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ENVIRONMENTAL AND SAFETY ASPECTS OF THE USE OF SULFUR IN HIGHWAY PAVEMENTS

Volume 1 - Evaluation of Environmental and Safety Hazards

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16. Abstract

The use of sulfur in highway paving mixtures has introduced questions regarding the pollutants generated, their environmental impact and the safety aspects associated with mix preparation and placement. This report presents the results of an investigation in which these factors are assessed.

The study considered the safety and environmental aspects of storage and handling, formulation, construction, operation and maintenance of highway pavements containing sulfur. These considerations included possible evolution of toxic and abnoxious fumes, dust and runoffs. Results of tests simulating in-service conditions such as traffic wear, skidding, freeze thaw, spills and fires are also discussed. The effects of these pollutants on humans, soils, highway structural materials, ground waters and vegetation is presented. Along with the laboratory study a detailed work plan which discusses methods and equipment for monitoring potential emissions and pollutants and recommended safety practices was generated. An annotated bibliography dealing with the safety and environmental effects on sulfur-modified paving materials was also prepared.

The final report was prepared in three volumes: Volume I - Evaluation of Environmental and Safety Hazards; Volume II - Field Evaluation Plan and Volume III - Annotated Bibliography.

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TABLE OF CONTENTS

Page

LIST OF TABLES

Table

Page

Figure

1 INTRODUCTION

1.1 Background

1.1.1 Sulfur - Asphalt Paving Mixtures.

Since 1973, the Texas Transportation Institute (TTI) has been actively engaged in a number of studies related to the use of sulfur in asphaltic pavement mixtures. Sulfur is unique in that it is one of the few materials which is expected to be in ample supply in the future. The primary reason for this potential over-supply is attributed to pollution abatement controls targeted at power plant stack gas emissions and the expected growth of recovered (secondary) sulfur supplies following commercialization of processes for synthetic natural gas, coal liquification, shale oil and other alternative energy sources. The present inventory of pollution abatement sulfur is increasing at a rate of about 4 million tons per year and it is predicted that by the latter part of this decade the supply will begin to exceed the demand. For this reason a considerable amount of research and development has been initiated to find uses for sulfur. One of the most promising areas being studied is in asphaltic pavement mixtures.

Depending on the manner in which it is introduced into the mix, sulfur can be used as a structuring agent (i.e. playing the role of an aggregate) in upgrading poorly graded sands or as an integral part of the binder in the form of sulfur-asphalt dispersions.

The first concept was pioneered by Shell Canada Ltd. [1-4] and resulted in a patented sand-asphalt sulfur (S-A-S) mix called Thermopave [5]. In S-A-S mixtures molten sulfur is added to asphalt at a sulfur/asphalt weight ratio, S/A, of 2 to 1. Sulfur fills the interstitial voids around the aggregate particles which, upon cooling, creates a mechanical interlock from which the material derives its strength. Developed primarily for use in areas where quality aggregates are scarce, S-A-S mixes prepared using locally available dune sands and beach sands have been shown to have performance characteristics equal to and in some cases superior to quality asphaltic concrete mixtures.

The Texas Transportation Institute (TTI) under the sponsorship of The Bureau of Mines and The Sulphur Institute [6] are currently extending the technology developed in Canada for application in the United States. This project started in 1973 and resulted in the successful placement of the first major domestic field test of Thermopave. The test section was a two-lane, 3000 ft (914 m) long, variable thickness pavement built on U. S. 77, south of Corpus Christi, Texas during April, 1977 [7]. This pavement is now in the third year of a post-construction evaluation. TTI participated in another Thermopave trial in Sulfur, Louisiana which took place during January 1977. This test section was 2000 ft. (610 m) in length and 24 ft (7.3 m) wide.

Considerable uncertainty about the future availability and cost of asphalt cement has been generated by the current energy squeeze and pricing as established by foreign suppliers. This has initiated considerable research activity in the United States [8, 9, 10], Europe [11] and Canada [12] directed to the partial or total replacement of the asphalt as the binder in asphaltic concrete. To this end, processes using sulfur as a substitute for up to 50 percent of the asphalt in asphaltic concrete mixtures are making inroads in the United States. These processes have been both developed and demonstrated independently by Societe' Nationale des Petroles d'Aquitaine (SNPA)* in France [11] and Gulf Oil Canada [12] using sulfur-asphalt "preblending" techniques and equipment which are proprietary to each. TTI, under the sponsorship of SNPA and The Sulphur Institute, conducted a series of

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*Currently Societe Nationale Elf d'Aquitaine (SNEA) verification studies using the SNPA process which culminated in a 3,650 ft. (1113 m) long, two-lane test section on U. S. 69 near Lufkin, Texas [13]. The test binder was a sulfur-asphalt blend in which 30 percent of the weight of the binder (i.e., 15 volume percent) consisted of sulfur. Gulf Canada has reported the placement of pavement mixtures with 50 weight percent sulfur in the binder [12].

In a cooperative effort with the Bureau of Mines' Metallurgy Research Laboratory in Boulder City, Nevada, TTI has been investigating paving mixtures which are prepared using "direct" mixing of the sulfur and asphalt [10]. This method would eliminate the need for specialized high shear-rate colloid mills or emulsifiers as proposed by Gulf and SNPA. During January 1977, a trial section of pavement using this concept was constructed in conjunction with the Nevada Highway Department on a portion of US 95 near Boulder City, Nevada. This pavement is also under post-construction evaluation by TTI for the Bureau.

Another SEA field trial took place in Bryan, Texas [14] in 1979 in which mixes prepared by both the "preblending" process and the Bureau of Mines' "direct" mixing process were utilized. The test section consisted of two lanes, 2,700 ft. (824 m) long and located on MH 153 in Brazos County, Texas.

TTI was also being sponsored by the Federal Highway Administration to carry out an extensive investigation to utilize sulfur as an asphalt extender [9]. This program studied a wide variety of asphalt cements and aggregates to generate and optimize mix design rationale in which asphalt demand is reduced by the use of sulfur.

An additional approach for the use of sulfur in road and highway construction is in the area of recycling old bituminous pavements [10,15]. This concept was conceived and is being developed as part of the TTI-Bureau of Mines cooperative effort. Only laboratory data has been generated at this time, but plans are being formulated to construct a field demonstration sometime during 1981. One successful sulfur-recycled pavement was constructed by the Minnesota Highway Department near Minneapolis during 1979 [16]. Most of the conventional asphalt pavement recycling processes require the use of some type of softening agent to peptize the age-hardened asphalt in the old pavement [17]. Sulfur has the ability to reduce the viscosity of sulfur-asphalt dispersions below that of the virgin asphalt [11, 12] at normal mix temperatures and to increase the stiffness of the sulfur-asphalt-aggregate mixtures when it cools. This characteristic is being investigated for city and urban streets where cut-backs have a tendency to produce mixtures with low stiffnesses.

A current on-going FHWA sponsored research program at TTI is studying the use of sulfur-extended asphalt (SEA) binder in open-graded friction courses (OGC) [18]. This project will produce a mix design procedure specifically oriented to sulfur-asphalt mixes. An experimental field demonstration project to construction an SEA-OFC pavement near Nacogdoches, Texas, was completed during the summer of 1980. The project utilized a dryer drum plant for preparing the mixes.

1.1.2 Sulfur Concrete Mixes

Mixes prepared without the use of asphalt are called sulfur concretes. Studies conducted by Southwest Research Institute [19] and the Bureau of Mines [20] have shown that sulfur concretes can be made with compressive strengths equal to or superior to portland cement concrete with an added capability of reaching full strength within hours. SWRI studies were generated primarily to develop a building material whereas the Bureau of Mines activity dealt primarily with the fabrication of acid resistant holding tanks and retaining walls.

When molten sulfur, which has been mixed with aggregate, solidifies and cools it undergoes an allotropic change from monoclinic to orthorhombic form. Orthorhombic sulfur being denser and smaller in unit volume than monoclinic brings about a high degree of shrinkage which creates high internal stresses. This renders the sulfur concrete susceptible to freeze-thaw deterioration. This has been partially overcome through the use of glass fibers or pumice as an intermediate filler and plasticizers such as dicyclopentadiene (DCPD) Dipentene (DP), etc.

Field tests on sulfur concrete slabs using 5% DCPD significantly out-performed the unmodified sulfur concrete in its resistance to weathering and temperature fluctuations. The flexural strength of modified sulfur concrete range from 18-25% of the compressive strength as compared to 10-15% of the compressive strength for straight sulfur and pcc materials.

1.1.3 Sulfur and Sulfur-Asphalt Chemistry

Elemental sulfur in its pure form is a yellow, crystalline solid. The melting/freezing point of sulfur is around 240°F (116°C), subject to its previous history and on its rate of heating and cooling [21, 22]. The heat of fusion is about 21.6 Btu/lb. (12 cal/g) [22]. Above the melting point, sulfur is a thin liquid up to about 320°F (160°C), after which the viscosity abruptly increases making pumping difficult [21, 23]. Figure 1 shows the viscosity of sulfur versus temperature. Liquid sulfur is normally handled at a temperature range 270 to 300°F (132 - 149°C) [21]. Within this range, it is not corrosive to steel or aluminum unless trapped water or acid is present [21, 24, 25]. Above 320°F (160°C), toxic gases form and increase as temperature continues to rise. In general, the amount of hydrogen sulfide (H_2S) generated is higher as the hydrocarbon content of the sulfur increases. The flash point of sulfur ranges from 335 to 370°F (169 to 188°C) [21, 26, 27] compared with 340 to 600°F (171 to 316°C) of asphalt cement. The auto ignition temperature of sulfur is around 500°F (260°C) [21, 28]. Sulfur is not soluble in water, but is moderately soluble in many other liquids [29] including asphalt.

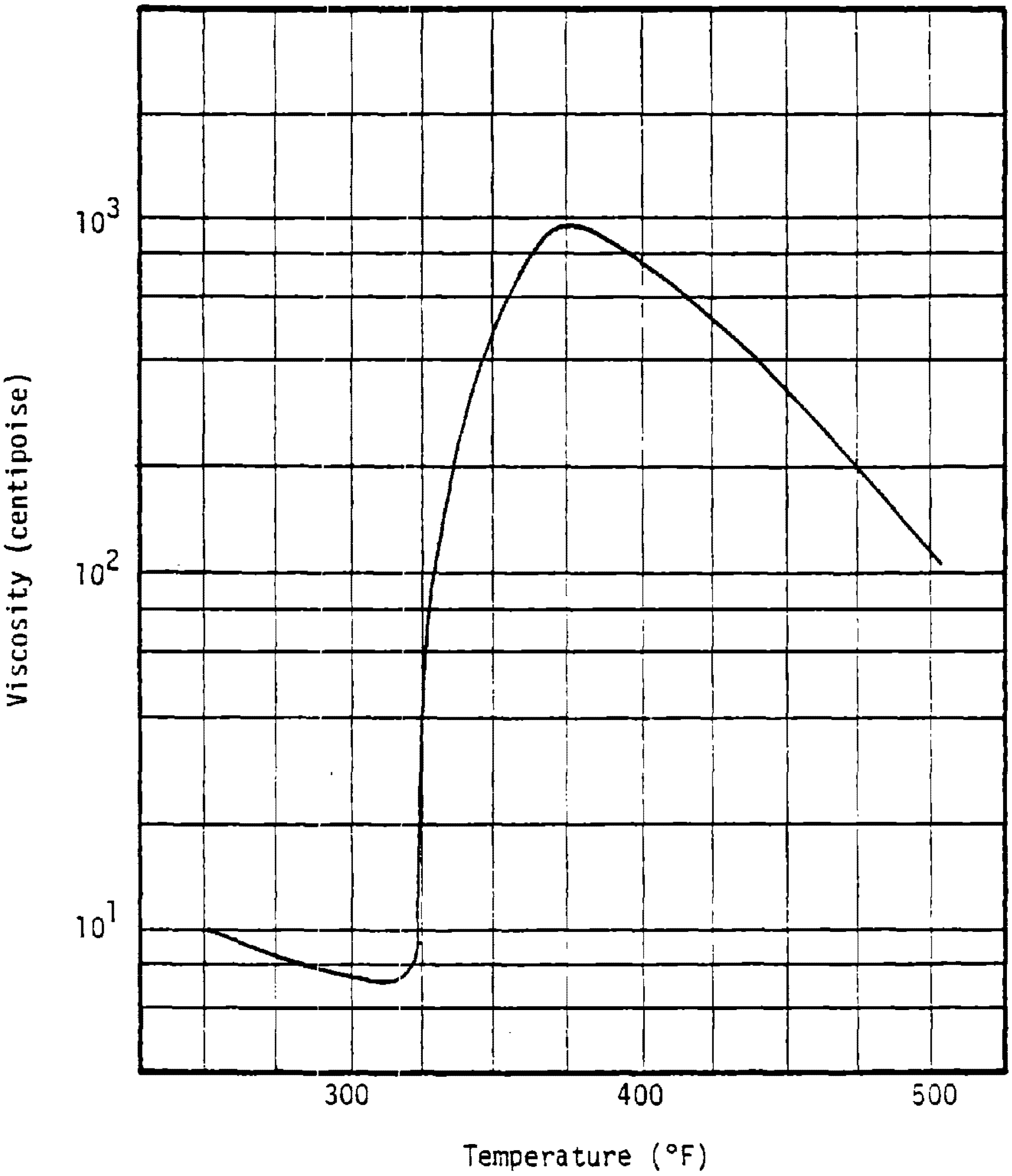


Figure 1 . Viscosity-Temperature Curve for Liquid Sulphur

°C = (°F - 32) x 5/9

The thermal conductivity of sulfur modified pavement mixes vary widely with composition. One series of tests found nearly comparable values for Sulfur-Asphalt-Sand (SAS) pavement systems and asphalt concrete of 11.7 and 15.7 x 10^{-4} cal/cm^2 - sec - °C, respectively [30].

The primary hazards due to the presence of sulfur in pavement operations and handling situations are gaseous emissions of hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) as well as airborne fumes and particulate (colloidal) sulfur. These primary hazards can usually be gauged in terms of temperature, time-duration under temperature, and dispersion factors. The relative toxicity of these pollutants will be discussed later in this report.

The sulfur-asphalt mixes are prepared using elemental sulfur and asphalt preheated to temperatures ranging from 265 to 300°F (130 - 149°C). Under these conditions the elemental sulfur can be oxidized to sulfur dioxide, which in turn can be converted to sulfur trioxide (Eqn 1).

$$(1) \qquad \tfrac{1}{8}S_8 \xrightarrow{\text{air}} SO_2 \xrightarrow{\text{air}} SO_3$$

The oxidation of sulfur dioxide to sulfur trioxide is rather slow in the absence of catalysts. In the presence of moisture these two oxides of sulfur will dissolve in any water droplets present. Sulfur dioxide, which is quite soluble in water, will be physically dissolved in the droplets with an exceedingly small part reacting with the water to form sulfurous acid (Eqn 2).

$$(2) \qquad SO_2 \xrightarrow{H_2O} SO_2 \text{ dissolved} \xrightarrow{H_2O} H_2SO_3$$

Aqueous solutions of sulfur dioxide possess acidic properties with a dissociation constant of 1.3 x 10^{-2} ascribed to the medium-strong sulfurous acid.

Sulfur trioxide will form the strong and corrosive sulfuric acid (Eqn. 3).

$$(3) \quad SO_3 \xrightarrow{H_2O} H_2SO_4$$

During the various operations carried out at elevated temperature, sulfur will be dispersed into the air in particulate form. This particulate sulfur can be deposited or be slowly oxidized.

Sulfur reacts with many organic compounds. Saturated hydrocarbons are dehydrogenated with formation of hydrogen sulfide (Eqn. 4). The, thus, generated olefins can add sulfur across the double bond forming

$$(4) \quad RCH_2\text{-}CH_2R' \longrightarrow RCH = CHR' + H_2S$$

organic sulfur derivatives, or can polymerize to hydrocarbons of higher molecular mass. Instead of olefin formation, sulfur may couple two hydrocarbon molecules (Eqn. 5) or yield an organic sulfide (Eqn. 6). Both of these reactions produce hydrogen sulfide.

$$\begin{tikzcd}[column sep=large] & & R\text{-}R + H_2S \quad (5) \\ 2RH \arrow[urr, "+1/8\ S_8"] \arrow[drr, "+n/8\ S_8"'] & & \\ & & R\text{-}(s)_{n-1}\ R + H_2S\ (n + 1,2,\ldots) \quad (6) \end{tikzcd}$$

The reactions of sulfur with organic compounds are very complex and have not yet been elucidated in detail. The organic products formed in these reactions are expected to be non-volatile at the temperatures prevalent during preparation, placement and normal use of the sulfur-asphalt mixture. Hydrogen sulfide is the most important gaseous product of these reactions. The extremely poisonous gas, hydrogen sulfide, can be detected at concentrations as low as 0.02 ppm by its revolting odor but tends to dull the sense of smell at higher concentrations and during longer exposure. It is thermally very stable. Only 75% of a sample is decomposed at 3000°F (1649°C). In air, hydrogen sulfide under normal atmospheric conditions was estimated to be approximately four days [31]. Hydrogen sulfide and sulfur dioxide can then react to form elemental sulfur (Eqn. 8) which would appear in the air as particulate matter.

(7) $$H_2S \xrightarrow{air} H_2O + SO_2$$

(8) $$2H_2S + SO_2 \longrightarrow 3/8\ S_8 + 2H_2O$$

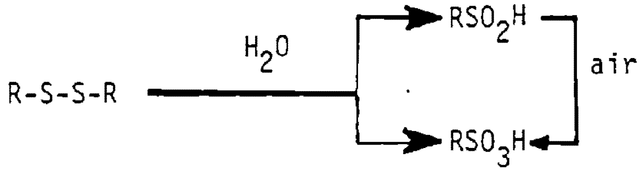
The reactions of sulfur with air or the hydrocarbons in the asphalt will produce large quantities of noxious gases at temperatures above 300°F (149°C). One can, therefore, expect to find sulfur dioxide, hydrogen sulfide and some sulfur trioxide and their reaction products with water in the air in the vicinity of locations where hot sulfur-asphalt mixes are handled, when the air is humid.

Under normal use, surface temperatures of sulfur-asphalt pavements are maintained below 300°F (149°C). Therefore, hydrogen sulfide and sulfur dioxide will very likely not be generated in amounts to exceed their Maximum Allowable Concentrations (MAC) [6, 7]. Slow oxidation of some of the sulfur will occur as described by (Eqn. 1).

An accident which causes a fire on such a pavement could locally raise the temperature of the mix high enough to generate hydrogen sulfide through reactions of sulfur with organic compounds (Eqn. 4, 5, 6). An additional part of the sulfur will burn to sulfur dioxide (Eqn. 1).

Sulfur-asphalt pavements are naturally exposed to the influence of atmospheric agents. The oxygen of the air will very slowly oxidize the sulfur to sulfur dioxide. This reaction is too slow to cause any pollution problems. It could also happen, that the organic sulfides in the mix are oxidized to sulfinic or sulfonic acids by oxygen (Eqn. 9).

(9)



$$R\text{-}S\text{-}S\text{-}R \xrightarrow{H_2O} RSO_2H \xrightarrow{air} RSO_3H$$

These acidic substances are more soluble in water than, for instance, the disulfides. They could be leached out by rain and enter surface and ground water streams. These compounds are related to snythetic surfactants, which are constituents of detergents, and should be biodegradable. Highly polar solvents such as water, deicing liquids, aqueous acids and alkalies are not expected to dissolve much more from the sulfur-asphalt pavement than from a pure asphalt mix. Depending on the strength of an alkaline solution part of the elemental sulfur can be converted to alkali polysulfides (Eqn. 10), which are soluble in an aqueous medium. In water containing dissolved oxygen these sulfides will be oxidized to sulfuric acid as the final product. Non-oxidizing acids, such as hydrochloric acid, do not dissolve sulfur. Oxidizing acids convert sulfur to sulfuric acid.

$$(10) \qquad \frac{n}{8}\ S_8 \xrightarrow[H_2O]{NaOH} Na_2S_n$$

Sulfur will not be dissolved to an appreciable extent by engine oil, grease and gasoline. The organic sulfur compounds are more likely to be extracted from the pavement by these materials. Through the mechanical action of the atmospheric agents, sulfur particles can be torn loose from the pavement and enter the run-off.

1.1.4 Pollutants Encountered in Sulfur-Asphalt Mixes

General: Throughout the development of the sulfur-asphalt concept one of the major concerns of the industry has been the potential hazards created at the construction site due to the evolution of toxic gases (H_2S and SO_2) and particulate sulfur. Over the years Shell and Gulf have monitored these pollutants both in the laboratory as well as in conjunction with their full-scale field trials. As yet, none of their data has been reported in the open literature. However, Shell [1, 4] has stated that as long as the temperature of the mix is maintained below 300°F (149°C) the concentrations of H_2S and SO_2 produced are well below the maximum allowable concentrations as suggested by the American

Conference of Governmental Industrial Hygienists (ACGIH) [32]. Similar studies at TTI and the Bureau of Mines support this claim [6, 33]. For the sake of clarification the nature of the safety problem associated with these types of contaminants will now be discussed.

RELATIVE TOXICITY OF H_2S

Hydrogen Sulfide is known for its characteristic "rotten egg" odor. Although this odor is noticeable at concentrations as low as 0.02 ppm [32], odor is not a good indicator of concentration level. Hydrogen sulfide can have a paralyzing effect on the sense of smell [34]. Therefore, high and potentially fatal concentrations of H_2S can escape recognition.

The basis used for establishing the relative toxicity of emissions data generated during this project were the relationships between H_2S concentrations and human effects as specified by ACGIH [32, 35]. These relationships are shown below:

Toxicity of Hydrogen Sulfide [35]

Concentration, ppm	Effect
0.02	Odor threshold
0.10	Eye irritation
5-10	Suggested Maximum Allowable Concentration (MAC) for prolonged exposure
70-150	Slight symptoms after exposure of several hours
170-300	Maximum Concentration which can be inhaled for 1 hour
400-700	Dangerous after exposure for 1/2 to 1 hour
600	Fatal with 1/2 hour exposure

On the basis of these effects a MAC value of 5 ppm is normally specified as the upper threshold limit for continuous exposure to H_2S emissions in areas normally expected to be occupied by construction or plant personnel.

RELATIVE TOXICITY OF SO_2

Sulfur Dioxide (SO_2) is a colorless gas with a pungent odor which, unlike H_2S, gives ample warning of its presence. The principle health hazard from SO_2 comes from inhalation of excessive quantities above its MAC. The basis for establishing the relative toxicity of emissions data generated during construction should be the relationships between SO_2 concentrations and human effects as specified by the National Institute for Occupational Safety by Health and The Manufacturing Chemists Association [36] and shown in the following table.

Toxicity of Sulfur Dioxide [36]

Concentration (ppm)	
0.3 - 1	Detected by taste
1	Injurious to plant foliage
3	Noticeable odor
5	MAC (ACGIH)
6-12	Immediate irritation of nose and throat
20	Irritation to eyes
50-100	MAC for 30-60 min. exposures
400-500	Immediately dangerous to life

The present Federal standard for SO_2 in an 8-hour time weighted average of 5 ppm (see 29CFR, 1910,93 published in the Federal Register, Volume 37, p. 22139, October 18, 1972) [37]. This is the MAC specified as the upper threshold limit concentration for SO_2 emissions in areas normally expected to be occupied by construction of plant personnel.

PARTICULATE SULFUR OCCURRENCE AND TOXICITY

Vapor given off during mixing and dumping operations contain a certain amount of undissolved and unreacted sulfur. As the vapors come in contact with air and cool, the sulfur vapor crystallizes into small particles which are carried by the wind in a manner similar to dust and fine sands. Since there is no practical way to eliminate this pollutant, its effects on both environment and personnel need to be considered.

This section will be devoted to a discussion of the relative hazards associated with sulfur dust on construction personnel as specified by the Manufacturing Chemists Association [38]. Assessments of the environmental impact of this pollutant in sulfur pavement construction do not exist.

The principal problems associated with sulfur dust lie in its contact with eyes. Sulfur is virtually nontoxic and there is no evidence that systemic poisoning results from the inhalation of sulfur dust. However, sulfur is capable of irritating the inner surfaces of the eyelids. Sulfur dust may rarely irritate the skin. This problem is minimized by the requirement that goggles be worn in areas subject to this pollutant such as at the hot mix plant and in the vicinity of the paver.

The primary hazard in handling solid sulfur results from the fact that sulfur dust suspended in air may be ignited. This problem is almost always limited to enclosures and unventilated areas. Since this is not typical of the hot mix plant or the paving area this particular hazard is not a major concern.

To minimize possible irritation, unnecessary contact with skin and eyes should be avoided. Following the work period, sulfur dust should be removed with mild soap and water. For relief of eye irritation, eyes should be thoroughly flushed with large quantities of plain water or physiological saline. Inadequate amounts of water may actually increase eye irritation.

1.1.5 TTI's Experience with Evolved Gases from Sulfur-Asphalt Mixes in the Laboratory.

Throughout all of its sulfur-asphalt-sand (SAS) and sulfur extended asphalt (SEA) studies TTI continually monitored H_2S and SO_2

emissions produced during mix preparation and sample fabrication. At the outset virtually no SO_2 was detected in any of the operations and concern was directed primarily to monitoring H_2S. The results of this activity are reflected in two reports [30, 39]. The H_2S emissions which were encountered as a function of sulfur-asphalt (S/A) ratio in the mix are tabulated below:

Sulfur-Asphalt Ratio	H_2S Concentration, ppm Mean	Range
2.25 (normal for Thermopave [1]	0.54	(0.20 - 1.80)
2.66	0.57	(0.54 - 0.60)
3.33	0.54	(0.54 - 0.60)
6.75	0.43	(0.30 - 0.50)
8.00	0.17	(0.15 - 0.20)
10.00	0.35	(0.08 - 1.0)

Both mean and ranges fell well within the suggested MAC levels for all S/A ratios tested. It should be mentioned that these data were taken 18 inches from the source (or surface of the mix) which was considered to be the normal working distance for laboratory personnel. All mixes were prepared at temperatures within the range suggested by Shell (i.e. 270°F to 300°F or 132°C to 149°C) the emissions above 300°F are shown in Figure 2.

The above data however do not reveal the true peak concentrations which occur upon initial mixing stages (i.e. when sulfur and asphalt are introduced into the mix). The peak loads detected produced more higher concentrations which dissipated in a matter of seconds. Such a comparison is shown in Figure 3 which compares the peak H_2S concentration during mixing (0 to 30 seconds after introduction of sulfur) with the concentration present at the end of a 3 minute compaction time for a mix with an S/A ratio of 2.5. Anticipated S/A ratio for sulfur-asphalt mixes range from 0.2 for SAE systems to 2.5 for sand-asphalt-sulfur mixes.

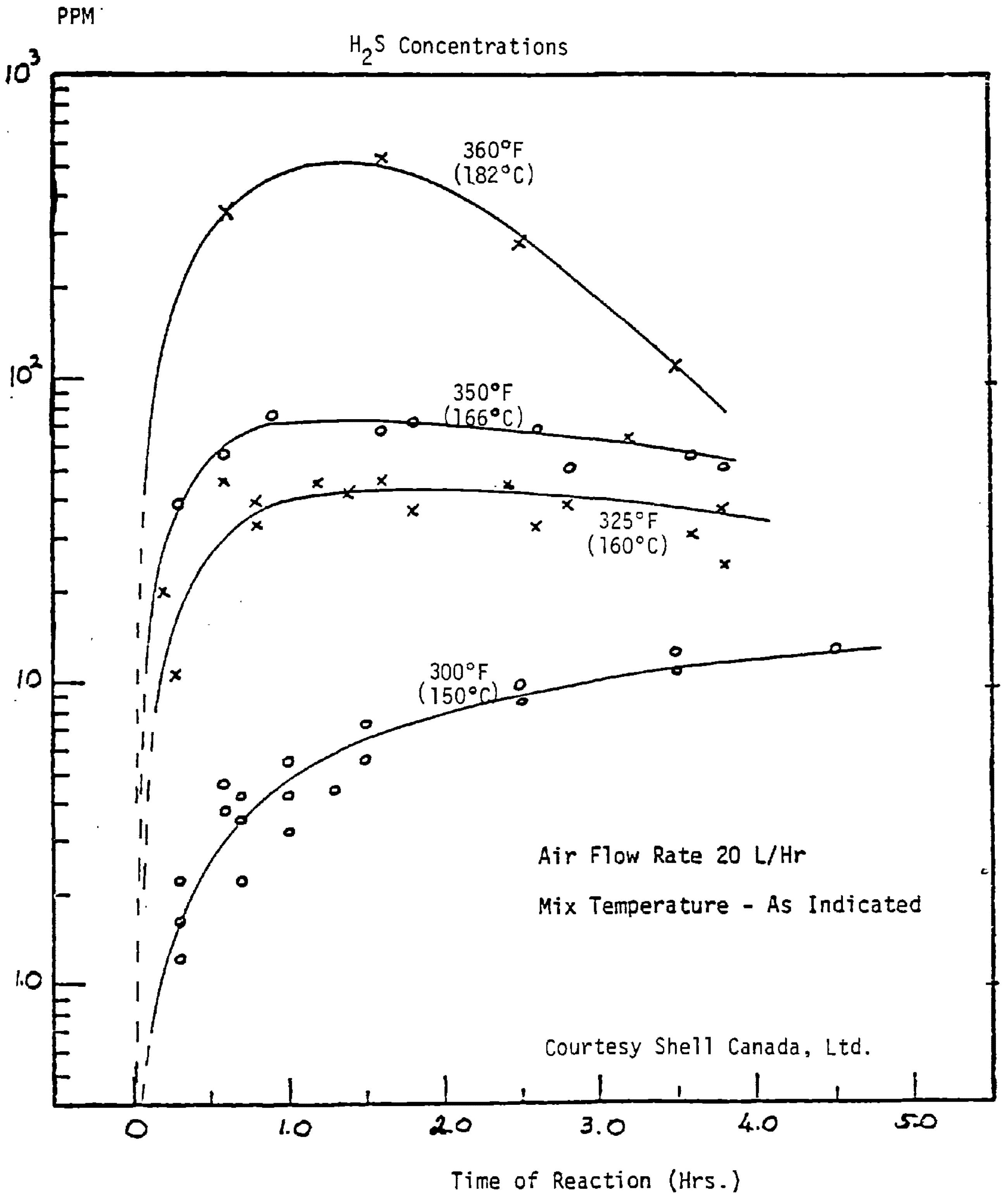


Figure 2. Effect of Temperature on Hydrogen Sulfide Concentration in SAS Mixtures as a Function of Reaction Time.

Figure 3 shows that the H_2S present within seconds after he contact of sulfur and asphalt took place during mixing was about 16.4 ppm. This concentration dipped to 0.4 ppm by the time the mix was ready for compaction about 3 minutes later. Although the figure does not indicate the total trace it was observed that H_2S concentrations were reduced to safe levels within 8-10 seconds after mixing was initiated.

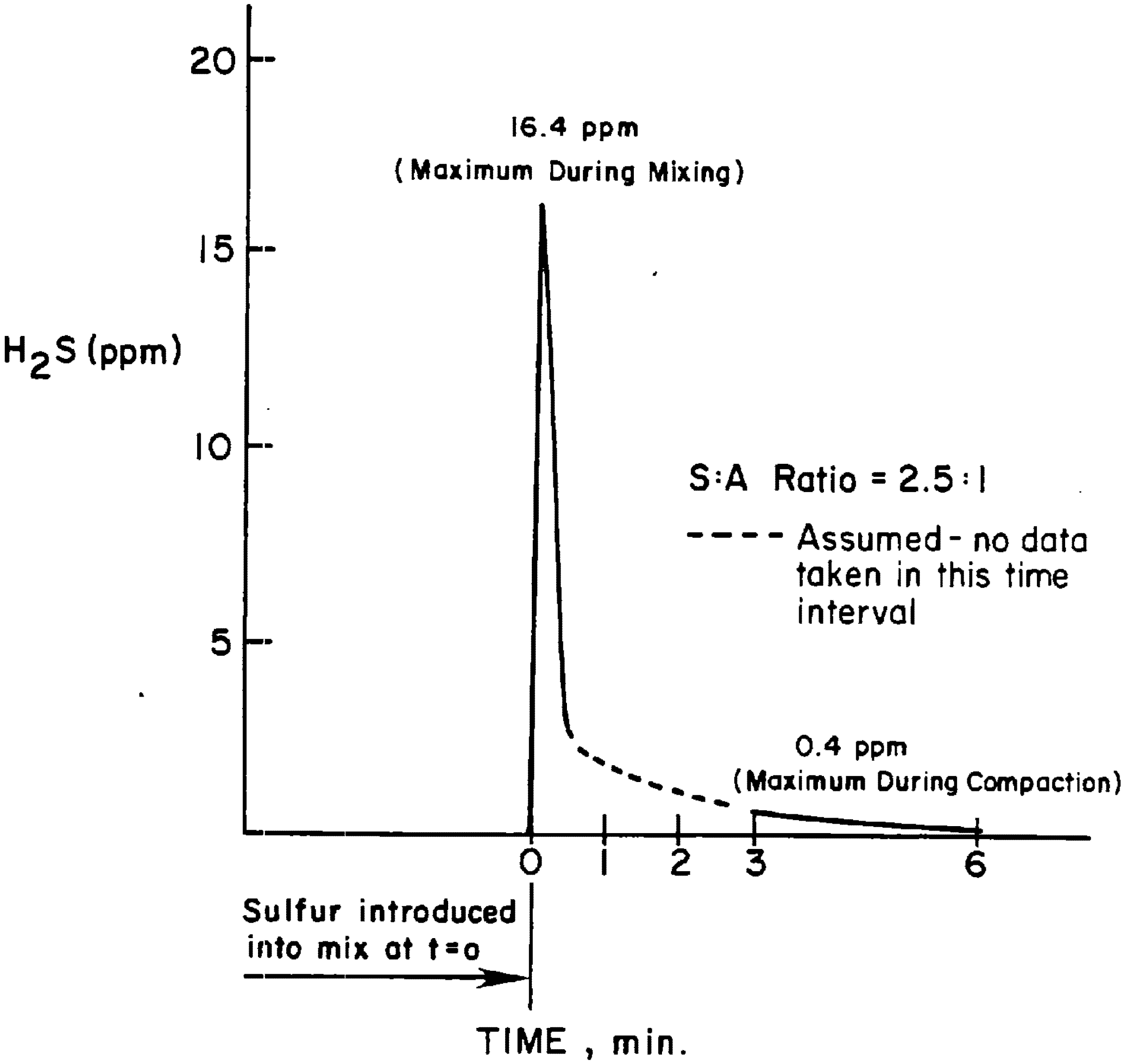


Figure 3. Comparison of H_2S Evolution During Mixing and Compaction.

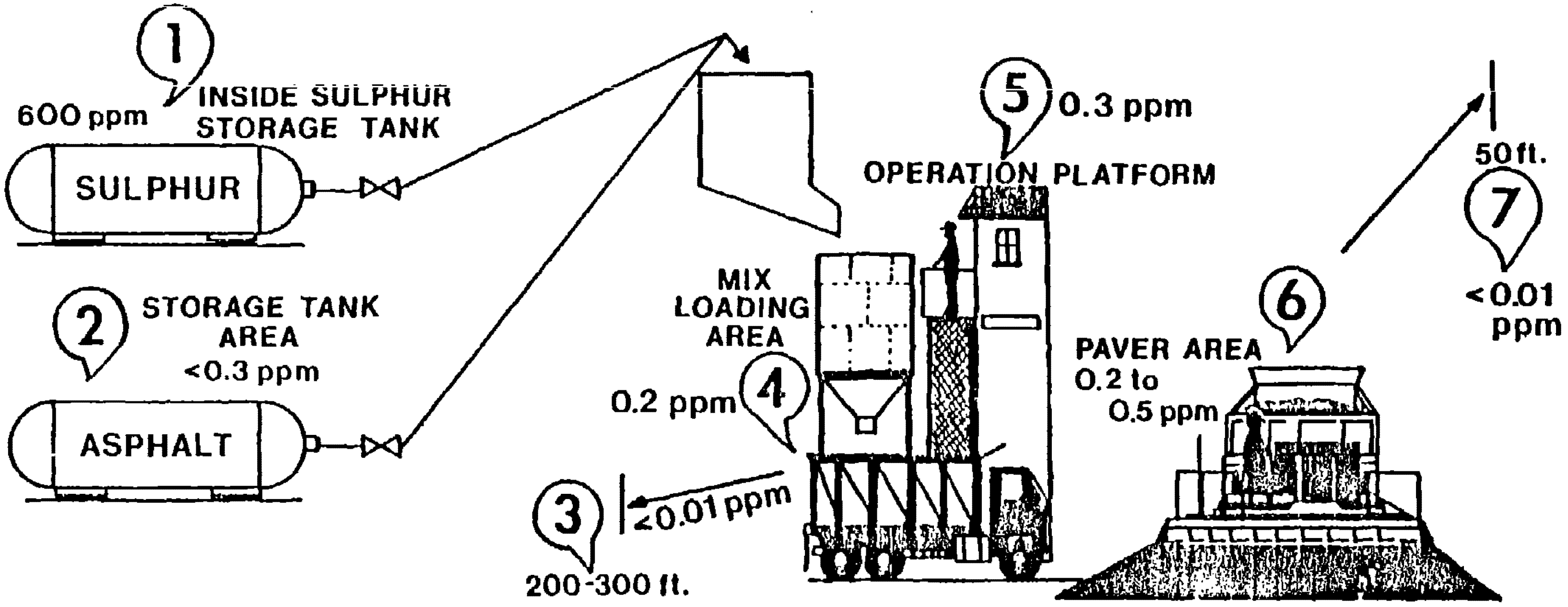
1.1.6 TTI's Experience with Evolved Gases from Sulfur-Asphalt Mixes-Field Trials.

Data on gaseous emissions were taken by TTI on both the Lufkin [13] and Kenedy County, Texas [7] sulfur-asphalt field trials. The Lufkin trials were only monitored for H_2S at virtually all important areas throughout the construction site. The results of this effort are indicated in Figure 4 which shows the H_2S concentrations at these locations. It should be noted that with the exception of the area inside the sulfur storage tank all H_2S concentrations were well below MAC values. Since this location is not considered to be a normal personnel area, safety considerations normally employed for sulfur handling would prevail [21].

Probably the most extensive emissions monitoring at a field test site was conducted by TTI along with personnel from the Bureau of Mines and the Texas Air Control Board (TACB) at the Kenedy County, Texas field trials. Details of that study are given in the construction report [7] for that project and will be summarized below.

The evolved gas measurements were taken during the construction period 5-7 April, 1977. TACB data were obtained using a mobile sampling van which moved about the various sampling sites. Specifically, measurements were taken at the following locations: Sulfur storage tank, hot-mix plant mixing chamber and the paver hopper and auger. Additional measurements were taken downwind of the plant and paver so as to establish dissipation factors.

Except for downwind samplings, most of the emissions readings generated by TACB were considered to be "source" type data; that is measurements were taken directly over the mixture. Samples were collected with a 5-ft. (1.5m) probe of 3/8 in. (9.5 mm) O.D. stainless steel tubing. Gases were sucked back to the analyzer through a 1/4 in. (6.4 mm) polyethylene tube by a Metal Bellows Company, Model MB-41 pump. Samples were collected by placing the probe tip at distances



1 ft. = 0.31 m

Figure 4. Anticipated H_2S Levels During Mixing and Paving

which ranged from 1 to 12 inches (25.4 mm to 305 mm) from the surface of the material from which the gases were being evolved. These distances are much less than that normally occupied by personnel which normally range from 2 to 6 ft. (0.6 to 1.8 m). Hence the designation "source data" were assigned to these samplings. As a backup to the source data collected by TACB, both TTI and the Bureau of Mines samplings were obtained at locations more representative of those which might be expected to be occupied by personnel.

One such area was on the platform of the hot-mix plant where the various mix ingredients were introduced into the pug mill. Continous samplings over a 24-hour period were taken in the vicinity of the manually operated feed controls at a height equal to nose level of the operator. Additional 24-hour continous samplings were taken at a point under the pug mill and just over the dump bodies of the trucks. Both of these points were monitored using a Houston-Atlas Sampler with a continuous read-out. This unit was furnished by the Bureau of Mines Metallurgy Research Laboratory of Boulder City, Nevada.

TTI personnel took samplings for both H_2S and SO_2 using two types of portable sensing instruments. A Metronics Model 721 "Rotorod" Gas Sampler [29] which is designed for monitoring only H_2S emissions was used to collect data in the vicinity of the plant, within the quality control testing laboratory, inside the cabs of hauling trucks, at the paver operator's seat, alonside the paver, at the paver's hopper and auger and in the vicinity of the sulfur storage tanks.

The other portable sampler employed was a Drager Tube with a manually operated bellows. Appropriate calibrated tubes for monitoring both H_2S and SO_2 were used with this device.

Samplings were taken at essentially the same locations monitored by the Metronics Rotorod Sampler. Drager tube measurements of H_2S concentrations thus provided a back up to those taken with the Rotorod Sampler.

KENEDY COUNTY TEST RESULTS

The results of the measurements taken of H_2S concentrations at various locations of the construction site and plant are given in Tables 1 to 3.

Table 1 includes data taken at and in the vicinity of the hot mix plant and sulfur storage area. Table 2 contains emissions monitored in the vicinity of the paving operation. Table 3 includes all other areas monitored. Data are presented in a manner to reflect locations, sampling agency (TACB, TTI or both), sampling equipment, average concentration and supporting remarks.

As has been reported, as long as the temperature of sulfur-asphalt systems were maintained below a maximum of 300°F (149°C), H_2S emissions were found to be well below suggested MAC values. Except for several occasions when screed temperature control was lost, H_2S concentrations as measured in locations normally frequented by construction personnel, were found to be significantly less than 5 ppm. The fact that no complaints were registered during the entire construction period supports this conclusion. In some cases "source type" emissions; that is, samplings taken directly over the mix material, appeared to be excessively high. However, in an open-air environment these concentrations are rapidly reduced with distance.

The highest concentrations encountered, as was the case at Lufkin, were at or near the loading port of the sulfur storage tank and inside the pug mill. Since these are not considered to be personnel areas the safety hazards are considered to be minimal".

All measurements of SO_2 concentrations were monitored by TTI using the Drager Tube. The data given below show the ranges of SO_2 concentrations measured at various locations at the paving site.

Table 1. H_2S Emissions at and in the Vicinity of the Hot Mix Plant.

Location	Sampling Agency	Sampling Equipment	Average Concentration (ppm)	Remarks NPA - non personnel area PA - personnel area
Sulfur Storage Tank Area				
a) Tank Inlet Port	TACB	Telematic	2939	NPA
b) 5 ft. from Tank Inlet Port	TACB	Telematic	23	NPA
c) On the ground at the base of the sulfur storage tank	TTI	Totorod	0.9	PA (moderate)
d) Ground level between sulfur tank and Hot Mix Plant Kiln	TACB	Telematic	0.02	PA (moderate to dense)
Hot Mix Plant Area				
a) Operator Platform	TACB	Telematic	0.007	PA (1-2 people)
	BOM	Houston - Atlas	0.5 to 2.0	PA (1-2 people)
	TTI	Rotorod	Trace	PA (1-2 people)
	TTI	Drager Tube	Trace	PA (1-2 people)
b) Base of Platform	TTI	Rotorod	Trace	PA (light)
Stairwell	TTI	Drager Tube	Trace	PA (light)
c) At Pugmill Discharge and Over Dump Body	BOM	Houston-Atlas	0.5 to 0.6	NPA
d) 125 ft. downwind of Hot Mix Plant	TACB	Telematic	0.01	PA (light)
	TTI	Rotorod	Trace	PA (light)

1 ft. = 0.31 m

Table 2. H_2S Emissions at and in the Vicinity of the Paver.

Location	Sampling Agency	Sampling Equipment	Average Concentration (ppm)	Remarks NPA - non personnel area PA - personnel area
Paver				
a) Floor at Paver Operator's Feet	TACB	Telematic	1.4	PA (1 person)
b) In Paver Operator's Chair	TTI	Rotorod	Trace	PA (1 person)
	TTI	Drager Tube	Trace	PA (1 person)
c) Paver Hopper	TACB	Telematic	4.3	NPA
	BOM/TTI	Drager Tube	2-5	NPA
d) Alongside Paver (at Auger) Downwind	BOM/TTI	Drager Tube	0-20*	PA (1-2 people)
e) Over Paver Auger	BOM/TTI	Drager Tube	20-80*	NPA
Paver Vicinity				
a) 300 ft. Upwind	TACB	Telematic	0	PA (light)
b) 25 ft. Downwind	BOM/TTI	Drager Tube	0	PA (light)
c) 100 ft. Downwind	TACB	Telematic	0.2	PA (light)
d) 200 ft. Downwind	TACB	Telematic	0	NPA
Over Pavement Behind Paver				
a) 0.5 ft. over surface	TACB	Telematic	1.3	NPA
b) 2 ft. over surface	BOM/TTI	Drager Tube	Trace	NPA

*Highest concentrations were encountered during a period when temperature control of the screed was lost causing mix temperature to exceed 320°F. (160°C). When temperature was reduced below 300°F (149°C) concentrations were reduced to near minimum values.

1 ft. = 0.31 m

Table 3. H_2S Emissions At Miscellaneous Locations.

Location	Sampling Agency	Sampling Equipment	Average Concentration (ppm)	Remarks
Dump Trucks				
a) Inside Cab at Hot Mix Plant	TTI	Rotorod	0.1	PA (1 person)
b) Inside Cab at Paver During Dump	TTI	Rotorod	0	PA (1 person)
c) Over Inlet to Dump Body	TTI	Rotorod	0.2	NPA
d. Inside Dump Body During Cleaning Operation	TTI	Rotorod	0.3	PA (1-2 persons)
Hot Mix Plant Quality Central Test Laboratory	TTI	Rotorod	Trace	PA (2-3 persons)
Hot Mix Plant Parking Area	TTI	Rotorod	0	PA (light)
At Sulfur Truck During Transfer to Storage Tank	TTI	Rotorod	0.4	PA (1-2 persons)

Location	Range (ppm)
Above paving hopper	0 - 0.5
Alongside paver (downwind)	0.5 - 20
Behind paver	0
Paver operator seat	0
Hot mix plant platform	Trace
Inside truck cab	Trace
Vicinity of sulfur storage tank	3 - 12
Directly over paved surface	0

As indicated, the values varied considerably with some concentration levels exceeding the MAC value recommended by ACGIH. These values were obtained primarily in areas of minimal worker exposure such as the vicinity of the sulfur storage tank and very close to the material in the paver. The latter were attributed to the deliberate overheating of the paver screed, a temporary event, which occurred near the end of construction. After these readings were taken the screed temperature was reduced and the concentrations were subsequently reduced to the lower values indicated above.

The paver screed without suitable temperature controls, would appear to be the main source of potentially high H_2S and SO_2 emissions. At typical operator and workmen locations on the paver and at the hot mix plant platform gas toxicity was negligible. As in the case with H_2S, gas evolution stayed well below established MAC limits when mix and paving temperatures were maintained under 300°F (149°C). Evolved gas analyses were carried out at a number of other field trials including Lufkin, Texas (1975), Bryan, Texas (1978) [14], Boulder City, Nevada (1977) and Tucson, Arizona (1979). In general, the emissions detected were well within the MAC values and consistent with the anticipated concentrations shown in Figure 4.

Only a limited amount of particulate sulfur measurements have been taken to date. The Bryan, Texas project [14], utilized a number of "Hi-Vol" dust collection units (Figure 5) stationed at various locations in the vicinity of the hot mix plant and at the paving site. Air was

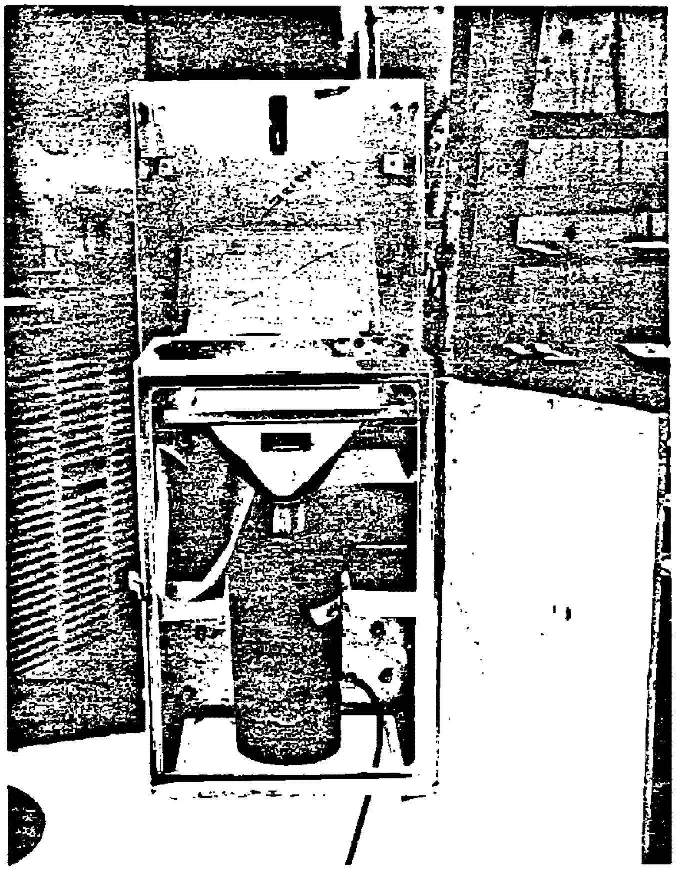


Figure 5. Hi Vol Dust Collector Utilized for Measuring Particulate Sulfur at the Plant and Job Site.

drawn into a covered housing and through a filter by means of a high flow-rate blower at a flow rate of 40 to 60 ft^3/min (1.13 to 1.17 m^3/min) which allowed suspended particles having diameters less than 10 m to pass to the filter surface. The mass concentration of the particulates in the ambient air (g/m^3) was computed by measuring the mass of collected particulates and the volume of air sampled. The total particulate matter collected by the four Hi-Vol units were analyzed in accordance with ASTM E30-40, the results of which are shown in Table 4. The amount of total particulate sulfur present was so minute that it was not deemed to be a hazard even regarding eye irritation.

1.1.7 Summary

The relative toxicity of three forms of sulfur pollutants (H_2S, SO_2 and sulfur dust) were discussed. As long as the mix temperature is not permitted to exceed 300°F (149°C), concentrations of the two gaseous pollutants can be expected to remain below recommended allowable threshold limits. This condition indicates the need to provide positive temperature controls at both the hot mix plant and the paver.

Although only limited amounts of data on sulfur dust generated during construction have been obtained to date, experience dictates that the only major hazard to personnel lies in irritation to eyes. Safety goggles are recommended to offset this problem. No on-the-job observations taken as yet would indicate that sulfur dust is present in sufficient quantities to create a health hazard. It has been recommended that additional data on sulfur dust be generated on any future sulfur-asphalt field trials.

The location where highest concentrations of H_2S and SO_2 can be expected at a job site will be in the sulfur storage area more specifically near the loading ports of the storage tank which is not considered a personnel area. Furthermore, the concentrations of the pollutants decrease rapidly with distance thus eliminating this area as a potential safety hazard to plant workmen. Normally

TABLE 4. Particulate Sulfur Measurements

Location	mg Total Sediment	mg Total Sulfur	Sediment Flux mg/m^3/day	Sulfur* Flux mg/m^3/day
Test Site, 35 ft Easterly from Engineer Station 57/10	120.07	0.654	205.73	1.12
Test Site, 35 ft Easterly from Engineer Station 58/20	139.5	0.630	249.98	1.13
Hot-Mix Plant, on Ground Between Binder Plant (Mill) and Pug-mill	1275.96	1.634	3198.40	4.10
same	1008.47	0.595	498.1	2.94
Hot-Mix Plant, Downwind Northerly	199.68	0.011	1126.2	0.06

* Not particulate Sulfur Exclusively - Test Results to follow (8-11-78)

Note: Measurements of Sediment Flux and Sulfur Flux are based 8-hour day.

The total matter collected by the High Volume units were analyzed by following ASTM Standard E 30-47.

accepted safety practices [24-26] should be employed during transfer of hot sulfur from delivery trucks to the storage tanks.

2 OVERALL PROGRAM PURPOSE, SCOPE, AND OBJECTIVES

2.1 Purpose

The purpose of this investigation was to evaluate the environmental and safety hazards along with the development of safety guidelines associated with the use of sulfur in highway pavements. This was accomplished by virtue of a series of laboratory and simulated field tests in which the safety and environmental aspects of materials storage and handling, formulation, construction, operation and maintenance of highway pavements containing sulfur were evaluated. The structuring of these tests and the evaluation of the results were complemented by the preparation of a field evaluation plan in which the sources, relative toxicity, safety and methods of monitoring and analyzing pollutants were identified. An annotated bibliography specifically oriented to the safety and environmental effects associated with sulfur-modified paving materials preparation and construction was also prepared.

2.2 Scope and Objectives

The long range objectives of the study were to evaluate the environmental and safety hazards and define some safety guidelines for the use of sulfur in highway pavements. Consideration was given to the possible evaluation and identification of toxic and obnosious fumes, dusts and runoffs which might be produced during formulation, storage, construction and maintenance of sulfur modified paving materials. This scope was extended to consider effects on humans, animals, soils, highway structural materials, ground waters and vegetation. The investigation was carried out in four tasks:

Task A - Laboratory Identification and Evaluation of Hazardous Materials and Conditions

Task B - Human Safety and Environmental Aspects

Task C - Field Evaluation Plan

Task D - Annotated Bibliography

and the final report was prepared in the following three volumes to provide a basis for selective and more cost effective distribution.

Volume I - Evaluation of Environmental and Safety Hazards

Volume II - Field Evaluation Plan

Volume III - Annotated Bibliography

Volume I contains primarily the results of the effort in Tasks A and B, the conclusion and recommendations generated in Task C and a discussion of the scope of Task D. Volume II provides a more detailed treatment of the field evaluation plan and Volume III the individually synopsized list of references. The latter have been codified, cross referenced and set up to permit easy updating.

3 TECHNICAL PROGRAM

3.1 Task A - Laboratory Identification and Evaluation of Hazardous Materials and Conditions

This task studied a number of different mix designs representative of typical sulfur-modified paving materials. Both sulfur-asphalt systems and sulfur concrete were considered. Mix designs were not selected on the basis of any structural capability and, as such, would not necessarily be considered optimum. They were chosen so as to represent a range of sulfur contents, and aggregate gradations, additives and specialty concepts (e.g., recycled mixes). The work plan for Task A is given in Figure 6.

Emissions, contaminants, environmental impact and possible anomolous behavior were examined under four conditions: (a) mix preparation, (b) weathering, (c) simulated fire and (d) chemical spills and surface treatments such as salt and deicers. Mix preparation was conducted over three temperatures, two within the normal working range for sulfur paving mixtures and one at an abnormally high temperature as might be encountered when temperature control is lost. Other process variables include humidity and oxygen levels.

Weathering studies were designed to look at the effects of long term exposure to the elements, run-off during rainfall conditons, of pavement materials and leachates produced by exposure to high surface temperatures, ultra-violet (actinic) light, freeze-thaw cycling and traffic wear. Biological activity and concomitant weathering were also considered.

The potential of the sulfur systems for catching fire, sustaining a burn and creating pollutants during combustion were also assessed. Finally, the resistance to attack by surface treatment chemicals such as brines and deicers were studied relative to safety and environmental impact.

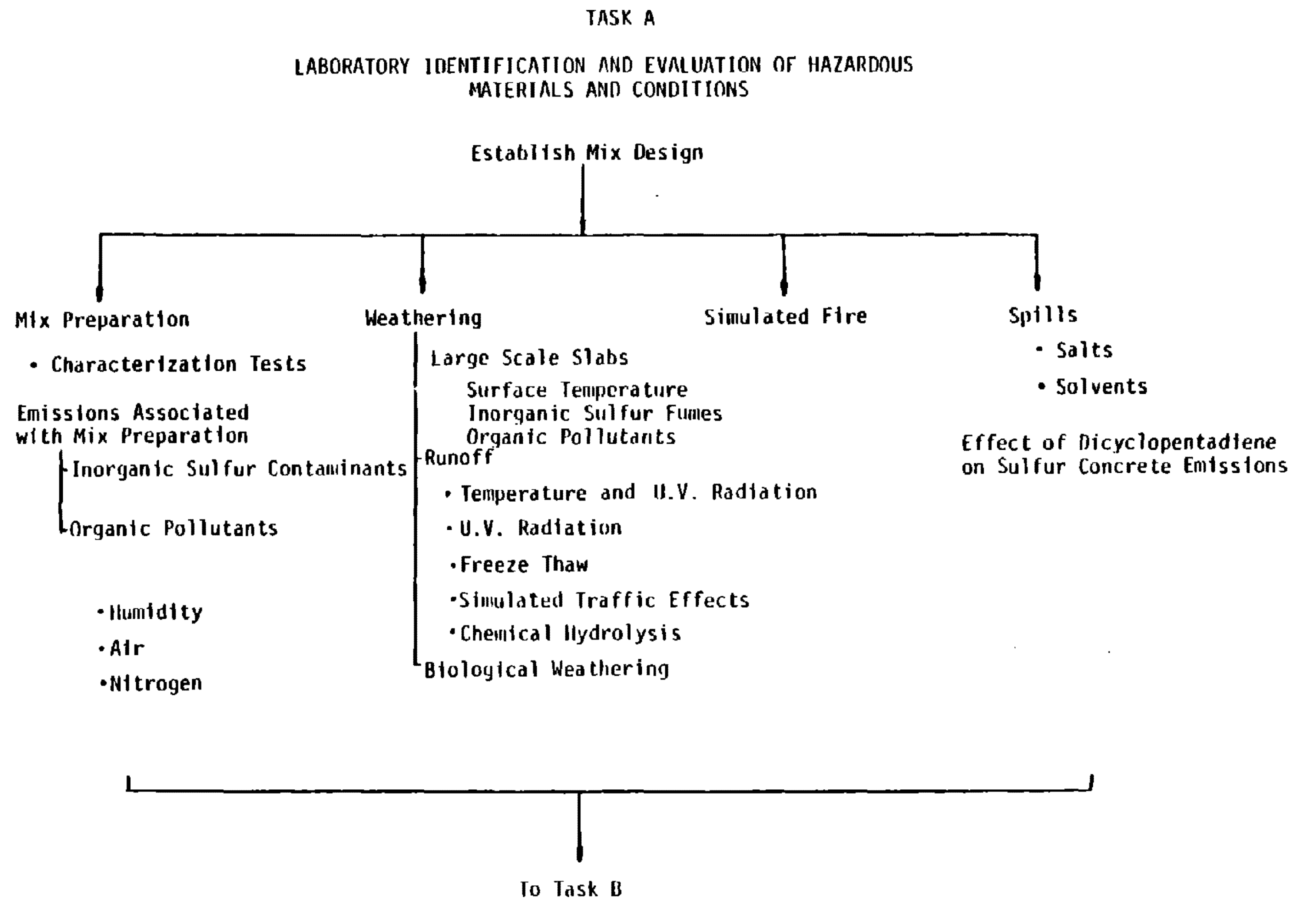


Figure 6. Task A Work Plan.

3.1.1 Mix Design Preparation.

The evaluation was conducted on three different types of sulfur-asphalt mixes; (a) aggregate-asphalt-sulfur (A-A-S), (b) sulfur extended asphalt (SEA) and sulfur recycled. Included in the SEA series were mixes prepared with both dense and open graded aggregate systems. For comparison purposes a conventional dense graded asphaltic concrete system was used as a control.

During the mix preparation phases difficulty was experienced with the AAS - open graded system. AAS mixes possess characteristically high sulfur contents (i.e. Sulfur/asphalt ratios ∿ 2 to 1). Because of the permeability of the open graded aggregates, seepage of the low-viscosity, liquid sulfur resulted in poor homogeniety in the samples prepared. The problem persisted until the sulfur content was reduced below 30 weight percent of binder. This approached the sulfur content of the direct blended SEA open graded mix. Therefore a "practical" AAS, open graded mix was considered to be unachievable.

In addition to the sulfur-asphalt systems, two sulfur concrete mixes were prepared. One mix was a sulfur-aggregate system with no additives while the other contained Dicyclopendadiene (DCPD) at 5 percent by weight of sulfur. The aggregate was a 50/50 rounded gravel/concrete sand blend.

The selection of the materials and the resulting mix designs for the preparation of laboratory samples which were used throughout the program are shown in Tables 5, through 8. Table 5 is a list of the selected mix materials and sources. Tables 6 and 8 contain the mix designs for seven sulfur-asphalt and four sulfur concrete systems, respectively. Table 7 contains the notations for Sulfur-Asphalt systems.

3.1.1.1 Characterization Tests.

The results of the characterization tests (see Table 9) conducted

Table 5. Selected Concrete Materials.

Asphalt Cement

Designation: AC-10

Source: American Petrofina
Mt. Pleasant, Texas

Elemental Sulfur

Designation: Sulfur

Source: Stauffer Chemical Co.
Specialty Chemical Division
Westport, Connecticut

Aggregates

Designation: Crushed Limestone

Source: Texas Crushed Stone
Burnett, Texas

Designation: Rounded Gravel

Source: Gifford-Hill
Bryan Pit

Designation: Concrete Sand

Source: Gifford-Hill
Bryan Pit

Designation: Beach Sand

Source: TAMU Stockpile -
obtained from Padre Island
Corpus Christi, Texas

Table 6. Selected Mix Designs and Materials for Laboratory Samples of Asphaltic Concretes.

Mix Number	Mixing*** System	Binder Proportions	Binder Content	AGGREGATE	
				Material	Gradation
1	Aggregate -Asphalt (AAS)	25% Sulfur 75% Asphalt	6.9 w/o	Crushed Limestone	Dense*
3		70% Sulfur 30% Asphalt	19.5 w/o	Beach Sand	Uniform
4		1.25% Sulfur 0% Asphalt	1.25 w/o	Nellis Runway Recycled Material	Dense
5		1.25% Sulfur 1.0% Asphalt	2.25%		
2	Aggregate -Emulsion (AE)	25% Sulfur 75% Asphalt	6.9% w/o	Crushed Limestone	Dense
7		20% Sulfur 80% Asphalt	≈4 w/o		Open**
6	Asphaltic Concrete (AC) (Control)	0% Sulfur 100% Asphalt	4.5%	Crushed Limestone	Dense

*Asphalt Institute Gradation IVb.

**Texas Highway Department Grade 4.

***Definitions of notations and symbols used in identifying mix types and designs are given in Table 7, page 35.

Table 7. Notations for Sulfur-Asphalt Systems.

Notation (Alphabetically)	Definition
AAS	Aggregate - Asphalt - Sulphur Mix System
AAS (SAND	AAS System with Sand as the Aggregate
AC	Asphaltic Concrete
ARM	Asphalt Recycled Mix
SEA	Sulfur Extended Asphalt (Asphalt and sulfur combined as an emulsion then added to aggregate)
SRM	Sulfur Recycled Mix
V/o	VOLUME Percent of Mix
v/o	VOLUME Percent of Binder
W/o	WEIGHT Percent of Mix
w/o	WEIGHT Percent of Binder

Table 8. Selected Mix Designs and Materials for Laboratory Samples of Sulfur Concretes.

Mix Number	Sulfur Content	Additive* Content	AGGREGATE	
			Material	Proportion
100	24%	0%	Rounded Gravel	50%
			Concrete Sand	50%
101	20%	by 5% Weight of Sulfur	Rounded Gravel	50%
			Concrete Sand	50%

*The Additive will be Dicyclopentadiene (DCPD).

Table 9. Properties of the Laboratory Sulfur-Asphalt Mix Design*.

Description of Mix	Resilient Modulus @ 68°F (M_r x10^{-6} psi)	Marshall Stability @ 140°F (lbs.)	Marshall Flow @ 140°F (0.01 in.)	Compacted Unit Weight lbs/cu.ft. (kg/M^3)	Air Voids (Percent Volume)
Mix 1 AAS 1.8 W/o S 5.1 W/o A	0.68	1970	9	152 (2430)	2.0
Mix 2 SEA 25 w/o S 75 w/o A	0.62	1977	9	151 (2420)	2.4
Mix 3 AAS (SAND) 13.5 W/o S 6.0 W/o A	0.40	3143	8	124 (1980)	8.6
Mix 4 SRM 1.25 w/o S 0.0 w/o A	2.90	6110	13.5	150 (2460)	2.0
Mix 5 SRM 1.25 w/o S 1.00 w/o A	1.60	3007	1.9	151 (2420)	1.6
Mix 6 AC 4.0 W/o A 0.0 W/o S	0.38	1790	8.5	146 (2340)	5.6

1 psi = 6.89 kPa
1 lbf = 4.45 N
1 in = 25.4 mm
1°F = 1.8 (°C) + 32

* These values are the average of tests made in triplicate.

on laboratory samples of sulfur extended asphalt were generated using the tests listed below:

1) Resilient Modulus at 68°F [40]
2) Marshall Stability and Flow (ASTM D 1559)
3) Compacted Unit Weight (ASTM D 1188)
4) Air Voids (ASTM D 1188)

A number of batches of sulfur concrete was prepared in accordance with the two mix designs given in Table 8 (i.e., one of sulfur concrete without additives, the other a sulfur concrete modified with 5 percent DCPD by weight of sulfur). The mixes were cast into 2-inch diameter by 4-inch long cylinders for compression and splitting tensile tests. Table 10 lists the results of these tests.

Table 10. Maximum Compressive and Tensile Stresses - Test Results for Sulfur Concrete.

Sample	Maximum Stress, psi Compressive	Splitting Tensile
SD-1	4490	1010
SD-2	5160	1160
SD-3	5190	1180
Average	4950	1085
S-1	2480	670
S-2	2610	860
S-3	2900	760
Average	2660	760

SD - Refers to sulfur concrete with DCPD (Mix Design 101 - Table 8).

S - Refers to sulfur concrete without plasticizer (Mix Design 100 - Table 8, page 35

The compression test was run in accordance with ASTM-C69 and the splitting tensile test was in accordance with ASTM-C496-71. It can be seen that sulfur concrete with DCPD had higher compressive and tensile strengths than did the unmodified mixtures. All samples were at least 14 days old when tested. As a matter of note the DCPD modified samples had normal failure characteristics whereas the unmodified specimens experienced localized failure indicative of poor aggregate-sulfur bonding.

3.1.2 Emissions Associated with Mix Preparation

Emissions generated during mix preparation were investigated as functions of mix design, temperature, and atmosphere (i.e., humidity, nitrogen). The primary objective of the experiment was to determine the concentrations, if any, of H_2S, SO_2, SO_3 elemental sulfur and organics released due directly to the incorporation of sulfur into formulation of sulfur-modified paving materials under the above environmental conditions.

The mix designs evaluated in this subtask are given in Table 11 and will be designated as MD-1 through MD-9. The specific environments selected for this evaluation are given below.

Temperature	(3),	°F	250	300	350
		(°C)	(121)	(149)	(176)
			Dry	Moist	Dry
Atmohspheres	(3),	%	5	95	N_2

3.1.2.1 Inorganic Sulfur Contaminants

The apparatus used to measure H_2S and SO_2 emissions is shown in Figure 7. Materials used in the study were prepared in bulk by proportioning the mix ingredients into a vat heated to 250°F (121°C) and mixing for 30 seconds. This was done to insure representative subsamples to differentiate between mix designs for the various

Table 11. Mix Designs Used in Task A Laboratory Evaluations.

Number	System	Weight Sulfur	Percent, w/o* Asphalt	Binder Content, w/o	Aggregate Material	Gradation
MD-1	AAS	1.8	5.1	6.9 (Asphalt)	Crushed Limestone	Dense
MD-2	SEA	25	75	6.9	Crushed Limestone	Dense
MD-3	AAS	70	30	19.5 (Asphalt)	Beach Sand	Uniform
MD-4	Recycled	1.25	0	1.25	Nellis AFB Runway	Dense
MD-5	Recycled	1.25	1.0	2.25	Nellis AFB Runway	Dense
MD-6	A/C	0	100	4.5	Crushed Limestone	Dense
MD-7	SEA	20	80	4.0	Crushed Limestone	Open
MD-8	Sulfur Concrete	24	0	24	Gravel/Sand	Dense
MD-9	Sulfur Concrete w/DCPD**	21	0	21	Gravel/Sand	Dense

*In SEA systems sulfur and asphalt proportions are given as weight percent of binder. All others are given as percent of total mix.

**Dicyclopentadiene (DCPD) was added at 5 percent by weight of sulfur.

parameters tested. Following the initial mix the materials were cooled immediately and ground to pass a 1 mm mesh sieve. Sample manipulation in this manner was necessary to reduce the variability within mix designs to a manageable level.

A 3 g sample of a given mix design was placed in a flask and heated at a rate of 7°F (3.9°C) per minute. Air was drawn over the sample at a measured rate of 1 to 3 liters per minute and subsequently mixed with a measured volume of dilution air. Sampling times were determined by emission levels. This was done so not to induce another variable associated with the amount of sulfur initially in the sample. For example, measured emissions would be erroneously diminished if air was continually drawn through the apparatus once sulfur losses were materially reduced. Sampling time for the 250°F (121°C) measurements averaged about 20 minutes. The interval was reduced to approximately 10 minutes for the 350°F (177°C) measurements. A suitable fraction of the air mixture was drawn through and monitored by H_2S and SO_2 meters (Interscan models 1176 and 1248), respectively.

Concentrations of H_2S and SO_2 were monitored at equilibrium formulation temperatures of 300°F (149°C) and 250°F (121°C) and 350°F (177°C). In addition, the impact of oxygen and relative humidity on gaseous emissions were evaluated for the high sulfur-asphalt blend (MD-3) relative to the above formulation temperatures.

Relative humidities of 5% and 95% for nitrogen and air drawn through the reaction vessel were achieved by either driving the sweep gas with anhydrous $CaSO_4$, or saturating with water vapor. Vapor flux values (See section 3.1.3.3 for definition of flux) were calculated by converting concentration expressed in μl/liter to total mg H_2S or SO_2 evolved, then dividing this number by sample weight in K_g and the time interval in minutes.

Particulates generated were trapped onto a pre-weighed 0.1 μm filter disc. The stainless steel filter housing was heated at a slightly higher temperature than the reaction vessel to circumvent the problem of clogging the filter with condensed vapors, which would hamper the ability to maintain the calibrated flow rates. The reaction vessel was cooled prior to removal of the heated filter in order to reduce the potential for condensation error. The filter was dismantled while still hot and the filter disc removed to a vacuum dessicator for cooling prior to gravimetric analysis.

The SO_3 emissions were quantified on separate subsamples by selective absorption into 80% isopropanol, followed by titrametric analysis [41] as sulfate expressed as elemental sulfur (SO_4-S). Isopropanol was prepared by diluting 80 ml of 100% peroxide free isopropanol with 20 ml deionized water. A 25 ml aliquote of the isopropanol was placed in a 100 ml pyrex bubbler. The bubbler was immersed in an ice bath and placed in line with the sweep gas downstream of the mixing chamber depicted in Figure 7.

In constrast to the closed or controlled environment provided by the test apparatus shown in Figure 7, another series of emissions measurements were made for mixes prepared in an open laboratory environment. Gases were monitored using the H_2S and SO_2 Interscan meters. To better simulate normal operating conditions the above measurements were made at approximately 18 inches (46 cm) from the surface of the mix.

3.1.2.2 Organic Pollutants

The apparatus used to collect organic emissions is shown in Figure 8. Collection of organic emissions entailed heating the sample to a desired temperature, followed by a sweep gas purge into refrigerated solvent (benzene, hexane or petroleum ether) traps. Sweep gas was drawn over the sample at 2 liters per minute for 15 minutes.

Contents of a 2-trap series were combined, passed through anhydrous Na_2SO_4, and reduced in volume by vacuum distillation for

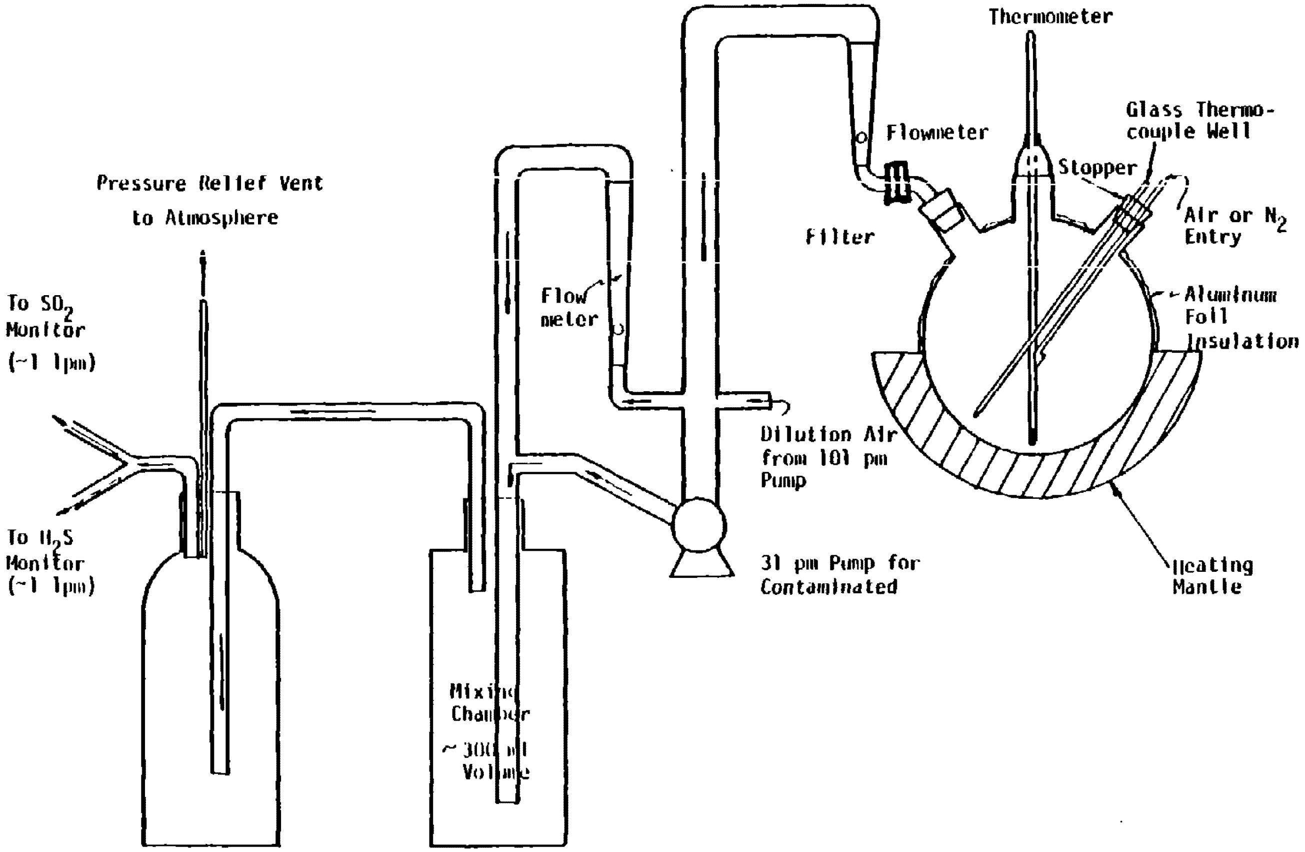


Figure 7. Apparatus for Collecting Inorganic Sulfur Contaminants - controlled environment.

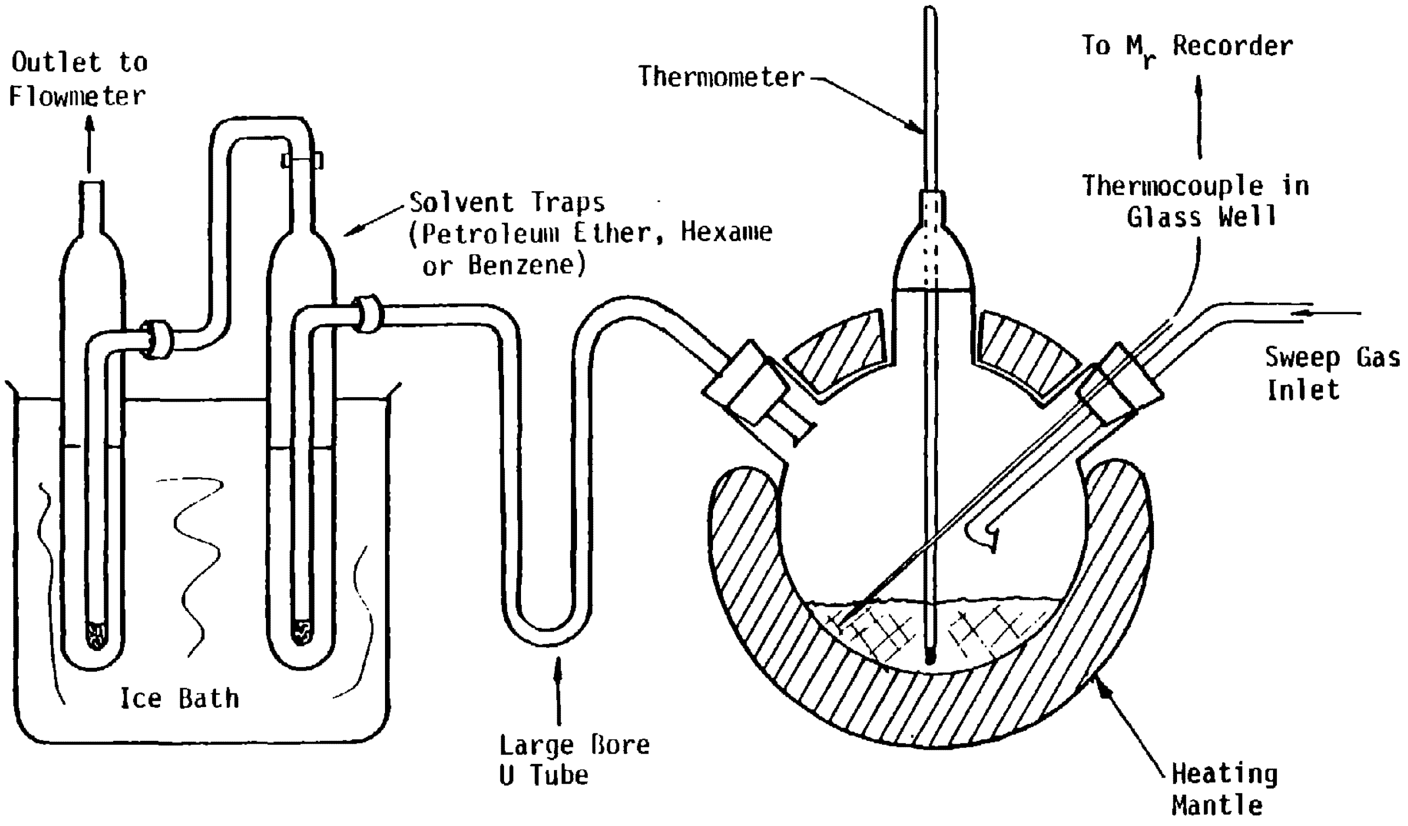


Figure 8. Apparatus Used to Collect Organic Emissions

subsequent gas chromatographic (GC) analyses.

Mercaptans were collected separately by a selective trapping technique [42, 43]. A bubbler containing 25 ml of 5% $HgCl_2$ solution with 0.3 ml of 5% NaOH added to adjust the pH was placed in line with the sweep gas in lieu of the refrigerated solvent traps. Two glass fiber filters impregnated with $KHCO_3$ and $ZnCL_2$ + H_3BO_3 immediately preceeded the bubbler to scrub SO_2 and H_2S gases, respectively. The SO_2 scrubber was prepared by saturating glass fibers, packed in a 0.1 in. (0.3 cm) I.D. by 2 in. (5 cm) glass tube, with a 5% $KHCO_3$ solution. A similar scrubber was constructed by saturating the glass fiber pack with a saturated $ZnCl_2$ solution adjusted to pH 4.7 with boric acid. Mercaptans and disulfide were purged with N_2 gas from the H_g complex into refrigerated pentane following acidification of the bubbler contents with 20% HCl. Organic solvent from the traps were combined, dried over anhydrous Na_2SO_4, and reduced to a suitable volume for gas chromatographic analysis.

The instruments used for analysis were a Tracor Model 550 and Tracor Model 560 Gas Chromatograph. The Model 550 is equipped with both a flame ionization detection (FID) and flame photometric detection (FPD) capability. An in-line 394 μm filter was used for operation of the FPD in a sulfur specific mode. FID is sensitive to carbon containing compounds. A standardization study was initiated to evaluate the detector response as measured in integration units (IU) relative to the moles of carbon injected. A similar study was conducted for sulfur containing compounds. Compounds employed in this effort and detector response corresponding to the instrument and detector employed are given in Table 12, while it should be noted that the technique quantifies material concentrations relative to carbon and sulfur only and underestimates the total mass. This technique is superior to those which quantify by either peak triangulation or inclusion of a single reference standard when dealing with unknown mixtures.

Table 12. Sulfur Compounds and Hydrocarbons Employed in Detector Response Study.

	DETECTOR RESPONSE	
	Flame Ionization	Flame Photometric
Hydrocarbon	IU*/mole of Carbon x 10^{12}	IU*/mole of Sulfur x 10^{13}
Anthracene	1.3	
Biphenyl	1.3	
Dibenzothiophene	1.4	3.8
Fluoranthene	1.5	
n-Hexadecane	1.4	
n-Hexacosane	1.5	
Napthalene	1.4	
n-Phenyls Carbazole	1.3	
o-Terphenyl	1.4	
Tetraphenylethylene	1.3	
1, 3, 5-Triphenylbenzene	1.3	
Triphenyl methane	1.4	
Xanthene	0.9	
-Butyl mercaptan		3.2
n-Hexyl mercaptan		4.3
n-Heptyl Mercaptan		4.4
Diethyl Sulfide		6.4
Diallyl Sulfide		6.1
Di-n-butyl Sulfide		5.2
Carbon Disulfide		3.8

*IU = Integration units.

Both GC's were fitted with 6 ft. (2.4 cm) by 1/4 in. (0.6) I.D. glass columns packed with 3% OV-1 on 80/100 mesh Chromosorb-W. The Model 550 was operated at a column temperature program between 86 and 464°F (30 and 240°C) at 1.7°F (3°C) per minute with an initial hold and final hold of 8 and 20 minutes, respectively. In general, the Model 550 was used to screen for sulfur containing compounds, and the Model 560 was used to screen for higher molecular weight hydrocarbons. The Model 560 column temperature was programmed between 212 and 464°F (100 and 240°C) at 5.4 °F/min (3°C/min) with an initial hold setting of 10 minutes and final hold of 40 minutes.

Quality control was maintained with daily monitoring of column efficiency and detector response. This was accomplished by injecting standard mixtures with widely varying retention times. The standard mixture was formulated from commercially available materials of high purity. Commercially available, standard compounds, similar to those expected to occur as emissions from asphalt were used in preparing the mixtures. These compounds were reasoned to be structurally similar moieties of asphalt, formed by thermal fragmentation and/or by reaction with sulfur during formulation of the various blends at high temperatures.

A combination GC-mass spectrometric analysis was made of the emissions from the highest sulfur containing mix design (MD-3) formulated at 350°F (176°C), and the control (i.e., no sulfur added).

Total sulfur was analyzed by the LECO Combustion Method whereby sulfur is oxidized in an induction furnace to SO_2, transferred to the LECO 532 Automatic Titrator and measured by idometric titration. Several NBS sulfur standards were used to calibrate the buret against known quantities of sulfur. Samples of unknown sulfur content are than assayed by comparison techniques.

3.1.2.3 Summary of Emissions Generated During Mix Preparation

Inorganic Emissions

Concentrations of H_2S and SO_2 emitted during the preparation of seven mix designs (MD 1-7) at 250, 300 and 350°F (121, 149 and 176°C) are shown in Tables 13a and 13b. Table 13a shows the concentrations generated using the controlled volume mixing chamber shown in Figure 7. The data shown in Figure 13b reflect the concentrations generated in the open atmosphere of the laboratory. The latter represent the peak concentrations which always occurred 5 seconds and 15 seconds after introduction of the sulfur and asphalt to the mix.

Examination of Tables 13a and 13b indicate the following:

1) The emissions collected in the closed environment were significantly higher than those taken under the more job-simulative conditions of the laboratory.
2) Peak load concentrations decay by an average factor of about five between 5 and 15 seconds after initiation of mixing.
3) Both H_2S and SO_2 emissions increase with temperature and with the rate of evolution once the temperature exceeds 300°F (149°C).
4) When mixes in the controlled environments are held at temperature above 300°F (149°C), the emissions rapidly approach and then exceed the MAC values for both H_2S and SO_2.
5) The emissions, where detectable, relative to the seven sulfur-asphalt mix designs appeared to be in the same proportions for both the closed and laboratory environments.
6) The high concentrations which appeared in MD-4 (recycled mix with no sulfur added) in both the controlled and laboratory test can not be explained. The fact that below 300°F (149°C) the H_2S emissions are about the same as for MD-5 (recycled with 1.0 percent sulfur added), indicate

Table 13. Variation of Gaseous Emissions with Mix Temperature As Generated During Mix Formulation.

Controlled Environment - Figure 13a

Gaseous Vapor	Temperature °F (°C)	Mix Design Number*						
		1	2	3	4	5	6	7
		Concentration, ppm						
H_2S	250 (121)	3.5	15	12	10	9	0.5	2.0
	300 (149)	8.0	280	305	110	90	2.0	78.0
	350 (176)	173.0	620	595	1100	500	2.5	385.0
SO_2	250 (121)	4.0	8.0	6.0	10	0.4	0.5	1.0
	300 (149)	9.0	140.0	160.0	39	83.0	2.0	17.0
	350 (176)	87.0	361.0	245.0	550	250	2.0	187.0

Laboratory Environment - Figure 13b

Gaseous Vapor	Temperature °F (°C)	Mix Design Number*						
		1	2	3	4	5	6	7
		Concentration, ppm						
H_2S 5 sec (15 sec)	250 (121)	Tr	Tr	1.1	Tr	>0.1	0.5	Tr
	300 (149	2.5 (Tr)	1.5 (Tr)	3.0 (Tr)	1.7 (Tr)	2.0 (Tr)	1.0 (Tr)	3.0 (>0.1)
	350 (176)	50 (7.0)	5 (1.5)	65 (14)	20 (5.0)	25 (5.0)	1.5 (0)	22 (3.0)
SO_2 5 sec (15 sec)	250 (121)	←			(Tr) (0)			→
	300 (149)	1.5 (Tr)	1.0 (0.3)	1.0 (0.1)	.5 (0)	1.7 (Tr)	1.2 (0.3)	0.4 (0)
	350 (176)	23 (4.0)	2.8 (2.0)	33 (7.8)	8 (2.0)	13 (2)	1.5 (Tr)	7 (1.5)

*Mix designs and numbers are given in Table 11, page 39 residual sulfur may have existed in the original unprocessed material.

7) The influence of DCPD in the sulfur concrete is discussed in Section 3.1.6.

Emissions are of approximately equal ratios of H_2S:SO at a formulation temperature of 250°F (121°C). At the highest formulation temperature of 350°F (176°C), a 2:1 ratio of $H_2S:SO_2$ was observed. It should be noted that the values represent peak concentrations observed and several factors such as the rate of heating may have affected the results. Although settings for the heating mantle were maintained, the same throughout the experiment, the different mix designs affected heating rates. Temperature differential across the samples thus resulted in less than definitive observations between mix designs, other than to point out the asphalt along released insignificant quantities of H_2S and SO_2 at even the highest formulation temperature.

In order to make comparisons between mix designs, the total H_2S and SO_2 emitted was expressed in a flux term (F) by dividing the total quantity of each gas emitted by the sample mass (M) and the time interval (t) for which the mix was heated; $F = \frac{Q}{Mt}$. The time interval employed varied not only between mix designs but within a single mix design relative to the formulation temperature. However, a minimum 10 minute reaction interval was employed to better validate the flux. Obviously a higher flux term corresponds to a higher emission level over longer time interval.

Flux values are presented in Table 14 and 15. The data suggest that similar masses of H_2S and SO_2 are emitted at corresponding formulation temperature for a given mix design. Vapor flux values are approximately equivalent at the highest mix temperature with the exception of the high-sulfur mix design (MD-3) and control (MD-6). Although the peak

Table 14. Variation of Vapor Fluxes of H_2S and SO_2 with Respect to Mix Temperatures Generated During Mix Formulation.

Vapor	Temperature		Mix Design*						
			1	2	3	4	5	6	7
	°F	(°C)	mg/kg/min						
H_2S	250	(121)	4	18	9	12	1	1	3
	300	(149)	9	260	114	26	42	2	90
	350	(176)	120	294	552	255	232	3	356
SO_2	250	(121)	9	14	5	22	1	1	3
	300	(149)	114	176	92	47	40	4	38
	350	(176)	240	267	610	240	218	4	326

*Mix designs and numbers are given in Table 11, page 39.

Table 15. Variation of Vapor Flux Values for MD-3 As Affected by Atmosphere.

	Temperature		Vapor Flux (mg/kg/min)	
	°F	(°C)	H_2S	SO_2
Air Dry	240	(121)	9.3	5.4
	300	(149)	114	92
	350	(176)	552	610
Air Wet	250	(121)	63	30
	300	(149)	320	531
	350	(176)	440	526
N_2 Dry	250	(121)	7.6	1.3
	300	(149)	417	234
	350	(176)	648	610

concentrations of H_2S and SO_2 for the MD-3 sample were equivalent to or lower than the other mix designs (Table 13), the concentrations were sustained for a longer time interval, due to the fact that MD-3 contained 5 to 8 times more sulfur in the mix initially. This resulted in larger H_2S and SO_2 flux values for the MD-3 material.

Comparisons of vapor flux values for MD-3 under different conditions are presented in Table 15. The increase in vapor flux with a corresponding increase in temperature was statistically significant at the 1% level. Although there were no statistically significant differences between vapor flux values with respect to atmospheric condition, the moist air (95% relative humidity) resulted in numerically higher H_2S and SO_2 emissions at lower temperatures. A statistical evaluation of the H_2S and SO_2 flux values using a "paired t" test suggested no difference in the magnitude of these fumes at corresponding mix temperatures and atmospheric conditions. No attempt was made to study atmospheric conditions on vapor flux values of the other mix designs due to negative results obtained on the high sulfur mix design.

A more thorough study of the high sulfur MD-3 material was made in a effort to mathematically model probable emissions levels relative to the mix temperature. Both H_2S and SO_2 gaseous emissions were described by an exponential function of the mix temperature (Figure 9). Regression coefficients approaching unity strongly suggest that temperature alone, if free sulfur is present in the mix, controls H_2S and SO_2 emission levels.

Sulfur trioxide was measured for all samples prepared at each of the respective mix temperatures. Only the high sulfur mix(MD-3) at the 350°F (176°C) mix temperature resulted in any measurable sulfur dioxide expressed as elemental sulfur (SO_2-S). Similarly, the SO_3-S flux value was 1.8 mg/kg/min.

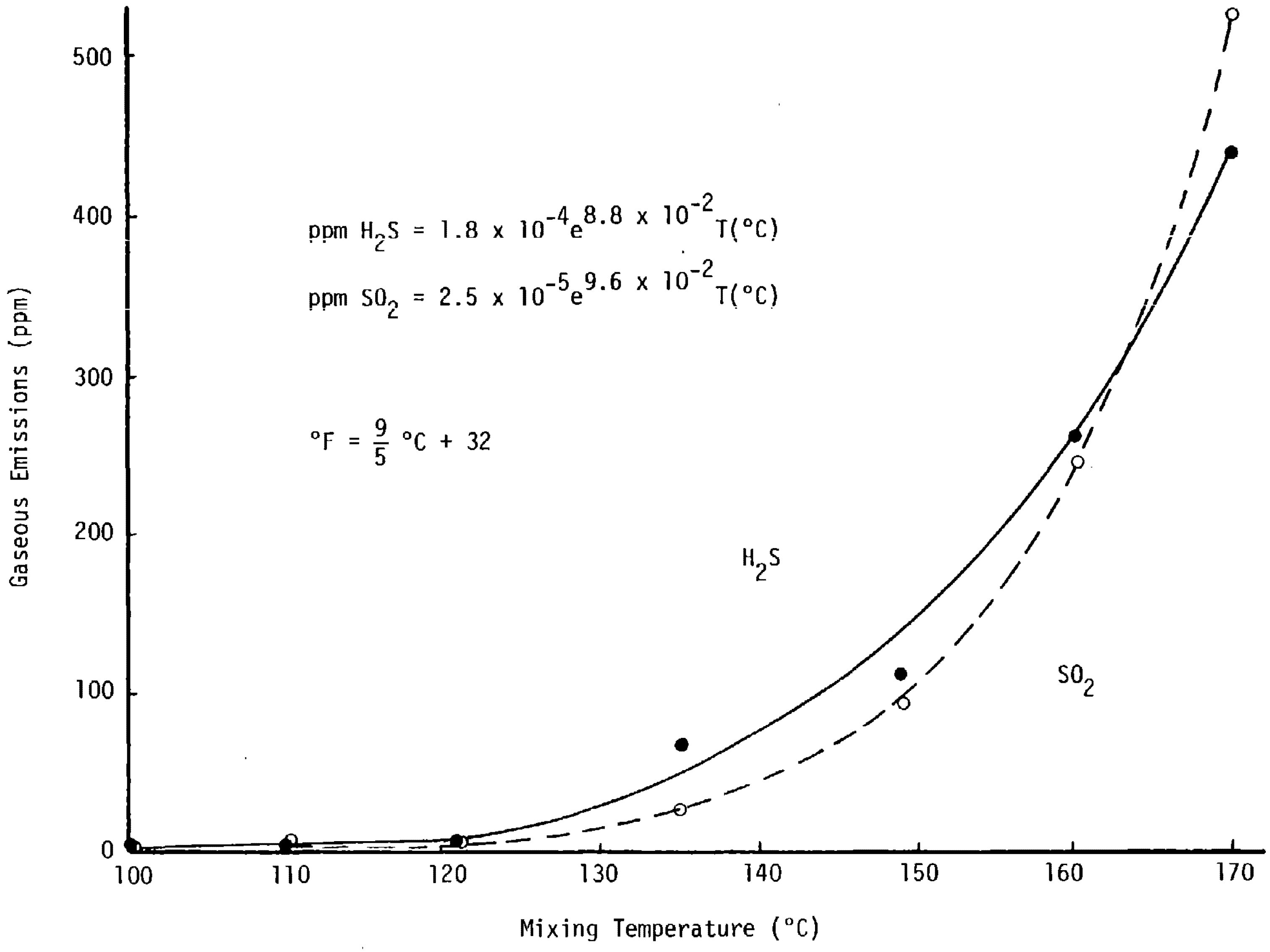


Figure 9. H_2S and SO_2 Emissions from MD-3 as Influenced by Mix Temperature - Controlled Environment.

Attempts to measure elemental sulfur were frustrated by unwanted deposition on apparatus surfaces which was impossible to recover and quantify. For this reason a mass balance was developed for sulfur in the various mix designs at the 3 mix temperatures. Elemental sulfur emissions were then estimated by the difference between total sulfur lost and the sum of that accounted for as H_2S, SO_2 and SO_3. Organic sulfur was too minute in quantity to have any effect on the material balance. The sulfur balance developed for the various formulations mixed at 250, 300 and 350°F (121, 149 and 176°C) are given in Table 16, 17, and 18 data. However, some organo-sulfur compounds of minute concentration may not be detected by FID, but show up as a large peak by FPD, due to the latter's much greater sensitivity.

Hydrocarbon emissions from mix designs formulated at 350°F are given in Figure 10. Two principles were used to determine which organic emissions, if any, would be considered significant. All emissions that can be attributed to normal asphalt are eliminated from consideration. This is not to imply that there is no hazard associated with these emissions, only that the scope of this work was limited to emissions induced by the use of sulfur. Also, organic emissions are not considered significant unless they exceed 1 ppm under the test conditions. Interpretation of the data according to these principles show no organic compound present in the emissions at the 1 ppm level. At the temperatures in the study no significant amounts of organic emissions, sulfur containing or otherwise, were detected above the normal to asphalt. FID scans of MD-2, MD-3, MD-4, MD-5, and MD-7, were developed following concentration to volumes suitable to detect 1 ppm of a $C_{11}H_{22}$ hydrocarbon relative to the total volume of air trapped. FID scans for MD-1 and MD-6 were concentrated more than required to demonstrate the similarities between characteristic GC profiles developed for a sulfur-asphalt mix and virgin asphalt.

Table 16. Sulfur Balance for Materials Mixed at 250°F (121°C).

	Mix Design Number*						
	1	2	3	4	5	6	7
	Weight of Sulfur, mg						
Total S	84.3	74.1	467.0	61.2	78.3	13.8	55.2
Residual	59.5	41.3	345.3	27.1	32.9	14.1	46.6
Total Emission	24.8	32.8	122.7	34.1	45.4	--	9.6
H_2S-S	0.1	0.5	0.4	0.4	0.2	--	--
SO_2-S	0.1	0.3	0.2	0.3	0.1	--	0.1
Total	0.2	0.8	0.6	0.7	0.3		
Elemental S	24.6	32.0	122.1	33.4	45.1	--	9.5

Table 17. Sulfur Balance for Materials Mixed at 300°F (149°C).

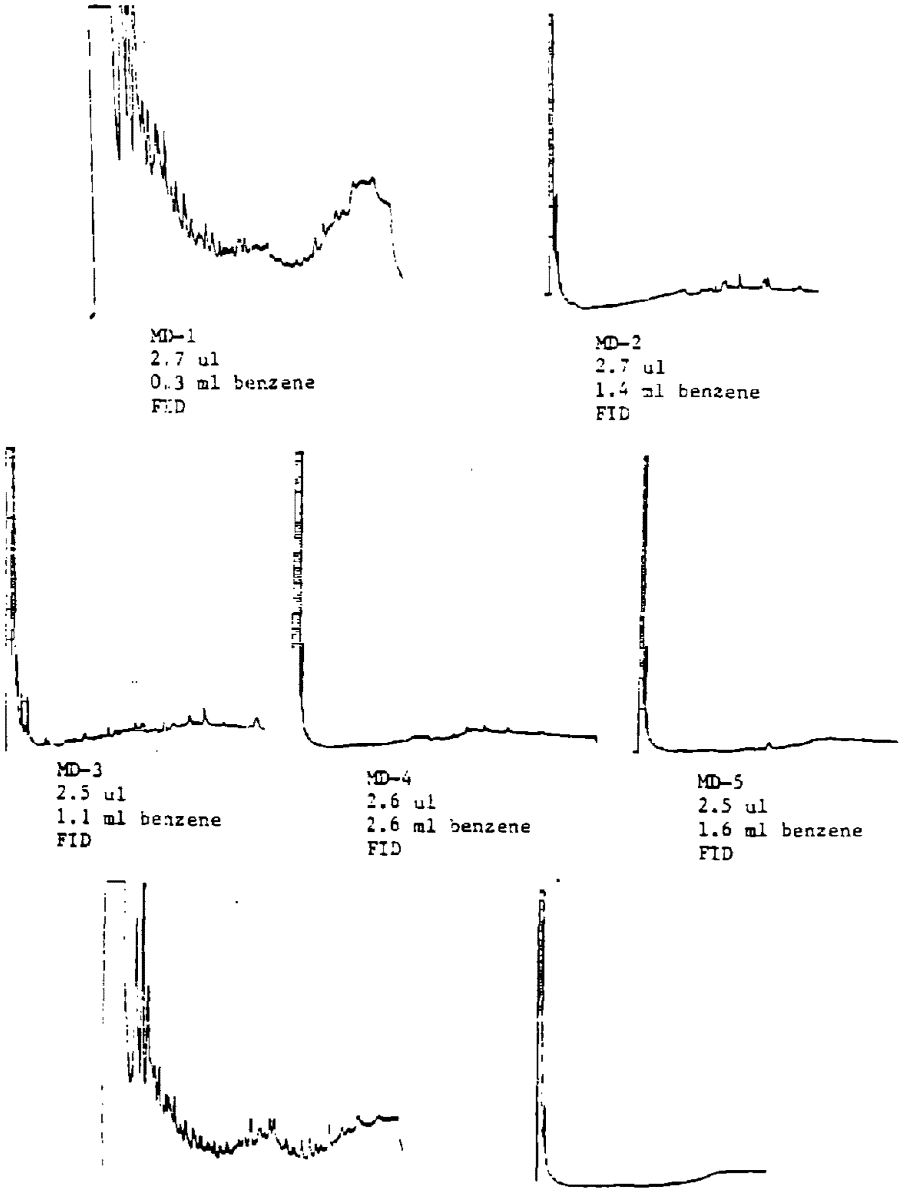
	Mix Design Number*						
	1	2	3	4	5	6	7
	Weight of Sulfur, mg						
Total	84.3	74.1	467	61.2	78.3	13.8	55.2
Residual	25.7	23.4	314.3	22.9	29.4	12.4	45.7
Total Emission	58.6	50.7	152.7	38.3	48.9	1.4	9.5
H_2S	0.4	8.3	12.5	1.1	1.3	.1	2.7
SO_2-S	0.4	3.9	2.8	0.6	0.6	.1	0.6
Total	0.8	12.2	15.0	1.7	1.9	0.2	3.3
Elemental S	57.8	38.5	137.7	36.6	47.0	--	6.2

*Mix designs are given in Table 11, page 39.

Table 18. Sulfur Balance for Materials Mixed at 350°F (177°C)

	Mix Design Number*						
	1	2	3	4	5	6	7
	Weight of Sulfur, mg						
Total S	84.3	74.1	467	61.2	78.3	13.8	55.2
Residual	18	24	207.5	18.7	26.1	13.6	40
Total Emission	66.3	50.1	259.5	42.2	43.3	0.2	15.2
H_2S-S	4.0	14.8	19.4	8.9	8.3	0.1	10.7
SO_2-S	2.1	7.5	9.2	4.2	3.9	0.1	4.9
SO_3-S	--	--	2.8	--	--	--	--
Total	6.1	22.3	31.4	13.1	12.2	0.2	15.6
Elemental Sulfur	60.2	27.8	230.9	29.1	31.1	0.0	0.0

*Mix designs are given in Table 11, page 39.



MD-1
2.7 ul
0.3 ml benzene
FID

MD-2
2.7 ul
1.4 ml benzene
FID

MD-3
2.5 ul
1.1 ml benzene
FID

MD-4
2.6 ul
2.6 ml benzene
FID

MD-5
2.5 ul
1.6 ml benzene
FID

MD-6
2.5 ul
0.3 ml benzene
FID

MD-7
2.6 ul
3.3 ml benzene
FID

Figure 10. Hydrocarbon Emissions from Mix Designs Formulated at 350°F (177°C).

Although the concentrations may be slightly attenuated due to an extended formulation time interval relative to sample mass, and the total volume of air drawn through the traps, the tests are conservative considering the high temperature, and the fact that asphlatic emissions would be expected to be of higher molecular weight and carbon number. Heavier materials of greater carbon number would result in a greater detector response than that calculated for a 154 AMU ($C_{11}H_{22}$) hydrocarbon, respectively, It can be seen from this data that the bulk of sulfur lost during formulation will be as elemental sulfur, particularly at the lower mix temperature. Asphalt bound sulfur was retained by the sample at even the excessive mix temperature of 350°F (176°C) - MD-7, Table 18. Although total sulfur lost by the sulfur-asphalt mix designs increased with increased temperature, that loss as elemental sulfur was diminished, corresponding to increased H_2S and SO_2 emissions. A much lower percentage of sulfur incorporated in MD-7 was lost compared to the other sulfur asphalt materials, and all emissions were conserved as H_2S and SO_2 at 350°F (176°C). The open graded design used in the mix may explain in part the lower sulfur emissions observed for MD-7. Possibly the void space associated with the mix design has much poorer heat transfer qualities, reducing the total heated surface, or causing temperature differentials within the microfabric of the sample such that elemental sulfur vaporized is condensed on adjacent cooler particles surface. H_2S and SO_2 are gases and would tend to be less affected by heat differentials. The lower total sulfur emissions for MD-7 reflect the lower heat transfer properties of the mix design.

Organic Emissions

To improve efficiency, the refrigerated solvent traps were placed in an immediate in-line position to the reaction vessel and combined prior to volume reduction and gas chromatographic analysis.

Trapped emissions were first screened for hydrocarbons using the flame ionization detector system (FID), followed by a second chromatographic analysis using a flame photometric detector system (FPD) in the sulfur mode. Compounds containing carbon and sulfur will show in both at 1 ppm. Hydrocarbons containing sulfur would be less sensitive using FID, but would be detected by FPD due to its greater sensitivity.

Sulfur containing emissions were found to increase significantly with increased mix temperature for all but MD-6. The temperature effect is demonstrated for MD-3 in Figure 11. All mix designs with the exception of MD-6 responded similarly to temperature. A comparison of the FPD scans at the high mix temperature of 350°F (Figure 12) clearly demonstrates that the sulfur containing peak is independent of the asphalt used in the mix. Only the large peak is of significant magnitude, although numerous other sulfur compounds were detected.

The one sulfur containing compound present in significant amounts was identified as elemental sulfur. All available information supports this identification, and is summarized as follows:

1. There is no FID peak corresponding to the magnitude of the FPD peak, indicating that the material is not carbon containing.

2. The FPD scan is clean for the control, MD-6.

3. A mass spectrum of the emissions concentrated for MD-3 and MD-6 formulated at 350°F was made, and revealed a significant peak corresponding to a mass/charge ratio of 32 percent for MD-3 but not for the MC-6.

4. An attempt was made to isolate any mercaptans by complexing with Hg^{+2} and partitioning the complex in water. The aqueous solution of the complex is separated and acidified to disrupt the complex. Mercaptans are then partitioned into a benzene phase, which was concentrated and analyzed by GC using the FPD mode. The chromotograms were clean suggesting the peaks found previously were not mercaptans.

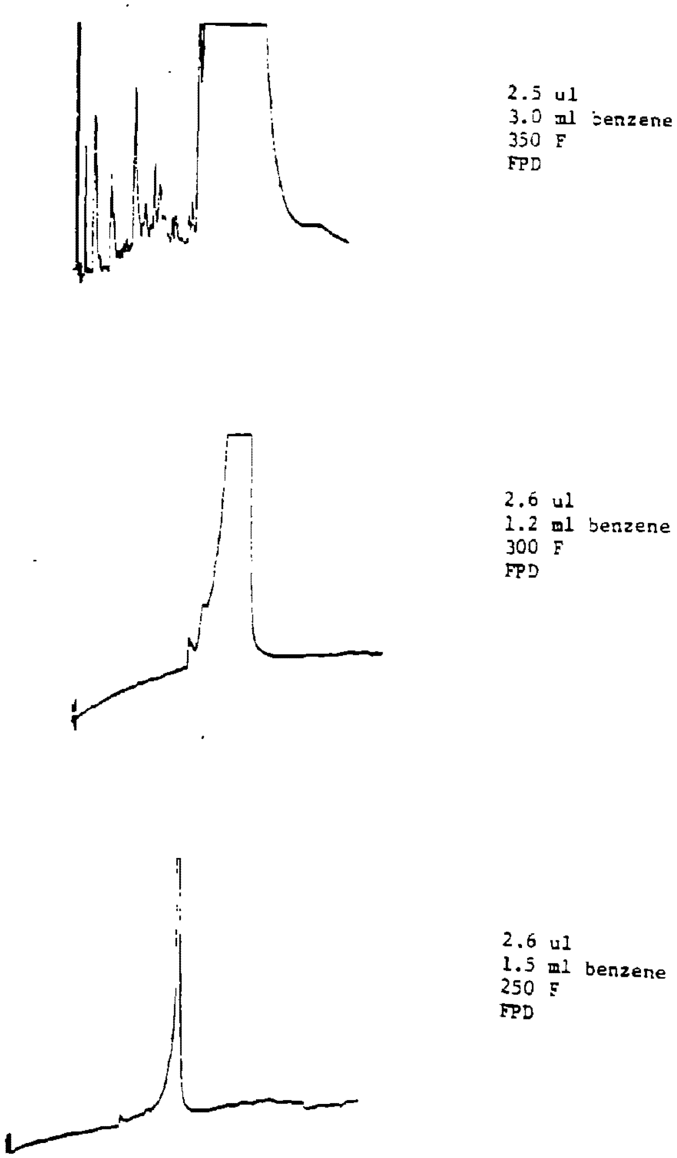
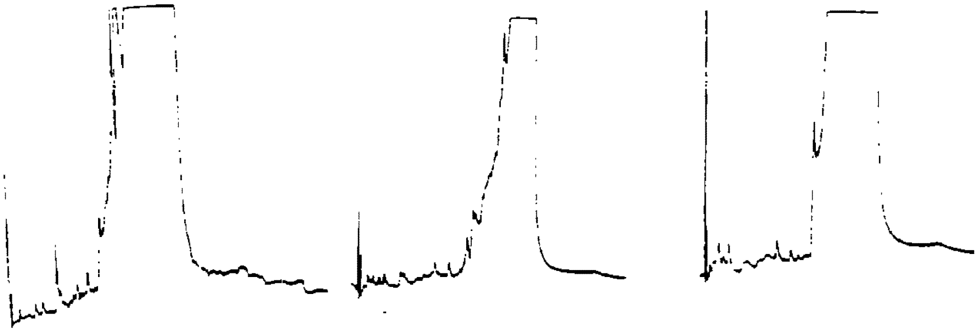


Figure 11. Sulfur Containing Emissions at 250, 300 and 350°F (121, 149 and 177°C) for MD-3.



MD-1
2.4 ul
1.4 ml benzene
FPD

MD-2
2.6 ul
2.0 ml benzene
FPD

MD-4
2.5 ul
1.8 ml benzene
FPD

MD-5
2.6 ul
3.3 ml benzene
FPD

MD-6
2.6 ul
3.0 ml benzene
FPD

MD-7
2.4 ul
2.5 ml benzene
FPD

Figure 12. Sulfur Containing Emissions at 350°F (177°C) for MD-1, MD-2, MD-4, MD-5, MD-6 and MD-7.

In summary, H_2S and SO_2 are produced in potentially lethal concentrations during formulation of sulfur-asphalt only when temperatures exceed 320°F (160°C) and when maintained in a closed environment such as that of heated storage silo. Concentrations of both gases will rapidly diminish under the open air conditions associated with the paving process.

Of greatest environmental concern is the vaporous elemental sulfur released during the dumping and paving process. Upon cooling the vapors will condense into fine particulates, which could be deposited on adjacent foliage and soil surfaces. Fines may also be transported from the pavement surface by wind, or in runoff following a rainfall event. Elemental sulfur would have an acidifying affect following any chemical and/or biological oxidation. The net impact will largely be determined by the buffer potential of soils and surface water affected. Maintenance of paving temperatures below 300°F (149°C) will reduce the potential of an adverse impact.

As will be discussed later, weathering of compacted sulfur-asphalt pavements by natural conditions is,at best,significant only in the long term. Concentrations of sulfur constitutents lost to the environment over a short term interval were found to be too low to have a measurable impact.

3.1.3 Weathering Studies

A series of tests were designed to assess the environmental and biological impact of sulfur modified pavements as caused by exposure to material weathering and simulated traffic wear. Sulfur induced fumes, dusts and runoff products were collected under a variety of in-service simulated environmental conditions including high temperatures, actinic light (UV radiation), simulated traffic wear, freeze-thaw cycling, rainfall, biological weathering, etc. These evaluations were made using two separate but complementary studies.

(a) Exposure to the elements of large scale (maximum surface area) pavement slabs.

(b) Analysis of runoff generated in simulated in-service conditions. In the first study (item a) slabs of pavement materials were exposed over a six month period including summer and winter months during which they experienced the combined effects of daily and seasonal temperature fluctuations, actinic light and rainfall. In the second study, small scale samples were evaluated using hydrolysis and mass balance techniques following exposure to each of the following four types of weathering conditions:

(a) High temperature
(b) UV radiation
(c) Freeze thaw
(d) Biological weathering

Seven mix designs numbered MD-1, 2, 3, 6, 7, 8 and 9 as given in Table 11 were used in these tests.

3.1.3.1 Exposure of Large Scale (Maximum Surface Area) Pavement Slabs

The temperature, actinic light and rainfall conditions were achieved by exposing slabs of selective mix designs on the roof of the six-story Soil and Crop Sciences, Entomology Center on the Texas A&M campus (Fig 13). The slabs were 2 ft. (61 cm) x 3 ft. (91.5 cm) x 2 in. (5 cm) thick cast into wooden frames, lines with aluminum to prevent any interaction between the wood and mixture ingredients.

A clear plastic box 1 ft. (30.5 cm) x 2 ft. (61 cm) x 0.5 ft. (15.3 cm) deep with a 2 in. (5 cm) diameter vent was constructed to fit over the slabs and provide a constant volume, controlled environment for emissions monitoring. Two 3.8 in. (1 cm) diameter ports (Fig 14) were drilled into the side of the box opposite from the vent to be used for sampling H_2S and SO_2 respectively. Air samples were monitored using Interscan monitoring devices. The vent was fitted with a 2 in. (5 cm) diameter x 39 in. (1 m)

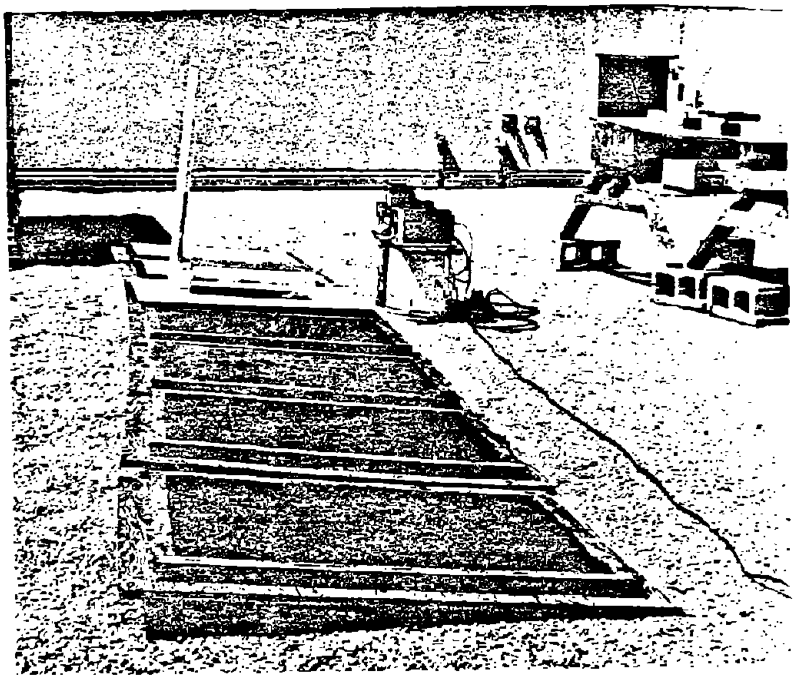


Figure 13. Pavement Slabs Under Exposure to the Elements for Weathering Studies.

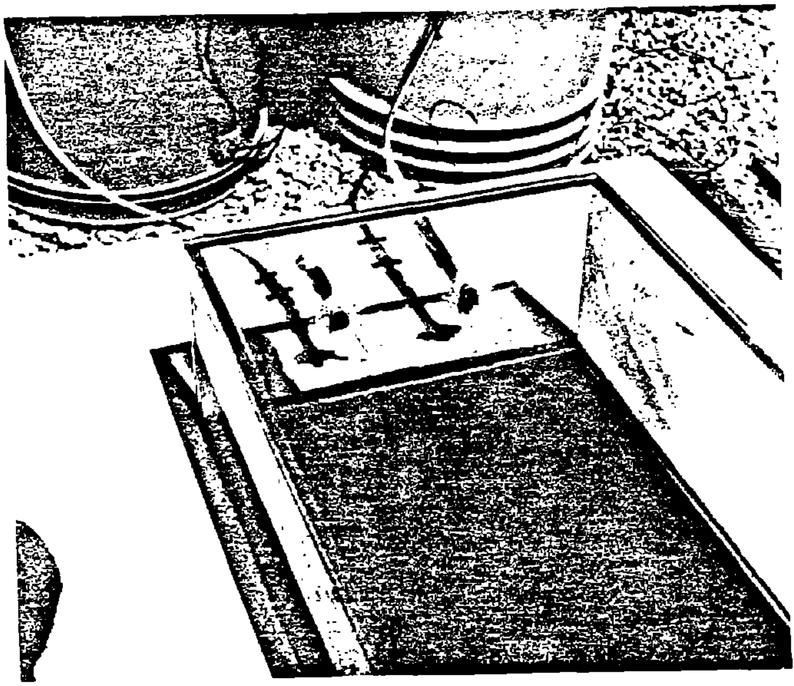


Figure 14. Exhaust Ports for Sampling H_2S and SO_2

long polyethylene stand pipe. This was to assure that air being drawn through the vent was not contaminated by emissions from adjacent slabs.

Surface temperature were measured using a copper-constantin thermocouple (Fig 15). Intimate contact between thermocouple and slab surface was maintained using transparent tape. After installation of the thermocouples, the plastic box, fitted with a white card board boarder, was placed over each slab and the surface temperature allowed to equilibrate. Outlets were combined then split 3 ways such that one air stream was drawn through an H_2S meter, one through an SO_2 meter, and the other through a series of refrigerated solvent traps. Air was drawn with a vacuum pump over the specimen surface, through each meter and solvent traps at a constant flow rate of 1 liter/min. Flow rates were controlled with calibrated flowmeters. The test set up is shown in Figure 16 with a close-up of the monitoring equipment shown in Figure 17.

Volatilized constituents were measured with respect to surface temperature and time following environmental exposure using 7 of the 9 mix designs given in Table 11. Measurements were made between 2 and 4 pm so as to effect a maximized surface temperature relative to daily and seasonal air temperature variability. A few air samples were drawn during the morning hours for evaluation at the lower surface temperatures.

A geometrically progressive sampling interval was employed to evaluate volatilized components with respect to time. Time-zero corresponded to initial sampling of air volatiles following exposure of pavement materials immediately after placement on the roof. Successive samples were collected at 1, 2, 4, 12 and 36 week intervals (June through December 1979).

Figure 15. Location of Thermocouple for Surface Temperature Measurements.

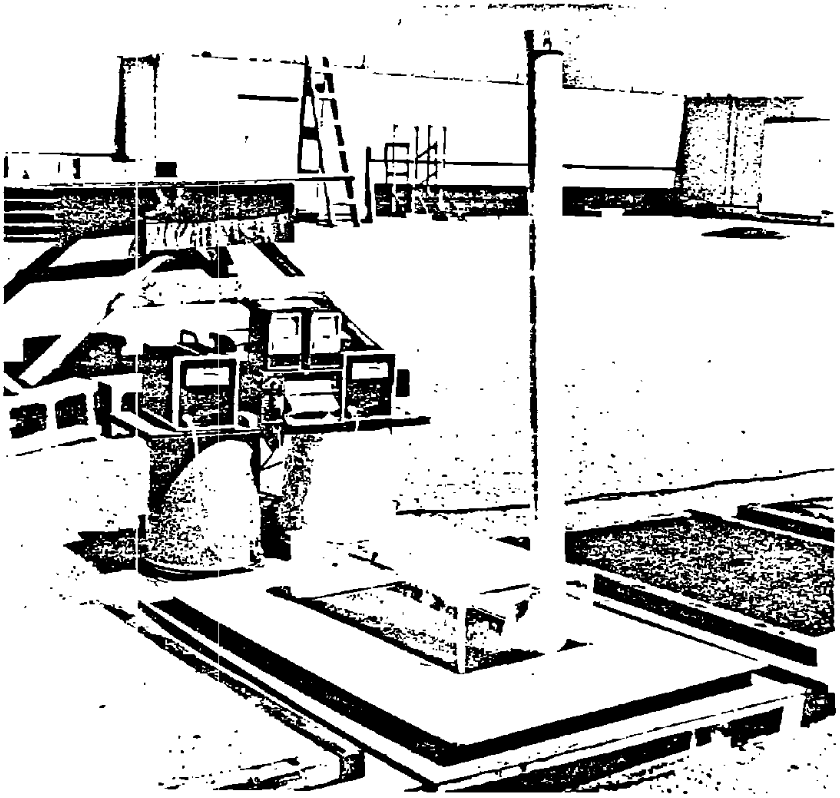


Figure 16. Weathering Test set-up for Exposure of Large Scale Pavement Slabs

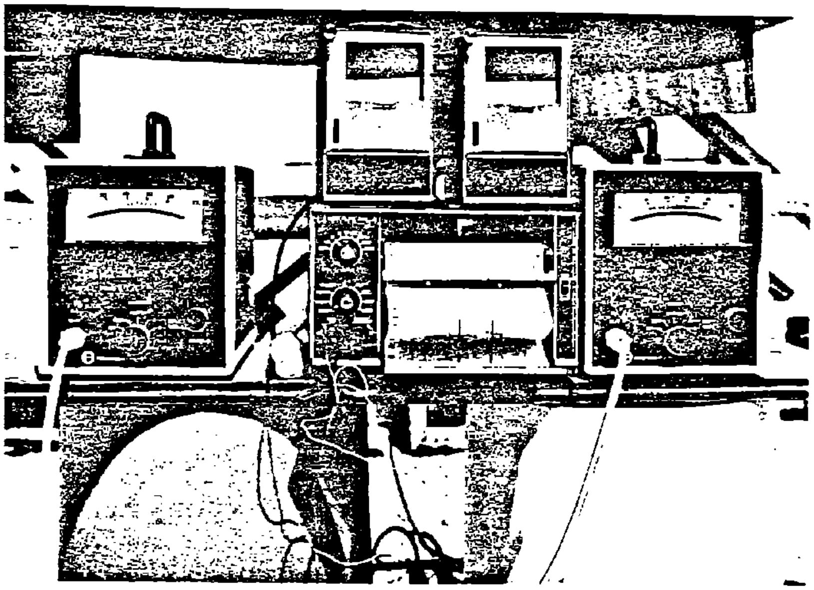


Figure 17. Close up of H_2S and SO_2 Monitoring Equipment Used In Weathering Studies.

Slab temperatures were monitored by continuously monitoring the output of the copper-constatin thermocouples. Output was calibrated against a mercury thermometer over temperatures ranging from 50°F to 212°F (10°C to 100°C), the range of surface temperatures anticipated.

H_2S and SO_2 emissions were monitored in ppm using Interscan Models 1176 and 1248, respectively. The meters were equipped with continuous strip chart recorders and were calibrated against commercially available span gases. Air samples drawn through refrigerated hexane traps were systematically screened by gas chromatographic analysis using a Tracor Model 550 GC equipped with flame ionization, and sulfur-specific flame photometric detector systems.

Solvents were dried over anhydrous Na_2SO_4 and reduced in volume by vacuum distillation prior to GC analysis. Generally, a 2.5 to 3.0 μ-liter sample was injected onto a 1/4 in. (0.6 cm) diameter x 6 ft. (183 cm) column packed with commercially available 3% OV-1 on 80/100 mesh gas chrom Q. Column temperatures were programmed to span between 86 and 464°F (30 and 240°C) at a 2.2°F/min (4°C/min.) rate. Detector response was measured by electronic integration of peak area. Integration units (IU) were assessed quantitatively by comparison with known quantities of reference material chromatographed at the same instrument settings. Analytical quality control was assured statistically by comparison of detector response to repeated injection of know hydrocarbons varying widely in molecular structure.

Inorganic and organic samples analyses were adjusted for background air quality as necessary. Meter readings in ppm by volume were normalized to volume at standard temperature and pressure to calculate moles of the respective gases volatilized relative to the total liters of air exhanged in the volatilization chamber. Vapor flux values were calculated by dividing the total gas evolved in milligrams by the surface area in square meters and the sampling time interval in hours.

Surface Temperature

The volatilization study was instigated during the first week of June 1979 and continued through the hot summer months to maximize the effect of surface temperature. Placement of the plastic box over the pavement resulted in a 15°F (8°C) increase in surface temperature due to a "greenhouse effect". Surface temperatures for the sulfur asphalt slabs generally ranged from 172 to 189°F (78 to 87°C), during the summer months, with the box in place. The maximum temperature recorded for the sulfur concrete material was 163°F (73°C) and 154°F (68°C) for sulfur concrete modified with dicyclopentadiene. Throughout the test, the surface temperature of DCPD-modified concrete was about 15 to 18°F (8 to 10°) cooler than the unmodified surface concrete.

Inorganic Sulfur Fumes

Once the box was placed on a slab specimen, the temperature recorder was turned on to determine an equilibrated maximum surface temperature. During the equilibration period, air flows were set through the meters and solvent traps without the volatilization chamber in line. Following the adjustment of flow rates to 1 liter/min., the background concentrations of H_2S and SO_2 were measured. Generally, pavement temperature was equilibrated to a maximum within 10 to 15 minutes, at which time the volatilization chamber was connected to the air flow lines.

A typical pattern for H_2S evolution continuously monitored with respect to time is shown in Figure 18. The concentration rose quickly to a maximum and then diminished to much lower levels, often that of the background air drawn into the volatilization chamber. The decline in concentration was attributed to a decrease in surface temperature as the cooler air passed over it. The pattern also suggests that vapor flux values, ultimately calculated from the total μ-liter gas evolved, are inflated due to permeation into a closed system.

H_2S and SO_2 vapor flux with respect to time for an asphalt pavement with no added sulfur is given in Table 19. The data demonstrate a relatively small net flux from sulfur-asphalt mixes. The same asphalt was used in the sulfur-asphalt systems. Corresponding vapor flux values for mix designs with approximately 2% added sulfur are given in Tables 20, 21, and 22 for the AAS-Limestone (MD-1), SEA-Limestone (MD-7), and SEA-Open graded (MD-2) systems, respectively. All demonstrated initially higher H_2S vapor flux over that of the asphalt pavement. Only the initial SO_2- vapor flux for the AAS-Limestone (MD-1) and AAS-Sand (MD-3) systems (Tables 20 and 23) exceeded that of the control, (MD-6) material (Table 19). Vapor flux for both H_2S and SO_2 was diminished to base detection levels within 2 to 4 weeks following placement on the roof. Flux values measured during the morning hours were either too low for meter detection or at the sensitivity level. Sensitivities level. Sensitivities varied somewhat, depending upon the surge characteristics of the scan as developed from continuous recording of the detector response. However, it should be noted that lower morning vapor flux values reflect the correspondingly lower surface temperatures as compared to that achieved in the afternoon sun.

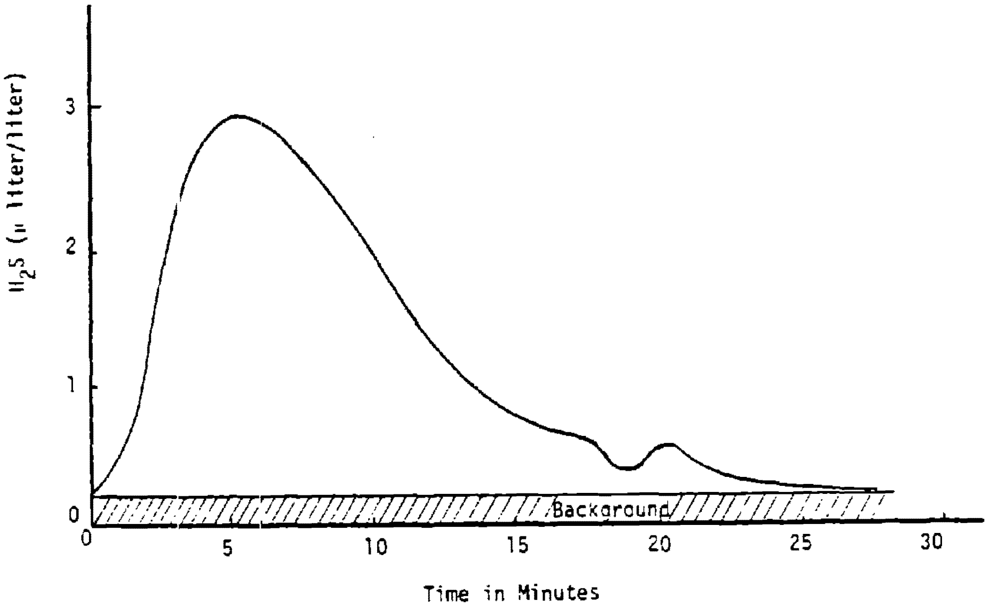


Figure 18. Typical Pattern of H_2S Evolution as Continuously Recorded with Respect to Time.

Table 19. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for MD-6 (See Table 11, page 39).

Time	Surface Temperature	Vapor Flux H_2S	Vapor Flux SO_2
weeks	°F (°C)	μg/m²/hour	
0	167 (75)	38.7	153
1	176 (80)	37.8	142
2	176 (80)	<37.8	< 74
4	172 (78)	ND	ND
12	169 (76)	ND	ND
24	86 (30)	ND	ND

Table 20. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for MD-1 (See Table 11, page 39).

Time	Surface Temperature		Vapor Flux H_2S	Vapor Flux SO_2
weeks	°F	(°C)	µg/m^2/hour	
0	181	(83)	262	352
1	181	(83)	119	140
2	185	(85)	75	69
4	178	(81)	< 37.7	< 71
12	172	(78)	ND	ND
24	86	(30)	ND	ND

Table 21. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for MD-7 (See Table 11, page 39).

Time [1/]	Surface Temperature		Vapor Flux H_2S	Vapor Flux SO_2
weeks	°F	(°C)	µg/m^2/hour	
0	181	(83)	165	135
1	189	(87)	147	138
2 (pm)	187	(86)	75	70
(am)	154	(68)	< 39	< 70
4	185	(85)	37.1	69
12 (pm)	181	(83)	< 37.0	< 71
(am)	113	(45)	ND	ND
24	122	(50)	ND	ND

[1/] pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

Table 22. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for MD-2 (See Table 11, page 39).

Time [1/]	Surface Temperature		Vapor Flux H_2S	SO_2
weeks	°F	(°C)	µg/m^2/hour	
0	172	(78)	183	141
1	181	(83)	119	126
2	172	(78)	114	143
4 (pm)	172	(78)	< 38.2	< 73
(am)	144	(62)	ND	ND
12 (pm)	163	(73)	ND	ND
(am)	115	(46)	ND	ND
24	86	(30)	ND	ND

[1/] pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

Table 23. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for MD-3 (See Table 11, page 39)

Time [1/]	Surface Temperature		Vapor Flux H_2S	SO_2
weeks	°F	(°C)	µg/m^2/hour	
0	181	(83)	955	872
1 (pm)	185	(85)	778	707
(am)	154	(68)	---	75
2 (pm)	189	(87)	637	699
(am)	169	(76)	462	435
4 (pm)	181	(83)	281	284
12 (pm)	181	(83)	150	141
(am)	158	(70)	< 39	< 74
24 (pm)	113	(45)	ND	ND

[1/] pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

The higher sulfur containing AAS-Sand mix (MD-3) produced considerably higher H_2S and SO_2 vapor flux values (Table 23). However, values were rapidly diminished to those approximating the initial flux values of asphalt alone with 12 weeks, which suggests that the vapor flux is dependent upon a surface temperature induced loss mechanism by volatilization, but that losses are finite, and materially diminished with weathering of the pavement surface.

Flux values for the sulfur concrete, perhaps best illustrate the temperature influence. Flux values for sulfur concrete and sulfur concrete plus dicyclopentadiene (Tables 24 and 25) were approximately equal in magnitude to those of the lower sulfur-asphalt pavement materials although they contained more than 10 times the total sulfur of the latter. Reduced flux values with time at comparable or higher surface temperatures demonstrated the attenuating influence of a weathered surface on H_2S and SO_2 evolved.

Organic Pollutants

At no time during the course of the volatilization study did vapors or fumes emanating from the pavement specimens exceed that of the background air quality with respect to organic or organic sulfur compounds.

At the end of 4 weeks, air samples were drawn separately for organic analysis in an attempt to increase sensitivity to organics. Thus all vapors from the chamber following temperature equilibration were passed through the refrigerated solvent traps for subsequent screening of volatile organics. A few samples were drawn into petroleum ether to determine if reduction of hexane volumes may have caused losses of more volatile organics. This effect, plus the ability to detect low levels of organics emanating in background air suggested that organics were simply not a significant constituent of the vapors drawn in the volatilization study.

Table 24. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for Sulfur Concrete - MD-8 (See Table 11, page 39).

Time[1/]	Surface Temperature		Vapor Flux H_2S	SO_2
weeks	°F	(°C)	µg/m^2/hour	
0	154	(68)	159	201
1	163	(73)	156	231
2	163	(73)	78	136
4	158	(70)	39	77
12 (pm)	163	(73)	39	73
(am)	140	(60)	ND	ND
24	79	(26)	ND	ND

[1/] pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

Table 25. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for Sulfur Concrete Modified with Dicyclopentadiene - MD-9 (See Table 11, page 39).

Time	Surface Temperature		Vapor Flux H_2S	SO_2
weeks	°F	(°C)	µg/m^2/hour	
0	142	(61)	164	232
1	154	(68)	199	300
2	153	(67)	120	150
4	144	(62)	82	115
12	140	(60)	41	77
24	79	(26)	ND	ND

Analyses of fumes during formulation temperatures for the various mix designs support these conclusions. Temperatures achieved during formulation which ranged from 250 to 350°F (121 to 177°C) exceeded the surface temperatures of the slab specimens yet resulted in comparatively low organic values relative to inorganic sulfur losses.

Although vapor flux values were still measurable up to 12 weeks following placement of the slab specimen on the roof, the impact of volatilization from these sulfur-asphalt test units was small relative to the magnitude of the flux term. It should also be noted that the samples were subjected to excessive surface temperatures, releasing fumes into a closed environment, prior to air withdrawal.

To put the magnitude of the flux values in perspective, consider that the 955 $\mu g/m^2$/hour reported for the initial H_2S from the high sulfur-asphalt blend, corresponds to a volume concentration in air of 2.6 ppm which is 50 percent of the MAC.

3.1.3.2 Analysis of Runoff Generated by Simulated In-Service Conditions

HIGH TEMPERATURE AND UV-RADIATION

Compacted specimens of the nine mix designs (MD-1 through 9) were prepared for exposure to temperature and ultra-violet (UV) light. Asphalt and sulfur-asphalt specimens were formed into 4 inch (10 cm) dia. x 3 1/2 inches (9cm) thick disc. The two sulfur concrete materials were shaped into rectangular bricks. Each formulation was made in quaduplicate. Two from each mix design were selected at random and wrapped in aluminum foil to eliminate the impact of ultra-violet light. Samples were set on a table on the roof of the Soil and Crop Sciences Building and exposed to direct sunlight for 6 months including the hot summer months (See Figure 19).

Following a 6 month exposure the outer edges of the compacted

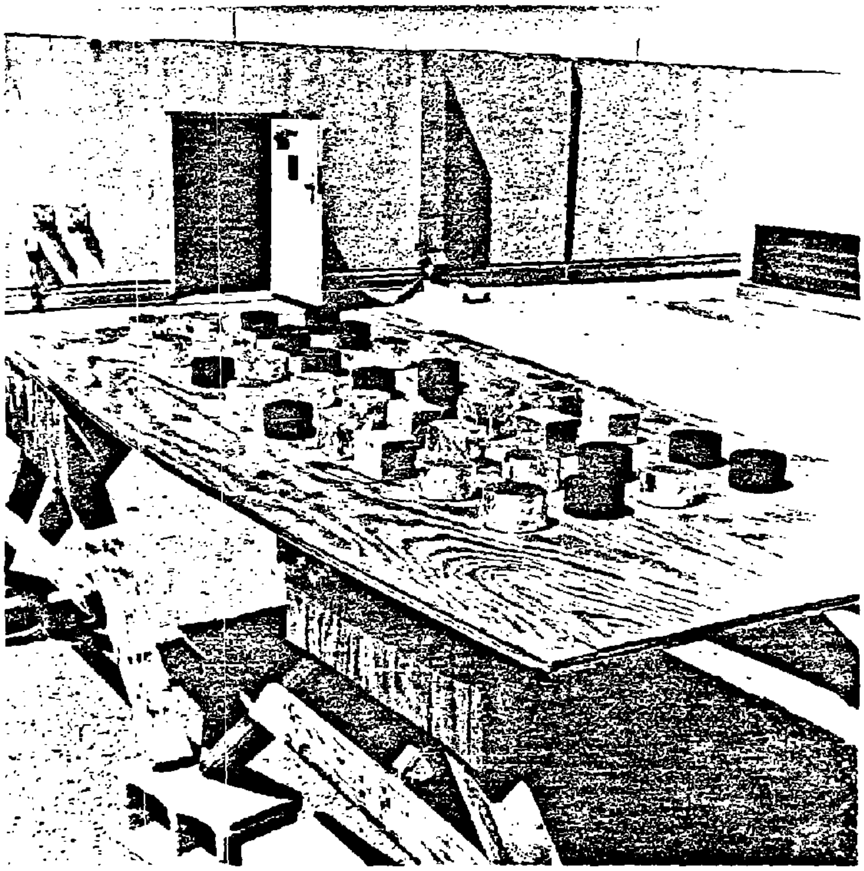


Figure 19. Samples Being Exposed to Ambient Temperature and Sunlight

specimens were chipped away using a hammer and chisel and subsequently ground in an ore crusher for total sulfur analysis. Materials were screened following the grinding process to give three size fractions; (a) that passing a 1 mm sieve (b) that retained on a 1 mm sieve but passing a 2 mm sieve, and (c) particles retained by the 2 mm sieve.

Total sulfur was determined for each mix design. Values obtained were utilized as a test statistics to determine the potential weathering affect of a combination high temperature and UV-light. In addition, the ground materials were subjected to both acid and base hydrolysis at a 187°F (86°C) reaction temperature to determine if a high temperature UV-light weathering combination resulted in subtle differences in emissions or hydrolysis products compared to laboratory control specimens.

Total sulfur relative to a particular mix design and exposure level to ultra violet radiation from full sunlight is summarized in Table 26. An Analysis of Variance (ANOVA) was carried out to aid interpreting the results. Initially, the variability between reps of sulfur concrete materials (MD-8 and MD-9) dominated as the greatest source of variation apart from MV design such that nothing could be interpreted for the sulfur-asphalt materials. A second ANOVA excluding the sulfur concrete data was determined, and results from this test given in Table 27. Results of this test show that reps were not significant, making definitive statements about the experiment relative to sulfur-asphalt possible.

Ultra violet radiation from full sunlight had no affect on the total sulfur measured. The greatest source of variation as one would expect was that of the mix design parameter due principally to the high sulfur content of AAS-Sand (MD-3) and low sulfur level of the control (MD-6). Surprisingly, results of the ANOVA revealed a UV-Light - Mix Design interaction which was statiscally significant at a 5% level. There was no distinct pattern in the data, and the only explanation for the interaction suggests that

Table 26. Total Sulfur of The Various Mix Designs Following Exposure to Full Sunlight at Normal High Surface Temperatures.

Exposure	Rep No.	Mix Design Number								
		1	2	3	4	5	6	7	8	9
		% Sulfur								
No UV-Light	1	3.1	2.0	15.1	2.4	2.8	0.4	1.6	21.0	36.3
	2	3.0	2.2	15.4	2.0	2.8	0.5	2.0	27.3	27.6
	Avg.	3.1	2.1	15.3	2.2	2.8	0.5	1.8	24.2	32.0
UV-Light	1	2.3	2.8	17.1	2.4	2.5	0.4	2.5	22.0	32.7
	2	2.6	2.3	15.8	2.9	2.4	0.4	1.5	28.4	28.8
	Avg	2.5	2.6	16.5	2.7	2.5	0.4	2.0	25.2	31.3

Table 27. Results of Analysis of Variance (ANOVA) For Mix Designs MD-1 through MD-7.

Source	Df	Sum of Squares	Mean Square	Fexp	F.01	F.05
Reps	1	0.481	0.481	4.45	9.07	4.67
Light (L)	1	0.241	0.241	2.23	9.07	4.67
Mix Design (No)	6	665.359	110.893	1026.78	4.62	2.92
LxMD	6	2.129	0.355	3.28	4.62	2.92
Error	14	1.398	0.108			
Total	27	670.144				

the samples randomly selected for exposure to sunlight had a slightly higher total sulfur content when processed.

Ground materials subjected to both acid and base hydrolysis reacted the same as the laboratory control samples, suggesting that actinic light gives no added inducement towards hydrolysis, or the effects are to subtle for the technique employed. The assessment was made relative to H_2S emission levels. No organics were detected in emissions trapped in refrigerated solvents, or dichloromethan extracts of filtered hydrolysates.

FREEZE-THAW TESTS

Compacted specimens for the 9 mix designs were subjected to the weathering impact of freeze-thaw cycling (ASTM C-666). The temperature of the cycle ranged from 0(-18) to 40°F (4°C), with each specimen subjected to a total of 100 cycles at 6 cycles per day.

Following the final thaw, the water used as the surrounding matrix was filtered and extracted by separatory funnel partitioning into 15% diethyl ether-dichloromethane. Extracts were dried over anhydrous Na_2SO_4 and reduced in volume to a very low volume then taken up to approximately 2ml with benezene. Aliquots were analyzed by gas chromatography using both flame ionization (FID) and flame photometric (FPD) detector systems.

The outer edges of the sample beam were chipped away from the bulk sample, ground to pass a 1 mm mesh sieve, and subsequently subsampled for total sulfur analysis. Subsamples were also subjected to acid base hydrolysis reactions to determine if freeze-thaw weathering results in enhanced chemical weatherability.

FID and FPD scans of freeze-thaw leachate waters partioned finally into benzene are given in Figures 20 and 28, for MD-1 through MD-9, respectively. Detector response to hydrocarbons (FID scans) suggests at first glance that there are significant quantities solubilized by freeze-thaw weathering. However,

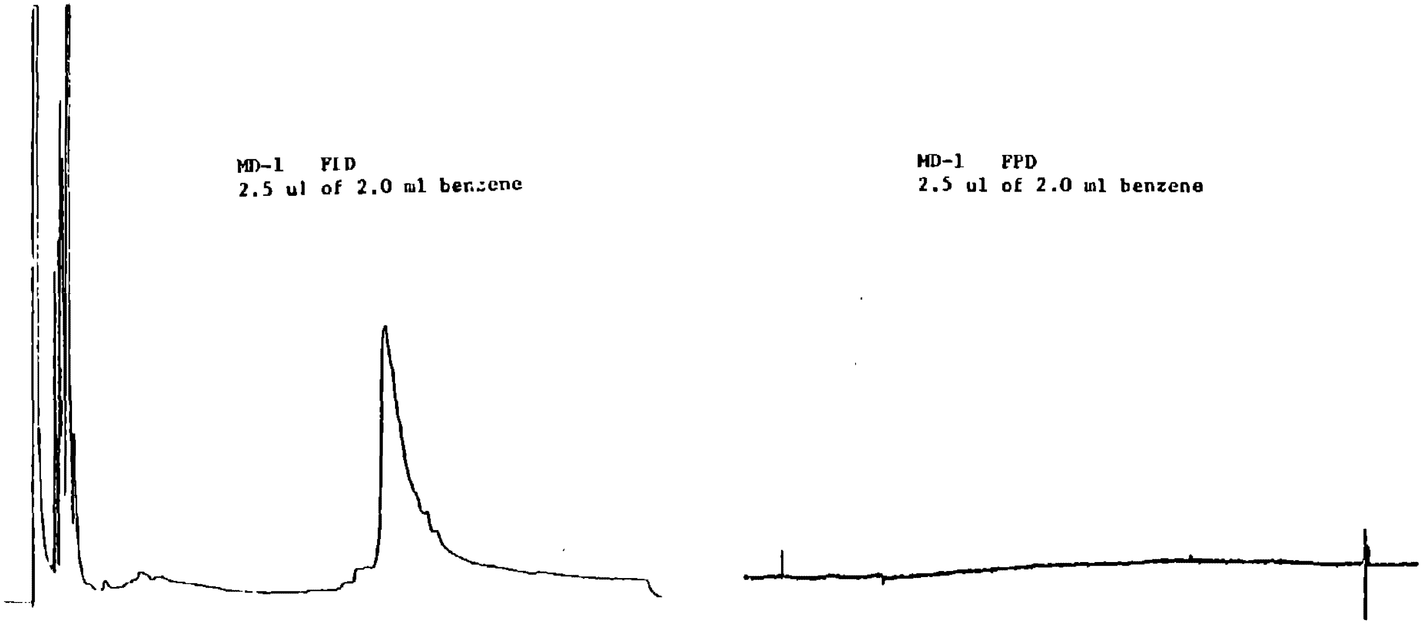


Figure 20. FID and FPD Scans for MD-1 Freeze-Thaw Leachates.

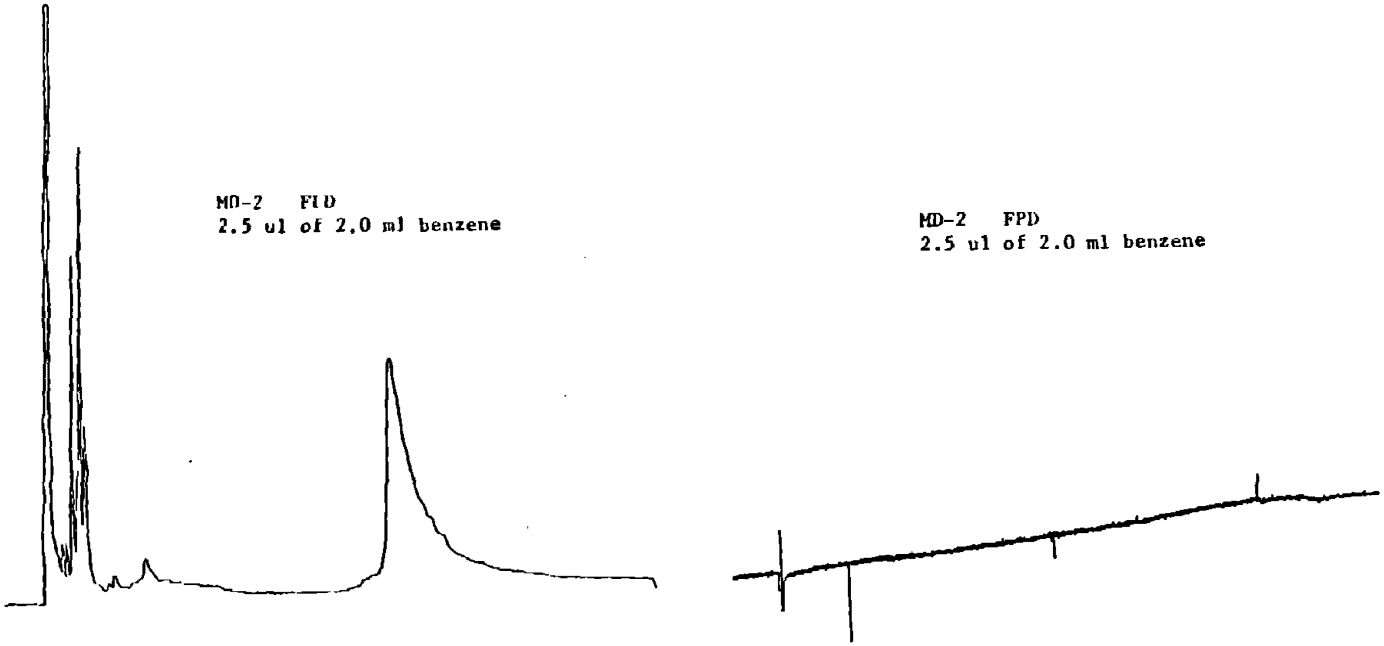


Figure 21. FID and FPD Scans for MD-2 Freeze-Thaw Leachates.

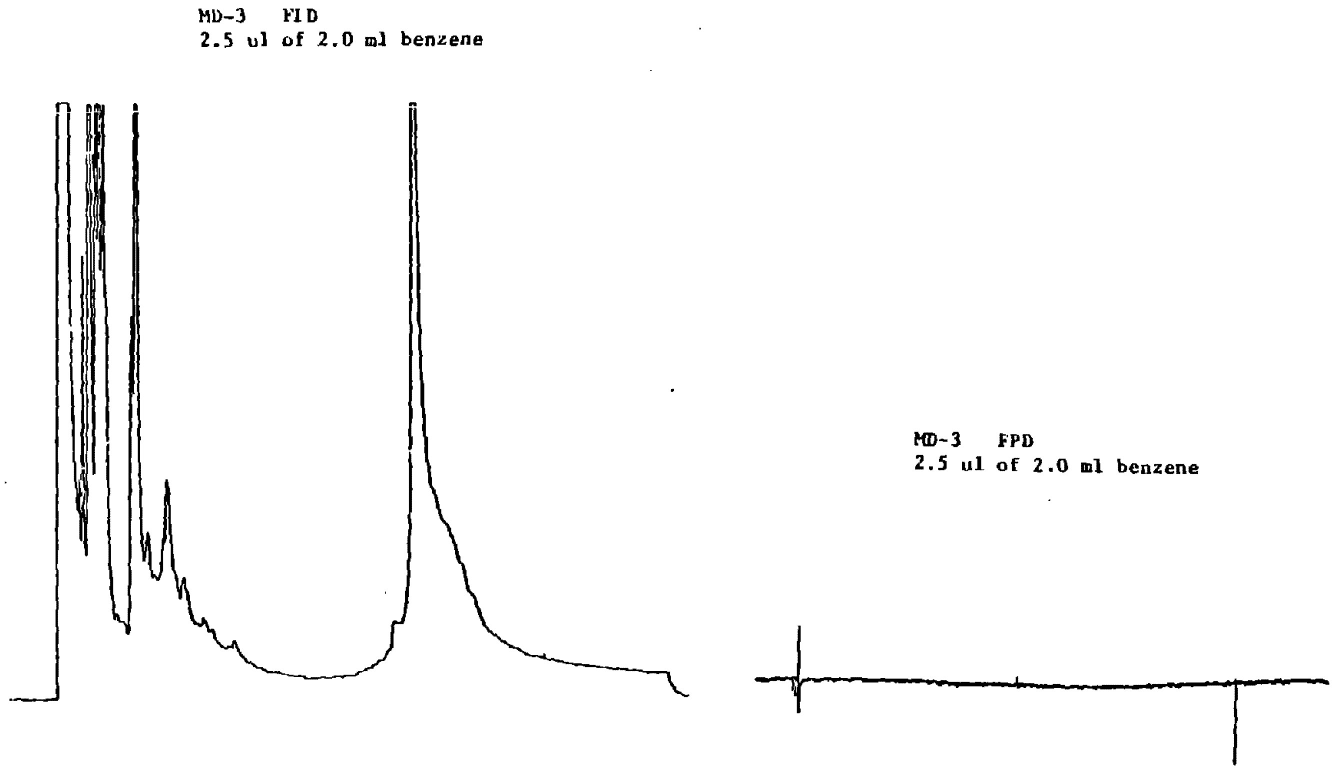


Figure 22. FID and FPD Scans for MD-3 Freeze-Thaw Leachates.

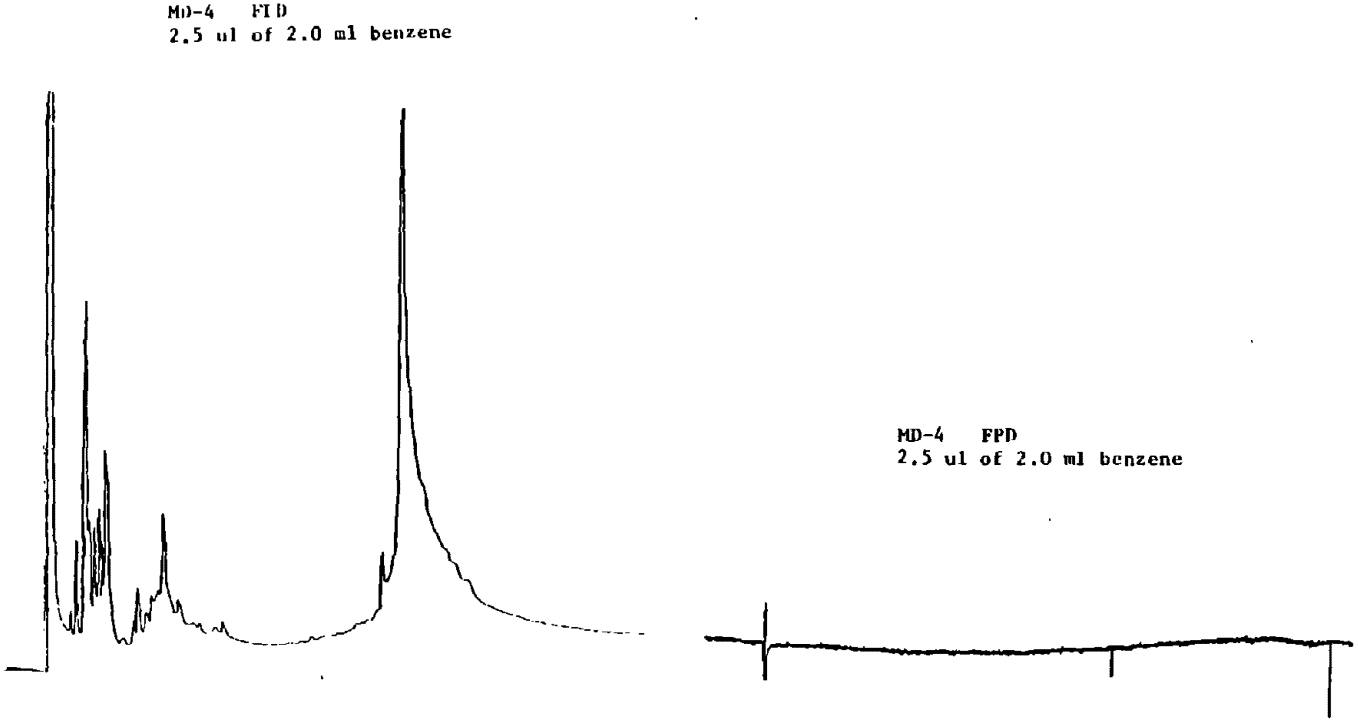


Figure 23. FID and FPD Scans for MD-4 Freeze-Thaw Leachates.

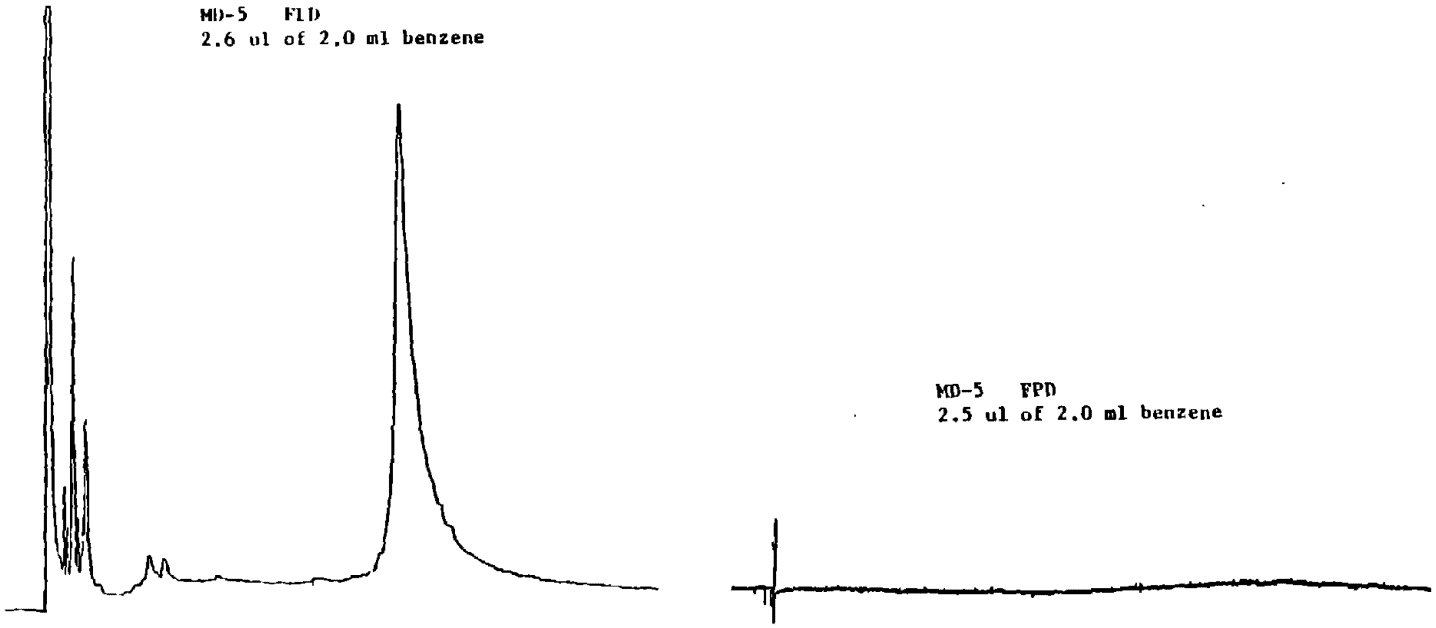


Figure 24. FID and FPD Scans for MD-5 Freeze-Thaw Leachates.

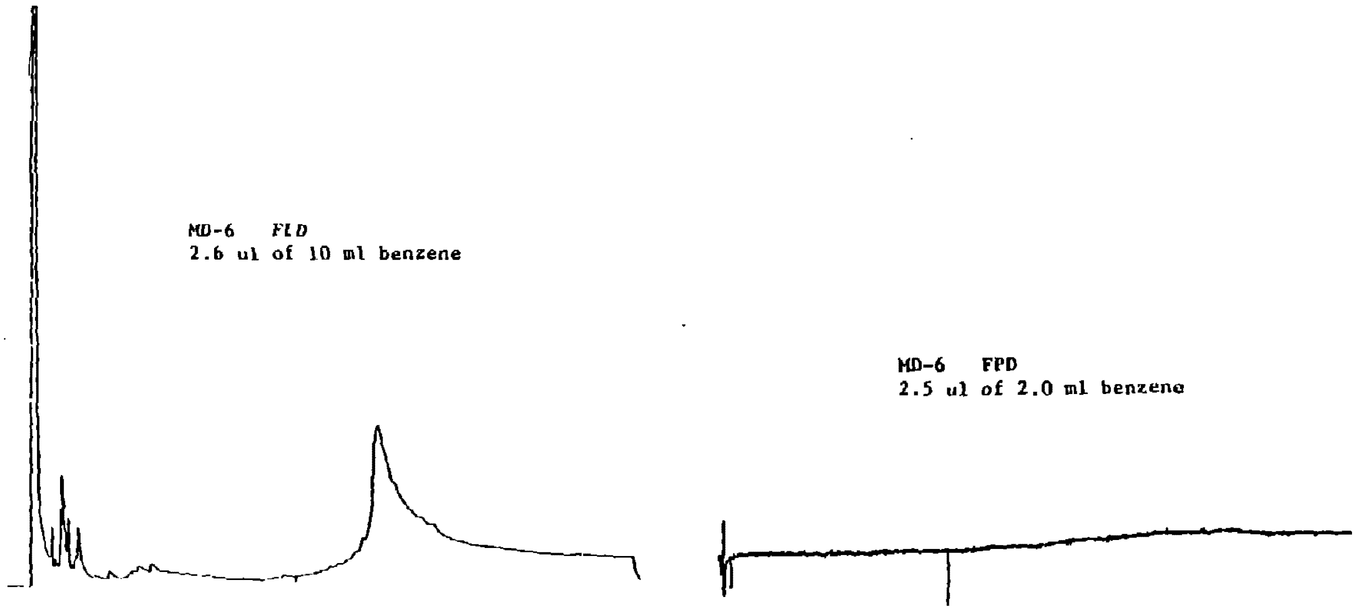


Figure 25. FID and FPD Scans for MD-6 Freeze-Thaw Leachates.

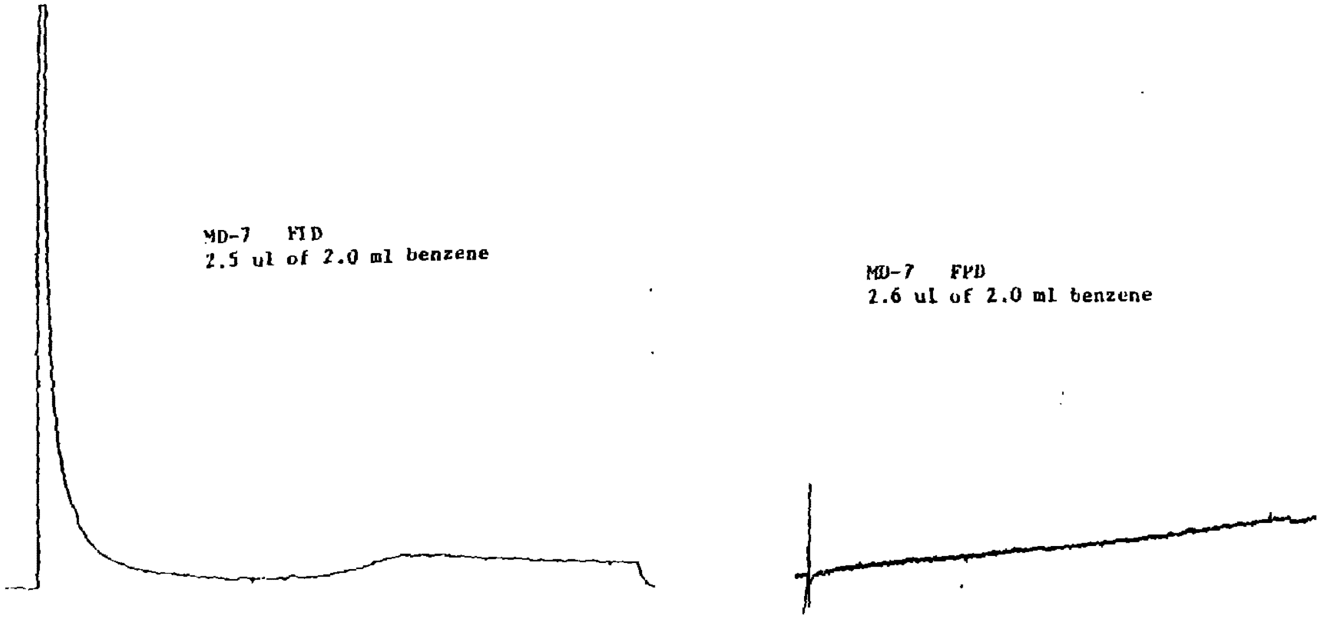


Figure 26. FID and FPD Scans for MD-7 Freeze-Thaw Leachates

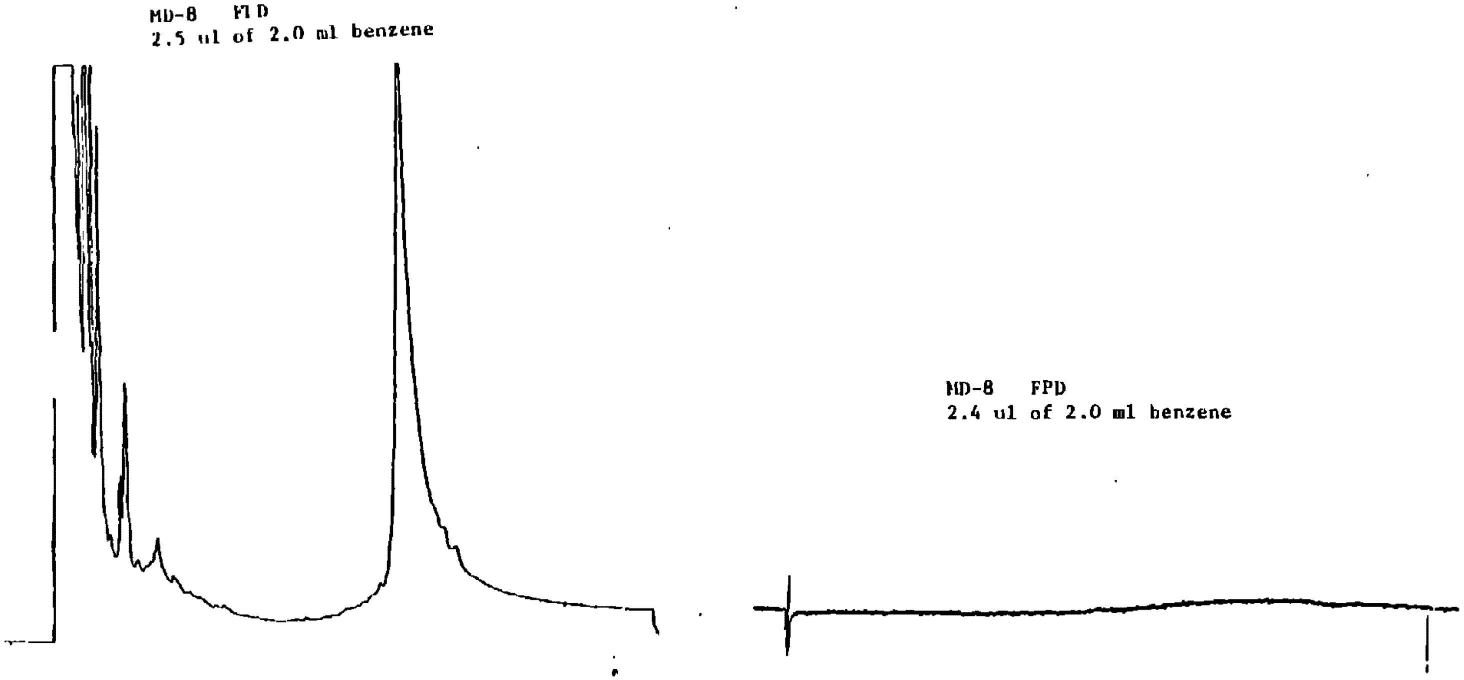


Figure 27. FID and FPD Scans for MD-8 Freeze-Thaw Leachates.

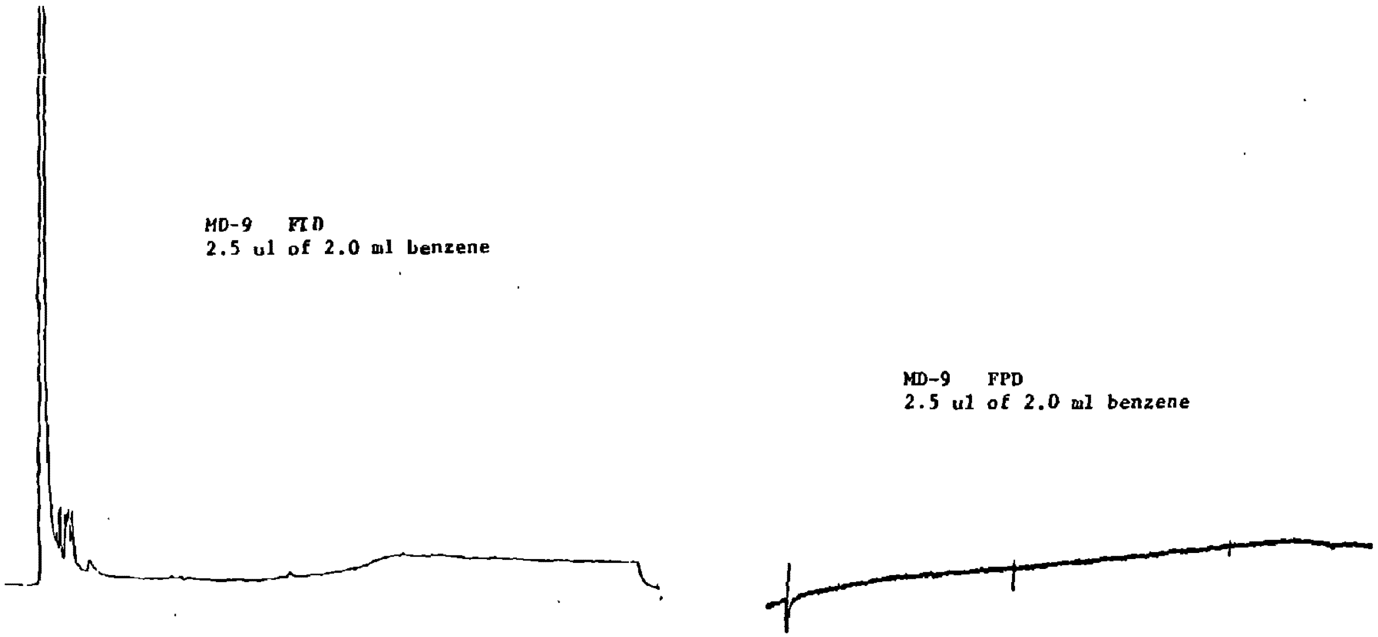


Figure 28. FID and FPD Scans for MD-9 Freeze-Thaw Leachates.

contamination appears to be a more logical explanation, due to the fact that even the sulfur concrete materials with no asphalt added reflected a significant FID detector response. FPD scans revealed that they hydrocarbons were not sulfur containing.

Samples chipped from the freeze-thaw beams and subjected to both acid and base hydrolysis reactions did not show any FID response. further supporting the conclusion that the leachate organics were actually freeze-thaw sample container contaminates and not sample constituents.

A total sulfur analysis (Table 28) suggested that there was no loss of sulfur from the sample following the multiple freeze-thaw weathering sequence.

Table 28. Total Sulfur Content of Compacted Specimens Following Freeze-Thaw Weathering.

	Mix Design								
	1	2	3	4	5	6	7	8	9
	% Sulfur								
Rep 1	3.12	2.90	17.0	1.87	3.02	0.42	2.02	25.44	18.62
Rep 2	2.68	1.56	15.7	1.98	2.42	0.57	1.93	22.50	18.90
Avg.	2.90	2.23	16.4	1.93	2.72	0.50	1.98	24.0	18.8

The difference between total sulfur values reported for MD-9 in the UV-light, high temperature study reported in Table 26, and those for the freeze-thaw test given in Table 28, resulted from sample treatment. Although materials from both studies were ground to pass a 1 mm mesh sieve, the freeze-thaw samples were ground to a powder prior to subsampling for total sulfur analyses. Rock fragments may have been excluded when subsampled in the previous study (Table 26) skewing the matrix towards sulfur particles, as indicated by a comparison to total sulfur reported for the MD-9 formulation.

With the exception for exhaust fumes which, it was felt, would have negligible effect on a sulfur-asphalt pavement, all the other conditions would manifest themselves in the creation of fine particles of dust through erosion or friction. This dust would eventually be blown by the wind or carried by rainfall run-off from the pavement to the soils or streams in the vicinity of the road.

It was decided that this dust could be created in the laboratory by grinding the test samples of the various mix design into 200 mesh particles and subjecting them to hydrolysis. The results generated would appear to be similar to those generated in the Freeze-Thaw tests. Since the basic ingredient being taken-off the road is elemental sulfur. The leaching effect on the rainwater would only have an effect on soils which have a low buffering capability. This can be offset by lime treatments. The potential for biological degradation is discussed in the next section.

SIMULATED TRAFFIC EFFECTS

There are numerous test apparatus which have been devised to evaluate pavement materials under simulated traffic conditions. The ensuing evaluations are usually made with respect to the materials structural integrity(i.e. rutting, fatigue life, etc). However, to the authors' knowledge no such test exists for specially evaluating the effect of traffic on the environment. The factors resulting from traffic which would impact the environment include:

(a) Skidding
(b) Snow plow friction
(c) Tire - pavement interaction
(d) Exhaust fumes

CHEMICAL HYDROLYSIS

Compacted specimens of the various mix designs were ground to pass a 2 mm mesh sieve. A 5 g sample was placed in a 500 ml reaction vessel, followed by 300 ml of pH 10 water. These extremes were selected as maximum potential weathering environments via chemical hydrolysis, that could result on the surface of an in-service pavement. The reaction vessel was heated to 185°F (85°C). Once the temperature was attained the hydrolysate solution was degassed with an airstream controlled at 1 liter/minute and continuous stirring. The airstream was passed through an H_2S meter.

Hydrolysate solution was filtered, and extracted, with 1:1 (v:v) acetone: benzene by a separatory partioning technique. The benzene layer was washed with deionized water to remove traces of acetone. Benzene was then reduced in volume and subsequently screened for hydrocarbons, and sulfur containing hydrocarbons by gas chromatography utilizing flame ionization and flame photometric detectors, respectively.

Filtered residues were analyzed for total sulfur using the LECO induction furnace to convert sulfur to SO_2 followed by idometric filtration of the SO_2.

A study was conducted to determine H_2S emissions as a function of time, pH and mix design at 185°F (85°C). This temperature corresponds to the maximum surface temperature measured for asphalt, and sulfur asphalt mats exposed to the elements in the volatilization study. The time factor was evaluated in ten minute intervals once the test temperature was attained. Results are summarized in Table 29 and 30. An

Table 29. H_2S Emissions as a Function of Mix Design, pH and Time.

		Mix Design [2]					
Solution pH	Time[1] (Min.)	1	2	3	4	5	6
				ppm $H_2.S$ [3]			
2.45	t_0	0.2	1.7	0.1	0.2	1.0	0.0
2.45	t_{10}	0.4	1.8	0.1	0.4	1.0	0.1
2.45	t_{20}	0.4	2.1	0.2	0.5	1.3	0.1
2.45	t30	0.3	1.4	0.2	0.5	1.5	0.1
10.7	t_0	4.4	2.7	8.7	0.7	5.5	0.2
10.7	t10	4.2	3.0	9.6	1.2	6.1	0.4
10.7	t_{20}	4.0	3.2	9.4	1.1	5.7	0.4
10.7	t_{30}	4.1	2.2	8.9	1.0	6.0	0.7

[1] t_0 taken at point where vapor T = 85°C

[2] Average of two determinations.

[3] For mix design details see progress report No. 6.

Table 30. ANOVA for H_2S as a Function of Mix Design, pH and Time at 185°F (85°C)

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Exponent F
pH	1	249.94	249.94	614**
Mix Design (MD)	5	222.29	44.46	109**
time (t)	3	1.10	0.37	0.91
pH x MD	5	224.4	44.88	110**
pH x t	3	0.44	0.14	0.36
MD x t	15	2.33	0.14	0.37
pH x MD x t	15	0.81	0.05	0.13
Error	48	19.51	0.41	
Total	95	720.72		

** Significant at the 1% level.

analysis of variance (ANOVA) revealed that mix design and pH had a highly significant affect on the H_2S measured, as shown in Table 30. Time of measurement was not a significant factor. A highly significant interaction occurred between pH and mix design, suggesting a neutralization reaction of the acidic media with the limestone aggregate. Equilibrium pH measurements on the hydrolysates support this premise. Mix Design 4, hydrolyzed in pH 2.45 acid solution, reacted to give an equilibrium pH of 7.55. Hydrolysis in a pH 10.7 base resulted in a hydrolysate pH of 8.7. There was very little difference in H_2S emission for MD-4 at 185°F (85°C) with respect to pH of hydrolyzing solution. This is shown in Table 31 with its associated ANOVA given in Table 32. Conversely a significant difference results in H_2S emissions for MD-3 between pH 2.45 and 10.7. Equilibrium pH values were 2.7 and 7.1, following hydrolysis in pH 2.45 and pH 10.7 solutions, respectively.

These data suggest that hydrolysis reactions may have some long term affect on sulfur-asphalt pavement. However, the effect tends to be mitigated by the aggregate system such that one would not expect environmentally significant quantities of sulfur emanating from sulfur-asphalt via chemical hydrolysis.

Analysis of hydrolysates by gas chromatographic techniques revealed that no organics were solubilized by hydrolysis reactions in either pH 2.45 or pH 10.7 water at a reaction temperature equivalent to the maximum surface temperature. Much more acidic or basic reactions, at the pavement surface, than could occur naturally would be required to induce chemical hydrolysis of sulfur asphalt pavements.

Total sulfur analysis of pavement residues, following the filtration of hydrolysates, revealed that all of the sulfur for the various mix designs was recovered in the residues. Statistically comparing mean values for percent total sulfur in the mix designs with corresponding values determined for the residues following hydrolysis using a paired t-test revealed no difference in the means. This suggests that

Table 31. H_2S Emissions as a Function of Mix Designs and pH.

Solution pH	Mix Design* 1	2	3	4	5	6
	H_2S ppm					
2.45	0.3	1.7	0.4	0.4	1.4	0.1
5.98	1.4	1.4	2.6	0.6	3.3	0.2
10.70	4.0	3.1	10.6	1.1	7.5	0.6

* Average of two determinations.

Table 32. ANOVA for H_2S as a Function of Mix Design and pH.

Source of Variation	Degree of Freedom	Sum of Squares	Mean Square	Exponent F
Between pH	2	110.44	55.22	448**
Between Mix Design	5	93.76	18.75	152**
Interaction	10	82.69	8.27	67**
Error	18	2.22	0.12	
Total	35	289.12		

** Significant at the 1% level.

the H_2S lost during hydrolysis was too low in magnitude to materially affect the total sulfur composition of the mix designs during the reaction time interval employed in this experiment.

3.1.3. 3 Biological Weathering

The various mix designs were ground to pass a 1 mm mesh sieve and incorporated into a 100 g fresh soil matrix to determine potential biological degradation. Degradation was followed by CO_2 evolution over a 90 day incubation period.

Soil was maintained at a field capacity moisuture level throughout the experiment. Field capacity is considered an optimum moisture level for soil microbial activity. The soil employed for this test was a sandy loam, which has a high native fertility, although low in nitrogen. No nitrogen was added in this study to better simulate natural conditions.

Biological degradation estimated as cumulative CO_2 evolved is given for the various mix designs in Table 33. The data suggest that sulfur tends to increase the biological activity of the soil. It should be noted that the material may behave quite differently had nitrogen been added to the system.

Although the experimental design tends to maximize the effects of biological degradation, it is certainly a plausible mechanism which will need further study at a field level. There are micro-organisms common to all soils which can utilize sulfur as an energy source. It is suggested from these data that soil microbes may be extremely important in the overall long term weathering of sulfur asphalt paving materials.

Weathering of in-service pavements by naturally occurring conditions should have no measurable impact on the environment, as assessed by simulated laboratory and relatively short term outdoor exposure studies.

Table 33. CO_2 Evolved from Asphalt, Sulfur/Asphalt and Sulfur Concrete Materials Incorporated into a Soil Matrix.

Mix Design	Cumulative CO_2 Evolved
	Mg
MD-1	194
MD-2	171
MD-3	149
MD-4	311
MD-5	373
MD-6	105
MD-7	136
MD-9	366
Soil Blank	183

3.1.4. Simulated Fire Tests

A number of samples approximately 3 x 4 x 1/2-inch thick (75 x 100 x 13 mm) were prepared from all of the sulfur mixtures for flamability tests in accordance with ASTM-D1692. Test specimens of sulfur, sulfur concrete, sulfur with DCPD, sulfur concrete with DCPD, sand-asphalt-sulfur and sulfur extended asphalt were exposed directly to a flame for a period of sixty seconds after which the flame was removed. While in contact with the flame, the sulfur and the sulfur concrete tended to melt, with only the foamed residue (intumescence) burning. Both samples, however, self extinguished when the flame was removed. The sulfur with DCPD also melted but the intumescent material burned more readily and continued to burn until the sample was totally consumed. The sand-asphalt-sulfur and sulfur extended asphalt samples burned with the evolution of a considerable amount of black smoke while in contact with the flame from the burner. When the flame was removed the smoke was reduced after about 6 seconds and both materials self extinguished. As expected, H_2S and SO_2 gases were emitted to a level beyond the range of the monitoring instruments (100 ppm) while maintaining direct flame contact, but reduced to trace levels within 10 seconds after the flame was removed and the temperature of the surface cooled.

A sample of asphalt cement was also exposed to direct flame. The sample did ignite and continued to smolder until the ash was created. The black smoke was generated in the asphalt samples but not in the pure sulfur sample. Only the sulfur containing samples emitted H_2S and SO_2. It was noticed that the presence of aggregate slowed the burning, and in all but the sulfur concrete with DCPD actually created a self extinguishing element.

It was concluded that barring any direct flame contact with a sulfur-asphalt or sulfur concrete, the surface would not readily ignite. Except for the DCPD sulfur concrete, none of the systems tested sustained a burn once the burner flame was removed. However, assuming ignition did take place the burning surface would self extinguish with only local environmental impact. Treatment of sulfur fires is discussed in the Field Evaluation Plan - Volume II.

Compacted specimens were also subjected to another laboratory simulated fire test using the controlled environment set-up given in Figure 29. It became clear on the initial test that the Interscan gas monitors were inadequate to measure the levels of H_2S and SO_2 emitted. Therefore the concentrations of these gases were monitored using a commercially available Drager appartus. A natural gas flame was used, and the flame tip placed on the specimen throughout each trial.

Organics were trapped in refrigerated hexane using a minumum 2 trap series. Contents of both traps were combined, dried over anhydrous Na_2SO_4, and reduced in volume by vacuum distillation prior to FID and FPD gas chromatographic analyses.

Compacted specimens resulted in a much different distribution of inorganic sulfur than anticipated, particularly with respect to the H_2S and SO_2 levels (Table 34). Neither H_2S and SO_2 were detected by Drager tube analysis of the asphalt control material (MD-6). Both sulfur concrete MD-8 and 9 produced extremely high concentrations of SO_2 relative to the sulfur-asphalt systems. H_2S was generated in the DCPD-modified material but not in the unmodified sulfur concrete.

Table 34. H_2S and SO_2 Concentrations Emitted during a Simulated Burn.

Sulfur Specie	Mix Design								
	1	2	3	4	5	6	7	8	9
	Concentration, ppm								
H_2S	25	18	350	75	25	0	20	0	25
SO_2	100	47	750	65	25	0	30	2800	3400

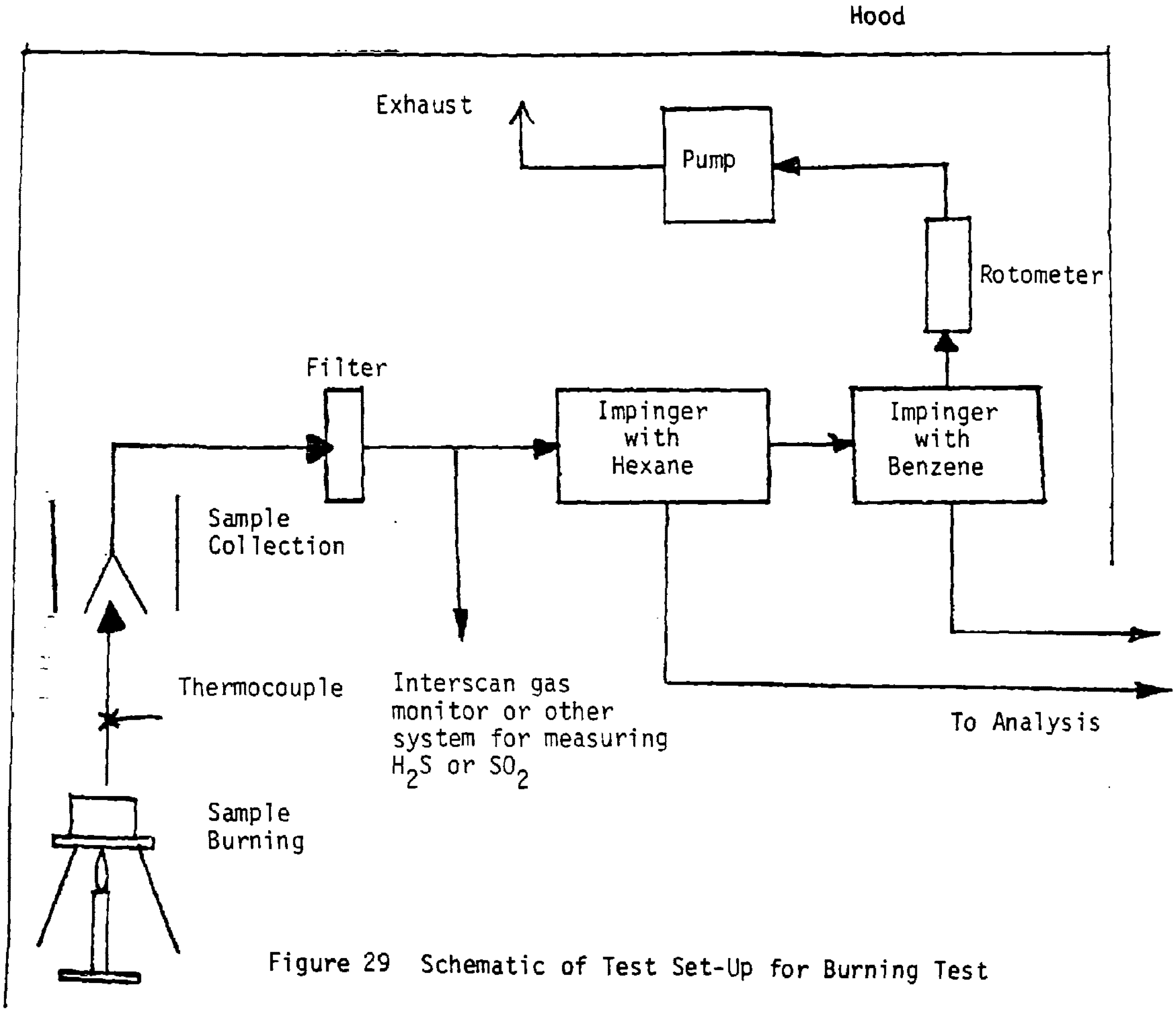


Figure 29 Schematic of Test Set-Up for Burning Test

Sulfur-asphalt materials, with the exception of the MD-3 design resulted in surprisingly low gaseous sulfur values, but with proportionally higher H_2S levels than anticipated. The high sulfur containing pavement (MD-3) and the sulfur concrete speciemsn (MD-8 and MD-9) yielded much higher SO_2 levels, with only MD-3 resulting in a significant H_2S level. The asphalt matrix definitely reduced sulfur emissions.

Attempts to recover particulate sulfur were completely frustrated due to immediate deposition on cooler surfaces of the apparatus glassware. Therefore a material sulfur balance was not attempted.

Although it was impossible to quantitate total organic emissions, FID scans revealed significant emissions for the sulfur asphalt pavements. Comparison of organic emissions trapped for MD-3 and MD-6 suggested that elemental sulfur mixed with asphalt does not materially affect the nature of the organics released on burning (Figure 30). Sulfur alone dominated the FPD scans, and is demonstrated in Figure 31, for a 1 to 10 dilution MD-3.

Although dense fumes were noticeable throughout the test, low levels of organics actually trapped in refrigerated solvent indicated an inadequate design of the test procedure. However, attempts to modify the system were completely thwarted by the physical nature of the fumes. Apparently the organics emitted were occluded with or onto sulfur particulates.

3.1.5 Simulated Spills

Compacted specimens of the asphalt and sulfur paving materials (Mix Designs 1 through 7) were fragmented into particles retained on a 2 mm sieve. Ten gram samples of each material were then placed in glass columns and leached with 100 ml saturaged NaCl at an elution rate of 4 ml per minute. Leachates were acidified to pH 6 and extracted by a separating funnel partition technique into benzene using 2.50 ml volumes of the latter. Benzene extracts were combined, dried over anhydrous Na_2SO_4, reduced in volume and subsequently analyzed by gas chromatography using both FID and FPD detector systems.

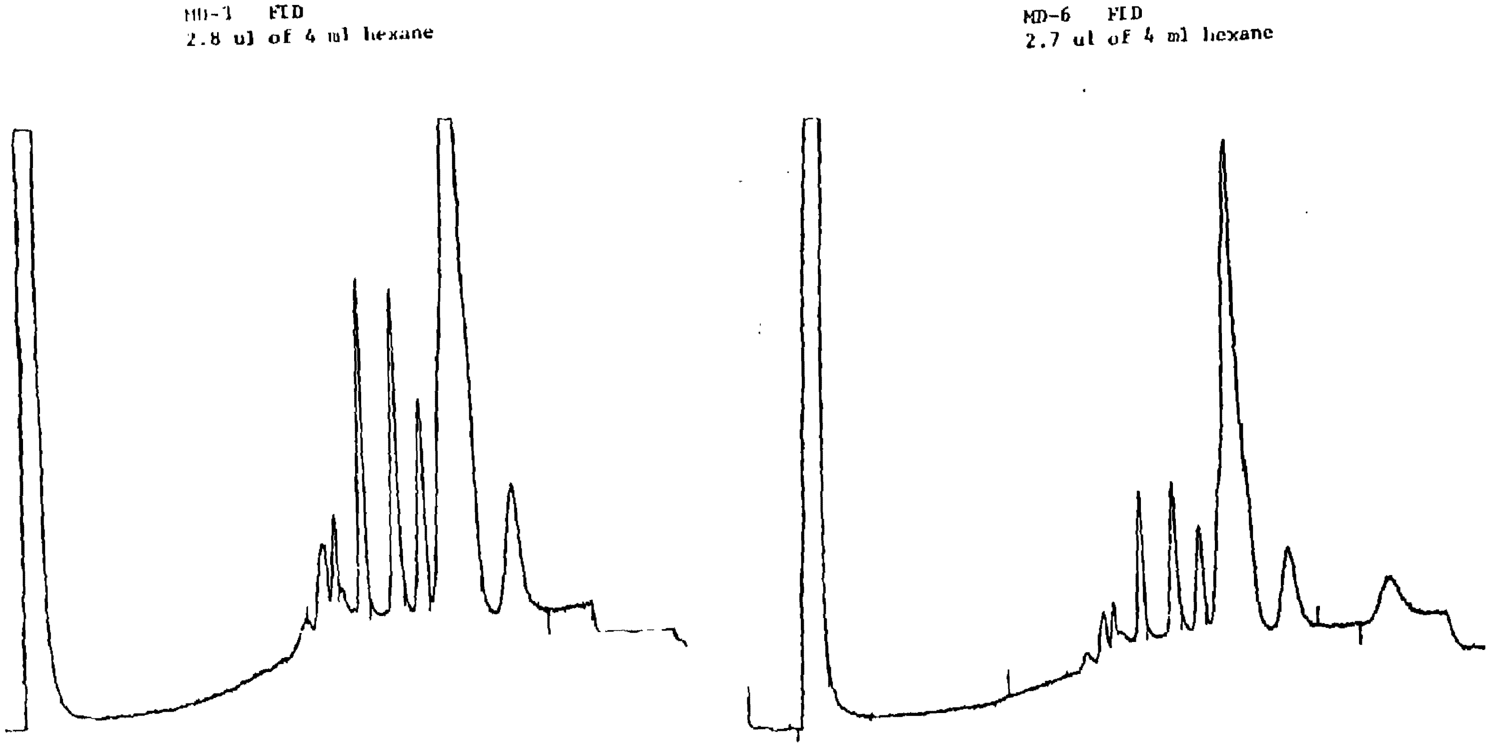


Figure 30. FID Scans of Emissions Generated on Burning Compacted Specimens of MD-3 and MD-6.

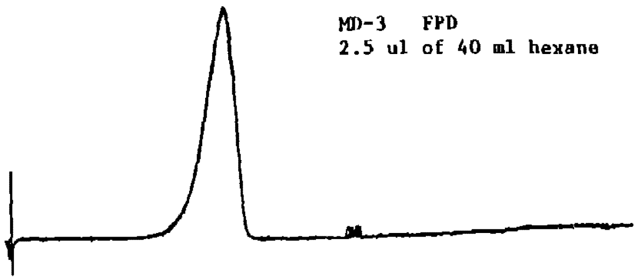


Figure 31. FPD Scan of Emissions Generated on Burning a Compacted Specimens of MD-3.

A separate 10g subsamples was leached with a 100 ml volume of nanograde quality iso-octane. Iso-octane extracts were simply dried over anhydrous Na_2SO_4 and analyzed by gas chromatography using both FID and FPD detector systems.

Saturated NaCl leach solution was used to simulate the affect of potential brines from deicing salts on sulfur-asphalt paving materials. FID scans of leachates (Figure 32) generated showed absolutely no organics were stripped from either asphalt or sulfur-asphalt materials with the column leach technique employed. The peaks showing up in several of the scans were found to be contaminates of the Na_2SO_4 used to dry the benzene extract. The elemental sulfur blank is designated as such. Straight line chromatograms were obtained in the FPD mode on analyses of the brine leach for sulfur containing components. The use of fractured pavement specimens in the test gave a much larger surface area than an intact pavement, and maximize the effectiveness of the brine leach on a comparative basis. One can only conclude from these results that brine of saturated deicing salts would have a minimal impact on run-off waters emanating from sulfur-asphalt or asphalt pavements.

Simulated gasoline spills, using iso-octane as a leach solvent, revealed that this may leach elemental sulfur from contacted surface materials (Figure 33 through 40). This is based on the fact that sulfur shows up on FPD detection with no commensurate peak in the FID model. The impact of a gasoline spill will of course be lessened with an intact compacted pavement surface. However, the fact remains that organic solvents or naptha mixtures will solubilize free sulfur.

The data suggests that a much longer contact time than that afforded by the column leach technique employed would be required to solubilize significant asphalt borne organics.

3.1.6 Effect of Dicyclopentadiene (DCPD) on H_2S and SO_2 Emissions From Sulfur Concrete Mixes

Dicyclopentadiene (DCPD) is one of the primary additives currently being used to plastize sulfur for use as a binder in sulfur concretes. The examination of gas evolution associated with the presence of DCPD in the system should be considered from

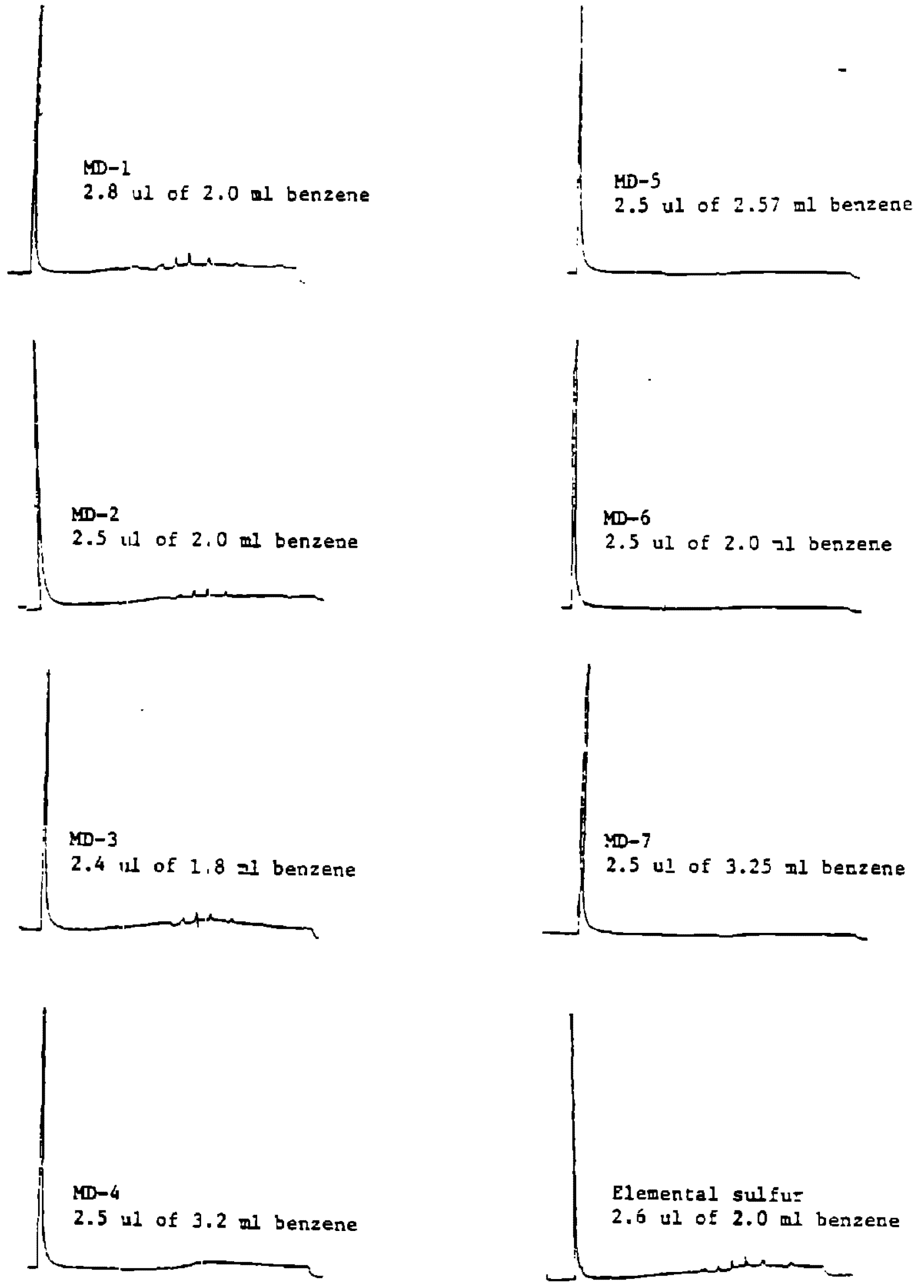


Figure 32. FID Scans of Fragmented Paving Materials Leached with Saturated NaCl.

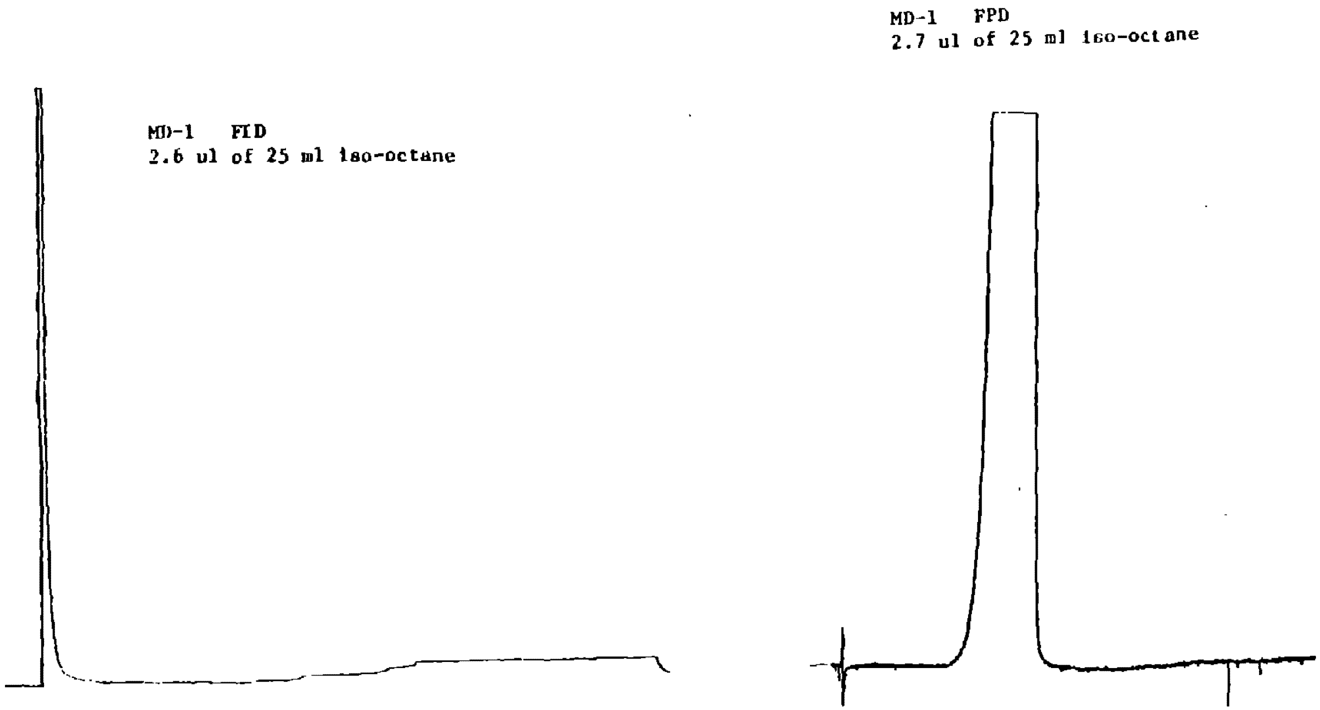


Figure 33. FID and FPD Scans of Fragmented MD-1 Paving Material Leached with Iso-Octane.

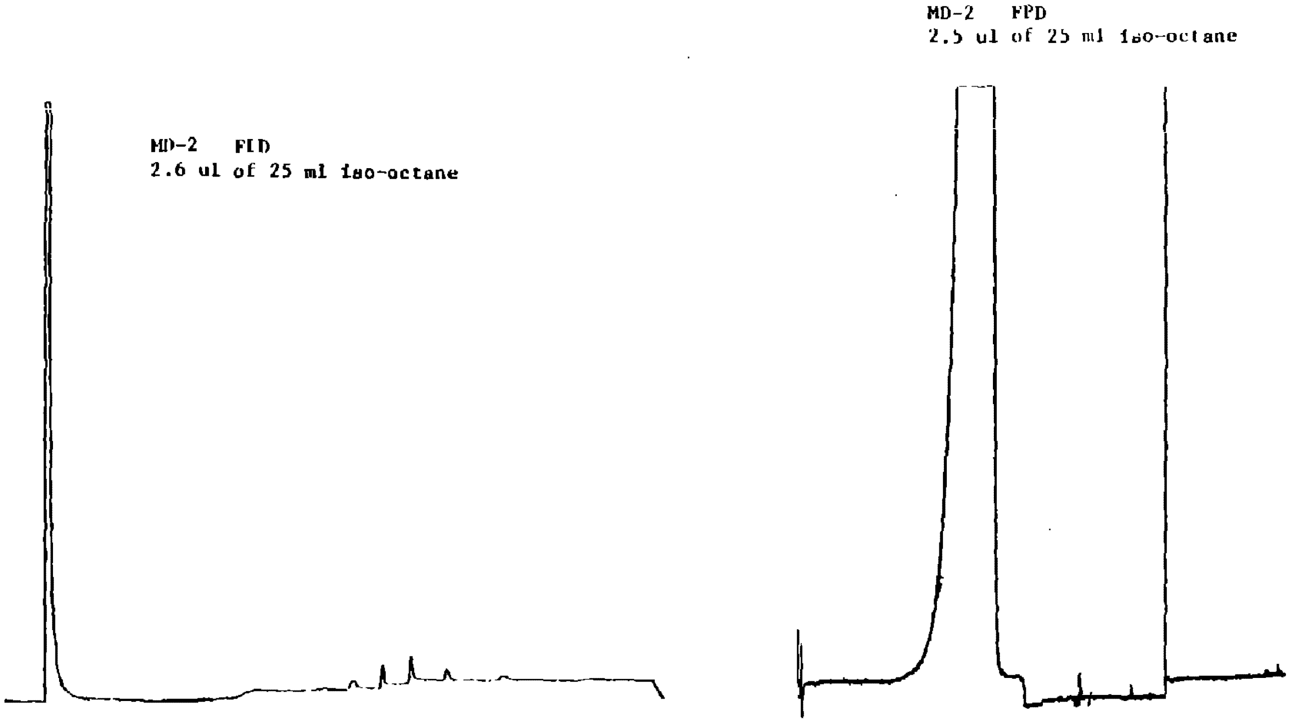


Figure 34. FID and FPD Scans of Fragmented MD-2 Paving Material Leached with Iso-Octane.

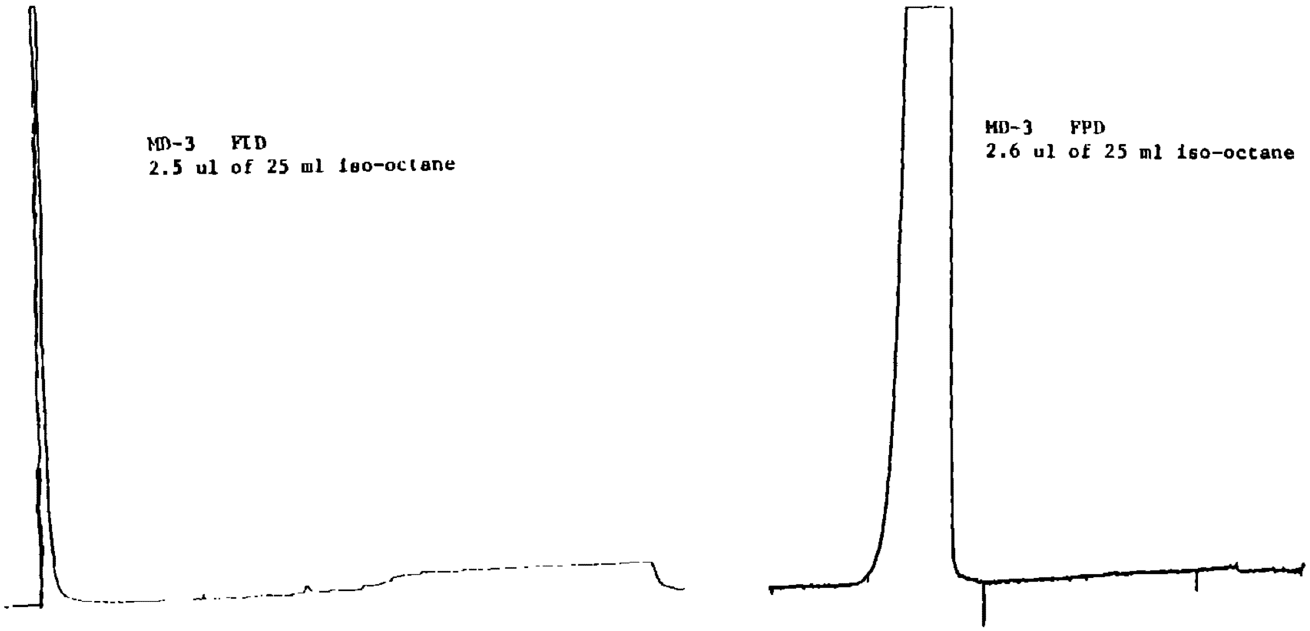


Figure 35. FID and FPD Scans of Fragmented MD-3 Paving Material Leached with Iso-Octane.

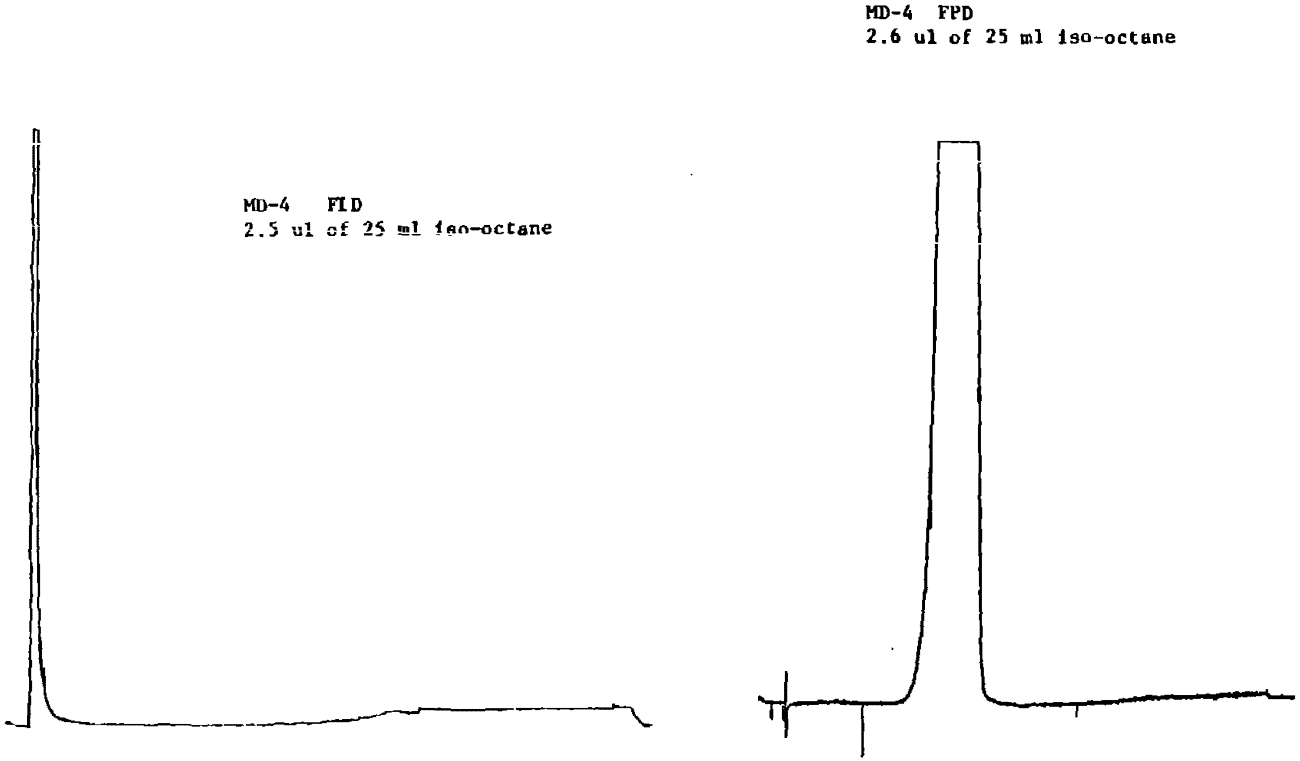


Figure 36. FID and FPD Scans of Fragmented MD-4 Paving Material Leached with Iso-Octane.

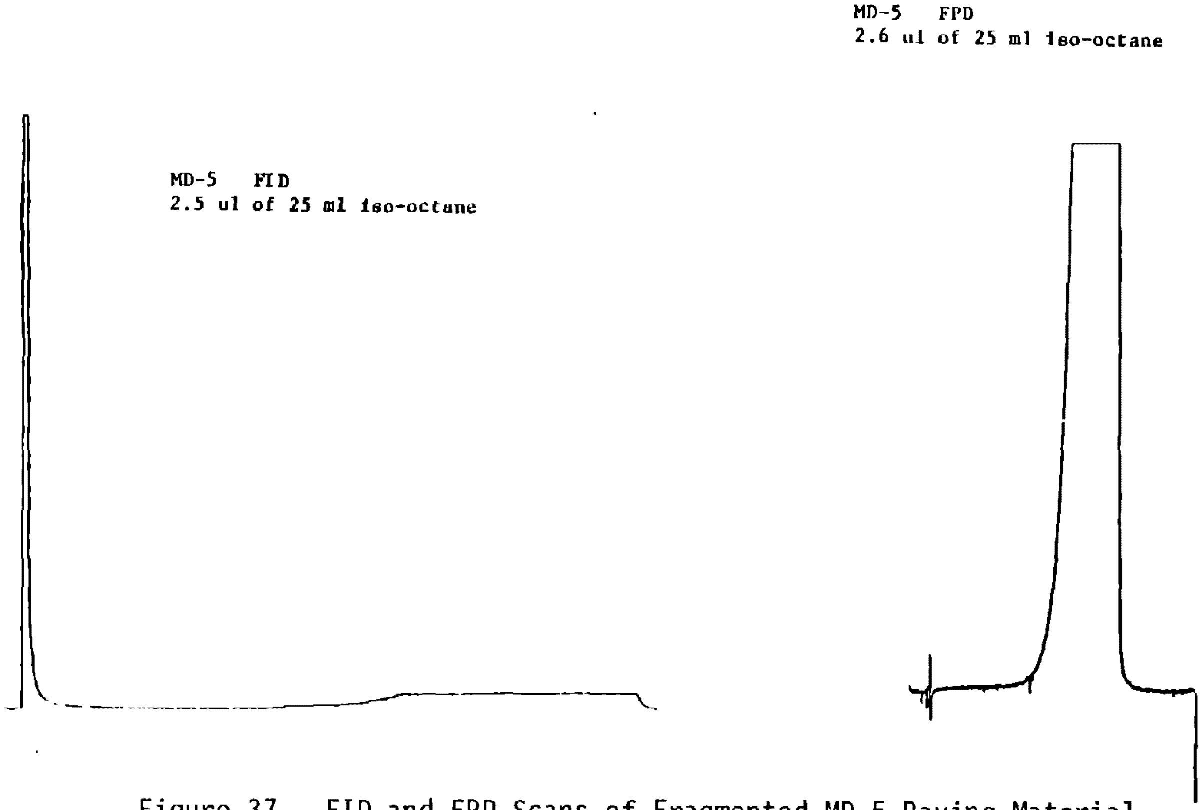


Figure 37. FID and FPD Scans of Fragmented MD-5 Paving Material Leached with Iso-Octane.

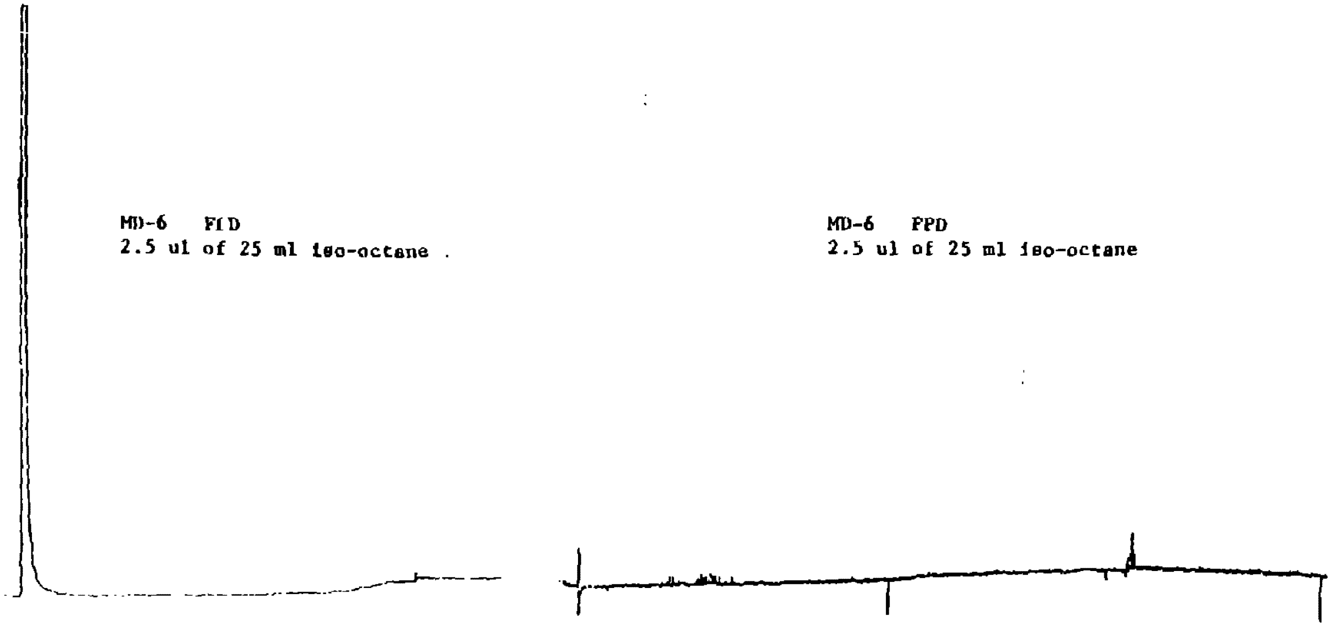


Figure 38. FID and FPD Scans of Fragmented MD-6 Paving Material Leached with Iso-Octane.

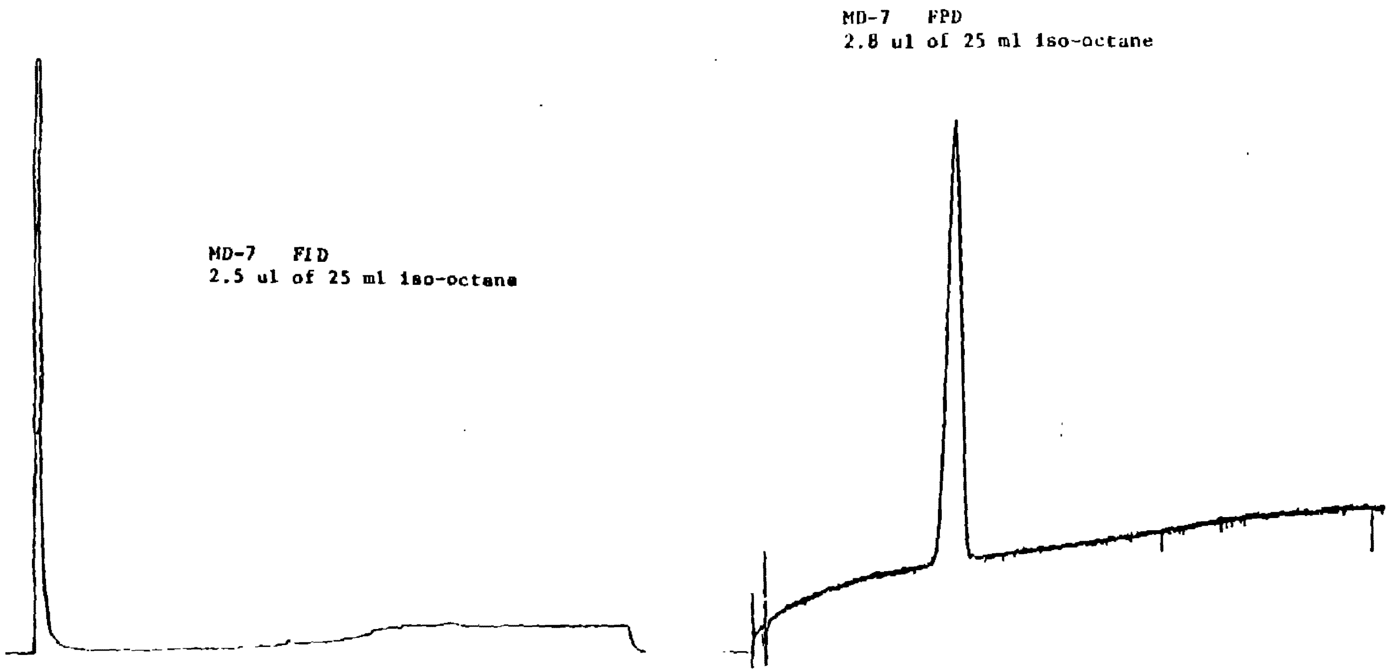


Figure 39. FID and FPD Scans of Fragmented MD-7 Paving Materials Leached with Iso-Octane.

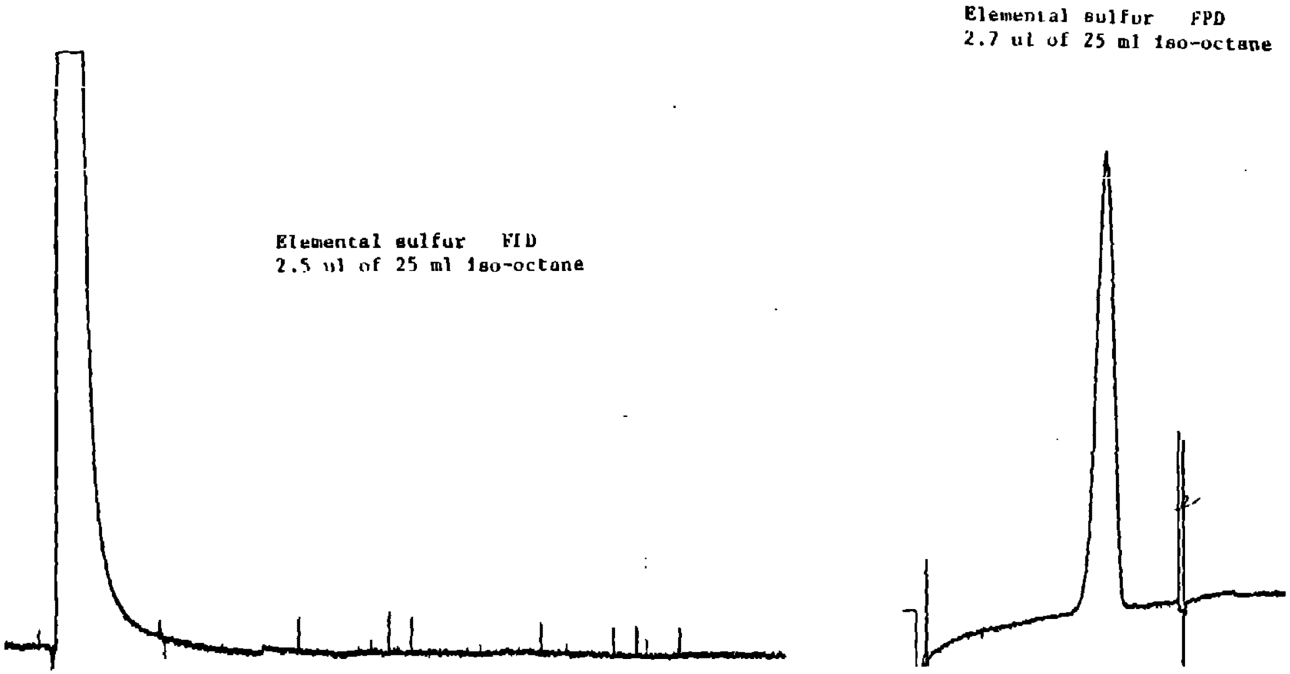


Figure 40. FID and FPD Scan of Fragmented Elemental Sulfur Leached with Iso-Octane.

two aspects; binder preparation and concrete production. In the former, the DCPD-sulfur reaction is of prime importance whereas in the latter the exposure of the binder to mixing temperatures of 250 to 350°F (121 to 177°C) is the main concern.

At the reaction temperature necessary for polymerization with sulfur 250 to 285°F (121 to 141°C), DCPD immediately depolymerizes to the cyclopentadiene (CPD) producing a highly exothermic reaction. If the exotherm is permitted to occur, the sulfur temperature can be raised to levels which may produce high levels of H_2S and SO_2. One way of controlling this reaction is to introduce the DCPD at a relatively slow rate or by premixing the DCPD and sulfur at room temperature prior to heating [19]. Another approach developed by The Bureau of Mines [20] utilizes a preblend of DCPD and its oligomer to slow down the reaction with sulfur and significantly reduce the exotherm. An in depth FHWA-sponsored research study [44] is looking into, not only H_2S and SO_2 generation, but other potentially hazardous pollutants which may be produced under the conditions that plasticized sulfur binders are processed. Therefore, the binder preparation aspect was not treated in this report.

This phase of the program dealt primarily with assessing the H_2S and SO_2 emissions generated during a typical sulfur concrete mixing operation. This was accomplished by monitoring the air space in the laboratory approximately 18 in (46 cm) over the mixing bowls using the H_2S and SO_2 Interscan monitors. Peak emissions from a DCPD-modified sulfur concrete mix (MD-9) were compared with the unmodified sulfur concrete (MD-8). The mixes were prepared at three temperatures; 250°F (121°C), 300°F (149°C) and 350°F (177°C). Total mixing time for each material never exceeded one minute. The peak dissipated after 15 seconds. The H_2S and SO_2 concentration, as measured, are shown in Table 35.

Table 35. Variation of H_2S and SO_2 Emissions with Mix Temperature Generated during Sulfur Concrete Mixing - Laboratory Environment

Gas		Temperature °F (°C)	Mix Design*	
			8	9
H_2S	5 sec.	250 (121)	Tr	1.0
	(15 sec.)		(0)	(Tr)
		300 (149)	0.8	1.1
			(Tr)	(Tr)
		350 (176)	23.1	31.2
			2.8	3.0
SO_2	5 sec.	250 (121)	Tr	Tr
	(15 sec.)		(0)	(0)
		300 (149)	Tr	1.0
			(0)	(Tr)
		350 (176)	16.8	22.3
			3.1	4.1

*Mix designs are given in Table 11, page 39

Consistent with that found for the sulfur-asphalt systems (see Table 13b), H_2S and SO_2 emissions remain at safe levels up to 300°F (149°F). Although the MAC values were exceeded for both MD-8 and MD-9 at the 350°F (177°C) temperature, they were rapidly diminished after 15 seconds of mixing. Where detectable, emissions from MD-9 were slightly higher than those generated in MD-8. It should be noted that at all temperatures, rather obnoxious odors were present during mixing which could prove objectionable to personnel. It is therefore recommended that sulfur concrete mixing be carried out at temperatures no greater than 300°F (149°C) and in well ventilated areas.

3.2 Task B - Human Safety and Environmental Aspects

3.2.1 Human Safety and Hazard Considerations

The results generated in Task A continue to support the fact that as long as sulfur-asphalt or sulfur concrete mixtures are maintained at temperatures which do not exceed 300°F (149°C) problems associated with the evolution of toxic pollutants are minimal. A more detailed treatment of the nature of the hazards and safety practices recommended for construction personnel is given in Volume II of this report.

The primary contaminants to which workers could be exposed in measurable amounts during production, placement and post construction maintenance of sulfur modified paving materials include Hydrogen Sulfide (H_2S), Sulfur Dioxide (SO_2), Sulfur Trioxide (SO_3) and particulate (elemental) sulfur. Each of these pollutants is capable of causing acute illness if the concentrations at which they exist exceed their respective Maximum Allowable Concentration (MAC) threshold. The relative toxity levels of H_2S, SO_2 and particulate sulfur have already been discussed in Section 1.1.4.

Results of Task A indicate that under normal recommended operating conditions it is unlikely that conditions could occur that would produce hazardous concentrations of SO_3 and subsequent illness. On the other hand, conditions could occur which could produce toxic levels of H_2S and SO_2. These include:

(a) Storage of hot sulfur-asphalt mixture in enclosed, poorly vented containers such as storage silos. Storage time of hot sulfur-asphalt mixes should be limited to a maximum of 4 hours. Overnight silo storage is not advised.

(b) Sulfur storage tanks can accumulate H_2S and SO_2 at concentrations well above the lethal level, and personnel working around open ports or sulfur discharge values for prolonged time periods should be equipped with a respirator.

(c) Pug Mill hoppers or feeds require periodic inspection for material "hang up" or clogging. Visual inspection by plant personnel is usually accomplished by climbing stairs or ladders to look inside the hoppers. Under certain atmospheric conditions, toxic fumes can accumulate to levels which may be hazardous to the workman.

Particulate sulfur can be generated during mixing, dumping into trucks under the pug mill, dumping into the paver hopper or the mixing action of the paver screw. Sulfur particles are carried into the air in a vapor wherein they cool and become fine sulfur dust. Except for the eyes, skin or mucosa, irritation is short term and can be prevented by wearing goggles and/or masks. Irritation is usually relieved by washing with water. Clothing recuirements for personnel who must work with hot, liquid sulfur are the same as for asphalt and is discussed in Volume II of this report.

Aside from eye or skin irritation, temporary discomfort can arise from odor. The extent of this discomfort is subjective and dependent on the specific sensitivity of each other. It is noteworthy that in communications with sulfur producers (e.g., Texas Gulf in Texas) records show that virtually no immediate or chronic illness related directly to sulfur has developed at their facility during the past 50 years.

Of the contaminants of interest, only SO_2, SO_3, and H_2S are suspected of causing chronic illness. Chronic illness due to exposure to SO_2, H_2S, or SO_3 is not expected based on the curent information available on these compounds and Task A. These results incicate that all exposures are anticipated to be at levels considerably below the maximum allowable concentration (MAC) considered acceptable for continuous exposure during an 8 hour working day.

Although sulfur-asphalt is combustible, the fire hazard associated with it is minimal. Liquid sulfur, sulfur vapor, and sulfur dust all are combustible, and fires can not be totally ignored. Although the likelihood of conditions suitable for a sulfur dust explosion is very slight this possibility should be recognized. Establishment procedures for the safe handling of liquid sulfur being used in that industry will minimize the fire and explosion hazard.

At the mix temperatures expected, asphalt will have only a minimal fire hazard associated with it. Correct safety and handling procedures are already known in the paving industry and are recommended for use on sulfur-asphalt systems, as well.

Under very extreme conditions, enclosed storage at excessive temperatures, it is theoretically possible that sufficient H_2S could be generated to form explosive mixtures with air. With adequate temperatures control, it seems very unlikely that this will occur in practice, however, all the materials involved in producing sulfur asphalt paving mixtures are heated to temperatures capable of producing a skin burn. Molten sulfur is a special problem, as improper handling could significantly increase the chances of personnel being burned.

Exposure limits for all the identified contaminants have been set by the American Conference of Governmental Industrial Hygienists (ACGIH) as threshold limit values (TLV's) and by OSHA as maximum allowable concentrations (MAC). In both cases the values for eight hours -- time weighted average (TWA) exposure are:

Contaminant	TLV
H_2S	10 ppm
SO_2	5 ppm
particulate sulfur	10 mg/m^3
asphalt fumes	2 mg/m^3
SO_3	2 mg/m^3

Although 10 ppm has been set as the TLV for H_2S by the ACGIH, the upper limit established for all of TTI's sulfur field trials programs has been set at 5 ppm.

3.2.2 Short Term Environmental Effects on Soils, Flora and Fauna

A shortage of sulfur-containing amino acids is one of the worlds most pressing problems with respect to human nutrition. Paradoxically, urban pollution is one of the most important sources of sulfur. Recent measures taken to reduce pollution have materially reduced this sulfur supply and rendered more and more soils to a sulfur deficient status. As sulfur enters the terrestrial environment, less oxidized forms will be converted to sulfates within the chemically and biologically active surface volume of aerated soils. Agronomically important soils have little capacity to absorb anions and SO_4 produced tends to be leached from the system. Acid soils tend to have adequate sulfur supplies fixed as precipitated metal sulfates. Weathered soils in humid moisture regimes are generally dependent upon sulfur containing fertilizers and sulfur pollutants to sustain supplies essential for plant growth.

It has been established that the bulk of sulfur released from the construction of sulfur-asphalt pavement materials, is inorganic sulfur. Principally the sulfur is in a free elemental form. Temperatures above 300°F (149°C) favor the formation of both H_2S and SO_2, which may exceed 500 ppm in a closed environment, such as that incurred during formulation, storage and transport. The potential hazards to human health and safety are addressed in Volume II.

The release of inorganic sulfur into the environment is most likely to occur during the paving process. Elemental sulfur released initially in a vaporous state will be rapidly cooled and condense to fine particulates. Elemental sulfur, due to its mass, will only be transported short distances via wind currents. H_2S and SO_2 released during the paving process can be transported relatively long distances since both are gases. The environmental impact of these gases are attenuated by distance transported via a dilution mechanism.

Elemental sulfur is not readily altered chemically due to insolubility in water. Elemental sulfur and its sulfides serve as electron donors for aerobic or anaerobic respiration by soil microflora with the formation of sulfates [45, 46]. Extremely acidic conditions accompany the oxidation of these reduced species, which can impart an adverse impact if the soil does not have sufficient neutralizing capacity to buffer the acidity produced. For weathered soils with insufficient buffer capacity the impact may induce aluminum and manganese concentrations toxic to sensitive agronomic crops. Soils of sufficient buffer capacity will in most cases benefit from the sulfur added. Marginal soils and those of insufficient buffer capacity can be limed by an inexpensive broadcast application to neutralize the acidity produced on oxidation of reduced sulfur.

Soils readily absorb H_2S and SO_2 gases [47, 48]. The absorption process is independent of microflora activity in soils. It had been demonstrated that SO_2 is chemically oxidized to SO_4. The reaction is not as acidifying as oxidation of the more reduced species.

The greatest potential for an adverse impact arising from sulfur-asphalt materials is from SO_2 generated during with mixing and paving process. Many oranamentals and agronomic plant species are adversely affected by relatively low concentrations of SO_2 [49-54]. However, the fact that the SO_2 generated will be rapidly dissipated and of short duration, grater reduces the potential for permanent plant damage [55]. Timing for a paving operation can also be used to lessen the potential for an adverse impact where sensitive plant species are in close proximity to the road bed. Research has shown that plants are more likely to be injured by low levels of SO_2 at high temperatures and high relative humidities [51, 56]. H_2S at the concentrations potentially emitted during the paving operation will have no adverse impact on plant communities. It has been suggested that low levels of H_2S may even be beneficial to agronomic crops [52].

Sulfur-asphalt pavements once constructed will have little impact on the environment. Gasoline spills may strip some sulfur as it runs off the pavement, but will rapidly penetrate soils such that only the road bed and adjacent soil zone would be affected. Liming materials used in the construction of road beds will more than neutralize potential acidity produced once in soil contact. The practice of stabilizing soils beyond the intended pavement surface will also negate potential acidity generated from sulfur dusts.

Large concentrations of SO_2 could result if a fire broke out following an accident, and cause damage to flora in the immediate area.

3.2.3 Short Term Environmental Effects on Structural Materials

Once the sulfur modified pavement is in service, the combined action of rain, wind and traffic could produce run-off or splashing that may have an effect on some of the structural materials normally found in the vicinity of a road. Under traffic wear, frictional forces between the tire and road surface will also produce a fine dust which could be transported to the side of the roady by wind or rain, or splashed onto moving or parked vehicles by back-spray from passing cars. To evaluate this effect, a number of materials were subjected to a series of tests simulating the activity just described. The materials evaluated included:

Material	Typical Location
Steel Reinforcing Rods	Sulfur Concrete Section
Galvanized Steel	Road Sign and Guard Rails
Chrome/Tin	Wheel Hubs

Material	Typical Location
Chrome Plating	Bumper
Painted Sheet Metal	Car Body and Roadway Signs
Aluminum	Nuts and Bolts, etc.
Copper	Tubing, Wiring, etc.
Rubber	Hoses, Sealants
Vinyl	Upholstery
Wood	Concrete Forms

Samples of the materials listed above were obtained from TTI's automobile "graveyard" and storage. It was decided by the project team that the test medium which would most nearly simulate the conditions described above would be a solution of finely ground paving material (i.e., minus No. 100 sieve) and water. Two particulate solutions referred to as "the leachates" were prepared using the sulfur DCPD concrete (Mix No. 102) and the sand-asphalt sulfur mix (Mix No. 3) designs. There were selected since they represented the mixes with the highest sulfur content. About 0.1 lb (45 grams) of each of the two crushed materials were added to about 1 gallon (3.8 liters) of water in a 2 ft. x 2 ft. x 1 ft. (0.51 m x 0.61 m x 0.30 m) open vessel. Three vessels were used; one for each of the two mix designs and one which contained only pure water. Samples were placed on a screen capable of being positioned so that the samples could be either totally submersed or completely above the leachate level in the vessel. The test was carried out at two temperatures; 75 and 140°F (24 and 60°C).

A sparger coil was located on the bottom of a vessel which was connected to an air supply. A control value was used to adjust air pressure to provide just enough turbulence to keep the particulate matter in suspension. The leachate was kept at a steady roll so as not to induce any abrasive action on the sample surfaces. This rolling agitation was maintained for 30 minutes after which the samples were removed from the leachate and left to dry. The test was repeated once a day for two months. After each 30 minute test, the samples were visually inspected for corrosion, chemical attack or change in surface characteristics. A schematic of the test set-up is shown in Figure 41.

Except for the copper which was chemically attacked by the sulfur-water solution, no permanent visual damage or changes were noted at either of the two test temperatures. The effect on copper was to be expected since it is an established material selection criteria not to use copper in handling or storing sulfur. The only visual effect noted was a film that formed on the painted surfaces upon drying. This was easily remedied by wiping with a clean, dry cloth.

A series of tests were also run on some steel samples in leachate solutions of varying pH. It was found that as the leachate became more acidic (i.e., pH $\leq$ 6) the steel samples were beginning to become pitted. At pH $\geq$ 7 no such activity was noted.

The results of these tests would indicate that exposure to sulfur-water solutions would be detrimental to copper and steel; the latter only in acidic solutions. This could be a problem in using reinforcing rods in moist sulfur concrete. The use of copper or copper alloys would not be advisable. Otherwise, there was no difference indicated between samples exposed to the two sulfur leachate and the pure water.

3.3 Task C - Field Evaluation Plan

The results of Tasks A and B along with pertinent information gleaned from the literature search (Task D) have been utilized to set up a detailed work plan for monitoring emissions and pollutants from operations and situations encountered in the construction and maintenance of sulfur-modified asphalt pavements. This Field Evaluation Plan in Task C of the overall project and is treated in detail in Volume II of the final report.

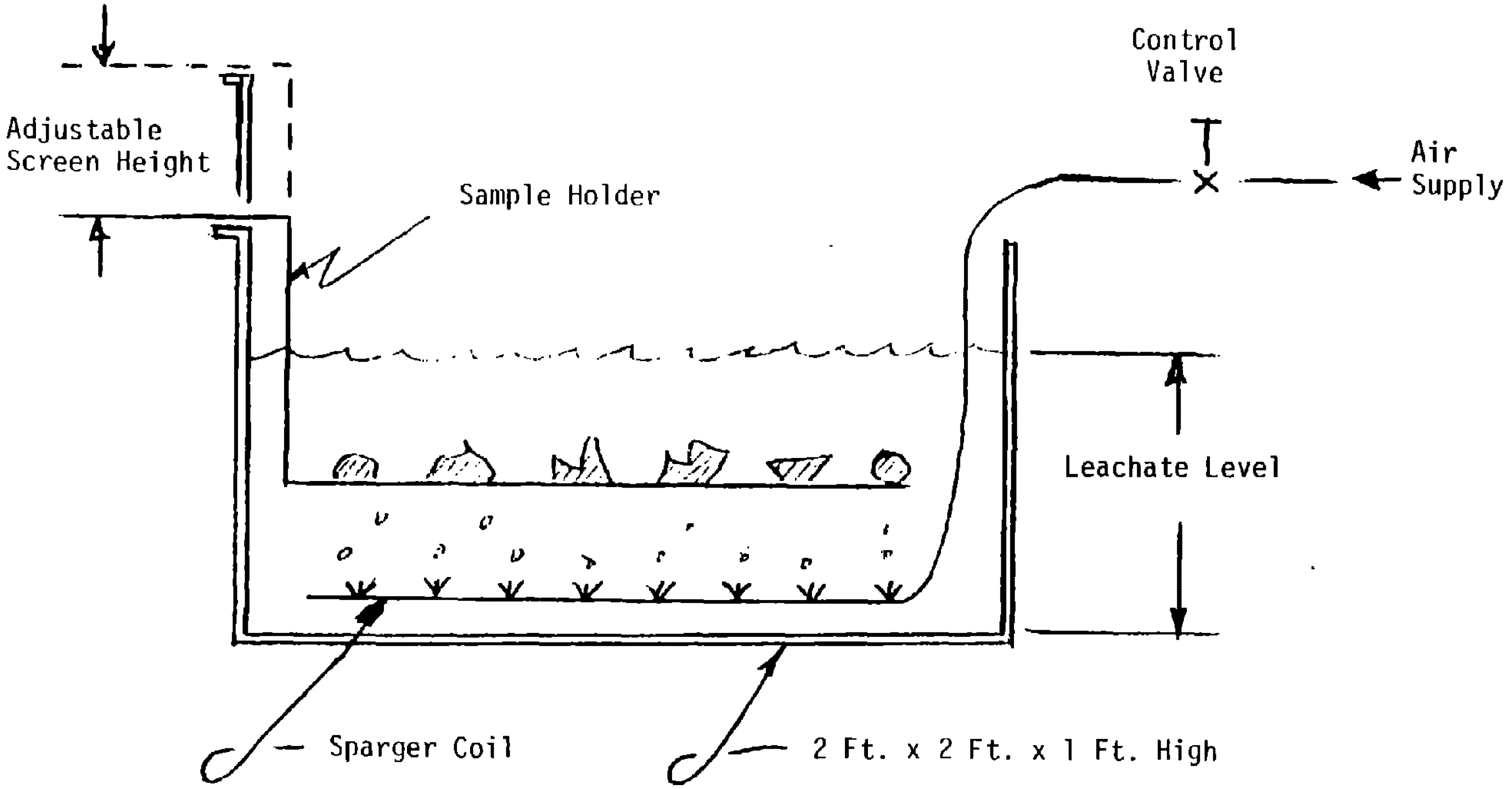


Figure 41. Schematic of Test Set-Up for Evaluating Short Term Environmental Effects on Structural Materials.

With the advent of the development of sulfur-modified asphalt pavements it has become necessary to properly evaluate the safety aspects of these materials lest the results of isolated, non-routine operating conditions misrepresent the true safety and environmental impact of this area of technology. The objective of the Field Evaluation Plan is to present a developed environmental and safety guideline for the use of sulfur in highway pavements. These guidelines include descriptions of hazards encountered in handling liquid sulfur. Symptoms of exposure to these hazards are described and first aid treatment is presented. The operations and situations encountered during construction of sulfur modified pavements are described in view of the hazards due to the presence of sulfur. Types of exposures, sources of the exposures, factors affecting the exposure levels, risk evaluation, and recommendations for appropriate safety apparel and monitoring equipment are given. The operations and situations are broken down into stationary and mobile sources of emissions and pollutants as follows:

Stationary	Qualtity Control Laboratory
	Sulfur Storage Tank
	Storage of Preblended Sulfur-Asphalt Binders
	Mixing Units
	Surge Silos
	Stacks
Mobile	Haul Trucks
	Paver

Types of maintenance operations and hot-mix recycling procedures have also been evaluated for exposure to noxious and obnoxious emissions due to the presence of sulfur in the pavement. Also included in the Field Evaluation Plan are methods of monitoring the potentially hazardous products as determined from the laboratory and simulated field tests.

Brief descriptions of some of the evolved gas analysis techniques have been presented for the types of monitoring common to the paving industry. The breakdown of emissions monitoring methods are: (1) area monitoring - continuous sampling techniques; (2) short term sampling - "grab" sampling, and (3) personnel monitoring - continuous sampling. In preparing this plan, every attempt was made to make the safety practices and working environment consistent with requirements already established by OSHA, NIOSH, and EPA in the paving and sulfur handling industries.

3.4 Task D - Annotated Bibliography

This phase of the project generated a synopsized review of the literature and appropriate patents, and provided for the establishment of a comprehensive annotated bibliography relative to the safety and environmental effects of the use of sulfur modified pavement materials. This resulting annotated bibliography is contained in Volume III of the final report for this contract and is comprised of over 500 abstracts derived from an extensive literature search. Each article has been classified into one or more of the following categories:

I. Environmental Effects
    1.0 Effects on Air and Water
    1.1 Effects on Plant Life
    1.2 Effects on Animal Life
    1.3 Bacterial - Microbiological Effects
    1.4 Effects on Soil

II. Health and Safety Aspects

III. Material and Structural Effects (Corrosive)

IV. Mechanisms and Monitoring Devices

V. Surface Abrasion and Contact of Sulfur Pavements

A suitable cross-referencing and coding system was also established. The code letters and numbers are given adjacent to each reference to indicate the particular category(s) covered in the reference.

Texas A&M University Library's Automatic Information Retrieval Service (AIRS), a computer search facility, was used to obtain over 1400 abstracts which were then reviewed, classified, and placed into the final report. The literature searched included such sources as the Chemical Abstracts, The Engineering Index, and the NTIS reports. The annotated bibliography, along with the abstractions and categorizations of the references, will facilitate updating as maybe required for any future efforts associated with sulfur-modified pavement construction.

4 CONCLUSIONS

A number of typical sulfur-asphalt and sulfur-concrete paving systems were evaluated to assess their potential environmental impact and establish safety considerations relative to their formulation, construction and maintenance. Their environmental impact was investigated from the formulation stages, through weathering, and included considerations of simulated fires and chemical spills.

In the formulation phase the influence of sulfur in nine mixtures was examined against mix temperature and humidity and oxygen content of the air. The results generated in this study tend to support the data generated by others in the laboratory as well as the field; that is, that as long as the mix temperature is kept below 300°F (149°C) evolved gases and pollutants can be maintained within safe limits. These conclusions do not apply when sulfur-asphalt or sulfur concrete are processed in closed environments or stored for prolonged periods of time. Effects of humidity and oxygen were found to be negligible. The recommended maximum allowable upper temperature limit for continuous handling of sulfur modified paving materials is therefore 300°F (149°C).

It was also found that exposure to the elements had a negligible effect on these pavement materials and run-off either by wind or rain produced little or no effect on the immediate environment. It should be noted that in both the formulation and weathering studies, were maximized the results may be considered conservative.

A large number of structural materials were evaluated for possible attack by run-off from a sulfur-asphalt pavement. Of the ten materials studied, copper and steel appeared to indicate a vulnerability. The former or its alloys should never be used in equipment or structure which could bring them in contact with sulfur due to the high probability of producing the sulfates of copper. Steel reinforcing rods would be susceptible to attack by H_2SO_4 produced by moisture on contact.

The possibility of accidental events such as fire and chemical spills revealed some possible short term undesirable effects. These were in the area of obnoxious fumes or short-time-interval pollution. Both the DCPD-modified and unmodified sulfur concretes generated high levels of SO_2 during burning. Virtually all of the sulfur pavement materials were difficult to ignite and were self extinguishing.

The effect of simulated brine and gasoline spills on sulfur pavement were studied. Whereas salt based deicers would have minimal effect, organic solvents or naphtha mixtures can solubilize free sulfur.

The results of this study also produced a Field Evaluation Document (Volume II) and an Annotated Bibliography (Volume III) containing over 500 relevant sources. The Field Evaluation Document was designed for use by contractors and state agencies to establish the relative safety and for identification of potential hazards at the various locations and work elements on a sulfur-asphalt construction project. Recommended clothing and first aid procedures were included in this document.

In summary the results contained herein would tend to support the conclusion that as long as hot sulfur paving mixtures do not exceed 300°F (149°C) all sulfur originating emissions (H_2S, SO_2, SO_3 and organic sulfur materials) levels will be below their respective Maximum Allowable Concentrations. Sulfur handling practices already established in the sulfur industry as well as those common to the hot asphaltic concrete community were sufficient to assure adequate personnel safety.

5 REFERENCES

1. Deme, I., Hammond, R., and McManus, D., "The Use of Sand-Asphalt-Sulphur Mixes for Road Base and Surface Applications", Proceedings, Canadian Technical Asphalt Association, Vol. XVI, November, 1971.
2. Deme, I., "The Use of Sulphur in Asphalt Paving Mixes", Presented to the Fourth Joint Chemical Engineering Conference, Vancouver, September, 1973.
3. Deme, I., "Basic Properties of Sand-Asphalt-Sulphur Mixes", Presented to the VII International Road Federation World Meeting, Munich, Germany, October, 1973.
4. Deme, I., "Processing of Sand-Asphalt-Sulphur Mixes", Presented at the Annual Meeting of the Association of Asphalt Paving Technologists, Williamsburg, Virginia, February, 1974.
5. U. S. Patent N. 3,783,853, June 12, 1973.
6. "Beneficial Uses of Sulphur-Asphalt Pavements", Volumes I-A, I-B, I-C, II, and III, Final Reports on Texas A&M Research Project RF 983, January, 1974.
7. Izatt, J. O., Gallaway, B. M., Saylak, D., "Sand-Asphalt-Sulphur Pavement Experimental Project, Highway U. S. 77, Kenedy County, Texas", Construction Report on Texas A&M Research Project 983, April, 1977.
8. Texas A&M Research Foundation Contract No. RF 3146, "Evaluation of Sulphur-Asphalt Emulsion Binder Systems for Road Building Responses".
9. "Extension and Replacement of Asphalt Cement with Sulfur", FHWA Report No. FHWA-RD-78-95. March, 1978.
10. McBee, W. C., et al., "Sulphur as a Partial Replacement for Asphalt in Bituminous Pavements", New Horizons in Construction Materials, Edited by H. Y. Fang, ENVO Publishing Co., Inc., p. 345, 1976.
11. Garrigues, C., and Vicent P., "Sulphur/Asphalt Binder for Road Construction", Advances in Chemistry Series 140, American Chemical Society, Washington, D. C., 1975.

12. Kennepohl, G. J. A., Logan, A. and Bean, D. C., "Conventional Paving Mixes with Sulphur-Asphalt Binder", Presented to the Annual Meeting of the Association of Asphalt Paving Technologists, Phoenix, Arizona, February, 1975.

13. Gallaway, B. M. and Saylak, D., "Sulfur/Asphalt Mixture Design and Construction Details, Lufkin Field Trials", Texas A&M Research for Texas State Department of Highways and Public Transportation, Study No. 1-10-75-512, January, 1976.

14. "Sulfur-Extended-Asphalt Field Trials - MH 153 Brazos County, Texas", A Detailed Construction Report, FHWA Report No. FHWA-TS-80-214, December, 1979.

15. Saylak, D., et al., "Recycling Old Asphalt Concrete Pavements", Proceedings of the Fifth Mineral Waste Utilization Symposium, Chicago, Illinois, April, 1976.

16. ___________, "Sulfur Extended Asphalt Pavements in Minnesota - 1979", Physical Research Section Report, Minnesota Department of Transportation.

17. Dunning, R. L., Mendenhall, R. L. and Fischer, K. K., "Recycling of Asphalt Concrete - Description of Process and Test Sections", Proceedings Association of Asphalt Paving Technologist, Phoenix, Arizona, February, 1975.

18. "Design of Open Friction Courses with Sulfur Extended Asphalt Binders", FHWA Contract No. DOT-FH-11-9588 with Texas A&M University, 1979.

19. Dale, J. M. and Ludwig, A. C., "Sulphur-Aggregate Concrete", Civil Engineering, Vol. 37, No. 12, pp. 66-68, 1967.

20. Sullivan, T. A. and McBee, W. C., "Bureau of Mines Develops Improved Sulphur Concretes", Vol. 12, No. 1, pp. 6-8, (Spring, 1976).

21. "Handling Liquid Sulfur", Data Sheet 592 prepared for the Engineering and Research Committee of the Fertilizer Section, National Safety Council, Chicago, Illinois.

22. "Properties of Sulphur", Texas Gulf Sulphur Company, New York, New York, 1961.

23. Bacon, R. F. and R. J. Fanelli, Journal of American Chemical Society, 65:639-648 (1943).

24. LeQue, F. L. and H. R. Copson, Corrosion Resistance of Metals and Alloys, 2nd ed. pp. 204, 426, Reinhold Publishing Corp., New York, 1963.

25. West, J. R., "Sulphur and Sulphides vs. Materials of Chemical Plant Construction", Chemical Engineering, (53) 10:255-234 (1946).

26. National Fire Protection Association, Boston, "Sulfur Fires and Explosions", National Fire Codes, June, 1959.

27. ASTM, Std. D92-57, Standard Method of Test for Flash and Fire Points by Cleveland Open Cup, 1957.

28. Mellor, J. W., Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. X, Longmans, Green and Co., Ltd., London, 1980.

29. Yost, D. M. and H. Russell, Systematic Inorganic Chemistry of Fifth and Sixth Group Nonmetallic Elements, p. 279, Prentice Hall, Inc., New York, 1944.

30. Ahmad, H., "A Laboratory Study of the Use of Sulphur in Sand-Asphalt Mixes for Flexible Pavements", a Ph. D. dissertation for Texas A&M University, May, 1974.

31. Heicklen, J., Atmospheric Chemistry, Academic Press, New York, p. 212, 1977.

32. Elkins, Hervey, B., The Chemistry of Industrial Toxicology, John Wiley and Sons, Inc., New York, pp. 95, 232, (1950).

33. Sullivan, T. A., "Studies of Sulphur-Asphalt Road Mixes", U. S. Bureau of Mines, Boulder City Metallurgy Research Laboratory, Boulder City, Nevada, Asphalt Research Meeting, August 9 and 10, 1973, Laramie Energy Research Center, Laramie, Wyoming, August 6, 1973.

34. Stolman, A., ed., Progress in Chemical Toxicology, Academic Press, New York, Vol. 1, p. 10, (1965).

35. Hydrogen Sulfide, Chemical Safety Data Sheet DS-36, Manufacturing Chemists Association, Washington, D. C., (Revised 1968).

36. Sulfur Dioxide, Chemical Safety Data Sheet SD-52, Manufacturing Chemists Association, Washington, D. C., (1959).

37. Occupational Exposure to Sulphur Dioxide - Criteria Document, U. S. Department of Health, Education, and Welfare document published by Public Health Service Center for Disease Control, National Institute for Occupational Safety and Health, (1974).

38. Sulfur, Chemical Safety Data Sheet SD-74, Manufacturing Chemists Association, Washington, D. C., (1959).

39. Conger, W. E., "A Laboratory Study of the Evolution of Hydrogen Sulfide Gas from Sand-Asphalt Sulphur Paving Material", Texas A&M Engineering Department Cooperative Study Report (Spring, 1974).

40. Schmidt, R. J., "A Practical Method for Determining the Resilient Modulus of Asphalt Treated Mixes", Highway Research Record 404, Material Academy of Sciences, Washington, D. C. (1972).

41. EPA, "Standards of Performance for New Stationary Sources - DPA Method 6", Federal Register, (December 23, 1971).

42. Adams, D. F., Bamesberger, W. L. and Robertson, T. J., "Analysis of Sulfur-Containing Gases in the Ambient Air Using Selective Prefilters and a Microcoulometric Detector", Journal of the Air Pollution Control Association, Vol. 18, No. 3, March, 1968.

43. Okita, T., "Filter Method for the Determination of Trace Quantities of Amines, Mercaptans and Organic Sulphides in the Atmosphere", Atmospheric Environment, Pergamon Press, Vol. 4, pp. 93-102, (1970).

44. FHWA Contract No. DTFH 61-80-C-00121, "Environmental and Safety Evaluation of Sulphlex Binders", with Peer Consultants, Inc. of Rockville, Maryland.

45. Peck, H. D., Jr., "Comparative Metabolism of Inorganic Sulfur Compounds", J. Bacterial, Vol. 82, pp. 933-939, 1962.

46. Postgate, J. R., "Recent Advances in the Study of Sulfate-Reducing Bacteria", Bacterial Review, Vol. 29, pp. 425-441, 1965.

47. Chiorse, W. C. and M. Alexander, "Effect of Microorganisms on the Sorption and Fate of Sulfur Dioxide and Nitrogen Dioxide in Soil", Journal Environmental Quality, Vol. 5, pp. 227-230, 1976.

48. Smith, K. A., J. M. Bremmer, and M. A. Tabatabai, "Sorption of Gaseous Atmospheric Pollutant by Soil, Soil Science", Vol. 116, pp. 313-319, 1973.

49. Karnosky, D. F., "Screening Urban Trees for Air Pollution Tolerance", J. Arboriculture, Vol. 5, p. 179, 1979.

50. Toivonen, P. M. A. and G. Hofstra, "The Interaction of Copper and Sulfur Dioxide in Plant Injury", Canadian Journal of Plant Science, Vol. 59, pp. 475-479, 1979.

51. Rist, D. L. and D. D. Davis, "The Influence of Exposure Temperature and Relative Humidity on the Response of Pinto Bean Foliage to Sulfur Dioxide", Phytopathology, Vol. 69, pp. 231-235, 1979.

52. Thompson, C. R., G. Kats and R. W. Lennox, "Effects of Fumigating Crops with Hydrogen Sulfide or Sulfur Dioxide", California Agriculture, Vol. 33, pp. 9-10, 1979.

53. Davis, D. D. and C. M. Gesalman, "Sensitivity of Bean Foliage to Sulfur Dioxide Observed", Science in Agriculture, Vol. 26, p. 16, 1979.

54. Laurence, J. A. "Response of Maize and Wheat to Sulfur Dioxide", Plant Disease Reporter, Vol. 63, pp. 468-471, 1979.

55. McLaughlin, S. B., D. S. Shriner, R. K. McConathy, and L. K. Mann, "The Effects of SO$_2$ Dosage Kinetics and Exposure Frequency on Photosynthesis and Transpiration of Kidney Beans (Phaseolus vulganis L)", Environmental and Experimental Botany, Vol. 19, pp. 179-191, 1979.

56. Elkiey, T. and D. P. Ormrod, "Pentunia Cultivar Sensitivity to Ozone and Sulfur Dioxide", Scientia Horticultural, Vol. 11, pp. 269-280, 1979.

6 APPENDIX

GC-MS Analysis and Original Data on Volatilized Products from Sulfur/Asphalt Mixes

GC-MS Analysis and Original Data Sheets on Volatilized Products from Sulfur Asphalt Mixes

The products of this study were to use gas chromatograph - mass spectroscopy (GC-MS) techniques to analyze and identify compounds volatilized during formulation of sulfur-asphalt at the excessive temperature of 350°F (176°C), and compare it to asphalt alone. This was initiated in particular to identify the relatively large peak showing up by gas chromatographic (GC) analyses using the flame photometric detector in a sulfur specific mode. It should be noted that initial GC analyses (see page 53) using a flame ionization detector system revealed no hydrocarbons were in excess of 1 ppm relative to the air volume trapped. However, the sulfur constituent was definitely in excess of 1 ppm for the sulfur-asphalt material. Mix design 3 (MD-3) described in Table 11, page 39 was utilized for the comparison to the asphalt (MD-6).

Volatilized components trapped in refrigerated solvent from 2 separate formulations at 350°F were combined and concentrated by vacuum distillation for GC-MS analysis. The mass spectrometer was a Hewlett-Packard Dodecapole 5890 A model with GC inlet. It has a mass resolution of one unit mass. A 18 m glass capillary column (2 mm I.D. coated with SP 2100) was used in the GC inlet. The SP 2100 capillary column was used instead of the OV-1 material because of better resolution at one-third the time.

The resultant GC scan of MD-6 is given in appendix Figure A-1. Mass spectra of sample, both in bar diagram and in Table form, were obtained. These spectra for peaks labeled +527, +583, +784, +859, +872 and +914 in Figure A-1 are given in Figures A-2, A-3, A-4, A-5 and A-6, respectively. These spectra were first compared with the 19,000 known mass spectra listed in "Registry of Mass Spectra Data" by S. Abrahamson; E. Stenhagen; F. W. McLafferty; Wiley, N. Y. 1974. Cornell University's computer program for mass spectra identification - PBM was also used to interpret some of MS obtained. The PBM has a data bank of 41,429 known mass spectra. Through telecommunication every known spectra in the data bank was retrieved and compred to the mass spectrum obtained. No match was ever found due principally to the low concentrations in combination with background matrix effects. However, possible structures were had computed from crack patterns for peaks labeled +527, +784, +872 and +914 (Figure A-1). The results of this effort are summarized in Table A-1. Of note is the fact that sulfur does not dominate any of the mass spectra, but did show up as moiety of peaks +784 and +914. The asphalt material was shown to contain approximately 0.5% sulfur.

The resultant GC scan of MD-3 is given in appendix Figure A-7. Adjustments were made to increase sensitivity levels of the flame ionization detector. An attempt was made to obtain the mass spectrum of a peak with a retention time of 15.5 minutes. The spectrum shown in Figure A-8 shows sulfur to dominate as a background. The initial mass spectrum for peak labeled +585 was initially dominated by sulfur Figure A-9. A second run negating the sulfur background is given in Figures A-10. The spectrum shows a similar framenting pattern as that noted for peak +527 obtained for the MD-6 sample. Mass spectrum of peak +638 is given in Figure A-11. Results of spectra are given in Table A-2.

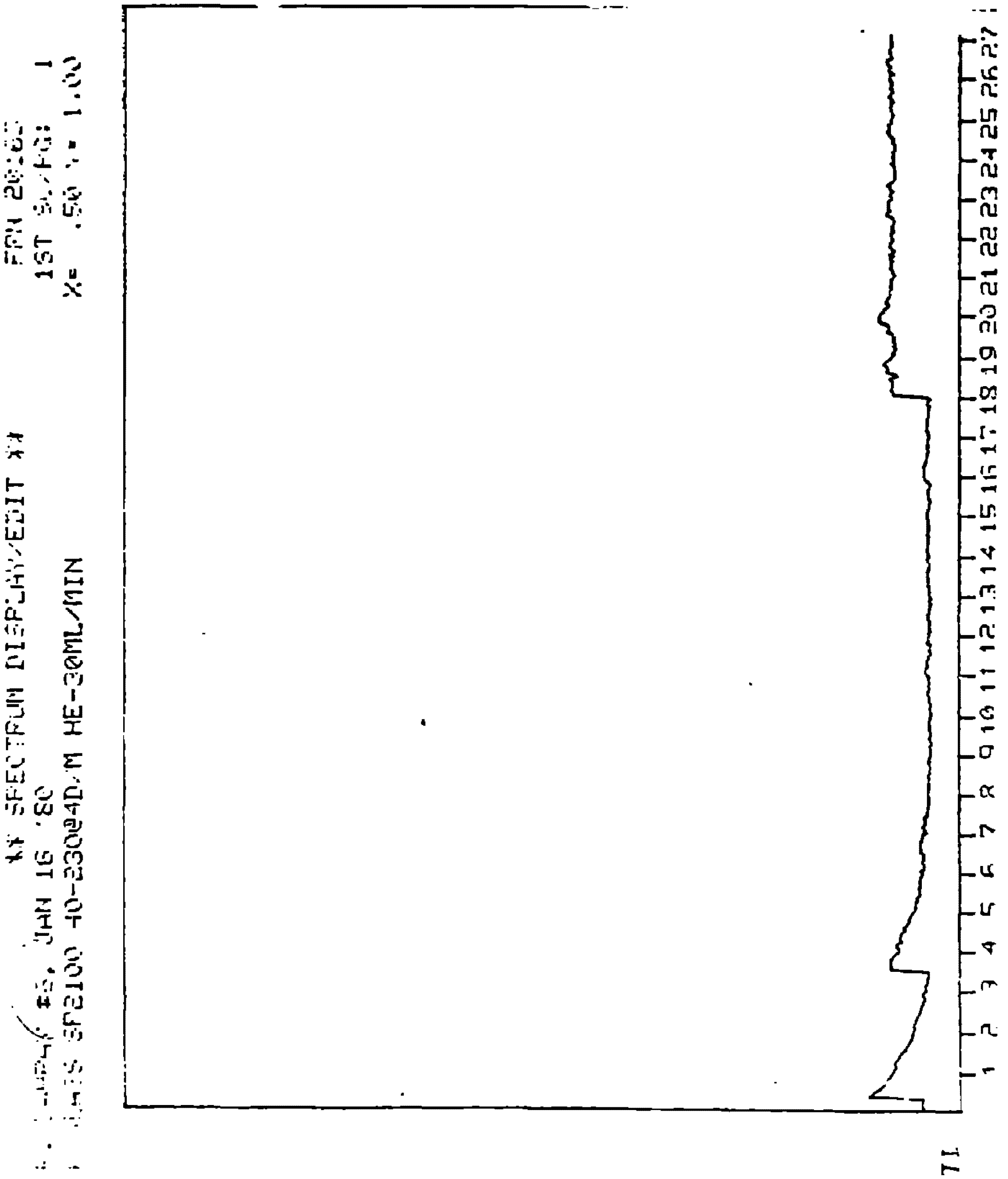


Figure A-1. Gas Chromatographic Scan of MD-6.

** SPECTRUM DISPLAY/EDIT ** FRN 20163

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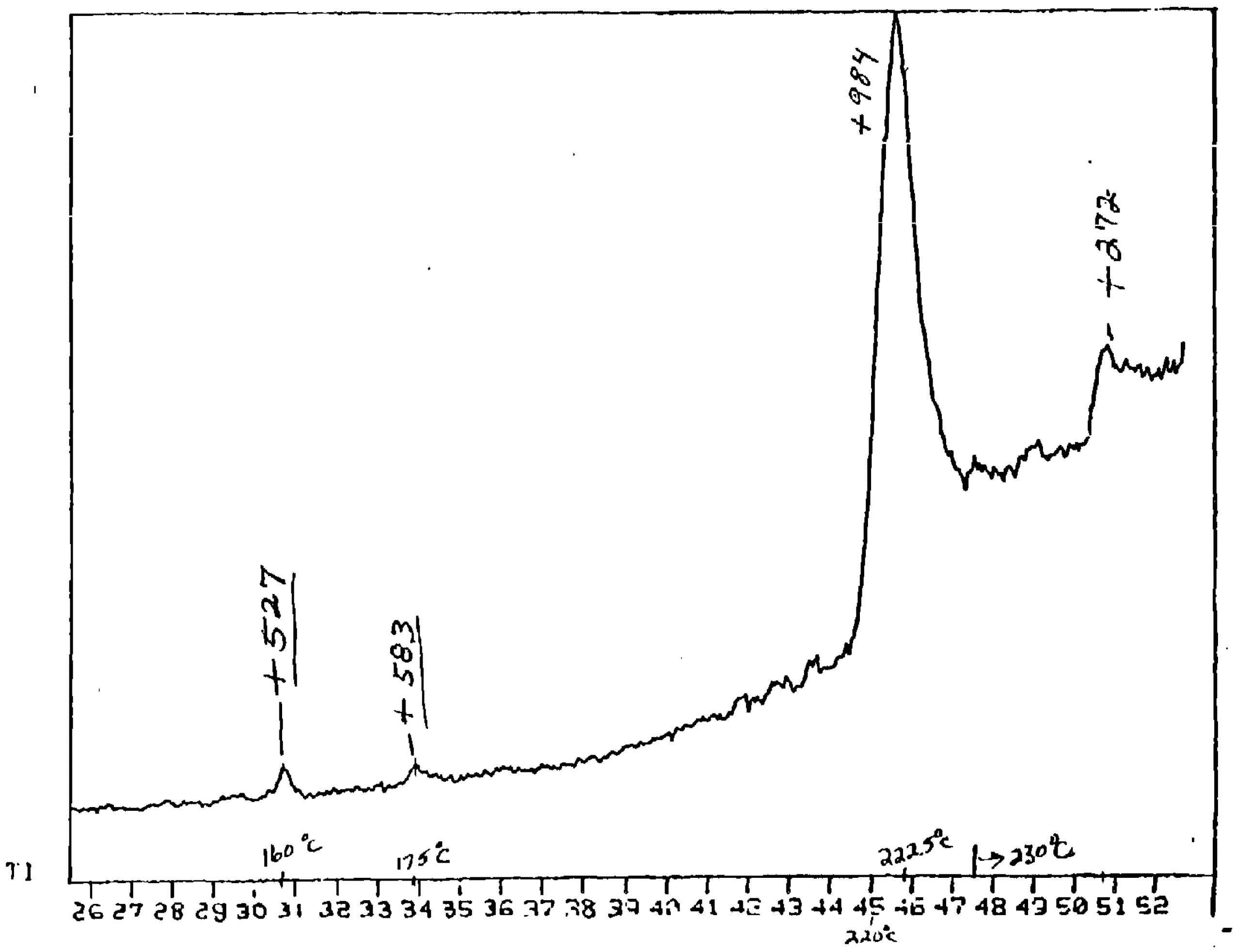

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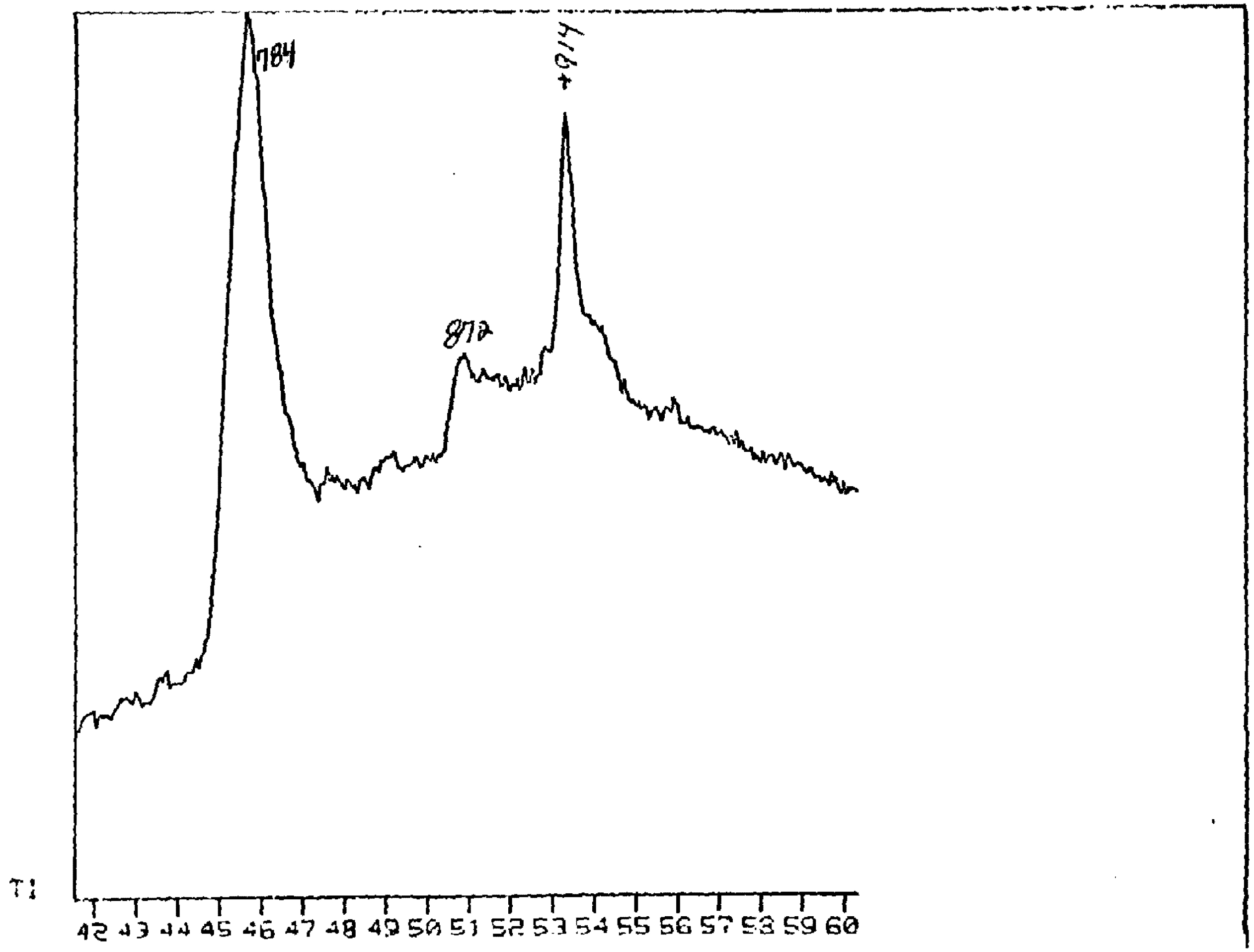


Reproduced from best available copy.

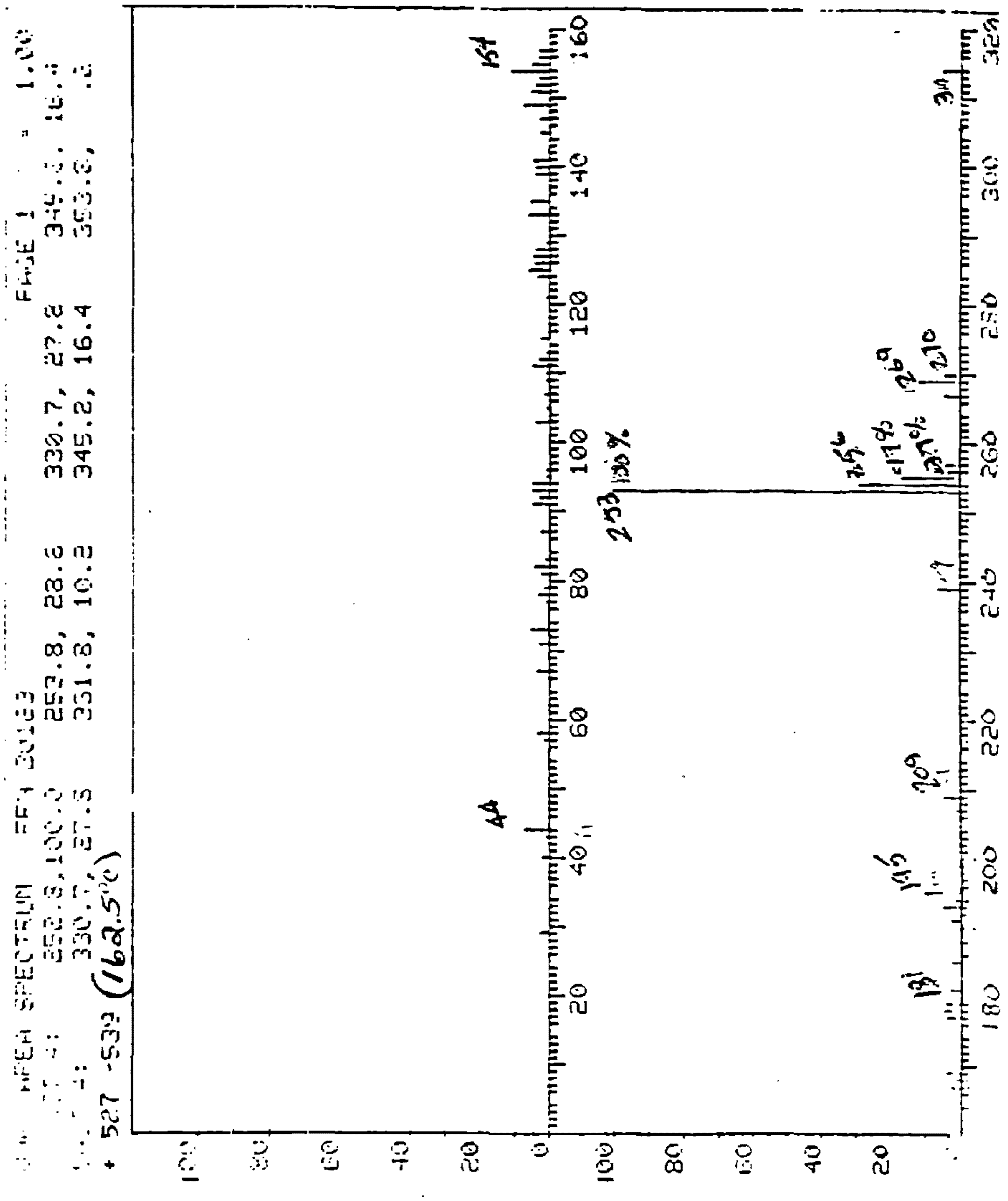
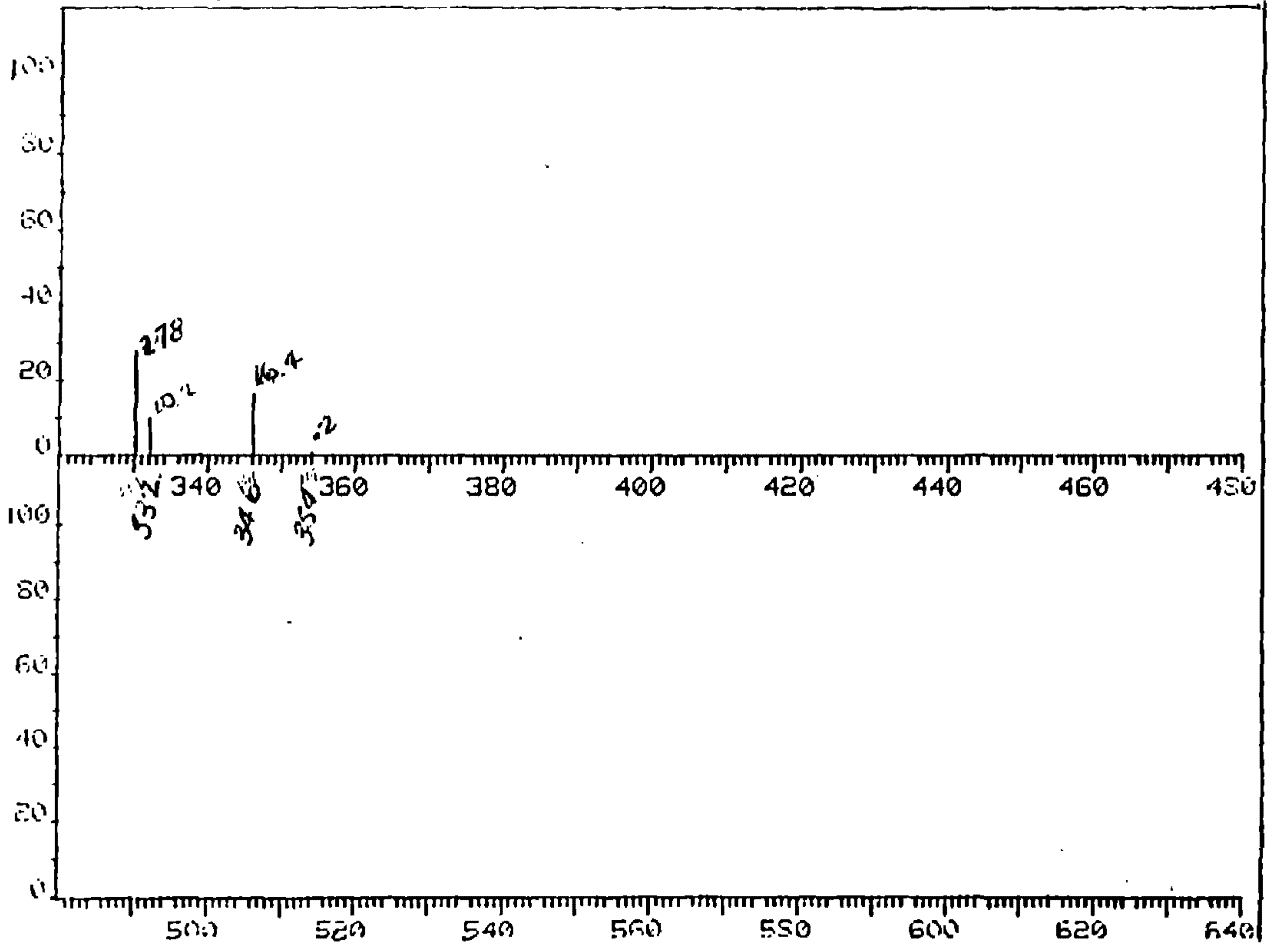


Figure A-2. Mass Spectrum of Peak +527.

```
[illegible] AREA SPECTRUM   FRN 20163                           PAGE 2  [illegible] = 1.00
[illegible] 4:    352.8,100.0    253.8, 28.6    330.7, 27.2    345.3, 16.4
[illegible] 4:    330.7, 27.8    331.8, 10.2    345.8, 16.4    353.8,    .2
+ [illegible] -539 (162.5°c
```



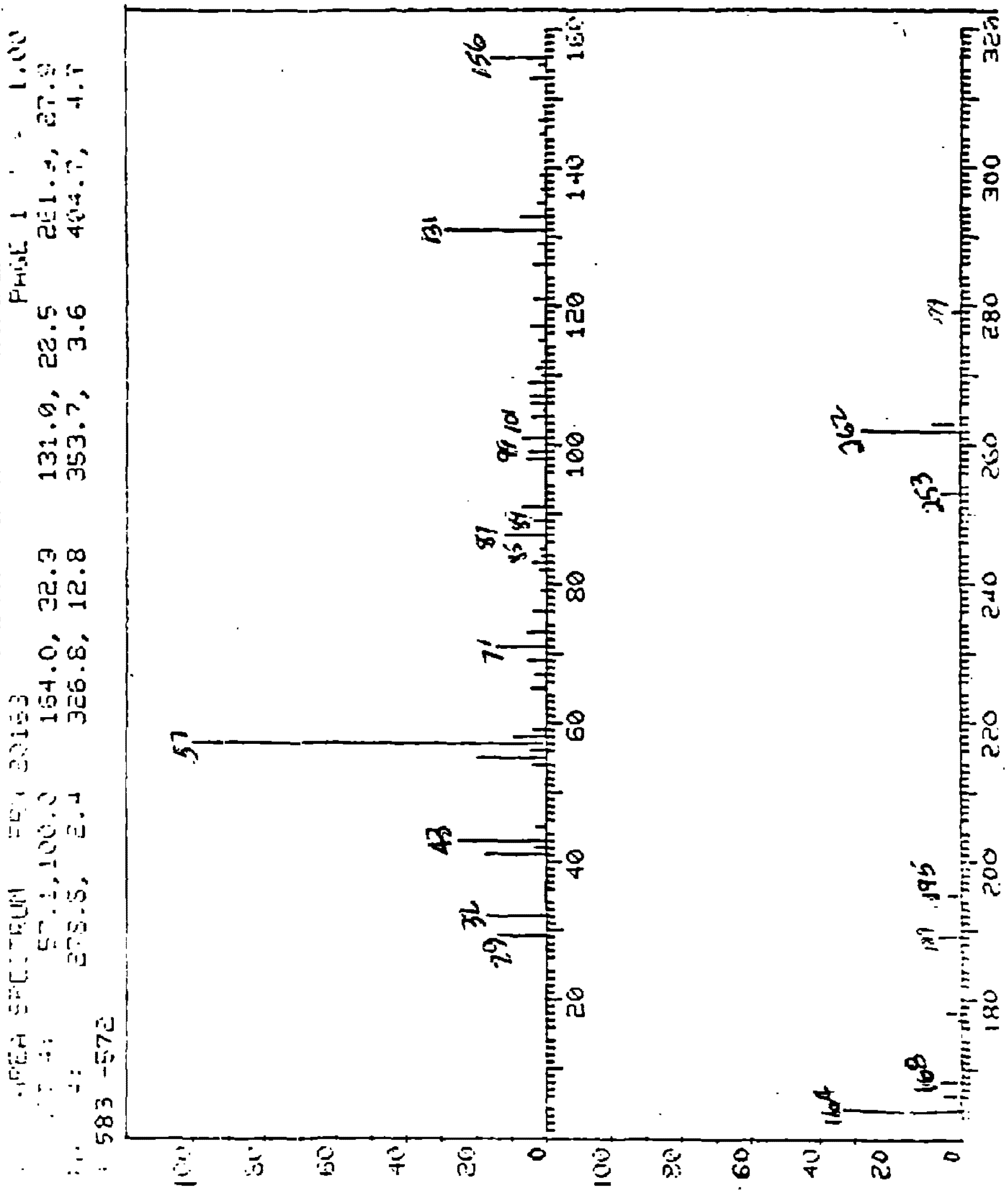
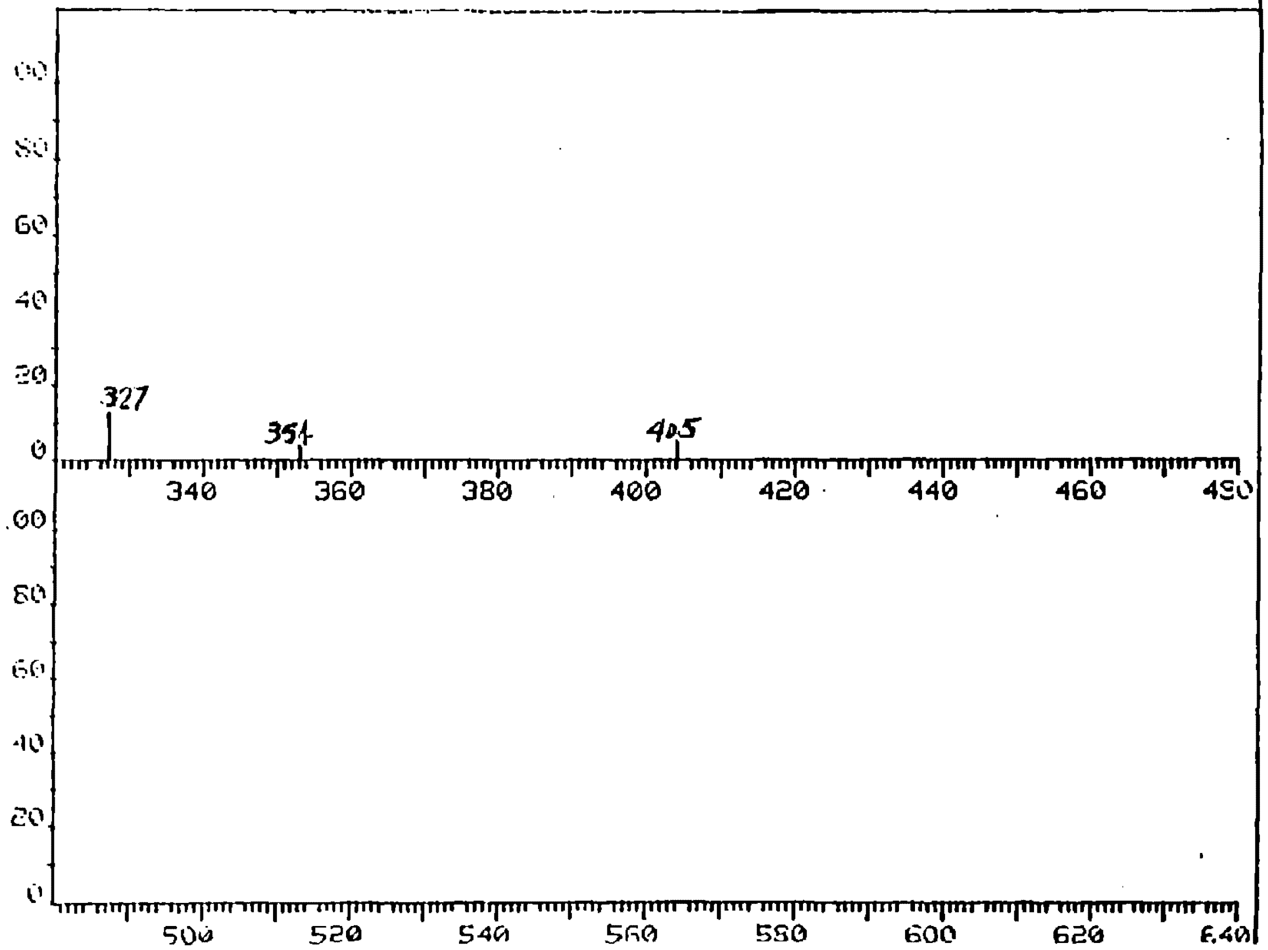


Figure A-3. Mass Spectrum of Peak +583.

```
NORM AREA SPECTRUM   FRN 20163                            PAGE 2  Y =  1.00
TARGET 4:      57.1,100.0     164.0, 32.9     131.0, 28.5     261.9, 27.9
LAST 4:        278.8,  2.4    326.8, 12.8     353.7,  3.6     404.7,  4.7
+ 503 -572
```



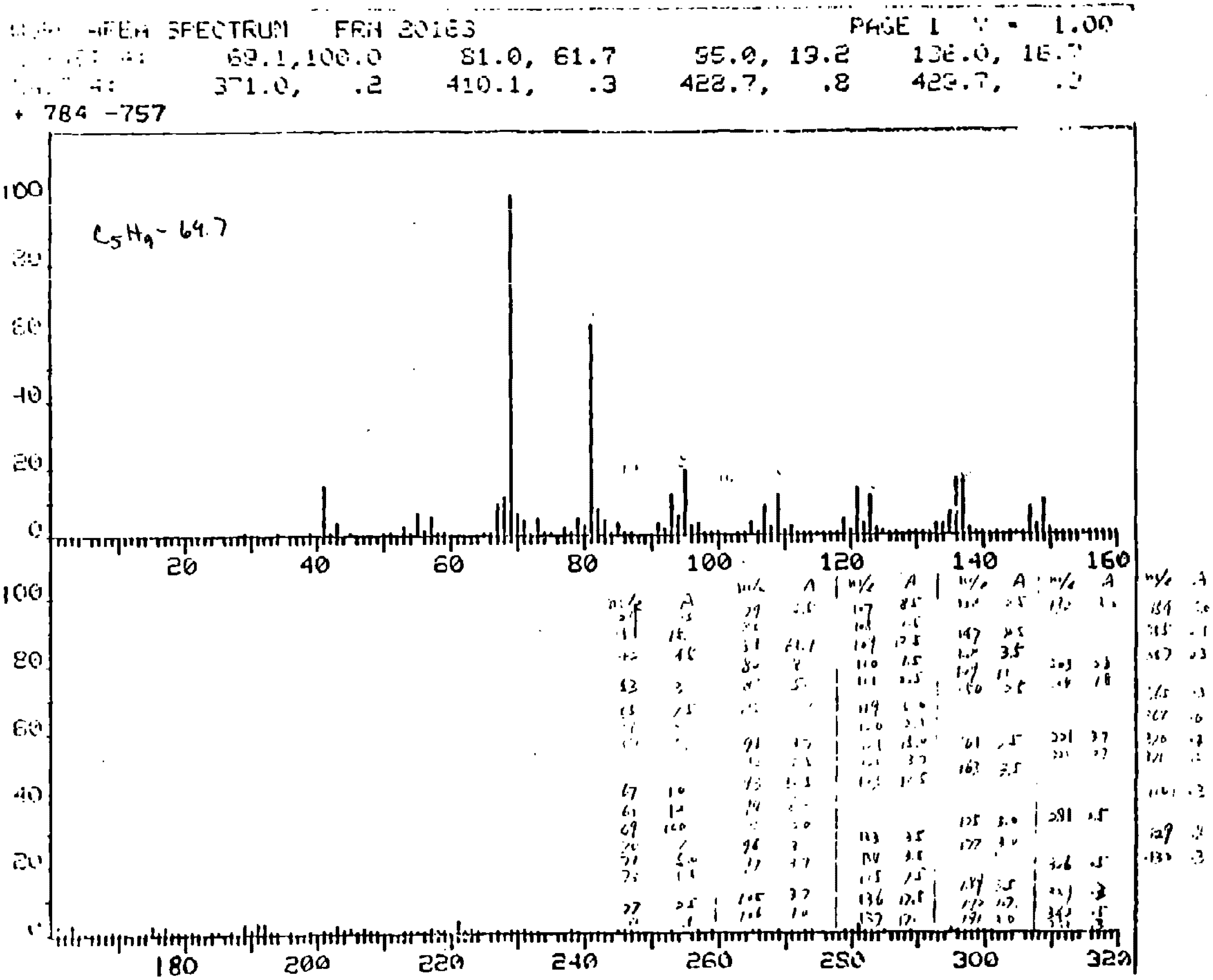
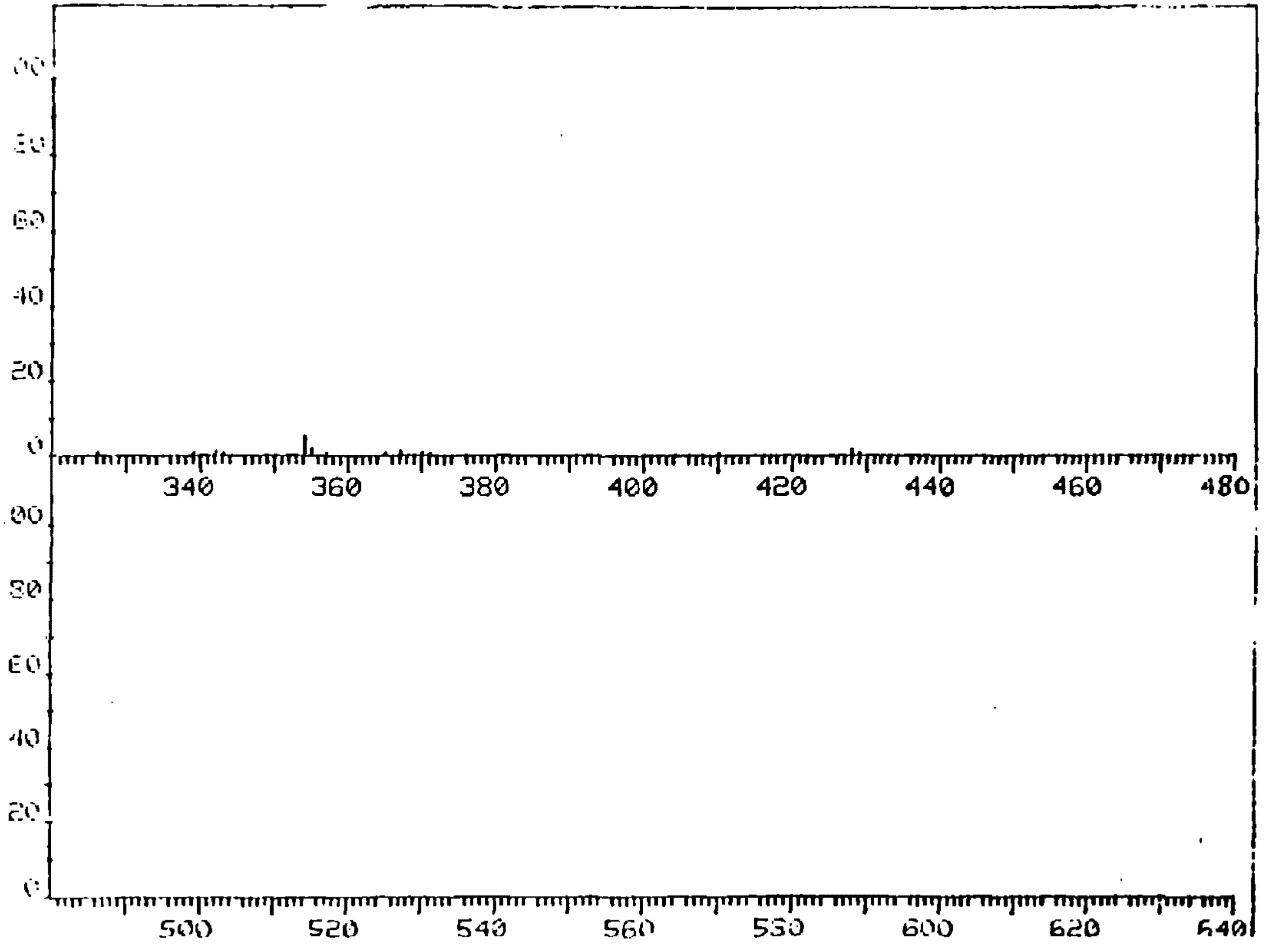


Figure A-4. Mass Spectrum of Peak +784.

```
[illegible] AREA SPECTRUM   FRN 20163                                PAGE 2  [illegible]   2.00
[illegible] 4:     69.1,100.0      81.0, 61.7      95.0, 19.2     126.0, 16.7
[illegible] 4:     371.0,    .2    410.1,    .3    428.7,    .8    429.7,    .5
[illegible] -757
```



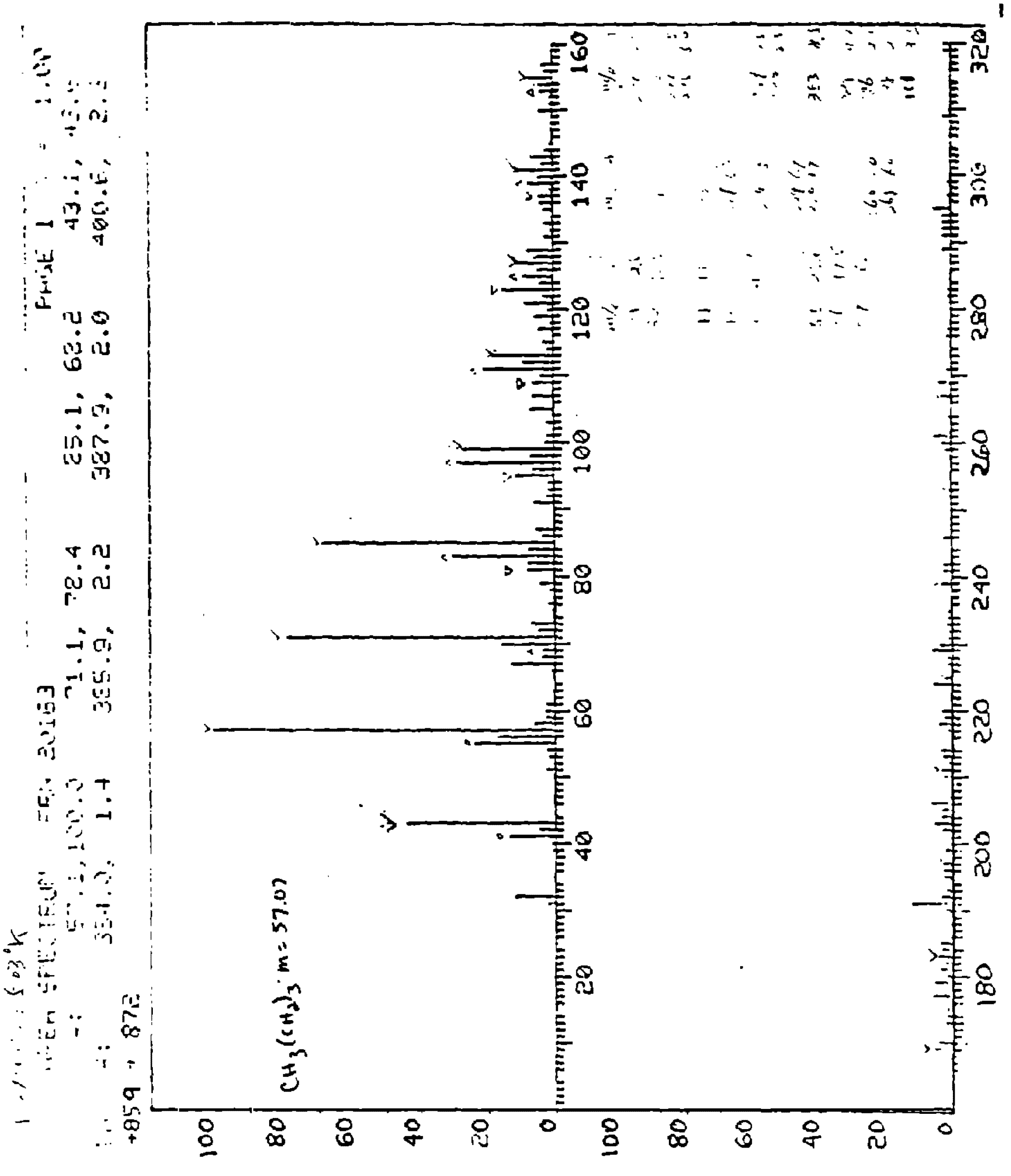
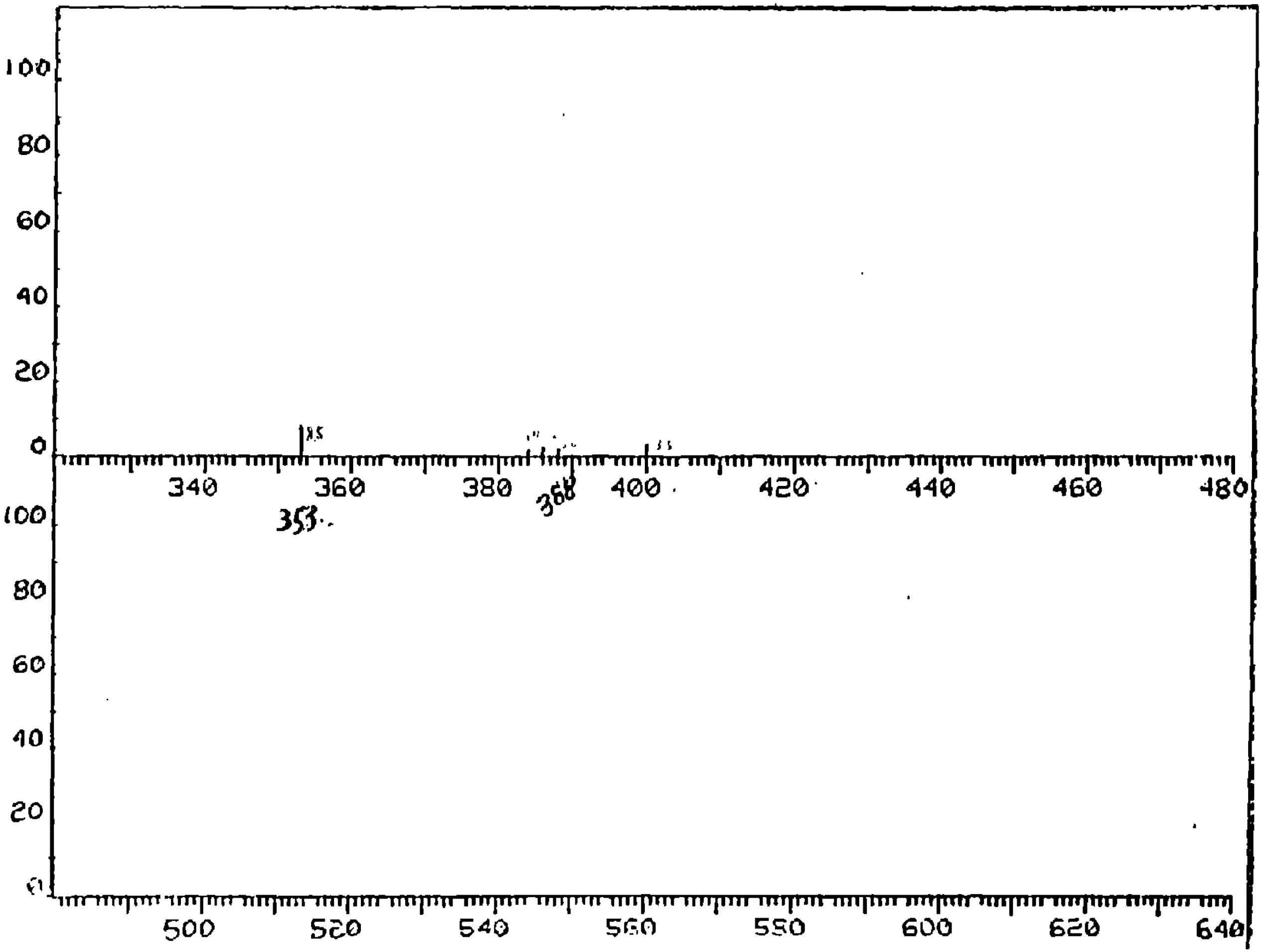


Figure A-5. Mass Spectrum of Peak +859.

```
NORM AREA SPECTRUM   FRN 20163                          PAGE 2  % =  1.00
LARGEST 4:     57.1,100.0     71.1, 78.4     85.1, 62.2     43.1, 43.6
LAST 4:        384.0,  1.4    385.9,  2.2    387.9,  2.0    400.6,  2.8
-859 + 872
```



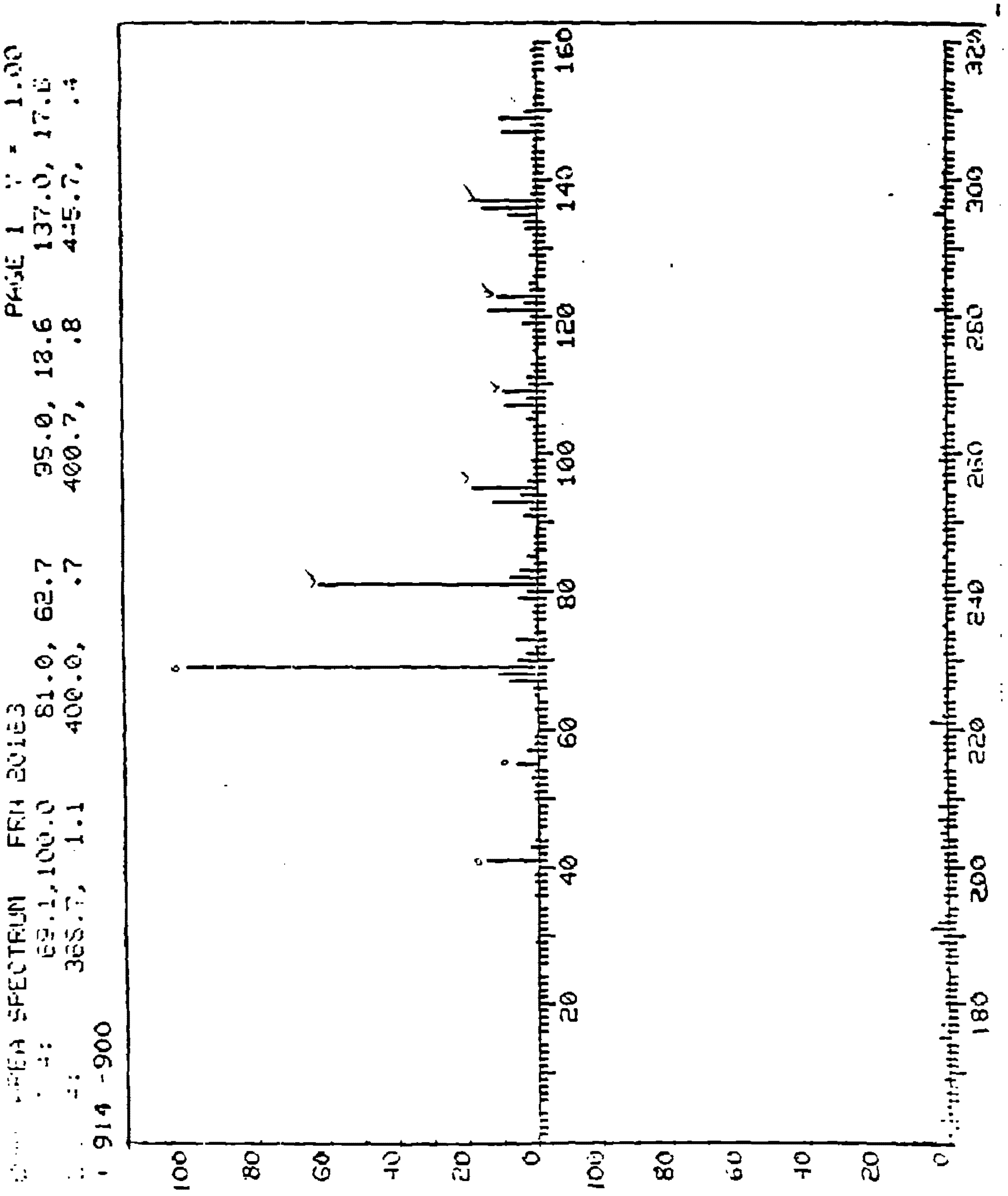


Figure A-6. Mass Spectra of Peak +914.

NORM AREA SPECTRUM FRN 20183 PAGE 2 % = 2.00

[illegible] 4: 69.1,100.0 51.0, 62.7 95.0, 18.6 127.0, 17.6

[illegible] 4: 365.7, 1.1 400.0, .7 400.7, .8 445.7, .4

\+ 914 -900

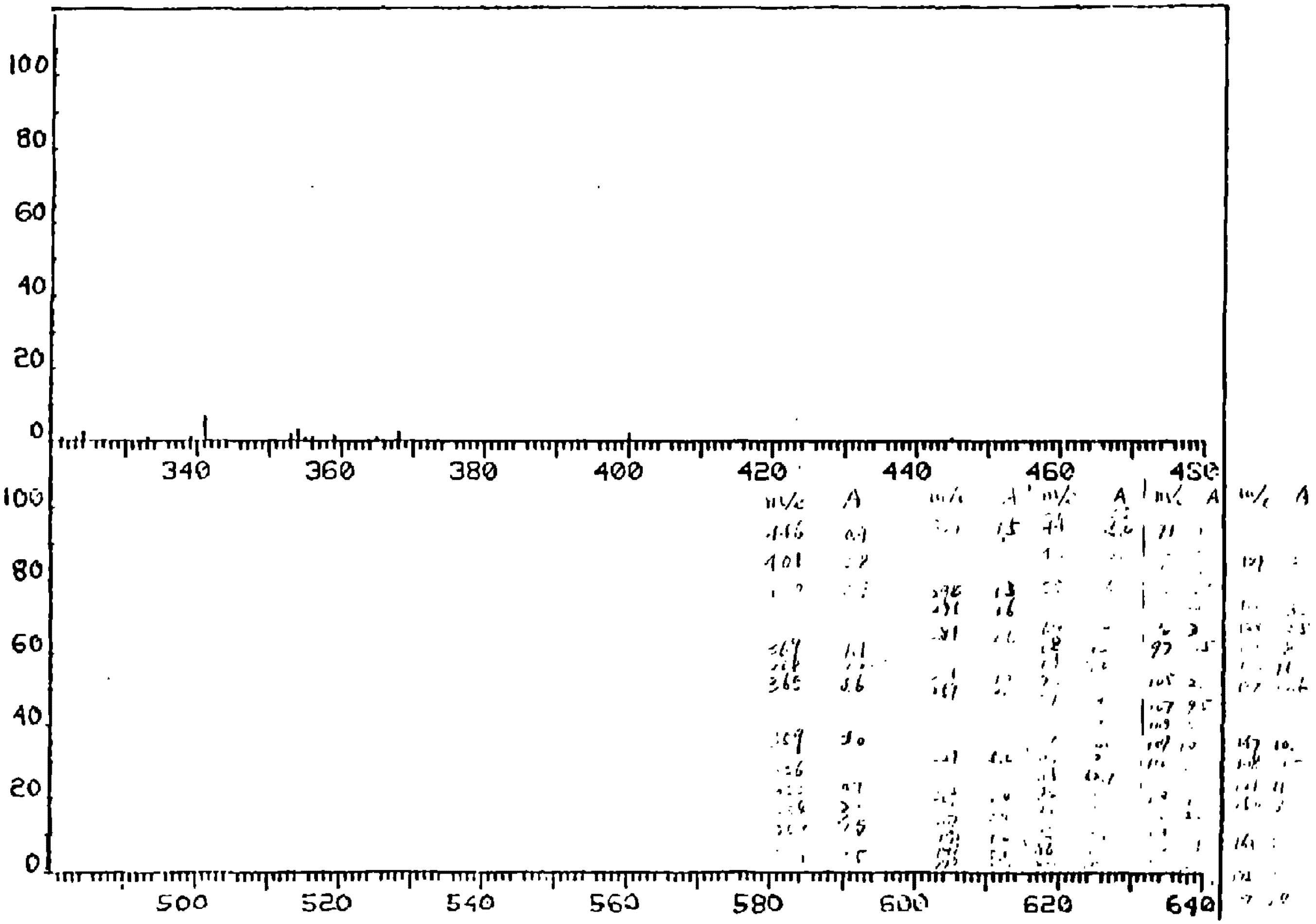
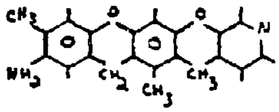
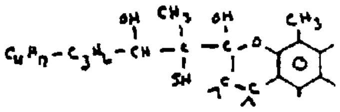
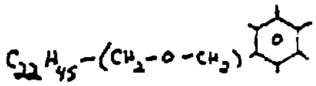
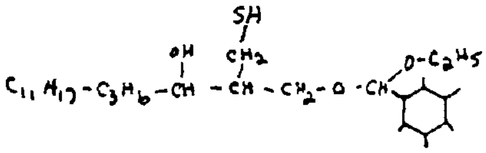


Table A-1. Summary of Mass Spectra of MD-6.

Peak no.	Retention Time (min)	Mass	Possible Structure
+527	30.7	346	
+784	45.7	444	
+872	50.9	430	
+914	53.4	446	

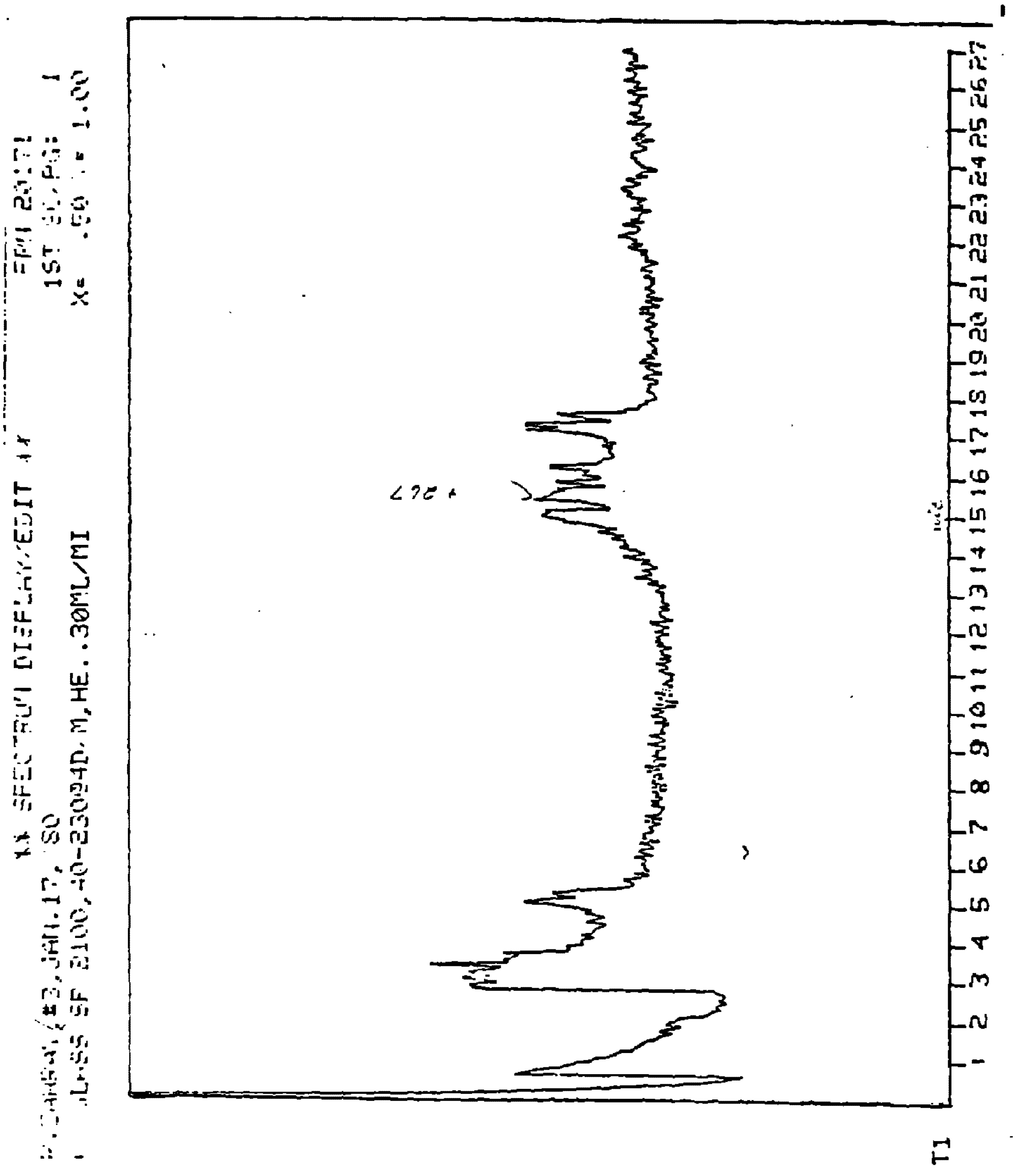
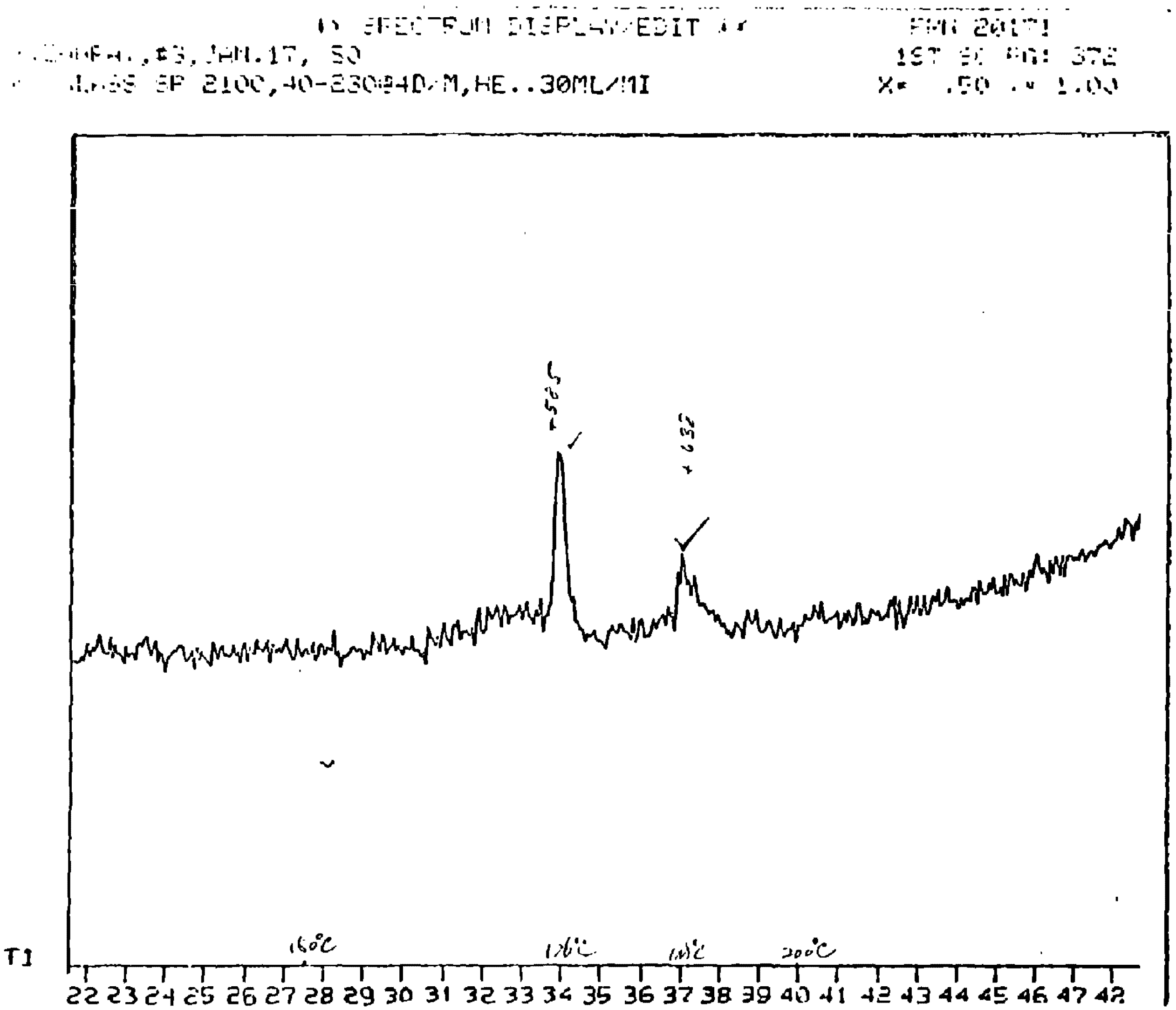


Figure A-7. Gas Chromatographic Scan of MD-3.

SPECTRUM DISPLAY/EDIT
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632
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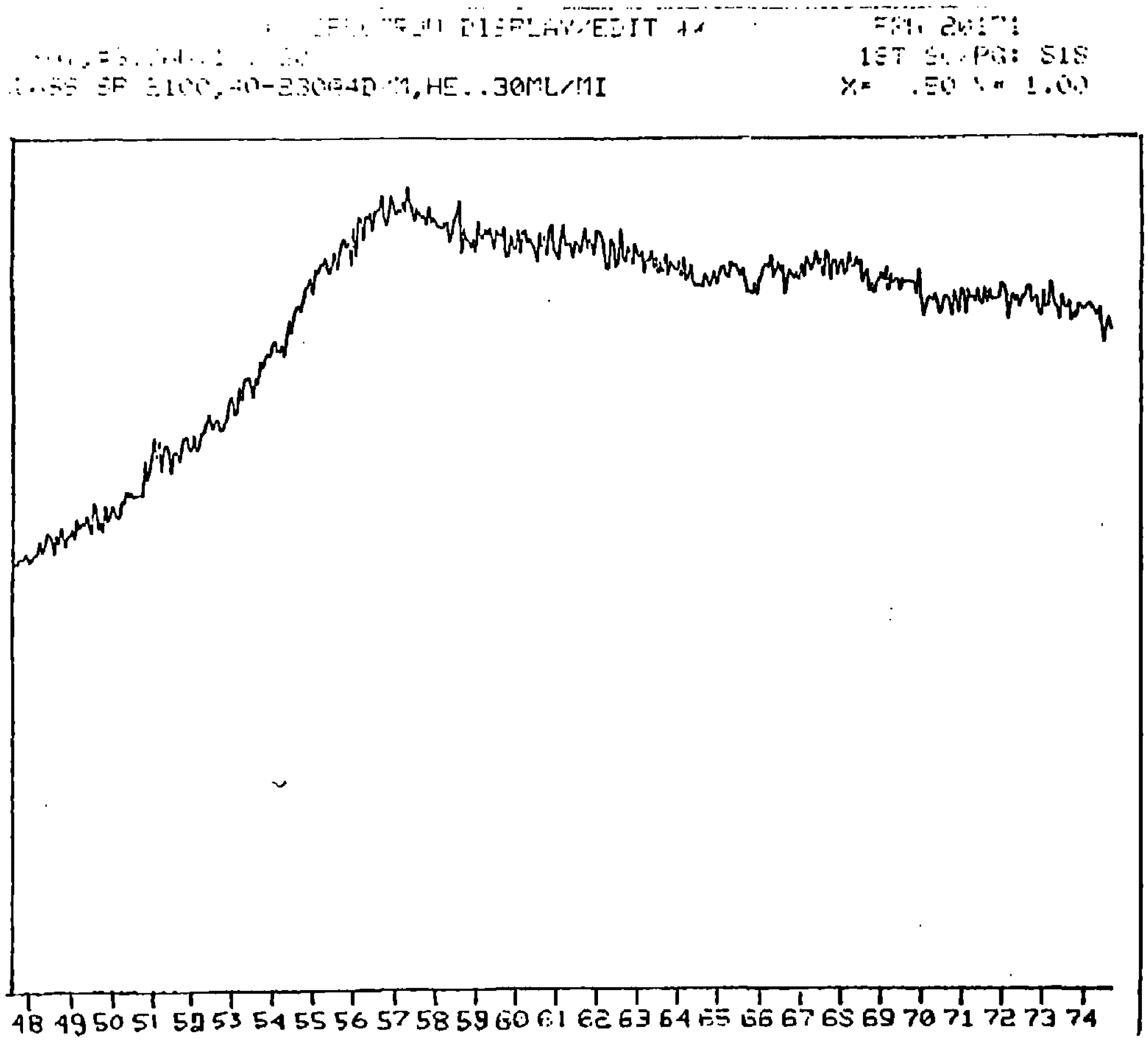
170°C
180°C
200°C
T1
22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48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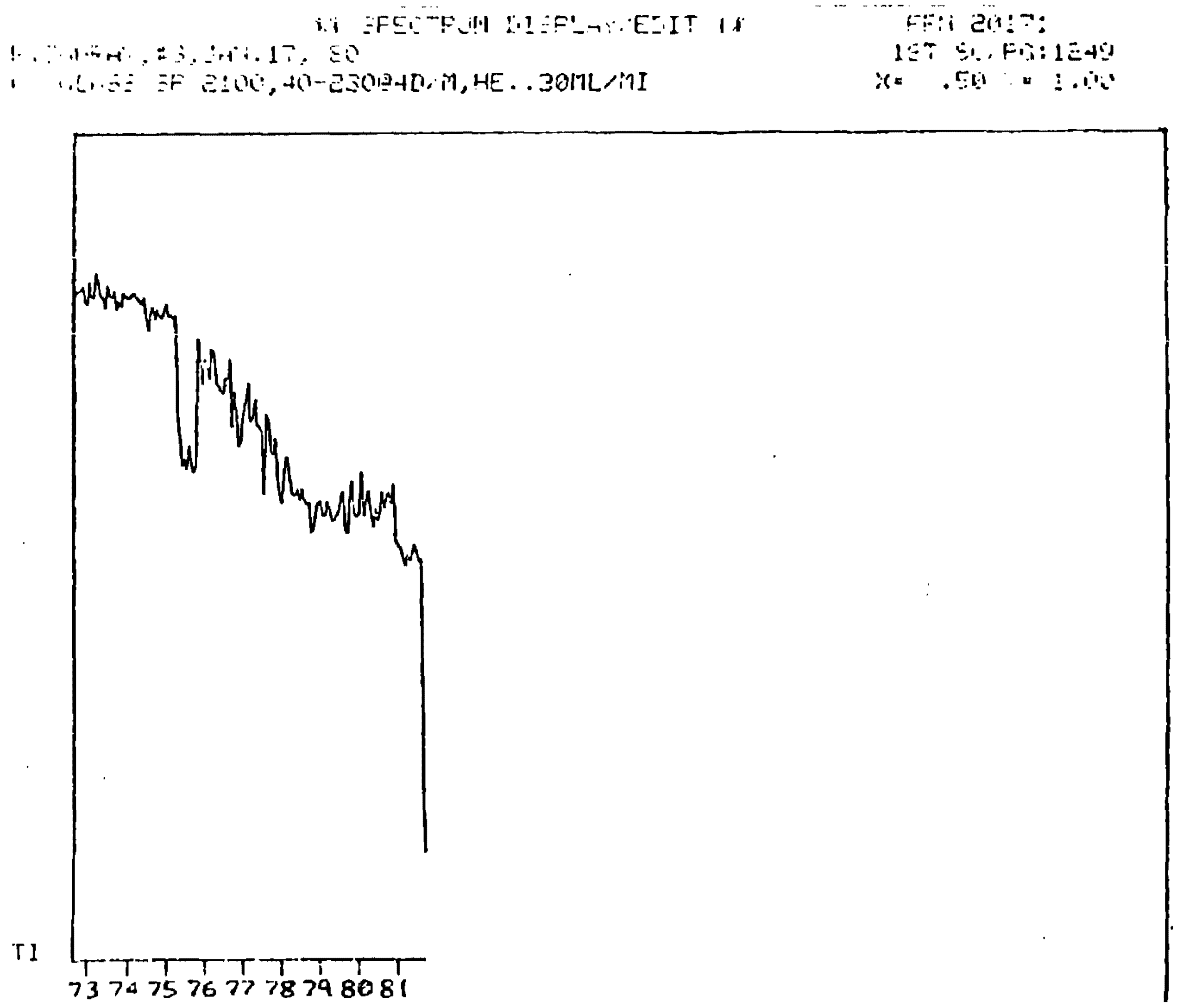
TI
48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74

SPECTRUM DISPLAY/EDIT
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81

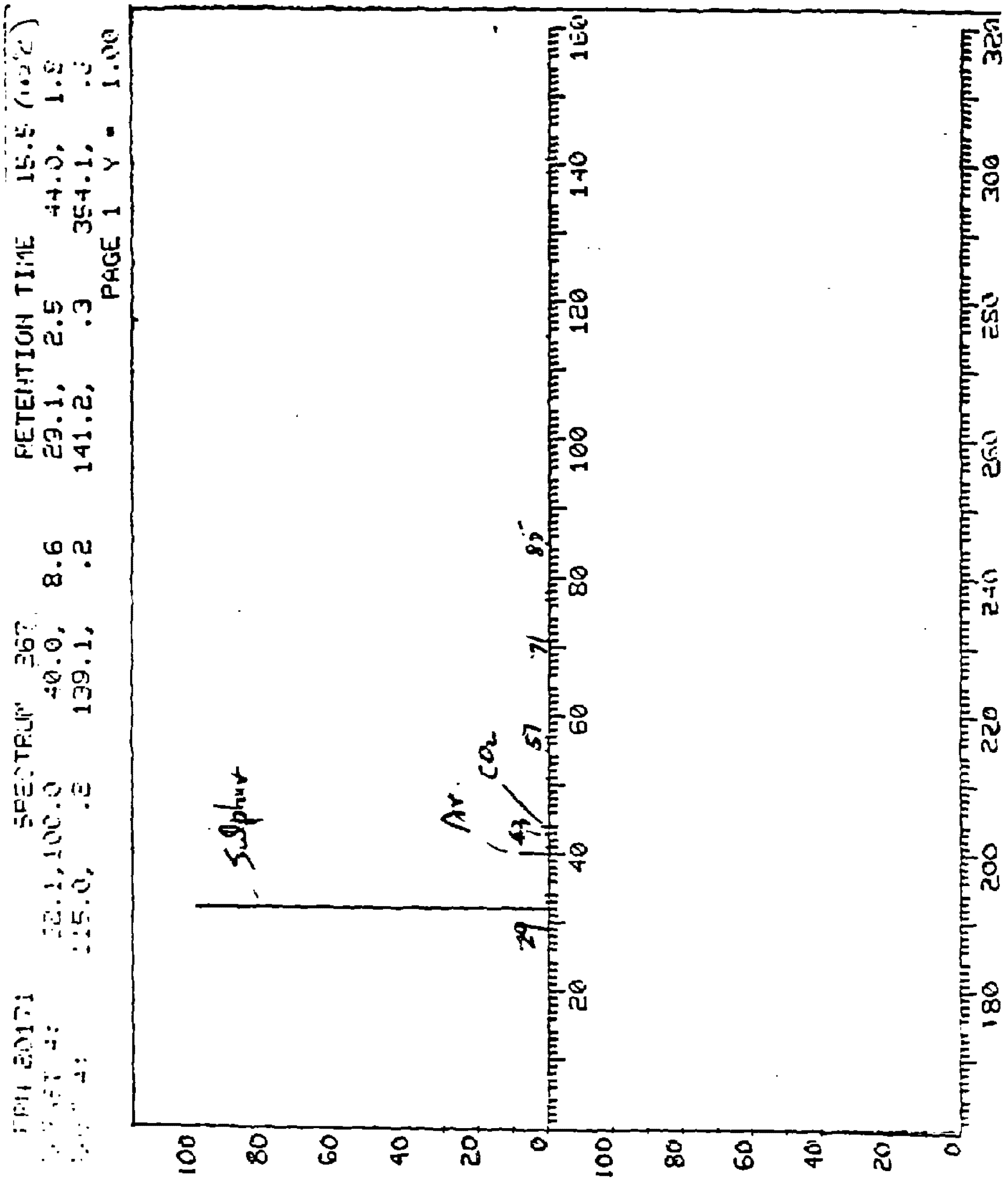


Figure A-8. Mass Spectrum of Peak +267.

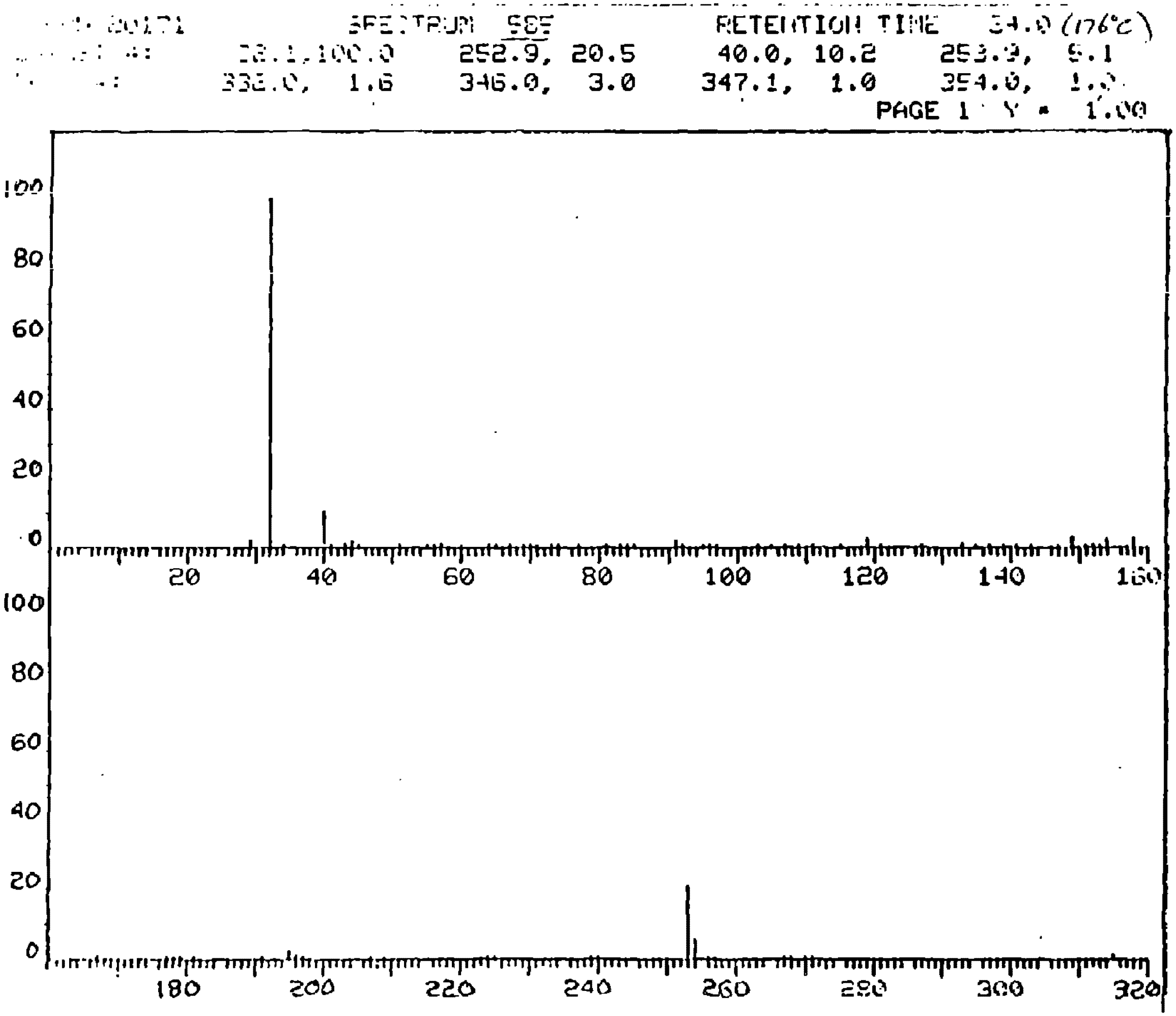
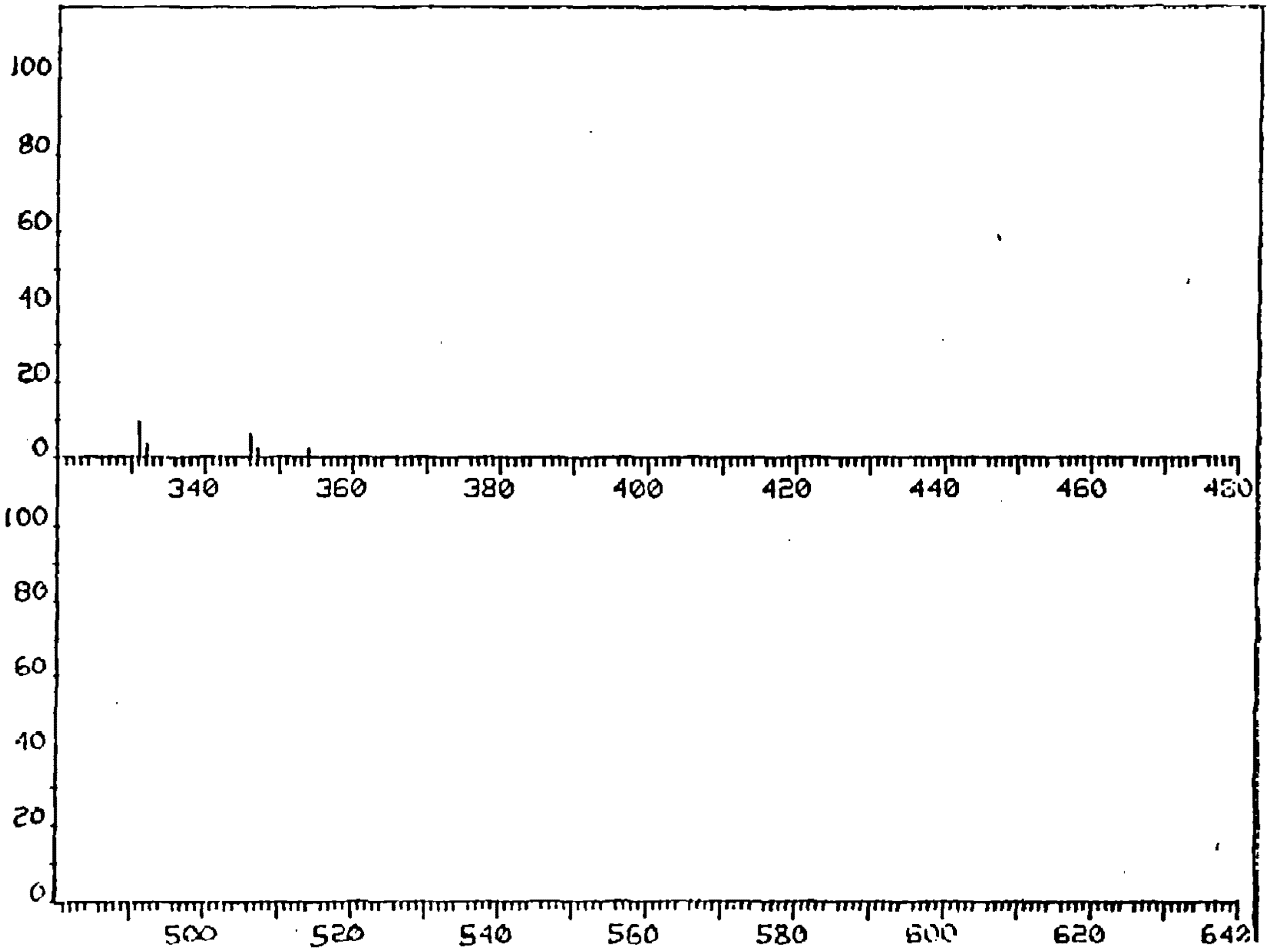


Figure A-9. Mass Spectrum of Peak +585.

```
FRN 20171          SPECTRUM  585          RETENTION TIME   34.0 (176°c)
LARGEST 4:     32.1,100.0     252.9, 20.5     40.0, 10.2     253.9,  5.1
LAST 4:       332.0,  1.6     346.0,  3.0    347.1,  1.0     354.0,  1.0
                                                    PAGE 2  Y =  2.00
```



RT 31/10

```
NORM AREA SPECTRUM   FRN 20171                                    PAGE 1      1.00
LARGEST 4:     352.9,100.0    253.9, 24.5    331.0, 22.1    149.0, 17.8
LARGEST 4:     331.0, 22.1    332.0,  7.4    346.0, 15.3    347.1,  6.2
+ 585 -570
```

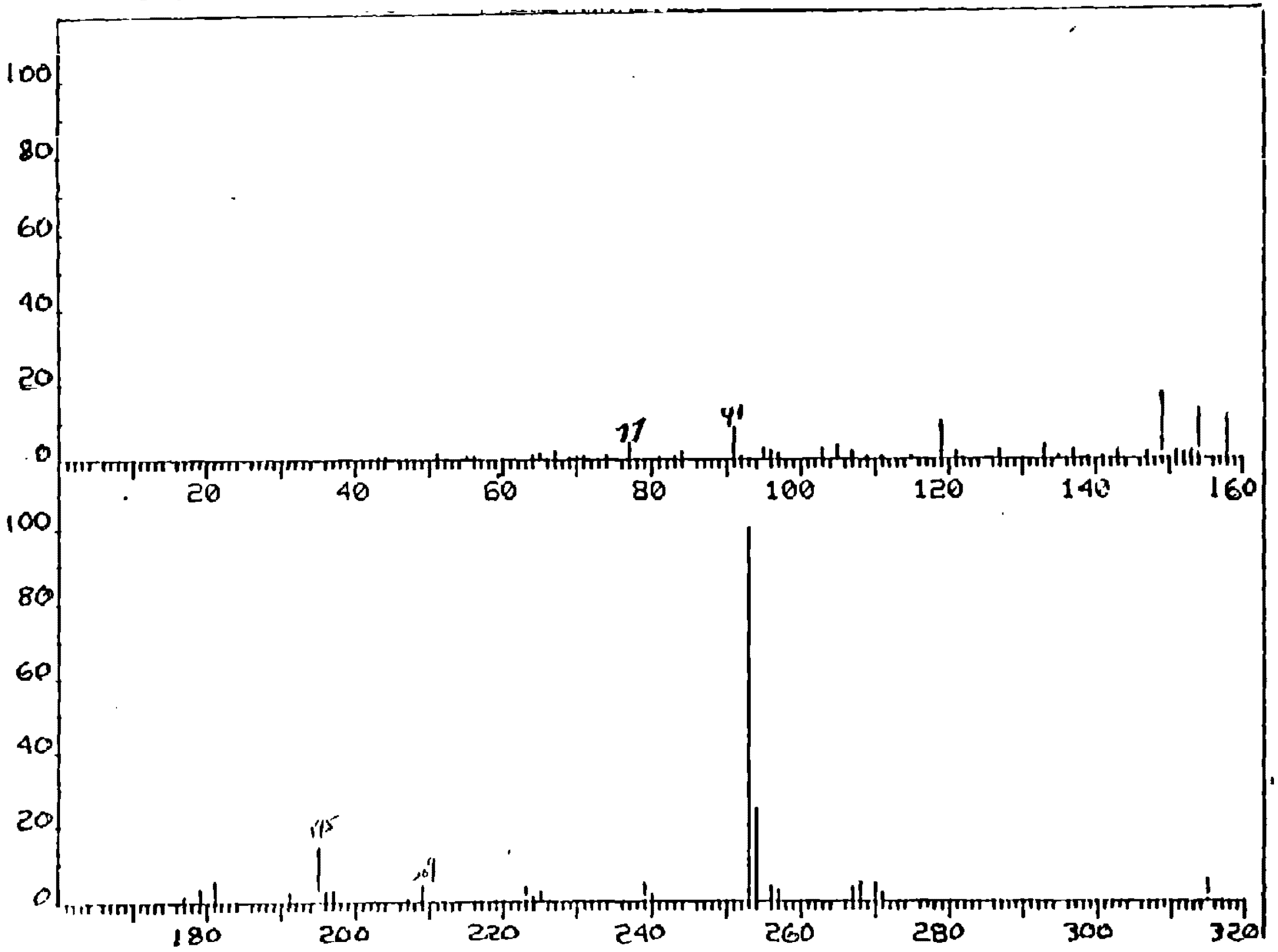
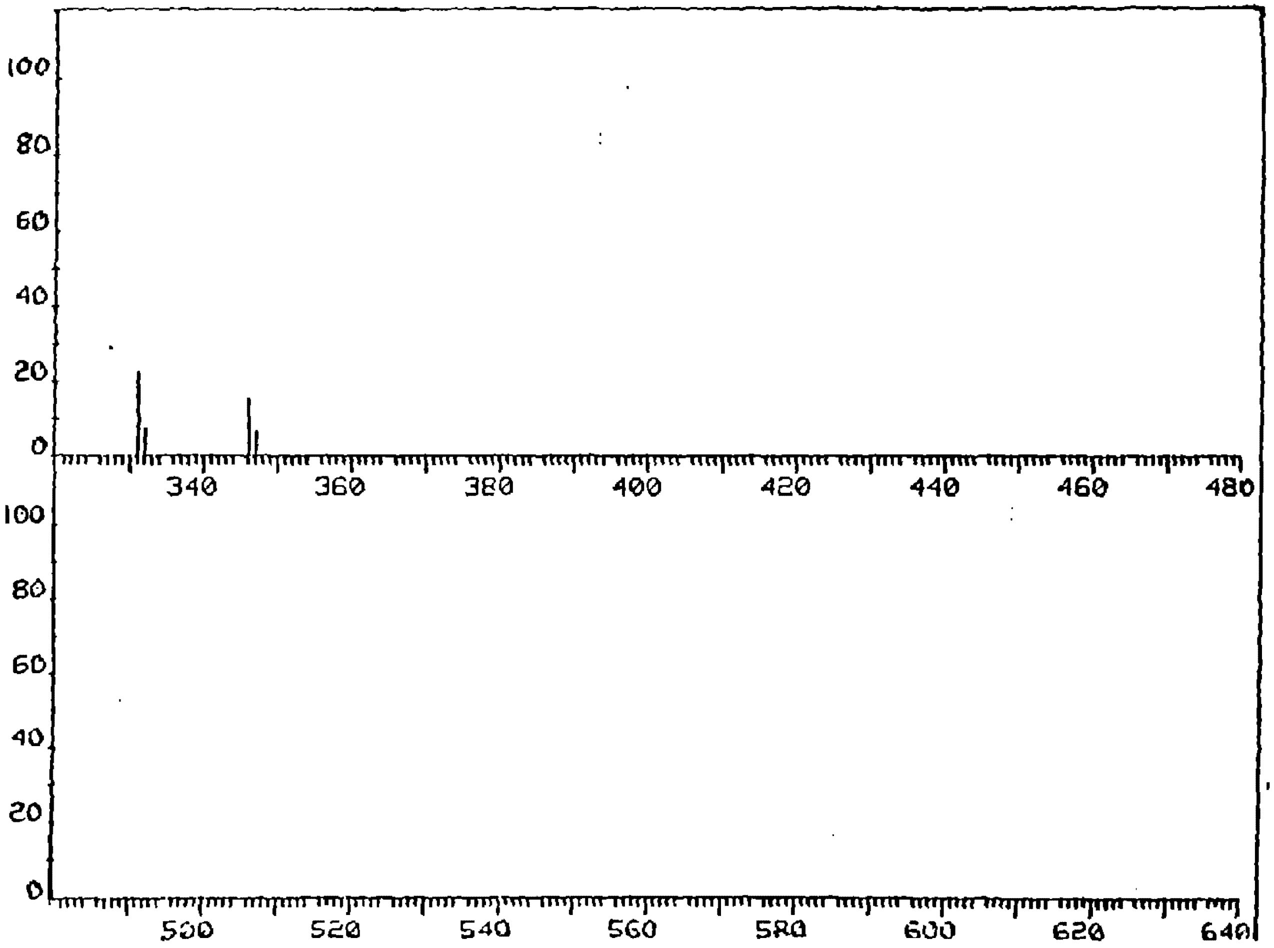


Figure A-10. Mass Spectrum of Peak +585, second run.

R7 34[illegible]

```
NORM AREA SPECTRUM   FRN 20171                                  PAGE 2  Y =  1.00
LARGEST #:     252.9,100.0     253.9, 24.5     331.0, 22.1     149.0, 17.5
LAST #:        331.0, 22.1     332.0,  7.4     346.0, 15.3     347.1,  6.2
+ 525 -570
```



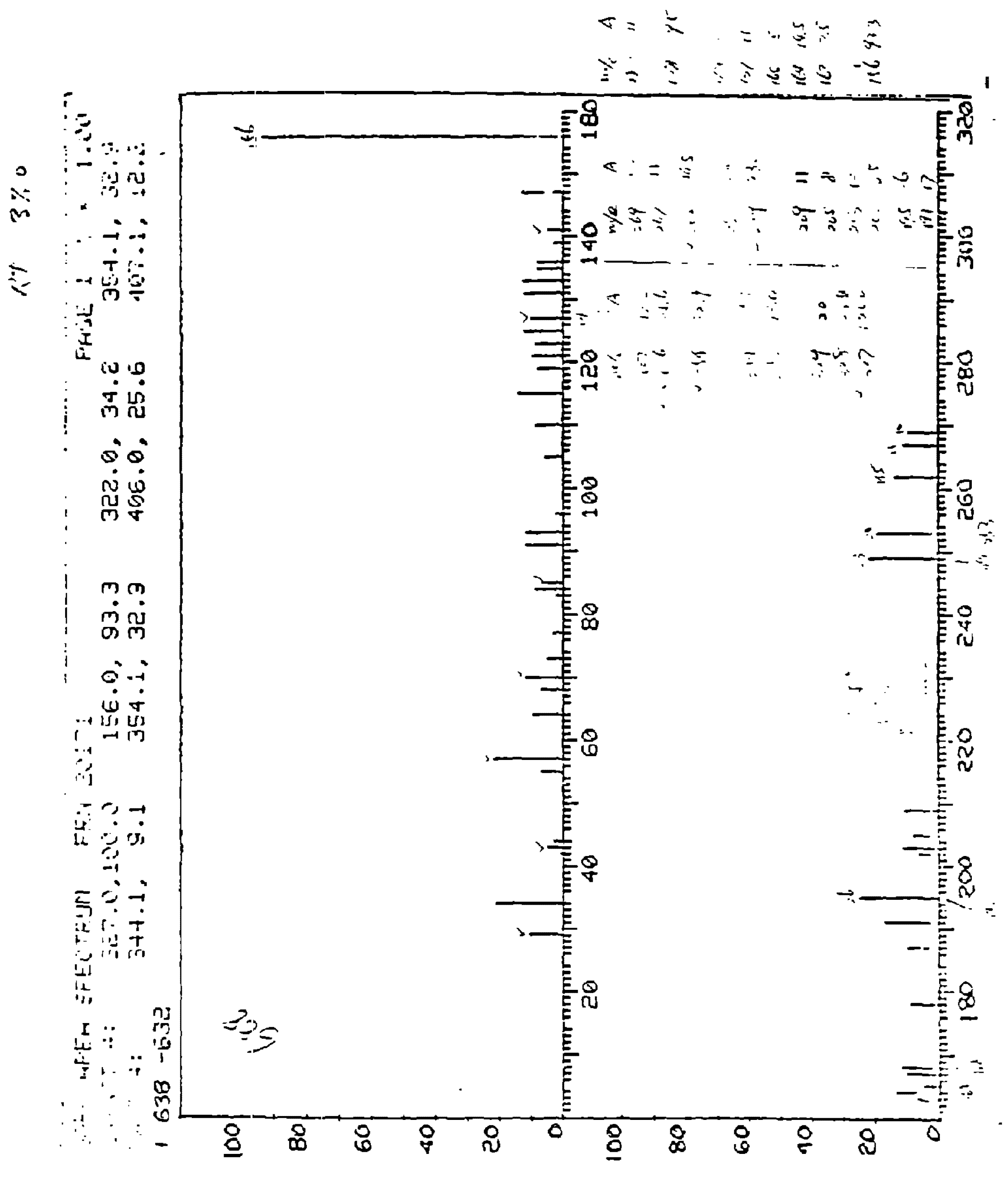


Figure A-11. Mass Spectrum of Peak +638.

RT 270

```
NORM. AREA SPECTRUM   FRN 20171                    PAGE 2  Y = 1.00
[illegible] #:   327.0,100.0    156.0, 93.3    328.0, 34.8    354.1, 32.9
[illegible] #:   344.1,  9.1    354.1, 32.9    406.0, 25.6    407.1, 12.2
+ 638 -632
```

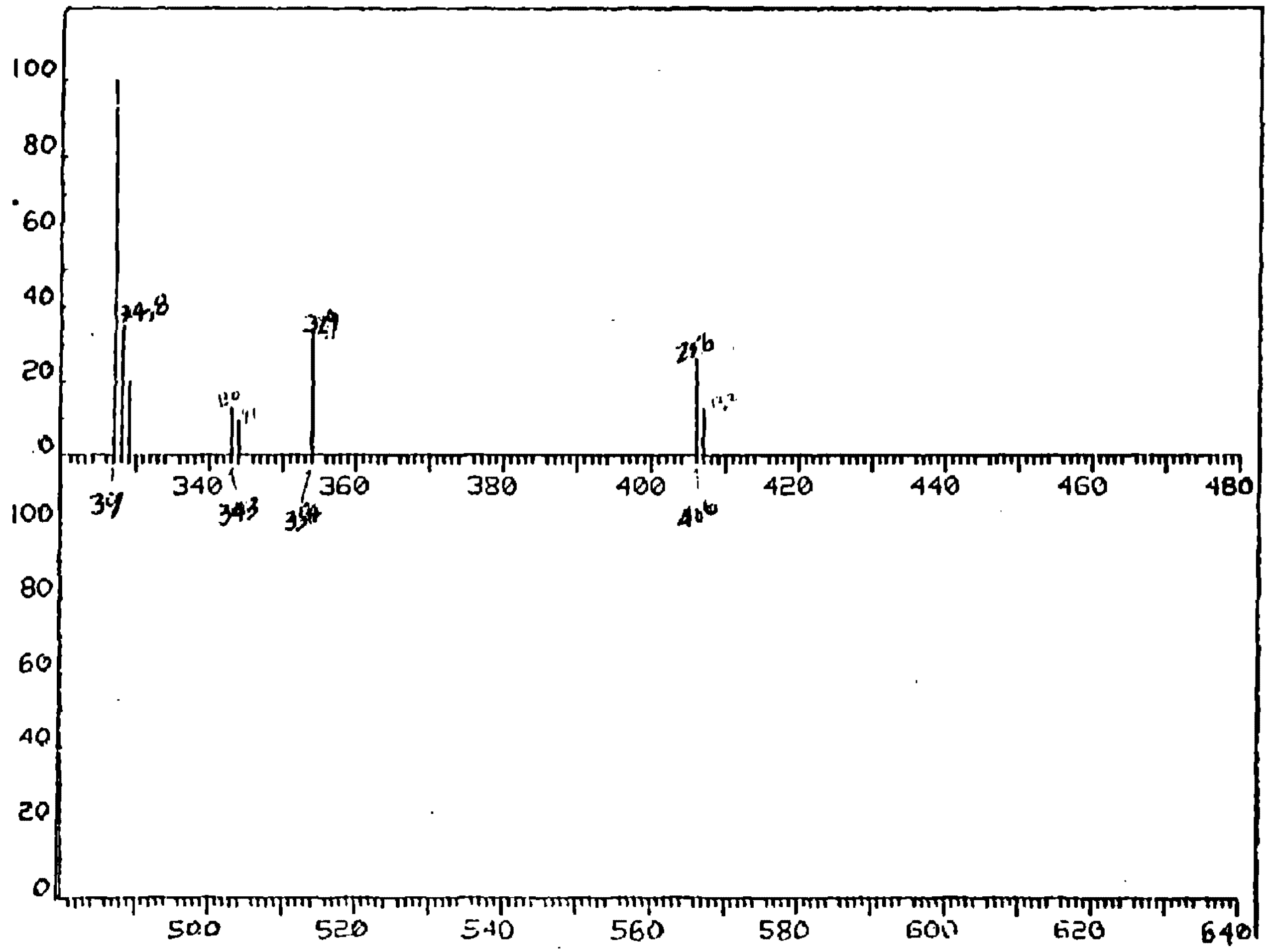
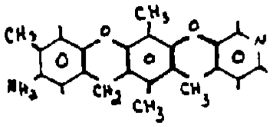


Table A-2. Summary of Mass Spectra for MD-3.

Peak no.	Retention Time (min)	Mass	Possible Structure
+267	15.5	32	Sulfur dominated spectra
+585	34	346	
+638	37	434