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Determination of iodide in ground water and soil by ion chromatography

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Abstract

Comprehensive elemental analysis of samples from the Bear Creek Valley near the Oak Ridge Y-12 Plant, and its floodplain have been performed in order to allow an unclassified assessment of possible elemental contamination within this area. A rapid ion Chromatographic method, with isocratic separation and micromembrane suppression is discussed within this paper for the analysis of iodide in soils, and floodplain ground waters. This developmental method will be used for future routine iodide analysis. Published by Elsevier Science B.V.

Keywords: Soil; Water analysis; Environmental analysis; Iodide

1. Introduction

The Upper East Fork Poplar Creek (UEFPC) and portions of the Y-12 Plant area have been exposed to actual and potential releases from the Y-12 Plant operations since the mid-1950s. The Y-12 Plant has been actively engaged in the development and manufacture of classified materials throughout its history. Comprehensive analyses of selected soils and waters from the UEFPC and selected Plant areas will allow an assessment of classified chemicals employed at the Y-12 Plant without specification of them. Iodide analyses, in conjunction with a wealth of other UEFPC analytical investigations, will document that classified chemicals were encompassed by the UEFPC remedial investigation. The intent of this screening exercise was not to provide data for risk assessment [1]. Specific procedures for sampling, chain of custody, laboratory analysis, laboratory quality control (QC) and reporting of data were followed during this assessment.

Within Lockheed Martin's Analytical Services Organization (ASO) Y-12 Plant Laboratory, iodide analysis has traditionally been done by wet chemistry methods. The leuco crystal violet method is applicable to iodide concentrations of 50 to 6000 $\mu g\,l^{-1}$ and the catalytic reduction method (e.g. the reduction of ceric ions by arsenious acid) is applicable to iodide concentrations of 80 $\mu g\,l^{-1}$ or less. Both methods require the preparation of several reagents that may be either expensive, require specialized preparation and containment apparatus, or create undesirable wastes. Both methods have interferences including high concentrations of chloride and the inhibitory effects of some metals [2].

Ion chromatographic analysis of iodide has been traditionally performed using a variety of columns such as the Dionex 125×3 anion separator precolumn [3], or the AS-1, 2, 3 and 4 columns [4], for example. Iodide is a part of the group of hydrophobic inorganic anions. Because of their large radii, it has been demonstrated that these ions have a strong affinity for the stationary phase of these columns and the use of highly concentrated carbon-

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ate eluents limited the use of the membrane suppressors. The introduction of the AS-5 column (with less hydrophobic functional groups on the latex particles) allowed standard carbonate–hydrogencarbonate eluents to be used and more effectively suppressed [5]. Later methods recommended the AS-7 column [6].

This paper describes the use of Dionex' new AS-11, 4-mm column to analyze iodide in ground waters and soils. Although the AS-11 column was specifically designed to resolve organic acids and inorganic anions in a gradient run within hydroxide eluent systems, the AS-11 column can also be used to provide rapid elution of iodide without interference from other anions. While carbonate-hydrogencarbonate eluents can be used for an isocratic determination of iodide, a hydroxide–methanol eluent was used for these analyses. Methanol (at a concentration of 20%) was added as a modifier to improve the ion-exchange process by minimizing the hydrophobic reactions and to eliminate peak tailing. This also increases the sensitivity of the analysis [7]. The AS-11 column is compatible with organic solvents due to its high degree of substrate cross-linking (55%, macroporous divinylbenzene polymer). Optimum column performance is obtained when the eluent and sample have a pH of between 0–14 [7]. The Dionex AMMS-II suppressor was used for all analyses and the eluent used did not exceed the suppressor's capacity. In order to minimize out gassing during the eluent makeup, the hydroxide–methanol eluent was premixed in working concentrations. The back pressure generated by column flow through will vary according to the flow-rate selected. Eluent flow-rates from 0.5 to 1.0 ml min^{-1} were used during this project which generated back pressures between 600 and 1150 p.s.i (1 p.s.i.= 6894.76 Pa). The practical pressure limit column is approximately 4000 p.s.i. [7]. Typical operating back pressures during this project were equal to or less than 1100 p.s.i.

2. Experimental

2.1. Apparatus

All chromatography was performed using a Model 2320i series Dionex ion chromatograph, with a 50 μl sample loop. The system components consisted of one anion HPIC AG-11 guard column (50×4 mm), an anion HPIC AS-11 separator column (25 mm), an anon micromembrane suppressor (AMMS-II), a CDM-3 conductivity detector, and an advanced gradient pump (AGP-1). The regenerant was delivered to the AMMS-II by plumbing the 'B' valve in conjunction with a helium-pressurized 4-l container. The eluents were delivered to the columns by a Dionex eluent degas module (EDM-2).

2.2. Materials

Deionized ultra-pure distilled water with a minimum conductivity of 15 MΩ cm (produced by a Millipore Milli-Q reagent water system) was used to make the eluent, regenerant and standards. Reagent-grade (Fisher Scientific) sulfuric acid (for regenerant) and sodium hydroxide (Fisher Scientific), and HPLC/Spectra grade (J.T. Baker) methanol (for eluent) were used. The standard solutions were made using reagent-grade (Mallinckrodt) potassium iodide.

2.3. Eluent and regenerant preparation

The eluent (0.027 *M* NaOH in 2% aqueous methanol) was made by dissolving 2.16 g 50% NaOH and 200 ml methanol per liter of solution in ultra-pure water. The regenerant (0.0025 *M* sulfuric acid) was made from reagent-grade sulfuric acid.

2.4. Standard preparation

The standards were prepared by diluting a 1000 mg l^{-1} stock iodide solution (1.3081 g KI to 1 l = 1000 mg l^{-1} iodide) to make appropriate working standards.

2.5. Flow-rates

The regenerate flow-rate used was 2.0 ml min^{-1}. The eluent flow used rate was 0.5–1.0 ml min^{-1}.

3. Sample history

Thirteen groundwater monitoring wells, two sur-

face water, two sediment, and six soil samples from various UEFPC and Y-12 Plant locations suspected of exhibiting high levels of defined contaminants of concern were selected and collected, or retrieved from archives, as appropriate. These samples were submitted to the Lockheed Martin Energy System's Y-12 Plant Analytical Services Organization for analysis. These samples represent primary contaminant areas in the UEFPC and Y-12 Plant area and would be typical of potential worst-case chemical contamination [1].

3.1. Waters

Water samples constituted both groundwater and surface water media in UEFPC and the Y-12 Plant area. Samples analyzed represented locations close to potential sources or within the potential depositional and/or accumulation areas [1].

3.2. Soils

Soil sampling for this study was conducted using media-specific standard operating procedures as applicable. Sampling was conducted employing simple spade and scoop methods. Samples were collected from the ground surface to approximately 6 inches (in.) below ground surface (1 in.= 2.54 cm). Samples were collected from various locations within the UEFPC and Y-12 Plant area [1].

3.3. Field quality control

Field quality control implemented during this study included, where appropriate: field duplicate for soil sampling; field duplicate for water sampling; and equipment washings from sampling equipment. Field blank waters were taken as required [1].

4. Results and discussion

4.1. Sample preparation

The initial step is the preparation of the samples. The liquid samples were filtered and diluted 100:1 with deionized water. The soil samples were prepared by adding 20 ml of carbonate-hydrogencarbonate solution (1.7 *M* $NaHCO_3$–1.8 *M* Na_2CO_3) to 0.25 g of soil. After agitation for 1 h and filtration through a 0.45 μm filter unit (Millipore, Millex-HV), 1 ml of the filtrate was diluted to 10 ml. The range of standards used was 0.5 mg l^{-1} to 10 mg l^{-1}.

4.2. Analysis of samples and quality control

After the samples were prepared and diluted, they were analyzed by ion chromatography under the conditions listed in Fig. 1. Additionally, the work plan for the characterization of UEFPC required the implementation of QC procedures during analysis and reporting to assure that the data obtained would be consistent with their laboratory use. Laboratory QC checks were performed throughout the work effort to generate data confidence [1]. Analytical QC measures were used to determine that the analytical process was in control. QA program and QC checks included: method blanks, laboratory control samples, laboratory duplicates, calibration verification sam-

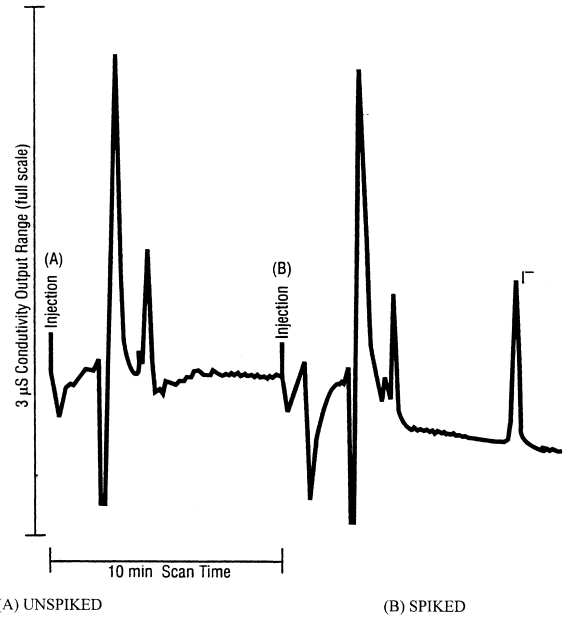

Fig. 1. Iodide groundwater analysis, (A) unspiked and (B) analyte spiked (1 mg l^{-1} iodide). Conditions: Millex-HV 0.45 μm filtered, 100:1 diluted; columns, AG-11 and AS-11; eluent: 0.027 *M* NaOH in 20% aqueous methanol; flow-rate, 0.50 ml min^{-1}; AMMS-II suppressor regenerant: 0.0025 *M* H_2SO_4, 2.0 ml min^{-1} flow-rate. 3 μS conductivity output range (full scale). Five min $in.^{-1}$ chart speed.

ples, laboratory duplicates, calibration verification samples, instrument blanks, and standard additions utilization. The standard solutions for the calibrations were prepared in the concentration range 0.5–10 mg l^{-1} and the calibration curves were found to be linear in this range. The precision of 6 replicates of water sample spikes of 1 mg l^{-1} was 3.3% R.S.D.. The precision of 4 replicates of soil sample spikes of 1 mg l^{-1} was 2.1% R.S.D..

Once the instrument was equilibrated and conditions optimized, the analyses and interpretation of the data was straight forward. (See Fig. 1 and Fig. 2) Early eluting peaks (i.e. chloride, nitrate, and sulfate) did not interfere with the iodide peak and quantification presented no problem. The iodide peak eluted in 7 to 8 min depending on the selected flow-rate (0.5 to 1.0 ml min^{-1}). The background conductivity was about 4 μS. Fifty samples (including field blanks, duplicates, and duplicate spikes) were analyzed for iodide for this study. The method detection limit based upon a signal-to-noise ratio of 3 is 0.3 mg l^{-1}.

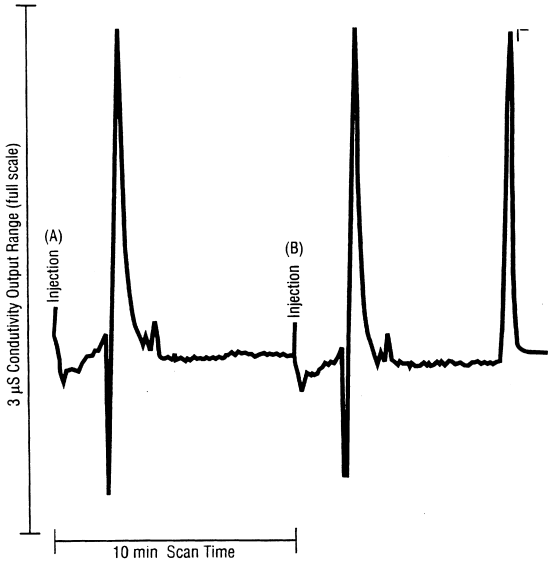

Fig. 2. Iodide soil analysis, (A) unspiked, and (B) analyte spiked (2 mg l^{-1} iodide). Conditions: 0.25 g. Sample leached in 20 ml hot water, Millex-HV 0.45 μm filtered, 10:1 diluted; columns: AG-11 and AS-11; eluent 0.027 *M* NaOH in 20% aqueous methanol; flow-rate 0.50 ml min^{-1}; AMMS-II suppressor, regenerant: 0.025 *M* H_2SO_4, 2.0 ml min^{-1} flow-rate 3 μS conductivity output range (full scale). Five min $in.^{-1}$ chart speed.

This is consistent with detection limits using conductivity detectors [8], although it has been reported that detection limits in the μg l^{-1} range can be obtained using amperometric detection [8], and isotope dilution mass spectrometry [9]. Other than matrix spikes, no amounts of iodide were determined in the samples, at or above the methods detection limit. Analysis time (not including preparation) was 8 min per injection. If thiocyanate and, or, thiosulfate were present in these samples, their corresponding peaks would elute after the iodide peak and not be a direct 'interferant'. The use of the organic modifier, methanol, has been shown to facilitate the separation of iodide, thiocyanate, and thiosulfate [7]. No chromatographic interferences were encountered during these analyses, nor was any degradation of chromatography performance observed.

5. Conclusions

Ion chromatography (IC) is a powerful separation technique which offers advantages for iodide analysis of aqueous and leached soil/sediment matrices with no observed interferences. This method provides a rapid and highly efficient separation of the iodide ion from the other ions present in the ground waters and leachates and the subsequent suppressed IC analysis is straight forward with excellent recoveries Table 1. The column used for these analyses (IonPac AS-11) is 100% HPLC solvent compatible [7], therefore organic solvent modifiers can be used to optimize ion-exchange selectivity. Highly retained surface anions like iodide have improved peak efficiency and the retention time is decreased significantly by the addition of methanol to the hydroxide eluent. This minimizes the hydrophobic interactions between the large hydrophobic anion, iodide, and the AS-11 column resin [4]. The AS-11 column is a significant advance in ion-exchange technology, far removed from the ion chromatography methods of identifying iodide in 1984 [10].

Although Dionex recommends a regenerant flow-rate of 10–15 ml min^{-1}, sufficient suppression of the eluent (at 0.5 ml min^{-1} flow-rate) was achieved at a significantly reduced regenerant flow (2 ml min^{-1}). A sufficiently stable baseline was achieved with the added benefit of less acidic waste being generated.

Table 1
Linearity of iodide matrix spikes

Standard linearity in water (water sample GW-169; Upper East Fork Poplar Creek Operable Unit-A)		Standard linearity in soil (soil sample 200A-SED; Upper East Fork Creek Operable Unit-A)	
Iodide added ($mg\ l^{-1}$)	Iodide recovered ($mg\ l^{-1}$)	Iodide added ($mg\ l^{-1}$)	Iodide recovered ($mg\ l^{-1}$)
0.5	0.47	0.5	0.48
0.5	0.48	1.0	0.95
1.0	0.98	1.0	0.95
1.0	1.0	2.5	2.5
5.0	5.2		
10.0	9.6		

This method can be adapted easily for the additional analysis of the halogens: fluoride, chloride, and bromide as detailed in a previously published paper by the authors [11].

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