Differential pulse polarographic trace level determination of iodate

P Sharma* & S Songara
Electroanalytical Laboratory, Department of Chemistry
J.N.V. University, Jodhpur 342 003, India
Email: sharma_pk00@yahoo.com

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A detailed voltammetric study was carried out for iodate ion which has resulted in optimization of analytical conditions for its trace level determination using differential pulse polarographic method. Chlorate and bromate did not interfere. The detection limit was 0.6 µg/mL. The method has successfully been applied for the analysis of iodate in different matrices.

Keywords: Iodate, DPP, Real samples
IPC Code(s): C25B1/04, G01N27/48

Iodate is not a natural component of water but may be formed during ozonation (disinfection) of raw water as a byproduct of iodide. It is added to food products particularly as table salt as a source of iodine, in order to prevent iodine deficiency and maintenance of thyroid hormone. Several methods such as spectrophotometry, ion chromatography, gas chromatography, and chemiluminescence are reported for determination of iodate. Most of these techniques are either not sensitive enough or require complicated and expensive instrumentation. Thus, it is appropriate to develop an alternate method of simple approach for the determination of iodate at sub-µg level.

Electrochemical methods such as stripping analysis and differential pulse polarography (DPP) have proved useful in such determinations. Different ionic forms of a species can also be characterized and determined by these methods. Luther and coworkers have determined iodine as iodate in sea water by cathodic stripping square wave voltammetry. Temerk et al. have shown sequential determination of iodate, periodate and bromate by DPP with a detection limit of $2.4 \times 10^{-6}$ M. A procedure of iodate determination in sea water at different pH values has been described by Lin using pulse polarography. Koltzoff and Belcher have reported cathodic stripping analysis of iodate and bromate in salts. The DPP determination of halides (bromide in presence of large concentration of chloride and iodide in food products) has been earlier reported by Sharma and coworkers. In the present work, the authors have found optimum DPP conditions for the analytical determination of iodate in presence of bromate using barium chloride medium. The method was employed in analysis of iodate contents in samples of natural waters, waste waters and salts.

Experimental Procedure

Instrumentation

A microprocessor based Pulse Polarographic Analyzer (Model CL-362) in combination with a drop-timer, of Elico (India), was used for the voltammetric measurements. Observations were recorded by a HP printer (model-3820). The instrumental settings for DPP were as follows: a dropping mercury electrode was used as the working electrode; pulse amplitude, 25 mV; pulse duration, 57 ms; clock time of pulse, 0.5 s and scan rate, 12 mV/s. Potentials were measured against a saturated calomel electrode (SCE) and platinum wire was used as an auxiliary electrode throughout.

A UV-Vis spectrophotometer (Model-108) of Systronics (India) was also used for sample analysis. It has a wavelength range of 190-900 nm. Tungsten halogen deuterium and wide range photo-multiplier were employed as the light source and detector, respectively. The spectral band width was 2 nm.

Sample preparation

(1) Water sample: 100 mL aliquot of water sample was treated with 1 mL of an oxidizing mixture of sulphuric acid and nitric acid to remove biological and other materials. 2 mL of 0.5 N ethylenediamine was added for preservation.

(2) Common salt sample: These were prepared by dissolving 1 g of common salt in 25 mL of distilled water.

All the experiments were carried out in an air-conditioned laboratory where the temperature was maintained at 25±1°C. Test solutions were deareated by bubbling purified nitrogen for 20 min, prior to voltammetric measurements. Traces of oxygen present in nitrogen were removed by passing the gas through a vanados chloride scrubbing solution kept in contact with amalgamated zinc. Chemicals used
were of analytical grade. Solutions were prepared in double distilled water.

Stock solution of iodate was prepared from potassium iodate of Qualigens Fine Chemicals, Bombay (Batch No. 134255110).

Quantitation in all determinations was made by the standard addition method\textsuperscript{19}.

**Results and Discussion**

**Polarographic characteristics**

The electroreduction of iodate ion was investigated in different supporting electrolytes such as potassium chloride, sodium chloride, ammonium chloride, barium chloride and acetate buffer. Among them 0.05M BaCl\textsubscript{2} was found to be the most adequate medium in which IO\textsubscript{3}\textsuperscript{−} produced a well-defined polarographic wave at –1.09V. The wave appeared to be diffusion controlled and its log–plot analysis indicated irreversible nature of the electrode process.

**Optimum DPP conditions**

IO\textsubscript{3}\textsuperscript{−} in presence of 0.05 M BaCl\textsubscript{2} also showed sharp DP peak (Ep: –1.09V). The peak current increased linearly with the iodate concentration up to 14.0 ppm. The calibration characteristics were as follows: slope, 0.0807; coefficient of correlation (\(r\)), 0.9993; intercept, 0.0573 and standard deviation, (±) 0.3632.

**Accuracy and precision**

The reproducibility of the method was evaluated by individual measurements of a solution containing known amount of iodate under the optimized experimental conditions. The data were in good agreement with a relative error of 2.7%, inferring that method is precise and accurate.

**Interference**

The coexisting interferant iodide with iodate in water supplies and common salt (added as food supplement) was monitored during the DPP determination of IO\textsubscript{3}\textsuperscript{−}. Peak potential of I\textsuperscript{−} in 0.05 M BaCl\textsubscript{2} polarographic medium was found to be more positive (> 0.0 V), indicating no interference. Similarly, BrO\textsubscript{3}\textsuperscript{−} is reduced at –1.65V which is well-separated from the IO\textsubscript{3}\textsuperscript{−} at –1.09 V. ClO\textsubscript{3}\textsuperscript{−} does not show a distinct wave in these experimental conditions. Common metal ions such as copper, lead and cadmium also gave distinguishable DP peaks as shown in Fig.1. Thus, these species did not interfere.

Fig. 1 — DP polarogram of iodate (18.69 ppm) in presence of copper, lead, cadmium and bromate in 0.05 M BaCl\textsubscript{2}. Cu (II), 0.93 ppm; Pb (II), 1.87 ppm; Cd (II), 3.74 ppm, IO\textsubscript{3}\textsuperscript{−} and BrO\textsubscript{3}\textsuperscript{−}, 18.69 ppm; Modulation amplitude, 50 mV; pulse duration, 57 ms; drop time, 0.5 s and scan rate 12 mV/s

The possibility of influence of iodide present in solution was also ruled out by analyzing a synthetic sample of iodate in presence of iodide. The results obtained were quantitative in terms of iodate concentration present in sample.

**Limit of determination**

The detection limit of iodate was found to be 0.6 µg/mL.

**Analytical applications**

The DPP method was applied for the determination of iodate contents in real samples.

**Analysis of iodate in natural waters and table salt**

A measured volume of the prepared sample of water and salt (as described in experimental section) was taken into the polarographic medium. DP polarograms were recorded between the potential of –0.9V and –1.2V. Peak currents were noted at –1.09V after substracting the blank current. The results of iodate determination in different samples are summarized in Table 1. These were further verified by carrying out additional recovery studies and the observations are presented in Table 2.

**Comparison**

The validity of the measurements has been demonstrated by comparing the results of DPP with UV-Vis spectrophotometric method based on the reaction of iodate with iodide in aqueous medium (pH ~ 4.0) at \(\lambda_{\text{max}}\) 352 nm\textsuperscript{20}. The comparative data are included in Table 3.
Table 1—DPP determination of iodate in different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>IO₃⁻ (ppm)</th>
<th>SD</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min.</td>
<td>Max.</td>
<td>Average</td>
</tr>
<tr>
<td>Waste water</td>
<td>2.37</td>
<td>2.50</td>
<td>2.44</td>
</tr>
<tr>
<td>Tap water</td>
<td>1.99</td>
<td>2.07</td>
<td>2.04</td>
</tr>
<tr>
<td>Drinking water</td>
<td>2.69</td>
<td>2.79</td>
<td>2.73</td>
</tr>
<tr>
<td>Pond water</td>
<td>2.08</td>
<td>2.21</td>
<td>2.10</td>
</tr>
<tr>
<td>Lake water</td>
<td>5.21</td>
<td>5.52</td>
<td>5.39</td>
</tr>
<tr>
<td>Bore well</td>
<td>1.06</td>
<td>1.09</td>
<td>1.08</td>
</tr>
<tr>
<td>Rock salt</td>
<td>1.09</td>
<td>1.13</td>
<td>1.12</td>
</tr>
<tr>
<td>Common salt</td>
<td>1.78</td>
<td>1.86</td>
<td>1.83</td>
</tr>
</tbody>
</table>

n = No. of determinations = 4

Table 2—Recovery studies on iodate determination

<table>
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<tr>
<th>Sample</th>
<th>IO₃⁻ (ppm)</th>
<th>Recovery</th>
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</thead>
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<tr>
<td></td>
<td>Added</td>
<td>Present</td>
</tr>
<tr>
<td>Waste water</td>
<td>4.0</td>
<td>2.44</td>
</tr>
<tr>
<td>Drinking water</td>
<td>4.0</td>
<td>2.74</td>
</tr>
<tr>
<td>Well water</td>
<td>4.0</td>
<td>1.08</td>
</tr>
<tr>
<td>Common salt</td>
<td>4.0</td>
<td>1.83</td>
</tr>
<tr>
<td>Average recovery</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3—Comparison of results of iodate determination by DPP and UV-Vis spectrophotometry

<table>
<thead>
<tr>
<th>Sample</th>
<th>IO₃⁻ (ppm)</th>
<th>DPP</th>
<th>UV-Vis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial waste</td>
<td>2.44</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td>Drinking water</td>
<td>2.73</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>Table salt</td>
<td>1.83</td>
<td>1.84</td>
<td></td>
</tr>
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</table>

Conclusion
The described differential pulse polarographic method for the determination of iodate is more specific, sensitive and rapid in comparison to the existing conventional techniques of estimation of halides and their oxyanionic forms. Further, it has enabled the determination of trace iodate without any interference of iodide usually present in food products particularly common salt. The results of iodate determination by present method are also in good agreement with other techniques including DPP¹³ (concentration limit, 2.4 × 10⁻⁶M).

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References