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**Determination of  
Iodine to Compliment  
Mass Spectrometric  
Measurements**



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Mass Spectrometric Measurements**

**Frederick A. Hohorst**

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**Lockheed Idaho Technologies Company**

PREPARED FOR THE  
**DEPARTMENT OF ENERGY**  
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**DETERMINATION OF IODINE  
TO COMPLIMENT MASS SPECTROMETRIC MEASUREMENTS**

Frederick A. Hohorst

**Introduction:**

The dose of iodine-129 to facility personnel and the general public as a result of past, present, and future activities at DOE sites is of continuing interest. WINCO received about 160 samples annually in a variety of natural matrices, including snow, milk, thyroid tissue, and sagebrush, in which iodine-129 is determined in order to evaluate this dose.

Currently, total iodine and the isotopic ratio of iodine-127 to iodine-129 are determined by mass spectrometry. These two measurements determine the concentration of iodine-129 in each sample. These measurements require at least 16 h of mass spectrometer operator time for each sample.

A variety of methods are available which concentrate and determine small quantities of iodine.<sup>1,2</sup> Although useful, these approaches would increase both time and cost. The objective of this effort was to determine total iodine by an alternative method in order to decrease the load on mass spectrometry by 25 to 50%. The preparation of each sample for mass spectrometric analysis involves a common step--collection of iodide on an

ion exchange bed. This was the focal point of the effort since the results would be applicable to all samples.

**Background:**

Measurement of iodine-129 concentrations in environmental samples is a necessary activity in order to estimate the dose of this radioisotope to personnel at DOE facilities and to the general public. Iodine-129 is of continuing interest throughout the DOE complex because of its long half-life ( $1.6 \times 10^7$  years) and the ease with which this essential element is absorbed by the human body.

Mass spectrometry is a sensitive tool for determination of the iodine-127 to iodine-129 ratio. To fully utilize this knowledge, the concentration of iodine in the sample, which is primarily iodine-127, must be known in order to interpret the data in relation to the body burden for iodine. Mass spectrometry can determine iodine-127 by isotope dilution techniques (IDMS) but it requires preparation of a second sample to which a known amount of natural iodine has been added. Remeasuring the ratio of iodine-127 to iodine-129 furnishes the information necessary to calculate the original iodine-127 concentration.

The approach proposed would determine iodine-127 in the same sample being used for the mass spectrometric determination of the ratio. This eliminates preparation and manipulation of different aliquots of sample which is a

significant potential source of error. Furthermore, activation analysis of a concentrated iodine sample located on  $0.5 \text{ cm}^3$  of ion exchange resin is less apt to generate significant waste.

#### Experimental:

All reagents used were analytical reagent grade unless otherwise stated. Deionized water was used. The anion exchange resin used in this work was BioRad AG1-X8, 100-200 mesh, in the acetate form. Iodine standards were prepared from sodium iodide in a solution  $0.009 \text{ M}$  in sodium hydroxide and  $0.009 \text{ M}$  in sodium sulfite. They were stored in a desiccator over water to minimize evaporative losses.

A dual head, variable speed, peristaltic pumping system was used as received. Polyvinyl chloride tubing was used in pulling a sample through an in-house fabricated glass "Y" into two  $0.5 \text{ mL}$  beds of anion exchange resin. These beds were held in  $1000 \mu\text{L}$  HDPE pipette tips with quartz wool. A second pipette tip inserted into the first kept the bed stationary. The target flows were about  $0.5 \text{ mL min}^{-1}$  and  $0.1 \text{ mL min}^{-1}$  for the two legs of the "Y". Samples contacted only glass, quartz wool, and HDPE before encountering the anion exchange resin. Pump effluents were directed to separate receptacles to permit measurement of individual flows through each leg of the "Y". The sample split was calculated from the mass of these flows.

After passage of a sample through a bed, that bed was rinsed with several

bed volumes of deionized water to minimize the sodium content of the bed. Excess water was drawn off, the second pipette tip removed, and the bed heat sealed in its pipette tip. A sample number was imprinted into a sealed end using clean steel numbering stamps before the sealed area cooled. These sealed tubes were then submitted for determination of iodine by neutron activation analysis (NAA).

Two "real" pairs of samples were included with each set sent for NAA. These pairs had been prepared by the combustion of Citrus Leaves, NBS SRM 1572, in an oxygen atmosphere followed by trapping in a 0.1 N sodium hydroxide - 0.1 N sodium sulfite solution. For the spiked samples, 10  $\mu\text{g}$  of NaI was placed on the leaves before burning. These solutions were also processed as described above.

### Results:

No iodine was detected in a blank which consisted of a sealed pipette tip containing quartz wool. The results of NAA of other samples are presented in Table 1 and Table 2. Facility A was a commercial activation analysis facility. The turn around time from the date we shipped the samples until the time results were FAXed to us was 11 calendar days. Facility B was a university based reactor; its turn around time was 65 calendar days.

The tables compare the iodine added to the net iodine found for each sample and report the percent difference. In the case of Facility A, the percent



difference was within 30% for the higher concentrations. This accuracy was considered acceptable for the proposed use of these analytical results. For Facility B, the percent differences were somewhat higher.

The most significant result of these NAA determinations is the higher than anticipated concentration of iodine in the anion exchange resin matrix. The current experimental values are 0.50 to 1.2  $\mu\text{g}$  per bed. The experimental value in 1979 as determined by NAA at the INEL's Advanced Test Reactor (ATR) was 0.16  $\mu\text{g}$  per bed for this same bottle of resin.

#### **Conclusions:**

The submission of selected samples for neutron activation analysis is a cost effective method for determination of iodine. Prudence dictates that appropriate blanks and controls be submitted with each set of samples submitted.

The higher than anticipated iodine blank for the anion exchange resin being used invites speculation. The cause may be inhomogeneous bottle contents, adsorption of airborne iodine, absorption of airborne iodine, or other unanticipated and unforeseen circumstances.

This higher blank has raised the detection limits to a higher than anticipated level. The simplest solution appears to be purchasing a new bottle of resin and testing a representative sample of it for iodine by NAA.

TABLE 1  
Irradiation of Samples at Facility A

| <u>Sample</u> | <u>Iodine Added</u><br>( $\mu\text{g}$ ) | <u>Gross Iodine</u><br>( $\mu\text{g}$ ) | <u>Net Iodine</u><br>( $\mu\text{g}$ ) | <u>Diff</u><br>(%) |
|---------------|--|--|--|--------------------|
| 1             | None <sup>a</sup>                        | 0.520 $\pm$ 0.094                        |  |                    |
| 2             | None <sup>b</sup>                        | 0.506 $\pm$ 0.049                        |  |                    |
| 3             | 0.0932                                   | 0.665 $\pm$ 0.086                        | 0.159 $\pm$ 0.099                      | + 71               |
| 4             | 0.361                                    | 0.840 $\pm$ 0.092                        | 0.334 $\pm$ 0.104                      | - 7                |
| 5             | None <sup>c</sup>                        | 1.20 $\pm$ 0.12                          | 0.694 $\pm$ 0.130                      | - 29               |
| 6             | Yes <sup>d</sup>                         | 2.85 $\pm$ 0.17                          | 2.344 $\pm$ 0.177                      | - 24               |

<sup>a</sup> Anion exchange resin in acetate form, unused. The high uncertainty was attributed to the presence of chlorine.

<sup>b</sup> Anion exchange resin, washed with dilute sodium hydroxide solution followed by deionized water,  $\approx$ 100 mL each.

<sup>c</sup> Original solution contained a calculated 3.9  $\mu\text{g}$  of iodine; 25.2% of solution (0.98  $\mu\text{g}$  I) passed through this bed.

<sup>d</sup> Original solution contained a calculated 4.1  $\mu\text{g}$  of iodine plus a 10  $\mu\text{g}$  spike of NaI; 22.3% of solution (3.1  $\mu\text{g}$  I) passed through this bed.

TABLE 2  
Irradiation of Samples at Facility B

| <u>Sample<sup>a</sup></u> | <u>Iodine Added</u><br><u>(<math>\mu\text{g}</math>)</u> | <u>Gross Iodine</u><br><u>(<math>\mu\text{g}</math>)</u> | <u>Net Iodine</u><br><u>(<math>\mu\text{g}</math>)</u> | <u>Diff</u><br><u>(%)</u> |
|---------------------------|--|--|--|---------------------------|
| 1                         | 2.65   | 3.80   | 1.15   |                           |
| 2 <sup>b</sup>            | None   | 1.213 $\pm$ 0.098<br>1.137 $\pm$ 0.091                   | 0.06 $\pm$ 0.11<br>-0.01 $\pm$ 0.11                    |                           |
| 3 <sup>b</sup>            | None   | 1.102 $\pm$ 0.103  | -0.05 $\pm$ 0.12                                       |                           |
| 4                         | 0.0971   | 1.115 $\pm$ 0.086  | -0.04 $\pm$ 0.10                                       |                           |
| 5                         | 0.149  | 1.229 $\pm$ 0.098  | 0.08 $\pm$ 0.11  |                           |
| 6                         | 0.299  | 1.520 $\pm$ 0.114  | 0.37 $\pm$ 0.13  | + 24                      |
| 7                         | 0.435  | 1.583 $\pm$ 0.127  | 0.43 $\pm$ 0.14  | - 1                       |
| 8                         | 0.581  | 2.153 $\pm$ 0.165  | 1.00 $\pm$ 0.17  | + 96                      |
| 9                         | No <sup>c</sup>  | 2.305 $\pm$ 0.139  | 1.15 $\pm$ 0.15  | + 31                      |
| 10                        | Yes <sup>d</sup>   | 7.511 $\pm$ 0.431  | 6.36 $\pm$ 0.44  | + 77                      |

<sup>a</sup> Submitted in random order; reordered and renumbered here for clarity.

<sup>b</sup> Mean blank was 1.151  $\pm$  0.0561  $\mu\text{g}$  iodine.

<sup>c</sup> Original solution contained a calculated 3.8  $\mu\text{g}$  of iodine; 23.1% of solution (0.88  $\mu\text{g}$  I) passed through this bed.

<sup>d</sup> Original solution contained a calculated 4.0  $\mu\text{g}$  of iodine plus a 10  $\mu\text{g}$  spike of NaI; 25.9% of solution (3.6  $\mu\text{g}$  I) passed through this bed.

The corollary to this hypothesis is to determine whether the iodine present on the resin is extractable under the experimental conditions being used. If it is extractable, corrections may have to be applied in order to accurately determine results by IDMS.

**References:**

1. R. R. Rao and A. Chatt, *Determination of Nanogram Amounts of Iodine in Foods by Radiochemical Neutron Activation Analysis*, *Analyst*, 1993, 118, 1247.
2. S. Palagyi and T. Braun, *Transport Extraction for Trace Element Separation and Preconcentration, II. Preconcentration of iodine from Aqueous Solution*, *Fresenius J. Anal. Chem.*, 1993, 346, 905.