RESL TECHNICAL PROCEDURE

CHEM-TP-Ni.1

DETERMINATION OF ^{63}Ni IN WATER

Preparer:	Date	Independent Review:	Date
Ray Randolph	4/19/99	George M. Hall	4/19/99
ES&H Review:	Date	Radiological Controls Review:	Date
Lynn Coleman	4/19/99	Richard Moore	4-19-99
QA Review:	Date	Supervisor Approval:	Date
Mohammed K Zaidi	4/19/99	Gary Mantooth	4-19-99

TITLE: CHEM-TP- Ni.1, DETERMINATION OF ^{63}Ni IN WATER

PURPOSE

The purpose of this procedure is to describe a method for the determination of ^{63}Ni in environmental and nuclear reactor water samples. This procedure incorporates and supersedes ACB-TP-Ni.01 (Rev 0).

APPLICABILITY

This procedure is applicable to the liquid-scintillation measurement of ^{63}Ni after its chemical separation from environmental waters and various liquids collected at nuclear reactor facilities.

RESPONSIBILITIES

RESL staff responsible for implementing this procedure are:
Radiochemist(s)

DEFINITIONS

H_2O - Demineralized water

Covered hotplate - Hotplate covered with 1.6-mm thick fiberglass mat

Dead water - Low-tritium background water obtained from offsite and distilled or demineralized to remove dissolved salts and particles.

PROCEDURE

1 **ABSTRACT** Nickel-63 is an activation product and a pure beta emitter that must be chemically separated from interfering radionuclides prior to counting. Radioactive nickel and the added nickel carrier are separated from most of the interfering impurities by using iron hydroxide as a scavenger. Further decontamination is provided by several nickel dimethylglyoxime (DMG) precipitations. The purified nickel is heated to formation of the black nickel oxide which is weighed to measure the chemical yield of the process. The oxide is dissolved and the ^{63}Ni is counted by liquid scintillation.

2 **LIMITATIONS AND INTERFERENCES** This method is suitable for most aqueous samples including those containing organic complexing agents. When nickel is complexed by organic compounds such as EDTA, these must be destroyed to obtain quantitative precipitation of nickel as nickel dimethylglyoxime. The only elements known to seriously interfere are palladium and hafnium, which if present in large quantities may give a high yield. Radioactive isotopes of these elements interfere with the counting of the ^{63}Ni. The volume of sample to be analyzed depends on the activity level as well as on the amount of stable nickel present, although the latter is seldom significant. Low activity samples can be concentrated by evaporation and high activity samples can be analyzed by taking small aliquants. The spectral capabilities of the liquid scintillation system provide a more reliable

means for quantifying ^{63}Ni and detecting the presence of interferences than older energy-window-type systems.

3 QUALITY ASSURANCE REQUIREMENTS

3.1 A reagent blank must be included with each set of samples. A ^{63}Ni standard must also be prepared and counted to determine the counting efficiency for each set of samples.

3.2 Correct performance of the liquid scintillation spectrometer must be verified by an Instrument Performance Analysis (IPA) at the end of counting each sample set. The IPA can be initiated automatically by the instrument.

4 SAFETY REQUIREMENTS

4.1 Follow Laboratory safety requirements in CHEM-AP-002 and proper use of fume Hoods as addressed in RESL-TP-IH.12.

4.2 Wear appropriate laboratory coat, gloves, and eye protection in accordance with RESL-TP-IH.7.

4.3 Dispose of all wastes in accordance with RESL-AP-10.

5 APPARATUS

5.1 Centrifuge with a 12-place rotor, trunnions, and cups for 100-mL centrifuge tubes

5.2 Centrifuge tubes, 100-mL glass

5.3 Erlenmeyer flasks, 250-mL

5.4 Fiberglass mat, 1.6 mm thick, to cover hotplate

5.5 Filter paper, S and S No. 576, 11 cm

5.6 Hotplate, 3600 W, 46 x 61 cm

5.7 Ultrasonic bath or vortex mixer

5.8 Vials, liquid scintillation, 22-mL glass

5.9 Burner, Bunsen

5.10 Fume hood

5.11 Boiling chips, Hengar, 10 mesh

6 **REAGENTS** NOTE: ALL SOLUTIONS ARE PREPARED WITH REAGENT GRADE CHEMICALS AND DEMINERALIZED WATER.

6.1 Ammonium Citrate Solution, 1 Molar: Dissolve 226 g of ammonium citrate in 500 mL of H_2O and dilute to 1 L.

6.2 Dimethylglyoxime Solution, 1% in 95% ethyl alcohol: Dissolve 10.0 g of DMG in 500 mL of 95% ethyl alcohol and dilute with 95% ethyl alcohol to 1 L.

6.3 Hydrochloric Acid, 1.0 Molar: Dilute 42 mL of concentrated (12 M) HCl to 500 mL with dead water.

6.4 Iron Carrier, 10 mg/mL: Dissolve 24.6 g of $FeCl_3 \cdot 6 H_2O$ in 200 mL of 1 M HCl and dilute to 500 mL with 1 M HCl.

6.5 Nickel Carrier, 10 mg/mL: Add 5 mL of 72% $HClO_4$ to 8.10 g of $NiCl_2 \cdot 6 H_2O$ and evaporate to fumes on a covered hotplate. Fume nearly dry and dilute to 200 mL with H_2O.

6.6 Scintillator, INSTA-GEL XF: Packard Instrument Company

7 **INSTRUMENTATION** Liquid scintillation, PC-controlled Packard Model 2770 TR/SL Liquid Scintillation Spectrometer.

8 **PREPARATION OF CALIBRATION STANDARD AND REAGENT BLANK**

8.1 Pipet an aliquant of ^{63}Ni standard solution (E4 to E5 dpm) into a tared counting vial containing 30 mg of nickel carrier and four boiling chips. Evaporate to dryness on the covered hotplate and then heat on the bare hotplate, just until the black nickel oxide (NiO) forms. Cool, weigh, and record the weight for later use in calculation of yields for the samples. Dissolve the NiO in 10 mL 1.0 M HCl, add 10 mL INSTA-GEL XF scintillator solution, and cap and shake until gel formation. This will be counted to determine the counting efficiency of ^{63}Ni.

8.2 Carry 50 mL of H_2O containing 30 mg of nickel carrier through the procedure in the same manner as the samples. This will be counted as the reagent blank.

9 **SEPARATION OF ^{63}NI AND PREPARATION FOR COUNTING**

9.1 Transfer an aliquant directly into a 100-mL centrifuge tube containing 30 mg of nickel carrier and proceed with Step 9.4 if the sample is known to be free of organic complexing agents. Transfer an aliquant into a 125-mL Erlenmeyer flask containing 30 mg of nickel carrier and 3 or 4 boiling chips if the sample contains organic complexing agents.

9.2 Add 2 mL of concentrated H_2SO_4 and evaporate on a covered hotplate to dense white fumes.

9.3 Continue heating and slowly add concentrated HNO_3 dropwise until the organic material is destroyed (black or brown residue disappears). Cool and transfer with water rinses to a 100-mL centrifuge tube. Dilute with H_2O to about 20 mL.

9.4 Add 10 drops of iron carrier. Heat with constant swirling over a low flame on the Bunsen burner to near boiling. Cool slightly and precipitate $Fe(OH)_3$ by slow dropwise addition of concentrated NH_4OH in excess while swirling continuously.

9.5 Centrifuge the sample at about 2000 rpm for 5 min and then filter the supernate through a folded 11-cm S and S No. 576 filter paper into a clean 100-mL centrifuge tube. Wash the filter paper with H_2O and collect the wash in the 100-mL tube. Discard the precipitate.

9.6 Add 3 mL of 1 M ammonium citrate to the filtrate and mix.

9.7 Add 15 mL of 1% dimethylglyoxime (DMG) in ethanol. Heat for 2 minutes in a hot water bath. Place the tube in an ultrasonic bath for 1 min to aid in packing the precipitate, or use a vortex mixer.

9.8 Centrifuge at about 2000 rpm for 5 min and carefully decant and discard the supernate.

9.9 Wash the precipitate with a mixture of 3 mL of 1 M ammonium citrate, 5 mL of H_2O, and 2 mL of 95% ethanol. Centrifuge, decant, and discard the wash solution.

9.10 Dissolve the precipitate with heat over a low flame in 2 mL of concentrated HNO_3 and 10 mL of H_2O. Cool, add 3 mL of concentrated NH_4OH, 3 mL of 1 M ammonium citrate, and repeat Steps 9.7 through 9.9 before proceeding to Step 9.11.

9.11 Dissolve the precipitate obtained from the repetition of Steps 9.7 through 9.9 in 5 mL of concentrated HNO_3 and 5 mL of H_2O. Transfer the solution to a tared counting vial containing 3 or 4 boiling chips (tare weight previously recorded).

9.12 Evaporate the solution to near dryness on the covered hotplate (do not allow the sample to dry and bake). Dissolve the residue, with heat on the covered hotplate, in 3 mL of concentrated $HClO_4$.

9.13 Heat the sample on the covered hotplate to fumes of perchloric acid to destroy DMG and other organics. Heat on the uncovered hotplate to dryness and formation of black NiO. Cool and weigh the vial for yield determination. Record the weight.

9.14 Add 10 mL of 1.0 M HCl to the vial and warm on a covered hotplate briefly to dissolve the NiO. Cool and add 10 mL of INSTA-GEL XF scintillator solution. Cap and shake well until formation of a gel. Mark the caps on the samples, standard, and reagent blank appropriately.

10 **COUNTING** Count the samples, standard, and reagent blank on the Packard Tri-Carb 2770 TR/SL liquid scintillation spectrometer which is operated by the dedicated instrument computer. Before attempting to count samples in this counter, the analyst should read and become familiar with the operating procedures in the Packard Tri-Carb Reference Manual. The Region settings (in keV) for counting ^{63}Ni are as follows:

	LL	UL	Information
Region A:	0.5	15.0	^{63}Ni counting region
Region B:	0.0	15.0	Alternative ^{63}Ni counting region
Region C:	20.0	2000	Monitor for other activity

Count the samples, standard, and reagent blank three times for 20 min. Once the samples, standard, and blank have been counted three (or more) times, mark the printout as to which sample was counted in which position.

11 **CALCULATION OF RESULTS AND UNCERTAINTIES** Calculate the results and uncertainties using the menu-prompted PC program LSNICKEL.WK3. The equation for the result is:

$$R, \mu Ci/mL = \frac{(A_G - A_B)}{(T)(V)(Y)(E)(2.22E6)}$$

where:

A_G = Average gross count in Region A from printout
A_B = Average gross count of reagent blank in Region A from printout
T = Count time in minutes (same for samples, ^{63}Ni standard, and blank)
V = Volume of sample, mL, corrected for dilution by acid used in sample preservation

Y= Yield = $\frac{\text{Gross wt sample - Sample vial tare wt}}{\text{Gross wt } ^{63}\text{Ni std. - Std. vial tare wt}}$

NOTE: ENTER WTS IN GRAMS TO 3 DECIMAL PLACES.

E = Counting efficiency from ^{63}Ni standard

$$= \frac{A_G(std.) - A_B}{(T)(dpm/mL\ std.)(e^{-\lambda t})}$$

11.1 Enter A_G, A_B, and T as defined above. Enter the time elapsed, t days, from the reference date of the ^{63}Ni standard solution used to the time the aliquant was counted (to the nearest day) and the mL used. Compare the current E value with the average $\overline{E}$ stored in the program. The current E value should be in statistical agreement with $\overline{E}$.

11.2 No additional input is required for calculation of uncertainties by the PC program. Enter the results, uncertainties, and other required data into the RESL database.

REFERENCES

Tri-Carb Liquid Scintillation Analyzers, Models 2770 TR/SL Reference Manual, Packard Instrument Co., Inc. 1995.

QUALITY RECORDS

The sample data and results that are entered in the RESL database.
The Liquid Scintillation Counter printout
The Sample Record Sheet.