

# IODOMETRIC MICRODETERMINATION OF PHOSPHORUS IN ORGANIC COMPOUNDS BY USE OF AN AMPLIFICATION REACTION

By

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## التقدير الأيودومتري الميكروئي للفوسفور في المركبات العضوية باستخدام تفاعل التكبير

عبد الله حسين الكبيسي و عبد الفتاح بسطاوي فرج و رجب رياض أمين

لقد تم إقتراح تفاعل تكبير كيميائي ذو معامل تكبير عالي للتقدير الميكروئي للفوسفور في المركبات العضوية . وتعتمد الطريقة أساساً على حرق المركب العضوي بواسطة طريقة قارورة الأكسجين ، وإمتصاص نواتج الحرق في ماء مقطر وتحويله إلى حمض الأرتوفوسفوريك بواسطة ماء البروم . يسمح بعد ذلك لتفاعل حمض الأرتوفوسفوريك الناتج بالتفاعل مع موليبدات الصوديوم في وسط حمضي ليكون حمض الفوسفوموليبيديك الذي يستخلص بواسطة مخلوط من الإثير وكحول البنتان ( ٥ : ١ بالحجم ) ، وينزع حمض الفوسفوموليبيديك من المذيب العضوي بعد ذلك بواسطة هيدروكسيد الصوديوم .

يُختزل الموليبدم السداسي إلى الموليبدم الخماسي بواسطة الخارصين في وسط حمض الخليك ، ويعاد أكسدة الموليبدوم الخماسي بواسطة أيون فوق اليودات في مدى للآس الهيدروجيني يتراوح من ٣,٤ - ٣,٩ . يتم بعد ذلك حجب الزيادة من أيون فوق اليودات بواسطة موليبدات الأمونيوم وتعابير اليودات الناتجة بواسطة ثيوكبريتات الصوديوم . تسمح الطريقة المقترحة بمعامل تكبير مقداره ٣٦ حيث أن كل ذرة فوسفور في المركب العضوي تنتج ٣٦ مكافئ يود .

*Key Words:* Iodometry, Microdetermination of phosphorus, Organic Analysis, Amplification reactions.

### ABSTRACT

A high chemical amplification method is described for the iodometric microdetermination of phosphorus in organic compounds. This method depends on combustion by the oxygen flask, absorption of the combustion products in distilled water and conversion to orthophosphoric acid with bromine water. The phosphoric acid produced is then allowed to react with sodium molybdate in acid medium to form phosphomolybdic acid which is extracted into a mixture of diethyl ether and pentanol (5:1, V/V), and back extracted with sodium hydroxide. The molybdate thus produced (12 atoms molybdenum (VI) for each original phosphorus atom) is reduced with zinc in acetic acid medium to the quinquivalent molybdenum, which is then oxidised with potassium periodate in the pH 3.4-3.9 range, into the hexavalent form. In the same pH range, the excess periodate is masked with ammonium molybdate and the released iodate is titrated with sodium thiosulphate. This method affords 36-fold amplification as each phosphorus atom liberates 36 equivalent of iodine.

### INTRODUCTION

Phosphorus is one of the most diversified elements in compounds. It is already realised[1] that organophosphorus compounds play an important role in life processes. Many of these compounds have useful applications in the fields of

agriculture and medicine. The determination of phosphorus in environmental and biological samples deserves attention.

Several methods have been described in the literature[1,2] for the determination of phosphorus in organic compounds. These methods include: titrimetric[3],

gravimetric[3] spectrophotometric[4], atomic absorption[1] and emission[5], spectrometric, X-ray fluorometric[6], potentiometric[7], polarographic[8] and neutron activation techniques[9]. Most of these procedures are based on quantitative conversion of phosphorus containing organic compound to orthophosphate ion prior to the application of any of the measurement techniques.

A simple titrimetric method, based on an iodometric amplification reaction, has been attractive as it affords sufficient accuracy for the determination of phosphorus at trace level. Two iodometric amplification methods have been developed[10-12] for the determination of phosphorus in organic compounds, but unfortunately, these methods allows only two or three amplification factors. These low amplification factors do not allow the application of the proposed methods for the analysis of organic compounds containing relatively low percentage of phosphorus with a reasonable accuracy.

The aim of the present work is to develop a simple and accurate iodometric method, based on a high chemical amplification reaction, suitable for the determination of phosphorus in a wide range of organic compounds.

## EXPERIMENTAL

### Reagent and Materials

Unless otherwise specified, all chemicals were of analytical reagent grade.

Ammonium molybdate solution, 10% aqueous solution of the tetrahydrate salt  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ .

Sodium molybdate solution (30 mg/ml), it was prepared and stored in a polyethylene bottle to avoid contamination from glass.

Potassium periodate solution, it was prepared by dissolving 1.75 g of the recrystallized solid reagent in 500 ml of distilled water containing 3 ml of saturated borax solution.

Sodium thiosulphate solution (0.02 M), standardized against potassium iodate.

### Apparatus

A 500 cm<sup>3</sup> oxygen flask of otherwise conventional specifications and ordinary microanalytical equipments were employed.

### Procedure

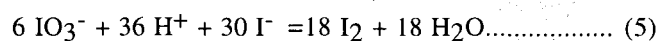
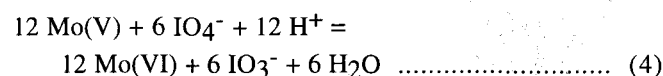
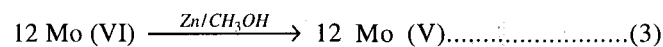
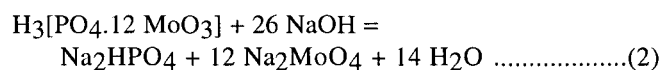
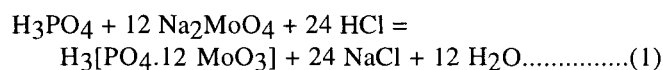
15 ml of redistilled water was taken in 500 oxygen flask. 3-6 mg of the organophosphorus compound was wrapped and combusted as usual with the closed flask technique[2]. 10 cm<sup>3</sup> of freshly prepared saturated bromine water was added to the absorption solution and allowed to stand for 5 minutes. The solution was boiled gently to remove bromine. Another 10 cm<sup>3</sup> portion of the bromine water was added and the boiling repeated. The solution was transferred to a 50 cm<sup>3</sup> measuring flask with water. To a 5 cm<sup>3</sup> aliquot, distilled water was added until the total volume was about 20 cm<sup>3</sup>. To this, 2 cm<sup>3</sup> of HCl (sp. gr. 1.18) and 5 cm<sup>3</sup> sodium molybdate were added and the

solution was brought to boiling temperature. After cooling the solution was transferred to a separatory funnel and the phosphomolybdic acid extracted with 20 cm<sup>3</sup> portion of a mixture of diethyl ether and pentanol (5:1, V/V). The organic layer was separated and washed three times with 5 cm<sup>3</sup> portions of 0.2 M H<sub>2</sub>SO<sub>4</sub>. The molybdate was back extracted with 10 cm<sup>3</sup> of NaOH (1M). 5 cm<sup>3</sup> of glacial acetic acid and ca. 0.3 g of zinc dust were added to the aqueous layer and the mixture boiled on a steam bath for 5 minutes, filtered through a filter paper and the filtrate collected in an Erlenmeyer flask containing ca. 0.3 g sodium carbonate. 5 cm<sup>3</sup> of potassium periodate was added and the solution was allowed to stand for 1-2 minutes. After this, 5 cm<sup>3</sup> ammonium molybdate (10%), few crystals of potassium iodide (ca. 0.1 g) were added and the liberated iodine titrated with 0.02M sodium thiosulphate using starch as indicator. A blank was run to correct the reagent error.

## RESULTS AND DISCUSSION

Generally, in acid media containing excess molybdate, orthophosphate forms phosphomolybdic acid which is readily extracted into various oxygen-containing organic solvents such as ethers, esters, ketones and aldehydes[13]. Recently, polyurethane foams have also been suggested for the extraction and separation of this heteropoly acid[13]. The appropriate conditions for the formation of phosphomolybdate and its extraction in many organic solvents have been described in detail in the literature[1,2,13].

The proposed iodometric method is based on complete conversion of organophosphorus compound to orthophosphoric acid, quantitative formation of phosphomolybdic acid, separation of the heteropoly acid using suitable organic solvent, back extraction of the molybdate in aqueous phase, reduction of sexivalent molybdenum to the quinquivalent form and the oxidation of molybdenum (V) with periodate. The unreacted periodate can then be masked[14] with ammonium molybdate and the released iodate can be determined iodometrically. The reactions involved can be illustrated as follows:



That is, each original phosphorus atom liberates 36 iodine atoms.

A literature survey reveals that quantitative formation of phosphomolybdic acid takes place in relatively wide range of acid concentrations (0.1-1.5 M HCl). In these acidic media,

the heteropoly acid thus produced is completely extracted in e.g., a mixture of diethyl ether and pentanol (5:1, V/V)[15].

Trials were made to separate phosphomolybdic acid formed in a dynamic extraction mode by using columns packed with unloaded or pentanol-loaded polyether, polyurethane foams. Unfortunately, it was observed that considerable amounts of free molybdic acid are retained on the foam column as well and cause serious interferences in the subsequent iodometric estimation. Accordingly, a solvent extraction procedure using a mixture of diethyl ether and pentanol was chosen in the present work for the quantitative separation of phosphomolybdic acid.

It is necessary to select a reducing agent, which quantitatively converts hexavalent molybdenum to the pentavalent state, without interference in the subsequent iodometric finish. A variety of reducing agents have been examined for this purpose, zinc in acetic acid solution has proven the most suitable. Carbon dioxide evolved from the reaction between sodium carbonate present in Erlenmeyer flask and the acidic filtrate, during filtration of zinc after the reduction process, prevents molybdenum(V) from any probable interaction with atmospheric oxygen.

The reaction of quinquevalent molybdenum with periodate was found to depend on the pH of the aqueous solution. At ambient temperature reaction (4) proceeds forward in the pH 3-4 range. Fortunately, however, this pH range is usually maintained after the reduction process due to the buffering effect of acetic acid originally present and sodium acetate, produced from the reaction of acetic acid and both sodium hydroxide and sodium carbonate. Moreover, in this pH range ammonium molybdate masks efficiently the unreacted periodate, which simplifies the procedure for the subsequent iodometric finish.

As is obvious from the above mentioned reactions, the proposed method affords 36-fold amplification which is quite favourable for the determination of phosphorus in organic compounds containing low percentage of phosphorus.

Organophosphorus compounds containing low phosphorus content were not available during this study. However, the proposed method was successfully employed for the determination of phosphorus in a variety of organophosphorus compounds (including organometallic compounds) containing chlorine, nitrogen and/or sulphur using only a small aliquot of the absorption solution which contains micro-amounts of phosphorus (Table 1).

**Table 1**

Iodometric microdetermination of phosphorus in organic compounds

Compound	Phosphorus %		Standard Deviation
	Expected	Average* Found	
Triphenyl phosphine	11.81	12.1	0.14
Triphenyl phosphin oxide	11.13	11.3	0.22
Diphenyl phosphazene derivative	21.56	21.8	0.26
Research compound (I)	5.24	5.3	0.28
Research compound (II)	6.12	5.8	0.37
Phosphazene	26.73	26.7	0.40

\*Average of four determinations

The proposed method gave also reasonable results in the determination of phosphazene (cf. Table 1) which is a cyclic inorganic phosphorus compound ( $N_3P_3Cl_6$ ) with high phosphorus content. Evidently, however, organic compounds containing lower percentage of phosphorus (<1%) can be analyzed by running directly the proposed procedure on the whole absorption solution after the oxygen flask combustion.

Application of the proposed amplification method to the determination of varying amounts of phosphorus (10-200  $\mu$ g), present as phosphate in aqueous solution gave very satisfactory results which suggests the application of the attractive iodometric titration to the analysis of traces of phosphorus in waters.

## REFERENCES

- [1] **Hassan, S. S. M., 1985.** Organic Analysis Using Atomic Absorption Spectrometry, Horwood, New York.
- [2] **Ma, T. S. and R. C. Rittner, 1979.** Modern Organic Elemental Analysis, Dekker, New York.
- [3] **Wilson, C. L. and D. K. Wilson, 1962.** Comprehensive Analytical Chemistry, Vol. IC, Elsevier, Amsterdam, 1962.
- [4] **Sun Deying and Huaxue Shiji, 1989.** 11, 312, CA: 112(22)210317r.
- [5] **Siroki, M., G. Vujicic, V. Milun, Z. Hudovsky and L. Maric, 1987.** Anal. Chim. Acta, 192: 175.
- [6] **Wang Yuesheng, Zhang Yiyin, Shan Jun, Xu Jian and Cui Jingrong, 1989.** Fenxi Ceshi Tongbao, 8 (4): 32.
- [7] **Pietrogrande Agostino and Zancato Mirella, 1989.** Talanta, 35: 664.
- [8] **Bishara, S. W. and M. E. Attia, 1971.** Talanta, 18: 634.
- [9] **Lisovski, I. P. and L. A. Smakhtin, 1971.** J. Radional. Chem., 8: 75.
- [10] **Gawargious, Y. A. and A. B. Farag, 1971.** Microchem. J., 16: 333.
- [11] **Idem, Ibid, 1971,** 16: 342.
- [12] **Burns, D. T. and A. Townshend, 1992.** Talanta 39: 715.
- [13] **Khan, A. S. and A. Chow, 1983.** Talanta, 30: 173.
- [14] **Belcher, R., 1968.** Talanta, 15: 357.
- [15] **Simon, S. J. and Boltz, D. F., 1975.** Anal. Chem., 47: 1758.