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Spectrophotometric Determination of Phosphorus in Aqueous and Organic Phases Obtained on Pyrolysis of Naphtha

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A method for the digestion of organophosphorus compounds and the determination of phosphorus in aqueous and organic phases, which are obtained on pyrolysis of naphtha, has been proposed. The method is based on the formation of molybdivanadophosphate (MVP) which exists as stable and true yellow solution. Sample oxidation (digestion) is achieved using concentrated sulfuric and nitric acid for 30 min on water bath and subsequent heating on a medium flame to expel out sulfur trioxide fumes. The absorbance of the resulting solution was measured after proper dilution at 450 nm. The recovery and accuracy of the present method were verified by spiking experiments. Influence of foreign substances was checked. The method was applied for the determination of phosphorus in aqueous and organic phases obtained on pyrolysis of naphtha as waste product. The collective recovery of phosphorus achieved from the two (organic and aqueous phases) samples is 86%, which was quite satisfactory, while the rest 14% of phosphorus is expected go out with major gaseous products during naphtha pyrolysis. The phosphorus released with the coke was almost negligible.

Key Words: Phosphorus, Phosphorus Determination, Naphtha, Pyrolysis, Spectrophotometric determination of phosphorus.

INTRODUCTION

Phosphorus occurs widely in the environment, its importance being due to its nutrient role. In the aqueous environment, phosphorus is a prerequisite for microbial growth. Heavy algal growth, *i.e.*, algal bloom is undesirable in water bodies since secondary pollution is created[1]. As a consequence of the increasing use of organophosphorus compounds as insecticides and in agriculture, medicine and industries, the concentration of many toxic organophosphorus compounds has been increasing in the environment causing a grievous pollution of the precious gifts of nature, namely air, water and land[2, 3]. The analysis of phosphorus is therefore of extreme importance to the limnologist and those concerned with pollution[1,3].

Naphtha is the most important feed stock in modern petrochemical industries for the production of light olefins but problem is faced due to undesirable coke

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formation during the pyrolysis of naphtha. Researches have shown that addition of organophosphorus compounds to hydrocarbon feed can significantly reduce coke formation[4]. We have been involved in the reduction of coke formation during naphtha pyrolysis using organophosphorus compounds like triphenylphosphine (TPP), triphenylphosphine sulphide (TPPS) and benzenediethylphosphite (BDP)[4]. Because of high toxic characteristics associated with organophosphorus compounds, the determination and monitoring of phosphorus in aqueous, organic and solid (coke) phases obtained on pyrolysis of naphtha are mandatory to control pollution by phosphorus.

Several different approaches have been employed for determination of phosphorus in various samples using emission spectroscopy, electrothermal atomic absorption spectroscopy and mass spectrometry. Recently, inductively coupled plasma optical emission spectrometry has been preferred and used for determination of phosphorus in copper-rich wastewater[3] but has been quite expensive. Diego *et al.*[5] have proposed a method for quantification of phosphorus content in cola drinks. Also Ramadoss *et al.*[6] have developed a method for phosphorus determination in titanium bearing minerals by potentiometric titration using ion-selective electrode while Zakharov *et al.*[7] have utilised electrothermal atomic absorption spectrometry for direct determination of phosphorus in vegetable oils. Masahiro and Isao[8] have examined a solid-phase extraction technique for pretreatment of colorimetric determination of soluble reactive phosphorus in sediment extracts. The method was then applied for the determination of iron-bound P (Fe-P) in sediment samples from the Tamagawa Estuary. Surprisingly, no method has been tried for determination of phosphorus in organophosphorus compounds in aqueous and organic samples obtained during pyrolysis of naphtha or hydrocarbons.

It is, therefore, desirable to standardise a micro procedure for the determination of phosphorus with simplicity, rapidity and reliability (accuracy and precision). The often employed spectrophotometric method for determination of phosphorus is based on an ammonium molybdate reaction, followed by stannous chloride reduction of the molybdophosphate complex in acidic medium which is catalysed by phosphate ion producing a complex known as molybdenum blue[9]. The molybdenum blue method has found application in the microchemical field but has a major disadvantage that the colour is not very stable. There have been many reports on various modifications of molybdenum blue method in order to enhance the stability and sensitivity[10]. The yellow colour produced on mixing of ammonium vanadate, molybdate and phosphate is suitable for micro determination of phosphorus in organic compounds. In the present paper we report the exploitation of MVP formation for determination of phosphorus in aqueous and organic phases obtained on pyrolysis of naphtha.

EXPERIMENTAL

All of the reagents used were of analytical reagent (AR) grade and the solutions were prepared with double distilled water. Nitric acid (S.D. Fine Chemicals) and sodium hydroxide (BDH) were used to maintain the desired pH values. Sulfuric acid (S.D. Fine Chemicals) was used for the digestion of organophosphorus compounds. Ammonium vanadate solution containing 0.20% vanadate was prepared by dissolving 2.3500 g of ammonium vanadate (NH_4VO_3, Rearan, Hungary) in 500 mL boiling water followed by addition of 100 mL diluted sulfuric acid (1 : 12). The solution was cooled and diluted to 1000 mL. Ammonium molybdate solution containing 5% MoO_3 was prepared by dissolving 6.9319 g of $(NH_4)_6MoO_7O_{24}\cdot 4H_2O$ (IDPL, Hyderabad) in 100 mL hot water with continuous shaking and filtered. These solutions are stable for several months.

A double beam Hitachi spectrophotometer model U-2000, comprised of matched silica cells with path lengths 1 cm, was used for measuring absorbance of the reaction mixtures. All pH measurements were made on an Elico digital pH meter model LI-120 using BDH buffers for standardisation. All glassware used was cleaned scrupulously.

Recommended procedure

Digestion of TPP, BDP and Preparation of the Calibration Curve: 0.5016 g of TPP was taken in a 250 mL digestion (Erlenmeyer) flask to which 4.0 mL of concentrated H_2SO_4 and 0.5 mL of concentrated HNO_3 were added. The resulting mixture (solution) was digested on a water bath for 30 min. Again 5 drops of concentrated HNO_3 were added and digested on a medium flame until the solution was clear and all sulfur trioxide fumes were evolved (30 min). The solution was diluted to 100 mL and transferred quantitatively by filtration to a 500 mL volumetric flask with several rinsings of the digestion flask. This gave the stock solution of 100 $\mu g\ mL^{-1}$ phosphorus in orthophosphate form.

Thirteen aliquot portions of the stock standard orthophosphate solution (digested TPP), in the range 1–30 $\mu g\ mL^{-1}$ phosphorus were taken into 50 mL volumetric flasks. A blank was also started simultaneously. The aliquots were diluted to 30 mL. Then 5.0 mL of 0.20% vanadate solution was added slowly with continuous swirling to each batch. This was followed by addition of 5.0 mL 5% molybdate solution. Finally all the solutions were diluted to 50 mL (leaving 1–2 drops gap). The pH of all these solutions were maintained at 1.50 ± 0.02. After standing for 30 min the absorbance measurements were made at 450 nm and the data obtained were used to prepare a calibration graph. For the digestion of BDP and preparation of the calibration graph 0.3684 g of BDP was accurately weighed out in a digestion flask and exactly similar procedure for digestion and calibration curve preparation was followed as for TPP.

To determine phosphorus in organic phases containing TPP or BDP, 1 mL of organic phase sample was taken in a digestion flask followed by addition of 1 mL concentrated H_2SO_4 and 0.1 mL concentrated HNO_3. To determine phosphorus in aqueous phases containing TPP or BDP, 20 mL of aqueous phase sample was taken in a digestion flask followed by addition of 2 mL concentrated H_2SO_4 and 1 mL of concentrated HNO_3. Thereafter the same digestion procedure, as for

TPP (*vide infra*), was followed for digestion of the samples in organic as well as in aqueous phases.

RESULTS AND DISCUSSION

The yellow colour produced on mixing of ammonium vanadate, molybdate and phosphate is suitable for micro determination of phosphorus in organophosphorus compounds. The coloured complex formed is known as phosphovanadomolybdate or MVP which exists in a true solution and is better reproducible than the molybdenum blue complex. The stability of this system, together with its relative freedom from interfering substances and its ease of colour development, recommend its use for the quantitative determination of phosphorus. This method requires phosphorus to be in orthophosphate state by wet decomposition (oxidation). The organophosphorus compound is converted to orthophosphate by digestion with sulfuric-nitric acid mixture. The blanks, consisting of the reagents without phosphate, also have an appreciable absorption; so it was necessary to measure the absorbances against reference blank.

The absorption behaviour of the MVP was shown to follow Beer-Lambert's law in range 1–30 μg mL^{-1} of phosphorus from which a calibration graph was obtained. The calibration graph used for the determination of phosphorus is affected by the concentration of acid in the solution. Moreover, the low acidity employed makes it necessary and undesirable to use large excess of molybdenum and vanadate which contribute to the absorbance of the blank. Hence it was established that an optimum pH 1.5 is required for maximum development of colour for determination of phosphorus. Also vanadate is added before the addition of molybdate to prevent the formation of the yellow molybdophosphate. The linear regression equations correlating absorbance at 450 nm (A_{450}) to phosphorus (μg ml^{-1}) in TPP and BDP were derived as

$$A_{450\,(TPP)} = 0.0825\,[P], \quad r = 0.999 \qquad (1)$$

$$A_{450\,(BDP)} = 0.0267\,[P], \quad r = 0.998 \qquad (2)$$

To validate the accuracy and precision of the adopted procedure, phosphorus in spiked water samples containing TPP and BDP was determined using equations (1) and (2) respectively. The analytical results of the two samples representing organophosphorus compounds are listed in Table-1. The excellent recovery results shown by TPP and BDP indicate that these organophosphorus compounds are quantitatively oxidised (digested) to the pentavalent state by digestion mixture employed. The procedure adopted gives results with better degree of accuracy and simplicity.

Influences of foreign substances: To judge the applicability of the method, the influences of foreign substances was checked in solutions containing 10 μg mL^{-1} P-PO_4^{3-} taking interfering substances up to concentrations of 1000 μg mL^{-1}. The effect of foreign ions on the determination of phosphorus is given in Table-2, where the criterion of interference being a relative deviation $\leq 4\%$ in the determination of 10 μg mL^{-1} phosphorus. This method has advantage that removal of small quantities of arsenic is not necessary.

Applications

The method was successfully applied to the determination of phosphorus in organic and aqueous samples obtained on pyrolysis of naphtha where TPP and BDP were added to reduce coke formation. It is worth mentioning that TPP and BDP added to various naphtha feed stocks were 100, 200 and 500 μg mL^{-1}; so the determination of phosphorus in twelve (six aqueous and six organic) samples were carried out and results are shown in Table-3. The feeding rates of naphtha containing varying amounts of BDP were less than the feeding rates of naphtha containing TPP, which explains the less quantities of phosphorus obtained from BDP samples (*cf.* Table-3). On the basis of mass balance calculation it was found that the quantity of phosphorus in aqueous phase was quite less than in organic phase while cumulative average recovery was found to be 86%. An attempt was made to determine the phosphorus content in coke formed during naphtha pyrolysis but could not be detected. It was, therefore, concluded that the rest 14% phosphorous came out with the useful gaseous products obtained during naphtha pyrolysis[4].

TABLE -1
ACCURACY AND PRECISION OF PHOSPHORUS DETERMINATION IN TPP AND BDP SPIKED WATER BY THE PROPOSED PROCEDURE

pH = 1.50, temp. = 25.0 ± 0.1°C.

Amount of [P] added (μg ml^{-1})	TPP		BDP	
	[P]* found ± s (%) (μg mL^{-1})	Error	[P]* found ± s (%) (μg mL^{-1})	Error
1.0	1.01 ± 0.03	+1.00	0.98 ± 0.02	–2.00
2.0	2.05 ± 0.03	+2.50	1.96 ± 0.03	–2.00
4.0	4.06 ± 0.08	+1.50	4.08 ± 0.07	+2.00
6.0	6.06 ± 0.11	+1.00	6.08 ± 0.10	+1.33
8.0	8.05 ± 0.11	+0.63	7.90 ± 0.11	–1.25
10.0	9.90 ± 0.11	–1.00	9.85 ± 0.07	–1.50
12.0	12.10 ± 0.13	+0.83	11.80 ± 0.08	–1.67
15.0	15.00 ± 0.07	0.00	15.08 ± 0.08	+0.53
18.0	18.30 ± 0.09	+1.67	17.65 ± 0.09	–1.94
20.0	19.50 ± 0.35	–2.50	19.60 ± 0.25	–2.00
23.0	23.00 ± 0.42	0.00	23.15 ± 0.32	+0.65
25.0	25.00 ± 0.50	0.00	25.55 ± 0.08	+2.20
30.0	29.70 ± 0.40	–1.00	29.60 ± 0.07	–1.33
	Av.= 1.05		Av.= 1.57	

*Mean of three determinations.

The ±s values represent the standard deviation of the mean for three determinations.

TABLE-2
EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 10 μg mL^{-1} OF PHOSPHORUS

pH = 1.50, temp.= 25.0 ± 0.1°C.

Ions added	Concentration (μg mL^{-1})	Relative error (%)
NH_4^+	1000	–21.3
Ba^{2+}	1000	–1.5
BO^{3-}	1000	–2.8
K^+	1000	+0.5
Na^+	1000	+0.5
Mg^{2+}	1000	+0.5
Ca^{2+}	1000	+2.3
Cl^-	500	–3.2
Ni^{2+}	200	+1.6
Cu^{2-}	200	+1.8
Co^{2+}	200	+1.9
Pb^{2+}	200	+1.8
F^-	40	–2.8
Fe^{2+}	20	+2.4
Fe^{3+}	20	–2.9
NO_3^-	20	–1.8
SO_3^-	20	–2.5
AsO_4^-	20	–3.0
Si(IV)	20	–3.5

TABLE-3
DETERMINATION OF PHOSPHORUS IN AQUEOUS AND ORGANIC SAMPLES, CONTAINING TPP AND BDP, OBTAINED ON PYROLYSIS OF NAPHTHA AND PERCENTAGE RECOVERY

pH = 1.50, temp. = 25 ± 0.1°C

Type of samples	TPP containing naphtha feed stocks μg mL^{-1}			BDP containing naphtha feed stocks		
	100	200	500	100	200	500
	Phosphorous found^{a,b} (μg mL^{-1})			Phosphorous founda, b (μg mL^{-1})		+
Organic phase	1365.5	2732.0	6525.5	797.0	1595.0	3986.0
Aqueous phase	65.4	131.0	325.0	38.2	77.3	193.0
Recovery* (%)	86.0	86.0	85.0	85.0	86.0	86.0

[a] Mean of three analyses.

[b] Phosphorus determined in total organic and aqueous phases obtained.

*Calculated on the basis of mass balance.

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