THE DETERMINATION OF HYPOPHOSPHITE AS AN IMPURITY IN PHOSPHITES

(UDC 543.7)

V. M. Masalovich, P. K. Agasyan, and E. R. Nikolaeva

Urals Scientific Research Chemical Institute and Moscow State University

Translated from Zavodskaya Laboratoriya, Vol. 32, No. 7,
pp. 790-792, July, 1966

The optimum conditions have been established for the quantitative oxidation of hypophosphite by iron (III). A systematic positive error in the determination of hypophosphite was obtained in the presence of more than $2.08 \cdot 10^{-3}$ mole/liter of phosphite, due to partial oxidation of the latter. A method is proposed for the determination of hypophosphite in sludges, in the presence of phosphites and phosphates, with the introduction of an appropriate correction found from a calibration curve.

The method used for determination of hypophosphite in the presence of phosphites was based on oxidation of $H_2PO_2^-$ with a boiling solution of an iron (III) salt, and titration of the Fe(II) ions formed with a solution of cerium (IV) sulfate [1], or sodium vanadate [2]. However, when we checked this method, the results were low or in the presence of appreciable amounts of phosphite were high and not fully reproducible. In the present work we established the conditions for the precise quantitative oxidation and determination of hypophosphite with an iron (III) salt.

We showed experimentally that the optimum conditions were as follows: Acidity of medium 1 to 1.4 M in HCl; duration of boiling 20 min; reagent ratios $^1/_2\,[H_3PO_2] \leq 6\,[Fe(III)] \geq [H_3PO_3]$. If the ratio of the mole concentrations of H_3PO_3 and Fe(III) exceeded the above limit, then oxidation of hypophosphite under the other conditions stated was incomplete (Fig. 1). It was clear that the Fe(III) was complexed in the presence of a large excess of phosphite ions [3].

TABLE 1. Results for the Determination of Hypophosphite in Pure Solutions (Boiling Time 20 min)

NaH_2PO_2 added mg	Sastri and Kalidas method [1] × (n = 3)	Verbitskaya and Romanova method [2] (n = 5)	Proposed method (n = 5)	S_1^2 for column 4	d_1^2 for columns 1 and 4
28.69	25.23±0.21	27.33±0.42	28.63	0.0036	0.0169
21.52	16.39±1.48	19.85±0.39	21.61	0.0120	0.0324
14.35	11.48±0.58	12.49±0.86	14.29	0.0278	0.0144
7.17	3.14±0.41	4.00±0.33	7.16	0.0040	0.0004
5.74	2.18±0.58	2.52±0.45	5.79	0.0053	0.0100
4.30	1.37±0.14	1.86±0.20	4.31	0.0112	0.0004
2.87	1.24±0.11	1.20±0.16	2.87	0.0045	0.0001

TABLE 2. Results for the Determination of Hypophosphite in the Presence of Phosphite

Added		NaH_2PO_2 found, mg		S_1^2 for column 4	d_1^2 for columns 2 and 4
$CaHPO_3$, g	NaH_2PO_2, mg	Without correction (n=5)	With correction (n = 5)		
	21.5	25.9	21.8	0.04	0.09
0.4	14.4	18.0	13.9	0.04	0.25
	2.9	6.7	2.6	0.01	0.09
	21.5	24.6	21.8	0.05	0.09
0.28	7.2	10.0	7.2	0.008	0.00
	2.9	5.6	2.8	0.005	0.01
	21.5	23.0	21.3	0.04	0.04
0.18	7.2	8.9	7.2	0.008	0.00
	2.9	4.5	2.8	0.005	0.01
	1.5	3.1	1.4	0.003	0.01

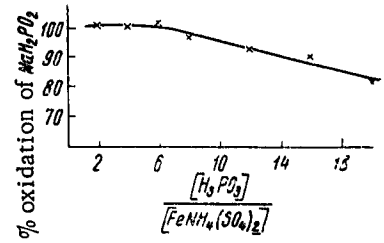

Fig. 1. The effect of phosphorous acid on the extent of oxidation of hypophosphite.

TABLE 3. Results of the Analysis of Sludges for Phosphite, Hypophosphite, Phosphate, and Total Phosphorus (Expressed as % P)

$CaHPO_3$ (n = 4), S_{rep} = 0.02	$Ca(H_2PO_2)_2$ (n = 3) S_{rep} = 0.001	$CaHPO_4$ (n = 3), S_{rep} = 0.003	ΣP for components S_{rep} = 0.02	ΣP by gravimetric method (n = 4) S_{rep} = 0.05	d_i^2
16.93	0.08	0.31	17.32	17.24	0.0064
16.15	0.06	0.23	16.44	16.39	0.0025
14.61	0.20	0.51	15.32	15.59	0.0729
15.54	0.23	0.45	16.22	16.11	0.0121
14.75	0.23	0.33	15.31	15.14	0.0289
16.48	0.11	0.10	16.69	16.61	0.0064
17.56	0.34	0.21	18.11	18.13	0.0004

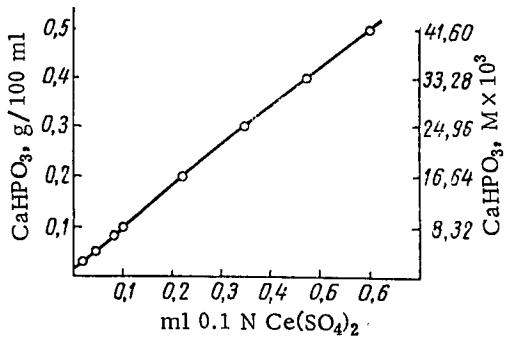

Fig. 2. The relation between $CaHPO_3$ content and consumption of titrant.

Table 1 compares the results for the analysis of a hypophosphite solution, containing 1.434 mg NaH_2PO_4 per ml (checked gravimetrically [4] and volumetrically*), under the conditions proposed by us and those suggested previously [1, 2].

Statistical treatment of the results, obtained by our method, showed that the dispersions were uniform for the samples, since $G_{calc} = 0.41 = 0.41$, and $G_{0.05}(4.7) = 0.43$. This made it possible to calculate the total error of the reproducibility ($S_{reproducibility} = 0.047$) and to check the hypothesis by the t criterion: $t_{calc} = 0.10$, but $t_{0.05}(6) = 2.45$, so that the difference between the amounts of NaH_2PO_2 added and found were inconsiderable [5].

It was found that there was also appreciable oxidation of phosphite by Fe(III) ions when $C_{CaHPO_3} > 0.25$ g/liter ($2.08 \cdot 10^{-3}$ mole/liter). However, the observed linear relation between the phosphite content of the solution and the consumption of titrant (Fig. 2) made it possible to apply an appropriate correction to the results for the determination of hypophosphite as an impurity in phosphite. Table 2 shows that satisfactory results were obtained when this correction was applied.

Statistical treatment of the data in the table showed: $G_{calc} = 0.24$; $G_{0.05}(4.10) = 0.33$; $S_{reproducibility} = 0.14$; $t_{calc} = 0.90$; $t_{0.05}(9) = 2.26$.

A method was developed for the determination of $Ca(H_2PO_2)_2$ in sludges from hypophosphite production.

A 0.5 g sample of sludge dried at 105°C, weighed to a precision of 0.0002 g, or 0.8 g of undried sludge, was placed in a 250 mm conical beaker, with a ground neck fitted to a reflux condenser. The sample was treated with 30 ml of 4 N HCl and 25 ml of 0.2 N $NH_4Fe(SO_4)_2$ (or $FeCl_3$) in 0.8 N hydrochloric acid and made up to 100 ml with distilled water. The solution was boiled for 20 min, cooled, and titrated with standard cerium sulfate solution (0.05 or 0.01 N, depending of the hypophosphite content of the sludge), in the presence of two drops of ferroin. A blank test, without any sludge, was carried out at the same time, under the same conditions.

The content of hypophosphite as $Ca(H_2PO_2)_2$ in the sludge was calculated from the equation:

$$\%\ Ca(H_2PO_2)_2 = \frac{[(V - V_1)N - 0.1V_2]E \cdot 100}{q \cdot 1000},$$

* All-Union State Standard 200-41. Sodium hypophosphites.

where N is the normality of the titrant; E is the equivalent weight of $Ca(H_2PO_2)_2$ = 42.51; q is the weight of the sludge sample, g; V and V_1 are the volumes of standard cerium (IV) solution used for titration of the sample and the blank; V_2 is the volume of titrant consumed in the partial oxidation of the $CaHPO_3$, with allowance for the first 0.025 g of $CaHPO_3$. The correction V_2 was found from a calibration curve. We found that it was equal to $(X-0.025) \times 1.263$ ml of 0.1 N titrant, where X is the content of $CaHPO_3$ in the weight of sample taken, as determined on a separate sample by our previously published method [6].

Table 3 shows some results for the analysis of sludges for their phosphorus-containing components. Phosphates were determined photometrically [7], phosphites iodometrically [6], and hypophosphites by the method described above. The total phosphorus contents, obtained by summation, differed little from the amount of phosphate determined gravimetrically [4].

Thus, our proposed method was shown to be quite satisfactory for the determination of hypophosphite in the three-component system investigated.

LITERATURE CITED

1. M. Sastri and C. Kalidas, Recueil trans. Chim., 75, 9-11, 1122 (1956).
2. T. D. Verbitskaya and N. K. Romanova, Zavodskaya laboratoriya, 25, 7 (1960).
3. V. M. Masalovich and others. Zhurnal neorganicheskoi khimii, 11 (2), 272 (1966).
4. L. Wolf and W. Jung, Z. anorg. allg. Chem., 201, 353 (1931).
5. V. V. Nalimov, The Use of Mathematical Statistics in the Analysis of Materials, [in Russian] Fizmatgiz (1960).
6. V. M. Masalovich, E. R. Nikolaeva, and P. K. Agasyan, Zavodskaya laboratoriya, 31, 12 (1965).
7. A. P. Dunaeva, Zhurnal prikladnoi khimii, 3, 1-3, 105 (1930).