

## Short Communication

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### SELECTIVE MICRODETERMINATION OF PHOSPHATE BY A NEW AMPLIFICATION METHOD

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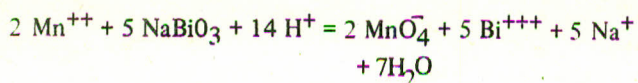
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#### Introduction

The manganous ion reacts with soluble phosphates in slightly ammoniacal solutions containing excess of ammonium salts to form the sparingly soluble precipitate of manganese ammonium phosphate,  $MnNH_4PO_4$ . This reaction has been proposed for the gravimetric determination of manganese<sup>1</sup> and also for phosphate.<sup>2</sup>

In the course of investigations of new micro-analytical methods for phosphate, it appeared that the above reaction should be capable of adaptation to the titrimetric determination of this ion if the amount of manganese in the precipitate could be determined volumetrically. Manganese may be determined titrimetrically after being oxidised to permanganate. On this basis the new method has been devised. The phosphate is precipitated as manganese ammonium phosphate, which after being filtered and washed free from reagents is dissolved in dilute nitric acid. The released manganese is oxidised to permanganic acid by excess of sodium bismuthate



The excess of bismuthate is removed by filtration, and the permanganate formed is titrimetrically determined in the filtrate. In this way the method involves a five fold amplification.

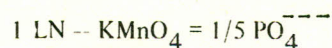
#### Experimental

##### Procedure

To the slightly acidic solution (5 - 10 ml), containing 5 - 20 mg of phosphate, add 0.5 g of ammonium sulphate and 2 ml of 5% manganous sulphate solution. Heat almost to boiling, and add dilute ammonia (1:10) dropwise with stirring until precipitation begins; immediately suspend the addition of ammonia. Continue the heating and stirring until the precipitate becomes crystalline. Then add

another drop or two of dilute ammonia, stir as before, etc., and so continue to complete precipitation. Cool in ice for 1 hr. Filter off on sintered-glass funnel (G4) and wash the precipitate with 10-15 ml of cold 1% ammonium nitrate solution. Dissolve the precipitate in 15 ml of 30% nitric acid, add 0.2 - 0.3 g of AR sodium bismuthate and stir the mixture for 2-3 min. Filter as before and wash the residue with 50 ml of 3% nitric acid, collecting the filtrate and washings in a clean 250-ml Buchner flask. Run in slowly 0.05N ferrous ammonium sulphate solution from a burette until a slight excess is present, and titrate immediately with 0.03N potassium permanganate solution.

Run a blank by mixing an equal volume of the ferrous solution used with 50 ml of 3% nitric acid and a little of sodium bismuthate, and titrating against the standard potassium permanganate. The difference between the titrations represents the permanganate equivalent to the phosphate in the sample.



$$\text{mg of phosphate} = (V_2 - V_1) \times N \times \frac{94.97}{5}$$

where  $V_1$  = ml of permanganate used in the determination,  
 $V_2$  = ml of permanganate used in the blank,  
 $N$  = normality of permanganate.

*Notes.* (1) The test solution must be made slightly acidic before analysis and boiled gently for 2-3 min to decompose any carbonate, sulphite or sulphide that may coexist. (2) If the sample solution contains cations such as  $Ca^{++}$ ,  $Mg^{++}$ ,  $Al^{+++}$ ,  $Fe^{+++}$ , etc., that form phosphate precipitates in basic medium, they must be removed before by passing the solution through a strong cation-exchange resin in the hydrogen form.

(3) The back titration with potassium permanganate must be carried out immediately the ferrous solution has been added, because the ferrous solution reacts slowly with nitric acid.

#### Results and Discussion

*Advantages of the Method.* The present method may be regarded as specific for phosphate since all common anions do not interfere. The low solubility of manganese ammonium phosphate, the 5-fold amplification reaction involved and the high sensitivity of the permanganate titration made it possible to determine microamounts of phosphate.

*Precision of the Method.* In Table 1 results for a series of ten determinations are arranged in ascending order of magnitude for test solutions containing 4.75 mg of phosphate. The results are reproducible with a coeffi-



cient of variation around  $\pm 1.2\%$ . Such results are considered to be satisfactory on the milligram scale.

TABLE 1. DETERMINATION OF PHOSPHATE  
(Phosphate taken 4.57 mg)

4.66	4.66	4.70	4.70	4.70
4.75	4.75	4.75	4.79	4.84
Mean value				4.73 mg
Standard deviation				$\pm 0.06$ mg
Co-efficient of variation				$\pm 1.2\%$

*Interferences from Cations.* Most metals interfere by forming insoluble phosphates. The use of EDTA as masking agent was found inappropriate because it masks manganous ions as well. Therefore, an ion-exchange column (hydrogen form) was used for removing interfering cations before determination. To test the effectiveness of this method, synthetic mixtures containing different cations were analysed after being passed through the column. The results obtained are recorded in Table 2. The mean error is  $\pm 0.83\%$  which is satisfactory on the micro-scale. It will be noted that the error is mostly shifted towards the negative side. This indicates that the error is mainly manipulative.

The present method may, therefore, be applied to

TABLE 2. ANALYSIS OF MIXTURES

( $\text{PO}_4^{3-}$  taken as  $\text{KH}_2\text{PO}_4$  9.50 mg in 10 ml of solution).

Cation	Concentration (M)	Added as	$\text{PO}_4^{3-}$ Found (mg)	Error (%)
$\text{Ca}^{++}$	0.01	$\text{Ca}(\text{NO}_3)_2$	9.40	-1.0
	0.02		9.31	-2.0
$\text{Mg}^{++}$	0.01	$\text{MgSO}_4$	9.40	-1.0
	0.02		9.40	-1.0
$\text{Zn}^{++}$	0.01	$\text{ZnSO}_4$	9.59	+0.9
	0.02		9.50	0.0
$\text{Al}^{+++}$	0.01	$\text{Al}_2(\text{SO}_4)_3$	9.45	-0.05
	0.02		9.36	-1.5
$\text{Fe}^{+++}$	0.01	$\text{Fe}_2(\text{SO}_4)_3$	9.50	0.0
	0.02		9.54	+0.4

the analysis of industrial materials such as fertilisers and drugs.

#### References

1. Arthur I. Vogel, *A Text Book of Quantitative Inorganic Analysis* (Longman, London, 1965), p. 264.
2. S.K. Shushich, Ref. Zhur. Khim., 23, 473 (1955).