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Spectrophotometric determination of trace amounts of iodide-ions in form of ionic associate with brilliant green using electrochemical oxidation

Research Article

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Abstract: A combined method involving electrochemical oxidation of iodide to iodate at a platinum electrode followed by extraction in CCl_4 of ionic associates of iodine-iodide complexes with brilliant green, formed in excess of iodide, was developed for the spectrophotometric quantification of iodide. The slope of the calibration curve yields a molar extinction coefficient of $\varepsilon = 3 \cdot 10^5$ L mol^{-1}cm^{-1}. This method can be used for the quantification of iodide in the concentration range of $3 \cdot 10^{-7}$ - $3 \cdot 10^{-6}$ mol L^{-1} with a detection limit of $5 \cdot 10^{-8}$ mol L^{-1}. The interfering effect of other ions on the determination of the iodide concentration was also investigated. The method was successfully applied for the determination of iodide in real samples of NaCl and spring water. Relative standard deviation is 1 – 2%.

Keywords: *Iodide • Electrochemical oxidation • Brilliant green • Spectrophotometric determination*

1. Introduction

Iodide ion is one of the main components among existing iodine-containing ions. Several methods can be used for the quantitative determination of iodide ions, including voltammetry [1,2], chromatography [3,4], kinetic [5,6], but spectrophotometric methods are the most common to date.

The spectrophotometric method based on the chemical oxidation of iodide to iodate, formation of iodine-iodide complexes and measurement of absorbance of the complexes [7] in near ultraviolet (λ = 290, 351 nm) is well-known among the photometric methods for the determination of iodide. Coefficients of absorption for iodine in the complexes are 30000 and 20000 L mol^{-1} cm^{-1}, respectively, at the two wavelengths selected. However, a great number of impurities present in real samples also absorb in this spectral region, yielding inaccurate results of the determination. Sensitivity of the determination in prior work [7] ensures detection of concentrations greater than 6×10^{-8} mol L^{-1}. However, such sensitivity was demonstrated only in a test solution. The real sample was diluted with rather great volume of water in the analysis under flow injection.

Spectrophotometric methods based on the extraction of ionic associates of iodide-ions with a cationic dye have been reported [8]. Selectivity for such methods is low because of formation of ionic associates of cationic dye with other ions. A high molar absorption coefficient is determined by aggregation of brilliant green under pH 6.0 and by extraction of associates of aggregated cationic dye in chloroform. The slope of the calibration curve in this method is not stable in time.

Methods involving controlled potential coulometry at a platinum electrode have a working range of 10^{-3} – 10^{-5} mol L^{-1} and are characterized by high selectivity, but their sensitivities are inferior to that of the spectrophotometric method [8]. Electrochemical reaction—the chemical basis of coulometric determination—can be used jointly with spectrophotometric determination of the products. Such unification eliminates usage of chemical oxidizing agents [7] and ensures measuring of absorbance in the visible spectrum.

The aim of this work is to develop a procedure for the determination of iodide ions using two methods – electrochemical oxidation at the platinum electrode and spectrophotometric determination of ionic associates with brilliant green.

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2. Experimental Procedure

2.1 Apparatus

Absorbance was measured using UV/Vis spectrophotometer SF – 46 (LOMO, Russia), equipped with 10 mm quartz cells. Measurements were carried out using potentiostat P – 5848 and coulometric integrator IPT – 1. (Gomel Plant for Measuring Instruments, Belarus). Electrochemical cell consisted of vessel with working wire platinum electrode (total area 75 cm^2) and auxiliary plate electrode (area 1.5 cm^2), placed in glass cylinder with filtering bottom. Saturated silver/silver chloride electrode (Gomel plant of Measuring equipment, Belarus) served as reference.

Electrochemical oxidation was carried out in the medium of sulphuric acid (H_2SO_4; c = 0.1 mol L^{-1}) at the platinum electrodes. Preparation of the electrodes and oxidation regime at 1.1 V *versus* saturated silver/silver chloride electrode reference electrode were described in prior work [9]. Sulphuric acid (c = 0.1 mol L^{-1}) was used as stock electrolyte and as solution in the cathode space. Volume of solution in cell was 85 mL. Mixing of solution was carried out with aid of magnetic stirrer.

Solution of KBr was injected for acceleration of oxidation reaction of iodides under 1.1 V, for obtaining appropriate concentration in test solution ~ 2×10^{-5} mol L^{-1}. Bromine formed by electrolysis was later removed from solution by boiling.

2.2 Reagents

All reagents used were of analytical reagent grade and all solutions were prepared with bidistilled water, saturated with gaseous nitrogen.

2.3 Preparation of the solutions

A standard solution of potassium iodide was prepared by dissolving 0.166 g potassium iodide (Reachim, chemically pure) in bidistilled water and diluting to the mark in 100 mL volumetric flask.

A standard solution of potassium bromide was prepared by dissolving 0.119 g potassium bromide (Reachim, chemically pure) in bidistilled water and diluting to the mark in 100 mL volumetric flask.

A 1 mol L^{-1} sulphuric acid solution was prepared by dilution of concentrated sulphuric acid (Reachim, chemically pure) with bidistilled water.

Saturated solution of brilliant green was prepared by dissolving 5 g of $C_{27}H_{33}N_2C_2O_4H\bullet H_2O$ (Reachim, pure for analysis) in 100 mL of bidistilled water, at which point undissolved residue was filtered out. Filtered saturated solution of brilliant green was further twice diluted with bidistilled water.

Carbon tetrachloride (Reachim, pure for analysis) was purified by distillation with activated carbon.

2.4 Sample preparation

Sample preparation of spring water for analysis included adding 75 mL of spring water, 10 mL of H_2SO_4 (c = 1 mol L^{-1}) and 10 mL of potassium bromide solution (c = 2×10^{-4} mol L^{-1}) to 100-mL volumetric flask and diluting to the mark with bidistilled water.

5 g of table rock salt sample was weighed and dissolved with 60 mL of bidistilled water, then filtered. Filtrate was transferred into 100 mL volumetric flask, and 10 mL of H_2SO_4 (c = 1 mol L^{-1}) and 10 mL of potassium bromide solution (c = 2×10^{-4} mol L^{-1}) were added. Solution was diluted to the mark with bidistilled water.

2.5 Procedure

Before each determination, electrodes were stored in solution of potassium iodide and subjected to chemical cleaning (HNO_3 (1:1)) and electrochemical cleaning (in H_2SO_4 under 1.1 V) [9].

10 mL of brilliant green solution and 2 mL of H_2SO_4 (c = 1 mol L^{-1}) were mixed in beaker and warmed before extraction, then this mixture was used in extraction-photometric determination. This procedure results in decreased aggregation of dye and, thereby, decreased absorbance value of the blank solution.

Warmed mixture of brilliant green and sulphuric acid, 10 mL of potassium iodide solution (c = 2×10^{-3} mol L^{-1}) and 20 mL of organic solvent were added to separating funnel and saturated with nitrogen. Extraction was carried out for 3 min, periodically passing nitrogen through solution in funnel. Organic phase was discarded after first extraction. Extraction was repeated once more. Absorbance of second extract was measured at absorption maximum band (λ = 645 nm) with path length of 1 cm. Absorbance value of second extract is absorbance of blank sample.

After second extraction, test solution was added to separating funnel, and then extracted with 20 mL of carbon tetrachloride. Extraction was carried out for 3 min, periodically passing nitrogen through solution in funnel. Organic phase was transferred into 50-mL volumetric flask. Extraction was repeated with new portion of solvent and extracts were combined. Volume of solution was diluted to the mark with extract after third extraction. Obtained solution was mixed and absorbance of combined extract was measured at absorption maximum band (λ = 645 nm) with path length of 1 cm.

3. Results and Discussion

A method for the determination of iodide in the form of an ionic associate with brilliant green has been described [8]. Associates of iodine-iodide complexes are characterized with higher efficiency of extraction than associates with other inorganic anions. For this reason, electrochemical oxidation allows for increased selectivity of the determination.

As previously demonstrated [10], iodide can be quantitatively oxidized to iodine, but some product remains on the surface of the platinum electrodes, yielding a falsely low result for the determination; this is especially important for determination of low concentrations of iodide. Oxidation to iodate ions in the presence of bromide ions allows increased sensitivity of the determination of iodide ions:

$$I^- + 3H_2O = IO_3^- + 6H^+ + 6e^- \quad (1)$$

$$2Br^- = Br_2 + 2e^- \quad (2)$$

Bromine was removed by boiling. It has been found experimentally that bromine from the solution may be removed after electrolysis by heating to the boiling point and keeping under boiling for 1 minute in the open vessel. Comparison of the experimental absorbance values of extracts of iodine-iodide complexes with brilliant green, obtained in the test solution, containing bromine and without it, leads us to conclude that bromine removal was complete.

However, in excess of iodide a stoichiometric quantity of iodine or iodine-iodide complex anions was obtained:

$$IO_3^- + 6H^+ + 8I^- = 3I_3^- + 3H_2O \quad (3)$$

Under these conditions, it should be expected that the sensitivity of the determination will go as 3 ε (R^+), where ε is the molar extinction coefficient, [ε] = L mol^{-1} cm^{-1}; R^+ is a cation of organic dye.

Completeness of the conversion of iodide to iodate depending on the quantity of charge passing through the cell, is shown in the Fig. 1.

Iodine can be quantitatively converted mainly to one form (iodate) only by passing through the cell an excess of charge. From Fig. 1 it is clear that for full oxidation of iodide to iodate, it is necessary to pass through a quantity of charge 1.1 times more than the theoretical value. The low limit of the required quantity of charge can be evaluated using the equation of Faraday's law and bromide concentration.

The calibration curve of the dependence of extract absorbance of ionic associates on concentration of iodide-ions in the electrochemical cell is represented in

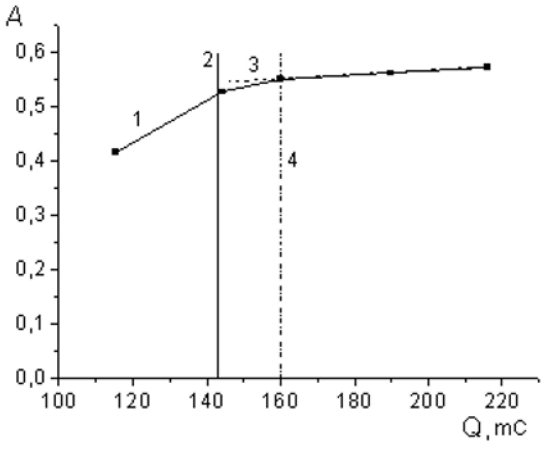

Figure 1. Absorbance vs. quantity of charge curve for iodine-iodide complexes with brilliant green in CCl_4. (1) C_{KI} = 1×10^{-6} mol L^{-1}, C_{KBr} = 2×10^{-5} mol L^{-1}; (2) point, conforming to the theoretical estimation of quantity of charge, which is necessary for cooxidation of iodide and bromide; (3) accumulation of residual current curve; (4) point, conforming to the experimental needed quantity of electricity for cooxidation of iodide and bromide.

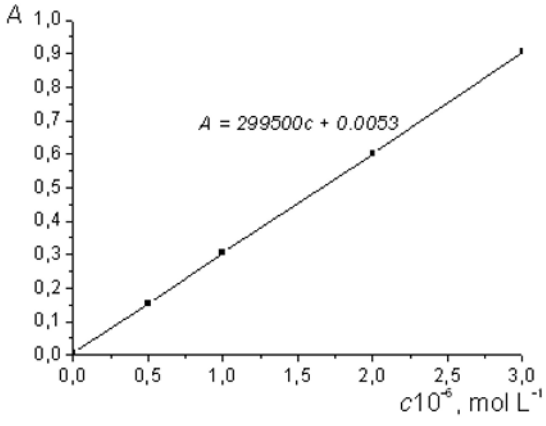

Figure 2. Calibration curve of the dependence of the absorbance of ionic associates of iodine-iodide complexes with brilliant green on concentration of iodide-ions in the electrochemical cell.

Fig. 2. The curve was plotted from data obtained after subtraction of the absorbance of the blank test. Values of the absorbance of the blank test were measured in the presence of 0.1 mol L^{-1} sulphuric acid solution. The value of the absorbance of the blank experiment is in the range of 0.080 – 0.082.

Slope of the calibration curve is a = 300000 L mol^{-1}cm^{-1} and it exceeds 3ε(R^+). This is most likely the result of extraction of the total volume of electrolyzed solution into a smaller volume of solvent.

This method can be used for the determination of iodide in the concentration range of 3×10^{-7} - 3×10^{-6} mol L^{-1} with a limit of detection 5×10^{-8} mol L^{-1}.

Characteristics of the selectivity of the determination of iodide-ions in the presence of interfering ions are given in Table 1.

It is shown that chlorate, nitrate and chloride ions do not interfere with determination of iodide, but that bromide, thiocyanate, perchlorate, oxalate, sulphate and sulphite ions do interfere with determination of iodide at the concentrations given in the table. Values were estimated according to the formula:

$$C_{\min}, mol\ L^{-1} = \frac{S_A}{\varepsilon_{cond}}, \quad (4)$$

where S_A = 0.005.

Table 1. Characteristics of the selectivity of the determination of iodide.

Interfering anion	ε_{cond}	C_{min}, mol L^{-1}	$K^{sel}_{I_3^-/Anion}$
I^-	88	5.7×10^{-5}	3.4×10^{3}
Br^-	2.4	2.1×10^{-3}	1.25×10^{5}
SCN^-	315	1.6×10^{-5}	952
$C_2O_4^{2-}$	0.9	5.8×10^{-3}	3.3×10^{5}
ClO_4^-	20.6	2.4×10^{-4}	1.5×10^{4}
SO_3^{2-}	9.8	5.0×10^{-4}	3.1×10^{4}
SO_4^{2-}	0.81	6.3×10^{-3}	3.75×10^{5}

Iodide forms ionic associates with brilliant green partly extracted into carbon tetrachloride. As mentioned in the experimental section, combined extract is diluted to the mark with organic phase after the third extraction. This method allows quantitative extraction of iodide-ion (blank extraction).

The described method for determination of iodide concentration was tested on two real samples: NaCl and spring water. Obtained results are given in the Table 2.

The proposed method allows the determination of iodide with high sensitivity and satisfactory precision. Relative standard deviation is 1–2%. Standard addition confirms the accuracy of the obtained results. Spectrophotometric determination of iodide was carried out in NaCl according to a more established method [7] for comparison. In the analysis, weight of sample and volume of solution were the same as in the proposed method. The molar extinction coefficient of I_3^- in the known method at λ=351 nm is 3 times less than the molar extinction coefficient in the proposed method. Comparison of the results indicates that analytical signal increases in the proposed method versus the known method [7]. Error of the determination by proposed method decreases.

4. Conclusions

The proposed method has advantages in comparison with the spectrophotometric method using brilliant green [8]. These advantages are connected with the strict

Table 2. Analysis of real samples (ω – mass fraction, s_ω - standard deviation of mass fraction).

Object of analysis	Added, ppm	Found, ppm			
	$\omega_{(I^-)}$	$\omega_{(I^-)total}$	$\omega_{(I^-)}$	ω_{av} (I^-)	$s_{\omega(I^-)}$
NaCl, Artyomovsk, Donetsk region, Ukraine	*Results by proposed method*				
	-	1.32	1.32		
	-	1.35	1.35	1.33	0.02
	-	1.33	1.33		
	1.03	2.35	1.32		
	1.03	2.32	1.29	1.30	0.01
	1.03	2.33	1.3		
	Results by known method [7]				
		1.36	1.36		
		1.33	1.33	1.36	0.03
		1.38	1.38		
Spring water, Kharkov, Ukraine	-	0.052	0.052		
	-	0.051	0.051	0.052	0.001
	-	0.052	0.052		
	0.057	0.109	0.052		
	0.057	0.107	0.05	0.051	0.001
	0.057	0.109	0.052		

stoichiometry of yield and stability of analytical form in time, and with great selectivity. In comparison with the flow injection spectrophotometric method [7], the proposed method is characterized by:
- higher sensitivity of determination;
- absence of excess chemical oxidizing agent;
- exclusion of influence of impurities absorbing in near UV-spectral region.

Combination of electrochemical oxidation and photometric determination allows a stoichiometric multiplication of the quantity of analyte and, as a result, increased sensitivity of determination. The selectivity coefficient, estimated from the ratio of sensitivities of determination, increases as well.

References

[1] V. Lucia, A.M. Campos, Marine Chemistry 57, 107 (1997)
[2] Y. Zhu, J. Guan, L. Cao, J. Hao, Talanta 80, 1234 (2010)
[3] T.K. Malongo, S. Patris, P. Macours, F. Cotton, J. Nsangu, J.-M. Kauffmann, Talanta 76, 540 (2008)
[4] B. Rebary, P. Paul, P.K. Ghosh, Food Chemistry 123, 529 (2010)
[5] O.M. Trokhimenko, V.N. Zaitsev, J. Anal. Chem. 59(5), 551 (2004)
[6] Z.O. Tesfaldet, J.F. van Staden, R.I. Stefan, Talanta 64, 1213 (2004)
[7] Z. Xie, J. Zhao, Talanta 63, 339 (2004)
[8] S.B. Niazi, M. Mozammil, Analytica Chimica Acta 115, 252 (1991)
[9] A.V. Drozd, V.M. Belik, Uzhgorod University Bulletin Chemical Series 9, 102 (2003) (in Ukrainian)
[10] A.V. Drozd, T.S. Tishakova, Kharkov University Bulletin. Chemical Series. 895(18), 101 (2010) (in Russian)