

Direct Determination of Phosphite in Fertilizers by Amperometric Titration

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Amperometric titration using two Pt microelectrodes for the determination of phosphite in fertilizers based on the oxidation of analyte by iodine is proposed. The influence of pH, buffer composition, temperature, and foreign species on the end point and titration time was investigated. For titrations carried out at 70 °C using the pH 6.8 phosphate buffer, samples containing ca. 0.4% (m/v) P₂O₅ could be titrated with 0.050 mol L⁻¹ iodine titrant, and the end point determined by extrapolating the linear portions of the plot to their intersection coincided with the end point identified by spectrophotometry. Accuracy was checked for phosphite determination in five fertilizer samples. Results were in agreement at the 95% confidence level (paired *t* test) with spectrophotometry. Recoveries of phosphite added to fertilizer samples ranged from 97% to 102% regardless of the amount of spiking in several determinations. The relative standard deviation (*n* = 10) was 1.0% for a diluted sample containing 0.050 mol L⁻¹ Na₂HPO₃.

KEYWORDS: Phosphite; direct determination; titrimetry; iodine

INTRODUCTION

Phosphorus is an important element to plant nutrition and is determined routinely in samples of agricultural interest (1). Phosphate-based fertilizers are well-known as sources of phosphorus to soil and crops (2). More recently, phosphite-based compounds have been used alternatively to phosphate because phosphite species act as a fungicide and move more rapidly than phosphate in the soil, reducing the phenomena of phosphorus fixation (3). Efficient methods for phosphite determination are relevant for production units to monitor the raw materials, the production process, and the quality of the final product and to provide capability for laboratories dedicated to chemical analysis.

Among analytical techniques usually employed for phosphorus determination are atomic absorption spectrometry—AAS (4), inductively coupled plasma optical emission spectrometry—ICP OES (5), gravimetry (6, 7), spectrophotometry (8–10), amperometry (11, 12), and titrimetry (13).

The AAS and ICP OES techniques are characterized by relative specificity and sensitivity but determine total phosphorus. Phosphite can be determined gravimetrically by the magnesium pyrophosphate or Hg₂Cl_{2(s)} formation (6, 7). The former method requires a previous oxidation of phosphite to phosphate (6), and the last one generates large amounts of mercury-based residue (7), counteracting the tendency toward clean chemistry (14). Regarding spectrophotometry, all methods available for phosphate (8) also can be used for phosphite. Nevertheless, a suitable sample pretreatment to convert phos-

phite to phosphate is required. A flow-injection spectrophotometric procedure already had been proposed for phosphite determination using the molybdenum blue method (9). The automated spectrophotometric flow injection analysis system with online sample treatment allowed the sequential determination of phosphite and phosphate (10). Electrochemical studies on the behavior of phosphorous acid on palladium surfaces showed a catalytic effect for oxidation of phosphite to phosphate (15). A palladium film on a platinum electrode has been proposed in a manual voltammetry procedure for phosphite, but the poor adherence of the palladium film at the electrode surface impaired its application to real samples (11). This cumbersome was circumvented after development of a new sensor based on a graphite electrode modified with a palladium–platinum–palladium film by a sequential cathodic deposition of palladium, platinum, and palladium on a graphite electrode (12). The determination of phosphite by classical titrimetry using iodine as titrant was proposed recently (13), but the identification of the end point, manifested by the appearance of faint yellow, was considered the main drawback of the method. This shortcoming could be avoided if a simple and low cost sensor were used to monitor the reaction between phosphite and iodine.

This study reports on the use of two platinum microelectrodes to determine phosphite by amperometric titration based on the oxidation of analyte with iodine titrant. The performance of the proposed procedure was checked after analyzing real liquid fertilizer samples.

MATERIALS AND METHODS

Reagents, Analytical Solutions, and Samples. High purity water (resistivity 18.2 MΩ cm) obtained using a Millipore Rios 5 reverse

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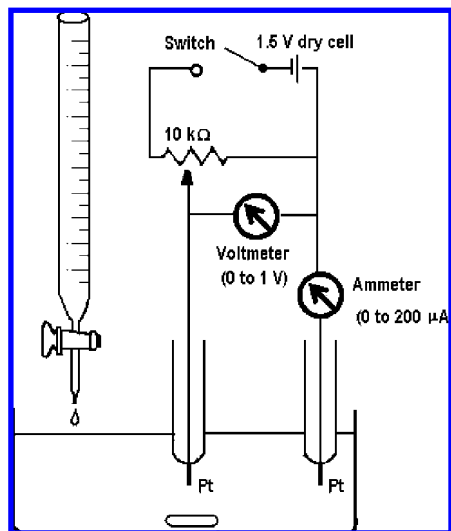


Figure 1. Assembly for the amperometric titration system proposed for phosphite determination.

osmosis and a Millipore Milli-Q academic deionizer (Millipore, Bedford, MA, USA) system was used throughout to prepare all solutions.

Iodine solution ($0.050 \text{ mol L}^{-1} \text{ I}_2$) was prepared by dissolving 10 g of KI (Mallinckrodt, Xalostoc, Mexico) in about 20 mL of water, followed by 6.3450 g of I_2 (Spectrum, Gardena, USA), and making the volume up to 500 mL with water. This solution was standardized with a $0.050 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ solution and stored in an amber glass flask. The optimum titrant and analyte concentrations were adapted from the determination of phosphite by classical titrimetry using iodine as titrant (13).

The $0.050 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ solution was prepared by dissolving 6.2048 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (Spectrum) in about 200 mL of water, and making the volume up to 500 mL with water. This solution was standardized with a $0.0067 \text{ mol L}^{-1} \text{ K}_2\text{Cr}_2\text{O}_7$ solution.

The $0.0067 \text{ mol L}^{-1} \text{ K}_2\text{Cr}_2\text{O}_7$ solution was prepared by dissolving 0.4928 g of $\text{K}_2\text{Cr}_2\text{O}_7$ (Mallinckrodt) dried at 140°C for 2 h, and making the volume up to 250 mL with water.

Phosphite stock standard solution ($0.050 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_3$) was prepared by dissolving 5.4010 g of $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ (Riedel-de Haën, Germany) in water and making the volume up to 500 mL with water.

Fertilizer samples containing potassium phosphite as a source of phosphorus were supplied by Samaritá Industry & Trading Ltd. (Artur Nogueira, Brazil). The samples were diluted (1:50 or 1:100 m/v) in water.

Amperometric Titration System. The amperometric titration system depicted in **Figure 1** comprised a Mesco DM 890 multimeter (200 mA sensibility), a homemade potentiostat (16), a MA 259 controlled temperature magnetic stirrer (Marconi, Brazil), and two short platinum wires ($30 \text{ mm} \times 0.3 \text{ mm}$) with a potential difference between them of 100 mV. A multimeter was first connected in parallel to the potentiostat for the potential settlement and then was connected in serial mode to measure the current in the system.

Procedure. The influence of the main parameters on the end point and titration time was evaluated with the system depicted in **Figure 1** by titrating aliquots of 10.00 mL of $0.050 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_3$ solution + 25.0 mL of buffer solution ($\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ and citric acid/ Na_2HPO_4) with $0.050 \text{ mol L}^{-1} \text{ I}_2$ solution as titrant at different pH (3.0, 4.0, 5.0, 5.8, 6.0, 6.8, 7.0, 7.8) and temperature (25° , 45° , and 70°C). The influence of the voltage difference between Pt microelectrodes on the current and end point determination was studied in the 25–200 mV range. A current was plotted against volume of titrant, and the end point was determined by extrapolating the linear portions of the plots to their intersection points.

The influence of the ions usually present in liquid fertilizers was evaluated by titrating 10.00 mL of solution of $0.050 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_3$ solution + 25.0 mL of phosphate buffer (pH 6, 8) containing $150 \text{ mg L}^{-1} \text{ Mg}^{2+}$, Mn^{2+} , $1000 \text{ mg L}^{-1} \text{ Ca}^{2+}$, $200 \text{ mg L}^{-1} \text{ Zn}^{2+}$, 30 mg L^{-1}

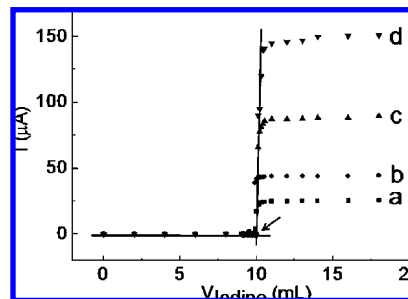


Figure 2. Typical plots of current against volume of iodine titrant added for phosphite determination. Data refer to 10.00 mL of $0.050 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_3$ solution + 25.0 mL of buffer solution ($\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$, pH = 6.8) titrated with $0.050 \text{ mol L}^{-1} \text{ I}_2$ solution at 70°C applying a 25 mV (a), 50 mV (b), 100 mV (c), or 200 mV (d) voltage difference between Pt electrodes. The black arrow indicates the end point.

Cu^{2+} , $10000 \text{ mg L}^{-1} \text{ Cl}^-$, CO_3^{2-} , SO_4^{2-} , and NO_3^- , with $0.050 \text{ mol L}^{-1} \text{ I}_2$ solution as titrant. After the parameters had been selected, the precision and accuracy were evaluated. The precision was evaluated after 10 successive titrations of a sample solution containing $0.050 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_3$. Accuracy was checked by applying the proposed procedure to the direct determination of phosphite in five commercial fertilizer samples. Recovery tests for spiked samples were done in two levels by adding aliquots of $0.050 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_3$ standard stock solution in diluted fertilizer samples before in order to obtain solutions with 0.020 and 0.040 mol L^{-1} of phosphite.

All samples were also analyzed by spectrophotometry (10). Other analytical characteristics such as reagent and sample consumption also were evaluated.

RESULTS AND DISCUSSION

Preliminary tests revealed the feasibility of two Pt microelectrodes to monitor the reaction between phosphite and iodine and use them as a basis of a titrimetric method for phosphite determination. The end points were identified easily from plots of current against volume of iodine titrant added. The influence of variation of voltage difference (25–200 mV) between electrodes on end point determination is depicted in **Figure 2**. When the voltage difference varied from 25 to 200 mV, the final current increased from 25 to $150 \mu\text{A}$, but the end point determination was not affected. For a 200 mV voltage difference, lengthy waiting times were observed for stabilization of readings at the final current. But this was not observed for 25, 50, and 100 mV. As a compromise between rapid stabilization of final current readings and broadest variation of current, a 100 mV voltage difference was then selected for further experiments.

Phosphite oxidation by iodine is a temperature-dependent reaction. The first experiments carried out at room temperature (25°C) showed an appreciable current flow immediately after first drops of titrant were added. The equivalence point before that time, given by the “excess” of iodine, suggested a slow reaction rate, in which case there was an end point error. The reaction rate increased when the titration was carried out at 45°C , but the volume of added titrant at the end point was still different from that at the equivalence point. For temperature fixed at 70°C , the consumption of iodine was almost instantaneous, and the end point coincided with the equivalence point. The titration time reduced from 150 to 12 min when temperature was varied from 25 to 70°C . So, this temperature was selected for further experiments.

The pH is another important parameter to be considered. The potential of reduction of the system iodine/iodide is unaffected for pH < 8. For higher pH, iodine may react with hydroxyl

Table 1. Comparative Results: Results (Mean \pm Standard Deviation) for Phosphite Determination ($n = 3$) in Liquid Fertilizers (Expressed as % (m/m) P_2O_5) Found by the Proposed Amperometric Titrimetric Method and by the Reference Method Based on Spectrophotometry (10)

sample	amperometric titration	spectrophotometry
1	19.4 \pm 0.7	19.4 \pm 1.3
2	27.0 \pm 0.3	28.2 \pm 2.4
3	29.1 \pm 0.3	29.5 \pm 2.1
4	36.7 \pm 0.9	35.4 \pm 2.7
5	40.0 \pm 0.2	40.4 \pm 3.2

anions, producing IO^- plus I^- (17). The influence of the pH and composition of the buffer system on phosphite oxidation were investigated by employing the Na_2HPO_4 – NaH_2PO_4 and citric acid– Na_2HPO_4 buffer systems at the following pH values: 5.8 – 6.8 – 7.8 (phosphate) and 3.0 – 4.0 – 5.0 – 6.0 – 7.0 (citric acid/phosphate). In both situations, aliquots of 10.00 mL of 0.050 mol L^{-1} Na_2HPO_3 reference solution plus 25 mL of each buffer solution were transferred to a flask and titrated with the 0.050 mol L^{-1} iodine solution until an abrupt increase in current had been observed.

The reaction between iodine and phosphite is fairly slow at $pH \leq 4$. When the pH was increased from 4 to 5, the reaction rate increased, but the titration time was relatively lengthy still. For the phosphate buffer at pH 5.8, 6.8, and 7.8, the titration time was 67, 12, and 10 min, respectively. For the acid citric/sodium phosphate at pH 5.0, 6.0, and 7.0, the end point was obtained after 98, 25, and 12 min, respectively. Despite the fact that the phosphate buffer at pH 7.8 presented the shortest titration time, the selected pH for further experiments was pH 6.8 to avoid consumption of iodine by OH^- (17). The buffer phosphate at pH 6.8 and the temperature of 70 °C were elected as optimum conditions for further experiments. It should be pointed out that determining phosphite in the presence of phosphate is an interesting application in the quality control of phosphite-based fertilizers. The determination of phosphite by conventional methods usually requires the determination of phosphate only and total phosphate, with the phosphite concentration being obtained then by difference. With the proposed procedure, the determination of phosphite is obtained after a single and direct analysis.

The influence of foreign ions on end point also was evaluated. The type and concentration of interfering chemical species was chosen as a function of the contents of macro- and micronutrients usually in liquid fertilizer samples. For a solution containing 0.050 mol L^{-1} Na_2HPO_3 in the presence of 150 mg L^{-1} Mn^{2+} , 150 mg L^{-1} Mg^{2+} , 200 mg L^{-1} Zn^{2+} , 30 mg L^{-1} Cu^{2+} , and 1000 mg L^{-1} Ca^{2+} , no interferences were observed. The presence of chloride, carbonate, nitrate, and sulfate at concentrations up to 10000 mg L^{-1} did not affect the end point.

The precision of the method was evaluated by means of the relative standard deviation (RSD) of 10 successive titrations. The RSD calculated for the proposed amperometric titration was 1.0% for a diluted sample containing 0.050 mol L^{-1} Na_2HPO_3 . Accuracy was assessed by analyzing liquid fertilizers without any previous treatment. The results obtained with the proposed procedure (Table 1) were not statistically different from those obtained by spectrophotometry at the 95% confidence level (t -test). The recoveries of 0.020 and 0.040 mol L^{-1} of phosphite added to fertilizer samples ranged from 97% to 102% regardless of the amount of spiking in several determinations. The titration time was approximately 12 min, corresponding to about 127 mg of I_2 , 200 mg of KI, 174 mg of Na_2HPO_4 , and 176 mg of NaH_2PO_4 consumed per determination.

The proposed procedure in this work comprises a biamperometric titration method for direct determination of phosphite in

liquid fertilizer. Besides the direct determination, high selectivity, low reagent consumption, and rapidity, high accuracy and precision are other favorable analytical characteristics. The method can be considered an alternative to the use of conventional methods already available for phosphite determination.

LITERATURE CITED

- (1) Mengel, K.; Kirkby, E. A. *Principles of Plant Nutrition*, 4th ed.; International Potash Institute: Bern, Switzerland, 1987; 687 pp.
- (2) Dias, L. E.; Fernandez, L. Q. P.; de Barros, N. F.; Novaes, R. F.; de Moraes, E. J.; Daniels, W. L. Availability of phosphorus in a Brazilian oxisol cultivated with eucalyptus after nine years as influenced by phosphorus fertilizer source, rate and placement. *Commun. Soil Sci. Plant Anal.* **2000**, *31*, 837–847.
- (3) Yogeve, E.; Sadowsky, A.; Solel, Z.; Oren, Y.; Orbach, Y. The performance of potassium phosphite for controlling Alternaria brown spot of citrus fruit. *J. Plant Dis. Prot.* **2006**, *113*, 207–213.
- (4) Coskun, N.; Akman, S. Direct determination of phosphorus in different food samples by means of solid sampling electrothermal atomic absorption spectrometry using Pd+Ca chemical modifier. *Spectrochim. Acta, Part B* **2005**, *60*, 415–419.
- (5) Yang, I.; Han, M. S.; Yim, Y. H.; Hwang, E.; Park, S. R. A strategy for establishing accurate quantitation standards of oligonucleotides: quantitation of phosphorus of DNA phosphodiester bonds using inductively coupled plasma-optical emission spectroscopy. *Anal. Biochem.* **2004**, *335*, 150–161.
- (6) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative chemical analysis*, 4th ed.; Macmillan: New York, 1969; 1199 pp.
- (7) Harris, D. C. *Quantitative Chemical Analysis*, 4th ed.; W. H. Freeman: New York, 1995; p 837.
- (8) Marczenko, Z. *Separation and Spectrophotometric Determination of Elements*; Ellis Horwood: Chichester, U.K., 1986; 708 pp.
- (9) Ito, H. A.; Gomes Neto, J. A.; Fernandes, K. G.; de Moraes, M.; Cardoso, A. A. Spectrophotometric determination of phosphite in fertilizer in a flow injection system with online sample preparation. *Lab. Rob. Autom.* **2000**, *12*, 286–290.
- (10) Dametto, P. R.; Franzini, V. P.; Gomes Neto, J. A. Phosphite determination in fertilizers after online sequential sample preparation in a flow injection system. *J. Agric. Food Chem.* **2007**, *55*, 5980–5983.
- (11) Ito, H. A.; Oliveira, M. F.; Neto, J. A. G.; Stradiotto, N. R. Eletrodo modificado em filme de paládio para a determinação voltamétrica de fosfito. *Eletica Quim.* **2002**, *27*, 161–168.
- (12) Franzini, V. P.; Fugivara, C. S.; Benedetti, A. V.; Ribeiro, C. A.; Cavalheiro, E. T. G.; Gomes Neto, J. A. Direct determination of phosphite in fertilizers by flow-injection amperometry. *Electroanalysis* **2007**, *19*, 1794–1798.
- (13) Franzini, V. P.; Gomes Neto, J. A. Método titrimétrico para determinar fosfito em amostras agroindustriais. *Quim. Nova* **2007**, *30*, 308–311.
- (14) Leitner, W. Reflections on “green chemistry” in 2005. *Green Chem.* **2006**, *8*, 125–125.
- (15) Trasatti, S.; Alberti, A. Anodic oxidation mechanism of hypophosphorous and phosphorous acid on palladium. *J. Electroanal. Chem.* **1966**, *12*, 236–249.
- (16) Flaschka, H. A.; Barnard, A. J., Jr.; Sturrock, P. E. *Quantitative analytical chemistry. Volume II: Short introduction to practice*; Barnes & Noble Book: New York, 1969; 290 pp.
- (17) Mendham, J.; Denney, R. C.; Barnes, J. D.; Thomas, M. J. K. *Análise química quantitativa*; LTC: Rio de Janeiro, 2002; 462 pp.

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