RP530[a]

Determination of Selenium-79 in Aqueous Samples

1.0 Scope and Application

This method describes the isolation of Se in aqueous samples by ion exchange, distillation if necessary, and precipitation for subsequent analysis of ^{79}Se by liquid scintillation counting (LSC). It has been applied to high-level radioactive samples from Hanford waste tanks and on defense waste processing facility (DWPF) samples from the Savannah River Site. The separation, although difficult, provides a decontamination factor of Se from other β-emitters of about 10^6 and a chemical yield of about 50% or better.

2.0 Summary

The oxidation state of Se is adjusted to the neutral molecular form, H_2SeO_3. In this form, the Se passes through a mixed-bed ion exchange column onto which most other elements are absorbed. Further purification of Se is accomplished by precipitating the elemental Se after reduction with hydroxylamine hydrochloride. The Se is dissolved in HNO_3 and prepared for LSC. A distillation process, which may be used for further purification, is also described. The chemical yield of Se can be determined gravimetrically or by elemental analysis of Se {e.g., inductively coupled plasma (ICP) optical emission spectroscopy (OES)}. Selenium-79 activity is determined from beta-decay measurement by LSC. A flow chart (Figure 1) indicates available paths for sample preparation.

3.0 Interferences

Selenium-79 is determined by LSC; therefore, the Se fraction must be well separated from other beta emitters. This method should satisfactorily remove these interferences before counting.

4.0 Safety

Selenium is considered a highly toxic material, and the carrier and sample preparative steps should be undertaken with appropriate safety considerations.

Bromine is a relatively strong oxidizer with a reasonably low boiling point (<100°C) and should be handled with due care.

(a) This method was consolidated by S. K. Fadeff (Pacific Northwest Laboratory, Richland, Washington) from two analytical procedures; one from Pacific Northwest Laboratory (Maiti and Kozelisky 1990) and one from Savannah River Laboratory (Dewberry 1991).

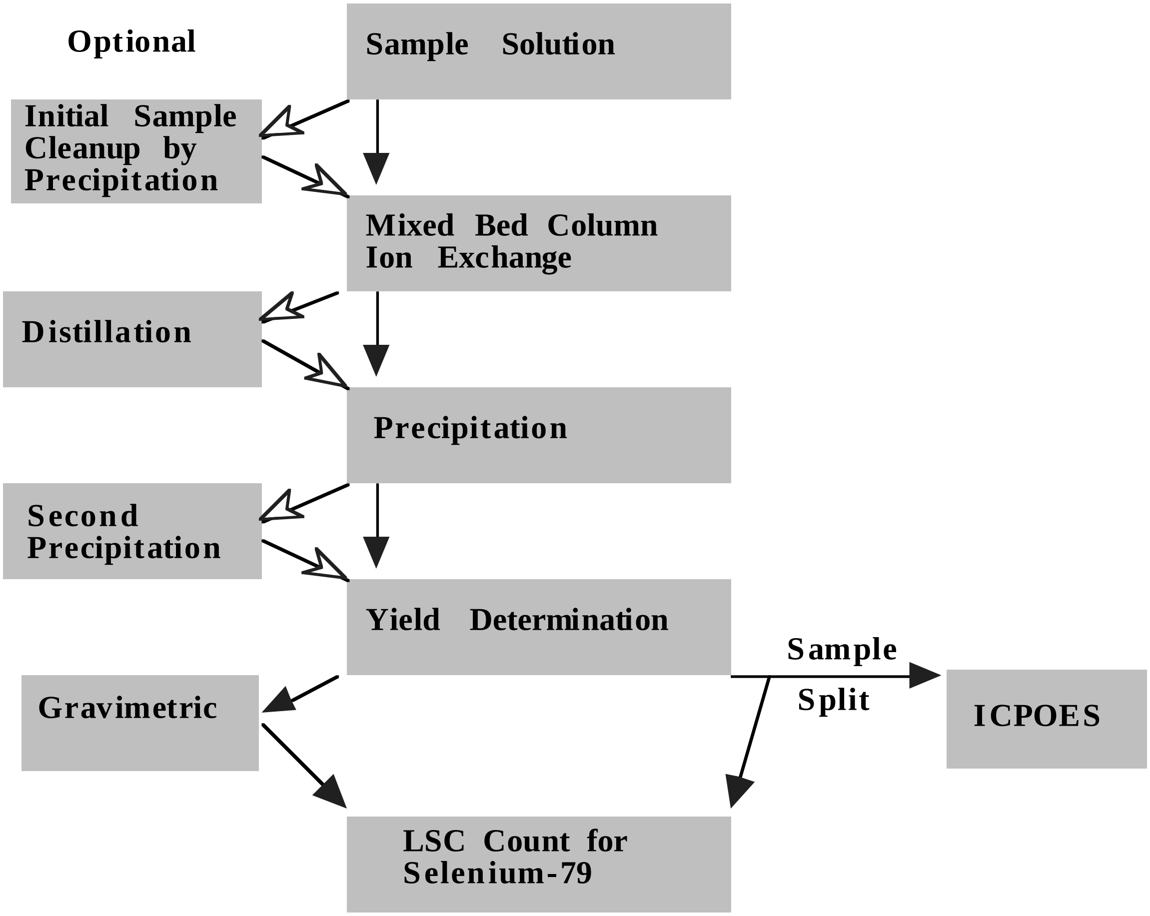

Figure 1. Pathways for Sample Preparation

5.0 Apparatus and Materials

- Beaker, appropriate sizes (e.g., 30 mL to 400 mL)
- Vials, 7 mL and 35 mL, glass, screw-cap, or equivalent (Note: 35-mL vials can be used in a centrifuge)

- Liquid scintillation vials
- Heating block (100°C), hotplate, or water bath
- Ion exchange column, approximately 0.5-cm internal diameter (A 7.5-mL plastic dropper with the top cut off and plugs of glass wool on resin top and bottom works well.)
- Transfer pipets, glass or plastic
- Filters, tared (e.g., Whatman 934AH glass microfiber filters). For the gravimetric yield determination, the filter should be small enough to lie flat on the bottom of the LSC vial. For spectrometric yield determination, filter size is not critical. Note: Some filters break apart in LSC cocktail; it is recommended filters be tested in LSC cocktail for suitability.
- Filtration unit suitable for selected filter
- Petri dishes or other suitable carriers for filters
- Centrifuge tubes (Note: 35-mL vials can be used in a centrifuge)
- Centrifuge

Distillation

- Selenium still (An example of a specially made still is shown in Figure 2.)
- Variac, 1.5-ampere output, 0 to 140 volts
- Heating mantle, 50 mL, round bottom
- Thermometer, including temperature range of ~20°C to 130°C
- N_2 gas, 2 psi (e.g., 99.99%)

6.0 Reagents

Reagent grade (or better) chemicals should be used in all tests, unless otherwise indicated. Other grades may be used if it is ascertained that the reagent quality will not adversely affect the method performance. Water purity should conform to American Society for Testing and Materials (ASTM) specification D 1193, Type II (or better), unless otherwise indicated.

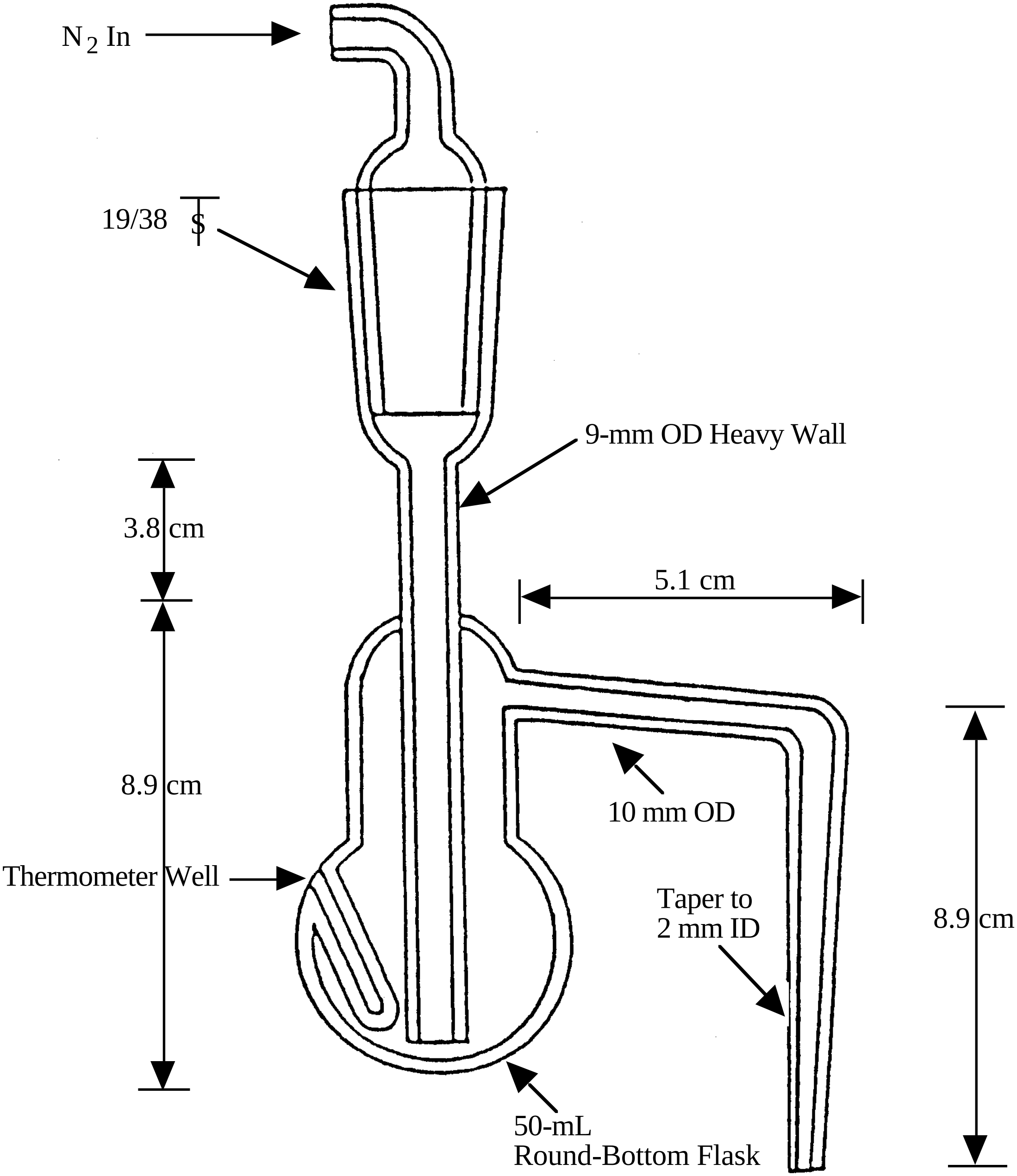

Figure 2. Selenium Still

- Selenium carrier, 10 mg/mL {This may be prepared by dissolving about 1.0 g (precisely known) of gray elemental Se in a 100-mL volumetric flask using 5 to 6 mL of hot concentrated HNO_3. When dissolution is complete, the selenium solution is diluted to slightly less than the volumetric mark with 0.5 M HNO_3. After cooling to ambient temperature, the solution is diluted to volume with 0.5 M HNO_3.}

- Carbon-14 standard, National Institute for Standards and Technology (NIST) traceable

- Nitric acid, fuming, 16 M, 8 M, 0.5 M, and 0.1 M

- Ion exchange resin, AG 50W-X8 (Bio-Rad, Richmond, California), or equivalent, 100 to 200 mesh, H^+ form

- Ion exchange resin, AG 1-X4 (Bio-Rad, Richmond, California), or equivalent, 100 to 200 mesh, Cl^- form

- Nitric acid saturated with bromine. (This may be prepared by adding ≈100 µL Br_2 to 15 mL of 0.5 M HNO_3.)

- Bromine water. (This may be prepared by adding ≈100 µL of Br_2 to 15 mL of deionized water.)

- Hydrobromic acid, 47% to 49% or 9 M

- Liquid scintillation cocktail, e.g., Ultima-Gold®

- Hydroxylamine hydrochloride, 0.25 g/mL in H_2O (The shelf life is approximately two weeks.)

- Sodium hydroxide, 0.3 M

- Ethanol, 95% or better

- Hydrochloric acid, 9 M

- Br_2

7.0 Sample Collection, Preservation, and Handling

Water samples should be preserved to pH <2 with HNO_3. Refrigeration is generally not required.

8.0 Procedure

For samples containing a high-salt matrix (e.g., fused samples), an initial sample cleanup should be performed as described in step 8.1. For low-salt samples, the initial sample cleanup can be omitted and the separation method begun at step 8.2.

8.1 Initial Cleanup of High-Salt Matrix Samples

8.1.1 An appropriate sample aliquot of the dissolved fused sample is transferred to an appropriately sized beaker or vial. (A 35-mL vial can be used for all of section 8.1, including centrifuging if the sample volume ≤ 10 mL). The sample volume must be recorded. A precisely known quantity (e.g., 20 mg) of Se carrier and 20 µL of Br_2 are added. Using a stir bar, the sample is mixed thoroughly; then it is allowed to stand 10 min.

8.1.2 To the sample, 10 mL of 25% $NH_2OH•HCl$ are added, and the solution is mixed.

8.1.3 The sample is heated until black Se precipitates; this takes about 45 min. The sample is then cooled.

8.1.4 The solution is transferred to a centrifuge tube, if necessary, and is centrifuged for about 5 min to provide a tightly-packed precipitation.

8.1.5 The supernate is removed using a transfer pipet. The container walls and precipitate are washed with ≈10 mL of ethanol.

8.1.6 The sample is again centrifuged for about 5 min. The ethanol is removed using a transfer pipet.

8.1.7 The sample is slightly warmed to vaporize residual ethanol.

8.1.8 To the Se, 0.5 mL concentrated HNO_3 are added.

8.1.9 The sample is heated until the Se dissolves.

8.1.10 Five milliliters of water and 50 µL of Br_2 are added to the sample. The method continues with step 8.3.

8.2 For low salt or non-fused samples, a solution aliquot is added to a beaker or vial. A precisely known quantity (e.g., 20 mg) of Se carrier is added, along with 0.5 to 1.0 mL of 0.5 M HNO_3, and an excess of Br^-. This HNO_3/HBr mixture has been prepared at 2 different sites as follows:

a) 100 µL Br_2 is mixed with 15 mL 0.5 M HNO_3; 0.5 to 1 mL of this mixture is added to each sample

b) 200 µL Br_2, 500 µL 9 M HBr, and 0.5 to 1 mL 0.5 M HNO_3 are added to each sample.

The choice will depend on preference and performance on the matrix type. The solution is swirled to mix thoroughly.

The excesses of Br^- *and* Br_2 *will hold Se as* H_2SeO_3.

8.3 Ion exchange columns are prepared by placing 1 mL of the AG 1-X4 anion resin in the column and by placing 1 mL of the AG 50W-X8 cation resin on top of the anion resin. The resin column is washed with 5 mL of deionized water.

8.4 The sample solution is transferred quantitatively to the ion exchange column using 0.5 M HNO_3•HBr (1 drop HBr per 1 mL 0.5 M HNO_3) to rinse the sample vial. The Se passes through the column and is collected in an appropriate vial (e.g., 35-mL screw-cap vial).

Selenium will not absorb onto the column, but will collect in the elution vial. Most of the other activity will absorb onto the mixed-bed resin.

8.5 At this point, purification may continue with distillation (step 8.6) followed by precipitation (step 8.7), or purification may continue with precipitation (step 8.7).

8.6 Distillation.

Distillation is an excellent purification technique for Se. If sample purity is not sufficient after ion exchange and precipitation, it may be appropriate to apply distillation to the separation scheme for that matrix. Distillation may not generally be necessary, but is included as an *option.*

8.6.1 The solution is quantitatively transferred from the vial to a Se still.

8.6.2 The vial is rinsed with two 5-mL portions of HBr, which are transferred to the still.

8.6.3 The round bottom of the still is placed in the heating mantle.

8.6.4 A vial containing 5 mL of 25% NH_2OH•HCl is placed in an iced-filled beaker (e.g., 400 mL). The vial is positioned so that the tip of the still's exit is below the liquid level of the NH_2OH•HCl in the vial.

8.6.5 The still inlet is connected to N_2, and the N_2 flow rate is adjusted to about five bubbles per sec.

8.6.6 The heating mantle variac is set to 110 V. The temperature should rise to ≈120°C. Distillation should be continued for about 35 min. When distillation is complete, the solution in the still should be pale yellow, as the red/brown Br_2 has been distilled.

8.6.7 After distillation, the variac is turned off, and the solution is allowed to cool for 2 to 3 min. Then the still is removed from the heating mantle, and the N_2 flow is shut off. The vial containing the distillate is removed. The still (shown in Figure 2) is cleaned as follows:

1. The waste in the still is discarded by vacuum suctioning through the still top into a radioactive waste jug.
2. While continuing to pull a vacuum through the top of the still, the still is flushed clean by allowing water to be pulled up the exit arm of the still. (The water in the beaker used for cooling may be used.) The still is cleaned with a series of flushes as above, with 25% $NH_2OH \cdot HCl$, deionized water, 8 M HNO_3, and finally with deionized water.

8.6.8 The sample preparation continues with step 8.7.2.

8.7 Precipitation

8.7.1 If the sample was not distilled, 4 mL HBr are added to the sample solution.

Bromide provides a more reducing matrix for the subsequent reduction of Se^{+4} *to elemental Se.*

8.7.2 To the sample from step 8.6.8 or 8.7.1, an excess (e.g., 5 to 10 mL) 200 mg/mL $NH_2OH \cdot HCl$ are added, and the sample is heated gently for about 30 min.

The low heat will speed the reduction of Se^{+4} *to elemental Se. The solution will turn orange or lavender.*

8.7.3 The solution is cooled, transferred to a centrifuge tube, if necessary, and then centrifuged. After the Se has settled, the major amount of supernate may be suctioned off with a disposable pipet.

If a second precipitation is to be performed for additional purification from other beta emitters, the following steps are taken:

1. Without removing the black precipitate, the supernate is removed with a transfer pipet and discarded.
2. The precipitate is washed with ≈10 mL of ethanol.
3. The sample is again centrifuged for about 5 min. The ethanol wash is removed, using a transfer pipet, and the vial is warmed to vaporize the residual ethanol.
4. Slowly, 500 µL of 16 M HNO_3 are added to the vial, and then the sample is heated until the Se dissolves.
5. Ten milliliters of deionized water are added to the vial, which is swirled to mix.
6. Ten milliliters of 25% $NH_2OH \cdot HCl$ are added to the vial, which is swirled to mix.
7. The sample is heated gently for about 30 min, cooled, then centrifuged. The major amount of supernate may be suctioned off with a disposable pipet.

8.7.4 Two alternatives for yield determination and LSC sample preparation are described, one in section 8.8 (gravimetric yield determination), and one in section 8.9 (spectrometric yield determination). One of these alternatives is selected for an analytical batch of samples.

8.8 Gravimetric Yield Determination and LSC Sample Preparation

8.8.1 A filter small enough to fit the bottom of an LSC vial is tared, then mounted onto the filtration unit.

8.8.2 The black elemental Se is mounted onto the center of the filter while vacuum is applied, using a glass transfer pipet.

8.8.3 The vial is washed with 3 to 4 mL of ethanol, and the residual Se is transferred to the filter.

8.8.4 The filter is removed from the filter holder, and the filter plus the Se are placed on a petri dish, or other suitable carrier, and dried in an oven at 110°C to 120°C for about 30 min.

8.8.5 The filter plus Se are then cooled in a desiccator for at least 10 min.

8.8.6 The filter plus Se are weighed, and the mass is recorded.

8.8.7 The filter plus Se are transferred to a LSC vial. The filter is placed such that it lies flat on the bottom of the vial.

8.8.8 The Se is dissolved with 150 µL of concentrated HNO_3.

The Se is allowed to dissolve completely before going to the next step.

8.8.9 To neutralize the acid, 1 mL of 0.3 M NaOH is added.

8.8.10 A background sample is prepared by adding a filter to an LSC vial, washing with 150 µL HNO_3, and adding 1 mL 0.3 M NaOH.

8.8.11 An appropriate liquid scintillation cocktail (e.g., Altex™, Ultima-Gold™, Opti-Flour®, etc.) is added to the Se sample solution and background sample. The vial is capped, and the solution is shaken until it is clear.

8.8.12 The sample is counted by LSC to measure the ^{79}Se activity.

8.9 Yield Determination by Spectroscopy and LSC Sample Preparation

8.9.1 A filter is mounted on a filtration unit. The sample is quantitatively transferred to the filtration unit and filtered using four 5-mL aliquots of 0.1 M HNO_3 as the vial rinse and wash solution.

8.9.2 The filter is transferred to a new vial, and the filtrate is discarded.

8.9.3 The Se precipitate is dissolved with a precisely known quantity (e.g., 2.0 mL) of fuming HNO_3.

8.9.4 A precisely known quantity, equal to the HNO_3 volume in step 8.9.3 (e.g., 2.0 mL) of distilled water is added to the sample, and then the filter paper is removed and discarded.

8.9.5 A background sample is prepared by washing a blank filter paper with the same volume (step 8.9.3) of fuming HNO_3, adding the same volume (step 8.9.4) of distilled water, and removing the filter paper.

8.9.6 An aliquot (e.g., 100 µL) is transferred to another vial for subsequent Se yield determination and analysis of Sr, Zr, Ni, and Na (radioisotopes that might interfere with the LSC determination) by ICP-OES (or equivalent). This step is also applied to the prepared background sample.

8.9.7 An aliquot (e.g., 1 mL) of sample is transferred to an LSC vial and mixed with an appropriate volume of scintillation cocktail (e.g., 14 mL of Opti-Flour®). The background sample is prepared in the same way and will constitute the LSC background-subtraction sample.

8.10 Standard Preparation. Since ^{79}Se standard is generally not available for calibrations, a ^{14}C standard is used. The maximum and average beta energies for ^{14}C and ^{79}Se are similar (maximum energy 156 keV and 160 keV, respectively), which makes ^{14}C an acceptable calibration standard for measuring ^{79}Se {see Radioactive Decay Data Tables (DOE/T/C-11026)}. Carbon-14 calibration standards are prepared in the same matrix as the samples. The ^{14}C standard activity should provide appropriate counting statistics in a reasonable count time.

8.11 Quench Factor. A series of ^{14}C standards are made up containing different amounts of Se carrier, from 0 to 20 mg, in the same matrix as the samples. These are measured by LSC to establish the quench correction. An additional quench curve may need to be prepared to accommodate acid quenching if the standards and samples vary in acid concentration.

9.0 Calculations

9.1 Gravimetric Yield Calculation

$$Y = \frac{\left(\text{Mass}_{\text{gross}} - \text{Mass}_{\text{filter}}\right)}{[\text{Se}] \bullet V} \qquad (9.1)$$

Y = yield as a decimal fraction

$\text{Mass}_{\text{gross}}$ = mass of Se plus filter as milligrams from step 8.8.6

$\text{Mass}_{\text{filter}}$ = mass of filter only as milligrams from step 8.8.1

$[Se]$ = Se concentration in carrier as milligrams/milliliter

V = volume of Se carrier added in milliliters

9.2 Spectrometric Yield Calculation

$$Y = \frac{[Se]_{smpl}}{[Se]_{added} \bullet CF} \tag{9.2}$$

where

$[Se]_{smpl}$ = the Se concentration found in the sample (e.g., mg/mL)

$[Se]_{added}$ = the Se concentration of the carrier solution originally added to the sample (e.g., mg/mL)

CF = correction factor for carrier dilution in preparation for the sample split (steps 8.9.3 and 8.9.4)

For example, 2.0 mL of a 10 mg/mL Se solution are added; the sample dilution results in the 20 mg of Se being diluted to 4.0 mL, resulting in a 5 mg/mL solution. The resulting correction factor is

$$\frac{2.0\ \text{mL}}{4.0\ \text{mL}} = 0.5$$

9.3 Selenium-79 Counting Efficiency

$$E = \frac{CR_{std} - CR_{bkg}}{DR_{std}} \tag{9.3}$$

E = ^{14}C and ^{79}Se counting efficiency

CR_{std} = Count rate of ^{14}C standard from liquid scintillation counting data

CR_{bkg} = Count rate of the ^{79}Se blank

DR_{std} = Disintegration rate of ^{14}C in the calibration standard

9.4 Quench Factor

$$F_q = \frac{CR_i}{CR_{unquenched}} \tag{9.4}$$

where

F_q = quench factor

CR_i = count rate of the quenched standard

$CR_{unquenched}$ = count rate of the unquenched standard

For Ultima-Gold™, no quench up to 20 mg of Se was found (Maiti and Kozelisky 1990).

9.5 Sample Activity Concentration

9.5.1 If a non-fused sample is being analyzed, the activity calculation is

$$A = \frac{CR_{Se} - CR_{bkg}}{E \cdot Q \cdot Y \cdot F_q} \cdot S \cdot C \tag{9.5}$$

where

A = sample ^{79}Se activity concentration

CR_{Se} = sample count rate obtained from the liquid scintillation counting data

CR_{bkg} = ^{79}Se background sample count rate obtained from the liquid scintillation counting data

E = ^{14}C and ^{79}Se counting efficiency

Q = quantity of sample (in mL)

Y = yield factor calculated for sample

F_q = quench Factor

S = sample split factor (if portion was removed for ICP yield determination)

C = conversion factor to produce the desired reporting units

9.5.2 If a fused sample is being analyzed, the calculation becomes:

$$A = \frac{CR_{Se} - CR_{bkg} \bullet V}{E \bullet Q \bullet Y \bullet F_q \bullet M} \bullet S \bullet C \qquad (9.6)$$

where

V = final volume of dissolved, fused sample

M = mass of the sample that was fused, in g

10.0 Quality Control

To check for possible sample contamination, a method blank should be run with each batch of samples. A batch should not exceed 20 samples. A Se carrier is used to determine recovery for each sample. Carrier recovery should be at least 50%. Use of duplicates should be considered to provide information on method precision.

11.0 Method Performance

This method was applied to four Hanford waste tank samples taken from two cores. Duplicate aliquots (nominally 0.5 g) of the tank-sludge cores were prepared by KOH fusion and diluted to 100 mL in the hot cell. The ^{79}Se analysis was performed using the initial cleanup from high-salt solutions, anion exchange, distillation, and two precipitations, followed by gravimetric yield determination. Sample ^{79}Se activities are summarized in Table 1. The RPD is relative percent difference and is a measure of the precision of the analysis, including core aliquoting. The percent uncertainty (U) includes random and systematic errors for the analysis only. Also included in the table is a summary of the major radioactive constituents measured in the tank sample matrix.

Table 1. Summary of ^{79}Se Activity in Hanford Waste Tank Samples

Core 29				Core 30			
Sample ID	^{79}Se (Bq/g)	% U	RPD	Sample ID	^{79}Se (Bq/g)	% U	RPD
4312-1	3.6	17		4316-1	2.2	29	
4312-2	3.2	18		4316-2	2.0	29	
Average	3.4		12	Average	2.1		10
4313-1	4.1	16		4317-1	1.5	40	
4313-2	3.4	17		4317-2	1.7	38	
Average	3.8		18	Average	1.6		13
Blank	<0.7			Blank	<1.1		

Principal Radioactive Matrix

Core 29		Core 30	
^{137}Cs	6.3 MBq/g	^{137}Cs	5.2 MBq/g
^{90}Sr	11 MBq/g	^{90}Sr	7.0 MBq/g
Pu (total)	0.004 MBq/g	Pu (total)	0.004 MBq/g
^{241}Am	0.0031 MBq/g	^{241}Am	0.0021 MBq/g
^{99}Tc	0.0048 MBq/g	^{99}Tc	0.0037 MBq/g
U	205 µg/g	U	190 µg/g

No evidence of higher energy (>157 keV) beta emitters was apparent in the samples. Therefore, decontamination factors for ^{137}Cs and ^{90}Sr are better than 10^6. Chemical yields averaged 88 ± 4% for the eight samples and two blanks.

Historically, the chemical yields average 85.4% (n = 37), including the set of data summarized in Table 1.

This method was tested on four defense waste processing facility (DWPF) sludge-only feed samples (and on six sludge-only glass product samples) by performing anion exchange and one precipitation process followed by ICP-OES analysis for chemical yield. The resulting decontamination factor from other beta emitters was $>10^6$. Gamma emitters were not detectable in the final product. Selenium recoveries on the 10 samples ranged from 21% to 63%. The average ^{79}Se activity in the four sludge-only feed samples was 3.3 ± 1.7 Bq/mL (200 ± 100 dpm mL). For the six glass product samples, < 20 Bq/mL (<1000 dpm/mL) ^{79}Se was observed.

12.0 References

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13.0 Further Reading

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