Procedure for determining the activity concentration of radium-228 in drinking water and ground water

H-Ra-228-TWASS-01

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1 Scope

This procedure is suitable for the determination of the activity concentration of Ra-228 in drinking water, but also in other waters such as ground, mineral or spring water with salt concentrations to about 2,5 g · l⁻¹ and barium concentrations of less than 1 mg · l⁻¹. A reduced yield must be expected in waters with higher salt loads as a result of incomplete radium enrichment.

Achievable detection limits range between 1,5 mBq · l⁻¹ and 2 mBq · l⁻¹ for a sample volume of 10 litres when the standard parameters of the procedure are properly applied.

2 Sampling

The general requirements for representative sampling and sampling techniques according to DIN Standard 38402 Parts 13 and 14 (1, 2) have to be complied with. In this conjunction, reference is also made to H-VORBEMERK-TWASS-01 and procedure H-γ-SPEKT-TWASS-01.

3 Analysis

3.1 Principle of the procedure

In analogy to (3), this procedure is based on the enrichment of radium and actinium through co-precipitation with barium sulphate, the conversion of the sulphate into a more easily soluble carbonate, a separation of actinium by means of extraction-chromatography, the micro-precipitation of actinium with cerium fluoride, and the measurement of the beta radiation of the short-lived Ac-228 with its half-life of 6 hours immediately thereafter. The chemical yield of the radium separation is determined with the aid of the carrier element barium, e. g., by using atom-absorption spectrometry. The sequence of the analytic steps is illustrated in Figure 1.

3.2 Sample preparation

In order to handle a 10 l-sample in the laboratory, its volume is either reduced through evaporation or split into four aliquots that will be combined again later in the analytic process.
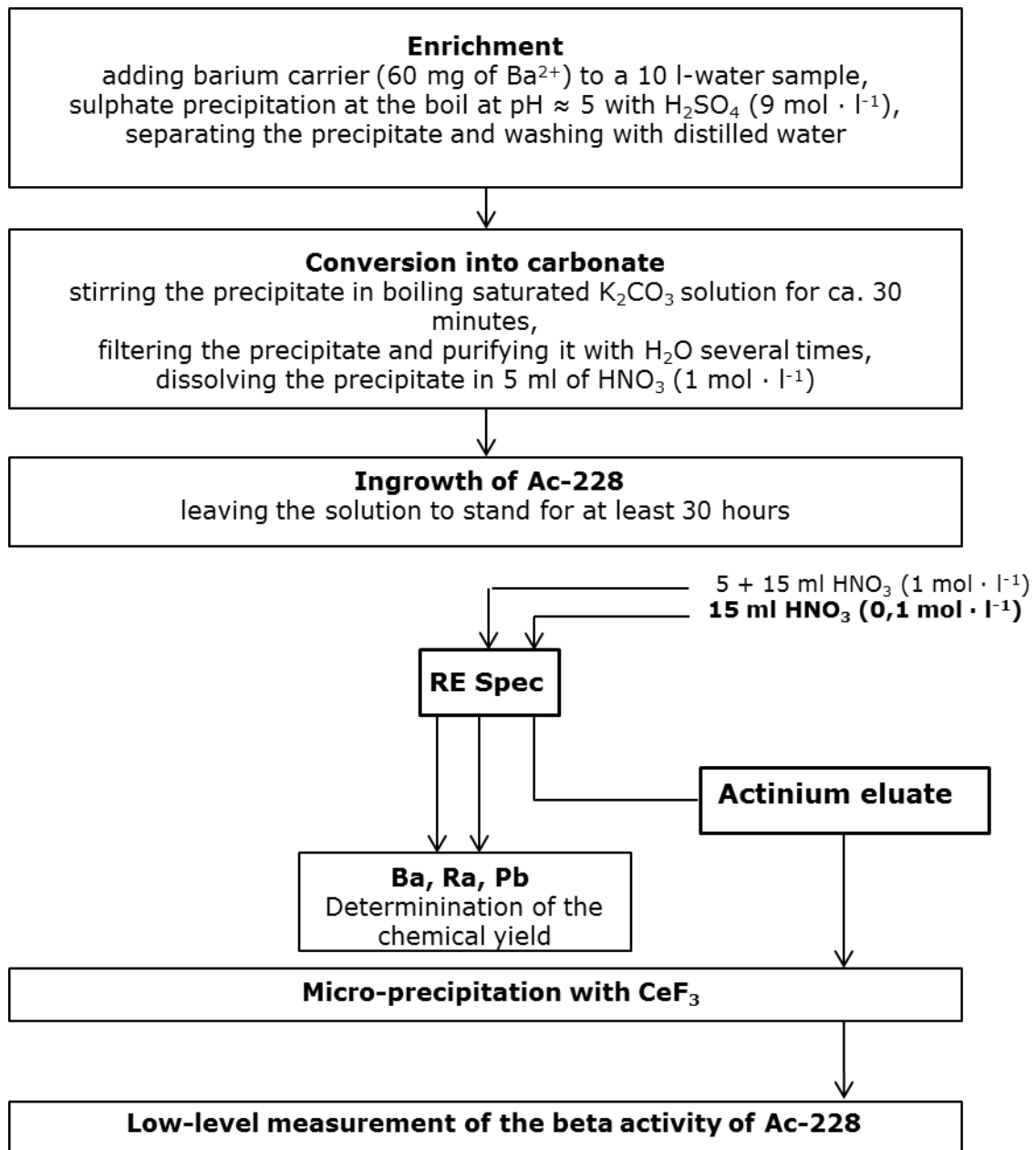
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Enrichment
adding barium carrier (60 mg of Ba^{2+}) to a 10 l-water sample,
sulphate precipitation at the boil at pH ≈ 5 with H$_2$SO$_4$ (9 mol · l^{-1}),
separating the precipitate and washing with distilled water

Conversion into carbonate
stirring the precipitate in boiling saturated K$_2$CO$_3$ solution for ca. 30 minutes,
filtering the precipitate and purifying it with H$_2$O several times,
dissolving the precipitate in 5 ml of HNO$_3$ (1 mol · l^{-1})

Ingrowth of Ac-228
leaving the solution to stand for at least 30 hours

5 + 15 ml HNO$_3$ (1 mol · l^{-1})
15 ml HNO$_3$ (0,1 mol · l^{-1})

RE Spec

Actinium eluate

Ba, Ra, Pb
Determinination of the chemical yield

Micro-precipitation with CeF$_3$

Low-level measurement of the beta activity of Ac-228

Fig. 1: Overview of the procedure for the determination of the activity concentration of Ra-228 in drinking water

3.3 Radiochemical separation

3.3.1 5 ml of citric acid (1 mol·l^{-1}) and a few drops of methyl red solution are added to each of the four 2,5 l partial samples in a 3 l-beaker or to the concentrate of the whole sample after evaporation, respectively. After adding 0,5 ml of barium carrier solution to each of the four partial samples or 2 ml to the concentrated solution (corresponding to 60 mg of barium to the whole sample), respectively, concentrated ammoniac solution (13 mol·l^{-1}) is added until the colour of the indicator turns to yellow. The solution is heated to boiling, and barium sulphate is then precipitated by adding ca. 3 ml of diluted sulphuric acid (9 mol·l^{-1}). Once the precipitate has completely sedimented, the clear supernatant is decanted and discarded.

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3.3.2   The precipitate and the remaining solution that could not be decanted without loss of precipitate are transferred to a filtering device where the remaining solution can be sucked off in a vacuum. The partial samples are combined again at this stage by using <u>one</u> filter for all four partial samples. The sulphate precipitate is washed with distilled water several times, then transferred together with the filter to a 50 ml-beaker, submerged under ca. 20 ml of distilled water. After adding ca. 700 mg of potassium carbonate, it is covered with a watch glass, heated to boiling, and stirred for ca. 30 minutes while maintaining the heat.

3.3.3   After the filter is rinsed it will be removed and vacuum filtration is applied on the carbonate precipitate and its supernatant solution. Washing with distilled water is continued until the pH of the wash water becomes neutral. The carbonate precipitate is dissolved in 5 ml of nitric acid (1 mol·l^{-1}) (point of time t_1) and left to stand for a minimum of 30 hours to facilitate the ingrowth of Ac-228.

3.3.4   For the subsequent extraction-chromatography, an RE resin column with a column bed volume of 2 ml and 0,7 g of a specific resin for the isolation of rare earth elements charged with CMPO (octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide) dissolved in TBP (tributyl phosphate)is employed. It is preconditioned with 5 ml of nitric acid (1 mol·l^{-1}). The run-off is discarded. For collecting the resultant solutions, a 50 ml-volumetric flask is placed under the drain of the column and the radium-charged solution is applied. The beaker is flushed with 5 ml of nitric acid (1 mol·l^{-1}) and the flush water added to the column as well (point of time t_2). Thereafter, remaining barium, radium and lead ions are washed out with 15 ml of nitric acid (1 mol·l^{-1}). The volumetric flask is filled to the calibration mark with distilled water and the solution is used for the determination of the chemical yield.

3.3.5   The actinium ions are eluted from the column with 15 ml of nitric acid (0,1 mol · l^{-1}).

3.3.6   Following the addition of 0,2 ml of cerium carrier (200 µg of cerium) and 1 ml of hydrofluoric acid 40 % (23 mol·l^{-1}) to the eluate, the solution is stirred at room temperature for 30 minutes. The formation of precipitates during the micro precipitating process will not be observable and the solution will remain clear. It is filtered through an acid-resistant membrane filter with a pore size of 0,1 µm using vacuum suction. The fluoride precipitate is washed with distilled water and dried by rinsing it with acetone. Using double sided adhesive tape, the dried filter is affixed to a labelled steel disc and its activity measured immediately (point of time t_3).

4   Measuring the activity

4.1   Principle of the procedure

The beta activity of the Ac-228 is measured in a low-level anti-coincidence gas-flow counter. The measurement employs the same geometric arrangement that was previously used for calibration purposes.

Note
Owing to the short half-life of Ac-228, measuring has to start right after the counting source has been prepared. Every delay prior to the start of the measurement will cause the achievable detection limit to rise; just one hour of delay will increase the latter by ca. 15 %.

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Checking the chemical yield by adding Ba-133 tracer, as has been described in (3), is not recommended, because the comparatively high Ba-133 activities that would need to be added for additional gamma-spectrometric measurement have a potential of interfering with the low-level beta measurement if barium and actinium are incompletely separated. After the Ac-228 has decayed, each counting source needs to be measured again for the determination of the background effect.

4.2 Calibration

Calibrating the measuring station needs to make use of drip-on calibration sources with known Sr-89 activities because calibration sources of Ac-228 are unavailable and the two radionuclides have comparable mean beta energies. A value typical of the calibration factor is 2,0 Bq·s

4.3 Measurement

The count rates are measured at intervals of 60 minutes over a period of at least 500 minutes. The mean value derived from the individual measurements is then used for calculating the activity, after eliminating obvious outliers if necessary. In order to exclude the possibility of contamination of the counting sources with, e. g., Pb-210 or Th-234, the decay curves of the measured activity are subjected to spot-checks. Figure 2 illustrates this, using a sample of mineral water as an example.

Possibly present Ac-227 does not interfere with the measurement, because the beta radiation of Ac-227 ($E_{\beta max}$ = 40 keV) is measured only with a detection efficiency of 1,5 % as opposed to the high-energy beta radiation of Ac-228 ($E_{\beta max}$ = 2100 keV).
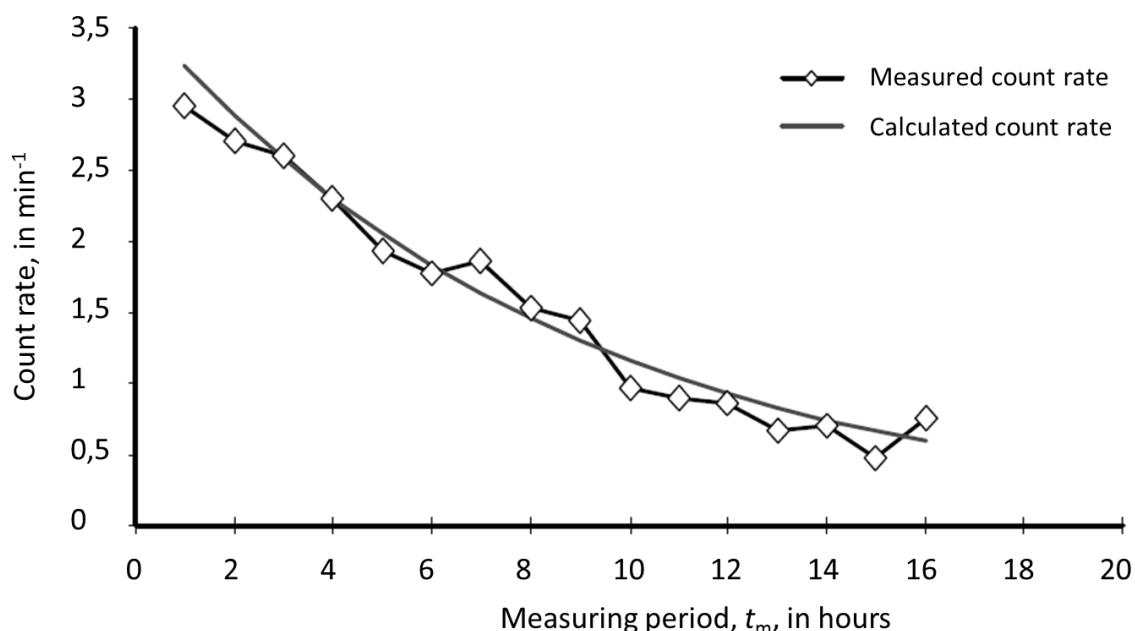

Fig. 2: Decay curve of the actinium counting source extracted from a sample of mineral water

5 Calculation of the results

5.1 Equations

The activity concentration of Ra-228 is calculated according to equation (1):

$$c = \frac{\varphi_A \cdot (R_g - R_0)}{V \cdot \eta} \cdot \frac{\lambda_r \cdot t_m}{1 - e^{(-\lambda_r \cdot t_m)}} \cdot \frac{e^{\lambda_r \cdot (t_3 - t_2)}}{1 - e^{-\lambda_r (t_2 - t_1)}} \tag{1}$$

where

c activity concentration of Ra-228, in Bq·l^{-1};
R_g gross count rate of the counting source, in s^{-1};
R_0 background count rate, in s^{-1};
V volume of the sample, in l;
φ_A calibration factor for the respective measuring chamber, in Bq·s;
η chemical yield;
λ_r decay constant of Ac-228, in s^{-1};
$t_2 - t_1$ the period of time for the ingrowth of Ac-228, in s,
      where: t_1 dissolution of the carbonate;
              t_2 start of the elution of the Ac-fraction;
$t_3 - t_2$ period of time for the decay of Ac-228, in s;
      where: t_3 start of the beta measurement;
t_m duration of measurement, in s.

Note
If the water samples are stored for more than 3 months, the decay of the Ra-228, which is not in radioactive equilibrium with Th-232, needs to be taken into consideration and equation (1) completed accordingly. About 3 % of the original Ra-228 activity will have been decayed after 3 months.

The chemical yield, η, is obtained according to equation (2):

$$\eta = \frac{m_E}{m_P} \tag{2}$$

in which the following factors are introduced in addition to the variables already defined:

m_E mass of the element barium in the Ba(Ra)-eluate, in mg;
m_P mass of the barium added to the sample as a carrier, in mg.

The relative standard deviation of the activity concentration is calculated according to equation (3), and the relative standard deviation of the net count rate according to equation (4):

$$\frac{s(c)}{c} = \sqrt{\left(\frac{s(R_n)}{R_n}\right)^2 + \left(\frac{s(\varphi_A)}{\varphi_A}\right)^2 + \left(\frac{s(\eta)}{\eta}\right)^2} \tag{3}$$

$$\frac{s(R_n)}{R_n} = \frac{1}{R_n} \cdot \sqrt{\frac{R_b}{t_m} + \frac{R_0}{t_0}} \tag{4}$$

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where

$\dfrac{s(c)}{c}$ relative standard deviation of the activity concentration;

$\dfrac{s(R_n)}{R_n}$ relative standard deviation of the net count rate R_n;

$\dfrac{s(\varphi_A)}{\varphi_A}$ relative standard deviation of the calibration factor φ_A;

$\dfrac{s(\eta)}{\eta}$ relative standard deviation of the chemical yield;

R_n net count rate, in s^{-1};

t_0 duration of the background measurement, in s.

5.2   Worked example

The following is a worked example for determining the Ra-228 activity concentration, with the following estimated numerical values being complemented with a relative standard deviation of the calibration factor of 10 % and that of the chemical yield of 15 %.

V = 10 l; $t_2 - t_1$ = 115200 s (32 h);

$t_3 - t_2$ = 7200 s; $\lambda_{Ac\text{-}228}$ = 3,13 10^{-5} s^{-1};

φ_A = 2,8 Bq·s; m_P = 60 mg ;

m_E = 48 mg; t_0 = 240000 s;

t_m = 57600 s; R_0 = 0,0045 s^{-1};

R_g = 0,025 s^{-1}.

Determining the chemical yield:

$$\eta = \frac{48}{60} = 0,8$$

Calculating the activity concentration:

$$c = \frac{2,8 \cdot (0,025 - 0,0045)}{10 \cdot 0,8} \cdot \frac{3,13 \cdot 10^{-5} \cdot 57600}{1 - e^{(-3,13 \cdot 10^{-5} \cdot 57600)}} \cdot \frac{e^{3,13 \cdot 10^{-5} \cdot 7200}}{1 - e^{-3,13 \cdot 10^{-5} \cdot 115200}} \, Bq \cdot l^{-1} =$$

$$= 0,0072 \cdot \frac{1,803}{1 - 0,164} \cdot \frac{1,253}{1 - 0,0271} \, Bq \cdot l^{-1} = 2,02 \cdot 10^{-2} \, Bq \cdot l^{-1}$$

Calculating the relative standard deviation of the activity concentration:

$$\frac{s(R_n)}{R_n} = \frac{1}{0,0205} \cdot \sqrt{\frac{0,025}{57600} + \frac{0,0045}{240000}} = 0,033$$

$$\frac{s(c)}{c} = \sqrt{0,033^2 + 0,1^2 + 0,15^2} = 0,183$$

The Ra-228 activity concentration of the sample thus amounts to:

$$c = (20 \pm 4) \, mBq \cdot l^{-1}$$

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5.3 Consideration of uncertainties

The relative standard deviation of the calibration factor is determined by the uncertainty of the activity of the calibration source used, and the relative standard deviation of the corresponding net count rate, as well as the uncertainty arising from using a radionuclide that is not identical to Ac-228; it is estimated at about 10 %. The relative uncertainty of the chemical yield is estimated to be 10 to 20 %, as the two final steps of the analysis, i. e., eluting the actinium and its co-precipitation with cerium fluoride, are not taken into consideration for the determination of the yield. Compared to these, errors incurred from pipetting and uncertainties relating to weighing are of lesser importance.

Note
If the analysis is conducted without checking the yield, the uncertainty of the results must be expected to be higher. Experience shows that chemical yields of 70 % to 80 % are typical, but values of less than 50 % are possible.

Considering the data provided and the extremely low level of activity, the relative total uncertainty of the procedure ranges around 30 %.

6 Characteristic limits of the procedure

6.1 Equations

The detection limit of the Ra-228 activity concentration is calculated according to equation (5):

$$g = \frac{\varphi_A \cdot (k_{1-\alpha} + k_{1-\beta})}{V \cdot \eta} \cdot \frac{\lambda_r \cdot t_m}{1 - e^{(-\lambda_r \cdot t_m)}} \cdot \frac{e^{\lambda_r \cdot (t_3 - t_2)}}{1 - e^{-\lambda_r \cdot (t_2 - t_1)}} \cdot \sqrt{\frac{R_0}{t_0} + \frac{R_0}{t_m}} \tag{5}$$

where

g detection limit of the Ra-228 activity concentration, in Bq$\cdot$l^{-1};

$k_{1-\alpha}$, $k_{1-\beta}$ quantiles of the normal distribution for type I and type II errors.

6.2 Worked example

Inserting the values of the worked example given in section 5.2 and $k_{1-\alpha} = 3,0$, $k_{1-\beta} = 1,645$, applying equation (5) will produce the following detection limit:

$$g = \frac{2,8 \cdot 4,645}{10 \cdot 0,8} \cdot \frac{3,13 \cdot 10^{-5} \cdot 57600}{1 - e^{-3,13 \cdot 10^{-5} \cdot 57600}} \cdot \frac{e^{3,13 \cdot 10^{-5} \cdot 7200}}{1 - e^{-3,13 \cdot 10^{-5} \cdot 115200}} \cdot \sqrt{\frac{0,0045}{240000} + \frac{0,0045}{57600}} \; Bq \cdot l^{-1} =$$

$$= 1,626 \cdot \frac{1,8}{1 - 0,164} \cdot \frac{1,269}{1 - 0,0271} \cdot \sqrt{9,675 \cdot 10^{-8}} \; Bq \cdot l^{-1} = 1,42 \cdot 10^{-3} \; Bq \cdot l^{-1}$$

The detection limit in this example amounts to 1,4 mBq$\cdot$l^{-1}.

7 Catalogue of chemicals and equipment

7.1 Chemicals

The extraction-chromatographic separation requires a carrier that is available under the name of RE-resin (Eichrom™).

All chemicals used should furthermore be of the purity grade "*pro analysi*":

— Concentrated nitric acid, HNO_3:   14 $mol \cdot l^{-1}$;
— Diluted nitric acid solutions: 1 $mol \cdot l^{-1}$ and 0,2 $mol \cdot l^{-1}$;
— Diluted sulphuric acid, H_2SO_4:   9 $mol \cdot l^{-1}$;
— Hydrofluoric acid 40 %, HF: 23 $mol \cdot l^{-1}$;
— Ammoniac solution 25 %, NH_3:   13,5 $mol \cdot l^{-1}$;
— Citric acid solution, $C_6H_8O_7 \cdot H_2O$:   1 $mol \cdot l^{-1}$:
  210,15 g of $C_6H_8O_7 \cdot H_2O$ dissolved in 1 l of H_2O;
— Methyl-red solution: 0,1 %;
— Potassium carbonate, K_2CO_3;
— Carrier solution for radium enrichment and determining the yield:
  5,31 g of $BaCl_2 \cdot 2H_2O$ dissolved in 100 ml of H_2O;
— Carrier solution for micro-precipitation with CeF_3:
  155 mg of $Ce(NO_3)_3 \cdot 6H_2O$ dissolved in 100 ml of HCl (1 $mol \cdot l^{-1}$).

7.2 Equipment

Aside from the basic equipment of a radiochemical laboratory, the following will be required:

— 3 l- to 5 l-beakers with watch glasses of corresponding sizes;
— Sand bath;
— Hotplate with magnetic stirrer;
— Accessories for extraction-chromatography (stands for columns, funnels, caps);
— Vacuum-suction apparatus and acid-resistant membrane filters with a pore size of 0,1 μm;
— Stainless steel discs (V2A steel, Ø 25 mm, thickness 0,3 mm);
— Low-level gas-flow counter with anticoincidence disposition;
— Atomic-absorption spectrometer;

References

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(3) W. C. Burnett, P. H. Cable, R. Moser: Determination of radium-228 in natural waters using extraction chromatographic resins, Radioactivity and Radiochemistry 6, Vol. 3, S. 36-44, 1995