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Sequential-Constant Current Coulometric Determination of Sulfite-Thiosulfate and/or Sulfite-Ascorbic Acid in a Solution

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A coulometric titration method is introduced for sequential determination of sulfite, thiosulfate and ascorbic acid in sulfite-thiosulfate or sulfite-ascorbic acid couple in a solution. Formaldehyde or acetaldehyde can be used to mask the sulfite component. Two sequential measurements of coulometric time, one for the both components in the mixture and one for the sample solution in which sulfite is masked by formaldehyde can be used to determine the concentrations of sulfite-thiosulfate and/or sulfite-ascorbic acid couples. Relative standard deviations (RSD) of all measurements lie in the range of 0.1-4 % . The effect of different parameters such as pH, concentration of reagents, ionic strength and effect of interferences are studied. The proposed method can determine 5.0×10^{-4}–1.0×10^{-6} mol of thiosulfate and also 6.0×10^{-5} - 5.0×10^{-7} mol of ascorbic acid in a sample solution in the presence of 1.3×10^{-5}–4.4×10^{-7} mol of sulfite. The current efficiency of the method is estimated to be ≥ 98.0 %. The proposed method can be used for the determination of sulfite-thiosulphate or sulfite-ascorbic acid in the presence of real sample matrixes (*e.g.*, mineral waters and vitamin C tablets) with good accuracy and precision.

Key Words: Coulometric titration, Sulfite, Thiosulfate, Ascorbic acid.

INTRODUCTION

The use of electrochemical methods in trace analysis is well documented. Their role and importance especially in routine analysis have been improved in recent decades due to the advent of powerful computerized electroanalytical techniques. Coulometric titration using electrogenerated I_2 has been used long in the determination of ascorbic acid, thiosulfates, sulfite and also iodination of some drug compounds[1-7]. This approach allows more precise analytical results than the usual iodometric titration owing to I_2 electrogeneration directly in the coulometric cell and better control over the regeneration rate. Moreover, the determination is rapid

because no titrant preparation, standardization and storage are required. Also the possibility of carrying out a few successive titrations without changing the supporting electrolyte and the simplicity of calculating the amount of the analyte is achieved.

A major weakness, common to titrimetric methods, is the lack of selectivity and also analyte detection[8]. Simultaneous determination of analytes and finding more sensitive methods of end-point detection remain an active research area in coulometric titrations[9-13]. Computers and electronics will play an increasing role in this effort[14].

The present paper aims at establishing a method for sequential determination (two stage coulometric titration) of two components, sulfite-thiosulfate and sulfite-ascorbic acid mixtures in a solution. The I_2-starch complex colour formation is used as end-point detecting system.

EXPERIMENTAL

The measurements were carried out on a JC 100 model coulometer equipped with two 7 × 4 mm Pt electrodes. The instrument can work at constant current selected in the range of 1-50 mA, (constant currents of 1-3 mA were used troughout). A E649 model Meterohm stirrer was used and measurements of pH were made using a Meterohm 625 pH-meter. A FORTUNA autosampler (± 0.05 mL) was used for taking small precise volumes of different samples.

Sodium sulfite, sodium thiosulfate, ascorbic acid, formaldehyde, potassium iodide and other chemicals were purchased from Merck. All other chemicals were of analytical reagent grade. All solutions were prepared with doubly distilled deionized water.

Stock solutions of sodium sulfite, 8.7×10^{-3} M; sodium thiosulfate, 1.02×10^{-2} M; ascorbic acid, 9.9×10^{-3} M; (all were standardized with standard iodine solution) KI, 0.5 M were prepared by dissolving appropriate amount of each compound in water. Solutions of different salts, 0.1 M were also prepared.

Procedure: 0.2 -2 mL of sample (sulfite, thiosulfate, ascorbic acid, sulfite-thiosulfate or sulfite-ascorbic acid) solution, 5 mL of 0.5 M of potassium iodide, 5 mL of bicarbonate buffer (pH = 8.5) and 4 drops starch indicator solutions were added to a 150 mL beaker. The solution was diluted to 75 mL with distilled water and then titrated with electrically generated I_2 titrant under selected constant current (3 mA) passed between two flat platinum electrodes. The end-point of the titration was distinguished by blue colour of iodine-starch complex.

The concentrations of analytes in the sample solution were obtained by the following equation[15],

$$n = it/zF \quad (1)$$

where 'n' is the number of moles of any component in the sample solution, 't' is the total transition time (the coulometric titration time for one pre-selected constant current chronopotentiometric run), 'z' is the number of electrons for the component under study and 'F' is the Faraday constant.

RESULTS AND DISCUSSION

A few articles about simultaneous and sequential coulometric determination of chemical species in a solution mixture are reported in literature[16-19].

In preliminary experiments, it is noted that both formaldehyde and acetaldehyde can be used as good masking agents for sulfite[20] and the second component of the solution mixture can be titrated with good accuracy and efficiency. It must be mentioned that both formaldehyde and acetaldehyde have no effect on the coulometric titration time. The results are shown in Table-1.

TABLE-1
EFFECT OF FORMALDEHYDE AND ACETALDEHYDE AS MASKING AGENTS FOR SULFITE IN THE COULOMETRIC TITRATION OF SULFITE-THIOSULFATE AND SULFITE-ASCORBIC ACID SOLUTIONS

Sample type	Titration time		Relative error (%)
	Theoretical	Experimental	
Blank[a]	0.0	4.5	–
Blank + formaldehyde[b]	0.0	4.6	–
Blank + acetaldehyde	0.0	4.7	–
Sulfite (4.4×10^{-6} mol)	279.9	278	-0.7
Sulfite (4.4×10^{-6} mol) + formaldehyde	–	4.6	–
Thiosulfate (1.02×10^{-5} mol)	326.8	327	+0.1
Thiosulfate (1.02×10^{-5} mol) + formaldehyde	326.8	327	+0.1
Ascorbic acid (4.45×10^{-6} mol)	319.0	321	+0.6
Ascorbic acid (4.45×10^{-6} mol) + formaldehyde	319.0	321	+0.6
Sulfite (4.4×10^{-6} mol) + Thiosulfate (1.02×10^{-5} mol) + formaldehyde	326.8	327	+0.1
Sulfite (4.4×10^{-6} mol) + Ascorbic acid (4.45×10^{-6} mol) + formaldehyde	319.0	321	+0.6

[a]Blank solution: 5 mL of 0.5 M of KI, 5 mL of buffer solution of pH = 5 and 4 drops of starch solution.
[b]3 mL of 0.1 M of formaldehyde is used.

The effect of pH of the test solution on the coulometric titration time of sulfite-thiosulfate and sulfite-ascorbic acid mixtures was studied and the results are shown in Table-2. It is observed that the lowest relative error (maximum current efficiency) is obtained at pH = 8.5 (bicarbonate buffer solution) for the test solution. The relation between pH of the test solution and per cent relative error of coulometric titration time of sulfite-thiosulfate is shown in Fig. 1. Bicarbonate buffer solution was used as optimum buffer throughout the experimental studies.

TABLE-2
EFFECT OF DIFFERENT BUFFERS ON THE COULOMETRIC TITRATION TIME FOR DIFFERENT MIXED SOLUTION

Sample	pH of buffer	Theoretical time (s)	Experimental time (s)	Relative error (%)
Sulfite-thiosulfate mixture	3.0	606.5	591.1	-5.5
	4.0		593.3	-2.2
	5.0		601.2	-0.9
	6.0		598.8	-1.3
	7.0		593.4	-2.2
	8.0		590.7	-1.6
	8.5		599.9	-1.0
	9.0		585.6	-2.9
	10.0		562.3	-10.4
	11.0		–	-15.3
Sulfite-ascorbic acid mixture	3.0	599.0	579.0	-3.3
	4.0		583.5	-2.6
	5.0		595.1	-0.7
	6.0		592.3	-1.1
	7.0		592.0	-1.2
	8.0		590.1	-1.5
	8.5		596.0	-0.5
	9.0		585.0	-2.3
	10.0		580.3	-9.1
	11.0		575.4	-14.0

The total titration time required for analysis depends on the concentration of components in the sample solution. For low concentrated solutions, small constant current values as low as 1 mA are used. By using small constant current trace analysis can be performed with small relative errors (< 2 %).

In order to study the effect of various species on the determination of sulfite-thiosulfate and sulfite-ascorbic acid system, a fixed amount of mixture components (2×10^{-5}–1×10^{-6} M of each component) was taken

with different amounts of foreign species and the recommended procedure was followed. A relative error of ± 2 % was considered tolerable. The results showed that ions or molecules such as Pb^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+} do interfere at concentrations more than 0.02 M. This effect may be due to complex formation of sulfite and thiosulfate ions with these cations[21].

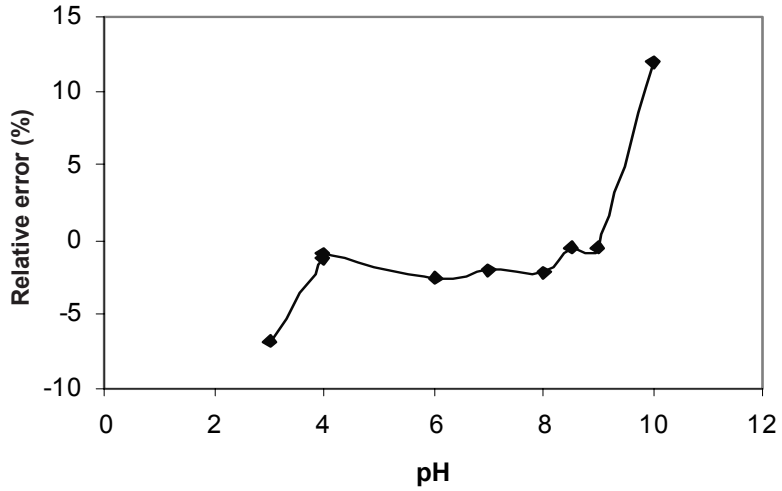

Fig. 1. Effect of pH of the test solution on the relative error of coulometric titration time of sulfite-thiosulfate mixture

From the results in Table-1, it is obvious that the proposed setup and method give good current efficiency and also very good recovery values (accuracy) and RSD for sequential trace analysis of sulfite-thiosulfate and sulfite-ascorbic acid system in different sample solutions. In order to compare the results of proposed method with another sensitive method, the square wave voltammetric method (SWV) was selected. The concentration of each component in the sample solution was determined by using the voltammogram with maximum peak current and using standard calibration graph obtained for each component (sulfite, thiosulphate and ascorbic acid) by SW voltammetric method. The results show good agreement between the methods but the SWV method results show larger RSD (less precise) values with respect to the proposed method.

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