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THE GAS CHROMATOGRAPHIC ANALYSIS OF
INTACT AND POST BLAST EMULSION EXPLOSIVES

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Major professor

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THE GAS CHROMATOGRAPHIC ANALYSIS OF INTACT AND POST BLAST EMULSION EXPLOSIVES

By

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ABSTRACT

THE GAS CHROMATOGRAPHIC ANALYSIS OF INTACT AND POST BLAST EMULSION EXPLOSIVES

By

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Emulsions are becoming more common place within the realm of explosives. Their ease of manufacturing, low cost of production, compositional stability, and performance in the field make emulsions a valuable and desired tool by mining companies. However, their ease of manufacturing has also allowed criminals to manufacture emulsions for potentially illegal purposes. Forensic chemists and criminal investigators will eventually become involved with a bombing case dealing with emulsions. Therfore, this thesis was based on the gas chromatographic analysis of intact and post blast emulsion samples. The emulsion samples were extracted using several different solvents to obtain the best extraction quality. Extracts were analyzed on a Perkin Elmer 8500 gas chromatograph. The resulting chromatograms revealed the wax, oil, and emulsifier combinations used within the various emulsions tested. These results prove to be a useful tool in the identification of emulsion explosives.

DEDICATION

This Thesis is dedicated to the person who has given me incentive, encouragement,
and hope. Her patience and support is greatly appreciated.
Thank you, Kymberly Anne McElgunn!

ACKNOWLEDGMENTS

During the Summer of 1992, I was involved in an internship program through the Criminal Justice Department, at Michigan State University. I had the pleasure of completing this internship at the Bureau of Alcohol, Tobacco, and Firearms National Laboratory in Rockville, Maryland. It was there where I was given the opportunity to complete the experimental research on emulsion explosives needed for this thesis project. I would like to extend my thanks and gratitude to Mr. Rick Tontarski, Mr. Richard Strobel, Mr. Ed Bender, and the rest of the staff at the ATF laboratory. Their abundant knowledge and help is greatly appreciated!

I would also like to thank Professor Jay Siegel for his patience and guidance in helping me write this thesis!

And to my family, who has believed in me from the beginning, I thank you very much!

TABLE OF CONTENTS

THES

LIST OF TABLES

LIST OF FIGURES

HE

HES

INTRODUCTION

Emulsion explosives are becoming more commonly used in criminal bombings since explosive manufacturers are turning away from the production of the once popular commercial dynamite, water gels, and slurries. Dynamite poses health risks while gels/slurries have limited shelf lives. Emulsions, however, avoid these disadvantages due to their composition. With the decrease in production of dynamite and increase in production of emulsions, the same pattern of usage has been observed in criminal bombings within the United States.

In 1990 there were 1,573 actual and attempted bombings according to data from the Bureau of Alcohol, Tobacco and Firearms (ATF), Federal Bureau of Investigation (FBI), and the United States Postal Service (USPS). Those bombings caused the deaths of 22 persons, injuries to 251 persons, and approximately $13 million in property damage. The most common targets are residential buildings, mail boxes, vehicles, and commercial buildings with motives typically of vandalism and revenge (Dept. of Treasury, ATF, 1990). The deaths and damages caused by bombings are gruesome and severe, while the potential destructiveness of further bombing incidents is

high. Although the destruction caused by bombings cannot be reversed, justice can be served if investigators are able to determine the type of explosive used, and the person responsible for making and planting the device.

Identification and characterization of the explosive can be paramount in the investigation of any bombing incident, and can serve as a case breaking lead for the investigator. With this information the investigator can concentrate his/her efforts on a certain manufacturer or supplier, and on evidence collected in connection with a certain suspect. Unfortunately, emulsions are made with the same or similar materials by all manufacturers making identification of a particular manufacturer quite difficult.

Essentially, emulsions are made with a carbonaceous fuel which serves as the fuel phase and acts like a catalyst, an inorganic oxidizer salt which acts as an oxidizing agent, microspheres which provide sensitization and density control, an oil/wax combination which helps retain consistency and adds to the fuel phase of the emulsion, an emulsifier to emulsify the mixture, aluminum which is used as an auxiliary fuel, and water which is needed in the reaction with the oxidizer salt (Wade 1978). Different ingredients can be used to act as an oxidizer, emulsifier, fuel, oil, or wax and it is assumed that manufacturers change ingredients depending upon price variation and the conditions (weather and soil) under which the emulsion will be used. Also, explosive manufacturers

consider their formulations to be proprietary, making it difficult to obtain compositional information. Therefore, analysis of emulsions may yield results that cannot be used to individualize a sample to a particular manufacturer, but analysis of an intact sample and a post-blast sample can yield data that will permit comparison.

The research completed here utilized a gas chromatograph (GC) to analyze the organic components (oil/wax/emulsifier) of five intact emulsions, one emulsion blasting agent, and one post-blast sample.

From the results obtained it is hoped that chromatograms from GC analysis will provide the necessary information to determine if different intact samples can be distinguished from each other, and if post-blast samples can be identified as emulsions and to one particular intact sample.

Combining the analysis of organic components in emulsions by GC with the analysis of inorganic components by spot tests, X-ray diffraction (XRD), and ion chromatography, allows forensic chemists to make a responsible conclusion as to whether an unknown explosive is an emulsion or if a post-blast sample reveals emulsion explosives that can be compared with suspect intact samples.

LITERATURE REVIEW

The era of high explosives began in 1846 when a chemist, named Ascanio Sobrero, at The University of Torino, nitrated glycerin and partially destroyed his lab in the process (Hopler, 1991). However, it was not until 1866 when Alfred Nobel received his patent on a mixture of kieselguhr and nitroglycerin (NG) commonly called dynamite (Hopler, 1991). Nobel solved the problem of NG exploding unexpectedly by making it more stable with the use of kieselguhr (diatomaceous earth) since this material is an absorbant and acts to protect the NG from shock. Giant Powder Company and Dupont were the two major companies to produce dynamite in the late 1800's after learning how to make it more stable and packageable. Mining and construction companies then learned that dynamite could produce a more desirable effect than could black powder so the use of dynamite spread rapidly.

Improvements in dynamite formulations began after recognizing that kieselguhr was an inert product, but other materials such as sodium nitrate would act as an oxidizer adding more strength to the mixture. NG was also mixed with nitrocotton to produce a very high strength explosive where the NG wasn't in the liquid form. Ammonium nitrate was also

used to replace part of the NG, leaving a powerful, water-resistant product.

In 1925 Hercules Powder Company marketed a brand of dynamite with a high ammonium nitrate concentration (Hopler, 1991). This product utilized inexpensive ingredients but still had strength enough to produce desired effects.

Then in 1935, Dupont marketed a mixture of AN, fuel oil, and dinitrotoluene (DNT) that had advantages of extreme insensitivity, easy handling, and decreased toxcicity (Hopler, 1991).

In the mid 1950's an explosive composed of only AN and a fuel oil was introduced. It was called ANFO (ammonium nitrate fuel oil). ANFO had the major advantage of low cost, but lacked water resistance and density. Therefore, it had to be packaged in water resistant liners for use in wet holes, which didn't allow for the cross-section of the hole to be completely filled. The low density limited the amount of the ANFO that could be used, thus limiting the energy released from detonation. In answer to this problem Dr. Melvin A. Cook invented an ammonium nitrate based explosive called a slurry, in 1957 (Hopler, 1991). Unlike ANFO the slurry itself contained water and a gelling agent, usually a guar gum, to thicken the solution. This added the water resistance and higher density lacking in ANFO.

In addition to slurry components, companies began adding sensitizers, which increase the detonation propagation. This

eliminates the need for a separate sensitizer. Commonly used components were chemical gassing, microballoons, aluminum powder or chips, Methylamine nitrate (MAN), ethylene glycol mononitrate (EGM), hexamethyl enetetramine nitrate (HMTAN), and monoethanol amine nitrate (MEAN) (Hopler, 1991).

Slurries became extensively used, especially "Tovex," produced by Dupont. Slurries had advantages over ANFO, however they had the disadvantages of exhibiting unexpected variability in performance, having a limited shelf-life, and having detonation problems at ambient temperature and pressure (Kaye, 1980).

In the 1980's a new explosive called an emulsion emerged with advantages over slurries. Emulsions exist either as an oil-in-water or water-in-oil composition where both exist as small droplets of one material enclosed in a continuous matrix of another material (Hopler, 1991). Emulsion explosives are usually of the water-in-oil type, where water droplets are surrounded by oil making the mixture water resistant. The water droplet however is actually a supersaturated solution of ammonium nitrate surrounded by the hydrocarbon fuel.

According to Hopler (1991) ANFO is the most used explosive material in the United States, but does not have the most efficient detonation reaction due to AN particle size. In emulsions the AN particle size has been drastically reduced, which increases the detonation reaction.

Besides the microscopic AN particles, emulsions contain

water, one or more inorganic nitrate oxidizers, oil with or without dissolved wax, and emulsifying agents. Emulsions generally contain a sensitizer such as a metal perchlorate, but all emulsions manufactured at Atlas contain bubbles or microspheres as a sensitizer (Midkiff 1992). Microspheres also provide density control as well as sensitization.

A more detailed composition comes from a patent by Wade (1978), but can also be found in a variety of patents on emulsion explosives and blasting agents. The cap-sensitive emulsion described by Wade (1978) contains from 3.5% - 8% by weight of a hydrocarbon fuel with an emulsifier. Typical fuels used are paraffins, olefins, naphthenes, aromatic compounds, and saturated or unsaturated hydrocarbon fuels. Included within the fuel is a combination of a wax and an oil. The wax content can range from 2.5% - 4.5% by weight in the emulsion, and the oil can range from 0.5% - 5.5% by weight in the emulsion (Wade, 1978). The waxes used can include petrolatum wax, microcrystalline wax, paraffin wax, mineral waxes, animal waxes, and insect waxes. Examples of oils used are petroleum oils, vegetable oils, or highly refined mineral oils.

The emulsifier is also combined with the carbonaceous fuel ranging from 0.5% - 2.0% by weight of the total composition (Wade, 1978). Examples of the emulsifiers are sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate, and sorbitan

tristearate. Mono- and diglycerides of fat-forming fatty acids and polyethylene sorbitol beeswax derivative materials can also be used as emulsifiers.

Particulate aluminum can be used as an auxiliary fuel within emulsions ranging up to 15% by weight (Wade, 1978).

Water is present from 10% - 22% by weight of the total emulsion (Wade, 1978).

An oxidizer salt ranging from 65% - 85% by weight of the emulsion is typically present (Wade, 1978). The salt is generally ammonium nitrate, however there may be up to 20% of another inorganic nitrate combined with AN, such as an alkali or alkaline earth metal. An ammonium perchlorate or earth metal perchlorate could also be used.

Ranging from 0.9% - 15% by weight are glass microbubbles (Wade, 1978). These can range from 10 - 70 microns in size, where the bulk density ranges from 0.1 - 0.4 g/cc. The microbubbles are used to achieve a density in the emulsion from 0.9 -1.35 g/cc (Wade, 1978). Commonly used microbubbles are sold by 3M Company with a trade designation of B15/250. Emerson & Cumming, Inc. sell microbubbles with a trade designation of Eccospheres. Philadelphia Quartz Company sells microbubbles under the trade designation Q-CEL.

Blasting agents are described as being an explosive, either a slurry or emulsion, that cannot be initiated by a No. 8 blasting cap, thus requiring a primer for detonation (Midkiff, 1992).

Emulsion blasting agents contain the same general components as do emulsion explosives except for the use of a sensitizer such as inorganic metal compounds like aluminum (Brockington, 1980)(Bluhm, 1969).

Published laboratory analyses of emulsion explosives or blasting agents is limited since emulsions are relatively new. However, due to the inorganic components within emulsions, unrelated experimental studies performed on inorganic materials can be applied to the analysis of emulsions.

Glass microspheres were analyzed by Midkiff (1992) using Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDX) which determined elemental composition of the microspheres. The elemental compositions were found to be different among samples allowing them to be associated with their respective producers. Particularly, elements of 3M glass microspheres are calcium and silicon. Philadelphia Quartz (PQ) glass microspheres contain sodium and silicon. PQ ceramic microspheres contained aluminum, calcium, iron, potassium, sulfur, silicon, and titanium. An unknown producer of phenolic microspheres contains aluminum, chlorine, iodine, sodium, sulfur, and silicon. An unknown producer of glass microspheres with a Hercules brand name contains the elements aluminum, calcium, chlorine, potassium, sulfur, and silicon.

Further inorganic analysis can be accomplished by a variety of tests such as spot tests, crystal tests, ion chromatography (IC), Fourier Transform Infrared (FTIR), and

XRD. Inorganic components of emulsion explosives and blasting agents can vary depending upon the different oxidizers and sensitizers used during manufacturing. As noted in several patents, inorganic oxidizing salts within emulsions are ammonium nitrate, sodium nitrate, potassium nitrate, calcium nitrate, ammonium perchlorate, sodium perchlorate, potassium perchlorate, or calcium perchlorate (Bluhm 1969)(Wade 1978)(Brockington 1980).

Spot tests and crystal tests offer a quick and easy determination of the inorganic composition of an emulsion. Nitrates and nitrites can be detected by the dipheynlamine, Griess, or nitron spot tests. With the addition of diphenylamine reagent to the test solution a deep blue color will appear (Hoffman and Byall, 1973), a blue to blue-black color indicating nitrates, and blue-black color indicating nitrites (Parker, Stephenson, McOwen, Cherolis, 1974). As noted by Hoffman et al. (1973) the diphenylamine test will also produce a blue color in the presence of other oxidizing agents, therefore this test is most useful as a screening test.

The Griess test will produce a pink to red color in the presence of nitrates when the reagent is added to the test solution. In the presence of nitrites a red to yellow color will appear (Parker et al. 1974). Hoffman et al. (1973) states that after the addition of the Griess reagent to the test solution addition of zinc dust will reduce the nitrate

ions to nitrite ions producing a deep red color.

The nitron reagent will produce a white precipitate in the presence of nitrates and a dirty white precipitate in the presence of nitrites (Parker et al. 1974).

The detection of ammonium is performed by the addition of Nessler's reagent to the test solution where a orange/brown color will appear (Hoffman et al. 1973)(Hayes, 1980)(Midkiff et al. 1992).

Perchlorates were detected by Parker et al. (1974) by adding cupric tetrapyridine reagent to the test solution yielding a purple crystalline precipitate, or by adding methylene blue reagent yielding a purple color to a purple precipitate. Midkiff et al. (1992) also used triphenylselenium chloride to detect perchlorates, which forms a white precipitate or white needles in clusters within the test solution. Tetrabutyl ammonium chloride, when added to the test solution will form a white precipitate or small crystals resembling glass chips in the presence of chlorates.

Sodium, potassium, and calcium can be detected through the use of a flame test on the dried extract. An intense yellow color will appear in the presence of sodium. A lilac flame coloration will appear under two thicknesses of cobalt blue glass to indicate the presence of potassium. An orange-red flame coloration will indicate the presence of calcium, however, this test is inconclusive if sodium is also present (Hayes 1980).

THE

Chemical spot tests can also be performed on sodium, potassium, and calcium. The detection of sodium is performed by the addition of zinc uranyl acetate reagent to solution yielding a slow developing yellow/green fluorescence under ultraviolet light. Potassium is indicated when a white precipitate forms upon addition of sodium tetraphenylboron to the test solution. Ammonium ions should be removed prior to this test by boiling with 2N sodium hydroxide. Calcium is indicated when a violet precipitate forms after addition of freshly prepared 0.2% aqueous sodium rhodizonate solution and 1N sodium hydroxide solution (Hayes 1980).

Beveridge, Greenlay, and Shaddick (1983) completed experimental studies on water gels and a wide range of "home-made" chemical mixtures utilizing IR and XRD in part. Their samples were confined in steel pipes and ignited leaving residue and unreacted material to be analyzed. The chemical mixtures were two component combinations of oxidizers with a fuel. Potassium chloride was identified by XRD, while chlorate and some unreacted perchlorate were identified by IR and XRD. Nitrate oxidizers were reduced to nitrites which were identified by IR.

Ion chromatography (IC) is increasingly becoming used to detect inorganic materials within suspect explosives. This technique is beginning to take the place of traditional chemical spot tests and XRD, or being used in conjunction with them. Reutter, Buechele, and Rudolph (1983) believe that the traditional methods have limitations in their efficiency to detect inorganic materials that IC would readily detect.

When the extortion bombing of Harvey's Resort Hotel, in Nevada, occurred in 1980, the extortionist told authorities that the explosive device contained TNT. However, debris collected after the bomb detonated was extracted with water and the extract was analyzed using chemical spot tests and XRD. These tests only showed positive results for calcium carbonate and calcium sulfate from pieces of cement and dry wall (Reutter et al. 1983).

With no success using those techniques they decided to analyze the water extract with IC where, in fact, traces of sodium, ammonium, and nitrates were detected on all fragments of the improvised explosive device (IED) (Reutter et al. 1983).

Analysis of post-blast residues of a commercial slurry revealed that IC detected sodium, nitrate, ammonium, monomethylamine, potassium, nitrite, choride, and sulfate where XRD of the same residue only detected sodium nitrate (Reutter et al. 1983).

X-ray diffraction (XRD) is by no means an obsolete tool in the analysis of pre- or post-blast residues, however, it proves most useful in the analysis of solid residues versus that of traces that may be recovered from a water extraction.

Rudolph et al. (1983) experimented with varying IC conditions to yield optimum results. They found that nitrates, nitrites, chlorates, phosphates, and sulfates can be detected in a single run using a sodium carbonate/bicarbonate eluent, and sodium, ammonium, potassium, and monomethylamine were detected using a 0.10 N HCL / 60% H2O / 40% methanol eluent.

The detection of divalent cations, such as calcium, has become more important since the use of calcium nitrate as an oxidizer along with ammonium nitrate. The divalent cations calcium, magnesium, strontium, and barium were detected using a 0.0025 N HCL / 0.0025 N phenylenediamine - 2HCL eluent (Reutter, Buechele 1983).

Aluminum is detectable in pre-blast samples since most aluminum used as sensitizers in gel/slurries and emulsions are in granular or chip form, and can be seen with the naked eye. Testing the particles for confirmation of aluminum has been done on a microscope slide with a drop of 10% NaOH. The aluminum should immediately react with the NaOH to release bubbles. The same test can be carried out with 6N HCL which also reacts with aluminum, forming gas bubbles (Midkiff et al. 1992).

Organic components that exist within emulsion explosives and blasting agents include oils, waxes, and emulsifiers. There is a large variety of oils, waxes, and emulsifiers that can be used in any number of combinations and concentrations, and since a single emulsion producer will use materials from different suppliers, the value of characterization of the

THE

oil/wax/emulsifier combination as being indicative of a particular producer is unknown (Midkiff et al. 1992).

It is possible that for this reason little research has been conducted on the organic analysis of emulsions. Little information on emulsions in particular, and especially the organic analysis of such, has been found in the literature.

Midkiff et al. (1992) used hexane and/or pentane to extract an emulsion sample. The extracts were combined and filtered through a micro filter to remove suspended particles, and then evaporated to a small volume to concentrate the extract.

Rudolph et al. (1983) used GC/MS to analyze the hydrocarbons of an ANFO sample. A mass spectrum was obtained through GC/MS to aid in the identification and characterization of oils and if, according to Rudolph et al. (1983), the same material is consistently being used by a particular group, this would reveal the groups identity if an unclaimed bombing were to occur.

Bender, Crump, and Midkiff (1992) used gas chromatography (GC) to analyze the organic extract of emulsions. They used iso-octane as the solvent and a homogenizer to break up the sample. After filtration the samples were analyzed by GC where the oil, wax, and emulsifier mixtures were observed.

From their research they revealed that the oil/wax combinations dominate the chromatograms, however the emulsifier can still be detected. Bender et al. (1983) also found that the emulsifying packages varied widely among the samples tested, thus leaving the possibility of using emulsifier identification as a viable option in the characterization of emulsions.

METHODS AND MATERIALS

The individual components of Atlas Powermax formulations were dissolved in Trichloroethylene(TCE), and analyzed on the Gas Chromatograph for comparison to chromatograms generated by intact emulsion extractions.

The emulsion samples have been extracted with different solvents in the hopes of finding a solvent that will better extract the organic components from the sample, thus producing better gas chromatographic (GC) results. Approximately 0.5-1.0 grams of the intact samples were used experimentally per each solvent. The intact emulsion samples used are listed in Table 3. After solvation, each sample was concentrated by evaporation. All samples were analyzed on a Perkin Elmer 8500 Gas Chromatograph using 1.0-2.0 ul sample injection sizes. The injection sizes varied in order to observe if 2 ul injection sizes produced better chromatographic results over 1 or 1.5 ul injection sizes.

Post-blast samples, also listed in Table 3, were prepared for GC analysis by using only Iso-octane as the solvent. Approximately 40-50 grams of each sample was combined with 30 ml of iso-octane to dissolve the organic components in the soil sample. A Supelco Supelclean LC-S1 column was used to remove contaminants from the post blast extractions. Each post column filtrate was then concentrated, and analyzed on the GC using a 1 ul injection size.

List of Materials:

Perkin Elmer 8500 Gas Chromatograph

Nelson Analytical 900 Series Interface

Wyse PC 286/10 computer

Pierce Reacti-therm heating module

Pierce Reacti-vap evaporating unit

Tissue Tearor: Model 985-370 type 2, Biospec Products, Inc.

Whatman Autovial: 0.45um, Nylon-66 membrane, w/glass microfilter prefilter, polypropylene housing

Supelco Supelclean LC-S1 column

Atlas products: Individual components & Intact emulsions.
From: Atlas Powder Company
P.O. Box 271
Tamaqua, PA 18252

Austin products: Intact emulsions.
From: Austin Powder Company
3690 Orange Place
Cleveland, OH 44122

Sovents were LC Grade, supplied by Burdick & Jackson Co.

Table 1. Gas Chromatograph Conditions.

Instrument	Perkin Elmer 8500 Gas Chromatograph
Column	Quadrex Aluminum clad fused silica 15 meter "400" methyl silicone 0.25 id., 0.10um film thickness
Temperature Program	Initial Temp. 100°C Initial Time 5 min. Rate 10°C/min. Final Temp. 420°C
Injector	Program Temperature Vaporizer(PTV) 430°C ballistically split/splitless
Carrier	Hydrogen at 15psi head pressure
Detector	Flame Ionization at 450°C

Preparation of standard.

Standards, C22, C32, and C44, were prepared separately with 1ml of Trichloroethylene(TCE). The separate samples were analyzed on the GC, and then mixed together, and analyzed in combination. The chromatogram of the combined sample is shown in Figure 1.

Preparation of individual components from Atlas Powermax formulations.

The samples were prepared as follows: Each sample was weighed and combined with 2ml of Trichloroethylene(TCE). To ensure that the sample dissolved as much as possible, shaking and a little heat was applied. The individual components themselves and their compositions, as stated by Atlas, are listed in Table 2. GC sample injection size was 1 ul. Chromatographic results are shown in Figures 2-7.

Table 2. Individual components and compositions

Individual component	Composition of component as stated by Atlas
#1	Contains the oils that are present in the external or fuel phase of the film packaged cap sensitive Powermax formulations.
#2	Contains the wax and oil combination used in fuel phase of Atlas' paper packaged product.
X-5	Contains the emulsifier combination that goes with #2.
#3	Contains #2 and X-5 in the approximate proportions in which they are used.
TN0115	This is the emulsifier used with #1.
TN0146	This is the mixture of TN0115 and #1.

Table 3. Intact and post blast emulsion samples.

Intact Samples	**Post Blast Samples**
Atlas Powermax 140	
Atlas Powermax 440	Atlas Powermax 440
Atlas Apex 840	
Atlas Apex 240 Blasting Agent	
Atlas 7D	
Austin Emulex 720	

Preparation of Intact Samples using Trichloroethylene (TCE).

Table 3 shows the intact emulsion samples and the post-blast emulsion samples that were used in this study. All samples listed in Tables 6-9 were taken from different locations within each packaged emulsion stick. This procedure was done to determine if any settling of components had occurred since the time of manufacturing that could cause differing analysis results. Intact samples were first dissolved using TCE, and prepared as follows: A spatula was used to break up the sample as much as possible, and by stirring and shaking vigorously to complete as much solvation as possible. After solvation, the entire sample was poured

into a Whatman autovial for filtering. The filtered samples were then ready for GC analysis, where 2 ul of each sample was used to obtain Chromatograms. Chromatographic results are shown in Figures 8-23 respectively.

Preparation of Intact Samples using Methylene Chloride.

Methylene Chloride was the next solvent used. Each sample, shown in Table 10, was mixed separately with 5-10 ml of methylene chloride, in a 30 ml beaker. The beakers were placed on a hot plate at 350°C for 5 min. A spatula was used to stir and break the larger pieces of the emulsion. The beakers were then placed into an ultrasonic bath to facilitate further solvation. The samples were then placed into a Centrex disposable centrifugal microfilter and placed into the centrifuge until all liquid had been displaced to the bottom of the tube. The liquid samples were then separately poured into test tubes and placed into the evaporating unit to evaporate all methylene chloride. After evaporation, 2 ml of TCE was added to each sample. GC sample injection size was 1 ul. Chromatographic results are shown in Figures 24-27.

Preparation of Intact Samples using Hexane.

Each sample, shown in Table 11, was separately placed into a 30 ml beaker, to which approximately 20 ml of hexane was added. Each beaker was placed on a hot plate at 350°C, and the hexane was allowed to boil down to approximately 5 ml

This remaining 5 ml was filtered through a Whatman autovial into a test tube. The test tubes were placed into the evaporating unit where all hexane was evaporated. To each sample 2 ml of hexane was added. A 1 ul sample injection size was used to obtain chromatographic results shown in Figures 28-31.

Table 12 shows previous samples used, plus the addition of two new samples: Atlas Apex Blasting Agent 240 and Atlas 7D. The corresponding weights used of each sample is also shown in Table 12. To each sample, approximately 25 ml of hexane was added in a 50 ml beaker. The beakers were placed on a hot plate at 350°C. Using a spatula the samples were broken up as much as possible. The samples were boiled down to approximately 5 ml and then each sample was filtered through a Whatman Autovial into a test tube. The test tubes were then placed into the evaporating unit where all hexane was evaporated, after which 2 ml of TCE was added to each sample. A 1.5 ul injection of each sample was used to obtain the chromatographic results shown in Figures 32-42.

Preparation of Intact Samples using Iso-Octane.

The seven emulsion samples shown in Table 13 had a representative sample taken from each. The corresponding weights of each are also shown in Table 13. Each sample was placed into a sample vial, to which approximately 3-5 ml of iso-octane was added. The Tissue Tearor was used to thoroughly homogenize each sample, then each sample was placed into a centrifuge tube and centrifuged for approximately 30 seconds, at 1200 rpm. The supernatant was decanted into a whatman autovial and filtered into a clean sample vial. If need be, the samples were evaporated down to a volume of approximately 2 ml. Samples were then injected into the GC for analysis using 1.5ul injections. Chromatographic results are shown in Figures 43-48.

Method of Post Blast Recovery.

A 1 pound sample of explosive was suspended approximately 1 ft above the ground, using the bare ground as a witness plate. The samples were detonated using an Austin Rockmaster instantaneous detonator. The soil from the blast craters was collected and placed into airtight canisters. Soil samples from underneath the blast site were taken as control samples before detonation.

Preparation of Post Blast Samples.

Approximately 40-50 g of each sample was placed in separate beakers. Thirty milliliters of iso-octane was added to each, and placed on a hot plate at 300°C, for 5 min. The mixture was then gravity filtered. Then, using a Supelco Supelclean LC-S1 column, 2 ml of iso-octane was poured into the column followed by the filtrate of the separate samples. The post column filtrate was placed into the Reacti-Vap &

Therm unit to concentrate the sample down to approximately 2 ml. A 1 ul sample injection size was used for GC analysis. Chromatographic results are shown in Figures 49-54.

Figure 55 shows an overlay of the emulsifier sample X-5, from Atlas, and an intact sample of Atlas Powermax 440.

EXPERIMENTAL RESULTS

The individual components found in most of Atlas' Powermax formulations, listed in Table 2, have a consistency ranging from a thick molasses to a hard wax. Table 5 shows the weight of each individual component dissolved in TCE. These components were relatively easy to dissolve in the Trichloroethylene, but at times, a little heat was applied to fully dissolve the samples.

The GC injection size of each sample was 1ul. Results from the GC analysis of the individual components can be seen in Figures 2-7.

Results of Standard Analysis.

Table 4. Carbon standard sample amounts.

STANDARD	WEIGHT	SOLVENT
C22	0.0046 g	1 ml TCE
C32	0.0049 g	1 ml TCE
C44	0.0018 g	1 ml TCE

Table 4 lists the standards, and their corresponding weights that were prepared with TCE.

Figure 1 shows C22 appearing at 8 minutes, C32 appearing at 15 minutes, and C44 appearing at 22 minutes.

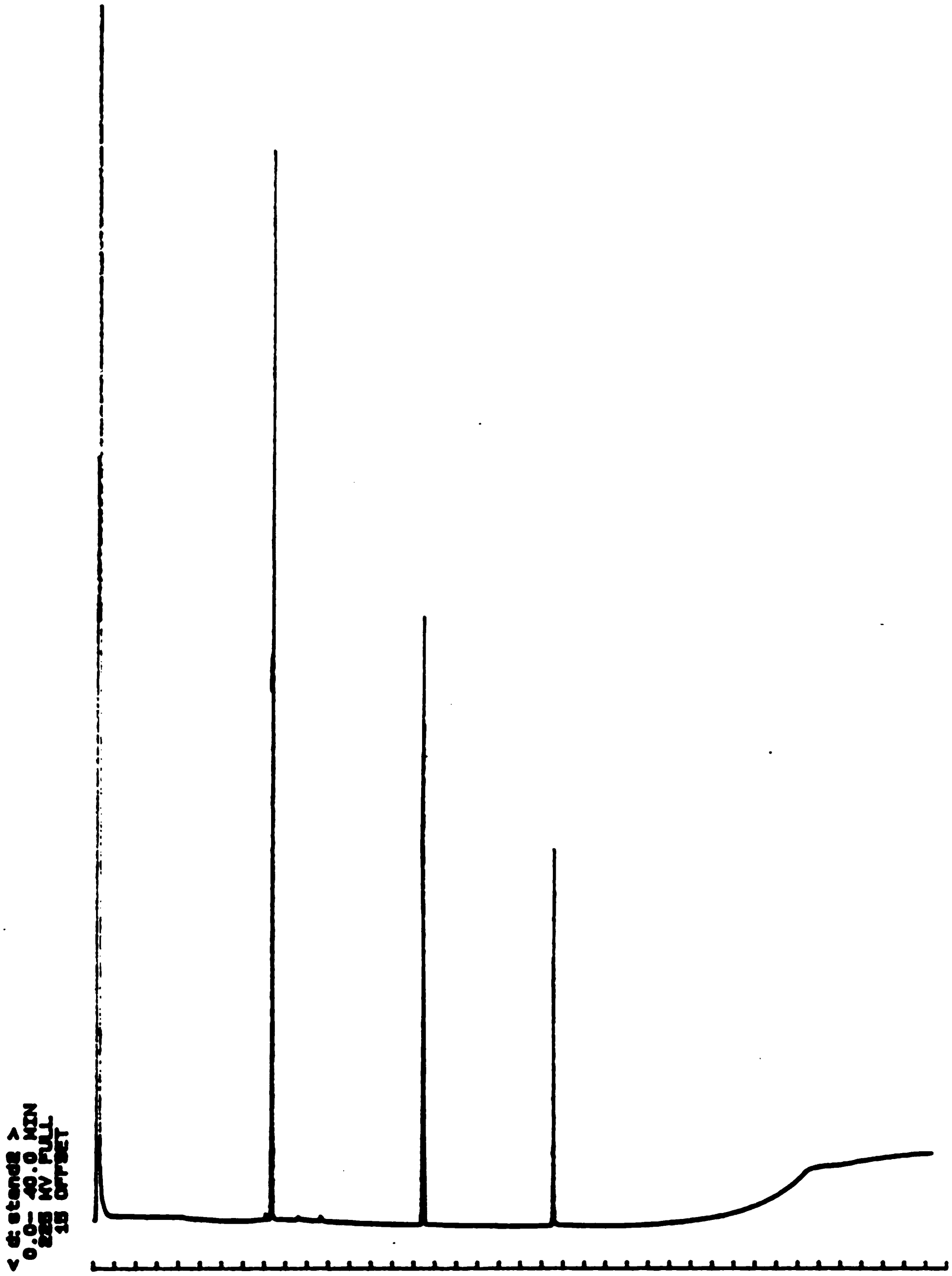

Figure 1: Chromatogram of the Carbon Standards C22, C32, and C44.

Results of Individual Components Prepared with TCE.

Table 5. Individual component sample amounts.

SAMPLE	WEIGHT	SOLVENT
#1	0.0760 g	2 ml TCE
#2	0.0810 g	2 ml TCE
#3	0.0570 g	2 ml TCE
X-5	0.0239 g	2 ml TCE
TN0115	0.0538 g	2 ml TCE
TN0146	0.0271 g	2 ml TCE

Figure 2 is of the individual component #1, containing the oils that are present in the fuel phase of the cap sensitive Powermax formulations. The GC produced one very large peak ranging form 7 to 26 minutes. This peak had no symmetry and had a large unresolved area underneath.

Figure 3 is the result of the GC analysis of individual component #2, which contains the combination of wax and oil used in the fuel phase of Atlas' paper packaged product. This chromatogram shows a series of consecutive sharp peaks ranging from 7-21 minutes. There is also a small unresolved area underneath the peaks within the same time range.

Figure 4 represents the individual component X-5, which contains the emulsifier combination that is used with the individual component #2. This chromatogram shows approximately 7 peaks of interest. The first two peaks,

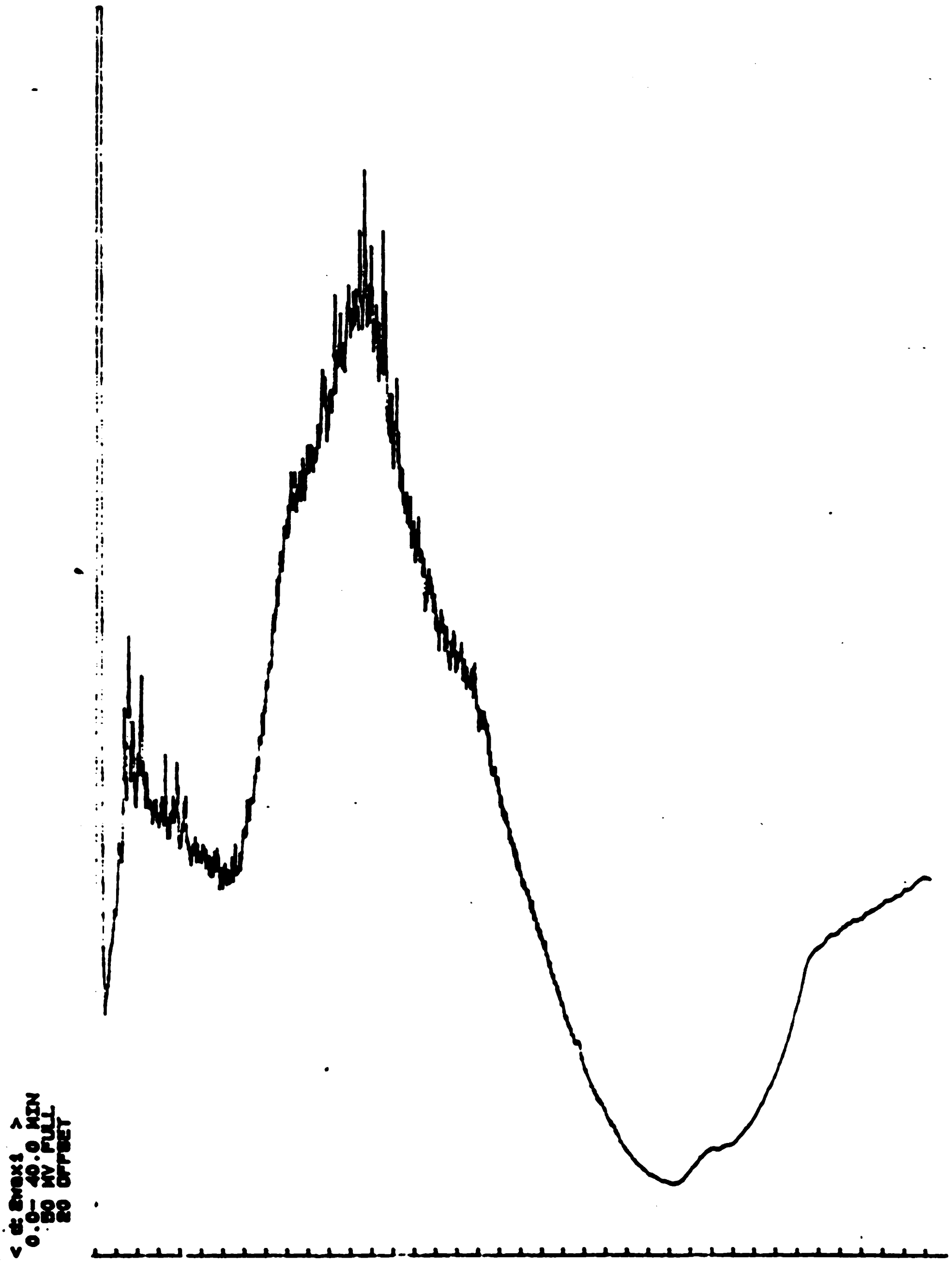

Figure 2: Chromatogram of Individual Component #1.

Figure 3: Chromatogram of Individual Component #2.

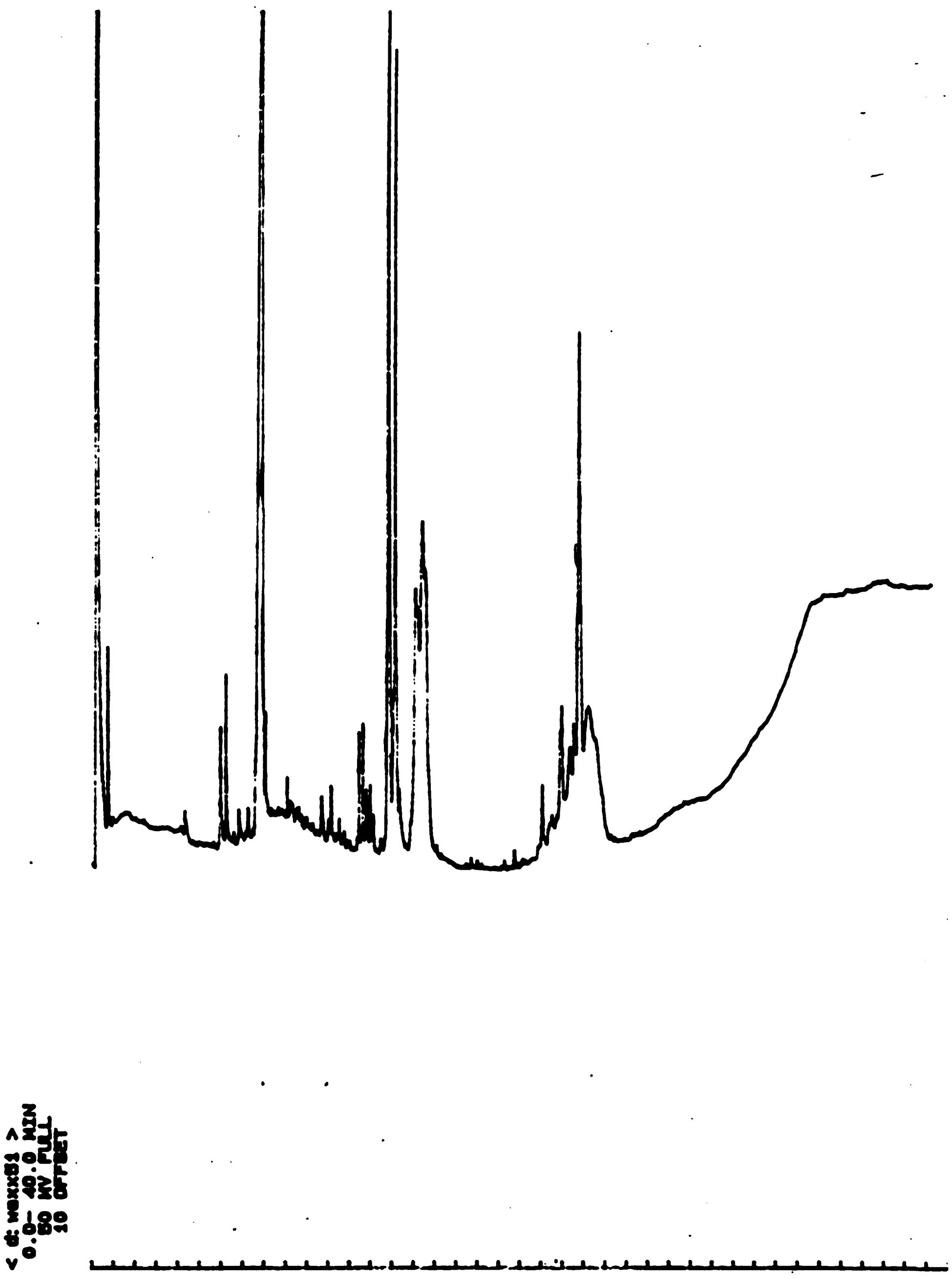

Figure 4: Chromatogram of Individual Component X-5.

becoming evident at 6 minutes, are right next to each other, and are not separated by the baseline. The second peak shows up at 8 min. and is very evident from its peak height. The next two peaks of interest show up at 14 min. These two peaks are not separated by the baseline, and both have a high peak height. Another peak that shows up at 15 min. is not completely defined but is combined with a second peak where they both share the same area beneath. The last peak of interest shows up at 23 min. This peak does not begin and end at the baseline, but is very evident from its height.

Figure 5 represents the individual component #3, which contains individual components #2 and X-5 in the approximate proportions in which they are used in the packaged emulsion. Within this chromatograph a series of consecutive peaks ranging from 7.5 to 22 min can be seen. Interspersed within the consecutive peaks are random peaks that are important. The first being at 8 min., the second at 14 min., the third at 23 minutes.

Figure 6 represents the individual component TN0115, which is an emulsifier used with the individual component #1. This chromatogram shows somewhat symmetrical groupings of 4 and 5 peaks per group. These groupings appear in the range of 5-26 minutes.

Figure 7 represents the individual component TN0146, which is the mixture of TN0115 and component #1. This chromatogram shows one large unresolved peak, with a large area beneath it, ranging from 6-23 minutes. Ranging from 23-28 min. are several groupings with 4 small peaks each.

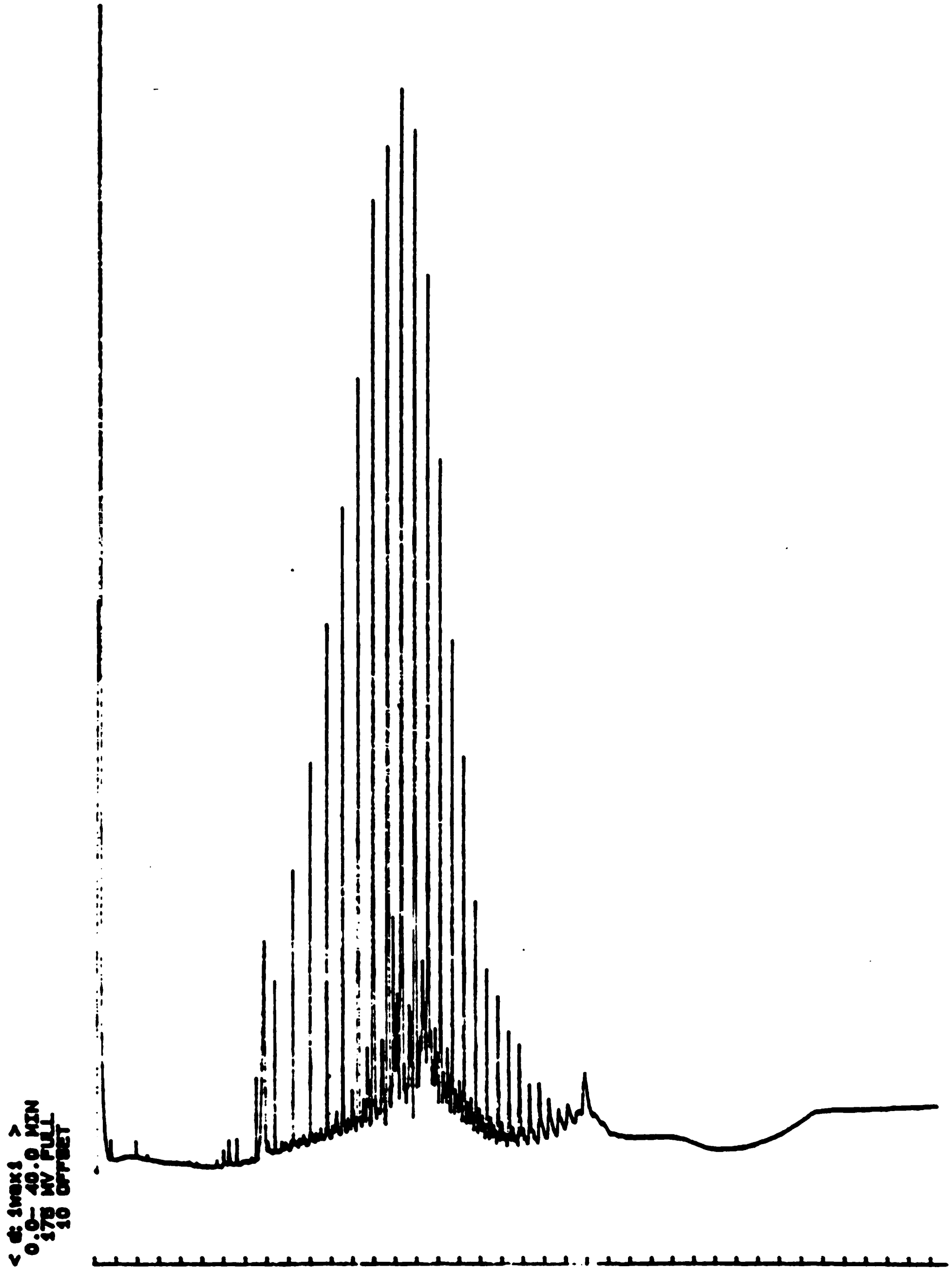

Figure 5: Chromatogram of Individual Component #3.

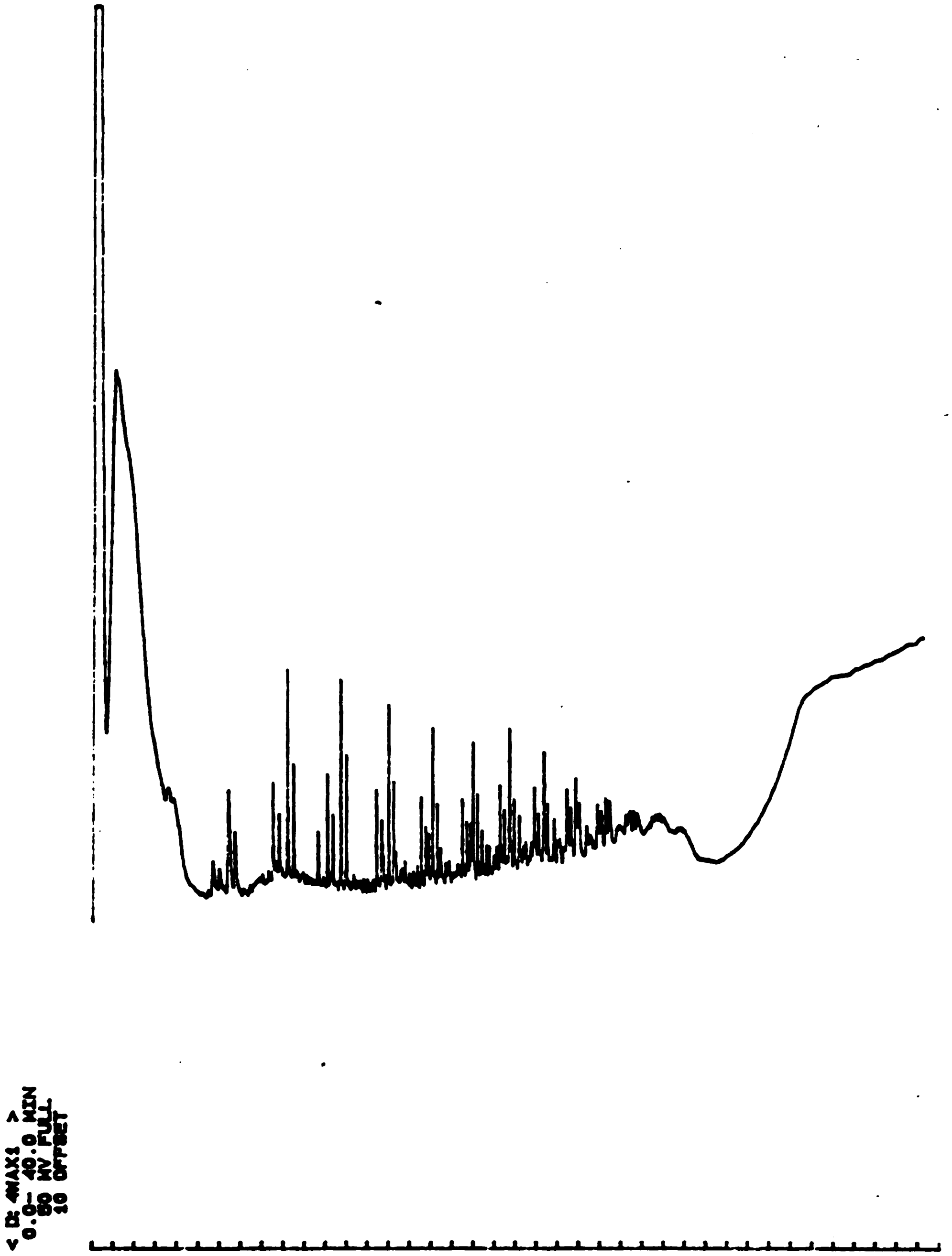

Figure 6: Chromatogram of Individual Component TN0115.

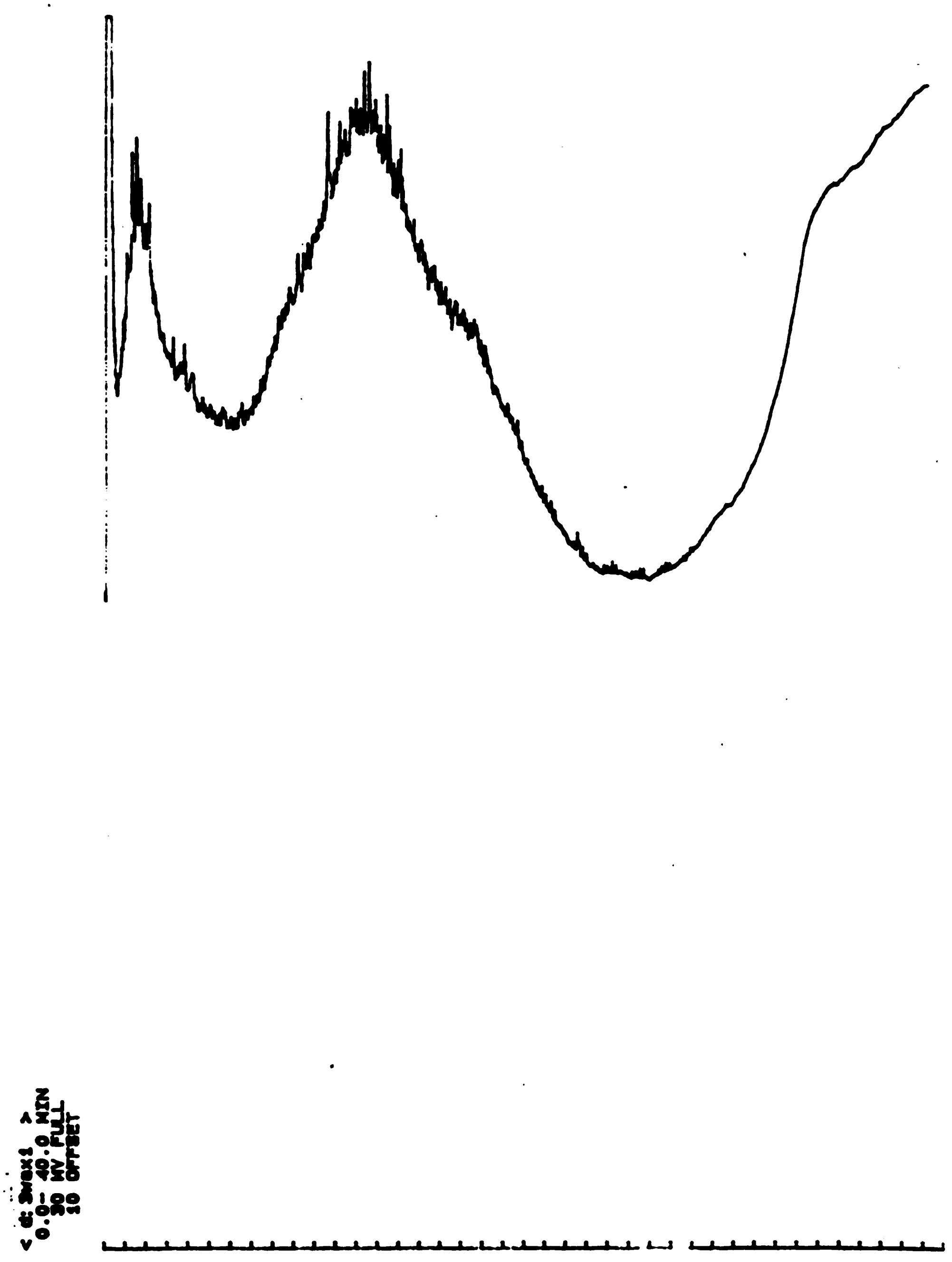

Figure 7: Chromatogram of Individual Component TN0146.

Results of Intact Emulsion Samples Prepared with TCE (Trial 1).

Table 6. Intact emulsion sample amounts prepared with TCE (Trial 1).

Sample	Weight	Solvent
Atlas Powermax 140	0.48 g	TCE-2 ml
Atlas Powermax 440	0.63 g	TCE-2 ml
Atlas Apex 840	0.46 g	TCE-2 ml
Atlas Apex (BA) 240	0.61 g	TCE-2 ml
Austin Emulex 720	0.42 g	TCE-2 ml

Table 6 lists each sample and its amount used to obtain the following chromatographic results.

Figure 8 represents a sample of Atlas Powermax 140. Within this chromatogram is a series of consecutive sharp peaks ranging from 9-21 minutes. There is a small unresolved area beneath these peaks that spans most of the same time range. There is a peak that appears at 7.5 min. with a substantial height, one at 14 min., and another at 23 minutes.

Figure 9 represents a sample of Atlas Powermax 440. This chromatogram shows the distinct consecutive series of sharp peaks that range from 9-21 minutes. Underneath this range of peaks is a somewhat large unresolved area. In addition are the distinct peaks that appear at 7.5 min., 14 min., and 23 minutes.

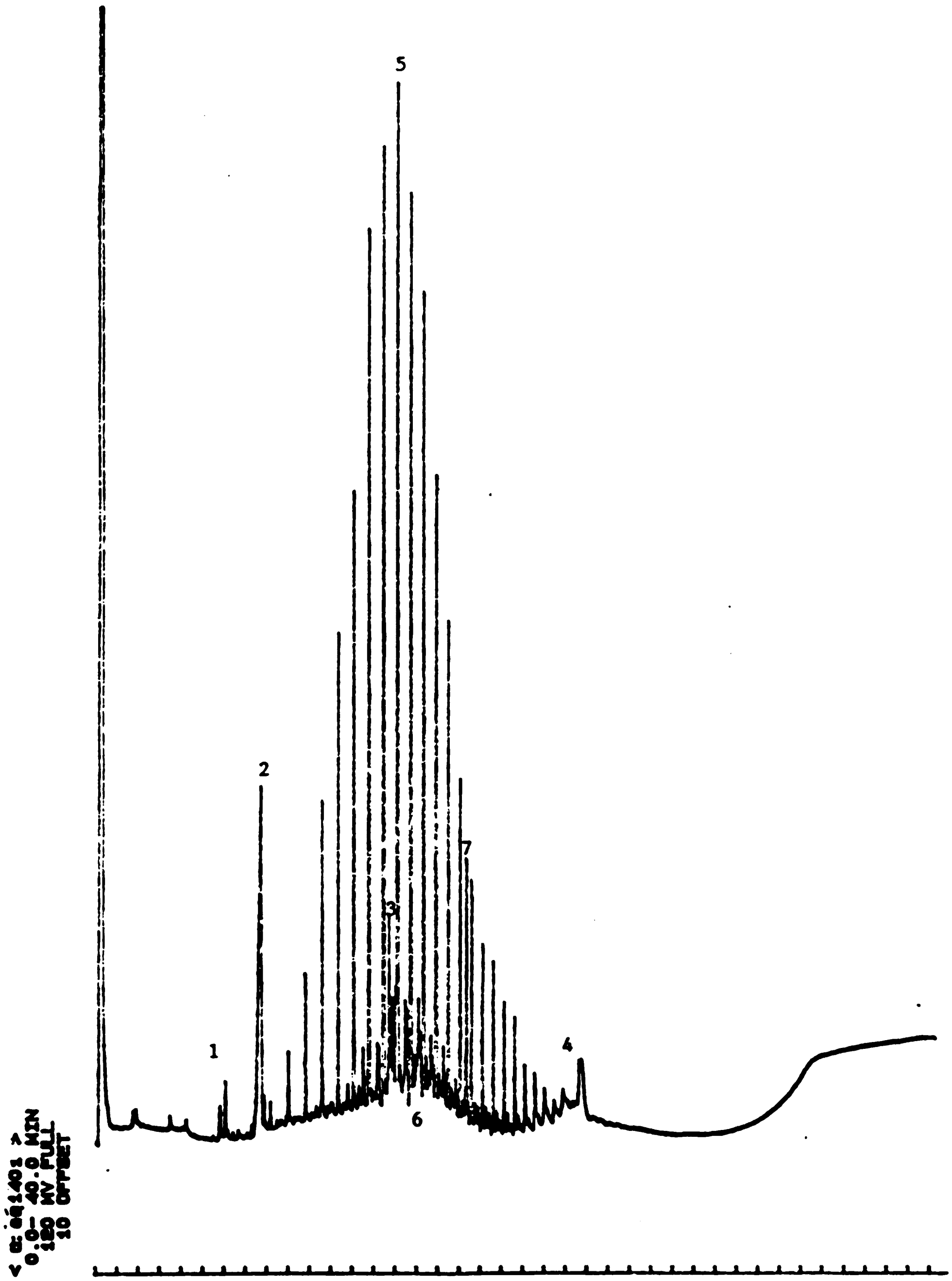

Figure 8: Chromatogram of Atlas Powermax 140 Prepared with TCE (Trial 1).

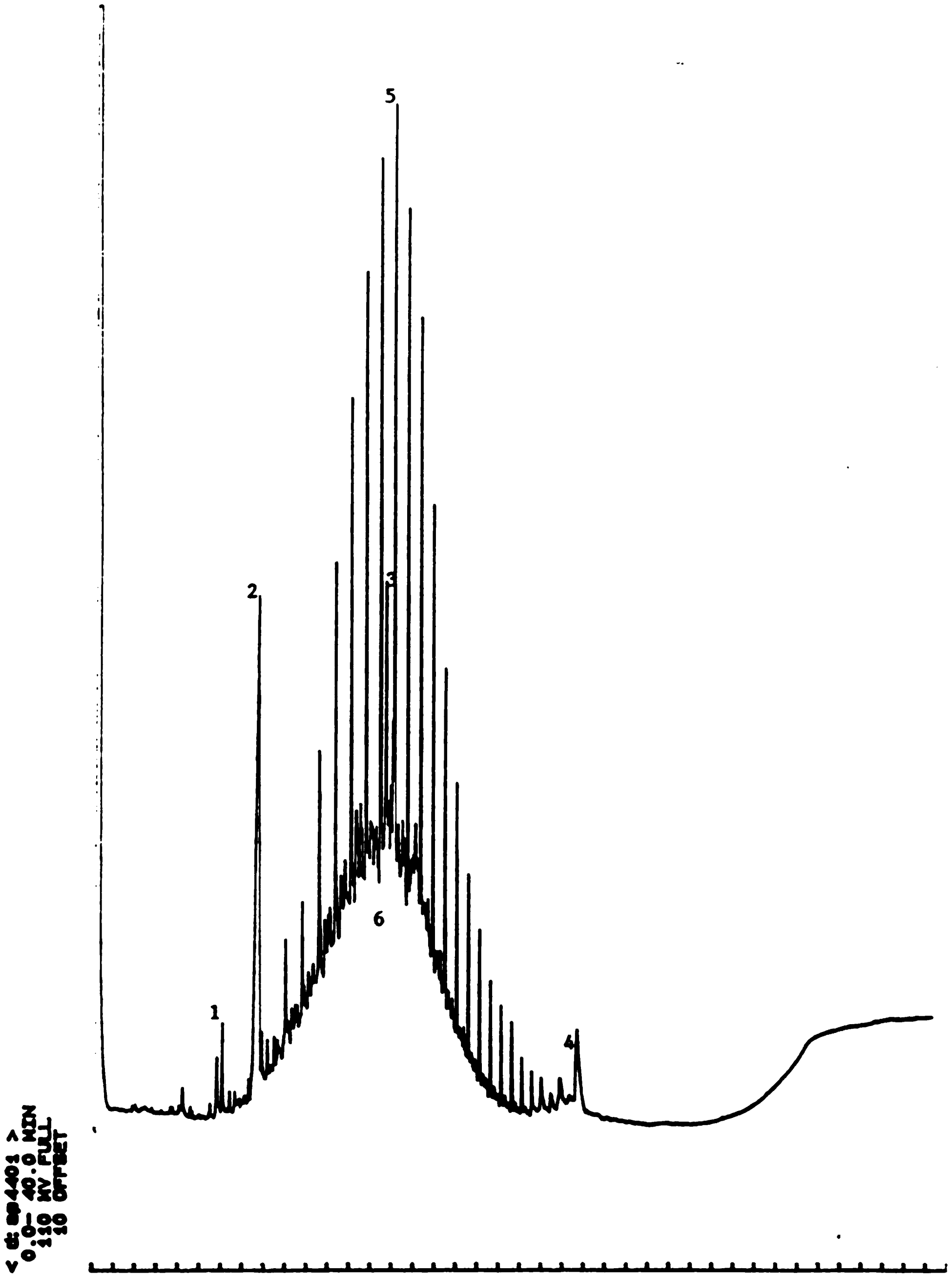

Figure 9: Chromatogram of Atlas Powermax 440 Prepared with TCE (Trial 1).

Figure 10 represents a sample of Atlas Apex 840. A series of consecutive sharp peaks range from 9-21 minutes. Additional important peaks appear at 7.5 min., 17.5 min., and 23 minutes.

Figure 11 represents a sample of Atlas Apex 240 blasting agent. This chromatogram shows a series of consecutive peaks ranging from 7-21 minutes. A quite large unresolved area is present throughout the same time range. Additional important peaks can be seen at 7.5 min., 14 min., 17 min., and 23 minutes.

Figure 12 represents a sample of Austin Emulex 720. This chromatogram reveals two large unresolved peaks. The first ranging from 0.5-6 minutes. The second ranging from 7-20 minutes. Near the trailing end of this chromatogram are two groups of 4 small consecutive peaks between 21-24 minutes.

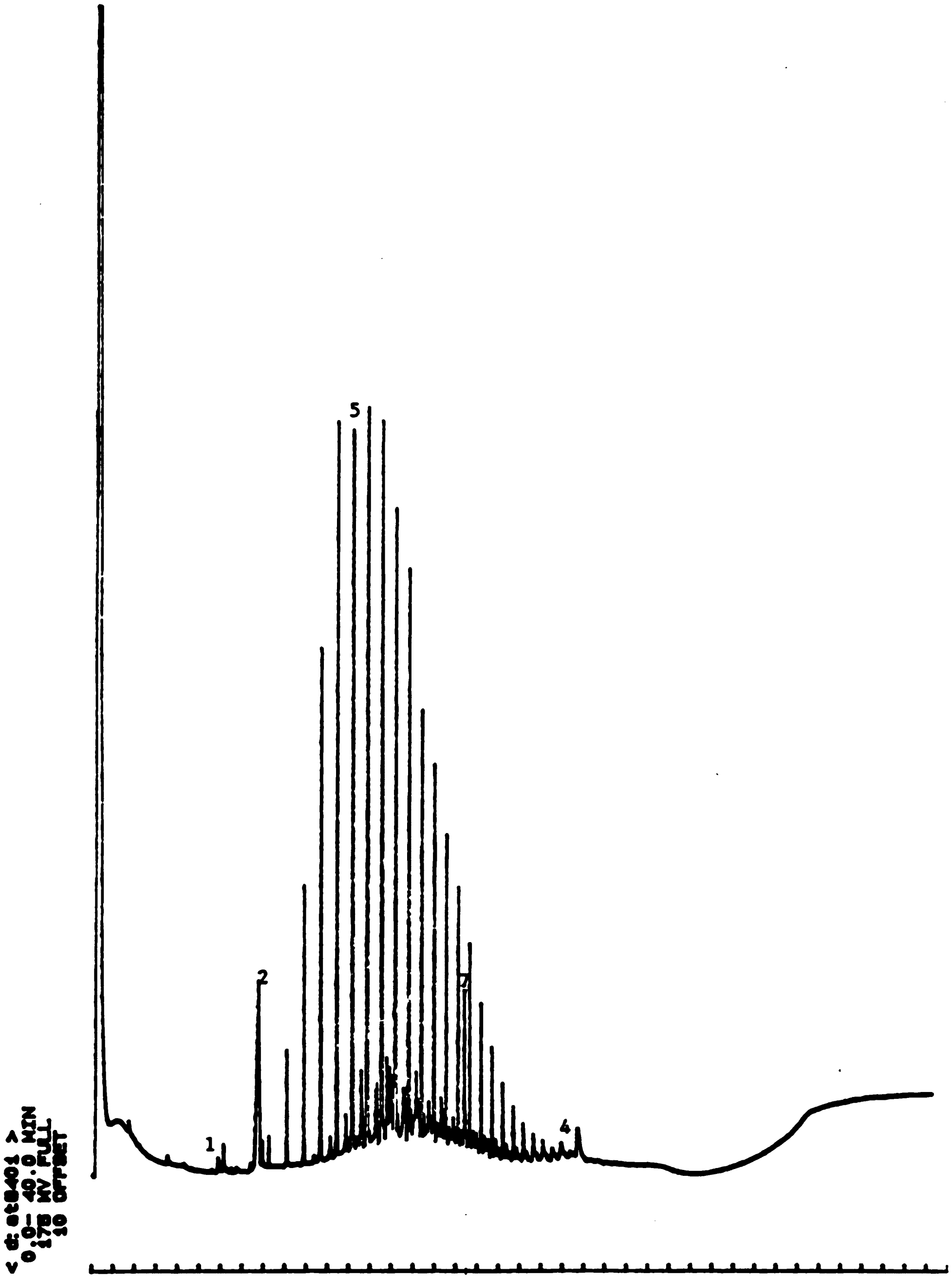

Figure 10: Chromatogram of Atlas Apex 840 Prepared with TCE (Trial 1).

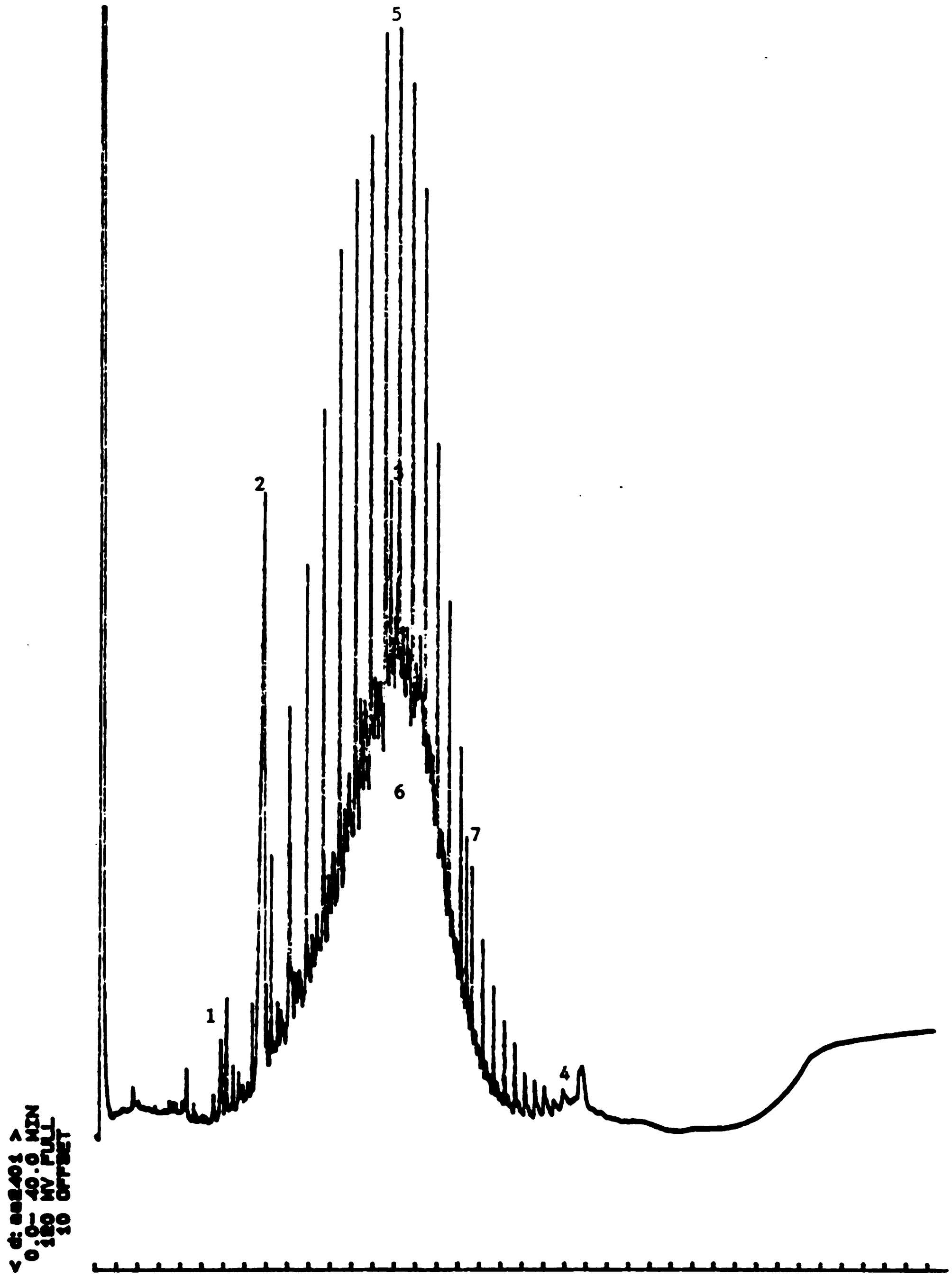

Figure 11: Chromatogram of Atlas Apex Blasting Agent 240
Prepared with TCE (Trial 1).

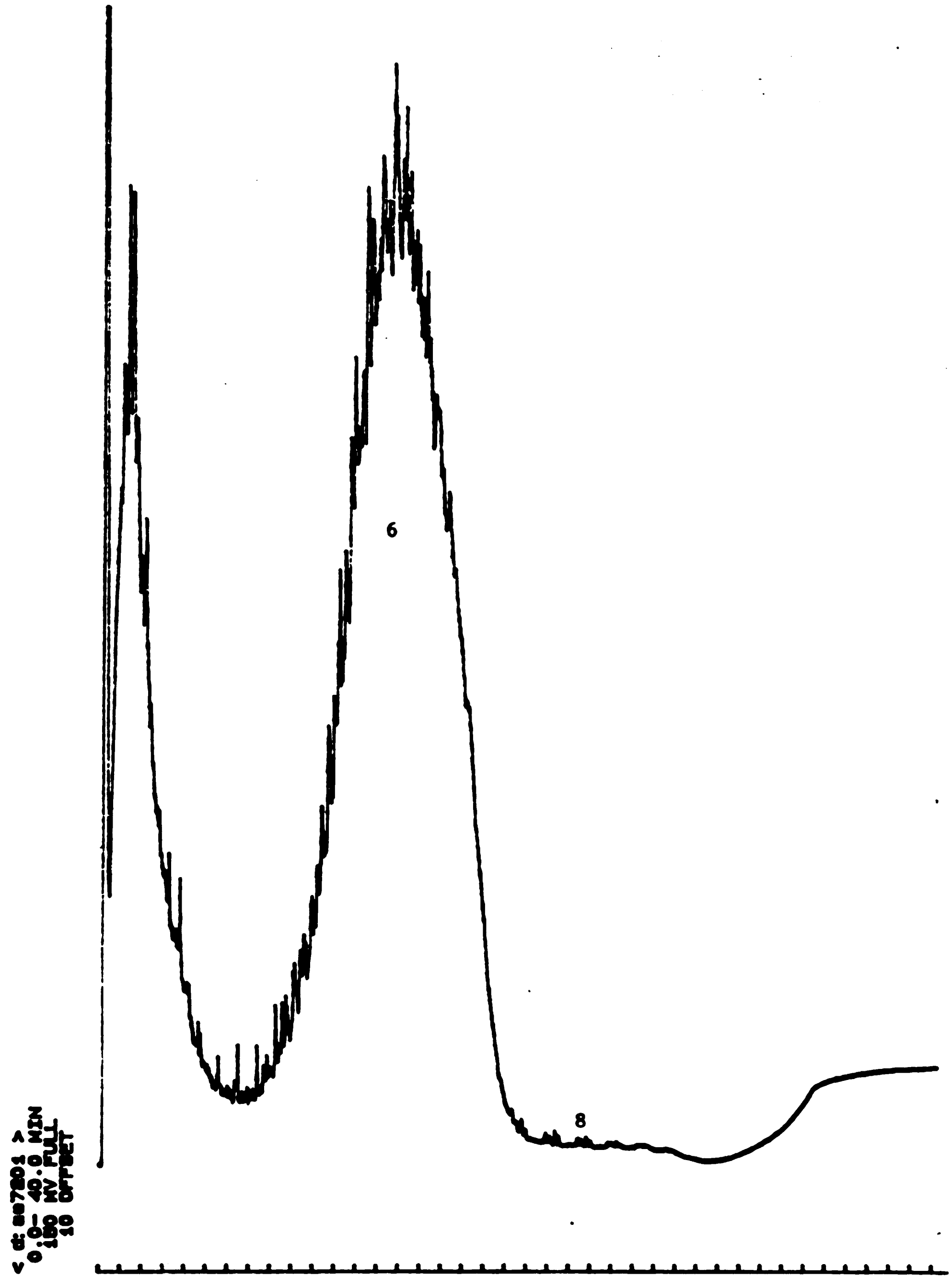

Figure 12: Chromatogram of Austin Emulex 720 Prepared with TCE (Trial 1).

Results of Intact Emulsion Samples Prepared with TCE (Trial 2).

Table 7. Intact emulsion sample amounts prepared with TCE (Trial 2).

Sample	Weight	Solvent
Atlas Powermax 140	0.57 g	TCE-2 ml
Atlas Powermax 440	0.63 g	TCE-2 ml
Austin Emulex 720	0.92 g	TCE-2 ml

Table 7 lists a second sampling of intact emulsion samples prepared with TCE. These samples were taken from different locations on the packaged sticks than those samples listed in Table 6.

Figure 13 represents a sample of Atlas Powermax 140. Again the familiar series of consecutive peaks ranging from 7-20 minutes can be seen. A small unresolved area beneath the peaks can also be seen within the same range. Additional important peaks can be seen at 7.5, 14 and 22.5 minutes.

Figure 14 represents a sample of Altas Powermax 440. This chromatogram shows an unresolved peak ranging from 4-6 minutes. The series of consecutive peaks is again present ranging from 7-20 minutes. The peaks of this series, ranging from 17-20 minutes, are small in height and not very sharp. Additional important peaks can be seen at 7.5, 14, and 23 minutes.

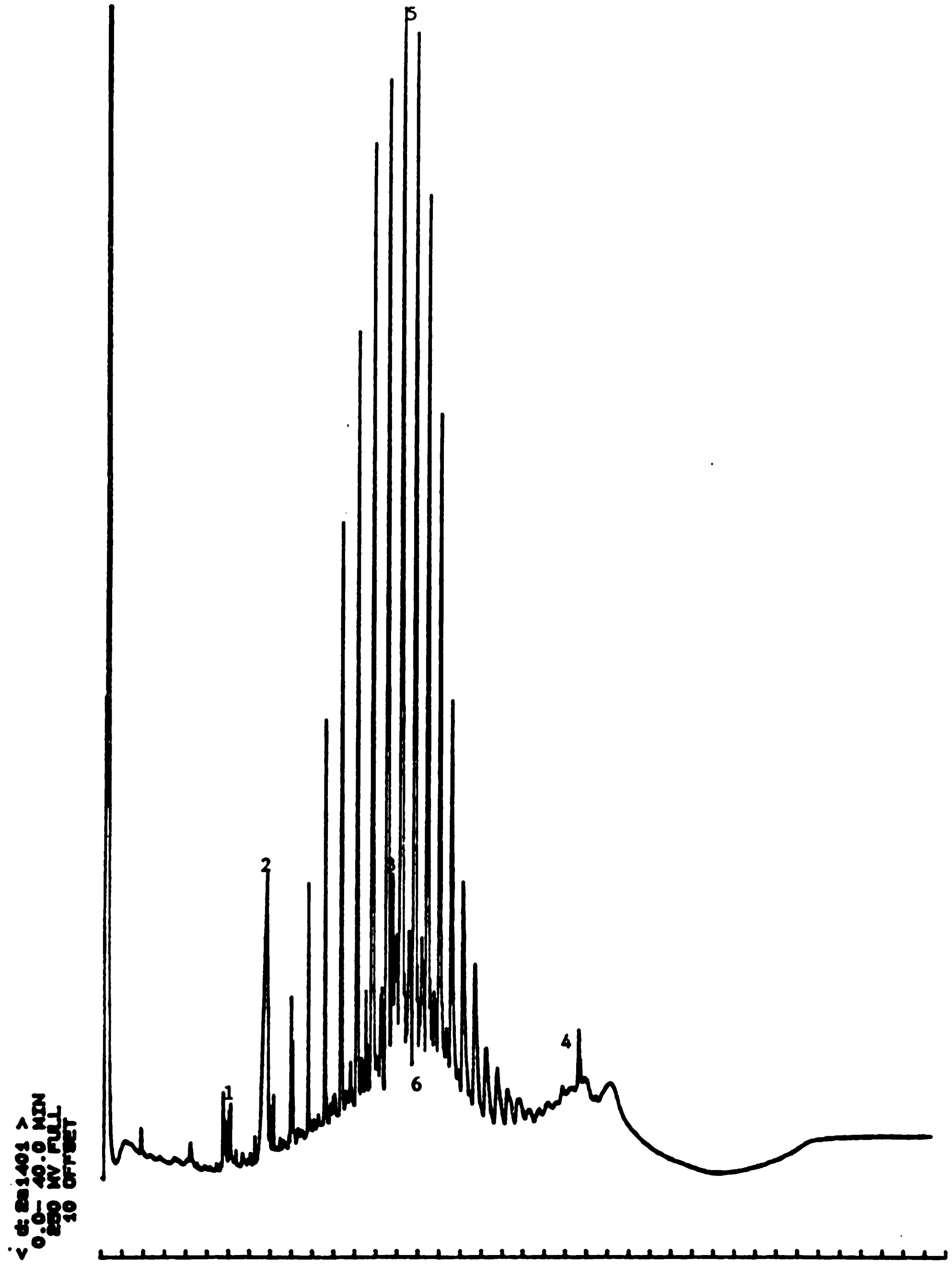

Figure 13: Chromatogram of Atlas Powermax 140 Prepared with TCE (Trial 2).

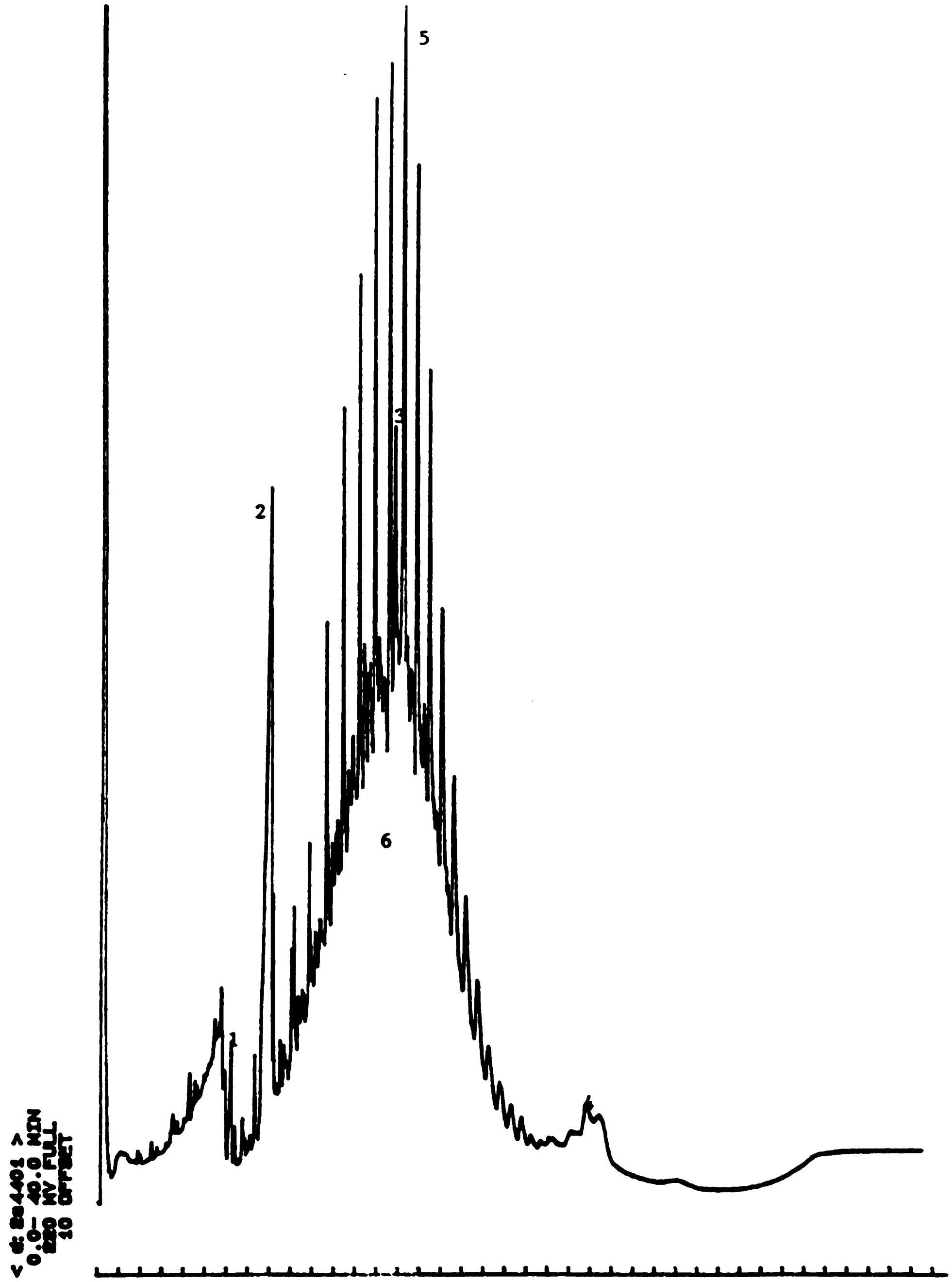

Figure 14: Chromatogram of Atlas Powermax 440 Prepared with TCE (Trial 2).

Figure 15 represents a sample of Austin Emulex 720. Within this chromatogram is an unresolved peak of substantial height that ranges from 0.5-5 minutes. Another larger unresolved peak, also at equal height, ranges from 7-20 minutes. From 21-23 min. are two groups of peaks with 4 peaks to a group.

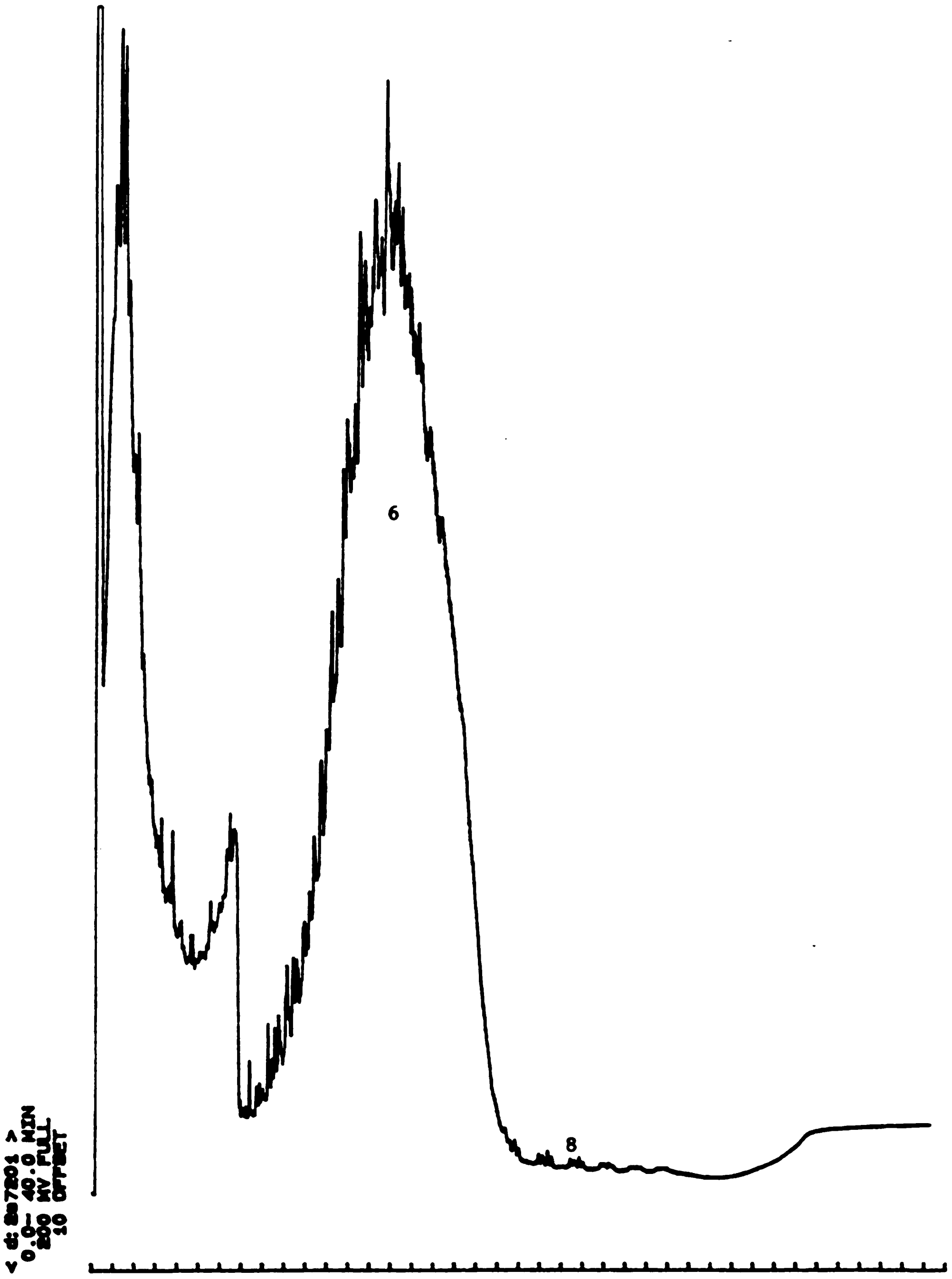

Figure 15: Chromatogram of Austin Emulex 720 Prepared with TCE (Trial 2).

Results of Intact Emulsion Samples Prepared with TCE (Trial 3).

Table 8. Intact emulsion sample amounts prepared with TCE (Trial 3).

Sample	**Weight**	**Solvent**
Atlas Apex 840	0.92 g	TCE-2 ml
Atlas Powermax 140	0.55 g	TCE-2 ml
Atlas Powermax 440	0.80 g	TCE-2 ml
Austin Emulex 720	0.78 g	TCE-2 ml

Table 8 lists a 3rd sampling of intact emulsion samples prepared with TCE. These samples were again taken from different locations on the packaged stick than those samples listed in Tables 6 & 7.

Figure 16 represents a sample of Atlas Apex 840. A series of consecutive sharp peaks is again present, ranging from 8-21 minutes, with a small unresolved area beneath the peaks. Additional peaks are seen at 7.5, and 23 minutes.

Figure 17 represents a sample of Atlas Powermax 140. Ranging from 8-21 min. is a series of consecutive sharp peaks, with a small unresolved area beneath the entire range. Additional peaks of interest are at 5, 7.5, and 23 minutes.

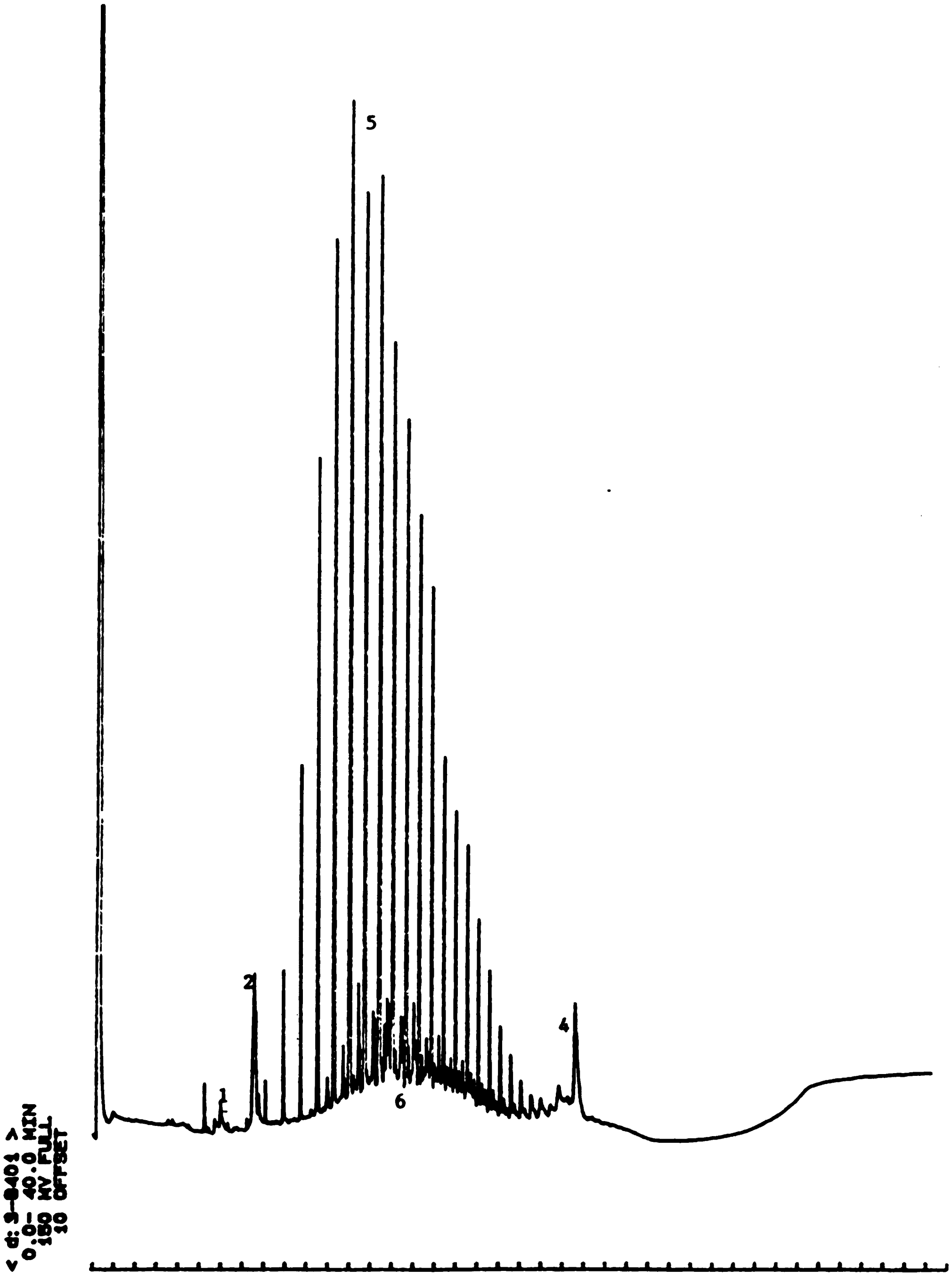

Figure 16: Chromatogram of Atlas Apex 840 Prepared with TCE (Trial 3).

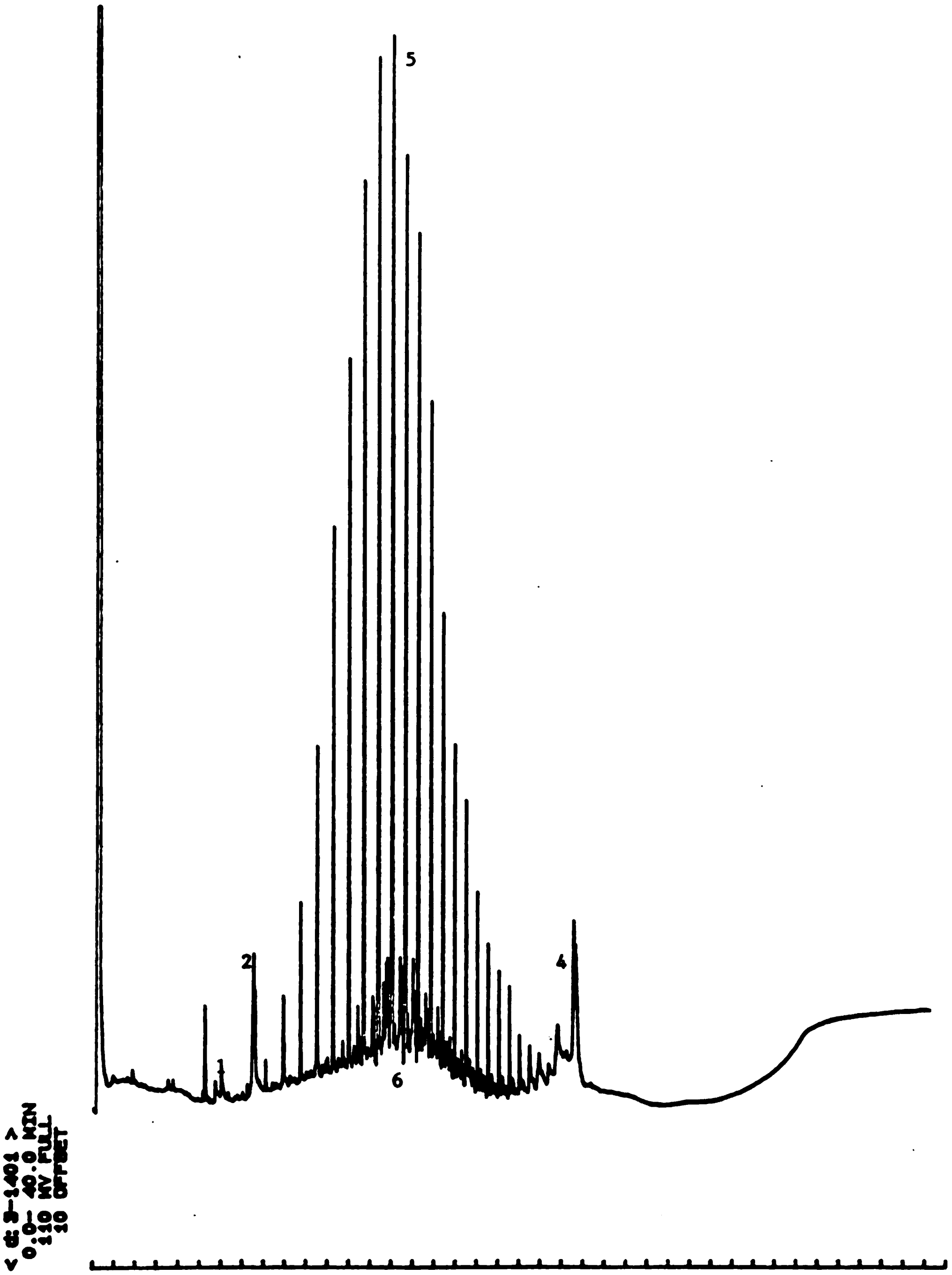

Figure 17: Chromatogram of Atlas Powermax 140 Prepared with TCE (Trial 3).

Figure 18 represents a sample of Atlas Powermax 440. Ranging from 8-21 min. is a series of consecutive peaks with a considerable area beneath the peaks, covering the entire time range. Additional peaks of interest are at 5, 7.5, and 23 minutes.

Figure 19 represents a sample of Austin Emulex 720. An unresolved peak ranging from 0.5-6 min. is shown, with an additional, larger unresolved peak ranging from 7-20 minutes. Ranging from 21-25 min. are 3 groupings of 4 peaks each.

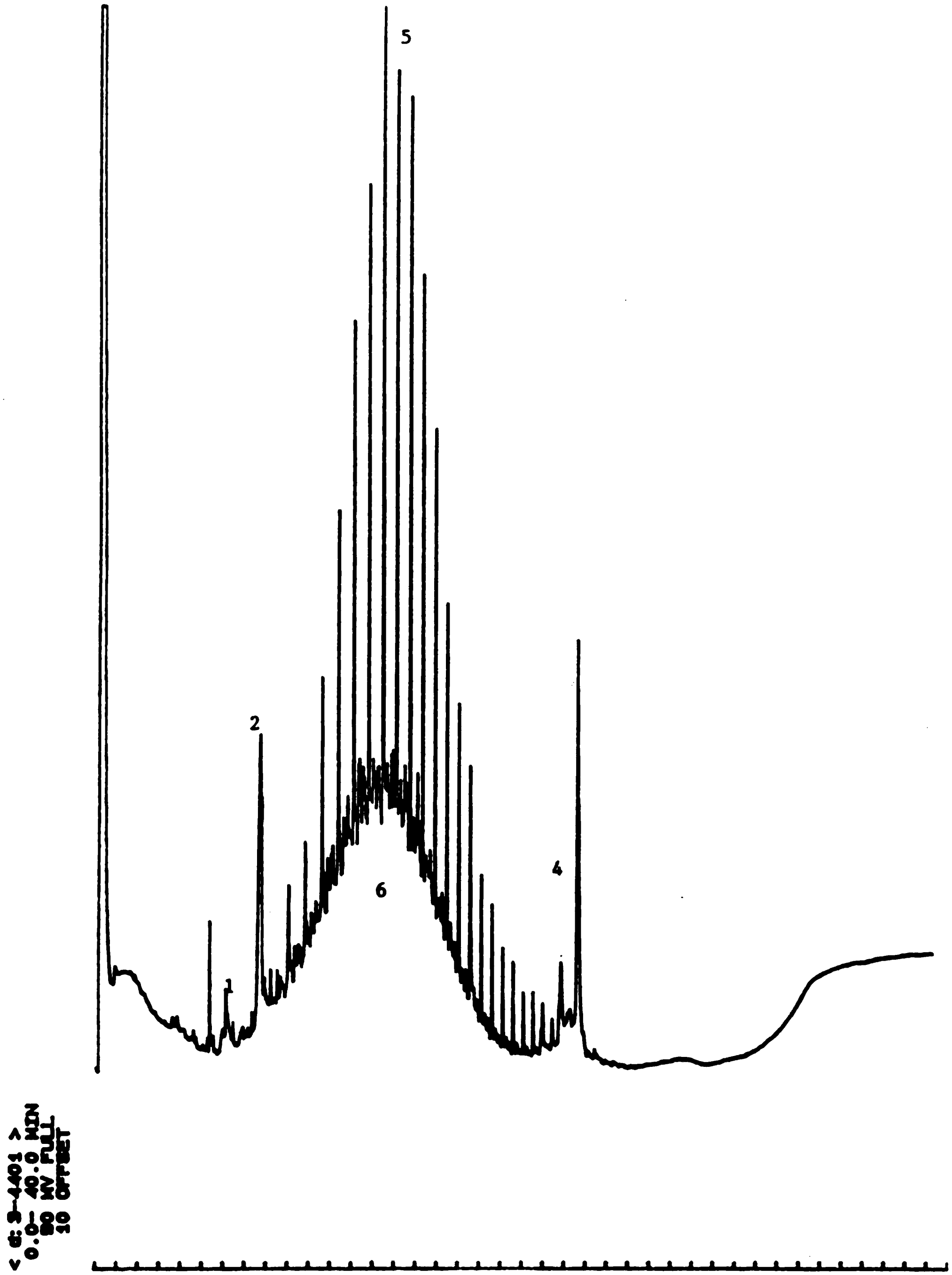

Figure 18: Chromatogram of Atlas Powermax 440 Prepared with TCE (Trial 3).

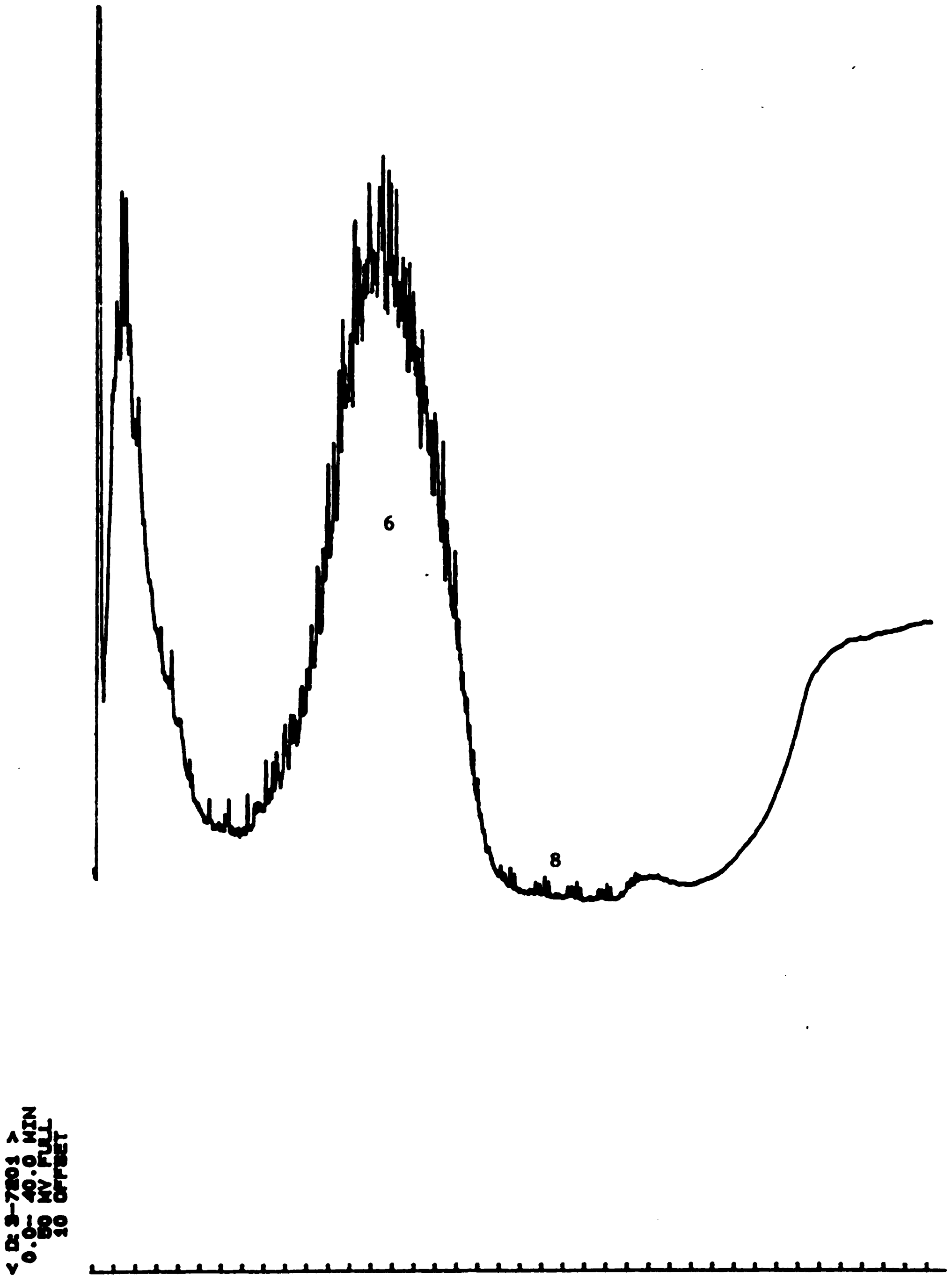

Figure 19: Chromatogram of Austin Emulex 720 Prepared with TCE (Trial 3).

Results of Intact Emulsion Samples Prepared with TCE (Trial 4).

Table 9. Intact emulsion sample amounts prepared with TCE (Trial 4).

Sample	Weight	Solvent
Atlas Apex 840	0.64 g	TCE-2 ml
Atlas Powermax 140	0.82 g	TCE-2 ml
Atlas Powermax 440	0.76 g	TCE-2 ml
Austin Emulex 720	0.54 g	TCE-2 ml

Table 9 lists the 4th sampling of intact emulsion samples from different locations on the packaged emulsion stick than those samples listed in Tables 6, 7, & 8.

Figure 20 represents a sample of Atlas Apex 840. Ranging from 8-20 min. is a series of consecutive peaks with a small unresolved area beneath these peaks. Additional peaks of interest can be seen at 5, 7.5, and 23 minutes.

Figure 21 represents a sample of Atlas Powermax 140. The familiar series of consecutive peaks ranging from 8-21 min., with a small unresolved area beneath these peaks. Additional important peaks can be seen at 5, 7.5, and 23 minutes.

Figure 22 represents a sample of Atlas Powermax 440. The familiar series of consecutive peaks is again present, ranging from 8-21 minutes. Additional important peaks are present at

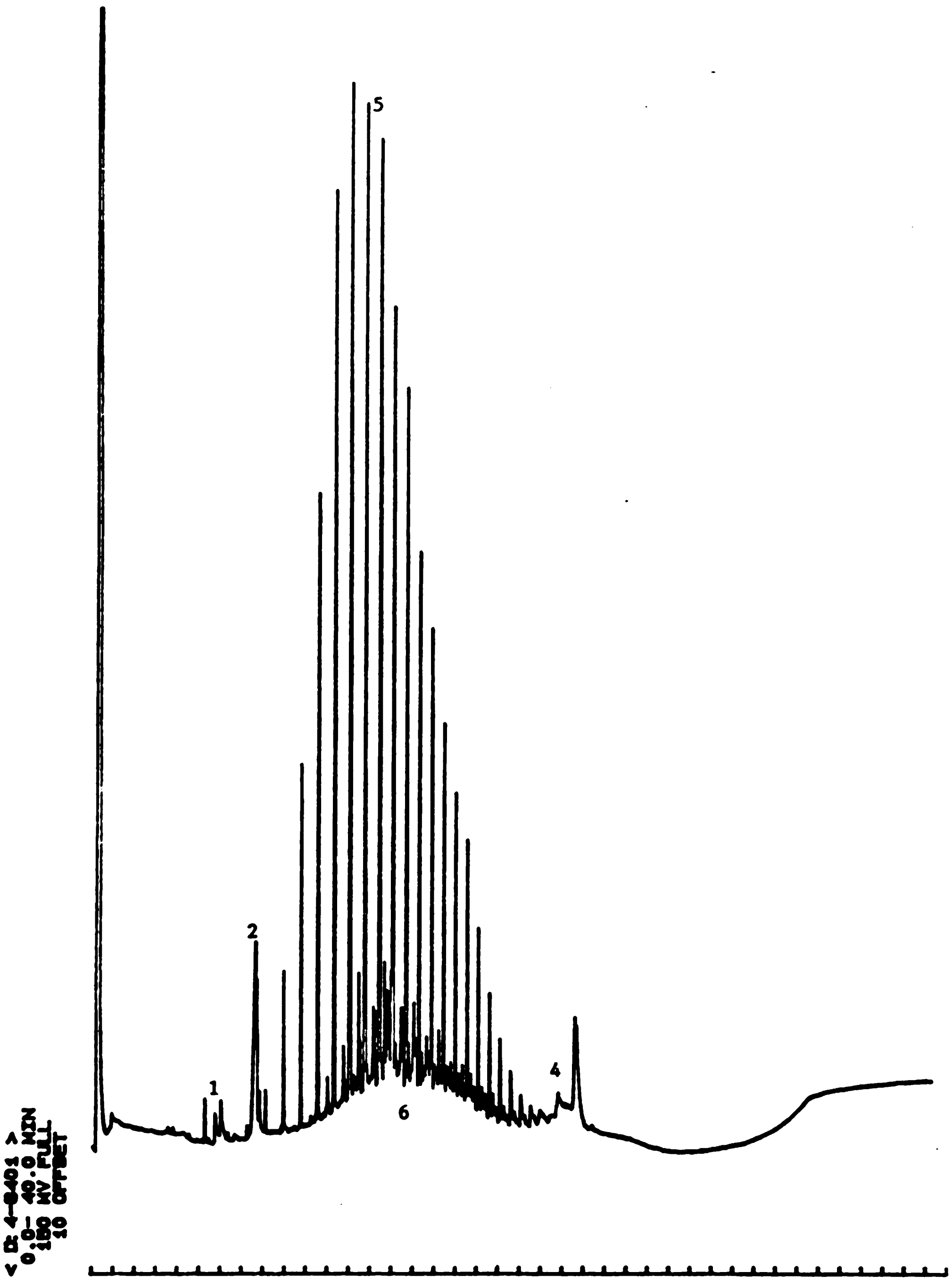

Figure 20: Chromatogram of Atlas Powermax 840 Prepared with TCE (Trial 4).

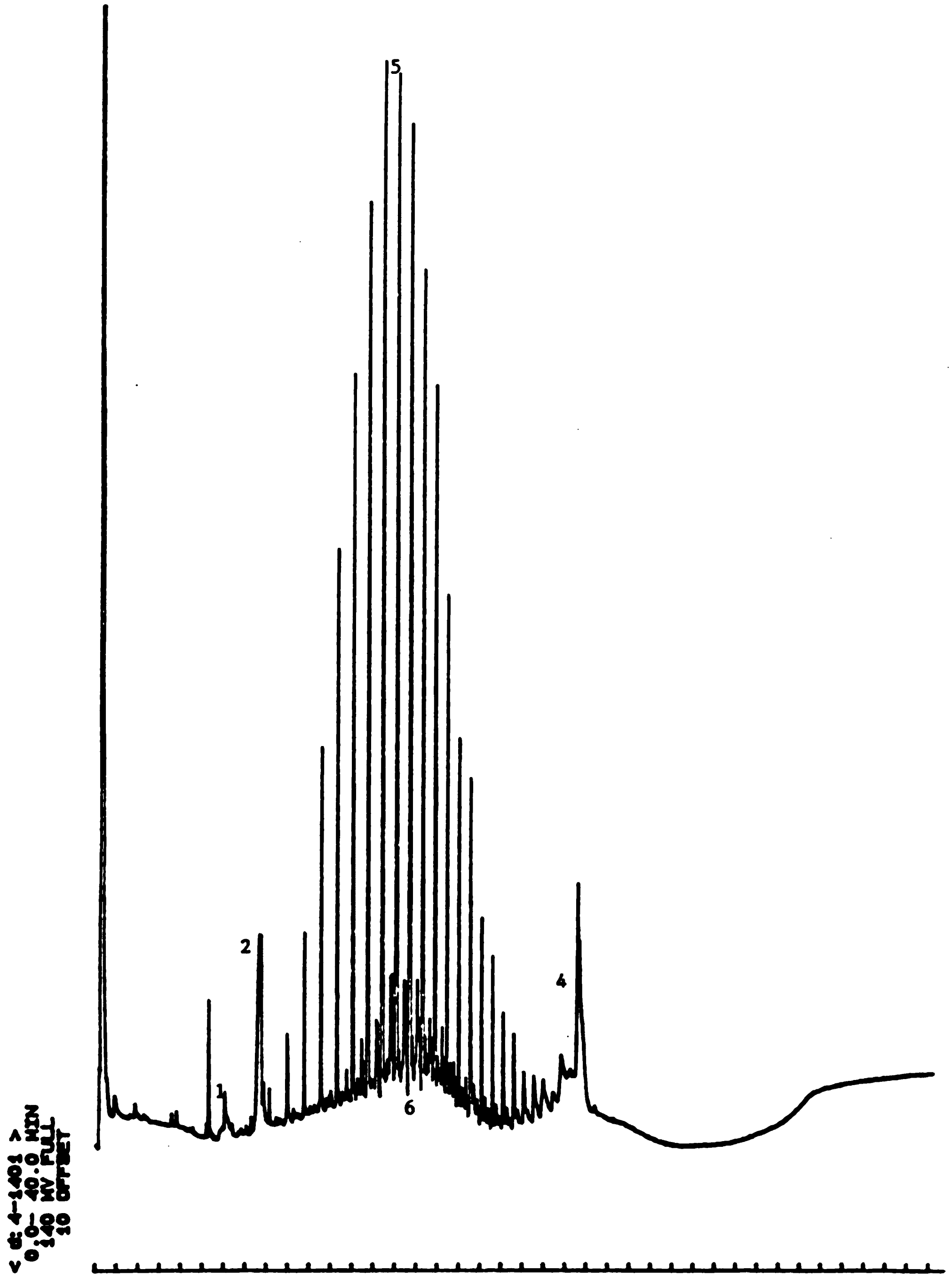

Figure 21: Chromatogram of Atlas Powermax 140 Prepared with TCE (Trial 4).

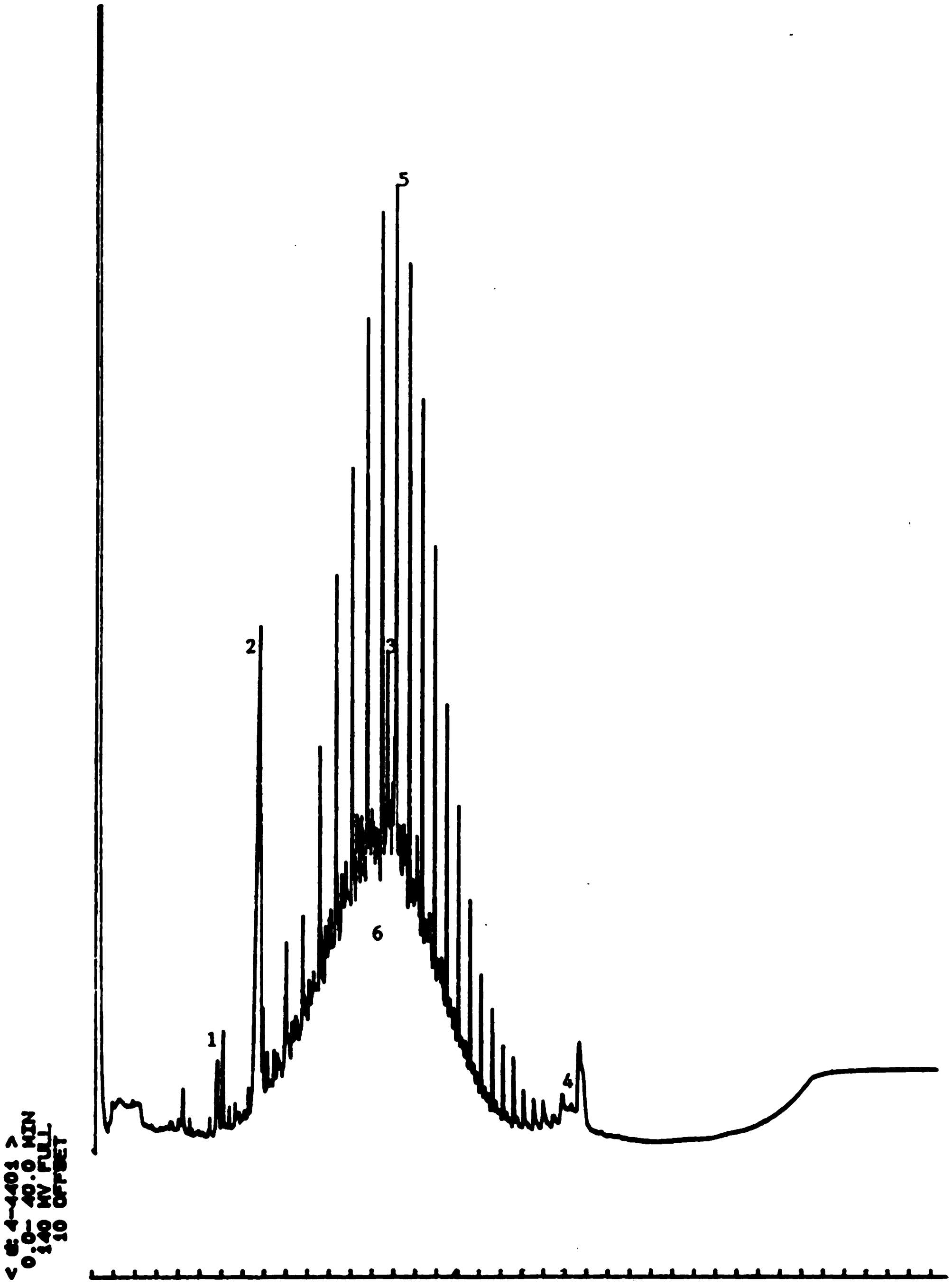

Figure 22: Chromatogram of Atlas Powermax 440 Prepared with TCE (Trial 4).

7.5, 14, and 22.5 minutes.

Figure 23 represents a sample of Austin Emulex 720. Ranging from 0.5-6 min. is an unresolved peak of considerable height. Ranging from 7-19 min. is a larger unresolved peak with equal height to the first. From 20-26 min., 4 groupings of peaks can be seen with 4 small peaks per group.

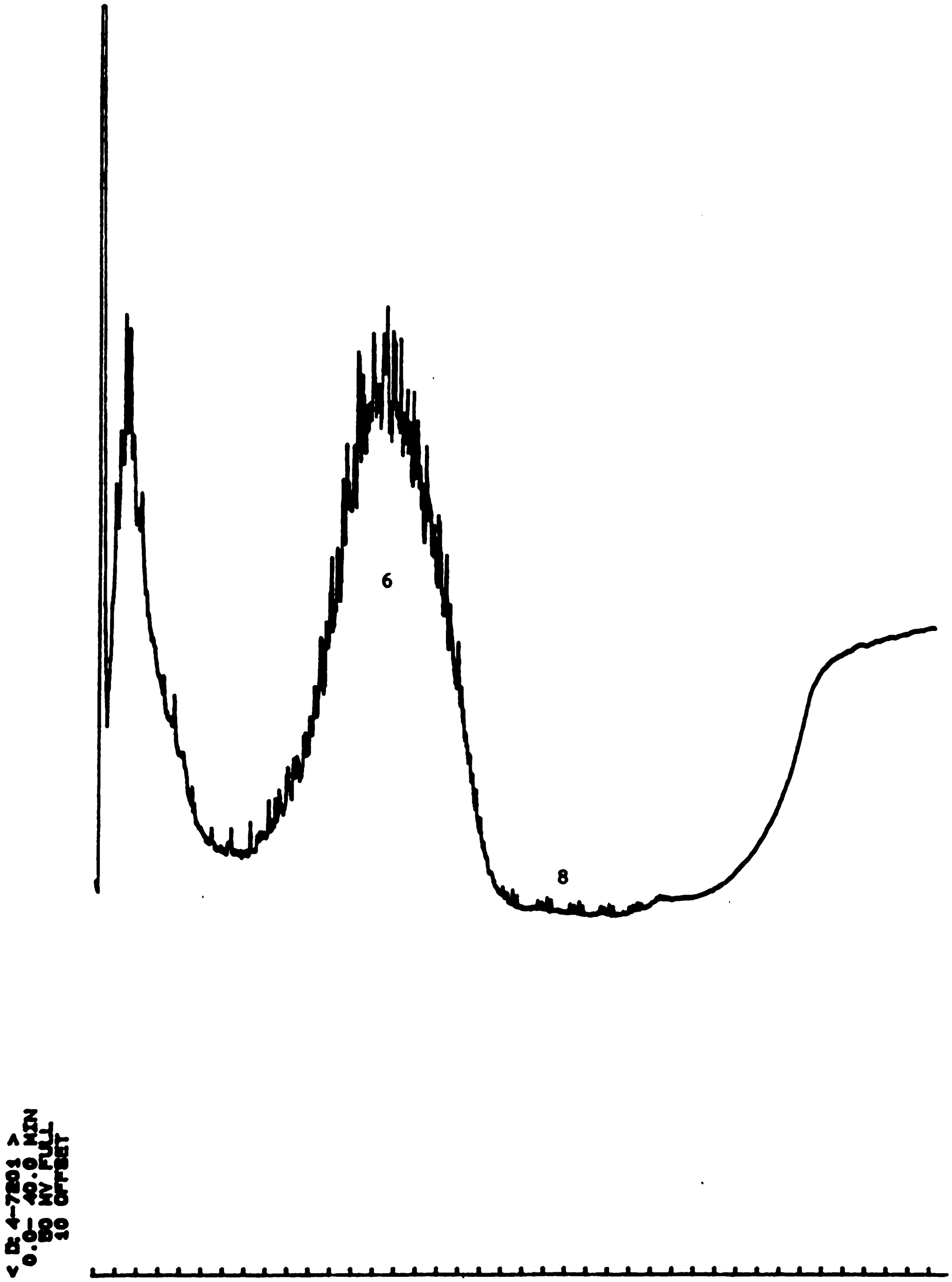

Figure 23: Chromatogram of Austin Emulex 720 Prepared with TCE (Trial 4).

Results of Intact Emulsion Samples Prepared with Methylene Chloride.

Table 10. Intact emulsion sample amounts prepared with Methylene Chloride.

Sample	**Weight**	**Methylene Chloride**	**TCE**
Atlas Powermax 140	0.35 g	5-10 ml	2 ml
Atlas Powermax 440	0.40 g	5-10 ml	2 ml
Atlas Apex 840	0.40 g	5-10 ml	2 ml
Austin Emulex 720	0.44 g	5-10 ml	2 ml

Table 10 lists the weight of intact samples that were prepared with Methylene Chloride initially, and then with TCE for GC use. The amounts of Methylene Chloride and TCE used are also indicated.

Figure 24 represents a sample of Atlas Powermax 140. Shown in this chromatogram is a series of consecutive peaks that range from 8-17 minutes. Also shown is one peak that appears at approximately 13.5 minutes. There is a small unresolved area that lies beneath the series of peaks.

Figure 25 represents a sample of Atlas Powermax 440. Again the series of consecutive peaks can be seen that ranges from 9-15 minutes. A separate peak lies at approximately 13.5 minutes. There is a large unresolved area beneath this series

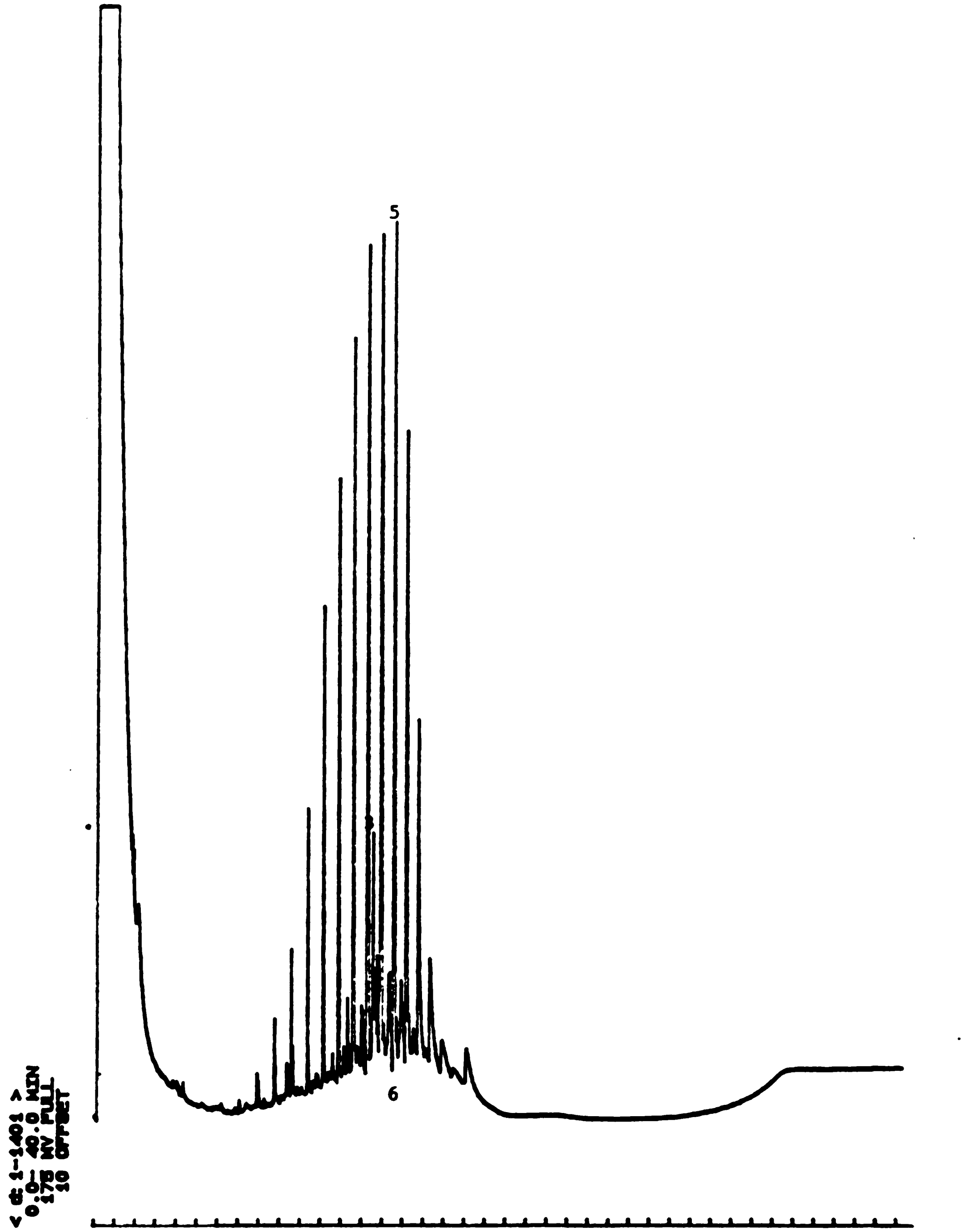

Figure 24: Chromatogram of Atlas Powermax 140 Prepared with Methylene Chloride.

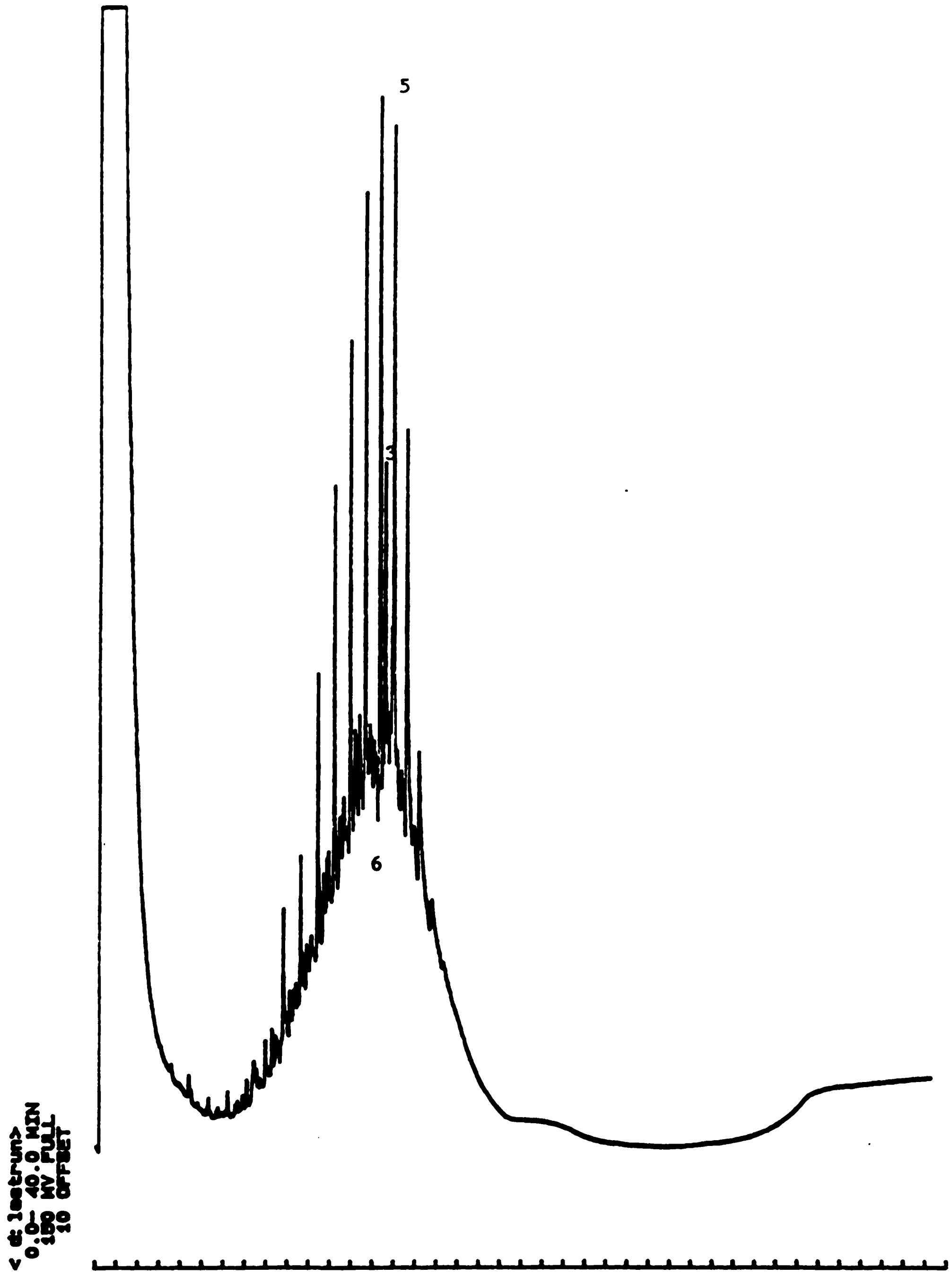

Figure 25: Chromatogram of Atlas Powermax 440 Prepared with Methylene Chloride.

of peaks.

Figure 26 represents a sample of Atlas Apex 840. A series of consecutive peaks ranging from 8-16 minutes can be seen. Two separate peaks can be seen at appx. 12.5 and 13.5 minutes.

Figure 27 represents a sample of Austin Emulex 720. This chromatogram only shows a large unresolved peak ranging from 7-19 minutes.

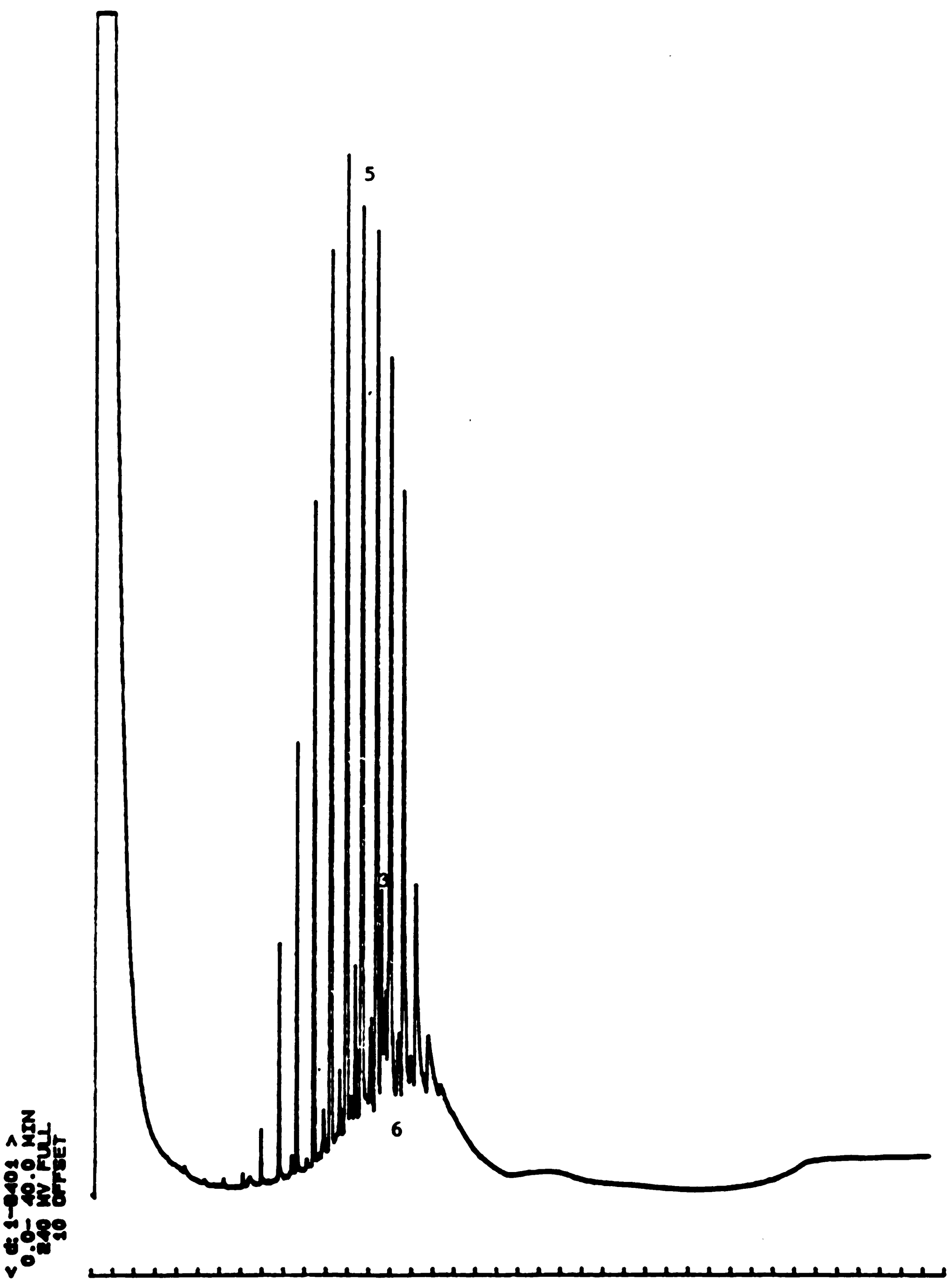

Figure 26: Chromatogram of Atlas Apex 840 Prepared with Methylene Chloride.

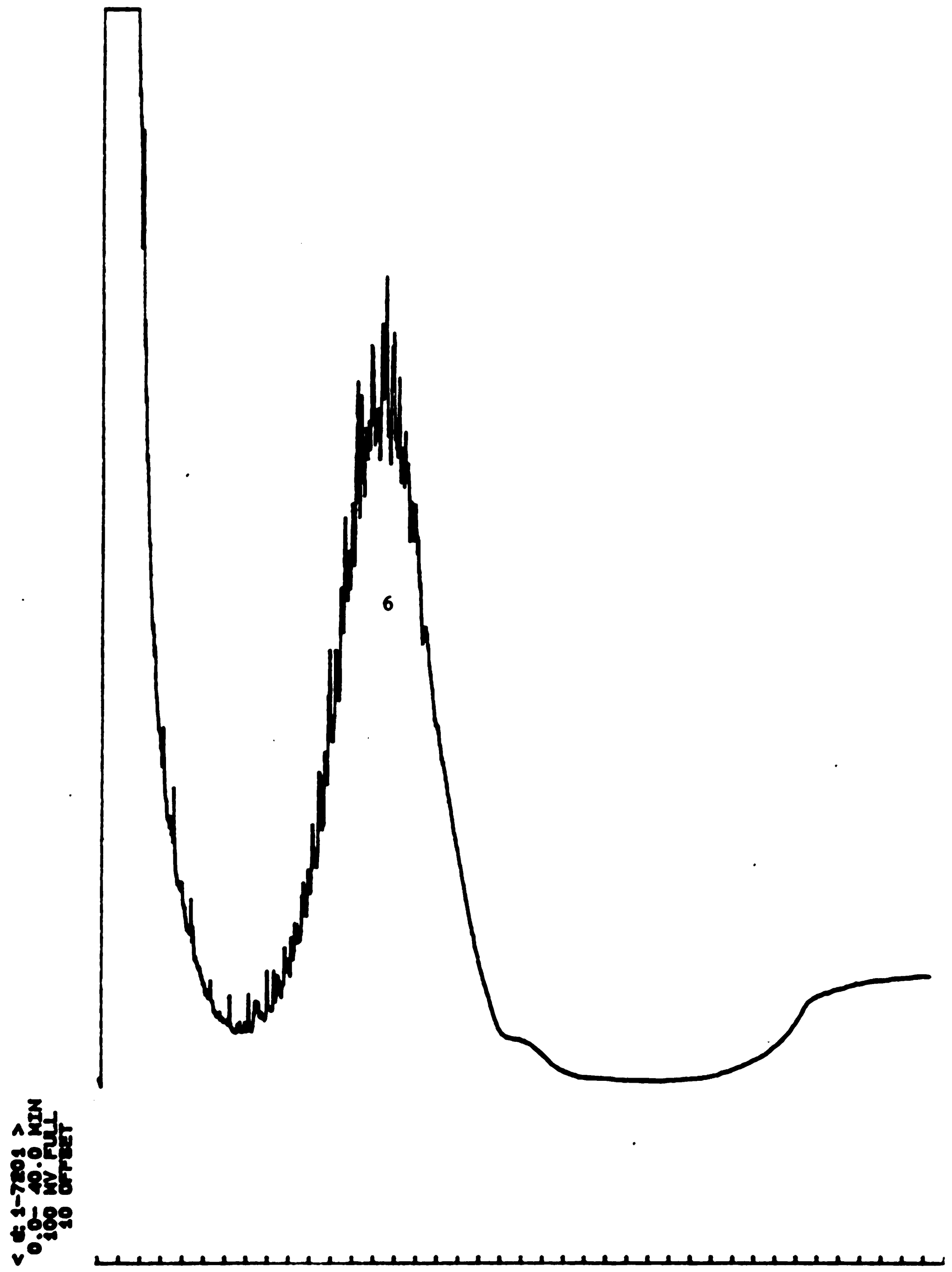

Figure 27: Chromatogram of Austin Emulex 720 Prepared with Hexane.

Results of Intact Emulsion Samples Prepared with Hexane and TCE (Trial 1).

Table 11. Intact emulsion sample amounts prepared with Hexane and TCE (Trial 1).

Sample	Weight	Initial Solvent: Hexane	Final Solvent: TCE
Atlas Powermax 140	0.45 g	20 ml	2 ml
Atlas Powermax 440	0.45 g	20 ml	2 ml
Atlas Apex 840	0.45 g	20 ml	2 ml
Austin Emulex 720	0.40 g	20 ml	2 ml

Table 11 lists the weights of the intact samples prepared with the initial solvent of Hexane, and then the final solvent of TCE.

Figure 28 represents a sample of Atlas Powermax 140 prepared with Hexane and TCE. This chromatogram shows a series of consecutive peaks ranging from 12-25 minutes. Additional important peaks can be seen at 11, 21, and 26 minutes.

Figure 29 represents a sample of Atlas Powermax 440. A series of consecutive peaks ranges from 12-25 minutes. Other peaks are shown at 9, 11, 21, and 26.5 minutes. A somewhat large unresolved area can be seen underneath the range of peaks.

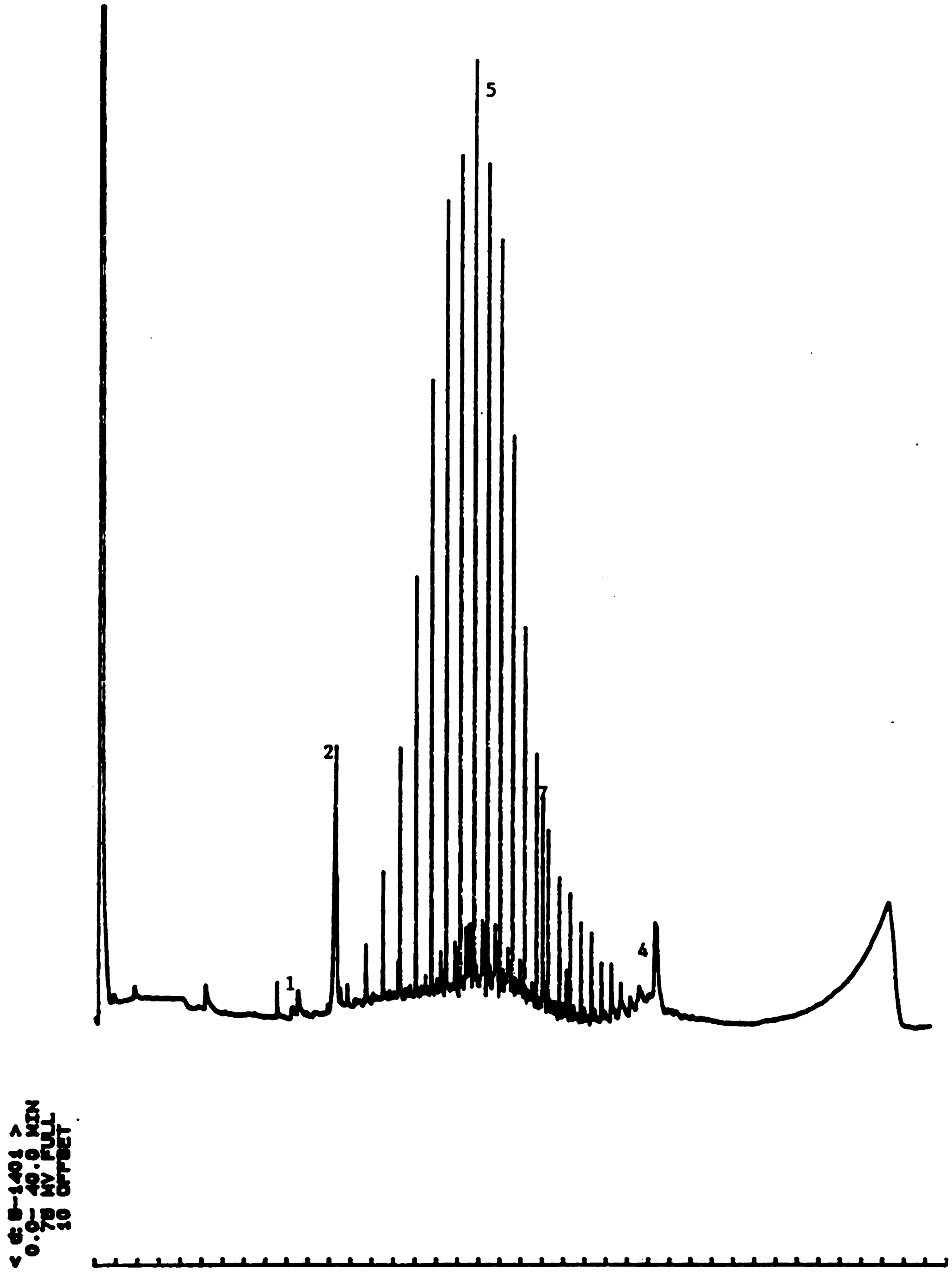

Figure 28: Chromatogram of Atlas Powermax 140 Prepared with Hexane.

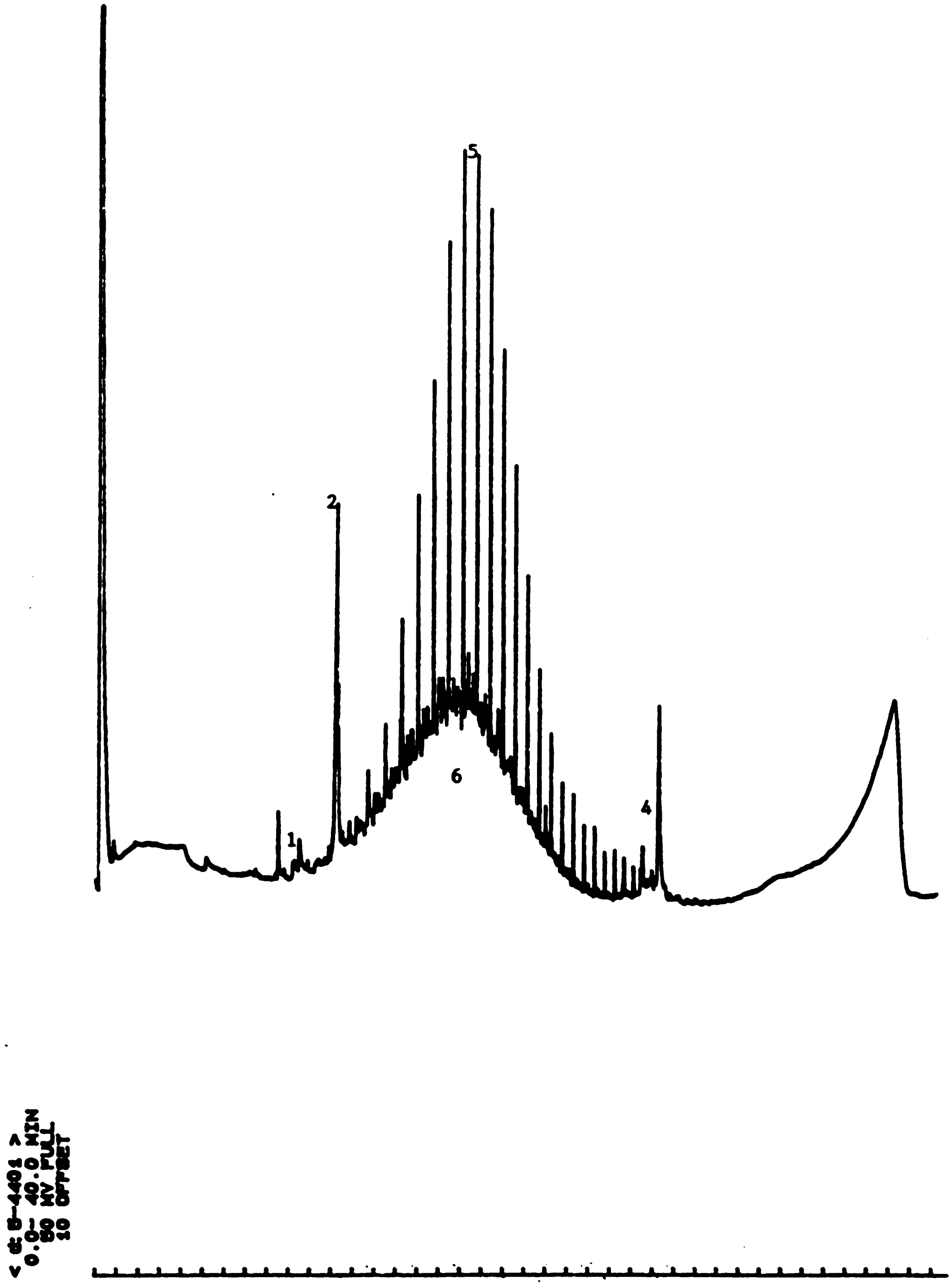

Figure 29: Chromatogram of Atlas Powermax 440 Prepared with Hexane.

Figure 30 represents a sample of Atlas Apex 840. A series of consecutive peaks can be seen ranging from 12-25 minutes, with additional peaks at 11 and 26.5 minutes. A small unresolved area beneath the peaks can be seen.

Figure 31 represents a sample of Austin Emulex 720. This chromatogram shows an unresolved peak ranging from 0.5-5 minutes, and another unresolved peak from 11 to 23 minutes. At 21 minutes is a sharp distinct peak. Ranging from 24-30 minutes are 4 groups of peaks, with 4 peaks per group.

Figure 30: Chromatogram of Atlas Apex 840 Prepared with Hexane.

Figure 31: Chromatogram of Austin Emulex 720 Prepared with Hexane.

Results of Intact Emulsion Samples Prepared with Hexane and TCE (Trial 2).

Table 12. Intact emulsion sample amounts prepared with Hexane and TCE (Trial 2).

Sample	Weight		Initial Solvent: Hexane	Final Solvent: TCE
Atlas Powermax 140	0.45 g		25 ml	2 ml
Atlas Powermax 440	0.47 g		25 ml	2 ml
Atlas Apex 840	0.50 g		25 ml	2 ml
Atlas Apex BA 240 (old)	0.53 g		25 ml	2 ml
Austin Emulex 720	0.50 g		25 ml	2 ml
Atlas Apex BA 240 (new)	End 1	0.87 g	25 ml	2 ml
	Middle	0.89 g		
	End 2	0.78 g		
Atlas 7D	End 1	0.58 g	25 ml	2 ml
	Middle	0.56 g		
	End 2	0.55 g		

Table 12 lists the intact samples that were prepared with hexane, and the corresponding weights of each sample used.

Figure 32 represents Atlas Powermax 140. There is a range of peaks from 12-25 minutes that are in a series and consecutive, with a very small area beneath the peaks that is unresolved. Other peaks of interest show up at 11.5, and 26.5

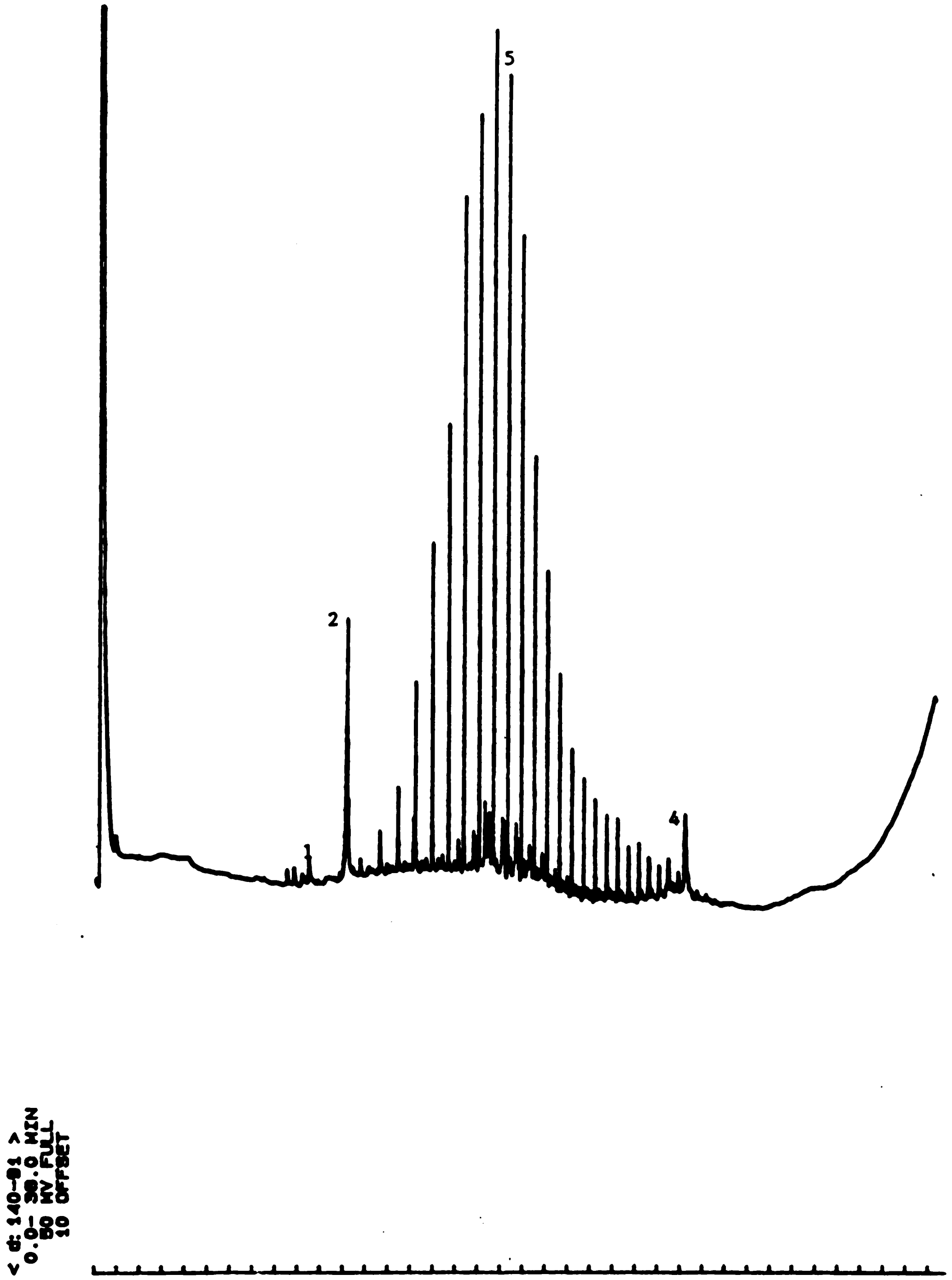

Figure 32: Chromatogram of Atlas Powermax 140 Prepared with Hexane and TCE.

minutes.

Figure 33 represents a sample of Atlas Powermax 440. From 12-25 minutes is a series of consecutive peaks with a somewhat large unresolved area beneath the peaks in the same range. Again, there are other peaks that appear at 11.5, and 26.5 minutes, and another peak at 17 minutes.

Figure 34 represents a sample of Atlas Apex 840. A series of consecutive peaks can be seen in the range of 12-25 minutes with a small unresolved area beneath these peaks, within the same time range. Again, there is the peak that appears at 11.5 minutes, and the other common peak which appears at 26.5 minutes.

Figure 35 represents a sample of Atlas Apex 240 BA (old). A series of consecutive peaks ranging from 12-25 minutes is again apparant, with a large unresolved area beneath this series, within the same time range. The commonly seen peaks at 11.5 and 26.5 minutes are also apparant.

Figure 36 represents a sample of Autin Emulex 720. This chromatogram shows a large unresolved peak that ranges from 10-21 minutes, with no series of consecutive peaks showing. In the range of 22-29 minutes is a grouping of peaks. These peaks appear as separate groups with 4 small peaks per group.

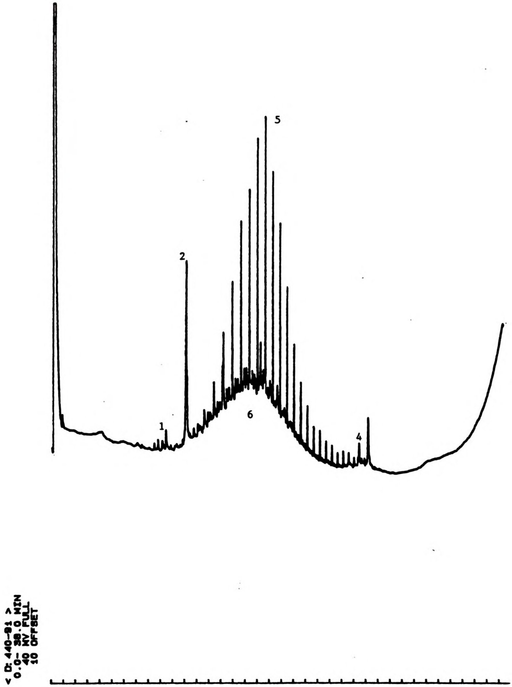

Figure 33: Chromatogram of Atlas Powermax 440 Prepared with Hexane and TCE.

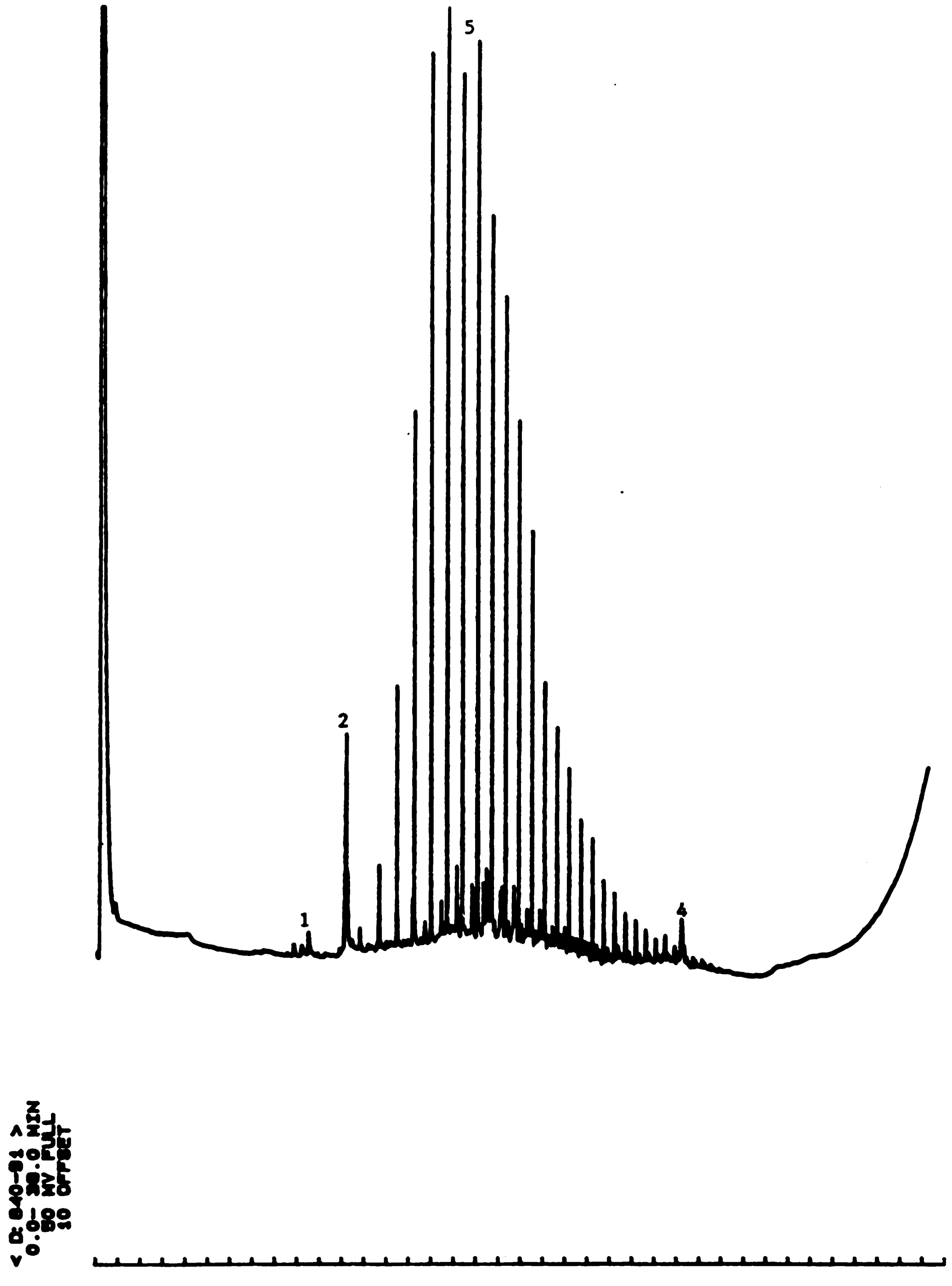

Figure 34: Chromatogram of Atlas Apex 840 Prepared with Hexane and TCE.

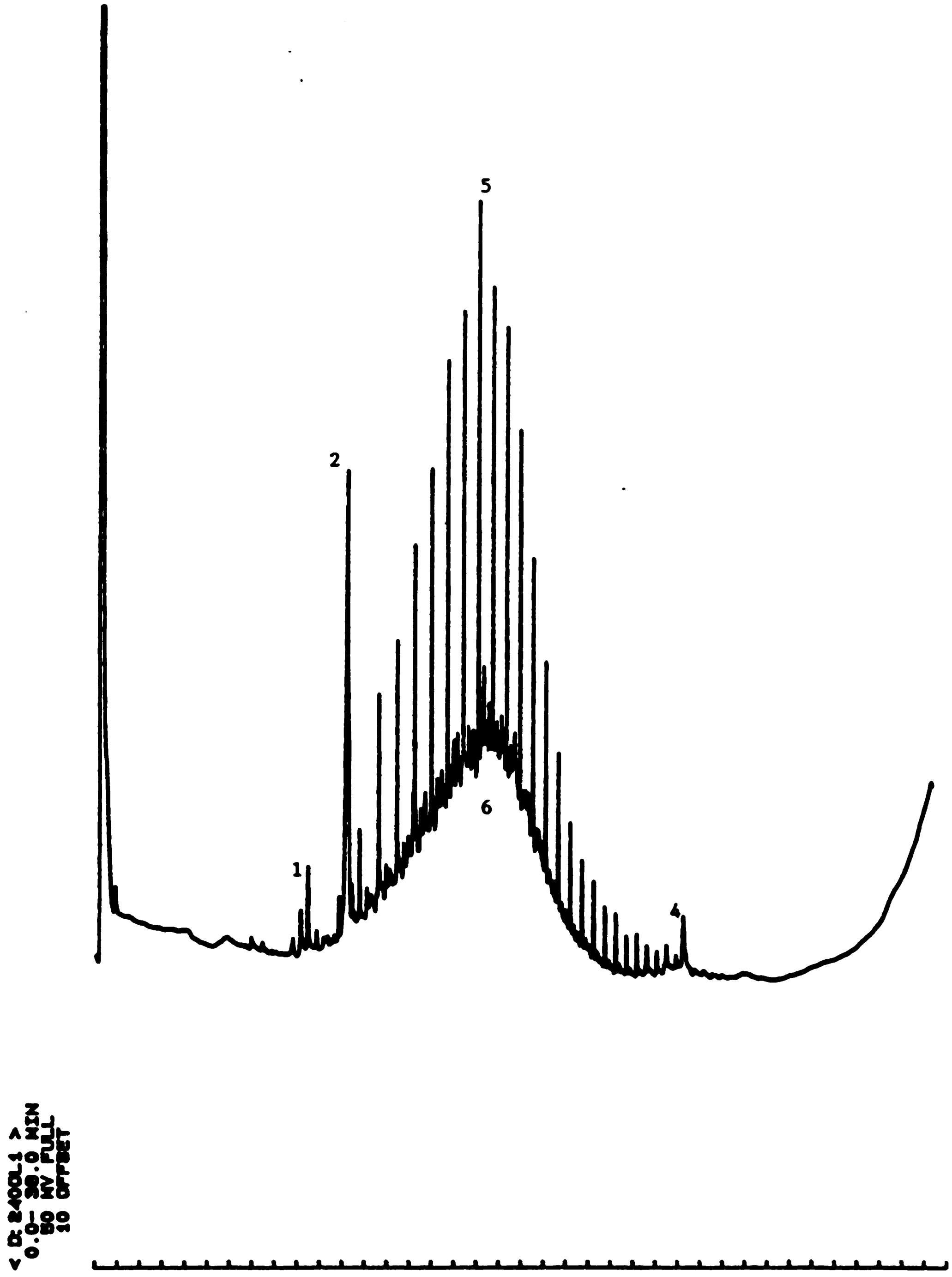

Figure 35: Chromatogram of Atlas Apex Blasting Agent 240 (old) Prepared with Hexane and TCE.

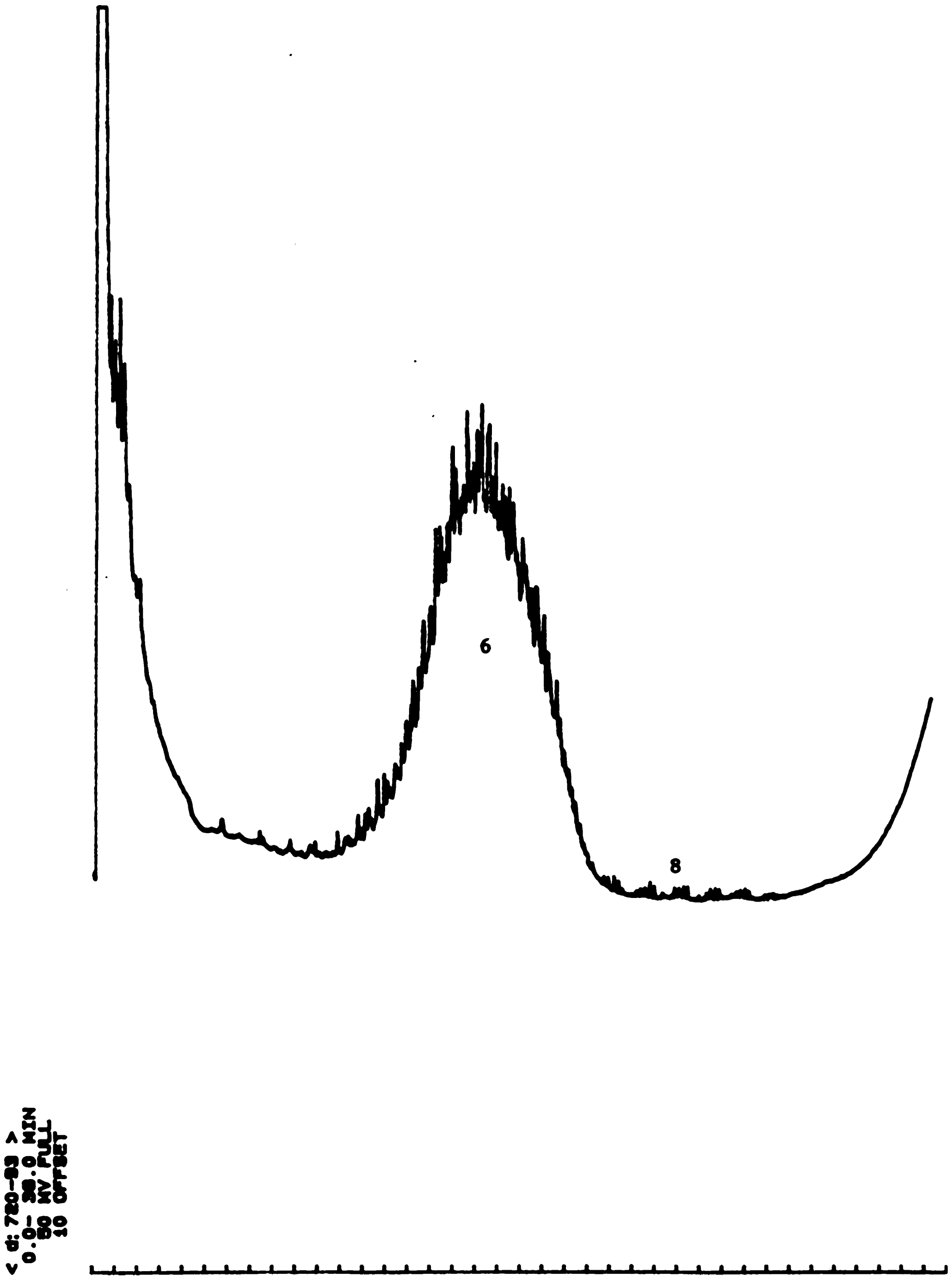

Figure 36: Chromatogram of Austin Emulex 720 Prepared with Hexane and TCE.

Figure 37 represents a sample of Atlas Apex BA 240 (new), taken from end 1 of the sample stick. This chromatogram does not show the common series of consecutive peaks, but does have the common unresolved area that ranges almost throughout the entire scale. At 21 minutes is a very distinct peak, followed by 4 groups of peaks with 4 peaks per group, ranging from 23-29 minutes.

Figure 38 represents a sample of Atlas Apex BA 240 (new), taken from the middle of the sample stick. Again, there is no series of consecutive peaks, but the unresolved area that is commonly present does exist, ranging throughout most of the time scale. Again, at 21 minutes is a very distinctive peak followed by the 4 groups of peaks with 4 peaks per group.

Figure 39 represents a sample of Atlas Apex BA 240 (new), taken from end 2 of the sample stick. A larger unresolved area can be seen within this chromatogram, that ranges from 5-31 minutes. No series of consecutive peaks exists, nor does groupings of peaks exist.

Figure 40 represents a sample of Atlas 7D, taken from end 1 of the sample stick. The common series of consecutive peaks can be seen that ranges from 12-25 minutes, with virtually no unresolved area beneath this range. Again, peaks of interest appear at 11.5, 21, and 26.5 minutes.

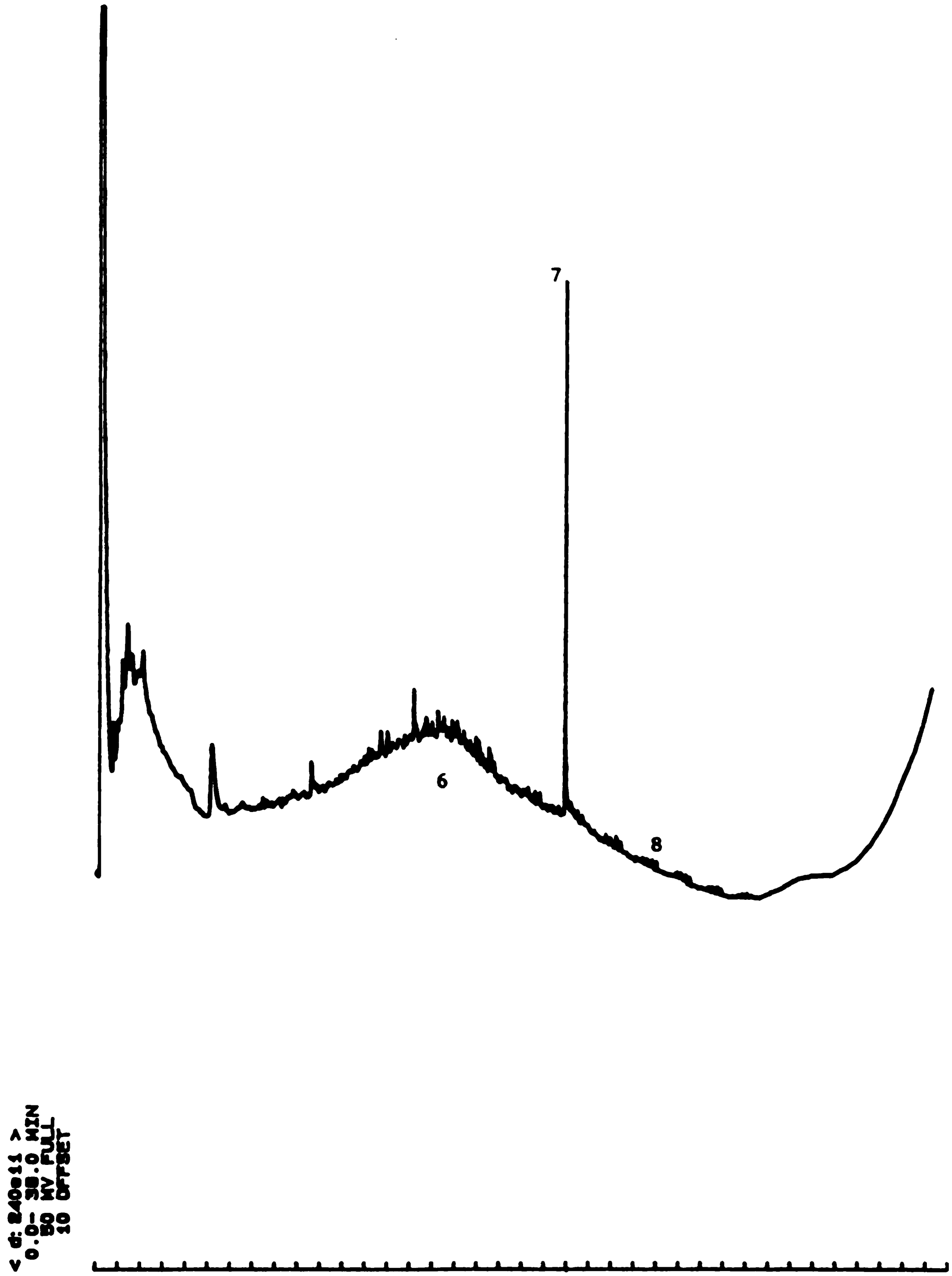

Figure 37: Chromatogram of Atlas Apex Blasting Agent 240 (new) End 1 Sample Prepared with Hexane and TCE.

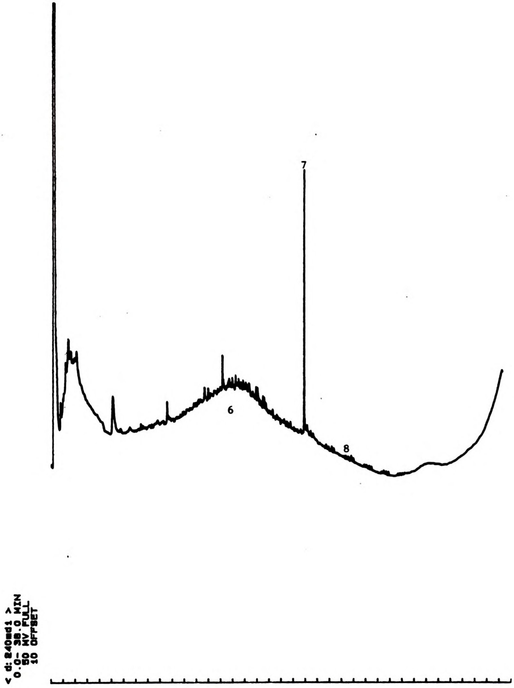

Figure 38: Chromatogram of Atlas Apex Blasting Agent 240 (new) Middle Sample Prepared with Hexane and TCE.

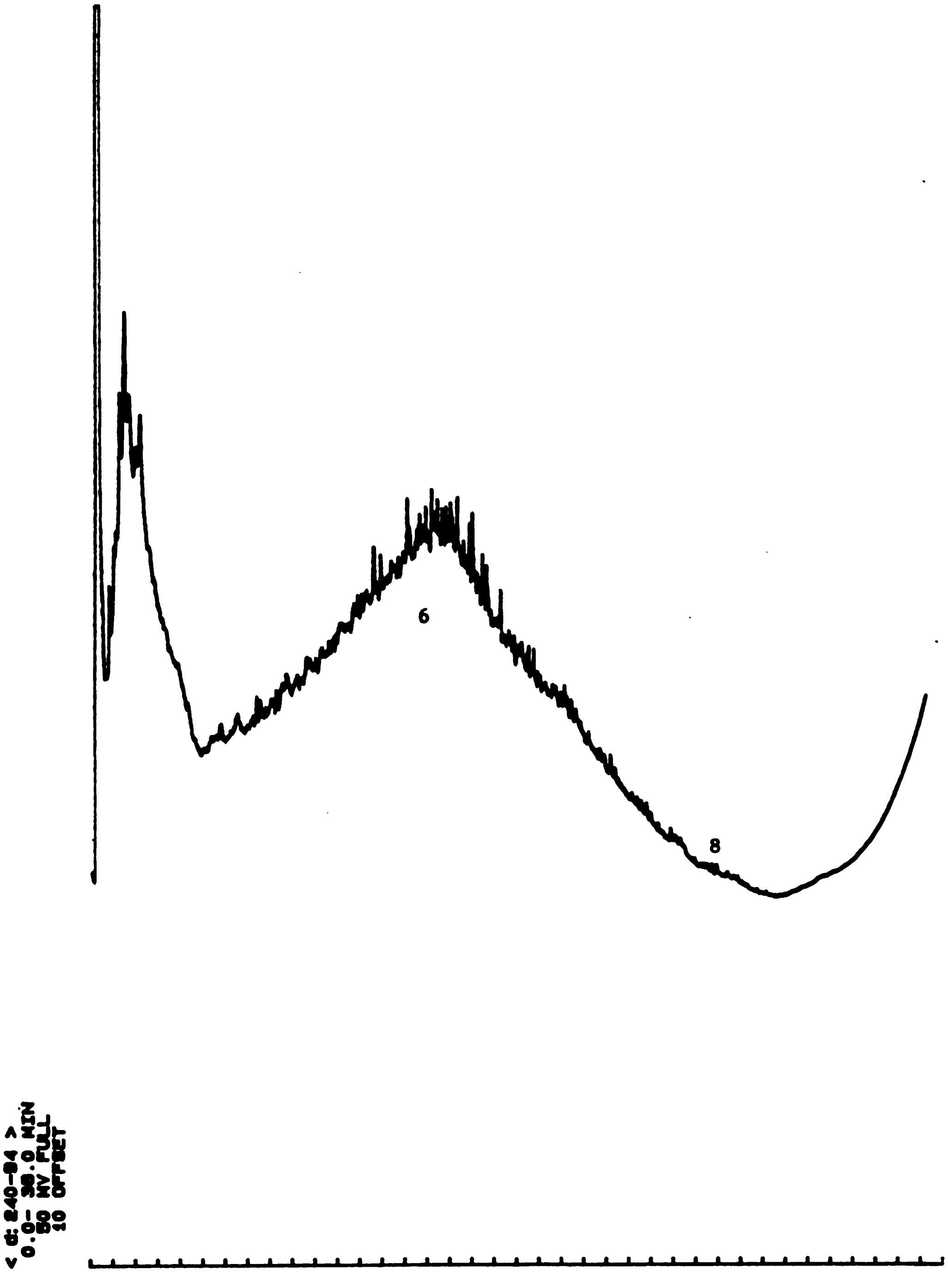

Figure 39: Chromatogram of Atlas Apex Blasting Agent 240 (new) End 2 Sample Prepared with Hexane and TCE.

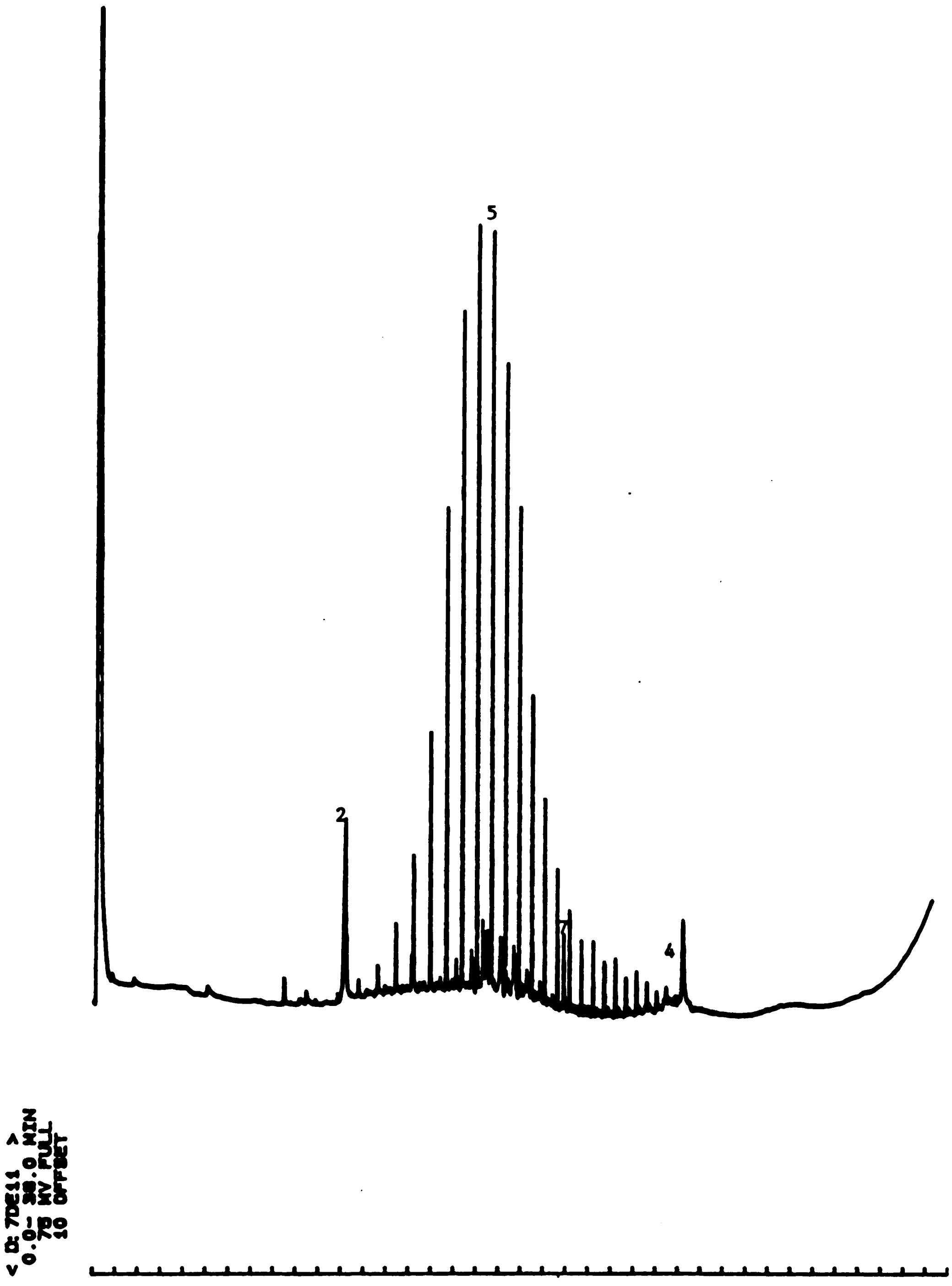

Figure 40: Chromatogram of Atlas 7D End 1 Sample Prepared with Hexane and TCE.

Figure 41 represents a sample of Atlas 7D, taken from the middle of the sample stick. Ranging from 12-25 minutes is the series of consecutive peaks, with a slightly larger unresolved area beneath this series than shown in chromatogram 40. Peaks at 11.5, 21, and 26.5 minutes are seen, with the peak at 21 minutes being larger than that shown in chromatogram 40.

Figure 42 represents a sample of Atlas 7D, taken from end 2 of the sample stick. Ranging from 12-25 minutes is the series of consecutive peaks, with a very slight unresolved area beneath the series. Other important peaks appear at 11.5, 21, and 26.5 minutes.

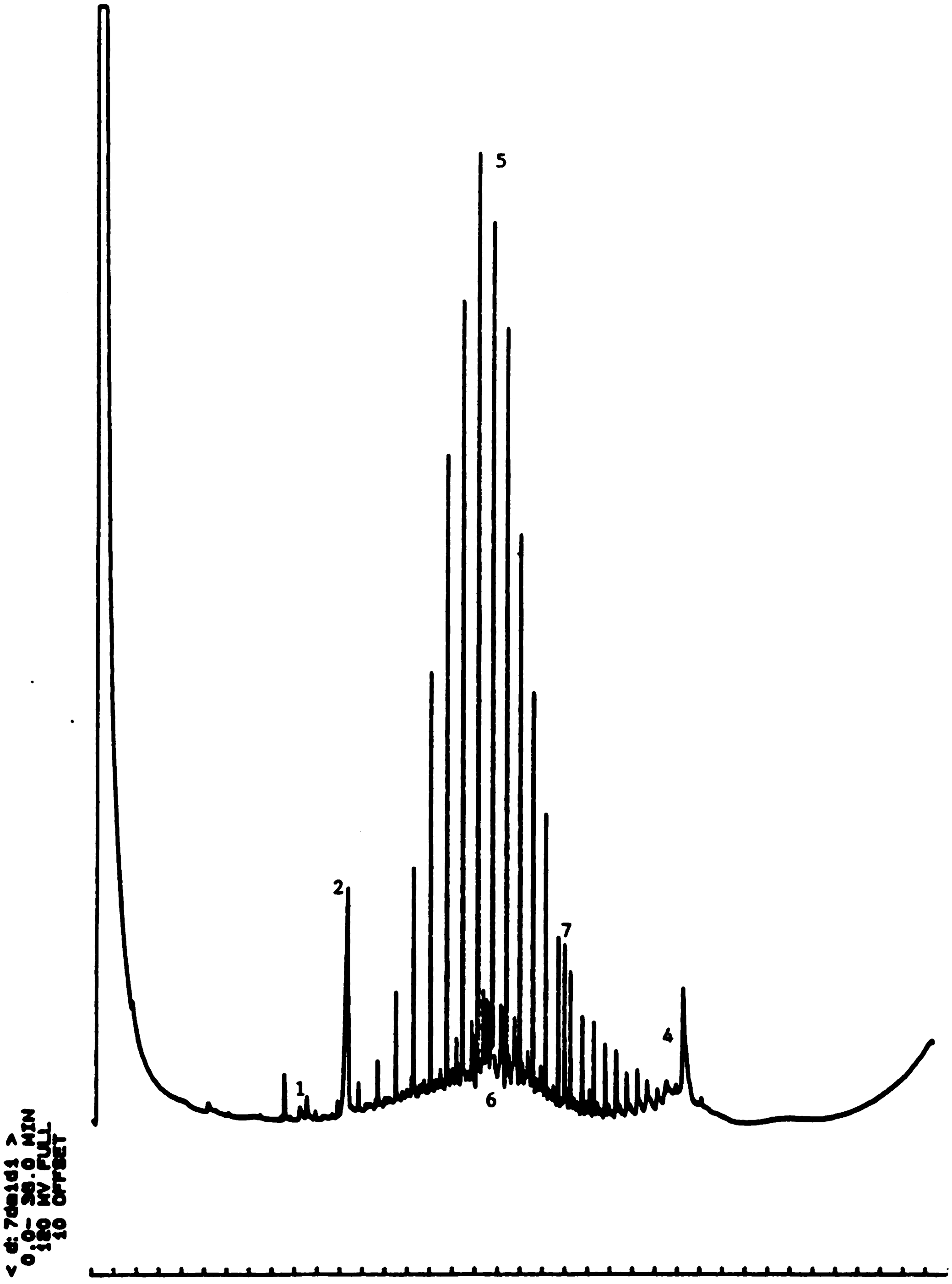

Figure 41: Chromatogram of Atlas 7D Middle Sample Prepared with Hexane and TCE.

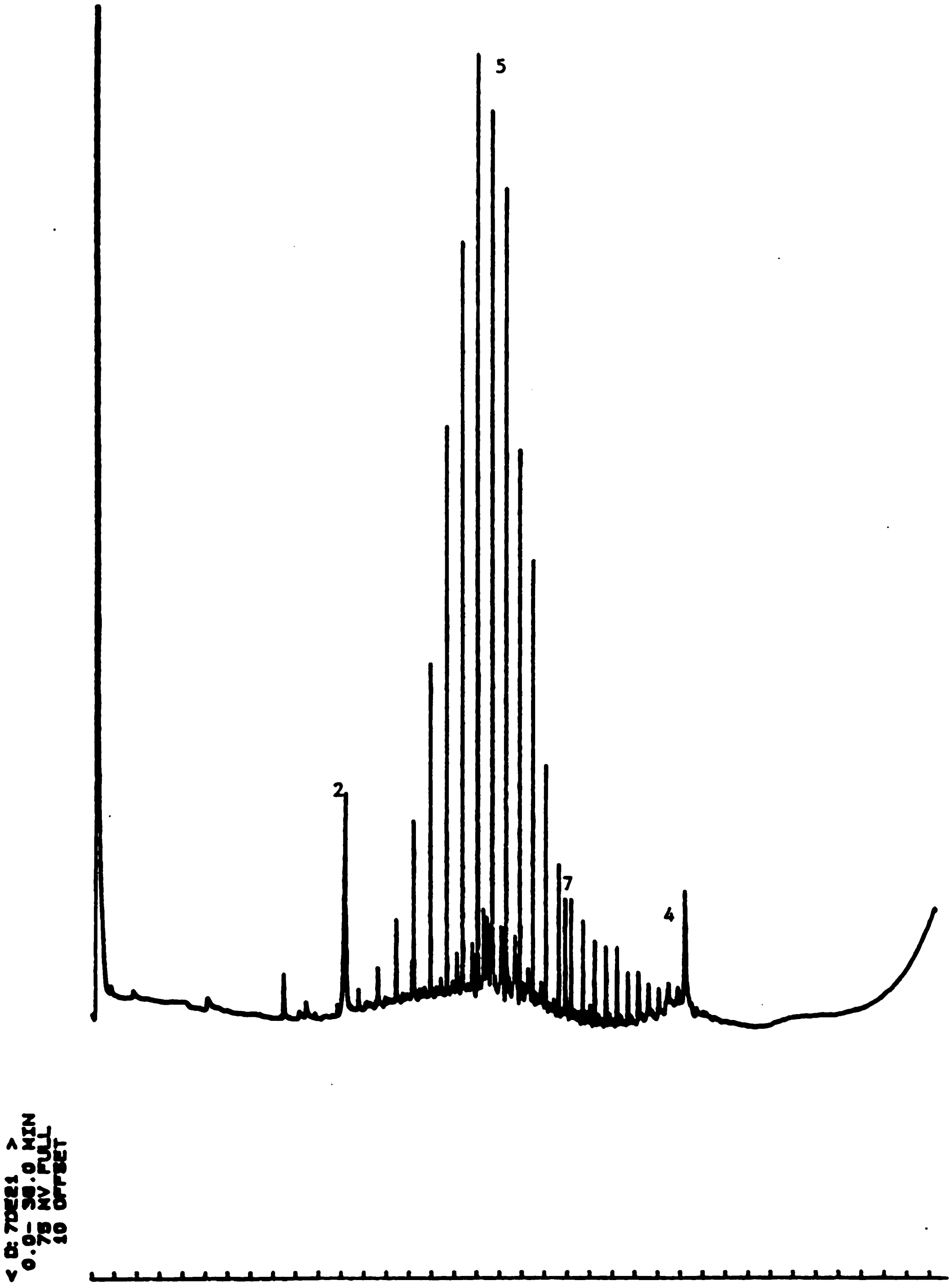

Figure 42: Chromatogram of Atlas 7D End 2 Sample
Prepared with Hexane and TCE.

Results of Intact Emulsion samples prepared with Iso-Octane.

Table 13. Intact emulsion sample amounts prepared with iso-octane.

Sample	**Weight**	**Solvent: Iso-Octane**
Atlas Powermax 140	0.41 g	3-5 ml
Atlas Powermax 440	0.77 g	3-5 ml
Atlas Apex 840	0.86 g	3-5 ml
Atlas Apex 240(old)	0.46 g	3-5 ml
Austin Emulex 720	0.74 g	3-5 ml
Atlas 7D	1.51 g	3-5 ml

Table 13 lists the intact emulsion samples prepared with iso-octane, including the corresponding weights of each sample used.

Figure 43 represents a sample of Atlas Powermax 140. In the range of 12-25 minutes is the common series of consecutive peaks, with a small unresolved area beneath this series. At 11.5, and 26.5 minutes are two other commonly seen peaks.

Figure 44 represents a sample of Atlas Powermax 440. Ranging from 12-25 minutes is a series of consecutive peaks, with a large unresolved area beneath this series. Other important peaks are seen at 11.5, 18, and 26.5 minutes.

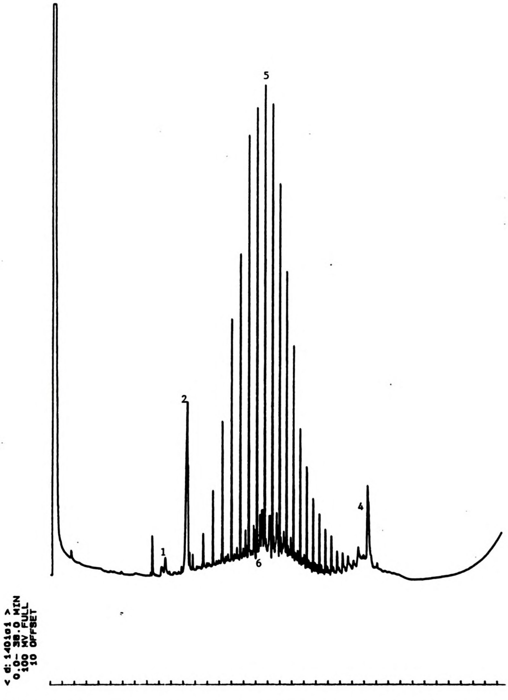

Figure 43: Chromatogram of Atlas Powermax 140 Prepared with Iso-Octane.

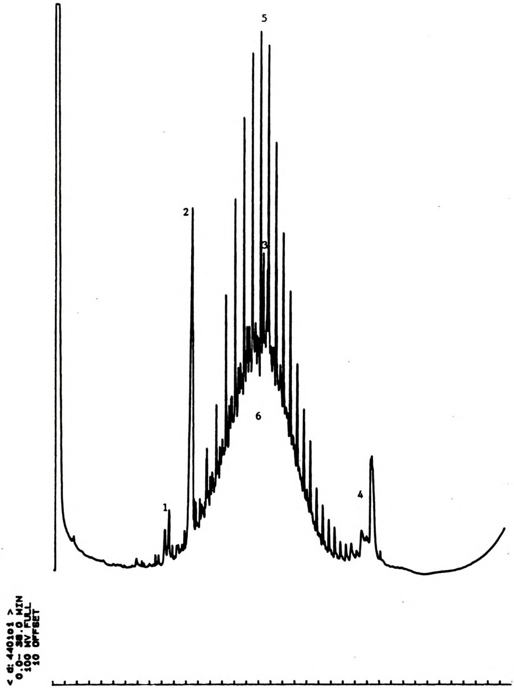

Figure 44: Chromatogram of Atlas Powermax 440 Prepared with Iso-Octane.

Figure 45 represents a sample of Atlas Apex 840. The common series of consecutive peaks is again seen from 12-25 minutes, with a small unresolved area beneath the series. Two other peaks of interest appear at 11.5, and 26.5 minutes.

Figure 46 represents a sample of Atlas Apex BA 240 (Old). Ranging from 12-25 minutes is a series of consecutive peaks, with a large unresolved area beneath this series. Two other important peaks appear at 11.5, and 26.5 minutes.

Figure 47 represents a sample of Austin Emulex 720. This chromatogram reveals one large unresolved peak that ranges from 11-24 minutes. Ranging from 24-30 minutes are 4 groups of peaks with 4 small peaks per group.

Figure 48 represents a sample of Atlas 7D. Ranging from 12-25 minutes is the common series of consecutive peaks, with a small unresolved area beneath this series. At 11.5, and 26.5 minutes are two other common peaks that appear.

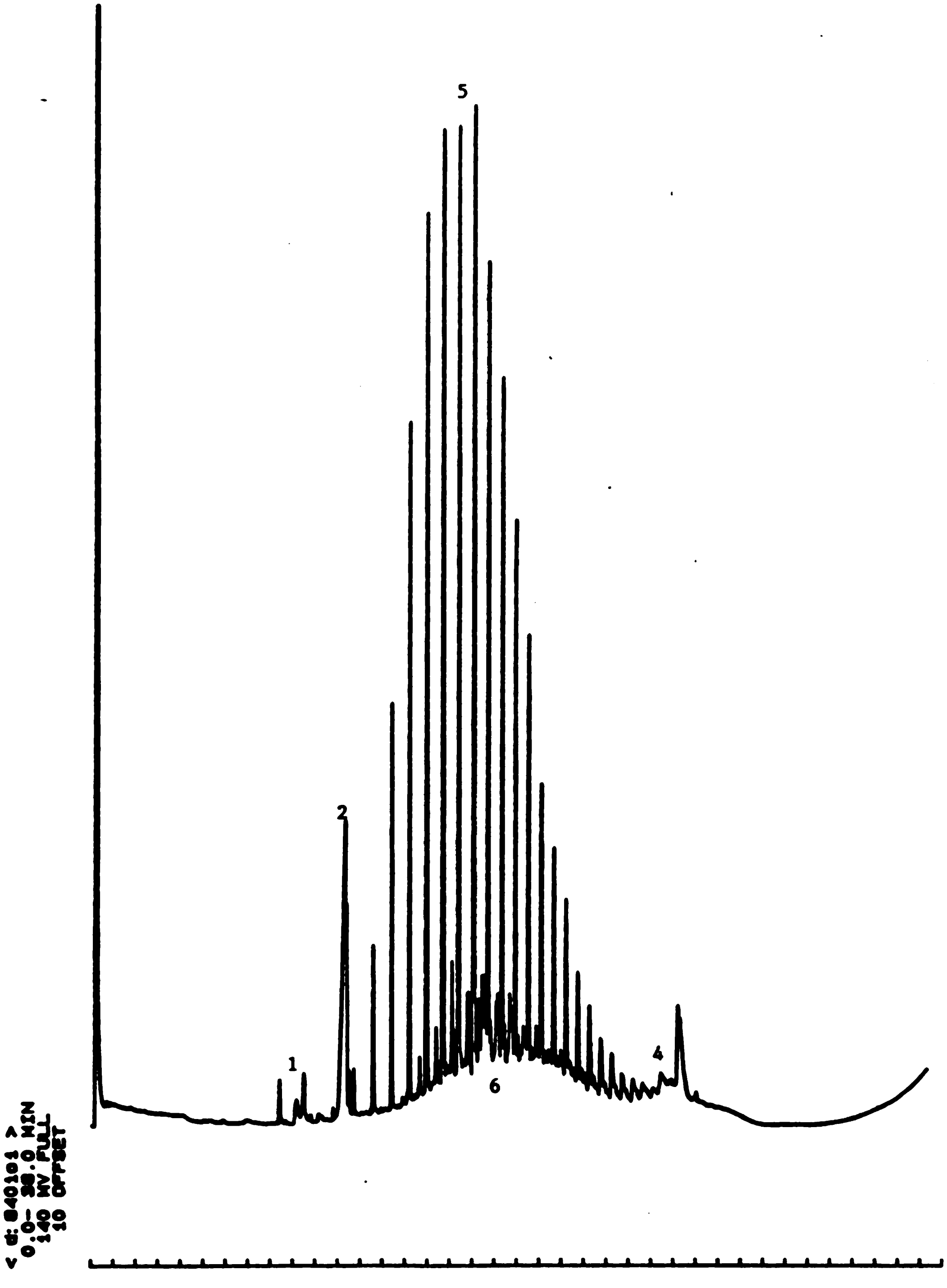

Figure 45: Chromatogram of Atlas Apex 840 Prepared with Iso-Octane.

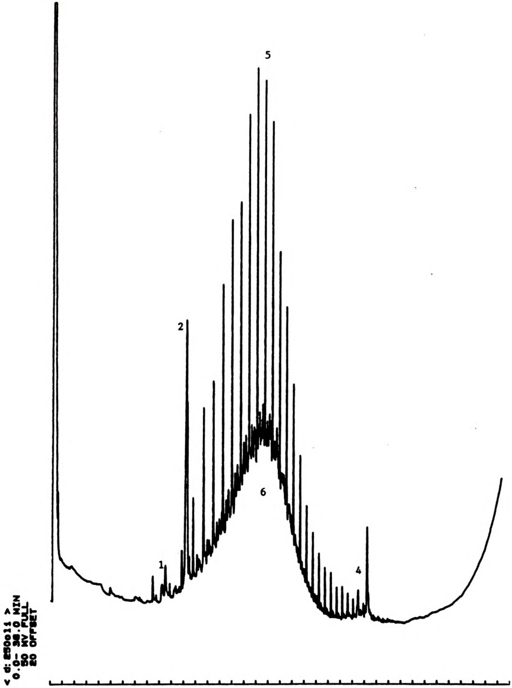

Figure 46: Chromatogram of Atlas Apex Blasting Agent 240 (old) Prepared with Iso-Octane.

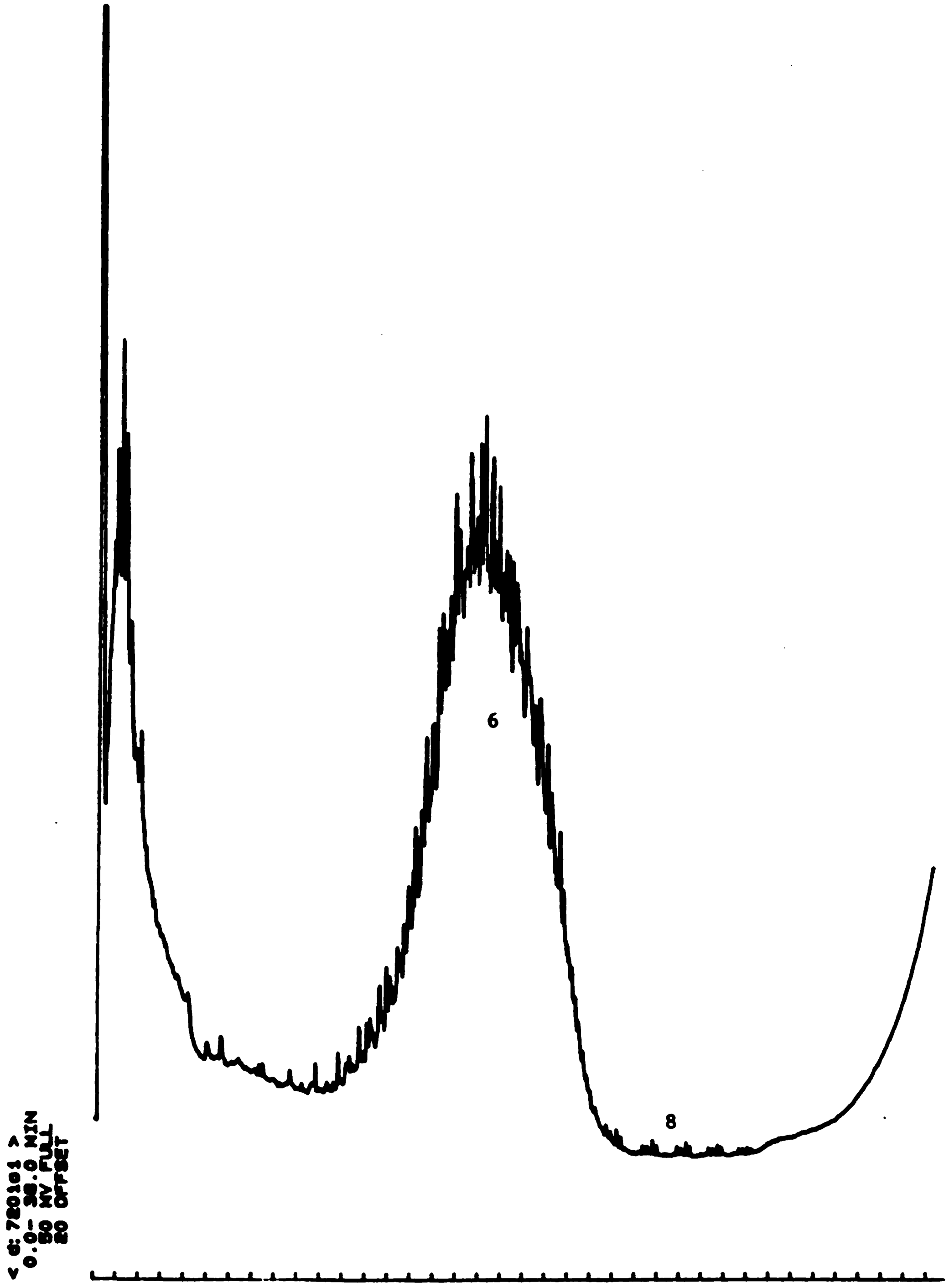

Figure 47: Chromatogram of Austin Emulex 720 Prepared with Iso-Octane.

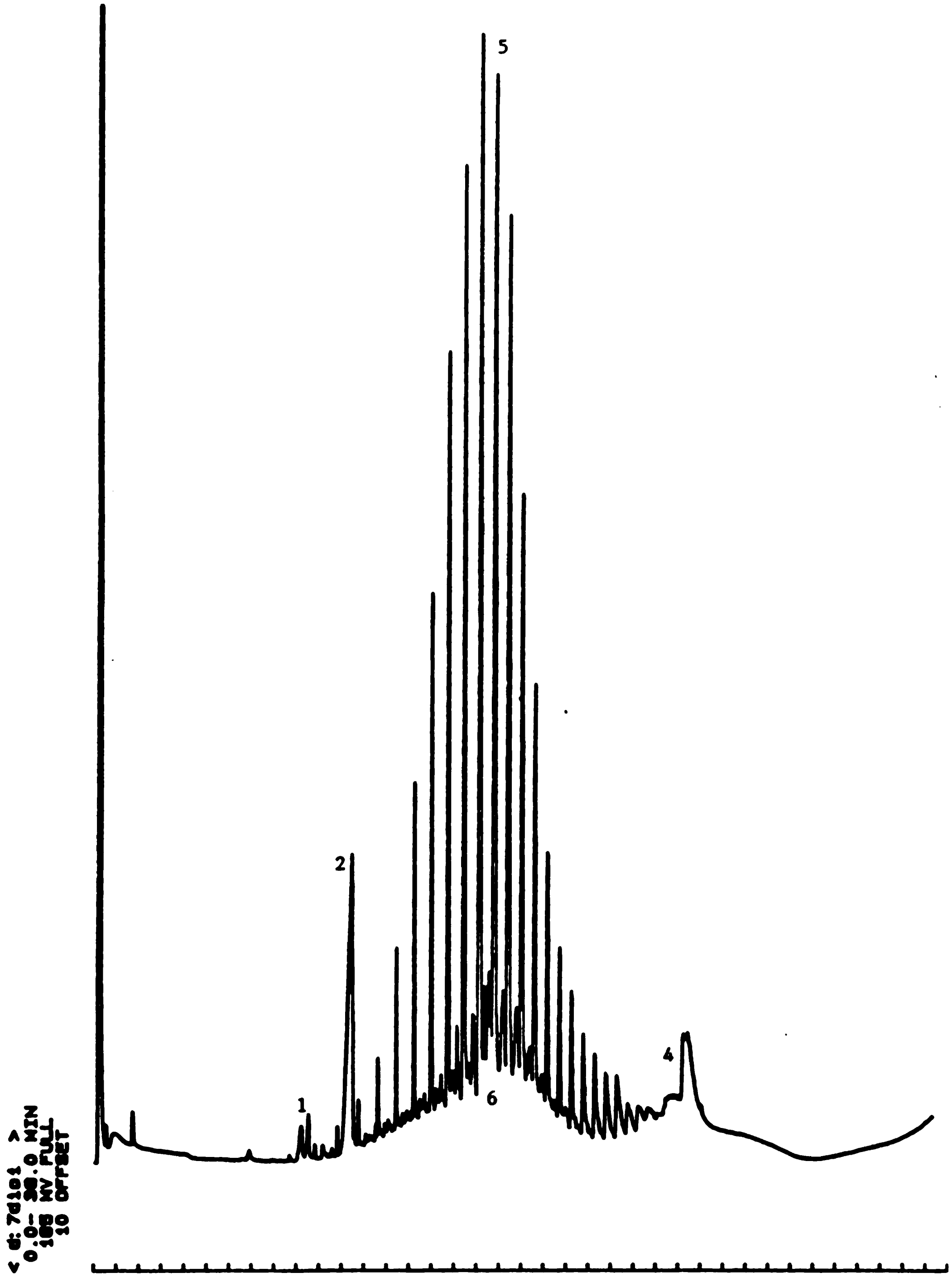

Figure 48: Chromatogram of Atlas 7D Prepared with Iso-Octane.

Results of Post Blast Analysis.

Table 14. Soil, Control, and Post blast sample amounts prepared with TCE and Hexane.

Sample	**Weight**	**Solvent**
Atlas Powermax 440 control	5.21 g	TCE
Atlas Powermax 440 post-blast	3.15 g	TCE
Atlas Powermax 440 post-blast	40.75 g	TCE
Atlas Powermax 440 post-blast	42.35 g	Hexane

Figure 49 represents a sample from the mixture of soil and intact Atlas Powermax 440 extract. Ranging from 8-22 minutes is a series of homologous peaks, with an unrelsolved area beneath.

Figure 50 represents a sample of the post-blast sample control soil. Ranging from 14.5-20 minutes is a series of small consecutive peaks.

Figure 51 represents a sample of the Atlas Powermax 440 post-blast, in which 3.15 grams of sample was extracted. Ranging from 14.5-20 minutes is a series of small consecutive peaks.

Figure 52 represents a sample of Atlas Powermax 440 post blast, in which 40.75 grams of sample were extracted. Ranging from 10.5-26 minutes is a series of consecutive peaks, with an

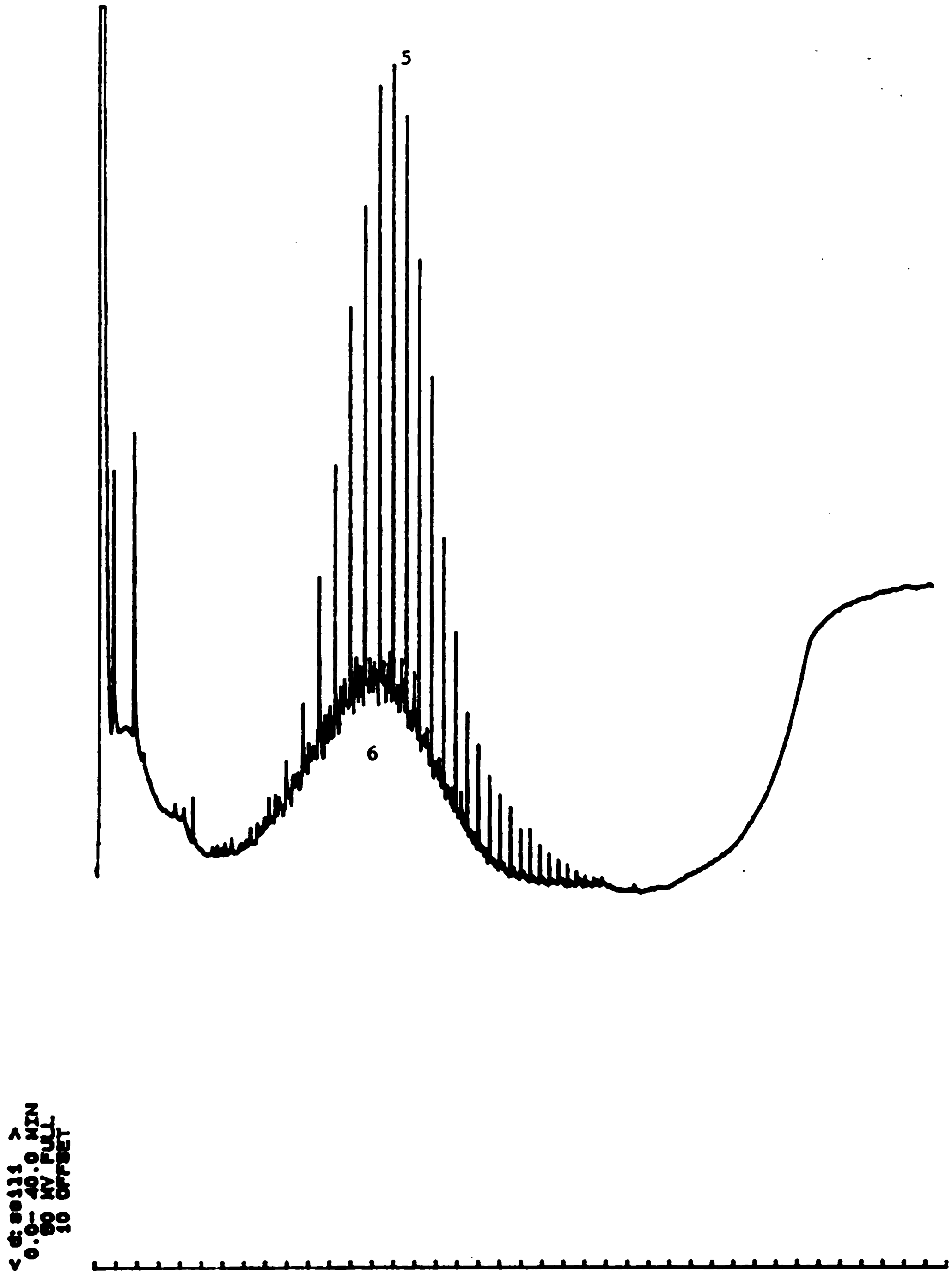

Figure 49: Chromatogram of Soil & Intact Atlas Powermax 440 Mixture Prepared with TCE.

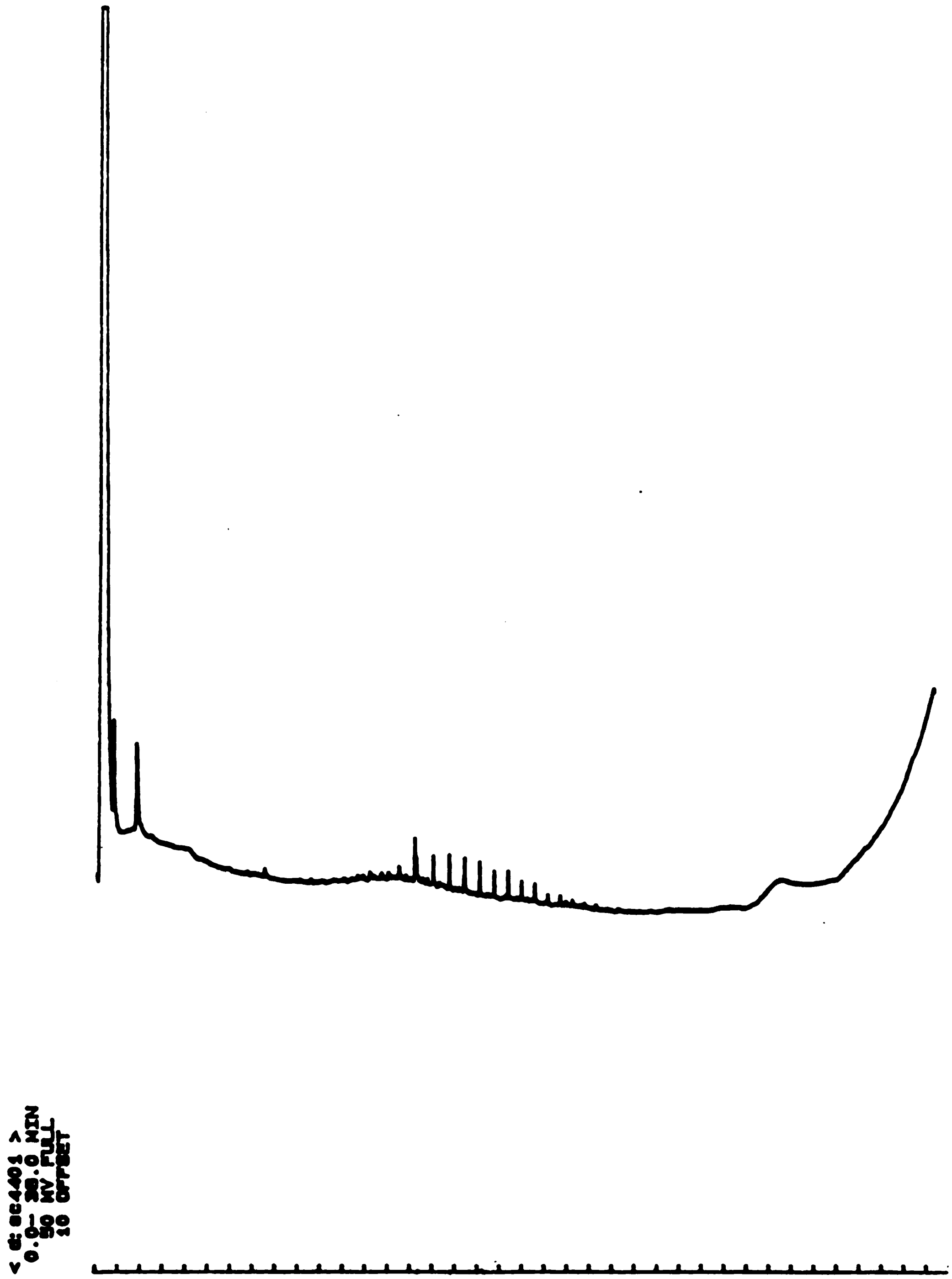

Figure 50: Chromatogram of Sample Control Soil Prepared with TCE.

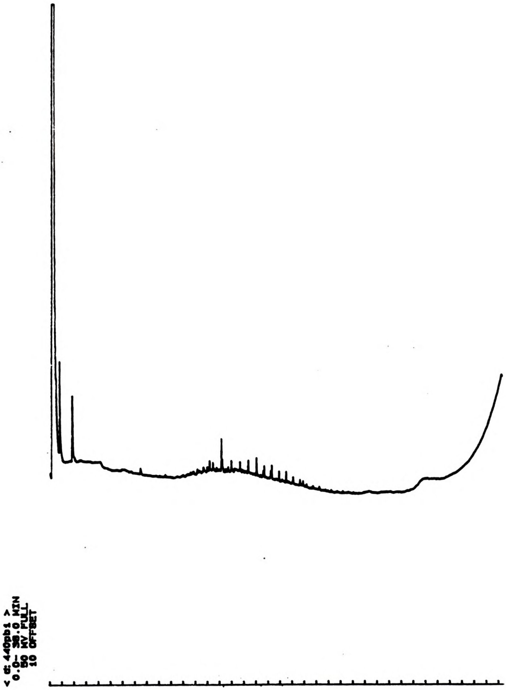

Figure 51: Chromatogram of Soil & Atlas Powermax 440 Post Blast Mixture Prepared with TCE (Trial 1).

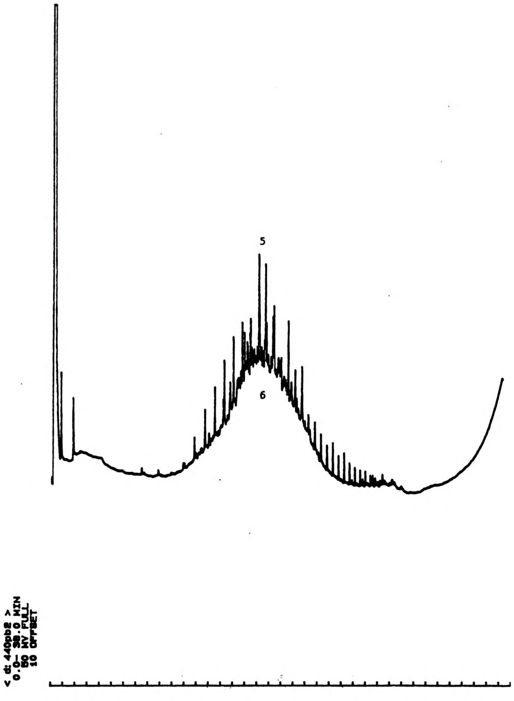

Figure 52: Chromatogram of Soil & Atlas Powermax 440 Post Blast Mixture Prepared with TCE (Trial 2).

unresolved area beneath.

Figure 53 represents a sample of Trichloroethylene after being filtered through the Supelco column. A small peak at 14.5 minutes is observed.

Figure 54 represents a sample of Atlas Powermax 440 post-blast prepared with hexane. Ranging from 11.5-26 minutes is a series of consecutive peaks with a large unresolved area beneath this series.

Figure 55 represents a sample of the individual component X-5, and a sample of Atlas Powermax 440 that have been overlaid on the same chromatogram.

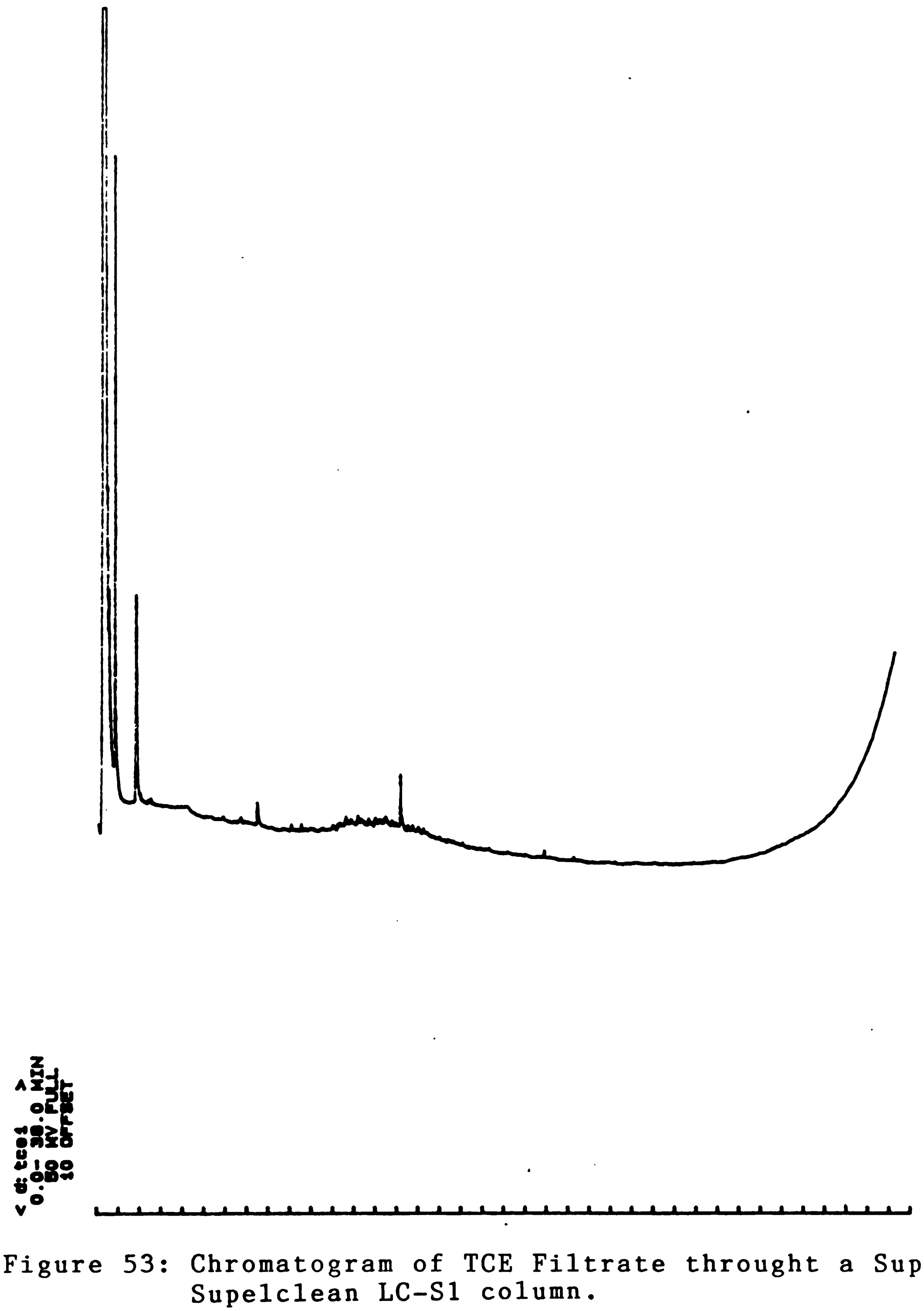

Figure 53: Chromatogram of TCE Filtrate throught a Supelco Supelclean LC-S1 column.

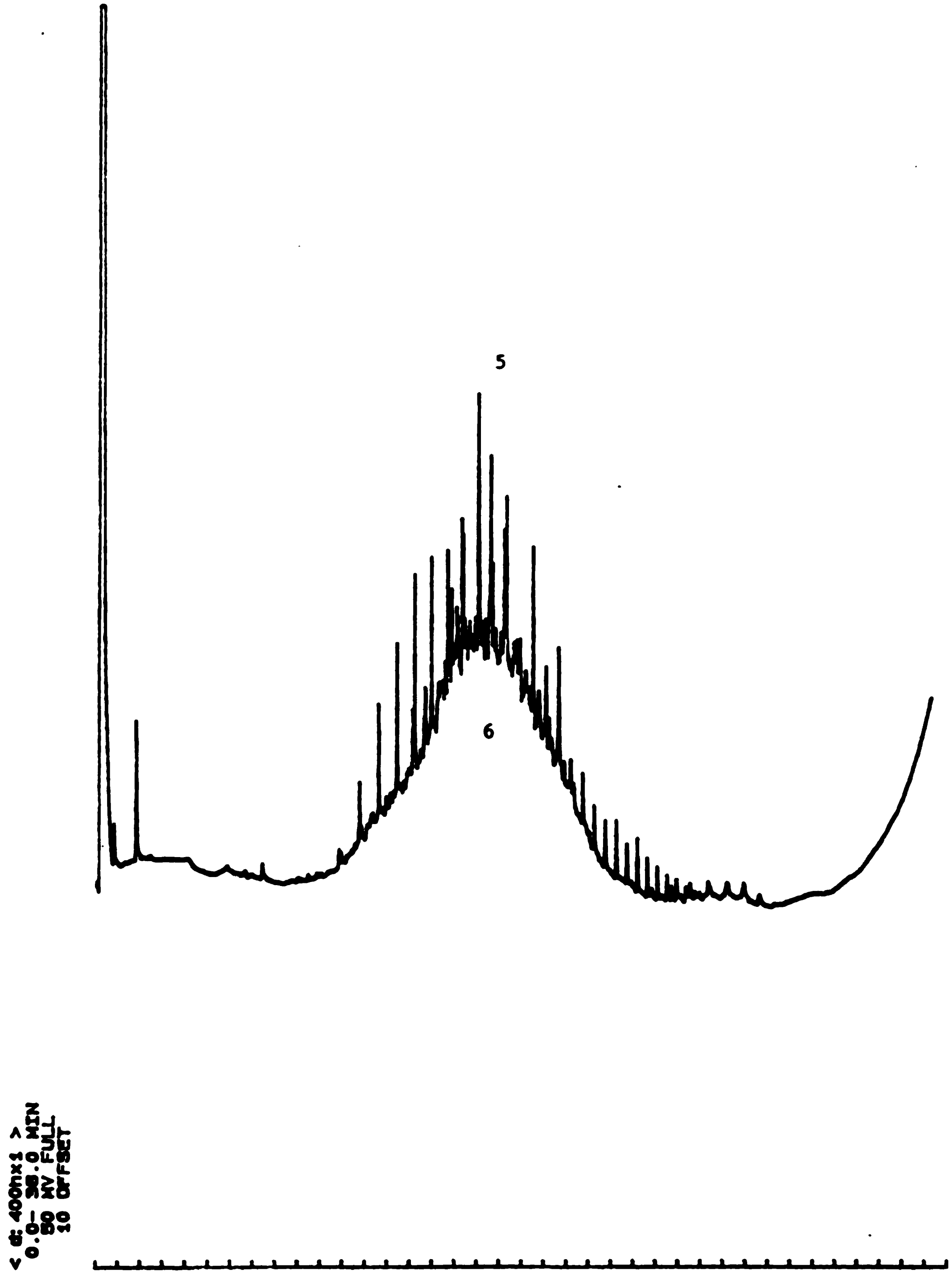

Figure 54: Chromatogram of Soil & Atlas Powermax 440 Post Blast Mixture Prepared with Hexane.

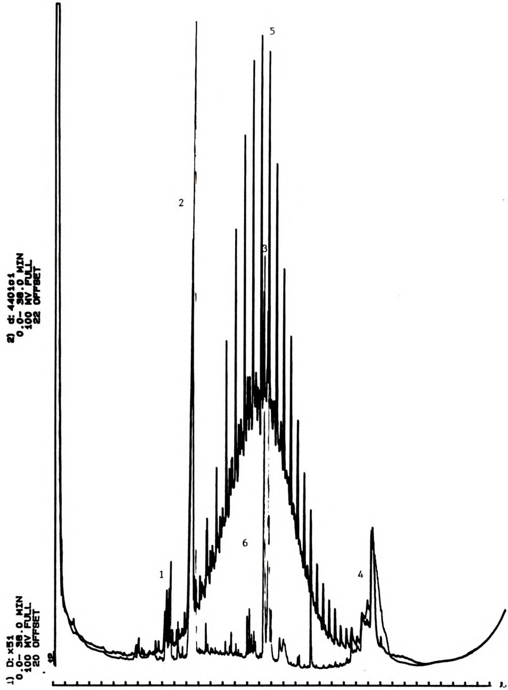

Figure 55: Overlay Chromatogram of Individual Component X-5 and Atlas Powermax 440.

DISCUSSION

Discussion of Results from Analysis of Individual Components.

Essentially, through gas chromatographic analysis of emulsion explosives, organic components within the emulsions will be revealed. The organic materials that are of concern within emulsion are waxes, oils, and emulsifiers.

Analysis of individual components, that were supplied by Atlas, on the Gas Chromatograph supplies the standards for what will be expected when intact and post-blast emulsion samples are analyzed.

Figure 2: Individual component #1.

This component contains the oils that are present in the fuel phase of the cap sensitive Powermax fromulations.

Within this chromatogram appears an unsymmetrical and unresolved peak between 1 and 5 minutes. This peak most likely represents the carbonaceous fuel such as a No. 1 or No. 2 fuel oil. Because fuel oil ranges from C8-C24 it is a more volatile oil than that of a vegetable or mineral oil. Therefore, the larger unsymmetrical and unresolved peak between 7 and 26 minutes would represent the vegetable or mineral oil that is less volatile.

Figure 3: Individual component #2.

This component contains the wax and oil combination used in fuel phase of Atlas' paper packaged product.

Within this chromatogram is a series of homologous peaks that ranges from 7-23 minutes. Since it is known that this sample represents a wax/oil combination, and that the oils that are present in the fuel do not generate a series of homologous peaks, then in conclusion, the homologous peaks must represent the wax itself. As for the small unresolved area beneath the peaks this must represent the oils present where it is partially dominated by the wax.

Figure 4: Individual component X-5.

This component contains the emulsifier combination that goes with individual component #2.

This chromatogram is representative of the emulsifier combination as mentioned above, where Points 1, 2, 3, and 4 are points of interest that will be seen in later figures of intact emulsion samples.

Figure 5: Individual component #3.

This component contains #2 and X-5 in the approximate proportions in which they are used.

Within this chromatogram Points 1, 2, 3, and 4 are observable, although Point 1 is small. However, these points do indicate the presence of the emulsifier combination of X-5.

Points 5 and 6 represent the presence of the wax and oil respectively.

Figure 6: Individual component TN0115.

This component contains the emulsifier used with individual component #1.

The chromatogram represented within this figure shows groupings of peaks with either 4 or 5 peaks per group. Similar smaller groupings will be seen in later figures and will be labelled as Point 8.

Figure 7: Individual component TN0146.

This component contains the mixture of TN0115 and #1.

The small unsymmetrical and unresolved peak from 1 to 5 minutes most likely represents the carbonaceous fuel found in component #1, whereas the larger unsymmetrical and unresolved peak most likely represents a vegetable or mineral oil found in individual component #1.

Near the end of the chromatogram, starting approximately at 23 minutes can be seen 3 groupings of peaks with 4 peaks per group, labelled as Point 8. Point 8 represents the individual component TN0115; the emulsifier.

Discussion of Results from Analysis of Atlas Powermax 140

The Atlas Powermax 140 formulations prepared with Trichloroethylene and analyzed on the GC show all of the same characteristics; those being the series of homologous peaks caused by a paraffinic wax, peaks that are characteristic of an emulsifier, and some small undefined areas beneath the peaks that indicate an oil is present.

These chromatograms are consistent with the chromatograms of the individual components that show the oils, waxes, and emulsifiers. Points 1, 2, 3, & 4 show peaks that are characteristic of the individual component X-5 of the emulsifier, which can be seen in Figure 4. Point 5 is characteristic of the waxes found in individual component #2, seen in Figure 3.

The sample of Atlas Powermax 140 in Figure 8 shows a peak that appears at 17.5 minutes, labelled Point 7. This peak is not consistent with the other samples of Atlas Powermax 140 prepared with TCE. It is believed that this peak is a contaminant arising during preparation of the sample. In Figures 8 & 13 the Points 1, 2, 3, & 4 characterize the emulsifier while Points 5 & 6 represent the wax and oil combinations repectively. Figures 17 & 21 also show Points 1, 2, & 4 that represent the emulsifier, and Points 5 & 6 represent the wax and oil respectively.

The 140 sample prepared with Methylene Chloride, in Figure 24, has few distinctive points compared to the other

Powermax 140 samples. What is comparable are points 5 & 6, which represent the waxes and oils respectively, and Point 3 representing the emulsifier X-5. Due to the injector port failing to reach 430°C ballistically, the chromatogram loses resolution and begins to trail off around 16 minutes.

Figure 28 represents a sample of Powermax 140 prepared with Hexane. Points 1,2 & 4 are present and indicate that an emulsifier is present, and again the wax/oil combination can be seen in points 5 & 6. Once again there is a peak, labelled Point 7, arising at 17.5 minutes that most likely represents a contaminant through preparation of the sample.

Another Powermax 140 sample prepared with Hexane is illustrated in Figure 32. As expected, the emulsifier can be distinguished from the wax/oil combination by Points 1, 2, & 4, and 5 & 6 respectively.

Figure 43 illustrates a sample of Powermax 140 prepared with iso-octane, in which the emulsifier is easily identified by points 1, 2 & 4, as is the wax/oil combination identified by points 5 & 6 respectively.

Discussion of Results from Analysis of Atlas Powermax 440

Figure 9 illustrates a sample of Atlas Powermax 440 that was prepared with TCE. The emulsifier, X-5, is identified by four specific points within this chromatogram; points 1, 2, 3 & 4. Points 5 & 6 easily distinguish the wax/oil combination with Point 6 being more pronounced, indicating a higher oil content than that seen in the Powermax 140 samples.

Another Powermax 440 sample, shown in Figure 14 and prepared with TCE, distinctively shows Points 2, 3, & 4 representing the emulsifier. Due to the changing of the millivolt scale during the GC run, Point 1 is not distinguishable. The wax/oil combination is again characterized by Points 5 & 6.

Figures 18 & 22 distinctively show the emulsifier by Points 1, 2, 3 & 4, although Point 3 is not seen in Figure 18. The wax/oil combination is also very distinctive in each chromatogram as seen by Points 5 & 6.

Figure 25 represents the Powermax 440 sample prepared with Methylene chloride. At this point, the injector temperature was not being achieved, causing the poor resolution towards the end of the chromatogram. However, it is still possible to observe the emulsifier, but only by Point 3. Points 5 & 6 characterize the wax/oil combination once again.

The remaining samples of Atlas Powermax 440 illustrated in Figures 29, 33, and 44, prepared with hexane for the first two and iso-octane for the latter, all show the typical points as compared to the previous Powermax 440 samples. Although Point 3 is virtually non-existent in Figure 29, the emulsifier is still detectable as well as the wax/oil combination. Again, Point 3 is only slightly observable in Figure 33. However, the emulsifier and wax/oil combination are

distinguishable from one another. Figure 44 unmistakeably distinguishes the emulsifier from the wax/oil combination, with point 3 being observable as further characterization of the emulsifier.

Discussion of Results from Analysis of Atlas Apex 840

Atlas Apex 840 samples prepared with the variety of solvents produced similar results throughout the GC analysis. As illustrated in Figures 10, 16, 20, 26, 30, 34, & 45 Atlas Apex 840 is characterized by its identifiable emulsifier and wax/oil combination. The only difference is observed in Figure 10 where a peak, Point 7, appears at approximately 17.5 minutes. Due to the fact that this peak does not appear in other chromatograms of the Apex 840 product or in chromatograms of the individual components themselves, it is concluded that this peak has arisen from contamination during preparation. Figure 26 has lost resolution near 15 minutes due to the injector port failing to heat to 450°C ballistically. The points that characterize the emulsifier are visable throughout the chromatograms; Points 1, 2, 3, & 4, as are the points that characterize the wax/oil combinations; Points 5 & 6. These samples are similar to the samples of Atlas Powermax 140, and both are almost identical to the chromatogram of individual component #3, which illustrates the combination of indivdual components #2 and X-5; a wax/oil combination and emulsifier combination respectively.

Discussion of Results from Analysis of Atlas Apex Blasting Agent 240 (old)

Atlas Apex Blasting Agent 240 (old) was analyzed fewer times than most of the other emulsion samples since it was determined that this sample would less likely be found at criminal bomb scenes, due to the fact that it is not cap sensitive.

Figures 11, 35, & 46 illustrate the old 240 samples. These illustrations are almost identical where the emulsifying package can easily be identified through Points 1, 2, 3, & 4. However, Point 4 is only observable in Figure 11. In Figure 11 there can also be seen a peak, Point 7, which appears at approximately 17.5 minutes. Again, this peak is not present in other Apex 240 samples or individual component samples, and therefore is most likely the result of contamination during preparation.

The wax/oil combinations are characterized by Points 5 & 6, and as can be seen, Point 6 has a substantial heighth, indicating that this emulsion sample has considerably more oil in its composition than do the Powermax 140 or Apex 840 samples.

Discussion of Results from Analysis of Austin Emulex 720

Austin Emulex 720 is a substantially different emulsion, as composition is concerned, compared to that of the Atlas products. Figures 12, 15, 19, 23, 27, 31, 36, & 47 illustrate this fact.

Essentially the Austin product is a composition of oil and emulsifier. A wax/oil combination is not indicated here due to the absence of homologous peaks that dominate other emulsion samples. Although this is an Austin sample rather that an Atlas sample it is still similar to the combination of individual components used by Atlas. From the addition of indivdual components #1 and TN0115; an oil(s) and emulsifier respectively, the result is seen in Figure 7 (TN0146), which is almost identical to all of the Austin samples analyzed. However it is likely that a different oil combination may have been used in the Austin sample, but the chromatograms indicate that the same or similar emlulsifier was used. Austin Emulex 720 is characterized by Points 6, 8, & 9.

Figure 15 shows a sudden change in plotting at 7 minutes due to a change in the millivolt scale at that time.

Figure 27 lacks any resolution after approximately 15 minutes due to the injector port reaching 450°C at the beginning of the GC program.

Figure 31 contains a random peak, Point 7, that appears at approximately 21 minutes. Being that this peak is random and not found in the other Emulex 720 samples it must have arisen through contamination of the sample during preparation.

Discussion of Results from Analysis of Atlas Apex Blasting Agent 240 (new)

Three separate samples of Atlas Apex BA 240 (new) were taken from a different location on the stick of packaged emulsion.

These samples are illustrated in Figures 37, 38, & 39. They are characterized by Points 6, 7, 8, & 9 as is the chromatograms of Atlas Apex BA 240 (old) sample. These samples do not have the homologous peaks that indicate a wax is present. These chromatograms only indicate that an oil(s) and emulsifier are present. It seems as though this newer sample of Apex 240 has a slightly lesser amount of oil within its composition as compared to the older sample of Apex 240.

Figures 37 and 38 have a distinctive peak, Point 7, arising at 21 minutes which has been assumed to be a product of contamination due to the fact that similar peaks have appeared randomly throughout analysis of all the different samples.

Discussion of Results from Analysis of Atlas 7D

Three separate samples of Atlas 7D were prepared with Hexane, and one sample with iso-octane. The three separate samples prepared with Hexane were taken from different locations on the packaged emulsion stick to determine if any differences in analysis would occur. Figures 40, 41, 42, & 48 illustrate the results of the GC analysis. Atlas 7D can be characterized as an emulsion with a wax/oil combination and emulsifier combination due to Points 5 & 6 and 1, 2, & 4 respectively.

This emulsion is very similar to Atlas Powermax 140 and Atlas Powermax 840 where neither of the three types of emulsions appear to have a significant oil composition as they do a wax composition.

Figures 40, 41, & 42 have a peak, Point 7, that appears approximately at 21 minutes, and although they appear more times than not, it is still regarded as a product of contamination due to the lack of a similar peak appearing in any individual component samples.

Discussion of Results from Analysis of Post Blast Samples

Figure 49 illustrates a sample of Atlas Powermax 440 that was manually added to a sample of soil, and tested after filtration. Most prominent on the chromatogram is the appearance of the homologous peaks, Point 5, that indicate a wax is present. In addition, is the unresolved peak indicated by point 6 that suggests an oil(s) is present. There is no indication that an emulsifier is present because it was removed during filtration throught the Supelco column.

Figure 50 shows a small series of homologous peaks. Since this chromatogram illustrates only a soil sample used as a control it is diffucult to determine what is causing the peaks other than the possibility of something extracted from the Supelco Supelclean column.

Figure 51 illustrates the GC analysis of a small sample of 440 post-blast; only 3.15 g of post-blast soil was extracted. Seeing that the results only yielded a small series of homologous peaks, much like that of the control sample, another sample was extracted using 40.75 g of post-blast soil. Figure 52 illustrates this larger post-blast sample used in which the series of homologous peaks is more pronounced, as is the unresolved peak marked by point 4. This indicates that a wax/oil combination is most likely present. But again, there is no indication that an emulsifier is present, since it was again removed during filtration through the Supelco column.

Figure 53 illustrates a sample of TCE only that was filtered through a Supelco Supelclean column to detect if any contaminants were originating from the column itself.

Figure 54 illustrates the same Atlas Powermax 440 post-blast sample that was prepared with TCE, that was again extracted, but with Hexane. Points 5 & 6 respectively mark the indicators of a wax and oil combination within the emulsion. The emulsifiers were removed during filtration through the Supelco column.

Discussion of Basic Methodology, Including Solvents.

The resulting chromatograms do not reveal that any one solvent has extracted the emulsion samples better than the other. In my opinion, any of the solvents used within this thesis will adequately extract the samples, however, the solvents should not be relied upon to perform all the work in breaking up the emulsion. To extract as much of the emulsion as possible, a homogenizer will perform an excellent job. Filtration through a Whatman Autovial will remove all solid materials leaving an extract which can then be evaporated (concentrated) down to approximately 2ml. This extract is then ready for injection into the gas chromatograph.

CONCLUSION

The purpose of this thesis experiment was to obtain gas chromatographic analyses of individual components in emulsion explosives, of intact emulsion explosives, and of post blast emulsion residues. The resulting chromatograms provided the necessary information to determine if different intact

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CONCLUSION

The purpose of this thesis experiment was to obtain gas chromatographic analyses of individual components in emulsion explosives, of intact emulsion explosives, and of post blast emulsion residues. The resulting chromatograms provided the necessary information to determine if different intact emulsion samples can be distinguished from each other, if post blast emulsion samples can be identified as emulsions and to one particular intact emulsion sample.

Chromatograms of intact samples can be used to characterize each sample as an emulsion since the characteristics of the individual components are revealed within the chromatograms. However, the chromatograms cannot be used to distinguish between one manufacturer or brand of a particular emulsion since the components of many emulsions are similar. In certain instances the chromatograms reveal results that indicate two samples cannot be from the same source, where other chromatograms of two different samples may not be indistinguishable. In this regard, it can be said that GC analysis can only be used as a screening test when individualizing emulsions to a specific brand. However, in my opinion, GC analysis can be used as a confirmatory test when identifying an explosive as an emulsion, but not to individualize the emulsion to a particular manufacturer or brand.

GC analysis of post blast emulsion residues detected the wax and oil combination used within the intact emulsion sample, however the emulsifiers were not detected since they were removed during separation in a Supelco column. The experimentation completed within this thesis showed that post blast emulsion residues were detected by GC when residues were extracted from a large amount (40-50 grams) of soil. Residues extracted from a smaller amount (3-5 grams) of soil were not detected such that they were clearly defined. Consequently, post blast residues may not always be detected through GC analysis, depending upon the amount of sample available.

Accordingly, from the results, GC analysis is an excellent tool for identifying an intact explosive sample as an emulsion. Through the use of other analytical techniques, such as ion chromatography (IC), spot tests, flame tests, and SEM/EDX in conjunction with gas chromatography, more precise data can be obtained to make conclusive identifications of post blast samples. However, it will always be difficult, if not impossible, to individualize intact samples and especially post blast samples to a particular manufacturer.

For forensic scientists and criminal investigators, identification of the explosive will prove to be satisfactory in most instances. Individualizing the explosive to a

particular manufacturer or brand becomes unnecessary in light of other evidence that can corroborate a suspects connection with a certain case. Galvanized pipes, intact explosive residues, packaging that contained explosives, separate ingredients used to make explosives, tape, wire, blasting caps, timing devices, etc., are all items that can be used as corroborative evidence.

In conclusion, the research presented here provides a basic methodology for analyzing emulsions using a gas chromatograph, and data that provided evidence that explosives can be identified as emulsions by their component characteristics. Future considerations for research on emulsions should include analysis by gas chromatography coupled with mass spectrometry (GC-MS). This analytical analysis should provide results that can be used to confirm the presence of an emulsion explosive from post blast samples. However, GC-MS will not be able to provide individualizable results as to who the manufacturer might be. Therefore, it would be extremely helpful for forensic chemists if manufacturers would agree to produce emulsions with an identifier. For example, taggets are placed within smokeless powder which allows identification of the manufacturer. If this method could be repeated for emulsions, the forensic science community could greatly benefit in its cases involving emulsions. Until then, relying upon GC and previously mentioned analytical techniques will prove to produce results

that will be accurate, reliable, and upheld in a court of law.

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