A PARAMETRIC STUDY OF LABORATORY SCALE MANUFACTURE OF SODIUMALLYLSULFONATE

by

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ABSTRACT

The main aim of this work involyes the manufacture of sodium allylsulfonate from allylbromide and sodiumsulfite by using laboratory scale testing of the commonly used industrial batch method(1). Yield of sodiumallylsulfonate by processing conditions were examined.

Sodiumallylsulfonate (SAS), is mainly used in nickel electroplating bath as a brightening and levelling agent. It improves the throwing power of the bath, thus; yielding deposits of high brightness and good adherence. At the same time, it possesses the other properties of brightening agents by being a rapid adsorber on the cathode with its subsequent incorporation into the electrodeposit. It has strong inhibition action on the discharge of nickel ions without significantly affecting the discharge of hydronium ion. SAS also possesses the ability to considerably decrease the Nickel current efficiency with increase in SAS concentration in the electrolyte. Sodiumallylsulfonate, besides the other unsaturated sulfonates, is an important copolymerizable emulsifying agent in copolymerization with larger proportions of acrylonitrile for the preparation of dyeable acrylic fibers with improved whiteness. Because of the molecular structure; having a double bond; a sulfonate group and low molecular weight, Sodiumallylsulfonate is the preferred copolymer among the other unsaturated sulfonates.

The compound was synthesized by using a new reagent other than recommended in literature. Allylbromide was used instead of allylchloride and methanol was used as the solvent in the reaction mixture. The analysis of the samples obtained from experiments, showed the identical properties with the commercial allyl used sample synthesized by allylchloride as the primary reagent.

A number of experiments were carried out based on the same procedure but with different experimental reaction parameters. Physical and chemical tests were carried out on the products obtained. A process was then chosen to optimize the cost and ease of manufacture with the optimum results. The repetition of the experiments at the selected reaction conditions were examined, and it was found that at 44°C and 180 minutes of reaction time the best yield and quality of SAS samples were obtained.

ÖZET

Bu çalışmada, alil bromür ve sodyum sülfit kullanılarak ve endüstriyel metodlarla, laboratuvar şartlarında sodyumalilsülfonat üretilmiştir. Reaksiyon parametrelerinde yapılan değişikliklerin, üretilen maddenin miktarı ve kalitesi üzerindeki etkileri incelenmiştir.

Sodyumalilsülfonatın (SAS) başlıca kullanım alanı Nikel elektrokaplama banyolarıdır. Kaplanan alanın düzgün, seviyeli ve herbir noktasının eşit miktarda kaplanma özelliğini geliştiren bu kimyasal madde, kaplamaya parlaklık ve iyi yapışma özelliklerini kazandırır.

SAS, aynı zamanda diğer doymamış sülfonatlar ile beraber tekstilde kullanılan önemli bir kimyasal maddedir. SAS molekülünün çift bağı, sahip bulunduğu sülfonat grubu ve alçak moleküler ağırlığı gibi moleküler yapısının özellikleri, onun, diğer doymamış sülfonatlar arasından tercih edilmesine neden olmaktadır. Akrilonitril ile polimer oluşturarak, beyazlığı gelişmiş ve boyanabilir akrilik elyaf üretiminde kullanılır. Akrilonitril, akrilik elyafa tek başına yeterli tekstil özellikleri kazandırırsa da, elyafın boyanabilmesi için SAS ile polimerizasyon gereklidir.

Bu deneysel çalışmamızda SAS, literatürde belirtilen başlangıç maddesi olan alilklorür yerine alil bromür ve çö-

zücü olarak metanol kullanılmak suretiyle üretilmiştir. Deneylerden elde edilen örnekler ile alil klorürü başlangıç maddesi olarak kullanan yöntemle üretilen ticari örneğin analiz sonuçları karşılaştırıldığında, her ikisinin de aynı özellikleri taşıdıkları saptanmıştır.

Aynı deneysel yönteme bağlı kalarak ve değişik reaksiyon parametreleri kullanarak çok sayıda deneyler yapılmıştır. Bu deneylerin sonucunda elde edilen örnekler, fiziksel ve kimyasal testlere tabi tutulmuşlardır. Sonuç olarak, üretimde kolaylık ve ucuzluk açısından en iyi üretim yöntemi seçilmiştir. Seçilen sabit reaksiyon parametrelerinde, elde edilen sonuçların doğruluğunu ve tekrarlanabilirliğini sağlamak için, birçok deney yapılmıştır. Bütün bu deneylerin sonucunda, miktar ve kalitesi en yüksek SAS örneklerinin, 180 dakikalık reaksiyon süresi ve $44^{o}C$ reaksiyon ısısı kullanılarak üretildiği saptanmıştır.

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I. INTRODUCTION

1.1. PROPERTIES AND USES OF SODIUMALLYLSULFONATE

Sodiumallylsulfonate is an odorless, white crystalline compound. Commercially, it's produced and purchased in powder form. It's soluble in water and methanol. Its' specific gravity is 1,24-1.275. Other specifications of sodiumallyl-sulfonate are listed in Table 1.1.1.1.

Table 1.1.1.1. Specifications of SAS(2)

Assay	93% min.
NaCl	1%
Na_2SO_3	0,05%
Losson drying	5%
pH	8,5-9,2

Sodiumallylsulfonate is mainly used in nickel electro-plating baths as a brightening agent to yield deposits of high brightness, good adherence and with good throwing power of the bath. It has all the other properties of brightening agents and nowadays it's the most widely and commonly used addition agent in nickel electroplating baths. Detailed functions of brightening agents and electroplating solutions

will be mentioned in Section 1.2.

Sodiumallylsulfonate, besides the other unsaturated sulfonates, is an important comonomer for the copolymerization with larger proportions of acrylonitrile for the preparation of dyeable acrylic fibers(3). The acrylics are the third major class of synthetic fibers. They should contain at least 85 per cent acrylonitrile while modacrylics should have between 35 and 85 per cent acrylonitrile. These fibers possess the properties of softhand, resistance to creasing and quick drying. They are highly resistant to degradation, to sun light and to various chemicals. They have properties similar to wool and have replaced wool in many markets such as for blankets, sweaters, etc.(4). The addition of SAS to a spinning solution composed of 20 parts of acrylonitrile-sodium p-styrene sulfonate-vinylidene chloride copolymer (66.5:1.5:3.2) in 80 parts of dimethylformamide (DMF), gave acrylic fibers with improved whiteness after coagulation and after thermal stretching(5).

Acrylic fibers with high density were prepared by first spinning mixtures containing an acrylic polymer into heated air. Then these fibers were treated with a coagulating liquor. Thus, a mixture containing 68,5 per cent 92:7.5:0.5 acrylonitrile-methylacrylate-SAS copolymer was first spun into air at 400°C. Then the mixture was immersed in a coagulating bath, washed and drawn 350 per cent in steam at

100°C. This process was used to produce 3-denier/filament fibers with bulk similar to that of wool. These kind of fibers have high affinity for basic dyes and reduced boiling water shrinkage(6).

The sulfonate group improves the dyeability of the fiber. Otherwise, acrylonitrile provides the necessary textile characteristics to the fiber by itself. These modified acrylic polymers (acrylonitrile-SAS copolymer) show hydrophilicity, antistatic property and dyeability increasing and viscosity decreasing. The copolymer has lower tensile strength than polyacrylonitrile(7).

Other main uses of SAS can be stated as below:

(a) Polyester warp is coated with an aqueous composition containing 7.8 per cent 0.5:99.5 SAS-vinylacetate copolymer. Then it's dried to give a warp with weaving efficiency of 97 per cent(8).

(b) SAS-vinylacetate copolymer and nylon-6 (thermoplastic resin) are spun together to produce bicomponent synthetic fibers. These fibers have improved affinity for basic dyes and they are useful for the manufacture of silklike yarns(9).

(c) SAS-vinylalcohol copolymers are used in the preparation of aminoplast which are used as wood adhesives(10).

As a conclusion, we may say that sodiumallylsulfonate finds its main applications in electroplating and textile industries, either by itself or by forming polymers with various chemical compounds. Additionaly, it can be used in many different fields of industry.

1.2. ELECTROPLATING

The electrochemical deposition of dissolution of metals is used in a number of metal working processes. Probably the most widely used and well known is electroplating. Electroplating is the electrodeposition of an adherent coating on an object in order to obtain a surface different from that of the underlying material(11). In contrast to various other processes of applying coatings, electroplated coatings are applied to improve appearance, corrosion resistance and physicochemical properties of the surfaces (hardness, electrical and thermal conductivity, solderability, reflectivity, etc.)(12). Some of the advantages of electroplated coatings over the other methods of applying coatings are as follows(13):

(a) Absence of an intermediate layer between the coatings and the substrate metal as in the case of hot dip and diffusion processes.

(b) Fine structure and often very valuable physical properties mentienod above.

(c) Easy control of the coating thickness to fractions of a micrometer.

(d) Most convenient method of applying coatings of metals with high melting points as for example copper, nickel, chronium, iron, silver, gold and platinum.

Electroplating is a surface treatment. The material being treated is made the cathode in an electroplating solution or bath. Anode is made of the metal being plated. Such baths are always aqueous solutions so that only those metals that can be reduced from aqueous solutions of their salts can be electrodeposited on one of the electrodes(14).

The basic components of an electroplating unit are, a cathode, an anode, an electrolyte and a suitable plating bath. Additional equipment may be necessary for stirring, for purification of the electrolyte, and to provide any automation. The electrical equipment usually consists of a step-down transformer and rectifiers. They provide the necessary low voltage directcurrent from the mains supply.

The metal is plated out in crystalline form. The size and packing of the crystals, determines the adhesion, continuity, appearance, strength and other characteristics of the deposit. The crystalline nature of the deposit is determined by the characteristics of the plating cell. The most important of these is probably the chemical composition of the electrolyte, followed by the applied current density. The physical characteristics of the cell are also important, particularly the temperature, the stirring rate, the size and the shape of the electrodes.

The thin layer being deposited sometimes is composed of two or more metallic elements, in which case, it's an

alloy. The solution or plating bath contains dissolved salts of all the metals which are being deposited. It often also contains an appropriate acid, base and/or salt added for the purpose of holding the pH at a desired fixed level. Other substances, called addition agents are often added to the plating bath for the purpose of giving the plate a desired texture. By this way, the plate can be strong, adherent and mirror smooth rather than rough, granular, loose and mechanically weak(15).

There is always a temperature range within which it's desirable to hold the plating bath. There is also a range of current density within which it is desirable to hold the current. The temperature affects the nature of the deposit and increase in temperature may lead to unsatisfactory plating. To stabilize the temperature, heating or cooling coils may be used. Solution can be also circulated through a heat exchanger. By current density, is meant the current per unit area of the object being plated. If the thickness of the deposit is to be uniform, the current density must be the same at all points on the cathode surface. Objects to be plated are often irregular in shape and with some plating baths such areas may receive very little deposition. The term "throwing power" is used to describe the ability of a plating system to produce an even deposit an irregular cathode(16). It is determined by the conductivity, the variation of current efficiency with current density and the variation of the polarization with current density.

The general properties conferred by electroplating include the following points: good adhesion, improved corrosion resistance, appearance, brightness, frictional characteristics, wear resistance and hardness, specific electrical properties, high optical reflectivity and many others.

Most of the metals consumed in electroplating are nickel, chromium, tin, gold, copper and silver.

1.2.1. Nickel Electroplating and Bath Properties

Nickel plate with or without an underlying copper strike, is one of the oldest protective-decorative electrodeposited metallic coatings for steel, brass and other basic metals(17). The first applications of nickel plate were for stove and bicycle components.

Nickel has almost innumerable uses. It's plated in all thicknesses and there are available many different nickel electroplating baths, each with its own advantages and limitations.

Most nickel-plating baths of today are based on the bath originally formulated by O.P.Watts, and these baths were named "the Watts bath". Watts bath is prepared with nickel sulfate, nickel chloride and boric acidas main chemicals. The concentrations of these constituents and conditions for operating the bath are given in Table 1.2.1.1(18).

Table 1.2.1.1. Watts Nickel Plating Bath

Constituent or Condition	Range
Nickel Sulfate, $NiSO_4.7H_2O$, gpl	300 to 450
Nickel Chloride, $NiCl_2.6H_2O$ gpl	45 to 60
Boric Acid, gpl	35 to 40
Wetting agent, gpl	0.5 to 1.0
pH	3.2 to 4.5
Temperature, ^oC	51.7 to 62.7
Cathode current density, amps/cm^2	$4.65x10^4$ to $7.43x10^4$
Anode current density, amps/cm^2	$1.86x10^4$ to $3.72x10^4$

For nondecorative (engineering) purposes, ductile, pore free and smooth nickel can be deposited from this solution without the need for addition agents. Brightening agents are consumed in appreciable quantities for plating bright nickel.

Electrodeposits of nickel possess a wide variety of properties, depending on plating bath composition and operating conditions. They may be classified according to application or appearance as general-purpose, special-purpose, black and bright(19).

General-purpose deposits (Semi-bright deposits)

They are produced by Watts, sulfamate and fluoborate baths. Primary uses are to protect alloys based on iron, copper or zine against corrosive chemical environments. They are used for plating wire, rod and strip and also for electroforming.

Special-purpose deposits

They are produced by all chloride or all sulfate baths and used for plating the inside of steel pipe and fittings, barrel plating and electroforming.

Black-nickel deposits

They are produced by baths containing zincsulfate or zinc chloride. They are primarily used to obtain a dark, nonreflective, decorative finish. Typical uses are for typewriter and camera parts, military instruments, clothes, fasteners and costume jewellery.

Bright nickel deposits

Bright nickel plating baths are modifications of the Watts nickel solution that contain inorganic or organic brightening agents. These additions serve to produce a higher than usual degree of brightness, reflectivity and hardness. Generally these deposits are used to provide decorative finishes on metals. They are also used as undercoatings for chromium or other precious metals.

In addition to these major applications, many other uses have been found for electrodeposition of nickel. One example is the use of nickel deposit to protect molybdenum and uranium against oxidation at elevated temperatures.

Every plating bath contains ingredients to perform the following functions (at least the first and usually several of them)(20):

(a) Provide a source of ions of metal to be deposited.

(b) Form complexes with ions of the depositing metal.

(c) Provide conductivity.

(d) Stabilize the solution against hydrolysis or other forms of decomposition.

(e) Buffer the pH of the solution.

(f) Regulate the physical form of the deposit.

(g) Aid in anode corrosion.

(h) Modify other properties peculiar to the solution involved.

Nickel plating bath contains $NiSO_4$ and $NiCl_2$, both of which provide nickel ions and the necessary conductivity. H_3BO_3 is added to buffer the solution and organic agents regulate the physical form and properties of the deposit.

1.2.2. Brightening Agents Properties and Uses

Brightening agents are small traces of organic compounds added to the salt solutions used in electroplating baths. These compounds modify, mainly by adsorption processes, the crystalline growth of the deposited metal(21). These organic additives produce brilliant deposits and have the following properties(22):

(a) Strong inhibition action on the discharge of nickel ions without significantly affecting the discharge of hydronium ion.

(b) Are not sensitive to metallic contaminations,

(c) Are not highly toxic or sensitive to anode effects,

(d) Produce deposits with fair ductility, low stress and more important bright and levelled over a wide range of current density,

(e) Improve the cathode efficiency of a plating bath

(f) Increase the hardness of the electrodeposit,

(g) Increase the throwing power of the bath.

These agents are key factors in the electroplating baths used for the deposition of decorative coatings as well as corrosion protective coatings. The addition agents which make possible the brilliant leveling nickel plate are more specific, more stable and more controllable in their effects. They are characterized by the presence of unsaturated bonds. Adsorption of these agents takes place on the freshly deposited nickel, through covalency with atomic d-orbitals of the nickel and the pi-electrons of the unsaturated bond.

Some examples of brightening agents can be named as the unsaturated sulfonic acids and their salts, such as vinylsulfonic acid, allylsulfonic acid, and sodiumallylsulfonate, quinaldine, acidine, furfural, aromatic sulfonic acid imides, aliphatic unsaturated tertiary amines and coumarin(23).

II. STATEMENT OF THE RESEARCH PROBLEM

The aim of this work was to manufacture sodiumallylsulfonate, an important and widely used brightening agent in nickel electroplating and also a copolymer in the production of acrylic fibers, by using laboratory scale testing of the commonly used industrial batch method. Sodiumallylsulfonate is not manufactured in Turkey and it's imported from various countries for commercial use.

The first aim of the research was to produce technical grade sodiumallylsulfonate that is suitable for commercial use. Experiments were performed to produce the desired compound and then by varying the experimental reaction parameters, the optimum conditions for the manufacturing process were obtained. As reaction parameters, temperature, pH, stirring rate and time were chosen. After satisfactory results were obtained, reproducibility of the experiments were tested. The obtained samples were analysed qualitatively using Infrared Spectrophotometry and quantitative experiments were also performed.

In summary, the following points were aimed in this research:

(a) To manufacture sodiumallylsulfonate in laboratory scale using allylbromide as the starting reagent,

(b) To choose the optimum reaction conditions with respect to technical and economical considerations.

III. CAPACITY ESTIMATION

The capacity estimation of sodiumallylsulfonate is based mainly on literature survey and market survey. Information obtained from literature is dependent on the reports of Başbakanlık Hazine ve Dış Ticaret Müsteşarlığı Fiat Tetkik ve Tescil Dairesi. Visiting certain companies that are the main consumers of sodium allylsulfonate is the basis of market survey.

In industry, SAS is consumed mainly in two fields. One is the nickel electroplating industry and the other one is the textile industry. Nickel electroplating processes are performed in rather small but by a great number of companies. Therefore; to get in contact with each of these firms was not possible. In textile industry, the plants manufacturing acrylic fiber consume this compound and among them, Yalova İplik ve Elyaf San. is the only company using SAS. Each of the individual firms consume SAS in different proportions but when the total consumption is estimated, a considerable amount is obtained.

Based on the information received both from market survey (Gamtaş, Nikelaj Galvano, Yalova Elyaf San.) and literature survey, the following approximate values are obtained for the years 1981, 1982 and 1983.

Year	Use of SAS(tons)
1981	680
1982	740
1983	1.200

Observing the demand for SAS in the previous years, an estimation can be done for the future demand roughly. It's seen that every year total consumption shows an increase. The demand in a five year period is calculated by increasing 1200 tons 20 per cent each year. By this method, it's found that in 1991, full capacity of the plant can be assumed as 5100 tons of SAS per year.

This result, as explained before is an approximate estimation of rough values obtained from literature and market surveys.

IV. EXPERIMENTAL

4.1. MATERIALS USED

Allyl bromide: It's purchased from Fisher Scientific Co., U.S.A., with the following specifications; boiling range: 69.4-71.6°C, specific gravity: 1.420 and used in chemically pure form.

Sodium Sulfite: It's purchased from Fisher Scientific Co., U.S.A., with the following specifications; anhydrous and assay: 98.4 per cent, and used in aqueous form.

Methanol: It's purchased from Rafineks Kimya Sanayi with the following specifications; boiling range: 64-65°C, density: 0.790-0.792, refractive index: 1.328-1.33 and used in chemically pure form (99 per cent).

Sodium hydroxide: It's purchased from E.Merck, Darmstadt and pellets were dissolved in distilled water to produce aqueous solution.

Diethyl ether: It's purchased from E.Merck, Darmstadt and used in chemically pure form (99.5 per cent).

Ethanol: It's purchased from Kızılay and used in chemically pure form (95 per cent).

4.2. EQUIPMENT

The system used in this study consists of the following components and is shown in Fig.4.2.1.1.

(a) Constant temperature bath

(b) Reaction vessel

(c) Heater

(d) Variable speed mechanical stirrer

(e) Extraction flask with a long thin tube at the bottom

(f) Thermometer.

Also, common laboratory glassware such as beakers, funnels, evaporation dishes, extraction flasks, graduated cylinders, etc., are used.

4.3. PRODUCTION METHODS OF SODIUMALLYLSULFONATE

Generally, the method to produce sodiumallylsulfonate in emulsion is by reacting allylchloride with aqueous Na_2SO_3 solution which is preheated to the desired beginning reaction temperature of 33-70°C. Allylchloride solution is stoichiometrically in excess of 10-40 per cent. The reaction is carried out by mixing intensively and by keeping the pH range between 7-11, preferably between 9 and 11 until the complete consumption

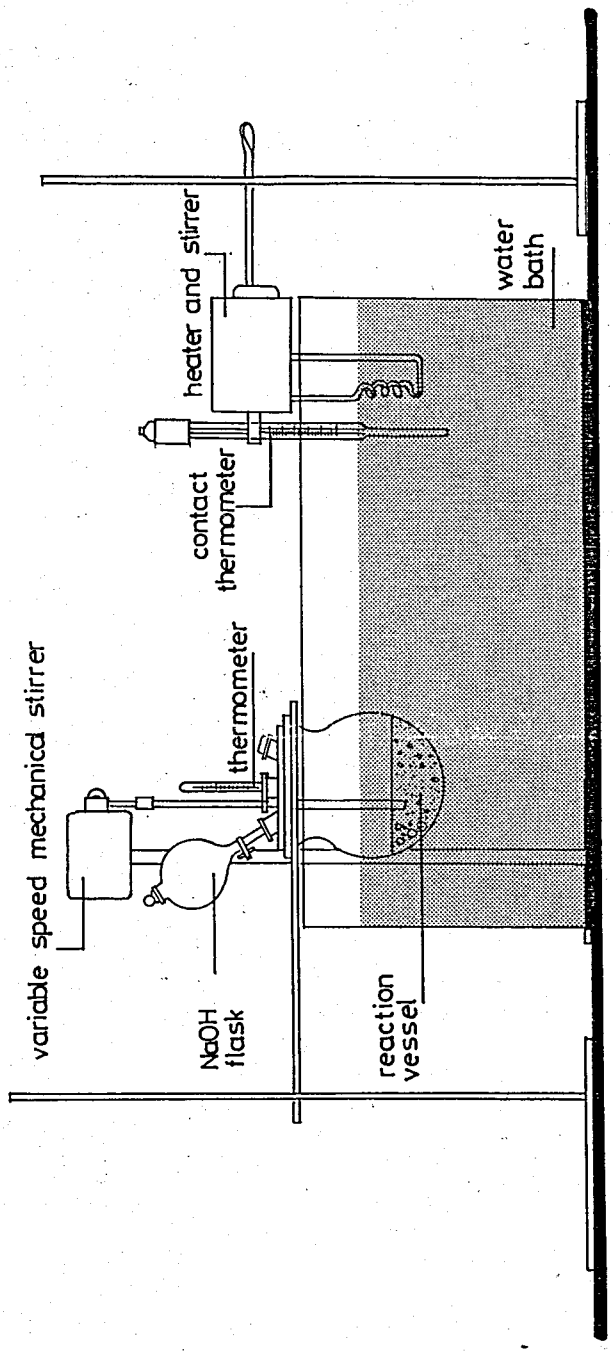

Fig. 4.2.1.1. Experimental System

of Na_2SO_3 is observed. NaOH is added to the solution in order to keep the pH at a constant value between 7 and 11.

Reaction is carried out with a Na_2SO_3 solution of 23.5 and 28 per cent by weight. 28 per cent Na_2SO_3 and 23,5 per cent Na_2SO_3 solutions are used for the initial reaction temperatures of 33°C and 70°C, respectively.

The production of SAS takes place by the reaction of allylchloride with sodiumsulfite in aqueous alcoholic solution according to the following equation:

$$CH_2 = CH\ CH_2Cl + Na_2SO_3 \xrightarrow{AlC\ /\ H_2O} CH_2 = CH\text{-}CH_2SO_3Na + NaCl$$

However; this method has low yields due to the considerable hydrolysis reactions. Therefore, the selectivity of the reaction is decreased. Besides, according to literature(24), reaction time of twelve hours are needed. Since the solubility of Na_2SO_3 in water-alcohol mixtures is low, relatively dilute reaction solutions will be used in order to optimize the energy needed for the evaporation. According to other methods(25), gaseous allylchloride is introduced in an aqueous Na_2SO_3 solution. A part of allylchloride is consumed and the rest remains unreacted and unconverted to the products. It can be returned by condensation and reevaporation, but these processes consume high energies because of constant evaporation and condensation. In addition, the method explained above requires relatively long reaction time as it takes longer for gas-liquid phase contact.

The unavoidable hydrolysis of allylchloride which runs simultaneously with the formation of SAS, is not considered by the two methods described here. During the reaction, HCl which is formed through the hydrolysis, decreases the pH of the end solution to a value of about 4. At these low pH values, the reaction is considerably slow. To avoid this, it's necessary to keep the pH value in the range 7 to 11, preferably between the range 9 and 10, by adding NaOH. During the addition of NaOH, pH value should not exceed 11, since the hydrolysis of allylchloride increases in strongly alkaline medium and accordingly selectivity decreases.

SAS is recovered from reaction mixture generally by evaporation of the solution. Extraction with alcohol and crystallization from alcohol proceeds at a later stage. Therefore; it's necessary to find a method which makes it possible to produce SAS through conversion of allylchloride in a Na_2SO_3 solution, concentrated as much as possible and also, in a short period with higher selectivity and low energy consumption.

A theoretically significant temperature for the reaction is $44^{o}C$. This is the boiling point of the attained azeotrope of allylchloride and water, under normal pressure. Therefore; the reactions at higher temperatures should be run under pressure. For a desired reaction temperature of $50^{o}C$, the necessary pressure is 1.3 bars, for $60^{o}C$ and $70^{o}C$,

it's 1.8 and 2.25 bars, respectively. At temperatures above 50°C, the reaction is carried out under nitrogen pressure. Reaction period is; about 240 minutes at 45°C, about 155 minutes at 50°C, about 75 minutes at 60°C and about 40 minutes at 70°C.

In spite of shorter reaction times, high temperatures are not recommended since the hydrolyzed amount of allylchloride increases with temperature, for example from 0.3 per cent at 36°C to 1.4 per cent at 70°C. Thus; further increases in reaction temperature, decreases the selectivity strongly.

The reaction of allylchloride with Na_2SO_3 is an exothermic reaction. Because of this exothermicity it is recommended to add the allylchloride into a sodium sulfite solution, which is preheated to a temperature sufficiently lower than the desired reaction temperature.

As the simplest case, the initial temperature will be chosen as 44°C. This method saves energy in two respects:

(a) At least a part of the reaction heat evolved is used to heat the reaction mixture (conservation of energy in large scale).

(b) At lower temperatures higher concentrations of Na_2SO_3 can be chosen, since the solubility of Na_2SO_3 decreases with increasing temperature (from 28 per cent at 33°C to 23.5

per cent at 70°C). By this way, concentrated reaction mixtures are obtained thus; evaporation costs are minimal.

According to this method(26), if the whole procedure is summarized, manufacture of SAS will involve the following steps:

Allylchloride is added to an aqueous Na_2SO_3 solution which is heated to the desired initial reaction temperature in the range between 33 and 70°C. The pH of the resulting solution will be between 9 and 10. Allylchloride is added under normal pressure at the initial temperatures up to 44°C. Over 44°C, the addition must be carried out under nitrogen pressure.

Effective stirring during the reaction period is necessary. Reaction temperature should lie between 45 and 70°C, especiallyl between 50 and 60°C.

During the reaction, aqueous NaOH solution is added to keep the pH value in the range between 7 and 11, preferably 9 and 10. When the sulfite content in the aqueous phase of the reaction mixture is decreased to ≦0.03 per cent, the reaction terminates.

The aqueous reaction mixture which contains essentially SAS and NaCl is evaporated and then extracted to purify SAS. Although it's difficult to obtain high yields of SAS using allylchloride because of the sensibility to hydrolysis, high yields of approximately 99 per cent are obtained by this method.

In another method(27), the preparation of SAS is improved by treating allylchloride with aqueous Na_2SO_3 solution containing a surfactant such as hydroxyethylated alkylphenol or sodiumstyromaleate and copperchloride catalyst. Methanol can also be added to the reaction mixture as the solvent in order to obtain a homogeneous mixture(28).

The experimental method carried out for the production of SAS in this work is generally based on the methods mentioned in this section. However; some modifications were made and the complete procedure is explained in Section 4.4.2.

4.4. EXPERIMENTAL PROCEDURE

4.4.1. Preliminary Work

Before starting the experiment, amounts of reagents necessary are calculated and then solutions are prepared according to stoichiometric ratios. Aqueous sodiumsulfite solution, allylbromide, methanol and 0.1 N sodiumhydroxide solution are the starting reagents for the reaction.

The following are the work outs of the solutions prepared and used throughout the reactions:

2500 gr, aqueous Na_2SO_3 solution and 483 gr allyl-bromide are needed. Na_2SO_3 solution is 26,5 percent by weight.

$$2500 \text{ gr.} \times 0.265 = 662.5 \text{ gr. } Na_2SO_3$$

$$662.5 \text{ gr. } Na_2SO_3 \times \frac{1 \text{ mole } Na_2SO_3}{126.04 \text{ gr. } Na_2SO_3} = 5.26 \text{ mole } Na_2SO_3$$

$$483 \text{ gr. } CH_2 = CHCH_2Br \times \frac{1 \text{ mole}}{120.98 \text{ gr.}} = 3.99 \text{ mole } CH_2=CHCH_2Br$$

$$\text{Mole Ratio} = \frac{\text{Allylbromide}}{\text{Sodiumsulfite}} = \frac{3.9924}{5.2563} = \frac{1}{1.3}$$

We want to reduce the amounts of reagents, therefore; without changing the mole ratio, the amounts are taken as 15 per cent of the calculated values.

$$\text{Then Mole Ratio is } \frac{0.15}{0.198} = \frac{\text{Allylbromide}}{\text{Sodiumsulfite}}$$

$$0.198 \text{ moles } Na_2SO_3 \times \frac{126.04 \text{ g } Na_2SO_3}{1 \text{ mole } Na_2SO_3} = 24.96 \text{ gr } Na_2SO_3$$

$$0.265 \text{ x} = 24.96 \Rightarrow \text{X} = 94.189 \text{ gr. solution}$$

Therefore; 24.96 gr Na_2SO_3 is dissolved in 70 ml of distilled water to have the desired aqueous solution.

$$0.15 \text{ moles allylbromide} \times \frac{120.98 \text{ g allylbromide}}{1 \text{ mole allylbromide}} = 18.147 \text{ g allylbromide}$$

$$18.147 \text{ g allylbromide} \times \frac{1}{1.483 \text{ gr/ml}} = 12.24 \text{ ml allylbromide}$$

0.1 N NaOH solution is prepared by dissolving 4 gr of NaOH pellets in one liter distilled water. Physical properties of the reagents are listed in Table 4.4.1.1.

TABLE 4.4.1.1. Physical Properties of Reagents

	Molecular Weight (g)	Melting Point (°C)	Boiling Point (°C)	Density (g / ml)	Solubilities					
					Cold Water	Hot water	alc.	eth.	ace.	bz.
Allyl Bromide	120.98	-119.4	70	1.398	insol.	insol	∞	∞	-	-
Sodium Sulfite	126.04	Decomposes	Decomposes	2.633	12.54g/100 cc	28.3g/100 cc	sl.sol.	-	-	-
Sodium Hydroxide	40.00	318.4	1390	2.13	42g/100 cc	347g/100 cc	v.sol.	insol	insol	-
Methanol	32.04	- 93.9	64.96	0.7914	∞	∞	∞	∞	∞	v

4.4.2. Experiment Part

The amounts of allylbromide and sodiumsulfite required are calculated according to their molar ratios. The temperature of the water bath is kept constant up to ± 0.5 by the aid of a contact thermometer and constant stirring. All of the sodiumsulfite solution is placed in the reaction vessel and by constant stirring, the solution is heated to the desired reaction temperature. The temperature of the reaction mixture is recorded by a thermometer inserted to the reaction vessel throughout the experiment. Sodium hydroxide solution is filled into an extraction flask and placed by the reaction vessel. Then the necessary amounts of allylbromide nad methanol are added to the sodium sulfite solution and the reaction starts. Methanol is added as solvent to produce a homogeneous reaction mixture (Physical properties of reagents are tabulated in Table 4.4.1.1). The reaction period varies from run to run and the reaction is carried out at the set temperatures for each experiment by operating the variable speed stirrer to achieve a thorough mixing. The reaction can be represented by the following chemical equation:

$$CH_2 = CHCH_2Br + Na_2SO_3 \xrightarrow{CH_3OH/H_2O} NaBr + CH_2 = CHCH_2\ SO_3Na$$

As the reaction starts, samples are taken from the reaction mixture at regular intervals in order to test the pH of the solution. To keep the pH of the mixture at the range

between 9 and 10, aqueous NaOH solution is added dropwise from the extraction flask situated on top of the reaction vessel. Sample taking and accordingly NaOH addition procedures are continued until the reaction period is terminated. Then the reaction mixture is filtered and unreacted Na_2SO_3 is removed from the reactionmixture. During all filtration processes throughout the experiments, ashless No:40 filter papers by W. and R.Balston, Ltd., are used.

The resulting reaction mixture is extracted with diethylether in order to remove the excess allylbromide from the solution. The aqueous phase obtained from extraction is put into an evaporating dish and evaporated.

The step following the evaporation involves treatment of the resulting precipitate with ethanol. The precipitated compound is dissolved partly in ethanol and then filtered to remove the undissolved sodiumbromide from the reaction mixture. This process is repeated twice and the resulting solution is again transferred to an evaporating dish and to the hot plate for further evaporation. When the alcohol is completely evaporated, the crude sample of sodiumallylsulfonate precipitates out of the reaction mixture.

To get rid of the remaining impurities, the sample is dissolved in methanol and it's recrystallized from the solution first by filtration and then by evaporation. This step is repeated more than once. The purified sample is dried in oven. At the end white crystals of sodiumallylsulfonate are obtained.

4.5. PURIFICATION OF THE CRUDE SAMPLE

After the completion of sodiumallylsulfonate production, small samples are taken for solubility tests in water and in methanol and later for infrared spectrophotometric analysis. The presence of extra peaks and deviations of the peaks from the original data in the infrared spectra show the existence of some impurities and insufficient purification. Therefore; further purification of the crude sample is necessary. This is achieved by dissolving the samples and washing them thoroughly in methanol. Undissolved particles are removed from the solution by filtration. Sodiumallylsulfonate crystals are obtained by evaporation of the solution on hot plate and drying in the oven. This procedure is repeated more than once to purify the crude sample and by this way the white color of the crystalls is also improved. However; since sodiumallylsulfonate is soluble in methanol, there is some loss of crystalls during this purification step. The effect of this loss is discussed in Section 6.1.1.

4.6. ANALYSIS OF THE SAMPLE

4.6.1. Infrared Spectrophotometric Analysis

The quality of the samples obtained from experiments are investigated by infrared spectrophotometer.

4.6.1.1. Infrared Spectroscopy

The infrared region of the electromagnetic spectrum extends from the end of the visible spectrum to the microwaves, that is, the region includes radiation at wavelengths between 0.7 and 500 μm or in wave-numbers, between 14000 cm^{-1} and 20 cm^{-1}. The spectral range of greatest use is in the mid-infrared region, which covers the frequency range from 200 cm^{-1} to 4000 cm^{-1} (50 to 2.5 μm). Infrared spectroscopy involves the twisting, bending, rotating and vibrational motions of atoms in a molecule. Upon interaction with infrared radiation, portions of the incident radiation are absorbed at particular wavelengths. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum, which is a unique characteristic of the functional groups comprising the molecule and of the overall configuration of the atoms as well(29). Infrared spectrophotometry is most useful for identifying organic compounds and deducing the structure of newly synthesized compounds. To establish a background for these uses, a brief introduction to the absorption of infrared radiation will be presented first, followed by statements of the instruments and sample handling.

Molecular Vibrations

Atoms or atomic groups in molecules are in continuous motion with respect to each other. A molecule can be viewed as a set of balls (representing atoms) connected by springs

(representing chemical bonds). In the ground state, the atom balls vibrate somewhat on the bond springs. Absorption of infrared energy at particular wavelengths (i.e., frequencies) increases this motion. The frequency of the incoming radiation must match that of the atom balls vibrating on their bond springs. This is called a "condition of resonance". Although the vibrational changes in a chemical molecule are caused by the absorption of only certain frequencies of infrared energy, there also numerous rotational energy changes. Because of these, spectra consists of absorption bands rather than lines.

The molecular vibrations observed are of two types; stretching and bending. Stretching is a rhythmical movement of the atoms back and forth along the bond axis. Bending is the vibration which implies movement of atoms out from the bonding axis. Four types can be distinguished:

(a) Deformation or scissoring: The two atoms connected to a central atom move toward and away from each other with deformation of the valence angle;

(b) Rocking or in-plane bending: The structural unit swings back and forth in the symmetry plane of the molecule;

(c) Wagging or out-of-plane bending: The structural unit swings back and forth in a plane perpendicular to the molecule's symmetry plane;

(d) Twisting: The structural unit rotates back and forth around the bond which joins it to the rest of the molecule.

Instrumentation

The essential components of an infrared spectrophotometer are given in the figure below:

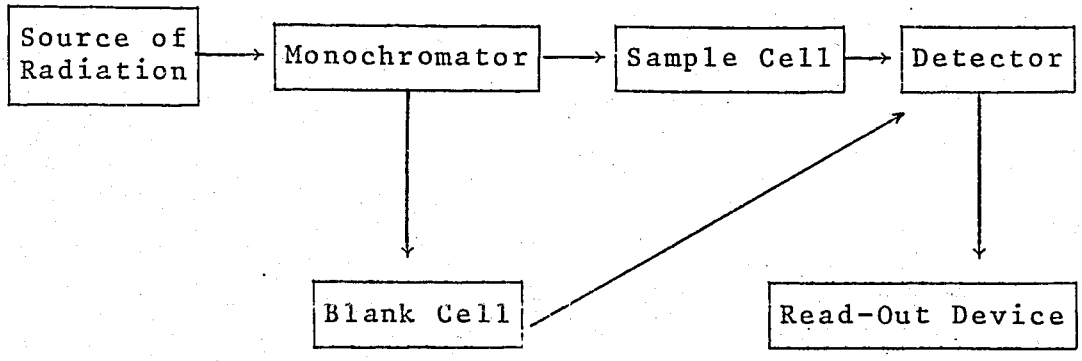

Fig.4.6.1.2. Components of Infrared Spectrophotometer

Ifnrared Radiation Sources

The only important infrared sources are continuous sources which emit radiation whose intensity varies smoothly over an extended range of wavelengths. Tungsten lamp is a source of infrared but its output is limited to about 2500 nm (2.5 μm). Therefore this source is more useful for the near infrared region. Two most important infrared sources are the Nernst glower and the Globar. Spectral energies of the Globar and the Nernst glower are comparable except in the region

below 5 μm (5000 nm), where the Globar provides a significantly greater output.

Monochromators

The function of a monochromator is to select a beam of one-wavelength radiation that can be varied over a wide range. key element is the dispersing device and the diffraction grating is used for wavelength selection. Light striking the grating is diffracted so that different wavelengths come off at different angles. Rotating the grating makes it possible to select light of the desired wavelength.

Infrared Detectors

Infrared radiation may be measured by detecting the temperature change of a material in the infrared beam; this type of a detector is a thermal detector. Another, but less used detector is the photon or quantum detector, which depends on internal photoconductive effects resulting from the transition of an electron from one valence bond to a conduction band within the semiconductor receptor. Quantum detectors are faster and more sensitive but restricted to range of wavelengths to which they can respond. Thermal detectors are usable over a wide range of wavelengths but they suffer from relatively low sensitivity and slow response. This is because of the radiant power of infrared radiation being so weak. The basic forms of thermal radiation detectors are the radiation thermocouple, the Golay detector and the bolometer.

Sample Handling

Gases, liquids in solution and solids are handled in infrared spectrophotometers. For gas samples, a variety of cells are used with path lengths that range from a few centimeters to several meters. For liquid samples, solvents such as carbon disulfide, carbon tetrachloride, tetrachloroethylene, chloroform, dimethylformamide, dioxane, cyclohexane and benzene are used. Because of the tendency for solvents to absorb, infrared cells are much narrower (0.1 to 1 mm) than those employed for cell windows in the infrared region. Insolubla samples or ones that, for some reason, cannot be analyzed in solution can be determined in two ways. In one a mull is prepared by dispersing a finely ground sample in a refined hydrocarbon oil (Nujol). The resulting mull is then examined as a film between flat salt plates. In the second technique, potassium bromide pellets are prepared and this method is explained in detail in Section 4.6.1.2.

4.6.1.2. Infrared Technique Used

In the analysis of sodiumallylsulfonate crystalls, pellet technique is used. This technique involves mixing the fine ground sample (a milligram or less) and dried KBr powder and pressing the mixture in an evacuable die at sufficient pressure (12 tons) to produce a transparent disk. KBr becomes quite plastic at high pressure and will flow to form a clear disk. Mixing is done in a vibrating ball-mill. The disk is

then held in the instrument beam for spectroscopic examination. The resulting spectra frequently exhibits bands at 2.9 and 6.1 μm (2900 and 6100 nm) due to absorbed moisture.

In the analysis of samples, disks are prepared by mixing one milligram of sample with approximately 300 milligrams of KBr. The mixture is put in a vibrating ball-mill for three minutes. Then the sample is placed in a steel cylinder and compressed using a vacuum pump (Shimadzu Rotary vacuum pump. Type SA18) up to 10 tons. The IR spectra of the KBr disc is then taken (Shimadzu IR Spectrophotometer IR-435) and compared with the original.

4.6.2. Qualitative Experimental Analysis

Qualitative analysis of the samples is based on the solubility, pH and experimental tests to determine the percent of sodiumallylsulfonate present.

The results of solubility tests are successful since all of the samples obtained are soluble in methanol and water. The results of pH tests are listed in Section V, Table 5.1.4.

4.6.2.1. Sample Preparation

For the experiments, the equipment used is the normal laboratory equipment.

Reagents

Bromine: Manufactured by Fisher Scientific Company and used in chemically pure form.

Sodium Bromide: Manufactured by Fisher Scientific Company and used as both saturated solution and chemically pure form.

Methanol: Manufactured by Rafineks Kimya Sanayi and used in chemically pure form (99 per cent).

Sodiumthiosulphate: Manufactured by Panreac and used as 0.1 N aqueous solution.

Potassium Iodide: Manufactured by Labor Kimya Sanayi and used as 10 per cent solution.

Solutions

(a) Bromine-Bromide Solution:

5.5 ml of bromine is introduced in one liter calibrated flask, containing 500 ml of methanol and 100 g of NaBr. It's diluted to one liter with methanol and shaken till complete dilution of NaBr.

(b) Saturated NaBr Solution:

200 g of NaBr is introduced in a volumetric flask containing 200 ml of distilled water and saturated solution

is prepared by using a stirrer (Corning hot-plate stirrer, Type PC-351).

(c) Potassium Iodide Solution

25 g of KI is introduced in a volumetric flask containing 225 ml of distilled water to prepare 10 per cent KI solution.

(d) Sodiumthiosulfate Solution

24,82 g of $Na_2S_2O_3 \cdot 5H_2O$ is dissolved in 2 lt of distilled water to prepare 0.1 N solution.

4.6.2.2. Experimental Procedure

0.1-0.2 g of sample is weighed exactly in a 200 ml glass stoppered volumetric flask. 10 ml of distilled water, 10 ml of saturated NaBr solution and about 5 g of NaBr are added. Then, from a burette 25 ml of the bromine-bromide solution is added.

The resulting solution is allowed to sit one hour with occasional swirling. Then 50 ml of methanol and 10 ml of 10 per cent KI solution are added and immediately titrated with 0.1 N thiosulfate until the color of the solution turns from dark brown to colorless. The blank test is carried out in the same way.

Expression of the result

$$\text{Per cent Sodiumallylsulfonate (SAS)} = \frac{(A-B)\times 0.0072}{P} \times 100$$

where:

A = ml $Na_2S_2O_3$ 0.1 N in the blank test

B = ml $Na_2S_2O_3$ 0.1 N in the proper test

P = g weighed substance.

The results of these tests are listed in Table 5.1.5.

V. EXPERIMENTAL RESULTS

In this work twelve experiments were carried out at various reaction temperatures and reaction periods for the manufacture of sodiumallylsulfonate. The mole ratio of allylbromide to sodiumsulfite is 1 to 1.32 and it is constant throughout the experiments. The operating temperature is varied between 35°C and 70°C and reaction period is varied between 60 minutes and 360 minutes.

The experimental conditions used throughout the experiments are all tabulated in Tables 5.1.1 through 5.1.6 and the results are discussed in Section VI.

The results of the infrared data for the experiments 1 through 12 and the original sample can be seen in the figures 6.2.1 through 6.2.16. They are compared and discussed in Section VI.

In Table 5.1.1. experimental conditions are tabulated in detail and amounts of product obtained are listed. The molar ratio of allylbromide to sodiumsulfite is kept constant throughout all the experiments as 1 to 1.32. In the first two

Table 5.1.1. Experimental Conditions and Results

Run No.	Molar ratio of allylbromide to sodium sulfite	Amount of allylbromide used(ml)	Amount of sodium sulfite used(g)	Amount of methanol used (ml)	Amount of 0.1 N NaOH added (ml)	Reaction Temperature (°C)	Reaction Period (min)	Amount of Na_2SO_3 unreacted (g)	Amount of NaBr obtained (g)	Amount of SAS obtained (g)
1	0.3/0.396	24.47	49.91	-		44	240	-	-	1.534
2	0.3/0.396	24.47	49.91	100		44	240	-	13.42	2.780
3	0.15/0.198	12.24	24.96	50	62	44	240	-	12.00	7.111
4	0.15/0.198	12.24	24.96	50		35	240	4.359	11.65	9.190
5	0.15/0.198	12.24	24.96	50	18	60	105	8.496	12.53	1.452
6	0.15/0.198	12.24	24.96	50	28	50	155	5.255	10.97	8.904
7	0.15/0.198	12.24	24.96	50	19	60	105	7.205	9.573	9.093
8	0.15/0.198	12.24	24.96	50	27	60	75	5.743	13.05	10.28
9	0.15/0.198	12.24	24.96	50	33	70	60	5.304	8.003	11.84
10	0.15/0.198	12.24	24.96	50	40	35	360	4.347	10.52	9.537
11	0.15/0.198	12.24	24.96	50	36	44	180	5.359	10.82	13.77
12	0.15/0.198	12.24	24.96	50	39	44	120	4.001	9.062	13.49

runs the amounts of reagents are two times more than the other runs and they are reduced in the following runs in order to consume less amounts of reagents. The amount of methanol added to the reaction mixture as solvent, is also kept constant throughout all the experiments. The amount of sodiumhydroxide added to the reaction solution in order to keep the pH value between the range 9 and 10, varies from one experiment to another. Since the function of sodiumhydroxide solution is to neutralize the forming HBr and allylalcohol in the reaction mixture, the consumption changes according to the formed amounts of both acids. Reaction temperature is varied between 35°C and 70°C. The last two experiments are carried out at 44°C to test the reproducibility of the desired result. Since satisfactory results are obtained at the end of twelve experiments, no further experiments were performed. The pH value of the reaction mixtures is kept in the range of 9 and 10 in all runs. This is tested in regular intervals by adding aqueous sodium hydroxide solution and using the special pH test paper. Reaction period is varied between 60 minutes and 360 minutes according to the selected reaction temperature. As temperature is increased, reaction period is decreased and also at constant temperatures different reaction periods are tested. In the experimental procedure, the first step after the reaction is finished is to filter and remove the unreacted sodiumsulfite content. The amount of unreacted sodiumsulfite varies from one experiment to another related to the reaction temperature, reaction period and stirring rate.

Table 5.1.2. Experimental Results

Run No.	Na_2SO_3 unreacted (moles)	NaBr obtained (moles)	SAS obtained (moles)	Yield of SAS (per cent)
1	-	-	0.0107	10.66
2	-	0.1305	0.0193	19.27
3	-	0.1167	0.0494	49.39
4*	0.0346	0.1132	0.0638	63.79±4
5	0.0674	0.1218	0.0101	10.08
6*	0.0417	0.1066	0.0618	61.83±5
7**	0.0572	0.0930	0.0632	63.15±3
8**	0.0456	0.1268	0.0714	71.38±5
9*	0.0421	0.0778	0.0823	82.25±3
10*	0.0345	0.1022	0.0662	66.23±2
11***	0.0425	0.1052	0.0956	95.55±2
12***	0.0317	0.0881	0.0937	93.67±4

*: Experiments performed twice
**: Experiments performed three times
***: Experiments performed four times

Amounts of sodium bromide obtained as a by-product of the reaction also depend on the experimental conditions and they are listed in the table. Finally the amounts of product obtained from each experiment are tabulated.

In Table 5.1.2 only the experimental results are tabulated. The molar concentrations of unreacted sodiumsulfite, sodiumbromide obtained as by-product and the desired product sodiumallylsulfonate are listed. This table is the brief representation of experimental results without relating the results to any experimental conditions and it's derived from Table 5.1.1. Yield of sodiumallylsulfonate in percent form is calculated using the one to one molar ratio of the reaction stoichiometry. The molar concentrations of allylbromide and sodiumsulfite are 0.15 and 0.198, respectively in experiments four through twelve. According to the stoichiometry of the reaction, the products should have molar concentrations of about 0.15 at the end of the reaction period when theoretically hundred per cent conversion is considered. The numerical values listed in this table as moles of sodiumbromide obtained and moles of sodiumallylsulfonate obtained show appreciable experimental results. As it's seen in the table, the last two experiments have the highest yields of the all experiments and therefore no further experiments were carried out.

In Table 5.1.3., per cent yield of sodiumallylsulfonate obtained from each experiment is listed and compared with both reaction temperature and reaction period. As the temperature is increased, the reaction period is decreased and vice versa as the temperature

Table 5.1.3. Correlation of Per cent Yield of SAS to reaction parameters

Run No.	Reaction Temperature (°C)	Reaction Period (min)	Per cent yield of SAS
1	44	240	10.66
2	44	240	19.27
3	44	240	49.39
4*	35	240	63.79±4
5	60	105	10.08
6*	50	155	61.83±5
7**	60	105	63.15±3
8**	60	75	71.38±5
9*	70	60	82.25±3
10*	35	360	66.23±2
11***	44	180	95.55±2
12***	44	120	93.67±4

*: Experiments performed twice
**: Experiments performed three times
***: Experiments performed four times

is decreased, the decreased, the reaction period is increased. In experiments 7 and 8, the temperature is kept constant at 60°C and the reaction period is decreased from 105 minutes to 75 minutes to observe any changes in the results. Likewise in experiments 4 and 10, the temperature is kept constant at 35°C and the reaction period is increased from 240 minutes to 360 minutes. When the per cent yields of the reactions are considered, it's seen that there are no large variations in the results. In runs 1, 2, 3, 11 and 12 the temperature is 44°C but in the last two, the reaction periods are changed. As the per cent yields are compared, it's seen that the last two have the highest yields even though the reaction period is decreased. This is due to experimental errors or trials done in the first runs to decide on the complete procedure for the following experiments. As the number of experiments increases, the per cent yields obtained show considerable improvement.

Table 5.1.4. pH of SAS Samples

Run number	pH
1	6.20
2	6.23
3	7.72
4	7.65
5	6.43
6	7.70
7	8.03
8	7.93
9	8.06
10	8.05
11	8.03
12	8.00

In Table 5.1.4, pH value of the obtained product sodiumallylsulfonate in each run is listed. According to literature(30), the pH value of a commercially used sodium-allylsulfonate sample is reported as in the range of 8.5 and 9.2. When the experimental results are observed, the values vary from 6.20 to 8.06. Generallly, the samples showing qualitatively and quantitatively similar properties have almost the same pH values.

In Table 5.1.5, per cent of sodiumallylsulfonate in each sample is calculated following a special experimental procedure explained in details in Section 4.6.2.2. According to the procedure, a weighed amount of sample is titrated with sodiumthiosulphate until the end point is observed. Then, the percent of sodiumallylsulfonate in the sample is calculated by using the amount of sodiumthiosulfate used both in the blank test and in the proper test and also the exact weight of the sample. Each of these values are listed in the table with the corresponding experiment number. The first row shows the results of the test performed on the obtained original sample of sodiumallylsulfonate. The lowest value obtained in this test is 48.96 in experiment one and the highest value belongs to the original sample.

The others vary in the range of 70.56 and 87.32 per cent purity. The original sample shows 98.64 per cent purity whereas the products of experiment number 2, 3, and 11 give very close values to 98.64 per cent purity.

Table 5.1.5. Per cent Purity of SAS in the samples

Run No.	$Na_2S_2O_3$ used in the blank test (ml)	$Na_2S_2O_3$ used in the proper test (ml)	Weight of sample (g)	SAS in the sample (%)
Original sample obtained	51.3	37.6	0.1000	98.64
1	51.3	44.5	0.1000	48.96
2	51.3	36.3	0.1168	92.46
3	51.3	37.1	0.1104	92.61
4	51.3	39.8	0.1000	82.80
5	51.3	40.5	0.1000	77.76
6	51.3	39.5	0.1034	82.17
7	77.1	65	0.1003	86.86
8	77.1	67.3	0.1000	70.56
9	77.1	66.2	0.1002	78.32
10	77.1	64.9	0.1006	87.32
11	77.1	63.2	0.1017	98.41
12	77.1	65.4	0.1042	80.84

Table 5.1.6. Experimental Results correlated to reaction parameters

Run No.	Reaction Temp. (°C)	Reaction Period (min)	Per cent Yield of SAS	Per cent Purity of SAS	pH of SAS
1	44	240	10.66	48.96	6.20
2	44	240	19.27	92.46	6.23
3	44	240	49.39	92.61	7.72
4	35	240	63.79±4	82.80	7.65
5	60	105	10.08	77.76	6.43
6	50	155	61.83±5	82.17	7.70
7	60	105	63.15±3	86.86	8.03
8	60	75	71.38±5	70.56	7.93
9	70	60	82.25±3	78.32	8.06
10	35	360	66.23±2	87.32	8.05
11	44	180	95.55±2	98.41	8.03
12	44	120	93.67±4	80.84	8.00

VI. DISCUSSION OF THE EXPERIMENTAL RESULTS

The aim of this research was to study and observe the effects of processing conditions on the sodiumallylsulfonate yield and quality using laboratory scale testing of the commonly used industrial method. Then the aim was to choose the optimum reaction parameters at the same time minimizing the economical costs. The procedure carried out during the experiments was based on the German Patent of sodiumallylsulfonate Manufacture (1). Basically the experiments explained in the result section were qualitative study and the main aim was to produce sodiumallylsulfonate that is suitable for commercial use.

6.1. DISCUSSION OF THE WET ANALYSIS

According to literature, various methods were recommended for the industrial scale manufacturing process, but all of them used allylchloride as the starting reagent. We wanted to obtain sodiumallylsulfonate with allylbromide as the starting material because it is never tried in literature. Allylchloride and allylbromide have similar physical properties

except for their molecular weight and allyl bromide being a more reactive compound. The use of allyl bromide brings the advantage of performing experiments up to 70°C without the need of inert gas pressure because this limit is 44°C when allylchloride is used. 70°C is the attained azeotrope of allyl-bromide and water and above this temperature, nitrogen gas pressure is used in order to prevent the escape of reaction mixture. Using allylbromide as the starting reagent, we wanted to observe the variation in SAS per cent yield and to see how this yield varies by changing the reaction parameters. Depending on the parameters and results obtained from each experiment, a general trend was found. This trend was correlated to reaction temperature and reaction time to obtain the most suitable conditions for the manufacture of sodiumallylsulfonate. The results obtained at the end of this work were discussed by correlating time and temperature to per cent yield, per cent purity and pH of the samples obtained.

6.1.1. Discussion of the Per cent Yield

Per cent yield was correlated to reaction temperature and time. But it was decided that to discuss each or a group of experiments together will give more detailed information about SAS manufacture in this work.

1- Experiments 1-2

As reported in literature, reaction period is dependent on reaction temperature. If reaction temperature is increased, reaction time should be decreased accordingly. At high temperatures, shorter reaction periods are used which seems quite effective, however; high temperatures at the same time require the use of inert gas pressure. Therefore; the first experiment was carried out at 44°C with a reaction period of 240 minutes. According to the procedure defined in Section 4.4.2, the experiment was performed and sodiumallylsulfonate was obtained. The first and the second experiments were carried out under the identical conditions and the results obtained weren't very satisfactory due to low SAS yield. This is because of some trial and error methods performed during these two runs. In the first experiment, a nonhomogeneous mixture was obtained since methanol was not added to the reaction mixture. Starting with the second experiment, because of methanol addition homogeneous solutions were obtained. Also various purification methods were tried on the products of these two experiments. Recrystallization both in deep-freeze and by evaporation were tested and then at the end it was decided to wash SAS obtained with methanol more than once. As a result of these tries, a major amount of the products were lost during this washing process and therefore low values for the per cent yield of the reactions were obtained. After the completion of the first two experiments, a general trend for the manufacturing process was decided and this procedure was accepted throughout the rest of the experiments. The molar ratio of the starting

reagents, pH of the reaction mixture and the amount of methanol added to the solution were kept constant throughout the experiments. Reaction temperature and reaction period were chosen as process variables and the effect of changes in these variables on the yields and purity of SAS produced were examined.

2- Experiments 1-5-7

The lowest SAS yields were obtained in the first and the fifth experiments which were carried out at 44°C and 60°C respectively (10.66 per cent and 10.08 per cent). The main reason for the low value of the first experiment is related to trial and error methods explained in the first section. For the fifth experiment, the inefficient yield can be related to experimental errors. As it's seen in Tables 5.1.1 and 5.1.2 the amount of sodiumsulfite unreacted in this experiment is the largest when compared with the rest of the experiments. The amount of sodiumbromide obtained as by-product is quite high (0.1218 moles) but the amount of product obtained (0.0101 moles) does not correspond to the 1/1 molar ratio of the reaction stoichiometry. This is due to incomplete separation of NaBr and SAS. Also it is due to the loss of sample resulting from the purification step. Therefore; the fifth experiment was repeated in the seventh run keeping the reaction conditions constant (60°C and 105 minutes). At the end of this experiment, an improved result was obtained (63.15 per cent yield).

3- Experiment 2

In the second experiment again a low yield of SAS was obtained (19.27 per cent). The main reason behind this low value is basically the same discussion valid for the first experiment, in order to achieve a general trend for the manufacturing process.

4- Experiment 3

In this run, the reaction parameters were 44°C and 240 minutes. The same conditions as the first two experiments were used. The amount of crude sample obtained was quite satisfactory but the loss of sample during the filtration and purification steps made the overall yield of the reaction 49.39 per cent. This value is considered low since with the used parameters a higher result should have been obtained.

5- Experiments 4-10

In the fourth experiment, the reaction temperature was decreased to 35°C keeping the reaction period at 240 minutes. At the end of this experiment, a yield of 63.79 per cent was obtained. In this run, the only variable was the temperature. It was decreased from 44°C to 35°C, but the reaction period remained constant. Therefore; to observe the effect of change in reaction period, the tenth experiment was performed. In the tenth experiment, following the recommendations

in literature, the reaction period was increased to 360 minutes. At the end, 66.23 per cent product yield was obtained. There were no great differences between the results of the two experiments. Therefore; it was decided that performing the experiment at 35°C both at long and shorter reaction periods does not give the desired results.

6- Experiment 6

In the sixth experiment, 50°C and 155 minutes were chosen as the reaction temperature and time respectively. The SAS per cent yield result showed that 61.83 per cent is not very satisfactory when compared with reactions of higher yield. The main reason behind this intermediate yield can be explained as not enough time is allowed for the reaction to complete at this temperature.

7- Experiments 8-7

To observe the effects of reaction time variation on the results, run numbers 7 and 8 were performed. In the eighth experiment, the temperature was kept constant at 60°C and time was decreased from 105 to 75 minutes. The result obtained at the end of this run was 71.38 per cent, but the difference was not very significant when compared with the previous run. Therefore; it was decided that increasing the reaction temperature from 44°C to 60°C and decreasing the reaction period to various values does not exhibit significant changes in per cent SAS yield.

8- Experiment 9

In this experiment, the temperature was further increased to 70°C and the reaction period was decreased to 60 minutes. At the end a yield of 82.25 per cent was obtained. This result was very satisfactory in industrial scale. To decide on the optimum conditions, this experiment seemed very suitable with short reaction period. Low temperatures and longer reaction periods were not very efficient because it was difficult to keep the reaction temperature and the other reaction parameters constant. In industry, runs at high temperatures were performed using an inert gas pressure. In laboratory, we avoid using pressure due to incontrollable reaction parameters. But it will be worthwhile to try higher temperatures and lower reaction periods with pressure. Since high temperatures and short reaction periods have the disadvantage of dependency on pressure, it was decided to repeat the experiment at 44°C to obtain the optimum conditions.

9- Experiments 11-12

In the eleventh experiment, the reaction temperature was 44°C and the reaction period was decreased from 240 minutes to 180 minutes. At the end, the highest yield of all the experiments was obtained (95.55 per cent). In order to check the reproducibility of the results obtained from this run the twelvth experiment was performed. In this run, keeping the temperature at 44°C, the reaction period was

further decreased to 120 minutes. When this run is compared with the first three experiments, it's seen that the reaction period is decreased 50 per cent and again a very good result of 93,67 per cent yield was obtained.

From the results obtained, it was shown that the most suitable temperature for this reaction is chosen as 44°C. The reaction period is to be decided after the interpretation of the data obtained from per cent purity tests and infrared measurements.

6.1.2. Discussion of the Per cent purity of SAS samples

When the per cent purity of the samples obtained from each experiment is compared with the original sample (98.64 per cent purity), it was observed that the results of experiments 2, 3 and 11 have the closest values (92.46, 92.61 and 98.41 per cent, respectively). The lowest value is the result of first experiment (48.96 per cent). This result is due to inefficient purification and the presence of impurities in the sample. The results of the remaining experiments vary in the range of 70.56 per cent and 87.32 per cent depending on the reaction temperature and reaction period.

In the fourth and tenth experiments, the reaction temperature is 35°C but the reaction period is increased from 240 minutes to 360 minutes. The per cent purity of the

samples also increase from 82.17 per cent to 87.32 per cent but the difference is not very significant.

In the fifth experiment, the purity is 77.76 per cent, whereas keeping the reaction temperature and period constant at the seventh experiment, the result increases to 86.86 per cent. As discussed before, this is due to experimental errors performed in the fifth experiment.

In the sixth experiment, the purity of the obtained sample is 82.17 per cent. When the reaction temperature and reaction period are observed, the results seemed satisfactory.

In the eighth experiment, the per cent purity decreases to 70.56 per cent. If we compare this result with the result of the seventh experiment (86.86 per cent), it's seen that keeping the temperature constant at 60°C, but decreasing the reaction period from 105 minutes to 75 minutes affects the result in the negative direction. This is mainly due to the incompleteness of the reaction.

In the ninth experiment, the result obtained is 78.32 per cent. Here, increasing the reaction temperature to 70°C and decreasing the reaction time to 60 minutes, decreases the purity of the sample obtained.

When the results of the last two experiments are compared, it's observed that the purity of the samples decrease from 98.41 per cent to 80.84 per cent with decreasing

reaction time at constant temperature. The highest per cent purity is obtained as a result of the eleventh experiment with a value of 98.41. At the end of the discussions of the product yields, it was decided that the optimum temperature was 44°C. This result is confirmed with the discussion of product purity and at the same time optimum reaction period is decided as 180 minutes. The validity of this result will be also confirmed by the interpretation of the obtained infrared data in Section 6.2.

6.1.3. Discussion of the pH Values

After each experiment, pH of the solution was obtained by adding miligrams of sample to about 20 ml of water gradually until the solution is completely saturated and the pH value stays constant over a period of five minutes. The values obtained in this way are compared with the values from the literature(2). It shows that the pH values range between 6.20 and 8.06 throughout the experiments. The lowest values obtained are 6.20 and 6.23, respectively and they are the result of samples obtained at the end of the first two experiments. Therefore; they are not considered seriously depending on the explanations made previously. The range stated in literature is between 8.5 and 9.2. Generally the experimental values are lower than the reported values. This result is related to differences between the recommended and the performed experimental procedures. In literature all pH values are given as the values of SAS obtained from

allylchloride. During the hydrolysis of allylchloride in the reaction mixture, formed HCl and allylalcohol are neutralized by adding NaOH. In the performed experiments, allylbromide was used as the reagent and HBr and allyl alcahol were formed during hydrolysis. The amount of NaOH used for neutralization of the acids formed, can be less in the experimental procedure. Consequently; the samples generally have low pH values when compared with the ones stated in literature. The amount of allyl alcohol produced in the reaction mixture should be checked in order to confirm the validity of this discussion.

As a result, low pH values will result when compared with the values of the literature, from;

(a) The differences in the production method of SAS
(b) The amount of NaOH used to neutralize HBr and allyl alcohol formed.

6.2. DISCUSSION OF THE INFRARED RESULTS

Infrared spectroscopy was chosen for the identification of our products obtained and comparisons were made according to the identified peaks. When we have a look at the original sample (Figs.6.2.1, 6.2.2) and compare it with the SAS characteristic peaks, firstly at 1600-1690 cm^{-1}, 920-998 cm^{-1} and 3000-3100 cm^{-1}, we saw C=C stretch and deformation motions associated with allylic double bond formation. These peaks exist in our samples in different sharpnesses. But

these were clearly seen in our samples obtained. Our ideal sample obtained from run 11 shows extremely similar behaviour as the original. But in general, the appearance of C=C peaks vary from sample to sample consistent with the percent yield and purity.

For sulphonate groups, we observe different peaks with the following wave numbers: 1100-1250 cm^{-1} (sharp), 1000-1050 cm^{-1} (medium) and 600-700 cm^{-1} (medium). All of these peaks existed and again at different proportions. Lower yield samples showed broader and not very definable peaks.

An absorption peak in 3300-3500 cm^{-1} region is ordinarily due to various O-H stretching vibrations. These peaks are often broad and appear in dilute and nonpolar solvents. Hydrogen bonding tends to broaden the peaks and move them toward lower wavenumbers. The broad peaks in our samples may be due to the absorbed water in our samples although the samples were kept in dessicators after drying and due to some methanol left overs after evaporation steps.

In order to check the improvement achieved during the washing of the SAS samples with methanol, several IR spectra were taken and they can be seen in Figs.6.2.3. through 6.2.16. As seen from these figures, peaks will get more definable, sharper and some new ones appear in the regions characterized above. In experiments 3, 9 and 11 further cleaning process will result in sharper and new peak

formation and can be seen in Figs. 6.2.7.1, 6.2.7.2, 6.2.13.1, 6.2.13.2, 6.2.15.1, and 6.2.15.2, respectively.

When we compare the IR results obtained, with literature (30) and original sample and also with percent yield and pH results, we see that they confirm the compound manufactured at a laboratory scale is Sodiumallylsulfonate.

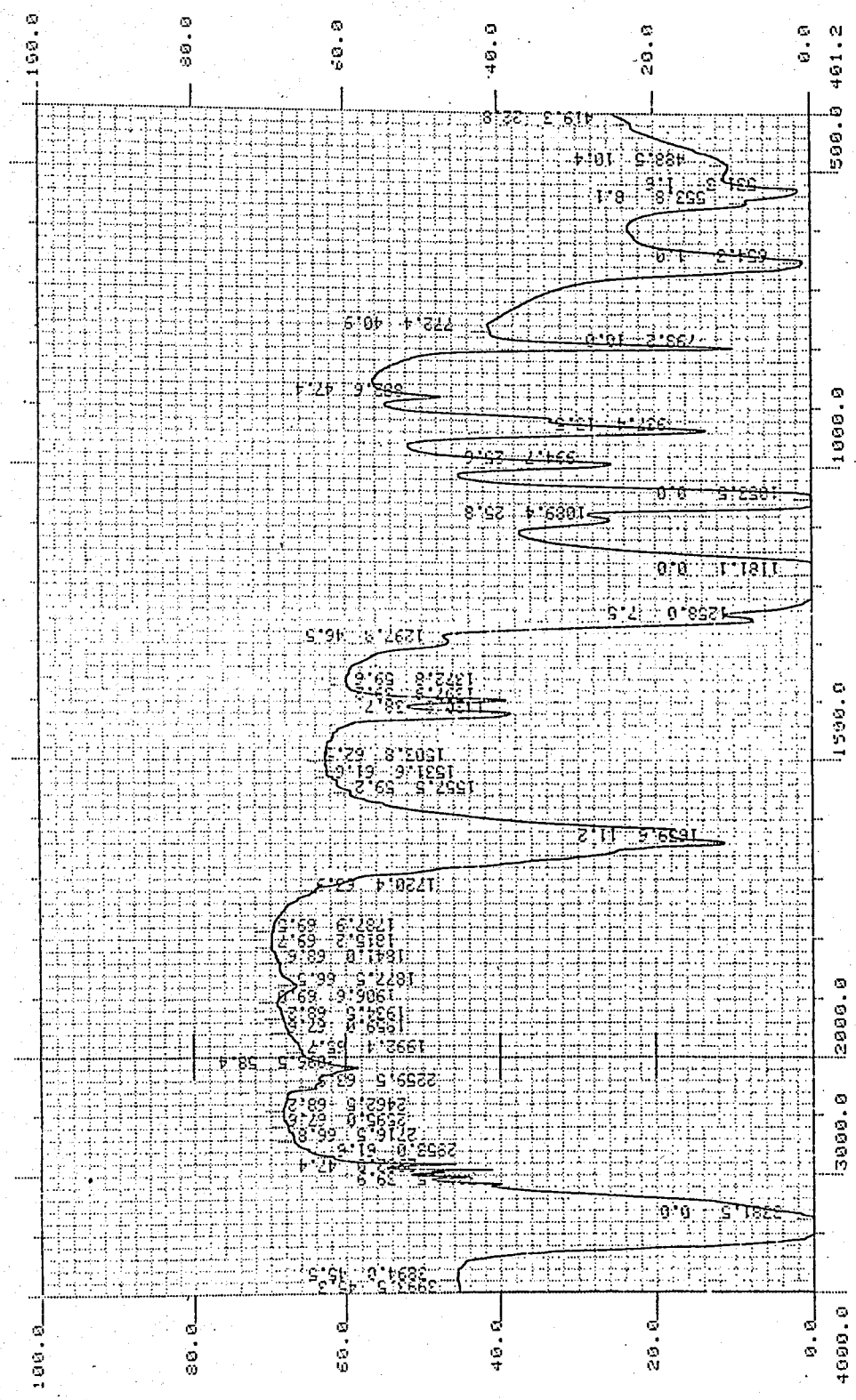
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Fig.6.2.1.

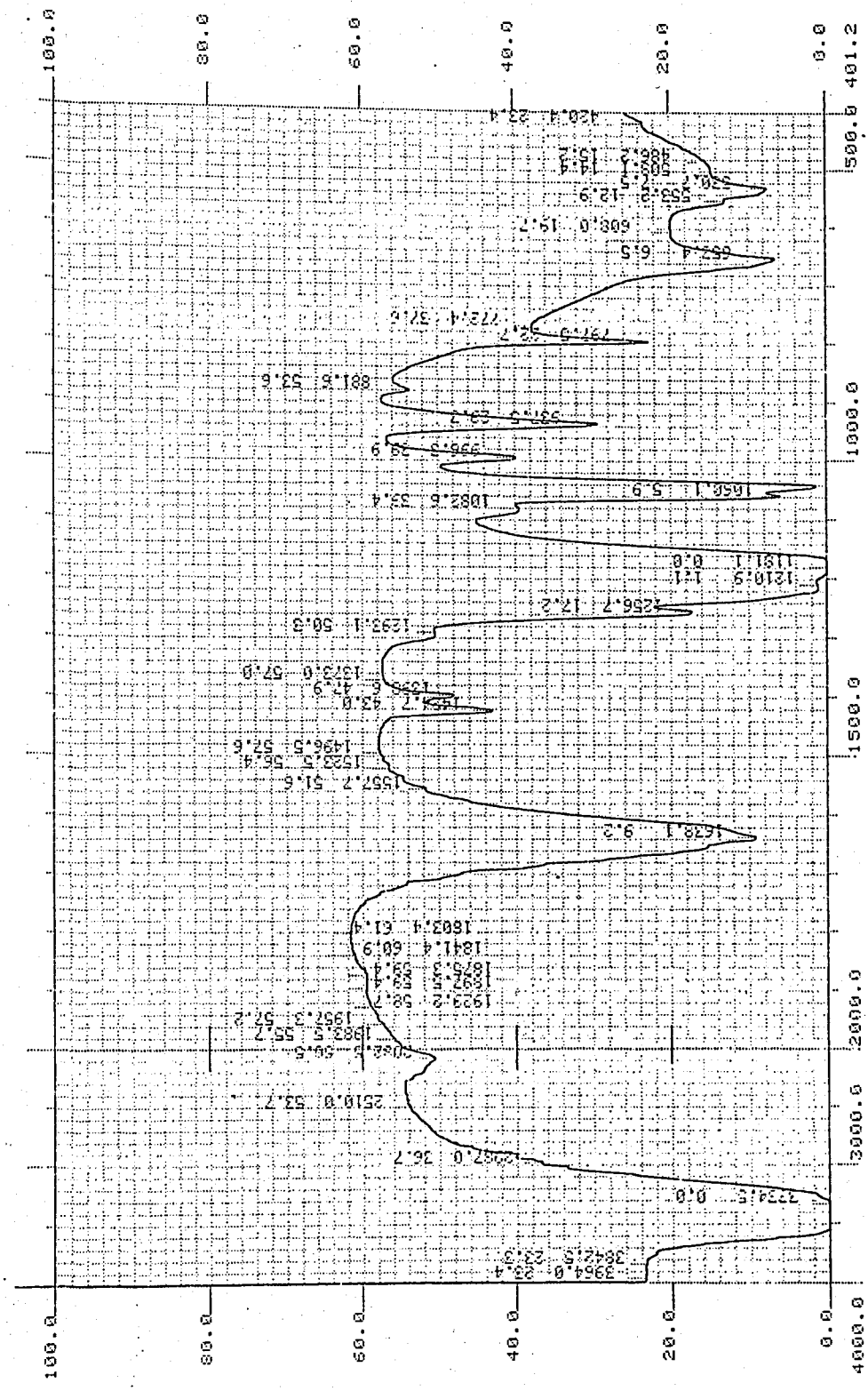
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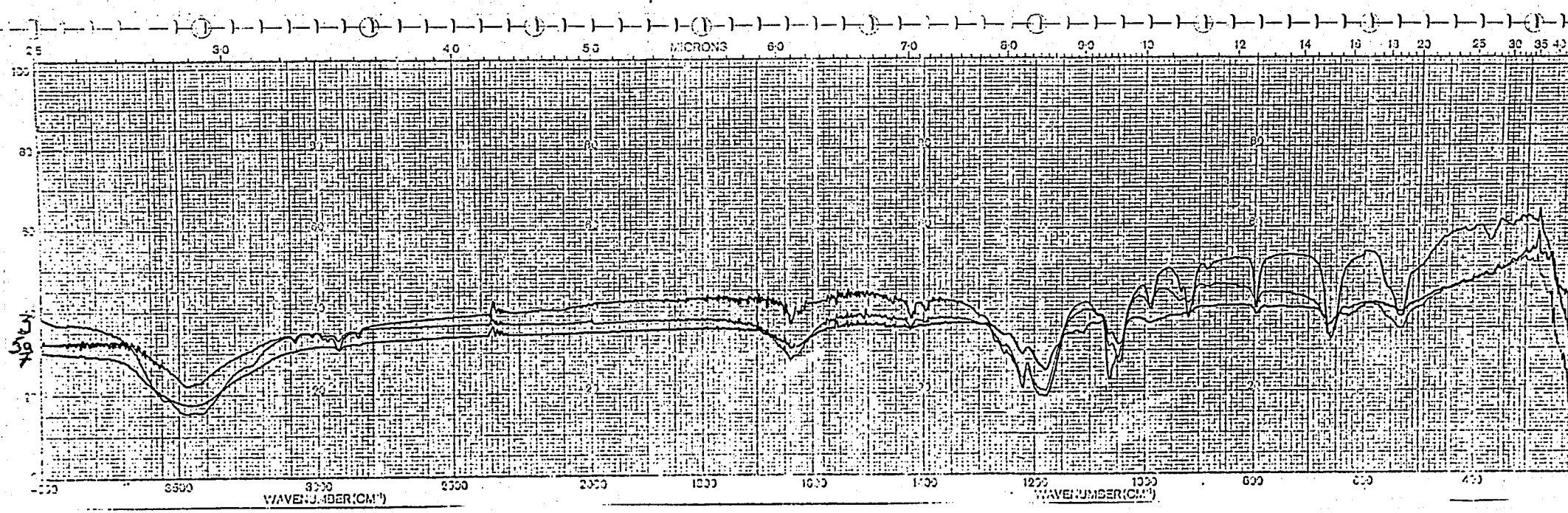
Fig.6.2.2.



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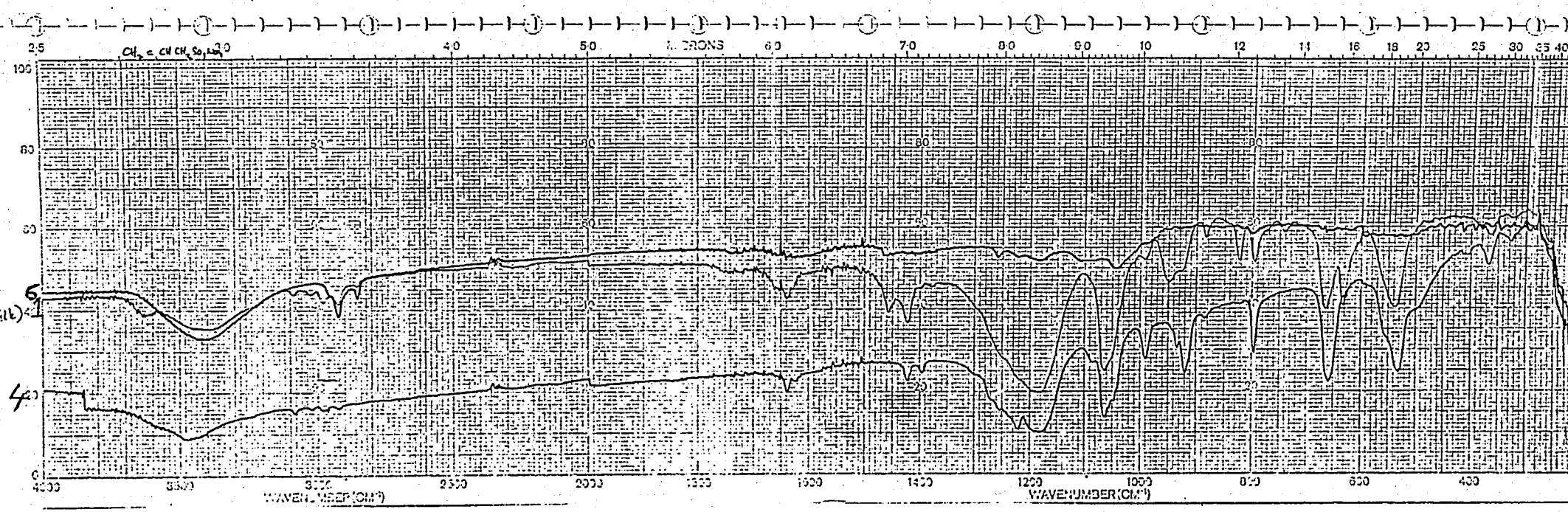

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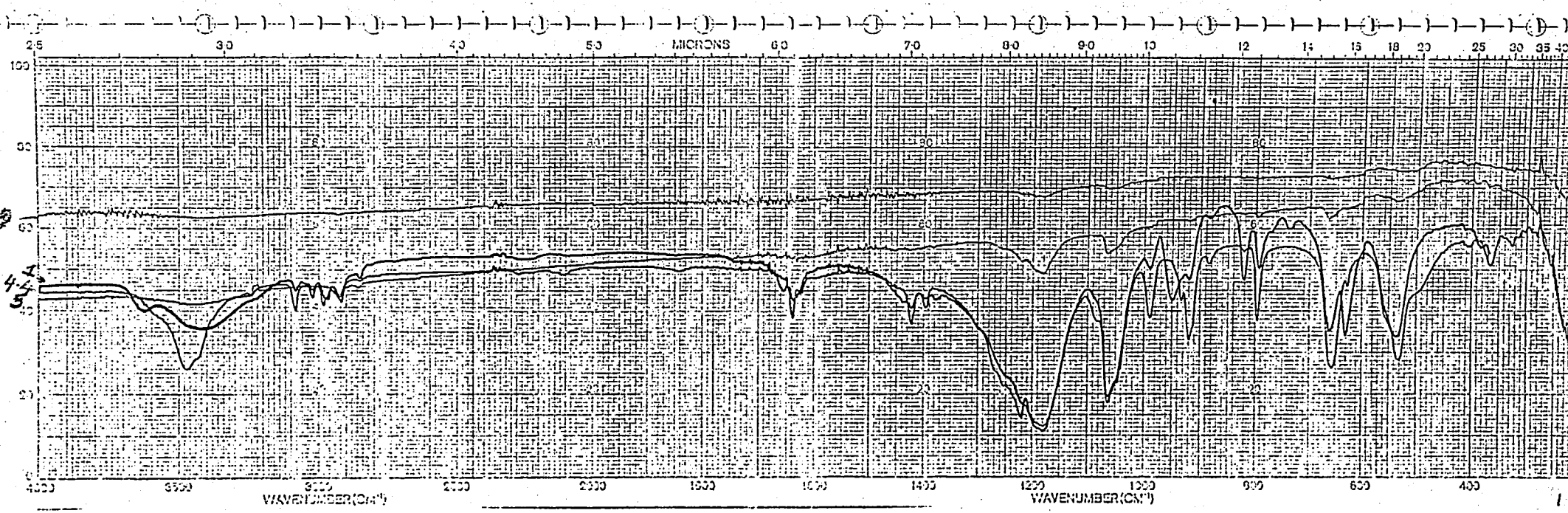

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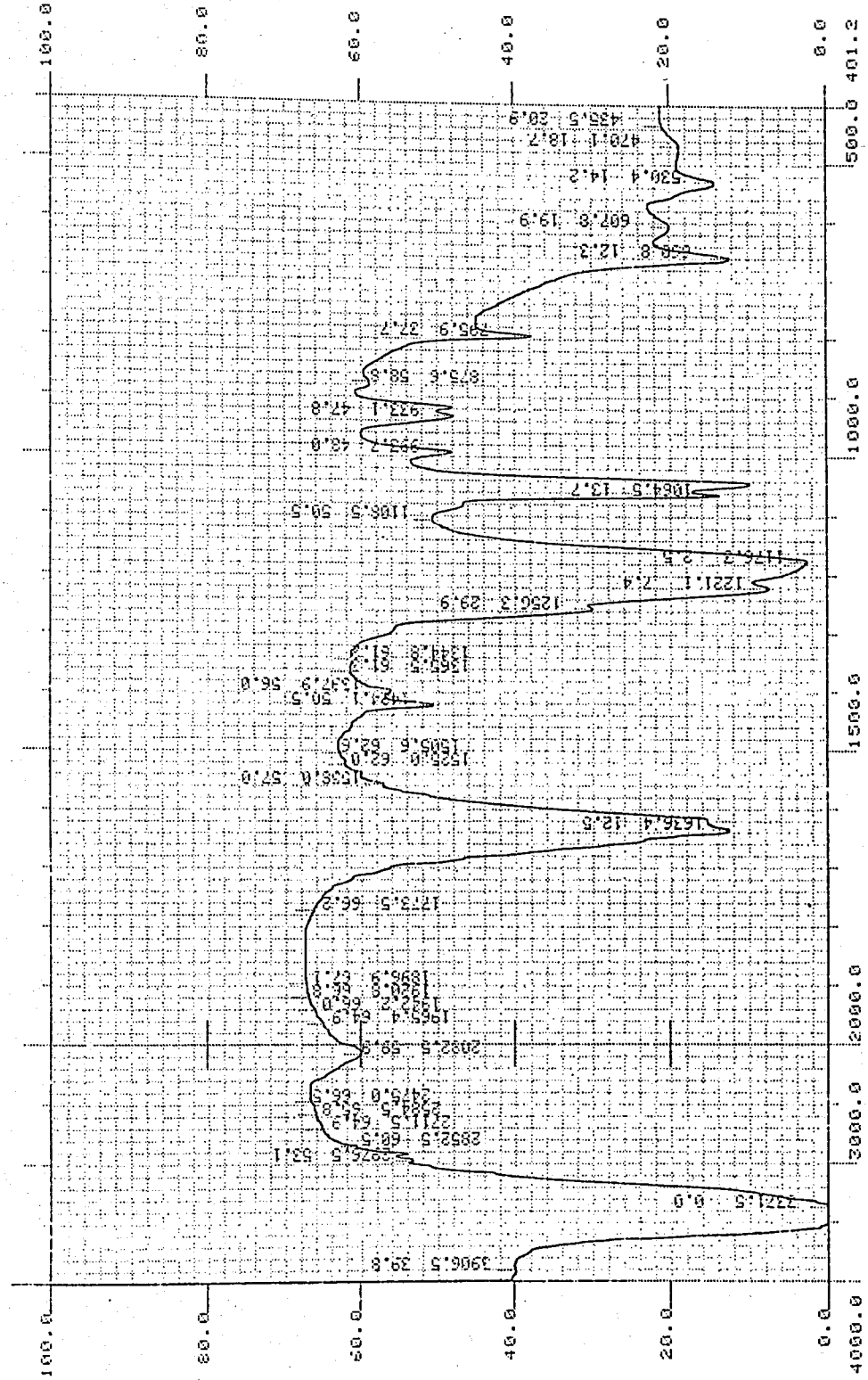
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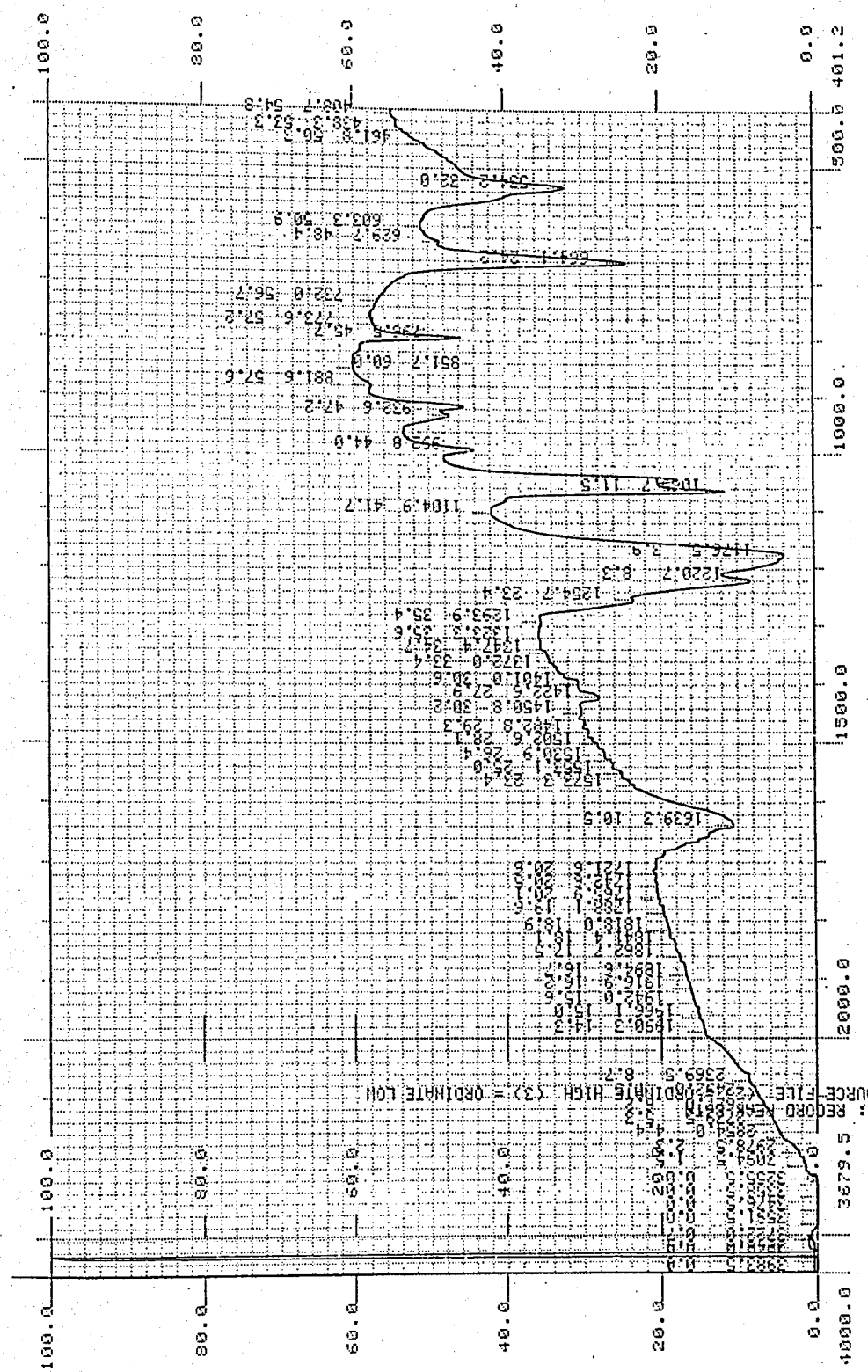
Fig.6.2.6.



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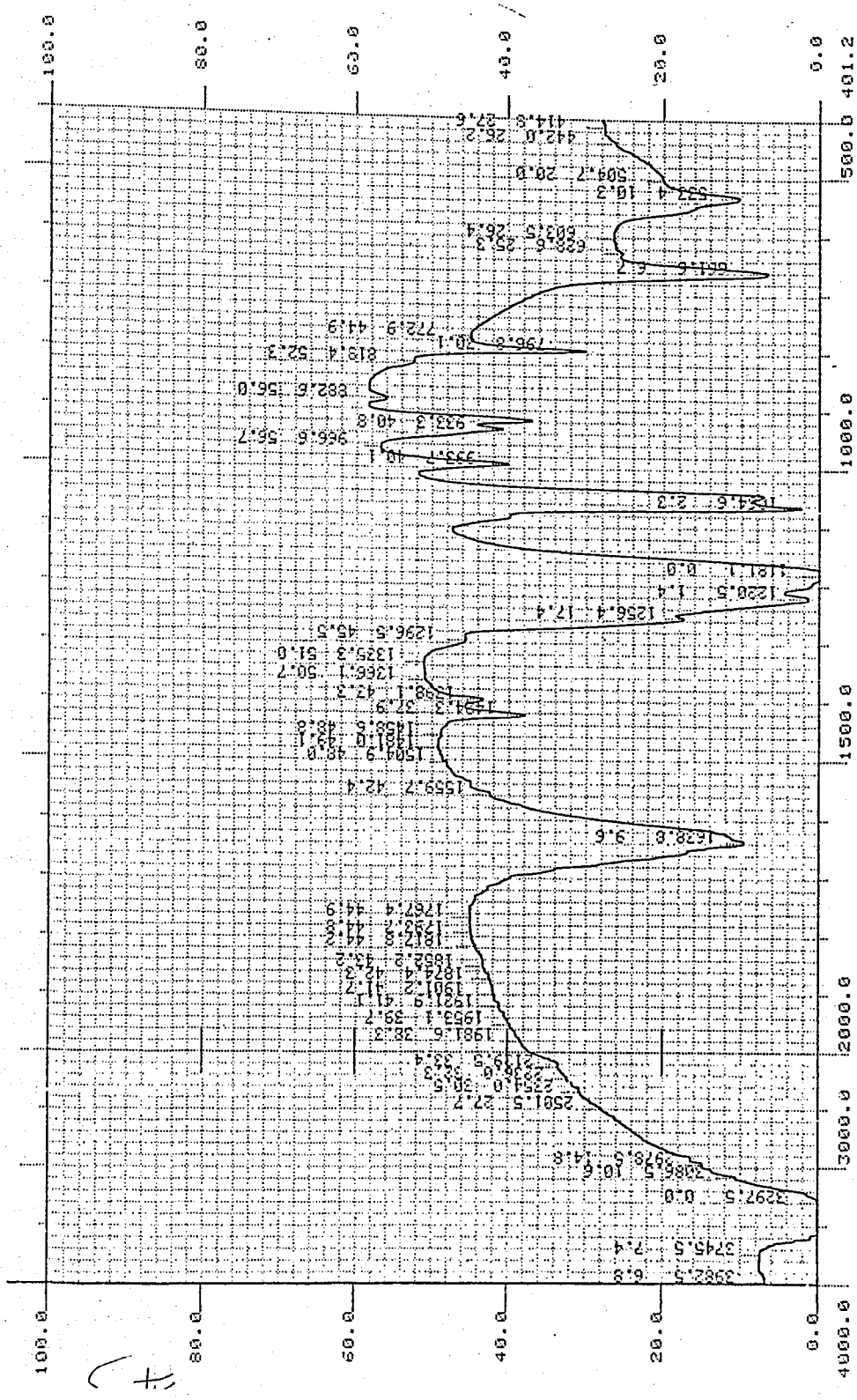
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Fig.6.2.7.2.

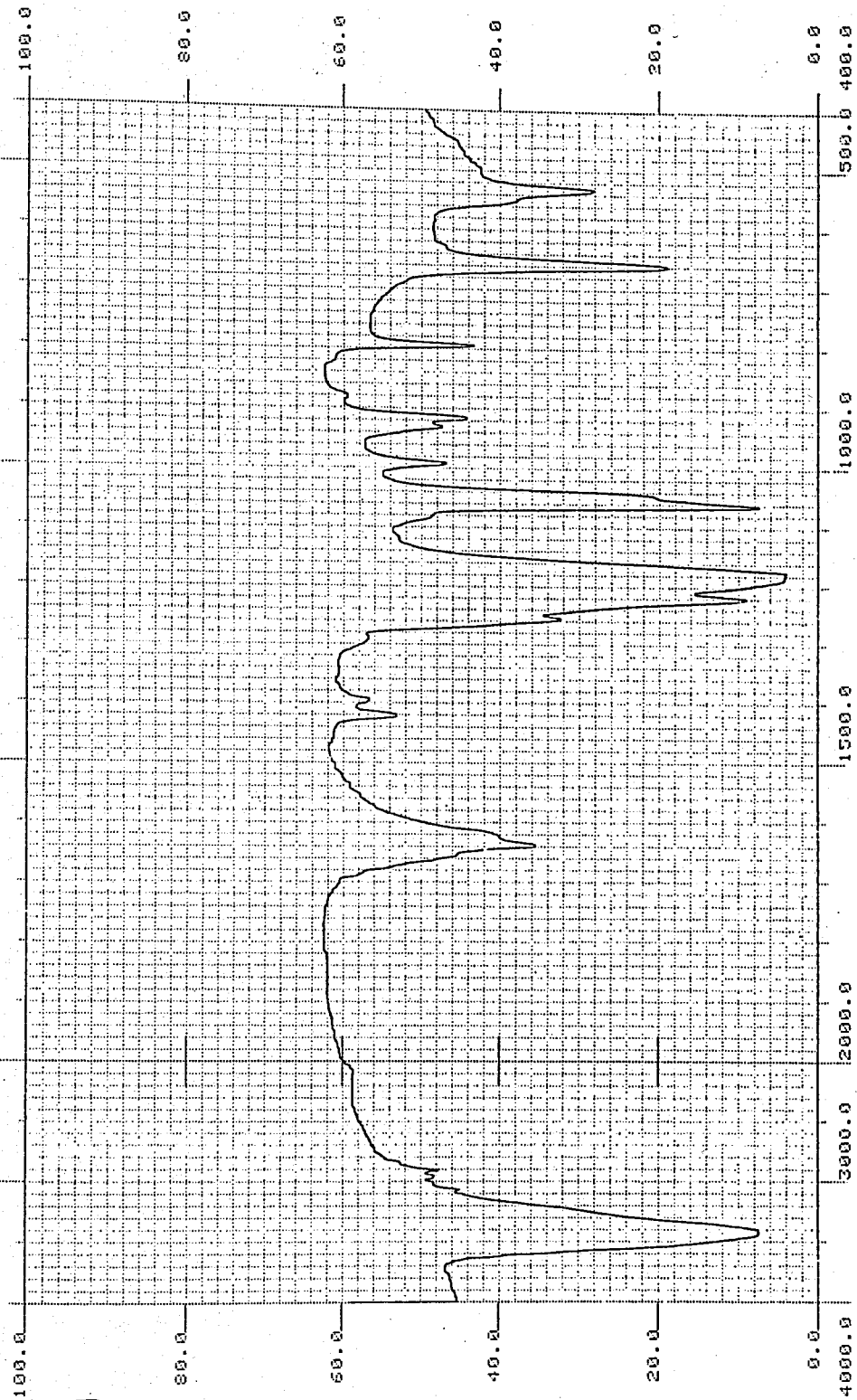
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Fig.6.2.8.

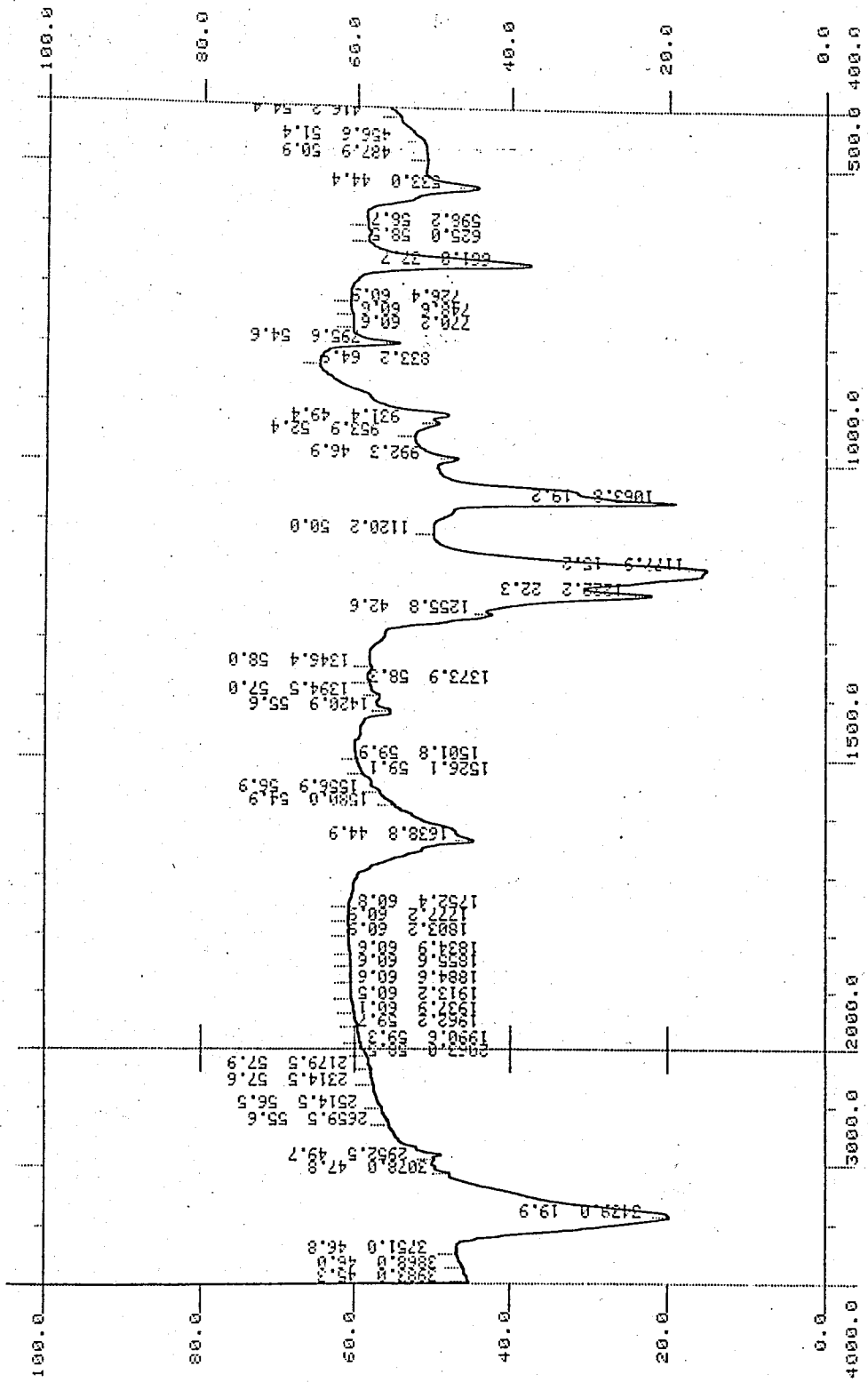
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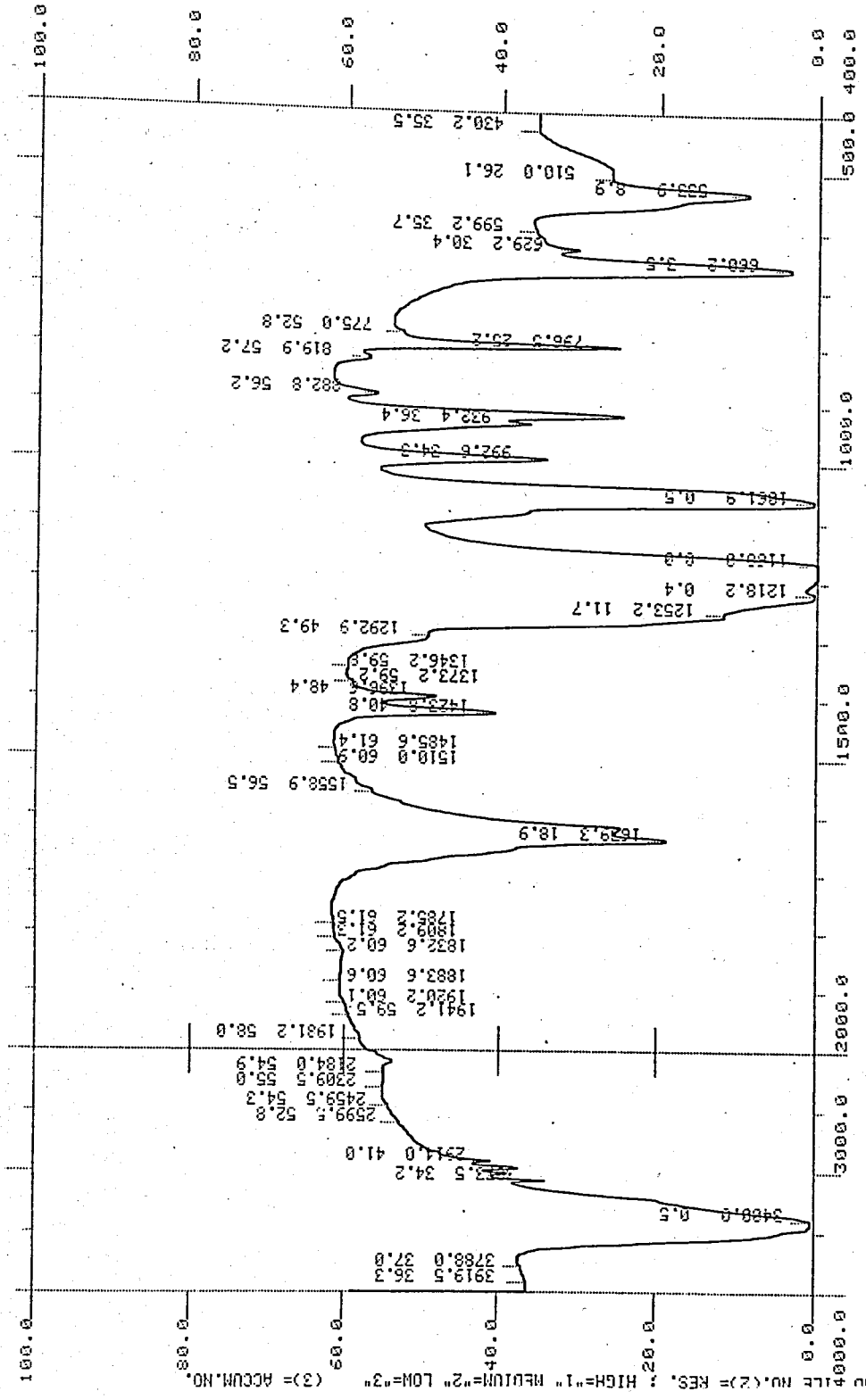
Fig.6.2.9.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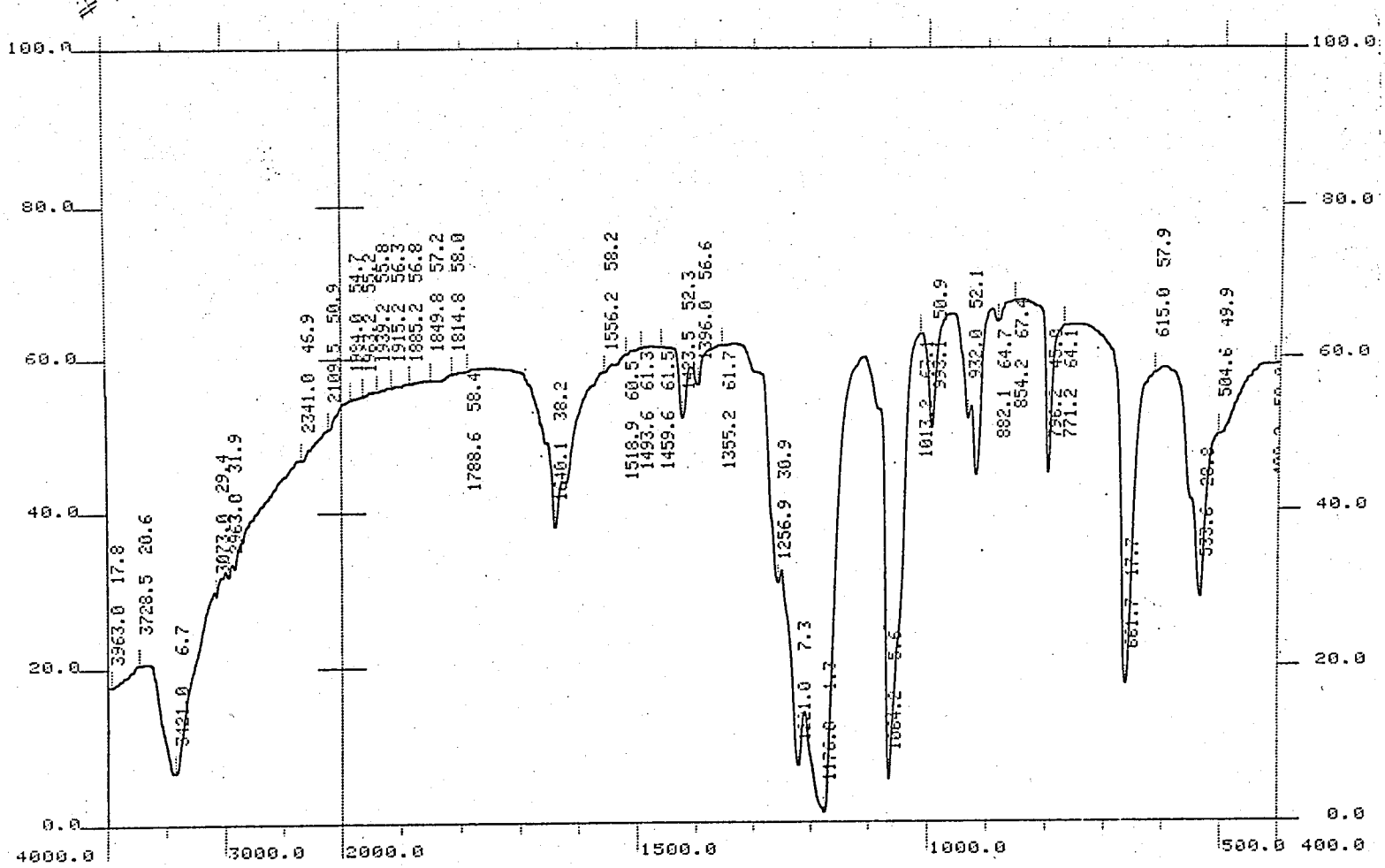
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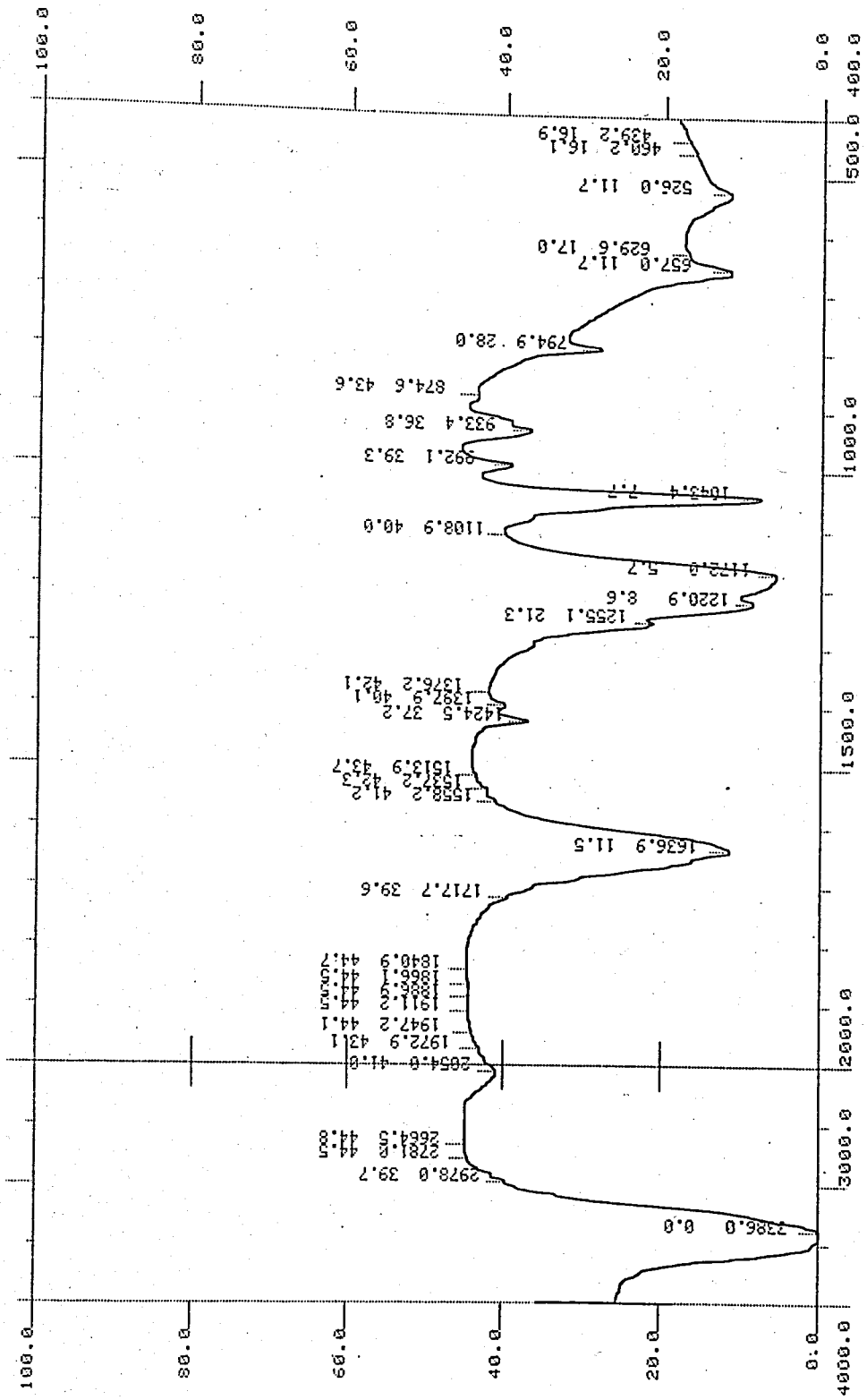
Fig.6.2.11.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439.2 16.9

Fig.6.2.12.

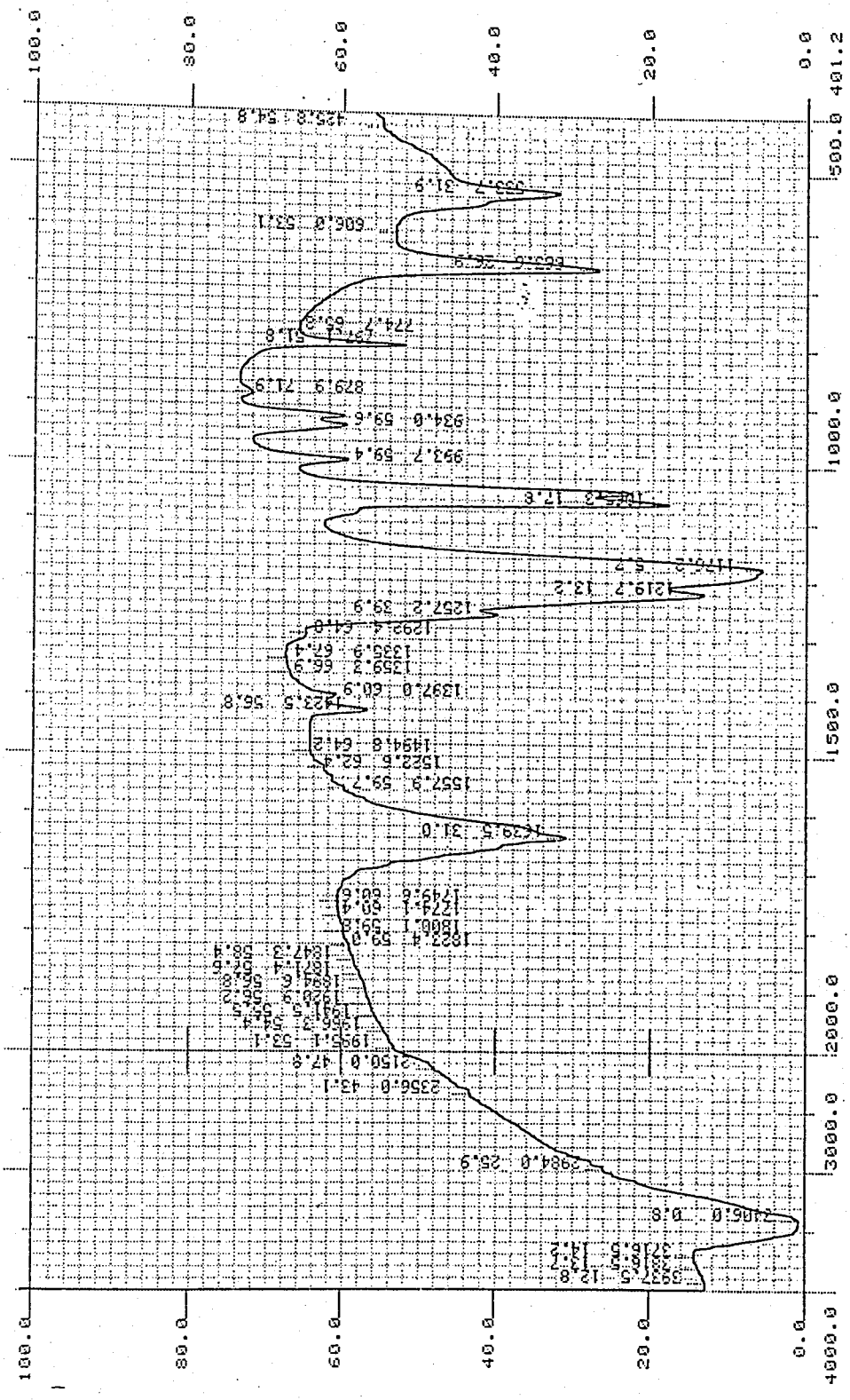
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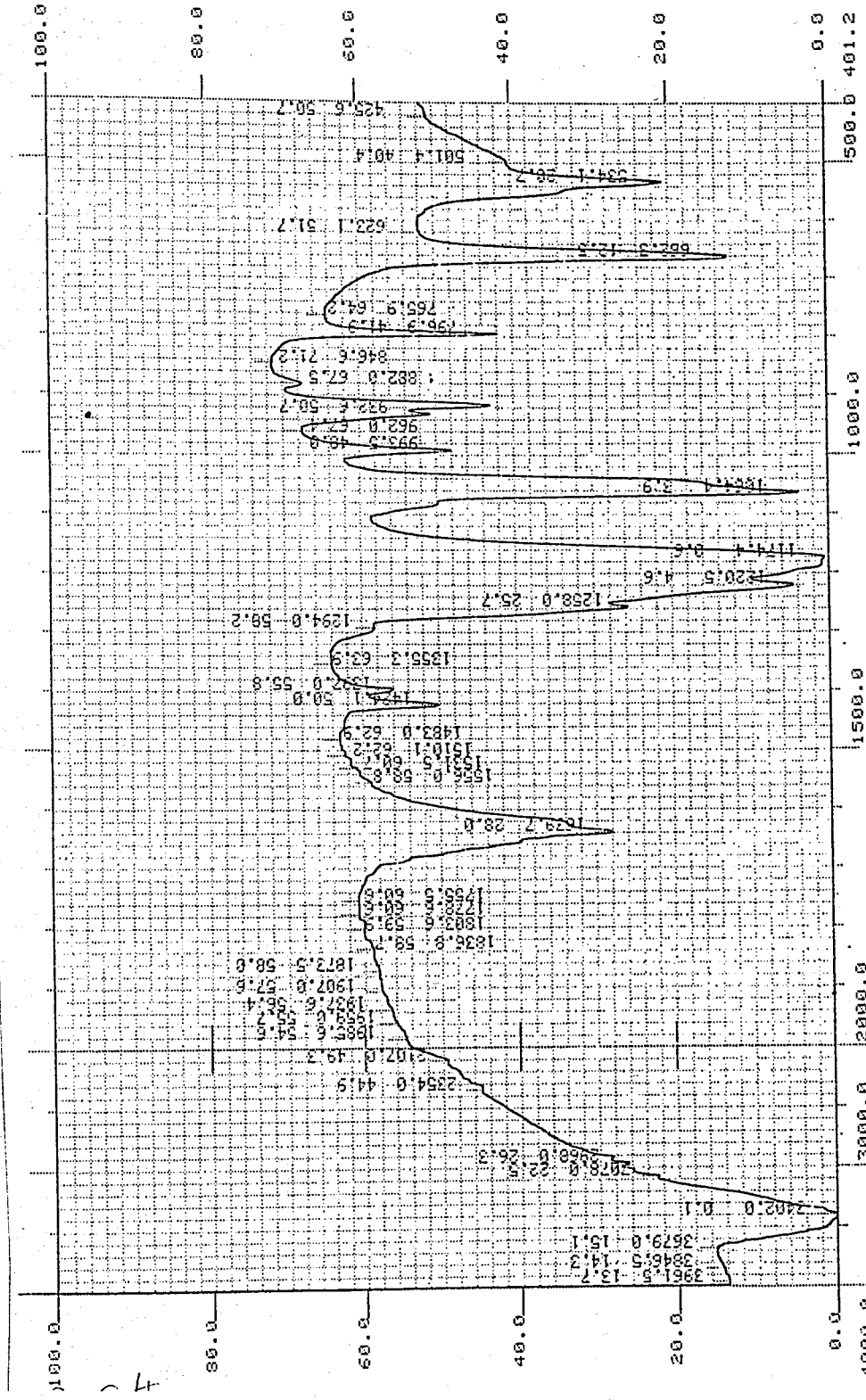
Fig.6.2.13.1.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3961.5 13.7
3846.5 14.2
3679.0 15.1
2402.0 0.1
2078.0 22.5
2360.0 26.3
2254.0 44.9
2102.0 49.2
1865.6 54.5
1554.0 55.7
1927.6 56.4
1907.0 57.6
1873.5 58.0
1826.9 58.7
1803.6 59.5
1728.5 60.5
1735.5 60.6
1629.7 28.0
1556.0 58.8
1531.5 60.2
1510.1 62.2
1483.0 62.9
1434.1 50.0
1392.0 55.8
1355.3 62.9
1294.0 58.2
1258.0 25.7
1220.5 4.6
1174.4 8.6
1064.4 3.9
995.5 46.9
962.0 67.1
922.6 50.7
882.0 67.5
846.6 21.2
796.3 41.5
765.9 64.2
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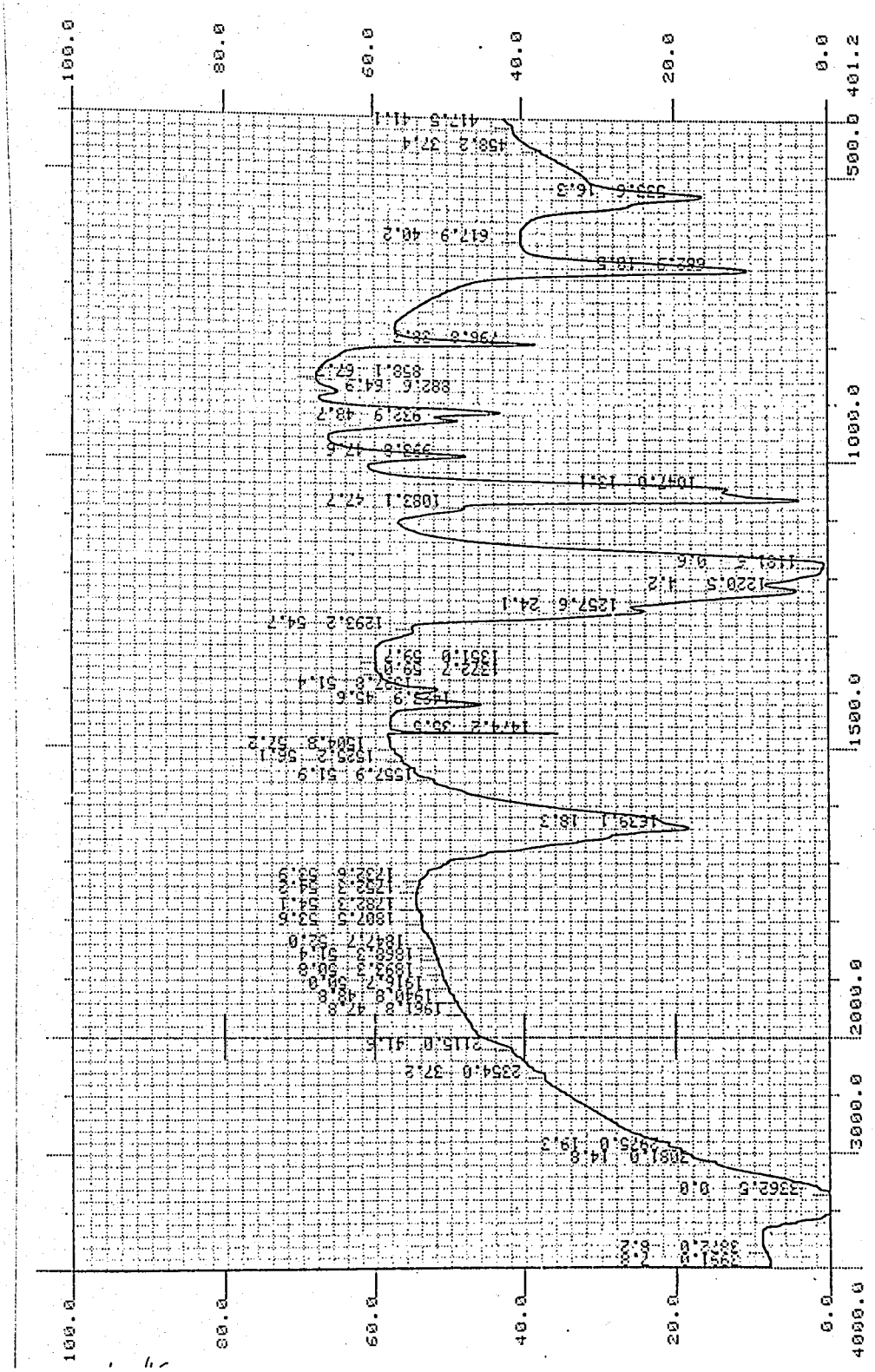
622.1 51.7
534.1 28.7
501.4 40.4
425.6 50.7

Fig.6.2.13.2.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4000.0
417.5 41.1
458.2 37.4
555.6 16.3
617.9 40.2
796.6 38.2
858.1 67.
882.6 64.3
932.9 48.7
993.8 17.6
1042.0 13.1
1083.1 47.7
1161.2 0.6
1220.5 4.2
1257.6 24.1
1293.2 54.7
1351.8 59.7
1392.7 59.0
1427.8 51.4
1463.9 45.6
1474.2 35.5
1504.8 52.2
1525.2 56.1
1557.9 51.9
1679.1 18.3
1807.5 53.6
1862.2 54.1
1884.7 52.0
1913.2 50.0
1940.8 48.8
1961.8 47.8
2115.0 41.5
2354.0 37.2
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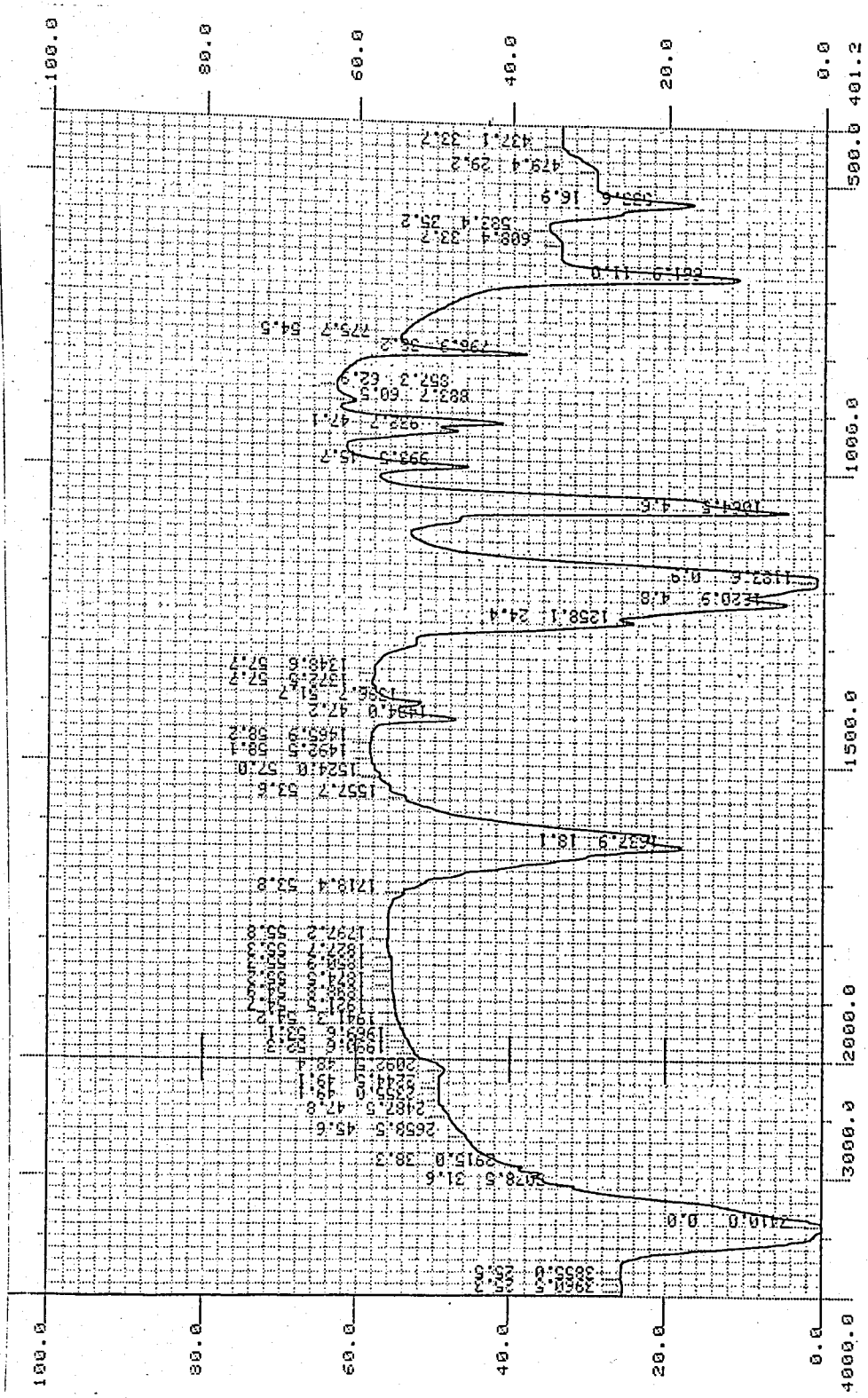
Fig.6.2.14.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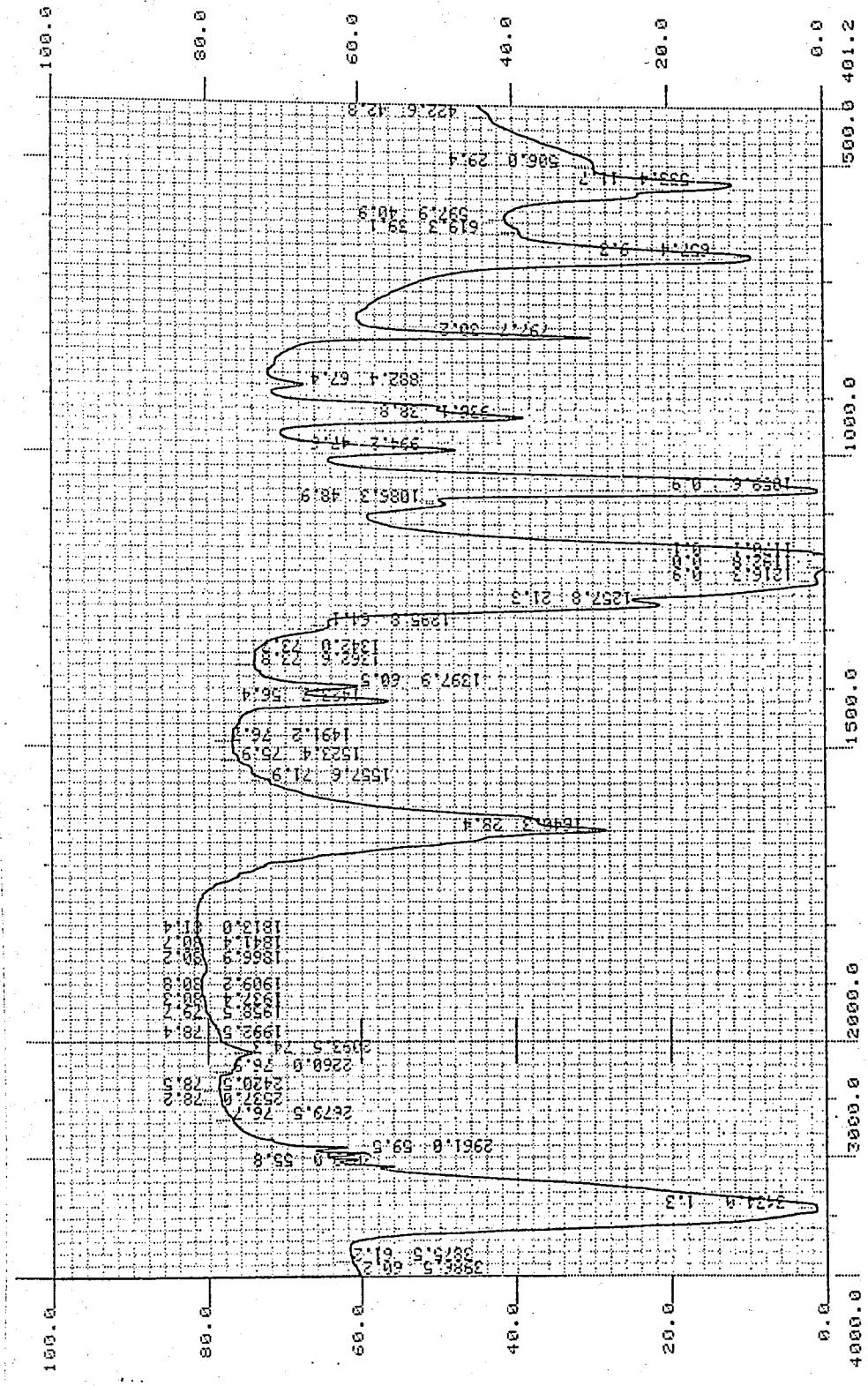
401.2

Fig.6.2.15.1.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1500.0
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500.0
401.2
3986.5 60.2
3875.5 61.2
3421.0 1.3
2961.0 59.5
2679.5 76.7
2537.0 78.2
2420.5 78.5
2260.0 76.9
2063.5 74.2
1992.5 78.4
1858.5 79.2
1837.4 80.2
1909.2 80.8
1866.9 80.2
1841.4 80.2
1813.0 81.4
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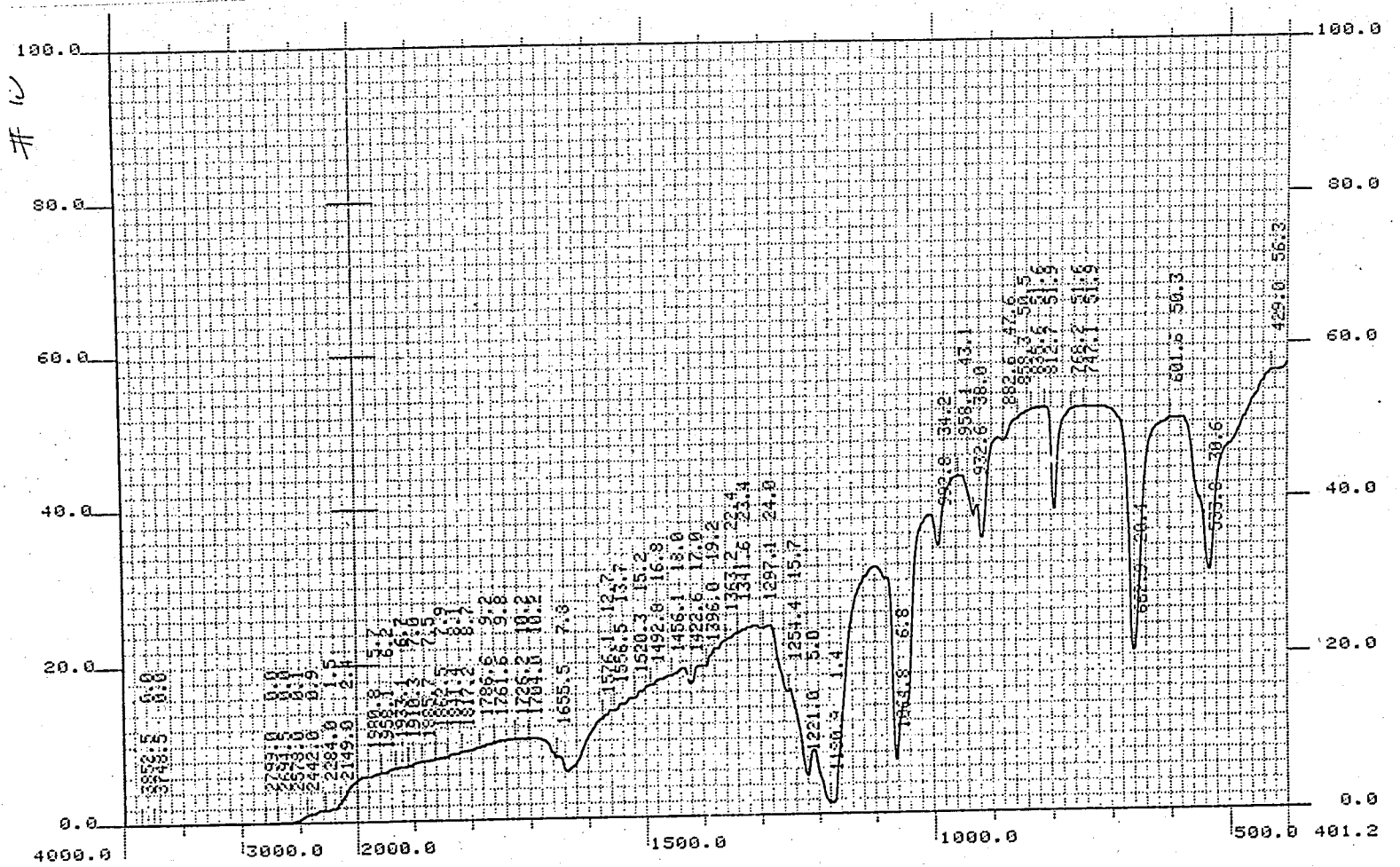
1295.8 61.1
1257.8 21.3
1152.8 55.8
1216.2 55.8
1085.3 48.9
1059.6 0.9
936.4 47.5
882.4 67.4
936.4 28.8
794.4 30.2
650.4 9.3
619.3 39.1
597.9 40.9
535.4 11.7
506.0 29.4
422.6 12.8

Fig.6.2.15.2.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401.2

Fig.6.2.16.

VII. CONCLUSION

The results obtained show that, the aims of this research were achieved. It's now proven that the reaction of allyl bromide instead of allylchloride with sodium sulfite using methanol as the solvent can be carried out at a constant temperature bath to obtain sodiumallylsulfonate.

The effects of changes in reaction parameters such as reaction period and temperature on sodiumallylsulfonate yield and quality were examined. As a result of twelve experiments performed at various conditions, it's concluded that the optimum temperature for this manufacturing process is 44°C. Also using a reaction period of 180 minutes which is lower than the preferred time in literature, is ideal for minimizing the economy since using allylbromide instead of allylchloride does not affect the total product cost significantly. Performing the experiment at 44°C and 180 minutes, gives the best yield and quality of sodiumallyl-sulfonate.

VIII. RECOMMENDATIONS FOR FUTURE WORK

In order to improve the quality and the per cent yield of sodiumallylsulfonate, the following points will be suggested for future work on this field regarding SAS manufacture.

1- The experimental system that will be used should be improved. Improvement should include a better and effective stirring rate, temperature control, the addition of NaOH and continuous monitoring system of pH control.

2- Materials used can be varied. Both allylchloride and allylbromide can be used as starting reagents and the effect of these materials on the results can be examined.

3- The manufacturing process can be improved on a pilot plant scale.

4- The experimental procedure followed in this work can be modified. In the experiments carried out at high temperatures, inert gas pressure can be tried.

5- Drying of the obtained product should be improved. Spray drying technique is recommended.

6- The sodiumallylsulfonate obtained from laboratory experiment should be tried for the brightening effects in nickel electroplating solutions.

7- The feasibility study can be made for the production of SAS both from allylchloride and allylbromide as the starting material.

8- Different solvents such as DMF and DMSO should be tried.

9- The reaction mechanism can be studied. SN_2 displacement reaction seems more suitable to this procedure than SN_1 displacement reaction.

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