



ELSEVIER

Journal of Chromatography A, 696 (1995) 257–263

JOURNAL OF
CHROMATOGRAPHY A

Extraction–gas chromatographic method for the determination of organophosphorus compounds as lubricating oil additives

Albertine E. Habboush*, Sabri M. Farroha, Hussain I. Khalaf

Chemistry Department, College of Science, University of Baghdad, Baghdad, Iraq

First received 16 March 1994; revised manuscript received 17 October 1994; accepted 18 October 1994

Abstract

A direct solvent extraction–gas chromatographic method was developed for the determination of organophosphorus compounds as additives in lubricating oil for control purposes. Ethanol (95%) was used as an extractant and Varian GC-Vista 6000 gas chromatograph with a 3% OV-17 column and dual flame photometric detector was used for the measurements under the optimum experimental conditions. The accuracy and precision of the method were determined by preparing model samples of different types of engine lubricating base oils blended with different amounts of triphenyl phosphate or *p*-tricresyl phosphate ranging from 0.002 to 1.0% (w/w), which correspond to 2.12–955 ppm of phosphorus. The results showed errors ranging from 0.40 to 2.96% and the relative standard deviation did not exceed 3%. This method was applied successfully to the determination of phosphorus compounds in different types of lubricating oils. Each sample requires 20 min for analysis and 72 samples can be analysed per 8-h day. The effect of storage on the amount of phosphorus as an additive in lubricating oils was also considered.

1. Introduction

An important industrial use of phosphorus is as organophosphorus additives in lubricating oils because of their oxidation-inhibiting, corrosion-inhibiting, anti-wear and extreme-pressure characteristics [1–3]. Lubricant additives are based on various organic and inorganic chemicals and the proportion of organophosphorus is 6–10% of the total additive content [2]. Limitations on the amount of phosphorus compounds is important when petroleum products are blended with additives. Hence an accurate, simple, rapid and reproducible method of analysis for control

purposes in blending or for performance testing on field samples taken during customer use is required. Chemical methods usually require the phosphorus in the sample first to be converted into inorganic orthophosphate, which is usually done by oxidation and/or hydrolysis of the sample [4–6]. The most popular chemical method seems to be spectrophotometry [7], but completeness of combustion and burning a sufficient amount of sample are common problems. Photometric titration for the determination of disubstituted dithiophosphates in lubricating oils was described by Płaza [8]. The method is simple and rapid and samples do not require separation or other preliminary stages prior to their analysis, but the method is specific for this type of

* Corresponding author.

additive and only at concentrations above 0.01%.

Emission spectroscopic methods [9] are also widely used. Their main advantage is the wide concentration range of additives that can be determined, but the disadvantages are poor precision (5–10%) and slowness and also HPO flame emission suffers from interferences from organic solvents which can affect the emission intensity of species to be detected [10].

Atomic absorption spectrometry (AAS) has also been used to determine phosphorus additives in lubricating oils [11,12]. The electrothermal AAS determination of phosphorus additive in lubricating oils and related products was reported by Russeva and Rhavezov [13]. The phosphorus content of the samples analysed ranged from 0.003% to 7%. Interference from inorganic phosphorus can be expected in this method.

Gas chromatography with flame photometric detection (GC-FPD) has been used to determine some organophosphorus compounds [14,15]. However, very little has been published on the use of GC for the determination of organophosphorus compounds as additives in lubricating oils or other petroleum products. Pospisilova et al. [16], determined tricresyl phosphate in lubricating oils using GC with nitrogen-phosphorus detection. The phosphorus content of the samples analysed varied from 0.049% to 0.093% with a relative error of 5–10%.

Habboush et al. [17] developed a direct GC method for the determination of organophosphorus compounds as gasoline additives. The

phosphorus content of the samples analysed ranged from 0.84 to 13.4 ppm with an error ranging from 1×10^{-4} to 7×10^{-4} % (w/w) and a relative standard deviation not exceeding 4.2%.

This work was aimed at developing a method for the determination of organophosphorus compounds as additives in lubricating oils by direct extraction of the additive from the sample in a suitable organic solvent and analysis by GC-FPD. Triphenyl phosphate and *p*-tricresyl phosphate were used as models for the organophosphorus additives in lubricating oils.

2. Experimental

2.1. Apparatus

A Varian GC-Vista 6000 gas chromatograph equipped with both a flame photometric detector and a flame ionization detector. The FDP was used during this work. Nitrogen of 99.99% purity was used as the carrier gas with an optimum volume flow-rate of 30 ml/min. The optimum volume flow-rates of the other gases were hydrogen 140 ml/min, and air-I 80 ml/min and air-II 170 ml/min. The detector and column inlet temperatures were set at 20°C above the column temperature. Isothermal column temperatures between 200 and 280°C were applied (Table 1) and 260°C was the most suitable for selective separation (Fig. 1). All the optimum conditions found during this work were fixed throughout the analysis. A linear 1200 paper recorder with capacity 1 mV and chart speed 1

Table 1
Retention times of organophosphorus compounds dissolved in 95% ethanol on 3% OV-17 at different column temperatures

Compounds	Retention time (min)								
	200°C	210°C	220°C	230°C	240°C	250°C	260°C	270°C	280°C
Triphenyl phosphate	17.6	12.2	7.91	5.33	3.77	2.62	1.88	1.49	1.01
<i>p</i> -Tricresyl	43.0	39.8	20.6	14.4	9.43	5.34	4.39	3.01	2.12

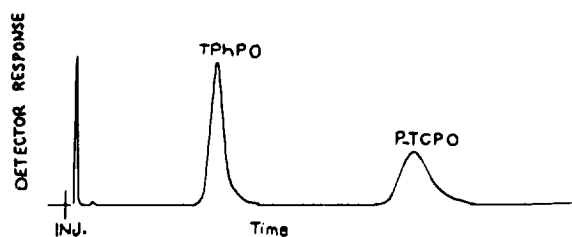


Fig. 1. Chromatogram of a mixture of triphenyl phosphate and *p*-tricresyl phosphate in gasoline engine lubricating oil obtained on a 3% OV-17 column with FPD at 260°C.

cm/min was used. Columns were made of stainless-steel tubing (2 m × 3.25 mm O.D. and 2.4 mm I.D.). They were packed with different percentages of different polysiloxane liquid stationary phases on Chromosorb W DMCS (80–100 mesh). The most selective for the analysis was found to be 3% OV-17 (50% phenylmethylpolysiloxane).

2.2. Materials

All compounds were of high purity purchased from Fluka and BDH and no further purification was needed. Engine lubricating oils (base and

improvement treated oil) were obtained from the Al-Dora Refinery, Baghdad, Iraq.

2.3. Preparation of samples

Samples of different types of engine lubricating oils were blended with different amounts of triphenyl phosphate ranging from 0.002 to 1.0% (w/w), which correspond to 2.12–955 ppm phosphorus; this range was selected based on the literature [2]. The preparation was done by weighing 1 g of triphenyl phosphate accurately and blending it with 100 g of oil by heating at 40°C for 1 min with shaking. Approximately 1 g of this sample was weighed accurately in a conical flask, then 20 ml of 95% ethanol were added, the mixture was shaken well and transferred into a 25-ml separating funnel, shaken vigorously for 1 min and then allowed to settle for 5 min and the ethanol layer (upper) was transferred into a 100-ml volumetric flask. The extraction with 95% ethanol was repeated five times to ensure completeness of extraction and 95% ethanol was used to complete the volume to 100 ml. The same procedure of blending and extraction was followed for *p*-tricresyl phosphate.

Table 2
Accuracy and precision of the determination of triphenyl phosphate as an additive in gasoline engine lubricating oils

Sample	Phosphorus added (ppm)	Phosphorus found ^a (ppm)	Error (%)	R.S.D. (%)	Recovery (%)
Base gasoline engine lubricating oil	951	944	-0.70	1.70	99.30
	92.5	91.5	-1.08	0.10	98.92
	9.24	9.11	-1.40	1.05	98.60
	4.65	4.55	-2.08	2.31	97.92
	2.10	2.04	-2.87	1.70	97.13
Treated gasoline lubricating oil ^b	952	941	-1.15	1.33	98.89
	92.0	91.0	-1.09	0.61	98.99
	9.09	8.95	-1.50	0.72	98.50
	4.58	4.50	-1.80	2.23	98.20
	2.12	2.05	-2.40	2.28	97.60

^a Mean of six values.

^b Gasoline engine lubricating oil treated with an improvement additive in the refinery.

Table 3
Accuracy and precision of the determination of triphenyl phosphate as an additive in diesel engine lubricating oils

Sample	Phosphorus added (ppm)	Phosphorus found ^a (ppm)	Error (%)	R.S.D. (%)	Recovery (%)
Base diesel engine lubricating oil	955	940	-1.57	0.58	99.47
	92.3	91.8	-0.54	0.35	98.41
	9.20	9.11	-0.98	0.59	99.02
	4.45	4.33	-2.62	1.76	97.38
	2.40	2.34	-2.36	2.42	97.64
Treated diesel engine lubricating oil ^b	949	939	-1.05	0.35	98.96
	95.6	94.2	-1.50	1.34	98.50
	9.11	9.02	-1.01	0.60	98.99
	4.55	4.43	-2.64	1.93	97.36
	2.50	2.44	-2.27	1.65	97.73

^{a,b} See Table 2.

2.4. Analysis

A 1- μ l volume of the extractant was injected into the gas chromatograph under the optimum experimental conditions found during this work. The calibration graph method was used to determine the amount of organophosphorus compound as an additive in lubricating oils. There-

fore, a series concentrations of these additives containing phosphorus ranging from 1.0 to 1000 ppm was prepared in 95% ethanol and 1 μ l of each sample was injected into the gas chromatograph.

Samples were prepared in 15-ml Quickfit stoppered, dark-glass tubes. The injections of all samples were made with a 1- μ l Hamilton syringe

Table 4
Accuracy and precision of the determination of *p*-tricresyl phosphate as an additive in gasoline engine lubricating oils

Sample	Phosphorus added (ppm)	Phosphorus found ^a (ppm)	Error (%)	R.S.D. (%)	Recovery (%)
Base gasoline engine lubricating oil	850	842	-0.61	0.61	99.03
	85.1	84.2	-1.08	0.30	98.92
	8.56	8.45	-1.32	0.65	98.68
	4.60	4.53	-1.45	1.11	98.55
	2.25	2.21	-1.96	1.40	98.04
Treated gasoline lubricating oil ^b	850	839	-1.29	0.23	98.69
	85.5	84.5	-1.16	0.56	98.84
	8.45	8.45	0.66	0.59	99.44
	4.35	4.45	2.25	1.42	97.75
	2.30	2.27	1.31	1.53	98.70

^{a,b} See Table 2.

Table 5
Accuracy and precision of the determination of *p*-tricresyl phosphate as an additive in diesel engine lubricating oils

Sample	Phosphorus added (ppm)	Phosphorus found ^a (ppm)	Error (%)	R.S.D. (%)	Recovery (%)
Base diesel engine lubricating oil	850	843	-0.92	1.25	99.15
	85.5	84.2	-1.52	0.42	98.44
	8.45	8.41	-0.40	1.72	99.60
	4.50	4.36	-2.96	2.07	97.04
	2.30	2.28	-0.73	2.80	99.27
Treated diesel engine lubricating oil ^b	855	845	-1.17	0.59	98.88
	86.6	85.1	-1.73	0.51	98.23
	8.55	8.38	-1.99	0.60	98.01
	4.44	4.35	-2.03	1.15	97.97
	2.60	2.55	-1.93	4.96	98.07

^{a,b} See Table 2.

and the value of each determination was the mean of six analyses. The results are given in Tables 2–5.

Samples of different types of engine lubricating oils blended with different amounts of *p*-tricresyl phosphate as an additive were stored for 1 month in the ambient atmosphere and the same procedures were followed for extraction

and analysis. The results are given in Tables 6 and 7.

3. Results and discussion

Triphenyl phosphate and *p*-tricresyl phosphate were used as models of organophosphorus addi-

Table 6
Effect of storage of *p*-tricresyl phosphate as an additive in gasoline engine lubricating oils

Sample	Mean value before storage (ppm)	Mean value after storage ^a (ppm)	<i>t</i> Value ^b	Significance ^c
Base oil (gasoline)	842	840	0.10	N.S.
	84.2	84.2	0.15	N.S.
	8.44	8.44	0.00	N.S.
	4.35	4.58	0.11	N.S.
	2.20	2.20	0.34	N.S.
Treated oil ^d	839	837	0.78	N.S.
	84.5	84.5	0.02	N.S.
	8.45	8.48	1.16	N.S.
	4.24	4.25	0.26	N.S.
	2.27	2.26	0.43	N.S.

^a Storage for 30 days.

^b Data were analysed statistically by using the *t*-test.

^c N.S. = Not significant.

^d See footnote B in Table 2.

Table 7
Effect of storage of *p*-tricresyl phosphate as an additive in diesel engine lubricating oils

Sample	Mean value before storage (ppm)	Mean value after storage ^a (ppm)	<i>t</i> Value ^b	Significance ^c
Base oil (diesel)	843	843	0.00	N.S.
	84.2	84.2	0.00	N.S.
	8.41	8.41	0.00	N.S.
	4.36	4.37	0.00	N.S.
	2.28	2.34	1.02	N.S.
Treated oil ^d	845	846	0.15	N.S.
	85.1	85.0	0.18	N.S.
	8.38	8.41	0.93	N.S.
	4.35	4.40	1.54	N.S.
	2.55	2.56	0.29	N.S.

^{a-d} See Table 6.

tives in lubricating oils. Ethanol was chosen the extraction solvent because of its high polarity, so it extracts the polar components particularly well, and also it is not toxic and easy to work with. The base oil consisted of 70–85% *n*-alkanes (C₂₄–C₃₅) and 15–30% naphthenes, which are not soluble in ethanol, so the expected negative peak interference from alkanes with FPD can be prevented [14,18].

A 3% OV-17 column was utilized for the separation of organophosphorus compounds according to the results obtained previously in our laboratory [19], and a dual flame photometric detector was used for the determination because of its high selectivity, linearity and sensitivity [20].

In order to examine the accuracy, sensitivity and precision of the method, 2.12 ppm was the minimum and 955 ppm the maximum amounts of phosphorus blended with engine lubricating oil as triphenyl phosphate or *p*-tricresyl phosphate.

Tables 2 and 3, for triphenyl-phosphate blended with gasoline and diesel engine lubricating oils, respectively, show errors ranging from 0.70 to 2.80% with relative standard deviations not exceeding 2.4%. Tables 4 and 5, for *p*-tricresyl phosphate blended with gasoline and diesel engine lubricating oils, respectively, show errors ranging from 0.4 to 2.96% with relative standard deviations not exceeding 2.80%.

Tables 6 and 7 indicate that storage for 30 days in an ambient atmosphere of different types of lubricating oils containing phosphorus with concentrations ranging from 2.20 to 845 ppm as *p*-tricresyl phosphate has no effect on the concentration of phosphorus additives in all samples. Finally, the developed method proved to be rapid, since the analysis of each sample requires 20 min and 72 samples can be analyzed per 8-hr day.

References

- [1] J.R. Van Wazer, *Phosphorus and Its Compounds*, Vol. II. Interscience Publishers, New York, NY, 1961, Ch. 31.
- [2] W.C. Gergel, *Lubricant Additive Chemicals*, Report No. C-9331, Lubrizol, Cleveland, OH, 1987.
- [3] E.S. Forbes, *Tribology*, August (1970) 145.
- [4] J.E. Barney, II, J.G. Bergmann and W.G. Tuskan, *Anal. Chem.*, 31 (1959) 1394.
- [5] *ASTM Standards on Petroleum Products and Lubricants*, American Society for Testing and Materials, Philadelphia, PA, 1958, Method D 1091-58T.
- [6] A. Pietrogrande, M. Zancato and G. Bontempelli, *Analyst*, 100 (1985) 993.
- [7] S.J. Gedanky, J.E. Bowen and O.I. Milner, *Anal. Chem.*, 32 (1960) 1447.
- [8] S. Płaza, *Analyst*, 109 (1984) 1313.
- [9] W.N. Elliot, C. Heathcote and R.A. Mostyn, *Talanta*, 19 (1972) 359.

- [10] B.G. Julin, H.W. Vanderborn and J.J. Kirkland, *J. Chromatogr.*, 112 (1975) 443.
- [11] P. Tittarelli and A. Mascherpa, *Anal. Chem.*, 53 (1981) 1466.
- [12] A. Prevot and M. Gente Janniaux, *At. Absorpt. Newsl.*, 17 (1978) 1.
- [13] E. Russeva and I. Rhavezov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 19 (1986) 422.
- [14] C.R. Vogt and S. Kapilla, *J. Chromatogr. Sci.*, 17 (1979) 546.
- [15] S. Sass and G.A. Parker, *J. Chromatogr.*, 189 (1980) 331.
- [16] K. Pospisilova, J. Senkyrova, J. Paryzkova and Z. Jelinek, *Chem. Prum.*, 38 (1988) 484; *C.A.*, 109 (1988) 233839q.
- [17] A.E. Habboush, S.M. Farroha and L.S. Umar, *Abstr. PITTCON 1990*, p. 321, New York.
- [18] S.O. Abdelrahman and L.N. Kvitkovski, *Izv. Vyssh. Uchebn. Zaved. Neft Gaz*, 12 (1987) 49; *Ca.*, 108 (1988) 189509k.
- [19] H.I. Khalaf, *M.Sc. Thesis*, College of Science, University of Baghdad, Baghdad, 1989.
- [20] P.L. Patterson, R.L. Howe and A. Abu-Shumays, *Anal. Chem.*, 50 (1978) 345.