

Procedure for determining nickel-63 in wastewater

H-Ni-63-AWASS-01

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1 Scope

The present measuring instruction is suitable for analysing wastewaters irrespective of their composition and specifically for wastewater samples from nuclear power plants. Elevated salt contents, in particular fluoride ions and detergents, may interfere with the analysis. The content of inactive nickel needs to be known or must be determined.

Differentiating between Ni-63, Ni-57 as well as Ni-66 on the one hand, and Ni-56 and Ni-59 on the other hand, is not possible with the measuring technique described here. The presence of Ni-56/Ni-57/Ni-66 has to be verified by means of gamma spectrometry and the results of measuring the beta-emissions may need to be corrected accordingly. Owing to the short half-lives of these nuclides, it is also an option to wait for their decay prior to starting the beta-measuring process.

2 Sampling

Under normal conditions, sample volumes of 0,5 l to 1 l will be sufficient for determining the Ni-63 content. The sample taken needs to be representative of the wastewater to be analysed (see procedure H- γ -SPEKTAWASS-01). The sample is acidified with 1 ml of nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$). The water samples can be stored in polyethylene bottles for extended periods of time.

3 Analysis

3.1 Principle of the procedure

The principle of the procedure is illustrated in Figure 1. After adding nickel ions and retainer ions, nickel hydroxide is precipitated from the solution. The precipitate is dissolved in acid and separated via potassium hexanitritocobaltate (III) precipitation and subsequent removal of cobalt isotopes (Co-57, Co-58, Co-60) by ion exchange. Nickel is thereafter separated from other radionuclides by chloroform extraction of the nickel dimethylglyoxime complex. Renewed precipitation of the oxime will serve to gravimetrically determine the chemical yield. Once the organic compound has been decomposed with nitric acid, the sample is converted into chloride form, Gel forming scintillation cocktail is added to the solution, and finally the measurement is performed in a liquid scintillation counter.

3.2 Sample preparation

10 ml of cobalt hold-back carrier solution ($0,5 \text{ mg}\cdot\text{ml}^{-1}$ of Co^{2+}), precisely 4,0 ml of nickel carrier solution ($5,0 \text{ mg}\cdot\text{ml}^{-1}$ of Ni^{2+}), 5 ml of sulphuric acid ($18 \text{ mol}\cdot\text{l}^{-1}$), and 5 ml of nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) are added to the sample and then evaporated on a sand bath until it starts giving off sulphur trioxide fumes. This step is repeated until all organic constituents have been decomposed.

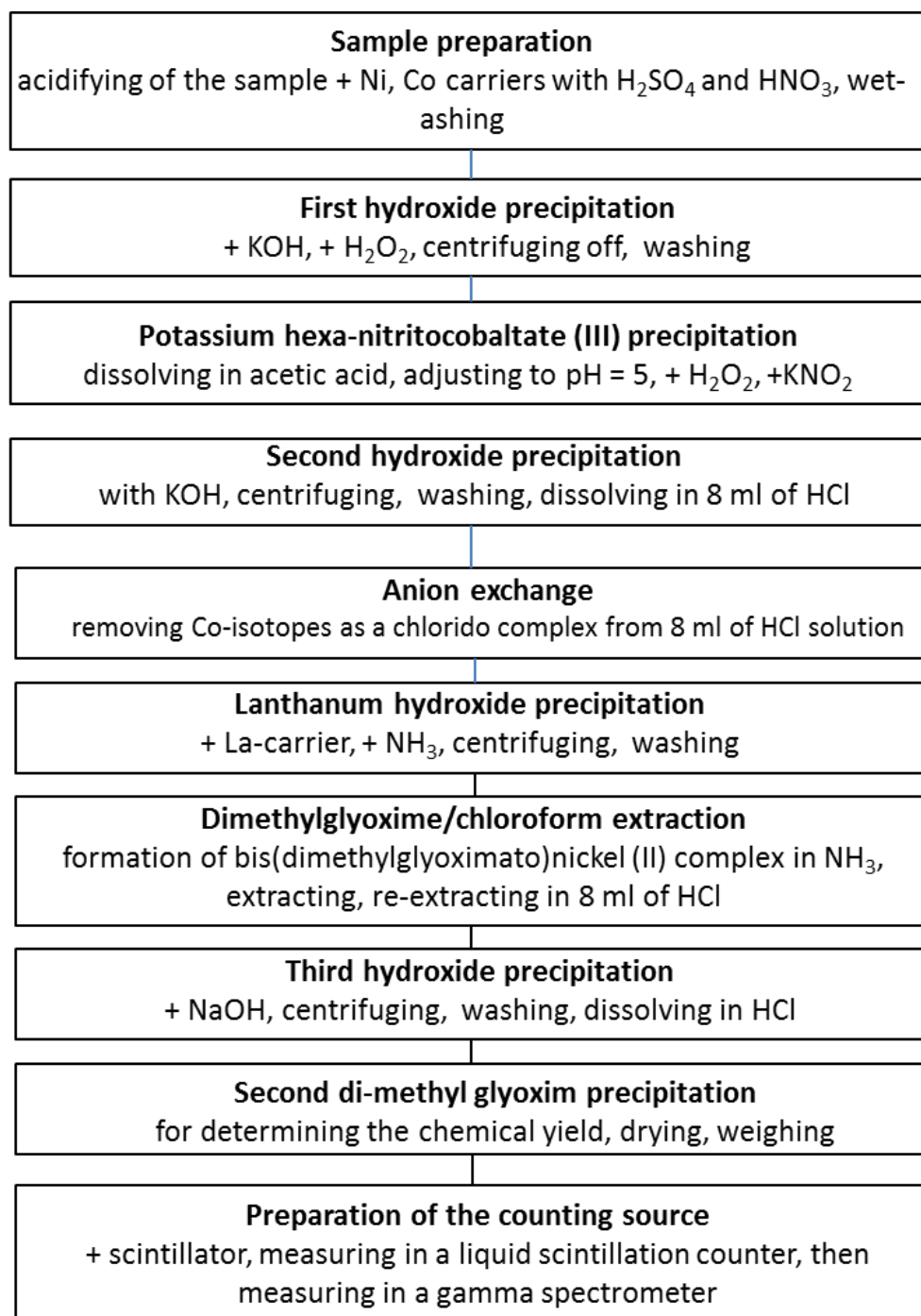


Fig. 1: Principle of determining Ni-63 in wastewater

3.3 Radiochemical separation

3.3.1 After having been left to cool to room temperature, a little distilled water is given to the sample and then it is transferred to a centrifuge tube (volume > 80 ml). Following the addition of a few drops of hydrogen peroxide ($10 \text{ mol} \cdot \text{l}^{-1}$), the hydroxides are precipitated by *adding* about 10 ml of potassium hydroxide ($6 \text{ mol} \cdot \text{l}^{-1}$) while stirring carefully until the point of alkaline reaction is reached. The precipitate is heated in a water bath until the hydroxides have agglomerated and sedimented. After having left the centrifuge tube cooling to room temperature, it is centrifuged. The supernatant solution is decanted and discarded.

3.3.2 The precipitate is dissolved in about 5 ml of acetic acid ($8 \text{ mol}\cdot\text{l}^{-1}$) and 2 drops of hydrogen peroxide ($10 \text{ mol}\cdot\text{l}^{-1}$) while being heated. Following dilution with distilled water to about 15 ml, 5 ml of ammonium acetate buffer ($\text{pH} = 5$) are added, heated on a boiling water bath, and 5 g of potassium nitrite dissolved in a little distilled water are carefully added while swivelling (emission of gas!). Yellow-coloured potassium hexanitritocobaltate (III) is formed. The sample is left on the water bath until the precipitate has agglomerated and sedimented. Following its cooling to room temperature, it is centrifuged off. The centrifugate is filtered via a blue-ribbon filter into another centrifuge tube. The walls of the first centrifuge tube and the precipitate are rinsed with a few ml of ammonium acetate. The rinsing solution and filtrate are combined and the precipitate discarded.

3.3.3 Nickel hydroxide is precipitated from the filtrate with about 5 ml of potassium hydroxide solution ($6 \text{ mol}\cdot\text{l}^{-1}$). After the precipitate has been heated on a water bath to make it agglomerate and sediment, it is cooled and centrifuged. The centrifugate is decanted and discarded. The precipitate is then thoroughly stirred up in 20 ml of distilled water and centrifuged once more; the supernatant water is discarded.

3.3.4 The precipitate is dissolved under warming in 2 ml of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) and another 5 ml of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) are added. The solution is slowly (about 0,5 ml per minute corresponding to 2 to 3 drops per second) applied to a conditioned anion exchanger (see section 7.1.1). The column is washed twice with 20 ml of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) each. The run-off and washing solution are combined and evaporated to near dryness.

3.3.5 The concentrate is elutriated with 10 ml of distilled water and quantitatively transferred to a centrifuge tube. Following the addition of 10 ml of lanthanum carrier ($1 \text{ mg}\cdot\text{ml}^{-1}$ of La^{3+}), lanthanum hydroxide is precipitated with ammonia ($13 \text{ mol}\cdot\text{l}^{-1}$) in excess. Once the precipitate has agglomerated and sedimented in a warm environment, it is centrifuged off. The centrifugate is transferred to a separation funnel. The precipitate is stirred up in 5 ml of ammonia ($0,1 \text{ mol}\cdot\text{l}^{-1}$) and centrifuged once more. The wash solution is also transferred to the separation funnel. The lanthanum hydroxide precipitate is discarded.

3.3.6 5 ml of sodium citrate solution ($0,5 \text{ mol}\cdot\text{l}^{-1}$), 10 ml of dimethylglyoxime/ethanol solution ($0,1 \text{ mol}\cdot\text{l}^{-1}$), as well as 400 ml of chloroform are added to the solution in the separation funnel. It is shaken for 5 minutes. Following the separation of phases, the organic (lower) phase is drained into a 600 ml-beaker. The extraction of the aqueous phase is repeated twice with 50 ml of chloroform each. The organic phases are combined and the aqueous phases discarded.

3.3.7 The organic phase is filled into the cleaned separation funnel and washed twice with 20 ml of ammonia ($0,1 \text{ mol}\cdot\text{l}^{-1}$) each. The wash solutions are discarded.

3.3.8 For the purpose of re-extraction, the organic phase is shaken with 25 ml of hydrochloric acid ($4 \text{ mol}\cdot\text{l}^{-1}$) for about 5 minutes. While the dimethylglyoximate complex will decompose, the nickel will concentrate in the aqueous (upper) phase. The chloroform phase is drained and collected for recycling by distillation.

3.3.9 The hydrochloric nickel solution is evaporated to near dryness in a 100 ml-beaker, 10 ml nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) are added for destroying remnants of dimethylglyoxime, and then evaporated to dryness once more. 4 ml of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) is given to the cooled residue and transferred with a little distilled water to a centrifuge tube.

3.3.10 Nickel is precipitated as hydroxide by adding about 10 ml of sodium hydroxide ($6 \text{ mol}\cdot\text{l}^{-1}$). Once the precipitate has agglomerated and sedimented in a warm environment, it is centrifuged off. The centrifugate is discarded. The hydroxide precipitate is dissolved in 1 ml to 2 ml of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) and diluted with distilled water to 5 ml.

3.3.11 The solution is made strongly alkaline by adding ammonia ($13 \text{ mol}\cdot\text{l}^{-1}$). By adding 5 ml to 10 ml of dimethylglyoxime/ethanol ($0,1 \text{ mol}\cdot\text{l}^{-1}$), nickel dimethylglyoxime is precipitated. It is left to stand for about an hour while it is occasionally stirred over. The precipitate is then siphoned off via a dry weighed glass filter crucible and washed with a water/ethanol mix (1:1). The sample is then dried at $105 \text{ }^\circ\text{C}$ until its weight remains constant, cooled to room temperature and weighed for determining the chemical yield.

3.3.12 The precipitate is dissolved in 2 ml of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) in the crucible and siphoned off to a 100 ml-beaker in a Witt's flask. The crucible is then rinsed twice with 5 ml of nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) each. The solution is evaporated to dryness. The residue is fumed off twice with 5 ml of nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) each and then once more with 5 ml of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$).

3.3.13 Finally, 2 to 3 drops of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) are given to the residue and the solution is transferred quantitatively with a little water (maximum volume 7 ml) to a small liquid-scintillation vial. After the sample – if required – has been filled with distilled water to a volume of 7 ml, 15 ml of gel forming scintillation cocktail are added, the vial is carefully capped, and shaken thoroughly.

4 Measuring the activity

4.1 General

The counting source produced according to the described separation procedure may contain a number of nickel isotopes. Table 1 is a compilation of some nuclear-physical data of nickel isotopes and their daughter nuclides, which may be of relevance here.

The short-lived nickel isotopes can be identified by gamma spectrometry on the basis of their own gamma lines or those produced by their decay products. If they are present, their complete decay needs to be awaited before the measuring process in the liquid scintillation counter can be repeated.

4.2 Calibration

When measuring the activity of a sample in a liquid scintillation counter, an external standard (e. g., Ra-226) is used to determine a quench value for each sample. This quench value depends on the nickel content of the sample and thus on the chemical yield. For its part, the calibration factor, ϕ_m , depends on the quench value. It is therefore necessary that a quench curve be recorded.

Calibration is based upon several calibration sources that have been produced according to section 3.3 with nickel masses of between 5 mg and 25 mg and supplemented with known activities of Ni-63 (in the range of 1000 Bq), after which the count yield in relation to the nickel mass can be determined. The calibration function can be displayed with sufficient approximation as a 2nd-order polynomial.

Tab. 1: Nuclear data of nickel isotopes and daughter nuclides (in brackets)

Nuclide	Half-life (d)	β - E_{\max} (keV)	Emission probability (%)	γ -energy (keV)	Emission probability (%)
Ni-56	6,1	7 (EC)	100	158 270 481 751 812 1562	99 40 41 53,8 90,5 12,5
(Co-56)	77,3	7 (EC)	81	847 1038 1238	100 14 67,6
Ni-57	1,50	7 (EC) 849 (β^+)	60 40	127 1378 1920	15 84,9 15
(Co-57)	270,9	7 (EC)	100	122 136	85,6 10,6
Ni-59	$2,74 \cdot 10^7$	7(EC)	100	-	-
Ni-63	$3,51 \cdot 10^4$	63	100	-	-
Ni-66 (Cu-66)	2,28 (5,1 min)	200 2630	100 100	1039	9

4.3 Measurement

The low-energy beta radiation of the isotope Ni-63 is measured by liquid scintillation counting. This requires that an energy range from 0 keV to 63 keV be set as to correspond to the energy of the beta radiation of Ni-63.

Using a measuring instrument with logarithmic energy scale is of advantage for measuring the low-energy X-rays of Ni-59, as quenched samples will otherwise have the recorded pulses distributed only over a very few channels. Fine-tuning the energy range might possibly allow a separate determination of Ni-63 and Ni-59. While the Ni-63 may then be determined «without errors» (provided that all other radionuclides have been properly separated or have decayed), a portion of the Ni-63 beta spectrum will impact on the range of the Ni-59 (spill over). For the mathematical correction of this effect, see, procedure H-C-14/H-3-AWASS-01. For measuring X-rays by liquid scintillation counting and the required setting of channels and calibration, see also procedure H-Fe-55-AWASS-01.

The sample should be measured together with a background effect sample. The latter is manufactured according to step 3.3.13 from ca. 25 mg of nickel. The measuring period should be at least 200 minutes in the case of low-level measuring. In order to be able to recognize chemo-luminescence, which will be recorded by the measuring instrument preferentially in the low-energy channels, the samples should be measured several times. If the measuring instrument used allows to record beta spectra, this option should be exploited.

In order to detect radioactive contaminations, in particular by the nickel isotopes Ni-56, Ni-57 and Ni-66, the sample is measured by gamma spectrometry after the liquid scintillation measurement has been completed. Repeating the measurement after allowing for an adequate decay period may be necessary.

5 Calculation of the results

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

and (2): $\eta = \frac{m_G \cdot f}{m_T}$

$$c = \frac{\varphi_A \cdot (R_g - R_0)}{V \cdot \eta} \quad (1)$$

$$\eta = \frac{m_G \cdot f}{m_T} \quad (2)$$

where

- c activity concentration of Ni-63, in Bq·l⁻¹;
- V sample volume, in l;
- φ_A calibration factor, in Bq · s;
- R_0 background count rate, in s⁻¹;
- R_g gross count rate, in s⁻¹;
- m_G mass of the nickel dimethylglyoxime, in g;
- m_T mass of the nickel carrier, in g;
- f conversion factor nickel dimethylglyoxime/nickel (= 0,2032).

5.1 Worked example

5.1.1 Calculating the chemical yield

By inserting numerical values of:

$$m_G = 0,0651 \text{ g}$$

$$m_T = 0,0200 \text{ g,}$$

equation (2) will produce $\eta = 0,661$ (66,1 %).

5.1.2 Calculating the activity concentration

The activity concentration c is calculated by inserting:

$$\varphi_A = 2,33 \text{ Bq} \cdot \text{s}$$

$$R_g = 1,70 \text{ s}^{-1}$$

$$R_0 = 0,27 \text{ s}^{-1}$$

$$V = 0,5 \text{ l,}$$

into equation (1) as $c = 10,1 \text{ Bq} \cdot \text{l}^{-1}$.

Subsequent gamma spectrometric measuring this sample did not detect the presence of further nickel isotopes.

5.2 Consideration of uncertainties

The total uncertainty of the measuring result depends for the largest part on the calibration uncertainty of the liquid scintillation counter and the uncertainty attached to determining the chemical yield. Systematic uncertainties, such as those caused by incompletely separated interfering radionuclides cannot be quantified and cannot therefore be taken into consideration mathematically.

In practical operations, the total uncertainty will amount to count rates that are clearly above that of the background effect, at about $\pm 10\%$.

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. The detection limit for the activity concentration, g , is calculated according to equation (3):

$$g = \frac{G}{\eta \cdot V} \quad (3)$$

Inserting the numerical values given above and a measuring period for the background effect of $t_0 = 12000$ s (200 min) will produce a detection limit, g , of the activity concentration of:

$$g = 0,22 \text{ Bq}\cdot\text{l}^{-1}$$

7 Catalogue of chemicals and equipment

7.1 Chemicals

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

- Ammonia, NH_3 : $0,1 \text{ mol}\cdot\text{l}^{-1}$ and $13 \text{ mol}\cdot\text{l}^{-1}$;
- Ammonium acetate buffer solution, $\text{NH}_4(\text{CH}_3\text{COO})/\text{CH}_3\text{COOH}$: $\text{pH} = 5$;
- Anion exchanger: e.g., DOWEX 1×8 , 20 mesh to 50 mesh, Cl^- -form;
- Chloroform, CHCl_3 ;
- Dimethylglyoxime, $(\text{CH}_3\text{CNOH})_2$: $0,1 \text{ mol}\cdot\text{l}^{-1}$ ethanol;
- Acetic acid, CH_3COOH : $8 \text{ mol}\cdot\text{l}^{-1}$;
- Ethanol, $\text{C}_2\text{H}_5\text{OH}$;
- Potassium hydroxide, KOH : $5 \text{ mol}\cdot\text{l}^{-1}$;
- Potassium nitrite, KNO_2 ;
- Cobalt hold-back carrier: $0,5 \text{ mg}\cdot\text{ml}^{-1} \text{ Co}^{2+}$ ($2,0 \text{ g}\cdot\text{l}^{-1} \text{ CoCl}_2\cdot 6\text{H}_2\text{O}$) ;
- Lanthanum nitrate: $1 \text{ mg}\cdot\text{ml}^{-1} \text{ La}^{3+}$ ($3,1 \text{ g}\cdot\text{l}^{-1} \text{ La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$) ;
- Sodium citrate, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\cdot 2\text{H}_2\text{O}$: $0,5 \text{ mol}\cdot\text{l}^{-1}$;
- Sodium hydroxide, NaOH : $6 \text{ mol}\cdot\text{l}^{-1}$;
- Nickel carrier: $5 \text{ mg}\cdot\text{ml}^{-1} \text{ Ni}^{2+}$ (e. g., nickel standard solution, Merck) ;
- Nitric acid, HNO_3 : $14 \text{ mol}\cdot\text{l}^{-1}$;
- Hydrochloric acid, HCl : $4 \text{ mol}\cdot\text{l}^{-1}$ and $8 \text{ mol}\cdot\text{l}^{-1}$;
- Sulphuric acid, H_2SO_4 : $1 \text{ mol}\cdot\text{l}^{-1}$;
- Scintillator, gelling, e. g., INSTAGEL® (Packard);
- Hydrogen peroxide, H_2O_2 : $10 \text{ mol}\cdot\text{l}^{-1}$.

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7.1.1 Conditioning the anion exchanger

The pre-soaked exchanger resin is filled without air bubbles into a column (inner diameter 10 mm) to a height of about 10 cm. It is washed with 50 ml of distilled water and 50 ml of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$). The column must not run dry.

7.2 Equipment

- Liquid scintillation counter (with an option of displaying beta spectra);
- Glass filter crucible (frit with a porosity of 4);
- gamma spectrometer;
- Basic equipment of a radiochemical laboratory.

References

- (1) Krieger, H. L., Gold, S.: Procedures of radiochemical analysis of nuclear reactor aqueous solutions. U. S. Environmental Protection Agency, EPA-R4 73-014, May 1973
- (2) Gans, I., Arndt, J.: Untersuchungen zur Emission von P-32, Fe-55 und Ni-63 mit Abwässern aus Kernkraftwerken in der Bundesrepublik Deutschland. WaBoLu-Berichte 3 (1982)