Scientific paper

Analysis of Zinc Dialkyldithiophosphate Additives in Commercial Lubricating Oil using Matrix Assisted Laser Desorption/Ionization-Time of Flight Mass Spectrometry

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Abstract

The zinc dialkyl/aryl dithiophosphates (ZDDPs) are multifunctional lubricating oil additives. In this research, the analysis of ZDDPs additive in lubricating oils using Matrix Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-Tof) has been developed. The complexes $[Zn(DTP)(DMSO)_2]^+$ from reaction between zinc dithiophosphate with dimethylsulfoxide were prepared. Analysis parameters for MALDI-Tof MS have been investigated; types of matrix and analyte: matrix ratio. The optimum condition of the analysis is dithranol as a matrix with tetrahydrofuran as solvent and the ratio of $[Zn(DTP)(DMSO)_2]^+$ to matrix is 1:75 by volume. And then, this developed method is applied for the analysis of ZDDPs additive in a commercial lubricating oil. Moreover, the results also suggested that additives in commercial lubrication oils can be separated to two groups; zinc dialkyldithiophosphates and zinc diaryldithiophosphates. Consequently, the pattern of ZDDPs can be used as a tool for producers of commercial lubricating oil products.

Keywords: MALDI-Tof MS, zinc dialkyldithiophosphate, lubicating oil additive

1. Introduction

The lubricating oils cannot satisfy the requirements of high performance lubricants without using the benefit of modern additive technology. Additives are synthetic chemical substances that can improve lots of different parameters of lubricants. They can boost existing properties, suppress undesirable properties and introduce properties in the lubricating oils.

One group of compounds widely used as multifunctional lubricating oil additives are the zinc dialkyl/aryl dithiophosphates (ZDDPs). They are added to base oils in low concentration and act as corrosion inhibitors, antiwear agents and oxidation inhibitors. They prevent or reduce rust and friction by forming a protective layer of additive on the metal surface, and also decompose peroxides in internal combustion engines. The ZDDPs complexes are manufactured by reaction of alcohols, phosphorus pentasulphide and zinc salts. The performance or effectiveness of the ZDDPs depends on the nature of the alkyl substituent of the metal complexes. Previous techniques which have been used in the analysis of ZDDPs in lubricating oils include thin-layer chromatography (TLC)[1] which were developed in ninhydrin and good separation.

Electrospray mass spectrometry (ES-MS)[2] has been used for the qualitative analysis of engine oil inhibitor and antiwear additives. From the analysis, neutral $Zn(DTP)_2$ compounds cannot be detected by ESIMS, ionic products formed by reaction with dimethyl sulphoxide or excess

dithiophosphate ions can be analysed. After that, the developed method has been applied to analyze commercial engine oil additives and was able to detect differences between ZDDPs which had been manufactured with different alcohols.

Capillary supercritical fluid chromatography (cSFC)[3] was used by Ashraf to analyze lubricating oil additives, including ZDDP. Moreover, Thibon et al. have shown an application of capillary electrochromatography (CEC)[4] in the analysis of ZDDP. The separation electrolytes were optimized speci?cally to ZDDP. Four commercial ZDDPs have been analysed but only the peak related to the structure of the ligands [(RO)(RO)PS_2] has been detected.

The other analyses were not directly related to analysis of ZDDPs but concerned their ability, such as Harrison and Brown[5] studied the thermal decomposition of ZDDPs on a stainless steel metal surface by using external reflection Fourier Transform infrared (FTIR) spectroscopy, ^{31}P-MAS NMR and scanning electron microscopy (SEM). No ?lms were seen on the metal surface at temperatures less than or equal to 150 °C but brown or black deposits were seen at 200 and 260 °C.

For the ESI-MS technique which has been applied for analysis of ZDDP in commercial lubricating oils, although this technique proved to be successful for the analysis of the ZDDP mixtures, several problems are associated with them and make their use difficult, such as contamination of the column, detector insensitivity, base oil content of the samples, thermal instability, and extended analysis time.

Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-Tof MS) has not previously been employed for the analysis of ZDDPs even though it has been demonstrated to have several advantages, such as spectral simplicity owing to the production of singly charged ions compared to multiply charge in ESI, faster analysis time. The inherent soft ionization of MALDI allows promotion of these large thermally labile molecules into the gas phase without extensive fragmentation. Only recently, MALDI-Tof MS has been used for analysis of ZDDPs. The objective of this research is to develop a mass spectrometric method as a method for analysis of the carbon number of the two alkyl chains and structures of zinc dithiophosphates (ZDDPs) and apply it for the analysis of commercial lubricating oils.

2. Experimental

2. 1. Reagents and Chemicals

The zinc dithiophosphate additive package for lubricating oil was a gift from Lubrizol. Eight commercial lubricating oils (A, B, C, D, E, F, G and H) were brought from local markets. Hexane, isooctane, ethyl acetate, methanol, dimethylsulfoxide (DMSO), tetrahydrofuran in HPLC and Analar grade were purchased from Labscan, Co., Ltd., Thailand. Matrices for MALDI-Tof analysis; dithranol (1,8,9-trihydroxyanthracene), DHB (2,5-dihydroxybenzoic acid), HABA (2,(-4hydroxyphenylazo)benzoic acid) and α-CHCA (α-cyano-4-hydroxycinnamic acid) were brought from Sigma-Aldrich Co., Ltd. Calibration standard for MALDI-Tof analysis are Angiotensin I and Bradykinin which were obtained from Sigma-Aldrich, Co., Ltd. Silica gel 60 (70–230 mesh) for column chromatography was obtained from Merck, Co., Ltd.

2. 2. Apparatus

All mass spectrometric analysis was performed by Matrix-Assisted Laser Desorption /Ionization-Time of Flight Mass Spectrometer (MALDI-Tof) Model Biflex (Bruker Daltonic, Germany).

2. 3. Procedure

2. 3. 1. The Optimal Conditions for the Analysis of Zinc Dithiophosphate in Additive Package.

2. 3. 1. 1. Sample and target preparation

The stock solution of ZDDP was prepared by diluting ZDDP additive package with tetrahydrofuran to yield the final concentration at 7,000 mg/L. And then, the analyte solution was prepared by mixing 75 μL of stock solution with 0.5 DMSO. After that, 1.0 μL of analyte solution, 1.0 μL of internal standard solution (1 mg/ml in water) and matrix solution were mixed and vortexed. Finally, 0.5 μL of the mixture of analyte, internal standard and matrix was deposited on a MALDI Target and allowed to dry. Internal calibration[6] involves the mixing of one or more standard compounds with the unknown analyte. The mixture was then mixed with the matrix solution for MALDI analysis. Using reference masses assigned to the standard ion peaks, calibration constants were calculated which were used to assign masses for the remainder of the peaks in the spectrum. The MALDI-Tof MS spectrum of Angiotensin I and Bradykinin exhibited the peak at m/z of 1297.51 and 1061.23, respectively.

2. 3. 1. 2. Type of Matrix

For MALDI-Tof MS analysis, the following conditions and parameters were studied: type of matrix, and analyte-to-matrix ratio. The following types of matrices in this experiment were separately used: dithranol, 2,5-dihydroxybenzoic acid (DHB), α-cyano-4-hydroxycinnamic acid (CCA) and 2-(4-hydroxyphenylazo)-benzoic acid (HABA). All matrices were prepared by dissolving 10 mg of matrix with 1 mL of THF. In addition, the analyte solution and various matrix solutions were mixed (1:75) and vortexed.

2. 3. 1. 3. Analyte-to-Matrix Ratio

The optimum ratios of analyte solution and matrix were studied by preparing the target which contains the ratios of analyte solution to matrix solution at 1:25, 1:50, 1:75 and 1:100.

2. 3. 2. Separation of Zinc Dithiophosphates (ZDDPs) from Commercial Lubricating Oil

The ZDDPs from commercial lubricating oils were extracted according to the following procedure. Silica gel (45 g) was packed in a Buchner porcelain funnel then attached to a suction flask. The commercial lubricating oils (5 g) were loaded into the funnel and were eluted with 150 mL of hexane for base oil removal. And then ZDDPs were eluted from funnel by using a 250 mL of isooctane-ethyl acetate-methanol (4:1.6:0.1, v/v). Then the fraction was evaporated to dryness using a rotary evaporator, prior to analysis using MALDI-Tof mass spectrometry.

2. 3. 3. Matrix Assisted Laser Desorption/Ionization Mass Spectrometry

All MALDI spectra were acquired in positive linear mode using a MALDI-Tof MS mass spectrometer from BIFLEX (Bruker Daltonic, Germany) with a pulsed nitrogen laser (λ = 337 nm). Spectra were acquired as the sum of 200 laser shots.

3. Results and Discussion

The extracted ZDDPs from additive and commercial oil has been analysed by MALDT-Tof MS. We also experienced problems with the ionization efficiency which has been reported earlier by Cardwell[2].

Then all the analyses were carried out by using the reaction between complexes of ZDDPs and DMSO. The conditions of MALDI which are the type of matrix and matrix ratio have been optimized and are reported later in this section. Moreover, the eight commercial lubricating oils have been chosen as representative of the developed method.

3. 1. The Optimal Conditions for Analysis of Zinc Dithiophosphates Additive in Lubricating Oil

3. 1. 1. Type of Matrix

The results suggested that the type of matrix is the most significant factor for MALDI analysis because the matrix corresponded to ionization efficiency of the sample[7]. Four matrices were selected to use in this experiment: dithranol, DHB, CCA and HABA. From the results, no peaks corresponded to native ZDDPs. The significant peaks in mass spectra from the matrices were related to $[Zn(DTP)(DMSO)_2]^+$. The MALDI-Tof MS spectrum of zinc dithiophosphate derivateives; [Zn(DTP)(DMSO)2]+ in which dithranol was used as a matrix (Figure. 1a) showed the peaks between m/z of 517 and 615 which were separated by 14 mass units. The increment of 14 atomic mass units corresponded to CH_2 groups which are located in the side chain of $[Zn(DTP)(DMSO)_2]^+$. Also, the MALDI-Tof MS spectrum from this figure led to complete calculation of the carbon number of two alkyl chains which will be explained in more detail later. The other matrices, that is DHB, CCA and HABA, also show similar results, but the ion intensity is much lower as compared to dithranol. The MALDI-Tof spectra of $[Zn(DTP)(DMSO)_2]^+$ which DHB (Figure. 1b), CCA (data not shown) and HABA (data not shown) showed only some peaks and spectral information on the carbon number of the two alkyl chains were not fully calculated. Consequently, dithranol was found to be the most suitable matrix for analysis of $[Zn(DTP)(DMSO)_2]^+$.

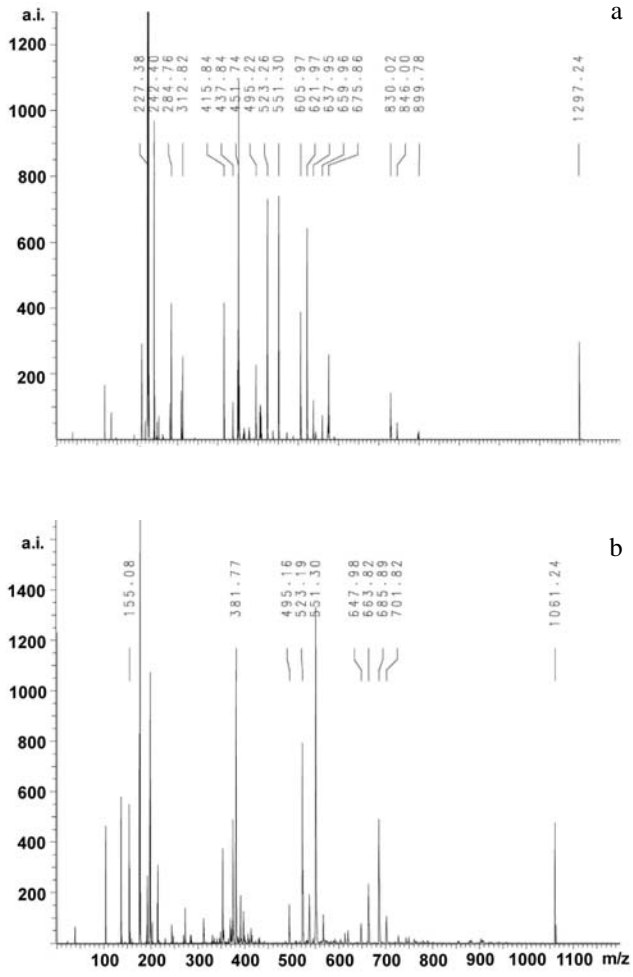


Figure 1. MALDI-Tof spectra of $[Zn(DTP)(DMSO)_2]^+$ when dithranol (a) and DHB (b) was used as the matrix.

3. 1. 2. Ratios of Analyte to Matrix

Dithranol was chosen for further optimum condition. The suitable analyte: matrix ratio was investigated. The analyte solution was diluted by using analyte: matrix 1:25, 1:50, 1:75 and 1:100.

We obtained MALDI-Tof MS spectrum of $[Zn(DTP)(DMSO)_2]^+$ in which dithranol was used as a matrix at analyte to matrix ratios 1:25, 1:50, 1:75 and 1:100 (data not shown). The sample peaks in mass spectra were found to be similar. The m/z of 545.53, related to ZDDPs, was selected for the representative of intensity comparison. From Table 1, it was shown that the ratio of analyte: matrix at ratio of 1:75 (Figure 2) gave the highest relative intensity. In the lower ratio, there might not be enough matrix to absorb the energy and generate the analyte ion. For the higher ratio, the amount of analyte molecules might be too low so the intensity was decreased.

Table 1. Relative intensity of various ratios of analyte-to-matrix of $[Zn(DTP)(DMSO)_2]^+$ of m/z of 545.53

Ratio of analyte to matrix	Relative Intensity	Comparative Relative intensity
1 : 25	950	41.3
1 : 50	2000	86.9
1 : 75	2300	100
1 : 100	700	30.4

3. 2. Analysis of Zinc Dithiophosphate in Additive Package by MALDI-Tof

The complex of the reaction between dimethylsulfoxide (DMSO) and ZDDPs are required for a further analysis using mass spectrometry[2]. The overall reaction can be described in Eq. 1 as follow:

$$\underset{\text{Zinc dialkyl/aryl dithiophosphate}}{Zn(DTP)_2} + \underset{\text{Dimethylsulfoxide}}{2DMSO} \qquad (1)$$

$$\underset{\text{Zinc-containg cation}}{[Zn(DTP)(DMSO)_2]^+} + \underset{\text{Dithiophosphate anion}}{DTP^-}$$

All peaks related to [Zn(DTP)(DMSO)2]+ were identified using the proposed structure as described below. The carbon number of alkyl residues in $[Zn(DTP)(DMSO)_2]^+$ can be calculated using Eq. 2. It is difficult to identify the individual alkyl chains, so the result is shown as the combination of alkyl chains (R1 + R2). The $[Zn(DTP)(DMSO)_2]^+$ at the optimum conditions is show in Figure 2. The calculation results of the peaks related to the complexes, which were calculated using Eq. 2, are reported in Table 2.

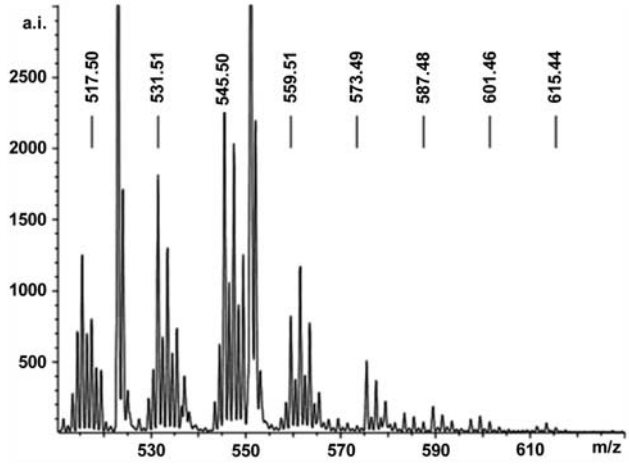
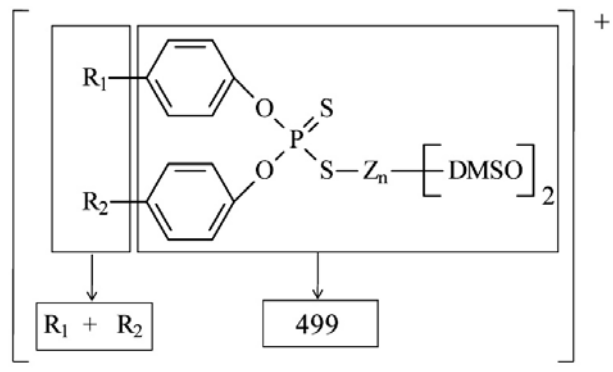


Figure 2. MALDI-Tof MS spectrum of [Zn(DTP)(DMSO)2]+ in additive package using dithranol as matrix, laser power 187 μJ, an analyte to matrix ratio of 1:75.

Table 2. Calculation of the carbon number of dialkyl residues using zinc dialkyldithiophosphate derivatives

Zinc-containing cation; $[(OR_1)(OR_2)PS_2Zn(DMSO)_2]^+$	Carbonnumberofalkyl residues;$(R_1 + R_2)$
517	12
531	13
545	14
559	15
573	16
587	17
601	18
615	19

$[Zn(DTP)(DMSO)_2]^+$ can be calculated using the following equation.



$$347 + (R_1+R_2) = M \qquad (2)$$

Where, M is the m/z value obtained from spectrum, R_1 and R_2 are the alkyl groups, such as CH_3, C_2H_5 and C_3H_7, etc.

3. 3. Application of MALDI-Tof MS for Analysis of Zinc Dithiophosphates in Commercial Lubricating Oil

Zinc dithiophosphates (ZDDPs) additives were separated from eight different commercial lubricating oils using flash column chromatography as described in the experimental section. Base oil in commercial lubricating oil was removed by elution with hexane. Then ZDDPs were successively eluted from the column later using mixture of isooctane-ethyl acetate-methanol (4:1.6:0.1, v/v). All the fractions were analyzed by MALDI-Tof mass spectrometry. No detectable amounts of ZDDPs were found in hexane.

The MALDI-Tof MS spectra of $[Zn(DTP)(DMSO)_2]^+$ in Commercial A, B, C, D, E had the similar pattern of m/z value which have peaks between m/z of 517 and 615, indicating the same type of ZDDPs. The MALDI-Tof MS of commercial A was chosen as representative for this group (Figure 3a). Then MS spectrum of ZDDPs additive package and commercial lubricating oil in this group was compared, the results suggested that two spectra have the same pattern. Consequently, the additive package in Commercial A, B, C, D, E is the package from ZDDPs additive package, that is, zinc dialkyldithiophosphate derivatives.

The MALDI-Tof MS spectra of $[Zn(DTP)(DMSO)_2]^+$ separated from Commercial F, G and H are very similar. Consequently, the mass spectrum of Commercial F (Figure 3b) was chosen as representative spectrum for this group. The peaks of MALDI-Tof MS spectrum of $[Zn(DTP)(DMSO)_2]+$ appeared between m/z of 697 and 795. The peaks in MALDI-Tof MS spectra of $[Zn(DTP)(DMSO)_2]^+$ in this group are different from MALDI-Tof MS spectrum of $[Zn(DTP)(DMSO)_2]^+$ in additive package. Nevertheless, the MALDI-Tof MS spectrum of $[Zn(DTP)(DMSO)_2]^+$ which were separated from Commercial F, G and H can be calculated using Eq. 3.

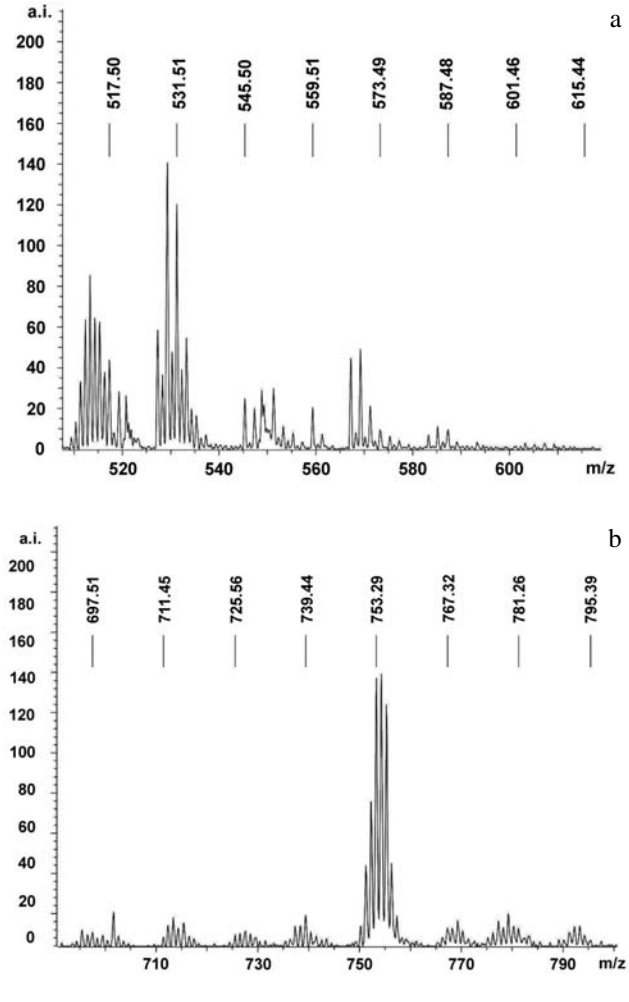
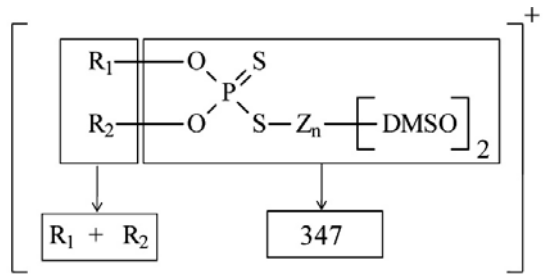


Figure 3. MALDI-Tof MS spectrum of $[Zn(DTP)(DMSO)_2]^+$ in commercial lubricating oils A (a) and F (b)



$$499 + (R1 + R2) = M \quad (3)$$

Where, M is the m/z value obtained from spectrum, R_1 and R_2 are the alkyl groups such as CH_3, C_2H_5 and C_3H_7, etc.

The ZDDPs in this group are related to zinc diaryldithiophosphate derivatives. The calculation results are reported in Table 3. The $[Zn(DTP)(DMSO)_2]^+$ provided information on the carbon number of the two alkyl chains ($R_1 + R_2$).

4. Conclusions

In this research, we have shown the ability of MALDI-Tof MS for the qualitative analysis of ZDDPs. In comparison to previous qualitative analysis methods, our method has proved to gain more information on structure elucidation and is less complicated. Moreover, MALDI-Tof MS analysis of zinc dialkyldithiophosphate and zinc diaryldithiophosphate derivatives in additive package also provided information on the carbon number of the two

Table 3. Calculation of the carbon number of dialkyl residues using zinc diaryldithiophosphate derivatives

Zinc-containing cation; $[(OC_6H_4R_1)(OC_6H_4R_2)PS_2Zn(DMSO)_2]^+$	Carbon number of alkyl residues; $(R_1 + R_2)$
697	14
711	15
725	16
739	17
753	18
767	19
781	20
795	21

alkyl chains which can be used as fingerprint of zinc dithiophosphates for any given commercial lubricating oil.

This method has been applied for the analysis of ZDDPs in eight commercial lubricating oils. From the results it is suggested that the mass spectrum pattern of each sample yields the information on the type of ZDDPs additives. Consequently, this method may be used as a tool for producers of commercial lubricating oils.

Furthermore, quantitative analysis and sensitivity enhancement of zinc dialkyl/aryl dithiophosphate analysis using MALDI-Tof MS should be investigated if relevant standard is available.

5. Acknowledgements

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Povzetek

Cinkovi dialkil/aril ditiofosfati (ZDDPs) so večnamenski dodatki v mazalnem olju. V pričujočem delu smo razvili masnospektrometrično metodo za določanje dodatkov ZDDP v mazalnem olju z ionizacijo z laserjem z desorpcijo v matriksu in masnim analizatorjem na čas preleta ionov (MALDI-ToF). Komplekse $[Zn(DTP)(DMSO)_2]^+$ smo pripravili z reakcijo med cinkovim tiofosfatom in dimetilsulfoksidom. Raziskali smo eksperimentalne pogoje masnospektrometrične meritve (MALDI-Tof MS), predvsem vrsto matriksa in razmerje mešanja vzorca v matriks. Optimalni pogoji analize so: matriks ditranol, topilo tetrahidrofuran in volumsko razmerje $[Zn(DTP)(DMSO)_2]^+$: matriks je 1 : 75. S tako optimizirano metodo smo analizirali dodatke ZDDPs v komercialnih mazalnih oljih. Rezultati analize kažejo, da lahko dodatke v mazalnih oljih razdelimo na dve skupini, cinkove dialkilditiofosfate in diarilditiofosfate. Tovrstne meritve dodatkov imajo veliko uporabnost za proizvajalce mazalnih olj.