

Spectrophotometric determination of phosphorus in coal and coal ash using bismuth-phosphomolybdate complex

RANDJEL P. MIHAJLOVIĆ,^{1#} NATAŠA R. IGNJATOVIĆ¹, MARIJA R. TODOROVIĆ,^{2#} IVANKA HOCLAJTNER-ANTUNOVIĆ^{3#} and VESNA M. KALJEVIĆ¹

¹Faculty of Science, University of Kragujevac, P. O. Box 60, YU-34000 Kragujevac, ²Faculty of Chemistry, University of Belgrade, P. O. Box 158, YU-1001 Belgrade and ³Faculty of Physical Chemistry, University of Belgrade, YU-11001 Belgrade, Yugoslavia

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Abstract: A modified spectrophotometric method using the bismuth phosphomolybdate complex for the determination of phosphorus in coal and coal ash is suggested. Bismuth together with phosphate and molybdate forms a very stable complex in acid medium which turns blue (“molybdenum blue”) by reduction with ascorbic acid. The apparent molar absorptivity of PBiMo is $1.66 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 720 nm and $2.10 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 670 nm in isobutyl methyl ketone (MIBK). Interference caused by the ions present are within the tolerance limits ($\pm 2\%$). Beer’s law is obeyed in the concentration range to 0.6 $\mu\text{g/mL}$ (aqueous solution) and to 1.2 $\mu\text{g/mL}$ P (MIBK). The sensitivity of the proposed method is 0.0078 $\mu\text{g/mL}$ (aqueous solution) and 0.0066 $\mu\text{g/mL}$ (MIBK).

Keywords: spectrophotometry, phosphorus determination, coal, coal ash, bismuth phosphomolybdate complex.

INTRODUCTION

The determination of phosphorus in natural samples is important in environmental chemistry and geochemistry, hence it is desirable to have available, a sensitive and accurate method for the determination of phosphorus available.^{1–17} Most of these methods are based on the absorption of yellow phosphomolybdic and vanadomolybdic acid or their reduction products in aqueous and organic solvents.

Various procedures have been used for the reduction of phosphomolybdic acid in to “molybdenum blue”: iron(II) ions,¹⁵ hydroquinone,¹⁶ tin(II) chloride,¹⁷ hydrozine sulfate,¹⁴ 1-amino-2-naphthosulphonic acid,¹⁸ ascorbic acid,¹⁹ mixture of Mo(V)/Mo(VI),²⁰ metol (4-(methylaminophenol) sulphate),²¹ 1-amino-2-naphthalene-sulfonic acid,²¹ ferrocene²² and potassium(II) oxalate.²³ The contents of the reduction product depends on the reductant applied. If the reduction of phosphomolybdenum acid is carried out using tin(II) chloride, “molybdenum blue” consists of a mixed oxide of tetravalent and hexavalent

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molybdenium, $(\text{MoO}_2 \cdot 4\text{MoO}_3)_2 \cdot \text{H}_3\text{PO}_4$. In the case when ascorbic acid is used as the reductant, the same reduction product is obtained.

In order to increase the sensitivity of the method for the determination of phosphorus in the form of phosphomolybdic acid, Ducret and Droullas²⁴ applied safranin T and crystal violet, while Babko *et al.*²⁵ applied crystal violet, methyl violet, malachite green, iodine-green, auramine, rodamine 6G, neutral red and safranin. Phosphorus was spectrophotometrically determined in natural waters with malachite green as the chromogen reagent.^{26–28} Micro quantities of phosphorus in nickel and its alloys were determined using a spectrophotometric method in which brilliant green was used as an organic hue. Tin(II) chloride²⁹ was used for the determination of phosphorus in coal ash in the reduction of phosphomolybdate acid.

In order to decrease the time needed for the reduction of molybdophosphoric acid, Marphy and Riley³⁰ introduced antimony(III) as potassium antimonyl tartrate in the investigated solution of phosphorus during the spectrophotometric determination of phosphorus. These authors stated that antimony ions(III) have the role of catalyzer. Somewhat later, Giong and Eisenreich³¹ surmised the stoichiometry of the reduced heteropoly acid to be $\text{PSb}_2\text{Mo}_{10}\text{O}_{40}$.

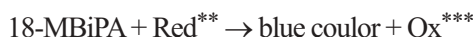
When phosphomolybdate is reduced with tin(II) or ascorbic acid in the presence of antimony, a blue complex that absorbs strongly at 882 nm is developed. The absorbance measurements may also be made at 700 nm with some loss of sensitivity. The reduction is not instantaneous, nor is the blue product stable; full color develops in 6–10 min and fades gradually thereafter.³²

Subsequently, the Murphy and Riley technique has become one of most frequently used procedures, achieving the tentative status in Standard Method for the Examination of Water and Waste Water³³ and inclusion in the Environmental Protection Agency's Method for Chemical Analysis of Water and Wastes.³⁴

As early as 1948, Boltz and Mellon¹⁴ noticed that the addition of bismuth to molybdophosphoric acid solution, with subsequent reduction, resulted in an increase in the blue hue. Campbell and Mellon used this catalytic effect for the determination of bismuth in an alloy for bearing metals.³⁵ By using a spectrophotometric study of bismuth phosphomolybdate, Hargis³⁶ established that this complex reduces with ascorbic acid much faster than with 12-molybdophosphoric acid (12-MPA, $\text{H}_3\text{PO}_4 \cdot 12 \text{MoO}_3$). Goldman and Hargis³⁷ established that phosphate reacts with bismuth in a solution of perchloric acid according to the reaction:



The formed complex is reduced with ascorbic acid according to the equation:



* 18-Molybdobismuthophosphoric acid

** Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$)

*** $\text{C}_6\text{H}_6\text{O}_6$

Since this complex is more stable than 12-MPA, these authors suggested this method for the determination of micro amounts of bismuth.

Considering the fact that the complex of antimony with phosphomolybdic acid is not stable enough and that bismuth forms a complex with phosphorus and molybdenum in the precise stoichiometric ratio (1:1:18)³¹ and that the formed complex is very stable over longer periods of time, the aim of this work was to develop a procedure for the direct spectrophotometric determination of phosphorus through the bismuth phosphomolybdate complex in coal and coal ash both from aqueous solutions and after extraction of the complex with isobutyl methyl ketone.

EXPERIMENTAL

Apparatus

All the experiments were performed with a spectrophotometer Carl Zeiss 11 Jena and a Perkin Elmer 300 double-beam atomic absorption spectrometer.

Reagents

Stock standard solution of bismuth: Bismuth metal (1.000 g) was dissolved in the minimum volume of 1:1 HNO₃. This solution was diluted to 1L with 2 % (v/v) HNO₃. The solution was further diluted to obtain a 0.001 M solution; a stock solution corresponding to 209 µg/mL of bismuth was thus obtained.

Standard phosphorus solution. Potassium dihydrogen phosphate, KH₂PO₄, (0.2197 g) was dissolved in distilled water to 500 mL. 1 mL of this solution contains 100 µg of phosphorus. The working solution of phosphorus (2 µg/mL) was prepared by dilution of the standard solution (100 µg/mL).

Ascorbic acid. Ascorbic acid (1 g) was dissolved in 100 mL of water. As ascorbic acid solutions are not stable for long periods of time at room temperature, they were freshly prepared immediately prior to use.

Ammonium molybdate solution (0.12 M). Ammonium heptamolibdate, (NH₄)₆Mo₇O₂₄·4H₂O, (2.2287 g) was dissolved in distilled water to 100 mL.

Perchloric acid (5 M). Concentrated HClO₄ (271.8 mL) was diluted to 500 mL with distilled water.

Sulphuric acid (2.5 M). Concentrated sulphuric acid (70 mL) was diluted to 500 mL.

Potassium antimonyl tartrate (1 mg/mL). Potassium antimonyl tartrate (KSbC₄H₄O₆·0.5 H₂O) 0.345 g was dissolved in distilled water and diluted to 100 mL.

Mixed reagent. Mix thoroughly 125 mL of 2.5 M sulphuric acid, 50 mL of ammonium molybdate, 50 mL of ascorbic acid and 25 mL potassium antimonyl tartrate solution. This reagent should be prepared as required as it is not stable for more than 24 h.

Sample preparation.

The coal and coal ash sample (about 0.3 g) were wet-ashed with 10 mL aqua-regia, 4 mL HF and 10 mL hydrogen peroxide solution. After the decomposition, solution was diluted to 50 mL.

Establishment of the calibration curve

1a) Various volumes (1, 2, 4, 8, and 15 mL) of the working solution were transferred to a 50 mL volumetric flask containing 2.5 mL 5 M HClO₄, 1 mL of 0.12 M ammonium molybdate and 2 mL of 0.001 M bismuth solution (8.36 µg/mL). Then 5 mL of the 1 % ascorbic acid solution was added and the volume was made up to 50 mL. The solution was allowed to stand for 10–15 min. The absorbance was measured at 720 nm against the blank solution in a 1 cm glass cell.

1b) A blue complex formed (procedure *1a*) and the solution was transferred into a 150 mL separating funnel. It was then extracted with 25 mL of isobutyl methyl ketone (MIBK) by shaking for ca. 1 min. The absorbance is measured at 625 nm against the blank solution.

The procedure of the determination of phosphorus

A certain volume of the sample (depending on the content of phosphorus) was measured into a 50 mL volumetric flask, and the same procedure as used for the establishment of the calibration curve was followed.

The procedure for the determination of phosphorus using the Sb-phosphomolybdate complex

Various volumes (1, 2, 4, 8 and 15 mL) of the working solution were transferred to a 50 mL volumetric flask, 8 mL of the mixed reagent were added and the volume was made up to the mark with water. After not less than 10 min the absorbance was measured at 882 nm using cells of an appropriate path length.

A certain volume of the sample was transferred to a 50 mL volumetric flask and made up to approximately 40 mL with distilled water, and the same procedure as used for the establishment of the calibration curve, was followed.

RESULTS AND DISCUSSION

Effect of pH

Boltz and Mellon¹⁴ established that 12-molybdophosphoric acid has maximum absorption in sulphuric acid solution of concentration 0.1–0.175 M, in HCl solution of concentration 0.2–0.3 mol/L and in HNO₃ solution of concentration 0.2–0.3 mol/L. The formation of the bismuth phosphomolybdate complex, as well as the formation of 12-molybdophosphoric acid, depend on the kind and the concentration of acid as well. The complex dissolves both in dilute and in concentrated solutions of strong mineral acids. However, the complex with bismuth is stable in a higher pH range than 12-molybdophosphoric acid.³⁷ Since the complex 18-BiPMo is the most stable in perchloric acid solutions, all our investigation were performed in solutions of this acid.

In order to determine the concentration of perchloric acid in which the reduced form of the BiPMo complex has maximum absorption, the absorbance of aqueous solutions of this complex in which the concentration P was 0.05–1.5 ppm and concentration of perchloric acid was 0.075–0.35 mol/L.

The results of the measurements of the influence of the acidity of aqueous solutions of the reduced form of the BiPMo-complex on the absorbance changes with time are shown in the Tables I and II. The results of the investigation show (Table I) that the absorbance of aqueous solutions of the reduced form of the BiPMo complex is the highest at the lowest concentration of perchloric acid (0.075 mol/L), which leads to the wrong conclusion that all determinations of phosphorus through the BiPMo complex should be performed at this concentration of the acid. However, the absorbance of this complex changes quickly with time at this concentration of perchloric acid and after a short period of standing there is no linear dependence between the measured absorbance and the concentration of phosphorus in the solution. This increase of the absorbance of aqueous solutions of the BiPMo complex in the solution of lower acidity is due to the reduction of the surplus molybdate into a blue product. Spectrophotometric determination of phosphorus in aqueous solutions of the BiPMo complex should, therefore, be performed at an acidity such that the absorbance of a solution of a certain concentration is high enough, the change of absorbance is minimum with respect to time and the dependence of the absorbance on the concentration is linear. All those demands are satisfied at a perchloric acid concentration of 0.25 mol/L. At this

concentration of acid, the absorbance of an aqueous solution BiPMo is stable for at least 89 hours. For this reason a perchloric acid concentration of 0.25 mol/L was used in all our investigations.

TABLE I. Effect of perchloric acid on the absorbance

Concentration of P/($\mu\text{g/mL}$)	Absorbance (λ^{720})			
	Concentration of perchloric acid/(mol/L)			
	0.35	0.25	0.15	0.075
0.05	0.019	0.026	0.033	0.036
0.10	0.039	0.057	0.068	0.072
0.15	0.057	0.077	0.119	0.129

TABLE II. Changes of the absorbance of aqueous solution of the bismuth phosphomolybdate complex with time at different concentrations of perchloric acid

Concentration of P/($\mu\text{g/mL}$)	Absorbance (λ^{720})							
	Concentration of perchloric acid/(mol/L)							
	0.35*	0.35**	0.25*	0.25**	0.15*	0.15**	0.075*	0.075**
0.05	0.019	0.019	0.026	0.027	0.033	0.042	0.036	0.222
0.10	0.039	0.040	0.051	0.052	0.068	0.093	0.072	0.333
0.15	0.057	0.057	0.077	0.077	0.119	0.136	0.129	0.389

*Absorbance measured 15 min after the complex was made; **Absorbance measured 90 min after the complex was made

If the BiPMo complex is extracted with MIBK, the concentration of perchloric acid should also be 0.25 mol/L. At lower acid concentrations the surplus molybdate is reduced into a product which dissolves in MIBK, thus disturbing the determination.

Absorption spectra

When a solution of ammonium molybdate, bismuth nitrate and ascorbic acid is added to an acid solution of phosphorus, a blue colour results from the formed BiPMo complex, which has a maximum absorption at a wave length of 720 nm (aqueous solutions). The maximum absorption (Fig. 1) of the BiPMo complex is 670 nm (MIBK).

Selection of solvent

Luech and Boltz³⁸ applied isobutanol, Klitina *et al.*³⁹ butanol, pentanol, isopentanol, and isobutyl methylketone and Jakubiec and Boltz propylene carbonate and CHCl_3 ⁴⁰ for the extraction of the BiPMo complex obtained by reduction with ascorbic acid. Gorjushina *et al.*⁴¹ applied *n*-butanol, isobutanol, diethyl ether, ethyl acetate, pentyl acetate, butyl acetate and isobutyl methylketone for the extraction of the antimonyl phosphor molybdate complex. Since the BiPMo complex is a product of the reduction of a phosphomolybdate polyacid such as phosphomolybdate and antimonylphosphomolybdate, which are 100 % extracted in MIBK, this solvent was employed in all our investigations of the extraction of the BiPMo complex.

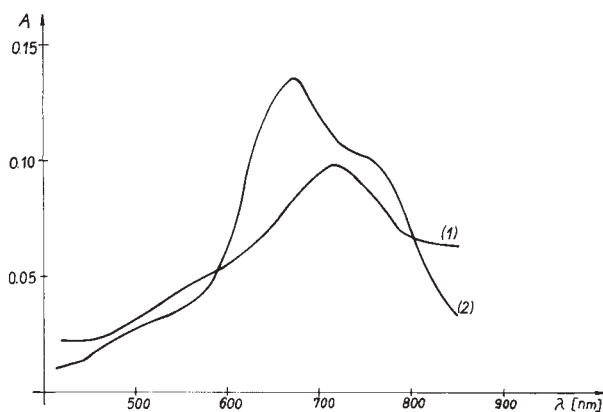


Fig. 1. Absorption curves for the bismuth phosphomolybdate complex in water (1) and MIBK (2)

Calibration graph, sensitivity and precision

The dependence of the absorbance on the concentration of phosphorus in an aqueous solution is linear in the range 0 – 0.6 ppm and 0 – 1.2 ppm in MIBK. The apparent molar absorptivity obtained from the slope of the calibration graph was $1.66 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 720 nm in water and $2.10 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 670 nm in MIBK.

The sensitivity of the proposed method is 0.0078 $\mu\text{g/mL}$ (aqueous solution) and 0.0066 $\mu\text{g/mL}$ (MIBK).

The precision given by the relative standard deviation of the absorbance was 2.10 and 1.07 % for 2.9 and 5.8 μg of phosphorus, respectively.

Effect of foreign ions

It is well known that not only P but also As, Si, Ge, Ti, Th, Zr, V, Nb, Ce and Sb react with molybdenum.³¹ All these ions can be expected to eject bismuth out of the ternary complex with phosphorus and molybdenum and so interfere with the phosphorus determination. Besides, data in the literature indicate that even other ions, such as Cr(VI), Fe(III), NO_2^- , WO_4^- , VO_2^- *etc.*,^{8,14} interfere with the formation of the phosphomolybdate complex. Since, in this paper, a modified spectrophotometric method for the determination of phosphorus in coal and coal ash is being proposed, it was decided to investigate the interference of only those ions whose presence in the analysed samples is to be expected, as well as of those for which ambiguous interference data exist in the literature. The contents of metal in coal and coal ash had been previously determined by the AAS method.⁴² In these investigations the concentration of the interferents and phosphorus were varied while the concentration of bismuth was kept constant (8.2 $\mu\text{g/mL}$). The interference of silicon on the spectrophotometric determination of phosphorus was not investigated because silicon is eliminated with HF before the determination of phosphorus.

The interference of the ions present are within the tolerance limits ($\pm 2\%$).

TABLE III. Determination of phosphorus in coal and coal ash

Sample	Coal/%			Coal ash/%			
	Spectrophotometry		Indirect AAS	Spectrophotometry			Indirect AAS
	A	B		A	B	C	
1.	0.27	0.28	0.28	1.05	1.05	1.00	1.05
2.	0.28	0.28	0.28	1.35	1.35	1.30	1.35
3.	0.28	0.27	0.27	1.00	1.00	0.95	1.00
4.	0.27	0.28	0.28	1.35	1.40	1.30	1.40
5.	0.27	0.28	0.28	1.60	1.50	1.45	1.50
6.				1.05	1.00	0.95	1.00
7.				1.35	1.40	1.30	1.40

A-BiPMo; B-SbPMo; C-BiPMo (IBMK)

The results of the determination of phosphorus in some samples of coal and coal ash are shown in Table III. The results presented in Table III are the average values of three measurements. The content of phosphorus was determined spectrophotometrically in three aliquots from each solution, or the phosphorus was determined after extraction with MIBK. The results of the determination of phosphorus were compared with the results of the determination obtained by application of the spectrophotometric method through SbPMo complex and an indirect AAS method. The analytical results obtained by the proposed method were in good agreement with those obtained by the standard spectrophotometric method (SbPMo) and by the indirect AAS method.

CONCLUSION

A modified spectrophotometric method for the determination of phosphorus in coal and coal ash is proposed. The sensitivity of the method is close to the sensitivity of the spectrophotometric method through the SbPMo complex, but the BiPMo complex is more stable. The absorbance of the solution does not change during more than 89 hours. A combination of reactants unstable at room temperature, is not needed for the determination of phosphorus by the proposed method. If the BiPMo complex is extracted with MIBK, the sensitivity of the suggested method is increased.

ИЗВОД

СПЕКТРОФОТОМЕТРИЈСКО ОДРЕЂИВАЊЕ ФОСФОРА У УГЉУ И ПЕПЕЛУ ПРИМЕНОМ БИЗМУТ-ФОСФОР-МОЛИБДАТНОГ КОМПЛЕКСА

РАНЂЕЛ П. МИХАЈЛОВИЋ¹, НАТАША Р. ИГЊАТОВИЋ¹, МАРИЈА Р. ТОДОРОВИЋ², ИВАНКА ХОЦЛАЈТНЕР-АНТУНОВИЋ³ и ВЕСНА М. КАЉЕВИЋ¹

¹Природно-математички факултет, Р. Домановића 12, 34000 Крагујевац, ²Хемијски факултет, Београд, Академски брз 16 и ³Факултет за физичку хемију, Академски брз 16, Београд

Предложена је модификована спектрофотометријска метода за одређивање фосфора у угљу и пепелу од угља преко бизмут-фосфор-молибдатног комплекса. Бизмут у киселој средини са фосфатом и молибдатом гради веома стабилан комплекс који редукцијом са аскорбинском киселином прелази у плаво обојење ("молибденско плаво"). Моларни апсорпциони коефицијент РВиМо комплекса износи $1,66 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ на 720 nm (водени раствор) и $2,10 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ на 670 nm (МИБК). Интерференције од присутних јона су у толерантним границама ($\pm 2\%$). Беров закон важи за концентрације до 0,6 $\mu\text{g/mL}$ (водени раствор) и за концентрације до 1,2 $\mu\text{g/mL}$ (МИБК). Осетљивост предложене методе износи 0,0078 $\mu\text{g/mL}$ (водени раствор) и 0,0066 $\mu\text{g/mL}$ (МИБК).

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