COULOMETRIC TITRATION OF PHOSPHITES, IN THE PRESENCE OF HYPOPHOSPHITES, WITH ELECTRICALLY GENERATED BROMINE

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A method has been developed for the coulometric titration of phosphite, in the presence of hypophosphite, with electrically generated bromine. Optimum conditions were established for bromine generation (> 0.5 M KBr, 0.5 to 4 mA/cm^2, pH 6.6 ± 0.3, t = 50°C). The sensitivity of the method was 0.4 μg/ml.

Phosphites, in mixtures with hypophosphites, can be determined by selective oxidation, in a neutral or weakly alkaline medium, with excess of iodine or bromine. The unreacted excess of halogen is titrated with an appropriate reducing agent [1, 2].

Phosphite can be determined iodometrically in the presence of a hundred times as much hypophosphite, but the reaction of phosphite with iodine is slow (> 20 min). Manchot and Steinhauser found that bromine reacted rapidly with phosphite in a weakly alkaline medium, but that hypophosphite was also partially oxidized [2]. It was not possible to determine < 0.05 mg/ml of H_3PO_3 by this method with adequate precision, and it was undesirable to use bromine as the titrant.

We have developed a coulometric method for determining microquantities of phosphite, based on its direct titration with electrically generated bromine. The stock solutions used were 0.0945 M H_3PO_3, 0.4 M NaH_2PO_2, 4 M KBr, 0.5 M NaH_2PO_4, 0.5 M Na_2HPO_4. Solutions of other concentrations were obtained by appropriate dilution. The titrations were carried out in a coulometer [3] by the constant current method. The electrodes were platinum plates (1 × 1 cm). These were treated with concentrated nitric acid, and then with distilled water, before each test. The end point of the titration was indicated potentiometrically, by means of an LPU-01 electronic potentiometer.

Experiments showed that the interaction of bromine with phosphite ions was slow at room temperature, in the pH range 6 to 7. It was accordingly necessary, towards the end of the titration, to interrupt the generation after 5 to 10 sec and wait for about a minute. At pH ≥ 8 or ≤ 5 the reaction was so slow that direct determination of phosphite was practically impossible. In the first case, this was probably associated with the generation of BrO^-, which reacted

TABLE 1. Percentage Efficiency of Bromine Generation by Current in a Phosphate Buffer Medium at Various Concentrations of Potassium Bromide in the Solution

Current density, mA/cm^2	pH = 6.6				pH = 5.0		pH = 8.0	
	0.2 M	0.5 M	0.8 M	1.6 M	0.5 M	1.6 M	0.5 M	1.6 M
0.5	99.5	99.7	99.8	99.8	99.8	99.8	99.7	99.8
1.0	96.6	99.8	99.9	99.9	99.9	99.9	99.8	99.9
2.0	96.5	99.9	99.9	100.0	99.9	100.0	99.9	99.9
3.0	97.2	99.9	100.0	100.0	100.0	100.0	99.9	100.0
4.0	97.5	99.9	100.0	100.0	100.0	100.0	99.9	100.0

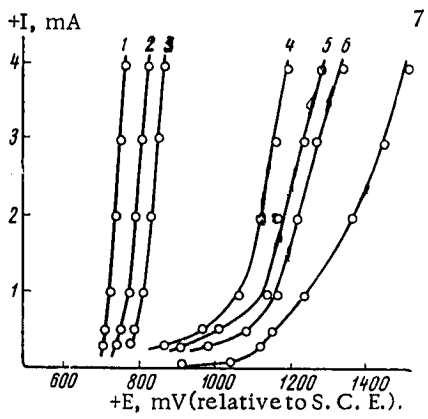
TABLE 2. Results for the Coulometric Determination of Phosphite Ion with Electrically Generated Bromine (n = 4, α = 0.95)

Current, mA	Taken, μg	Found, μg
1.0	19	19±2
	28	26±4
	38	39±2
3.0	77	77±4
	154	149±9
	308	311±9
	461	469±10

TABLE 3. Results for the Coulometric Titration of H_3PO_3 with Electrically Generated Bromine in the Presence of Various Amounts of Sodium Hypophosphite (0.5 M KBr, n = 3, α = 0.95).

Added		Weight ratio HPO_2^-: HPO_3^{2-}	H_3PO_3 found, μg	
H_3PO_3 μg	NaH_2PO_2 mg		x_i	$\bar{x}$
19*	0.7	28:1	21; 18; 21	20±4
	1.4	55:1	21; 17; 20	19±5
	2.1	83:1	18; 20; 18	19±3
	3.5	138:1	19; 20; 16	18±5
	4.5	178:1	20; 20; 23	21±4
	7.0	277:1	21; 21; 20	21±1
77*	0.7	7:1	78; 78; 75	77±4
	1.4	14:1	78; 80; 76	78±5
	2.1	21:1	78; 76; 79	78±4
	3.5	34:1	80; 72; 79	77±10
	4.5	44:1	78; 79; 82	80±5
	7.0	136:1	82; 80; 82	81±3
	14.0	68:1	83; 88; 83	85±7
483†	0.7	1:1	479; 484; 486	483±8
	1.4	2:1	504; 481; 484	490±31
	2.1	3:1	482; 492; 486	487±12
	3.5	5:1	502; 476; 494	491±31
	4.5	7:1	515; 494; 496	502±28
	7.0	10:1	515; 504; 516	512±16

* Current 1 mA
† Current 4 mA



Anodic polarization curves for the buffer solution 0.3 M NaH_2PO_4 and 0.2 M Na_2HPO_4) (curve 7), and for the buffer solution with KBr at concentrations 1.6, 0.8, 0.5, 0.2, 0.1, and 0.05 M (curves 1 to 6 respectively).

more slowly than bromine with phosphite. In the second case, the oxidation-reduction reaction between Br_2 and phosphite was retarded by the high acidity of the medium.

Increasing the temperature to 50°C, in the presence of a phosphate buffer to control the pH at 6.6 ± 0.3, enabled us to obtain a marked jump in potential at the end point with continuous generation of bromine, but not if the pH was outside the above limits.

We investigated the curves relating I and E for a phosphate buffer solution and for the same buffer containing 0.05 to 1.6 M KBr, all at 50°C, with a platinum working electrode. It was found that the efficiency of electrical generation of bromine increased with increasing potassium bromide concentration, since the anodic polarization curve shifted to a less positive region of potential, as compared with the curve for the buffer only (see figure). With the pH between 5 and 8, and with KBr concentration greater than 0.5 M, the generation efficiency was 99 to 100% at the current densities investigated (Table 1).

On the basis of these results we established the optimum conditions for the coulometric titration of phosphites with electrically generated bromine: KBr ≥ 0.5 M, phosphate buffer giving pH = 6.6 ± 0.3, t = 50°C, V = 50 ml.

Before each test, the buffer solution was oxidized to the potential at the end point of the titration, namely 0.62 V (relative to S.C.E.).

Table 2 shows some results for the determination of phosphite in known amounts of H_3PO_3. The sensitivity of the method was 0.4 μg/ml (about 5×10^{-6} M).

We investigated the effects of various amounts of hypophosphite on the results for the coulometric determination of phosphite (Table 3).

These experiments showed that the effect of hypophosphite depended, not on the weight ratio of the components, but on the absolute amount of hypophosphite present. For equal quantities of hypophosphite, there was a constant relative error which depended on the phosphite content. It is therefore recommended that the method should be used either for the determination of small amounts of phosphite (≤ 100 μg) in cases when the phosphite content does not exceed 4 to 5 mg in 50 ml of solution to be analyzed, or else with prefatory dilution of the test solution to create the necessary optimum conditions.

LITERATURE CITED

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