# EXPERIENCES IN THE RADIOCHEMICAL ANALYSIS OF THE PRIMARY COOLANT OF WWER TYPE NPPs USING INORGANIC ION EXCHANGERS

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## Summary

A simple and fast chromatographic separation procedure based on zirconium-phosphate has been developed to remove the matrix activities of $^{42}K$, $^{24}Na$ and $^{18}F$ from the primary coolant of WWER type NPPs* thus allowing the radiochemical $\gamma$-spectrometric analysis of the majority of fission products ($^{131}I$, $^{132}I$, $^{133}I$, $^{134}I$, $^{135}I$, $^{134}Cs$, $^{136}Cs$, $^{137}Cs$, $^{86}Rb$) within a couple of hours after sampling.

## Introduction

From the results of monitoring the radiochemical concentrations of the primary coolant conclusions can be drawn on the chemical and corrosion state of the construction materials, and the hermeticity of the fuel elements.

Radiochemical concentration measurements in permanent use at the WWER type NPPs are based on instrumental $\gamma$-spectrometry combined with certain radiochemical group separations. At the time of sampling the radioactivity of the primary coolant can be attributed to $^{42}K$, $^{24}Na$ and $^{18}F$ masking the $\gamma$-spectra of the majority of radioactive isotopes. Owing to the 12- and 15-hour-long half lives of $^{42}K$ and $^{24}Na$, respectively radiochemical concentrations can be determined by means of a direct instrumental method only after a cooling time of 4–5 days loosing all information on the isotopes with half-lives shorter than 10 hours. The routinely used method which analyses some radioactive isotopes of special interest in order to monitor the primary circuit conditions includes the following radiochemical group separations which can be carried out in some hours:
— iodine separation based on solvent extraction or isotope exchange;
— cesium–rubidium separation based on isotope exchange;
— strontium–barium separation based on isotope exchange and precipitation;

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— separation of corrosion products by filtering the floating particles with a membrane filter of pore size 0.45 μm.

A simple and fast radiochemical separation procedure applicable in an automated processor has been looked for to remove matrix activities of [42]K and [24]Na (perhaps that of ^{18}F, too) selectively shortening the time of analysis and offering information on radioactive isotopes of short half-lives as well. For such purposes inorganic ion exchangers are favoured because of their resistance to irradiation and their special characteristics in terms of selectivity.

The radiochemical separation procedure successfully applied to remove [24]Na and [42]K matrix activities from biological samples in neutron activation analysis has been adapted. In strong acid media hydrated antimony pentoxide (HAP) proved to be a selective sorbent for sodium and titanium-phosphate (TP) is said to be a selective sorbent for potassium [1]. Acidifying the primary coolant sample with concentrated HCl to at least $6M/dm^3$ then passing the solution through a column filled with HAP and TP, potassium and sodium are assumed to remain on the column and the effluent must contain all elements of interest.

The other investigated procedure is based on amorphous zirconium-phosphate, an inorganic sorbent, well-known for its high capacity towards the majority of mono-, di-, tri- and tetravalent cations in neutral solutions. Sodium and potassium ions are at the very end of the selectivity row thus allowing their selective removal by a properly chosen eluent [2]. The separation procedure consists of passing the neutral primary coolant sample through a column filled with amorphous zirconium-phosphate. The effluent will contain all the anions. Sodium and potassium are to be eluted, the sorbent free of the matrix activities can be dissolved and analysed by $\gamma$-spectrometry.

## Experimental

HAP is prepared and characterized according to reference [3]. TP is prepared and characterized according to reference [4]. ZP is prepared and characterized according to reference [5].

Radiochemical separation based on using HAP and TP sorbents: 250 $cm^3$ of primary coolant (containing carriers of the most important fission products) is added to a distillation flask, heated to refluxing, 10 $cm^3$ of cc. $HNO_3$ and 30% $H_2O_2$ respectively, are added. The oxidizing procedure is repeated in half an hour. The total time of refluxing is one hour. After cooling 250 $cm^3$ of cc. HCl is given to the solution which is passed through a column filled with 3 g of HAP and 3 g of TP (both of particle size of 0.25–0.50 mm) at a flow rate of about 5 $cm^3/min$. The effluent is collected in a measuring vessel of 500 $cm^3$ and measured by $\gamma$-spectrometry. During heating the volatile elements

## Table 1

### Comparative evaluation of radioactive concentrations in the primary coolant

| Radioactive isotope | Half life (hour) | Radioactive concentrations of the primary coolant at the time of sampling (Bq/dm$^3$) | | Standard group separations applied to monitor water chemistry | |
| --- | --- | --- | --- | --- | --- |
| | | Separation using HAP and TP sorbents cooling time = 8 h | Direct instrumental analysis cooling time = 5 h | Iodine fraction cooling time = 1 h | filtrate after prolonged cooling cooling time = 167 h |
| $^{42}$K | 12.4 | 188 600 | 1 640 200 | | |
| $^{24}$Na | 15.0 | | 247 800 | | 195 000 |
| $^{18}$F | 1.9 | | 525 000 | | |
| $^{131}$I | 192 | 160 | | 675 | 788 |
| $^{132}$I | 2.3 | | 13 300 | 17 200 | |
| $^{133}$I | 20.9 | 2 360 | 9 060 | 9 300 | 9 440 |
| $^{134}$I | 0.9 | | | 29 400 | |
| $^{135}$I | 6.6 | 4 200 | | 21 700 | |
| $^{133}$Xe | 126 | | | | 1 170 |
| $^{135}$Xe | 9.1 | | 11 100 | | |
| $^{99}$Mo | 66 | 1 390 | | | 1 700 |
| $^{187}$W | 23.7 | 3 430 | 24 900 | | 19 800 |
| $^{54}$Mn | 7500 | 230 | | | 106 |
| $^{134}$Cs | 2 years | | | | 83 |
| $^{136}$Cs | 3240 | | | | 26 |
| $^{137}$Cs | 30 years | | | | |
| $^{86}$Rb | 445 | | | | 740 |
| $^{110m}$Ag | 6050 | | | | 55 |
| $^{7}$Be | 1300 | | | | 2 170 |
| $^{140}$La | 40 | | | | 392 |

# Table 2

Comparative evaluation of radioactive concentrations in the primary coolant

| Radioactive isotope | Half life (hour) | Radioactive concentrations of the primary coolant at the time of sampling (Bq/dm$^3$) | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | Separation using amorphous zirconium-phosphate | | Direct instrumental analysis cooling time = 8 h | Standard group separations applied to monitor water chemistry | | |
| | | Primary coolant effluent cooling time = 2 h | Dissolved sorbent cooling time = 9 h | | Iodine fraction cooling time = 0.8 h | Cesium-rubidium fraction cooling time = 0.5 h | Filtrate after prolonged cooling cooling time = 143 h |
| $^{42}$K | 12.1 | | 30 400 | 1 401 900 | | | |
| $^{24}$Na | 15.0 | | | 236 900 | | | 68 800 |
| $^{18}$F | 1.9 | | 111 500 | 456 500 | | | |
| $^{131}$I | 192 | 560 | | | 598 | | 570 |
| $^{132}$I | 2.3 | 14 300 | | 16 600 | 15 000 | | 2 970 |
| $^{133}$I | 20.9 | 7 270 | | 6 700 | 6 600 | | |
| $^{134}$I | 0.9 | 14 220 | | | 15 800 | | |
| $^{135}$I | 6.6 | 12 600 | | 12 260 | 14 700 | | |
| $^{133}$Xe | 126 | | | | | | 755 |
| $^{135}$Xe | 9.1 | 3 960 | | 7 550 | | | |
| $^{99}$Mo | 66 | 28 | 16 | 780 | | | 1 020 |
| $^{187}$W | 23.7 | | 16 950 | 17 400 | | | 12 600 |
| $^{54}$Mn | 7500 | | | 65 | | | 121 |
| $^{134}$Cs | 2 years | | 110 | | | | 115 |
| $^{136}$Cs | 3240 | | 25 | | | | |
| $^{137}$Cs | 30 years | | 19 | | | | |
| $^{138}$Cs | 0.5 | | | | | 20 600 | |
| $^{86}$Rb | 445 | | 400 | | | | 958 |
| $^{89}$Rb | 0.2 | | | | | 2 020 | |
| $^{97}$Zr | 16.9 | | 24 | | | | 99 |
| $^{140}$Ba | 307 | | 101 | | | | |
| $^{110m}$Ag | 6050 | | + | | | | + |
| $^{7}$Be | 1300 | | | | | | + |

are collected in a vessel containing 2 M KOH and 2 M KI, this fraction can be measured, too.

Radiochemical separation based on using ZP sorbent:

$1000$ cm$^3$ of the primary coolant (containing the carriers) is passed through a column filled with 2 g of ZP (particle size 0.25–0.50 mm) at a flow rate of 5 cm$^3$/min 100 cm$^3$ of the effluent is directly measured. Sodium and potassium ions are eluted with 500 cm$^3$ of 0.05 M HCl at a flow rate of 15 cm$^3$/min ZP is dissolved in 10 cm$^3$ of $H_2F_2$ prior to $\gamma$-spectrometric analysis.

$\gamma$-spectrometry:

$\gamma$-spectra were taken with Ge(Li) semiconductor detector system (energy resolution 3.5 keV; efficiency 7%) and a 4k MCA, data were evaluated by an on-line HP 9825/A desk-top calculator. Measuring time varied between 300–2000 s, cooling times are listed in tables 1–2. Radioactive concentrations were calculated in Bq/dm$^3$ units referring to the time of sampling.

## Results, discussion

The radioactive concentrations of the isotopes in an experimental run for each separation procedure are given in Tables 1 and 2. Data obtained by radiochemical separations using inorganic sorbents can be compared both with the results of the direct instrumental $\gamma$-spectrometry without any separation after some hour-long cooling and with those obtained by standard group separations either after short cooling or prolonged cooling.

### Separation using HAP and TP sorbents

The selective removal of sodium and potassium matrix activities by the combination of HAP and TP, successfully applied to radiochemical neutron activation analysis for the determination of Cu, Zn, Mn, Co, Mo traces, proved to be insufficient for the analysis of the primary coolant of WWER type reactors (see Table 1).

The activity of $^{24}$Na can be reduced by three orders of magnitude, that of $^{42}$K only by one order of magnitude. The capacity of TP to retain potassium is low in 6 M HCl; namely approximately 1 mg/g sorbent. The concentration of potassium can reach the 20 mg/dm$^3$ value as a maximum in the primary coolant requiring 4–5 g of TP for each separation.

The selectivity of HAP and TP in 6 M acid media is not sufficient. Analyzing the sorbents HAP turned out to retain W and Rb, TP sorbed Cs ions. Increasing the acidity of the solution — presumably improving the selectivities — the capacities would still decrease.

The analysis of the iodine isotopes can be carried out by measuring both the effluent and the fraction containing the volatile compounds. The more agressive the conditions of oxidation are the greater losses of the volatile elements can occur. On the other hand oxidation is needed to dissolve colloid or floating particles to pass them through the sorption columns into the measuring vessel and to assure the highest and uniform valency states of the radionuclides. ([54]Mn could be detected in the effluent only after oxidation to manganate anion.)

### Separation using ZP sorbent

The separation procedure based on ZP seems promising (see Table 2). The main advantages can be summarized as follows:
— The capacity of ZP in neutral medium is relatively high, about 0.8 mequ/g (salt splitting capacity in distilled water). Passing 1 dm$^3$ of the primary coolant (the concentration of K$^+$ was 3.1 mg/dm$^3$) through a column of ZP of 2 g the radioactivities of [42]K and [24]Na were at background level (Table 2).
— Even fluorine is retained on ZP forming Zr–F complexes.
— The effluent contains the anions and the noble gases. All radioactive nuclides of iodine can be analysed quantitatively in this fraction free of [42]K, [24]Na and ^{18}F in a very short time: A fraction of 100 cm$^3$ can be collected during 20 minutes. It is superfluous to enrich iodine isotopes.
— Eluting with 0.05 M HCl sodium can be removed from the sorbent. The potassium elution is partially selective, about 5% of [42]K remains on ZP. The selectivity for cesium is complete, but that for rubidium is far from excellent. Analysing the eluent fraction about 50% of ^{86}Rb was found in the solution and only the other half of it was retained on the sorbent.
— Cations can be enriched on the sorbent by two orders of magnitude: 1 dm$^3$ of the primary coolant is passed through the ZP column, which is dissolved in 10 cm$^3$ of $H_2F_2$ finally.
— Good measuring geometry can be assured by dissolving the sorbent.
— High flow rates of 5–15 cm$^3$/min can be allowed during both flowing processes.
— Making use of the selectivity of ZP a special fission product analysis can be developed (iodine, cesium, rubidium, barium nuclides).

The main drawbacks of this separation procedure are the incomplete potassium — rubidium separation, and the difficulties to remove fluorine from the sorbent. Some ions are eluted even with 0.05 M HCl, for example La and Be.

According to the results of the separation experiments based on inorganic ion exchangers it could be established that HAP combined with TP can be used only with restrictions for the fast radiochemical analysis of the primary coolant of WWER type reactors while separation processes based on ZP are promising.

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