Trace level determination of bromide in presence of large concentration of chloride by differential pulse polarography

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The optimum conditions for the determination of bromide at low concentrations has been developed employing differential pulse polarography. A detection limit of 0.3 μg/ml has been achieved. The method has been successfully applied for the analysis of bromide content in underground waters and food products.

The application of voltammetric methods to analysis of natural waters has been mainly for the determination and speciation of metal ions, even though many non-metal inorganic species are also electroactive1-3. Thus, it is of interest to investigate the suitability of voltammetric methods for characterising the different anionic forms in aqueous systems. The present work is focused on electrochemical determination of bromide based upon the fact that all halide ions depolarise the dropping anode with the formation of the slightly soluble mercuric halide. The applicability of cathodic stripping voltammetry in the determination of bromide along with chloride and iodide has been described by Dhaneshwar and Patrecha4. More recently, Zhang and coworkers5 have shown the adsorptive polarographic determination of bromide. In the present note we report the optimal conditions for the trace determination of bromide using differential pulse polarographic (DPP) technique in presence of chloride which is usually present at higher concentrations.

Experimental

A polarographic analyzer (Model 174-A) in combination with X-Y recorder (Model RE 0074) and drop-timer (Model 174/70), (EG&G, U.S.A.) was used for polarographic measurements. The instrumental settings for DPP were as follows: a dropping mercury electrode was used as working electrode; pulse amplitude, 50 mV; pulse duration, 57 ms; clock time of pulse, 1s and scan rate 5 mV/s. Ag/AgCl and platinum wire were used as reference and auxiliary electrodes respectively. To avoid the contamination of chloride, Ag/AgCl electrode was connected to the polarographic cell by a saturated potassium nitrate salt bridge.

A Shimadzu UV-vis spectrophotometer (Model UV-1601) with a wavelength range of 190-1100 nm was also used for sample analysis. A 50 W halogen lamp and silicon photodiode were used as the light source and detector respectively. The spectral band width of resolution was 2 nm. Double beam optics was used as a photometric system and the photometric range in terms of absorbance was 0.5-3.99 nm.

Underground water samples were collected in clean polyethylene containers. These were filtered in order to separate any suspended particulate matter, and acidified with hydrochloric acid to pH 2.0 for storage. During sampling, pH1 was kept at 7.5. To an aliquot of the water samples (100 ml) was added 1 ml of a mixture of zinc acetate and sodium hydroxide (1:1) to remove sulfide in the form of precipitate6.

Determination of bromide

The prepared samples were taken into the polarographic cell with 0.01 M H2SO4 and DP polarograms were recorded in the potential range of 0.0 - +0.4 V. The peak currents were measured at +0.25 V after making blank corrections. The concentrations were determined by standard addition method7.

All the experiments were carried out in an air-conditioned laboratory where the temperature was maintained at 25±1°C. The test solutions were deaerated by bubbling purified nitrogen for 20 min prior to voltammetric recordings. Nitrogen was purified by passing it through a vanadous chloride scrubbing solution.

Chemicals used were of reagent-grade purity. Solutions were prepared in doubly distilled water. The bromide and chloride standard solutions were prepared each day freshly.

Results and discussion

Preliminary electrochemical observations of bromide ion on a DME indicated the suitability of 0.01 M H2SO4 among other supporting electrolytes studied viz: HNO3, HClO4, KNO3, NaClO3, and acetate buffer. A well-defined DC polarographic wave
was obtained with a half-wave potential of +0.20 V. Bromide also gave a DP peak in sulfuric acid medium at +0.25 V. A linearity between peak height and bromide concentration was found in the range of 0.3 - 22.0 μg/ml. The characteristics of calibration curve were as follows: slope, 0.434 ± 9.89x10⁻²; coefficient of correlation (r), 0.997; intercept, -0.274 ± 0.112 and standard deviation (s.d.), 0.243.

A very small peak was also noticed at low concentrations just before the appearance of main sharp DP peak of bromide. It might be due to the adsorption of free halides at the electrode surface, present in solution.

Since the physiochemical analysis of underground water showed the presence of a large concentration chloride it was necessary to check this during the determination of bromide. Therefore, DP polarograms of bromide were also recorded in presence of chloride. DP peaks of these species were distinguishable from each other (Ep : Br⁻, +0.25 V; Cl⁻, +0.32 V vs Ag/AgCl), illustrating no interference as shown in Fig. 1.

Thus, DP peak was found suitable for quantitation of bromide where a limit of determination of 0.3 μg/ml was achieved.

UV-vis spectrophotometric method was used to compare the results obtained by DPP. The results of determination of bromide in underground waters and food products like milk and beer are summarised in Table 1. The proposed DPP method for the determination of bromide is more specific, sensitive and rapid in comparison to the existing conventional methods for estimation of halides as it has enabled sequential determination of trace bromide in presence of large concentration chloride.

The standard phenol red method for the determination of bromide was automated by segmented flow analysis by Basel et al. which enabled bromide estimation in ground waters (0.15 mg/L). Chloride caused significant interference at a level as low as 100 mg/L. Samples in the range of 1-10 mg/L could be measured by flow injection analysis. It has been used for bromide determination in sea water (48-70 mg/L). The results of bromide determined by present method are in good agreement with other techniques including DPP (concentration limit, 1x10⁻⁵ M) in terms of measurement and precision (RSD, 0.35%).

![Fig. 1—Differential pulse polarogram of trace bromide in presence of large concentration of chloride in 0.01 M H₂SO₄ (modulation amplitude, 50 mV; pulse duration, 57 ms; clock time of pulse 1 s, scan rate 5 mV/s).](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bromide (μg/ml)</th>
<th>DPP (SD)</th>
<th>RSD(%)</th>
<th>UV-vis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Underground waters*</td>
<td>(213.21)</td>
<td>0.6894±0.0054</td>
<td>0.78</td>
<td>1.0812</td>
</tr>
<tr>
<td>Of Suraj Kund</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milk</td>
<td>(102.37)</td>
<td>1.2580±0.0042</td>
<td>0.33</td>
<td>1.2030</td>
</tr>
<tr>
<td>Beer</td>
<td>(118.63)</td>
<td>1.0431±0.0038</td>
<td>0.36</td>
<td>0.9775</td>
</tr>
</tbody>
</table>

n = No. of determinations; (n)=4

Values shown in parentheses is chloride determined by DPP in μg/ml.
Acknowledgement

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References