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A method for the determination of ZnDDP in lubricant oils by applying solid-phase extraction with mixed resin

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Abstract

One of the major applications of zinc dialkyldithiophosphates (ZnDDPs) is their usage as an anti-wear additive in lubricants including greases, hydraulic oils, and motor oils. ZnDDPs also could be used as corrosion inhibitors and anti-oxidants. In this study, GC/MS with solid-phase extraction (SPE) pretreatment was used to effectively remove base oils in lubricants and qualitative and quantitative analysis method for ZnDDPs in automotive lubricants. As a pretreatment method, liquid–liquid extraction (LLE) and SPE were applied. The SPE method using mixed absorbent containing 1.0% of active carbon in silica gel base showed the best results in both recovery and reproducibility. The LOD and LOQ of the developed method were 2.2 µg/ml and 6.7 µg/ml, respectively. And this method showed very good reproducibility of less than 0.1% RSD for the standard sample analysis. The developed method was successively applied to qualitative and quantitative analyses of ZnDDP in various real automotive lubricant samples.

Keywords: ZnDDP, Lubricant oil, SPE, Mixed resin, GC–MS

Introduction

Oil additives are chemical compounds that improve the lubricant performance of base oil (or oil “base stock”). Manufacturers of many different oils can utilize the same base stock for each formulation and can choose different additives for each specific application. Additives comprised up to 5% by weight of some oil (Bartels et al. 2003). Nearly all commercial motor oils contain additives, no matter whether the oils are synthetic or petroleum-based.

Some of the most important additives include those used for anti-wear additives which are one of the most important oil additives for automotive lubricants. Zinc dialkyldithiophosphates (often referred to as ZDDPs or ZnDDPs) (ZnDDP Engine Oil - Mustang Monthly XXXX) are typically used the most. These uncharged

compounds are not the salts. They are soluble in nonpolar solvents, and the longer-chain derivatives easily dissolve in mineral and synthetic oils used as lubricants. The main application of ZnDDPs is anti-wear additives in lubricants including greases, hydraulic oils, and motor oils. ZnDDPs also perform various functions such as corrosion inhibitors, coolants, and antioxidants (Barnes et al. 2001). They can be seen almost anywhere in the lubricants, and usages are usually between 600 and 2000 ppm depending on the type of automobiles.

The analysis of lubricant additives was generally applied to obtain information about the age and condition of the product. Various techniques have been applied to the analysis of oil additives including energy-dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA), and mass spectrometry (MS) (Çelik et al. 2013; Zhang et al. 2013; Kassler et al. 2011). Using mass spectrometry, highly detailed information about the chemical composition of lubricants can be generated, and quantification of additives is possible. Mass spectrometry is typically hyphenated with chromatographic techniques, such

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as supercritical fluid chromatography (Lavison-Bompard et al. 2009, 2012), gas chromatography (Bernabei et al. 2000), 2D gas chromatography (Liang et al. 2017), and liquid chromatography (Kassler et al. 2014) for the separation. However, these techniques are often time-consuming and may require sample preparation, such as derivatization prior to an analysis (Becker et al. 1997; Becchi et al. 2001).

A quantitative analysis of the lubricant antioxidant additives was reported by the real-time direct analysis method combined with the mass spectrophotometry that was applied to the analysis of oil additives in lubricants. Although the paper regarding the quantitative analysis of various lubricant additives was published, no specific analysis method for the lubricant anti-wear additive was reported (Costa et al. 2001).

We present in this report the GC–MS analysis method for the commercially available lubricant oil anti-wear additives. Due to the advantages of GC/MS, such as universality and a huge amount of database, the GC/MS method was chosen instead of LC/MS. However, the procedure of GC/MS method shall include a sample pre-treatment phase of removing the matrix of the base oil. To extract ZnDDP from a lubricant, a solid-phase extraction method was applied, using a mixture of resins (silica gel + active carbon). It has been confirmed that the technology developed in this paper can well be applied to a quantitative analysis of ZnDDPs in the lubricants.

Experimental

Materials and methods

Chemicals

The subject of the experiment was zinc dialkyldithiophosphate (ZnDDP), used as an anti-wear agent for automobiles, and various types of compounds exist depending on the type of the alkyl group. Among various ZnDDP compounds, this experiment was conducted on Zinc O, O-dibutyl dithiophosphate manufactured by BOC Science. As an internal standard (IS), pentachlorophenol (98%, Sigma-Aldrich, St. Louis, USA), was used. The solvents used for extraction were HPLC grade, and methanol, dichloromethane, and hexane (n-hexane), used as extraction solvents in solid-phase extraction and liquid–liquid extraction, were obtained from JT Baker (Phillipsburg, NJ, USA). The solvents included: tetrahydrofuran (JT Baker, Phillipsburg, NJ, USA), toluene (JT Baker, Phillipsburg, NJ, USA), acetonitrile (Burdick & Jackson, MI, USA), acetone (Burdick & Jackson, MI, USA), ethyl ether (Burdick & Jackson, MI, USA), ethyl acetate (Sigma-Aldrich, St. Louis, USA), and dimethyl sulfoxide (Duksan Pure Chemical Co., Ansan, South Korea). HPLC grade ones were purchased, and they were used without further purification. The engine oils

and transmission oils, used in the experiments, were the products used in our vehicle, including two engine oils (gasoline 0W-20 and diesel 0W-30) and two transmission oils (manual DCTF TGO & automatic SP4MI).

Instrument and parameters

In this study, gas chromatography-mass spectrometry (GC–MS) was used to analyze the anti-wear agent in automotive engine oil and to calculate its content. Gas chromatography was performed, using Chromatec-Crystal 9000 (C9000) from JSC SDO Chromatec (Russia), and the column was HP-Ultra 2 capillary column (25 m × 0.11 mm × 0.2 film thickness) from J & W Scientific (Folsom, CA, USA). AS-2M (3D) auto-sampler manufactured by JSC SDO Chromatec (Russia) was used as a sample injector. A total of 2 µl samples were injected and analyzed in splitless mode (Added: SIM mode). The inlet temperature was set at 250 °C, and the flow rate of helium carrier gas was 1 ml/min. The solvent delay time was 3.0 min, and a one-ramp temperature gradient was used. The initial temperature was maintained for 3 min at 50 °C; the heating rate was 8 °C/min to 300 °C, and the holding time was 10 min. A Chromatec-Crystal mass detector manufactured by JSC SDO Chromatec (Russia) was used as a mass spectrometer. As for the ionization method, electron impact ionization (EI) was used at 70 eV. The MSD ion source temperature was maintained at 200 °C in full-scan mode (25–1000 m/z) for qualitative and quantitative analysis.

Sample preparation methods

Standard sample manufacturing A standard sample was prepared by diluting Zinc O, O-dibutyl dithiophosphate, used as an anti-wear agent in 10 ml of solvent to 500 µg/ml (extraction solvent: hexane and methanol).

Liquid–liquid extraction (LLE) LLE, which extracts analytes from liquid samples, first extracted the 500 µg/ml standard sample dissolved in hexane, using a separation funnel using various solvents (DMSO, acetonitrile, and methanol). The recovery rate was measured.

Solid-phase extraction (SPE) A 24-port SPE Vacuum Manifold from Honeywell Burdick & Jackson was used for SPE (Standard sample extraction). 10 ml of hexane was flowed at a rate of 5 ml/min to condition a SPE cartridge. Zinc O, O-dibutyl dithiophosphate, used as an anti-wear agent in the activated cartridge, was diluted in 10 ml of hexane to 500 µg/ml and poured into the cartridge by flowing that at a rate of 5 ml/min. As an extraction solvent, 10 ml of methanol was extracted at a rate of 5 ml/min.

Validation test

Recovery To confirm the recovery, ZnDDP standard samples were dissolved in methanol and added at the concentrations of 50 µg/ml. Pentachlorophenol 10 µg/ml was added to sample. After the extraction (pretreatment) process was added, they were analyzed five times. The control group was extracted by adding the internal standard material at the same concentrations and then pretreated by adding the ZnDDP standard samples. Relative recovery was measured, using the area ratio of the ZnDDP standard sample and the internal standard of the comparison group and the control group.

Linearity To prepare the calibration curve, the ZnDDP standard samples were dissolved in methanol to make 8-point standard samples from 0.2 to 500 µg/ml at 10 µg/ml of pentachlorophenol to each sample. The samples were prepared by addition. The analysis was repeated three times with GC–MS, and the concentration of the calibration curve was selected to 8 points (0.2, 1, 5, 10, 50, 100, 200, and 500 µg/ml) for ZnDDP based on calibration limits. Linearity was evaluated by the correlation coefficient, which is the R^2 value of the calibration curve.

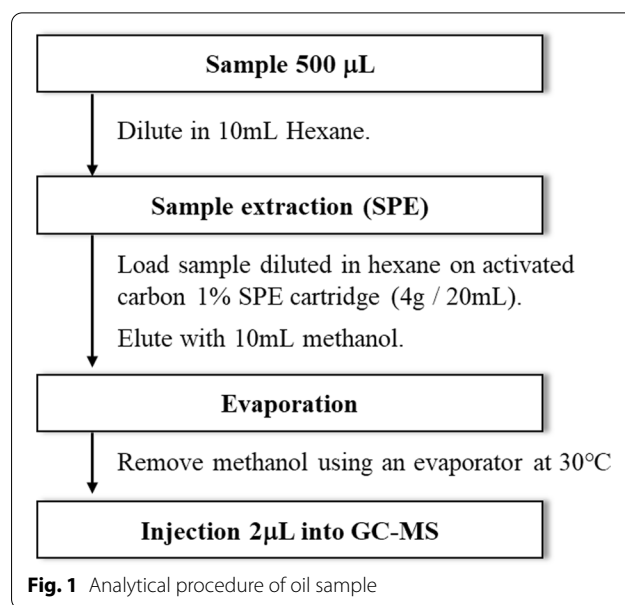
Limit of detection and quantification In order to measure the limit of determination (LOD) and limit of quantification (LOQ), concentrations of the ZnDDP standard samples in methanol were added at 0.2, 1, 5, 10, 50, 100, 200, and 500 µg/ml. The analysis was repeated three times per each concentration. Concentrations with a signal to noise (S/N) of 3.3 were selected as detection limits, and concentrations with that of 10 were selected as limit of quantification.

Precision and accuracy In order to evaluate the precision, 500 µg/ml ZnDDP standard sample was added repeatedly five times and expressed as a relative standard deviation (% RSD, CV). Accuracy was selected based on the calibration limits: low-quality control (LQC) concentration at 1 µg/ml; medium-quality control (MQC) concentration at 50 µg/ml; and high-quality control (HQC) concentration at 100 µg/ml. Percent bias (%) was:

$$\frac{(\text{Average measurement concentration} - \text{known concentration})}{\text{known concentration}} \times 100$$

Analytical procedures (Actual sample extraction)

10 ml of hexane was flowed at a rate of 5 ml/min to condition the SPE cartridge. The activated cartridge was injected with 500 µl of gasoline and diesel engine oils, and transmission oils, DCTF and SP4MI. 10 ml of hexane was flowed at a rate of 5 ml/min to remove the base oil,



which is an analyte. 10 ml of methanol, an extraction solvent, was extracted at a rate of 5 ml/min. The analytical procedure is shown in Fig. 1.

Results and discussion

Mass spectrum of standard sample

ZnDDPs are family of coordination compounds developed in the 1940s that feature zinc bound to the anion of dialkylthiophosphoric acid (e.g., ammonium diethyl dithiophosphate). The mass spectrum of ZnDDP standard, dissolved in a solvent, was obtained. The spectrum of ZnDDP with the internal standard is shown in Fig. 2.

As shown in Fig. 2, ZnDDP had a molecular ion of 552 and fragment ions with two ligands amputated from the compound of 243. ZnDDP is not salt. Thus, it was soluble in nonpolar solvents. However, the results of the mass analysis showed that the compound tended to break down into ligand and metal ions in the solvent. In this case, the degree of disassembly of this compound is depended on the electrolyte capacity of the solvent. That is, the ratio of fragment ion/molecular ion is depended

on the solvent. In addition, the sensitivity of the calibration curve in a quantitative analysis might vary depending on the solvent and might affect the reproducibility of the results. Therefore, to compensate for this problem in quantitative analysis, all of the ZDDP parent ions were ionized into fragment ions, and an experiment was

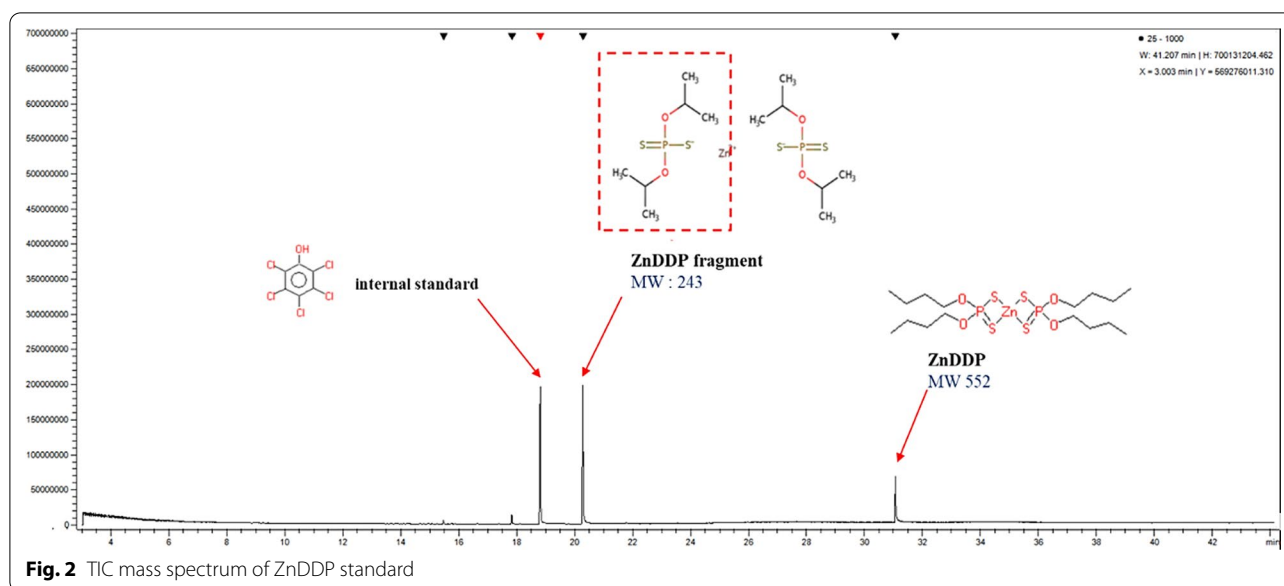


Fig. 2 TIC mass spectrum of ZnDDP standard

conducted for the solvent condition with the highest base peak sensitivity of the fragment ions.

Figure 3 shows the correlation between the abundance of the fragment peak and the number of acceptors of various solvents. The acceptor number of the solvent is an empirical parameter that quantitatively describes the electrophilic properties of the solvent. As the acceptor number of the solvent increased, the abundance of the fragment ion increased. This indicates that molecular and fragment ions are significantly interrelated with each other, and the ratio of the fragment ion/molecular ion can be confirmed quantitatively according to the properties of the solvent. In this study, methanol was used as a sample GC injection solvent to maximize the sensitivity in a quantitative analysis using 243, the base peak of fragment ions.

Pretreatment for ZnDDP extraction

To analyze ZnDDP from automotive lubricants, pretreatment is required to remove base oil from the original automobile lubricant samples and to extract ZnDDP. In this study, the optimum extraction conditions were identified by comparing both liquid–liquid extraction (LLE) and solid-phase extraction (SPE). For the LLE method, the recovery was measured by extracting ZnDDP from the 500 µg/ml standard dissolved in hexane coupled with various solvents. Methanol showed the highest recovery of 73% among the counter solvents used (DMSO: 53%, and acetonitrile: 45%). The SPE method first tested the SPE filler that could absorb samples. Methanol is currently used as an extraction solvent for silica gel, which is mainly used for automobile lubricant analysis. In an

experiment with silica gel, ZnDDP had a very low recovery rate of 25.7%. This is because silica gel did not absorb ZnDDP sufficiently and, thus, lost much of the sample in the first elution and cleaning processes to remove the base oil. Recently, a paper (Motamen Salehi et al. 2018) was published in which ZnDDP had very high adsorption characteristics for the soot (carbon) produced in the engine. Therefore, we applied silica gel mixed resin containing activated carbon. The same SPE experiment was performed by mixing activated carbon with silica gel at a weight ratio of 0, 0.5, 1, 2, and 5%

As a result, the recovery rate increased until 1% of the activated carbon was mixed, as shown in Fig. 4, and then, the recovery rate tended to decrease rapidly. That is, it was judged that ZnDDP did not escape during the final elution of SPE containing more than 2% active carbon because activated carbon had very high absorbency

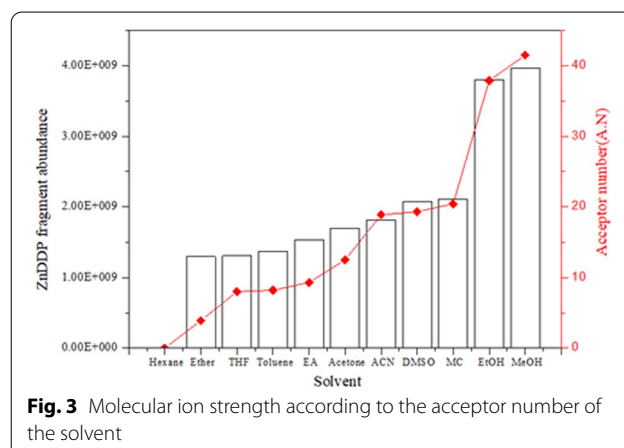


Fig. 3 Molecular ion strength according to the acceptor number of the solvent

in ZnDDP. For SPE with 1% activated carbon mixed filler, the recovery rate was close to 80%. Thus, in this study, the optimized SPE method, which reduces the amount of solvent used and analysis time, was applied as a pre-treatment method. In this case, the filler was a mixture of silica gel and active carbon at a 99:1 weight ratio.

Calibration curve and validation

A calibration curve was drawn, using the internal standard method for a quantitative analysis. Standard samples were prepared by dissolving the ZnDDP standard into methanol. The calibration curve was made of 8 points (0.2, 1, 5, 10, 50, 100, 200, and 500 µg/ml) of the standard sample from 0.2 to 500 µg/ml. 10 µg/ml of pentachlorophenol was added to each sample as its internal standard. The calibration curve is shown in Fig. 5.

The calibration curve shows excellent linearity ($R^2 = 0.9991$) in the concentration range.

Quantification of validation and actual samples

In order to confirm the effectiveness of the developed analytical method, validation was carried out. The results of the evaluation are summarized in Table 1. The detection limit was 0.0881 µg/ml at the signal-to-noise ratio of 3.3, and the calibration limit was 0.2669 µg/ml at the signal-to-noise ratio of 10.

The calibration curve was obtained by selecting 8 points based on the determined calibration limit. The calibration curve of the ZnDDP standard sample was: $y = 0.1123 \times X + 0.2358$ ($R^2 = 0.9991$), and the linearity was verified. The precision (%RSD) was 2.33% at 1 µg/ml, 4.56% at 50 µg/ml, and 3.03% at 100 µg/ml. The accuracy (%bias) was 2.11% at 1 µg/ml, 3.13% at 50 µg/ml, and 2.17% at 100 µg/ml. The accuracy was considered valid

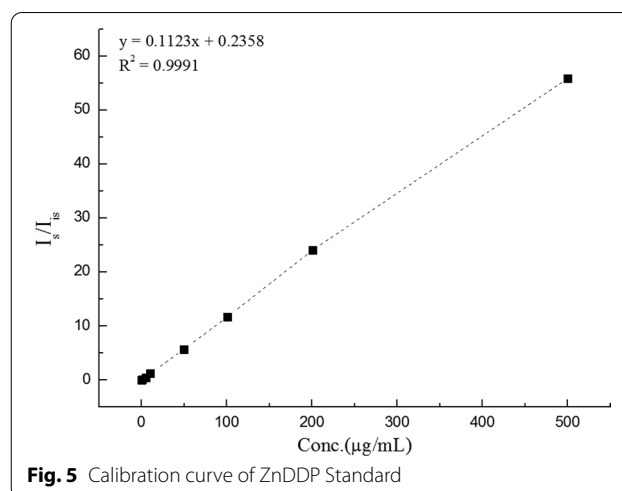


Fig. 5 Calibration curve of ZnDDP Standard

because it had a value within $\pm 20\%$. Thus, this experiment confirmed that the method would be reproducible.

Analysis of the actual samples

According to the method developed, qualitative and quantitative analyses of two motor engine oils (0W-20, 0W-30) and two transmission oils (manual, automatic) were conducted. The results of the analysis of actual samples through the developed method are summarized in Table 2. In addition, the total ion chromatogram (TIC) of engine oils and transmission oils added with the internal standard is shown in Fig. 6. Through this process, it was confirmed that ZnDDP, an anti-wear agent, could effectively be separated from the base oil and analyzed selectively at the same time.

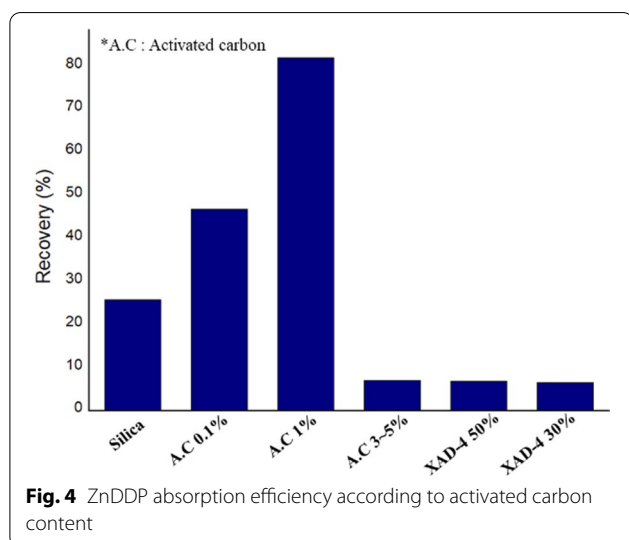


Fig. 4 ZnDDP absorption efficiency according to activated carbon content

Table 1 Detection limits and calibration limits of ZnDDP, precision, and linearity

ZnDDP (µg/ml)	LOD (µg/ml)	LOQ (µg/ml)	Precision (% RSD)	R^2
1	0.0881	0.2669	2.33	0.9991
50			4.56	
100			3.03	

Table 2 Results of the analyses of the actual samples

Sample	Result (µg/mL)
Gasoline engine oil (0W-20)	1.039 ± 0.19
Diesel engine oil (0W-30)	0.586 ± 0.15
Transmission oil (DCTF)	0.863 ± 0.19
Transmission oil (SP4MI)	0.305 ± 0.09

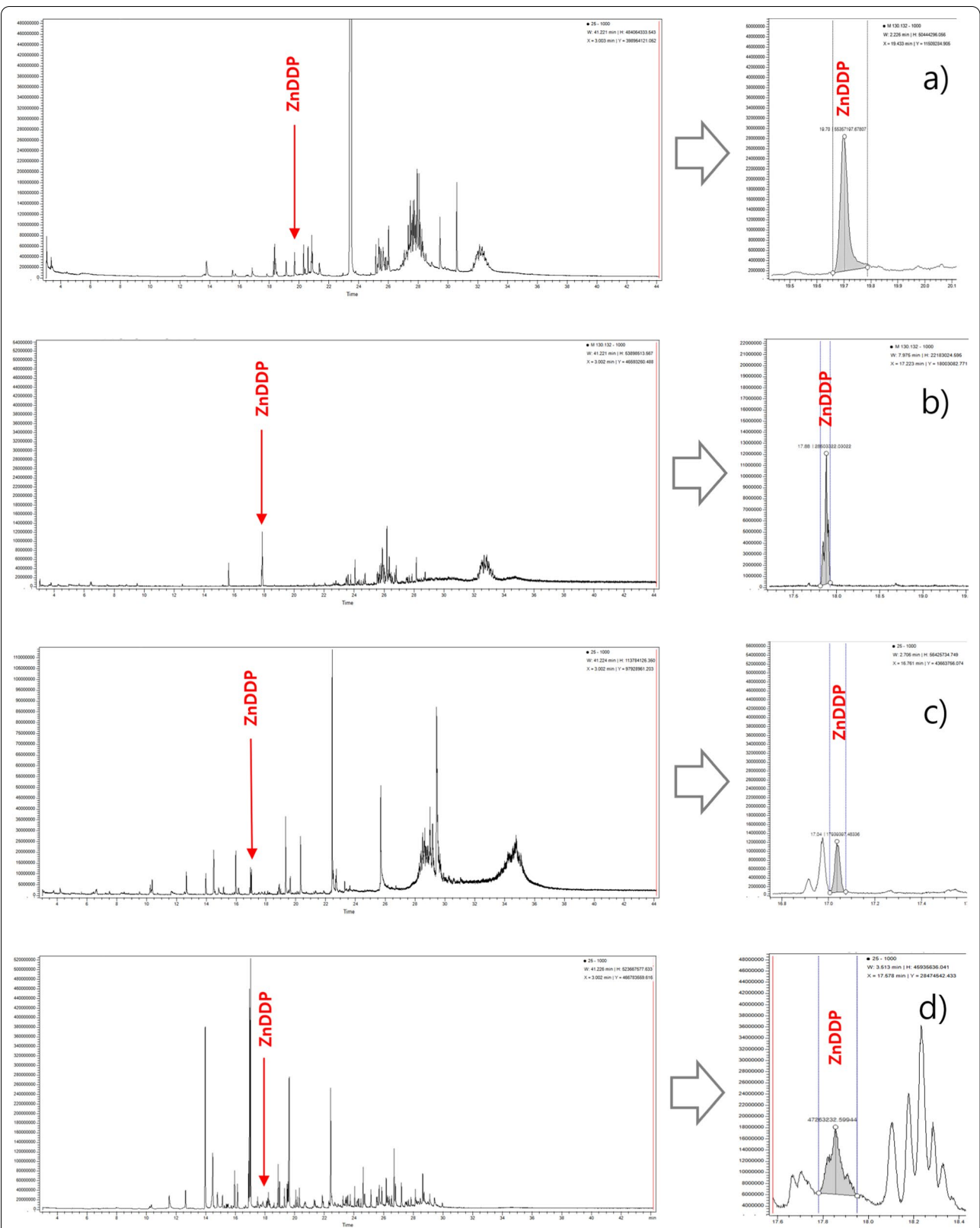


Fig. 6 Total ion chromatogram: **a** gasoline engine oil (0W-20), **b** diesel engine oil (0W-30), **c** transmission oil (DCTF TGO), **d** transmission oil (SP4MI)

Conclusion

- (1) The base oil of the lubricant was effectively removed, using SPE pretreatment and GC/MS, and the anti-wear ZnDDP, contained in automotive lubricants, was qualitatively and quantitatively analyzed
- (2) Both LLE and SPE were applied as pretreatment methods. The SPE method with a mixed adsorbent containing 1.0% of active carbon in the silica gel base showed the best results in both recovery and reproducibility.
- (3) The LOD and LOQ of the developed method were 0.0881 and 0.2669 µg/ml, respectively, and the standard sample analysis showed good reproducibility below 5% RSD.

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Author contributions

K-SS and S-JL contributed to conceptualization, S-JL and LC/MS were involved in project administration, E-YK and GC/MS contributed to experiment and validation, D-SL was involved in total analysis, and K-JP contributed to project administration and writing. All authors have read and agreed to the published version of the manuscript.

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Availability of data and materials

There are no supporting data.

Declarations

Ethics approval and consent to participate

This article does not contain any studies with human participants or animals performed by any of the authors.

Competing interests

The authors declare that they have no competing interests.

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