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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

Abstract

The aims of this project were to develop a method to measure the amount of ^{59}Ni in stainless steel and to determine the detection limit for this method. ^{59}Ni is produced by neutron activation in the construction material close to the core in a nuclear reactor and it is important to know the amount of ^{59}Ni present as it governs the classification of the waste. If the amount of ^{59}Ni is known at different locations in relation to the core, it is also possible to refine the calculation models of the neutron flux in the reactor.

Accelerator mass spectrometry (AMS), an ultra-sensitive method for measuring small concentrations of radionuclides as well as stable nuclides, has been used in this investigation to determine the concentration of ^{59}Ni (and thereby the activity) in stainless steel.

As the cobalt content in stainless steel is the main contributor to the background in a measurement of ^{59}Ni , a method for the chemical extraction of nickel from stainless steel, including a purification step to reduce the cobalt content in the sample, has been developed.

The detection limit for ^{59}Ni has been determined to 100 ± 30 Bq per gram nickel (100 ± 30 Bq/g_{nickel}) with the present status of the system.

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Summary

A method to measure the amount of ^{59}Ni in stainless steel has been developed at the Pelletron accelerator in Lund. As the cobalt content in stainless steel is the main contributor to the background in a measurement of ^{59}Ni , a method for the chemical extraction of nickel from stainless steel, combined with a purification step to reduce the cobalt content in the sample by several orders of magnitude, has been developed. The detection limit for ^{59}Ni has been determined to be $100 \pm 30 \text{ Bq/g}_{\text{nickel}}$ with the present status of the system. By improving the system in various ways, a reduction of the detection limit by a factor of 10 would be possible.

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1 Introduction

In nuclear waste management ^{59}Ni is an important radioisotope, as it is produced by neutron activation in the stainless steel of a nuclear reactor. Three main areas of interest can be identified.

1. Classification of the construction material in the plant on the basis of the activity concentration, in order to be able to define how the different parts are to be stored.
2. Refinement of calculation models of the neutron flux in the reactor. This can be done if the content of ^{59}Ni in the different parts of the reactor is known.
3. Classification of operational waste on the basis of its activity concentration, e.g. ion exchangers.

The amount of a radioactive isotope can be determined in two ways. Either by measuring the radiation emitted from the decaying isotope or by counting the number of radioactive atoms and comparing it to the number of atoms of a stable isotope. If the half-life of the isotope and the decay-path are known, both methods will give the same information. Which method is to be preferred varies from case to case. For isotopes with long half-lives – when the number of atoms of the radioactive isotope is large compared to the number decaying during the period of measurement – the method of counting atoms will be more effective. In the case of measuring decays, the technique is well known. The equipment is easy to use and available at a reasonable price. In the case of counting atoms one needs advanced equipment, including an accelerator, at a total cost of at least 10–15 MSEK.

It is difficult to measure ^{59}Ni by ordinary radiometric techniques due to its long half-life, $7.6 \cdot 10^4$ year /1-1/, and because it decays only via electron capture, i.e. only characteristic radiation is emitted. A more efficient way to measure radionuclides such as ^{59}Ni , is to use accelerator mass spectrometry (AMS), which is a highly sensitive method for measuring rare isotopes /1-2/.

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2 The aims of this project

The aims of this project are:

1. To investigate and to present the possibility of **handling active substances** at the Department of Nuclear Physics in Lund in connection with the determination of the ^{59}Ni content of these substances.
2. To develop a method for the **preparation of high-quality nickel samples** suitable for the ion source of the Lund AMS system. The nickel samples are produced from small pieces of stainless steel. The samples have to provide a stable current of negative nickel ions for a period of time sufficiently long for an AMS measurement (that is 1–2 hours). The minimum weight of nickel required per sample is 5–10 mg.
3. To **optimise the AMS ion source** to provide a high-quality current of ^{59}Ni ions. Before this project started, most of the investigations carried out with the Lund ion source involved graphite samples. The ion source should be optimised to provide a current of nickel ions of 5–10 μA .
4. To develop a method to **chemically reduce the cobalt content** of the original substance. Suitable methods are described in international research literature. The cobalt content is reduced in an anion-exchange process. This may lower the ^{59}Ni detection-limit by three orders of magnitude.
5. To build an **experimental chamber** as well as to purchase an **X-ray detector** with suitable electronic equipment. Further, to optimise the geometrical set-up for the experimental chamber and the detector.
6. To **determine “the machine background”** of cobalt and also to determine the level of suppression of the other nickel isotopes (^{58}Ni , ^{60}Ni). This analysis will involve measurements on samples, which as far as possible are free of ^{59}Ni and ^{59}Co .
7. Finally, after step one to six have been carried out, to **determine the detection limit** for ^{59}Ni .

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3 The experimental technique

3.1 The AMS technique

The Lund AMS system /3-1/ is based on a 3 MV Pelletron tandem accelerator provided with a caesium-sputtering ion source containing a multiple sample holder /3-2, 3-3/. The beam extracted from the ion source passes several filters (magnetic and/or electric fields) which are tuned to single out the mass of interest. In this investigation the charge state 8+ and the ion energy 20 MeV were selected. By switching the setting of the filters between the mass of a stable isotope and the rare one, an abundance ratio between them can be determined, and thereby the number of ^{59}Ni atoms.

3.2 Detection of projectile X-rays

After analysis in the AMS system, the ions are slowed down by letting them pass through a 2 μm thick layer of germanium evaporated on a 100 μm thick mylar foil. Characteristic X-rays are produced, both from the target atoms and from the bombarding ions. By measuring characteristic X-rays the ions are identified by their atomic number. The X-rays were measured by a high-resolution germanium detector (Canberra, LEGe GL0210P, active area 200 mm^2 , resolution 145 eV FWHM at 5.9 keV) placed at zero degrees to the incoming ion beam.

To measure the stable isotope, characteristic X-rays (if the count rate is below 40,000 s^{-1}) or the beam current (if a beam current of a few nA is available) can be used. For these nickel experiments the stable isotope ^{61}Ni (with a natural abundance of 1.13%) has been selected, as this gives the possibility to detect characteristic X-rays. This simplifies the normalisation between ^{59}Ni and ^{61}Ni since neither the X-ray production rate nor the detection efficiency need be considered.

In a preliminary investigation different target materials and ion energies were tested /3-4/. The use of germanium as a target reduced the production of X-rays from Co ions compared to other target materials tested (Fe, Cu, Zn, Ga, Se). Another advantage of using germanium as a target is that, due to self-absorption, almost no Ge X-rays are seen in the spectra when a germanium detector is used. The thickness of the backing foil was not optimised for the detection of nickel ions, but was found to be sufficient for these experiments.

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4 Results

We describe below the realisation of the different sub-projects according to paragraph 2.

4.1 The handling of radioactive substances

As a first step, the possibility of handling active substances at the Department of Nuclear Physics in Lund for the determination of the ^{59}Ni content was investigated.

The isotopes, which contribute 99% of the total activity including ^{59}Ni , are calculated to be as given in Table 4-1.

Table 4-1. Isotopes contributing to 99% of the total activity in stain less steel.

Isotope	Half-life (year)	Activity in steam separator * (kBq/kg)	Activity in core grid ** (GBq/kg)
^{55}Fe	2.64	30	226
^{60}Co	5.34	4.0	69.6
^{59}Ni	76 200	0.014	0.876
^{63}Ni	93.5	1.6	100

*) Data provided by B. Bjurman, Forsmark Nuclear Power Station:

The activity in a steam separator at a distance of one metre from the core. The calculations assume 15 years of operation and that the separator has not been contaminated. The calculations were carried out at the Risø National Laboratory in Denmark.

**) Data provided by P.O. Aronsson, Ringhals Nuclear Power Station:

The calculations assume 10 years of operation, i.e. 75500 Full Power Hours (FPH).

The main reason for the difference in the calculated activities lies in the distance to the reactor core. The steam separator operates at a distance of one metre, while the core grid carries the fuel poles. Therefore, the core grid experiences a much larger neutron flux and therefore has a higher activity.

As a complement to these calculations, a measurement of the ^{60}Co activity was performed on a piece of a steam separator at the Ringhals nuclear power plant. The activity measured was ten times higher than the calculated activity. It is reasonable to believe that the theoretical model used for the calculations concerning the steam separator can be improved. Therefore the steam separator calculation will be recalculated by an improved method.

All the activities indicated above can be handled, without problems, at the Department of Nuclear Physics in Lund. As only a very small amount of activated steel (0.5-1 g) is needed to provide a sufficient amount of nickel, a possible increase in activity of one

order of magnitude should still not cause any handling problems in Lund. Based on these considerations, a suitable method of reducing the cobalt content of the samples has been chosen. This cobalt reduction can be performed without problems at the Department of Nuclear Physics in Lund.

4.2 Sample preparation for the detection of ^{59}Ni in stainless steel

As the raw material is stainless steel, nickel has to be extracted from the steel and separated from cobalt. The chemical composition of the sample used in the ion source is therefore dependent on the outcome of the above-mentioned chemical process. Once the chemical processing of the stainless steel was established, the sample requirements¹ guided our choice of sample material to be used in the Lund ion source.

4.2.1 Current quality

A current of good quality is, in this case, a high and stable current of negative nickel ions (“nickel current”). Preferably, this current is free of cobalt ions. The current intensity and stability are highly dependent on the sample substance used, the amount of substance pressed into the sample holder and the sample pressing process. The chemical process yields three different substances for investigation: Ni, NiO and a complex between nickel and dimethylglyoxime (Dmg).

Eight different types of samples were investigated:

1. A solid nickel sample (sol. Ni).
2. Nickel filings pressed over silver powder (Ni+Ag).
3. Industrial nickel and carbon powder, mixed 1:1 (Ni+C).
4. Nickel powder from the chemical process, recessed $\sim 0.5\text{mm}$ (Ni).
5. Nickel powder from the chemical process, recessed 2.5mm (Ni, rec.).
6. Nickel oxide, home-made from nickel powder (NiO).
7. Nickel oxide from the chemical process.
8. Ni-Dmg complex pressed on silver powder.

Metallic nickel samples seem to satisfy the above requirements best: They give a high and stable nickel current (up to $\sim 4\ \mu\text{A}$ when pressed into optimised sample holders and 10% current decrease per hour), see Figure 4-1.

Samples of nickel oxide give only half the current of a metallic nickel sample, and furthermore the current decreases fairly quickly. An explanation for this rapid decrease of the nickel oxide current may be that the material is “sputtered away” as the samples are investigated.

¹ The sample is required to provide a high and stable current of negative nickel ions during a period of time sufficiently long for AMS-measurements.

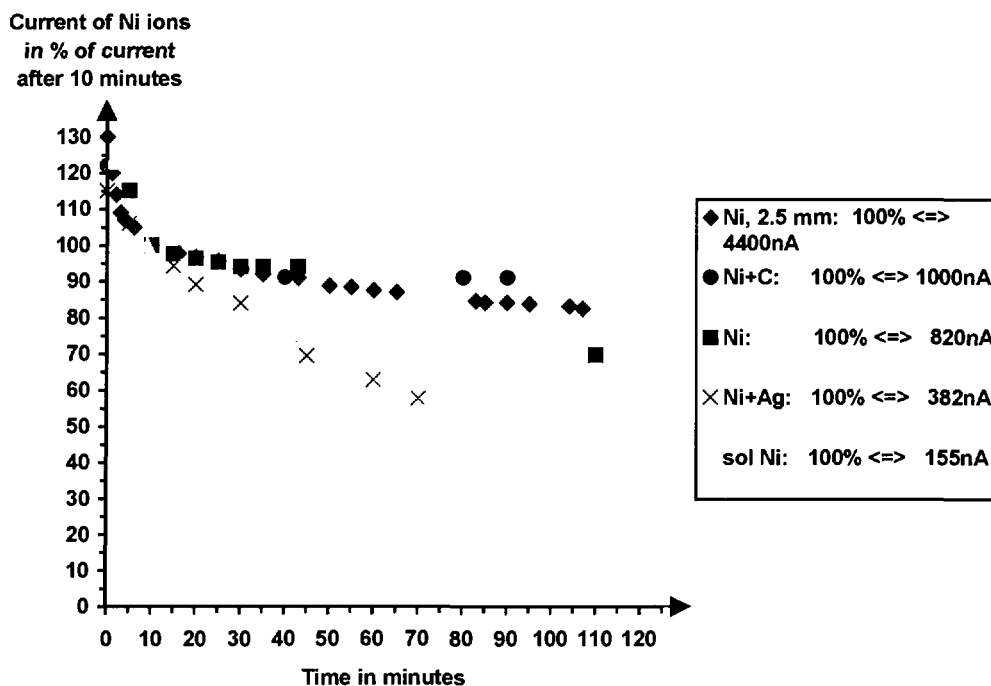


Figure 4-1. The nickel current measured after the inflection magnet as a function of time after an initial stabilisation of 10 minutes. Current stability is very important for quality measurements. Nickel pressed over silver (Ni+Ag) decreases too fast like the current from a solid nickel sample (sol Ni). Nickel mixed with carbon (Ni+C) is stable but mixtures should be avoided as they may contribute cobalt. Metallic nickel powder pressed to a depth of 0.5 mm (Ni) and 2.5 mm (Ni, 2.5 mm) is very stable, it decreases 10% per hour after initial stabilisation.

The solid nickel sample and the sample with nickel filings pressed onto silver powder gave low and steadily decreasing current.

Ni-Dmg complex pressed onto silver powder gives less than a tenth of the nickel current of a metallic nickel sample. Moreover, it was quite laborious² to press the Dmg powder onto the silver powder.

4.2.2 Cobalt contamination from sample holders

Originally, the sample material was pressed into copper holders. However, the copper holders were found to be a major source of cobalt in the AMS measurements. To avoid this, sample holders made of electrolytically produced copper or aluminium were investigated. Both substances proved to be very low in cobalt: Electrolytically produced copper holders currently do not interfere with AMS measurements at all, while aluminium sample holders interfere slightly.

Aluminium has now become the material of choice for sample holders as aluminium sample-holders provide the higher nickel current.

² The Dmg powder turned black, as if heated, when pressed onto the silver powder and stuck to the pressing tool rather than to the silver powder.

4.3 Optimisation of the Lund ion source

A common experience is that making a concavity in the sample with a depth equal to the diameter gives better beams, increasing the nickel current. A “lens effect” is created, possibly due to space charge distribution.

As the lens effect depends on the depth in relation to the diameter of the hole, finding the optimal lens effect means investigating a “matrix” of possible depths and diameters. Sample holders with a hole diameter of ~3.5 mm and various sample depths (0.5–7 mm) have been examined, with metallic nickel as the sample material. The maximum lens effect for metallic nickel occurs at a sample depth of approximately 2.5 mm, Figure 4-2. At this depth, the nickel current is 4–4.5 μA , an increase of four to five times compared to a standard metallic nickel sample with a sample recession of ~0.5 mm.

The sample, metallic nickel, is pressed into sample holders to a depth of 2.5 mm. To avoid contamination with cobalt from the steel pressing tools we have used a highly pure polymer, an 8 μm Kapton™-sheet, inserted between the pressing tool and the sample.

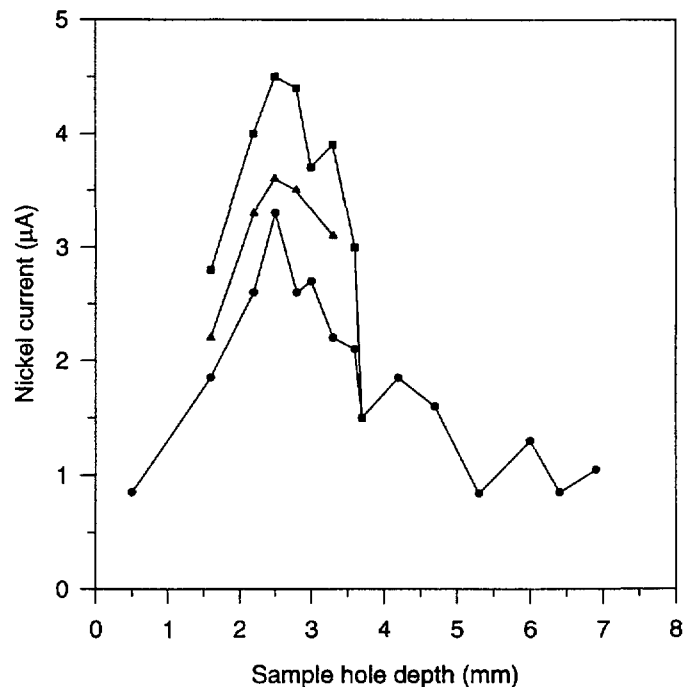


Figure 4-2. Three series of measurements of the nickel current after the inflection magnet as a function of sample hole depth relative to the sample holder surface. The current of nickel ions can be increased 4-5 times, up to ~4 μA , by making a concavity in the sample. In all three series of measurement, the sample with a depth of 2.5 mm gave the highest current.

4.4 Chemical reduction of the cobalt content in samples

4.4.1 Nickel chemistry

Available in the literature are two descriptions of methods for the chemical reduction of cobalt in a nickel sample /4-1, 4-2/. As our starting material is stainless steel, we also need a method to separate nickel from all of the non-nickel elements, about 90% of the weight of stainless steel³. This separation has to be carried out before we can utilise any of the cobalt-reduction processes described. To simplify the dissolution of the stainless steel when using the method described above, the sample to be analysed should preferably consist of metal chips weighing totally 0.5–1 g.

In short the method involves precipitating nickel with dimethylglyoxime (Dmg)⁴ /4-2/ after dissolving the steel in concentrated HCl. As nickel forms complex ions with (Dmg) this process removes essentially all other elements except nickel.

In more detail, the process is as follows:

- Dissolution of stainless steel in concentrated HCl /4-4/.
- Removal of all elements other than nickel by nickel precipitation with Dmg /4-3/.
- Main cobalt reduction by cobalt fixation on an anion exchange resin⁵ /4-2/.
- Final cobalt reduction by nickel precipitation with Dmg /4-2/.
- The nickel-Dmg complex is dried, baked to nickel oxide (NiO) and reduced to metallic nickel, which is then pressed into sample holders and put into the ion source /4-2/.

Of course, the cobalt reduction with Dmg in this process can be repeated as many times as desired but we have found that more than two reduction cycles do not improve the purity of the final product.

For a detailed description of the chemical process for nickel see Appendix 1: Nickel chemistry (in English) and Appendix 2: Nickel kemi (in Swedish).

Preliminary investigations of the efficiency of the nickel chemistry, done with AMS, indicate that the cobalt content of nickel was reduced to at least ppm level. In this case the chemically treated nickel was pressed into sample holders with stainless steel tools. It is a common experience that it is necessary to avoid all contact with metal objects after the nickel has been chemically treated. The preliminary investigations also indicated that the anion exchange resin increased the cobalt concentration in analysed samples rather than lowering it, probably because the solution became contaminated on its passage through the resin.

³ 18–8 stainless steel and SS2333 stainless steel /4-3/.

⁴ Nickel precipitation with dimethylglyoxime is described in, e.g. /4-4/.

⁵ Dowex 1x8, 50–100 mesh.

By using radioactive Co we were able to investigate the reduction efficiency without using the AMS system. A stainless steel sample was chemically treated to insure a cobalt concentration below a known level in the resulting nickel sample solution⁶. An activity of about 170 kBq ⁶⁰Co was added to the solution. Nickel was precipitated with Dmg and filtered off. The Dmg-precipitate was then dissolved in a well-known quantity of distilled water and ethanol. Finally, the activity of the processed solution was compared with the original activity by means of gamma-ray spectroscopy. This comparison indicates the potential efficiency for reducing cobalt by precipitation with Dmg. The activity measured was recalculated as the ratio of ⁵⁹Co to ⁵⁸Ni and was found to be $5.5 \pm 2.4 \cdot 10^{-9} : 1$, see Appendix 3. The experiment was repeated, with consistent results.

These findings also appear to be consistent with the maximal reduction efficiencies normally associated with this kind⁷ of chemical reduction of cobalt (ratios of 10^{-8} to 10^{-9}) /4-5/. Detection of characteristic X-rays allows for up to 500 times more cobalt than nickel. If no contamination takes place after the final precipitation of nickel by Dmg, the cobalt content of the processed samples is low enough to allow the detection of ⁵⁹Ni concentrations corresponding to 2–3 Bq per kilogram steel.

AMS measurements so far indicate cobalt levels of about 10^{-6} of the nickel content. Although these results are reliable, we cannot exclude the possibility of contamination not related to the chemical process (the sample material was exposed to air and possible dust contamination for 3–4 days). It is possible to improve the cleanliness of the handling of the chemically processed sample material, mainly by cleaning the laboratory equipment in hydrochloric acid and by using high quality, distilled, deionised water. The processed samples should also be kept in a desiccator to avoid dust contamination.

4.4.2 Alternatives and future investigations

Even if this method of chemical cobalt reduction is developed to its full efficiency, it may be that cobalt will still be a limiting factor in the ⁵⁹Ni detection-limits. It then becomes interesting to investigate another chemical method for reducing cobalt in nickel.

J.E. McAninch et al. /4-5/ report a preliminary ⁵⁹Co to ⁵⁸Ni ratio of 10^{-8} , corresponding to $1 \cdot 10^{11}$ atoms of cobalt in a 1mg nickel sample. This is comparable to our expected cobalt reduction when neglecting contamination. Essential in their method is nickel extraction by using the reaction between nickel and carbon monoxide to form nickel carbonyl ($\text{Ni}(\text{CO})_4$).

⁶ See Appendix 1 and 2 for details.

⁷ Nickel precipitaion by Dmg and cobalt fixation on an anion-exchange resin.

4.5 Experimental set-up

4.5.1 The X-ray detector

The X-ray detector should have as good a resolution as possible to make it possible to separate the different peaks in the spectra, especially the Ni K_{α} and the Co K_{β} peaks. It should also have as big an active area as possible to optimise the detection efficiency. A detector was purchased from Studsvik Instrument with the following specifications: (Canberra, LEGe GL0210P, active area 200 mm², resolution 145 eV FWHM at 5.9 keV). The detector was equipped with the necessary electronic equipment.

4.5.2 The experimental chamber

The experimental chamber was designed and built at the mechanical workshop of the Department of Physics in Lund. To optimise the detection efficiency a zero degree geometry was chosen, Figure 4-3. To be able to monitor the total charge transported by the beam, the end plate of the target chamber was electrically insulated from the beam system and an electron suppressor was installed. At the centre of the end plate was an opening of ($\phi=20$ mm), covered with an 8 μm KaptonTM exit window for the X-rays. The target foil was positioned three millimetres upstream of the exit window.

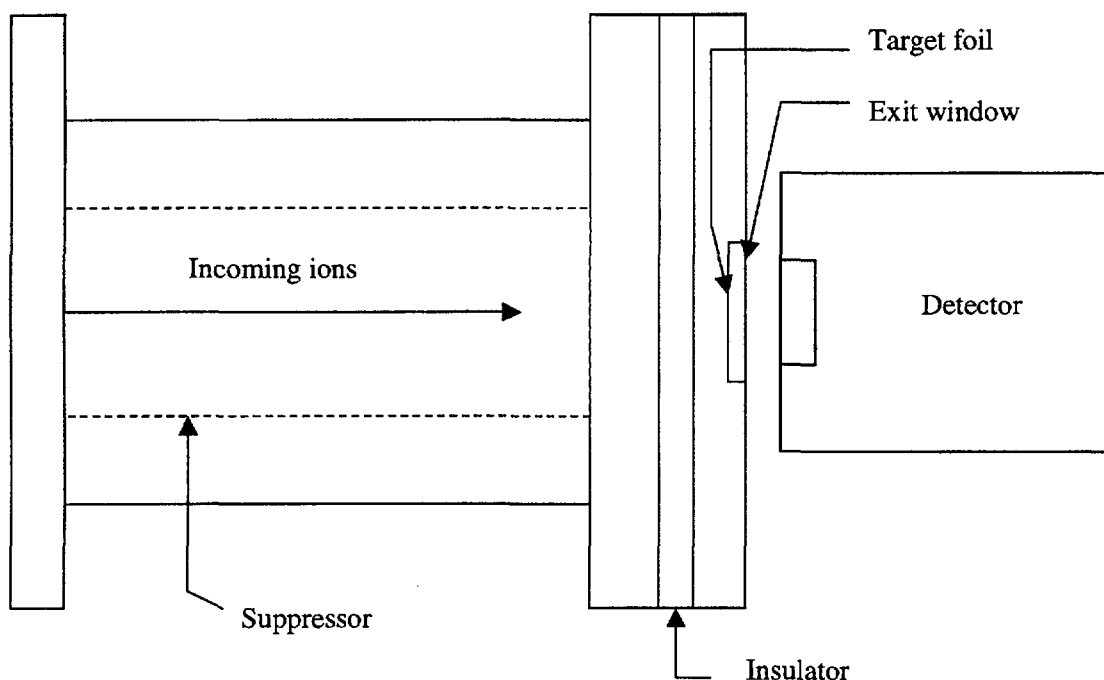


Figure 4-3. An outline of the experimental chamber.

4.6 Background

4.6.1 Mass resolution

Figure 4-4 shows X-ray spectra from the accelerator system tuned for mass 59. Figure 4-4a) shows the result when the ion source was loaded with a sample of nickel powder with a given $^{59}\text{Ni}/\text{Ni}$ ratio of $3.4 \cdot 10^{-7}$ (corresponding to 1000 Bq/g). This sample, with a stated accuracy of $\pm 25\%$, was activated at the research reactor at Risø, Denmark and was measured eight times, giving a mean value of the $^{59}\text{Ni}/\text{Ni}$ ratio of $3.7 \pm 0.7 \cdot 10^{-7}$ (1100 \pm 200 Bq/g). Figure 4-4b) shows the result with a ^{59}Ni -free sample, from the same source material as the activated sample. These two samples have not passed through the chemical purification. The Co/Ni ratio was measured to be $1 \cdot 10^{-7}$, i.e. a relatively low cobalt content, and therefore the result in Figure 4-4b) shows the capability of the AMS system to separate ^{59}Ni from the neighbouring stable nickel isotopes (i.e. ^{58}Ni and ^{60}Ni). The background in the Ni K_{α} window in Figure 4 4b) corresponds to a count rate of 10 Ni K_{α} counts/600s. This corresponds to a sample containing a $^{59}\text{Ni}/\text{Ni}$ ratio of $1 \pm 0.3 \cdot 10^{-8}$ (30 \pm 9 Bq/g). Notice, however, that this figure for the background related to the mass resolution is valid only for a sample with a low cobalt content.

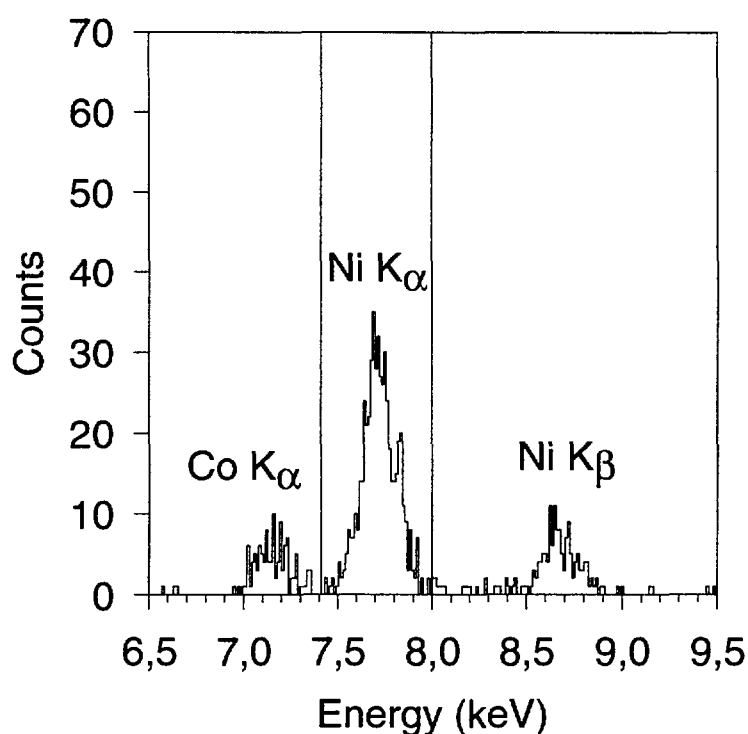


Figure 4-4a. Part of an X-ray spectrum from a beam originating from an activated nickel sample ($^{59}\text{Ni}/\text{Ni}$ ratio of $3.4 \cdot 10^{-7}$). The accelerator system was tuned for mass 59. The peaks are Doppler-shifted. Figures 4-4a, 4-4b and 4- 6 are normalised to the same integrated current.

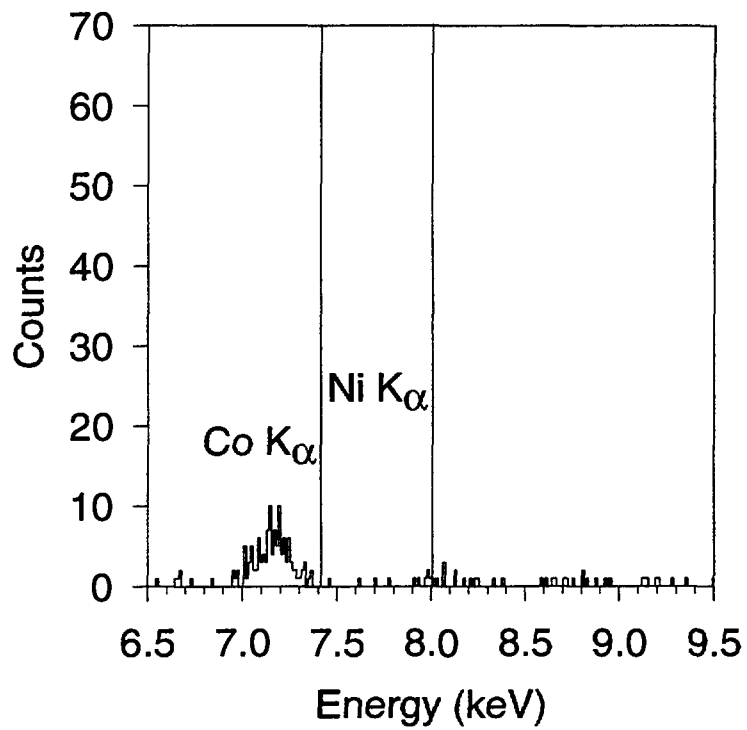


Figure 4-4b. Part of an X-ray spectrum from a beam originating from a ^{59}Ni -free nickel sample. The accelerator system was tuned for mass 59. The peaks are Doppler-shifted. Figures 4-4a, 4-4b and 4-6 are normalised to the same integrated current.

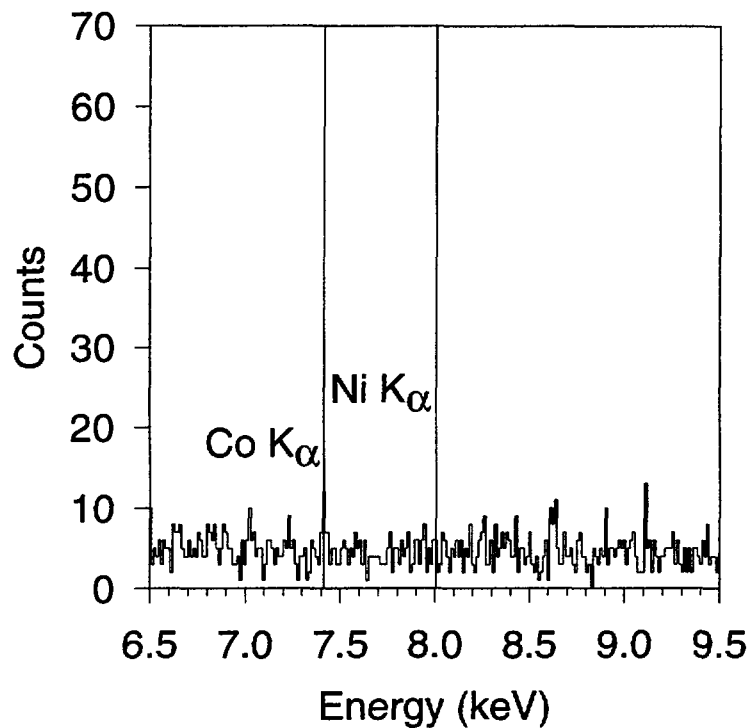


Figure 4-5. Part of a background X-ray spectrum obtained with the accelerator turned off. Measuring time: 12 h.

4.6.2 The natural background

Measurements of the X-ray background made with the accelerator turned off as well as with the accelerator at high voltage, but with the beam stopped at the low energy side of the system give, in both cases, 4 counts/600 s in the Ni K_{α} window, Figure 4-5. I.e. the machine operation does not contribute to the background. We conclude that a considerable proportion of the counts in the Ni K_{α} window, in Figure 4-4b, is due to the natural background and has nothing to do with the mass resolution of the accelerator system. With the count rate available of the stable isotope (20,000 Ni K_{α} count/s from ^{61}Ni) and the present target-detector geometry, the count rate of the natural background in the Ni K_{α} window corresponds to a sample containing a $^{59}\text{Ni}/\text{Ni}$ ratio of $5 \pm 0.3 \cdot 10^{-9}$ (15 ± 1 Bq/g).

4.6.3 Cobalt background

The spectrum in Figure 4-6 is obtained with a ^{59}Ni -free nickel sample, which has been produced by passing a stainless steel sample through the chemical purification process. As before, the AMS system was tuned for mass 59. The cobalt K_{α} and K_{β} peaks are here much more pronounced than in the previous figures. The tails from the cobalt peaks enhance the count rate in the Ni K_{α} window to about 9 times that for an unprocessed, ^{59}Ni -free sample. Accordingly, for a sample that has passed the chemical purification process, the background corresponds to a $^{59}\text{Ni}/\text{Ni}$ ratio of $1 \pm 0.12 \cdot 10^{-7}$ (290 ± 35 Bq/g).

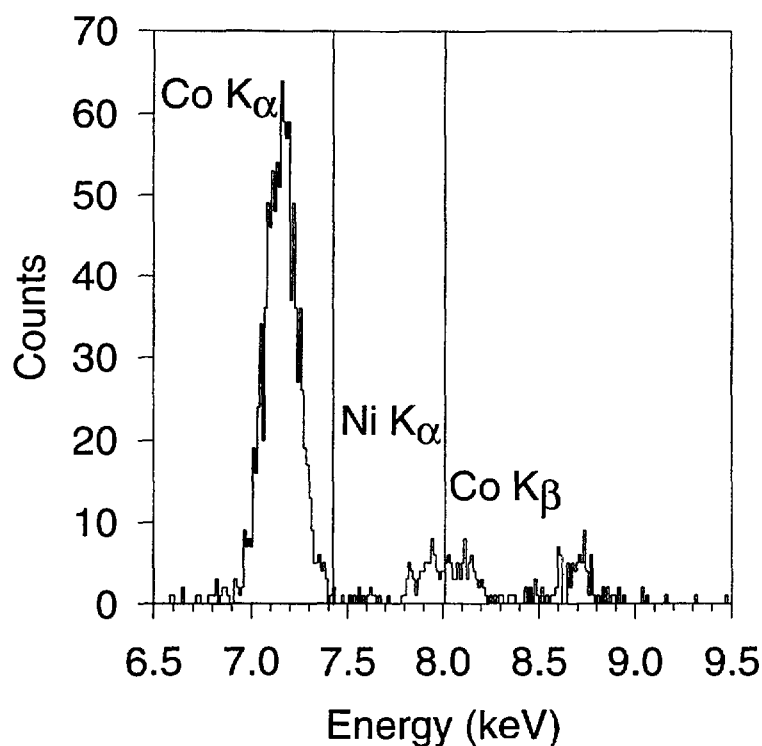


Figure 4-6. Part of an X-ray spectrum from a beam originating from a ^{59}Ni -free nickel sample, obtained by passing a stainless steel sample through the chemical purification process. The accelerator system was tuned for mass 59. The peaks are Doppler-shifted. Figures 4-4a, 4-4b and 4-6 are normalised to the same integrated current.

5 Discussion and conclusions

The different backgrounds of the Lund system to date, presented in section 4.6 above are summarised in Table 5-1.

Table 5-1. Summary of the different backgrounds of the Lund AMS system.

	Background from present system		Estimated background from improved system
	($^{59}\text{Ni}/\text{Ni}$)	($\text{Bg}/\text{g}_{\text{nickel}}$)	($\text{Bq}/\text{g}_{\text{nickel}}$)
Mass resolution (sample with low Co content)	$1 \pm 0.3 \cdot 10^{-8}$	30 ± 9	15 (terminal pumping) 2–5 (better injector)
Natural background	$5 \pm 0.3 \cdot 10^{-9}$	15 ± 1	5–10
Cobalt background	$1 \pm 0.12 \cdot 10^{-7}$	290 ± 35	25–30

As can be seen in the table the component totally dominating the background is due to the cobalt from the chemical purification process. By adopting various improvements – as described below – it is hoped that the background will be reduced as described in Table 4-2.

By improving the target-detector geometry, the radiation shield around the detector and by making some technical modifications to the system to increase the beam current (such as optimisation of the source), it should be possible to increase the signal-to-noise ratio and thereby decrease the disturbance from the natural background by a factor of two, down to $2-3 \cdot 10^{-9}$ ($5-10 \text{ Bq}/\text{g}_{\text{nickel}}$).

Equipment for gas stripping with terminal pumping is being tested in the high voltage terminal of the accelerator /5-2/. This will probably improve the mass resolution of the accelerator somewhat. A realistic estimation is that the background associated with the mass resolution will be lowered by a factor of two, down to $5 \cdot 10^{-9}$ ($15 \text{ Bq}/\text{g}_{\text{nickel}}$). A long-term project is to build a high-resolution injector, which will improve the mass resolution by at least an order of magnitude, down to $1 \cdot 10^{-9}$ ($2-5 \text{ Bq}/\text{g}_{\text{nickel}}$).

The tail of the cobalt K_{β} peak is the single factor that is at present the most serious limitation to the detection limit of ^{59}Ni . By improving the chemical purification process, using cleaner chemicals, ultra clean equipment, tools washed in concentrated HCl and filters in the ventilation system etc. we believe that the cobalt background can be lowered by a factor of 10 down to $1 \cdot 10^{-8}$ ($25-30 \text{ Bq}/\text{g}_{\text{nickel}}$). To further reduce the background it will be necessary to change to another and more complicated cobalt separation technique, for example, using the reaction between nickel and carbon monoxide, to form gaseous nickel carbonyl ($\text{Ni}(\text{CO})_4$) /5-1/.

This report describes a study of the detection limit of ^{59}Ni that can be reached by combining X-ray detection with the AMS system of our 3 MV Pelletron accelerator. The present status of the system is a $^{59}\text{Ni}/\text{Ni}$ background ratio of $1 \cdot 10^{-7}$, which corresponds to a detection limit (3σ above the background) of $3 \pm 1 \cdot 10^{-8}$ or 100 ± 30 Bq/g nickel. This is sufficient for some applications, for instance, the determination of the activity concentration in steel close to the core in nuclear reactors. In nuclear waste from power plants it is estimated that the activity concentration of ^{59}Ni reaches from below 1 Bq/g nickel some metres from the core to some MBq/g nickel close to the core.

The detection limit at the Lund AMS system is comparable to what other laboratories have reached. The detection limit of $^{59}\text{Ni}/\text{Ni}$ has been both measured and calculated by Wagner et al. /5-3/ to be of the order of 10^{-8} for 18 MeV Ni ions. This value includes the chemical processing necessary to reduce the Co/Ni ratio in the sample. McAnich et al. /5-3/ have reached a detection limit $^{59}\text{Ni}/\text{Ni}$ of the order of 10^{-11} by using the more complicated cobalt separation technique mentioned above.

The plan in Lund for the near future is to test samples produced by a cleaner chemical purification process and to test the terminal pumping system as described above. It is hoped that this will be done early in 1999.

Thus, using AMS at a small tandem accelerator ($< 3\text{MV}$), in combination with the detection of characteristic X-rays of the projectile, is a useful and economic alternative to large accelerators and sophisticated techniques.

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Appendix 1: Nickel chemistry

Dissolution of SS2333 stainless steel⁸ and precipitation of nickel by addition of a solution of Dimethylglyoxime in alcohol (4–5 hours)

1. Weigh out accurately 0.4 g of stainless steel, corresponding to 0.032–0.044 g nickel (Ni), into a 100–150 ml Erlenmeyer flask.

Smaller quantities are difficult to work with as the hydrochloric acid then boils away too quickly.

2. Dissolve the steel in a minimum volume of concentrated HCl. About 10 ml should be sufficient. Heat carefully. Hydrogen gas is generated.

1 g of stainless steel is dissolved in 20 ml of concentrated HCl. A minimum volume of concentrated HCl should be used for two reasons: To minimise the generation of chlorine gas when HNO₃ is added in step 3, and to facilitate the neutralisation of the solution in step 7. The colour of the solution is green, due to the Ni-ions.

3. Boil carefully with successive additions of concentrated HNO₃ (a total of 2–3 ml) poured down the sides of the Erlenmeyer flask. The colour of the solution will change to black, and the vapours leave a yellow condensate on the sides of the Erlenmeyer flask.

The ions of iron are oxidised by HNO₃, from Fe(II) to Fe(III). Boiling facilitates the oxidation. A lot of hydrogen gas is generated by the addition of HNO₃. Therefore, add a little at the time. About 5 ml of concentrated HNO₃ is needed for 1 g of stainless steel. The colour of Fe(III) is yellow in aqueous solution.

4. Dilute with distilled water to twice the current volume. If necessary, filter off any solid material and wash the filter paper with hot water.

Any solids remaining originate from the steel, and consist of salts of low solubility in conc. HCl, and/or precipitates.

5. Make up the filtrate with distilled water to a volume of 200 ml in a 400 ml beaker.

The larger volume facilitates the perception of the change in colour at neutralisation in step 7. The solution is green in colour.

6. Add approximately 2 g of tartaric acid (C₄H₆O₆).

Tartaric acid reacts with Fe(III) to form a complex. However, the presence of Fe(III) should be avoided when Dmg is used to precipitate Ni. About 5 g of tartaric acid is needed for 1 g of stainless steel.

⁸8,00–11,0% Ni; 17,0–19,0% Cr; ≤2,00% Mn; ≤1,00% Si; ≤0,05% C; ≤0,045% P; ≤0,030% S. Remaining substance is Fe.

7. Neutralise with 2 M NH_3 . The colour of the solution darkens.

Nota bene: If a precipitate appears or if the solution is not clear when rendered basic, more tartaric acid must be added until a perfectly clear solution is obtained when 2 M NH_3 is added. Any insoluble matter should be filtered off and washed with hot water containing a little NH_3 .

The previously rust-coloured or green and yellow solution becomes dark green as Ni^{2+} forms a complex ion with NH_3 , namely, $\text{Ni}(\text{NH}_3)_6^{2+}$.

Litmus paper is light red in acetose solutions and retains its (blue) colour on contact with basic solutions. The closer to neutral the solution is, the slower is the colour change.

8. Barely acidify the solution with 2 M HCl.

An acetose solution provides favourable conditions for the formation of the complex between Dmg and Ni, as the formation of $\text{Ni}(\text{NH}_3)_6^{2+}$ is suppressed.

9. Warm the solution to 60–80 °C.

10. Add a slight excess of a 1% alcoholic solution of Dmg (25–30 ml), immediately followed by 2 M NH_3 until the solution is slightly alkaline. Stir well.

The formation of $\text{Ni}(\text{Dmg})_2$ is facilitated by the addition of NH_3 , which reacts with the hydrogen ions which are created as $\text{Ni}(\text{Dmg})_2$ is precipitated as red crystals. For 80 mg of Ni, a slight excess of a 1% alcoholic solution of Dmg means about 50–60 ml.

11. Leave the solution on a bain-marie for 20–30 min. Stir from time to time.

Some of the solution is absorbed by the porous precipitate. The Ni-Dmg complex will re-crystallise and in this process, will absorb less and less of the solution. Heat facilitates the process of crystallisation.

12. Leave the solution for at least one hour to cool to room temperature.

13. Filter off the precipitate.

Preferably, use a filter pump to speed up the filtration. Make sure that the system is tight. Tighten, with wet paper between the filter-crucible and the filtering flask.

14. In the filter-crucible, wash the precipitate 6–7 times with small amounts of distilled water.

Nota bene: The precipitate should not be allowed to become dry.

Small amounts of distilled water means, 3–4 times the volume of the precipitate. The precipitate is cleaned from any unwanted, dissolved substances by washing. Every time the precipitate is washed, about 90% of the remaining contaminants are removed.

15. Save the last wash in a beaker and check for the presence of Cl^- -ions with an 0.1 M solution of AgNO_3 and some HNO_3 .

In an acetose solution AgCl forms as a pale precipitate. The presence of Cl^- -ions shows that other unwanted substances are present. The filtered solution must be made acidic with 1 M HNO_3 after the last wash, as AgNO_3 is dissolved in distilled water.

16. Check the filtrate for complete precipitation with a little Dmg solution.
If an unacceptable amount of precipitate is formed when Dmg solution is added, return to step 8.

Avoid contamination with Co from any possible source from now on!

17. Dry the precipitate in the filter-crucible at 110–120 °C for 45–60 minutes **or go on to the anion-exchange process.**

18. Combust the precipitate to nickel oxide (Ni(II)O) at 600–800 °C.

Transfer the Ni(Dmg)₂ (with a quartz spatula, or the like) into a quartz crucible with a lid. Heat carefully to above 600 °C. Ni(Dmg)₂ will ignite, forming black smoke. Nitric oxides are formed in the combustion. Continue heating the ash until the precipitate is completely black.

The lid of the quartz crucible ensures that the NiO does not escape from the crucible. A fairly violent circulation of gas is created by the combustion. A similar situation arises when evaporating the soot from the quartz crucible. Some Ni(Dmg)₂ will remain after the visible combustion of the complex, seen as red spots in the black NiO. This is combusted by further heating.

19. In a hydrogen gas environment, reduce Ni(II)O to metallic Ni at about 800 °C.

Transfer the NiO to a quartz combustion boat, with a piece of folded paper for example. In a hydrogen gas environment, the NiO is heated until it turns a dull grey. Nota bene: If the hot, metallic Ni is exposed to oxygen, it will react and form NiO again.

Procedures to further reduce the Co in the purified Ni

Removal of Co by an ion-exchange process (4–5 hours)

20. Dissolve Ni(Dmg)₂ in 10M HCl.
Dowex 1x8, 50–100 mesh is used as the ion-exchange resin.
21. Feed the solution onto the ion-exchange resin.
In the ion-exchange resin, Co is adsorbed as the complex {CoCl₄}²⁻ which is formed in concentrated HCl. Ni remains uncomplexed and therefore passes through the column. The {CoCl₄}²⁻ ions are blue, while the solution leaving the column is green due to the presence of Ni²⁺.
22. Add 10 M HCl corresponding to “the free volume” of the ion-exchange column.
This ensures that all of the Ni(Dmg)₂ solution has passed through the ion-exchange resin.

Precipitation of nickel by addition of a solution of Dimethylglyoxime in alcohol (Following step 5 to step 18, above)

23. Make up the volume of the filtrate to 200 ml with distilled water in a 400 ml beaker.
24. Add an additional amount of tartaric acid (C₄H₆O₆).
The tartaric acid reacts with any remaining Fe(III) ions. The FeCl₄⁻ radicals should have remained on the ion-exchange resin, but this precautionary addition of tartaric acid to the solution has no negative effects.
25. Neutralise with 2 M NH₃.
As the solution becomes alkaline, the Ni(Dmg)₂ complex is precipitated.
26. Make the solution weakly acidic with 2 M HCl.
Some of the Dmg complex dissolves. Any complex formation between tartaric acid and Fe(III) will turn the solution rust-brown.
27. Warm the solution to 60–80 °C.
On heating, most, if not all of the Dmg complex dissolves.
28. Again, add a slight excess of a 1% alcoholic solution of Dmg (7–8 ml), immediately followed by 2M NH₃ until the solution is slightly basic. Stir well.
29. Leave the solution on a bain-marie for 20–30 min. Stir from time to time.
The solution is clear, the precipitate red.
30. Allow the solution to stand for at least one hour to cool to room temperature.
31. Filter off the precipitate.

32. In the filter-crucible, wash the precipitate 6–7 times with small amounts of distilled water. Nota bene: All water should be filtered off between the washings. The precipitate should not be allowed to become dry.

33. Save the last wash in a beaker and check the presence of Cl⁻ ions with a 0,1 M solution of AgNO₃ and some HNO₃.

In an acetose solution AgCl forms as a pale precipitate. The presence of Cl⁻ ions shows that other unwanted substances are present. The filtered solution must be made acidic with 1 M HNO₃ after the last wash, as AgNO₃ is dissolved in distilled water.

34. Check the filtrate for complete precipitation with a little Dmg solution.

If unacceptable amounts of precipitate are formed when Dmg solution is added, repeat from step 25.

Avoid contamination with Co from any possible source from now on!

35. Dry the precipitate in the filter-crucible at 110–120 °C for 45–60 minutes **or repeat the ion exchange procedure.**

36. Combust the precipitate to nickel oxide (Ni(II)O) at 600–800 °C.

Transfer the Ni(Dmg)₂ (with a quartz spatula for example) into a quartz crucible with lid. Heat carefully to above 600 °C. Ni(Dmg)₂ will ignite, forming black smoke. Nitric oxides are formed in the combustion. Continue heating until the precipitate is completely black.

The lid of the quartz crucible ensures that the NiO does not escape from the crucible. A fairly violent circulation of gas accompanies the combustion. A similar situation arises when evaporating the soot from the quartz crucible. Some Ni(Dmg)₂ will remain after the visible combustion of the complex, seen as red spots in the black NiO. This is combusted by additional heating.

37. In a hydrogen gas environment, reduce Ni(II)O to metallic Ni at about 800 °C.

Transfer the NiO to a quartz combustion boat, with a piece of stiff paper or the like. In a hydrogen gas environment, the NiO is heated to a dull grey.

Nota bene: If the hot, metallic Ni comes into contact with oxygen, it will react and form NiO again.

After the ion-exchange process

38. Wash away the Co ions with 2 M HCl (see also: “preparations”).

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Appendix 2: Nickelkemi

Förberedelser

Se till att det finns rikliga mängder

- 2 M ammoniaklösning (NH_3 -lösning).
25% NH_3 är ca 14M. Till 250 ml 2M NH_3 behövs alltså $250/7 \approx 36$ ml 25% NH_3 .
- 1 M salpetersyra (HNO_3 -lösning).
65% HNO_3 är ca 12 M. Till 250 ml 1 M HNO_3 behövs alltså $250/12 \approx 21$ ml 65% HNO_3 .
- 2 M saltsyra (HCl -lösning).
37% HCl är ca 14 M. Till 250 ml 2M HCl behövs alltså $250/14 \approx 36$ ml 37% HCl .
- 1% etanollösning av dimetylglyoxim⁹ (Dmg).
Blandningsinstruktioner finns längre ned i denna text
- 0.1 M AgNO_3 -lösning i destillerat vatten.
Lösningen ska förvaras i en brun flaska.

Iakttag största renlighet efter den sista kemiska koboltreningen!

Undvik all kontakt med metallföremål! Glasdetaljer behöver kanske tvättas i kokande saltsyra och de kemikalier som används ska kanske vara högrena.

Blötning av jonbytarmassan och förberedelse av jonbytarkolonnen

- Tillför 2 rågade teskedar till 2 M HCl .
Mängden beror naturligtvis på jonbytarkolonns storlek.
- Låt massan svälla i 10–15 minuter.
- Lägg kvartsull som massans nedre begränsning i jonbytarkolonnen.
- Håll massan i kolonnen och låt den sedimentera.
- Sug bort eventuell överflödlig massa.
- Skölj med 2 M HCl tills eluatet ej längre är gult, för att spola rent jonbytarmassan.
- Lägg kvartsull ovanpå jonbytarmassan för att definiera en tydlig gräns.

⁹ $\text{CH}_3\cdot\text{C}(\text{:NOH})\cdot\text{C}(\text{:NOH})\cdot\text{CH}_3$.

Rening av jonbytarkolonnen

- Häll på 2 M HCl motsvarande hälften av kolonnens fria volym¹⁰ (5–7 ml) och låt den rinna av tills ytan är i höjd med kvartsullen. Upprepa proceduren tre gånger. Detta spolrar bort kobolt (Co)-jonerna som fastnat i jonbytarmassan.
- Häll på 10M HCl motsvarande hälften av kolonnens fria volym (5–7 ml) och låt den rinna av tills ytan är i höjd med kvartsullen. Detta förbereder jonbytarmassan för nästa Co-rening.
- Häll på ytterligare 10 M HCl och låt stå med ett urglas som lock.

OBS! *Låt inte jonbytarmassan torka i jonbytarkolonnen! Då bildas små luftbubblor som gör att lösningen inte passerar genom jonbytarmassan med ett jämnt flöde.*

Blandning av Dmg-etanollösning

Varje mol Ni kräver 2 mol Dmg för att bilda Ni(Dmg)₂. 0,04 g Ni kräver således $x/116 = 2 \times 0.04/58 \Rightarrow x = 0.16 \text{ g Dmg}$.

Molvikterna för Dmg och Ni är: M[Dmg]=116 g/mol och M[Ni]=58 g/mol. 0.16 g Dmg löses i 15.8 g etanol för att utgöra 1% av vikten. 15.8 g etanol motsvarar $15.8/0.789 \approx 20 \text{ ml etanol}$, då etanols densitet är 0.789 g/cm³.

- Väg respektive mät upp lämpliga mängder Dmg respektive etanol.
- Lös upp Dmg under försiktig uppvärmning.

Annat

- Avsluta alltid sköljningar med destillerat vatten för att undvika föroreningar från kranvattnet. Om tiden för torkning är knapp, kan man därefter skölja med etanol.
- Se till att luft kan komma ut om något hålls i en sluten volym.
- Häll inte tillbaka överflödigt lösning av något som finns på förråd, med eventuella föroreningar, i den ”rena” ursprungslösningen.
- Lös och värm i allmänhet i bägare. För sedan över lösningen till flaska.
- Rör inte om med termometern! (Många kemiska upptäckter om kvicksilver har gjorts på detta sätt!)
- Ha i allmänhet inte glasstaven i kärl som värms – den kan hoppa till och slå hål i botten på kärlet.

¹⁰ Med kolonnens fria volym menas volymen från jonbytarmassans övre kant till kranens öppning. Volymen är uppskattningsvis 10–15 ml.

Upplösning av SS2333 stål¹¹ och utfällning av nickel med Dimetylglyoxim [6] (4–5 timmar)

1. Ca 0.4 g rostfritt stål, motsvarande 0.032–0.044 g nickel (Ni) placeras i en 100–150 ml E-kolv¹².
2. Lös det rostfria stålet i minimal volym koncentrerad HCl, ca 10 ml borde räcka. Värm något¹³.

Rostfritt stål löses i 20 ml koncentrerad HCl per gram stål. Använd minimal volym koncentrerad HCl för att minimera klorgasutvecklingen vid tillsättning av HNO₃ (punkt 3) och för att senare lätt kunna neutralisera lösningen (punkt 7). Lösningen är grönfärgad.

3. Koka försiktigt och tillsätt successivt koncentrerad HNO₃ (totalt 2–3 ml) längs E-kolvets väggar tills lösningens färg ändrats till nästan svart med gul kondens på E-kolvets väggar.

HNO₃ oxiderar tvåvärt järn, Fe(II), till trevärt järn, Fe(III)¹⁴. Kokningen underlättar oxidationen. Vid tillsättning av HNO₃ bildas mycket klorgas, därför ska lite tillsättas åt gången. Ca 5ml koncentrerad HNO₃ behövs för 1g stål. Fe(III) är gul i vattenlösning.

4. Späd ut lösningen till ca dubbla volymen¹⁵ med destillerat vatten, filtrera¹⁶ bort eventuella fasta beståndsdelar om det behövs och skölj igenom resterna av lösningen med hett vatten.

De fasta beståndsdelarna kan vara delar av stålet som är svårlösliga i HCl och eventuella fällningar.

5. Späd lösningen med destillerat vatten till 200 ml i en 400 ml bägare.

Lösningens större volym gör att neutraliseringen blir enklare, dvs indikatorns omslag blir lättare att se.

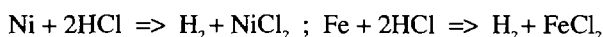
6. Tillsätt ca 2 g vinsyra (C₄H₆O₆).

Vinsyran bildar komplexa joner¹⁷ med Fe(III) jonerna som inte får vara närvarande då Dmg fäller ut Ni. För 1g stål krävs 5 g vinsyra.

¹¹8,00–11,0% Ni; 17,0–19,0% Cr; ≤2,00% Mn; ≤1,00% Si; ≤0,05% C; ≤0,045% P; ≤0,030% S; resten Fe [C W Wegst: "Stahlschlüssel", 396 (1995)].

¹² Lite lösning kondenserar på väggarna i 3. men rinner förhoppningsvis ned på grund av E-kolvets utformning.

¹³ H₂-utveckling svarar mot oxidation av metallen till högre oxidationsnivåer: Vi vill ha Fe(II) och Fe(III) för att ta hand om dem med vinsyran.



¹⁴ $3\text{H}^+ + \text{HN(V)O}_3 + 3\text{Fe}^{2+} \Rightarrow \text{N(II)O} + 3\text{Fe}^{3+} + 2\text{H}_2\text{O}$

¹⁵ För att lösningen ska flyta någorlunda lätt, men inte ta för lång tid, dvs ha för stor volym.

¹⁶ Vik och fukta filterpapperet med destillerat vatten. Om trattens öppning ligger an mot bägareväggen drar kapilläreffekten ned filtratet snabbare. Håll längs en glasstav för hög precision.

¹⁷ $\text{Fe}^{3+} + \text{citrat}^{3-} \Rightarrow [\text{Fe}(\text{citrat})_2]^{3-}$; $[\text{Fe(III)(OH)}_2\text{OH}]^{2+}$ är gul.

7. Neutralisera den starkt sura lösningen med 2 M NH_3 . Lösningen ändrar färg till mörkare grönt.

Lösningen färgas mörkt grön då Ni^{2+} bildar komplex med NH_3 , $\text{Ni}(\text{NH}_3)_6^{2+}$. Ursprungsfärgen är rostaktig i gröngult eller grön gul.

OBS! Om det bildas en fällning vid tillsatsen av NH_3 , eller om lösningen inte är helt klar, måste mera vinsyra tillsättas tills lösningen är helt klar vid tillsats av NH_3 . Eventuella fasta beståndsdelar filtreras bort och resterna av lösningen sköljs igenom med varmt vatten innehållande lite NH_3 .

Lackmuspapper färgas ljusrött i sur lösning och behåller sin blåa färg i basisk lösning. Papperet ändrar färg långsammare ju neutralare lösningen är.

8. Gör lösningen svagt sur genom att tillsätta 2 M HCl .

Lösningen behåller sin rostaktiga färg på grund av komplexet mellan vinsyra och Fe(III) . Den sura lösningen skapar förutsättningarna för att Dmg lätt ska kunna bilda komplex med Ni eftersom $\text{Ni}(\text{NH}_3)_6^{2+}$ inte finns i sur lösning.

9. Värm lösningen till 60–80 °C.

10. Tillsätt ett litet överskott av 1% alkohollösning av Dmg (25–30 ml); tillsätt omedelbart 2 M NH_3 tills lösningen är svagt basisk och rör om väl.

NH_3 tar hand om de vätejoner som bildas då $\text{Ni}(\text{Dmg})_2^{18}$ fälls ut i form av rödaktiga kristaller och underlättar på så sätt bildningen av $\text{Ni}(\text{Dmg})_2$.

11. Låt lösningen stå på ångbad i 20–30 min och rör om då och då.

Porösa fällningar tar till sig en del av lösningen. Genom värmen kommer Ni-Dmg komplexet att omkristallisera sig upprepade gånger och tar då till sig mindre och mindre av lösningen. Värmen underlättar även kristallisationsprocessen. Lösningen är svart, fällningen röd.

12. Låt lösningen svalna till rumstemperatur i ungefär 1 timme.

13. Filtrera fällningen:

Koppla vattensugen till filterkolven och håll lösningen i filterdegeln. Undertrycket på grund av vattensugen gör att filtreringen går snabbare.

14. Skölj ned $\text{Ni}(\text{Dmg})_2$ -fällningen som fastnat på filterdegelnns väggar med destillerat vatten och skölj 6–7 gånger med små mängder destillerat vatten. OBS! Fällningen får inte bli för torr!

Om fällningen blir för torr, bildas sprickor som det destillerade vattnet kan rinna igenom och sköljeffekten försämras. Sköljningen renar vätskan i fällningen från alla lösta substanser. Effekten av sköljningen är beroende av hur många sköljningar som görs: Varje sköljning avlägsnar ungefär 90% av de resterande substanserna. En liten del $\text{Ni}(\text{Dmg})_2$ kan ha gått förlorat vid filtreringen.

¹⁸ $2\text{Dmg} + \text{Ni}^{2+} \Rightarrow \text{Ni}(\text{Dmg})_2 + 2\text{H}^+$

15. Fånga upp den sista sköljningen i en bägare och kontrollera förekomsten av Cl⁻ joner med en 0,1 M lösning av silvernitrat (AgNO₃) och lite HNO₃.
- I sur miljö bildas silverklorid (AgCl) en ljus, ostlik fällning. Förekomsten av Cl⁻ joner visar på förekomsten av andra oönskade substanser. Eftersom AgNO₃ är löst i destillerat vatten, måste den filtrerade lösningen efter sista sköljningen först göras sur med t ex 1M HNO₃.*
16. Kontrollera att så gott som allt Ni har fällts ut genom att tillsätta lite Dmg-lösning till filtratet.
- Om för mycket fällning av Ni(Dmg)₂ bildas, gå tillbaka till punkt 8!*
17. Torka fällningen i filterdegeln vid 110–120 °C i 45–60 minuter **eller fortsatt med jonbytarkolonnen.**
18. Föraska fällningen till nickeloxid (Ni(II)O) vid 600–800 °C¹⁹: Skrapa loss Ni(Dmg)₂ med en kvartsspatel och för över det till en kvartsdegel. Upphetta den försiktigt, helst med lock, till över 600 °C. Efter ett tag tar Ni(Dmg)₂ fyr och kväveoxider bildas vid förbränningen av komplexet. Värm den föraskade substansen ytterligare tills den är helt svart.
- På samma gång kan man bränna bort soten från sidorna av degeln. Luta degeln så att luften kan cirkulera. **OBS!** Om det bara finns lite NiO i degeln finns risk för att den flyger ur degeln om luftcirkulationen är för stark. Detta gäller speciellt den första förbränningen, därför rekommenderas ett lock till kvartsdegeln. Efter den synliga förbränningen finns fortfarande lite Ni(Dmg)₂, NiC och annat kvar. Dessa förbränns när substansen värms ytterligare.*
19. Reducera Ni(II)O till metalliskt Ni i vätgasatmosfär vid 800 °C²⁰: NiO förs över till ett glödskepp av kvartsglas som placeras i ett provrör. Provröret fylls med vätgas i laboratoriets grafitiseringsanläggning och upphettas tills substansen är matt silvergrå. Sedan pumpas vätgasen ut och provröret får svalna. När provröret har svalnat släpps luft in i systemet.
- Om den varma substansen tillåts att komma i kontakt med syre, bildas åter igen en del NiO. Överföringen kan till exempel ske genom att vika ett papper och låta NiO glida ned i kvartsskeppet längs skåran.*

¹⁹ Molmassan för Ni(Dmg)₂ är 290g/mol och molmassan för NiO är 74g/mol.

a/290 mol Ni(Dmg)₂ ger således x/74 mol NiO ⇔ x=74a/290 [gram].
100 mg Ni(Dmg)₂ ger ca 25,5 mg NiO.

²⁰ b/74 mol NiO ger y/58 mol Ni. y=58b/74 [g]. 25,5 mg NiO ger ca 20,0 mg Ni.

Co-rening med anjonbytarkolonn (4–5 timmar)

20. Lös upp Ni(Dmg)_2 i 10 M HCl.
Som anjonbytarmassa används Dowex 1x8, 50–100 mesh.
21. Håll provlösningen i jonbytarkolonnen.
Co fixeras i jonbytaren eftersom Co bildar komplexa $\{\text{CoCl}_4\}^{2-}$ joner i koncentrerad HCl, medan Ni inte bildar komplexa joner. $\{\text{CoCl}_4\}^{2-}$ jonerna är stark blåfärgade. Lösningen som passerat jonbytarmassan färgas grönt av NiCl.
22. Tillsätt 10M saltsyra motsvarande kolonnens fria volym (ca. 10–15 ml) för att ”driva igenom” Ni-lösningen.

Utfällning med Dmg (som ovan, punkt 5ff)

23. Späd ut lösningen till 200 ml i en 400 ml bägare.
24. Tillsätt ytterligare lite vinsyra.
Detta för att ta hand om eventuella kvarblivna Fe(III) joner. FeCl_4^- bör ha fastnat på jonbytarkolonnen, men för säkerhets skull tillsätts ytterligare lite vinsyra. Citratet påverkar inte lösningen i övrigt.
25. Neutralisera lösningen med 2 M NH_3 .
 Ni(Dmg)_2 -komplexet fälls ut då lösningen blir basisk.
26. Gör lösningen svagt sur genom att tillsätta 2 M HCl.
Lite av Dmg-komplexet löses. Lösningen färgas rostaktig av eventuellt komplex vinsyra och Fe(III).
27. Värm lösningen till 60–80 °C.
Det mesta om inte allt av Dmg-komplexet löses vid uppvärmningen.
28. Tillsätt åter igen ett litet överskott av 1% alkohollösning av Dmg (7–8 ml); tillsätt omedelbart 2M NH_3 tills lösningen är svagt basisk och rör om väl.
29. Låt lösningen stå i ångbad i 20–30 min och rör om då och då.
Lösningen är klar, fällningen röd.
30. Låt lösningen svalna till rumstemperatur i ungefär 1 timme.
31. Filtrera fällningen.
32. Skölj ned Ni(Dmg)_2 -fällningen som fastnat på filterdegelns väggar med destillerat vatten och skölj 6–7 gånger med små mängder destillerat vatten. OBS! Fällningen får inte bli för torr!

33. Fånga upp den sista sköljningen i en bägare och kontrollera förekomsten av Cl⁻ joner med en 0,1M lösning av AgNO₃ och lite HNO₃.
- Sista sköljningen måste göras sur med t ex 1M HNO₃ för att utfällning av AgCl ska kunna ske.*
34. Kontrollera att så gott som allt Ni har fällts ut genom att tillsätta ytterligare lite Dmg-lösning.
35. Torka fällningen vid 110–120 °C i 45–60 minuter **eller upprepa processen.**
36. Föraska fällningen till nickeloxid (Ni(II)O) vid 600–800 °C²¹: Upphetta försiktigt en kvartsdegel med Ni(Dmg)₂ till över 600 °C. Efter ett tag tar Ni(Dmg)₂ fyr och kväveoxider bildas vid förbränningen av komplexet. Värm den förskade substansen ytterligare tills den är helt svart.
- På samma gång kan man bränna bort soten från sidorna av degeln. Luta degeln så att luften kan cirkulera. **OBS!** Om det bara finns lite NiO i degeln finns risk för att den flyger ur degeln om luftcirkulationen är för stark.*
37. Reducera Ni(II)O till metalliskt Ni i vätgasatmosfär vid 800 °C²²: NiO förs över till ett glödskepp av kvartsglas som placeras i ett provrör. Provröret fylls med vätgas i laboratoriets grafitiseringsanläggning och upphetas tills substansen är matt silvergrå. Sedan pumpas vätgasen ut och provröret får svalna. När provröret har svalnat släpps luft in i systemet.
- Om den varma substansen tillåts att komma i kontakt med syre, bildas åter igen en del NiO.*

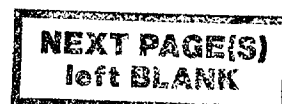
Efterarbete

38. Skölj bort Co-jonerna med 2 M HCl (se ”förberedelser”).

²¹ Molmassan för Ni(Dmg)₂ är 290g/mol och molmassan för NiO är 74g/mol.

a/290 mol Ni(Dmg)₂ ger således x/74 mol NiO ⇔ x=74a/290 [gram].
100 mg Ni(Dmg)₂ ger ca 25,5 mg NiO.

²² b/74 mol NiO ger y/58 mol Ni. y=58b/74 [g]. 25,5 mg NiO ger ca 20,0 mg Ni.



Appendix 3: Monitoring the chemical removal of cobalt with ⁶⁰Co

The test of efficiency was set up to monitor the absolute amount of cobalt removed chemically from a typical nickel solution. The easiest way to “measure” the absolute amount of cobalt in the nickel solution, is to subject a typical amount of stainless steel to chemical treatment (described in detail below). In this way, the concentration of cobalt in the chemically treated solution (extrapolated from AMS measurements on chemically treated nickel samples) should be well below the cobalt concentration of the radioactive solution of ⁶⁰Co. Finally, the cobalt concentration in the radioactive solution can be calculated from γ -spectrometry measurements.

A typical amount of stainless steel (≈ 0.5 g) was dissolved in concentrated hydrochloric acid (HCl). Nickel was precipitated with dimethylglyoxime (Dmg) and the remaining solution filtered off. The nickel-Dmg complex was then dissolved again in hydrochloric acid. 1.00 ml of a ⁶⁰Co solution was added to the solution.

To determine the amount of activity added and thus the amount of cobalt, two small glass flasks were filled with 1.00 ml of the same solution. The cobalt activity of these “calibration solutions” was measured to be 171 kBq and 173.5 kBq. From this, the amount of ⁵⁹Co added could be calculated, as ⁵⁹Co acts as a carrier substance at a concentration of 50 times that of ⁶⁰Co (see Tables App:3-1 and App:3-2, below).

Nickel was again precipitated from the active solution with Dmg. The remaining solution was filtered off and the nickel-Dmg complex was dissolved in a known quantity of concentrated hydrochloric acid and ethanol. 1.00 ml of this solution was subjected to γ -spectrometry. The remaining activity was measured to be of the order of tens of Becquerel (see Tables App:3-1 and App:3-2).

The comparison between the added and the remaining activity yields a ⁵⁹Co/⁵⁸Ni ratio of $5.5 \pm 2.4 \cdot 10^{-9} : 1$. When repeated, a ⁵⁹Co/⁵⁸Ni ratio of $2.9 \pm 1.5 \cdot 10^{-9} : 1$ was found, which is consistent with the results of the first experiment.

Table App:3-1. First attempt to monitor the chemical removal of cobalt with ^{60}Co .

Comments	Number of Ni-atoms	Number of Co-atoms	Approximate uncertainty
Solution containing 15–20 mg Ni, chemically treated. Co concentration extrapolated from AMS measurements.	$2.1 \cdot 10^{20}$	$<8 \cdot 10^{13}$	34% [1]
Approx. 173 kBq ^{60}Co was added to the solution, containing 50 times as much ^{59}Co as ^{60}Co .	$2.1 \cdot 10^{20}$	$2.2 \cdot 10^{15}$	10% [2]
Ni precipitation with Dmg. Remaining solution is filtered off.	$1.6 \cdot 10^{20}$	$1.6 \cdot 10^{15}$	25% [3]
The precipitate is dissolved in 12 ml of HCl and ethanol.			4.2% [4]
γ -spectrometry on 1.00 ml of solution Activity: 4.15 Bq.			8.4% [5]
Total activity of the solution: $12 \cdot 4.15 \text{ Bq} = 49.8 \text{ Bq}$.	$1.6 \cdot 10^{20}$	$6.2 \cdot 10^{11}$	
Results: Amount of ^{58}Ni (68.3% of the amount of Ni) and amount of ^{59}Co (98% of the amount of Co).	$1.1 \cdot 10^{20}$	$6.1 \cdot 10^{11}$	44% [6]
$^{59}\text{Co}/^{58}\text{Ni}$ ratio: $5.5 \pm 2.4 \cdot 10^{-9} : 1$.			

- [1] The nickel content of stainless steel is 8–11% Ni. The uncertainty is due to the chemical treatment and should not exceed 34%.
- [2] Calibration samples containing 1.00 ml of the active solution were subjected to γ -spectrometry. From these measurements, the β -activity was calculated to be 173.1 kBq and 171 kBq, in the two samples. (Systematic error: negligible.)
- [3] Loss of $\text{Ni}(\text{Dmg})_2$ -complex when transferred to a small beaker to be dissolved in concentrated HCl and ethanol: approximately 15%. Ni and Co are assumed to be lost in proportion to each other.
- [4] Systematic error in the volume measurement: ± 0.5 ml.
- [5] Statistical error (2σ) in γ -spectrometry.
- [6] Probable systematic error of the test of efficiency.

Table App:3-2. Second attempt to monitor the chemical removal of cobalt with ⁶⁰Co.

Comments	Number of Ni-atoms	Number of Co-atoms	Approximate uncertainty
Solution containing 16.8 mg Ni, chemically treated. Co concentration extrapolated from AMS measurements.	$1.74 \cdot 10^{20}$	$<7 \cdot 10^{13}$	[1]
Approx. 173 kBq ⁶⁰ Co was added to the solution, containing 50 times as much ⁵⁹ Co as ⁶⁰ Co.	$1.74 \cdot 10^{20}$	$2.2 \cdot 10^{15}$	10% [2]
Ni precipitation with Dmg. Remaining solution is filtered off.	$1.5 \cdot 10^{20}$	$1.9 \cdot 10^{15}$	15% [3]
The precipitate is dissolved in 10 ml of HCl and ethanol.			[4]
γ-spectrometry on 1.00 ml of solution. Activity: 2.33 Bq.			50% [5]
Total activity of the solution: $10 \cdot 2.33 \text{ Bq} = 23.3 \text{ Bq}$.	$1.5 \cdot 10^{20}$	$3.0 \cdot 10^{11}$	
Results: Amount of ⁵⁸ Ni (68.3% of the amount of Ni) and amount of ⁵⁹ Co (98% of the amount of Co).	$1.0 \cdot 10^{20}$	$2.9 \cdot 10^{11}$	53% [6]
⁵⁹ Co/ ⁵⁸ Ni ratio: $2.9 \pm 1.5 \cdot 10^{-9} : 1$.			

- [1] The Ni(Dmg)₂-complex was weighed before adding the active ⁶⁰Co solution. Uncertainty: negligible.
- [2] Calibration samples containing 1.00 ml of the active solution were subjected to γ-spectrometry. From these measurements, the β-activity was calculated to be 173.1 kBq and 171 kBq, in the two samples. (Systematic error: negligible.)
- [3] Loss of Ni(Dmg)₂-complex when transferred to a small beaker to be dissolved in concentrated HCl and ethanol: approximately 15%. Ni and Co are assumed to be lost in proportion to each other.
- [4] Systematic error in the volume measurement: ± 0.1ml (negligible).
- [5] Systematic error in γ-spectrometry due to the sensitivity to the distance between sample and detector.
- [6] Probable systematic error of the test of efficiency.

It is assumed that ⁶⁰Co is removed in proportion to ⁵⁹Co. It is also assumed that nickel precipitation with Dmg will remove cobalt down to a certain, absolute, ⁵⁹Co-to-⁵⁸Ni ratio.