Procedure for determining iron-55 in wastewater

H-Fe-55-AWASS-01

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ISSN 1865-8725 Version May 1997

Procedures manual for monitoring of radioactive substances in the environment and of external radiation
(Messanleitungen für die „Überwachung radioaktiver Stoffe in der Umwelt und externer Strahlung“)

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1 Scope

The procedure described here is suitable for analysing wastewaters of any composition and specifically those from nuclear power plants. Elevated salt contents, in particular fluoride ions and detergents, may interfere with the analysis. The content of inactive iron needs to be known or must be determined.

Differentiating between Fe-55 and Fe-59 is not possible with the measuring technique portrayed here. The presence of Fe-59 has to be verified by means of gamma spectrometry and the result of measuring the beta emissions may need to be corrected accordingly.

2 Sampling

A representative sample of 1 l of the wastewater to be analysed is acidified with 1 ml of nitric acid (14 $mol \cdot l^{-1}$) (see procedure H-γ-SPEKT-AWASS-01). Filled in polyethylene bottles, the water samples can be stored for extended periods of time.

Note
Samples severely polluted with salts or dirt will often produce poor chemical yields if their original volumes exceed 100 ml.

3 Analysis

3.1 Principle of the procedure

The principle of the procedure is illustrated in Figure 1. After adding Fe^{3+}-ions as carrier and retainer ions if necessary, iron is precipitated as hydroxide from the solution and then converted to a hexachlorido complex by ion exchange. To allow the measurement of the activity by liquid scintillation, a colourless hexafluoride complex has to be formed. The calculation of the chemical yield requires that the iron content of the sample be titrimetrically determined before and after the separation process.

3.2 Sample preparation

5 ml of sulphuric acid (18 $mol \cdot l^{-1}$) and 5 ml of nitric acid (14 $mol \cdot l^{-1}$) are added to the sample and evaporated on a sand bath until sulphur trioxide fume is visbile. This step is repeated until all organic constituents have been decomposed. After it has been left to cool to room temperature, the sample is diluted to a volume of about 200 ml with distilled water. The sample is then covered with a watch glass and left on the sand bath in a moderately warm environment overnight.

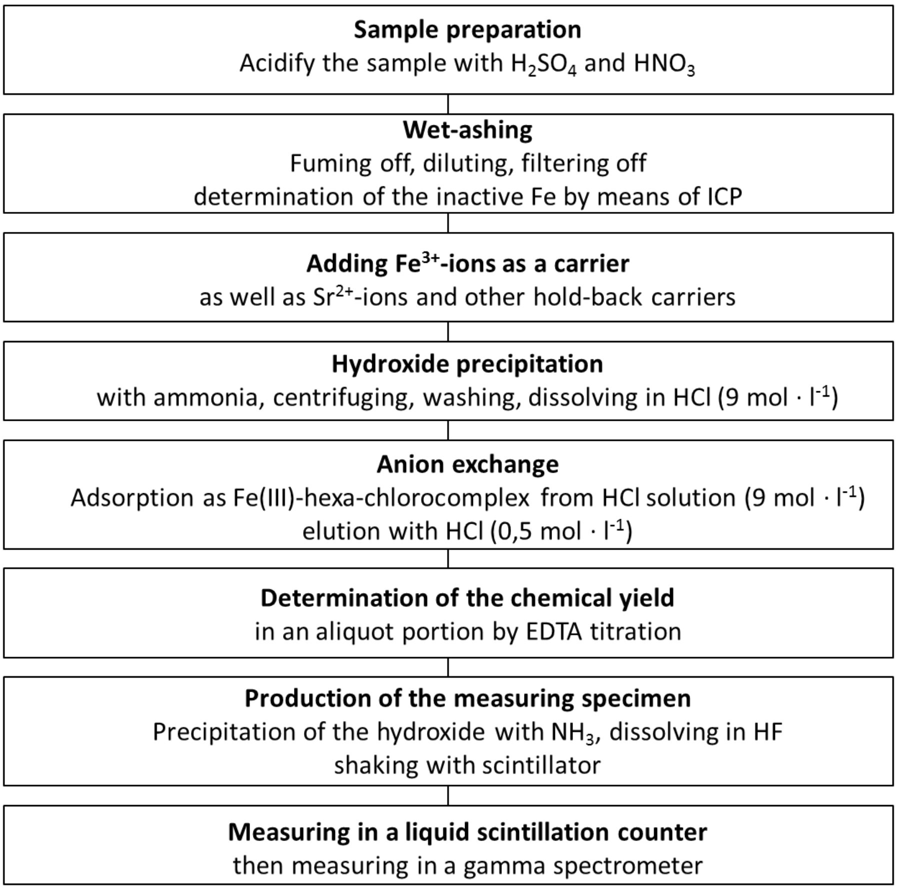

Fig. 1: Principle of determining Fe-55 in wastewater

The sample is filtered into a 500 ml-volumetric flask and washed with distilled water (the washing water is added to the filtrate). It is then filled with distilled water to the mark. For determining the content of inactive iron, 25 ml are taken and analysed, e.g., by spectrometry using inductively coupled plasma (ICP) (detection limit about 30 ppm).

If necessary, 5 ml of iron carrier solution is added to the remaining solution for determining the chemical yield of the separation process, with 10 ml of Sr-carrier, and, if required, with other retainer carriers.

3.3 Radiochemical separation

3.3.1 Ammonia (13 mol·l^{-1}) is added to the solution in a 500-ml-centrifuge beaker until it is alkaline, stirred and centrifuged. The supernatant is decanted and discarded. The precipitate is flushed with ammonia (0,1 mol·l^{-1}) into smaller centrifuge tubes and centrifuged once more. The supernatant is discarded. Ammonia (0,1 mol·l^{-1}) is used for washing the precipitate while it is thoroughly stirred up. The washing solution is discarded.

3.3.2 The residue is dissolved in 20 ml hydrochloric acid (9 mol·l^{-1}) and applied to a conditioned anion exchanger (see section 7.1.1) at a rate of about 1 ml per minute. The exchanger is washed twice with 25 ml of hydrochloric acid (9 mol·l^{-1}) and 50 ml of hydrochloric acid (4 mol·l^{-1}) each; the throughflow from the column and washing solutions are discarded.

3.3.3 After exchanging the receiver, iron is eluted with 40 ml of hydrochloric acid (0,05 mol·l^{-1}). The eluate is evaporated to about 1 ml, quantitatively transferred to a 10 ml-measuring flask, and filled with distilled water to the mark. For determining the yield, 50 ml of distilled water in an Erlenmeyer flask are adjusted to a pH of 1,5 to 2,5 (determined by a pH-meter) and warmed to 40 °C. Precisely 1 ml of the iron solution is added.

3.3.4 The content of the Erlenmeyer flask is titrated with EDTA solution (0,01 mol·l^{-1}) against variamine blue B indicator to the point of colour change from bluish red via grey to pure yellow.

Note

The variamine blue B indicator may be replaced with 5-sulphosalicylic acid, which will change colour from violet to colourless.
The yield may also be determined by ICP spectrometry.

3.3.5 The remaining 9 ml of the solution are transferred quantitatively with as little distilled water as possible to a previously weighed measuring plastic vial (for the liquid scintillation measurement to be carried out later) and ammonia (13 mol·l^{-1}) is added in excess. The hydroxide precipitate is centrifuged, and the supernatant solution decanted and discarded. The precipitate is washed three times with 15 ml of ethanol/water (1:1) each and finally once with distilled water.

3.3.6 The iron hydroxide precipitate is dissolved with 0,5 ml of hydrofluoric acid (28 mol·l^{-1}) in a counting vial and filled with distilled water to exactly 5,0 g. Subsequently, 15 ml of a gel forming scintillator is added, e. g., INSTAGEL, and shaken well for 1 minute (close the bottle tightly).

4 Measuring the activity

4.1 General

The low-energy X-radiation of 5,9 keV is measured by liquid scintillation counting. This requires that an energy range from 0 keV through 6 keV be preselected as to correspond to the energy of the X-radiation. Using a measuring instrument with logarithmic energy scale is of advantage for measuring this nuclide, as quenched samples will otherwise have the recorded pulses distributed only over a very few channels.

4.2 Calibration

Calibration is based upon several calibration sources with iron masses of between 25 mg and 100 mg and supplemented with known activities of Fe-55 (in the range of 1000 Bq), after which the detection efficiency in relation to the iron mass is determined. The calibration function can usually be displayed with sufficient approximation as a linear function (Figure 2).

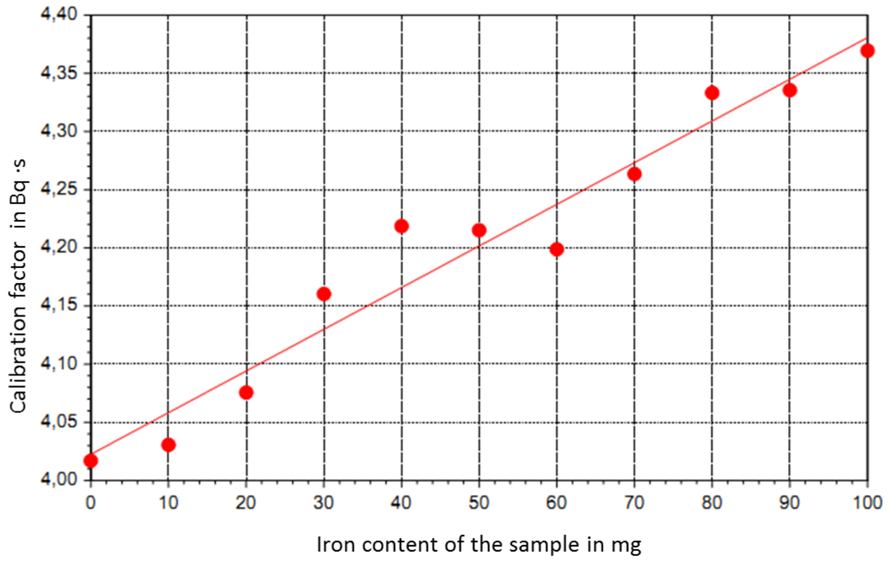

Fig. 2: Calibration factor relative to the iron content of a sample

4.3 Measurement

The sample should be measured together with a background effect sample. The latter is manufactured according to section 3.3 from ca. 100 mg of iron. The measuring period should be at least 100 minutes in the case of low-level measuring. In order to be able to observe chemo-luminescence, which will be recorded by the measuring instrument preferentially in the low-energy channels, several cycles should be measured. If the measuring instrument allows to record the beta spectra, this option should be exploited. A beta spectrum of Fe-55 (with logarithmic amplification) is shown in Figure 3.

In order to detect radioactive contaminations, in particular by Fe-59, the sample is measured by gamma spectrometry after the liquid scintillation measurement has been completed. Applying a correction with regard to the Fe-59 might be required. To this end, the detection efficiency for Fe-59 of the liquid scintillation counter may be supposed to be near 100 % ($\varphi_{Fe\text{-}59}$ = 1).

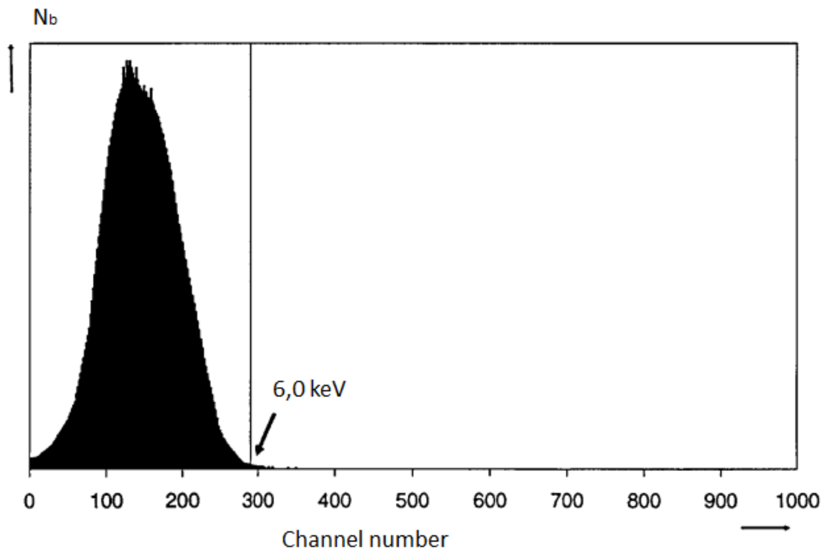

Fig. 3: Beta spectrum of a Fe-55 sample, recorded with logarithmic energy scale

5 Calculation of the results

The activity concentration, c, of the sample is calculated according to equation (1):

$$c = \frac{\varphi_A \cdot f_4}{V' \cdot \eta} \cdot f_1 \cdot \left(R_g - R_0\right) \tag{1}$$

where

- c activity concentration of Fe-55, in $Bq \cdot l^{-1}$;
- φ_A calibration factor, in Bq·s;
- R_0 background count rate, in s^{-1};
- R_g gross count rate, in s^{-1};
- f_4 correction factor based upon an aliquot portion taken from the sample for determining the yield (here f_4 = 10/9);
- V' volume of the sample, in l, see equation (4);
- η chemical yield (count < 1), see equation (3).

Equation (2) applies for the decay factor f_1:

$$f_1 = e^{\left(\ln 2 \cdot \frac{t_A}{t_r}\right)} \tag{2}$$

where

- t_A period of time between sampling and measuring, in s;
- t_r half-life of Fe-55, in s.

The chemical yield, η, is obtained according to equation (3):

$$\eta = \frac{V_T \cdot f_2 \cdot f_3}{Fe_T + Fe_0} \tag{3}$$

where

- V_T volume of the EDTA solution used for titration, in ml;
- Fe_T mass of the iron carrier, in mg;
- Fe_0 iron content of the sample prior to adding carrier, in mg;
- f_2 conversion factor EDTA/Fe (at 0,01 $mol \cdot l^{-1}$ EDTA, f_2 = 0,5585 $mg \cdot ml^{-1}$);
- f_3 correction factor for the removal of an aliquot portion (if 1/10 is taken out, f_3 = 10).

For the actually measured sample volume, V', equation (4) applies:

$$V' = V - \frac{V \cdot a}{b} \tag{4}$$

where

- V original volume of the sample, in l;
- a, b the aliquot portion a with the volume b, removed from the sample for determining the content of inactive iron (here: a = 0,025 l; b = 0,5 l).

5.1 Worked example

5.1.1 Calculating the chemical yield

With:

V_T = 9,00 ml of EDTA
Fe_T = 48,73 mg
Fe_0 = 8,008 mg,

equation (3) will produce: η = 0,886 (88,6 %).

5.1.2 Calculating the actually measured sample volume *V'*

With:

V = 0,8 l
a = 0,025 l
b = 0,5 l,

equation (4) will produce: V' = 0,76 l.

5.1.3 Decay factor

With:

t_A = $6{,}826 \cdot 10^6$ s (79 d)
t_r = $8{,}68 \cdot 10^7$ s (2,75 a),

equation (2) will give a decay factor of: f_1 = 1,056.

5.1.4 Activity concentration

With:

φ_A = 4,20 Bq·s
R_g = 5,798 s^{-1}
R_0 = 0,14 s^{-1}
f_4 = 1,111,

equation (1) will show the activity concentration at time of sampling as:

$$c = 41{,}4 \text{ Bq} \cdot \text{l}^{-1}.$$

Subsequent gamma spectrometric measurement of this sample did not detect the presence of Fe-59.

5.2 Consideration of uncertainties

For calculating the standard deviation, s, of the activity concentration, reference is made to chapter IV.5, equations (2.7) and (4.13) of this procedures manual. According to equation (5), $t_0 = t_m$ applies to the standard deviation, s:

$$s = s(R_n) \cdot \frac{c}{R_n} \quad \text{with} \quad s(R_n) = \sqrt{\frac{R_0 + R_g}{t_m}} \tag{5}$$

Using the values given in the example above and applying a measuring period of t_m = 6000 s, equation (5) will produce a result of s = 0,2 Bq·l^{-1}.

Equation (5) supposes that uncertainties in the detection efficiency, determination of the volume, determination of the chemical yield, and decay time are small compared to count uncertainties and may be neglected.

In practice, the total uncertainty will amount to count rates that are clearly above that of the background effect, at about ± 10 %.

6 Characteristic limits of the procedure

For calculating the detection limit for the activity, G, reference is made to equations (2.4) and (2.5) in chapter IV.5 of this procedures manual. Applying a measuring period for both the sample and the background effect of $t_m = t_0 = 6000$ s and $k_{1-\alpha} + k_{1-\beta} = 4{,}645$, will produce a value of:

$$G = 0{,}11 \text{ Bq}.$$

The detection limit for the activity concentration, g, is calculated according to equation (6):

$$g = \frac{G}{V' \cdot \eta} \cdot f_1 \tag{6}$$

Inserting the numerical values given in section 5.1 will thus show the detection limit, g, of the activity concentration as:

$$g = 0{,}17 \text{ Bq} \cdot \text{l}^{-1}.$$

7 Catalogue of chemicals and equipment

7.1 Chemicals

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

- Ammonia, NH_3: 0,1 mol·l^{-1} and 13 mol·l^{-1};
- Anion exchanger: e.g. DOWEX™ 1 × 8, 50 mesh to 100 mesh, Cl^--form;
- Iron carrier: 10 mg·ml^{-1} of Fe^{3+} (48,4 g·l^{-1} $FeCl_3 \cdot 6H_2O$);
- Ethanol, C_2H_5OH;
- Ethylenediaminetetraacetate, disodium salt (EDTA): 0,01 mol·l^{-1};
- Hydrofluoric acid, HF: 28 mol·l^{-1};
- Hold-back carrier mixed solution (see H-γ-SPEKT-AWASS-01);
- Nitric acid, HNO_3: 14 mol·l^{-1};
- Hydrochloric acid, HCl: 0,05 mol·l^{-1}, 4 mol·l^{-1} and 9 mol·l^{-1};
- Sulphuric acid, H_2SO_4: 18 mol·l^{-1};
- Strontium carrier: 10 mg·ml^{-1} of Sr^{2+} (30,43 g·l^{-1} $SrCl_2 \cdot 6H_2O$);
- Scintillator, gelling, e.g., INSTAGEL® (Packard)*;
- Variamine blue B hydrochloride (e.g., Merck 8506): 0,5 g of hydrochloride in 50 ml of distilled water.

*) Analyses conducted by the Coordinating Office have demonstrated this scintillator to be particularly suitable for the purpose.

7.1.1 Conditioning the anion exchanger

The pre-steeped exchanger resin is filled without air bubbles into a column (inner diameter 10 mm) to a height of about 12 cm. It is washed with 50 ml of distilled water and 50 ml of hydrochloric acid (9 $mol \cdot l^{-1}$). The column must not run dry.

7.2 Equipment

— Liquid scintillation counter (with an option of illustrating beta spectra);
— ICP-spectrometer or another device capable of accurately determining iron contents;
— pH-meter;
— gamma spectrometer;
— Basic equipment of a radiochemical laboratory.

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