



ELSEVIER

Journal of Chromatography A, 905 (2001) 207–222

JOURNAL OF  
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

# Structural determination of zinc dithiophosphates in lubricating oils by gas chromatography–mass spectrometry with electron impact and electron-capture negative ion chemical ionization

M. Becchi<sup>a,\*</sup>, F. Perret<sup>a</sup>, B. Carraze<sup>b</sup>, J.F. Beziau<sup>b</sup>, J.P. Michel<sup>c</sup>

<sup>a</sup>Service Central d'Analyse, CNRS, B.P. 22, 69390 Vernaison, France

<sup>b</sup>PSA, Service Central d'Analyses Physico-Chimiques, 78140 Velizy, France

<sup>c</sup>PSA, Service Lubrifiants, 25420 Belchamps, France

Received 11 July 2000; received in revised form 18 September 2000; accepted 19 September 2000

## Abstract

Pentafluorobenzyl ester derivatives were used to identify zinc dialkyldithiophosphates and diaryldithiophosphates anti-wear engine oil additives by GC–electron impact ionization (EI) MS and GC–electron-capture negative ion chemical ionization (ECNCI) MS analysis. GC–EI-MS of the dialkyldithiophosphate–pentafluorobenzyl derivatives afforded characteristic fragment ions corresponding to the cleavage of one and two alkyl radicals. In most cases, information was only obtained on one alkyl chain. Additional and complete information was obtained with retention time indices using synthetic derivatives and with GC–ECNCI-MS analysis. ECNCI afforded characteristic dithiophosphate anions which allowed the determination of the total number of carbon atoms in the alkyl radicals. The diastereoisomer mixtures of 2-hydroxy-*sec*-alkyl radicals were completely separated on GC analysis. © 2001 Elsevier Science B.V. All rights reserved.

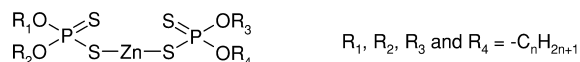
**Keywords:** Oils; Derivatization, GC; Zinc dithiophosphates; Dithiophosphates; Phosphates; Dialkyldithiophosphates; Diaryldithiophosphates

## 1. Introduction

Zinc dialkyldithiophosphates (ZnDDTPs) have been used for many years in automobile lubricants. They protect the lubricant against oxidative deterioration and serve as anti-wear agents. The ZnDDTPs consist of a polar organometallic core, usually a zinc atom with two dithiophosphate esters, surrounded by an alkylated side. The alkyl sidechains increase the

solubility in the base oil (Fig. 1). Their typical concentration is about 1% in engine oils.

Electron impact ionization mass spectrometry (EI-MS) has been used to characterize ZnDDTP mixtures [1]. Interesting results were obtained with liquid ionization mass spectrometry mode producing quasi-molecular ions [2].



$\text{R}_1, \text{R}_2, \text{R}_3$  and  $\text{R}_4 = -\text{C}_n\text{H}_{2n+1}$

Fig. 1. Dialkyl ZnDDTPs structure;  $\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4 = \text{C}_n\text{H}_{2n+1}$ .

\*Corresponding author. Tel.: +33-4-7802-2283; fax: +33-4-7802-7187.

E-mail address: m.becchi@sca.cnrs.fr (M. Becchi).

Direct analysis of ZnDDTPs was established by using electrospray ionization (ESI) MS [3,4]. This technique can quickly characterize ZnDDTPs in oil samples without extensive preparation and provides information on the molecular ion distribution of the various types of alkyl groups. In the positive ESI ion mode ZnDDTPs form cationized molecular ion with sodium [4] or adduct ions by reaction with dimethyl sulfoxide [3]. The negative ESI ion mode leads to the characterization of dialkyldithiophosphate anions. Nevertheless, in all cases, it was impossible to determine the precise structure of each compound and only information on the total carbon atom number of the different alkyl groups was obtained ( $R_1+R_2$  and/or  $R_1+R_2+R_3+R_4$  in Fig. 1).

There are currently no published optimal chromatographic separation method for ZnDDTPs. Normal-phase high-performance liquid chromatography (HPLC) could not resolve isomer mixtures [5] and mixed aqueous and organic-based solvents used in reversed-phase HPLC lead to the dissociation of zinc complexes [6].

More recently a method has been described that fully characterizes alkyl groups in zinc dialkyldithiophosphates. Methyl esters were formed and gas chromatography–mass spectrometry with electron impact ionization (GC–EI–MS) carried out, with a second method *p*-nitrobenzyl esters were formed and liquid chromatography–mass spectrometry (LC–MS) using atmospheric pressure chemical ionization (APCI) in the negative ion mode was used [7]. The GC–EI–MS of methyl esters enabled separation of isomers and determination of alkyl chain length by use of synthetic reference compounds. In some cases, however there were no reference compound available and only one alkyl chain could be identified. In these cases, LC–MS could be used to yield molecular ion information on the dithiophosphate anion (deprotonated molecular ion).

We investigated a more convenient derivatization pathway to fully characterize ZnDDTPs by GC–MS. Pentafluorobenzyl (PFB) ester derivatives were suitable for both GC–MS with EI and/or electron-capture negative ion chemical ionization (ECNCl) analysis. Zinc diaryldithiophosphates were also tentatively analyzed by this new method.

## 2. Experimental

### 2.1. Chemicals, reagents and samples

All solvents and reagents were of analytical-grade purity. The following compounds were obtained from Aldrich (St. Quentin Fallavier, France): 1-propanol; 2-propanol; 1-butanol; 2-butanol; 2-methyl-1-propanol; 1-pentanol; 2-pentanol; 4-methyl-1-pentanol; 4-methyl-2-pentanol; 1-hexanol; 2-hexanol; 2-methyl-1-pentanol; 3-methyl-1-pentanol; 3-methyl-2-pentanol; 2-methyl-3-pentanol; 3-hexanol; 2,3-dimethyl-2-butanol; 3,3-dimethyl-2-butanol; 2-ethyl-1-butanol; 2-methyl-2-pentanol; 3-methyl-3-pentanol; 2-ethyl-1-hexanol; 2,3,4,5,6-pentafluorobenzyl bromide and phosphorus pentasulfide ( $P_2S_5$ ). Tetramethylammonium hydroxide (TMAH) 0.1 M solution in 2-propanol and methanol were purchased from Merck (article 1 08124 0250; Nogent-sur-Marne, France). 5 $\beta$ -Androstane-3,17-dione was purchased from Steraloids (Interchim, Montluçon, France). Solid-phase extraction (SPE) was carried out on Bakerbond SPE columns filled with 500 mg of silica gel (J.T. Baker, 7086-03, Noisy le Sec, France).

### 2.2. Samples

The eight engine oil sample analyzed and namely OS1 to OS8 were obtained from different petroleum and lubricant manufacturers.

### 2.3. Synthesis of dithiophosphoric acids

Reference dialkyldithiophosphoric acids were prepared following the method of Brazier and Elliott [8]. 10 mmol (2.22 g) of  $P_2S_5$  were carefully added to 40 mmol of the well-stirred alcohol or respective alcohol mixture (1:1), while a temperature of 60–80°C was maintained, except for the octanol which was 100°C. The solution was stirred for 6 h and then cooled overnight in a refrigerator (4°C). The dithiophosphoric acids were then filtered from any excess of  $P_2S_5$ . Finally, 20  $\mu$ l of the final solution was used to prepare the PFB derivatives.

#### 2.4. Extraction of zinc dialkyldithiophosphates from oil samples

About 40 mg of each oil sample was dissolved in 3 ml of hexane. The sample solution was poured through a silica gel SPE column and washed with 40 ml of hexane. The zinc dithiophosphates (ZnDTPs) were eluted with 10 ml of dichloromethane and 10 ml of dichloromethane–acetone (90:10, v/v) mixture. These two fractions were combined and the solvent was evaporated to dryness to obtain the ZnDTP fraction. Half of the dried extract was used to prepare the PFB derivatives for GC–MS analysis. The other half was kept to use for other analytical studies: IR, ICP (inductively coupled plasma), ESI-MS.

#### 2.5. Pentafluorobenzyl derivatization

The dried extracts (from oil samples or dithiophosphoric acid syntheses) were treated with 0.6 ml of 0.03 M of a TMAH solution in acetonitrile–water (95:5, v/v) mixture in an ultrasonic bath for 30 min. Then, 1 ml of pentafluorobenzyl bromide solution in acetonitrile (0.02 M) was added. This was left in the ultrasonic bath for 30 min. Dithiophosphate–pentafluorobenzyl (DTP–PFB) esters were extracted successively by 4 ml and 2 ml of hexane. The upper organic phases were collected and concentrated to dryness.

The DTP–PFB ester derivatives from oil samples were redissolved in 0.2 ml of acetonitrile. Those from dithiophosphoric acid syntheses were first diluted in 1.5 ml and then diluted again to 1/15 in acetonitrile.

#### 2.6. GC–MS analysis

GC–MS analyses were performed on a Hewlett-Packard HP 6890 gas chromatograph (Agilent Technologies) equipped with a HP5-MS [poly(dimethyldiphenylsiloxane) containing 5 mol% diphenylsiloxane groups] fused-silica capillary column (30 m×0.25 mm I.D.; 0.25 μm film thickness) linked to a HP 5973 mass-selective detector.

Before injections, the 0.1 ml solution of DTP–PFB ester derivatives was diluted with 0.1 ml of the

internal standard solution (5β-androstane-3,17-dione, 10 μg/ml in acetonitrile). Injections (1 μl) were made in the pulsed splitless mode at 280°C, using helium as carrier gas (constant flow 1.2 ml). The oven temperature was increased from 100°C (1 min) to 175°C by 25°C/min, then to 310°C at 5°C/min, and maintained at the final temperature for 2 min.

In the EI mode, the source and the quadrupole temperatures were set at 230°C and 150°C, respectively. The electron energy was 70 eV. A mass range between 45 and 650 u was scanned.

In ECNCI, an appropriate chemical ionization (CI) source device from Hewlett-Packard was used. The source and the quadrupole temperatures were set at 150°C and 106°C, respectively. Methane was used as the reactant gas and the electron energy was set at 136 eV by the NCI autotune software. The scanning mass range was 130 to 700 u.

### 3. Results and discussion

#### 3.1. Synthesis of dithiophosphoric acids

To fully characterize alkylated side of ZnDDTPs the dithiophosphoric acid units were analyzed. Different C<sub>3</sub> to C<sub>8</sub> alkyl dithiophosphoric acids were synthesized using definite alcohol structures in the reaction with phosphorus pentasulfide [8]. An equimolecular mixture of two different alcohols in the reaction led to the formation of three compounds:

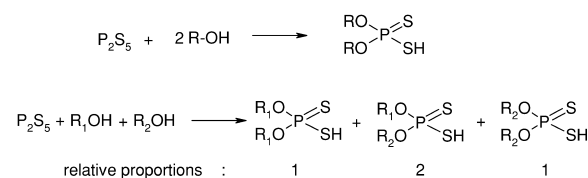


Fig. 2. Dialkyldithiophosphoric acids synthesis (R, R<sub>1</sub>, R<sub>2</sub>=C<sub>3</sub> to C<sub>8</sub> alkyls).

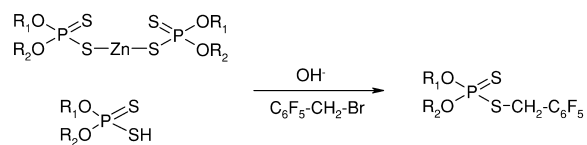


Fig. 3. Pentafluorobenzyl ester formation from ZnDDTPs or dithiophosphoric acids.

Table 1  
GC–MS (EI and ECNCI) analyses of synthetic dialkyl DTP–PFB ester derivatives

Dialkyldihiphosphate–PFB ester derivatives	$t_R$ (min)	Relative retention time (RRT)	EI, $m/z$ ions	ECNCI, $m/z$ ions
2-Propyl/2-propyl	8.18	0.441	353	213
1-Propyl/2-propyl	8.85	0.477	353	213
2-Propyl/2-methyl-1-propyl	9.30	0.502	353	227
1-Propyl/1-propyl	9.59	0.517	353	213
2-Propyl/2-pentyl	10.16	0.548	353	241
	10.27	0.554	353	241
2-Butyl/2-butyl	10.38	0.560	367	241
	10.45	0.564	367	241
	10.51	0.567	367	241
2-Methyl-1-propyl/2-methyl-1-propyl	10.51	0.567	367	255
2-Propyl/4-methyl-2-pentyl	10.62	0.573	353	255
	10.77	0.581	353	255
2-Propyl/3,3-dimethyl-2-butyl	10.79	0.582	353	255
	10.82	0.584	353	255
2-Propyl/2-methyl-3-pentyl	11.03	0.595	353	255
2-Propyl/3-hexyl	11.16	0.602	353	255
	11.22	0.606	353	255
2-Propyl/3-methyl-2-pentyl	11.17	0.603	353	255
	11.30	0.609	353	255
2-Propyl/2-hexyl	11.31	0.610	353	255
	11.50	0.620	353	255
1-Propyl/4-methyl-2-pentyl	11.42	0.616	353	255
	11.53	0.622	353	255
2-Propyl/2-methyl-1-pentyl	11.66	0.629	353	255
2-Propyl/2-ethyl-1-butyl	11.68	0.631	353	255
2-Butyl/4-methyl-2-pentyl	11.83	0.638	367; 395	269
	11.90	0.642	367; 395	269
	11.98	0.646	367; 395	269
	12.02	0.648	367; 395	269
1-Butyl/1-butyl	11.94	0.644	367	241
2-Methyl-1-propyl/4-methyl-2-pentyl	11.90	0.642	367; 395	269
	11.99	0.647	367; 395	269
2-Propyl/4-methyl-1-pentyl	12.03	0.649	353	255
2-Propyl/3-methyl-1-pentyl	12.03	0.649	353	255
2-Pentyl/2-pentyl	12.35	0.666	381	269
	12.44	0.671	381	269
	12.52	0.675	381	269
2-Methyl-1-propyl/3-methyl-2-pentyl	12.47	0.673	367	269
	12.54	0.677	367	269
2-Propyl/1-hexyl	12.60	0.680	353	255
2-Methyl-1-propyl/2-hexyl	12.62	0.681	367; 395	269
	12.74	0.688	367; 395	269
2-Pentyl/4-methyl-2-pentyl	12.84	0.693	381; 395	283
	12.94	0.698	381; 395	283
	12.95	0.698	381; 395	283
	13.03	0.703	381; 395	283
2-Methyl-1-propyl/2-methyl-1-pentyl	12.96	0.699	367; 395	269
1-Butyl/1-pentyl	13.30	0.718	367; 381	255
4-Methyl-2-pentyl/4-methyl-2-pentyl	13.32	0.718	395	297

Table 1. Continued

Dialkyldihiphosphate–PFB ester derivatives	$t_R$ (min)	Relative retention time (RRT)	EI, $m/z$ ions	ECNCI, $m/z$ ions
	13.43	0.724	395	297
	13.53	0.730	395	297
3,3-Dimethyl-2-butyl/3,3-dimethyl-2-butyl	13.66	0.737	395	297
	13.84	0.746	395	297
	13.96	0.753	395	297
2-Propyl/2-ethyl-1-hexyl	13.94	0.752	353	283
2-Methyl-3-pentyl/2-methyl-3-pentyl	14.17	0.764	395	297
3-Hexyl/3-hexyl	14.44	0.779	395	297
3-Methyl-2-pentyl/3-methyl-2-pentyl	14.45	0.779	395	297
	14.58	0.786	395	297
	14.69	0.792	395	297
1-Pentyl/1-pentyl	14.64	0.790	381	269
2-Hexyl/2-hexyl	14.78	0.797	395	297
	14.93	0.806	395	297
	15.04	0.811	395	297
2-Butyl/2-ethyl-1-hexyl	15.20	0.820	367	297
2-Methyl-1-propyl/2-ethyl-1-hexyl	15.25	0.823	367; 423	297
2-Methyl-1-pentyl/2-methyl-1-pentyl	15.45	0.833	395	297
2-Ethyl-1-butyl/2-ethyl-1-butyl	15.48	0.835	395	297
4-Methyl-1-pentyl/4-methyl-1-pentyl	16.28	0.878	395	297
3-Methyl-1-pentyl/3-methyl-1-pentyl	16.30	0.880	395	297
1-Hexyl/1-hexyl	17.43	0.940	395	297
2-Ethyl-1-hexyl/2-ethyl-1-hexyl	19.77	1.067	423	353

Table 2

Determination of the carbon atom number of one alkyl chain using ion A formation from EI mass spectra of DDTP–PFB ester derivatives

Dialkyldithiophosphate–PFB esters, ion A $[M-R_2+2H]^+$ $=[(OH)(OR_1)P(SH)(SCH_2C_6F_5)]^+$	Alkyl residue carbon atom number, $n$ ( $R_1=C_nH_{2n+1}$ )
353	3
367	4
381	5
395	6
423	8

Table 3

Determination of the total carbon atom number of dialkyl residues using the dithiophosphate anion from ECNCI mass spectra of DDTP–PFB ester derivatives

Dialkyldithiophosphate–PFB esters, dithiophosphate anion $[M-181]^- = [(OR_1)(OR_2)PS_2]^-$	Total carbon atom number of alkyl residues $R_1+R_2$
213	6
227	7
241	8
255	9
269	10
283	11
297	12
353	16

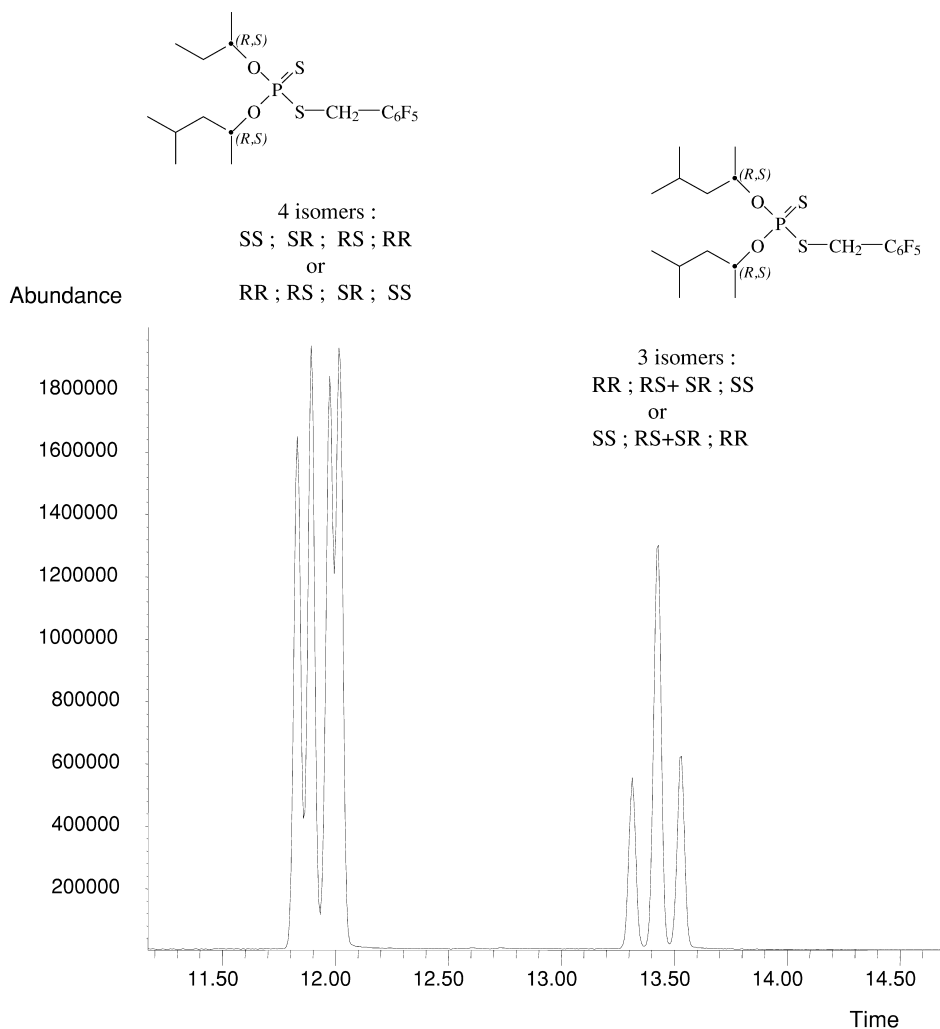


Fig. 4. GC separation of diastereoisomer mixtures from dialkyl DTP-PFB esters. Time scale in min.

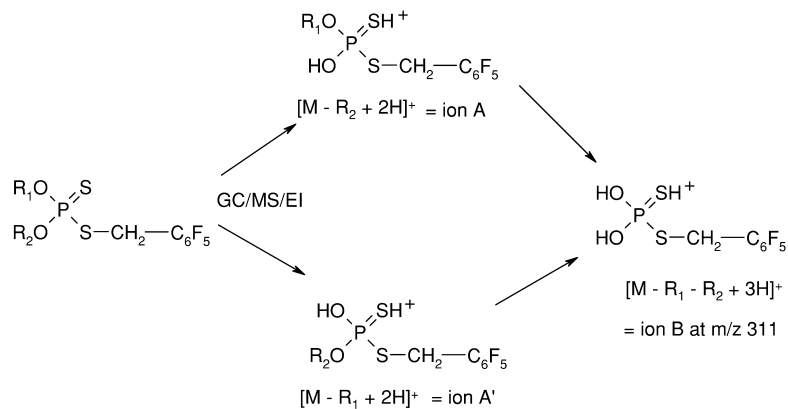


Fig. 5. Electron impact mass spectra fragmentation of DDTP-PFB esters.

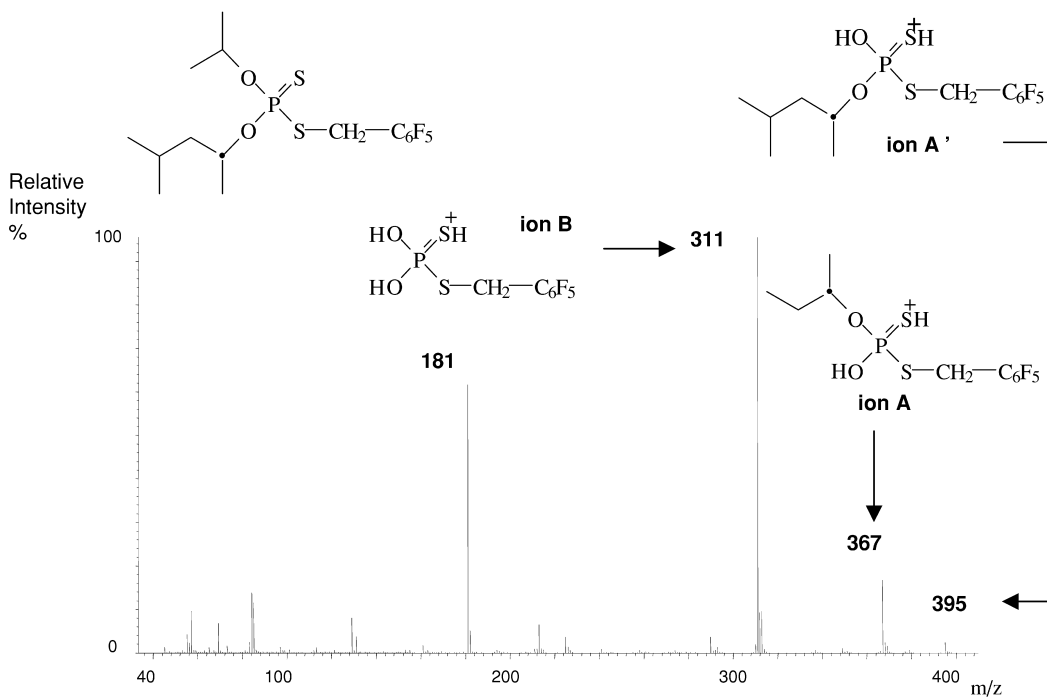
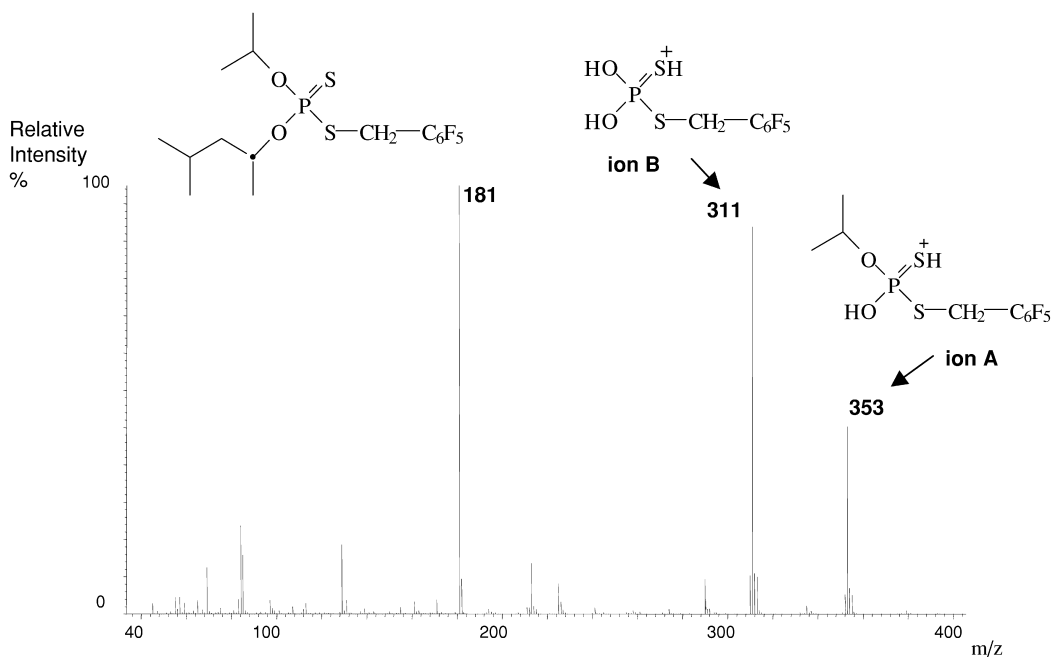


Fig. 6. EI mass spectra of DDTP–PFB ester derivatives.

two symmetrical compounds ( $R_1R_1$  and  $R_2R_2$ ) and a mixed compound ( $R_1R_2$ ) (Fig. 2).

The dialkyldithiophosphoric acids could only be synthesized with primary or secondary alcohol, no product was obtained using tertiary alcohols such as 2,3-dimethyl-2-butanol, 2-methyl-2-pentanol or 3-methyl-3-pentanol.

### 3.2. Derivatization

Pentafluorobenzyl ester derivatives (Fig. 3) were

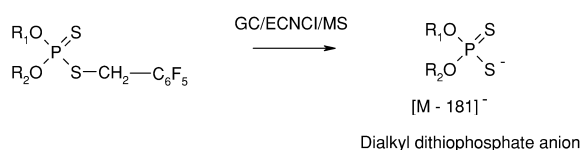


Fig. 7. ECNCl-MS fragmentation of DDTP–PFB esters.

chosen for several reasons: the reaction was efficient and rapid, the derivatization reagents were easier and safer to prepare than diazomethane and they could be

Table 4

GC–EI-MS and GC–ECNCl-MS analyses of engine oil sample DTP–PFB ester derivatives: fully characterized dialkyldithiophosphate derivatives

Dialkyl DTP–PFB ester derivatives	RRT	EI-MS, <i>m/z</i>	ECNCl-MS, <i>m/z</i>	Engine oil samples								
				OS1	OS2	OS3	OS4	OS5	OS6	OS7	OS8	
2-Propyl/2-propyl	0.441	353	213	++ <sup>a</sup>	++	+	+	+	+	+	+	
2-Propyl/2-methyl-1-propyl	0.502	353	227	++				+			+++	
2-Butyl/2-butyl	0.560	367	241								+++	+++
	0.564	367	241	+								
	0.567	367	241									
2-Methyl-1-propyl/2-methyl-1-propyl	0.567	367	241	+		(+)		+			+++	
2-Propyl/4-methyl-2-pentyl	0.573	353	255	+++	+++	+++	+++	+++	+++	+++		
	0.581	353	255									
2-Methyl-1-propyl/4-methyl-2-pentyl	0.642	367; 395	269	+		(+)		+				
	0.647	367; 395	269									
4-Methyl-2-pentyl/4-methyl-2-pentyl	0.718	395	297									
	0.724	395	297	+++	+++	+++	+++	+++	+++	+++		
	0.730	395	297									
2-Propyl/2-ethyl-1-hexyl	0.752	353	283	+++	+			++			+++	
2-Methyl-1-propyl/2-ethyl-1-hexyl	0.823	367; 423	297	+++				++			+++	
2-Ethyl-1-hexyl/2-ethyl-1-hexyl	1.067	423	353	+++	++	(+)		++			+++	

<sup>a</sup> Estimated relative concentration: high +++; medium ++; low +; trace (+).

Table 5

GC–EI-MS and GC–ECNCl-MS analyses of engine oil sample DTP–PFB ester derivatives: partially characterized dialkyl and diaryldithiophosphate derivatives

Dialkyl DTP–PFB ester derivatives	RRT	EI-MS, <i>m/z</i>	ECNCl-MS, <i>m/z</i>	Engine oil samples								
				OS1	OS2	OS3	OS4	OS5	OS6	OS7	OS8	
Butyl/pentyl	0.637	367; 381	255			(+) <sup>a</sup>					+	
Butyl/pentyl	0.675	381	255								+	
Butyl/octyl complex mixture	0.81–0.92	367; 423	297							++		++
Octyl/octyl complex mixture	1.02–1.24	423	353							+++		
Diaryl DTP–PFB ester derivatives	0.72–1.03	287; 301; 315	247; 261	++	++		++	++	++	++	++	++
		329; 343; 357	275; 289									
		371; 385; 399	303									
		413										

<sup>a</sup> Estimated relative concentration: high +++; medium ++; low +; trace (+).



used for both GC (in the EI-MS and/or ECNCI-MS modes) and LC studies [9].

### 3.3. Gas chromatography

An internal standard was used in order to improve retention time comparison between the different derivatives and isomers. 5 $\beta$ -Androstane-3,17-dione, a compound not present in automotive oils, which did not co-elute with any other compound was used. The results are reported in Table 1.

In some cases we obtained unexpected GC chromatograms: three or four compounds instead of one for a derivative. This only occurred with racemic secondary alcohol on carbon number 2 of the alkyl chain. When the dialkyldithiophosphate derivatives only had one racemic structure in duplicate as 2-butyl/2-butyl, 2-pentyl/2-pentyl, 2-hexyl/2-hexyl, 4-methyl-2-pentyl/4-methyl-2-pentyl and 3-methyl-2-pentyl/3-methyl-2-pentyl, they appeared as triplets in the ratio 1/2/1 corresponding to the differentiated structures of *R+R*, *R+S* and *S+R*, and *S+S* (or vice versa) (Fig. 4). This type of separation was not

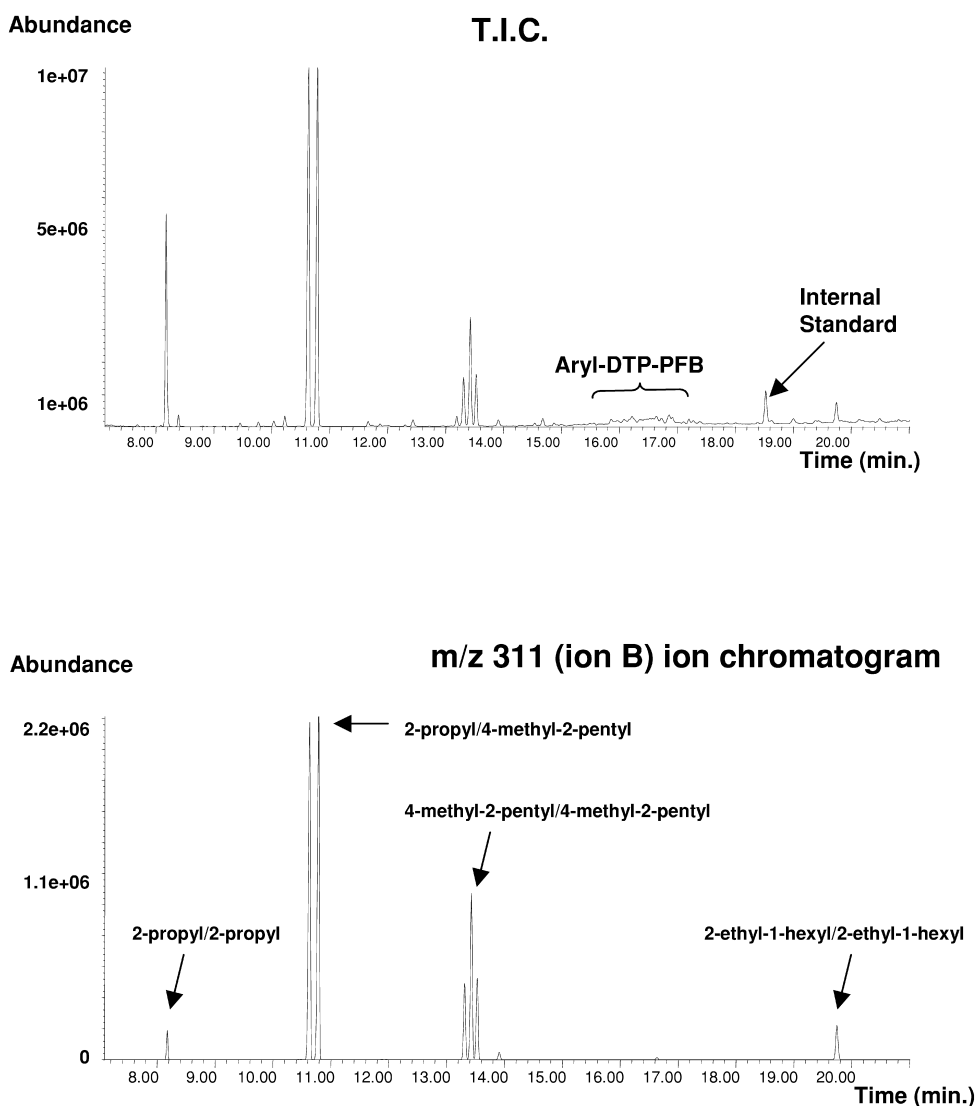


Fig. 8. GC–EI-MS analysis of DTP–FFB derivatives from OS2.

observed for racemic alcohol on carbon 3 like 3-hexyl or 2-methyl-3-pentyl derivatives (Table 1).

When the dialkyldithiophosphate derivatives had two different alkyl structures with two different asymmetrical carbon atoms, a quadruplet separation for *R+R*, *R+S*, *S+R* and *S+S* structures (or vice versa) was observed in 1/1/1/1 ratio, as shown for 2-butyl/4-methyl-2-pentyl and 2-pentyl/4-methyl-2-pentyl (Table 1 and Fig. 4).

Diastereoisomer mixture derivatives were separated on other column types, such as DB-XLB (12% diphenylsiloxane) or DB17 (50% diphenylsiloxane).

### 3.4. Electron impact mass spectrometry

The molecular ion was not observed for DDP–PFB derivatives, except for the propyl derivatives: 1-propyl/1-propyl and 2-propyl/2-propyl. With all other derivatives, the main fragmentation ions

corresponded to the loss of alkyl radical and a proton transfer (Fig. 5).

The successive losses of the two alkyl radical lead to the formation of the protonated dithiophosphoric acid pentafluorobenzyl ester ion B at  $m/z$  311. The  $m/z$  311 ion chromatogram afforded rapid location of PFB ester from DDTPs.

Ion A types could either have a characteristic ion by loss of only one alkyl radical, loss of  $R_1$  or  $R_2$ , or have both ions A and A', by losses of alkyl radical  $R_1$  and  $R_2$  from the molecular ion. In the former case, the derivative was not fully characterized as the elimination of the greatest alkyl radical was observed and spectral information on only one alkyl chain was evident (Tables 2 and 3, Fig. 6). In the latter case, ions A [ $M-H-R_1$ ]<sup>+</sup> and A' [ $M-H-R_2$ ]<sup>+</sup> were present and led to complete determination of the two alkyl chain carbon numbers (Table 1 and Fig. 6).

In all spectra the fragment ion from the PFB

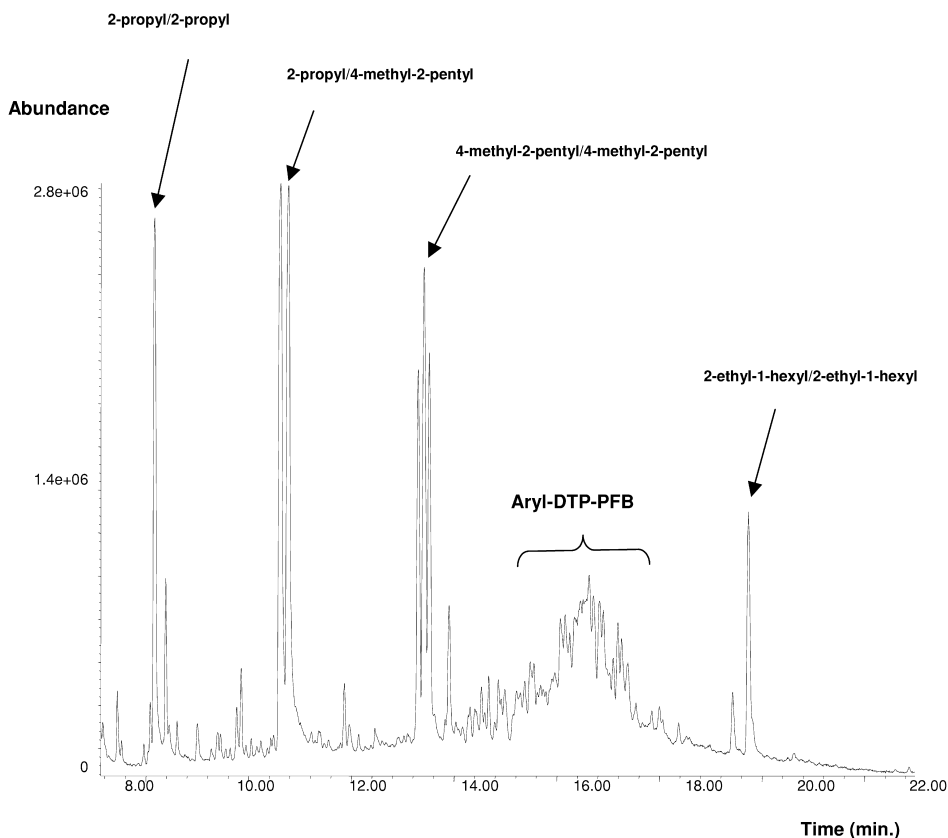
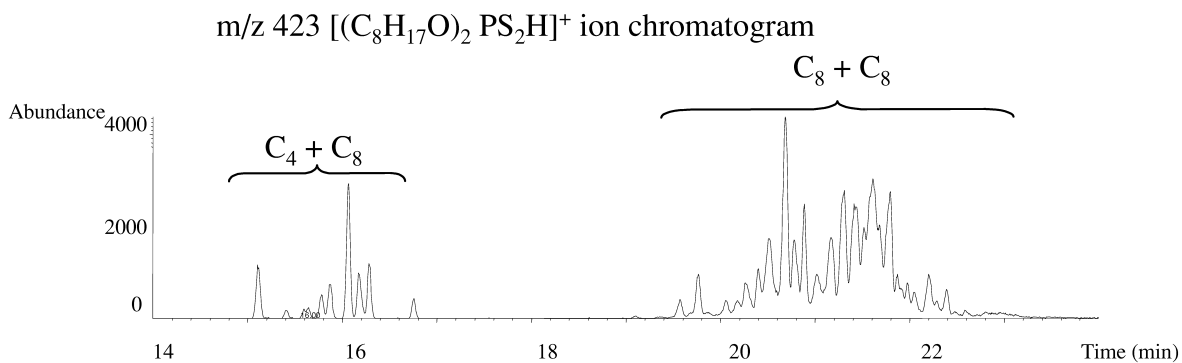
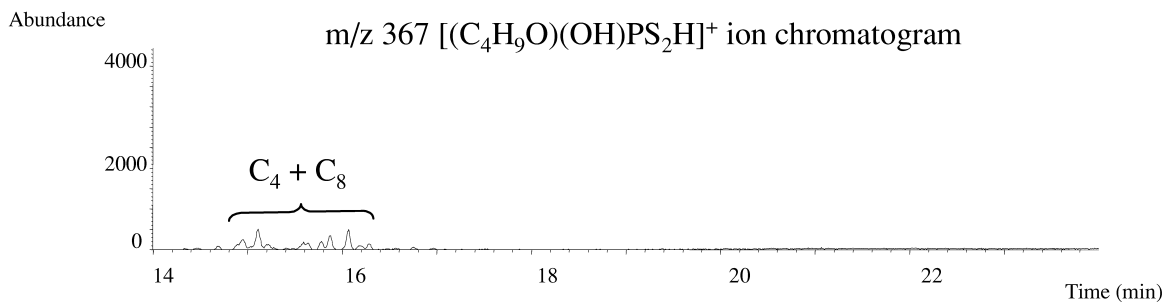
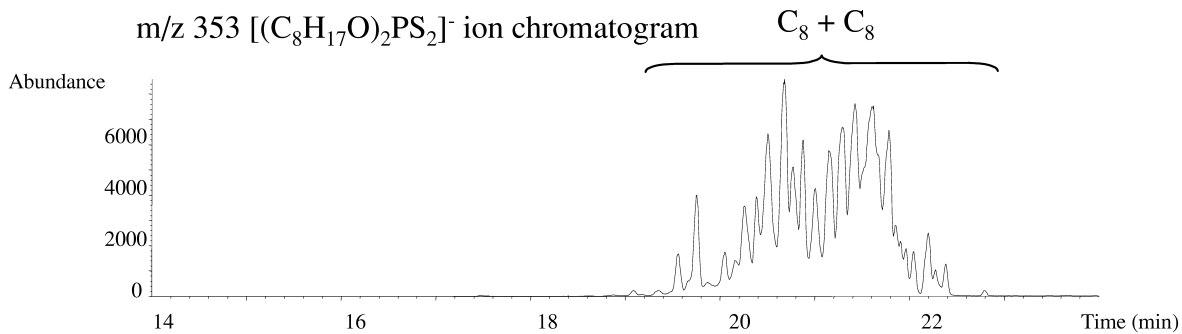
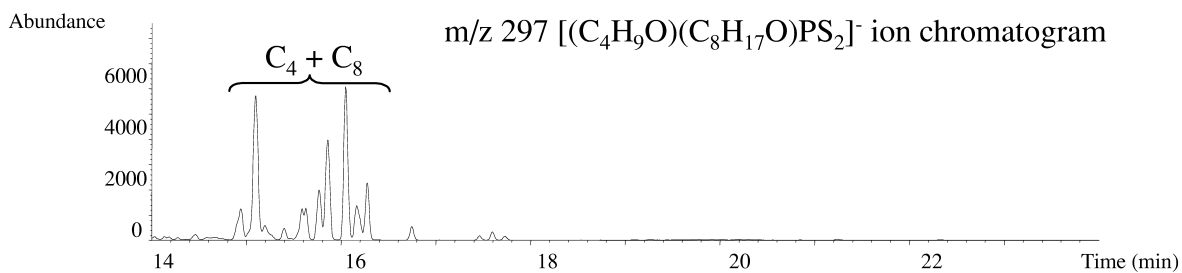


Fig. 9. GC–ECNCl–MS analysis of DTP–PFB derivatives from OS2.

**EI-GC/MS****ECNCl-GC/MS**Fig. 10. GC–MS characterization of  $C_4/C_8$  and  $C_8/C_8$  DTP–PFB mixtures from OS6.

derivatives at  $m/z$  181 corresponding to the benzylium ion  $[C_6F_5CH_2]^+$  was observed.

### 3.5. Electron-capture negative ion chemical ionization mass spectrometry

GC–ECNCI–MS experiments were performed under the same GC conditions as EI–MS. As expected no significant differences were observed if methane or ammoniac were used as reactant gas. The source temperature was decreased to 130°C however, no improvements were observed at temperature lesser than 150°C.

ECNCI mass spectra were very simple as only one ion was present, its mass corresponded to the loss of the PFB radical (Fig. 7), the molecular ion was not observed.

The dialkyldithiophosphate anion  $[M-181]^-$  provided information about the carbon atom number of the two alkyl chains  $R_1+R_2$ . If the EI data yielded information regarding only one alkyl chain then the ECNCI data could be used to derive the identity of the unknown alkyl chain. Therefore, it was possible to determine all the combinations of  $R_1+R_2$ . Table 3

summarizes all the combinations of  $R_1+R_2$  observed for the dialkyldithiophosphate anions.

### 3.6. Zinc dialkyldithiophosphates extraction from oil samples

ZnDDTPs additives were extracted from oil samples by SPE on silica gel columns. Mineral base oil was first eliminated by washing with hexane. The ZnDDTPs were successively eluted using a dichloromethane and dichloromethane–acetone (90:10, v/v) mixture. In order to check the efficiency of the SPE extraction, two subsequent wash with more polar solvents, acetone and methanol, were used. All the fractions were analyzed by GC–EI–MS after DTP–PFB ester formation. No detectable amounts of ZnDDTPs were found in the hexane wash fraction and either in the two extra fractions of acetone and methanol.

### 3.7. Oil samples analysis

ZnDDTPs from eight different oil samples were extracted, derivatized and analyzed by GC–MS. The results are summarized in Tables 4 and 5 for the

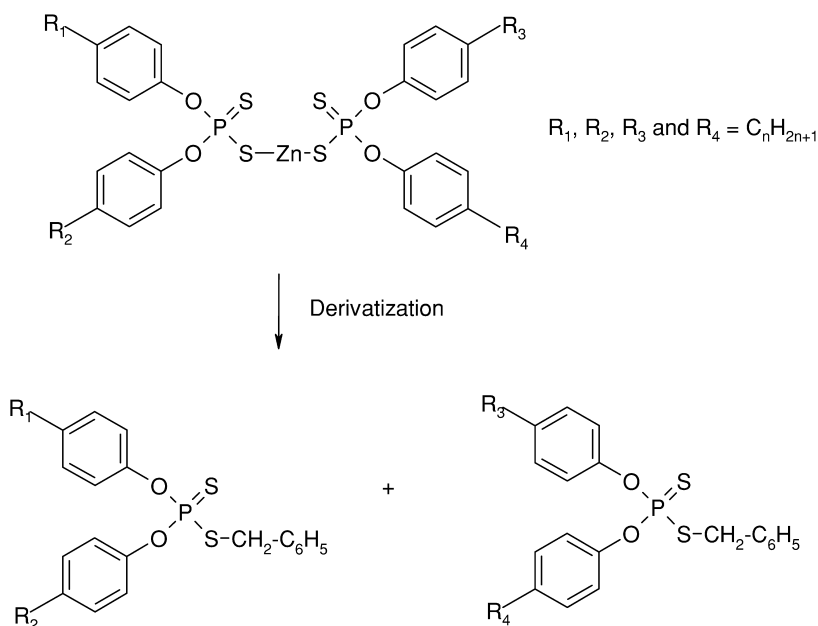


Fig. 11. Zinc diaryldithiophosphates structure and PFB derivatization.

fully identified and partially identified compounds, respectively.

The main derivatives from ZnDDTPs were fully characterized (Table 4) and corresponded to C<sub>3</sub>, C<sub>4</sub>, C<sub>6</sub> and C<sub>8</sub> combinations for alkyl chains. GC–EI–MS and GC–ECNCl–MS results for engine oil sample OS2 were given as an example in Figs. 8 and 9, respectively.

Incomplete structures were proposed for some

derivatives (Table 5). Butyl/pentyl DTP–PFB esters were minor compounds in oil samples OS3 and OS7. They appeared as single GC peak that was characteristic of the absence of diastereoisomer mixtures from butyl and pentyl derivatives (absence of alkyl substitution in position 2 on an asymmetrical carbon atom).

Derivatives from C<sub>4</sub>/C<sub>8</sub> and C<sub>8</sub>/C<sub>8</sub> alkyl combinations were present with many different structures

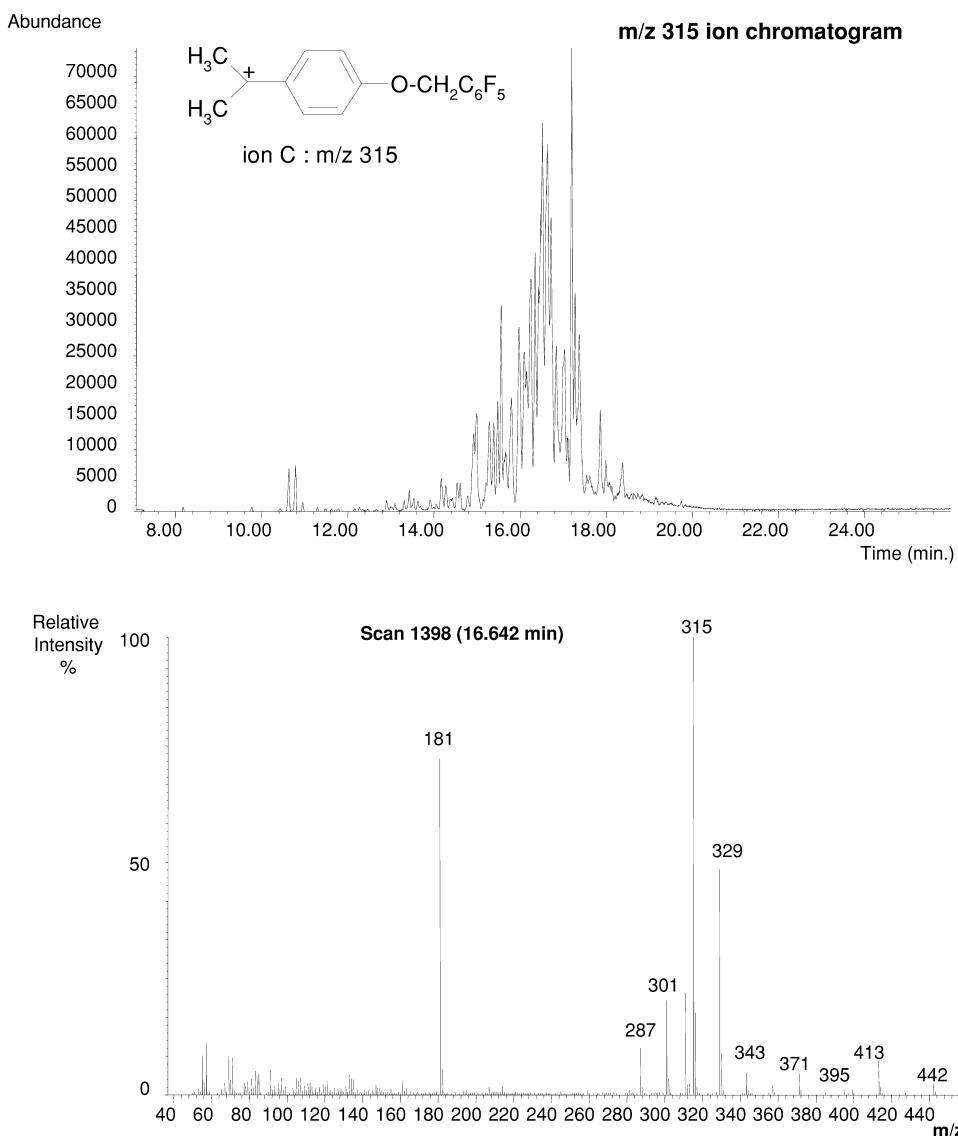


Fig. 12. GC–EI–MS analysis of OS2: *m/z* 315 ion chromatogram and mass spectrum of diaryl DTP–PFB derivatives.

as appeared as non-baseline resolved (Fig. 10). They were only detected in oil samples OS6 and OS8 for C<sub>4</sub>/C<sub>8</sub> and in oil sample OS6 for C<sub>8</sub>/C<sub>8</sub> ZnDDTP mixtures, respectively.

The ZnDDTPs concentrations were similar for all oil samples. We also observed the absence of linear dialkyl DTPs because of the use of only branched-chain alkyl structures for additive preparation.

### 3.8. Diaryldithiophosphates characterization

Another class of derivatives had been characterized: zinc diaryldithiophosphates as PFB ester derivatives (Fig. 11). They also were characterized as complex mixtures by GC–MS (Figs. 8 and 9).

EI mass spectra were very difficult to interpret as they consisted of mixed spectra from many com-

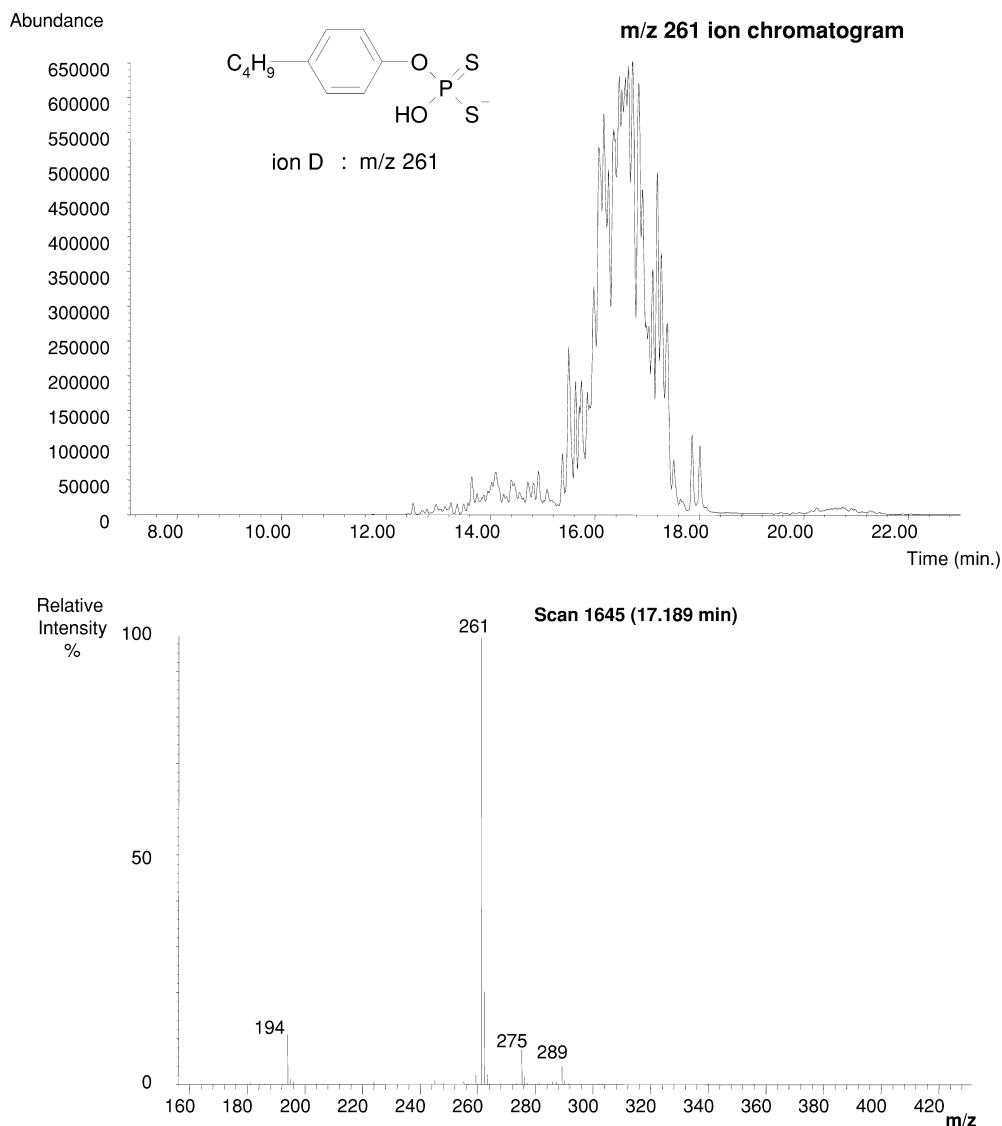


Fig. 13. GC–ECNCl–MS analysis of OS2: *m/z* 261 ion chromatogram and mass spectrum of diaryl DTP–PFB derivatives.

Table 6

Determination of the carbon atom number of one alkyl-aryl chain using ion D formation from ECNCI mass spectra of aryl DTP–PFB ester derivatives

Diaryldithiophosphate–PFB esters, dithiophosphate anion [(OH)(C <sub>n</sub> H <sub>2n+1</sub> -C <sub>6</sub> H <sub>4</sub> -O)PS <sub>2</sub> ] <sup>-</sup>	Carbon atom number, <i>n</i> for (C <sub>n</sub> H <sub>2n+1</sub> C <sub>6</sub> H <sub>4</sub> O)(OR)PS <sub>2</sub> -PFB
247	3
261	4
275	5
289	6
303	7

pounds. Furthermore, molecular ions were absent and the main ions observed did not correspond to simple fragment ions as observed with dialkyldithiophosphate PFB esters. These ions were due to rearrangement coming from the lost of the dithiophosphate moiety and transfer of the PFB to the alkylphenol part (Fig. 12) with ion C formations from *m/z* 287 to 413 with 14 mass units difference. This rearrangement/decomposition during EI ionization was also confirmed using other derivatives, we noticed fragment ions (ions C) at *m/z* 135, 149, 163 until 247 for methylated derivatives and at *m/z* 193, 207, 221 until 305 for trimethylsilylated derivatives, respectively.

Molecular ions also were absent in ECNCI mass spectra, however fragment ions could be used for identification. These anions, ions D, were generated by loss of the PFB radical and one of the alkylphenyl radical with a proton transfer (Fig. 13). Therefore, information was only present concerning the remaining alkylphenyl group on the dithiophosphate anion. With ECNCI, the shortest chains for the alkylphenyl part remained on the dithiophosphate anion, which was consistent with the losses of the largest alkylphenyl radicals (Table 6). The main representative ion D was at *m/z* 261, indicating a 4 carbon atom alkylphenyl chain.

These results were in accordance with those obtained by LC–APCI-MS analyses in the negative ion mode (unpublished results) of diaryl DTP–PFB esters: we found that alkyl parts R<sub>1</sub>+R<sub>2</sub> or R<sub>3</sub>+R<sub>4</sub> (Fig. 11) on the phenyl moiety corresponded to C<sub>3</sub>+C<sub>16</sub>, C<sub>3</sub>+C<sub>19</sub>, C<sub>4</sub>+C<sub>8</sub>, C<sub>4</sub>+C<sub>12</sub>, C<sub>4</sub>+C<sub>13</sub>, C<sub>4</sub>+C<sub>14</sub>, C<sub>4</sub>+C<sub>16</sub>, C<sub>4</sub>+C<sub>20</sub>, C<sub>5</sub>+C<sub>16</sub>, C<sub>5</sub>+C<sub>20</sub>, C<sub>6</sub>+C<sub>7</sub>, C<sub>6</sub>+C<sub>20</sub>, C<sub>7</sub>+C<sub>20</sub> as the main alkyl combinations with probably many isomeric possibilities.

All the oil samples tested, except sample OS3 contained diaryl-DTPs. They were characterized with difficulty by GC–EI-MS total ion current (TIC), but use of ion C type chromatograms lead to an easier characterization. GC–ECNCI-MS analyses of diaryl-DTP–PFB esters showed characteristic complex mixtures as well in TIC as in ion D type chromatograms (Figs. 8, 9 and 13).

#### 4. Conclusion

GC–MS analysis of pentafluorobenzyl ester derivatives provided an individual fingerprint of zinc dialkyldithiophosphates for any given lubricating oil sample. This enabled the relationships between anti-wear properties and alkyl chain structure of Zinc DDTPs to be studied. GC–EI-MS and GC–ECNCI-MS were very complementary for structure and carbon atom number determination of alkyl residues. Retention time indexes afforded identification of all common DDTP derivatives. We observed unexpected diastereoisomer GC separation for 2-hydroxy-*sec.*-alkyl derivatives. Use of dithiophosphate pentafluorobenzyl esters allowed identification of diastereoisomer mixtures of 2-hydroxy-*sec.*-aliphatic alcohols. The presence of diaryldithiophosphates could also be characterized using the same procedure.

#### Acknowledgements

The authors thank Dr. T.E. Chapman (Bioscreen, Torrance, CA, USA) and Dr. R. Aguilera (UCLA, Los Angeles, CA, USA) for useful comments during manuscript preparation.

**References**

- [1] P. Bartl, A. Schaaff, *Fresenius Z. Anal. Chem.* 312 (1982) 319.
- [2] M. Tsuchiya, H. Kuwabara, *Anal. Chem.* 58 (1986) 695.
- [3] T.J. Cardwell, R.C. Colton, N. Lambropoulos, J.C. Traeger, *Anal. Chim. Acta* 280 (1993) 239.
- [4] V.P. Nero, D.D. Drinkwater, in: 43rd ASMS Conference on Mass Spectrometry and Allied Topics, Atlanta, GA, 1995.
- [5] N. Lambropoulos, T.J. Cardwell, D. Caridi, P.J. Marriott, *J. Chromatogr. A* 749 (1996) 87.
- [6] K.L. Windhal, T.J. Cardwell, *J. Chromatogr. A* 765 (1997) 181.
- [7] R. Becker, W. Hoffmann, A. Knorr, W. Walther, A. Lehmann, *Fresenius J. Anal. Chem.* 357 (1997) 688.
- [8] A.D. Brazier, J.S. Elliot, *J. Inst. Petrol.* 53 (1967) 63.
- [9] K. Blau, J. Halket, *Handbook of Derivatives for Chromatography*, Wiley, Chichester, 1993.