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Detection of iodide in geologic materials by high-performance liquid chromatography

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Abstract

A method for the detection of iodide in geologic materials including surface and ground waters, brines, and extracts from sediment, plants, soil and crude oil is presented. The detection limit of the HPLC system under ideal conditions is 0.45 ng. Applications of the method are related to the use of the ^{129}I isotope system in environmental science and geology. Ion chromatography is used to monitor extraction of I and to determine total I concentrations from samples prepared for measurement of $^{129}\text{I}/\text{I}$ ratios by accelerator mass spectrometry. Methods of extraction and sample preparation are described.

1. Introduction

Geologic sample materials such as ground water, saline formation water, meteoric and surface water, and aqueous derivatives of soil, sediment, crude oil and vegetation may have iodine concentrations ranging from a few ppb to thousands of ppm (mass/mass). Methods of sample preparation for these materials, and measurement of iodide by HPLC are described here. Solid samples require off-line, pre-column derivatization, as iodine is bound in organic compounds. Our motivation for developing these methods is in the geochemical interpretation of iodine concentrations in natural waters and sediments, and for the preparation of samples for ^{129}I iodine/iodine ratio determination. The ^{129}I isotope system has recently come into use in hydrogeologic studies, in marine chemistry and

in investigations of releases from nuclear facilities.

A variety of methods have been used for the detection of iodine in geologic samples. Notable examples are Ce–As reduction catalysis [1], colorimetry [2,3], X-ray fluorescence spectrometry [4], and neutron activation [5–7]. Analysis by HPLC has several advantages over these methods, principal among them the greater dynamic range and lower detection limit for the ion chromatography (IC) system described below. These features are essential for the measurement of a wide range in I concentrations in the variety of sample materials analyzed. The small sample volume required to make a concentration measurement is also advantageous, especially if the sample will be used for ratio determination. ^{129}I iodine/iodine ratios are measured by accelerator mass spectrometry, which requires a sample size of approximately 1 mg I. Low I concentrations in some materials make extraction of 1 mg a significant challenge. Depending on the sample matrix, interferences present and

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concentration level, HPLC has greater accuracy and better reproducibility than neutron activation or colorimetric methods. Interfering elements or compounds in geologic materials often make detection of I by GC or neutron activation impractical [6,7]. Unlike X-ray spectrometry, inductively coupled plasma, GSC, or neutron activation analyses, HPLC requires iodide in dilute aqueous solutions for sample injection. Extraction and conversion of iodine from solid samples into this form are accomplished in various ways, as described below. Lastly, the speed, ease, and relatively low cost with which iodide measurements can be carried out using this HPLC set-up make possible large-scale investigations involving numerous samples.

General anion-exchange columns and conductivity detectors are capable of separating and detecting iodide at levels of a few ppm in matrices with similar levels of other anions. However, natural materials typically contain much lower levels of iodine, and levels of other constituents that are several orders of magnitude higher. An HPLC system that relies on pre-column derivatization of halides to organohalogen compounds and UV detection [8] and a flow-through electrode system [9], used for detection of trace iodide in natural waters and biological samples have previously been reported. In addition, an HPLC detection method for iodinated halogens which incorporates post-column, on-line UV irradiation prior to oxidative electrochemical detection, was developed for determination of trace levels of organoiodides in pharmaceuticals [10]. Compared to the method used here, those systems require more extensive sample treatment and are less versatile in the types of starting materials that can be analyzed. The detection limits and accuracy levels are similar to those reported here. Despite its advantages, this HPLC method is limited by its ability to detect only iodide. Therefore, if precise determination of concentrations for each of the various iodine species in the original sample matrix is critical, one of the methods referred to above may be more appropriate than the HPLC method described here.

The IC system configuration described here

has excellent selectivity for iodide in a variety of matrices and a working range of a few ppb to approximately 100 ppm, which are required for analysis of geologic materials. Naturally occurring interferences are quite rare, and are restricted to organic derivatives. Under ideal conditions, this system has a detection limit (method limit of detection = $3s$, s = standard deviation at zero level) of 0.45 ng (equating to 1.8 ppb) with a reproducibility of 3 ppb standards of 7%. Reproducibility of standards, prepared from reagent grade KI diluted with distilled deionized water (18 M Ω), in the range 50 ppb–3 ppm is 3%.

2. Experimental

The IC system set-up described here was modified from the version suggested by the manufacturer, Dionex (Sunnyvale, CA, USA) for a series 2000i Dionex BioLC. Development of the system parameters is described in [11]. The separation column used is the Dionex AG7—this is the “guard” column which is normally used to protect the longer analytical column (AS7). The AG7 column (5 cm \times 4 mm I.D.) consists of 10- μ m packing material and 350-nm microbeads with 5% latex cross-linking. Separation is by adsorption rather than by ion exchange with the hydrophobic functional groups on this column. The guard column is used alone for two reasons: the typical lifetime of a column used for derivatives of geologic materials is about 6 months (using 0.45- μ m and organic filters for samples when necessary, and with an average daily use of approximately 5 h), so the lower expense of the guard column is attractive, and the time for a single analysis is shortened from 16 to 8 min, without degradation of peak separation. Detection is by amperometry (at a fixed potential: +0.8 V) with a Pt working electrode and a Ag/AgCl reference electrode. Results are improved by soaking the working electrode in a saturated KI solution after approximately 40 h use. The mobile phase used is 45 mM HNO₃, made with Ultrex ultrapure reagents. Using the shorter column, with a flow-

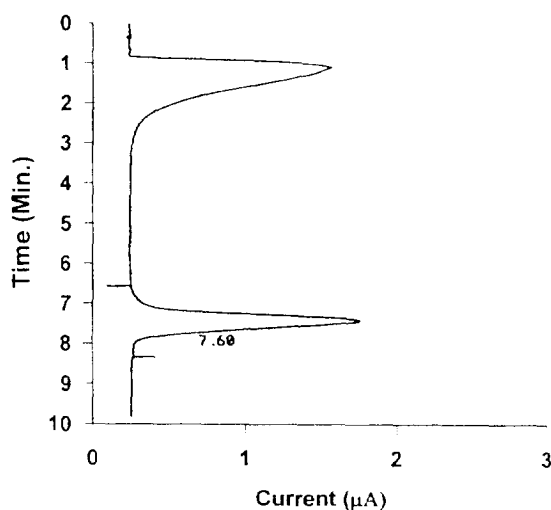


Fig. 1. Chromatogram from a sediment sample extract. Iodide concentration is 1.86 ppm; peak is labelled with a retention time of 7.60 min. The leading peak is 2 mM (sodium) hydrogensulfite—the collection solution and reducing agent. Injection volume is 250 μ l; detection is by amperometry.

rate of 1.0 ml/min, the retention time for iodide is approximately 7 min. A SP 4400 Spectra-Physics integrator plots peak areas which are used for quantification. Good separation is achieved between iodide and other common anions, and between iodide and sodium hydrogensulfite, the reducing agent commonly used to convert any iodate present to iodide (Fig. 1). Sodium hydrogensulfite concentrations of up to 10 mM do not interfere with the iodide peak. For solutions with low I concentrations, a 250 μ l

sample is injected, however smaller sample loops can be used at concentrations above approximately 1 ppm. Organic pre-filters must be employed when organic compounds potentially exist in the sample matrix.

3. Off-line pre-column sample preparation

Table 1 shows the various types of materials from which iodine has been extracted, the preparation required for analysis by HPLC, and typical concentrations with associated accuracy. In general, our results for iodine concentrations in the original materials agree with concentrations determined by the other methods listed above. Direct comparisons were made with the colorimetric method for some saline water samples, and with the neutron activation method for two sediment samples. For the water samples, the absolute difference between the concentration values for the two methods was less than or equal to 5%, while results for the sediments agreed to within 12%.

For dilute waters from oxidizing environments including rainwater, snow, ice and some ground waters, iodine may exist primarily as iodate. Addition of a reducing agent, such as sodium hydrogensulfite is necessary to convert iodate to iodide. Experiments carried out on laboratory standards made from reagent grade KIO_3 and KI

Table 1
Summary of results for HPLC analysis of iodide in various sample matrices

Material	Preparation	Typical concentration range	Representative R.S.D. for HPLC method (%)
Meteoric waters	Conversion to I ⁻ concentration	<0.5 ppb–10 ppb	10
Hydrothermal and ground waters	Conversion to I ⁻	10 ppb–0.5 ppm	3
Saline water	Dilution	0.5 ppm–300 ppm	7
Sediment/soil extracts	Chemical breakdown and distillation	0.1 ppm–10 ppm	5
Plant/animal extracts	Single combustion or alkali leach and fusion	20 ppb–3 ppm	5
Crude oil extracts	Continuous combustion	0 ppb–50 ppb	10

salts indicate that 99.7% (R.S.D. of 0.4%) of IO_3^- is converted to I^- in the presence of excess sodium hydrogensulfite. While natural waters contain other species that will compete for reduction with iodate, the high sodium hydrogensulfite concentrations allowed by the system configuration (up to 10 mM; pH 5–6) are sufficient for most water compositions. For filtered natural water samples (in which only iodide and iodate are present and thermodynamically stable) iodate concentrations can be determined by the difference (iodide + iodate) – iodide. Pre-concentration by vacuum distillation of extremely dilute samples such as continental rainwater may be required.

Oil field brines and other saline formation waters, which typically contain 100 g/l or more total dissolved solids, must be diluted by at least 10:1 for analysis by HPLC. Reproducibility is compromised and retention times are shifted for these solutions, because of extremely high anion (especially chloride) concentrations. Chloride/iodide ratios are generally in the range 500:1 to 1000:1. Although these fluids have naturally high levels of chloride, bromide, sulphate, nitrate, sodium, calcium, magnesium, ammonium and potassium, none of these was found to interfere with the iodide peak. Repeated measurements (at least 3) at various dilutions (at least 2) must be performed for each sample to achieve errors of <10%. Dilutions of up to 500:1 (in which iodide concentrations would be ca. 0.5 ppm) may still be in a range well above the detection limit, in which the best results are achieved. In these waters, iodine should exist only as iodide given that the brines reside in a strongly reducing environment. Conversion to iodate may take place during sampling and/or storage, therefore treatment with a reducing agent may be necessary. If separation of inorganic and organic I species is desired, a solid-phase extraction filter such as Envirelut (Varian) can be used on fluid volumes of up to 2 l prior to sample preparation and concentration determination by HPLC.

Iodine is biophilic, and is bound to organic compounds in sediments and soils. Depending on the organic content of the sediment or soil, I levels may be <1 ppm to several hundred ppm.

Although as yet untested, the method of extraction described here would also presumably work for ground or crushed rock material. Extraction of iodine from these materials is accomplished by chemical breakdown of organic molecules in an all-glass apparatus with nitric acid and 30% hydrogen peroxide. Iodine in the gaseous form (i.e., as I_2) is forced into a gas-washing bottle with nitrogen gas. The collection solution is 10–100 mM sodium hydrogensulfite, which reduces the iodine to iodide, and the concentration in the solution is then measured by HPLC. (See [12] for a more thorough description of the chemical procedure.) Depending on the sample size and the composition of the sample, extraction of the 1 mg of I necessary for ratio determination may take several days. Recovery rates for samples spiked with 1-iodooctadecane were 80–90%.

For samples with high iodine concentrations, or when removal of only a relatively small amount of iodine is necessary, extraction can be accomplished by a single combustion [13], or by alkali leach and fusion [14,15]. Combustion in oxygen of 10 g or less of material in a pressurized bomb is appropriate for samples consisting mainly of organic material. This includes plant and animal parts and hydrocarbons. Incomplete combustion due to the presence of inorganic compounds in the matrix results in poor reproducibility for soils and sediments. The alkali leach and fusion method involves heating a sample mixed with sodium hydroxide and sodium peroxide for 2 h at 600°C, and is likewise appropriate for relatively small sample sizes. Reported recovery rates for this method are approximately 80% for meteorite samples [14]. In these methods, the final collection solution contains a reducing agent and iodine as iodide. The collection solution can be injected for concentration determination after filtration through a 0.45- μm filter.

Once iodine concentrations have been measured, and 1 mg or more is collected in solution, the procedure for extraction of iodine into carbon tetrachloride and subsequent precipitation as silver iodide, as described in [16] is followed. Measurements of $^{129}\text{I}/\text{I}$ are made by accelerator mass spectrometry using a cesium sputter source

on solid AgI targets [17,18]. Ratios for pre-anthropogenic samples are in the range $20 \cdot 10^{-15}$ – $1500 \cdot 10^{-15}$.

4. Applications

Iodine and its long-lived isotope ^{129}I have been used in a wide variety of applications in marine geochemistry and hydrogeochemistry. Iodine concentrations and pre-anthropogenic $^{129}\text{I}/\text{I}$ ratios have been used for identification of sources and tracing of migration pathways for hydrothermal waters [16] and sedimentary basin brines [12,19], and in other ground water studies [20–22]. For these applications, extraction of sufficient iodine for ratio measurement by accelerator mass spectrometry is straightforward, and the principal use of the IC system is in concentration determination. The advantages of the HPLC system described here are high selectivity, a high level of accuracy, and very little sample preparation at a low cost.

Natural $^{129}\text{I}/\text{I}$ ratios have also been used in the study of organic material dating and diagenesis in marine sediments [12]. HPLC is used for monitoring the extraction of iodine from the sediments, the course of which shows significant variation from sample to sample. This is due to variable sediment sample compositions, including organic contents ranging from 0.1 to 10% organic carbon and matrices consisting of, e.g., primarily silicates or primarily carbonates.

Investigations using anthropogenic ^{129}I have focused on tracking point source emissions from nuclear facilities [15,23,24], and using the anthropogenic input signal as a tracer for the marine carbon cycle and ocean circulation [25,26]. Because ^{129}I levels are quite high in most of these samples (which may be ground water, surface water, meteoric water, seawater, soil, seaweed or other plant or animal parts) the iodine extracted from them can be combined with carrier material of a known ratio to increase bulk material to form a suitably sized sample for measurement by accelerator mass spectrometry (AMS). Using this method, the overall accuracy of the ratio measurement depends on knowledge

of the amount of I contributed from the sample and from the carrier material, so precise measurement of I concentration by HPLC is invaluable. I concentrations in the original material are determined from average recovery rates for the derivitization method chosen.

5. Conclusions

The HPLC method for detection of iodide described here has been applied to samples from a variety of geologic materials, including meteoric waters, ground waters, surface waters, saline formation waters, and derivatives of soils, sediments, crude oil and plant and animal parts. $^{129}\text{I}/\text{I}$ ratios were subsequently measured on AgI samples made from these materials. The HPLC method has the advantages of having a wider range and lower detection limit than other wet chemistry methods, and is more versatile with greater selectivity than GC or neutron activation methods. Under ideal conditions, this method has a detection limit of 0.45 ng and a reproducibility of standards of 3% in the optimum working range.

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