การหาการกระจายน้ำหนักโมเลกุลของสารช่วยกระจายตัวชนิดพอลิไอโซบิวทีนิลซัคซินิไมด์ โดยแมสสเปกโทรเมทรี

นางสาวสายน้ำผึ้ง ศิลป์เจริญ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2545

ISBN 974-17-3160-4

DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTION OF POLYISOBUTENYLSUCCINIMIDE-TYPE DISPERSANT BY MASS SPECTROMETRY

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Program of Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2002

ISBN 974-17-3160-4

Thesis Title DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTION OF POLYISOBUTENYLSUCCINIMIDE-TYPE DISPERSANT BY MASS SPECTROMETRY
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สายน้ำผึ้ง ศิลป์เจริญ : การหาการกระจายน้ำหนักโมเลกุลของสารช่วยกระจายตัวชนิดพอลิไอโซบิวทีนิลซัคซินิไมด์โดยแมสสเปกโทรเมทรี (DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTON OF POLYISOBUTENYLSUCCINIMIDE-TYPE BY MASS SPECTROMETRY) อ. ที่ปรึกษา : ผศ.ดร.พลกฤษณ์ แสงวณิช, อ.ที่ปรึกษาร่วม : อ.ดร.ธรรมนูญ หนูจักร จำนวนหน้า 87 หน้า. ISBN 974-17-3160-4

งานวิจัยนี้เกี่ยวข้องกับการพัฒนาเทคนิคสำหรับการหาการกระจายน้ำหนักโมเลกุลของสารช่วยกระจายตัวชนิดพอลิไอโซบิวทีนิลซัคซินิไมด์ โดยใช้เทคนิคแมสสเปกโทรเมทรีแบบเมทริกซ์แอสซิสเทดเลเซอร์ดีซอร์พชันไอออไนเซชัน (MALDI-MS) การวิเคราะห์ทำได้โดยผสมสารช่วยกระจายตัวกับเมทริกซ์ชนิดต่าง ๆ เช่น ไดทรานอล อัลฟาไฮดรอกซิไซยาโนซินนามิกแอซิด 2,5-ไดไฮดรอกซีเบนโซอิกแอซิด ออลทรานสเรตินโนอิกแอซิด อินโดลอะคริลิกแอซิด และ 2-(4-ไฮดรอกซีเฟนิลอะโซ)เบนโซอิกแอซิด หลังจากที่ของผสมถูกทำให้แห้งกลายเป็นสารละลายของแข็งแล้ว ทำการยิงของผสมที่แห้งด้วยแสงเลเซอร์เพื่อให้สารตัวอย่างกลายเป็นไอออน พบว่าภาวะของ MALDI-MS ต่อไปนี้ให้แมสสเปกตรัมที่ดีที่แสดงถึงการกระจายน้ำหนักโมเลกุลของสารช่วยกระจายตัว: การเตรียมตัวอย่างด้วยวิธี dried droplet ใช้ CCA เป็นเมทริกซ์โดยมีเตตระไฮโดรฟูแรนเป็นตัวทำละลาย อัตราส่วนของสารละลายสารช่วยกระจายตัวต่อสารละลายเมทริกซ์เท่ากับ 1:5 โดยปริมาตรและใช้พลังงานเลเซอร์ที่ 170 ถึง 180 ไมโครจูล จากนั้นได้ใช้วิธีที่พัฒนาขึ้นนี้ในการหาการกระจายน้ำหนักโมเลกุลของสารช่วยกระจายตัวชนิดพอลิไอโซบิวทีนิลซัคซินิไมด์ในตัวอย่างน้ำมันดีเซลที่จำหน่ายในท้องตลาด

หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือนิสิต...
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมืออาจารย์ที่ปรึกษา...........................
ปีการศึกษา 2545 ลายมืออาจารย์ที่ปรึกษาร่วม.........................

4372443623 MAJOR : PETROCHEMISTRY
KEYWORD : MALDI / DISPERSANT / MOLECULAR WEIGHT DISTRIBUTION / MASS SPECTROMETRY / POLYMER

SAINAMPUENG SINJAROEN: DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTION OF POLYISOBUTENYLSUCCINIMIDE-TYPE DISPERSANT BY MASS SPECTROMETRY THESIS ADVISOR : ASSISTANT PROFESSOR POLKIT SANGWANIT,Ph.D., THESIS CO-ADVISOR : THUMNOON NHUJAK, Ph.D., 87 pp. ISBN 974-17-3160-4

This research involves the development of a method for determination of molecular weight distribution of polyisobutenylsuccinimide dispersant, using matrix assisted laser desorption ionization-mass spectrometry (MALDI-MS). The MALDI-MS analysis was carried out by mixing the dispersant with various types of matrix such as dithranol, α-hydroxycyanocinnamic acid (CCA), 2,5-dihydroxy benzoic acid, *all-trans* retinoic acid, indole acrylic acid, and 2-(4-hydroxyphenylazo)-benzoic acid. After the dispersant-matrix mixture was dried to form a solid solution, the dried mixture was bombarded with laser light to obtain ionic analyte. The following MALDI-MS conditions were found to provide the good MS spectrum of molecular weight distribution of the polymer dispersant: sample preparation using a dried droplet method, CCA as a matrix with tetrahydrofuran as a solvent, the dispersant solution: matrix solution of 1:5 by volume, and the laser power of 170 to 180 μJ. The developed MALDI-MS was used to be an excellent method for determination of the molecular weight distribution of polyisobutenylsuccinimide dispersant in the commercial diesel oils.

Program: Petrochemistry and Polymer Science	Student's signature……………….
Field of study: Petrochemistry and Polymer Science	Advisor's signature……………….
Academic year: 2545	Co-advisor's signature…………...

ACKNOWLEDGEMENT

She wish to express her deepest gratitude to her advisor, Assistant Professor Dr. Polkit Sangvanit and co- advisor, Dr. Thumnoon Nhujak, for their guidance, advice and kindness throughout the course of this research and to Associate Professor Dr. Amorn Petsom for his valuable suggestions, helping and advice. In addition, She is also grateful to Associate Professor Dr. Supawan Tantayanon and Associate Professor Dr. Wimonrat Trakarnpruk for their discussions and comments.

She also thanks the Institute of Biotechnology and Genetic engineering, Chulalongkorn University for support MALDI-TOF MS and many thanks are going to Khun Rungroj Ampha from BRS Intertrade Ltd., Part who provided the additives package for using in this research work.

She would like to express her gratitude to her friends and Khun Piboon Pornmanee who have contributed suggestion and support during this research.

Finally, she owed very deep thanks to her family for their love, support and encouragement.

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LIST OF SCHEMES

LIST OF ABBREVIATION

UV = Ultraviolet
IR = Infrared
HPLC = High Performance Liquid Chromatography
MALDI = Matrix-Assisted Laser Desorption Ionization
TOF = Time of Flight
MS = Mass spectrometry
mmHg = millimeter of Hg
Da = Dalton
cm = centimeter
kV = kilovolt
m/z = mass to charge ratio
nm = nanometer
FTIR = Fourier Transform Infrared spectroscopy
SEC = Size Exclusion Chromatography
NMR = Nuclear Magnetic Resonance spectroscopy
PS = Polystyrene
PMMA = Polymethyl methacrylate
PPG = Polypropylene glycol
PEG = Polyethylene glycol
LS = Light Scattering
VPO = Vapor Pressure Osmometry
ml = milliliter
µl = microliter
µJ = microjoule
(V/V) = volume by volume
PIB = Polyisobutene
PIBSN = Polyisobutenylsuccinimide
PIBSE = Polyisobutenylsuccinate ester

CHAPTER I

INTRODUCTION

The purpose of investigation

The use of diesel oil as passenger car engine oil has had dramatic volume growth and improved technology, leading to progressively better performance properties. Fuel oil contains two major components which are base oil and additives. Dispersant is one of the important additives in fuel oil. It plays a major role in the fuel oil to provide fuel injector, carburetor and valve cleanliness. Engine life is prolonged and under desirable engine exhaust emissions are reduced.

Dispersant has a long chain hydrocarbon with polar ends containing oxygen and/or nitrogen. In engine oils, the harmful products of combustion and other contaminate are rendered harmless by the polar ends and the long chain hydrocarbon of this additive helps to solubilize or suspend the debris in the oil.

Previous techniques for determination of dispersant in fuel oil include HPLC and GPC[1], UV-visible and IR spectroscopy[2]. However, UV-visible and IR spectroscopy suffer from interference from base oil. In this work, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was used for determination of molecular distribution of polyisobutenylsuccinimide. MALDI-TOF MS was shown to be very useful tool for polymer characterization[3]. It can be used to determine average molecular weights and molecular weight distributions of polymers, and to provide structural information on end-group, repeating unit and chemical modification of a polymeric system. However, the success of this technique for polymer analysis depends on the availability of a suitable sample/matrix preparation. The advantage of this technique for such analysis includes low sample consumption; ease of sample preparation, short analysis time and soft ionization which leads to negligible or no fragmentation of analytes.

Objective

The objective of this work is to develop mass spectrometry as a method for determination of polyisobutenylsuccinimide dispersant.

Scope of work

In initial work, polyisobutenylsuccinimide dispersant will be separated from dispersant package. The MALDI-TOF MS conditions were studied for determination of molecular weight distribution of polyisobutenylsuccinimide dispersant. After that, a developed method will be used to determine polyisobutenylsuccinimide dispersant in commercial fuel oil.

CHAPTER II

THEORITICAL AND LITERATURE REVIEWS

Fuel oil is a complex mixture of base oil and numerous additives: detergents, anti-oxidants, corrosion inhibitors, viscosity improver, and dispersants which are polymer of polyolefinic or methacrylate type. Among these additives, dispersant of the polyisobutenylsuccinimide type is particularly important as it prevents agglomeration of particles produced by the oil degradation and metallic parts wear and maintains them in suspension in the oil.[2]

2-1 Dispersant [4]

Prior to 1955, the additives used for the purpose of keeping and engine clean were sulfonates, phenates, salicylates and phosphonates. These materials did a good job so long as the service did not involve an excessive amount of low-temperature, short distance, or stop-and-go type driving.

In the 1950s a new type of additive, a non-metallic or ashless dispersant, was introduced to help keep engines clean. This product, known as a succinimide dispersant, was a relatively high molecular weight polyisobutenyl group attached to a polar end group.

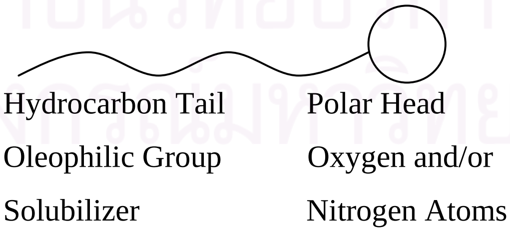


Figure 2-1 Stylized dispersant.

Dispersant is non-metallic or ashless cleaning agents. Figure 2-1 shows the stylized structure of an ashless dispersant, which is similar to the structure of a detergent in that the dispersant has a hydrocarbon tail or oleophilic group which enables the dispersant to be fully soluble in the based oil used. The dispersant also has a polar head. The polarity of dispersant is derived from the inclusion of oxygen, phosphorus, or nitrogen atoms into the molecule.

The sludge and varnish-forming precursors, resulting as a by-product of engine fuel combustion, contaminate the engine oil as they blow by the piston rings into the engine crankcase. Prior to the introduction of dispersants, these contaminants would settle out on critical parts of the engine hampering operation and eventually requiring engine overhaul. The presence of water in gasoline engine low-temperature stop-and-go operation accelerates the contaminant drop-out process. Dispersants are a vital component in gasoline engine oils and are also used to advantage in diesel engine oils to suspend harmful soot contaminants in order to provide longer engine life between overhauls. Diesel engine oil temperatures are generally sufficiently high enough to vaporize water from the oil.

Ashless dispersants are designed to have their polar chemical heads attached to rather large hydrocarbon groups. As shown in Figure 2-2, these polar heads interact with sludge. The hydrocarbon groups provide the solubilizing action with maintains the potentially harmful debris in suspension in the oil. By use of an engine oil well fortified with a dispersant additive, as well as by practicing engine manufacturers’ oil drains recommendations; virtually all of the harmful deposit-forming debris is removed from the engine when the oil is periodically drained.

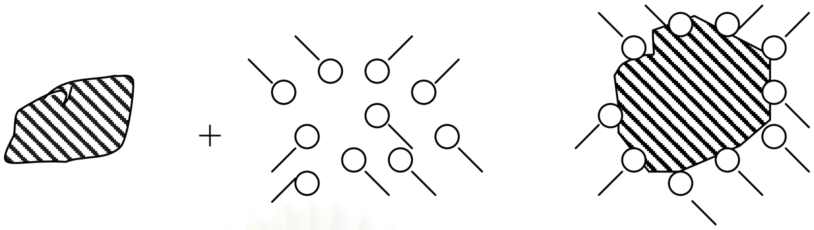
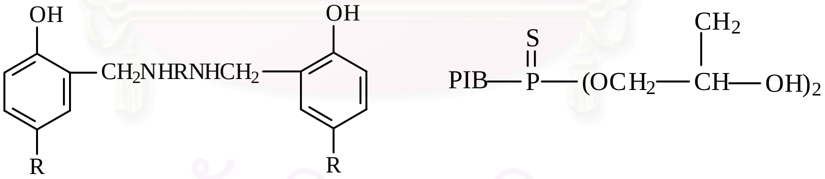


Figure 2-2 Sludge dispersion.

There are four different types of ashless dispersants: (1) succinimides, (2) succinate esters, (3) Manich types and (4) phosphorus types. Their structures are shown in Figure 2-3

Succinimide type

Succinate Ester type



Manich type

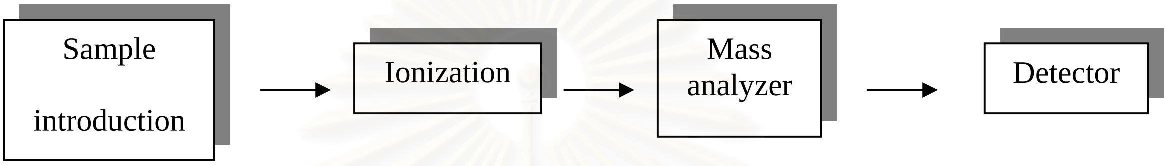
Phosphorus type

Figure 2-3 Four types of dispersants**.**

2-2 Mass Spectrometry (MS) [5]

MS is a highly useful technique for molecular structure elucidation. It has been applied throughout the biological and earth science. MS is a tool for accomplishing measurement in many areas of science.

Mass spectrometry is distinguished by its extremely high sensitivity and by its applicability to samples in all physical states (including aqueous solutions and solid materials) and to samples of high as well as low molecular weight. The methods available for sample ionization are paralleled by an equally wide variety of methods of mass analysis, as shown in Scheme 2-1.



- Direct insertion probe	- Electron ionization	- Tof	- Photomultiplier
- Chromatograph (online)	- Chemical ionization	-Quadrupole mass filter	- Electron multiplier
- Batch inlet	- Desorption ionization	- Quadrupole ion trap	
- Membrane introduction	- Spray ionization	- Ion cyclotron resonance	

Scheme 2-1 Sequence of operations in a mass spectrometer.

Mass spectrometry is usually performed to determine the molecular weight of compounds. To accomplish this end, one of the several ionization methods for producing intact molecular ions must be used. These methods generate either positive or negative ions related to original molecule by adding or subtracting an electron or by adding or subtracting an anion or cation.

1) Sample Introduction

When samples are introduced into the mass spectrometer in a suitable form (such as aqueous), the analytes are ionized to create gas phase ions that are analyzed for their mass-to-charge ratios and then detected. Although mass spectrometers are capable of subnanogram sensitivity, solid samples are normally required to be in microgram range.

Similarly, solutions can sometimes be analyzed at the parts per trillion levels, but concentrations in the parts per million levels are more common. Mass spectrometers are operated under a vacuum, often 10^{-6} torr (mmHg) or less, which is maintained by a combination of mechanical forepump with diffusion pumps, turbomolecular pumps or ion pumps. Many instruments can be vented to atmosphere and a working vacuum can be reachieved in a matter of minutes. Samples can be introduced into the ion source by the following methods.

(1) Batch gas and vapor inlets
(2) Direct insertion probe
(3) Membrane interfaces
(4) Gas or liquid chromatographs

2) Ionization

Various procedures are used to form gas phase ions from molecules, depending on the physical state of the analytes. Choices are available as to the types of ions produced (positively and negatively charged, radical cations and protonated molecules, etc.) and the degree, which these ions are internally excited. Internally excited molecular ions dissociate to produce fragment ions, which may reveal details molecular structure. On the other hand, an intact molecular ion (such as the protonated molecule or radical anion) provides information on molecular weight.

The major ionization methods used for organic and biological compounds can be divided into four categories:

(1) Electron ionization (EI)
(2) Chemical ionization (CI)
(3) Laser desorption ionization (LDI)
(4) Electrospray ionization (ESI)
(5) Atmospheric pressure chemical ionization (APCI)

3) Mass Analyzer

Ions can be separated on the basis of their mass-to-charge ratios using electric or magnetic fields arranged so as to spread them in time or space. Five types of mass analyzers are

(1) Magnetic sectors
(2) Time-of-flight analyzers
(3) Quadrupole mass filters
(4) Quadrupole ion traps
(5) Ion cyclotron resonance

4) Ion Detection

These are major instruments for ion detection

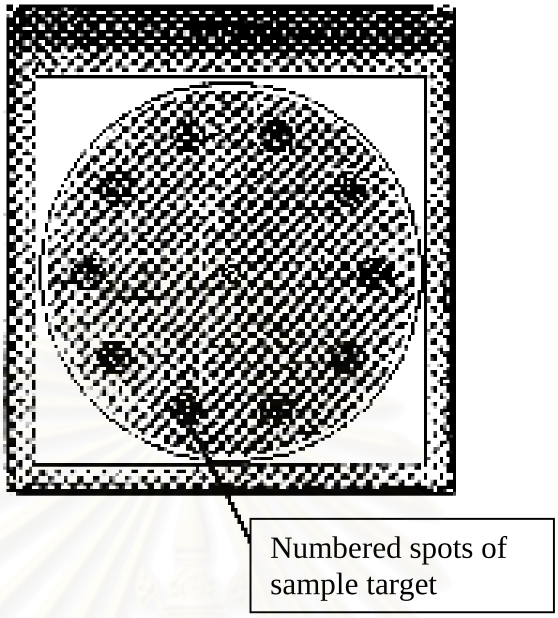
(1) Photomultiplier
(2) Electron multiplier

2-3 Matrix-Assisted Laser Desorption Ionization (MALDI) [6]

MALDI was introduced independently in 1988 by Hillenkamp et.al as a method of transferring large, labile molecules into the gas phase as intact ions. This technique of sample preparation allows for precise and the fast molecular weight determination of peptides, proteins, carbohydrates, nucleic acids, synthetic polymers or other natural products. A remarkable characteristic of MALDI is its extraordinary sensitivity. Total amounts of sample load onto the target surface are often in the picomole to femtomole range and much of this sample is not used. The experiment yields singly charge ions from compounds having molecular weight in excess of 100 kDa. This high range has led to the choice of the time-of-flight mass analyzer for use with this ionization technique because of their compatibility with high mass ions and pulse production.

2-3-1 Basic component of MALDI-TOF-MS

1. Laser System – The laser system provides the pulsed laser light at defined wavelength and intensity on a small spot on the target. In general, the laser system consists of a pulsed UV or IR laser (standard is a N_2 laser with 337 nm wavelength and 3 ns pulse width for use with matrix components absorbing light of this wavelength), an attenuator which allows fine adjustment of the laser influence, beam splitters to direct a fraction of a laser light to a photodiode starting the time-of-flight measurement, a lens system to focus the laser beam and a mirror system to direct the beam into ion source on target.
2. Ion Source – The ion source consists of a positively or negatively charged metal electrode, i.e., the sample probe, and a grounded accelerating grid at the distance of about 1 to 2 cm. Possible accelerating potentials are in the range of +30/-25 kV. The analyte/matrix mixture is deposited on this electrode and exposed to the pulsed laser beam. When the analyte/matrix mixture is hit by the laser beam, gaseous analyte ions are formed which are accelerated by the electrical field, exit the source and pass though focusing lenses into the field-free drift region.
3. Multiprobe – The multiprobe ion source has a manually operated sample loading facility. The sample selection and movement is totally computer controlled and performed on a circular area, which can be rotated around its own axis, as illustrated in Figure 2-4. Probe tips are available with 8, 10 or 20 defined sample position. The classical ion optical design of a charged electrode facing a grounded grid provided high performance for stable as well as for metastable ions.



Numbered spots of sample target

Figure 2-4 Multiprobes.

2-3-2 Basic principle of TOF mass spectrometry

Its extremely high mass-to-charge range and its high sensitivity characterize time-of-flight analyzer, since all ions in the pulse are injected into the flight tube and are mass analyzed. A further advantage is its simplicity. Mass measurements in excess of 10^4 Da/charge were first made on biological molecules with TOF instruments, and molecular mass determinations in the hundreds of thousands of Dalton represent the current state of the art. The resolution and dynamic range mass spectrometers are relatively low; so that individual carbon isotopes are not normally resolved for organic compounds above 5,000 Da. Mass measurement accuracy approaches 0.01%. This accuracy of specifying molecular weight is much better than is possible by conventional techniques in biochemistry.

The time-of-flight method is simple in concept. A beam of ions is accelerated through a known potential *V*, and the time *t* taken to reach a detector at a distance *d* in a linear flight tube is measured. If all ions fall through the same potential *V*, their velocities

v must be inversely proportional to the square roots of their masses m (eq.2-1). The source must be pulsed in order to avoid simultaneous arrival of ions of different mass-to-charge ratios. The flight time is related to the mass-to-charge ratio, m/z, by eq.2-2 and in common units of Da/atomic charge, microseconds, volts, and cm by eq.2-3.

$$\frac{1}{2}mv^2 = zV \qquad 2\text{-}1$$

$$t = \sqrt{\left(\frac{m}{2zV}\right)}\,d \qquad 2\text{-}2$$

$$m/z = 1.93t^{2}V/d^{2} \qquad 2.3$$

This simple relationship allows the mass determination from the flight times after proper calibration.

Typical features of TOF mass spectrometers are:

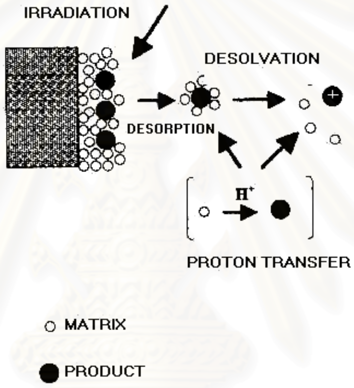
1. A spectrum over the complete mass range can be obtained in microseconds
2. In principle, no upper mass limit exists for this type of mass analyzer
3. A very high sensitivity is achievable due to the high ion transmission
4. The operation is rather simple and straightforward

2-3-3 Ion mechanism

The dilute analyte is present in a solid matrix chosen to absorb radiation at the laser wavelength, often 308 nm. The analyte, which is present in high dilution in the matrix, is not energized directly. As the matrix molecules vaporize, the intermolecular forces that bind the analyte break and the analyte molecules desorb into the gaseous state. The analyte ions leave the surface with significant kinetic energies, entrained as they are in a microsupersonic molecular beam of expanding matrix vapor. The analyte may be percharged, such as a salt, and the intact cation, C^+, may simply be transferred as an ion form the solid to the vapor state on laser irradiation of the matrix.

$$C^+ \text{ (solid)} + \text{energy} \longrightarrow C^+ \text{ (vapor)}$$

Alternatively, a neutral analyte may be ionized through ion- molecule reactions occurring in the energized selvedge. Ionization mechanisms shown in schematic 2-2



Scheme 2-2 Ionization mechanisms.[7]

2-3-4 The important of Matrix

The MALDI matrix compounds are usually organic acids that have strong electronic absorption features in the region of laser wavelength used. Samples are usually present in very high dilution in the matrix, often 10^4 or more, to prevent analyte-analyte interactions. The pK_a of the matrix correlated with the degree of fragmentation observed-highly acidic matrices tend to cause more fragmentation. An unwelcome characteristic is that the analyte-matrix mixture must yield good crystals, presumably those in which intimate mixing of the analyte and matrix occurs. Some experience in preparing samples may be required.

In order to desorb intact non-volatile and thermolabile molecules, it is necessary to introduce energy into the system in such a way preventing thermal decomposition. Lasers with their characteristic short pulses of high intensity light are ideal for such purposes. Before the advent of MALDI, molecules were directly irradiated with lasers in order to transfer them into gas phase (Laser Desorption; LD) for mass spectrometric analysis. However, this approach was limited to low molecular weight materials because the energy required for ion desorption was sufficient to cause molecular fragmentation. The incorporation of matrix materials overcomes this problem by several means:

1) The matrix strongly absorbs the laser light at the wavelength at which the analytes are only weakly absorbing; thermal relaxation of excited matrix molecules leads to evaporation of the matrix and, at the same time, transfers the non-volatile analyte molecules into the gas phase without comparable excitation and fragmentation.

2) The matrix reduces intermolecular contacts beyond analyte-matrix interactions thereby reducing the desorption energy.

3) The matrix acts as a protonating (positive ion detection) or deprotonating (negative ion detection) agent either in solution/solid phase or in the gas phase and is therefore essential in the ion formation process. All these effects are necessary and combine to provide high ion yield of the intact analyte, giving rise to sub-picomole sensitivity.

Matrix selection is shown in Table 2-1

Table 2-1 Matrix Selection

Matrix	Substrate
Alpha-cyano-4-hydroxycinnamic acid (CCA)	Peptides, lipids, polymers
2,3-amino-4-hydroxybenzoic acid	Sugars
2,5-dihydroxybenzoic acid (DHB)	Polymers, sugars, peptides
Indole acrylic acid (IAA)	Polymers
Dithranol	Polymers

To analyze this experiment with the above technique, following factors should be considered

2-3-5 Factors for MALDI analysis

1. Sample preparation

Sample preparation is of prime importance to get a good MALDI mass spectrum and depends significantly on the operator and their ability to communicate with the sources of the particular analytical problem. A homogeneous distribution of small crystals usually gives best results, and also the purity of the matrix material can hardly be overemphasized. There’re two methods for sample preparation. They are dried droplet method and two layer method.

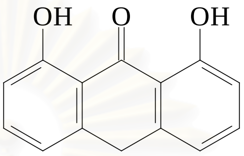
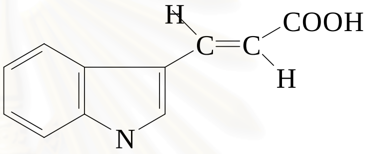
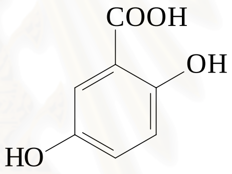
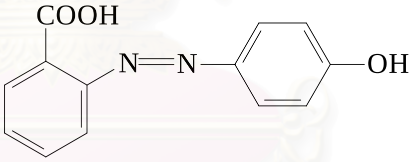
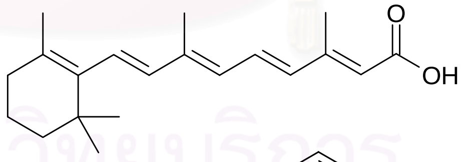
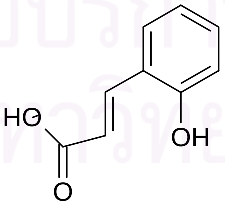
2. Type of matrix

The ability of matrix molecules to separate analyte molecules is facilitated by the chemical nature of the interacting molecules. Because of their similar chemical properties, polar matrix molecules (e.g., 2,5-dihydroxybenzoic acid (DHB)) interact well with polar analyte molecules. Through trial and error, some polar matrices such as 2-(4-hydroxyphenylazo)-benzoic acid (HABA), all-trans retinoic acid (RTA), 2,5 -DHB and dithranol have been found to work for hydrocarbon polymers. For example, HABA and all-trans-RTA have been applied to polystyrene.[10, 11] The matrix all-trans-RTA has also been applied to polybutadiene and polyisoprene.[12] DHB and trans-indole acrylic acid have also been used for hydrocarbon polymers. The most commonly used matrix for hydrocarbon polymers to date is dithranol.

Matrix is selected by considering their similar properties such as polarity.

The matrices in this research are shown in Table 2-2.

Table 2-2 Structures of matrices[8]

Matrix	**Structure**	**Molecular weight**
Dithranol		226.23
Trans-3-Indoleacrylic acid (IAA)		187.2
2,5-Dihydroxybenzoic acid (DHB)		154.12
2-(4-Hydroxyphenylazo)- benzoic acid (HABA)		242.23
all-Trans Retinoic acid (RTA)		300.
α-Hydroxycyanocinnamic acid (CCA)		164.

Comparison of MALDI-TOF MS spectra obtained for PS by using different matrices is shown in Figure 2-5.

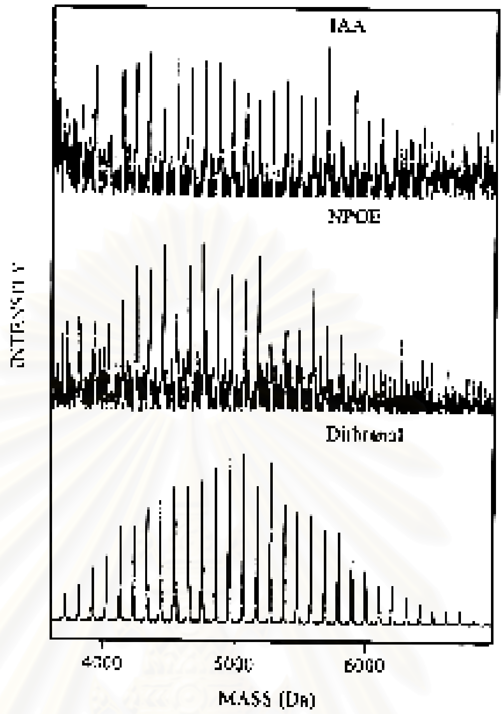


Figure 2-5 Comparison spectra of PS with different matrices.[8]

3. Solvent considerations

Several studies have shown that a number of factors in sample preparation can affect the MALDI results. For example, Yalcin et.al examined the effect of solvent, particularly solvent mixtures, used to prepare polymers, matrix and cationization reagent solutions on MALDI analysis[3]. Figure 2-6 is shown different solvents using for sample preparation.

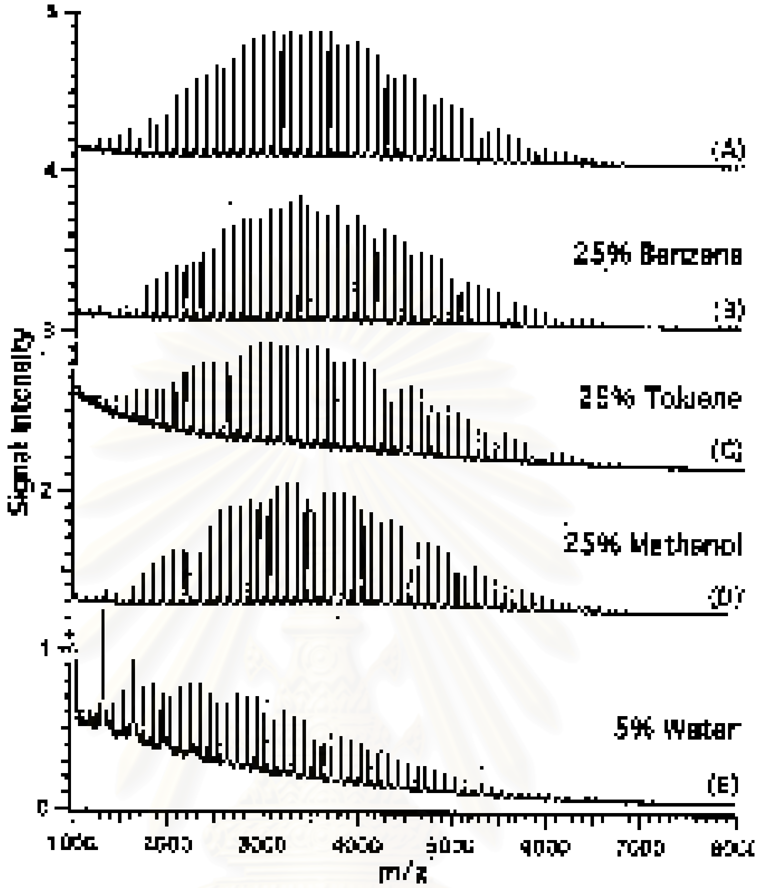


Figure 2-6 MALDI spectra of PMMA obtained by using different solvent systems for sample preparation: (A) 99.5%THF/0.5% methanol, (B) 25% benzene/74.5% THF/0.5% methanol, (C)) 25% toluene/74.5% THF/0.5% methanol, (D) 25.5% methanol/74.5% THF and (E) 5% water/94.5% THF/ 0.5% methanol. All *trans*-retinoic acid was used as the matrix and NaCl was used as the cationizing agent.[3]

4. Laser Power

Different degrees of laser power have influence on the analysis of sample. Some samples may require high degree of laser power, whereas in some cases, spectrum can be shown by using low degree of laser power. Variation in laser power is shown in Figure 2-7.

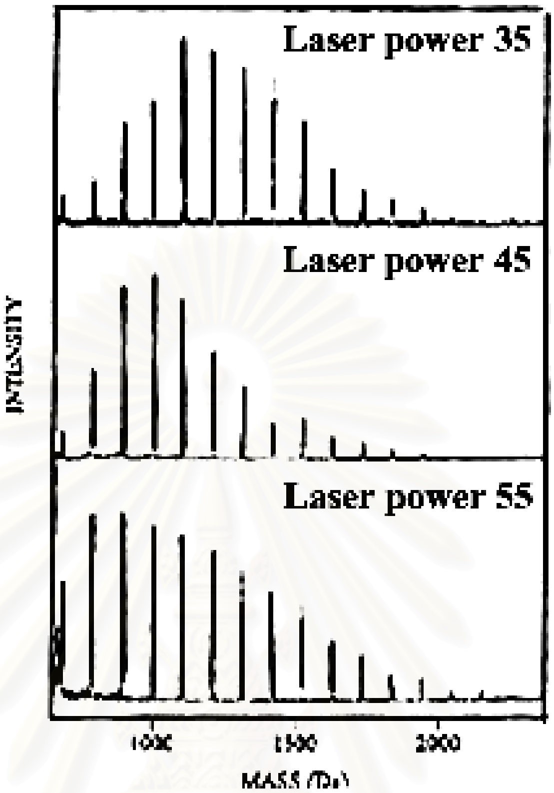


Figure 2-7 Changes in molecular weight distributions of PS due to variations in laser power.[8]

5. Cationizing agent [9]

In MALDI-MS the primary means of forming gas-phase ions is by proton or metal ion attachment. Most MALDI amenable analyte molecules contain heteroatoms such as N or 0 in their molecular structures which provide lone pairs of electrons on which cationization can take place. Similarly, hydrocarbon polymers with unsaturated double bonds have polarizable ¶ bonds on which cationization reagents, mainly metal ions, can be attached. For saturated hydrocarbon polymers like polyethylene, the typical MALDI experiment does not yield reliable results due to the inert nature of such analytes. While ionization of biopolymers in MALDI occurs by protonation, the ionization of synthetic polymers is achieved through cationization by metal ions; group 1 metal salts are good cationization reagents for polar synthetic polymers. Cationization by using cationizing agent is shown in Figure 2-8

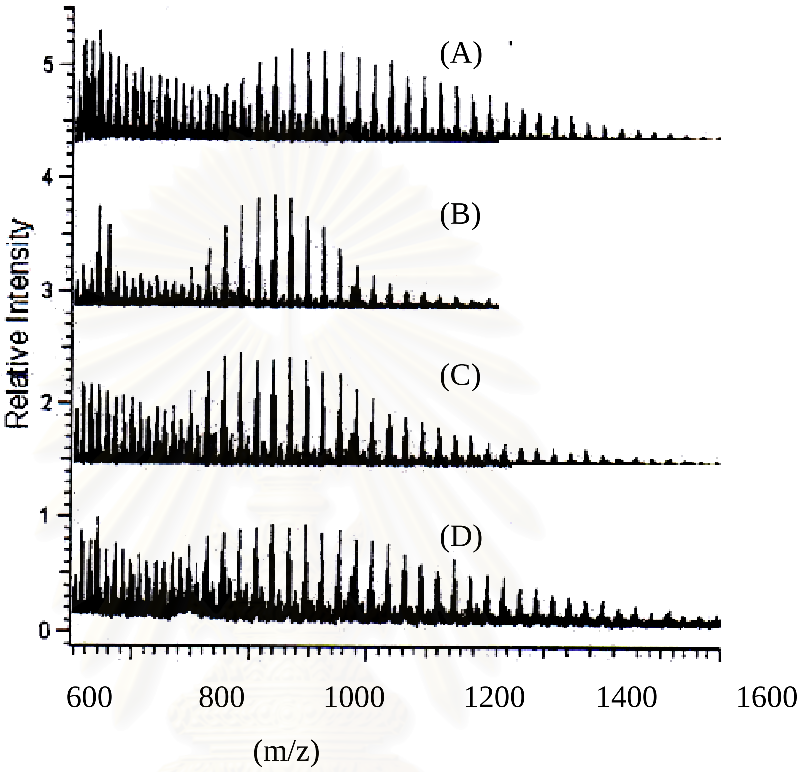


Figure 2-8 MALDI mass spectra of PE obtained by using silver cationization with (A) dithranol, (B) trans,tran-2,4-diphenyl-1,3-butadiene, (C) all-trans-retinoic acid and (D) no matrix.[9]

In general, MALDI-MS has been more successful for the analysis of polar synthetic polymers than for nonpolar synthetic polymers. It has been established that analysis of hydrocarbon polymers such as polystyrene, polybutadiene or polyisoprene requires a different approach; standard MALDI protocols do not work for these types of polymers. Hydrocarbon polymers do not undergo protonation or metal cationization by monovalent Group 1 metal salts ions. To date, only silver (Ag^+) and copper salts (Cu^+ or Cu^{2+}) have been found to work relatively well for nonpolar polymer cationization in MALDI. The performance of these two metal salts is matrix dependent.

2-3-6 Determination of average molecular weights of polydispersity polymer

1) Mass- average molecular weight; $\overline{M}w$

$$\overline{M}w = \Sigma (N_iM_i^2) / \Sigma (N_iM_i)$$

2) Number- average molecular weight; $\overline{M}n$

$$\overline{M}n = \Sigma (N_iM_i) / \Sigma N_i$$

Where N_i ,M_i represent signal intensity in peak area and mass for the oligomer containing *i* monomers.

2-4 Literature Reviews

Dispersant of the polyisobutenylsuccinimide type are important as they prevent agglomeration of particles produced by the oil degradation and metallic parts wear and maintain them in suspension in the oil. Three research groups published work on analysis of polyisobutenylsuccinimide dispersant with other technique. The first group, Hui and rosset[15] isolated polybutenylsuccinimide-type dispersant from monograde and multigrade lubrication oil by classical liquid-adsorption chromatography on a florisil column and characterize through FT-IR and size exclusion chromatography (SEC). In 1997 Ampha[1] determined dispersants in gasoline and diesel oil by separated dispersant from fuel oil with alumina and monitored the results with FT-IR, GPC and NMR. Aléman et.al[16] synthesized polyisobutenylsuccinimide as a dispersants and detergent in fuel. They synthesized polyisobutenylsuccinimide by reaction of polyisobutenylsuccinic anhydride and primary amine and identified by FT-IR. The alkenylsuccinimide showed bands 1700 to 1707 cm^{-1} of C=O stretching, in addition to a C-N band at 1390 cm^{-1}. The absorption of N-H stretching in case of polyamines in the 3000-3500 cm^{-1} range was also observed.

MALDI is a useful technique for biological and polymer. In the field of polymers, many studies were reported on measurements of molecular weight distributions (polydisperse) for a variety of polymers including polystyrene (PS), polyethylene glycol (PEG), polypropylene glycol (PPG), polymethyl methacrylate (PMMA), polybutylene and polyisobutylene etc.. In these works, the following optimum factors and parameters were studied: types of matrix, solvent effect, cationization reagent effect for obtained good spectra. Belu[8] et.al studied MALDI MS for polymer characterization with different polymers, different matrices, different laser power and different cationizing agent. The results showed that optimum quantities of polymer, matrix and cationizing agent were established specifically for PS. Dithranol is the best matrix for PS, and the addition of $\text{Ag}^{๕}$ for cationization of molecules was necessary. Polymers up to 49 ku were analyzed. Effects of laser power were found to be the most significant for lower molecular weight polymers and skew the distribution of oligomers. In 1998 Zhu et.al[11] determined the average molecular weight of narrow polydispersity polymers by MALDI-TOF MS. Polymers in this experiment are PS 5050, PS 7000 and PS 11600 which used all-trans retinoic acid as a matrix, $AgNO_3$ and LiOH were used as a cationizing agent. The results showed that under the experimental conditions used in this work, asymmetric distortion of the molecular weight function did not occur during the MALDI analysis of the PS 5050 and PS 7000. It was concluded that MALDI mass spectrometry can provide accurate molecular weight and molecular weight distribution information for narrow polydispersity polymers.

The success of MALDI-TOF MS for the characterization of polymer structures and for determination of average molecular weight and distributions depends on the use of proper sample/matrix preparation. Yalcin et.al[2] examined the effect of solvents, particularly solvent mixtures, used to prepare polymer matrix and cationizating agent solutions on MALDI analysis. It was demonstrated that sample morphology and polymer distribution on the probe can be greatly influenced by the type of solvents used.

Dispersant in this work has PIB as a polymer and a succinimide group at the end of a molecule. Ji et.al[17] studied four types of PIB by MALDI. The sulfonation samples were employed before analysis by MALDI. All MALDI-TOF MS spectra reported in this paper were generated using all-trans retinoic acid matrix. Tetrahydrofuran was used as solvent for both polymers and matrix. Because the difficulty in attaching ions for such materials, the ionization for MALDI-TOF MS analysis is realized by sulfonating the olefin end groups to introduce a readily ionized moiety into the polymer. The number-average molecular weights and weight-average molecular weights of these materials were also measured by LS and VPO.

CHAPTER III

EXPERIMENTAL

3-1 Materials

1. LZ 9530T; as dispersant additive package for diesel
   Lubrizol
2. Aluminium oxide 90 (70-230 mesh)
   For column chromatography; Merck
3. Hexane
   Analytical grade; Fisher
4. Tetrahydrofuran
   HPLC grade; Lab scan.
5. Acetonitrile
   Solvent grade; J.T. Baker
6. Ethyl alcohol
   Solvent grade; J.T. Baker
7. Acetone
   Commercial grade; J.T.Baker
8. Methyl alcohol
   Solvent grade; J.T. Baker
9. Dithranol
   Aldrich
10. 2,5-Dihydroxybenzoic acid
    Aldrich
11. 2-(4-Hydroxyphenylazo)-benzoic acid
    Aldrich
12. *all- trans* Retinoic acid
    Sigma
13. α-Hydroxycyanocinnamic acid
    Sigma

14. Indole acrylic acid
    Sigma
15. Angiotensin II
    Sigma
16. Neurotensin
    Sigma
17. Silver trifluoroacetate
    Sigma
18. Silver nitrate
    Sigma

3-2 Apparatus and Instruments

1. Matrix-Assisted Laser Desorption Ionization Mass spectrometer (MALDI-MS)
   BIFLEX, BRUKER
2. Vortex mixer
   Vortex-genie No.2, Scientific Industries
3. Multichannel probe
   BRUKER
4. Autopipett
   pipetman, Gilson
5. Electronic Balance
   Fx-180, A&D
6. Pipette tip
7. Eppendorf

3-3 PROCEDURE

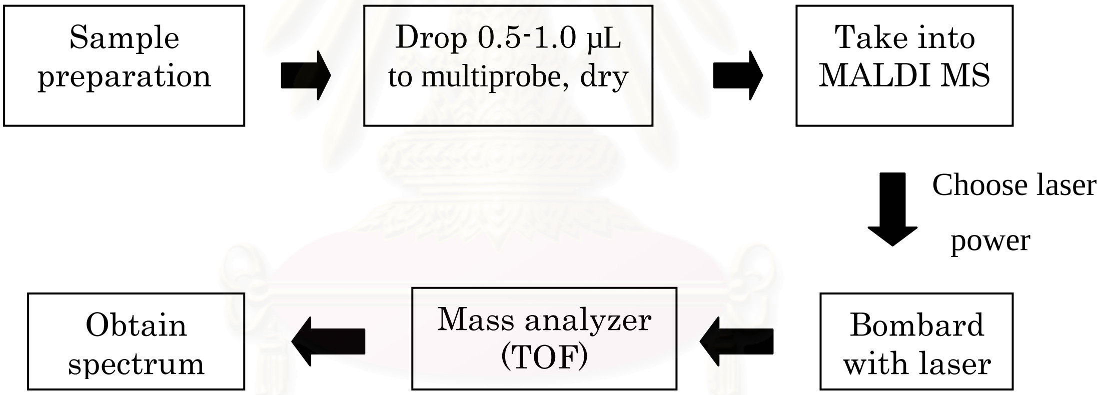
1. Separation of LZ 9530T from base oil

Alumina (50 g) was packed in glass column. The dispersant package (50 ml of LZ 9530T) containing base oil and dispersant 50 ml was loaded into the column. Hexane (100 ml) was added into the column to elute base oil and the tetrahydrofuran 50 ml was added to elute dispersant from alumina. The solvent in this fraction was evaporated using a rotary evaporator.

Prior to analysis using FTIR and MALDI-TOF mass spectrometry, the dispersant was dissolved in THF with a ratio 1:3.

2. MALDI-TOF MS Analysis

The overall process of MALDI is shown in Scheme 3-1.



Scheme 3-1 The overall process of MALDI analysis.

Sample and reagent preparation for MALDI

Polymer sample (dispersant) for MALDI analysis was prepared by combining the dispersant solution and various matrix solutions. The following types of matrices in this experiment were separately used: dithranol, α-hydroxycyanocinnamic acid (CCA), 2, 5-dihydroxybenzoic acid (DHB), *all*- trans retinoic acid (RTA), 2-(4-hydroxyphenylazo)-benzoic acid (HABA), indole acrylic acid (IAA).

- 10 mg/ml dithranol was prepared in THF.

- CCA was prepared in a variety of ways to investigate sample effect

a) at 10 mg/ml in water/acetonitrile (70:30, 0.1% (V/V) TFA) vortex and allow saturated solution to settle.

b) at 10 mg/ml in ethanol/acetonitrile (50:50, 0.1% (V/V) TFA) vortex.

c) at 10mg/ml in CCA in THF. CCA can dissolve in organic solvent.

- 10 mg/ml DHB was prepared in acetone.
- 10 mg/ml IAA was prepared in acetone.
- 10 mg/ml *all- trans* Retinoic acid was prepared in THF.
- 10 mg/ml HABA was prepared in THF.

.

Cationizing agent preparation

- 0.15 M $AgNO_3$, AgTFA dissolved in ethanol were separately prepared.

For MALDI-TOF mass spectrometric analysis, the following conditions and parameters were studied:

- Sample preparation
- Analyte-to-matrix ratio (A/M)
- Type of matrix
- Laser power
- Solvent effect
- Cationizing agent

2.1 Sample preparation

Two methods for sample preparation were carried out.

1) Dried droplet method – sample and matrix were mixed and vortexed. Then a mixture solution of 0.5-1.0 µl was deposited on a multiprobe and allowed to dry.

2) Thin layer method – The matrix solution was deposited on a multiprobe and allowed to dry to form a microcrystal layer. A sample solution containing analyte was added to the top of the matrix layer and dry. The matrix was droped again on the top of the sample layer and allowed to dry.

2.2 Analyte-to-matrix ratio (A/M)

The amount ratio of analyte to matrix were varied

- 1:1
- 1:2
- 1:3
- 1:4
- 1:5
- 1:6

2.3 Types of matrix

Samples for MALDI analysis need a suitable matrix to obtain good spectra. The following matrices were selected for this experiment.

- Dithranol
- CCA
- DHB
- IAA
- RTA
- HABA

2.4 Laser power

Different degree of laser power has influence on the MS spectrum. Some samples may require high degree of laser power, whereas in some cases, spectrum can be shown by using low degree of laser power. The values of laser power 150, 160, 170 and 180 μJ were used for this experiment.

2.5 Solvent effect

Solvents are important for obtaining good spectra. CCA is a good matrix for polymer wherever solvents may affect the MS spectrum. Thus, various solvents were used.

1) CCA in water/acetonitrile (70:30, 0.1% (V/V) TFA)
2) CCA in ethanol/acetonitrile (50:50, 0.1% (V/V) TFA)
3) CCA in THF

2.6 Cationizing agent

These metal solutions, $AgNO_3$ and AgTFA were used.

CHAPTER IV

RESULT AND DISCUSSION

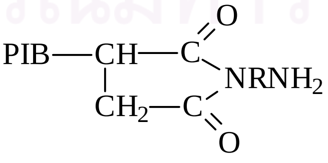
This research was related to development of mass spectrometry for determination of the dispersant additive in diesel. As proposed in the previous chapter, the results will be shown and discussed in each part, respectively.

1. Characterization of polyisobutenylsuccinimide dispersant by infrared spectroscopy

Dispersant obtained from removal of base oil in dispersant package was identified by FTIR. The spectrum is shown in Figure A1 and the results are shown in Table 4.1.

Table 4-1 FTIR of dispersant from LZ9530T

Wavenumber (cm^{-1})	Bond type
1037	$C-NH_2$
1390	C-N
1465	$-CH_3$
1710	C=O
2950	CH_2 , CH_3
3428	Amine, amide



Polyisobutenylsucinimide

Figure 4.1 Polyisobutenylsuccinimide type

Aléman-Vázquez and Villagómez-Ibarra[16] studied polyisobutenylsuccinimides by FTIR. The results showed that the polyisobutenylsuccinimide showed C=O at 1700- 1707 cm^{-1}, C-N at 1390 cm^{-1} and N-H at 3000-3500 cm^{-1}. From IR spectrum of this experiment, it was concluded that the dispersant in LZ9530T package might be polyisobutenylsuccinimide.

2. Determination of molecular weight distribution by matrix-assisted laser desorption ionization mass spectrometry

The optimized conditions and parameters for determination of molecular weight distribution of polymer dispersants were performed to obtain good spectra. The results are shown as follow;

2.1 Sample preparation

For MALDI-MS analysis, a comparison of MALDI spectra of dispersants from a dried droplet and thin-layer method was investigated. The results in Figures A2 and A3 showed that the dried droplet method gave higher intensity of mass spectrum for molecular weight distribution. This may be because the dried droplet preparation method is more homogeneous than the thin-layer preparation method.

2.2 Analyte-to-matrix ratio

The amount ratio of suitable analyte: matrix ratio was investigated. When analyte-to-matrix ratio is too high, the spectrum showed many peaks of matrices. Whereas, at low analyte: matrix ratio, ionization cannot occur. Since the matrix will transfer a proton to sample after irradiated with laser light. Consequently, the lower amount of matrix, the lower number of transfer proton, then it is difficult for ionization.

The samples, which have the amount ratio of analyte: matrix (CCA); 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6 were prepared. The obtained MALDI-MS spectra are shown in Figures A4-A8. At sample: matrix ratio 1:1, no significant peak was observed. This indicates that the sample is not ionized. At sample: matrix ratio 1:2 (Figure A4), the obtained MALDI–MS spectrum of dispersant was poor because of a narrow range of molecular weight distribution and low intensity detection response. The obtained spectrum of sample: matrix ratio 1:3 (Figure A5) has narrower range of molecular weight distribution than do the spectra of sample: matrix ratios 1:4 and 1:5 (Figures A6 and A7). At sample: matrix ratios 1:4 and 1:5 (Figures A6 and A7), the patterns of molecular weight distribution were found to be similar, but the MALDI-MS spectrum of sample:matrix ratio 1:5 has higher intensity of detection response. At sample: matrix 1:6 (Figure A8), the higher noise was obtained. Thus, a suitable dispersant:matrix ratio was chosen to be 1:5.

2.3 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 have selectivity for particular sample. The matrices; dithranol, CCA, DHB, all-trans retinoic acid (RTA), HABA and IAA were used in the experiment.

2.3.1) Dithranol

The obtained MALDI-MS spectra of dispersant with dithranol as a matrix at laser power values of 150, 160, 170 and 180 µJ are shown in Figures A9-A12. From Figure A9, no spectrum of dispersant was observed. This indicates that the laser power of 150 is not enough for ionization of dispersant. The obtained MALDI-MS spectra of dispersant with dithranol at laser power 160 and 170 µJ (Figures A10 and A11) were found to be similar. In comparison with MALDI-MS spectra of dispersant with dithranol at laser power 160 and 170 µJ(Figures A10 and A11), the MALDI-MS spectrum of dispersant with dithranol at laser power 180 µJ has higher intensity of detection response and wider molecular weight distribution. Molecular weight distribution of MALDI-MS spectrum of dispersant with dithranol is in a m/z range of 700-1400, with a repeating unit of 56 Da.

2.3.2) α-Hydroxycyanocinnamic acid (CCA)

The obtained MALDI-MS spectra of dispersant with CCA as a matrix at laser power value of 150, 160, 170 and 180 µJ are shown in Figures A13-A16. All of laser power values can give acceptable spectra of dispersant. However, the laser power of 180 µJ gave highest intensity of detection response. Molecular weight distribution of

MALDI-MS spectrum of dispersant with CCA is in a m/z range of 800-2200, with a repeating unit of 56 Da.

2.3.3) 2, 5-Dihydroxybenzoic acid (DHB)

DHB as a matrix at a laser power range of 150-180 µJ for dispersant analysis by MALDI-MS was used. At laser power values of 150 and 160 µJ, no significant peak was observed because ionization of sample at this condition did not occur. Laser power 170 and 180 µJ (Figures A17 and A18), the MALDI-MS spectra of dispersant with DHB as a matrix were found to be similar, but MALDI-MS spectrum of dispersant with DHB at laser power 180 µJ has higher intensity of detection response.

2.3.4) all Trans- retinoic acid (RTA)

RTA is a popular matrix for molecular weight distribution determination of polymers. In this experiment, the MALDI-MS spectra of dispersant with RTA as a matrix at a laser power range of 150-180 µJ are shown in Figures A19-A22. Figure A19 shows spectrum of dispersant with RTA at laser power 150 µJ, with molecular weight distribution in m/z range of 400-1200. At laser power values of 160 and 170 µJ (Figures A20 and A21), the MALDI-MS spectra were found to be similar. These spectra have lower intensity of detection response when compared to MALDI-MS spectrum of dispersant with RTA at laser power 150 µJ. At laser power 180 µJ (Figure A22) the higher noise was obtained. The MALDI–MS spectra of dispersant with RTA show a different molecular weight distribution range with previous spectra of dispersant using dithranol, CCA or DHB as a matrix. Molecular weight distribution of MALDI-MS spectrum of dispersant with RTA is in a m/z range of 400-1200, with a repeating unit of 56 Da.

2.3.5) 2-(4-hydroxyphenylazo)-benzoic acid (HABA)

The MALDI-MS spectra of dispersant using HABA as a matrix at a laser power range of 150-180 µJ are shown in Figures A23-A26. Laser power 150 µJ (FigureA23) show no spectrum of dispersant because it is not enough for ionization of dispersant. The MALDI-MS spectra of dispersant with HABA at laser power 160, 170 and 180 µJ (Figures A24-A26) were poor because the mass spectra of dispersant were not observed.

2.3.6) Indole acrylic acid (IAA)

The MALDI-MS spectra of dispersant with IAA as a matrix at a laser power range of 150-180 µJ are shown in Figures A27-A30. All MALDI-MS spectra of dispersant with IAA were found to be similar. However, laser power 180 µJ (Figure A30) gave the best result of dispersant analysis. The MALDI–MS spectra of dispersant with RTA show a different molecular weight distribution range with previous spectra of dispersant using dithranol, CCA, DHB or RTA as a matrix. Molecular weight distribution of MALDI-MS spectrum of dispersant with IAA is in a m/z range of 400-900, with a repeating unit of 44 Da.

From MALDI-MS spectra of dispersant, it is concluded that three ranges of molecular weight distribution were found. The fist range is m/z of 800-2200 with molecular weight of repeating unit of 56 Da, using dithranol, CCA or DHB as a matrix. However, the use of CCA as a matrix and laser power 180 µJ was found to be the best condition for determination of the first range of molecular weight distribution. The second range is m/z of 400-1200 with molecular weight of repeating unit of 56 Da, using RTA as a matrix. The third range is m/z 400-900 with molecular weight of repeating unit of 44 Da, using IAA as a matrix.

2.4 Solvent effect

The types of solvents have an effect on intensity and resolution of spectrum. The methods for sample preparation were described in Section 2.5, Chapter III. The MALDI-MS spectra of dispersant using different solvent are shown in Figures A31-A33. The MALDI-MS spectra of dispersant with CCA using THF and ethanol/acetonitrile (Figures A31 and A32) showed good spectra, which have a wide range of molecular weight distribution and high intensity of detection response. Figure A33 shows MALDI-MS spectrum of dispersant with CCA using water/acetonitrile as a solvent. From Figures A31-A33, both THF and ethanol/acetonitrile are good solvent for dispersant analysis, using CCA as a matrix.

2.5 Cationizing agent

The MALDI-MS spectra of dispersants using CCA as a matrix and $AgNO_3$ or AgTFA as a cationizing agent are shown in Figures A34 and A35. MALDI-MS spectra of dispersant with and without cationizing agent (Figures A34, A35 and A16) show a similar pattern of molecular weight distribution.

Data processing from MALDI analysis

From the previous results and Figures 4-2, 4-3 and 4-4, molecular weight distribution of dispersant in dispersant package (LZ9530T) may be divided into three ranges as shown in Table 4-2.

Table 4-2 Three kinds of polymers from MALDI-MS spectra

Range	MW of Repeating unit (Da)
❶ m/z of 400-900	44
❷ m/z of 400-1200	56
❸ m/z of 800-2200	56

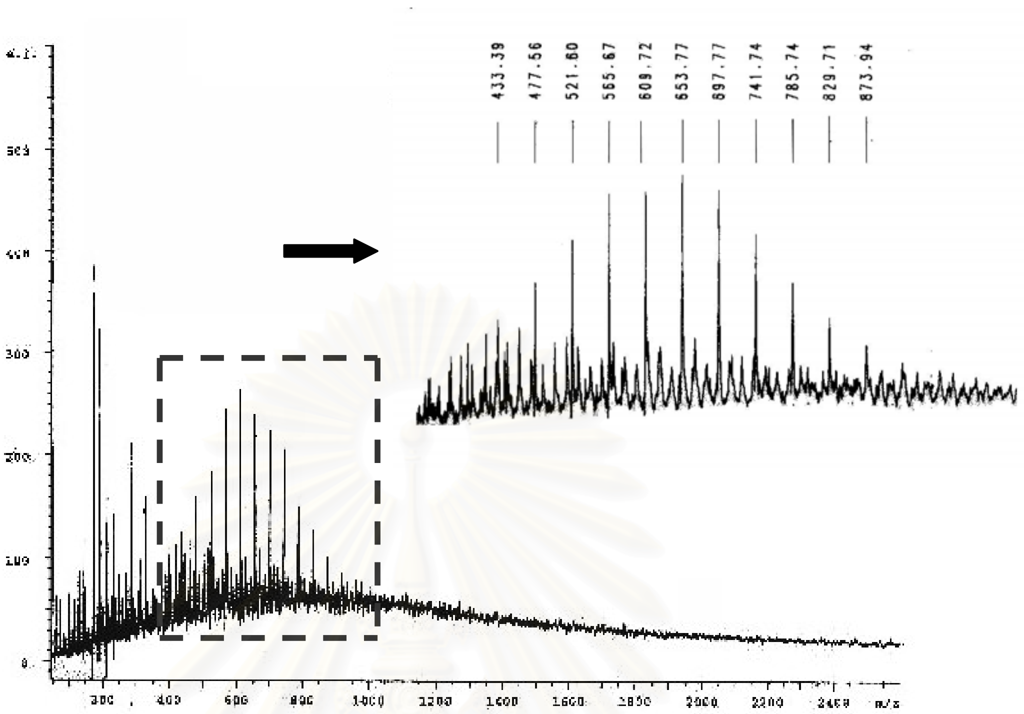


Figure 4-2 Molecular weight distribution of polymer range ❶ m/z of 400-900

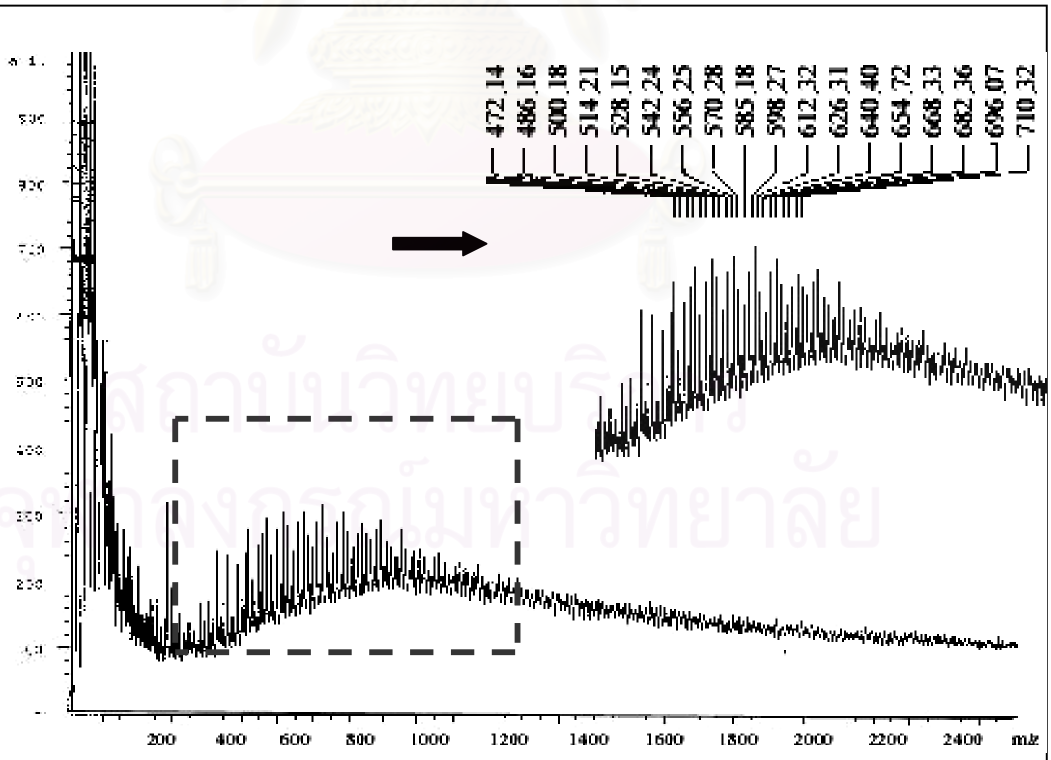


Figure 4-3 Molecular weight distribution of polymer range ❷ m/z of 400-1200

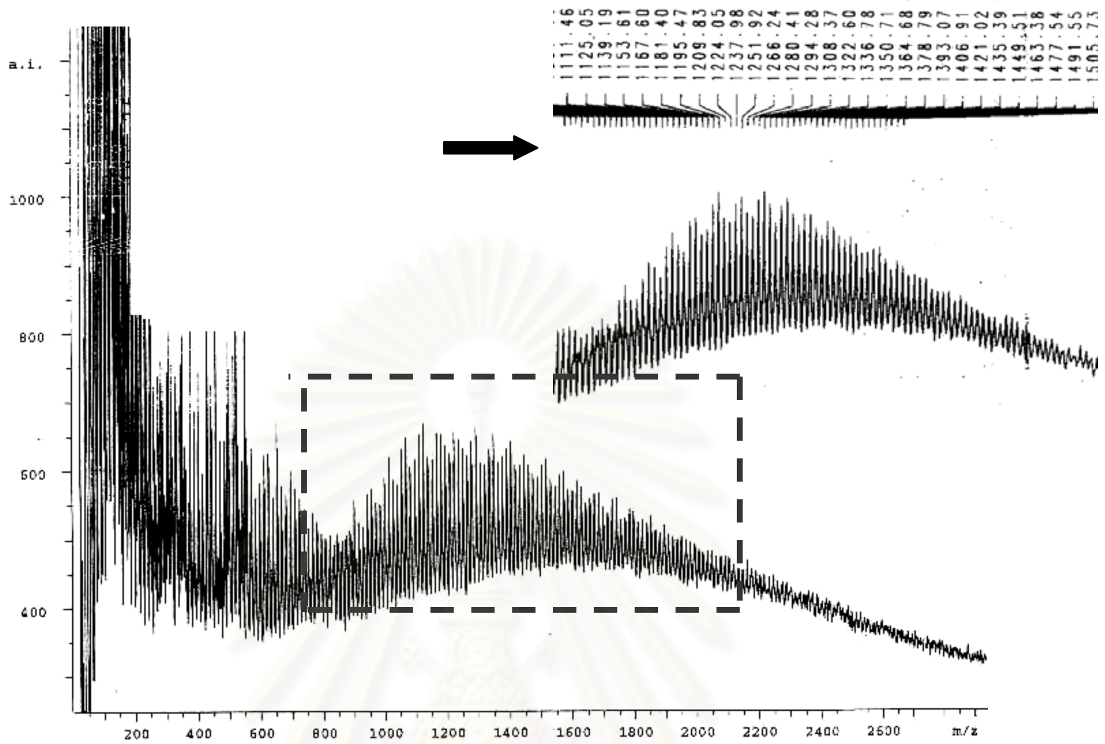


Figure 4-4 Molecular weight distribution of polymer range ❸ m/z of 800-2200

Calculation of average molecular weights of polydispersity polymer

Mass- average molecular weight and number- average molecular weight are calculated using the following equations.

1) Mass- average molecular weight; $\overline{M}w$

$$\overline{M}w \quad = \quad \Sigma\,(N_iM_i^2) \,/\, \Sigma\,(N_iM_i) \ldots\ldots\ldots\ldots\ldots\ldots \text{ 4-1}$$

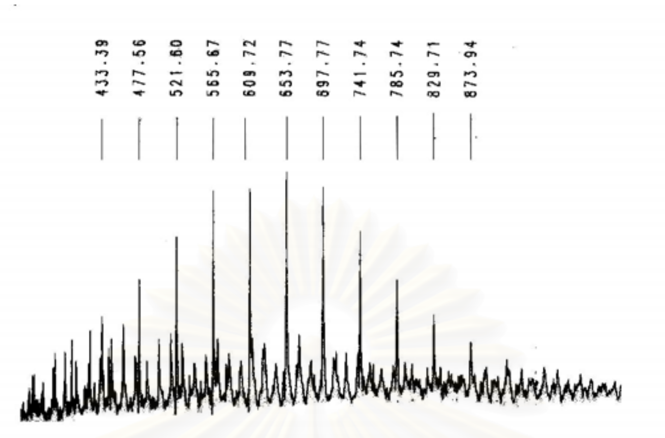
2) Number- average molecular weight; $\overline{M}n$

$$\overline{M}n \quad = \quad \Sigma\,(N_iM_i) \,/\, \Sigma\, N_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots\text{4-2}$$

Where N_i ,M_i represent signal intensity in peak area and mass for the oligomer containing *i* monomers.

Example

Range 1) 400 -900



$\overline{M}w$ = $[(3.8x433.39^2) + (5.2x477.56^2) + (6.6x521.60^2) + (8.5x565.67^2) +$
$(9.4x609.72^2) + (9.9x653.77^2) + (8.6x697.77^2) + (6.7x741.74^2) +$
$(4.5x785.74^2) + (3.0x829.71^2) + (2.2x873.94^2)]/ [(3.8x433.39) +$
$(5.2x477.56) + (6.6x521.60) + (8.5x565.67) + (9.4x609.72) +$
$(9.9x653.77) + (8.6x697.77) + (6.7x741.74) + (4.5x785.74) +$
$(3.0x829.71) + (2.2x873.94)]$
= 656.0111

$\overline{M}n$ = $[(3.8x433.39) + (5.2x477.56) + (6.6x521.60) + (8.5x565.67) +$
$(9.4x609.72) + (9.9x653.77) + (8.6x697.77) + (6.7x741.74) +$
$(4.5x785.74) + (3.0x829.71) + (2.2x873.94)] /$
$(3.8+5.2+6.6+8.5+9.4+9.9+8.6+6.7+4.5+3.0+2.2)$
= 636.0051

The overall values of $\overline{M}w$ and $\overline{M}n$ of three polymers are shown in Table 4.3.

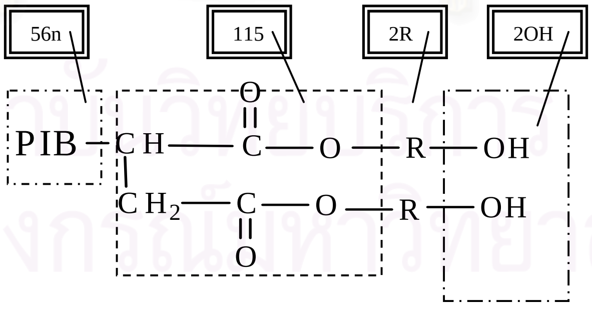
Table 4-3 $\overline{M}w$ and $\overline{M}n$ of polymers

Range	MW of Repeating unit (Da)	$\overline{M}w$	$\overline{M}n$
❶ m/z of 400-900	44	656.01	636.00
❷ m/z of 400-1200	56	751.51	730.61
❸ m/z of 800-2200	56	1406.64	1337.32

Polyisobutenylsuccinimide (PIBSN) consists of the combination of succinimide at the end of PIB with molecular weight of repeating unit of 56 Da. From Table 4.3, the peaks in a m/z range of 400-900 with molecular weight of repeating unit of 44 Da should not belong to PIB. It is possible that the m/z range of 400-900 with repeating unit is polyethylene oxide (–CH_2CH_2-O–).

There are three types of commercial dispersant containing PIB; polyisobutenylsuccinate ester (PIBSE), polyisobutenylsuccinimide (PIBSN) and phosphorus types[4]. FT-IR spectrum in Figure A1 indicates that dispersant in dispersant package is not phosphorus type. Consequently, PIB in range ❷ and ❸ might be PIBSN and/or PIBSE.

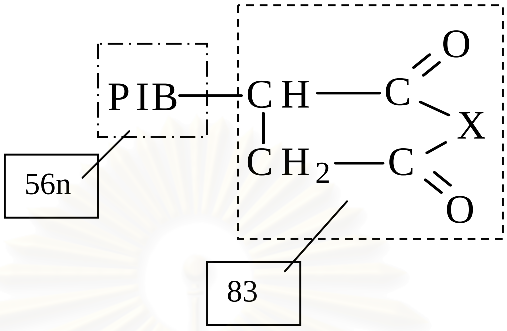
Molecular wight of PIBSN and PIBSE can be calculated from the equations below.



Polyisobutenyl succinate ester

$$56n + 115 + 2R + 34 \qquad = \qquad M \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4\text{-}3$$

Which n is the number of repeating unit, R the alkenyl group such as CH_2, and M the m/z value obtained from spectrum.



Polyisobutenylsuccinimide

$$56n + 83 + X \quad = \quad M \qquad \text{………………..4-4}$$

X is amine derivative. It is known that the derivative of tetraethylenepentamine or ethylenediamine is used as dispersant substances[16].

One peak from MALDI-MS spectra in range ❷ and range ❸ (Figures A36 and A37) is chosen to substitute the Equations 4-3 and 4-4.

From Equation 4-3, all parameters are known (R is CH_2; Mw =14, M is chosen from spectrum) except n.

$$n \quad = \quad \frac{M - 34 - 115 - 2(14)}{56} \qquad \text{……………..4-5}$$

In Figure A36, peak m/z of 851.39 Da was chosen from range ❷.

$$n \quad = \quad \frac{851.39 - 34 - 115 - 2(14)}{56}$$

$$n \quad = \quad 12.04$$

If the equation was substituted with peak m/z 1056.02 Da from range ❸ (Figure A37).

$$n \quad = \quad \frac{1056.02 - 34 - 115 - 2(14)}{56}$$

$$n \quad = \quad 15.69$$

Thus, range ❷ (m/z 400-1200) should be PIBSE and not PIBSN. Moreover, other peaks in this range ❷ such as m/z values of 627.56, 683.80, 739.68 and 795.81 Da (see Figure A36) were also indicated that this range of molecular weight distribution should belong to PIBSE.

From Equation 4-4, X is substituted with molecular weight of a derivative of ethylenediamine ($M_w = 58$) or tetraethylenepentamine ($M_w = 187$)

$$n = \frac{M-83-X}{56} \qquad \text{..................4-6}$$

If X is molecular weight of derivative of ethylenediamine.

$$n = \frac{M-83-58}{56}$$

The peak m/z of 851.39 Da from Figure A36 and the peaks 1056.02 Da from Figure A37 were substituted in the above Equation.

→ m/z of 851.39 $$n = \frac{851.39-83-58}{56}$$

$$n = 12.68$$

→ m/z of 1056.02 $$n = \frac{1056.02-83-58}{56}$$

$$n = 16.34$$

If X is molecular weight of derivative of tetraethylenepentamine.

$$n = \frac{M-83-187}{56}$$

→ m/z of 851.39 $$n = \frac{851.39-83-187}{56}$$

$$n = 10.38$$

→ m/z of 1056.02 $$n = \frac{1056.02-83-187}{56}$$

$$n = 14.03$$

Thus, range❸ (m/z 800-2200) should be PIBSN and not PIBSE. Moreover, other peaks in this range such as m/z values of 1111.46, 1167.60, 1224.05 and 1280.41 Da (see Figure A37) were also indicated that this range of molecular weight distribution should belong to PIBSN of tetraethylenepentamine.

Therefore, three kinds of polymers found in dispersant package (LZ9530T) are polyethylene oxide, PIBSE and PIBSN.

This research focuses on polyisobutenylsuccinimide, which found with this condition; using dried droplet preparation method with analyte: matrix ratio 1:5, CCA as a matrix at laser power180 μJ. This condition was used for determination of molecular weight distribution of dispersant in commercial diesel oil.

3. Application of MALDI-MS for analysis of dispersant in commercial diesel oil

The MALDI-MS spectra of dispersant in PTT and SHELL diesel oils are shown in Figures A38 and A39. The MALDI-MS spectra of dispersant from PTT and SHELL diesel oils had the similar molecular weight distribution, indicating the same type of dispersant. The MALDI-MS spectra of dispersant in PTT and SHELL diesel oil were different from the MALDI-MS spectrum of dispersant from dispersant package LZ9530T (Figures A38 and A39). This indicated that PIBSN of tetraethylenepentamine was not used in PTT and SHELL diesel oils.

From Equation 4-6, X is substituted with molecular weight of derivative of ethylenediamine (M_w = 58) or tetraethylenepentamine (M_w= 187)

$$n = \frac{M - 83 - X}{56}$$

Dispersant in LZ9530T is PIBSN of tetraethylenepentamine, but dispersant in PTT and SHELL diesel is not the same with LZ9530T. Thus, X in this equation is not molecular weight of tetraethylenepentamine. It may be molecular weight of ethylenediamine.

The peak m/z of 1150.01 Da from figure A38 was substituted.

$$n = \frac{1150.01 - 83 - 58}{56}$$

$$n = 18.01$$

Therefore, dispersant in PTT and SHELL diesel oil should be polyisobutenylsuccinimide of ethylenediamine.

CHAPTER V

CONCLUSION

In this research, MALDI-MS was developed for determination of molecular weight distribution of polyisobutenylsuccinimide dispersant. The dispersant was separated from dispersant package (LZ 9530T). Then, the dispersant was analyzed by MALDI-MS. The optimum conditions and parameters were studied for determination of molecular weight distribution of polyisobutenylsuccinimide dispersant.

The results showed that a dried droplet method is suitable for sample preparation of MALDI-MS analysis, in comparison with a thin-layer method. The best analyte-to-matrix ratio was found to be 1:5. Additionally, use of α-hydroxycyanocinnamic (CCA) as a matrix and laser power 180 μJ provided good MALDI-MS spectrum for determination of molecular weight distribution of polyisobutenylsuccinimide dispersant. Cationizing agent was found to not improve ionization of dispersant.

The type of solvent also was found to have an effect to sample intensity. The best solvent system is THF or ethanol/acetonitrile (50:50, 0.1% (v/v) TFA) because of their similar polarity of matrix and analyte.

From MALDI- MS analysis of LZ9530T dispersant package, three kinds of polymer were found, polyethylene oxide (m/z of 400-900), polyisobutenylsuccinate ester (m/z of 400-1200) and polyisobutenylsuccinimide of tetraethylenepentamine (m/z of 800-2200).

A developed method was used to analyze dispersant in PTT and SHELL diesel oils. Results showed that dispersant in PTT and SHELL diesel oils was found to be polyisobutenylsuccinimide of ethylenediamine with the repeating unit of 56 Da, which is different from polyisobutenylsuccinimide of tetraethylenepentamine in LZ9530T.

It is concluded that MALDI-MS is an excellent method for determination of type and molecular weight distribution of dispersant. This method can be used for identification of dispersant in commercial diesel oils.

It is suggested that a developed MALDI-MS method may be used for quality control of dispersant production. For further work, other polymer additives in other fuel oils could be determined by MALDI-MS.

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APPENDIX

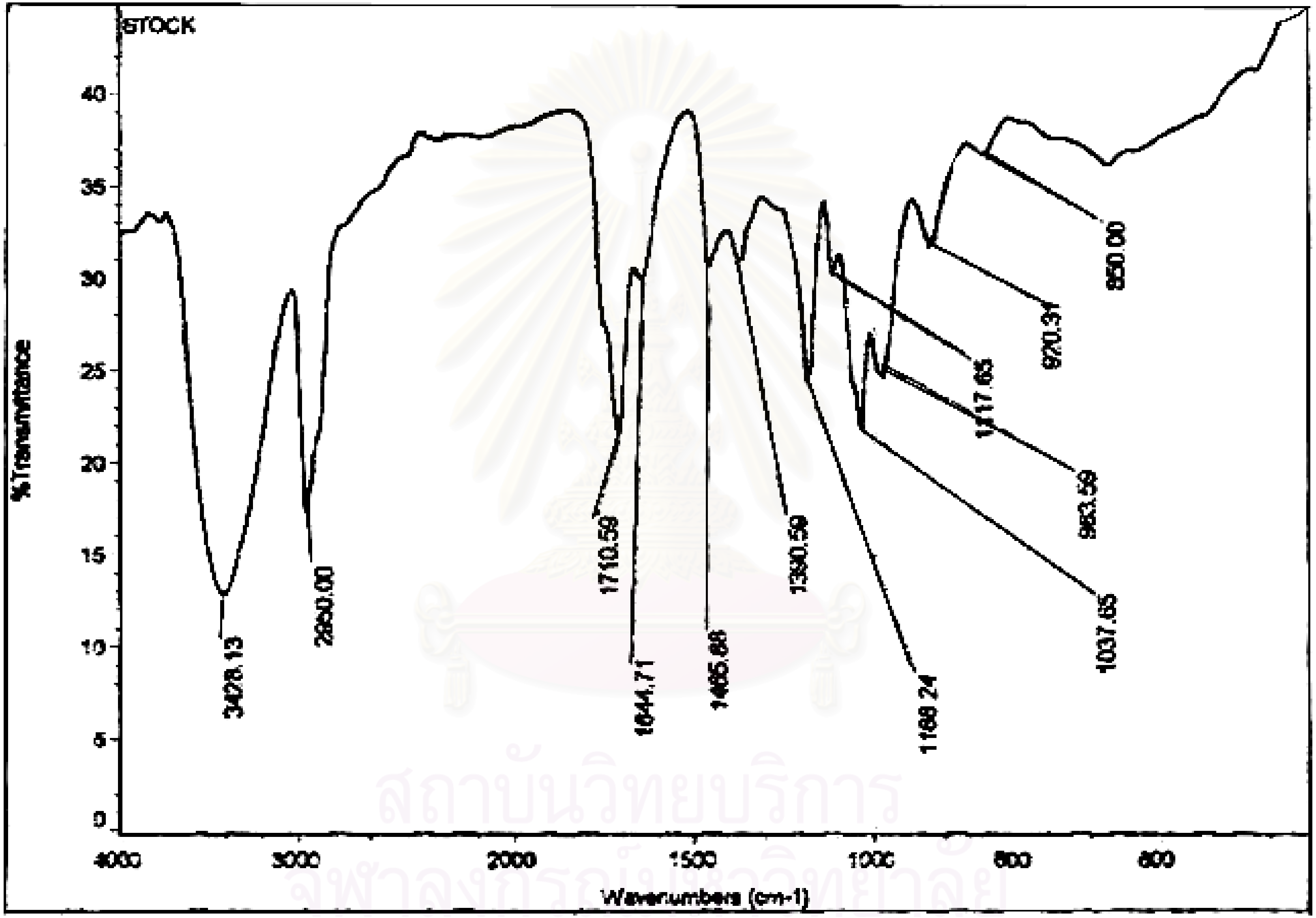


Figure A1 FT-IR spectrum of dispersant separated from LZ 9530T.

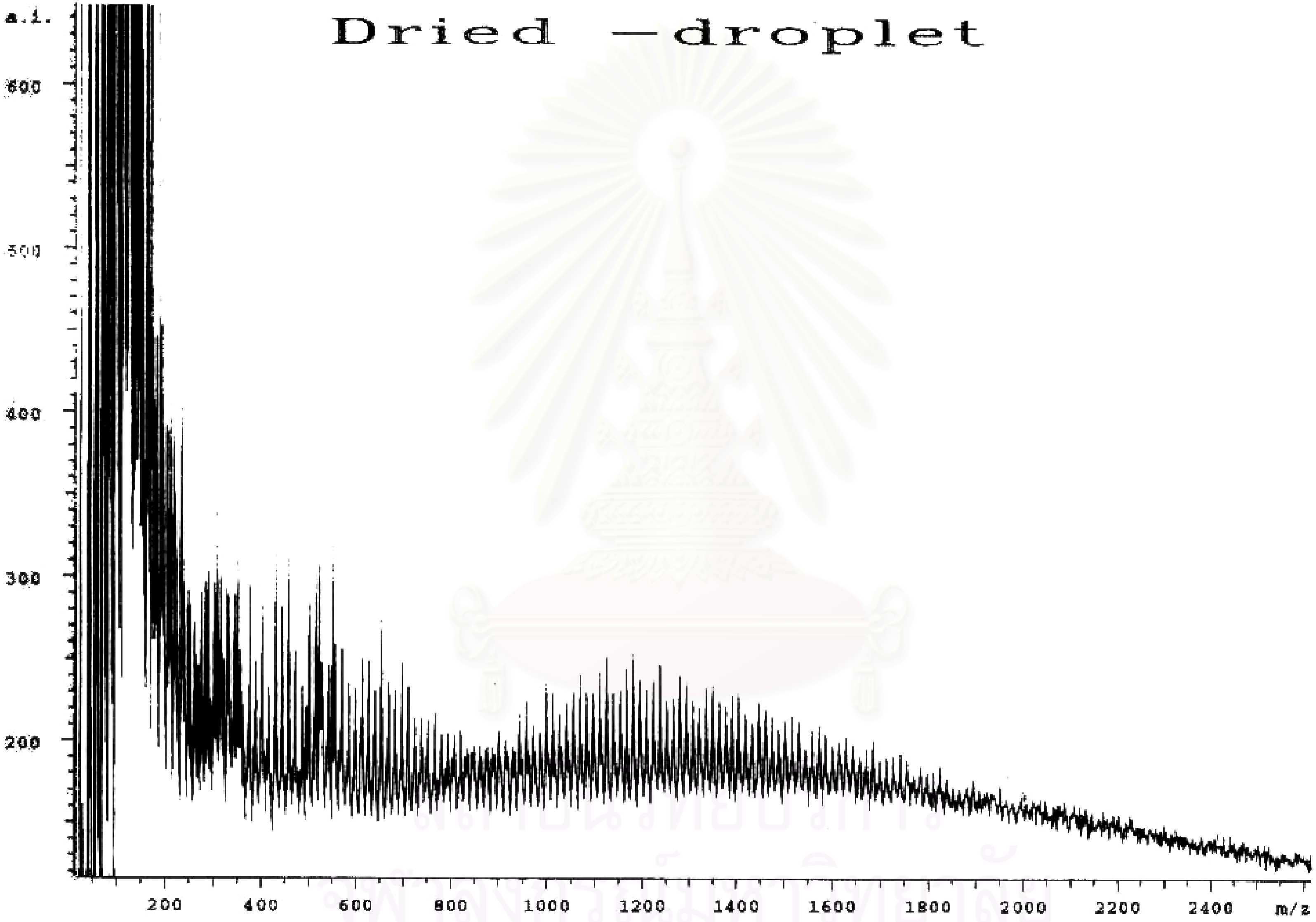


Figure A2 MALDI-MS spectrum of dispersant using a dried droplet method.

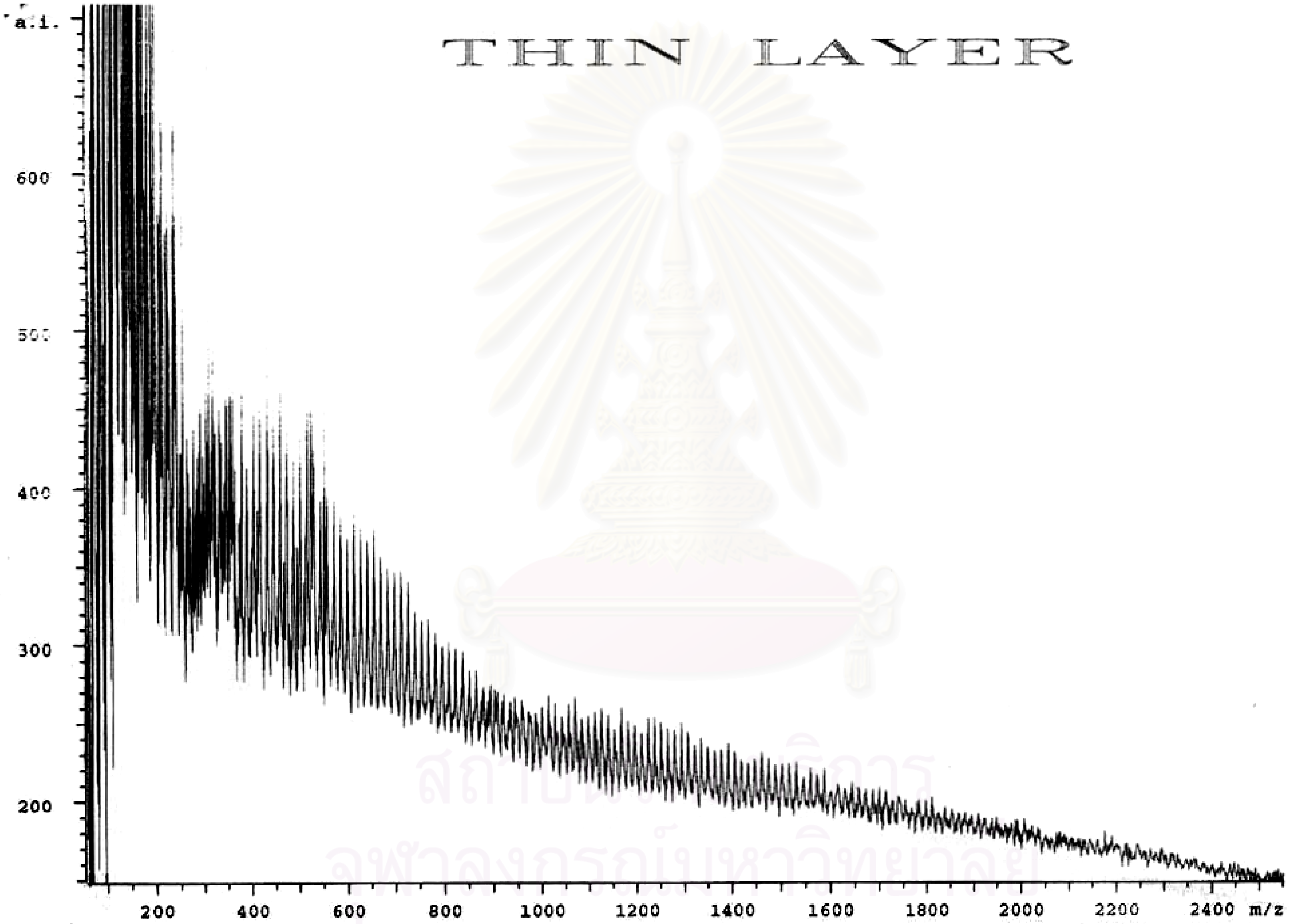


Figure A3 MALDI-MS spectrum of dispersant using a thin-layer method

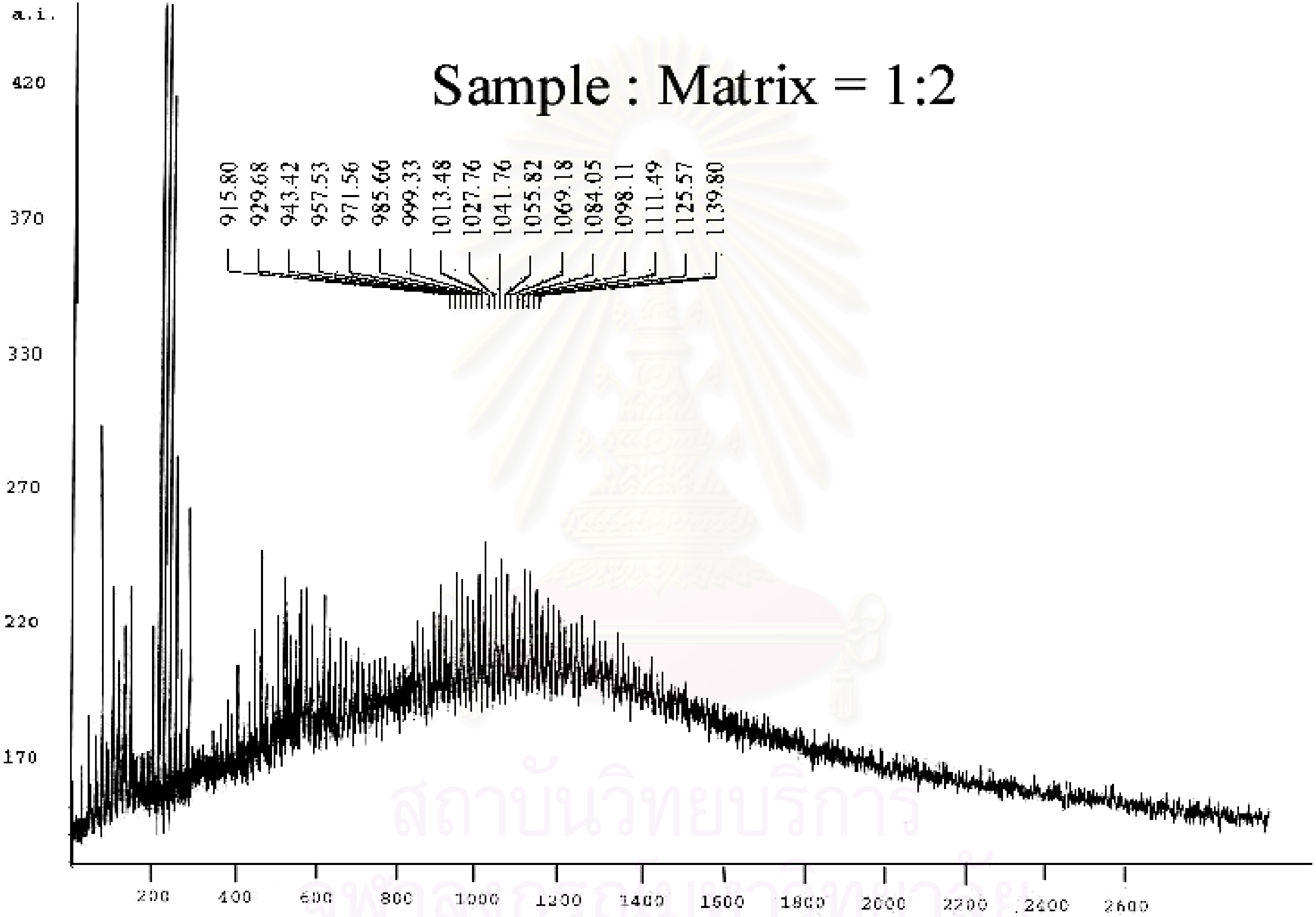


Figure A4 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA ratio of 1:2, laser power of 180 μJ.

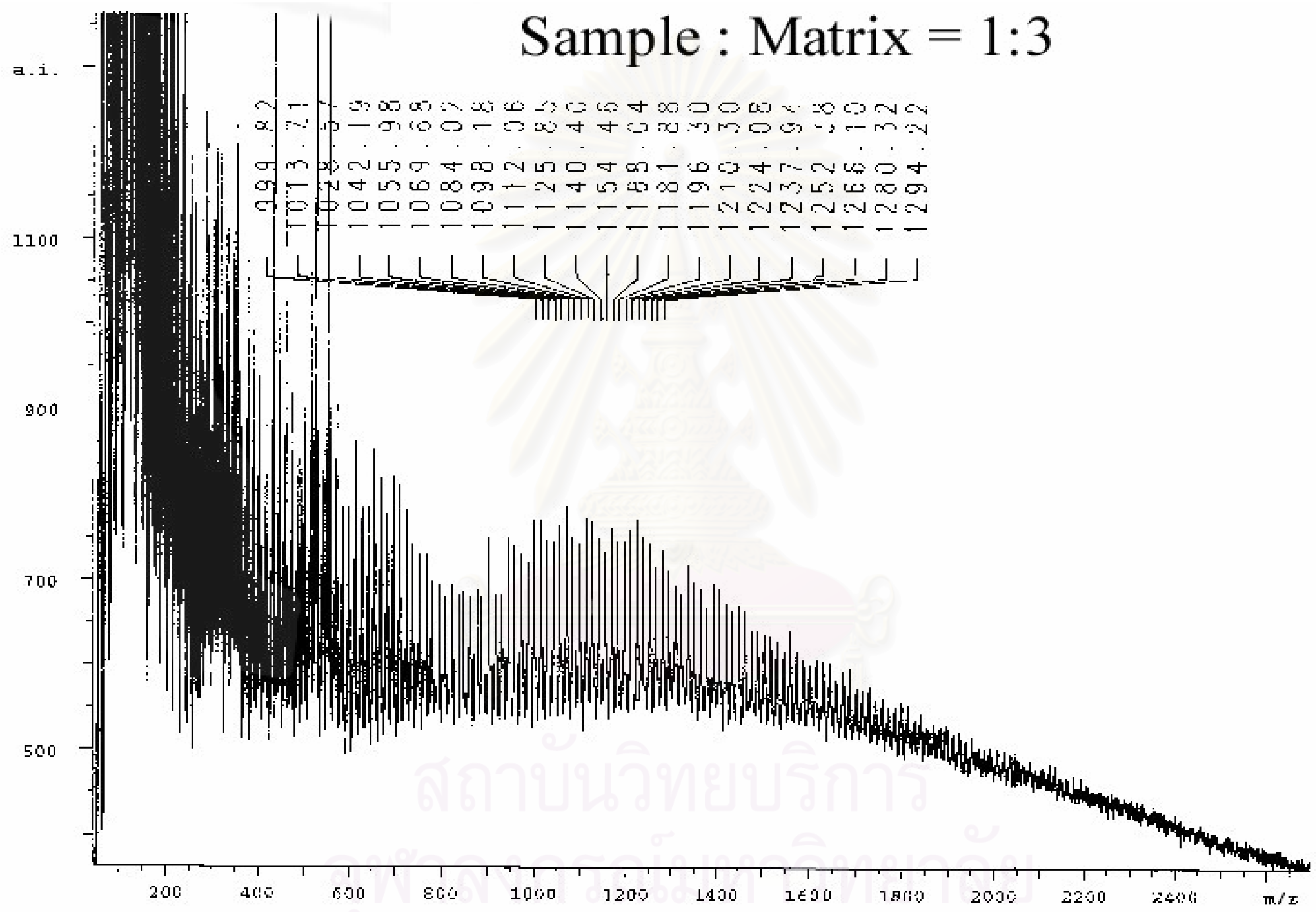


Figure A5 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA ratio of 1:3,laser power of 180 μJ.

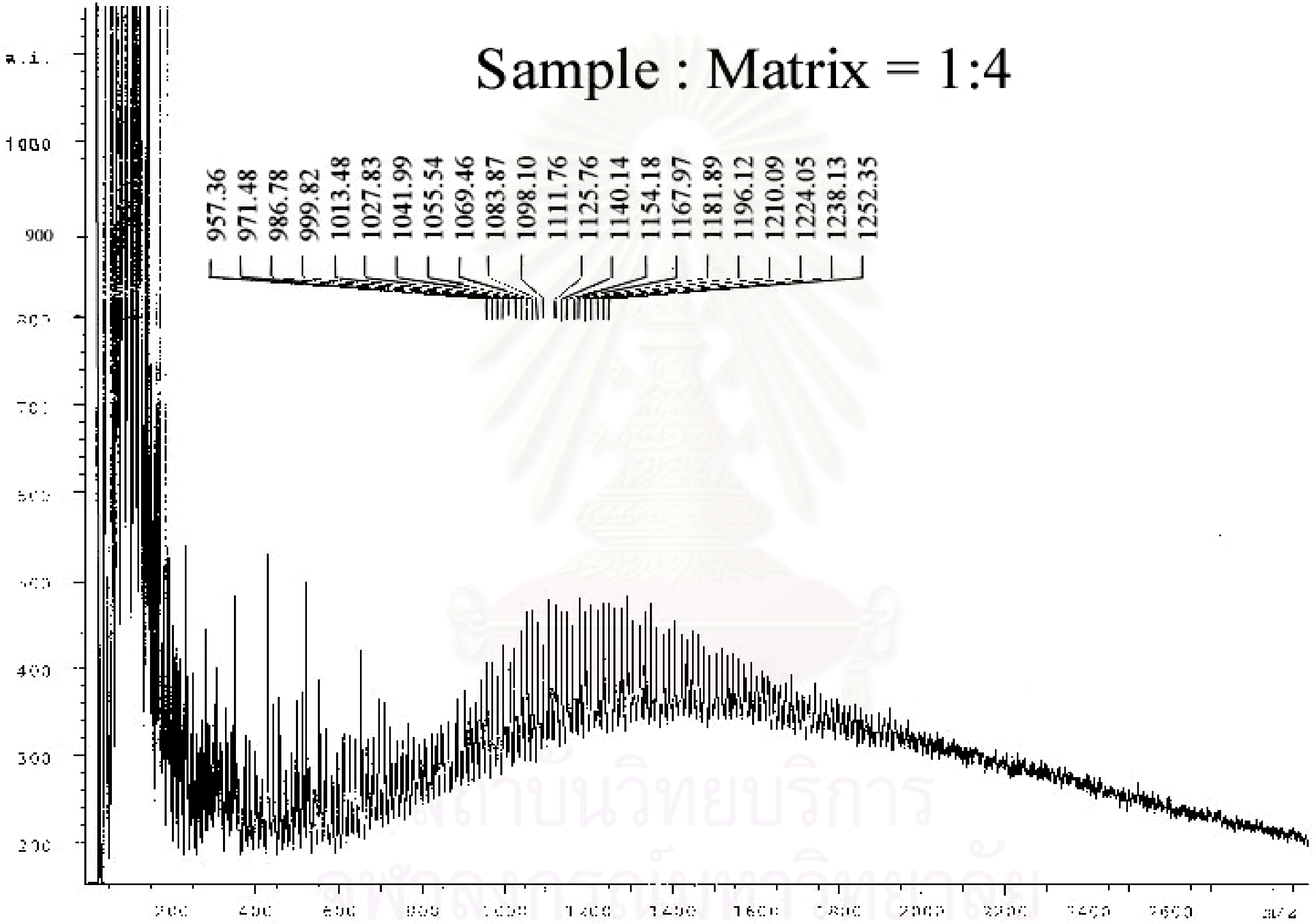


Figure A6 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA ratio of 1:4, laser power of 180 μJ.

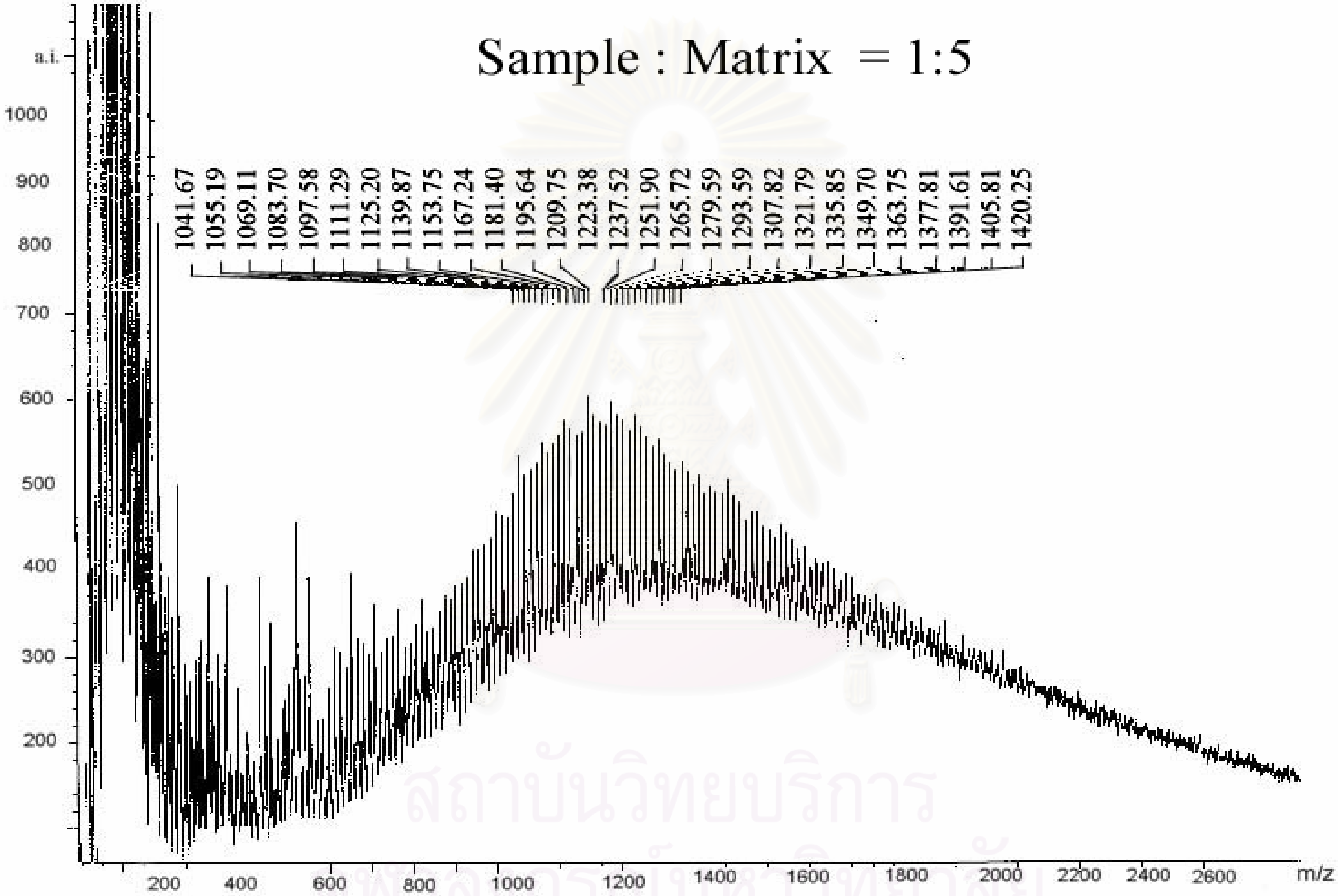


Figure A7 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA ratio of 1:5, laser power of 180 μJ.

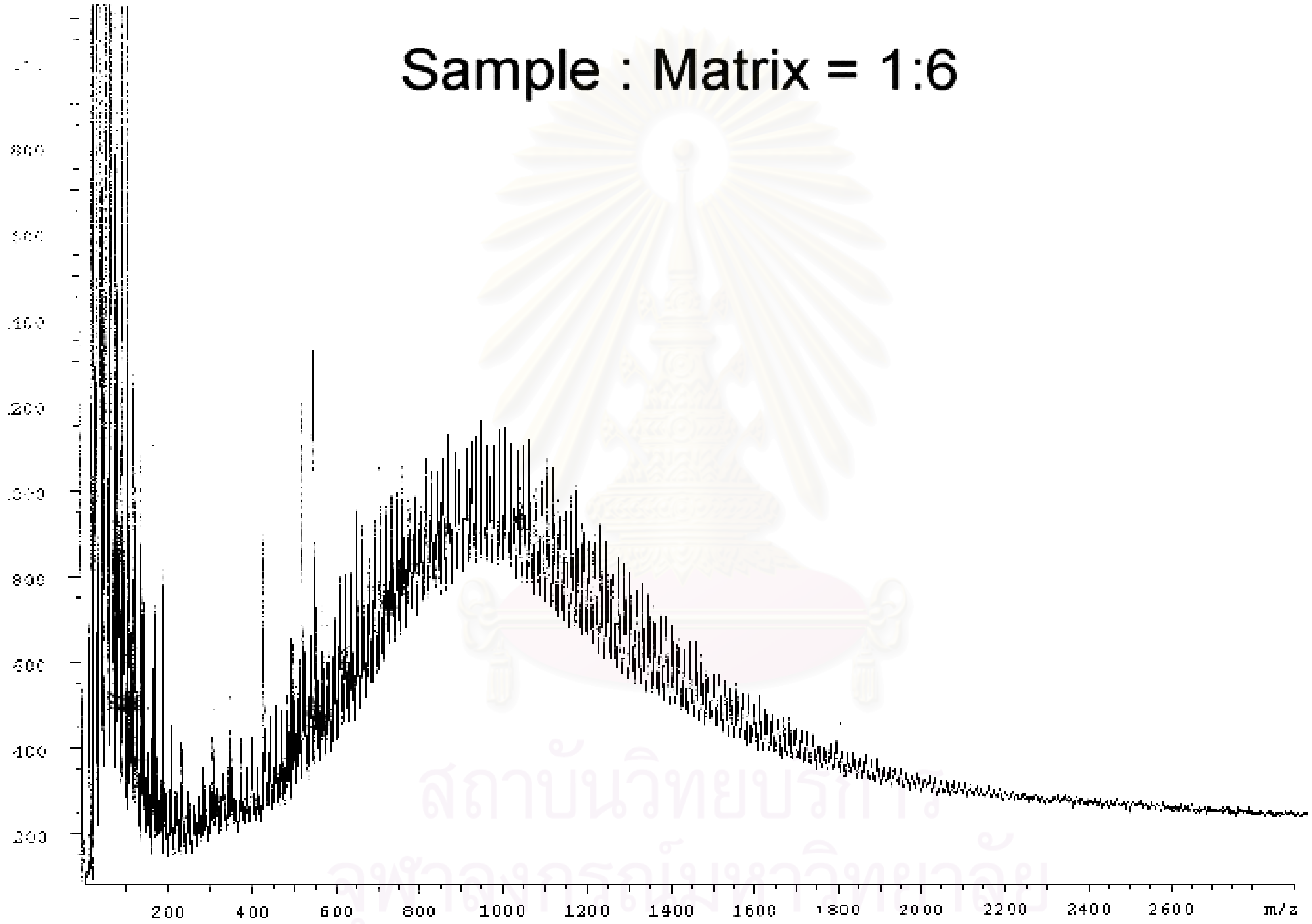


Figure A8 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA ratio of 1:6, laser power of 180 μJ.

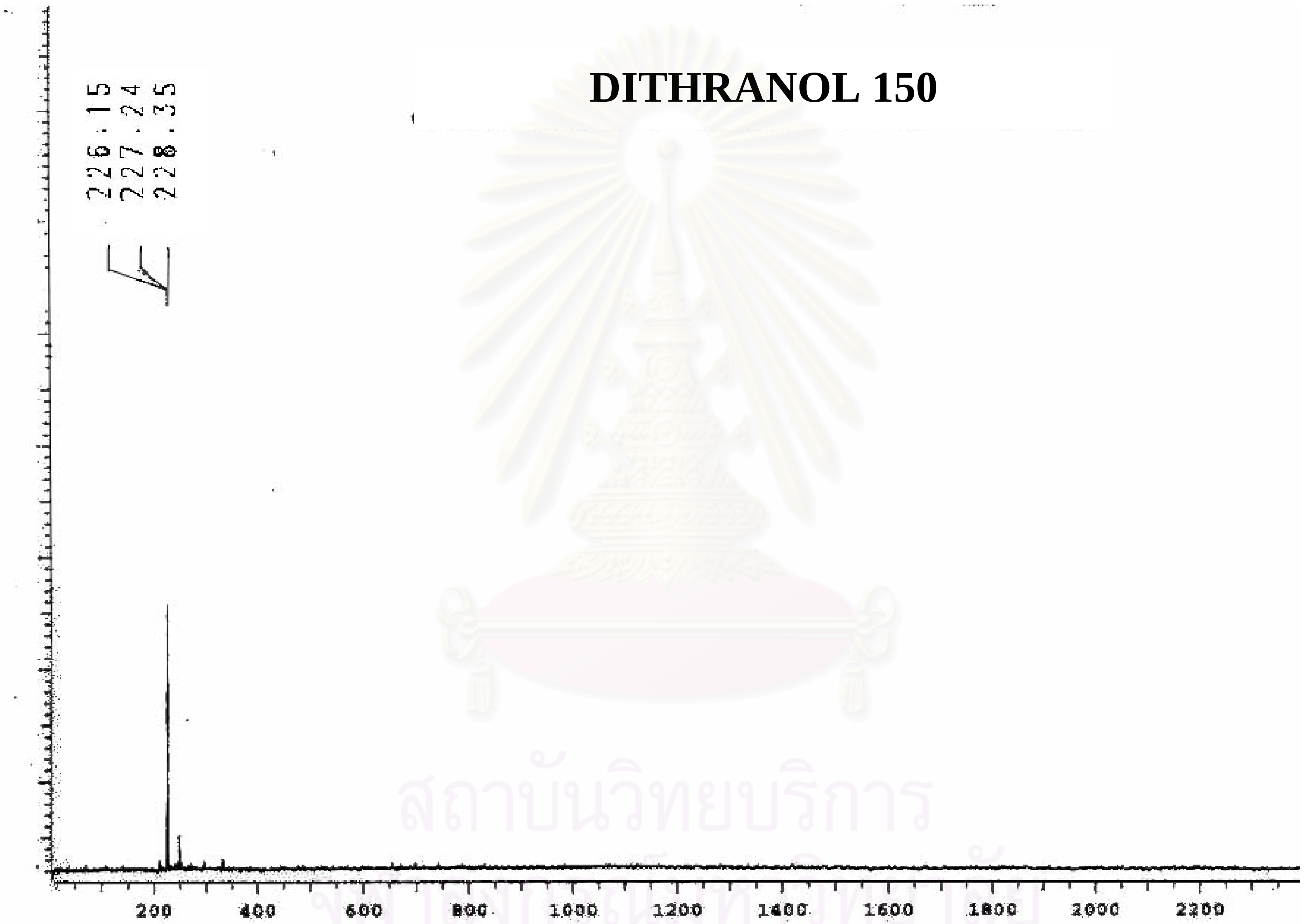


Figure A9 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:dithranol ratio of 1:5, laser power of 150 μJ.

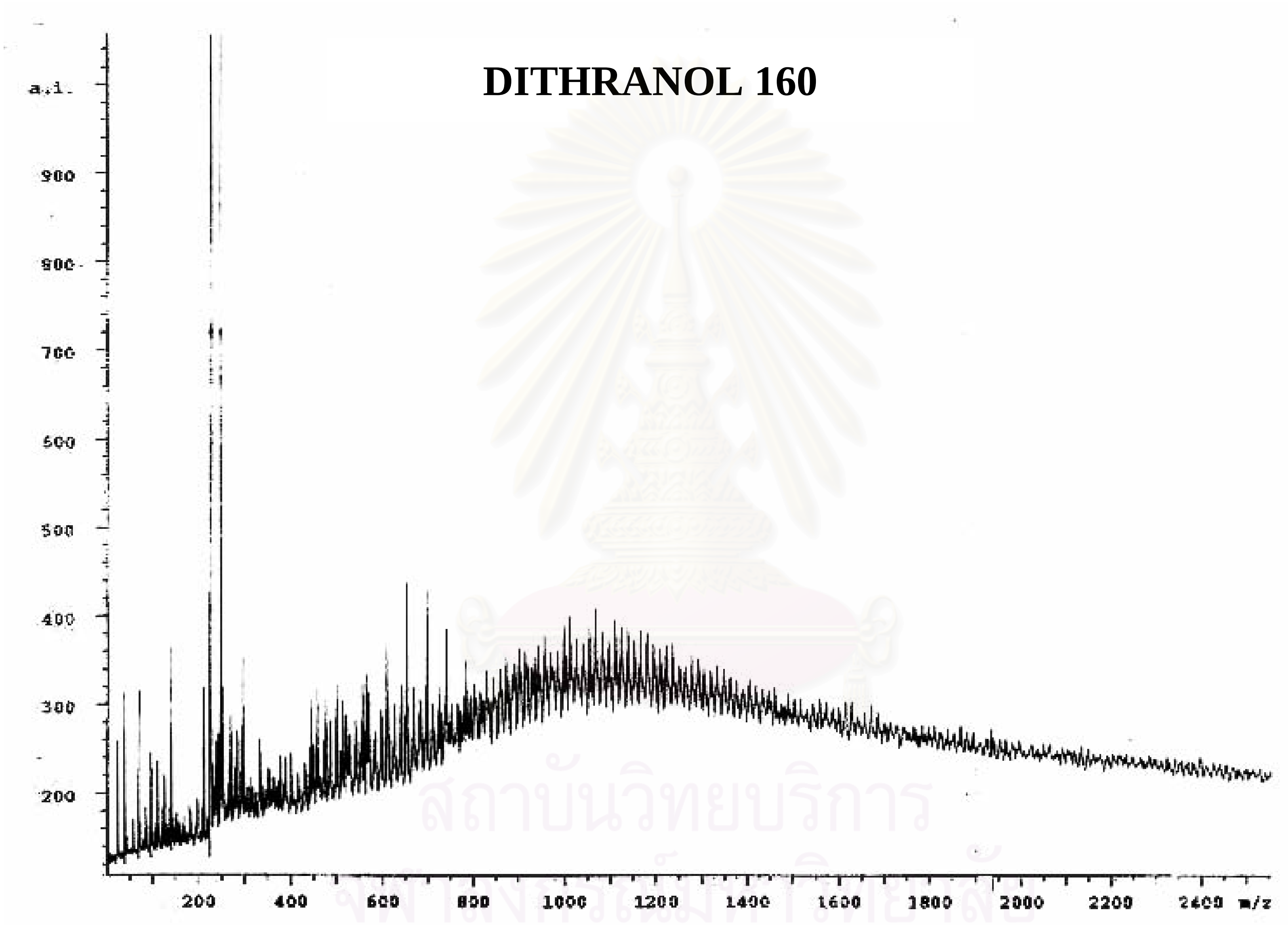


Figure A10 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:dithranol ratio of 1:5, laser power of 160 μJ.

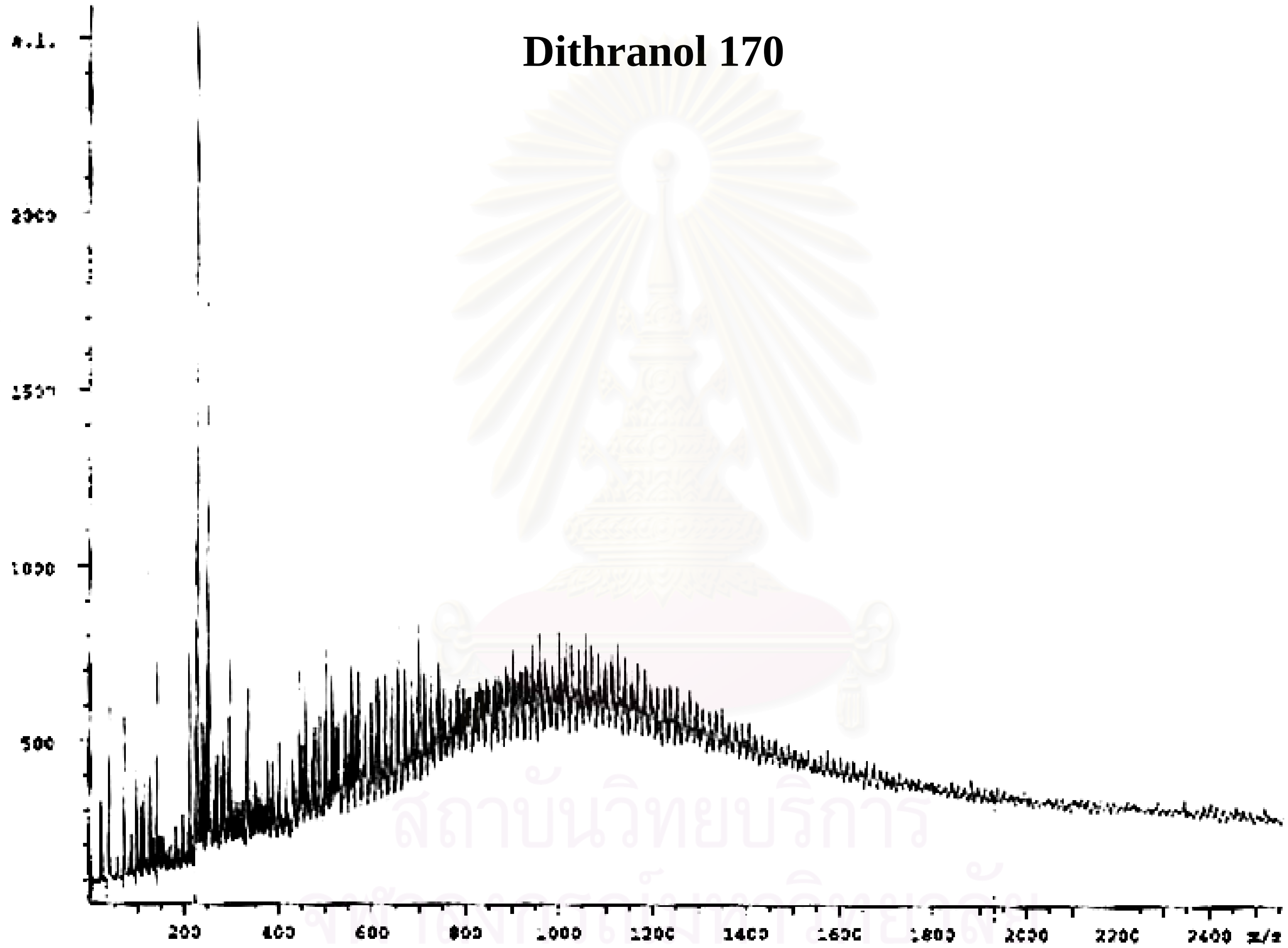


Figure A11 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:dithranol ratio of 1:5, laser power of 170 μJ.

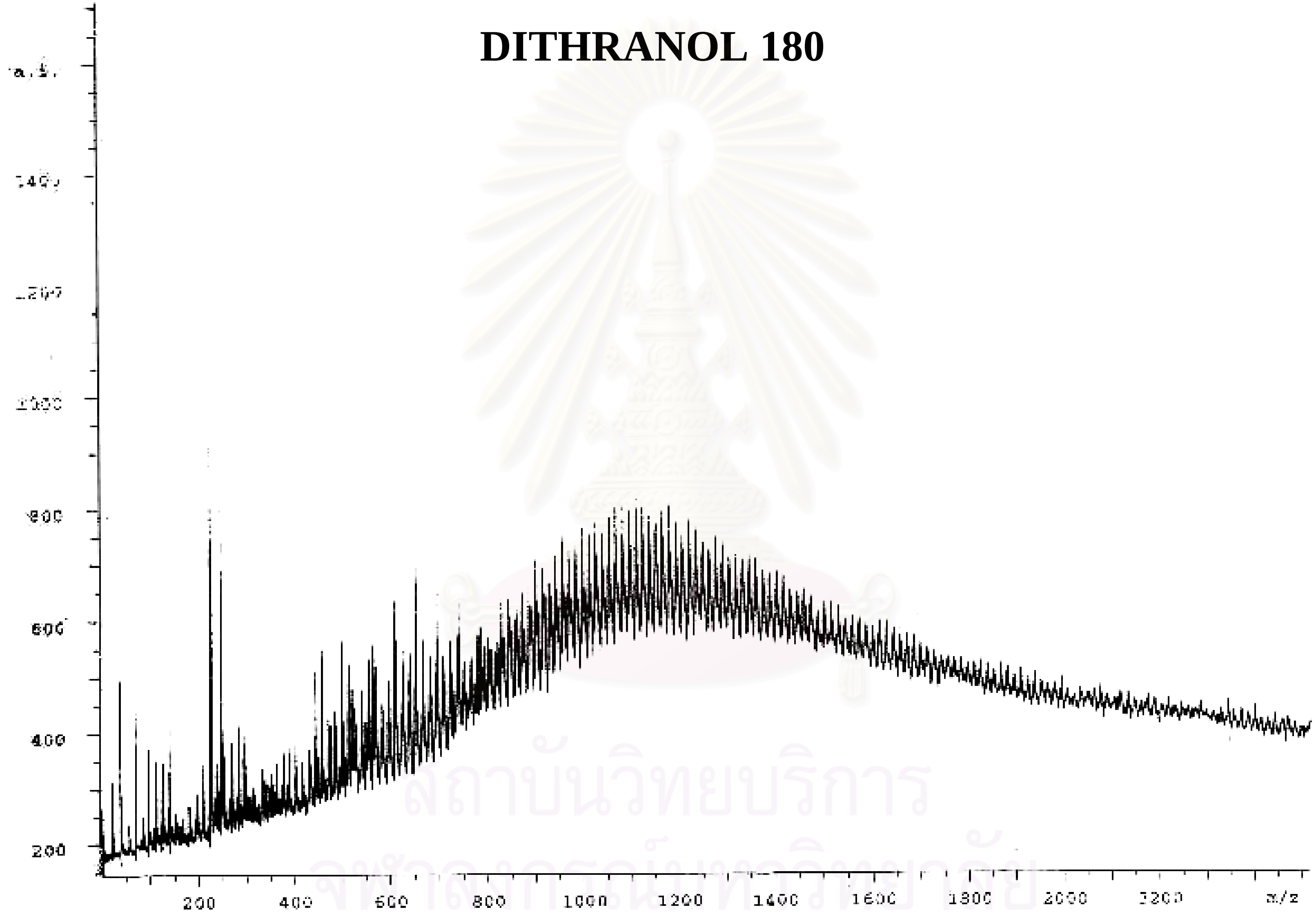


Figure A12 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:dithranol ratio of 1:5, laser power of 180 μJ.

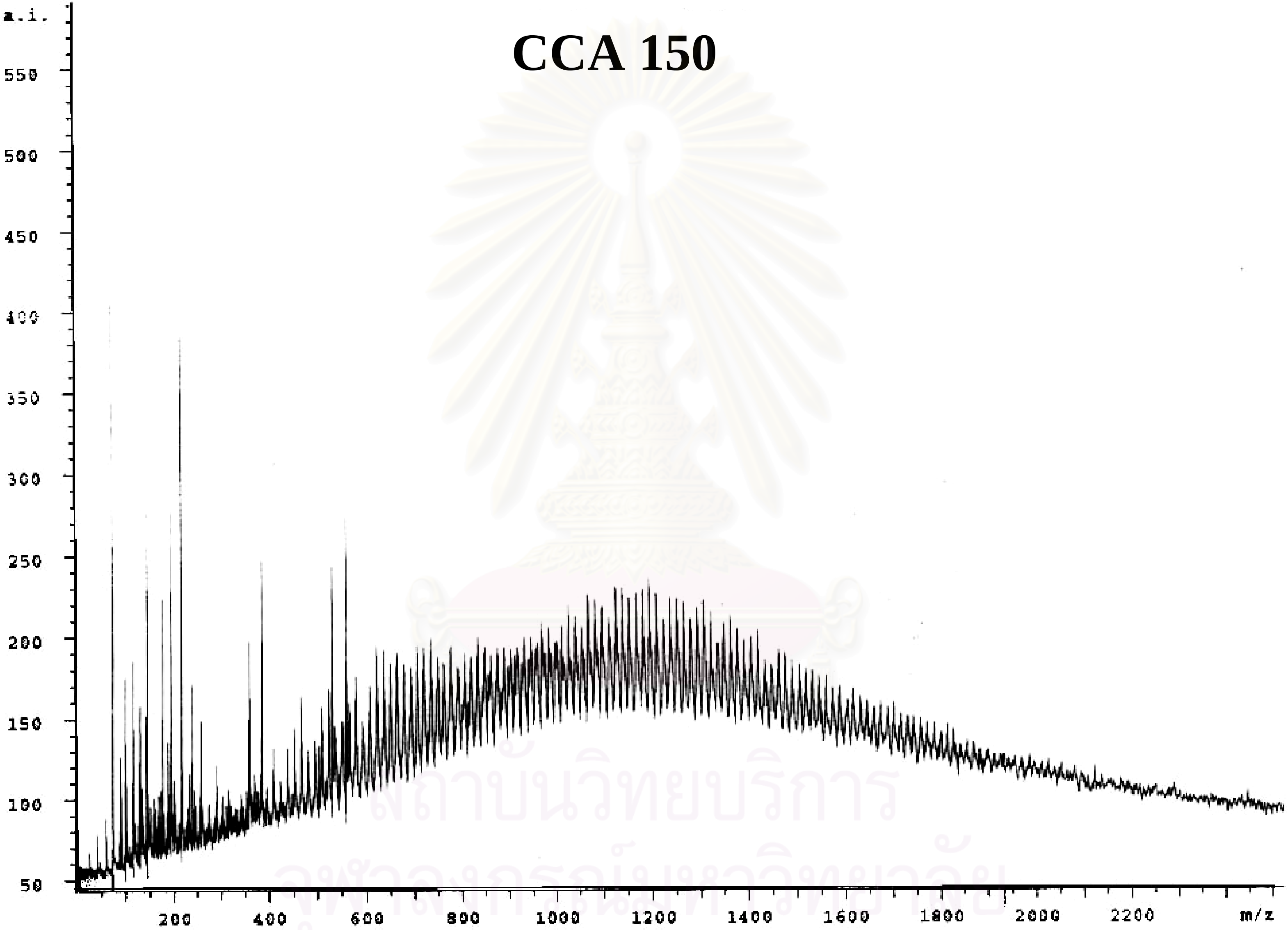


Figure A13 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA ratio of 1:5, laser power of 150 μJ.

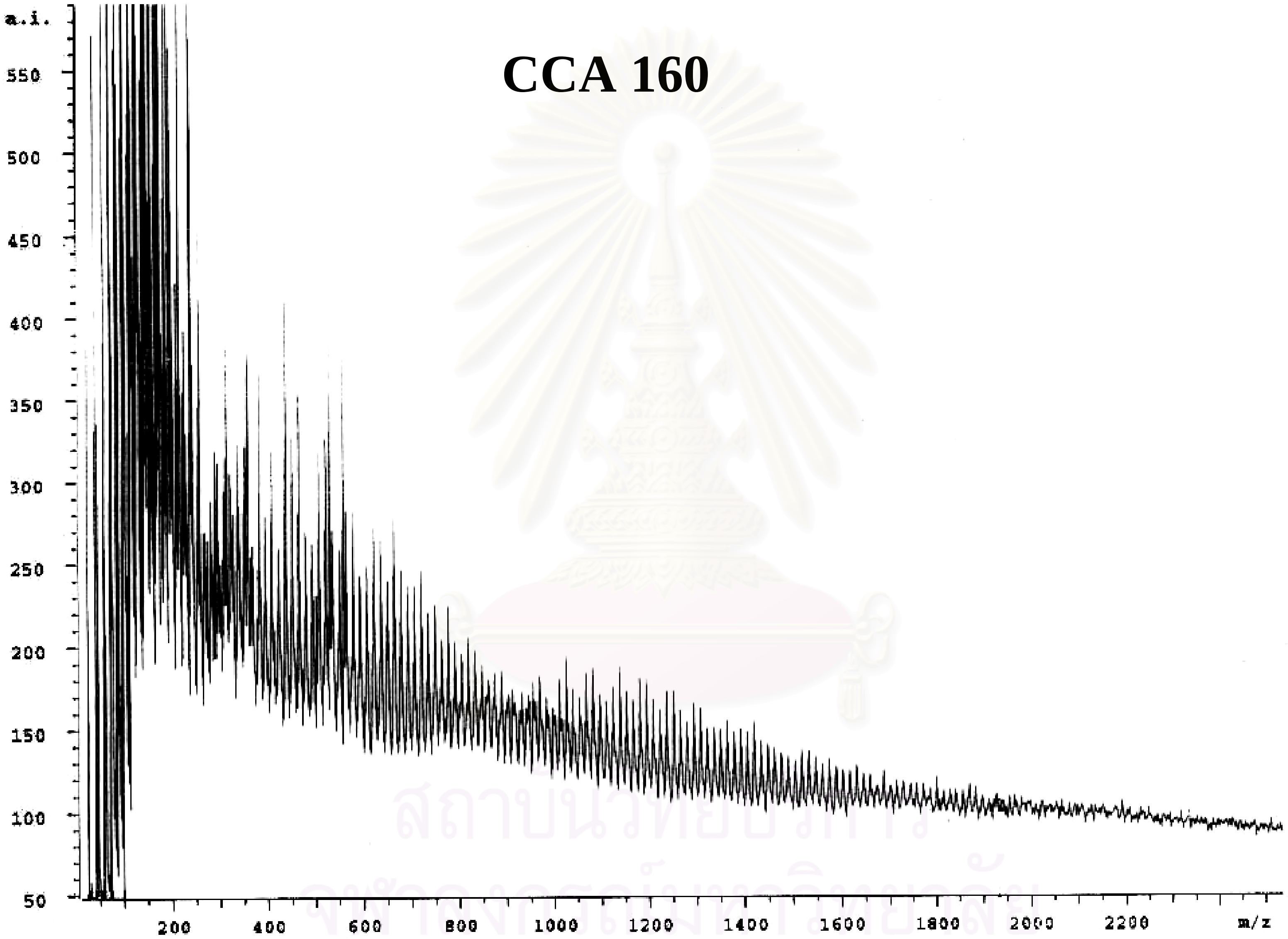


Figure A14 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA ratio of 1:5, laser power of 160 μJ.

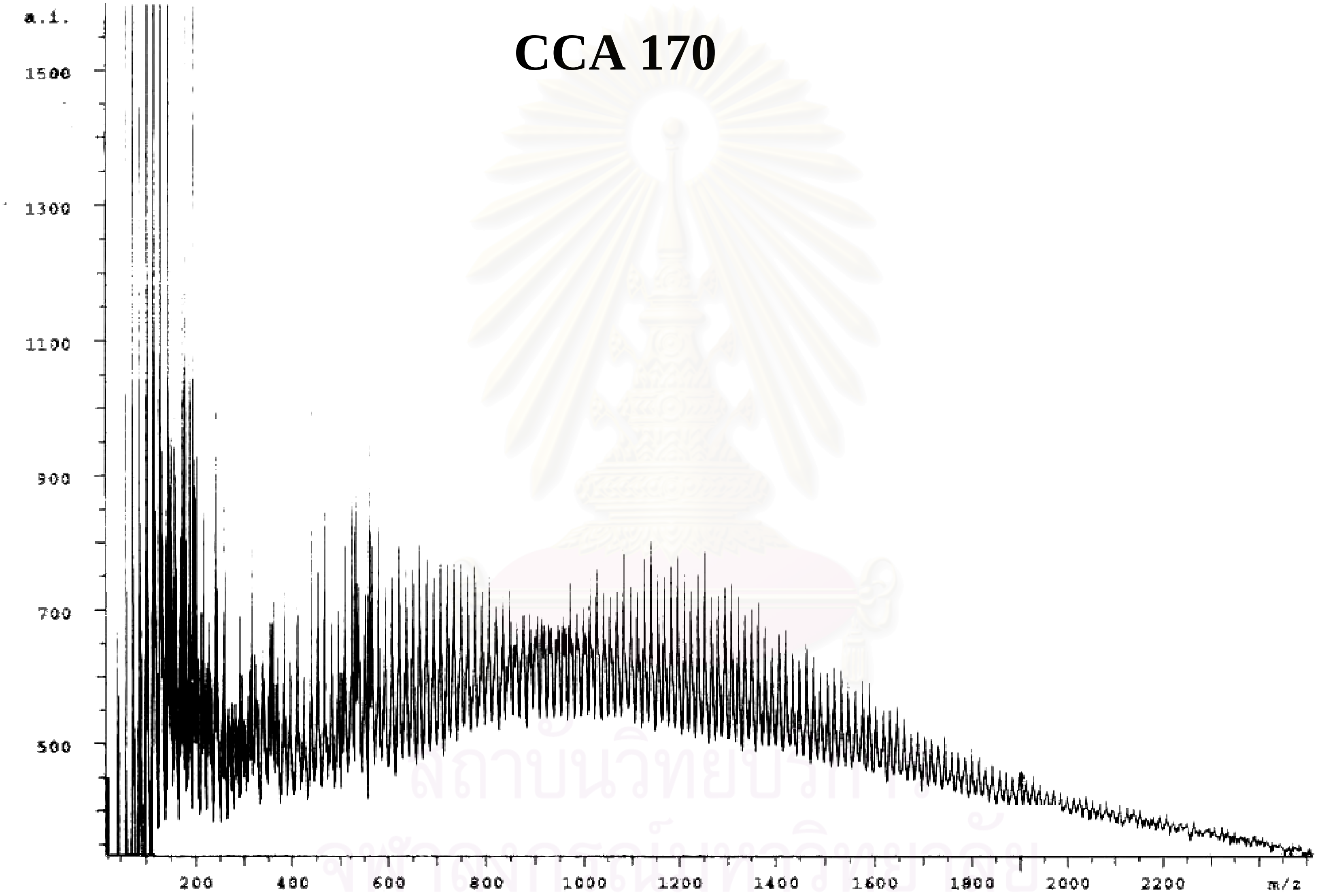


Figure A15 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA ratio of 1:5, laser power of 170 μJ.

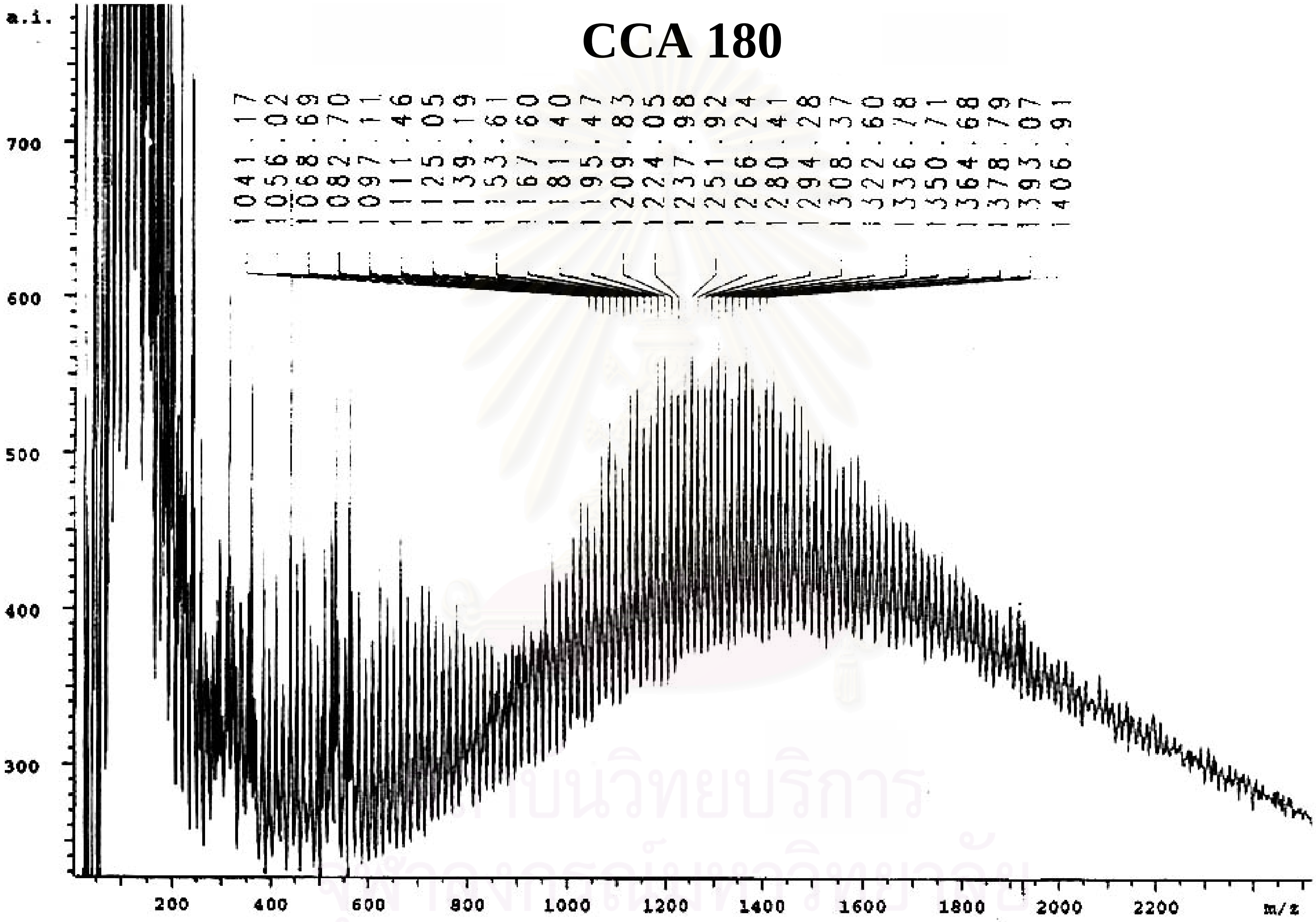


Figure A16 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA ratio of 1:5, laser power of 180 μJ.

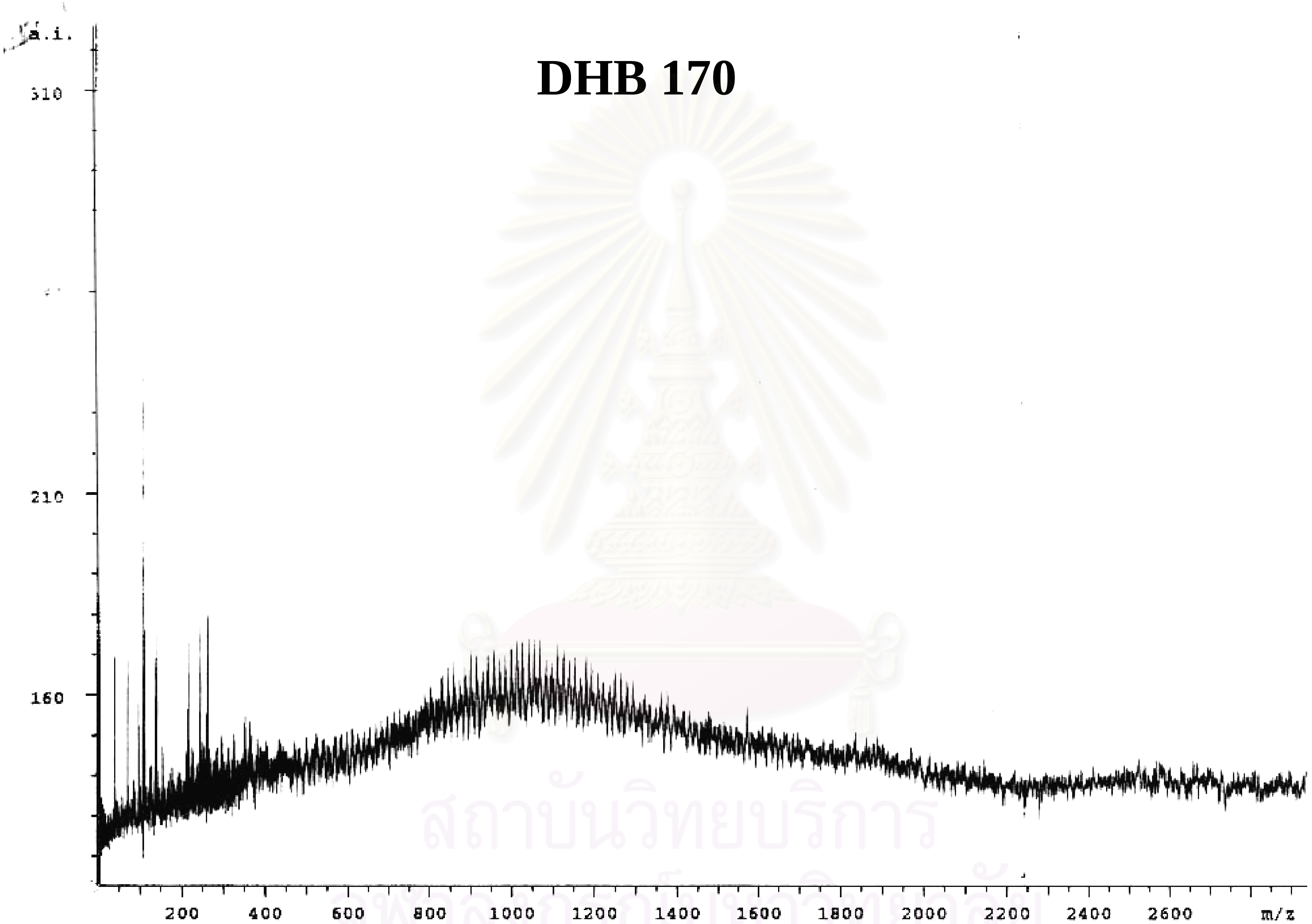


Figure A17 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:DHB ratio of 1:5, laser power of 170 μJ.

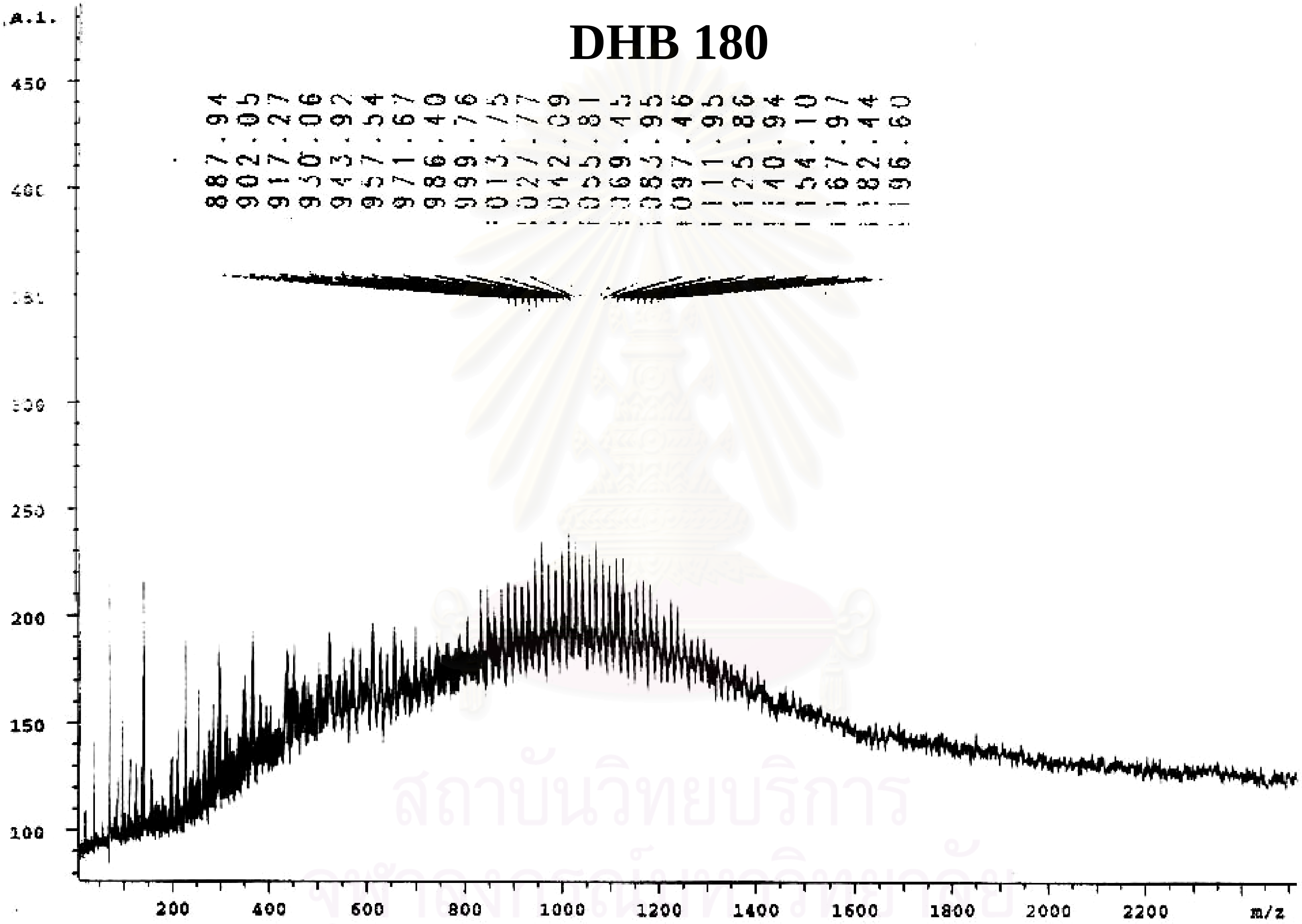


Figure A18 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:DHB ratio of 1:5, laser power of 180 μJ.

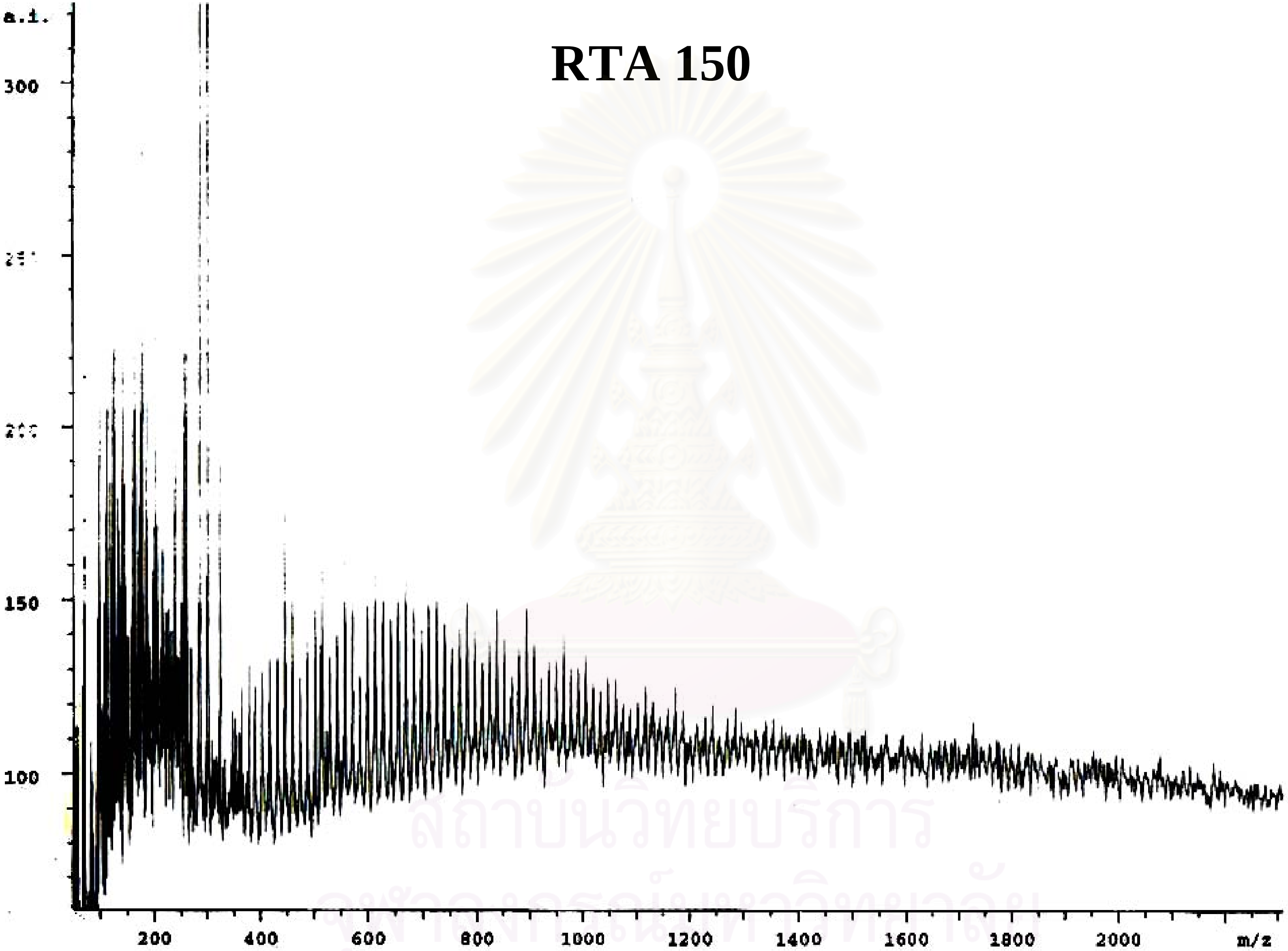


Figure A19 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:RTA ratio of 1:5, laser power of 150 μJ.

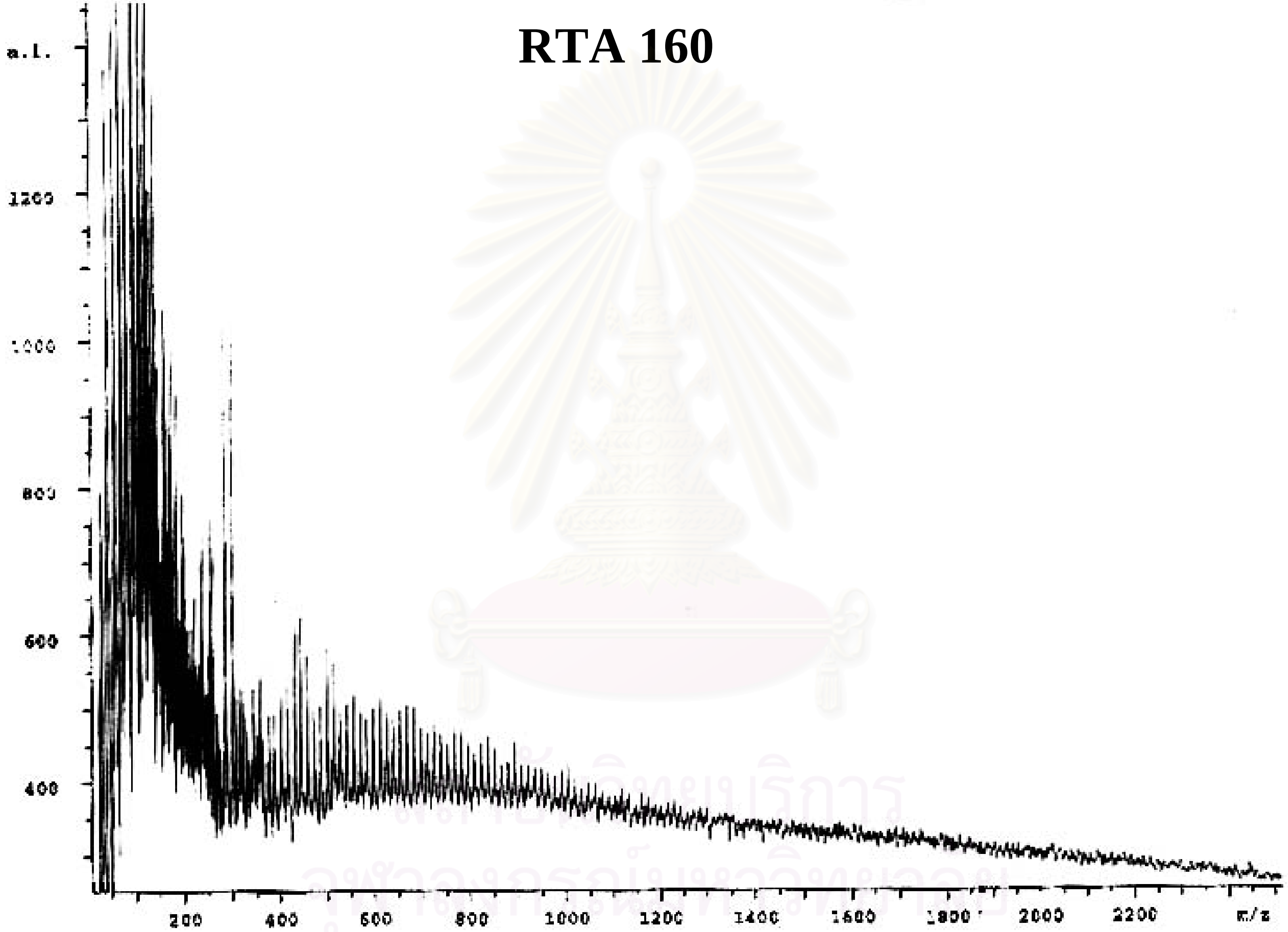
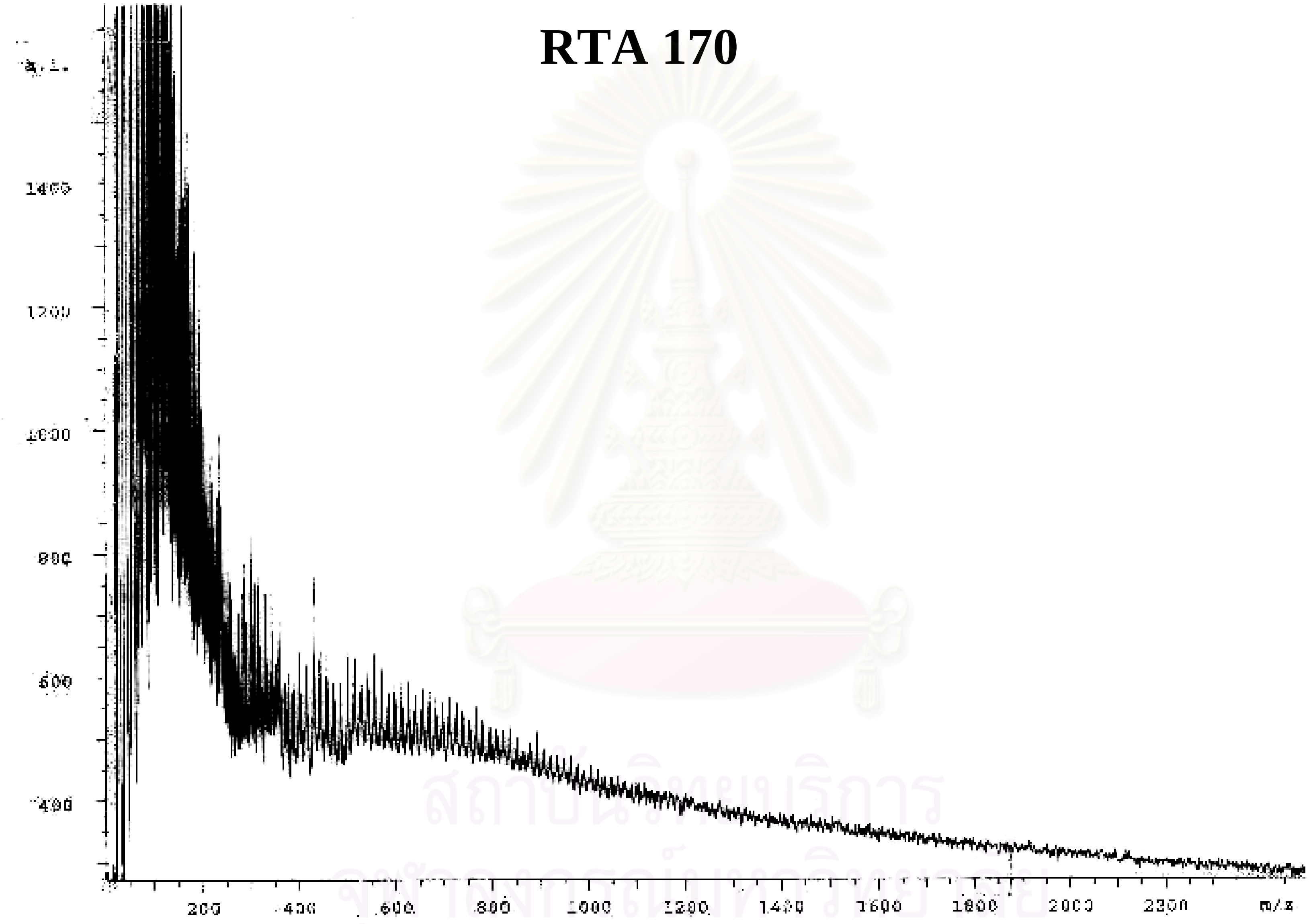


Figure A20 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:RTA ratio of 1:5, laser power of 160 μJ.



RTA 170

Figure A21 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:RTA ratio of 1:5, laser power of 170 μJ.

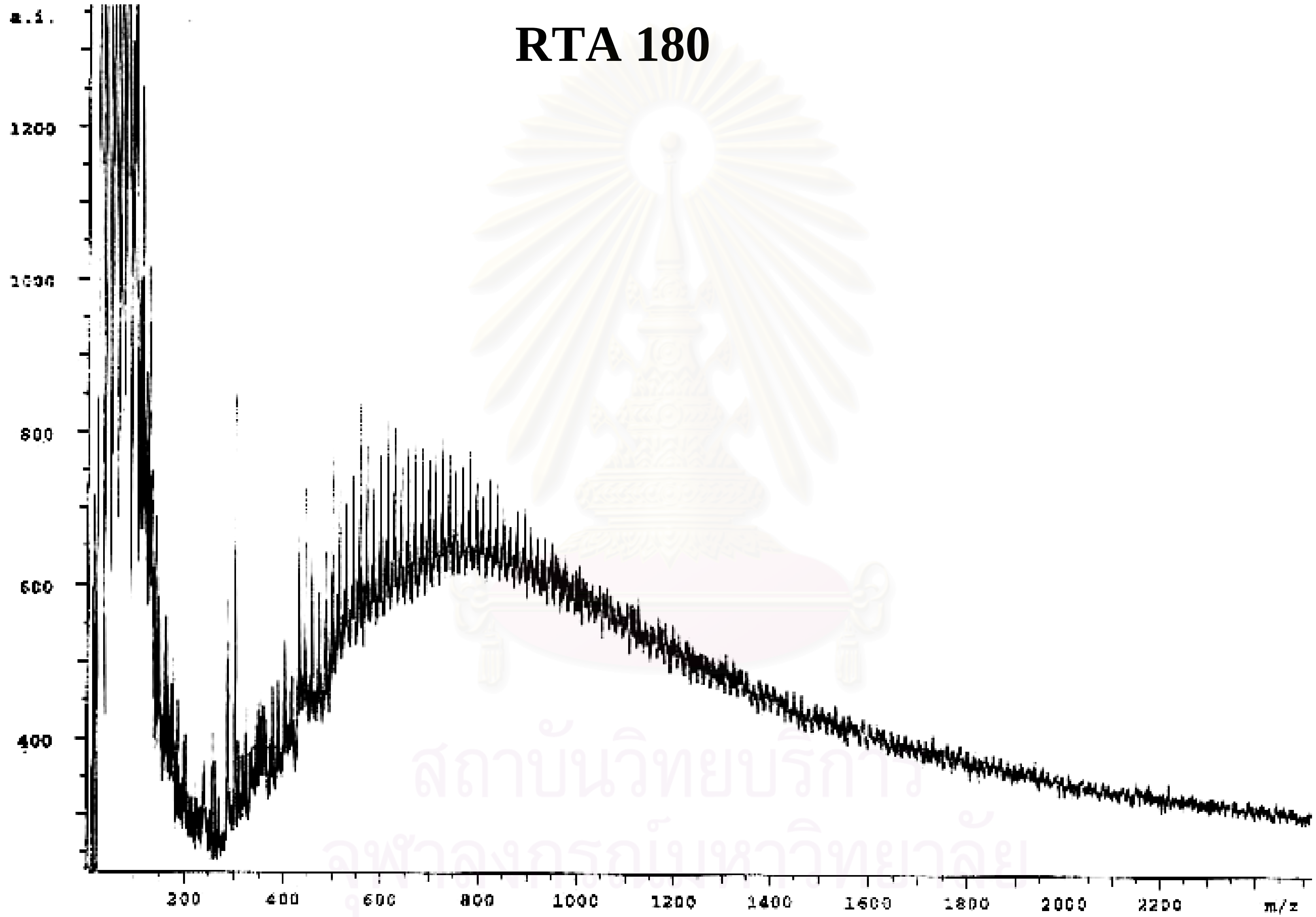


Figure A22 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:RTA ratio of 1:5, laser power of 180 μJ.

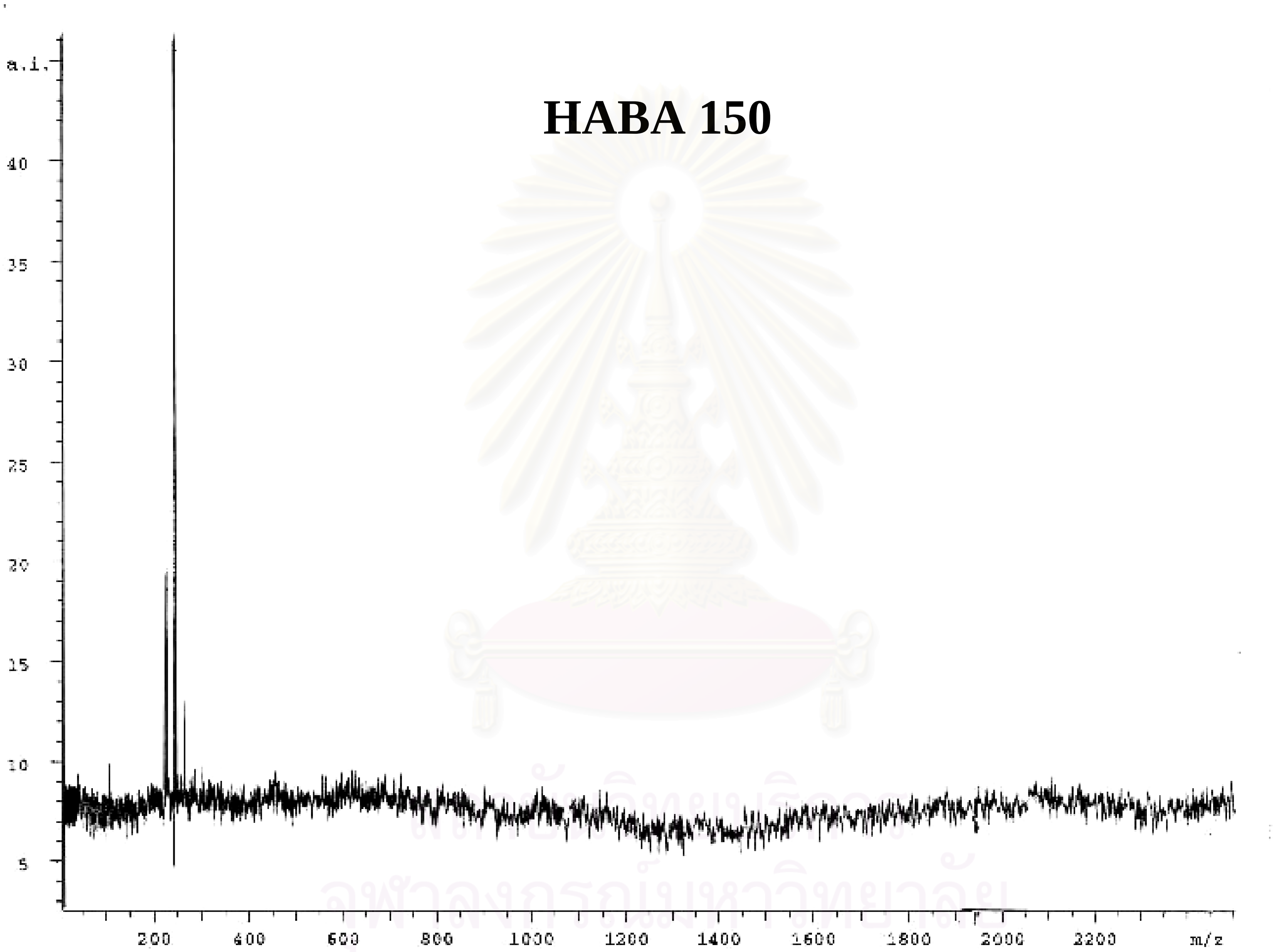


Figure A23 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:HABA ratio of 1:5, laser power of 150 μJ.

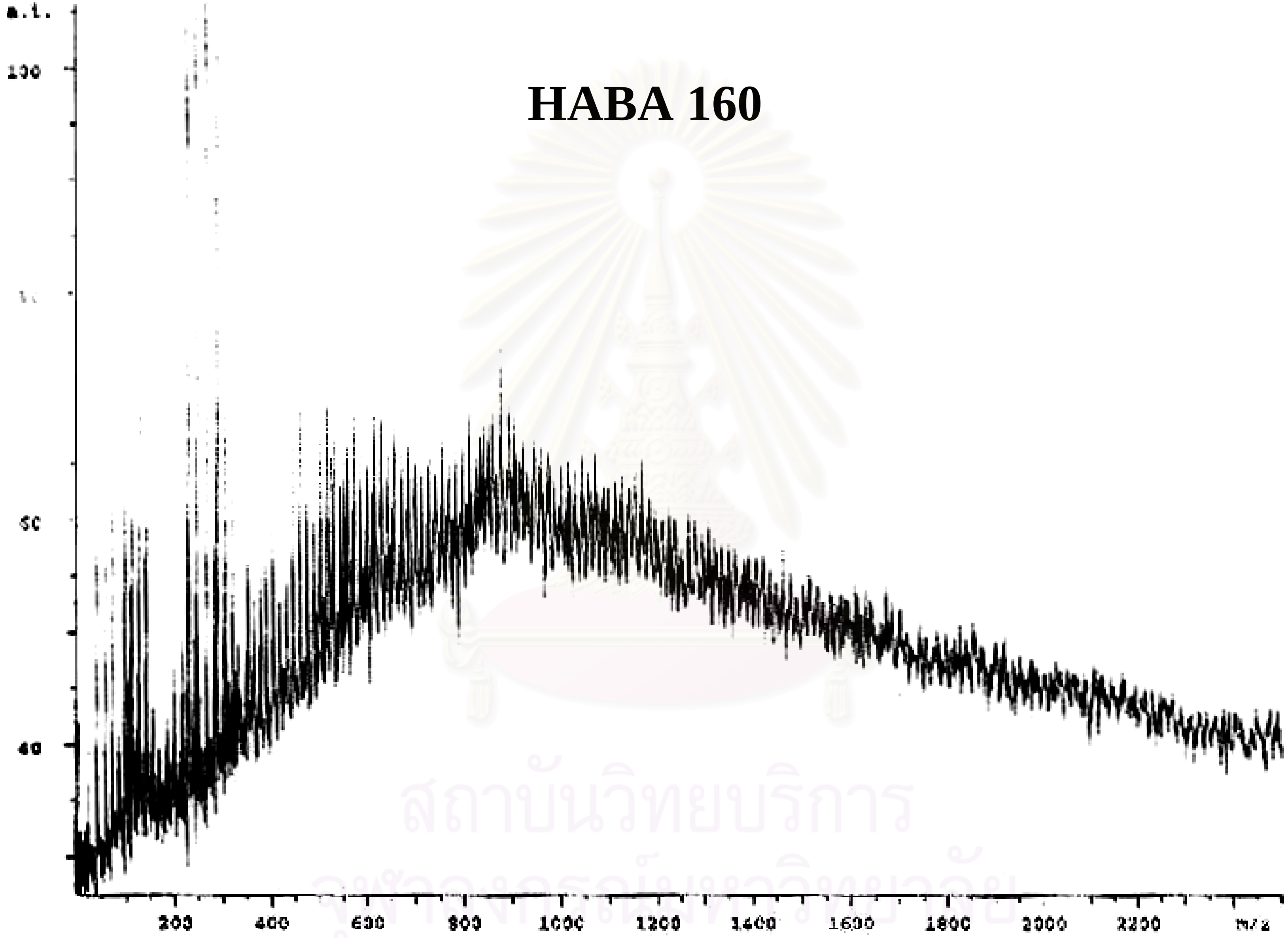


Figure A24 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:HABA ratio of 1:5, laser power of 160 μJ.

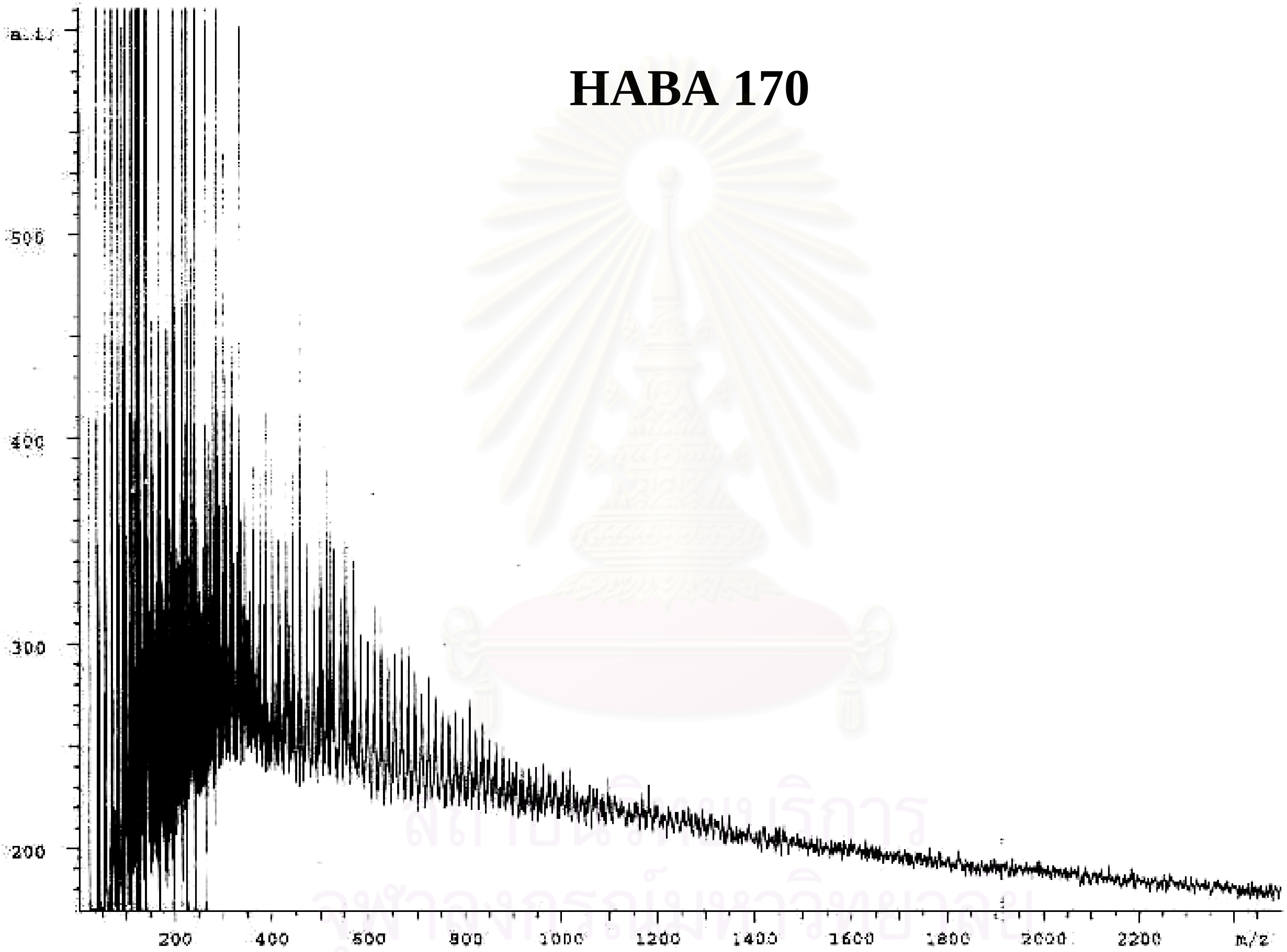


Figure A25 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:HABA ratio of 1:5, laser power of 170 μJ.

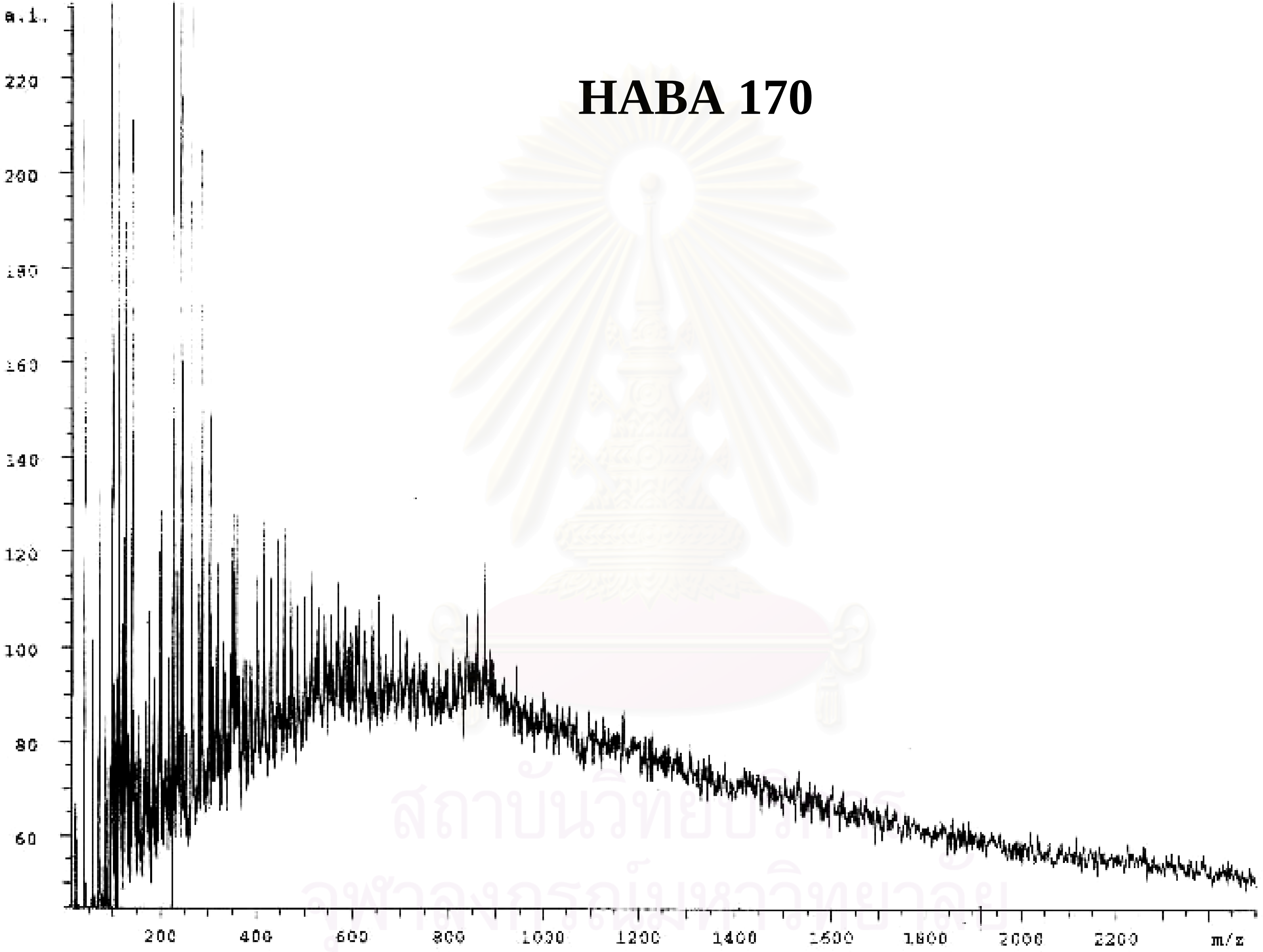


Figure A26 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:HABA ratio of 1:5, laser power of 180 μJ

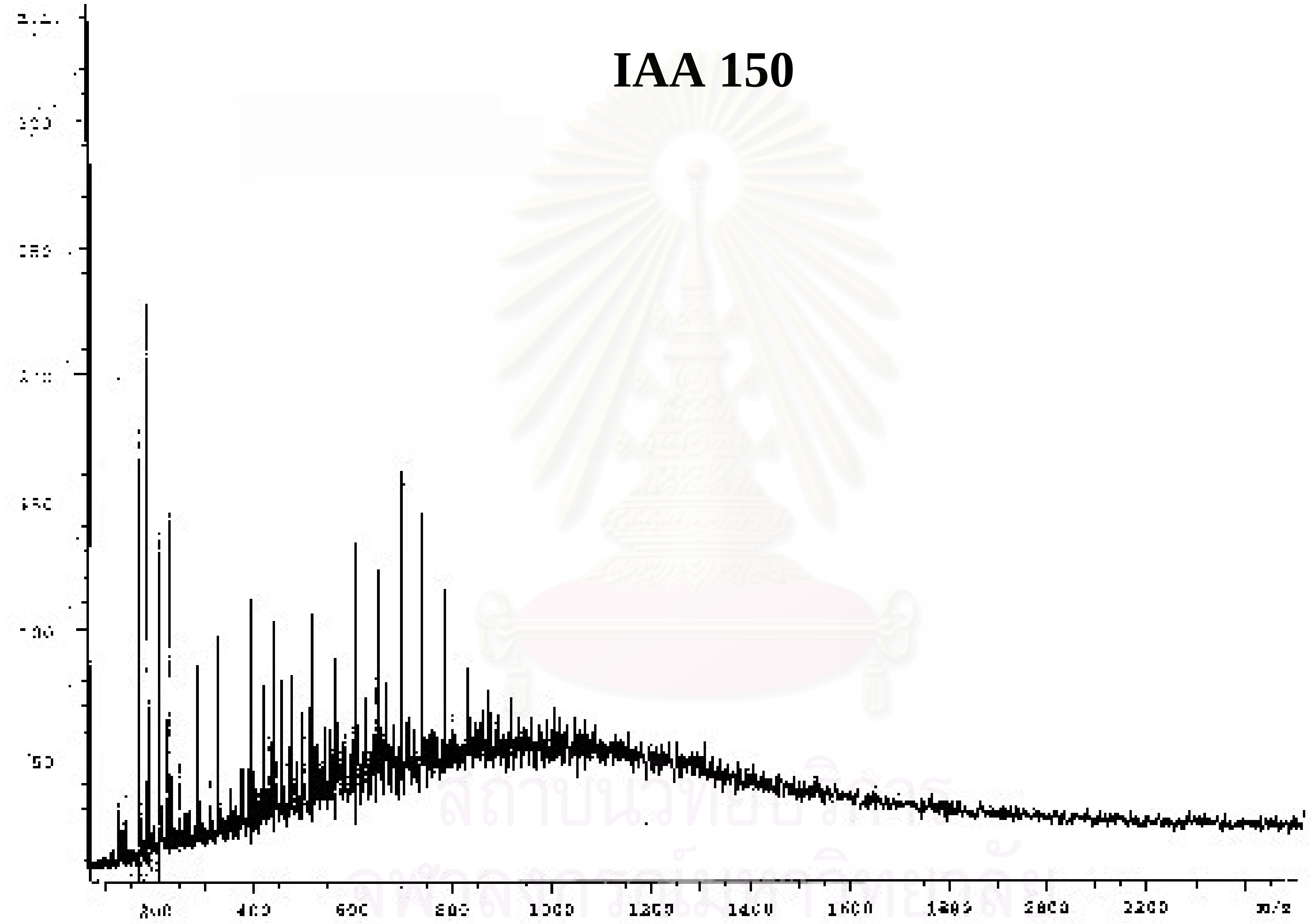


Figure A27 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:IAA ratio of 1:5, laser power of 150 μJ.

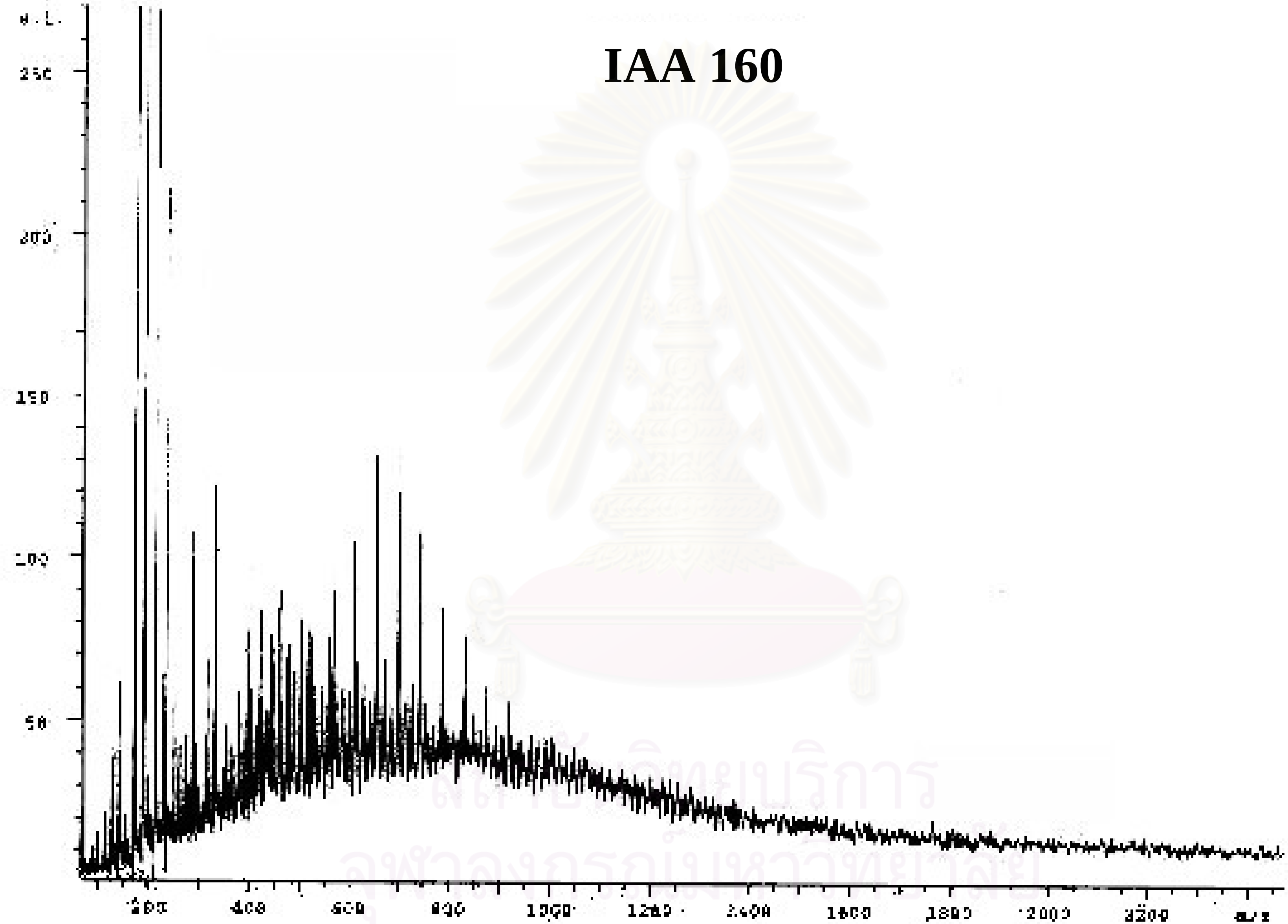


Figure A28 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:IAA ratio of 1:5, laser power of 160 μJ.

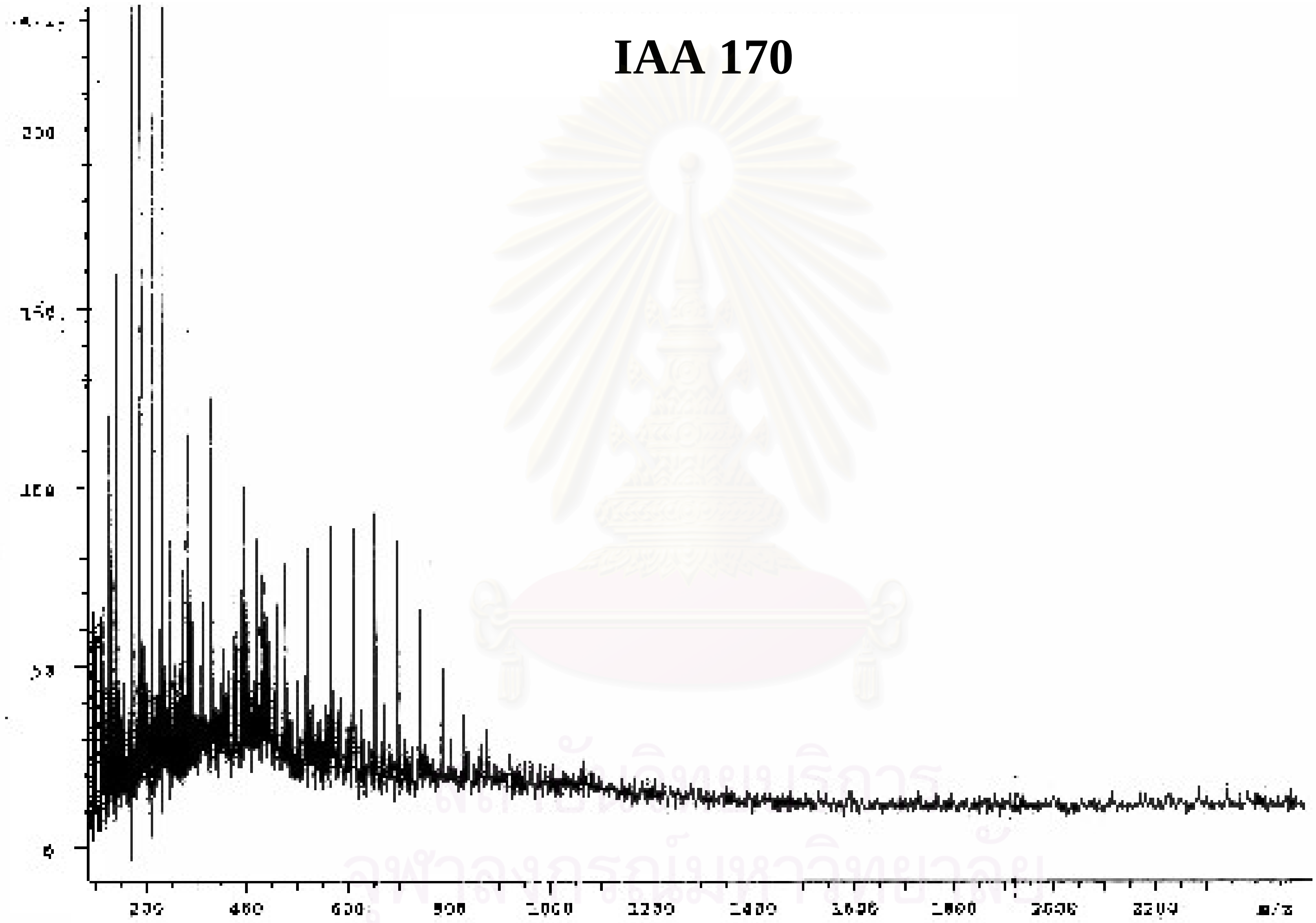


Figure A29 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:IAA ratio of 1:5, laser power of 170 μJ.

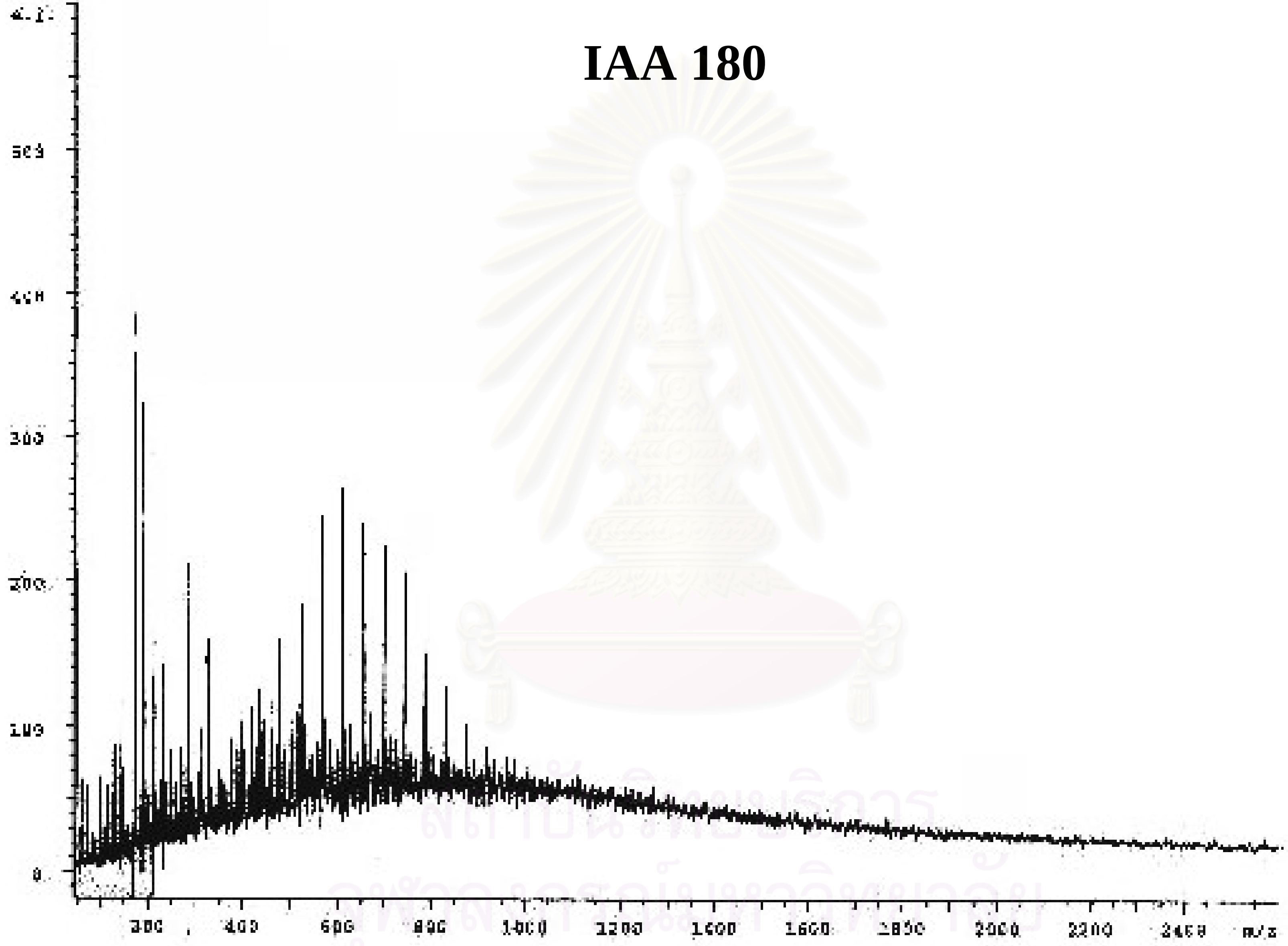


Figure A30 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:IAA ratio of 1:5, laser power of 180 μJ.

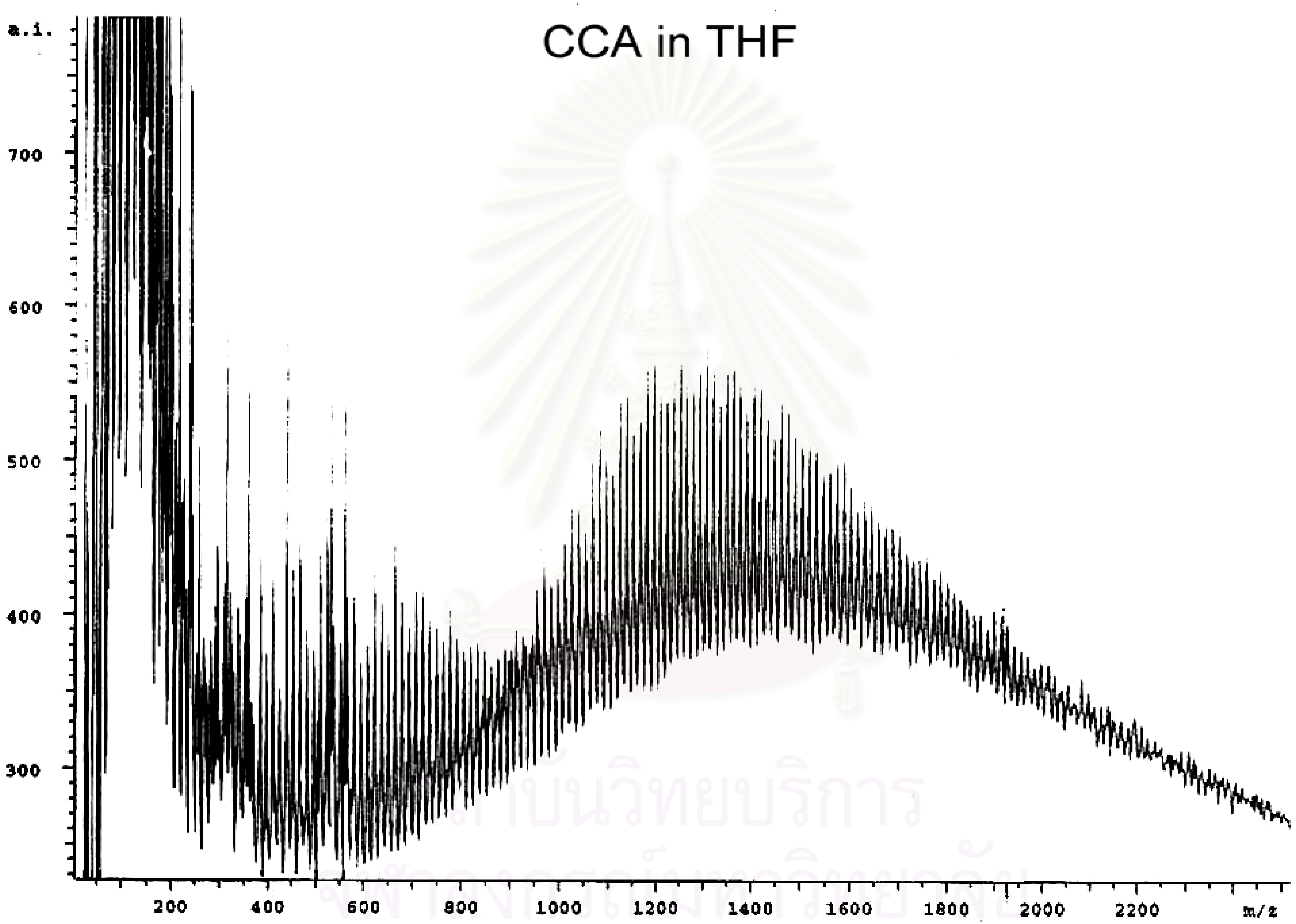


Figure A31 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA (THF as a solvent) ratio of 1:5, laser power of 180 μJ.

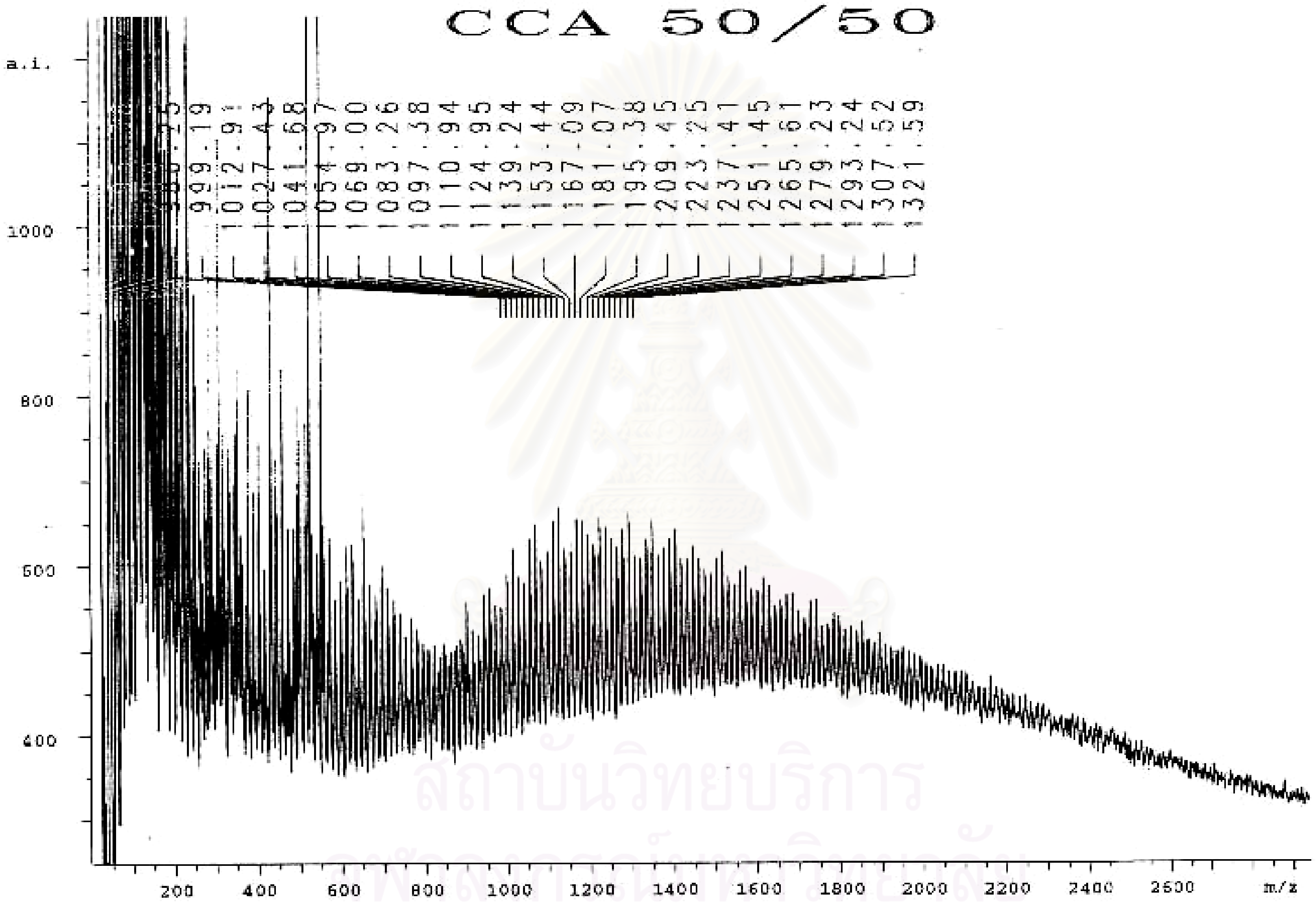


Figure A32 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA(ETOH /ACN (50:50, 0.1%(v/v) TFA as a solvent) ratio of 1:5, laser power of 180 μJ.

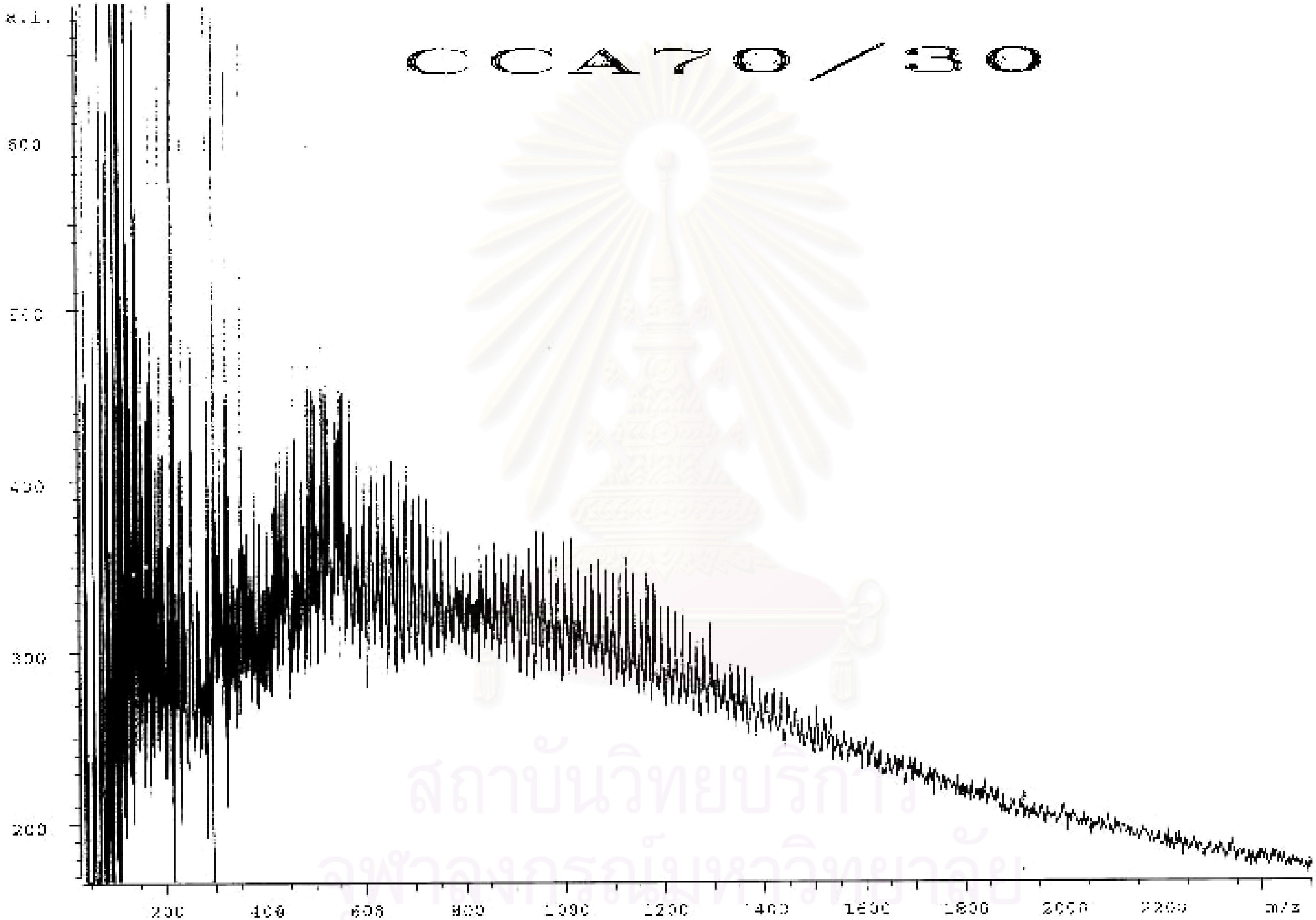


Figure A33 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA (H_2O /ACN (70:30, 0.1%(v/v) TFA as a solvent) ratio of 1:5, laser power of 180 μJ.

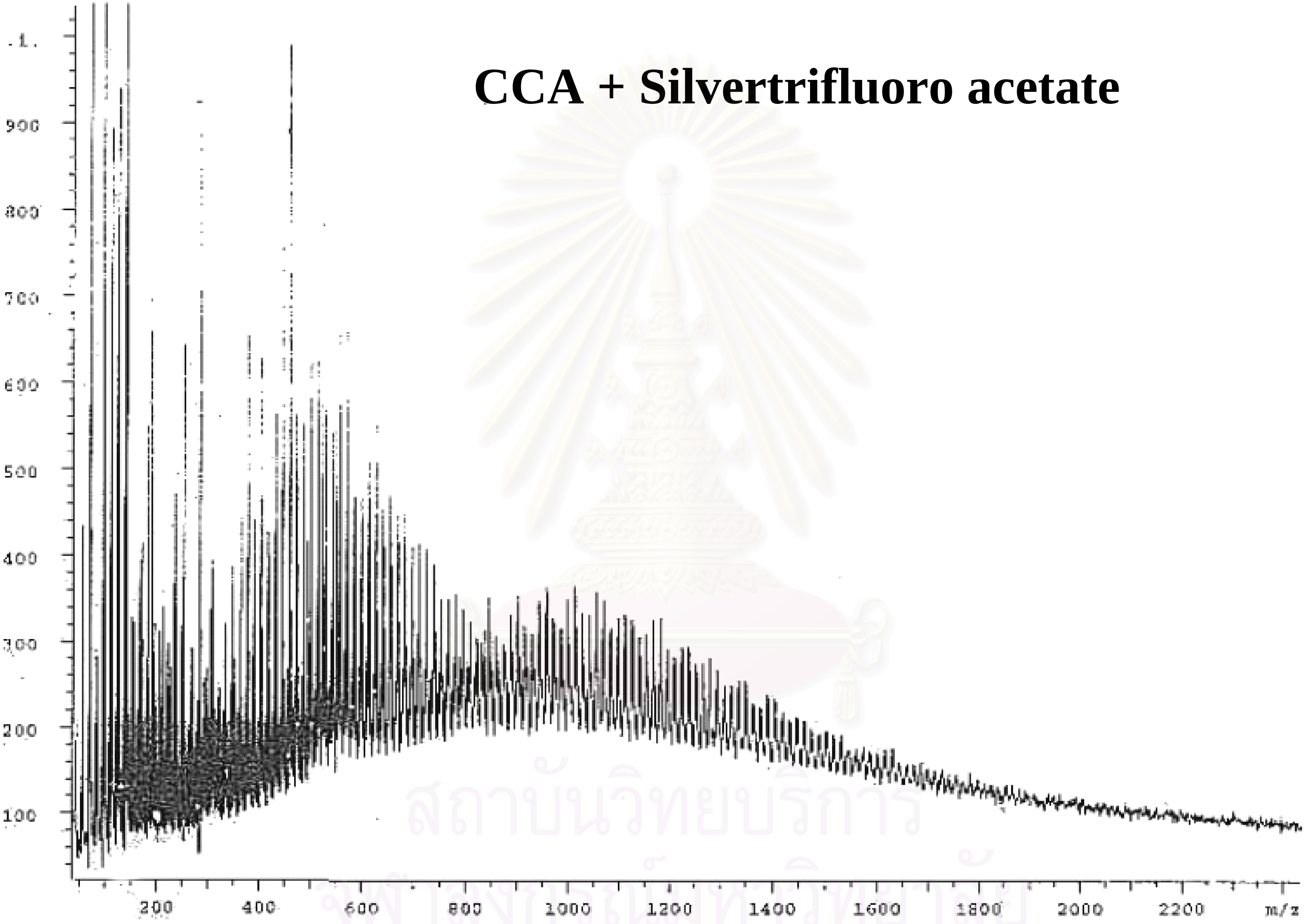


Figure A34 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA (THF as a solvent) ratio of 1:5, AgTFA as a cationizing agent, laser power of 180 μJ.

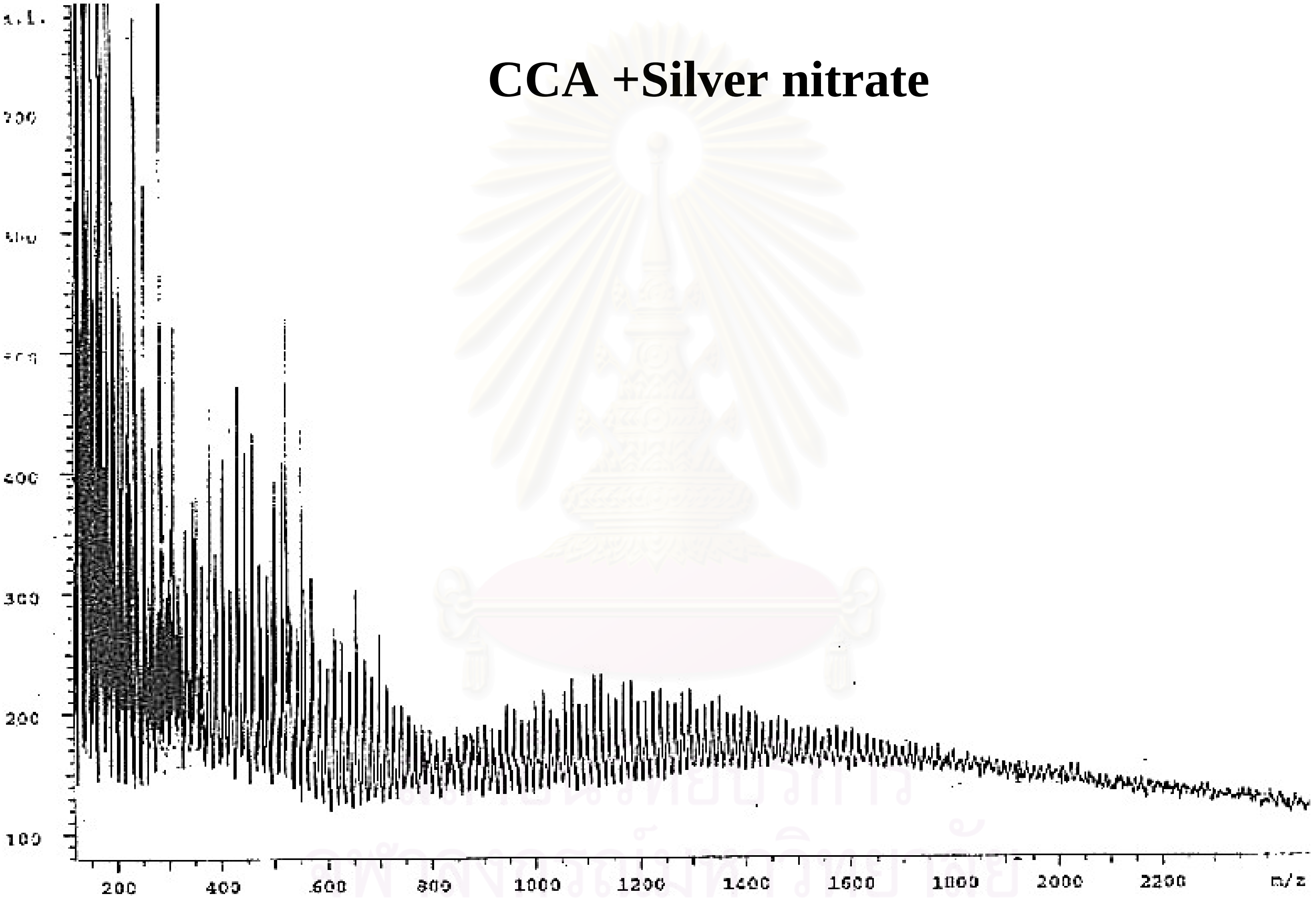


Figure A35 MALDI-MS spectrum of dispersant using a dried droplet method, an analyte:CCA (THF as a solvent) ratio of 1:5, $AgNO_3$ as a cationizing agent, laser power of 180 μJ.

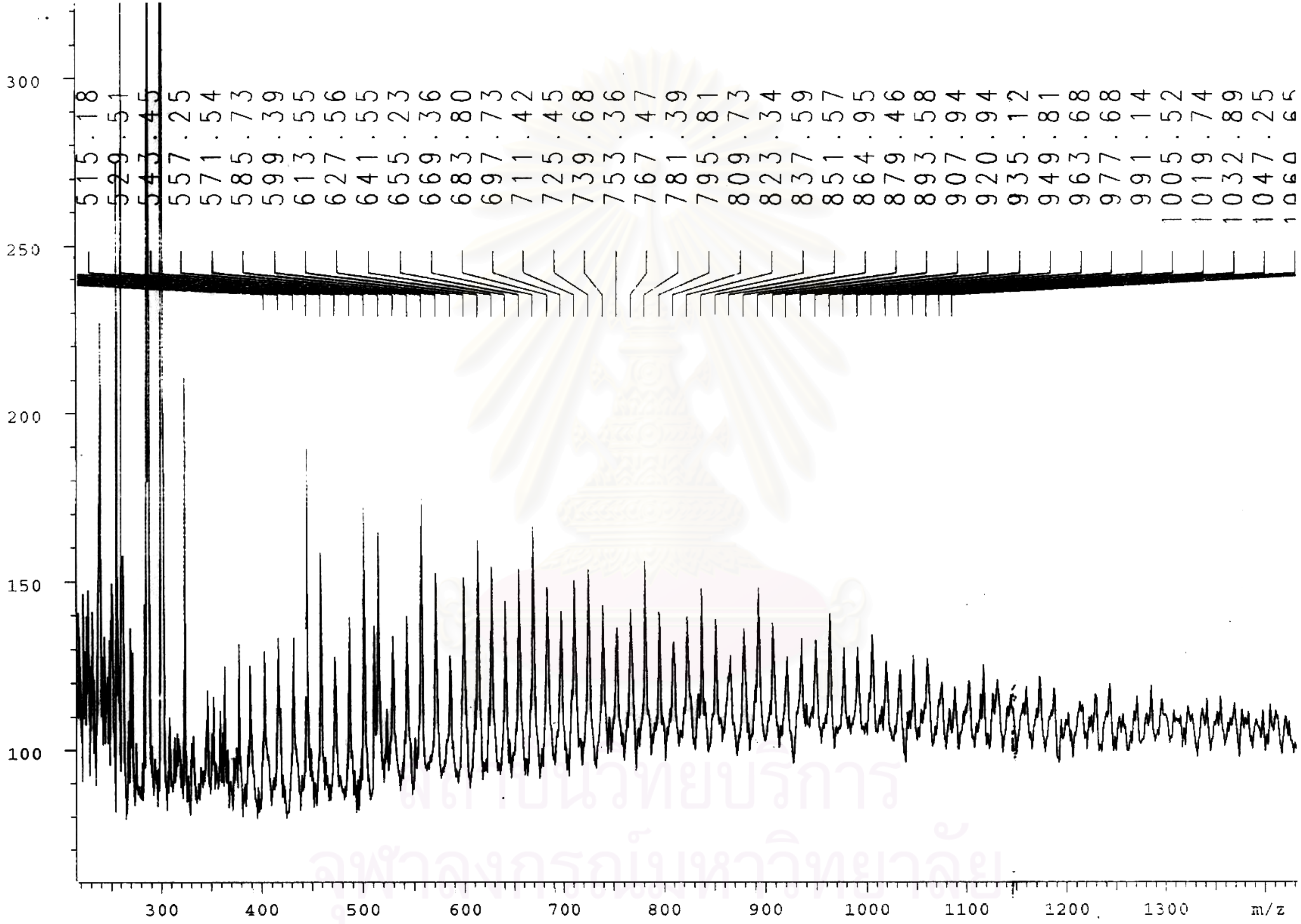


Figure A36 Molecular weight distribution of polymer range m/z of 400-1200.

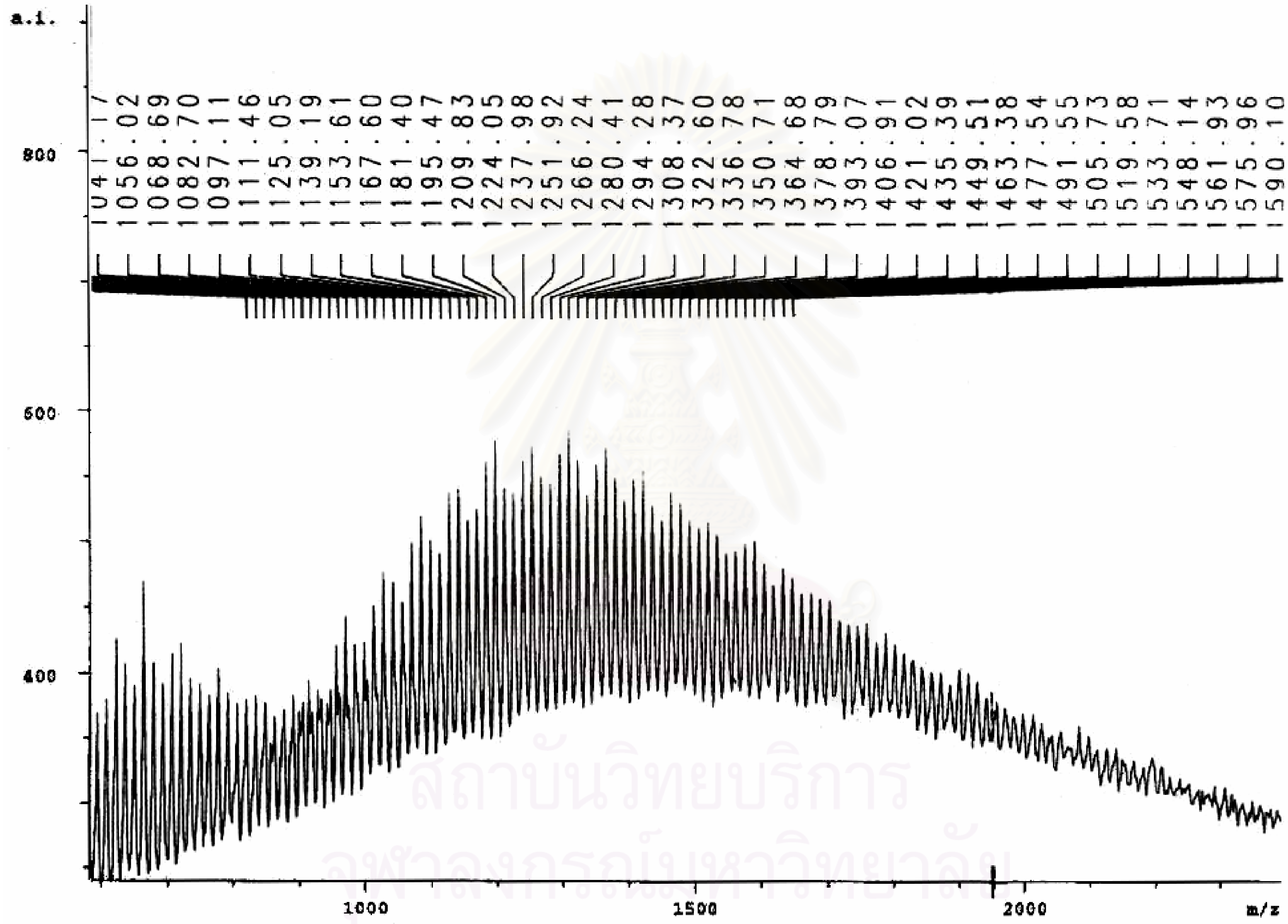


Figure A37 Molecular weight distribution of polymer range m/z of 800-2200.

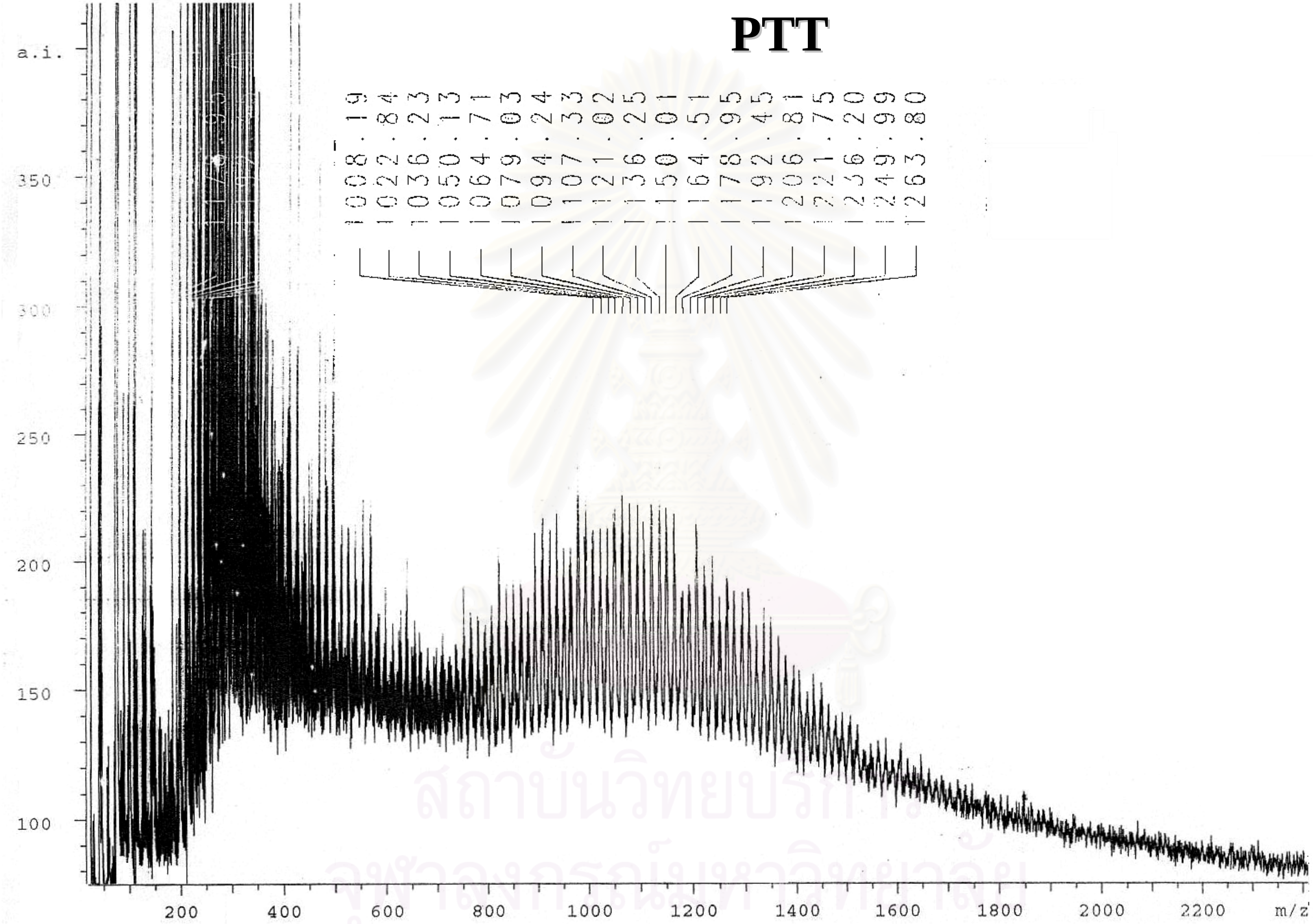


Figure A38 MALDI-MS spectrum of dispersant separated from PTT diesel oil : MALDI-TOF MS conditions as shown in Figure A16.

SHELL

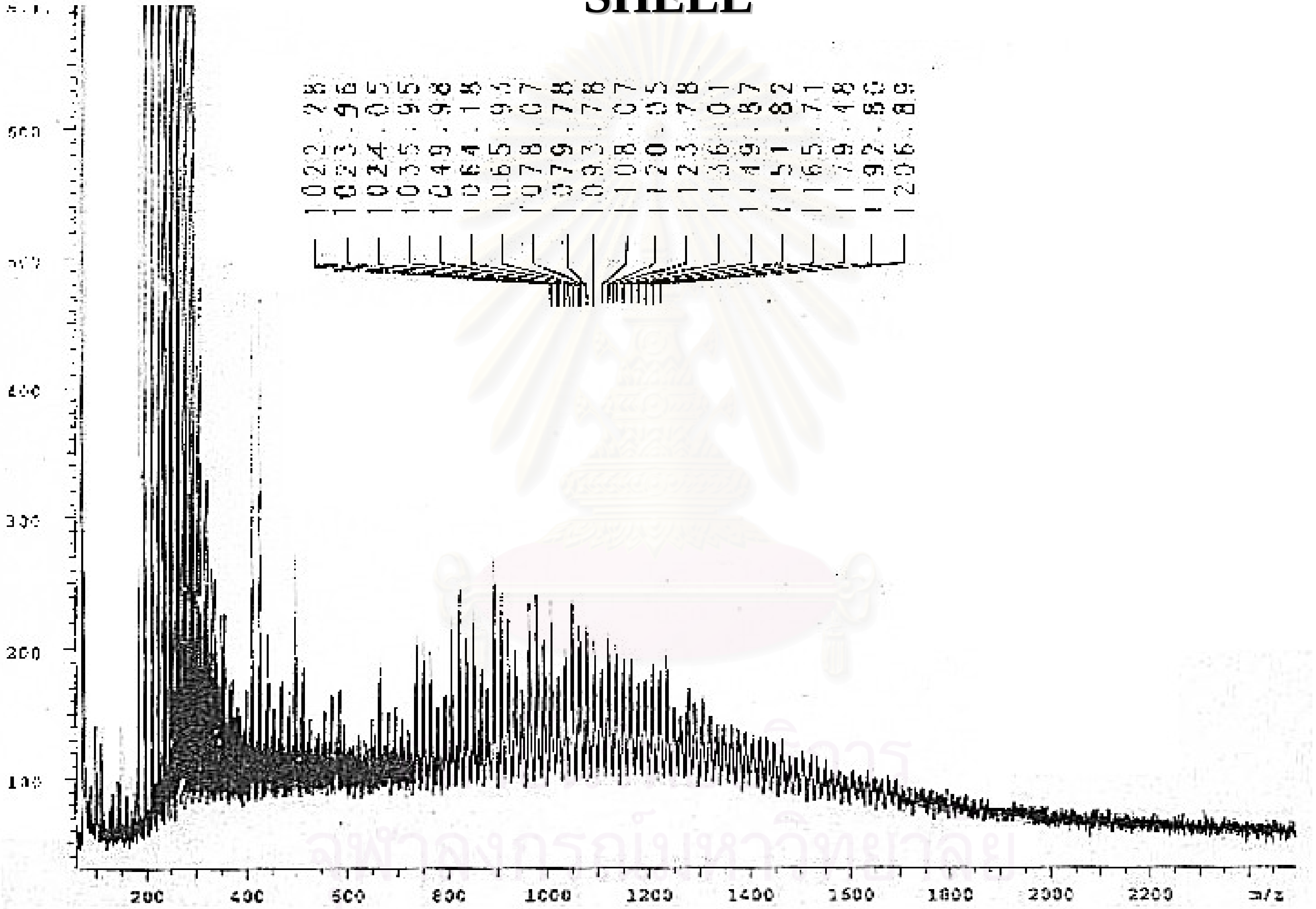


Figure A39 MALDI-MS spectrum of dispersant separated from SHELL diesel oil: MALDI- MS conditions as shown in Figure A16.

VITA

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