

Short Communication

Photometric determination of phosphate using metal oximates— an indirect method

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Abstract

The colour fading action of phosphate on coloured complexes of uranium(VI) and iron(III) with salicylaldoxime (SAO), 2-hydroxy-1-naphthaldoxime (OHNAO), piconol-oxime (MRPO) and 2-hydroxy-5-methyl propiophenone oxime (HMPOX) is utilised for the determination of phosphate in microgram quantities. The method is applied for the determination of phosphate percentage in various NPK fertilizers. The effect of various foreign ions is also studied.

Key words: Di-sodium hydrogen phosphate, iron(III), uranium(VI), molybdenum(VI), decrease in absorbance, spectrophotometry.

1. Introduction

Determination of small amounts of phosphate is important in many branches of industry and also in geochemical, biochemical and agrochemical materials. The most extensively used spectrophotometric methods for the determination of phosphate, utilise either molybdo-phosphoric acid or molybdo-vanado phosphoric acid¹⁻³. In some of these methods, thorium, zinc and nitrate interfere seriously necessitating an extraction step^{4,5}. A few indirect methods based on the colour bleaching effect of phosphate over the coloured complexes of ferric iron with thiocyanate and 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazene are also reported in literature^{6,7}.

In these laboratories, the use of oximes as analytical reagents has been extensively studied. During our studies, it was found that metal-oxime complexes can be successfully utilised for the indirect determination of phosphate. Moreover, the oximes can be easily prepared in the laboratory in pure colourless crystalline form which avoid the problem of blank correction. Uranium(VI) and iron(III) form coloured complexes with various oximes. These metal ions also form stable complexes with phosphate.

Since the stability constants of metal-phosphate complexes are higher than the corresponding values of the metal oximates, we have attempted to determine phosphate spectrophotometrically by displacing oxime from the metal oximates, thereby decreasing the absorbance of the coloured metal oximates.

Uranium(VI) forms soluble orange-red coloured complexes with salicylaldoxime (SAO), 2-hydroxy-1-naphthaldoxime (OHNAO), peonol oxime (4-methoxy resacetophenone oxime, MRPO) and 2-hydroxy-5-methyl propiophenone oxime (HMPOX) in the pH range 5–11. The complexes showed maximum absorbance at 400 nm. Iron(III) forms a wine-red coloured complex with SAO in the pH range 6.5–7.0 (λ_{max} : 480 nm), bluish-green coloured complex with OHNAO in the pH range 1–2.5 and violet coloured complexes with MRPO and HMPOX in the pH range 1–3.5 having absorption maximum at 400 nm in the visible range. Addition of small quantities of phosphate to any of these complexes resulted in the proportional decrease of their absorbance with the amount of phosphate. This observation is utilised for the determination of phosphate in microgram amounts.

2. Experimental

2.1. Apparatus and reagents

ECIL Spectrophotometer Model GS 866 B and ELICO Digital pH Meter Model Li-120 were employed for the absorbance and pH measurements respectively.

The oximes SAO, OHNAO, MRPO and HMPOX were prepared in the laboratory in pure crystalline form using the standard procedures^{8–10}. 0.1 M and 0.05 M alcoholic solutions of oximes were employed for the studies.

0.01 M solution of uranyl nitrate was prepared by dissolving requisite amount of the AnalaR grade sample in distilled water.

Ferric ammonium sulphate (0.1 M) was prepared by dissolving requisite amount of M and B sample in distilled water containing a few drops of sulphuric acid. Solutions with lower concentrations were prepared by proper dilution of the stock solution.

The stock solution of phosphate (4.71×10^{-4} M) was prepared by dissolving 0.1286 g of AnalaR grade di-sodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$) in distilled water in a 250 ml volumetric flask. Lower concentrations were prepared by appropriate dilution of the stock solution.

Sodium acetate-acetic acid buffer solution of pH 6.0 and sodium acetate-hydrochloric acid buffer solution of pH 2.5 and 3.0 were used in the studies.

2.2. Procedure

Uranium(VI)-oxime method

To various aliquots of di-sodium hydrogen phosphate (1 to 5 ml) corresponding to 4 to 20 μg of phosphate taken in a set of five 25 ml volumetric flasks, 1 ml of salicylaldoxime (0.1 M), 5 ml of methanol, 12 ml of buffer solution of pH 6 and 1 ml of uranyl nitrate (1×10^{-2} M) were added to each flask. The contents were made up to the mark with distilled water and the absorbance was measured at 400 nm against water as blank. A linear plot was obtained when the absorbance values were plotted against the amount of phosphate added. The experiment was repeated using other oximes, viz., OHNAO, MRPO and HMPOX. The results are presented in Table I.

Iron(III) oximate method

In each of a set of five 25 ml volumetric flasks, 1 ml of salicylaldoxime (5×10^{-2} M) 5 ml of methanol, 12 ml of buffer solution of pH 6.5 and 1 ml of ferric iron solution (5×10^{-3} M) were taken. Then various aliquots of di-sodium hydrogen phosphate (1 to 5 ml), corresponding to 0.9 to 4.5 μg of phosphate, were added to these flasks and the contents were made up to the mark with distilled water. The absorbance measurements of these solutions were made at 480 nm against water as blank. A linear plot resulted on plotting the absorbance values against the amount of phosphate.

Similar procedure was adopted for the determination of phosphate using the oximes OHNAO, MRPO and HMPOX. The results are recorded in Table I.

Table I

Metal oximates	pH	Colour	Abs. maxima (nm)	Phosphate detd. ($\mu\text{g}/\text{ml}$)
Uranium(VI)-SAO complex	6.0	Orange-yellow	400	4.0-20.0
Uranium(VI)-OHNAO complex	6.0	Orange-yellow	400	1.8- 9.0
Uranium(VI)-MRPO complex	6.0	Orange-yellow	400	1.8- 9.0
Uranium(VI)-HMPOX complex	6.0	Orange-yellow	400	1.8- 9.0
Iron(III)-SAO complex	6.5	Wine-red	480	0.9- 4.5
Iron(III)-OHNAO complex	2.5	Bluish green	400	1.8- 9.0
Iron(III)-MRPO complex	3.0	Violet	400	0.9- 4.5
Iron(III)-HMPOX complex	3.0	Violet	400	0.9- 4.5

3. Interferences

Interference of various anions and cations which are generally encountered with phosphate was studied in the determination of 0.9 ppm of phosphate. Sodium, potassium, calcium, barium, strontium, magnesium, manganese(II), zinc, thorium, cadmium, chloride, bromide, iodide, sulphate, nitrate, acetate and chromate did not interfere even when present in 1000-fold excess. Three-fold excess of carbonate, silicate, citrate, tartrate, arsenate and oxalate did not interfere. Traces of copper(II), nickel(II), vanadium(V) and titanium(IV) interfered by forming precipitates. Cobalt(II) interfered due to its colour.

4. Discussion

The results in Table I show that among the metal-oximates used, iron(III) complexes with SAO, MRPO and HMPOX offer more sensitivity in the determination of phosphate (0.9 to 4.5 $\mu\text{g/ml}$). For each addition of 1.8 μg of phosphate the absorbance of uranium(VI) oximates decreases by 0.04. In the case of iron(III) oximates, the absorbance decreases by 0.035 for each addition of 0.9 μg of phosphate. This may be due to the formation of stronger and stable complexes between iron(III) and phosphate than between uranium(VI) and phosphate. This may result in the displacement of organic chelating agent (oxime) from the metal complex by phosphate. Since organic reagents (oximes) employed are colourless and have no absorbance in the visible region, blank correction is not required. Further, the method provides the advantage of determining phosphate in presence of thorium, zinc, manganese(II), magnesium, chloride, sulphate, nitrate, cadmium and chromate and moderate amounts of silicate, carbonate, citrate, tartrate and arsenate and eliminates extraction step. In this respect, the method is superior to the methods proposed by Wadelin *et al*⁴ and Tsutomu *et al*⁵. The present method offers equal sensitivity (1–5 ppm) as those of Mehra and Sogani⁷ and Henrickson¹¹.

The colour development of uranium(VI) and iron(III) metal oximates is instantaneous. Uranium(VI) oximates and the iron(III) oximates are stable for over 72 hr and 2 to 3 hr respectively.

5. Analysis of NPK fertilizers for phosphate

The percentage of phosphate in various NPK fertilizers was determined by using iron(III)-peonol oxime complex. A calibration curve was constructed using standard phosphate solutions and iron(III)-peonol oximate. The fertilizer sample solutions were also treated in a similar manner with iron(III)-peonol oxime complex and the absorbance was measured as usual. Using these absorbance values, the amount of phosphate in the samples was computed from the calibration curve. The results (Table II) indicate that the values obtained by the present method are well comparable with those obtained by standard method¹².

Table II

Fertilizer N P K	Percentage of phosphate	
	Present* method	Standard method
Sample 1 (15 : 15 : 15)	14.90	15.04
Sample 2 (14 : 35 : 14)	35.70	35.71
Sample 3 (17 : 17 : 17)	17.20	16.19

* Average of 3 determinations.

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