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Abstract

An inductively coupled plasma - mass spectrometry (ICP-MS) method was developed to determine the ^{129}I content in aqueous environmental samples. Due to interference from xenon, direct measurement of ^{129}I could not be made on the ICP-MS. An ion-exchange technique is used to concentrate the Iodine from one liter samples to 30 mL. The 30 mL eluant from the anion-exchange column is then introduced to the ICP-MS. The detection limit of the procedure is $\leq$0.5 pCi/L.

Several samples from the Savannah River near the Savannah River Site (SRS) have been analyzed for ^{129}I by this procedure. Concentrations of ^{129}I in the Savannah River ranged from 0.05 $\pm$0.12 to 0.21$\pm$0.49 pCi/L (95% CL). Below a seepage basin, in Four Mile Creek on the Savannah River Site, ^{129}I concentrations were as high as 2.31$\pm$1.22 pCi/l. Before exiting the SRS the ^{129}I concentration had decreased to 0.30$\pm$0.16 pCi/L by dilution in Four Mile Creek.

Introduction

Nuclear fission processes produce ^{129}I. It may be released to the environment by nuclear reactors and separation processes. Analysis of environmental samples is required to ensure that the ^{129}I concentration in the environment around nuclear facilities does not exceed dose limits as set forth in DOE Orders 5400.1 and 5400.5. Aqueous samples of ^{129}I had been measured previously at the SRS by neutron activation techniques (Anderson, 1980). There are currently no operating reactors at the SRS to perform the neutron activation analysis, thus a new method for detection of ^{129}I had to be developed.

Mass spectrometric techniques are more sensitive than counting techniques for radionuclides with half-lives of over 1000 years. The half-life of ^{129}I is 1.6 x 10^7 years. The mass spectrometric technique chosen for measuring ^{129}I was inductively coupled plasma - mass spectrometry (ICP-MS). At the Savannah River Technology Center (SRTC), at the SRS, we are using a Turner TS Sola ICP-MS to measure ^{129}I in aqueous samples. The detection limit of the instrument is 3 ppt (0.53 pCi/l) of ^{129}I, providing we have Xenon-free Argon. To date we have been unable to obtain sufficiently Xenon-free

Argon, thus our detection limit is approximately 17 pCi/L ^{129}I. To ensure that the dose limit in DOE Order 5400.1 is not exceeded and to calculate the environmental impact of the SRS, a detection limit of ≤1.0 pCi/L of ^{129}I was desired. To reach the desired detection limit of ≤1.0 pCi/L we have developed a concentration technique which provides a 33-fold concentration factor, giving us a procedural detection limit of ≤0.5 pCi/l.

Concentration Procedure

The concentration procedure is similar to that used for the previous SRTC neutron activation technique. The natural Iodine in the sample is used as a yield monitor. One milliliter of 5% NaOCl per liter of sample is added to ensure all of the iodine exists in the oxidized state. The Iodine is then reduced by adding 5.0 mL of 1M NH_2OH-HCl and 2.0 mL of freshly made $NaHSO_3$ per liter. The pH of the sample is adjusted to 6.4 - 6.6 with NaOH and the Iodine concentrated on 2.0 mL of Bio-Rad AG 1X8, Cl^- form anion-exchange resin. 30 mL of 4M HNO_3 was used to elute the Iodine from the resin (Dolan, et al. (1991). The 4M HNO_3 eluant is introduced directly into the ICP-MS for the analysis.

Inductively Coupled Plasma - Mass Spectrometer Analysis

Figure 1 shows the spectrum of a 10 ppb ^{127}I (natural Iodine) solution. The peaks at mass 129, 131, and 132 are xenon, at 26.4%, 21.2%, and 26.9% respectively. Figure 2 shows a standard with a 129/127 Iodine radio of 0.1, the ^{127}I at 10 ppb. When making ^{129}I measurements, the ^{131}Xe peak is monitored to correct for ^{129}Xe at n/z=129. In natural samples ^{132}Ba may bias a ^{132}Xe based correction at n/z=129 , thus the smaller ^{131}Xe peak was chosen for making the ^{129}Xe correction.

The TS Sola ICP-MS has two detectors: a Faraday detector is used for counting signals >1 x 10^6 counts per second, and a multiplier for counting smaller signals. After concentration of an aqueous sample the count rate is too high for the ^{127}I to be counted on the multiplier detector; however, the ^{129}I must be counted on the multiplier to achieve the desired sensitivity. To obtain the 129/127 ratio, indium is used as an internal standard. Indium has two isotopes, 113 at 4.3% and 115 at 95.7%. By correctly choosing the indium concentration, the ^{115}In and ^{127}I can be counted on the Faraday detector, while the ^{113}In, ^{129}I, and ^{131}Xe are counted on the multiplier detector. By setting the Faraday and multiplier detector sensitivities to 1.0 for both elements, and setting the isotope equations so that the ^{127}I isotopic abundance is 100% on the Faraday detector and the ^{129}I isotopic abundance is 100% on the multiplier, the 129/127 Iodine ratio can be determined directly from the ICP-MS results. The 129/127 ratio can then be multiplied by the Iodine concentration in the original sample to obtain the ^{129}I concentration of the original sample.

Sample Results

Blanks were prepared by adding a known amount of Iodine to deionized water. The 129/127 Iodine ratios and calculated ^{129}I concentrations are shown in Table 1. These values are consistent with our predicted detection limit of ≤0.5 pCi/L. Samples are

collected quarterly from the Savannah River above and below the SRS. The results from the first two quarters show ^{129}I concentrations below our detection limit (see Table 2.).

Near the F- and H- separations areas on the SRS are seepage basins known to have elevated concentrations of ^{129}I (Anderson, 1980). The headwater of Four Mile Creek is above the seepage basins; the creek is just under 15 miles long. At approximately river mile 3 the creek passes the seepage basins. As seen in Figure 3, the ^{129}I concentration in Four Mile Creek increases dramatically upon passing the seepage basins. By the time the creek exits the SRS and enters the Savannah River, the ^{129}I concentrations are at the procedure detection limit, similar to the Savannah River values above the SRS.

Conclusions

At the SRTC we have developed a method to analyze aqueous samples for ^{129}I by ICP-MS. We are currently measuring the ^{129}I concentrations in streams on the SRS and in the adjacent Savannah River. We have just added an ultrasonic nebulizer to our ICP-MS which appears to have decreased the Xenon interference. By using the ultrasonic nebulizer and by increasing the sample size we hope to decrease our detection limit to <0.1 pCi/L.

Acknowledgments

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Dolan, S.P., Sinex, S.A., Capar, S.G., Montaser, A., and Clifford, R.H., "On-Line Preconcentration and Volatilization of Iodine for Inductively Coupled Plasma - Atomic Emission Spectrometry", *Analytical Chemistry, 63*, 1991, pp. 2539-2542.

Table 1. Iodine-129 Blank Results

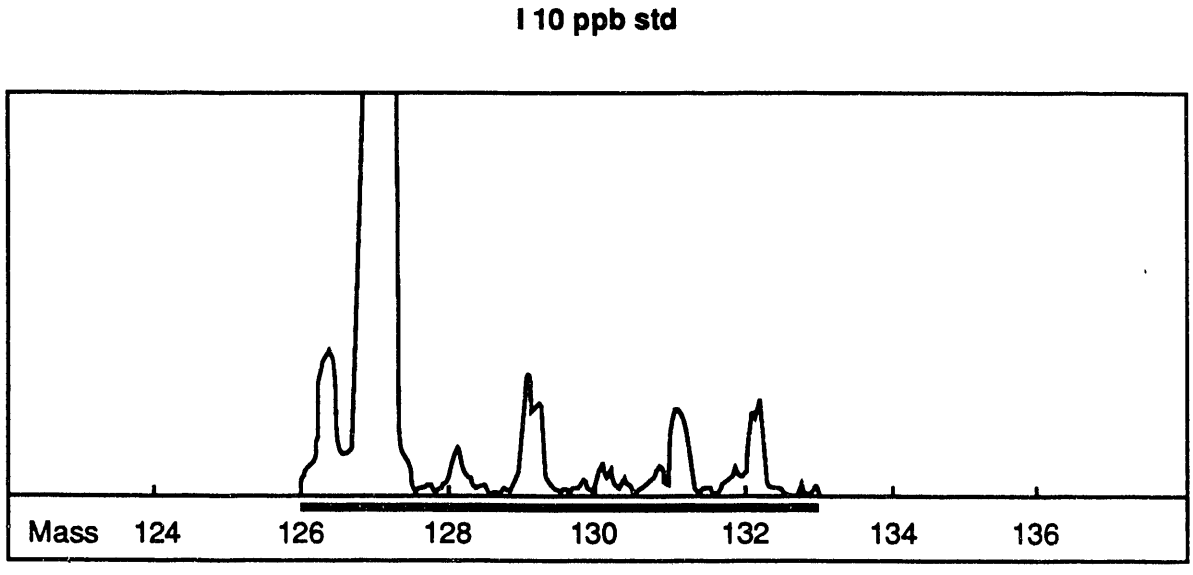
Sample Number	129/127 Iodine Ratio		^{129}I pCi/L
1	1.23×10^{-6}		0.328
2	1.00×10^{-6}		0.314
3.	1.49×10^{-6}		0.144
4	0.94×10^{-6}		0.173
		mean	0.24 ± 0.10 (1σ)

Table 2. Iodine-129 Concentration in the Savannah River

Location	1st Quarter (pCi/L)*	2nd Quarter (pCi/L)*
Shell Bluff	0.05 ± 0.12	0.16 ± 0.47
Above Vogtle	0.16 ± 0.58	0.11 ± 0.42
Below Vogtle	0.21 ± 0.49	0.12 ± 0.28
Highway 301 Bridge	0.12 ± 0.24	0.14 ± 0.39

* 95% CL

Figure 1. **10 ppb Iodine-127 (Natural Iodine)**



Scale	: 1.0E + 3 cps	Dwelltime per Channel	: 32 ms
Plot Type	: Linear	Channells per AMU	: 16
Detector	: Mutiplier	Number of Passes	: 8

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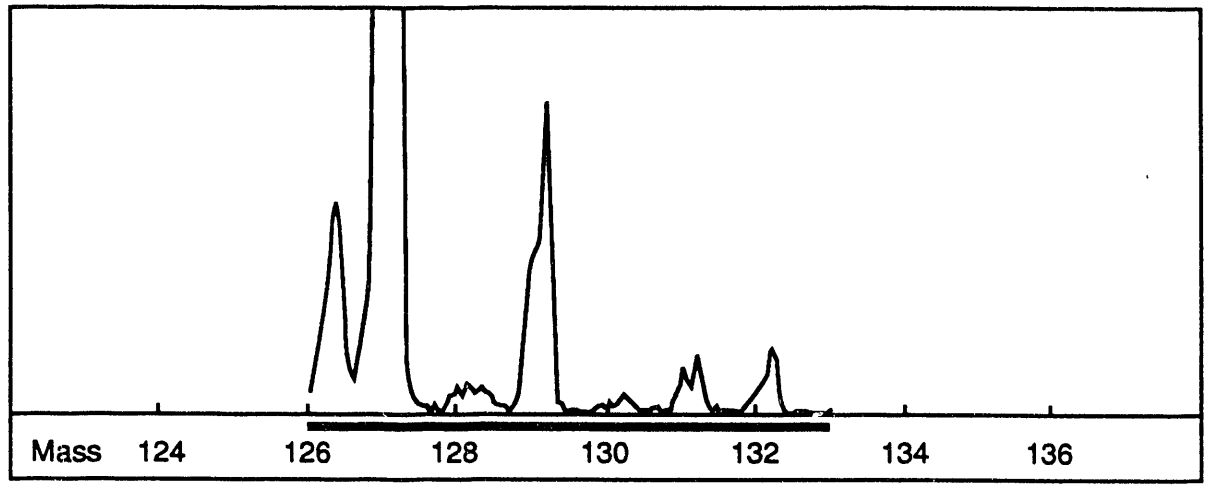
Figure 2. **10 ppb Iodine-127 Standard - 129/127 Ratio = 0.1**



Scale	: 1.0E + 3 cps	Dwelltime per Channel	: 32 ms
Plot Type	: Linear	Channells per AMU	: 16
Detector	: Mutiplier	Number of Passes	: 16

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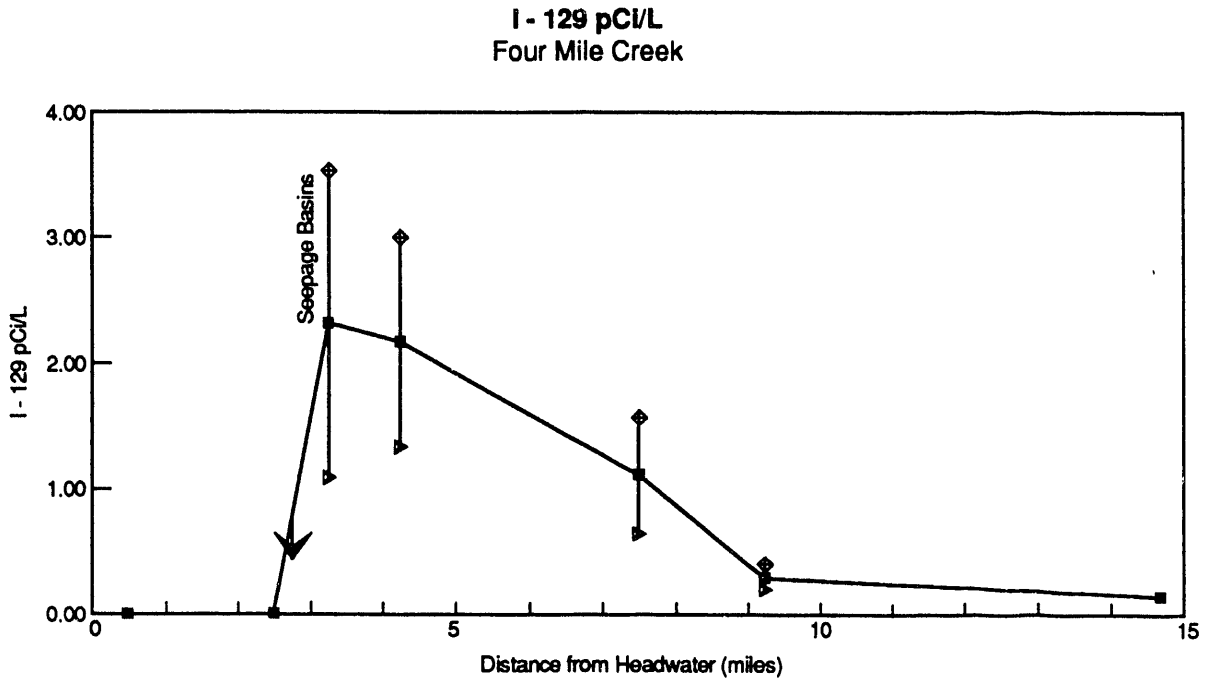
Figure 3. Iodine-129 Concentration in Four Mile Creek



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