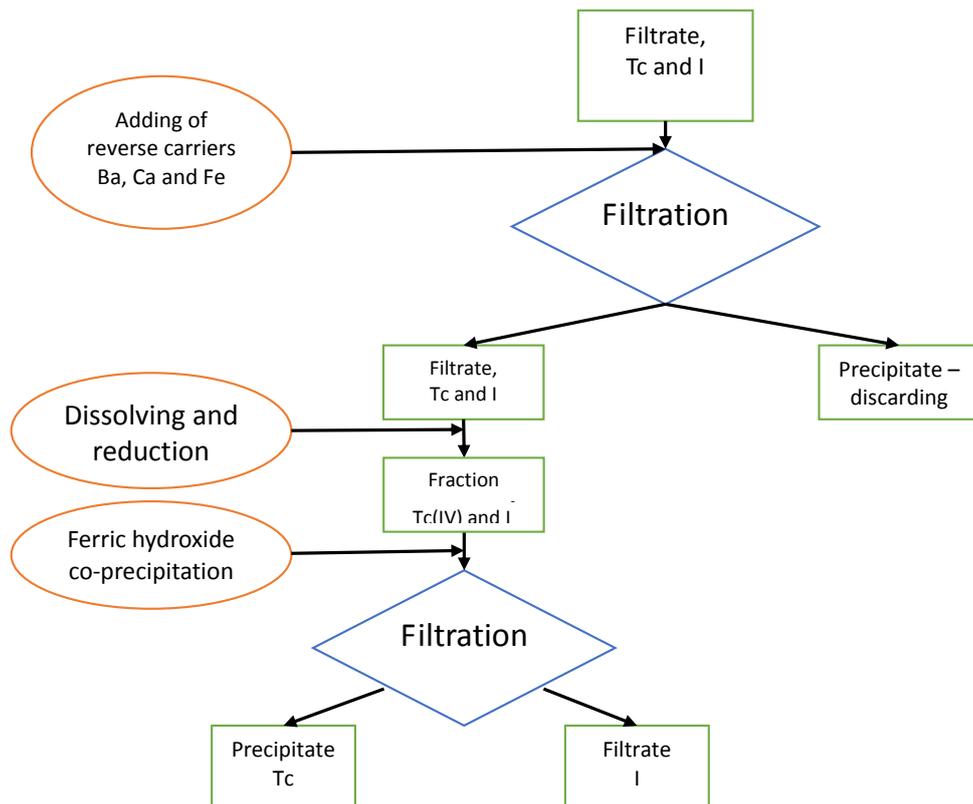
way there is large extent the reduction of the various forms of iodine in the sample (iodides, hypiodide, iodates, periodates, iodine associates and organically bound iodine) to iodide. Nickel will be present in the sample as a complex ion –  $\text{Ni}(\text{NH}_3)_6^{2+}$  and will not precipitate. Samples were treated for the removal of ammonium ions in the presence of oxidizing agent to store technetium to technetate and iodine as iodate.

Nickel is precipitated with sodium hydroxide as a hydroxide, wherein the iodate and technetate remain in the solution above the precipitate.

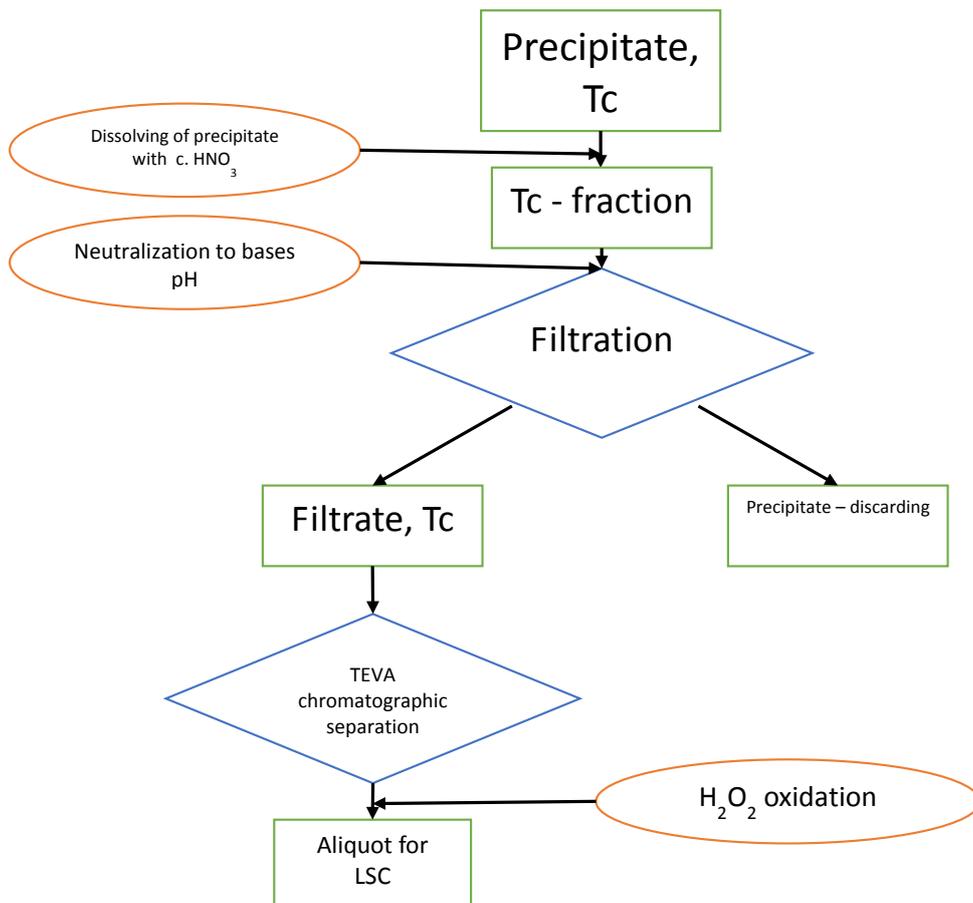
The precipitate of nickel was dissolved in acid and purified by an extraction – chromatography from interfering beta radionuclides by applying anion – exchange resin AG1X8, 100–200 mesh, chloride form.



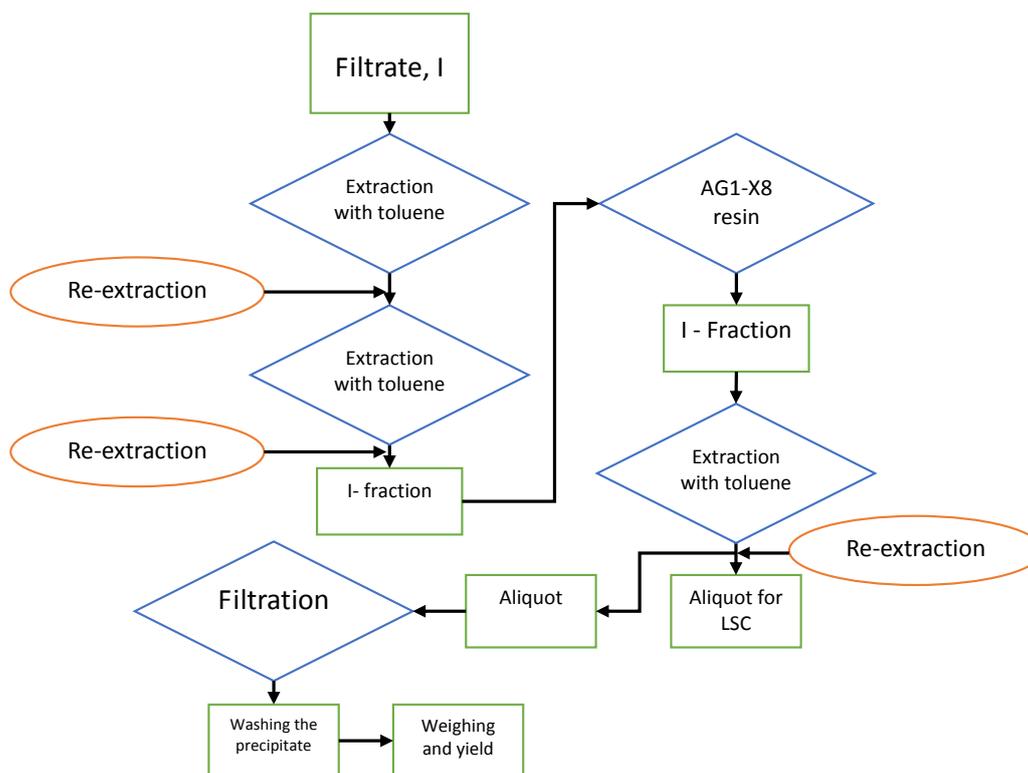
Scheme 2. Stage of preparation of nickel for measurement.



Scheme 3. Stage of separating technetium from iodine.



Scheme 4. Stage of preparation of technetium to measurement.



Scheme 5. Stage of preparation of iodine measurement.

Nickel fraction is purified and concentrated by two successive extractions with dimethylglyoxime (DMG) in chloroform. Re-extraction of nickel and the resulting aqueous phase is treated to remove traces of organics. A suitable aliquot of the sample is mixed with liquid scintillation cocktail, and was measured on a liquid scintillation.

To determine the effectiveness of the liquid scintillation spectrometer is prepared secondary calibration sources of certified reference source with known activity of  $^{63}\text{Ni}$ .

Another aliquot was taken for establishing radiochemical yield by measuring in inductively coupled plasma – optical emission spectrometry (ICP-OES).

To the solution containing technetate and iodate are added inverse carriers Ba, Ca and Fe and co-precipitation the interfering metals. The precipitate was collected and technetate and iodine forms from liquid above the precipitate are reduced accordingly to Tc [IV] and I. Follows a step of separating technetium from iodine by co-precipitation of the technetium with the ferric hydroxide, wherein the iodide remains in the solution.

After oxidation of Tc (IV) from the precipitate to Tc [VII] with concentrated  $\text{HNO}_3$ , the solution is carefully neutralized and the fallen alkaline sludge is removed as radioactive waste.

Final Tc-fraction is separated again with highly specific extraction chromatographic resin type TEVA-Spec®. Eluted from the chromatography column technetate is oxidized in the presence of  $\text{H}_2\text{O}_2$ , mixed with scintillation cocktail and measuring in liquid scintillation.

Iodate in the solution is reduced to elemental iodine and extracted in toluene. The extraction of iodine allows a high degree of separation of a very large part of the elements and isotopes present in the matrix except the halides (especially  $\text{Cl}^-$  and  $\text{Br}^-$ , which are interfering for determining the chemical yield of the procedure). The extraction of iodine followed by re-extraction. Re-extracted iodine is purified by anion exchange. Second extraction for further purification and concentration after controlled oxidation to elemental iodine eluted from the column iodide. The extracted elementary iodine is re-extracted once again as iodide. Aliquot is divided quantitatively into two parts – one is for determined of weight yield, the iodide is precipitated as AgI, but along with it there are precipitated chlorides and bromides of the silver.

The lower solubility of AgI enables purification of the precipitate of AgI by sequentially and repeatedly treated with ammonia water and ethyl alcohol (see Table 1).

Table 1. Solubility of chlorides, bromides and iodides of silver

Salt	Solubility
AgCl	$1.6 \times 10^{-10}$
AgBr	$5.0 \times 10^{-13}$
AgI	$1.5 \times 10^{-16}$

The other part of the aliquot is quantitatively transferred to pre-weighed scintillation vial, mixed with scintillator UG LLT and is measured by LSC (maximum energy of  $\beta$ -spectrum 154 keV, average energy – 40.9 keV) with appropriate standards and "empty" (white) sample.

### 3 An Alternative Method for Measurement of TC and I

Because of the long half-life of the nuclides  $^{129}\text{I}$  ( $1.57 \times 10^7$  years) and  $^{99}\text{Tc}$  ( $2.15 \times 10^5$  years) can be defined their mass concentration in aliquot by mass spectrometry with inductively coupled plasma (ICP-MS), and by the law of radioactive decay can recalculate their specific activity.

The apparatus used is model VARIAN 820-MS with quadrupole mass-spectrometer and fully digital detector with high concentration range, including innovative CRI-interface to remove polyatomic interferences.

This method is subject of standard EPA 200.8.

The use of two independent methods will result the verifying of the whole procedure and results.

Inductively coupled plasm – mass-spectrometry (ICP-MS) as a method of reaching levels 10–6 g/L of the desired elements – this will allow to guarantee the authenticity of MDL for levels corresponding to the environment. As regards of definition of the above radionuclides, laboratory use external standards, and for concentration calibration of apparatus are prepared a multi-element standard solutions from Merck®.

The conditions under which will be carried out specific measurements:

Index	Value
Plasma flow	16.00 L/min Ar
Auxiliary flow	2.00 L/min Ar
Sheath Gas flow	0.20 L/min Ar
Nebulizer flow	1.00 L/min Ar
Sampling depth	6.50 mm
Power	1.35 kW
Pump rate	5 rpm
Spray chamber temperature	3.00°C
Replicate time	21.03 sec
Scan time	1052 msec
Nebulizer	Cross flow – Scot type nebulizer
Skimmer and sampler cones	Ni – cones

### 4 Conclusion

The procedure presented for analysis of  $^{129}\text{I}$ ,  $^{63}\text{Ni}$  and  $^{99}\text{Tc}$  will be verified by two independent methods, leading to

proof of its accuracy and reproducibility.

The results obtained are essential for determining environmental impact assessment (EIA), which in itself is a necessary for the realization of the project for the construction of a National Radioactive Waste Repository (NRWR). This is one of the commitments of the Bulgarian government to the European Commission.

So established procedure can be used for continuous monitoring of the environment in the controlled area of future NRWR.

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