

RiO5 METHOD (39)

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Protocol for the preparation of samples from solid or liquid matrices for the measurement of ^{129}I by accelerator mass spectrometry (AMS)

Disclaimer

It is the responsibility of the analyst to follow established safety and health practices. Although each laboratory identified as the source has tested the methods, each user should perform an individual validation procedure.

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1 SCOPE

This document is a summary of the protocol for the preparation, measurement and analysis of samples for ^{129}I employed by the Lalonde Laboratory at the University of Ottawa. Details of the methods are available in the document: *Protocol for the Analysis of Iodine-129 at the IsoTrace Laboratory version 3.07, 2007.*

2 EQUIPMENT and CHEMICAL REAGENTS

2.1 Equipment and consumables

- Calibrated balance
- Micropipettes
- Volumetric Flasks
- Thermolyne programmable muffle furnace (Model F1500)
- 20 ml scintillation vial
- ICP-MS or INAA (detection of ^{127}I)

2.2 Reference Material

- All samples are analysed with respect to a reference material which can be traced to a NIST standard. Two reference materials have been used at IsoTrace: IsoT2 for measurements between 1993 and 2004 and IsoT6 for measurements during and after 2004.
- The IsoT6 reference material is produced by dilution from the NIST 4949C Iodine-129 standard. The dilution factor is verified by comparison measurements with the NIST 3230 low level iodine-129 standards.
- IAEA-375 soil reference material

2.3 Chemical reagents

- Doubly De-Ionized Water
- Acids, bases, solvents, Na_2O_2 , NaNO_2 , NaHSO_3 , etc.
- AgI, NaI- solution
- 350 mesh Nb powder

2.4 Solutions

- NaI carrier solution

3 PROCEDURE

Standard sample preparation procedures are used for the extraction of iodine from a variety of sample materials, the determination of the iodine content, the addition of carrier (if necessary) and the precipitation of the final iodide. All procedures are tested on a specified seaweed from Japan or on IAEA-375 soil before being applied to a submitter's sample. These sample preparation procedures are to serve as guidelines only.

Complete flow records for the preparation procedures on each sample are maintained with all weights, measures and procedures. These records include the calibration results of the measurement and test equipment used in the sample preparation process.

As the ^{127}I content of the sample is usually quite low, if a concentration (atoms of ^{129}I /gram) is required, carrier is added at the start of the extraction procedure and either the solution is brought to equilibrium (for liquid samples) or is mixed to a uniform condition (solid samples) before processing. A measurement of the $^{129}\text{I}/^{127}\text{I}$ ratio using AMS and the weight of the carrier added is usually sufficient to determine the concentration as the quantity of ^{127}I added in the carrier usually exceeds that in the sample by several orders of magnitude. If the concentration of ^{127}I in the original sample (before the addition of carrier) is known, it can be added to the amount of ^{127}I in the carrier when determining the concentration.

If isotope ratios are required and the ^{127}I content of the sample is unknown, the ^{127}I content of an aliquot of the original sample is determined by ICP-MS or INAA.

3.1. Calibration of Measuring and Test Equipment

3.1.1. Balances

The calibrated balance is the fundamental instrument for all sample preparation procedures. Before the preparation of each batch of the iodide carrier solution, or at least every three months, the balance used to weigh the NaI must be calibrated according to the procedure outlined in the manual for the balance. For the AND Model ER-120A balance currently in use, this procedure is on page 6 of the manual. This calibration must then be checked using the weights from a calibrated weight set traceable to NIST, with the results recorded on a calibration sheet, dated and signed by the calibrator. Significant discrepancies ($>0.1\%$) in the ranges used for calibration of volumetric flasks and micropipettes as well as measuring NaI carrier will necessitate servicing of the balance.

3.1.2. Micropipettes

At the same time as the balance calibration and before any preparation work requiring such certification, the micropipettes used in the sample preparation process are to be calibrated according to the manufacturers procedure. These are then to be checked by dispensing DDIW (section 3.2) into a tared beaker using the balance calibrated as per section 3.1.1. The results are to be recorded on a signed and dated calibration sheet.

3.1.3. Volumetric Flasks

At the same time as the balance calibration the calibration of the volumetric flasks used in the preparation of NaI carrier solution is to be checked by taring the empty flask, then filling the flask to the scribed mark with DDIW (section 3.2) weighing the filled flask using the balance calibrated as per section 3.1.1. The results are to be recorded on a signed and dated calibration sheet.

3.2. Water Preparation

3.2.1. De-ionized water, obtained locally is passed through an anion de-mineralization column and an ultrapure de-mineralization column before use in any sample preparation process. This water is referred to as DDIW (Doubly De-Ionized Water) in the following text.

3.3. Sample Pre-treatment

Extensive sample pre-treatment is not required. At present, samples are pretreated to produce stable material for storage purposes only.

- Solid samples are dried at low temperature (if required), and stored in plastic containers
- Aqueous samples are stored in sealed opaque containers in a light free environment

3.4. Solid Organic and Inorganic Materials

3.4.1. An alkali fusion technique is used, based on the one described by Nishizumi et al (Nature 305 (1983) 611- 612 and references therein).

3.4.2. Approximately 5 grams of material is weighed out and placed in a 100 ml iron Crucible.

3.4.3. 15 g NaOH and 10 g Na₂O₂ together with a sufficient quantity of DDIW are added to and mixed well with the 5 g of sample material.

3.4.4. When carrier is required, approximately 5 – 20 mg I- in the form of a NaI solution with concentration of 1 mg I- per 10 µl is added to the above mixture and mixed well.

3.4.5. The mixture is covered and left at room temperature for 24 hours.

3.4.6. The covered crucible is placed in a furnace, for which the heating pattern depends on the particular furnace:

3.4.6.1. For heating strategies for the Thermolyne programmable muffle furnace (Model F1500), see Kieser, 2007.

3.5. Leaching

3.5.1. 40 ml of DDIW are added to the crucible and mixed thoroughly with the contents.

3.5.2. All free material is transferred into a 250 ml beaker

3.5.3. Step 3.5.1 is repeated until all the contents crucible are transferred to the beaker

3.5.4. The soluble and insoluble fractions are separated by centrifugation.

3.5.5. The insoluble fraction is reserved (treatment described in section 3.7)

3.6. Water soluble extraction

3.6.1. Concentrated HNO₃ is added to the aqueous phase obtained in step 4.5.4

3.6.2. The pH of this solution is checked (must be between 1 – 3)

3.6.3. The solution is transferred to a 250 ml separatory funnel

3.6.4. The beaker which contained the solution is rinsed 3 times with 1 – 2 ml of 6N HNO₃ which is added to the separatory funnel.

3.6.5. 25 ml of hexane or carbon tetrachloride and 0.1 - 0.3 ml of 6M NaNO₂ are added to the separatory funnel.

3.6.6. The mixture is shaken with frequent venting, then the layers are allowed to separate.

3.6.7. If a second extraction is necessary, the aqueous layer is drained, reserved and used to repeat the process from step 3.6.3. Otherwise, the aqueous layer is drained to waste.

3.6.8. 10 ml of DDIW and sufficient 4M NaHSO₃ are added to the separatory funnel to obtain clear separation of the aqueous and hexane or carbon tetrachloride layers.

3.6.9. The mixture is shaken and the layers are allowed to separate.

3.6.10. The I- aqueous layer is drained into a clean beaker and the pH recorded.

3.7. Extraction of the water insoluble precipitate

3.7.1. The precipitate obtained in step 3.5.5 is washed 3 times with DDIW.

3.7.2. 5 ml of 6N HCl are used to dissolve the precipitate and the supernatant is decanted into a clean beaker.

- 3.7.3. Step 3.7.2 is repeated with the remaining precipitate.
- 3.7.4. The supernatant is added to that obtained in step 3.7.2 and the precipitate is discarded.
- 3.7.5. The combined supernatant is mixed with 0.5 ml of 1M NaHSO₃ for 3 minutes before transfer to a 250 ml separatory funnel.
- 3.7.6. 25 ml hexane or carbon tetrachloride and 0.1 – 0.2 ml 6M NaNO₂ are added to the separatory funnel.
- 3.7.7. The mixture is shaken and the layers are allowed to separate.
- 3.7.8. The aqueous layer is drained to waste, leaving the hexane or carbon tetrachloride
- 3.7.9. The aqueous fraction from step 3.6.10 and sufficient 4M NaHSO₃ are added to the separatory funnel to obtain clear separation of the aqueous and hexane or carbon tetrachloride layers.
- 3.7.10. The mixture is shaken and the layers are allowed to separate.
- 3.7.11. The I- aqueous layer is drained into a clean 50 ml beaker and the pH is recorded.

3.8. Purification of I-

- 3.8.1. The aqueous layer from step 3.7.11 is transferred into a clean 250 ml separatory funnel
- 3.8.2. The beaker is rinsed 3 times with 1 – 2 ml hexane or carbon tetrachloride which is added to the separatory funnel.
- 3.8.3. 25 ml hexane or carbon tetrachloride and 0.5 ml 6M NaNO₂ are added to the separatory funnel.
- 3.8.4. The mixture is shaken and the layers are allowed to separate.
- 3.8.5. The aqueous phase is drained and discarded
- 3.8.6. 10 ml of DDIW and sufficient 4M NaHSO₃ are added to the separatory funnel to obtain clear layer separation.
- 3.8.7. The mixture is shaken and the layers are allowed to separate.
- 3.8.8. The I- aqueous layer is drained into a clean 50 ml beaker.

3.9. Second Purification of I-

- 3.9.1. Section 3.8 is repeated with the aqueous layer obtained in step 4.8.8.

3.10. Precipitation of Silver Iodide

- 3.10.1. The aqueous solution is transferred to a 20 ml scintillation vial
- 3.10.2. 100 µl of concentrated HNO₃ are added and gently mixed in
- 3.10.3. The temperature of the mixture is raised to 85 - 90°C
- 3.10.4. 600 µl of 0.1M AgNO₃ are added
- 3.10.5. The precipitate is allowed to settle.
- 3.10.6. The supernatant is poured off and discarded and the precipitate is rinsed 3 times with DDIW
- 3.10.7. The precipitate is taken to dryness at 50°C.
- 3.10.8. The sample is sealed and stored in a dark location.

3.11. Aqueous Samples

The procedure used is a modification of the one outlined by J. Kleinberg and G. Cowan, *The Radiochemistry of Fluorine, Chlorine, Bromine, Iodine*, Los Alamos National Laboratory.

- 3.11.1. Select a 200 ml aliquot of the sample (quantity may be varied depending on the iodine concentration of the sample).
- 3.11.2. Add HNO₃ to acidify water sample to pH ~1.

- 4.11.3. Sufficient NaHSO₃ is added to the water sample to obtain a NaHSO₃ concentration of 0.01M in the sample.
- 3.11.4. 2 mg of I- carrier is added to the sample (for a 200 ml aliquot) and mixed thoroughly on a shaker for 0.5 hours and left to stand for 16 hours.
- 3.11.5. Add 15 ml of hexane and 0.1-0.3 ml of NaNO₂ (6M) into the sample obtained from 3.11.4. and mix on a shaker for 15 min. Then transfer into the 250 ml separatory funnel. Layers are allowed to separate.
- 3.11.6. Collect the hexane into a 50 ml centrifuged tube and return the aqueous phase to the aliquot bottle. Repeat steps 3.11.5 to 3.11.6 with fresh hexane (15, 10, 10 ml), but no NaNO₂ added until hexane became colorless, usually 4 times in all.
- 3.11.7. Return hexane collected in 3.11.6 to the separatory funnel. Add 10 ml DDIW and sufficient (usually 0.1-0.3 ml) 1M NaHSO₃ until both phases became colorless. Discard hexane.
- 3.11.8. To the aqueous solution from 3.11.7 add 0.2 ml HNO₃ (6N) to obtain pH=1. Add 15 ml hexane, 0.1 ml NaNO₂ (6M), shake well, then vent the separatory funnel and allow the layers to separate. Discard aqueous phase.
- 3.11.9. To the hexane obtained in 3.11.8 add 10 ml DDIW, 0.2 ml NaHSO₃ (1M), shake well, vent and then allow the layers to separate. Drain the aqueous layer into a 20 ml scintillation vial.
- 3.11.10. Precipitate as in section 3.10

3.12. Silver Iodide Samples

- 3.12.1. Samples are sorted according to the expected level of ¹²⁹I
- 3.12.2. Low (less than 10⁻¹¹) are handled separately
- 3.12.3. AgI is mixed with 1.5 times the weight of 350 mesh Nb powder
- 3.12.4. The mixture is pressed into cathode to produce machine ready samples

3.13. Cathode Pressing Procedure

- 3.13.1. A clean sample press is used.
- 3.13.2. A disposable stainless steel foil anvil liner is used
- 3.13.3. Cathodes are made of 304 stainless steel and sealed with a C18700 copper press pin
- 3.13.4. AgI/Nb mixture is inserted into the 1.6 mm hole in cathodes with a disposable micropipette tip.
- 3.13.5. Small samples may be backfilled with additional Nb powder as required.
- 3.13.6. Cathode number is recorded

3.14. Reference Material

All samples are analysed with respect to a reference material which can be traced to a NIST standard. Two reference materials have been used at IsoTrace: IsoT2 for measurements between 1993 and 2004 and IsoT6 for measurements during and after 2004.

3.14.1. The IsoT2 reference material was produced by dilution from the NIST 4949B Iodine-129 standard. The isotope ratio for this material, calculated from the dilution factor is $^{129}\text{I} / ^{127}\text{I} = (1.174 \pm 0.022) \times 10^{-11}$.

3.14.2. The IsoT6 reference material is produced by dilution from the NIST 4949C iodine-129 standard. The dilution factor is verified by comparison measurements with the NIST 3230 low level iodine-129 standards. (*Work currently in progress; hence no isotope ratio quoted at present.*)

3.15. Background Samples

Sodium Iodide is pressed directly into cathodes to produce sample for monitoring spectrometer background levels. This material has an isotopic ratio of $^{129}\text{I} / ^{127}\text{I} < 2 \times 10^{-14}$

3.16. Process Blanks

3.16.1. Process blanks for aqueous samples are produced by substituting DDIW for the sample material and processing as for aqueous samples (procedure 3.10).

3.16.2. Process blanks for solid samples are produced by omitting the sample material from the caustic fusion stage and processing with all reagents as for solid samples (procedures beginning in section 3.3).

3.17. Accelerator Mass Spectrometer Analysis

Samples are measure by accelerator mass spectrometer analysis. For details of machine analysis, calculation of results, precision, reporting and operating procedures, refer to Kieser (2007).

4 REFERENCES

Kieser, L., 2007. Protocol for the Analysis of Iodine-129 at the IsoTrace Laboratory version 3.07.

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