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Journal of Chromatography A, 706 (1995) 271–275

JOURNAL OF
CHROMATOGRAPHY A

Matrix-elimination ion chromatography with post-column reaction detection for the determination of iodide in saline waters

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Abstract

An ion chromatographic method has been developed for the determination of traces of iodide in saline waters. A Dionex IonPac AS11 anion-exchange column was used with a mobile phase containing sodium chloride in order to remove interferences of the sample matrix in both the chromatographic separation and detection. This matrix-elimination procedure was reinforced by a post-column reaction detection that was both selective and sensitive for iodide and was based on the reaction of iodide with 4,4'-bis(dimethylamino)diphenylmethane in the presence of N-chlorosuccinimide. Detection was carried out at 605 nm. The detection limit for iodide in seawater is at about 0.8 ppb for a 150- μ l injection, and the relative standard deviation at 5 ppb is better than 4%. Bromide is a potential interference, but is well separated from iodide. No interferences from dissolved organic matter in natural samples have been observed.

1. Introduction

There are many reasons to measure trace levels of iodine. It is an essential micronutrient for many organisms—both terrestrial and marine. It is released as one of the by-products from the operation of nuclear reactors. Iodine is also a useful element to characterize soils, ground waters, saline formation waters and other

brines [1], and in its different forms or species, it is a possible indicator of oceanic biological productivity [2], and is useful in studying the redox chemistry of natural waters [3].

In natural waters, iodine exists almost exclusively as the anions, iodate and iodide. The prevalence of one over the other depends on redox chemistry: iodate is dominant under oxidizing conditions, iodide under reducing conditions. Of the several methods that can be used to determine iodate in natural waters, automated

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colorimetry [4] and polarography [5,6] operate well even in saline¹ waters. Very few methods allow trace iodide to be determined directly in natural waters, and only a couple in saline waters. The voltammetric method of Luther et al. [7] with a detection limit of 0.01–0.03 ppb (mass/volume, equivalent to $\mu\text{g I/l}$) is very sensitive. Its drawback is that it is not a very rapid method of analysis. Dissolved organic matter might also interfere in some natural waters. Nakayama et al. [8] have described another electrochemical procedure that is very sensitive, too, for iodide measurement in seawater. It uses a flow-through iodide-selective electrode, and is automated. However, the instrumentation appears quite complex and is not readily available. As far as we know the originators are the only ones to have used this procedure to determine iodide.

Ion chromatography (IC) seems to offer advantages for the determination of iodide. The halide elutes late both in anion-exchange chromatography and ion interaction chromatography, so that it is usually well separated from interferences. There have been two problems for saline water analysis: (i) deterioration of chromatographic efficiency with injection of the high-chloride matrix, and (ii) lack of sensitivity. The first has been solved by using the matrix-elimination technique, where chloride is added to the mobile phase [9–11]. Although various detectors have been tried including UV absorption [9,11], amperometry [9,12] and potentiometry [13], sensitivity remains an obstacle.

In this study, we have addressed both problems for determining iodide in saline water by IC by combining the matrix-elimination technique with a sensitive and selective post-column reaction for iodide. The post-column reaction is derived from an IC method described earlier [14,15] which uses the reaction of iodide with 4,4'-bis(dimethylamino)diphenylmethane ("tetra-base") in the presence of chloramine T. Several modifications of this reaction necessary in combination with the matrix-elimination tech-

nique are described in this paper, and results from an application to analysis of seawater samples are presented.

2. Experimental

2.1. Instrumentation

The IC instrumentation consisted of two 510 solvent-delivery systems (Waters, Milford, MA, USA), a 7010 injection valve (Rheodyne, Cotati, CA, USA), an AS 11 column (Dionex, Sunnyvale, CA, USA), a temperature-control module (Waters), a knitted reaction coil made from PTFE tubing (114 cm \times 0.5 mm I.D.), a Model 450 variable-wavelength UV-visible absorbance detector (Waters) and a Maxima 820 chromatography data workstation (Waters). The second pump was fitted with pulse dampener (Waters).

2.2. Reagents and procedures

The mobile phase was prepared by dissolving 0.4 ml methanesulphonic acid (Fluka, Buchs, Switzerland) and 5.84 g sodium chloride in 700 ml water, adding a solution containing 0.8 g 4,4'-bis(dimethylamino)diphenylmethane (Merck, Darmstadt, Germany) in 200 ml of methanol, and making up to 1 l. The post-column reagent comprised 1.5 g/l N-chlorosuccinimide and 15 g/l succinimide (both obtained from Aldrich, Milwaukee, WI, USA) in a succinate buffer prepared from 11.8 g/l succinic acid adjusted to pH 4.0. All chemicals used were of analytical grade. Water was treated with a Milli-Q (Millipore, Bedford, MA, USA) water-purification system. The mobile phase and the post-column reagent were filtered through a 0.45- μm filter and degassed before use.

Seawater samples were injected directly without sample preparation apart from a filtration through a 0.2- μm filter. The flow-rate of the mobile phase was 0.9 ml/min and that of the post-column reagent 0.3 ml/min. The detection wavelength was 605 nm.

¹ By saline, we mean natural waters that are dominated by sodium chloride.

3. Results and discussion

3.1. Optimization of the post-column reaction

Originally discovered by Feigl and Jungreis [16], iodide catalyses the reaction between the tetrabase and hypochlorite (generated by the hydrolysis of chloramine T) yielding a quinoidal product of intense blue color which gradually turns into green. These reagents have been used successfully in IC and post-column reaction detection for iodide [14,15], though the stability of chloramine T solutions as a source of hypochlorite was not completely satisfactory. Therefore, substitution of chloramine T by other reagents with better stability was attempted. The use of N-chlorosuccinimide/succinimide seemed to be a promising alternative. Considerable experience with this reagent was already available from earlier work dealing with the post-column reaction detection of cyanide [17] which involved the oxidation of cyanide to cyanogen chloride. Although chloramine T was the usual oxidation reagent for cyanide, the alternative reagent N-chlorosuccinimide was found to be more suitable for application in a post-column reaction system. Therefore, this reagent suggested itself for employment in the detection of iodide.

As mentioned above, the blue color of the post-column reaction is not stable and careful optimization of the reaction conditions is necessary. The optimum of the reaction time is in the order of 14 s depending strongly on the temperature and other reaction conditions. We tried to keep the length of the mixing capillary as short as possible so that a high backpressure would be avoided. This was done with respect to an eventual use of alternative post-column reagent-delivery systems that are driven by pressure. These systems would allow a generally pulseless flow and therefore a minimum of baseline noise, but do not tolerate high backpressures.

It should be remembered that one of the reagents, namely the tetrabase, is a component of the mobile phase so that only one post-column reagent pump is necessary for the addition of the N-chlorosuccinimide/succinimide reagent (a post-column reaction solution consisting of a

mixture of tetrabase and the oxidizing reagent would not be stable so that both reagents must be pumped individually; the incorporation of the tetrabase into the mobile phase does not interfere with the chromatographic separation and does not lead to side reactions with iodide during the separation process). The practicable pH for the reaction is limited to a range below 4.5 because the tetrabase is not soluble at higher pH values. Generally, sensitivity decreases with decreasing pH. In practice, a pH not higher than 4.0 was chosen in order to avoid precipitation in the reaction coil under all circumstances. Increasing the tetrabase concentration from 0.4 to 0.8 g/l results in a four-fold increase in sensitivity. Higher concentrations can lead to solubility problems and have not been investigated. The temperature effect was investigated in a range from 35 to 65°C. Up to 55°C, the sensitivity increased linearly and was roughly doubled for each 10°C. This increase in sensitivity leveled off at temperatures above 55°C. Unfortunately, the signal-to-noise ratio did not increase to the same extent because of increased background absorption (even without iodide, the reaction between hypochlorite and tetrabase does occur, although the reaction kinetics are slow). A temperature of 45°C yielded the best signal-to-noise ratio. Finally, the sensitivity depends on the concentration of the N-chlorosuccinimide. An increase in its concentration from 1 to 1.5 g/l yields an increase in sensitivity of approximately 50%. Higher concentrations pose problems with respect to solubility and have not been investigated further.

3.2. Analysis of seawater samples

Generally, samples of high ionic strength such as seawater cannot be injected directly onto the separation column due to severe peak broadening as a result of self-elution by the sample matrix itself and loss of band-compression effects. Special techniques such as on-column matrix elimination can overcome these problems. In this case, the matrix ion is used as component of the eluent in a concentration close to—or even higher than—the sample matrix. In reality, high eluent concentrations may lead to

retention times that are too short. Therefore, a compromise must be found and the optimum concentration will be low enough to achieve a reasonable retention time but high enough to avoid poor peak shapes. Fig. 1 shows the dependence of the number of theoretical plates for the iodide peak as a function of sodium chloride concentration of the matrix and injection volume (in all cases, the concentration of sodium chloride in the eluent was kept at 5.84 g/l, at which concentration a reasonable retention time of approximately 5.5 min can be achieved, while still providing effective matrix elimination). With respect to separation efficiency, a decrease in injection volume is preferable to a dilution of the sample matrix. An injection volume of 150 μl was chosen as a compromise between sensitivity and separation efficiency. One should be aware of the fact that the data in Fig. 1 indicate just a moderate separation efficiency achievable with this mobile phase. This is not a big obstacle as we are not dealing with a complicated separation problem. The only interfering peak (reacting in the tetrabase/N-chlorosuccinimide system) would be bromide, but it elutes near the void volume well separated from iodide. The pseudohalide, thiocyanate, might be expected to show some reaction with the reagent; nevertheless, the

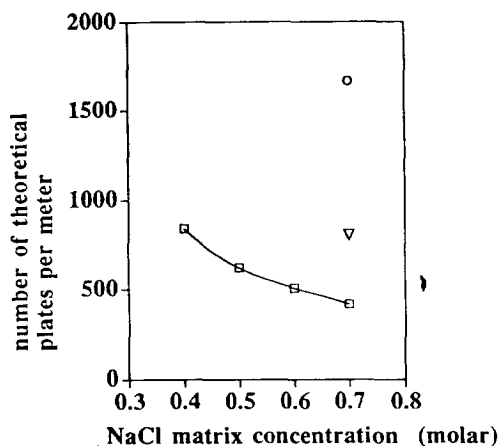


Fig. 1. Dependence of the number of theoretical plates for the iodide peak as a function of the sodium chloride concentration of the matrix and the injection volume. Injection volumes: □ = 200 μl ; ▽ = 150 μl ; ○ = 100 μl .

experiments indicated no interferences from thiocyanate up to 1.5 ppm.

The response of the post-column reaction detector was found to be linear in a range up to 100 ppb for an injection volume of 150 μl . The detection limit (given as signal-to-noise ratio of 3) was approximately 0.8 ppb (injection volume of 150 μl) corresponding to an absolute amount of 120 pg injected. This detection limit is approximately five times poorer than that obtained earlier with a mobile phase containing methanesulfonic acid without sodium chloride [14,15]. Obviously, the relatively high concentration of sodium chloride in the eluent decreases the sensitivity of the post-column reaction. Nevertheless, detection limits are still good enough for the application described in this paper. Most of the baseline noise could be attributed to small irregularities in the flow-rates of the pumps used for delivering the mobile phase and the post-column reagent. Therefore, efficient pulse dampeners are crucial. The use of syringe pumps instead of reciprocating piston pumps might have some potential for further reduction of baseline noise. Unfortunately, this sort of instrumentation has not been available for this study.

Fig. 2 shows a typical chromatogram for the determination of iodide in seawater. The reproducibility was checked by injecting a seawater sample six times which yielded a relative stan-

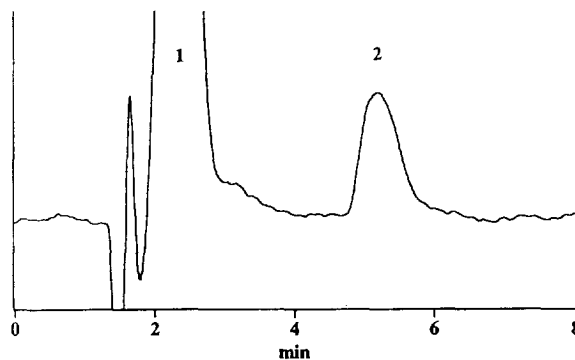


Fig. 2. Typical chromatogram for the determination of iodide in seawater. Injection volume: 150 μl ; wavelength: 605 nm; 0.01 AUFS; other conditions as in Experimental section. Peaks: 1 = bromide; 2 = iodide (5 ppb).

dard deviation of 3.2% for 5 ppb iodide. Quantification was done by external standards. Generally, the range of iodide concentrations to be expected in seawater samples is relatively narrow. Therefore, it seemed justified to use only two external standards covering the lower and higher end of this range. The following injection sequence was observed: standard 1–sample 1–sample 1–standard 2–sample 2–sample 2–standard 1–sample 3–. . . . For each sample, the standards enclosing this sample were used for quantification.

Organic matter present in natural waters can interfere with voltammetric methods, but we have not observed any problems with our IC method in the analysis of several marine and estuarine water samples. Even if organic interference was subsequently noted in different samples, we believe that it could be removed by pre-treatment of the sample by passing it through a small cartridge containing a suitable reversed-phase substrate.

If other salts in addition to sodium chloride are present in a saltwater sample, then it is possible that the eluent recommended above will not be adequate for good chromatography. However, by appropriate adjustment of the eluent to include other major salts to restore effective matrix elimination [11], and then re-optimization of the post-column reaction, it should be possible to determine iodide in an even larger range of water samples.

We will be looking to apply this method to iodide determination in various marine and other natural waters as part of ongoing work in our laboratories.

4. Conclusions

Matrix-elimination IC in combination with selective post-column reaction detection shows a range of attractive features that should make this technique an interesting alternative to existing methods for trace determination of iodide in high-ionic-strength matrices. Ion chromatography can easily be automated and adapted to a high sample throughput. The instrumentation is

robust and can be made compatible with the requirements of remote operation, such as ship-board analysis. In this way, problems associated with sample transport and sample preservation might be reduced considerably. The detection limit of this technique for iodide is low enough (and can still be improved to some extent by instrumental modifications as indicated above) to be a valuable tool for investigations of iodine speciation in diverse saline waters.

Acknowledgement

Technical support from Dionex Corporation is gratefully acknowledged.

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