

**Procedure for determining the activity
concentrations of iron-55 and nickel-63
in wastewater**

H-Fe-55/Ni-63-AWASS-01

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Procedure for determining the activity concentrations of iron-55 and nickel-63 in wastewater

1 Scope

This procedure is used to determine the activity concentrations of iron-55 (Fe-55) and nickel-63 (Ni-63) in wastewater samples from nuclear facilities and installations by liquid scintillation counting (LSC) in accordance with KTA Safety Standard 1504 [1]. The iron content in the sample must be less than $20 \text{ mg}\cdot\text{l}^{-1}$ and its nickel content less than $10 \text{ mg}\cdot\text{l}^{-1}$. Other radioisotopes of iron and nickel must be taken into account when calculating the Fe-55 and Ni-63 activity concentrations, respectively. When using a sample volume of 0,25 litres, the detection limits are about $1 \text{ Bq}\cdot\text{l}^{-1}$ for Fe-55 and about $0,5 \text{ Bq}\cdot\text{l}^{-1}$ for Ni-63 and are thus below the required detection limits according to KTA Safety Standard 1504 [1].

Other aqueous samples may also be analysed using this procedure.

2 Sampling

With regard to representative sampling and addition of the inactive iron and nickel carriers, it is referred to the Procedure H- γ -SPEKT-AWASS 01.

A sample volume of one litre is usually taken. The water sample is acidified with about 10 ml nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) per litre to a pH value of 1 for stabilisation.

3 Analysis

3.1 Principle of the procedure

In this extraction chromatographic procedure, a sample volume of about 0,6 litres is required for the double determination of the activity concentrations of Fe-55 and Ni-63.

Iron and nickel are enriched by hydroxide precipitation from the sample solution. The dissolved hydroxide precipitate is then applied to a carrier (TRU-Resin) loaded with octyl(phenyl)-N,N-diisobutyl-carbamoyl-methyl-phosphine oxide in tri-n-butyl-phosphate (CMPO/TBP) to separate iron [2, 3, 4]. The rinse and the first wash solution are combined and used for nickel determination; a second wash solution contains interfering lanthanides (Ln) and actinides (An) and is discarded. Iron is then eluted with dilute hydrochloric acid.

Note:

If high concentrations of alpha emitters such as uranium isotopes are present, iron is eluted with 10 ml nitric acid ($1 \text{ mol}\cdot\text{l}^{-1}$) in order to safely retain the alpha emitters. However, this reduces the detection efficiency of the liquid scintillation counting.

The nickel fraction is again subjected to hydroxide precipitation. The dissolved hydroxide precipitate is placed on a carrier (NI-Resin) loaded with butanedioxime-(2,3) [older designation: dimethylglyoxime, DMG] [5]. The rinse and the first wash solution are discarded. Nickel is washed from the column with dilute nitric acid.

The contents as well as the chemical yields of iron and nickel are determined, for example, by inductively coupled plasma optical emission spectrometry (ICP-OES) or flame atomic absorption spectrometry (AAS). The activity of radioactive iron and nickel isotopes is measured using LSC [6].

Note:

The nuclide-specific activity determination of the radioactive iron and nickel isotopes with an LSC is only possible via spectrum deconvolution. Since the considered activity concentrations of Fe-55 and Ni-63 dominate over those of other radioactive iron and nickel isotopes, spectrum deconvolution is rarely necessary. If the presence of Fe-59 cannot be excluded, a gamma spectrometric analysis is recommended (see Section 4.1).

The procedure is shown schematically in Figure 1.

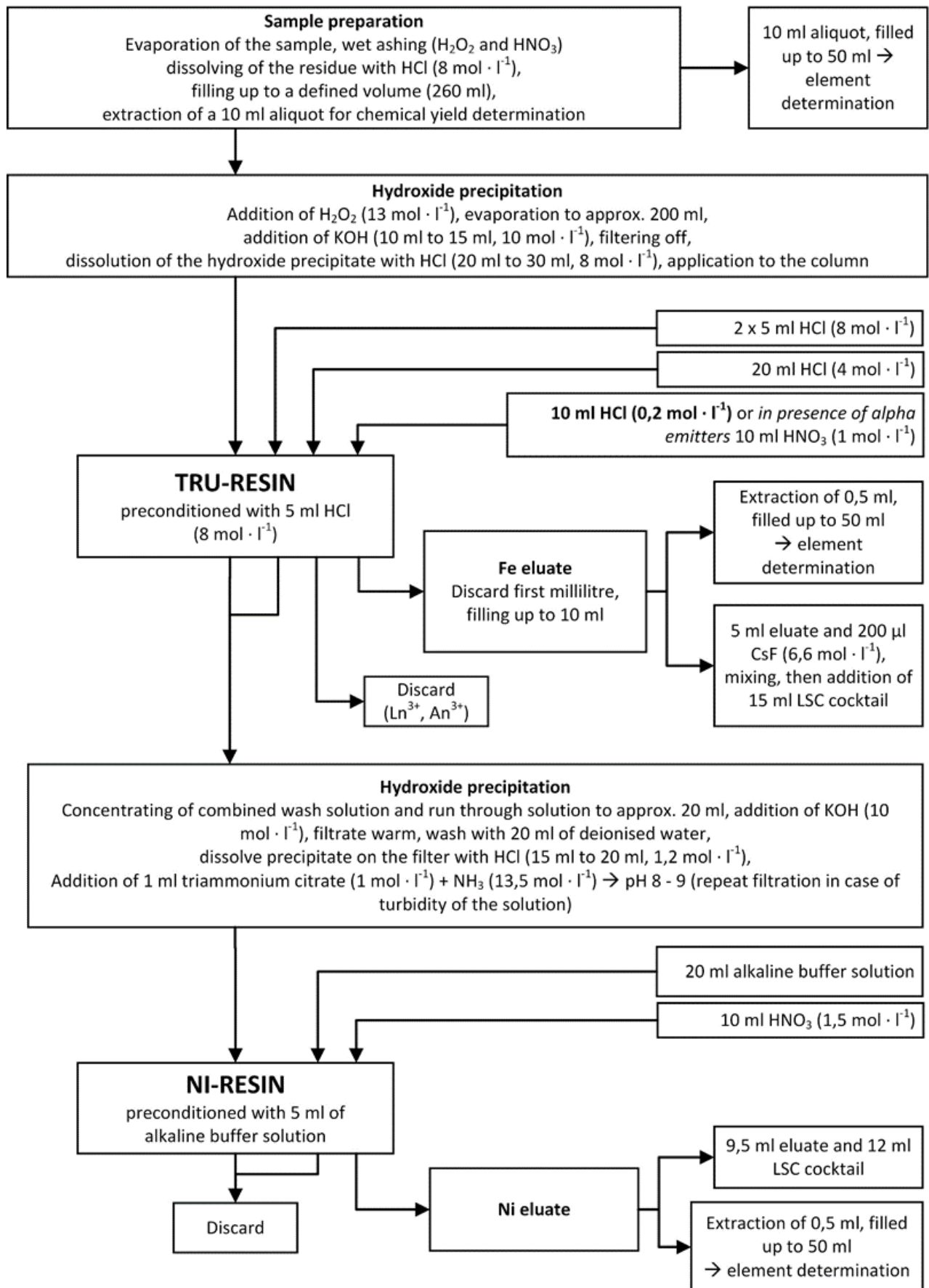


Fig. 1: Scheme of the extraction chromatographic separation process

3.2 Sample preparation

3.2.1 Determination of iron and nickel in the entire water sample

3.2.1.1 The entire water sample is homogenised by intensive mixing.

Note:

Wet digestion of the entire water sample is recommended for water samples with a high suspended solids content or sedimented components. The procedure corresponds to Steps 3.2.2.1 and 3.2.2.2. The prepared total sample is taken up with approx. 10 ml of concentrated hydrochloric acid ($10 \text{ mol}\cdot\text{l}^{-1}$) and the solution is then made up to the original sample volume with deionised water.

3.2.1.2 An aliquot of approx. 10 ml is taken and filtered through a syringe filter.

3.2.1.3 The iron and nickel contents in the filtrate are determined by AAS or ICP-OES. If the iron or nickel concentrations are below $4 \text{ mg}\cdot\text{l}^{-1}$, iron or nickel carrier is added to achieve a concentration of approx. $4 \text{ mg}\cdot\text{l}^{-1}$.

3.2.2 Determination of iron and nickel in the analysis solution

3.2.2.1 From the homogenized water sample, an aliquot of 260 ml is transferred for analysis in a 400-ml-beaker and evaporated on a sand bath to dryness.

3.2.2.2 The residue is dissolved by adding 10 ml of concentrated nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) and 5 ml of hydrogen peroxide solution ($9 \text{ mol}\cdot\text{l}^{-1}$). The solution is slowly evaporated to dryness. This step is repeated until all organic components are decomposed.

3.2.2.3 Afterwards, the residue is dissolved by adding approx. 5 ml concentrated hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) while stirring and heating.

3.2.2.4 After cooling and, if necessary, filtering, the clear solution is filled up to the initial volume of 260 ml with deionised water.

3.2.2.5 To determine the iron and nickel contents before the radiochemical separation, $c_{e,0}$, 10 ml of the solution are transferred to a 50 ml volumetric flask. The volumetric flask is filled up to the mark with deionised water.

3.2.2.6 The concentrations of iron and nickel are determined by AAS or ICP-OES.

3.3 Radiochemical separation

3.3.1 Enrichment of iron and nickel

3.3.1.1 The remaining solution from step 3.2.2.3 (250 ml) is mixed with a few drops of a hydrogen peroxide solution ($9 \text{ mol}\cdot\text{l}^{-1}$) to oxidise Fe^{2+} to Fe^{3+} . The solution is then evaporated to a volume of approx. 200 ml.

3.3.1.2 The iron and nickel hydroxides are completely precipitated in the heat as a voluminous precipitate by adding 10 ml to 15 ml potassium hydroxide solution ($10 \text{ mol}\cdot\text{l}^{-1}$).

Note:

The alkalinity of the solution is checked by using pH paper. If necessary, further potassium hydroxide solution ($10 \text{ mol}\cdot\text{l}^{-1}$) is added.

3.3.1.3 The precipitate is collected on a white band filter using a fast filtration funnel, the filtrate in a 400-ml-beaker.

3.3.1.4 The beaker which contained the precipitate, is washed by adding a few millilitres deionised water. The wash solution is transferred to filter with the precipitate (Step 3.3.1.3). The collected filtrates are discarded.

3.3.1.5 The hydroxide precipitate on the filter is dissolved by adding 20 ml to 30 ml hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$). The filtrate is collected in a 50-ml-beaker.

3.3.1.6 The filter is rinsed with a little hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$). The rinsing solution is also collected in the beaker from Step 3.3.1.5.

3.3.2 Separation of iron

3.3.2.1 The TRU-column used for iron separation is conditioned with 5 ml hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$).

3.3.2.2 The solution in the beaker from Step 3.3.1.6 is added to the conditioned TRU-column. The rinsing solution is collected in another beaker.

Note:

Chloridoferrate ions ($[\text{FeCl}_4]^-$) retained on the TRU-column form a broad yellow band (see Figure 2).

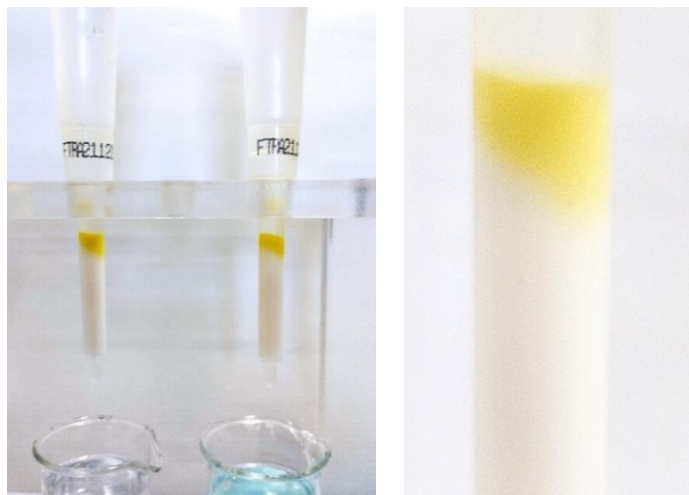


Fig. 2: Yellow band of chloridoferrate ions on the TRU-column

3.3.2.3 The beaker from Step 3.3.1.6 is washed twice with 5 ml hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) and the wash solutions are also added to the column. The wash solutions are collected in the beaker from Step 3.2.2.2. These eluates are used for the Ni-63 determination according to Section 3.3.3.

3.3.2.4 If interfering trivalent lanthanides and actinides such as americium cannot be excluded, these are washed off the column with additional 20 ml hydrochloric acid ($4 \text{ mol}\cdot\text{l}^{-1}$). The wash solution is discarded.

3.3.2.5 If yellow colouration only occurs in the upper third of the column, 0,5 ml of hydrochloric acid ($0,2 \text{ mol}\cdot\text{l}^{-1}$) are added to the column. The eluate is discarded.

3.3.2.6 Fe^{3+} is then eluted from the TRU-column with 10 ml hydrochloric acid ($0,2 \text{ mol}\cdot\text{l}^{-1}$).

Note:

For concentrations of alpha emitters (see Section 4.4) greater than $1 \text{ Bq}\cdot\text{l}^{-1}$ elution should be carried out with 10 ml nitric acid ($1 \text{ mol}\cdot\text{l}^{-1}$) instead of 10 ml hydrochloric acid ($0,2 \text{ mol}\cdot\text{l}^{-1}$) in order to retain the alpha emitters on the TRU column. The disadvantage of this procedure is that LSC quenching is increased.

3.3.2.7 To determine the chemical yield of iron, 1 ml of the eluate is pipetted into a 50 ml volumetric flask. After filling up to the mark with deionised water, the iron concentration is determined.

3.3.2.8 Transfer 5 ml of the eluate to a 20 ml polyethylene counting vial and decolourise by adding 100 μl to 200 μl caesium fluoride solution ($6,6 \text{ mol}\cdot\text{l}^{-1}$). Subsequently, 15 ml of scintillation cocktail is added. The counting source is homogenised by shaking.

3.3.3 Separation of nickel

3.3.3.1 The solution from Step 3.3.2.3 is concentrated on the heating stirrer to a volume of approximately 20 ml.

3.3.3.2 After cooling the solution, nickel hydroxide is completely precipitated as a voluminous precipitate by adding 10 ml to 15 ml potassium hydroxide solution ($10 \text{ mol}\cdot\text{l}^{-1}$).

Note:

The alkalinity of the solution is checked using pH paper. If necessary, potassium hydroxide solution ($10 \text{ mol}\cdot\text{l}^{-1}$) is added. The solution can heat up considerably.

3.3.3.3 The warm solution is filtered through a white band filter in a fast filter funnel. The beaker is rinsed with up to 20 ml of deionised water. The rinsing solution is transferred to filter with the precipitate. The filtrate is discarded.

3.3.3.4 The white band filter is transferred to a 100 ml beaker. The hydroxide precipitate in the filter is dissolved with 15 ml to 20 ml hydrochloric acid ($1,2 \text{ mol}\cdot\text{l}^{-1}$). The filter is then removed while rinsing carefully with a little bit of hydrochloric acid ($1,2 \text{ mol}\cdot\text{l}^{-1}$).

3.3.3.5 After adding 1 ml diammonium hydrogen citrate solution ($1 \text{ mol}\cdot\text{l}^{-1}$), the pH is adjusted to a value from 8 to 9 with approx. 2 ml ammonia solution ($13,5 \text{ mol}\cdot\text{l}^{-1}$).

3.3.3.6 If turbidity occurs in the solution, the solution must be filtered again through a white band filter. Then rinse the beaker with approx. 2 ml to 5 ml of a basic buffer solution (pH value 8 to 9, see Section 8.1). The filter with the residue is discarded.

Note:

The turbidity consists of hydroxides of interfering metal ions that have not formed amine complexes. These would clog the NI column used below.

3.3.3.7 The NI column is conditioned with 5 ml of a basic buffer solution (pH value 8 to 9, see Section 8.1).

3.3.3.8 The solution from Step 3.3.3.3 or 3.3.3.6 is applied to the conditioned NI-column. The nickel-DMG complex precipitating on the column can be recognised after a short time as a red band (see Figure 3). The solution that has run through is discarded.

Note:

The column capacity is about 3 mg Ni²⁺; if the nickel content in the solution is higher, the solution must be divided into several NI-columns. As the nickel-DMG complex precipitates on the carrier material, the solution may run through slowly. Therefore, the column may only be operated without pressure. Each NI-column may only be used once.

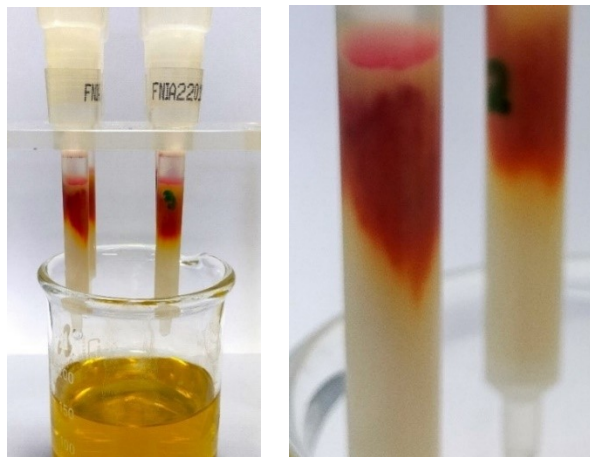


Fig. 3: View of the nickel-DMG complex as a red band on the NI-column

3.3.3.9 The column is then washed with 20 ml basic buffer solution. The wash solution is discarded.

Note:

If high levels of radioactive cobalt isotopes are expected, wash with approx. 60 ml of basic buffer solution until the wash solution is colourless (see Section 4.3).

3.3.3.10 The nickel-DMG complex is destroyed by adding 10 ml nitric acid (1,5 mol·l⁻¹); the released Ni²⁺ ions are eluted. The eluate is collected in a 20 ml counting vial.

3.3.3.11 An aliquot of 1 ml from the eluate is transferred to a 50 ml volumetric flask and filled with deionised water. This solution is used to determine the chemical yield of nickel.

3.3.3.12 Add 12 ml of scintillation cocktail to the remaining eluate and mix by shaking.

4 Measuring the activity

4.1 General

4.1.1 Measurement of iron-55

The activity of Fe-55 is determined by measuring the low-energy X-rays (K_{α} : 5,9 keV and K_{β} : 6,5 keV) in an LSC in an energy range from 0 keV to 6 keV. The energy range from 6 keV to 2 000 keV should also be recorded and compared with the corresponding energy range of the measured blank source (see Section 4.3) in order to be able to recognise impurities of interfering radionuclides (see Section 4.4). The pulse height distribution is shown in Figure 4 using the example of an Fe-55 counting source.

Note:

The LSC measurement of Fe-55 activity is interfered by the presence of Fe-59, as both emission spectra overlap. The Fe-59 component must be subtracted from the total count rate. The proportion of the count rate originating from Fe-59 in the total count rate in the energy range of Fe-55 depends on the Fe-59 activity and is approx. 15 % if comparable Fe-55 and Fe-59 activities are present in the counting source. A more precise estimate is possible by linear deconvolution of the overlapping LSC spectra. However, the interference can also be minimised by adjusting the Fe-55 energy range.

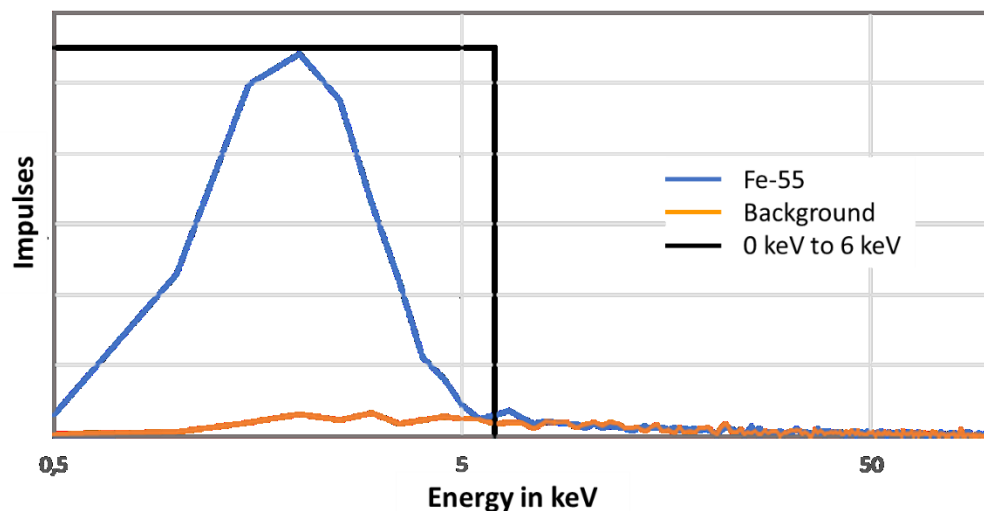


Fig. 4: LSC spectra of an Fe-55 counting source and a co-measured background in the energy range from 0 keV to 6 keV.

4.1.2 Measurement of nickel-63

The activity of Ni-63 is determined by measuring the beta radiation with a maximum beta energy $E_{\beta, \max}$ of 67 keV in an LSC in the energy range from 0 keV to 30 keV. The pulse height distribution is shown in Figure 5 using the example of a Ni-63 counting source.

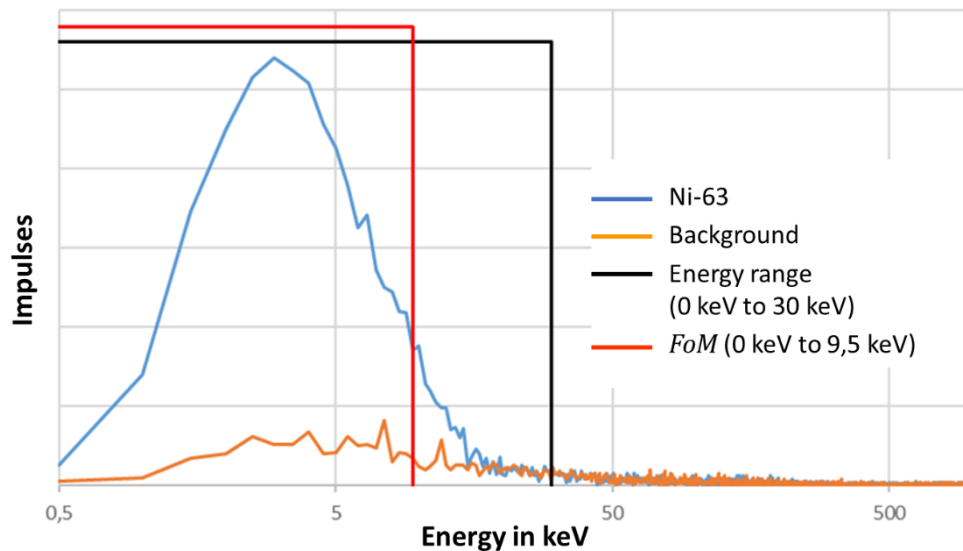


Fig. 5: LSC spectra of a Ni-63 counting source and a co-measured background in the energy range from 0 keV to 30 keV or from 0 keV to 9,5 keV at optimum FoM .

To optimise the evaluation, the energy range of interest should be selected so that the figure of merit (FoM) of a co-measured LSC calibration source of known activity is maximised. Equation (1) applies here:

$$FoM = \frac{\varepsilon_r^2}{R_0} = \frac{(R_{g,Std} - R_0)^2}{A_{Std}^2 \cdot R_0} \quad (1)$$

Herein are:

A_{Std} activity of the standard solution used, in Bq;

$R_{g,Std}$ gross count rate of the LSC calibration source, in s^{-1} ;

R_0 background count rate, in s^{-1} ;

ε_r detection efficiency for the radionuclide r, in $Bq^{-1} \cdot s^{-1}$.

Note:

Depending on the sample composition, the scintillation cocktail and the measuring device, further optimisation of the energy range based on the FoM may be necessary.

4.2 Calibration

Calibration sources with different activity concentrations whose activities are traceable to an Fe-55 or Ni-63 activity standard are used for calibration. The calibration sources are prepared in the same way as the counting sources (see Steps 3.3.2.8 or 3.3.3.12).

In LSC measurements, for example, impurities in the counting source cause a shift in the pulse height spectrum to lower and lower energies, resulting in a decrease in detection efficiency. This effect is known as quenching [7, 8]. A quench curve is recorded to correct

for this effect. For this purpose, the concentration of the radionuclide of interest is systematically increased by adding quenching substances such as nitromethane or carbon tetrachloride in the volume range from 0 μl to 30 μl to the calibration sources while keeping their activity constant. The calibration sources are measured with the energy range settings described in Section 4.1, whereby the manufacturer-specific quench parameter, e. g. $tSIE$, is determined automatically.

The detection efficiency of the radionuclide of interest, ε_r , is determined as a function of the quench parameter as a regression polynomial. These functions for determining the Fe-55 and Ni-63 activity are shown graphically in Figures 6 and 7. The activity-related calibration factor for the radionuclide r , $\varphi_{A,r}$, is calculated according to Equation (2).

$$\varphi_{A,r} = \frac{1}{\varepsilon_r} \quad (2)$$

For the quench parameter $tSIE$ considered here, the detection efficiency is calculated according to Equation (3), whereby a polynomial function (here second degree) with the coefficients v_1 , v_2 and v_3 is fitted to the measurement data.

$$\varepsilon_r = v_1 + v_2 \cdot tSIE + v_3 \cdot tSIE^2 \quad (3)$$

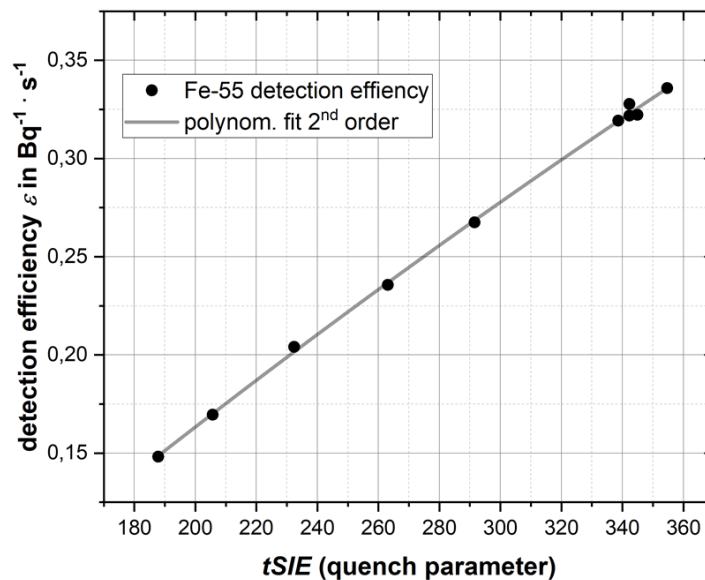


Fig. 6: Detection efficiency for iron-55, $\varepsilon_{\text{Fe-55}}$, as a function of the device-specific quench parameter $tSIE$.

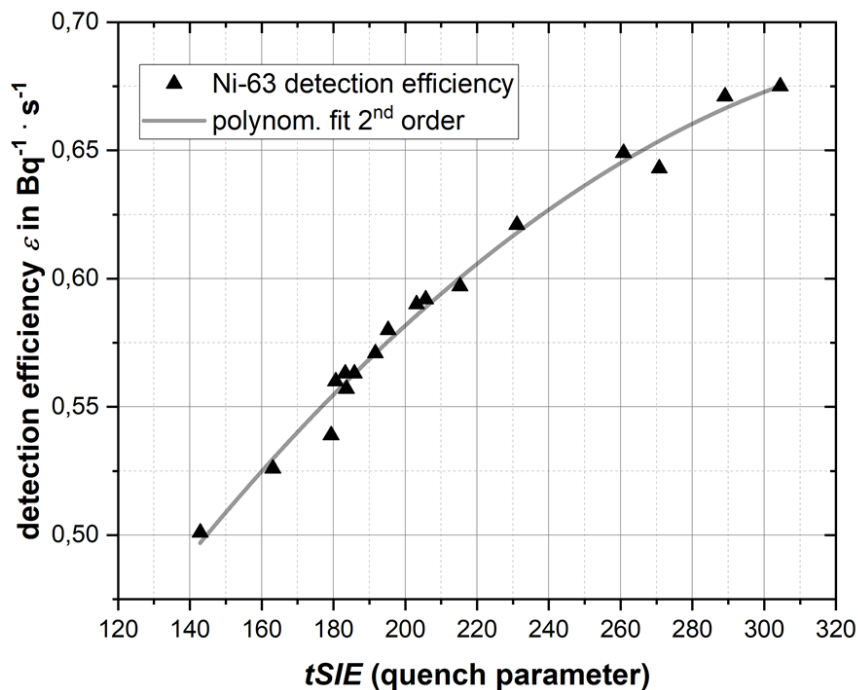


Fig. 7: Detection efficiency for nickel-63, $\varepsilon_{\text{Ni-63}}$, as a function of the device-specific quench parameter $tSIE$.

With the usual quench values

- for the measurement of the Fe-55 activity of $tSIE = 300$ and
- for the measurement of the Ni-63 activity of $tSIE = 200$

the calibration factors $\varphi_{A,\text{Fe-55}}$ of 2,78 $\text{Bq} \cdot \text{s}$ and $\varphi_{A,\text{Ni-63}}$ of 1,73 $\text{Bq} \cdot \text{s}$ result.

4.3 Measurement

The activities of iron-55 or nickel-63 in the corresponding counting sources are measured with an LSC, usually for 6 000 seconds, after the chemiluminescence has decayed for at least three hours in the dark and in the cool, ideally in the sample chamber of the measuring device. Similar blank sources are also measured in each series of measurements.

Note:

The eluate used for measurement must be decolourised according to Step 3.3.2.8, otherwise a very high colour quench will occur. After the addition of scintillation cocktail, chemiluminescence often disappears after three hours, but in the case of Fe-55 counting sources it may only have decayed to a negligible level in the energy range from 0 keV to 200 keV after approx. 20 hours (see Section 4.1).

If the LSC has an automatic luminescence correction, this option must be used. If this option is not available, the decaying luminescence can only be recognised by repeat measurements.

4.4 Interferences

Both the chemical separation and the LSC measurement can be interfered by high cobalt concentrations above $30 \text{ mg} \cdot \text{l}^{-1}$ as well as by the presence of iron-59 and beta-emitting actinides.

4.4.1 Interference of nickel determination by iron and cobalt

The nickel determination is interfered by the formation of DMG complexes of Fe^{2+} (coloured red) or Co^{2+} (coloured brown) if the separation of the iron isotopes is incomplete and/or in the case of high cobalt concentrations. In contrast to the Ni-DMG complex, which precipitates on the column, these complexes are soluble in aqueous diammonium hydrogen citrate solution. A larger volume of wash water may be required to completely wash out these complexes (see Step 3.3.3.9). To check the quality of the cobalt separation, the pulse height spectrum in the energy range from 30 keV to 2 000 keV is analysed. In this energy range, the count rate must correspond to that of the measured background spectrum.

4.4.2 Interference in iron determination by beta-emitting actinides

In the determination of Fe-55, beta-emitting actinides such as Pu-241 interfere, since tetravalent plutonium and thorium ions as well as uranyl ions in hydrochloric acid solution in the TRU-column show a similar retention behaviour as trivalent iron ions [2, 4]. For this reason, nitric acid ($1 \text{ mol} \cdot \text{l}^{-1}$) is used for the elution in step 3.3.2.6 instead of hydrochloric acid ($0,2 \text{ mol} \cdot \text{l}^{-1}$). The actinides remain on the TRU-column and the iron ions are washed out. Nevertheless, if Pu-241 or Th-234 are present in the Fe-55 counting source, their emitted beta radiation is also registered in the Fe-55 energy range. To check the quality of the actinide separation, the pulse height spectrum is analysed in the energy range from 6 keV to 2 000 keV. In this energy range, the count rate must correspond to that of the measured background spectrum.

Note:

The LSC measurement of the iron eluate is carried out as described in Section 4.1. Changing from hydrochloric acid to nitric acid increases the quench and reduces the detection efficiency.

5 Calculation of the results

5.1 Output quantity

The activity concentration for the radionuclide r of interest is calculated according to Equation (4)

$$c_r = \varphi_r \cdot R_{n,r} = \varphi_r \cdot (R_{g,r} - R_0) \quad (4)$$

with

$$\varphi_r = \frac{\varphi_{A,r}}{\eta_e} \cdot \frac{V_E}{V_P \cdot V_M} \cdot f_1 \quad (5)$$

The chemical yield of iron or nickel, η_e , is obtained with the volumes used in this procedure for the removal of the aliquots and their replenishment according to Equation (6):

$$\eta_e = \frac{c_{E,e}}{c_{0,e}} \quad (6)$$

The decay correction factor f_1 is calculated according to Equation (7):

$$f_1 = e^{\ln 2 \cdot \frac{t_A}{t_r}} \quad (7)$$

In the Equations (4) to (7) are:

- c_r activity concentration of the radionuclide r , in Bq;
- $c_{E,e}$ concentration of the element of interest, e , in the diluted eluate, in $\text{mg} \cdot \text{l}^{-1}$;
- $c_{0,e}$ concentration of the element of interest, e , in the diluted starting solution before the separation process, in $\text{mg} \cdot \text{l}^{-1}$;
- f_1 decay correction factor for the period between reference time and start of measurement;
- $R_{g,r}$ gross count rate of the radionuclide r , in s^{-1} ;
- $R_{n,r}$ net count rate of the radionuclide r , in s^{-1} ;
- R_0 background count rate, in s^{-1} ;
- t_A time period between reference date and start of measurement, in s;
- t_r half-life of the radionuclide r , in s;
- V_E volume of the eluate, in l;
- V_M volume of the aliquot of the eluate for the preparation of the counting source, in l;
- V_P sample volume used for the chemical separation process, in l;
- η_e chemical yield of the element e ;

- $\varphi_{A,r}$ activity-related calibration factor of the radionuclide r , in Bq·s;
 φ_r procedural calibration factor of the radionuclide r , in Bq·s·l⁻¹.

5.2 Standard uncertainty of the output quantity

Uncertainty contributions arising from sampling are not taken into account in the framework of this Procedures' Manual, as these can depend on many different and often not quantifiable factors.

The combined relative standard uncertainties of the activity concentrations of Fe-55 and Ni-63 are calculated according to Equation (8):

$$u_{\text{rel}}(c_r) = \frac{u(c_r)}{c_r} = \sqrt{u_{\text{rel}}^2(R_{n,r}) + u_{\text{rel}}^2(\varphi_r)} \quad (8)$$

The relative standard uncertainty of the net count rate, $u_{\text{rel}}(R_{n,r})$, is calculated according to Equation (9):

$$u_{\text{rel}}(R_{n,r}) = \frac{u(R_{n,r})}{R_{n,r}} = \frac{1}{R_{n,r}} \cdot \sqrt{\frac{R_{g,r}}{t_m} + \frac{R_0}{t_0}} \quad (9)$$

Note:

The contribution of $u_{\text{rel}}(R_{n,r})$ to the overall uncertainty of the activity concentration only plays a significant role at low count rates or short measurement durations.

The relative standard uncertainty of the procedural calibration factor as carrier of the type B uncertainties is determined according to Equation (10):

$$u_{\text{rel}}(\varphi_r) = \frac{u(\varphi_r)}{\varphi_r} = \sqrt{u_{\text{rel}}^2(\varphi_{A,r}) + u_{\text{rel}}^2(\eta_e) + u_{\text{rel}}^2(f_1) + \sum_j u_{\text{rel}}^2(V_j)} \quad (10)$$

and

$$u_{\text{rel}}(f_1) = \frac{u(f_1)}{f_1} = \frac{\ln 2}{t_r} \cdot \sqrt{u^2(t_A) + \left[u(t_r) \cdot \frac{t_A}{t_r} \right]^2} \quad (11)$$

In Equations (8) to (11) are:

- t_m duration of counting source measurement, in s;
 t_0 duration of background measurement, in s;
 $u(x)$ standard uncertainty of any variable x or a tabulated constant, in the respective unit;
 $u_{\text{rel}}(x)$ relative standard uncertainty of any quantity x or a tabulated constant.

When considering the uncertainties of the analysis result, it should be noted:

- The contribution of the relative standard uncertainty of the net count rate to the overall uncertainty of the activity concentration only plays a significant role at low count rates or short measurement durations.
- The relative standard uncertainties of the calibration factors result from the statistical parameters of the regression (calculation of the counting yield functions) or are estimated on the basis of repeated calibrations.
- The relative standard uncertainty of the chemical yield already takes into account the uncertainties of pipetting and dilution processes.
- The absolute standard uncertainties of the volume data, e.g. for pipettes and measuring vessels, correspond to the manufacturers' specifications.
- The standard uncertainty of the decay correction factor f_1 is taken into account if the time span between the reference date and the start of measurement, t_A , comprises several half-lives of the radionuclide of interest. The uncertainty of t_A depends on the accuracy of the reference and measurement times.
- The uncertainty of the half-life of the radionuclide of interest is taken from the literature [9].
- The standard uncertainty of the measurement time is generally negligible.

6 Characteristic limits of the procedure

The calculation of the characteristic limits follows the standard series ISO 11929 [10]. Further considerations are to be found in the General Chapter CHAGR-ISO-01 of this Procedures' Manual [11].

6.1 Decision threshold

The decision threshold of the activity concentrations of the radionuclides of interest, c_r^* , is calculated according to Equation (12):

$$c_r^* = k_{1-\alpha} \cdot \varphi_r \cdot \sqrt{R_0 \cdot \left(\frac{1}{t_m} + \frac{1}{t_0} \right)} \quad (12)$$

Where $k_{1-\alpha}$ is the quantile of the standardised normal distribution for the first type of error. For measurements according to [1], the value is 1,645.

Note:

The quantile $k_{1-\alpha}$ must be adapted to the measurement purpose [11].

6.2 Detection limit

The detection limit of the activity concentrations of the radionuclides of interest, $c_r^\#$, is determined according to Equation (13):

$$c_r^\# = c_r^* + k_{1-\beta} \cdot \sqrt{[c_r^\# \cdot u_{\text{rel}}(\varphi_r)]^2 + \varphi_r^2 \cdot \left[\frac{c_r^\#}{t_m \cdot \varphi_r} + R_0 \cdot \left(\frac{1}{t_m} + \frac{1}{t_0} \right) \right]} \quad (13)$$

Equation (13), which can be solved iteratively, can be transformed into the explicit Equation (14) after squaring and applying the solution formula for quadratic equations.

$$c_r^\# = \frac{c_r^* \cdot \psi}{\theta} + \left[1 + \sqrt{1 - \frac{\theta}{\psi^2} \cdot \left(1 - \frac{k_{1-\beta}^2}{k_{1-\alpha}^2} \right)} \right] \quad (14)$$

The auxiliary quantities used in Equation (14) are composed as follows:

$$\theta = 1 - k_{1-\beta}^2 \cdot u_{\text{rel}}^2(\varphi_r) \quad (15)$$

$$\psi = 1 + \frac{k_{1-\beta}^2}{2 \cdot c_r^*} \cdot \frac{\varphi_r}{t_m} \quad (16)$$

Where $k_{1-\beta}$ is the quantile of the standardised normal distribution for the second type of error. The value is usually 1,645 [1, 11].

6.3 Limits of the coverage interval

In this procedure, the limits of the probabilistic symmetric coverage interval are used [1].

For the limits of the coverage interval for a probability $1 - \gamma$, the probabilities for the quantiles of the lower and upper coverage interval are first calculated according to Equations (17) and (18):

$$p = \omega \left(\frac{c_r}{u(c_r)} \right) \cdot \left(1 - \frac{\gamma}{2} \right) \quad (17)$$

$$q = 1 - \omega \left(\frac{c_r}{u(c_r)} \right) \cdot \frac{\gamma}{2} \quad (18)$$

For measurements according to [1], the value 0,9 is used for $1 - \gamma$.

The lower and upper limits of the coverage interval are then determined according to Equations (19) and (20):

$$c_r^{\Delta} = c_r - k_p \cdot u(c_r) \quad (19)$$

$$c_r^{\nabla} = c_r + k_q \cdot u(c_r) \quad (20)$$

In the Equations (17) to (20) are:

- p probability for the quantile of the lower limit of the coverage interval;
- q probability for the quantile of the upper limit of the coverage interval;
- k_p quantile of the standardised normal distribution for probability p ;
- k_q quantile of the standardised normal distribution for probability q ;
- c_r^{Δ} lower limit of the coverage interval of the activity concentration, in $\text{Bq}\cdot\text{l}^{-1}$;
- c_r^{∇} upper limit of the coverage interval of the activity concentration, in $\text{Bq}\cdot\text{l}^{-1}$.

7 Worked examples

The evaluation can be carried out either manually (see Section 7.1) or software supported by Excel[®] or by the software UncertRadio (see Section 7.2). An Excel[®] spreadsheet as well as a project file for the software UncertRadio are available on the website of this Procedures' Manual.

7.1 Manual evaluation

In the manual evaluation, the interim results and the result are given rounded with four significant digits.

In the following, the calculation of the Fe-55 activity concentration, the associated standard uncertainty and the characteristic limits is carried out using the following numerical values as an example.

$R_g = 0,475 \text{ s}^{-1};$	$R_0 = 0,08 \text{ s}^{-1};$
$t_m = 6\,000 \text{ s};$	$t_0 = 6\,000 \text{ s};$
$t_A = 24,192 \cdot 10^6 \text{ s};$	$u(t_A) = 86,4 \cdot 10^3 \text{ s};$
$t_{\text{Fe-55}} = 86,69 \cdot 10^6 \text{ s};$	$u(t_{\text{Fe-55}}) = 0,25 \cdot 10^6 \text{ s};$
$V_E = 10 \cdot 10^{-3} \text{ l};$	$u(V_E) = 0,2 \cdot 10^{-3} \text{ l};$
$V_M = 5 \cdot 10^{-3} \text{ l};$	$u(V_M) = 0,1 \cdot 10^{-3} \text{ l};$
$V_P = 0,25 \text{ l};$	$u(V_P) = 2 \cdot 10^{-3} \text{ l};$
$c_{\text{E,Fe-55}} = 1,92 \text{ mg}\cdot\text{l}^{-1};$	$c_{0,\text{Fe-55}} = 2,00 \text{ mg}\cdot\text{l}^{-1};$
$v_1 = -9,86 \cdot 10^{-2};$	$tSIE = 300;$
$v_2 = 1,42 \cdot 10^{-3};$	$u_{\text{rel}}(\eta_{\text{Fe}}) = 0,05;$
$v_3 = -5,48 \cdot 10^{-7};$	$u_{\text{rel}}(\varphi_{\text{A,Fe-55}}) = 0,1.$

The activity-related calibration factor for the radionuclide Fe-55 is calculated according to Equation (2), the chemical yield for iron according to Equation (6) and the decay correction factor according to Equation (7).

$$\varphi_{A,Fe-55} = \frac{1}{-9,86 \cdot 10^{-2} + (1,42 \cdot 10^{-3} \cdot 300) + (-5,48 \cdot 10^{-7} \cdot 300^2)} \approx 3,596$$

$$\eta_{Fe} = \frac{1,92 \text{ mg} \cdot \text{l}^{-1}}{2,00 \text{ mg} \cdot \text{l}^{-1}} = 0,96$$

$$f_1 = e^{\ln 2 \cdot \frac{24,192 \cdot 10^6 \text{ s}}{86,89 \cdot 10^6 \text{ s}}} \approx 1,213$$

The procedural calibration factor is determined according to Equation (5):

$$\varphi_{Fe-55} \approx \frac{3,596}{0,96} \cdot \frac{10 \cdot 10^{-3} \text{ l}}{0,25 \text{ l} \cdot 5 \cdot 10^{-3} \text{ l}} \cdot 1,213 \approx 36,35 \text{ l}^{-1}$$

This gives the activity concentration of Fe-55 according to Equation (4):

$$c_{Fe-55} \approx 36,35 \text{ l}^{-1} \cdot (0,475 \text{ s}^{-1} - 0,08 \text{ s}^{-1}) \approx 14,36 \text{ Bq} \cdot \text{l}^{-1}$$

For the calculation of the combined standard uncertainty, the value of the relative standard uncertainties of the net count rate is calculated according to Equation (9):

$$u_{\text{rel}}(R_{n,r}) = \frac{1}{0,475 \text{ s}^{-1} - 0,08 \text{ s}^{-1}} \cdot \sqrt{\frac{0,475 \text{ s}^{-1}}{6000 \text{ s}} + \frac{0,08 \text{ s}^{-1}}{6000 \text{ s}}} \approx 0,0243$$

Using the values for the relative standard uncertainty according to Equation (11) and the relative standard uncertainties for the volumes used

$$u_{\text{rel}}(f_1) = \frac{\ln 2}{86,69 \cdot 10^6 \text{ s}} \cdot \sqrt{(86,4 \cdot 10^3 \text{ s})^2 + \left(0,25 \cdot 10^6 \text{ s} \cdot \frac{24,192 \cdot 10^6 \text{ s}}{86,69 \cdot 10^6 \text{ s}}\right)^2} \approx$$

$$\approx 8,879 \cdot 10^{-4}$$

$$\sum_j u_{\text{rel}}^2(V_j) = \left(\frac{0,2 \cdot 10^{-3} \text{ l}}{10 \cdot 10^{-3} \text{ l}}\right)^2 + \left(\frac{0,1 \cdot 10^{-3} \text{ l}}{5 \cdot 10^{-3} \text{ l}}\right)^2 + \left(\frac{2 \cdot 10^{-3} \text{ l}}{0,25 \text{ l}}\right)^2 \approx 0,864 \cdot 10^{-3}$$

the relative standard uncertainty of the procedural calibration factor is determined according to Equation (10):

$$u_{\text{rel}}(\varphi_{\text{Fe-55}}) = \sqrt{0,1^2 + 0,05^2 + (8,879 \cdot 10^{-4})^2 + 0,864 \cdot 10^{-3}} \approx 0,1156$$

With these values and after conversion of Equation (8), the standard uncertainty of the activity concentration is determined as follows:

$$u(c_{\text{Fe-55}}) \approx 14,36 \text{ Bq} \cdot \text{l}^{-1} \cdot \sqrt{0,0243^2 + 0,1156} \approx 1,697 \text{ Bq} \cdot \text{l}^{-1}$$

The Fe-55 activity concentration in the sample is thus:

$$c_{\text{Fe-55}} \approx (14,36 \pm 1,697) \text{ Bq} \cdot \text{l}^{-1}$$

The decision threshold of the Fe-55 activity concentration is calculated using the value for the quantile of the standardised normal distribution for the first type of error $k_{1-\alpha} = 1,645$ according to Equation (12):

$$c_{\text{Fe-55}}^* \approx 1,645 \cdot 36,35 \text{ l}^{-1} \cdot \sqrt{0,08 \text{ s}^{-1} \cdot \left(\frac{1}{6000 \text{ s}} + \frac{1}{6000 \text{ s}} \right)} \approx 0,3088 \text{ Bq} \cdot \text{l}^{-1}$$

Using the value for the quantile of the standardised normal distribution for the second type of error $k_{1-\beta} = 1,645$ and the values for the auxiliary quantities θ and ψ determined according to Equations (15) and (16)

$$\theta \approx 1 - 1,645^2 \cdot 0,1156^2 \approx 0,9638$$

$$\psi \approx 1 + \frac{1,645^2}{2 \cdot 0,3088 \text{ Bq} \cdot \text{l}^{-1}} \cdot \frac{36,35 \text{ l}^{-1}}{6000 \text{ s}} \approx 1,027$$

the detection limit can be calculated according to Equation (14):

$$c_{\text{Fe-55}}^{\#} \approx \frac{0,3088 \text{ Bq} \cdot \text{l}^{-1} \cdot 1,027}{0,9638} \cdot \left[1 + \sqrt{1 - \frac{0,9638}{1,015^2} \cdot \left(1 - \frac{1,645^2}{1,645^2} \right)} \right] \approx 0,6580 \text{ Bq} \cdot \text{l}^{-1}$$

To calculate the limits of the probabilistically symmetrical coverage interval, the probabilities for the quantiles of the lower and upper coverage intervals are calculated according to Equations (17) and (18):

$$p \approx \omega \left(\frac{14,36 \text{ Bq} \cdot \text{l}^{-1}}{1,697 \text{ Bq} \cdot \text{l}^{-1}} \right) \cdot 0,95 \approx 0,9499$$

$$q \approx 1 - \omega \left(\frac{14,36 \text{ Bq} \cdot \text{l}^{-1}}{1,697 \text{ Bq} \cdot \text{l}^{-1}} \right) \cdot 0,05 \approx 0,950$$

The following values are determined for the limits of the probabilistically symmetrical coverage interval according to Equations (19) and (20):

$$c_{\text{Fe-55}}^{\Delta} \approx 14,36 \text{ Bq} \cdot \text{l}^{-1} - 1,6448 \cdot 1,697 \text{ Bq} \cdot \text{l}^{-1} \approx 11,57 \text{ Bq} \cdot \text{l}^{-1}$$

$$c_{\text{Fe-55}}^{\nabla} \approx 14,36 \text{ Bq} \cdot \text{l}^{-1} + 1,6449 \cdot 1,697 \text{ Bq} \cdot \text{l}^{-1} \approx 17,15 \text{ Bq} \cdot \text{l}^{-1}$$

7.2 Software supported evaluation

7.2.1 View of the Excel® spreadsheet

Procedure for determining the activity concentrations of iron-55 and nickel-63 in wastewater

H-Fe-55/Ni-63-AWASS-01

Version July 2023

Procedures' manual for monitoring of radioactive substances in the environment and of external radiation (ISSN 1865-8725)

SAMPLE IDENTIFICATION:

wastewater

ANALYTE: Fe-55

#Number of input quantities	
k_alpha	1,645
k_beta	1,645
gamma	0,1

Create Excel
variables!

User-Input:	definition quantities/Excel variables
	Input of Excel variables
	Input of values of quantities
Excel-VBA:	#Keywords
	Values from Vbasic

DATA INPUT					UNCERTAINTY BUDGET		
#Values of input quantities	Unit	Excel variable	Input values	StdDev	partial derivatives	uncertainty budget:	budget in %
p 1 #Number of gross counts Ng		Ng	2850	53,385	0,006060293	0,323531111	3,635472184
p 2 duration of counting source measurement	s	tm	6000	0	-0,00287864	0	0
p 3 background count rate	1/s	R0	0,08	3,651E-03	-36,3617578	0,132774367	0,612290052
p 4 duration of background measurement	s	t0	6000	0	0	0	0
p 5 half time iron	s	_tFe	8,669E+07	0	-3,2048E-08	0	0
p 6 time period ref. date to start of measurement	s	tA	2,419E+07	0	1,14841E-07	0	0
p 7 volume eluate	l	VE	1,000E-02	2,000E-04	1436,289433	0,287257887	2,865976661
p 8 volume aliquot eluate	l	VM	5,000E-03	1,000E-04	-2872,57599	0,287257599	2,865970929
p 9 sample volume	l	VP	0,25	2,000E-03	-57,4515199	0,11490304	0,458555349
p 10 chemical yield		_eta	0,96	4,800E-02	-14,9613333	0,718143999	17,91231831
p 11 activity-related calibration factor (List can be continued here)	Bq*s	_phiA	3,596	3,596E-01	3,994130794	1,436289433	71,64941652
MODEL SECTION					Result = phi * Rn		
Derived quantities					(Formulae)		
h 1 #Gross count rate Rg	1/s	Rg	0,475				
h 2 Decay correction factor iron (List can be continued here)		_f1	1,2134				
#Net count rate Rn	1/s	Rn	0,3950				
#Calibration factor, proc.dep.	Bq*s/l	phi	36,362				
#Value output quantity	Bq/l	Result	14,3629	0,65796138	<-- output value modifiable by VBA		
#Standard uncertainty output quantity	Bq/l	uResult	1,6968				
#Decision threshold	Bq/l		0,3089				
#Detection limit	Bq/l		0,6580				
FURTHER DERIVED QUANTITIES					Calculate!		
Auxiliary quantity Omega		Omega	1,0000				
Best estimate	Bq/l	BestEst	14,3629				
Standard uncertainty best estimate	Bq/l		1,6968				
Coverage interval (lower limit)	Bq/l		11,5719				
Coverage interval (upper limit)	Bq/l		17,1539				

The corresponding Excel® spreadsheet is available on the website of this Procedures' Manual.

7.2.2 View of the UncertRadio result page

The screenshot displays the 'Results' tab of the UncertRadio software. The main window title is 'UncertRadio: Calculation of uncertainty budget and detection limits - H-Fe-55+Ni-63-AWASS-01_V2023-07_EN.bxp'. The interface includes a menu bar (File, Edit, Options, Help) and a toolbar with various icons. The 'Results' tab is active, showing the following data:

Final measurement result for c :

Value output quantity:	14.357	Bq/l
extendend (Std.-)uncertainty:	1.6961	Bq/l
relative ext.(Std.-)uncertainty:	11.814	%
Best Bayesian Estimates:		<input type="checkbox"/> min. Coverage interval
Value output quantity:	14.357	Bq/l
extendend (Std.-)uncertainty:	1.6961	Bq/l
lower range limit:	11.567	Bq/l
upper range limit:	17.146	Bq/l

Coverage factor k: 1.0
Probability (1-gamma): 0.90

Decision threshold and detection limit for c :

Decision threshold (DT):	0.3087	Bq/l	Iterations:	1
Detection limit (DL):	0.6576	Bq/l	Iterations:	4

k_alpha=1.645, k_beta=1.645 Method: ISO 11929:2019, by iteration

Monte Carlo Simulation:

Number of simul. measurements:	100000	<input type="checkbox"/> min. Coverage interval		
Number of runs:	1			
primary estimate:	14.402	relSD%:	Bq/l	0.038
uncertainty primary estimate:	1.7122	Bq/l	0.224	
Value output quantity:	14.402	Bq/l	0.038	
extendend uncertainty:	1.7122	Bq/l	0.224	
relative extd.(Std.-)uncertainty:	11.889	%		
lower range limit:	11.686	Bq/l	0.098	
upper range limit:	17.293	Bq/l	0.066	
Decision threshold (DT):	0.31406	Bq/l	0.406	
Detection limit (DL):	0.65037	Bq/l	0.295	

active run: 1 IT: 10 Start MC

The corresponding UncertRadio project file is available on the website of this Procedures' Manual.

8 Catalogue of the chemicals und equipment

8.1 Chemicals

The chemicals used should be of analytically pure quality.

- ammonia solution, NH₃: 13,5 mol·l⁻¹ (25 %);
- basic buffer solution: 0,2 mol·l⁻¹:
diammonium hydrogen citrate solution (1 mol·l⁻¹)
adjusted to pH 8,5 with ammonia solution (13,5 mol·l⁻¹);
- caesium fluoride solution, CsF: 6,6 mol·l⁻¹;
- diammonium hydrogen citrate solution: 1 mol·l⁻¹;
- Fe-carrier solution: 1 mg Fe³⁺ per ml solution:
2,42 g iron(III) chloride hexahydrate (FeCl₃·6 H₂O) in
500 ml nitric acid (0,1 mol·l⁻¹);
- hydrochloric acid, HCl: 10 mol·l⁻¹, 8 mol·l⁻¹, 1,2 mol·l⁻¹,
0,2 mol·l⁻¹;

-
- hydrogen peroxide, H₂O₂: 9 mol·l⁻¹ (30 %) in water.
 - NI-Resin: prefabricated column with 2 ml column bed volume (corresponding to 0,5 g resin);
 - Ni-carrier solution: 1 mg Ni²⁺ per ml solution:
0,81 g nickel(II) chloride hexahydrate (NiCl₂·6 H₂O) in 200 ml hydrochloric acid (0,1 mol·l⁻¹);
 - nitric acid, HNO₃: 14 mol·l⁻¹, 1,5 mol·l⁻¹;
 - potassium hydroxide solution, KOH: 10 mol·l⁻¹;
 - scintillation cocktail: e. g. Quicksafe A, Insta Gel Plus;
 - sulphuric acid, H₂SO₄: 18 mol·l⁻¹;
 - TRU-Resin: prefabricated column with 2 ml column bed volume (corresponding to 0,7 g resin);

8.2 Equipment

The following equipment is used for the procedure:

- standard equipment of a radiochemistry laboratory;
- optical emission spectrometer with inductively coupled plasma (ICP-OES) or flame atomic absorption spectrometer (AAS);
- counting vials with a volume of 20 ml;
- liquid scintillation spectrometer (LSC).

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