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โดยมัลติแมสสเปกโทรเมทรี



นางสาวเจนเนตร ตั้งเจริญ

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จุฬาลงกรณ์มหาวิทยาลัย

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

**ANALYSIS OF METAL DIALKYL DITHIOPHOSPHATE ADDITIVES IN
LUBRICATING OIL BY MALDI MASS SPECTROMETRY**



Miss Jannate Tungcharoen

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย
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By Miss Jannate Tungcharoen
Field of Study Petrochemistry and Polymer Science
Thesis Advisor Associate Professor Amorn Petsom, Ph.D.
Thesis Co-advisor Assistant Professor Polkit Sangvanich, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Master's Degree

..... Dean of the Faculty of Science
(Professor Piamsak Menasveta, Ph.D.)

THESIS COMMITTEE

..... Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

..... Thesis Advisor
(Associate Professor Amorn Petsom, Ph.D.)

..... Thesis Co-advisor
(Assistant Professor Polkit Sangvanich, Ph.D.)

..... Member
(Professor Sophon Roengsumran, Ph.D.)

..... Member
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

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ปฏิกิริยาของซิงค์ไดไทโอฟอสเฟต และไดเมททิลซัลฟอกไซด์ได้ $[Zn(DTP)(DMSO)_2]^+$ ถูกนำมาใช้ในการวิเคราะห์สารเติมแต่งซิงค์ไดแอลคิลไดไทโอฟอสเฟต และไดเอริลไดไทโอฟอสเฟตซึ่งเป็นสารเติมแต่งในน้ำมันหล่อลื่นโดยวิธีแมสสเปกโทรเมทรีแบบเมทริกซ์แอสซิสเทดเลเซอร์ดีซอร์พชันไอออนไนเซชัน (MALDI-MS) การวิเคราะห์โดยมัลติแมสสเปกโทรเมทรีทำได้โดยผสมอนุพันธ์ของซิงค์ไดไทโอฟอสเฟตกับเมทริกซ์ชนิดต่างๆ เช่น 2,5-ไดไฮดรอกซีเบนโซอิกแอซิด ไดทรานอล และอัลฟาไซยาโน-4-ไฮดรอกซีซินนามิกแอซิด ของผสมของอนุพันธ์ของซิงค์ไดไทโอฟอสเฟตและเมทริกซ์ถูกนำมาวางบนผิวโพรบโลหะแล้วฉายรังสีเลเซอร์เพื่อตัวอย่างเปลี่ยนเป็นไอออนของสารที่ต้องการวิเคราะห์ ภาวะการวิเคราะห์โดยมัลติแมสสเปกโทรเมทรีต่อไปนี้พบว่าให้แมสสเปกตรัมที่ดีของอนุพันธ์ของซิงค์ไดไทโอฟอสเฟต: ใช้ไดทรานอลเป็นเมทริกซ์โดยมีเตตระไฮโดรฟูแรนเป็นตัวทำละลาย อัตราส่วนของสารละลายอนุพันธ์ของซิงค์ไดไทโอฟอสเฟตต่อสารละลายเมทริกซ์เท่ากับ 1 : 75 โดยปริมาตร และพลังงานเลเซอร์ที่ 187 ไมโครจูล สเปกตรัมการวิเคราะห์โดยมัลติแมสสเปกโทรเมทรีของอนุพันธ์ของซิงค์ไดแอลคิลไดไทโอฟอสเฟตแสดงพีคระหว่าง m/z 517 ถึง 615 และอนุพันธ์ของซิงค์ไดเอริลไดไทโอฟอสเฟตแสดงพีคระหว่าง m/z 697 ถึง 795 การวิเคราะห์โดยมัลติแมสสเปกโทรเมทรีของอนุพันธ์ของซิงค์ไดไทโอฟอสเฟตให้ข้อมูลเกี่ยวกับจำนวนคาร์บอนของสายโซ่แอลคิลทั้งสองซึ่งถูกนำมาใช้ระบุความแตกต่างจากลักษณะเฉพาะของซิงค์ไดไทโอฟอสเฟตแต่ละชนิดในน้ำมันหล่อลื่นที่จำหน่ายในท้องตลาด

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

ปีการศึกษา 2547

ลายมือชื่อนิติ

ลายมือชื่ออาจารย์ที่ปรึกษา

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Reaction of zinc dithiophosphate with dimethylsulfoxide was used to analyze zinc dialkyldithiophosphates and diaryldithiophosphates lubricating oil additives by matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) analysis. The MALDI-MS analysis was carried out by mixing the $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ with various type of matrix such as 2,5-dihydroxybenzoic acid, dithranol and α -cyano-4-hydroxycinnamic acid. The mixture of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ and matrix was applied to the multiprobe and bombarded with laser to generate ionic analyte. The following MALDI-MS conditions were found to provided the good MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$: dithranol as a matrix with tetrahydrofuran as solvent, the ratio of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$: matrix was 1 : 75 by volume and laser power was 187 μJ . The MALDI-MS spectrum of zinc dialkyldithiophosphates showed the peaks between m/z 517 and 615 and zinc diaryldithiophosphates showed the peaks between m/z 697 and 795. The MALDI-MS analysis of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ provided information on the carbon number of the two alkyl chains (R_1+R_2) which is an individual fingerprint of zinc dithiophosphates for any given commercial lubricating oils. Therefore, the developed MALDI-MS was used to analyze zinc dithiophosphates in commercial lubricating oils.

Field of study Petrochemistry and Polymer Science Student's signature _____

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Co-advisor's signature _____

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LIST OF ABBREVIATIONS

AW	=	Antiwear
CI	=	Chemical Ionization
C	=	Coulomb
Da	=	Dalton
dm ³	=	cubic decimeter
DPDA	=	Dialkylphosphorodithioic acid
DPTA	=	Dialkylphosphorotrithioic acid
DMSO	=	Dimethylsulfoxide
EI	=	Electron Impact
ESI	=	Electrospray Ionization
EP	=	Extreme Pressure
FD	=	Field Desorption
FTICR	=	Fourier-Transform Ion Cyclotron Resonance
GC	=	Gas Chromatography
HPLC	=	High Performance Liquid Chromatography
IR	=	Infrared
KE	=	Kinetic Energy
kv	=	kilovolt
kg	=	kilogram
MALDI	=	Matrix-Assisted Laser Desorption Ionization
MS	=	Mass Spectrometry
m/z	=	mass to charge ratio
MDDP	=	Metal dithiophosphate
mg	=	milligram
ml	=	milliliter
nm	=	nanometer
PAO	=	Polyalphaolefin
SIMS	=	Second Ion Mass Spectrometry
TLC	=	Thin Layer Chromatography
TOF	=	Time-of-flight

UV	=	Ultraviolet
v/v	=	volume percent
w/w	=	weight percent
ZDDP	=	Zinc dithiophosphate
μJ	=	microjoule
μL	=	microliter
μm	=	micrometer



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CHAPTER I

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 substituents of the metal complexes.

Previous techniques which have been used in the analysis of ZDDPs in lubricating oils include thin-layer chromatography (TLC) [1], electrospray mass spectrometry (ES-MS) [2] and gas chromatography (GC) [3].

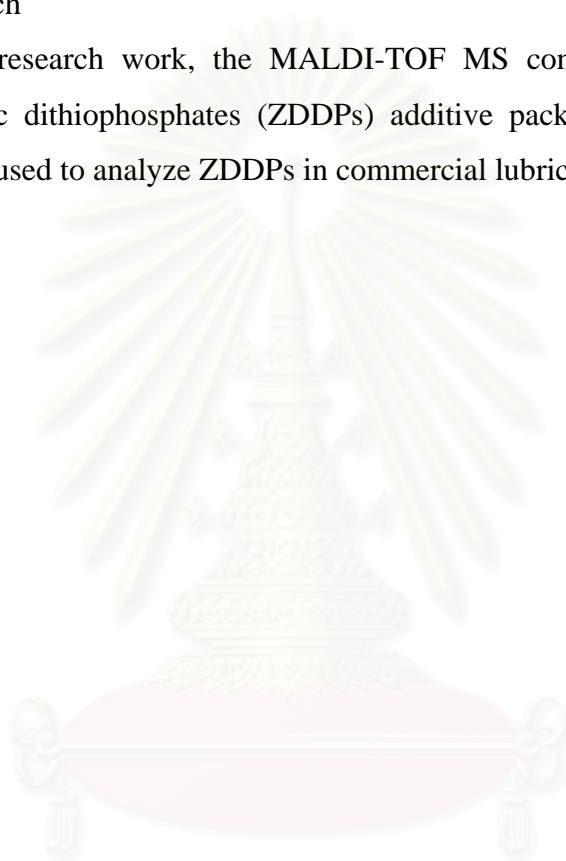
Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) has not previously been employed for the analysis of ZDDPs even though it has been demonstrated to have several advantages, such as spectral simplicity owing to the production of singly charged ions and the inherent soft ionization of MALDI allows promotion of these large thermally labile molecules into the gas phase without extensive fragmentation. Only recently, MALDI-TOF MS was used for analysis of ZDDPs.

Objectives

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).

Scope of research

In this research work, the MALDI-TOF MS conditions were studied for analysis of zinc dithiophosphates (ZDDPs) additive package. Then, a developed method will be used to analyze ZDDPs in commercial lubricating oil.



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CHAPTER II

THEORETICAL AND LITERATURE REVIEWS

2.1 Additives [4-8]

Additives can be classified from different aspects. Important and helpful for the understanding of additives is the following differentiation that takes into consideration which part of the tribo system is influenced by the additives. According to this considerations additives can be classified into types that

1. influence the physical and chemical properties of the base fluids
 - physical effects: *e.g.* demulsibility and low-temperature properties, *etc.*
 - chemical effects: *e.g.* oxidation stability, anticorrosion properties, and high-pressure lubricating properties, *etc.*
2. affect primarily the metal surface by modifying their physicochemical properties: *e.g.* reduction of friction, increase of extreme pressure behavior, wear protection, corrosion inhibition.

Additives are used at treat rates of a few ppm. They can assist each other, resulting in a synergistic effect, or they can lead to antagonistic effects. Many modern additives have several functions (multi-propose additives) and thus reduce the possibility of additives interfering with each other.

Also well balanced and optimized additive systems can improve the performance of lubricants enormously. The formulation of high performance lubricants requires also excellent high quality lubricating oils. The present trend is to use more and more hydrocracked and severely hydrotreated highly refined mineral oils as well as synthetic esters and PAOs.

2.2 Zinc dithiophosphates and metal dithiophosphates

Metal dithiophosphates, illustrated in Figure 2.1, are a class of lubricant oil additives widely used since 1940 in the formulation of lubricants such as industrial, diesel engine, and gasoline engine oils. The substituent R can be an alkyl, aryl, or alkyl-aryl and the metal M is usually zinc.

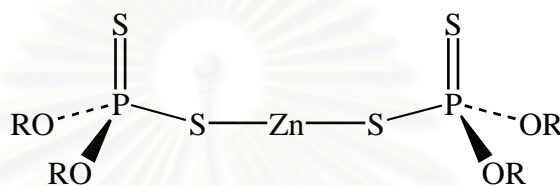


Figure 2.1 Zinc dialkyldithiophosphate structure; R_1, R_2, R_3 and $R_4 = C_nH_{2n+1}$

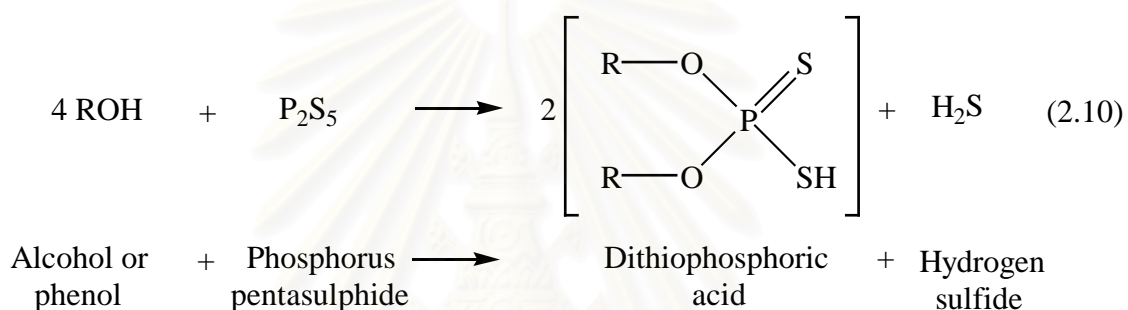
The ZDDPs consist of a polar organometallic core, usually a zinc atom with two dithiophosphate esters, surrounded by an alkylated side. The compounds zinc dialkyldithiophosphates (ZDDPs) are classified as multifunctional additives in lubricants, particularly in engine oils. They have the ability to combine antiwear, antioxidation, and corrosion-inhibiting properties to protect the engine against deterioration. The ZDDPs are mainly used to formulate anti-wear engine oils and hydraulic fluids. Their typical concentration is about 0.65-1.30 %w/w or 0.50-1.00 %v/v in engine oils.

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2.2.1 Synthesis

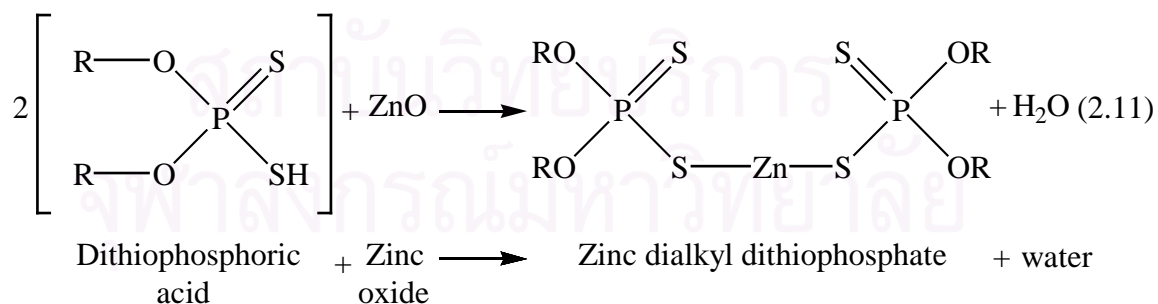
ZDDPs or ZDTPs can be synthesized in two steps. The synthesis of O,O-dialkylphosphorodithioic acids (DPTA or DPDA) *via* reaction (2.10) followed by their conversion to zinc dialkyl dithiophosphates (ZDDP) or metal dialkyl dithiophosphates *via* reaction (2.11).

STEP 1 : synthesis of O,O-dialkylphosphorodithioic acids (DTPA or DPDA)



(ROH = an alcohol or phenol, such as lauryl, octyl, cyclohexyl, or methyl cyclohexyl alcohol or amyl or butyl phenols)

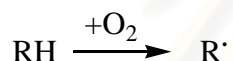
STEP 2 : synthesis of zinc dialkyl dithiophosphates (ZDDP)



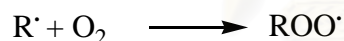
2.3 Oxidation of based lubricants [4]

The aging of lubricants can be differentiated into two processes: the oxidation process by reaction of the lubricant molecules with oxygen and the thermal decomposition (cracking) at high temperatures. In practice the oxidative aging of the lubricant is the dominating process which influences significantly the life time of the lubricant. Caused by steadily increased power density and reduced lubricant volumes (higher load-to-oil ratio) as well as extended service life in the last years, the thermal stress on the lubricant molecules grows constantly. The oxidation of hydrocarbons can be described by the well-known free radical mechanism via alkyl and peroxy radicals. The main reaction steps can be described by Figure 2.2.

Initiation



Chain propagation



Chain branching



Termination



Figure 2.2 Mechanism of autoxidation

The initiation of the so-called autoxidation consists of the hydrogen abstraction of the hydrocarbon by oxygen that will lead to the formation of an alkyl radical. The alkyl radical can react with oxygen to form an alkyl peroxy radical. The next step in the chain propagation scheme is the hydrogen abstraction by a peroxy radical from another hydrocarbon that will lead to a hydroperoxide and an alkyl radical which can again react with oxygen as described above. The difference in reactivity of the miscellaneous radicals explains why linear and unbranched hydrocarbons exhibit a much higher oxidation stability compared to branched, aromatic and unsaturated hydrocarbons. Further steps are chain branching (homolytic cleavage of hydroperoxides, increase number of reactive free radicals, autocatalytic phase of the autoxidation) and the termination of the radical chain reaction by recombination of two radicals to yield unreactive, non-radical species.

The typical oxidation products that will be formed by these oxidation processes are alkylhydroperoxides (ROOH), dialkyl peroxides (ROOR'), alcohols (ROH), aldehydes (RCHO), ketones (RR'C=O), carboxylic acids (RCOOH), esters (RCOOR') and so forth. By polycondensation processes high molecular weight oxidation products are formed. These products are responsible for the typical viscosity increase of aged oil. Further polycondensation and polymerization of these still oil soluble oxidation products lead finally to oil-insoluble polymers that can be observed as sludge and varnish-like deposits. Products of oxidation include sludge, gum, varnish, lacquer, carbon deposits and acidic compounds [5].

Sludge

The type of sludge depends on the conditions (1) under which it is created and (2) to which it is afterward exposed. Its composition includes water, carbon, engine oil, organic residue, and dirt that finds its way into an engine through the breather and carburetor. Sludge can be removed by petroleum solvents. As found in the crankcase, it is for the most part a black tar-like substance that can be broken into fine oily particles when squeezed by hand, at which time abrasive grit may be felt. This grit may be sand (foreign material), or hard carbonaceous particles formed from the oil in high-temperature regions of the engine. In crankcases not properly ventilated, such as those located in the rear of buses, the sludge often has the appearance of coffee grounds. Sludge usually settles to the bottom of the crankcase.

Lighter particles, however, circulate with the oil, and some become separated in the filter. The major factor in the creation of engine sludge is temperature. Water, where conditions tolerate its presence, acts in its development. Acids in such forms as sulfur and carbon compounds accelerate its formation.

Engine gum

A combination of phenolic compounds formed by selected hydrocarbons and formaldehyde. It is generated in the crankcase, generally, under high temperature and other environmental conditions prevailing there. Gum also forms in the combustion area and acts as a binder causing the residue to adhere to piston rings, ring grooves, valves, etc., and also causing agglomeration.

Varnish

A product of oxidation involving both the lubricating oil and fuel, particularly gasoline. Other fuels are also susceptible to gumming, which is the basic cause of varnish, but not to the extent of gasoline. Petroleum gum when exposed to the temperatures prevailing on piston and bearing surfaces bakes to a moderately soft oil-insoluble substance and/or is ironed out to form a tenacious coating by the motion and pressure of such components.

Carbon deposits

A combination of soot (from excessive fuel), tar-like carbon residues from oxidized lubricating oil, and foreign materials drawn into the engine and held by the gasoline gum. It bakes to a black, hard substance found in piston ring grooves and on the internal surfaces of the engine head, top of pistons, valves. *etc.*

Acidic compounds

The deterioration of lubricating oils is accompanied by the formation of certain oil-soluble acids that not only cause metal corrosion but also react with elements contained in the oil to hasten the decomposing process, which, in turn, initiates a continuing cycle leading to a condition approaching complete oil destruction.

2.4 Antioxidants in lubricating oil [6]

The use of additives to control lubricant degradation requires a focus on alkyl radicals ($R\cdot$), alkylperoxy radicals ($ROO\cdot$) and hydroperoxides ($ROOH$). Primary alkoxy radicals ($RCH_2O\cdot$) and hydroxy radicals ($HO\cdot$) rapidly abstract hydrogen from the substrate. It is therefore very unlikely that they can be deactivated by natural or synthetic antioxidants. In practice three additive types have proven to be successful in controlling the degradation of lubricating oils:

- radical scavengers
- hydroperoxide decomposers
- synergistic mixtures of these

Radical scavengers

The most widely used types of radical scavengers are phenolic and aminic antioxidants. Recently, organo-copper salts have been introduced to control the oxidative degradation of engine oils.

Hydroperoxide decomposers

These compounds convert hydroperoxides into non-radical products thus preventing the chain propagation reaction. Traditionally organosulfur and organophosphorus additives have been used for this purpose. They can be classified according to their structure as follows:

- Organosulfur compounds
- Zinc dialkyl dithiocarbamates
- Organophosphorus compounds

Multifunctional additives

Zinc dithiophosphates or metal dithiophosphates

The dominating position of ZDDPs as additives for lubricating oils is due to their multifunctional performance. Not only do they act as antioxidants, but they also improve the wear inhibition of the lubricants, and protect metals against corrosion. The mode of action of ZDDPs is believed to be in the decomposition products that react with the metal surface to form a protective surface coating.

Organomolybdenum compounds

These compounds are of general interest in the engine oil area. They are antioxidants and in addition improve the frictional and anti-wear characteristics of the lubricants. Such compounds impart oxidation stability to the oil by decomposing hydroperoxides and scavenging peroxy radicals.

Overbased phenates and salicylates

Both phenates and salicylates of magnesium and calcium behave as antioxidants at high temperatures.

Sulfur/nitrogen and sulfur/phosphorus compounds

Other multifunctional sulfur/nitrogen, sulfur/phosphorus based additives have antioxidant and anti-wear properties. These additives interact with peroxy radicals and hydroperoxides thus stabilizing industrial lubricants and engine oils.

2.5 Zinc dithiophosphates and metal dithiophosphates as antioxidants

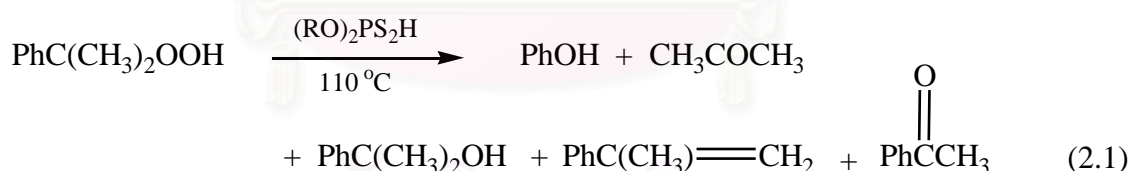
ZDDPs and MDDPs are antioxidants which have reaction mechanism and prepared by reaction as follow:

2.5.1 Reaction mechanism

The performance of ZDDPs is strongly influenced by the type of alcohols used for their synthesis. Table 2.1 gives an overview of the variance of performance with type of alcohol.

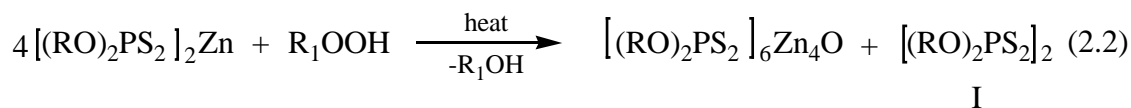
The way ZDDP performs as an antioxidant is a complex interaction pattern involving hydroperoxides and peroxide radicals. The performance matrix is additionally influenced by other additives which are present in industrial or engine oil formulations.

In a model system comprising cumene hydroperoxide and diverse ZDDPs it was demonstrated that the antioxidant mechanism proceeds by an acid catalysed ionic decomposition of the hydroperoxide. The catalyst species is O,O'-dialkylhydrogendithiophosphate, $(RO)_2PS_2H$, derived from the ZDDP.

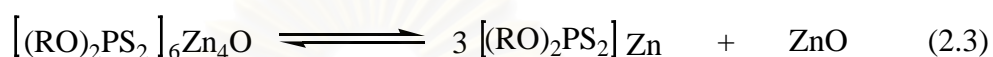


While the first four products are the result of an acid-catalysed cationic chain reaction, the acetophenone is formed by a free radical mechanism.

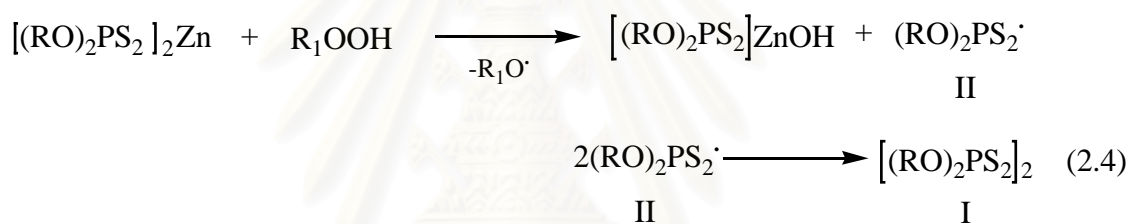
There are two inter-related mechanisms for the formation of the acid catalyst. In the first mechanism, a rapid, initial reaction of ZDDP and hydroperoxide forms a basic ZDDP and disulfide (I)



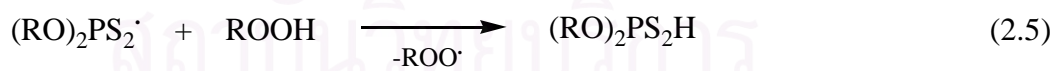
An induction period follows where the rate of decomposition of the hydroperoxide is slow. In this reaction phase the basic ZDDP dissociates to form ZDDP and ZnO.



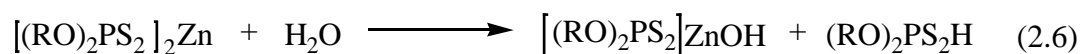
The ZDDP then reacts with hydroperoxide to form additional disulfide (I) *via* the dithiophosphoryl radical (II)



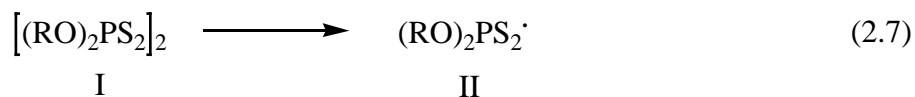
The kinetics of the reaction result in a final rapid decomposition of the hydroperoxide provided the concentration of the basic ZDDP is low. Under these conditions the sulfur radical is unable to dimerise. Instead it reacts with hydroperoxide leading to the catalytically active acid:



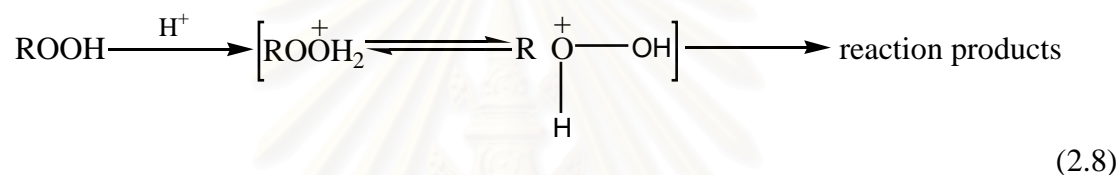
The second source of this acid arises when the ZDDP concentration falls below a critical level. Then traces of water interact with the ZDDP forming the acid catalyst:



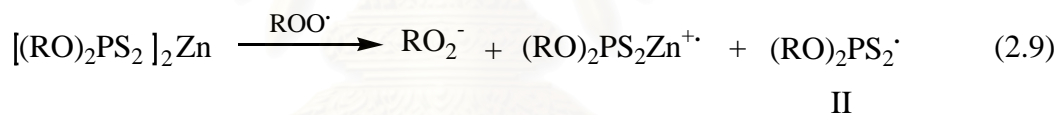
It was demonstrated that at temperatures above 125 °C, the disulfide (II) could be an additional source of the acid catalyst *via* reaction (2.7) followed by reaction (2.5).



A general scheme for the decomposition of hydroperoxides may be:



ZDDP may also interact with peroxy radicals according to the following mechanism:



The radical (II) may react again with hydroperoxide according to reaction (2.5) thereby regenerating the acid $(\text{RO})_2\text{PS}_2\text{H}$, which is a better inhibitor than the ZDDP.

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2.6 Antiwear (AW) and Extreme Pressure (EP) Additives [4, 7]

When two contacting parts of a machinery start to move and the hydrodynamic lubrication has not yet build up or in the case of severe stress and strong forces the lubricating system runs in the area of mixed friction. In this case antiwear and extreme pressure additives are necessary in any engine oil, metalworking fluid, lubricating grease to prevent welding of the moving parts respectively to reduce wear.

Function of Antiwear (AW) and Extreme Pressure (EP) Additives

Because of their polar structure these additives form layers on the metal surface by adsorption or chemisorption that guarantees their immediate availability in the case of mixed friction conditions. When the hydrodynamic lubricating film is not yet or no longer valid temperature will increase and the antiwear and extreme pressure additives can react with the metal surface forming tribochemical reaction layers that will prevent direct contact between the sliding metals. These friction reducing, slide-able reaction layers can smooth the asperity of the metal surface and reduce wear. Layers formed by only physically adsorbed polar substances like fatty oils, fatty acids and others to exhibit only poor or moderate high pressure properties. More effective and more stable are chemically reactive products (antiwear and extreme pressure additives) that can form tribochemical reaction layers. Corrosion inhibitors can interfere in the action of antiwear and extreme pressure additives.

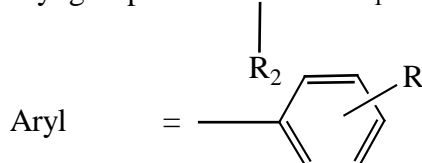
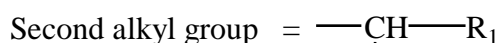
Antiwear additives are mainly designed to reduce wear when the running system is expose to the moderate stress whereas extreme pressure additives are much more reactive and are used when the stress of the system is very high in the order to prevent the welding of the moving parts that otherwise would lead to severe damage. Typically extreme pressure additives increase wear effects due to their high reactivity.

2.7 ZDDP as antiwear and extreme pressure additives

ZDDPs based on isopropanol or *n*-butanol are solids, whereas mixtures of short and long chain alcohols are liquid. The thermal and hydrolytic stability of ZDDPs and thus their reactivity (AW/EP-performance) can be influenced by the structure of the alkyl groups. So the thermal stability increases with the chain length of the alkyl groups and their structure in the sequence secondary, primary and aromatic. By carefully directed alcohol composition the specific requirements of different application can selectively be adjusted. The influence of alcohol composition and structure on the properties of zinc dithiophosphates is shown in Table 2.1.

Table 2.1 Influence of alcohol composition and structure on the properties of ZDDPs

Alkylgroup R	Function		Property	
	Oxidation inhibition	Wear protection	Thermal stability	Hydrolytic stability
R = C ₃ ↓ R = C ₈	No systematic influence	+	-	-
Structure of R		↑ -	↓ +	↓ +
Primary alkyl	satisfactory	satisfactory	good	satisfactory
Secondary alkyl	good	good	moderate	good
Aryl	moderate	bad	very good	bad

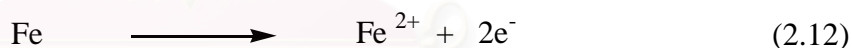


2.8 Corrosion inhibitors [6, 7]

Corrosion inhibitors are used in nearly every lubricant to protect the metal surface from the attack of oxygen, moisture and aggressive products. These moisture acidic products may be formed by the thermal and oxidative decomposition of the lubricant (base oils and additives), brought in directly from the environment (acid atmosphere) or caused by the specific application (aggressive blow-by gases in internal combustion engines). The base oils itself will of cause form a kind of protective layer on the metal surface. But in general this will not be sufficient especially when deeply refined oils without natural inhibitors are used. Then highly efficient anticorrosion additives are necessary.

The process of corrosion [3]

An electrochemical couple is formed between the ferrous metal and its oxide layer, invariably present. The anodic partial reaction generates electrons:



In neutral or alkaline conditions prevalent in the lubrication environment, the corresponding cathodic partial reaction is:



Further oxidation results in the formation of hydrated ferric oxide or Fe(III) hydroxide, *i.e.* rust. Corrosion inhibitors interfere with the anodic or cathodic partial reaction, or with both, resulting in a reduction in the corrosion current.

Mechanism of corrosion inhibitors

The mechanism of anticorrosion additives is relatively simple. Anticorrosion additives can be prevented by the formation of a nonmetallic protective layer which prevents the access of water and oxygen to the metal. Effective inhibitors must adhere strongly to the metal and form a film which is impermeable to water and oxygen. Inhibitors with physical action can be distinguished from chemically action inhibitors. The physical inhibitors are molecules with long alkyl chains and with polar groups which adsorb on the metal surface to form a densely packed, oriented hydrophobic layer. The chemical inhibitors react with the metal and form protective layers which alter the electrochemical potential. Because of this high surface activity, anticorrosion additives compete with other polar additives like antiwear and extreme pressure additives for the metal surface and can therefore reduce their efficiency. Corrosion inhibitors can be divided into two main groups: antirust additives for the protection of ferrous metals and metal passivators for non-ferrous metals.

Metal Passivators (Non-ferrous Metals) can be classified into three groups: film forming compounds (*e.g.*, ZDDPs, benzotriazole *etc.*), complex forming chelating agents (*e.g.*, *N,N'*-disalicylidene-propylenediamine *etc.*) and sulfur scavengers (*e.g.*, dialkyl-2,5-dimercapto-1,3,4-thiadiazole *etc.*). The fundamental function of the film forming types consists in the building of passivating protective layers on the non-ferrous metal surface thus preventing the of solubilization of metal ions that would work as pro-oxidants. The complex forming agents are able to build oil-soluble complexes with significantly reduced catalytic activity regarding the influence of non-ferrous metal ions on the oxidative aging process of lubricants. Sulfur scavengers are even able to catch corrosive sulfur by integrating sulfur into their molecule structure.

Antirust additives (Ferrous Metals)

Example;

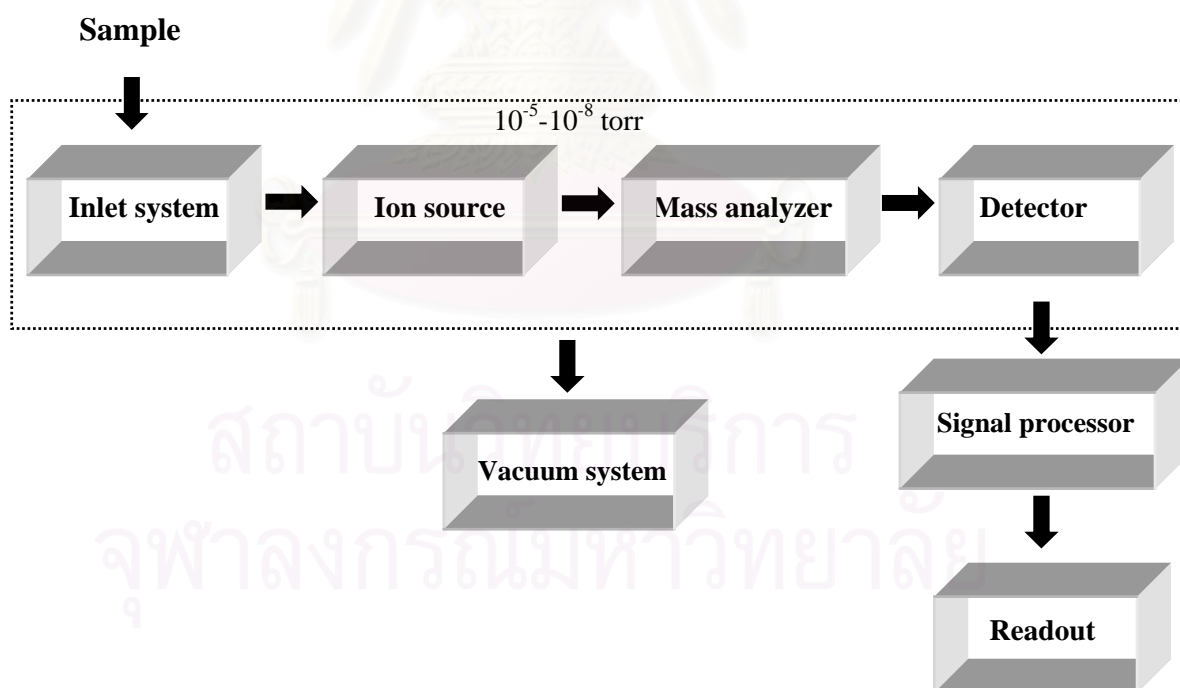
- Sulfur compounds
- Nitrogen compounds
- Carboxylic acid derivatives *etc.*

2.9 Mass spectrometry [9-16]

A mass spectrum is obtained by converting components of a sample into rapidly moving gaseous ions and separating them on the basis of their mass-to-charge ratios. Mass spectrometry is perhaps the most widely applicable of all the analytical tools available to the scientist in the sense that the technique is capable of providing information about (1) the qualitative and quantitative composition of both inorganic and organic analytes in complex mixtures, (2) the structures of a wide variety of complex molecular species, (3) the structure and composition of solid surfaces, and (4) the mixture analysis are some of the major applications.

Mass spectrometer

General description of instrument components



Scheme 2.1 Components of a mass spectrometer

The block diagram in Scheme 2.1 is shown the major components of mass spectrometers. The purpose of the *inlet system* is to introduce a very small amount of sample (a micromole or less) into the mass spectrometer, where its components are converted to gaseous ions. Often the inlet system contains a means for volatilizing solid or liquid samples. The *ion source* of a mass spectrometer converts the components of a sample into ions by bombardment with electrons, ions, molecules or photons. Alternatively, ionization is brought about by thermal or electrical energy. The function of the *mass analyzer* is analogous to that of the grating in an optical spectrometer. In the former, however, dispersion is based upon the mass-to-charge ratios of the analyte ions rather than upon the wavelength of photon. Like an optical spectrometer, a mass spectrometer contains a *detector* (for ions) that converts the beam of ions into an electrical signal that can then be processed, stored in the memory of a computer, and displayed or recorded in a variety of ways. A characteristic feature of mass spectrometers, which is not shared by optical instruments, is the requirement of an elaborate vacuum system to maintain low pressures (10^{-4} to 10^{-8} torr) in all the instrument components except the *signal processor* and *readout*. The overall analytic capability of a mass spectrometry system depends on the combined performance of these individual units. Several ionization techniques and mass analyzers have emerged, each with special purpose.

Ionization methods

- Ionization of volatile Materials
 - Electron Ionization (EI)
 - Chemical Ionization (CI) *etc.*
- Desorption/Ionization Methods
 - Field Desorption (FD)
 - Secondary Ion Mass Spectrometry (SIMS)
 - Matrix-Assisted Laser Desorption Ionization (MALDI) *etc.*
- Spray Ionization Methods
 - Electrospray Ionization (ESI) *etc.*

Mass Analyzers

- Scanning Mass Analyzers
 - Quadrupole Mass Filter
 - Quadrupole Ion Trap
 - Magnetic and Electric Sectors
- Nonscanning Mass Analyzers
 - Time-of-Flight (TOF) Analyzers
 - Fourier-Transform Ion Cyclotron Resonance (FTICR)

Detectors

- Electron Multipliers
- Photon Multipliers
- Array Detectors
- Photographic Plates and Faraday Cylinders

For this research, the ionization technique which was chosen for analysis of ZDDPs is Matrix-Assisted Laser Desorption Ionization and the mass analyzer is Time-of-Flight. The principals of these techniques were explained, respectively.

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2.10 The Matrix-Assisted Laser Desorption Ionization Technique

The matrix is the key component in MALDI-MS. The most commonly used matrices are DHB (2,5-dihydroxybenzoic acid), HABA (2,(-4-hydroxyphenylazo)benzoic acid), dithranol (1,8,9-trihydroxyanthracene) and α -CHCA (α -cyano-4-hydroxycinnamic acid). Their structures are shown in Figure 2.3. Properties essential to a MALDI matrix are (1) high molar absorptivity at the laser wavelength employed, (2) matrix solubility in the same solvent as the analyte material, (3) appropriate physical properties such as lattice structure and heat of sublimation, (4) ability to promote ionization, and (5) good vacuum stability. In practice, the matrix should provide maximum analyte ion intensity and signal reproducibility, and should minimize fragmentation and adduct formation with the molecule. It must also retain its properties in the presence of contamination.

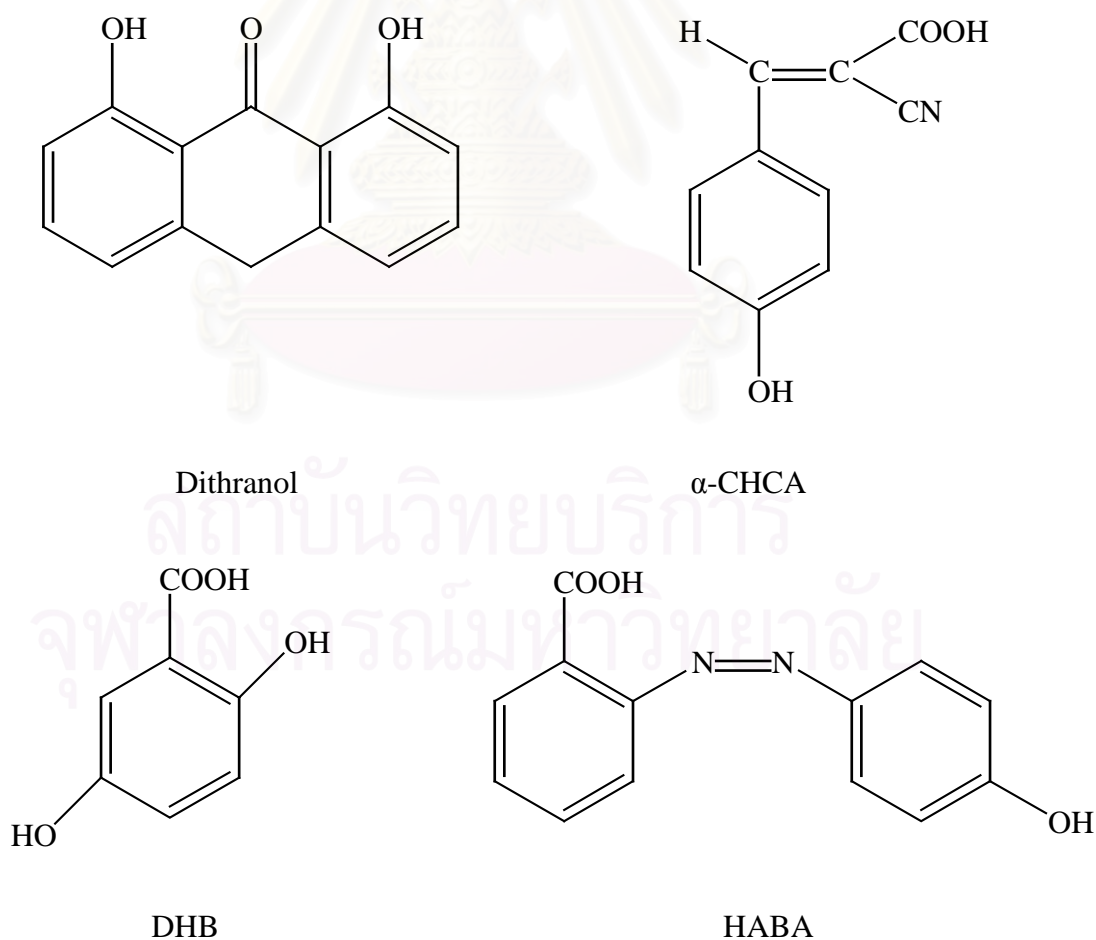


Figure 2.3 Common MALDI matrices

Ionization of the molecule is thought to occur in the condensed phase or just above the target in the volume of solid that was ablated by the laser pulse. It has been suggested that the matrix provides a source of gas-phase protons for ionization (proton transfer reaction) in the positive ion mode. However, in some cases even in the presence of cationization with a metal (*e.g.*, Na^+ , K^+) is the preferred pathway for ionization.

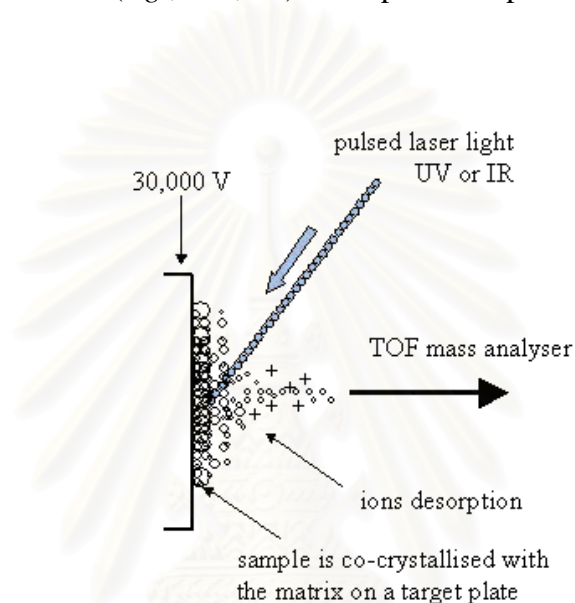


Figure 2.4 MALDI formation of ions by laser desorption

Sample Preparation

There are several methods of sample preparation, including the dried-droplet, fast evaporation, and smashed crystals methods--all with numerous variations. Since the dried-droplet and fast evaporation methods are the most commonly used (in part, owing to their simplicity), they will be described here. The matrix and analyte are dissolved in the appropriate mixture of organic solvent/water and either applied sequentially to the target plate or mixed together in a vial and deposited on a target plate (typically, polished stainless steel), where solvent evaporation occurs under ambient conditions or accelerated drying using compressed air or N₂. The molar ratio of analyte:matrix is usually 1:10³-1:10⁵; clearly, there is a large molar excess of matrix. The matrix crystallizes upon drying and concurrently individual analyte molecules are isolated in it. In the dried-droplet technique, a 1-μL portion of this mixture is applied to a stainless-steel or gold-coated sample well. In order to obtain a fine-grained morphology of the crystal formation, the sample spot is evaporated slowly in the ambient air or by a gentle stream of cold air. Other researchers have advocated a fast evaporation of the matrix-sample mixture. In this procedure, a 0.5-μL drop of the matrix solution in acetone that contains 1-2% water is rapidly deposited on the probe. The acetone rapidly evaporates to leave behind a homogeneous surface of small crystals. This procedure yields enhanced resolution, sensitivity, and mass accuracy.

After the crystallization step, the sample is inserted into the vacuum system of the spectrometer and pumped down to ca. 10⁻⁸ torr. At this point, the laser is fired at the target the matrix absorbs the laser light energy which vaporizes it (it desorbs from the surface) and this carries some of sample with it. At the time that the laser is pulsed a voltage is applied to the target plate to accelerate the ionized sample towards a time-of-flight mass analyzer. It can be illustrated in Figure 2.4. In the vacuum system, a column of material is ablated (matrix and analyte), and positive or negative ions are mass analyzed.

Various laser systems have been used to rapidly deposit energy into the matrix-sample combination. Most applications have used UV lasers, such as the N₂ (337 nm), the frequency-tripled (355 nm) and frequency-quadrupled (266 nm) Nd : YAG laser, and the ArF excimer laser (193 nm). IR lasers have also been used to produce the MALDI effect. The TEA CO₂ laser (10.6 μm), the Q-switched Er : YAG laser (2.94 μm), and the Cr : LiSAF or Nd : YAG pumped optical parametric oscillators (OPO) laser (3.28 μm) are the most common IR lasers. UV and IR lasers both yield similar spectra for proteins, although a better resolution has been obtained for some proteins with and IR laser.

Time-of-Flight Mass Analysis of MALDI-Produced Ions

A time-of-flight (TOF) mass analyzer is commonly used for MALDI-MS because the pulses of ions generated in this way provide the sampling mode required by TOF analyzers. Advantages of TOF mass analyzers over other mass spectrometry platforms include simplicity, high transmission, theoretically unlimited mass range, detection of all species simultaneously (multiplex advantage), high speed of analysis, and direct compatibility with pulsed ionization sources.

In MALDI, the ions are created by a laser pulse that strikes the matrix-covered surface. To measure the time-of-flight of a particular ion, the TOF clock needs to be set like a stopwatch (*i.e.*, $t = 0$ need to be defined). This can be accomplished in several ways: when the laser is fired, when a photodiode placed near the sample is activated by the laser pulse, or when the mass spectrometer extraction voltage is turn on.

The ions formed from the laser pulse are extracted into the TOF analyzer by an electrical field (U_{ex}). The kinetic energy (KE) given to an ion by the electric field is the product of the charge of the ion and the electrical field strength:

$$KE = zeU_{ex} \quad (2.14)$$

where z is the charge of the molecular ion, e is the charge of an electron in coulombs, and U_{ex} is the electric field strength in volts. In the ideal case, all ions (regardless of mass) enter the field-free region with identical kinetic energy. From Newtonian mechanics, we know the following relationship:

$$KE = (1/2)mv^2 = (1/2)m(dx/dt)^2 \quad (2.15)$$

Therefore the right side of equation (2.14) is equal to the right side of equation (2.15)

$$zeU_{\text{ex}} = (1/2)m(dx/dt)^2 \quad (2.16)$$

Since the ions are extracted in a very short source region relative to the time they spend in flight, the velocity is a constant in these equations; thus, we can replace the instantaneous velocity with the total flight time (Δt) and the total field-free flight path (Δx). By rearranging equation (2.16), m/z for a given can be determined:

$$m/z = 2eU_{\text{ex}}\Delta t^2/\Delta x^2 \quad (2.17)$$

where m is the mass in kilograms, (Δx) is the flight path length of the ion in meters, and (Δt) is the flight time in seconds. The total flight time is $t_{\text{arrival}} - t_0$; thus, Δt becomes t .

Equation (2.17) can also be written to determine the arrival time of a given molecular ion if the experimental conditions are known:

$$t = \Delta x (m/2zeU_{\text{ex}})^{1/2} \quad (2.18)$$

In more convenient terms, equation (2.17) can be written so that m is the molecular mass of the ion in daltons; and since 1 Da is equal to 1.660×10^{-27} kg and $e = 1.60 \times 10^{-19}$ C, the equation can be written

$$m/z = (9.638 \times 10^7)2U_{\text{ex}}(\Delta t^2/\Delta x^2) \quad (2.19)$$

The production of primarily singly charged ions ($z = 1$) in MALDI clearly demands high m/z mass analyzers. As previously mentioned, TOF has a theoretically unlimited mass range (e.g., if a Boeing 747 enters into one end of an empty tube a Boeing 747 will come out the other end—assuming no collisions). This places stringent requirements on the detection system because they are velocity-dependent (velocity-sensitive) detectors. This can be seen rearranging equation (2.16)

$$V = (2zeU_{\text{ex}}/m)^{1/2} \quad (2.20)$$

Thus the velocity decreases inversely with the square root of the mass, and therefore the sensitivity is reduced for high molecular weight species.

Because of the large kinetic energy difference of the ions produced at the surface, linear TOF analyzers do not afford high mass resolution because the initial kinetic energy distribution (which increases with mass) is not being compensated for. The linear mode operation is depicted in Figure 2.5.

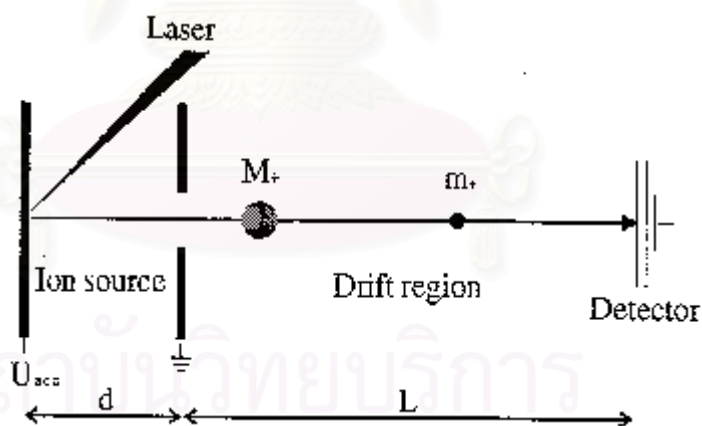


Figure 2.5 Schematic diagram of a linear time-of-flight (TOF) mass spectrometer

The reflectron TOF configuration was introduced in 1966 and several variations have subsequently appeared. The reflectron-TOF (reTOF) consists two linear field-free regions and an ion mirror (depicted in Figure 2.6) which compensates for different, nonzero initial kinetic energies of ions of the same m/z . Figure 2.6 depicts what occurs if two ions (1 and 2) of the same mass but different initial kinetic energy ($E_1 > E_2$) are desorbed from a surface and mass analyzed by a reTOF. Ions extracted from the surface (U_{ex}) traverse the first field free region (L_1). Thus the kinetic energy of ion 1 is ($U_{ex} + E_1$) and of ion 2 is ($U_{ex} + E_2$).

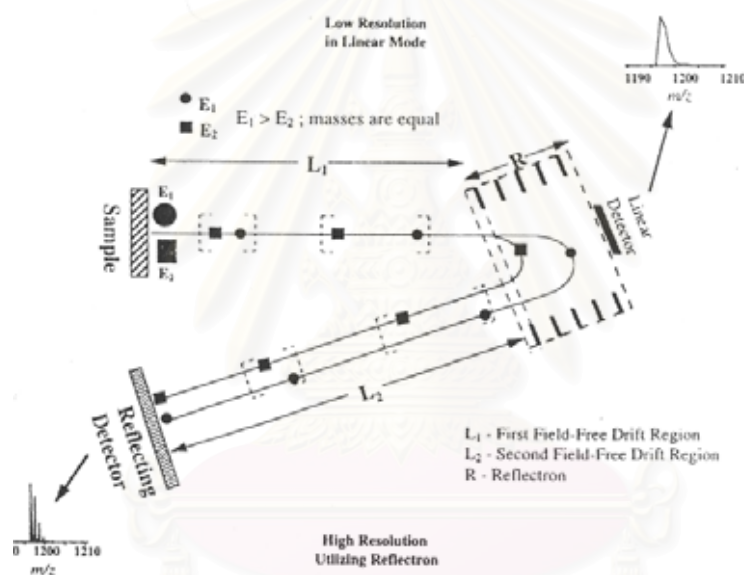


Figure 2.6 Schematic diagram of a reflectron time-of-flight (TOF) mass analyzer

The time required for each ion to arrive at the entrance to the ion mirror can be determined:

$$t = L_1/v \approx 1/KE^{(1/2)} \quad (2.21)$$

where t is the time, L_1 is the length of the first linear region, v is the velocity of the ion, and KE is the total kinetic energy of the ion. If E_1 has a greater kinetic energy than E_2 , E_1 will traverse the field-free region first. This is illustrated in Figure 2.6. with the brackets indicating the pair of ions that originated at the surface from the desorption laser pulse.

In the reflecting region (R), the ion with the greater kinetic energy (E_1) will penetrate further into the ion mirror, as shown in Figure 2.6. The distance the ion travels

into the ion mirror, which is proportional to flight time, depends on the ion's energy. Thus, the ion with the initial kinetic energy E_1 will traverse further into the field than the ion of energy E_2 and will therefore spend a longer time in region R. When the ions leave the reflecting field they enter into a second field-free linear region (L_2) and will ultimately strike the detector. However, note that the ion with energy E_2 is in front of ion E_1 at the exit of the ion mirror even though E_1 is still greater than E_2 . Time focusing is achieved by changing R (the length of the reflecting region) by altering the voltage of the ion mirror, since it is not experimentally feasible to change L_1 and L_2 . As the ions travel through the second field-free region (L_2), ions E_1 and E_2 become time focused at the plane of the detector because ion E_1 catches up to ion E_2 owing to its greater kinetic energy. This time focusing phenomenon results in significantly improved mass resolution, as depicted in Figure 2.6.

Recently, the implementation of delayed ion extraction, an important innovation originally proposed by Wiley and McLaren, has greatly improved mass resolution. Delayed extraction allows the ions to disperse in the source region (acceleration region just above the surface) owing to their initial velocity, while the density of neutrals is decreased by pumping them away. The number of ion-molecular collisions before extraction of the ions into the field-free drift region is therefore reduced, which decreases the width of the translational energy distribution. Simultaneously, ions having higher initial kinetic energy move further away from the extraction field in the source region and thus are given less kick; those of lower kinetic energy experience a higher extraction field. This approach has proven so successful that limitations in mass resolution are now focused on detection systems (the time resolution).

2.11 Literature Reviews

In 1971, Coates [1] analyzed oils and additives by thin-layer chromatography (TLC). The zinc dialkyl/aryldithiophosphates (ZDDPs) could be separated on silica gel thin layers by development with a mixture of ethyl acetate, acetic acid and isooctane in a saturated tank.

In 1993, Cardwell and coworkers [2] analyzed ZDDPs in engine oil additives by electrospray mass spectrometry (ES-MS). They found that the positive ion ES mass spectrum revealed a complex mixture of dithiophosphates based upon aryl alcohols. The peaks between m/z 697 and 879 were separated by 14 mass units, corresponding to a CH_2 group in the side chain of the zinc dithiophosphate derivatives.

In 1996, Lambropoulos and coworkers [17] separated ZDDPs by normal-phase high-performance liquid chromatography (normal-phase HPLC) on a 5- μm silica column using an isopropylamine-acetic acid-methanol (0.4:0.2:1.0 % v/v) in *n*-heptane-dichloromethane (60:40 % v/v) eluent. They found that the zinc complexes were eluted from the column without decomposition.

In 1997, Windahl and Cardwell [18] investigated ZDDPs in aqueous-based media indicating that the species retained in reversed-phase HPLC on a C_{18} column was not the zinc complex. They found that this technique was unsuitable for identification and analysis of ZDDPs.

In 1999, Thibon and coworkers [19] analyzed ZDDP in lubricating oils by nonaqueous capillary electrophoresis. Nonaqueous systems composed of methanol, tetrahydrofuran and acetonitrile with tetraethylammonium, tetramethylammonium or ammonium hydroxide and acetic acid were employed to separate the metal complexes accordingly to the different hydrocarbon chain lengths and structures of the alkyl substituents.

In 1999, Becchi and coworkers [3] used pentafluorobenzyl ester derivatives to identify ZDDPs in engine oils by GC-MS with electron impact and electron-capture negative ion chemical ionization. This procedure provided the structure and carbon atom number of alkyl residues.

CHAPTER III

EXPERIMENTAL

3.1 Materials

1. LZ 1395; as zinc dithiophosphate additive package for lubricating oil
Lubrizol
2. Commercial lubricating oils
 - E Superflo Premium Mineral; API SL/CF, SAE 20w-50
 - C Havoline Formula; API SL/CF, SAE 20w-50
 - D3 Gold Fully Synthetic; API CI-4, SAE 5w-30
 - Local Brand Fully Synthetic; API SL/CF, SAE 5w-50
 - T Lubricating Oil for Gasoline Engine; API SH/CD, SAE 20w-50
 - P V-120; API SD/CC, SAE 40
 - S Helix Plus; API SJ/CF, 15w-50
 - Q Formula Advanced Semi Synthetic; API SL/CF, SAE 15w-50
3. Silica gel 60 (70-230 mesh): For column chromatography; Merck
4. Hexane: Commercial grade; J.T. Baker
5. Isooctane: Puriss. p.a. ACS; > 99.5% (GC) ; Fluka
6. Ethyl acetate: Analytical grade; Fisher Chemicals
7. Methanol: Analytical grade; Labscan
8. Dimethylsulfoxide: Commercial grade; Labscan
9. Tetrahydrofuran: HPLC grade; Labscan
10. Dithranol (1,8,9-trihydroxyanthracene); Sigma-Aldrich
11. DHB (2,5-dihydroxybenzoic acid); Sigma-Aldrich
12. HABA (2,(-4-hydroxyphenylazo)benzoic acid); Sigma-Aldrich
13. α -CHCA (α -cyano-4-hydroxycinnamic acid); Sigma-Aldrich
14. Angiotensin I; Sigma-Aldrich
15. Bradykinin; Sigma-Aldrich

3.2 Apparatus and Instruments

1. Matrix-Assisted Laser Desorption Ionization Mass Spectrometer (MALDI-MS): BIFLEX; BRUKER
2. Vortex mixer: Vorttex-genie No.2; Scientific Industries
3. Multichannel probe; BRUKER
4. Autopipette: Pipetman; Gilson

3.3 Procedure

3.3.1 Sample and target preparation

The material safety data sheet (MSDS) of Lubrizol 1395 [20] indicated the composition of zinc dithiophosphate in additive package LZ 1395 at 90 % w/w. First, zinc dithiophosphate additive package LZ 1395 was dissolved in tetrahydrofuran (7,000 mg/L). Second, 0.5 μL DMSO was added into 75 μL of zinc dithiophosphate solution to get the analyte solution. Third, 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 multiprobe and allowed to dry.

Internal calibration [9] involves the mixing of one or more standard compounds with the unknown analyte. The mixture was then mixed with 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-MS spectrum of angiotensin I and bradykinin exhibited the peak at m/z 1297.51 and 1061.23, respectively.

3.3.2 Conditions for the analysis of zinc dithiophosphate in additive package LZ 1395

For MALDI-TOF MS analysis, the following conditions and parameter were studies:

- Type of matrix
- Laser power (μJ)
- Analyte-to-matrix ratio

Type of matrix

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). In addition, the analyte solution and various matrix solution were mixed (1 : 75) and vortexed.

- 10 mg/ml dithranol prepared in THF
- 10 mg/ml DHB prepared in THF
- 10 mg/ml CCA prepared in THF
- 10 mg/ml HABA prepared in THF

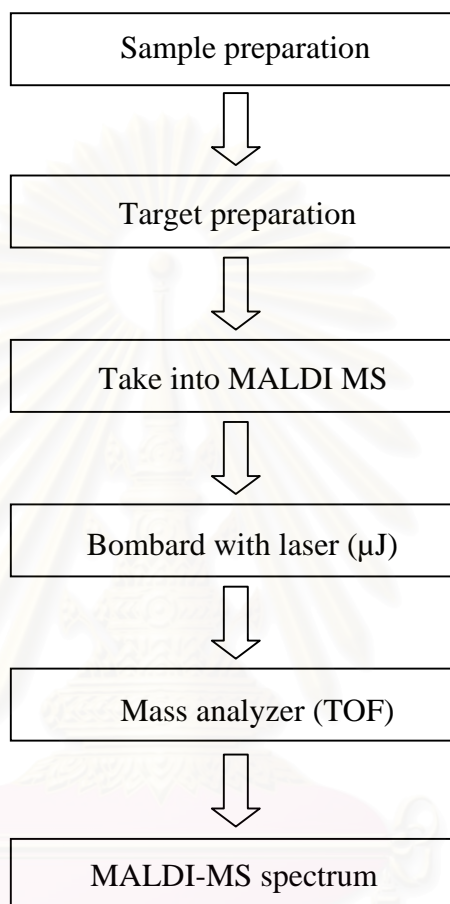
Analyte-to-matrix ratio

The ratios of analyte solution to matrix solution were

- 1 : 25
- 1 : 50
- 1 : 75
- 1 : 100

MALDI-TOF MS Analysis

The overall process for MALDI-TOF MS analysis is shown in Scheme 3.1.



Scheme 3.1 Schematic diagram for MALDI-TOF MS analysis

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3.3.3 Separation of zinc dithiophosphates (ZDDPs) from commercial lubricating oil

Commercial lubricating oil for flash column chromatography was prepared by mixing the lubricating oil (5 g) with the small amount of silica gel. Then silica gel (45 g) was packed in buchner porcelain funnel attached to a suction flask. The lubricating oil sample was loaded into the buchner porcelain funnel and eluted with 150 ml of hexane. The zinc dithiophosphates (ZDDPs) were eluted with 250 ml of isooctane-ethyl acetate-methanol (4 : 1.6 : 0.1, v/v) eluent. The solvent in this fraction was evaporated to dryness using a rotary evaporator, prior to analysis using MALDI-TOF mass spectrometry.



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As the peak at m/z value of the MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ was closed to the matrix, the matrix was deposited on multiprobe and allowed to dry to obtain MALDI-MS spectra of dithranol, DHB, CCA and HABA for used as a blank as shown in Figure A1 (a), A1 (b), A1 (c) and A1 (d), respectively.

4.1.2 Ratios of analyte to matrix

The ratio of suitable analyte : matrix ratio was investigated. The same concentration of analyte solution, which had the ratio of analyte : matrix (dithranol); 1 : 25, 1 : 50, 1 : 75 and 1 : 100 were prepared. The relative intensity from each spectrum is shown in Table 4.1.

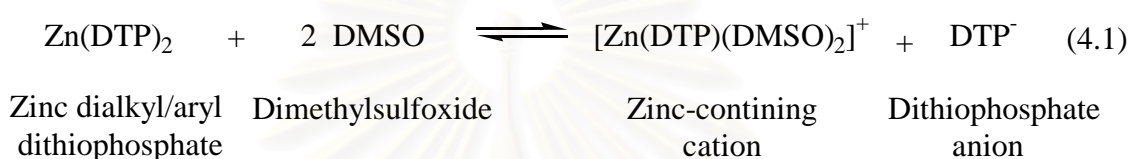
Table 4.1 Relative intensity of various ratios of analyte-to-matrix of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$

Ratio of analyte to matrix	Relative intensity
1 : 25	0.1253
1 : 50	0.2299
1 : 75	0.2991
1 : 100	0.0480

The obtained MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ which dithranol was used as a matrix and analyte to matrix ratios; 1 : 25, 1 : 50, 1 : 75 and 1 : 100 are shown in Figure A3 (a), A3 (b), A3 (c) and Figure A3 (d), respectively. The sample peaks in mass spectrum were found to be similar. From Table 4.1, it was shown that the ratio of analyte : matrix 1 : 75 gave the highest relative intensity. As a result, this ratio is the most suitable for analysis.

4.2 Analysis of zinc dithiophosphate in additive package LZ 1395 by MALDI MS

MALDI-TOF MS has been used for analysis of zinc dialkyl/aryl dithiophosphate derivatives; $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$. The neutral $[\text{Zn}(\text{DTP})_2]$ compounds cannot be observed by MALDI-TOF MS, but reaction with dimethylsulfoxide (DMSO) generates ionic product [2] which can be observed by this technique. The overall reaction can be described as follow:



In the following discussion, all peaks in the mass spectrum were identified by the m/z value of the most abundant peak in the characteristic isotopic mass distribution of sample containing zinc.

CHAPTER IV

RESULTS AND DISCUSSION

This research was related to the development of mass spectrometric method for analysis of the zinc dithiophosphate additive in lubricating oil. As proposed in previous chapter, the results will be shown and discussed in each part, respectively.

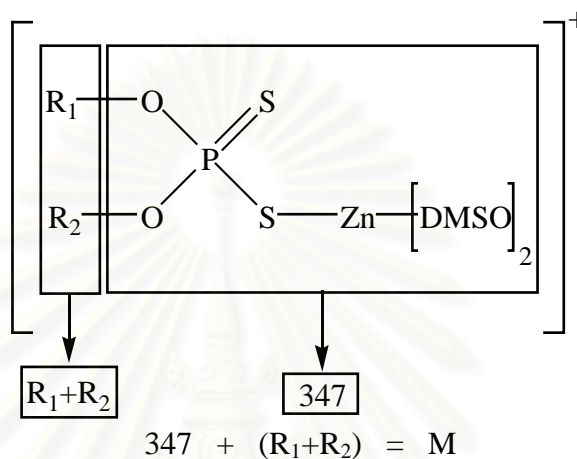
4.1 The optimized conditions for analysis of zinc dithiophosphates additive in lubricating oil

4.1.1 Type of matrices and laser power

Type of matrices and laser power are the most significant factors for MALDI analysis because the matrix and laser power corresponded to ionization efficiency of the sample [15]. The matrices: dithranol, DHB, CCA and HABA were used in this experiment. The MALDI-MS spectrum of zinc dithiophosphate derivatives; $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ which dithranol was used as a matrix (Figure A2 (b)) showed the peaks between m/z 517 and 615 which were separated by 14 mass units and corresponding to a CH_2 groups in the side chain of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$. Also, the MALDI-MS spectrum from Figure A2 (b) was present and led to complete calculation of the carbon number of two alkyl chains. Consequently, dithranol was found to be the most suitable matrix for analysis of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$. Whereas, the MALDI-MS spectra of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ which DHB (Figure A2 (d)), CCA (Figure A2 (f)) and HABA (Figure A2 (h)) were used as matrices showed only some peaks and spectral information on the carbon number of the two alkyl chains were not fully calculated. Therefore, DHB, CCA and HABA were not chosen to be the matrices for analysis of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$. Moreover, the sample peak intensity in the mass spectrum using dithranol as a matrix was the highest when compared with those using DHB, CCA and HABA as matrices.

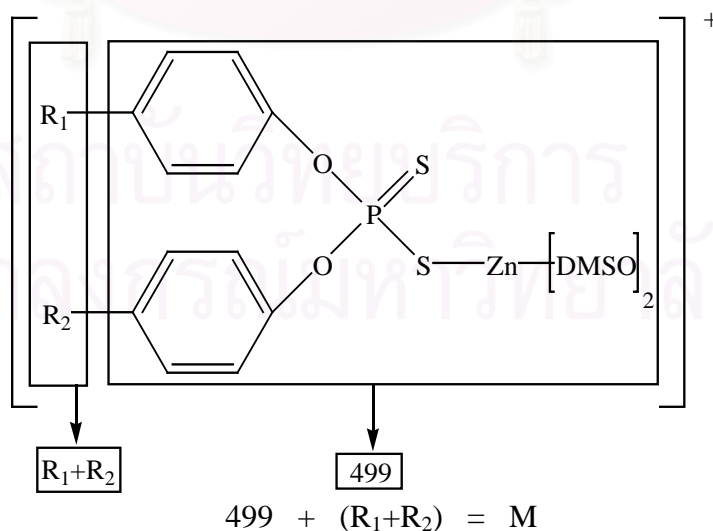
4.2.1 Calculation of the carbon number of zinc dithiophosphate derivatives

- (1) The carbon number of dialkyl residues using zinc dialkyldithiophosphate derivatives; $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ can be calculated using the following equation.



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.

- (2) The carbon number of dialkyl residues using zinc diaryldithiophosphate derivatives; $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ can be calculated using the following equation.



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.

When $[\text{Zn}(\text{DTP})_2]$ in additive package LZ 1395 was reacted with DMSO, the neutral complex undergoes ligand exchange and zinc-containing cations; $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ were observed in the positive ion mode.

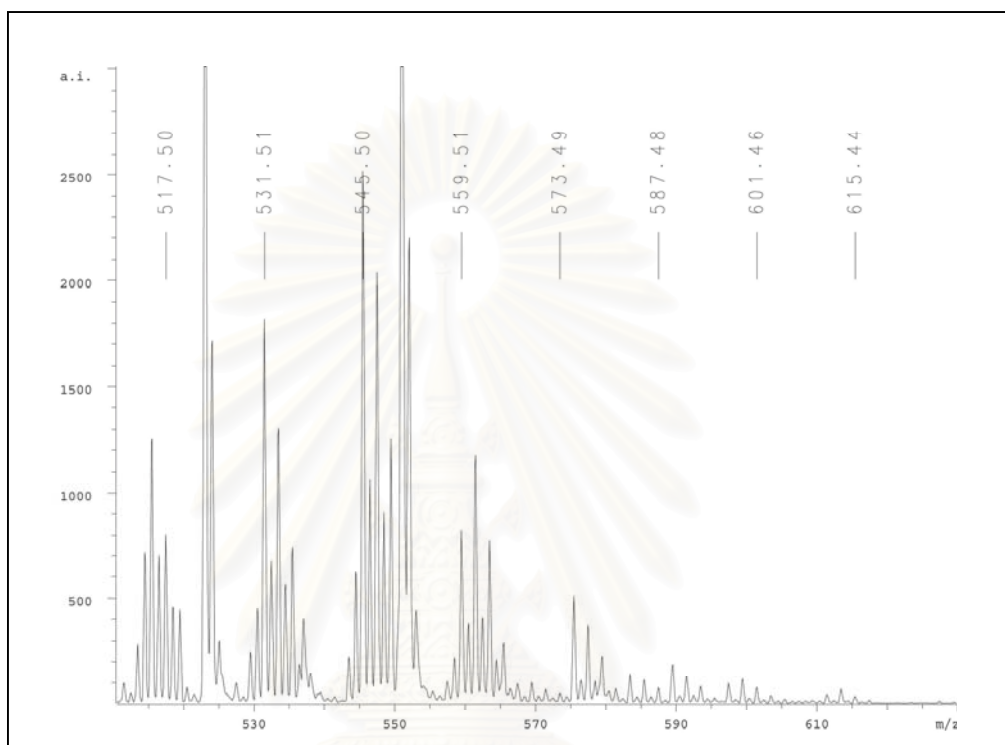


Figure 4.1 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in additive package LZ 1395 using dithranol as matrix, laser power 187 μJ , an analyte to matrix ratio of 1 : 75.

Upon reaction of $[\text{Zn}(\text{DTP})_2]$ in additive package LZ 1395 with DMSO, all of the peaks in the positive ion mass spectrum revealed the characteristic zinc isotope pattern. The MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ is shown in Figure 4.1 which the peaks between m/z 517 and 615 were separated by 14 mass units, which corresponding to a CH_2 group in the side chain of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$. The additional CH_2 groups in m/z 615 due to the longer alcohol molecule were used as a starting material.

The carbon number of dialkyl residues using $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ can be calculated using the equation (4.2). The calculation results are reported in Table 4.2. The $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ provided information on the carbon number of the two alkyl chains (R_1+R_2). They did not provide the information on the type of R_1 and R_2 . For example, the peak at m/z 545 could be defined as various types of alkyl groups such as two groups of $\text{C}_{14}\text{H}_{30}$, $\text{C}_7\text{H}_{15}+\text{C}_7\text{H}_{15}$, $\text{C}_6\text{H}_{13}+\text{C}_8\text{H}_{17}$, *etc.*

Table 4.2 Calculation of the carbon number of dialkyl residues using zinc dialkyldithiophosphate derivatives (MALDI-MS spectrum as shown in Figure 4.1)

Zinc-containing cation; $[(\text{OR}_1)(\text{OR}_2)\text{PS}_2\text{Zn}(\text{DMSO})_2]^+$	Carbon number of alkyl residues; ($\text{R}_1 + \text{R}_2$) ($\text{R}_1 + \text{R}_2 = \text{C}_n\text{H}_{2n+2}$)
517	12
531	13
545	14
559	15
573	16
587	17
601	18
615	19

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4.3 Zinc dithiophosphates separation from commercial lubricating oil

Zinc dithiophosphates (ZDDPs) additives were separated from eight different commercial lubricating oils by flash column chromatography. Base oil was removed by extraction with hexane. The ZDDPs were successively eluted using isooctane-ethyl acetate-methanol (4 : 1.6 : 0.1, v/v) eluent. All the fractions were analyzed by MALDI-TOF mass spectrometry. No detectable amounts of ZDDPs were found in the hexane and methanol extract.

4.4 Application of MALDI-MS for analysis of zinc dithiophosphates in commercial lubricating oil

Eight commercial lubricating oils were analyzed for their zinc dithiophosphate constituents using the DMSO method.

The MALDI-MS spectra of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from E Superflo, C Havoline Formula, D3 Gold, Local Brand and T lubricating oils are shown in Figure A4 (b), Figure A5 (b), Figure A6 (b), Figure A7 (b) and Figure A8 (b), respectively. The MALDI-MS spectra of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in E Superflo, C Havoline Formula, D3 Gold, Local Brand and T lubricating oils had the similar m/z value of the sample peaks which the peaks between m/z 517 and 615, indicating the same type of ZDDPs. In addition, the peaks in MALDI-MS spectra of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in E Superflo, C Havoline Formula, D3 Gold, Local Brand and T lubricating oils were the same as the peaks in MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in additive package LZ 1395 as shown in Figure 4.1. Consequently, the additive package LZ 1395 was used in E Superflo, C Havoline Formula, D3 Gold, Local Brand and T lubricating oils.

The MALDI-MS spectra of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from P V-120, S Helix Plus and Q Formula Advanced lubricating oils are shown in Figure A9 (b), Figure A10 (b) and Figure A11 (b), respectively. The MALDI-MS spectra of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in P V-120, S Helix Plus and Q Formula Advanced lubricating oils had the similar m/z value of the sample peaks which the peaks between m/z 697 and 795, indicating the same type of ZDDPs. In addition, the peaks in MALDI-MS spectra of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in P V-120, S Helix Plus and Q Formula Advanced lubricating oils were different from those in MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in additive package LZ 1395 as shown in Figure 4.1. Accordingly, the additive package LZ 1395 was not used in P V-120, S Helix Plus and Q Formula Advanced lubricating oils. For instance, the MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from Q Formula Advanced is shown in Figure 4.2.

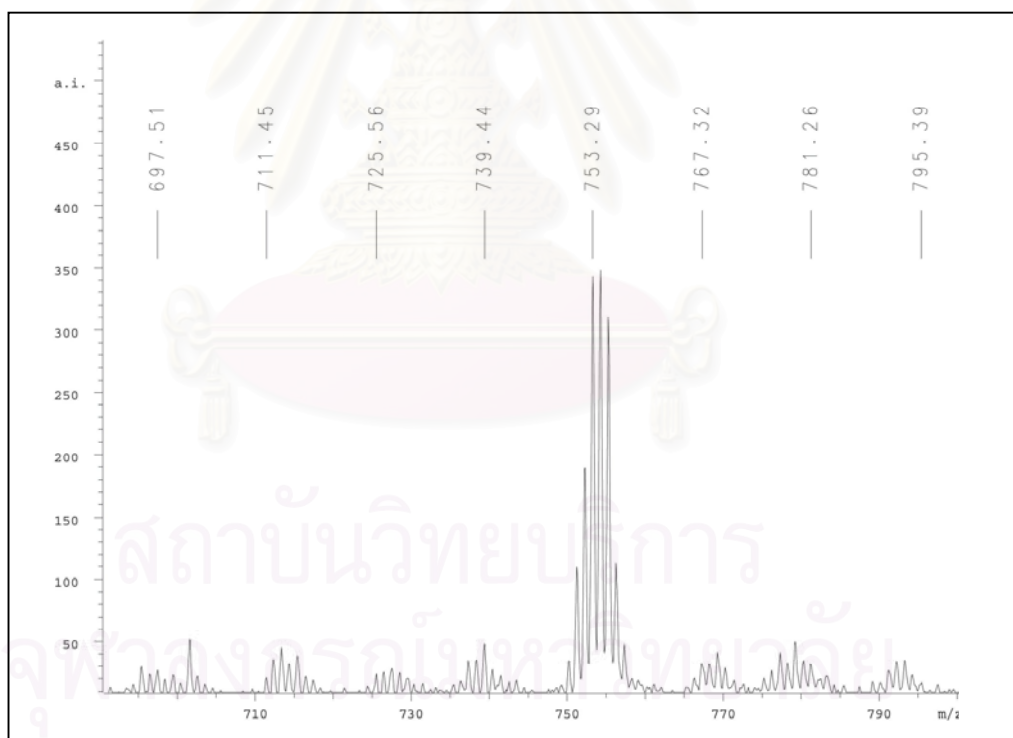


Figure 4.2 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from Q Formula Advanced lubricating oil using dithranol as matrix, laser power 187 μJ , an analyte to matrix ratio of 1 : 75.

The carbon number of dialkyl residues using $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ can be calculated using the equation (4.3). The calculation results are reported in Table 4.3. The $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ provided information on the carbon number of the two alkyl chains (R_1+R_2). They did not provide the information on the type of R_1 and R_2 . For example, the peak at m/z 725 could be defined as various types of alkyl groups such as two groups of $\text{C}_{16}\text{H}_{34}$, $\text{C}_8\text{H}_{17}+\text{C}_8\text{H}_{17}$, $\text{C}_9\text{H}_{19}+\text{C}_7\text{H}_{15}$, *etc.*

Table 4.3 Calculation of the carbon number of dialkyl residues using zinc diaryldithiophosphate derivatives (MALDI-MS spectrum as shown in Figure 4.2)

Zinc-containing cation; $[(\text{OC}_6\text{H}_4\text{R}_1)(\text{OC}_6\text{H}_4\text{R}_2)\text{PS}_2\text{Zn}(\text{DMSO})_2]^+$	Carbon number of alkyl residues; ($\text{R}_1 + \text{R}_2$) ($\text{R}_1 + \text{R}_2 = \text{C}_n\text{H}_{2n+2}$)
697	14
711	15
725	16
739	17
753	18
767	19
781	20
795	21

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CHAPTER V

CONCLUSIONS

In this research, the neutral zinc dithiophosphate $[\text{Zn}(\text{DTP})_2]$ cannot be observed by MALDI-MS, but reaction with DMSO generates ionic product $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ [2] which can be observed by this technique. The optimum conditions for analysis of zinc dithiophosphate were studied.

The results indicated that the optimal condition for this analysis is dithranol (1,8,9-trihydroxyanthracene) as a matrix with 1 : 75 analyte to matrix ratio and laser power value 187 μJ which provided good MALDI-MS spectrum for analysis of zinc dithiophosphate.

MALDI-MS analysis of zinc dialkyldithiophosphate derivatives in additive package LZ 1395 provided information on the carbon number of the two alkyl chains which is an individual fingerprint of zinc dithiophosphates for any given commercial lubricating oils. The presence of zinc diaryldithiophosphates could also be analyzed using the same procedure.

A developed method was used to analyze zinc dithiophosphate in E Superflo, C Havoline Formula, D3 Gold, Local Brand, T, P V-120, S Helix Plus and Q Formula Advanced lubricating oils. The results indicated that zinc dithiophosphate in E Superflo, C Havoline Formula, D3 Gold, Local Brand and T lubricating oils were found to be the same as zinc dialkyldithiophosphate in additive package LZ 1395. This indicated that zinc dialkyldithiophosphate in additive package LZ 1395 was used in E Superflo, C Havoline Formula, D3 Gold, Local Brand and T lubricating oils but different kind of zinc dialkyldithiophosphate was used in P V-120, S Helix Plus and Q Formula Advanced lubricating oils. Furthermore, zinc diaryldithiophosphate was found in P V-120, S Helix Plus and Q Formula Advanced lubricating oils.

It is concluded that MALDI-MS is an excellent method for analysis of zinc dithiophosphates. This method can be used for identification of zinc dialkyl/aryl dithiophosphates in commercial lubricating oils by observation information about the pattern of zinc dithiophosphates.

It is suggested that a developed MALDI-MS method may be used as a tool for commercial lubricating oils analysis. Furthermore, quantitative analysis and sensitivity enhancement of zinc dialkyl/aryl dithiophosphate analysis using MALDI-MS should be investigated if relevant standard is available.



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APPENDICES

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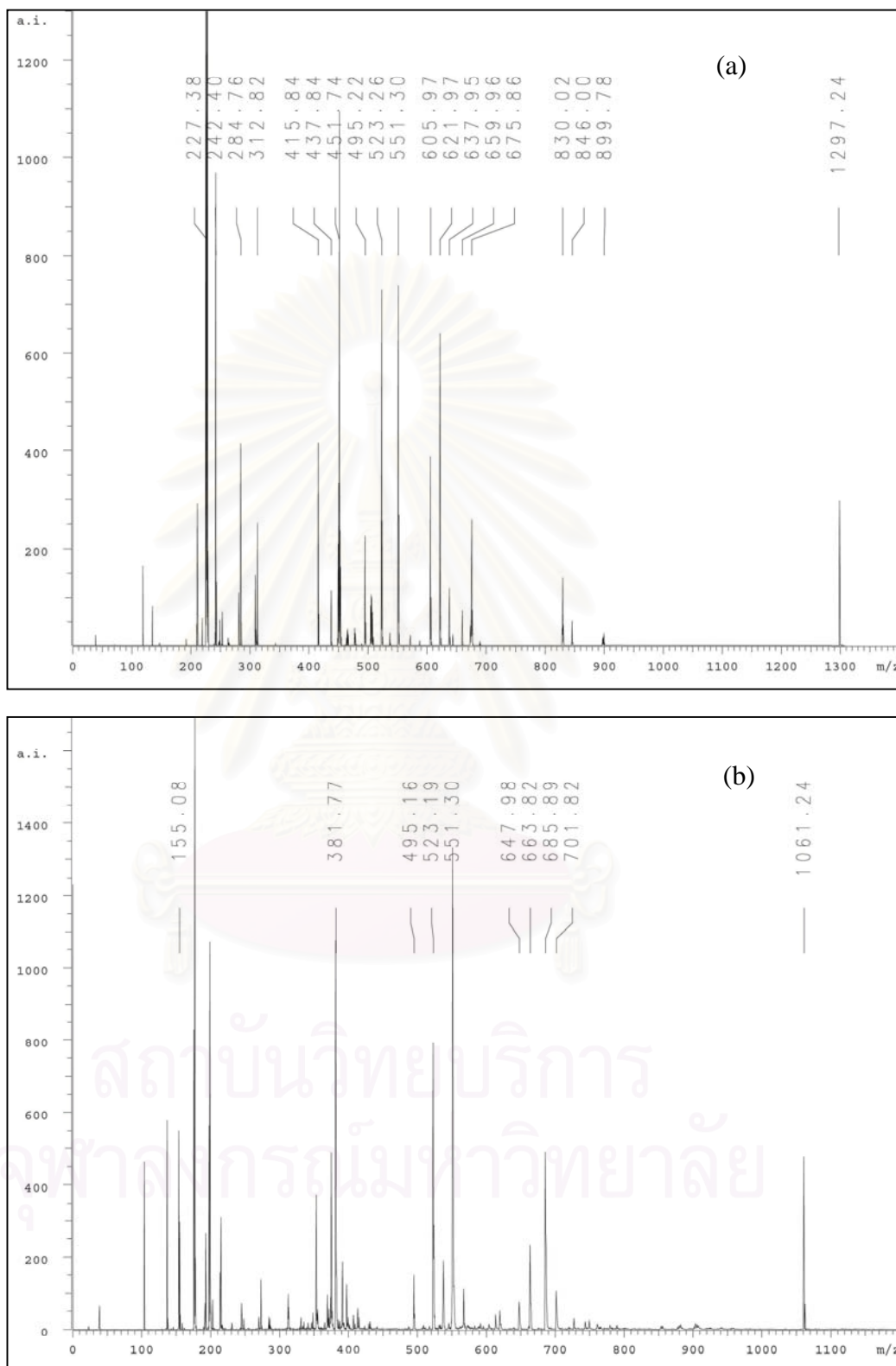


Figure A1 MALDI-MS spectrum of matrix: (a) Dithranol, (b) DHB.

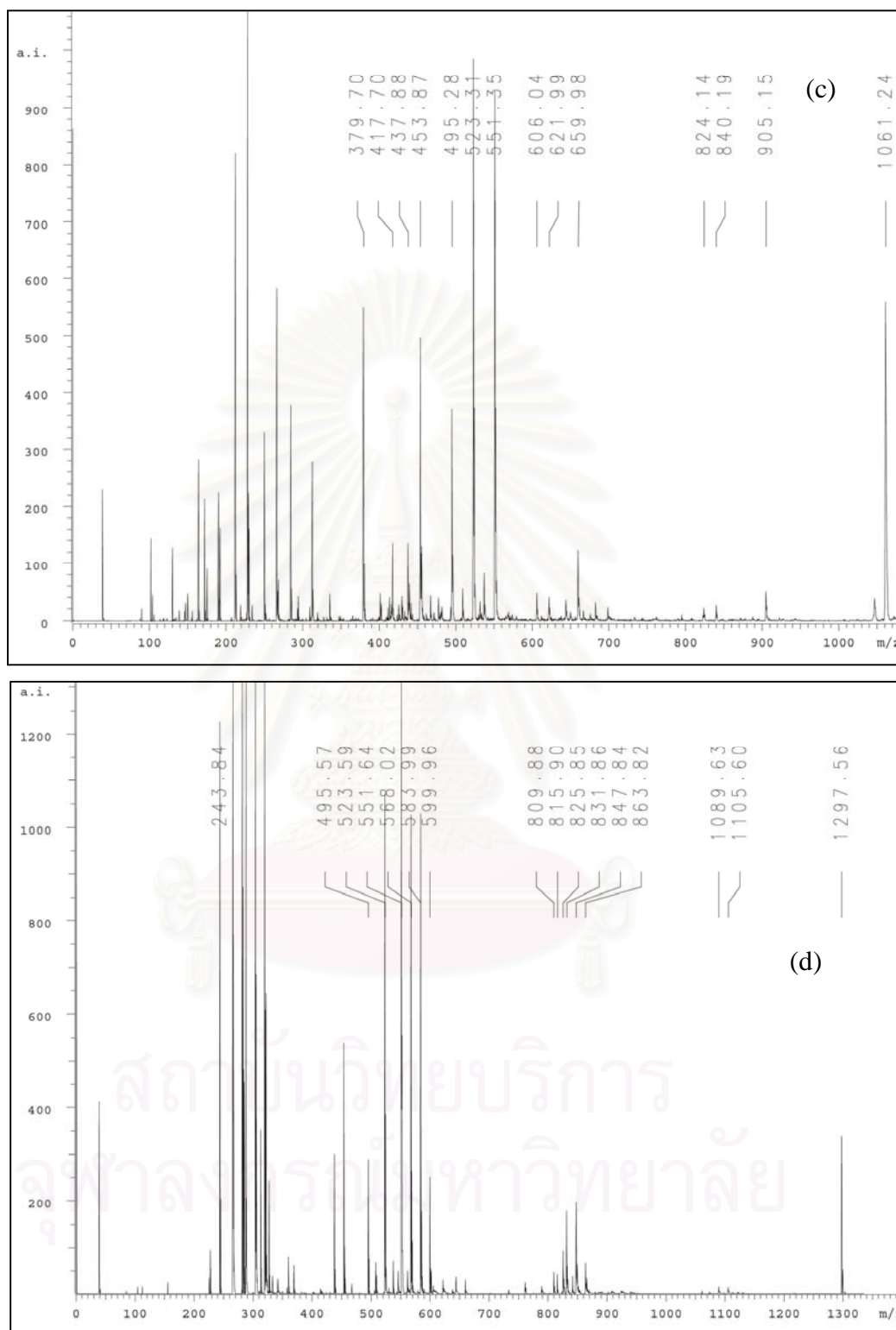


Figure A1 MALDI-MS spectrum of matrix: (c) CAA, (d) HABA.

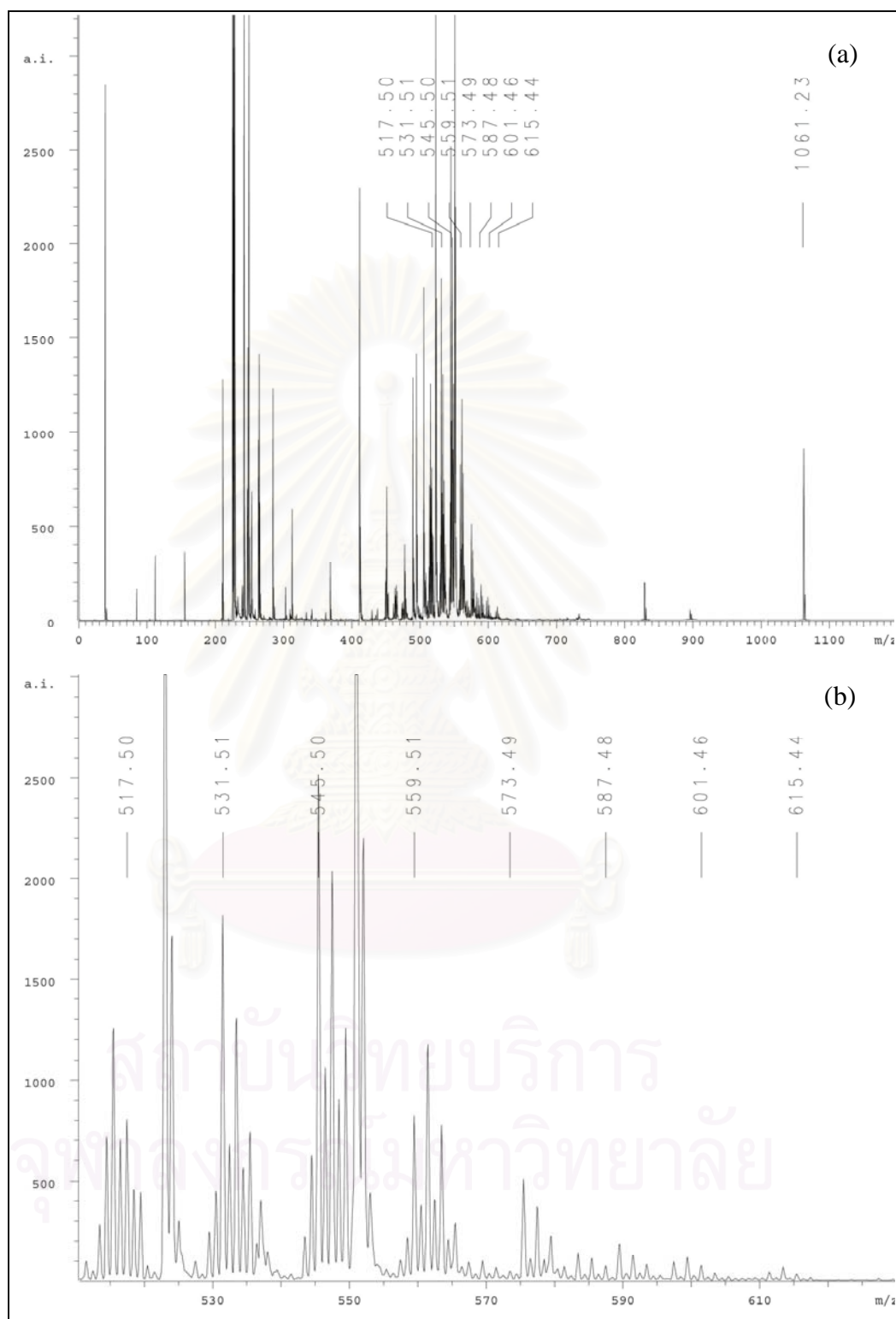


Figure A2 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in additive package LZ 1395 using dithranol as matrix, laser power 187 μJ .

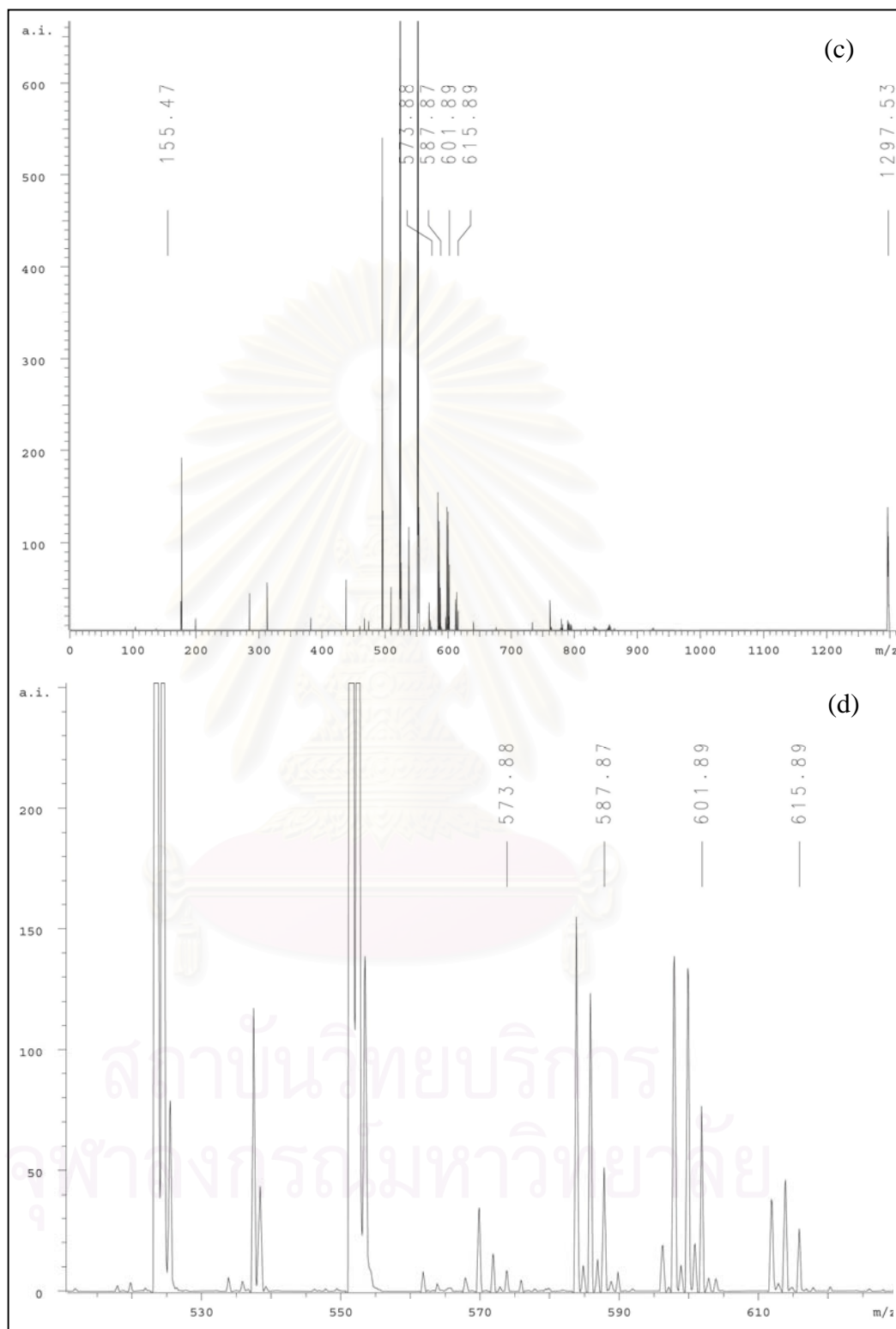


Figure A2 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in additive package LZ 1395 using DHB as matrix, laser power 194 μJ .

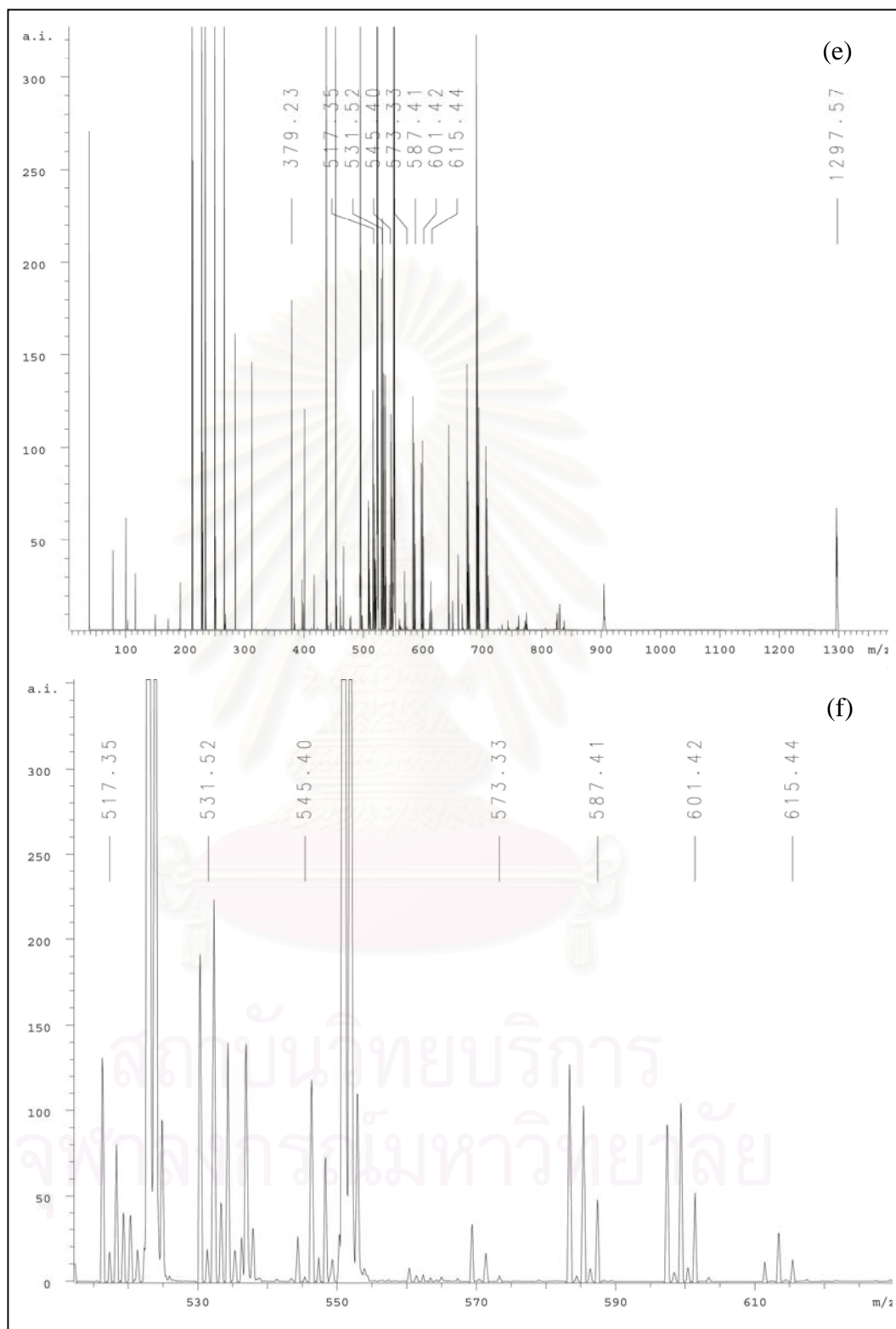


Figure A2 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in additive package LZ 1395 using CCA as matrix, laser power 184 μJ .

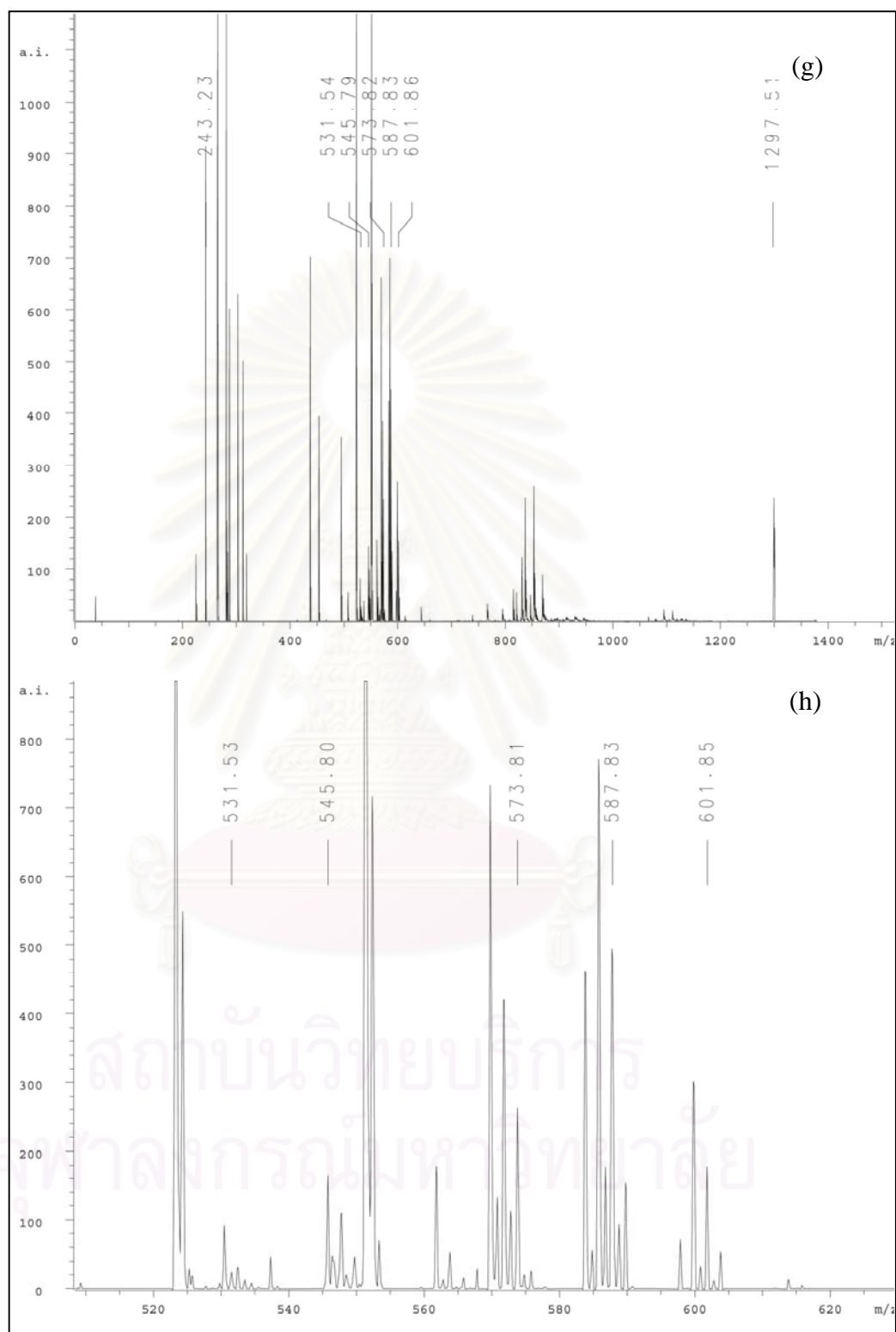


Figure A2 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in additive package LZ 1395 using HABA as matrix, laser power 186 μJ .

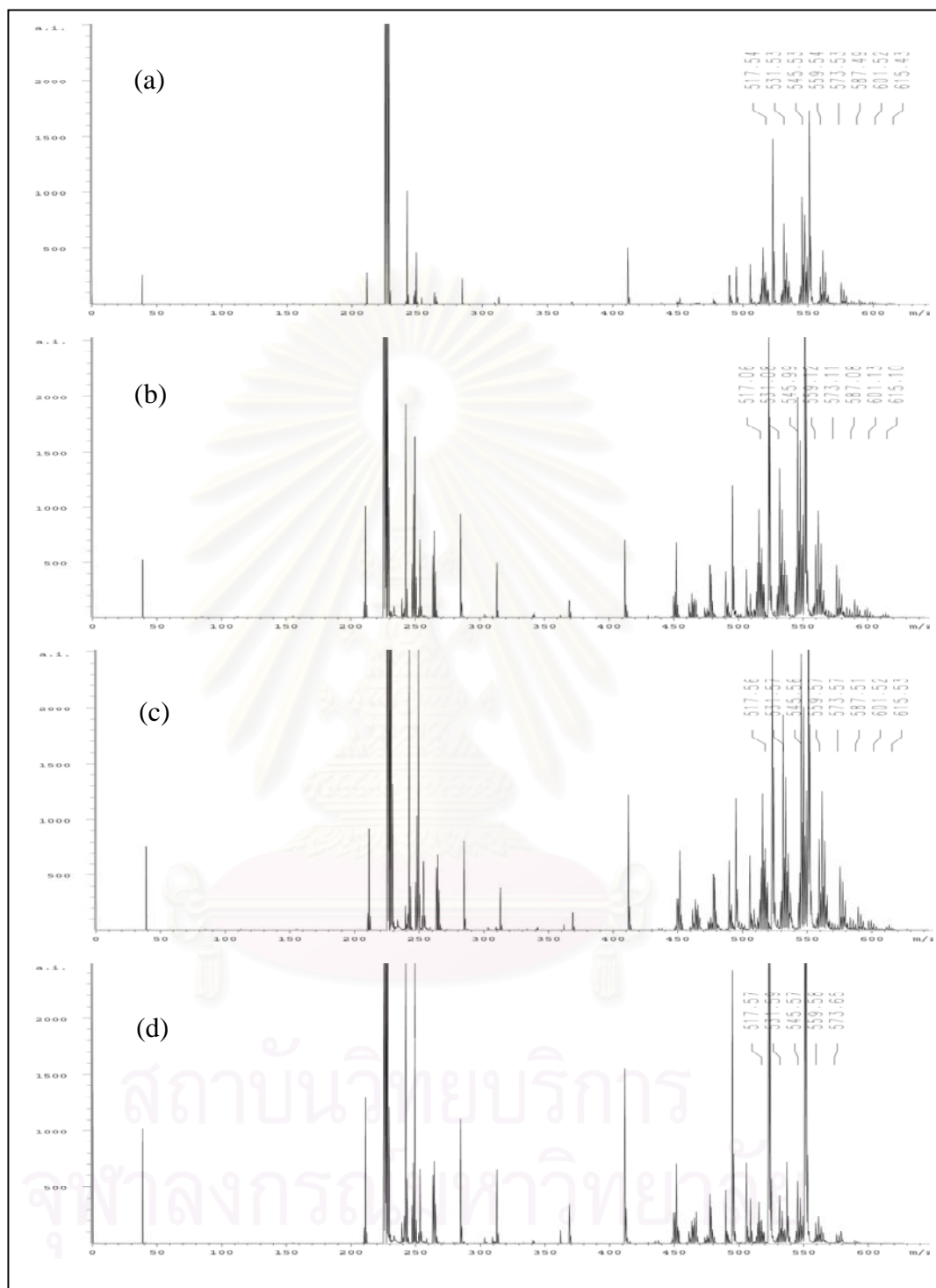


Figure A3 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ in additive package LZ 1395 using dithranol as matrix, laser power 187 μJ , an-analyte to matrix ratios: (a) 1:25, (b) 1:50, (c) 1:75, (d) 1:100.

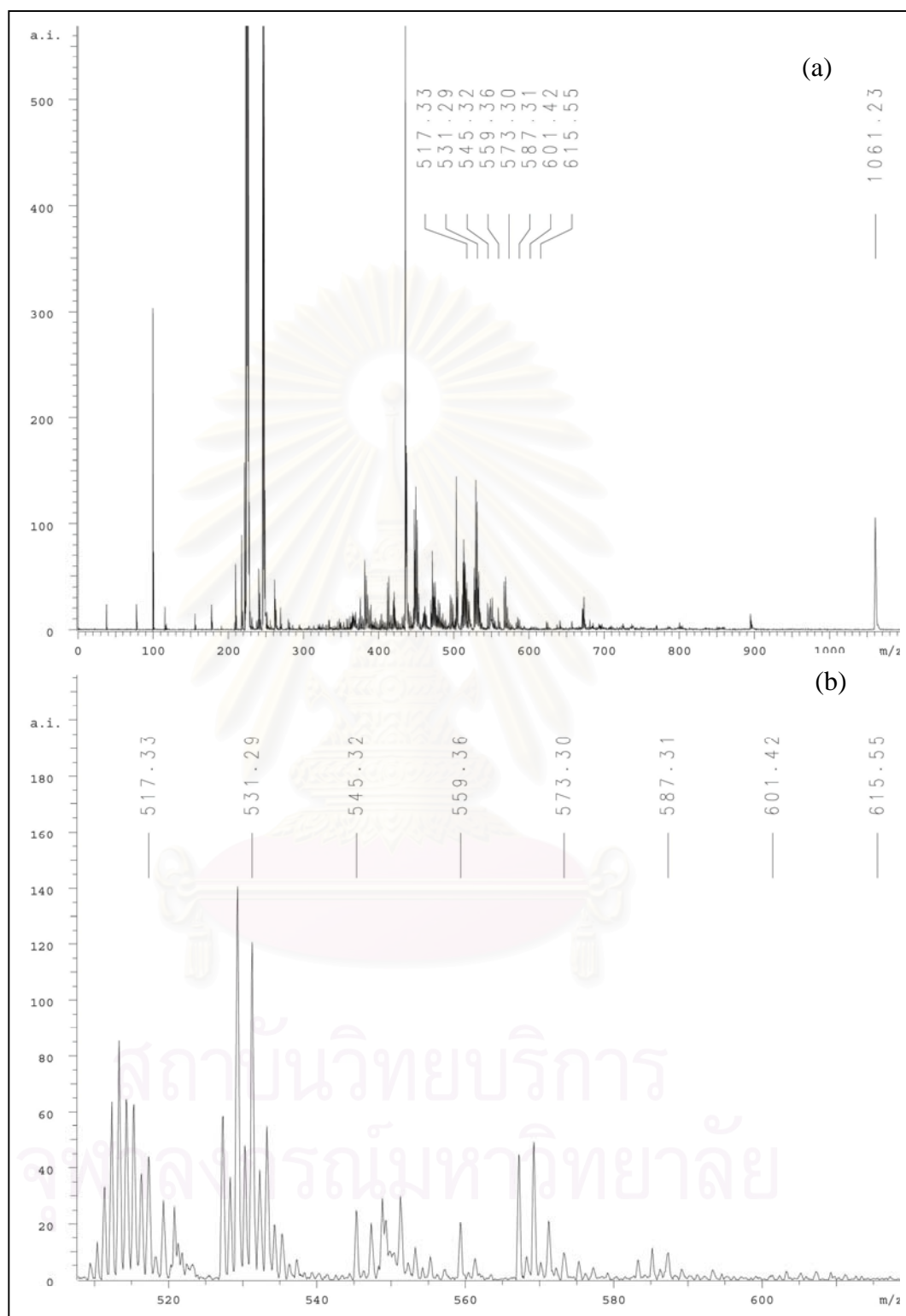


Figure A4 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from E Superflo lubricating oil (MALDI-TOF MS condition as shown in Figure A3 (c)).

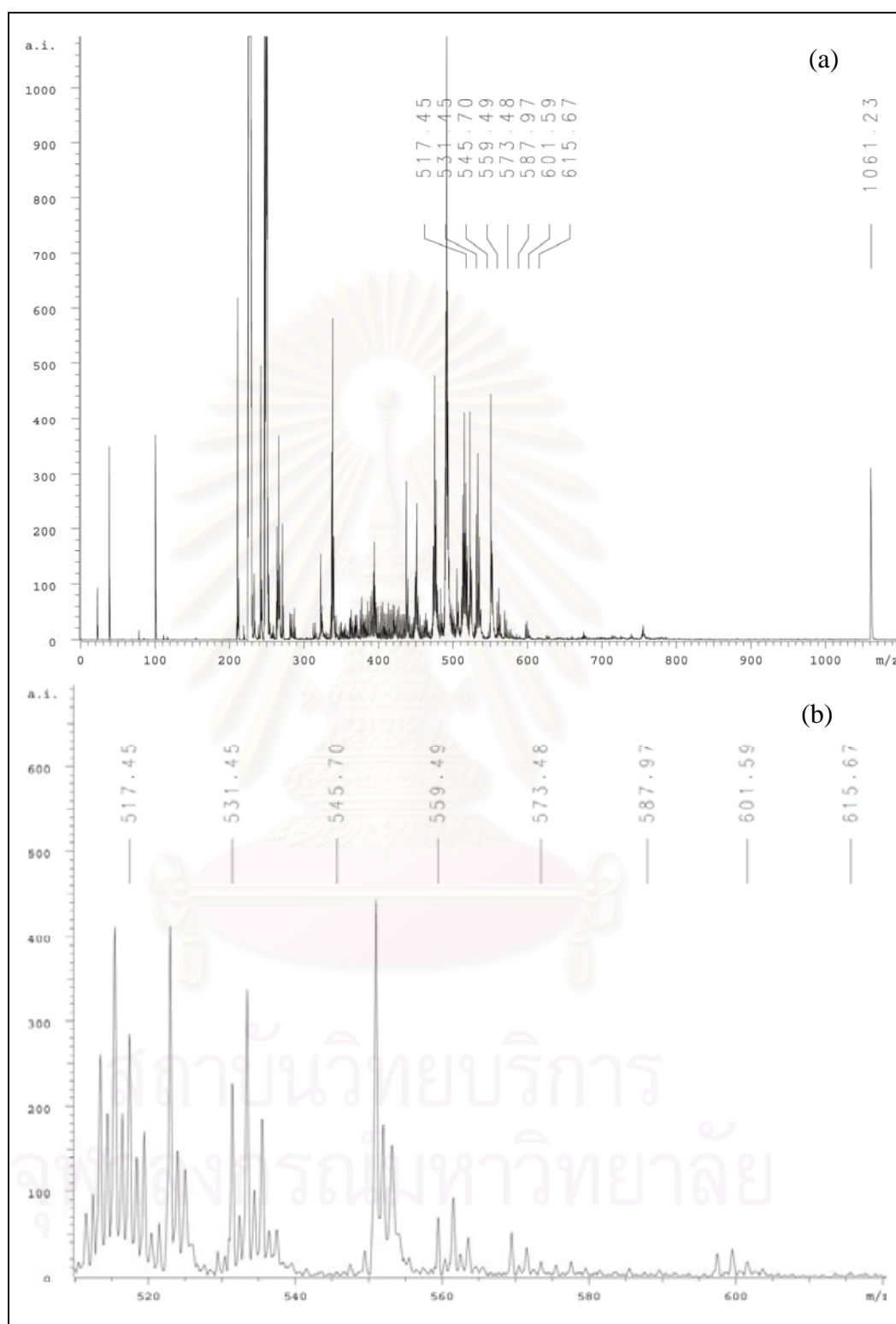


Figure A5 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_6]^+$ separated from C Havoline Formula lubricating oil (MALDI-TOF MS condition as shown in Figure A3 (c)).

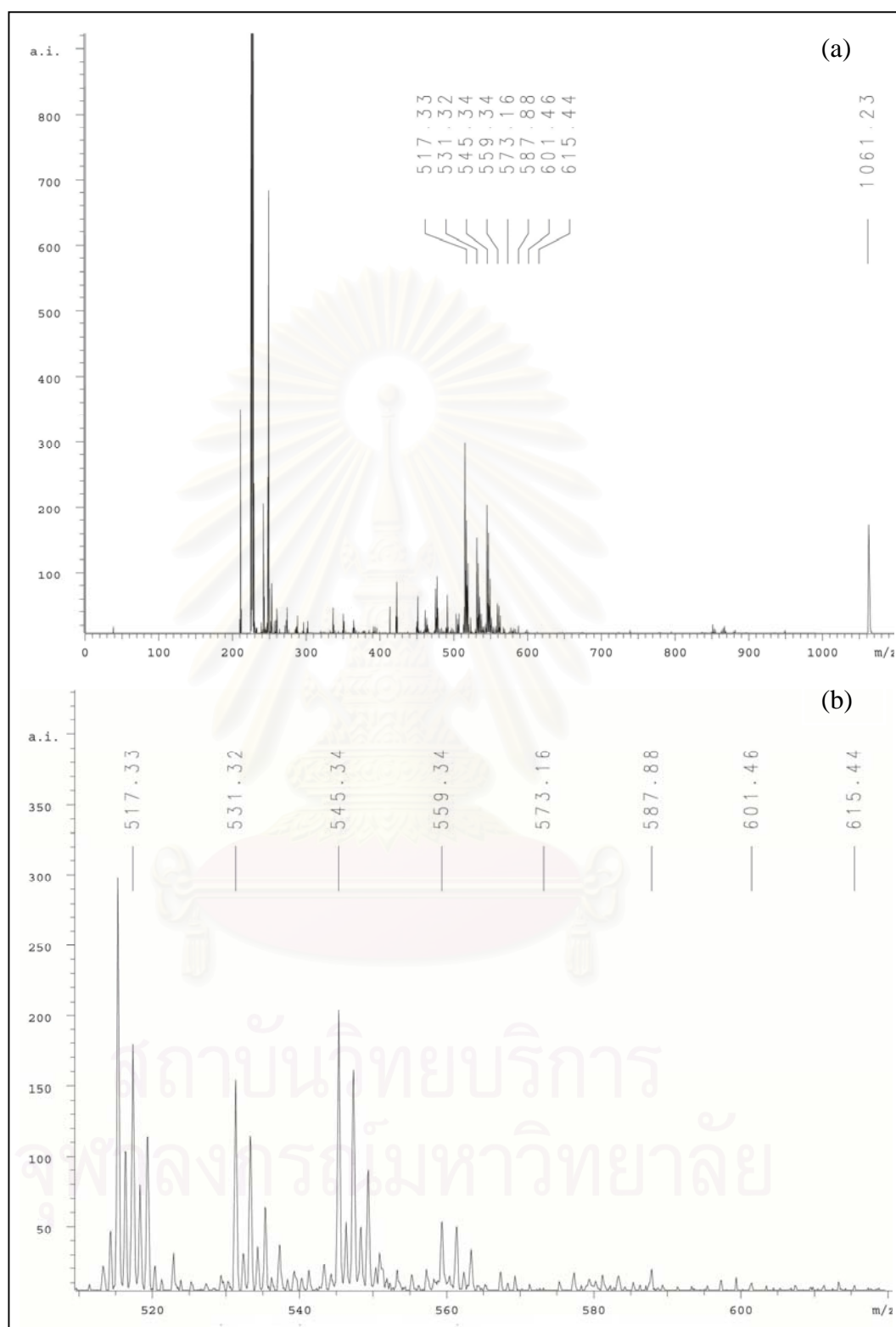


Figure A6 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from D3 Gold lubricating oil (MALDI-TOF MS condition as shown in Figure A3 (c)).

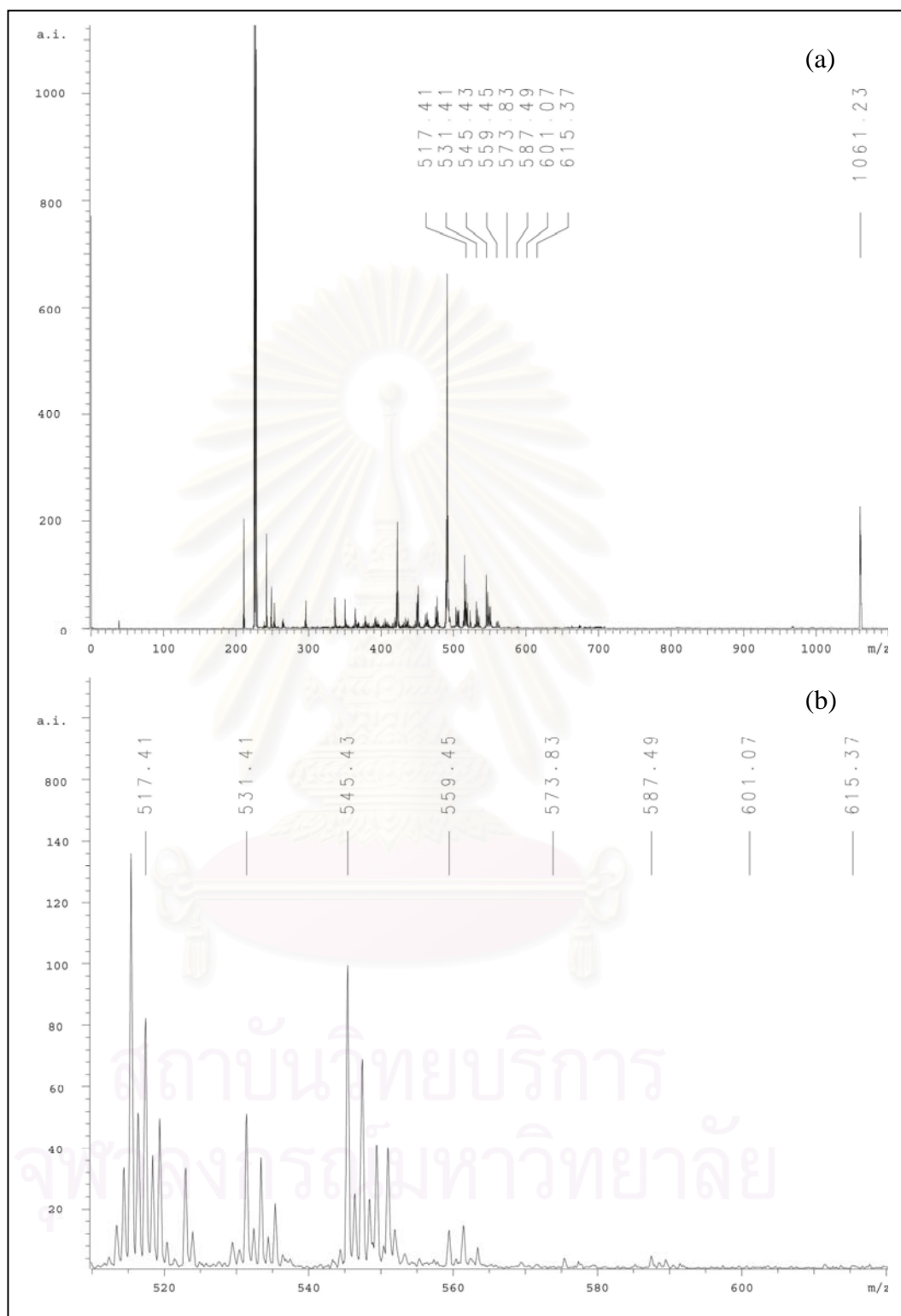


Figure A7 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from Local Brand lubricating oil (MALDI-TOF MS condition as shown Figure A3 (c)).

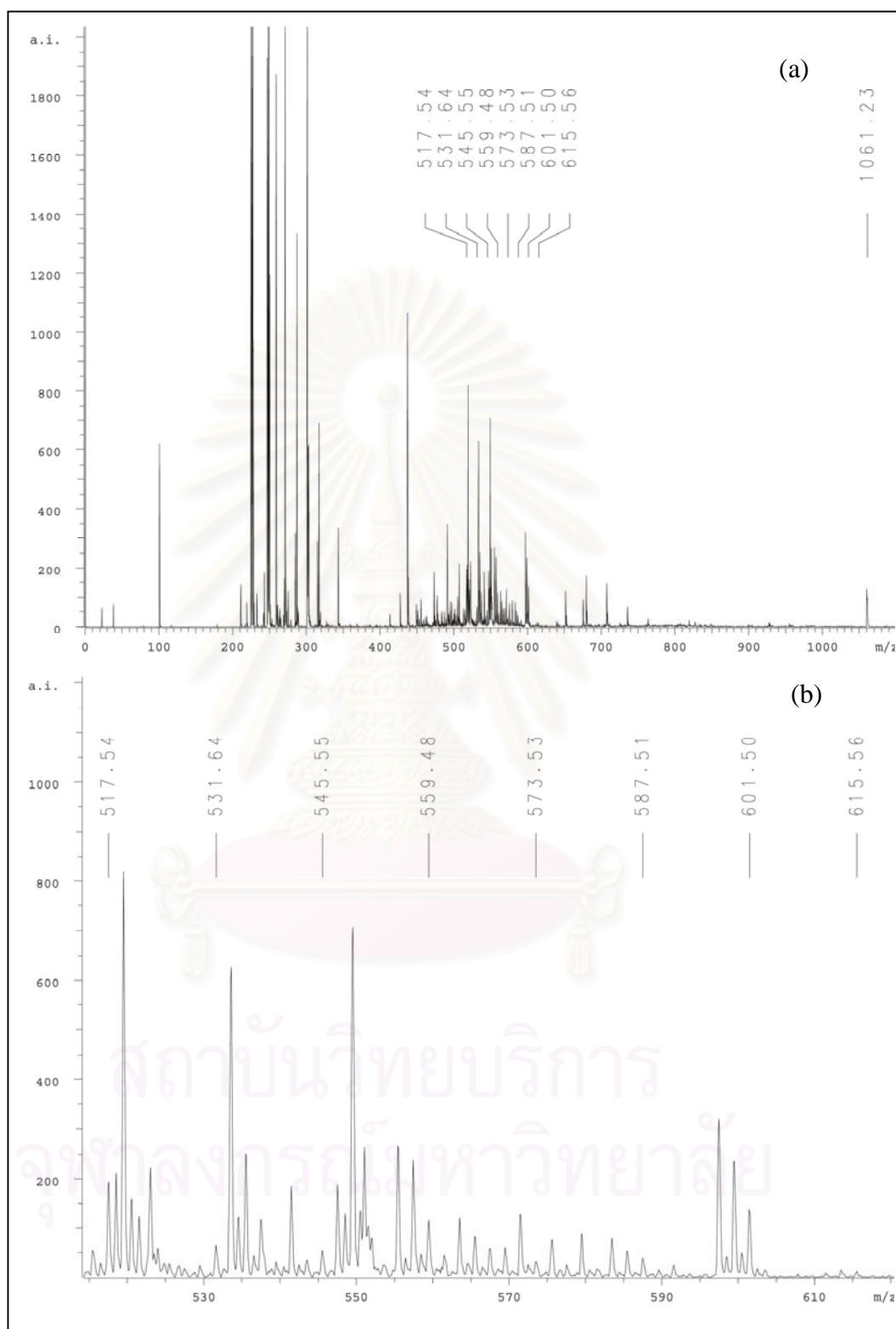


Figure A8 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from T lubricating oil for Gasoline Engine (MALDI-TOF MS condition as shown in Figure A3 (c)).

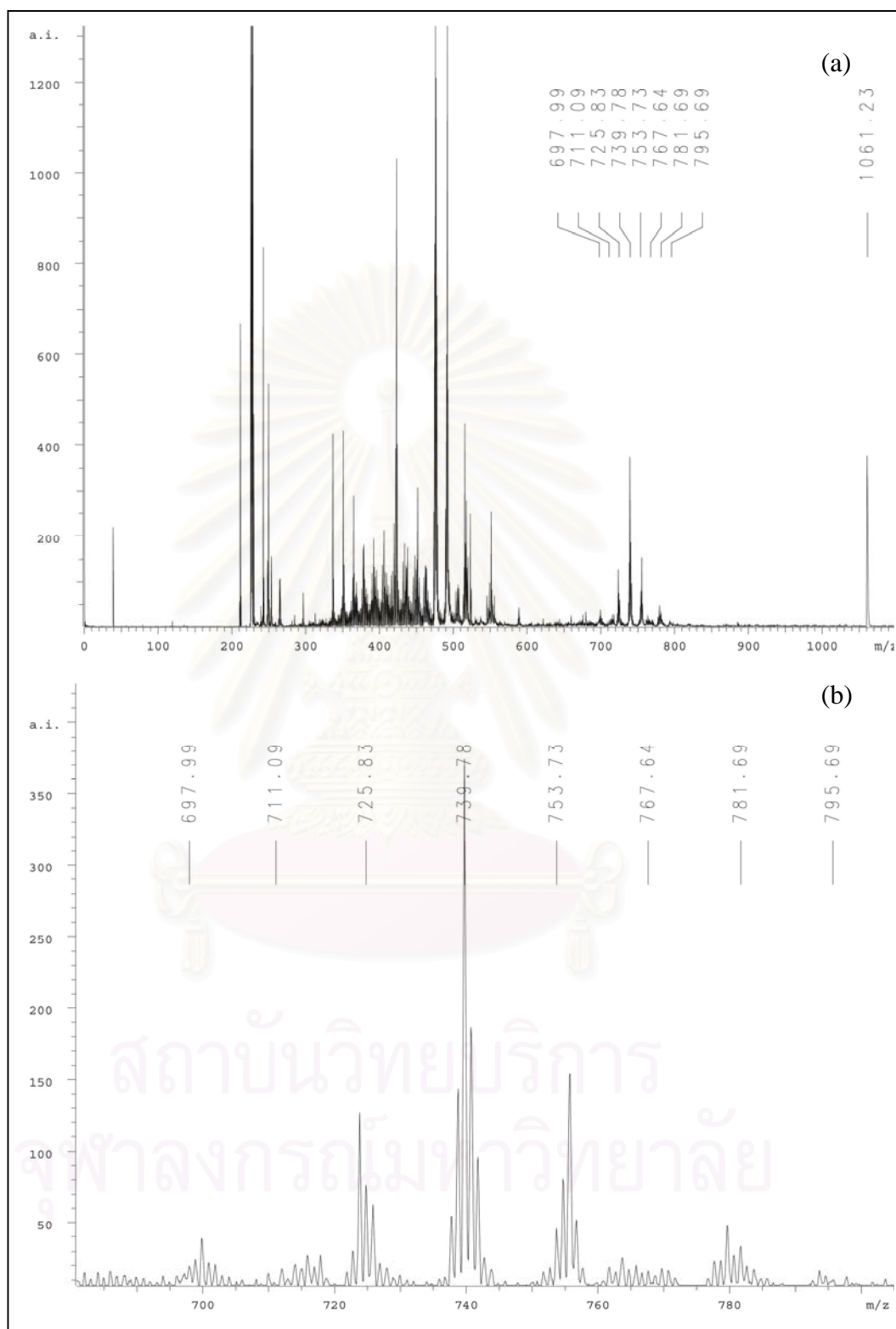


Figure A9 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from P V-120 lubricating oil (MALDI-TOF MS condition as shown in Figure A3 (c)).

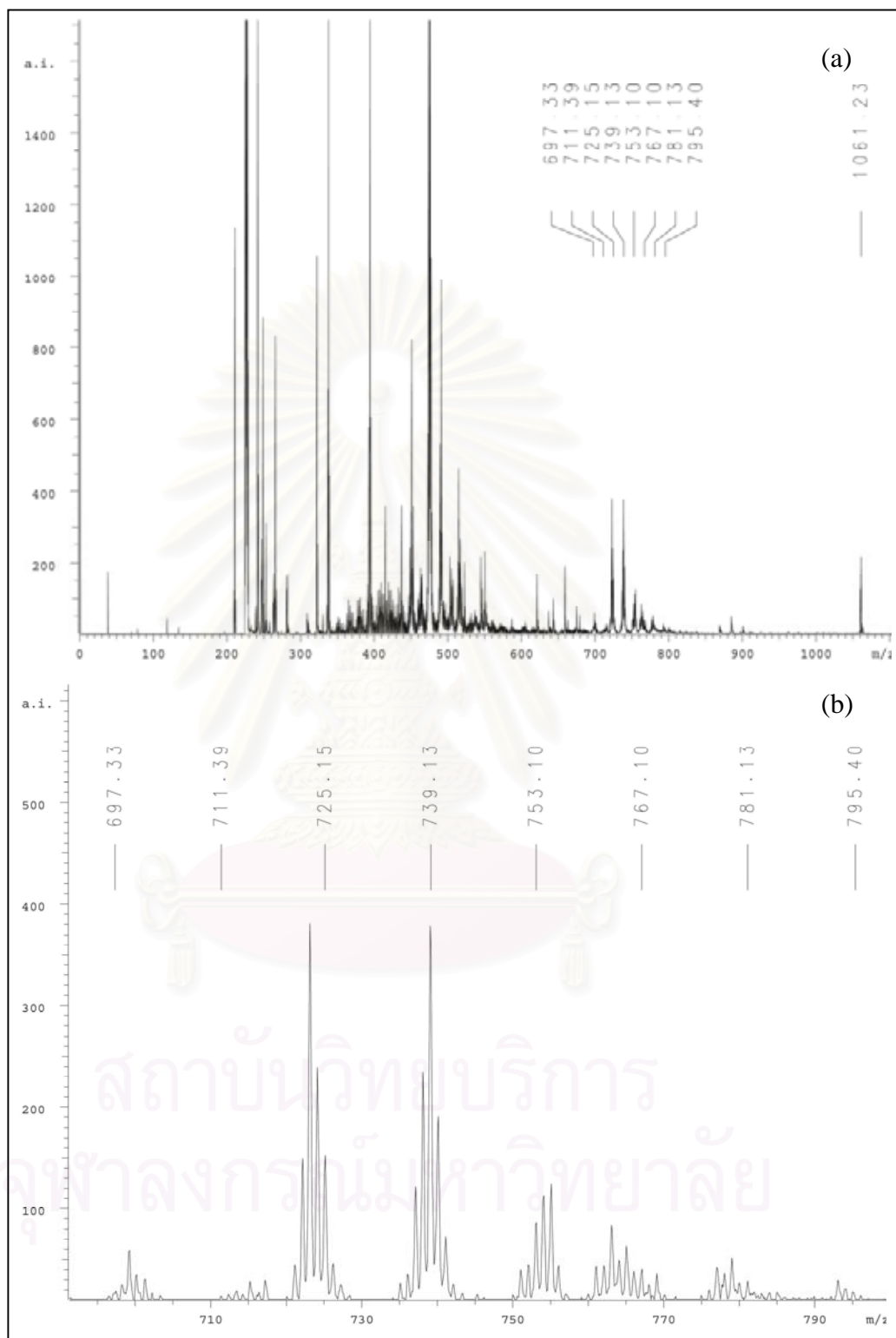


Figure A10 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from S Helix Plus lubricating oil (MALDI-TOF MS condition as shown in Figure A3 (c)).

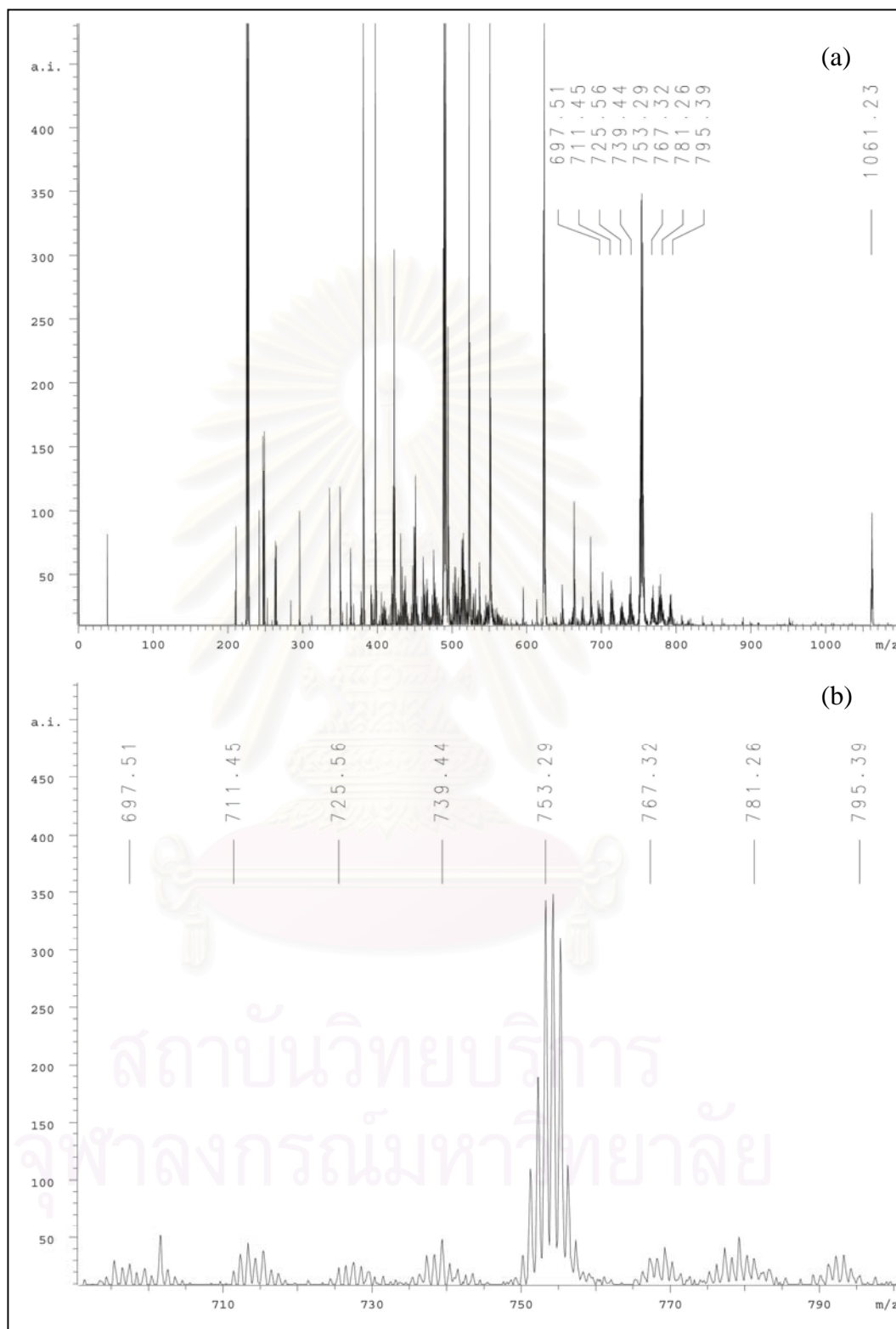


Figure A11 MALDI-MS spectrum of $[\text{Zn}(\text{DTP})(\text{DMSO})_2]^+$ separated from Q Formula Advanced lubricating oil (MALDI-TOF MS condition as shown in Figure A3 (c)).

CURRICULUM VITAE

Name : Miss Jannate Tungcharoen
Date of Birth : 26 Nov 1979
Address : 29/5 Bankaeng Road, Bankaeng, Nakhonsawan,
Thailand 6000
Education :
High School : Nakhonsawan School
Nakhonsawan Province
Undergraduate : Bachelor of Science Program (Chemistry) in 2002
Naresuan University, Phitsanulok Province
Trainee : King Mongkut's University of Technology Thonburi in 2001
Graduate : Master's Degree of Science in Petrochemistry
and Polymer Science Program, Faculty of Science
Chulalongkorn University in 2005



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จุฬาลงกรณ์มหาวิทยาลัย