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Short Communication

THE DETERMINATION OF BROMIDE IN NATURAL WATERS BY FLOW INJECTION ANALYSIS

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Summary. Bromide can occur in well waters as a result of sea water intrusion. The phenol red method is adapted to a flow-injection system and interferences are studied by using a two-channel valve. Standards are injected from one loop of the valve while the possible interferent is injected from the other loop, this provides a fast means of evaluating interferences. Ammonia, cyanide and humic substances interfere. Bromide can be determined down to 2 μM at a rate of 80 samples per hour.

The contamination of well waters from sea-water intrusions can be a serious problem in coastal areas. A rapid and accurate method for following the bromide/chloride ratio is of interest not only for tracing sea water in fresh water but also for monitoring pollution, e.g., from the petroleum industry.

Bromide can be determined in various ways. Direct potentiometric determination lacks selectivity as well as sensitivity. Spectrophotometric methods are well suited for automation and normally possess adequate sensitivity. Various methods have been used to determine bromide [1, 2]. The phenol red method [3–6] is probably most widely accepted as the standard method for bromide; it is based on the bromination of phenol red to bromophenol blue after oxidation of bromide to bromine with chloramine-T in an acetate buffer. The method is sensitive and selective enough to meet most requirements. Basel et al. [6] presented a thorough study of interferences in an automated segmented flow system under fully equilibrated conditions. Ammonia and chloride were identified as the most important interferents.

Flow injection analysis is now a well established technique for automating procedures, one of its most appreciated properties being its simplicity. It also offers a simplified and time-saving way of studying possible interferences. The aim of the present communication is to show how the phenol red method can be adapted to a flow-injection system and to explain a simple, quite general, way of studying interferences when a new method is applied.

Experimental

Reagents. The stock solutions were 2% (w/v) phenol red (Merck) in ethanol,

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1% (w/v) chloramine-T trihydrate in water, and sodium acetate/acetic acid buffer to a total concentration of 0.8 M. Preliminary studies showed that the optimal pH to reach the highest sensitivity was 5.2. Both the chloramine-T and the indicator stock solutions had to be renewed weekly because of degradation. The reagent solutions used were prepared daily from the stock solutions. Reagent 1 was prepared by diluting 1 ml of the indicator stock solution to 100 ml with acetate buffer. Reagent 2 was prepared by diluting 10 ml of the chloramine-T stock solution to 100 ml with acetate buffer.

All bromide standards were prepared by diluting 0.1 M potassium bromide with deionized water. Freshly prepared solutions of possible interferents were used.

Apparatus. The Tecator 5020 Flow Injection Analyzer used was equipped with a V-200 double-channel, variable-volume valve. The manifold used was a Chemifold III. A Tecator 5023 spectrophotometer was used as detector at 590 nm.

For the study of possible interferences, mixing of interferent solutions with bromide standards was easily done by using a two-channel valve. Thus, in the manifold used (Fig. 1), two carrier streams were first merged and then reagents were added at lower flow rates to avoid unnecessary dilution in the system. The single reaction coil before the detector was varied in a preliminary study to decide the optimal length in terms of sensitivity and sampling rate. Lengths greater than 60 cm gave only slight increase in sensitivity at the expense of decreased sample throughput. The flow rates for the carrier streams (C in Fig. 1) were 1.5 ml min^{-1} each. The reagents (R in Fig. 1) were propelled at a flow rate of 0.6 ml min^{-1}.

Results and discussion

Bromide concentrations in natural waters can vary quite extensively. In order to establish the lower limit of detection, two matched 200-μl loops

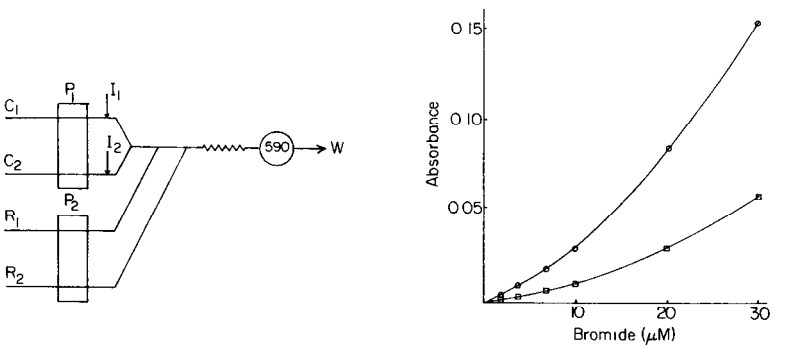

Fig. 1. Manifold for the determination of bromide. Loops I_1 and I_2 were normally 200 μl in volume. The teflon reaction coil was 600 mm long (0.7 mm i.d.). Flow rates of the carrier streams were 1.5 ml min^{-1} each and for the reagent 0.6 ml min^{-1} each.

Fig. 2. Calibration curves in the 0—3 × 10^{-5} M bromide range: (○) when both loops (200 μl each) are used to inject standards; (□) when only one loop is used to inject standards.

were installed in the injection valve. Further increase in the injected volume did not increase the peak height but only the peak width. Figure 2 shows calibration curves in the lower concentration region with standards in both channels or in only one channel. The curvature of the calibration in this region can probably be ascribed to the low reaction rate. In order to test this assumption, the pumps were stopped at the peak and the increase in absorbance was observed. A steady state was reached after 2 min, the peak height being increased about 2.5 times. The increase is greater for the lower concentrations of bromide. It would thus be possible to increase the sensitivity considerably by using a stopped-flow technique, but the loss in sample throughput could be a drawback for some purposes. When the sample is injected from only one of the loops, it is diluted about 1:2 by the other carrier stream. The dispersion of the sample in the rest of the system is low when high loop volumes are used. It can be seen from the calibration curves that the ratio of the responses is about 1:2 when one or two loops in the valve are used. The double-loop injection technique can be regarded as a way of premixing the samples before the reaction step. This feature of the system was conveniently used in studying the interferences from other substances and as a means of spiking the samples.

A large number of measurements with interferents could be studied within a reasonable time. Because natural waters always contain chloride, its possible interference was examined in detail, though initial experiments showed very little effect. Sodium chloride at two different concentrations was injected from one loop and a series of calibration solutions was injected from the other loop. The results are shown in Table 1. The chloride interference decreases slightly as the concentration of bromide increases, probably because of the faster rate of the main reaction at higher bromide concentrations. Also, any matrix effects in the detector will be greater at low bromide concentrations. The interference can be described as the ratio of Cl^-/Br^- concentrations at which the two ions contribute equally to the overall signal. For

TABLE 1

The interference of chloride on different concentrations of bromide

KBr conc.[a] (μM)	Absorbance with H_2O added[b]	Change in absorbance with NaCl added	
		0.1 M NaCl	0.7 M NaCl
2	0.0012	+0.0026	—
4	0.0028	+0.0024	+0.0256
7	0.0062	+0.0022	+0.0252
10	0.0092	+0.0026	+0.0260
20	0.0288	+0.0012	+0.0246
30	0.0582	+0.0012	+0.0192
50	0.1178	+0.0004	+0.0192

[a]Solution injected from loop 1. [b]Injection from loop 2.

chloride, this ratio is around 3.5×10^4, i.e., chloride at 3.5×10^4 times the concentration of bromide will produce a signal equal to that of bromide. The interference from chloride is thus usually negligible.

Other interferences which may have a greater influence are more easily studied by keeping the bromide concentration constant in one loop and varying the interferent concentration in the other loop. The results are shown in Table 2. Hydrogencarbonate, iodide and iron(III) all produced positive interferences. Hydrogencarbonate probably affects the pH and interferes only slightly except at concentrations well above the natural level. The reaction with iodide is, not surprisingly, more sensitive than that with bromide; however, the concentrations of iodide in natural waters are usually well below those of bromide. Iron(III) also interferes directly. The Fe^{3+}/Br^- interference ratio, calculated as described above, is approximately constant throughout the bromide concentration range at around 2.5×10^2. Both ammonium ion and cyanide produce negative interferences which are proportional to the concentration of the interfering ion. Cyanide would prove a considerable problem in the analysis of waste waters. Insertion of a cation-exchange column before the reagents are merged with the carrier stream avoids the interference from ammonium ion [6]; this was confirmed in tests for 0—30 μM bromide injections with 1 mM ammonium nitrate injected from loop 2. Apart from the interferences mentioned above, other substances can cause serious problems. Humic substances, normally present in natural waters, give negative interferences, but it is not easy to evaluate the extent of interference; the substances are partly removed by the cation-exchange column.

In order to study the applicability of the method, brackish water samples were taken from the Baltic Sea, two from the innermost archipelago of Stockholm (Edsviken and Värtan) and another at Öresund, at the west coast of Sweden, where the Baltic flows into the North Sea. The chloride contents of the samples were determined by flow injection analysis, using the standard method, after appropriate dilution. The results are shown in Table 3. The chloride/bromide ratio, expressed in molar units, for the water sample taken

TABLE 2

Effects of varying concentrations of interferents injected from one loop on the determination of 10 μM potassium bromide injected from the other loop. Interference is described by the change in peak absorbance, ΔA The peak absorbance for 10 μM bromide alone is 0.0102

$NaHCO_3$		KI		$Fe(NO_3)_3$		KCN		NH_4NO_3	
mM	ΔA	μM	ΔA	mM	ΔA	μM	ΔA	μM	ΔA
1	+0.0008	0.5	+0.0012	0.1	+0.0004	5	−0.0014	10	−0.0004
10	+0.0012	1	+0.0040	0.5	+0.0018	10	−0.0038	50	−0.0040
100	+0.0068	5	+0.0154	1	+0.0040	50	−0.0182	100	−0.0068
		10	+0.0318	10	+0.0362	100	−0.0252	1000	−0.0196

TABLE 3

The concentration of bromide and chloride in sea-water samples

Sample	Br^- found (μM)	Cl^- found (mM)	[Cl]/[Br]
Edsviken	45	27	600
Värtan	42	26	619
Öresund	321	208	648

from the more saline Öresund is normal for North Atlantic waters whereas the ratios for the samples taken in the Stockholm archipelago are below normal for Baltic sea water.

The proposed method for bromide can be used down to 2 μM at a sample throughput of 80 h^{-1}. There are few interferences in natural waters, but care must be taken with ammonium ion, cyanide and humic substances. The method can, of course, be tailored to fit required concentration ranges above 2 μM.

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