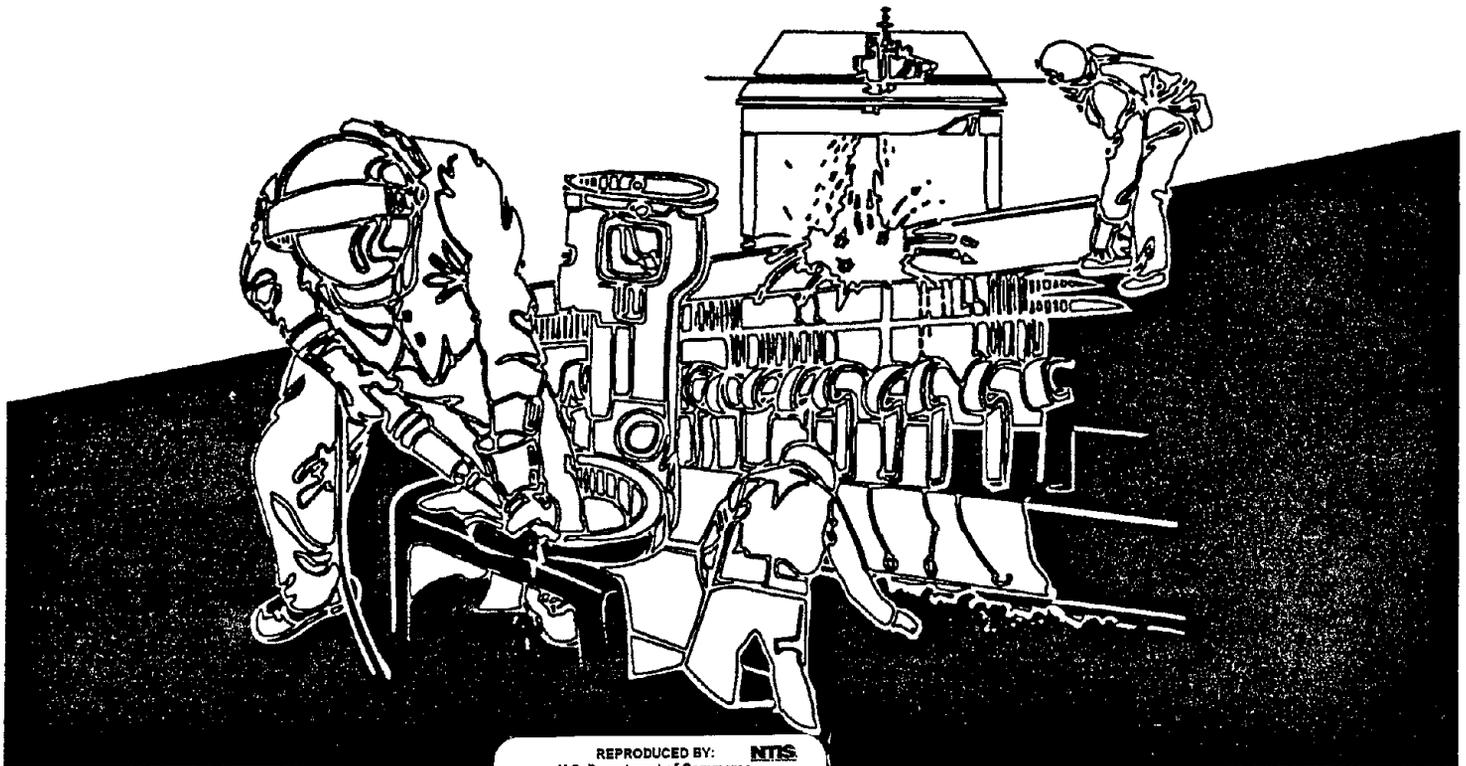




NIOSH HEALTH HAZARD EVALUATION REPORT

HETA 96-0100-2636
Harley-Davidson Motor Company
Tomahawk, Wisconsin

Beth Donovan Reh
Richard J. Driscoll
Eric J. Esswein



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PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, technical and consultative assistance to Federal, State, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Beth Donovan Reh, with the contributions of Dr. Richard J. Driscoll and Eric J. Esswein, of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Eric J. Esswein, Richard Hartle, and David Marlow. Laboratory assistance was provided by the Measurements Research Support Branch, Division of Physical Science and Engineering, and by the Immunology Investigations Branch, Division of Respiratory Disease Studies. In particular, Ardith Grote performed the extensive thermal desorption tube analyses. Desktop publishing by Ellen Blythe.

Copies of this report have been sent to employee and management representatives at Harley-Davidson and the OSHA Regional Office. This report is not copyrighted and may be freely reproduced. Single copies of this report will be available for a period of three years from the date of this report. To expedite your request, include a self-addressed mailing label along with your written request to:

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**Health Hazard Evaluation Report 96-0100-2636
Harley-Davidson Motor Company
Tomahawk, Wisconsin
April 1997**

**Beth Donovan Reh
Richard J. Driscoll
Eric J. Esswein**

SUMMARY

The National Institute for Occupational Safety and Health (NIOSH) received a confidential employee request to conduct a health hazard evaluation (HHE) at the Harley-Davidson plant in Tomahawk, Wisconsin. The requesters reported symptoms of chest tightness, breathing difficulties, headaches, heart irregularities, and hoarseness that were thought to be related to their work environment, and they listed the paint and clear-coat booths as primary concern areas. NIOSH investigators conducted an initial site visit on May 2, 1996, and then two follow-up visits on August 13-15, 1996, and November 18-20, 1996. During the site visits, exposures to organic compounds, microbial contamination, and endotoxins were measured; the ventilation system was evaluated; and employees were asked to complete a symptoms questionnaire. Using thermal desorption tubes, organic compounds were measured in 18 locations throughout the plant, and 18 specific compounds were quantified for comparison by location and season. Many exposures were slightly higher during the November site visit, but all were orders of magnitude below any occupational exposure limits. The microbial contamination in the water pits was up to 10^6 colony forming units per milliliter of water (CFU/mL) of gram negative bacteria and 10^4 CFU/mL of fungi; these measurements were higher than the concentrations being measured by the plant maintenance personnel. The endotoxin air concentrations ranged from 0.1-1359.1 endotoxin units per cubic meter of air (EU/m³) during the August site visit, and from 0.4-12.2 EU/m³ during the November site visit. Currently, occupational exposure limits for endotoxins do not exist. The symptom questionnaire results were analyzed by department, work area, and season. The pin-stripping and masking areas had the highest prevalence of symptoms, and no statistically significant increase of symptoms was reported during the heating season in any area.

In comparison to current occupational exposure limits, no overexposures were documented; however, there were low levels of many different chemical and biological exposures. The health effects from exposures to mixtures such as the ones in this plant are not known, but many of the compounds are irritants or sensitizers individually, and it is plausible that some of them could have at least additive, if not synergistic health effects, as a mixture. The highest concentrations (which were still low relative to occupational exposure limits) were found in the pin-stripping area and special repairs booth. In conjunction, the questionnaires showed that employees in and near these areas reported more symptoms than employees in other areas. Recommendations were made for added local exhaust ventilation, routine symptoms surveillance and industrial hygiene monitoring, and improved communications.

Keywords: SIC (3714, Motor vehicle parts and accessories) paints, solvents, thermal desorption tubes, endotoxins, microbial contamination, ventilation, direct gas-fired heating, respiratory symptoms, chest tightness, breathing difficulties, headaches

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INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) received a confidential employee request to conduct a health hazard evaluation (HHE) at the Harley-Davidson plant in Tomahawk, Wisconsin. The requesters reported symptoms of chest tightness, breathing difficulties, headaches, heart irregularities, and hoarseness that were thought to be related to their work environment, specifically the paint and clear-coat booth areas. NIOSH investigators conducted an initial site visit at the plant on May 2, 1996. An industrial hygienist reviewed work processes, Material Safety Data Sheets (MSDSs), and industrial hygiene sampling records; and an epidemiologist conducted voluntary confidential interviews with employees who had been experiencing symptoms. Based on this initial site visit, a second site visit was conducted on August 13-15, 1996, during which a team of NIOSH investigators performed an industrial hygiene and symptom surveillance evaluation. This evaluation was repeated on November 18-20, 1996, so that results could be compared between the heating and non-heating seasons.

BACKGROUND

This plant, built by and operated in the 1950's as Tomahawk Boat, was purchased by Harley-Davidson in 1963. The primary function of the plant was manufacturing fiberglass parts but, in the last 10 years, painting processes have been added. The plant still produces fiberglass parts and accessories for Harley-Davidson motorcycles. Sheet molding compound (SMC) is shipped to the plant where it is cut and formed in a compression mold. The parts are then aired, rough sanded, and any defects are repaired with a two-part epoxy. All parts are washed with distilled water and then transferred to a painting area. There are three enclosed paint booths, and also a clear-coat booth. After parts are painted and cured, they are sprayed with the clear-coat. Parts with observable paint defects are fine-sanded, buffed, repainted, and then sent to the final assembly area.

Both management and union representatives provided NIOSH investigators with a history of the health symptoms that led to this HHE request. In August 1995, one worker began having asthma-like attacks and had to go to a hospital emergency room. After about three weeks, that worker's breathing difficulty subsided, but a few others began experiencing respiratory problems. When the company published the respiratory problems to the general workforce, the number of complaints tripled among the day shift employees. The symptoms were reported to be flu-like (fever, chills, colds) and chest burning, and employees noted that their symptoms improved on weekends and on days away from work. One employee had not been able to return to work at all because of a potential work-related illness, but was back at work by the time of the second site visit. The symptomatic workers were from all ranges of seniority, although there did appear to be a higher prevalence among second shift employees, who tended to have less seniority.

In an effort to improve product quality, Harley-Davidson management renovated the building a few years ago, which resulted in a much more tightly-sealed building with fewer windows. The plant is divided into separate rooms that have separate ventilation systems and connect to each other through overhead doors which are kept closed when not in use. The east paint line and dealer parts pin-striping and masking areas are all in one room; all the parts painted in here are sent directly to dealers. The north and south paint lines, the clear-coat line, and the main pin-striping and masking areas are all in another room in the southwest part of the building.

Several changes have been made to the processes in the past few years. The north paint line, which used to operate with a filtered air system, was changed during the 1993 Christmas shut down. The line is now an enclosed paint booth with laminar flow ventilation from ceiling to floor. Operators stand on a grated floor over a recirculating water bath. Air flows through the floor, across the water surface, up along the back wall, which is an enclosed vertical water-wall, and then is exhausted outside. The recirculated water is filtered to remove the paint, which is sent to a municipal landfill. The east and south paint lines once operated with a

horizontal water-wash system, but these lines were changed in the summer of 1994 to a control system similar to the one used on the north paint line. Each of these booths has the same direct gas-fired air-handling unit (AHU). Air flows across the open flames and through several sets of filters, including one water filter for humidification, and then into the booths.

The clear-coat line was installed in 1991. In July 1995, the conveyor system was extended (increased from 600 to 950 parts per shift), a robotic arm was added to spray the clear-coat, and the coating was changed to a 100% acrylic-based paint. The line is similar to the paint booths except for the water pit and AHU. The water is aerated in the pit prior to draining. The AHU system, which was installed during the 1995 Christmas shut-down, is called a target-air system and has a direct gas-fired heating system like the other AHUs. However, instead of a water filter for humidification, water is sprayed directly into the gas flame.

These open-flame gas burners operate automatically in response to the heating need; whenever they initially ignite, workers reportedly can smell natural gas and complain of headaches and dizziness. The air supplied by these paint room AHUs can range from 100% outside air to up to 40% recirculated air. During the heating season, air is recirculated to reduce heating costs, and several employees report that symptoms increase during this time.

The routine industrial hygiene sampling data had not detected any concentrations higher than exposure limits. However, there are numerous chemicals in this plant, and every MSDS reviewed listed the product as a respiratory, eye, and skin irritant. Although bioaerosols do not have standardized occupational exposure limits, the endotoxin concentrations previously detected in one location were in the range that has been associated with acute respiratory effects such as chest tightness and cough.

To address the health concerns, the company had conducted air monitoring and had all the direct gas-fired air-handling units (AHUs) reset to minimize the production of nitrogen oxides. (It had

been hypothesized that since these AHUs can produce nitrogen oxides, which are respiratory irritants, their presence could exacerbate the respiratory irritation that might result from the other exposures in the plant.) Also, during the end of the most recent heating season, the AHUs were operated with 100% outside air. In an effort to contain exposures from the water system, the back of the clear-line booth had been enclosed with plastic from winter 1996 to the July 1996 shut-down when the water pit was modified. As spring began, fewer employees were reporting symptoms, although some symptoms persisted throughout the summer and into the next winter. To date, all of the environmental sampling and ventilation changes have not helped the company identify the cause(s) or potential cause(s) of the symptoms being reported by employees or whether or not these symptoms are related to the work environment.

May 2, 1996 Site Visit

NIOSH investigators first visited this plant on May 2, 1996. The site visit began with an opening conference attended by the United Paper Workers Local 7460 vice-president, management representatives, two representatives from Travelers Insurance (the company that conducts the industrial hygiene sampling for the plant), and the two NIOSH investigators – an industrial hygienist and an epidemiologist. The NIOSH investigators were briefed on the plant processes, the health complaints that had been occurring, and the actions that had been taken to try to address the problems. Following the opening conference, NIOSH investigators toured the facility and conducted a preliminary environmental evaluation and epidemiologic review. Based on this initial site visit, NIOSH investigators planned to return to this plant to evaluate exposures and health complaints both during the non-heating season and the heating season.

August 13–15, 1996 Site Visit

The second site visit began with an opening conference attended by the United Paper Workers Local 7460 vice-president, a United Paper Workers

International industrial hygienist, Harley-Davidson management representatives, an industrial hygienist and a ventilation engineer hired by the company, and a team of NIOSH investigators. Both consultants that were hired by the company were asked to participate in this site visit to facilitate the implementation of any NIOSH recommendations. During the opening conference, labor and management representatives explained that throughout the spring and summer, the reported health symptoms appeared to decrease, but at least two employees were still experiencing symptoms. Very few changes had been made during the July 1996 shut-down. The pump configuration in the clear-line water pit was altered by removing the aerators to try to reduce mist generation, and the temporary plastic enclosure was removed from behind the clear-line. There were no product changes between the first and second site visits.

November 18–20, 1996 Site Visit

This third site visit did not have an opening conference, but there was a meeting held with the United Paper Workers Local 7460 vice-president, management representatives, and an industrial hygienist contracted by the company so that the NIOSH representatives could go over the interim report and explain the sampling results in more detail. During this meeting, it was emphasized that no over-exposures were documented, but that there were many chemicals and microbes detected, and that the synergistic effects of this mixture of exposures is unknown. There was also a discussion about allergic and hypersensitivity reactions to make clear that once an individual becomes sensitized to an exposure, even a very small amount can trigger a reaction and occupational exposure limits are not effective for protecting those sensitized individuals. During this meeting, NIOSH investigators learned that two more employees had to leave work suddenly due to respiratory distress since the last site visit. Also, one day in November there had been a problem with the clear-line booth exhaust and there was an increase in employee complaints that corresponded with it.

METHODS

Environmental Evaluation

May Site Visit

The initial environmental evaluation consisted of observing the operations and ventilation systems, reviewing past industrial hygiene sampling data, and reviewing Material Safety Data Sheets (MSDSs). Based on this initial evaluation, a detailed sampling protocol was designed to be performed in the summer and then again during the heating season.

August Site Visit

Most of the sampling was conducted during the second shift because both the company and the union agreed that employees reported more symptoms on that shift. During the days of the survey, the south paint line was not in operation, and the east line was only operated during the first part of the third shift. Sampling times were adjusted so that sampling in the east paint room occurred during the third shift.

To evaluate the many volatile organic compound (VOC) exposures, a systematic sampling strategy was performed to evaluate the types and quantities of airborne compounds present in different areas of the plant and to possibly identify compounds whose presence was not previously known, thus providing an exposure map of the plant. Also, a few of the sampling locations were chosen to determine whether ventilation exhaust was being re-entrained into the building. Thermal desorption tubes and Gillian® low-flow air sampling pumps calibrated to 25 milliliters per minute (mL/min) were used to collect 4-hour general area (GA) air samples at 18 locations throughout the plant. The stainless steel tubes, configured for the Perkin-Elmer ATD 400 thermal desorption system, were analyzed using the ATD 400 automatic thermal desorption system interfaced with a HP5890A gas chromatograph and a HP5970 mass selective detector (TD/GC/MSD). (The method is detailed in Appendix A.)

Bulk samples from the paint line water pits were collected and sent to a contract laboratory for microbial analysis. For each sample, serial dilutions were made and plated onto growth media and incubated appropriately – R2A agar and 29°C for bacterial analyses, malt extract agar and about 25°C for fungal analyses, and tryptic soy agar and 55°C for *Thermoactinomyces*. After incubation, the plates were counted and representative species were identified.

To determine the potential for endotoxin exposure in the work areas, GA air samples were collected at each water pit and nearby work areas, and sent to a NIOSH laboratory for analysis by the *Limulus* amoebocyte lysate (LAL) assay. Another GA air sample was collected outside the north paint line and analyzed for hexahydrophthalic anhydride (HHPA), a sensitizing compound that is a component of the white paints used in the plant. There is no standard NIOSH analytical method for HHPA, so a modified version of the Occupational Safety and Health Administration (OSHA) sampling and analytical method for phthalic anhydride was used; the details of this method are described in Appendix B. All of the endotoxin and HHPA air samples were collected on 0.8-micron (μm), 37-millimeter (mm) polyvinyl chloride (PVC) filters using Gilian® high-flow air sampling pumps at 2.0 liters per minute (L/min).

November Site Visit

As with the August site visit, most of the sampling was conducted during the second shift. The thermal desorption tube sampling was repeated in the same manner that it was performed in August, except that a few locations were not sampled for practical reasons. Only one sample was collected in the east line area (instead of three) because the area was not operating full-time during second or third shift, and no samples were collected at the outside-air intakes because the gas fires prevented internal access to the AHUs. The endotoxin air sampling was also repeated, but again in fewer locations; and no bulk samples were collected for microbial analyses. If any white paint had been used during this site visit, sampling for HHPA would have been repeated.

Epidemiologic Evaluation

Harley-Davidson management and union representatives cooperatively identified a group of workers who were known to have become ill at work and to have associated the illness with work related exposures. Of this group, 13 persons from either the first or second shift volunteered to be informally interviewed by an epidemiologist from NIOSH (third shift workers were not interviewed). Based upon the symptoms described by the workers during these interviews, all employees were asked to complete a symptom questionnaire during the August and November site visits. These occasions were selected to assess whether symptom prevalences differed during periods in which the building was not heated (Symptom Survey 1) and when it was heated (Symptom Survey 2).

RESULTS AND DISCUSSION

Environmental Evaluation

Thermal Desorption Tube Sampling Results and Discussion

The results from the thermal desorption tube sampling are presented in Tables 1-7 and Figures 1-3 at the end of this report. (The raw data is presented in Appendix B.) Figure 1 shows the locations where samples were collected; one 4-hour (6-liter) sample was collected in each of the 18 locations on each day (only 14 locations during the November site visit). On the first day of each site visit, a few duplicate samples were collected for the laboratory to use to determine what compounds to quantitate. Based on these samples, 18 compounds were quantitated. Tables 1 and 2 present the compounds and their analytical limits of detection and quantification for each site visit.

Since this method is not standardized, the data should only be considered semi-quantitative, and therefore

should be interpreted using a relative scale. A scale from 0–10 was used to assign the measurements a relative number for the purpose of comparing the sampling results between locations (Table 3). “Not detected” values were assigned a “0,” trace values were assigned a “1,” values between trace and 1 microgram per sample were assigned a “2,” and so on. Each raw data point was converted to the relative scale, and then the relative scale numbers were averaged by location. These averages are presented in Tables 4–5 and Figure 2. Each chart in Figure 2 can be compared with the other charts in order to visualize differences in exposures by location and season. Also, the averages for each compound were summed by location to compare total relative concentrations. These totals are presented in Tables 6–7 and Figure 3.

Thermal desorption tubes are sensitive and will detect compounds at very low concentrations. To put these data in perspective, the sampling data for the pin-stripping location was compared to NIOSH recommended exposure limits (RELs) and then a mixture calculation was made to determine whether workers in that area might be overexposed to the mixture of the quantified compounds that have numerical RELs (see Tables 8–9). All the concentrations were orders of magnitude below the RELs, and the mixture calculation revealed no overexposure to the specific chemicals that were quantitated and have RELs. These results are consistent with the previous industrial hygiene sampling in this plant. However, this mixture calculation only accounts for compounds that were quantified and had RELs, which only represents a part of the total exposure mixture.

The thermal desorption tube sampling results reveal that employees in the main paint room (north, south, and clear lines; staging area, pin-stripping, and masking area; and touch-up spray room) are exposed to many different compounds in low concentrations. The highest exposures appear to be in the pin-stripping area and the touch-up spray booth, but again, these exposures are low relative to occupational standards. There was no quantifiable re-entrainment of compounds through the outside air (OA) intakes during the August survey.

There was generally no detected difference in the types of compounds detected on the thermal desorption tubes between the non-heating and heating season. However, the semi-quantitative data do suggest that there might be a slightly higher total concentration of compounds present during the heating season. (See Tables 6–7 and Figure 4).

Microbial Contamination Sampling Results and Discussion

Microorganisms (including fungi and bacteria) are normal inhabitants of the environment. The saprophytic varieties (those utilizing non-living organic matter as a food source) inhabit soil, vegetation, water, or any reservoir that can provide an ample supply of a nutrient substrate. Under the appropriate conditions (optimum temperature, pH, and with sufficient moisture and available nutrients) saprophytic microorganism populations can be amplified; the paint booth water pits provide an ideal environment for microbial amplification.

The bulk microbial sampling results are displayed in Table 10. (The raw data were previously communicated to Harley-Davidson by fax on September 24, 1996.) The samples from the paint booth water pits contained gram-negative bacteria concentrations up to 10^6 colony forming units per milliliter (CFU/mL) and fungi concentrations up to 10^4 CFU/mL. The sample collected from the clear line water pit did not contain bacteria at detectable concentrations, but did contain the highest concentration of fungi (12,000 CFU/mL *Acremonium* species and 30 CFU/mL *Paecilomyces* species). The microbial concentrations measured by NIOSH in the water pits were higher than the semi-quantitative measurements that are taken almost daily by the company. The debris found in the north line AHU contained high concentrations of both gram-positive and gram-negative bacteria and fungi. Currently, there are no occupational exposure limits for microbial contamination (in either the air or in water pits), but microbial exposures can be associated with health effects that are summarized in the following paragraph.

Some individuals manifest increased immunologic responses to bacteria, fungi, or their metabolites encountered in the environment. These responses and the subsequent expression of allergic disease is based, partly, on a genetic predisposition. Allergic respiratory diseases resulting from exposures to microbial agents have been documented in agricultural, biotechnology, office, and home environments.^{1,2,3,4,5,6,7,8} Acceptable levels of airborne microorganisms or bioaerosols have not been established, primarily because allergic reactions can occur even with relatively low air concentrations of allergens, and individuals differ with respect to immunogenic susceptibilities.

Endotoxin Sampling Results and Discussion

Endotoxins are lipopolysaccharides (LPS) that are part of the outer membrane of all gram-negative bacteria (GNB). GNB, and therefore endotoxins, are ubiquitous in nature; they are found in water, soil, and living organisms. Endotoxins are released when the bacterial cell is lysed (broken down) or when it is multiplying.^{9,10} The GNB growing in the water pits could result in higher than background concentrations of endotoxins in this plant, and therefore air sampling for endotoxins was performed.

The endotoxin sampling results are displayed in Tables 11-12. Blank filters were also submitted and the average endotoxin concentrations detected on these blanks were subtracted from the concentrations detected on the sample filters. The results from the August site visit ranged from below the average blank concentration to 1359.1 endotoxin units per cubic meter (EU/m³), and from the November site visit ranged from below the average blank concentration to 12.20 EU/m³. Currently, occupational exposure limits for endotoxins have not been established. However, Rylander has reported that sufficient toxicological data exists to establish an occupational exposure limit for endotoxins based on acute changes in pulmonary function. The following eight-hour time-weighted average (TWA) concentrations have been suggested: 200 endotoxin units per cubic meter (EU/m³) for airway inflammation with increased airway activity,

2000 EU/m³ for over-shift decline in forced expiratory volume in one second (FEV₁), 3000 EU/m³ for chest tightness, and 10,000-20,000 EU/m³ for toxic pneumonitis. Castellan has reported a calculated a no-effect level for pulmonary function of 90 EU/m³.¹¹

The concentrations measured during the August survey were higher than those measured during the November survey. Whether this is a seasonal change or due to improved control of microbial growth in the water pits is not known. The endotoxin concentrations measured by an outside consultant during the heating season of 1995 were lower than those of the August survey, but slightly higher than those of the November survey.

The three highest endotoxin concentrations detected in August were over the north paint line water pit, but the one air sample collected in the work area before the north paint line did not contain a concentration higher than the average of the blanks. Although the concentrations detected over the clear line water pit were relatively low (which is not surprising since no gram-negative bacteria were detected in the water sample), the concentrations in the work area in front of the clear line and the pin-striping area were higher than could be attributed to the clear line water pit or to the outside air. The endotoxin exposure source for this area has not yet been determined, but the concentrations are lower than those associated with acute lung function effects (reported to Harley-Davidson by Dr. Donald Milton as 42.5 EU/m³). Although the concentrations detected over the east and north paint line water pits are relatively high, these are not areas where employees work. Nevertheless, endotoxin exposures are associated with health effects, which are summarized in the following paragraphs.

Health effects from exposure to endotoxins have been documented in human case studies, human experimental studies, and animal studies. Common effects associated with endotoxin exposure include: fever, malaise, subjective chest tightness, increased respiratory and pulse rate, airway irritation, acute bronchoconstriction, chronic bronchitis, cough, dyspnea (shortness of breath), wheezing, changes in

white blood cell counts (mostly an increase in neutrophils), and decreased pulmonary function (although some studies did not document any decrements in pulmonary function).^{9,10,14,15,1213,14,15,16,17}

Hexahydrophthalic Anhydride (HHPA) Sampling Results and Discussion

The air sample collected in August and analyzed for HHPA did not contain a detectable concentration (<0.01 mg/m³). However, white paint was only used minimally throughout this shift. Another sample was not collected because white paint was not used any other time during this survey. Although there are no occupational exposure limits for HHPA, it is a known respiratory sensitizer at very low exposures.¹⁸

Evaluation of Ventilation Systems (August site visit)

The facility uses general dilution ventilation in the main plant areas and has several local exhaust ventilation systems, including the enclosed paint booths with vertical water-walls on the north, south, east and clear paint lines. The south mix room and the main paint room were confirmed to be under slight negative pressures. The main exhaust fan for these areas was not working at the time of the evaluation, the reason for which could not immediately be determined. Paint booth pressurization was evaluated using smoke traces and a TSI VelociCalc® Model 8360. Air gaps were visible where the doors met the door jambs. Make-up air enters these booths through filters in the ceiling and through either end of the hood-line where parts enter the booth via the conveyor line. The north and south booths were under a slight negative pressure (verified by chemical smoke entrained into an airstream). The east and clear line paint booth were both at neutral pressure with respect to the rest of the plant.

The water sump behind the clear paint line was inspected because previous environmental sampling by Harley-Davidson suggested that it was possibly a bioaerosol reservoir. Smoke traces confirmed a strong

and consistent pattern of air movement upwards out of the sump and towards the top of the clear paint line. The heat radiating from the dryer section downstream of the clear paint booth added to the upward convection current. It is possible that aerosols from the sump could be dispersed towards the front of the clear line and the pin-stripping area by the convective currents confirmed to exist above the sump.

Paint Booths

Operators access the enclosed paint booths by steps leading to doors at either end. The four-sided booths are constructed of metal and glass and are trapezoidal in shape. The operators stand on grated metal decking, which is over the water sump, and use hand-held spray guns to paint the parts which move through the booth via a conveyor. When inside the booths, operators wear supplied air respirators with loose fitting hoods.

The paint booth in the pin-stripping area is not used for painting operations, but only for storage of containers of paints and for paint mixing. Thus, it only serves to control fugitive emissions from the stored products and some mixing operations performed within five feet of the rear of the booth. To evaluate the efficacy of the booth, face velocity was measured. The booth measured 12'1" in width and 6'9" in height (84 square feet), and had an internal depth of 6 feet. Tape was used to mask the perimeter, and marks were made at one foot intervals on the horizontal and vertical perimeters. Eighty-four center-point measurements were made using a TSI VelociCalc® Model 8360 velocity meter configured in the velocity function mode measuring airflow in feet per minute (fpm). The average face velocity for the booth was determined to be 47 fpm. Volumetric flow was determined to be 3948 cubic feet per minute.

Using smoke traces, effective capture was observed up to five feet from the inside slots of the plenum for this booth. Beyond five feet, turbulence from overhead high velocity drum diffusers affected capture and compromised this control. The American Conference of Governmental Industrial Hygienists

(ACGIH) recommends face velocities of 100 fpm and 60 fpm, respectively, for air spray and airless spray painting booths. This booth lacked particulate filtration, but did have a carbon filter that the air passed through before recirculating back into plant. Information about the maintenance of the carbon filter was not available.

In the touch-up spray room, there is a bench-top ventilation booth that is used except when working on side-cars, which are too large to fit into the booth. This paint booth was also evaluated using the same method described for the pin-stripe paint booth. This booth measured 5' X 4' (20 square feet), and a total of 20 center-point velocity measurements were made. The average face velocity for the booth was determined to be 149 fpm. Volumetric flow was determined to be 2980 cubic feet per minute. Several factors impeded the performance of the spray booth and created turbulent air flow in the touch-up spray area. A set of metal cabinets were partially obstructing the transfer grill for room make-up air, a portable fan was used in this room, and the door to this room was left open. When the transfer grill was free of obstructions, the fan was turned off, and the door was closed a smooth laminar air movement was evident.

Air-handling Units (AHUs)

The main and east paint room AHUs (general building ventilation) and the north, south, and clear paint line AHUs were all inspected during this survey. Each AHU was composed of six sections — the make-up air intake, the direct gas-fired burner, the rough and final filters, the coils and condensate pan, the evaporative cooling system, and the fan room — and each section was accessible through a maintenance door. The clear line AHU was slightly different; it did not contain an evaporative cooler, but instead contained a "target-air" system — water-injection directly into the gas flame for humidification and a mist eliminator upstream of the pre-filters. The humidification system was not active at the time of the survey; water scale was found on the mist elimination matrix, but it was otherwise clean. No obstructions were evident in any make-up air

intakes. Although the burners were not operating and the flame path could not be visually observed during the site visit, the burner sections appeared to be located at a sufficient distance from the building return-air plenum to effectively isolate the flame head from building return air. Under normal AHU operation building return air would not be expected to pass across or through the burner section of these direct gas-fired units.

All AHUs were equipped with appropriate mechanical filtration — 24" x 24" x 2" pleated panel pre-filters (estimated at 40% ASHRAE dust spot efficiency) and 24" x 24" x 26" 90–95% efficient final pocket-type filters. No filters were missing and, with the exception of a lot of insects on the pre-filters, the filters appeared clean. Both sets of filter media were dry to the touch and free of any visible microbiological growth. No evidence of filter bypass (e.g. dust streaking, obvious gaps in filter frames, blowby, or filter collapse) was noted; this was supported by the clean condition of the coils. No evidence of visible microbiological growth was observed in the condensate pans, which appeared to drain appropriately. The evaporative cooler sections were not functioning at the time of the ventilation system survey, and several inches of water was present in the evaporative cooling reservoirs. The water was clear and free of any slime; the sumps were also free of any notable slime or visible microbiological contamination.

A five-gallon bucket, half full of used cotton rags, was found in the make-up air section of the main paint room air handling unit. The rags had been wet at one time but were dry at the time of the inspection and appeared to be free of any visible microbiological growth. Pieces of metal hardware (fasteners of some type) and a used tube of caulk were found on the floor inside of the outdoor-air intake section of this AHU. Downstream of the filter sections, the fan rooms were clean and free of significant visible debris on the floors.

An accumulation of dry, granular, brown debris was found scattered downstream of the evaporative cooler section of the north paint line AHU. The source of the material was not apparent, but vacuum cleaning

attachments were also left in this area suggesting that the debris was intended to be cleaned up, or that it was previously cleaned up and accumulated again. A bulk sample was collected for analysis of microbial contamination, and the results are presented in the microbial analysis section of this report.

Based on visual observation of the rooftop stacks and rooftop AHUs, it appeared possible that under certain wind conditions stack emissions could be entrained into make up air intakes for several air handlers. However, entrainment of stack emissions was not confirmed by the air sampling during this survey.

Epidemiologic Evaluation

Harley-Davidson management and union representatives cooperatively identified a group of workers who had become ill at work and associated their illness with work-related exposures. Of this group, a total of 13 persons from the first and second shift volunteered to be informally interviewed. The average age of the workers interviewed was 38, the majority were female (61%), and they had worked at Harley Davidson 7 or more years. Virtually all of these workers reported fatigue, and respiratory symptoms such as difficulty breathing, shortness of breath, and chest tightness. With one exception, the workers indicated that their symptoms began in the fall of 1995, and they associated the onset of symptoms with a redesign of the air-handling system. The one remaining worker not associating symptoms with the air-handling system reported experiencing respiratory-related symptoms for over two years. In general, the symptoms reported during the interviews tended to occur within hours of reporting to work, worsen by the end of the week, and tended to resolve after leaving work at the end of shift or on weekends or holidays. Two workers reported a flu-like illness that occurred during the fall of 1995. This illness was characterized by chills, muscle aches, and fever. These flu-like symptoms were reported to have occurred while the worker was at home, approximately 2-6 hours after the end of shift. Furthermore, these symptoms were reported to persist for several weeks.

Symptoms Questionnaire

Based upon the symptoms described by the workers during informal interviews, employees at Harley-Davidson, Tomahawk Division, were asked to complete a symptom questionnaire on two separate occasions. These occasions were selected to assess whether symptom prevalences differed during periods in which the building was not heated (Symptom Survey 1) and heated (Symptom Survey 2). Age, work experience and the gender of participants were similar in both symptom surveys (Table 13). Overall, employees reported slightly lower symptom prevalences while the building was heated (Table 14). The differences in symptom prevalences between the two heating periods, however, were not statistically significant.

Comparisons by Department

Survey 1 (no building heat) symptoms were compared by department (Table 15). A majority of respondents (74%) and a majority of symptoms (71-87%) were reported by workers in Departments 453 and 456. Furthermore, in 9 of the 10 symptoms recorded, the prevalence of symptoms was higher among workers in Department 456, compared with those in Department 453; however, only differences in chest tightness and flu-like symptoms were statistically significant. Thus, workers in Department 456 were twice as likely as workers in Department 453 to report chest tightness (Prevalence Rate Ratio (PRR) 1.96, 95% Confidence interval (CI) 1.16, 3.32), and more than 3 times as likely to report flu-like symptoms (PRR 3.67, 95% CI: 1.06, 12.67). No further comparisons were made between the remaining departments because of the limited number of respondents.

With the exception of dry cough (Department 452 and 456), aches (Department 453 and 456), and wheezing (Department 456), the reported symptom prevalences during symptoms survey 2 (heating season) were slightly lower or unchanged compared with the initial symptom survey. The slightly higher reports of dry cough, aches, and wheezing during the heating season were not statistically significant.

Among respondents for survey 2, workers in Department 456 were more than 7 times as likely to report chest tightness (PRR 7.0 95% CI: 1.08, 51.84), 4 times more likely to report muscle aches (PRR 4.0 95% CI: 1.05, 15.31), and 6 times more likely to report unusual fatigue (PRR 6.0 95% CI: 1.62, 22.56) than were workers in Department 452. Additionally, workers in department 456 were more than 4 times as likely to report itchy watery eyes as workers in department 453 (PRR 4.31 95% CI: 1.44, 12.94).

Symptoms by Work Area

In addition to departmental affiliation, questions in the second survey asked workers to indicate where they work in the plant. Of the 15 work areas surveyed, only 8 of these areas had 5 or more employees reporting symptoms (Table 16). Overall, prevalences for 10 out of 14 symptoms were highest among workers in masking (not East Line). Workers in the pin-stripping area reported symptom prevalence rates that are comparable to those in the masking department and reported the highest prevalences of chest tightness, chest pain, unusual fatigue, and shortness of breath. Symptoms consistent with chronic bronchitis (cough with phlegm, wheezing and shortness of breath occurring often or always) were compared by work area, as were symptoms consistent with an interstitial pneumonitis (chills, fever, and aches occurring often or always and getting worse at home). Although 10 workers had symptoms consistent with chronic bronchitis and one worker had symptoms consistent with an interstitial pneumonitis, no relationship was found between either of these conditions and any of the work areas at Harley Davidson.

CONCLUSIONS

Environmental Conclusions

The thermal desorption tube sampling results reveal that employees in the main paint room are exposed to many different compounds in low concentrations. The highest exposures appear to be in the pin-stripping area and the touch-up spray booth, but again, these

exposures are low relative to occupational standards. There was no quantifiable re-entrainment of compounds through the outside air (OA) intakes during the August survey. It did appear that there were higher concentrations of chemicals present during the heating season compared to the non-heating season, but still the concentrations were low.

Several of the chemicals detected on the thermal desorption tubes do have occupational exposure limits, such as NIOSH RELs, OSHA permissible exposure limits (PELs), or ACGIH Threshold Limit Values® (TLVs®). In the past all the monitoring performed in this plant was for chemicals that do have occupational exposure limits and the results were all well below the limits. The semi-quantitative data from the thermal desorption tube sampling were also well below any occupational exposure limits, as was shown in Tables 8-9. Because of this, NIOSH investigators can conclude that there is no documented overexposure to the chemicals sampled in this plant. The term overexposure is defined in this case as over a standard occupational exposure limit. However, occupational exposure limits are most often set based on acute or chronic health effects, not based on allergic reactions. By nature, hypersensitivity (allergic) reaction depends upon individual genetic predispositions; not every person exposed will have a reaction, and of those that do have a reaction, the health effects can vary widely. For example, some people exposed to pollen do not experience any problems, some may experience a runny nose or watering eyes, and others may experience asthma. It would be very difficult to establish exposure criteria based on allergic reactions because of the individuality of responses, and also because once a person is sensitized to an exposure (once they have become allergic to it), it often only requires a very small amount to cause an allergic or hypersensitivity reaction.

Also, there are many chemical and some biological exposures in this plant that do not have occupational exposure limits, and there are no occupational exposure limits for mixtures that can be applied here. A mixture of exposures can have three kinds of effects on a person: (1) each component of the

mixture may cause their own health effect regardless of the other components in the mixture, (2) the health effects may be additive, in that the effect from one component may be added to the effect of another to double the effect, and (3) the components of the mixture may act synergistically, which means that the effect of the components together is multiplicative, or greater than additive. With mixtures of many components, as in this plant, there may be many different health effects — some individual, some additive, and some synergistic. Unfortunately, this area of research is just beginning to be explored. For example, it is known that cigarette smoking and asbestos exposure act synergistically in causing lung cancer, and a few other two-component mixtures have been studied; but, complex mixtures such as those that exist in this plant have not yet been studied and probably will not be well understood for many years. **In this case then, what is important to understand is that we do not know the health effects associated with mixtures such as the ones in the plant, and that there is a possibility that all the very low concentrations here could together be responsible for some health effects.**

Another consideration is that many of the chemicals in this environment have low odor thresholds, meaning that people can smell them at very low concentrations that are well below occupational exposure limits. For example, humans can smell styrene at 0.1 parts per million (ppm), but the NIOSH REL is 50 ppm and the OSHA PEL is 100 ppm. Odors can be irritating or make people uncomfortable because they can smell that something is there and may worry that it is unhealthy.

In addition to odors, most of the exposures (both chemical and biological) in this plant can cause mucous membrane (eye, nose, throat) irritation, respiratory irritation, or slight central nervous system irritation (headaches, dizziness). These irritant effects are reversible and rarely considered in the development of occupational exposure limits (unless they are very severe acute effects). Nevertheless, these irritations can be very uncomfortable for employees.

Dilution ventilation in the main paint room may not be adequate to completely control exposures and the

irritant effects of solvent vapors emitted from the pin-stripping work area. Observing the work and the amounts of solvent and paints used, it appears unlikely that any occupational health criteria would be exceeded in this area, but sufficient solvent vapor may be released to produce upper airway and neurologic (headache) irritant effects and lead to employee complaints.

In August, the endotoxin concentrations in the air near the water pits were relatively high; however, since the endotoxin concentrations in the areas where employees actually worked were not high, the microbial contamination in the water may not be a significant issue. The bioaerosol sampling conducted by the company should help to determine if better control of the microbial growth in the water baths is necessary.

All AHUs were operational and appeared to be well maintained. The units were clean (except for the dry, granular debris in the north line AHU), appropriate filtration was installed, and no evidence of microbiological contamination was found except for the debris in the North paint line AHU.

The paint booths were at negative or neutral pressure with respect to the plant. Ideally, the booths should be under a slight negative pressure to prevent the release of solvent vapor into the plant.

Face velocity measurements show that, on the day of the evaluation, the pin-stripping paint booth was operating below sufficient face velocity recommended for this type of control. Average velocity was measured at 47 fpm. Sixty feet per minute should be considered an absolute minimum face velocity due to the location of the overhead drum diffusers, whose airflow affected performance at the face of the booth.

The bench-top paint booth in the touch-up spray room was determined to be operating at the minimum adequate face velocity. ACGIH and OSHA recommend 150 — 200 fpm for bench-type spray painting booths.

Epidemiologic Conclusions

In general, reported symptom prevalences were slightly lower during the heating season compared with symptom prevalences reported during the non-heating season. This finding differs from the generally held perception among workers that symptoms worsen during the heating season. Also, workers in the masking area (not East Line) and the pin-stripping areas reported slightly higher symptom prevalences than workers in other production areas. While these differences were not statistically significant, they are consistent with the industrial hygiene sampling data that showed: (1) no appreciable differences in thermal tube sampling results between the two heating seasons and, (2) that employees in both the pin-stripping and masking areas had consistently higher relative exposures to the compounds sampled.

The symptom questionnaires were collected without personal identifiers, and therefore, we are not able to identify the workers who had self-reported symptoms consistent with chronic bronchitis, and interstitial pneumonitis. These persons were not located in any one area of the plant and did not share job titles or tasks. Furthermore, these conditions cannot be determined simply on the basis of a questionnaire, but rather require a comprehensive medical evaluation. Workers who experience unusual shortness of breath, have a chronic productive cough (cough with phlegm), or have recurrent flu-like conditions (fever, chills, muscle aches) should bring these symptoms to the attention of their physician.

RECOMMENDATIONS

NIOSH investigators agree with the actions previously taken by Harley-Davidson management to try to address the health concerns, but employees are still reporting health effects. Based on the previous actions and the results of this HHE, NIOSH investigators offer the following recommendations.

Interim Report Recommendations

1. The brown debris downstream of the evaporative cooler in the north line AHU should be cleaned-up and its origin should be determined. If the evaporative cooling media is found to be the source of the material, and the material is determined to present a possible health hazard, the cooling media should be replaced.
2. A face velocity of 60-100 fpm is recommended for the pin-stripping booth, in accordance with the ACGIH recommendation for large spray booths when the operator is outside of the booth.
3. The door should remain closed for proper operation of the ventilation system in the special repairs area. Since the operator must move in and out of the area frequently with parts, it is suggested that the hinged door be removed and replaced with a self-closing or sliding-pocket door. In addition, portable fans should not be used in this room, and the transfer grill should be kept clear of obstructions such as cabinets or drawers.
4. Because HHPA is a confirmed respiratory sensitizer, Harley-Davidson should sample for it during a shift when white paint is being used. The sampling should be done near the sources (where freshly painted parts leave the enclosed, ventilated paint booth and at the doors to the paint booth) and in nearby areas where employees work without respiratory protection. Sampling should also be performed when white paint is used in the pin-stripping or special repairs areas.
5. Because the NIOSH microbial sampling results are so much higher than the concentrations measured by the company using the semi-quantitative dipslides, Harley-Davidson should confirm that the dipslides are being used properly (incubated at appropriate temperatures and for appropriate lengths of time).
6. Because employees are reporting a variety of non-specific symptoms, and the number of reports

appear to be higher in the pin-stripping area of the main paint room, Harley-Davidson should consider adding local exhaust ventilation (LEV) in the pin-stripping area. Another area to consider adding LEV is in the staging area. Although the chemical concentrations are below occupational standards, there are many different chemicals present that are irritants. Exposures to low levels of solvents can cause headaches, dizziness, respiratory irritation, and eye, nose, and throat irritation.

Final Report Recommendations

1. During the November site visit, NIOSH investigators observed that there was the same or similar debris in the North paint line AHU. This needs to be cleaned out and prevented from re-occurring, especially since there were high concentrations of microbial contamination in the debris. Since NIOSH investigators were told that it had been cleaned out after the August site visit, we must conclude that it accumulated again. Therefore, we recommend that the source of this debris be identified, and that all AHUs are routinely checked and cleaned to ensure that no debris is accumulating in them. After cleaning or any AHU maintenance, no equipment, tools, or rags should be left inside the AHUs.

2. Employees have been reporting various health symptoms since before this HHE began, and it was not clear whether the symptoms were worse in one area, on one shift, or at different times. To try to better clarify symptom incidence and prevalence over time, NIOSH investigators recommend that Harley-Davidson implement a system of symptom surveillance. Employees could report to the health and safety office whenever they have experienced a health symptom at work or thought to be associated with work. Maintaining consistent and standardized information (such as specific problem, onset of symptoms, whether symptoms lessen when away from work, any illnesses, whether the employee sought medical attention and the diagnosis, job title, department, location, compounds used, date, heating and ventilating conditions) about each incident will

help Harley-Davidson to better track symptoms in this plant. This could be maintained by the health and safety office in a similar manner to an OSHA Injury and Illness 200 log, but employees should be able to report anonymously through the union using a standard form. In order for a surveillance system to work well, employees must believe in the system, and therefore its specific design should be a joint labor-management decision. Routine analysis of the surveillance data could help to identify an emerging problem, and analysis of surveillance data along with exposure data could help when trying to resolve an on-going problem.

3. Along the same lines as recommendation #2, Harley-Davidson should also perform routine environmental monitoring of both the air, ventilation systems, and water pits. This has been done for chemicals with occupational exposure limits in the past, and has just begun to be done for other exposures. We recommend the continuance of monitoring for the purpose of characterizing the entire workplace rather than merely the compliance monitoring; the new contracts with the outside industrial hygienist and ventilation engineer should help to achieve this recommendation.

4. Communication between management and labor, although not totally lacking, could be improved at this plant. This could be facilitated by the establishment of routine symptom surveillance (mentioned above) because such a system would clearly identify if an area of the plant is suddenly experiencing health complaints and would thus force a discussion of possible causes. Also, when a difficult situation arises, such as the one that resulted in this HHE, it is important to continue to communicate and refrain from accusations. While very difficult to do (in all aspects of life), it can really help to focus on alleviating the problem rather than assigning blame for the problem. Continuing the joint labor-management health and safety meetings and making an effort to listen to both sides will help. If a health problem is suspected, management should listen to employee hypotheses about what might be the cause; those who work with something daily are likely to have good ideas about what the problems are or what might improve the work environment. Some

hypotheses might obviously not be feasible to an occupational health scientist, and, in that case, it is important for management to educate the employees as to why that hypothesis does not make sense rather than merely to dismiss the suggestion as wrong. Likewise, it is important for the employees to listen to those in management who were trained in health and safety. In situations that become controversial or where there is not a clear answer, an outside expert can be helpful. To help improve health and safety communications in this plant, NIOSH investigators have offered their consultative services whenever necessary; Harley-Davidson employees or management are welcome to call with questions or ask for specific assistance in evaluating a potential health hazard.

5. People with more serious health complaints who are seeking outside medical care – at least the two who had trouble returning to work at one point – should be advised to bring this report and any other exposure assessment reports to their physicians. Each chemical and biological exposure mentioned in this report or listed on a MSDS from this plant should be considered a *potential* cause for the health problems. Of course, all non-work exposures and personal medical history must also be considered.

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Table 1. Analytical Limits of Detection (LOD) and Limits of Quantitation (LOQ) for Thermal Desorption Tube Sampling Results. Harley-Davidson. Tomahawk, Wisconsin, HETA 96-0100, 8/13-15/96.

Analyte	LOD (µg/sample)	LOQ (µg/sample)
acetone	0.05	0.18
isopropanol	0.04	0.13
methylene chloride	0.05	0.17
methyl ethyl ketone (MEK)	0.04	0.12
butanol	0.04	0.12
1-methoxy-2-propanol	0.05	0.16
heptane	0.02	0.07
toluene	0.02	0.07
butyl acetate	0.03	0.10
propylene glycol methyl ether acetate (PGMEA)	0.03	0.11
xylenes	0.03	0.09
methyl amyl ketone (MAK)	0.02	0.07
styrene	0.02	0.06
2-butoxyethanol	0.04	0.12
butoxypropanol*	0.07	0.22
diisobutyl ketone*	0.07	0.22
2-butoxyethanol acetate*	0.07	0.22
total aliphatics**	0.25	0.83

* Reported values are estimates based on using 2-butoxyethanol as a standard.

** Reported values are estimates based on using Stoddard solvent as a standard.

Table 2. Analytical Limits of Detection (LOD) and Limits of Quantitation (LOQ) for Thermal Desorption Tube Sampling Results. Harley-Davidson. Tomahawk, Wisconsin, HETA 96-0100, 11/18-20/96.

Analyte	LOD (µg/sample)	LOQ (µg/sample)
acetone	0.09	0.29
isopropanol	0.10	0.34
methylene chloride	0.05	0.18
methyl ethyl ketone (MEK)	0.09	0.29
butanol	0.02	0.07
1-methoxy-2-propanol	0.09	0.29
heptane	0.05	0.15
toluene	0.06	0.19
butyl acetate	0.06	0.20
propylene glycol methyl ether acetate (PGMEA)	0.08	0.28
xylenes	0.05	0.17
methyl amyl ketone (MAK)	0.05	0.18
styrene	0.07	0.22
2-butoxyethanol	0.03	0.12
butoxypropanol*	0.03	0.12
diisobutyl ketone*	0.03	0.12
2-butoxyethanol acetate*	0.03	0.12
total aliphatics**	0.22	0.73

* Reported values are estimates based on using 2-butoxyethanol as a standard.

** Reported values are estimates based on using Stoddard solvent as a standard.

Table 3. Relative Scale Assigned to Evaluate Thermal Desorption Tube Sampling Results. Harley-Davidson. Tomahawk, Wisconsin, HETA 96-0100.

Relative Number	Estimated Concentration Range (µg/sample, each sample 6 liters)
0	ND (below limit of detection, see Table 2)
1	trace (below limit of quantitation, see Table 2)
2	trace - 1.0
3	1.1 - 7.5
4	7.6-15.0
5	15.1-22.5
6	22.6-30.0
7	30.1-37.5
8	37.6-45.0
9	45.1-52.5
10	52.5-60.0

Table 4. Thermal Desorption Tube Sampling Results. August 13–15, 1996. Harley–Davidson. Tomahawk, Wisconsin, HETA 96–0100.

Location (#) (see Figure 1 for locations)	Average Relative Amounts of Analytes Detected (scale of 1 to 10, see Table 1)								
	acetone	isopropanol	methylene chloride	methyl ethyl ketone	butanol	1-methoxy-2-propanol	heptane	toluene	butyl acetate
Conference Room (1)	2	2.7	0.3	0.3	1.7	1	0.3	2	1.7
Assembly area (2)	2.7	2.3	0	0.7	0.7	0.7	0	3	1.3
East line: before booth (3)	0.5	1	0	0	0	0	1.5	2	0
East line: at booth (4)	2	1.3	0	1	0	0.3	0.3	1.7	1
East line: pin-striping (5)	3	2	0	0	0	0.5	0.5	2	2
Press area (6)	2.7	2.3	0.7	1	0.7	1	0.7	2.3	1.7
North line: at booth (7)	5.3	3.8	1.3	3	2.5	3	2	3	3
Staging (8)	6.3	4.7	1.3	1	2.3	0.3	0.3	3.7	3
Clear line: at booth (9)	6.3	4.7	1.7	1.7	2.3	0.7	0.7	4	3
Clear line: pin-striping (10)	7.5	5.5	1.8	1.7	1.3	0.3	0.8	4.8	3.3
Masking (11)	4.7	3.7	1.3	0.7	2.3	0.3	2.3	3.3	2.7
Special repairs booth (12)	6.7	3.7	1.7	4	2.3	2	2.7	5	3
Clear line room AHU supply (13)	3.3	2	0.7	0.7	1.3	0	0	2.7	1.7
Clear line room OA intake (14)	0.7	0.7	0	0	0.3	0	0	1.3	1
Fairing assembly (15)	3	3	0.7	0.7	1.7	1	1	2.7	1.7
Buffing (16)	3.7	5.6*	0.5	0.5	1	1	0.5	2	1.3
East line room OA intake (17)	0	0	0	0	0	0	0	0	0
Outside (18)	0.7	0.7	0.3	0.3	0.7	0.3	0	2	1

Table 4 (continued). Thermal Desorption Tube Sampling Results. August 13–15, 1996. Harley–Davidson. Tomahawk, Wisconsin, HETA 96–0100.

Location (#) (see Figure 1 for locations)	Average Relative Amounts of Compound Detected (scale of 1 to 10, see Table 1)								
	PGMEA	xylenes	MAK	styrene	2-butoxy-ethanol	butoxy-propanol ¹	diisobutyl ketone ¹	2-butoxy-ethanol acetate ¹	total aliphatics ²
Conference Room (1)	1	1	1.7	2	1.7	0	0	0	1.7
Assembly area (2)	1	1.3	1	1.7	0.7	0	0	0	1
East line: before booth (3)	1	1.5	0	1	1	0	0	0	3
East line: at booth (4)	0.7	2	0	1.3	0.3	0	0	0.3	0.7
East line: pin-striping (5)	0.5	1.5	0	1.5	1	0	0	0	1.5
Press area (6)	1.3	2	0.7	8	0.7	0	0	0	0.7
North line: at booth (7)	3	2.8	2.5	1.5	2	1.7	1.7	0	3
Staging (8)	1	2	2	0	2	1.7	1.7	1	0
Clear line: at booth (9)	1	2	2.3	0	2	1	1	0.5	0
Clear line: pin-striping (10)	1.3	2	2.3	0.8	2	2	2	1	0
Masking (11)	1.3	2	2	0	1.7	1.3	1.3	0.7	1.3
Special repairs booth (12)	5.7	2.7	2	0.3	2	1.3	1.3	0.7	3.3
Clear line room AHU supply (13)	1	1	1.3	0	0.7	0.7	0.7	0.3	0
Clear line room OA intake (14)	0.7	0.7	0.7	0	0.3	0	0	0	0
Fairing assembly (15)	1.3	1.7	1.7	2	1.7	0	0	0	3.3
Buffing (16)	0.7	1.3	0.7	1.3	1.3	0	0	0	4.3
East line room OA intake (17)	0.5	0.5	0.5	0	0	0	0	0	0
Outside (18)	0.7	1	1	1	0	0	0	0	0

¹ 2-Butoxyethanol was used as the standard.

² Stoddard solvent was used as the standard.

Table 5. Thermal Desorption Tube Sampling Results. November 18–20, 1996. Harley–Davidson. Tomahawk, Wisconsin, HETA 96–0100.

Location (#) (see Figure 1 for locations)	Average Relative Amounts of Analytes Detected (scale of 1 to 10, see Table 1)								
	acetone	isopropanol	methylene chloride	methyl ethyl ketone	butanol	1-methoxy-2-propanol	heptane	toluene	butyl acetate
Conference Room (1)	2	2	0.5	1	1	0.5	0.5	1.5	1
Assembly area (2)	5.3	3	1.3	2.3	2	1	1	3	2
East line: at booth (4)	8.7	5	7	3.3	2.3	2.3	0.7	4	3
Press area (6)	4.7	2.7	0.7	2	2	1	0.3	2	2
North line: at booth (7)	8.3	3.3	0.8	3	2	2.8	1.5	3	3
Staging (8)	6.7	4.7	1	1.7	3	0.3	0.3	4.3	3
Clear line: at booth (9)	8	4	1	2.3	3	0.3	0.7	3.7	3
Clear line: pin-striping (10)	8.5	5.8	1.3	1.8	3	0.5	0.8	4.3	3
Masking (11)	6.3	4.3	0.7	1.3	3	0.3	2.3	3.7	2.7
Special repairs booth (12)	8	3	1	3.3	2.7	1	2.3	4	3.7
*Clear line room AHU supply (13)	3.7	2.3	0.7	0.7	2	0.3	0.3	2.7	1
Fairing assembly (15)	4.7	4.3	1	1.7	2	1	1	3	2
**Buffing (16)	3.7	3.7	0.7	1.3	1.7	0.7	0.7	2	1.3
***Outside (18)	1.3	1	0.3	0	0.7	0	0.3	0.7	0.7

* The first day results were noticeably higher than the next two days.

** The first day results were noticeably lower than the next two days.

*** The first day results had detectable concentrations, but the next two days did not.

Table 5 (continued). Thermal Desorption Tube Sampling Results. November 18–20, 1996. Harley–Davidson. Tomahawk, Wisconsin, HETA 96–0100.

Location (#) (see Figure 1 for locations)	Average Relative Amounts of Compound Detected (scale of 1 to 10, see Table 1)								
	PGMEA	xylenes	MAK	styrene	2-butoxy- ethanol	butoxy- propanol ¹	diisobutyl ketone ¹	2-butoxy- ethanol acetate ¹	total aliphatics ²
Conference Room (1)	0.5	1	0.5	0.5	1	1	0.5	0.5	1
Assembly area (2)	1.7	2	1.3	0.3	1.3	1.7	1.3	1	3
East line: at booth (4)	2.3	3.3	2	1	1.7	1.7	1.3	2	2.7
Press area (6)	1	2	1	4.3	1	1	1	0	1.7
North line: at booth (7)	2.8	3	3	1	1.5	2	2	1.5	3
Staging (8)	0.7	2.7	3	0.3	2	3	2.7	2	2
Clear line: at booth (9)	0.7	3	3	0	2	3	3	1.7	1.7
Clear line: pin-striping (10)	0.5	3	3	0	2	3	3	2	2.5
Masking (11)	1.3	2.3	2.3	0	2	2.3	2.3	1.3	2.7
Special repairs booth (12)	3.7	3	2.3	0.7	2	2.3	2.3	1.7	3
Clear line room AHU supply (13)	0.7	1	1.7	0.3	0.7	1.7	1.7	0.7	0.3
Fairing assembly (15)	1.3	2	1.7	1.3	1.7	2	2	2	4
Buffing (16)	1.3	1.3	0.7	1.3	2	1	1.3	1.3	6
Outside (18)	0.3	0.7	0.3	0	0.7	0.3	0.3	0.3	0.7

¹ 2-Butoxyethanol was used as the standard.

² Stoddard solvent was used as the standard.

* The first day results were noticeably higher than the next two days.

** The first day results were noticeably lower than the next two days.

*** The first day results had detectable concentrations, but the next two days did not.

Table 6. Totals of Average Quantifiable Concentrations from Thermal Desorption Tube Sampling. (Corresponds with Figure 4.) Harley-Davidson. Tomahawk, Wisconsin, HETA 96-0100, 8/13-15/96.

Location (#) (see Figure 1 for locations)	Average Total Concentration (µg/sample, each sample 6 liters)
Conference Room (1)	2.49
Assembly area (2)	6.25
East line: before booth (3)	2.43
East line: at booth (4)	0.55
East line: pin-striping (5)	3.05
Press area (6)	48.27 (39.55 µg was styrene)
North line: at booth (7)	53.36
Staging (8)	60.36
Clear line: at booth (9)	49.31
Clear line: pin-striping (10)	85.89
Masking (11)	34.45
Special repairs booth (12)	109.7
Clear line room AHU supply (13)	13.18
Clear line room OA intake (14)	0
Fairing assembly (15)	16.03
Buffing (16)	46.21 (22.30 was isopropanol)
East line room OA intake (17)	0
Outside (18)	0.13
Total	531.66

Table 7. Totals of Average Quantifiable Concentrations from Thermal Desorption Tube Sampling. (Corresponds with Figure 5.) Harley-Davidson. Tomahawk, Wisconsin, HETA 96-0100, 11/18-20/96.

Location (#) (see Figure 1 for locations)	Average Total Concentration (µg/sample, each sample 6 liters)
Conference Room (1)	0.00
Assembly area (2)	33.17
East line: at booth (4)	107.63
Press area (6)	34.40
North line: at booth (7)	53.60
Staging (8)	74.49
Clear line: at booth (9)	79.96
Clear line: pin-striping (10)	102.39
Masking (11)	65.84
Special repairs booth (12)	94.23
Clear line room AHU supply (13)	18.38
Fairing assembly (15)	48.10
Buffing (16)	54.79
Outside (18)	0.00
Total	766.98

Table 8. Mixture Calculation for Compounds Quantified from Samples Collected in the Pin-stripping Area, 8/13-15/96. Harley-Davidson. Tomahawk, Wisconsin, HETA 96-0100.

Compound	average µg/sample	mg/m ³	NIOSH REL (mg/m ³)	concentration/ REL
acetone	38.76	6.5	590	0.01
isopropanol	21.11	3.5	980	0.004
butanol	1.06	0.2	150	0.001
methylene chloride	0.35	0.1	occupational carcinogen	can't calculate
toluene	17.30	2.9	375	0.008
butyl acetate	4.35	0.7	710	0.001
xylene	0.66	0.1	435	0.0002
methyl amyl ketone	0.77	0.1	465	0.0002
2-butoxyethanol	0.53	0.1	24	0.004
Mixture Calculation: if sum of fractions (concentration/REL) is greater than 1, then overexposure to the mixture				0.03

µg/sample – micrograms per sample

mg/m³ – milligrams per cubic meter

NIOSH REL – National Institute for Occupational Safety and Health recommended exposure limit

Table 9. Mixture Calculation for Compounds Quantified from Samples Collected in the Pin-stripping Area, 11/18-20/96. Harley-Davidson. Tomahawk, Wisconsin, HETA 96-0100.

Compound	average µg/sample	mg/m ³	NIOSH REL (mg/m ³)	concentration/ REL
acetone	43.46	7.2	590	0.01
isopropanol	23.42	3.9	980	0.004
butanol	3.71	0.6	150	0.004
methyl ethyl ketone	0.43	0.07	200	0.0004
toluene	15.28	2.6	375	0.007
butyl acetate	5.79	1.0	710	0.001
xylene	1.53	0.3	435	0.0006
methyl amyl ketone	2.55	0.4	465	0.0009
2-butoxyethanol	0.33	0.06	24	0.003
diisobutyl ketone	1.68	0.3	25	0.01
2-butoxyethanol acetate	0.34	0.06	5	0.01
Mixture Calculation: if sum of fractions (concentration/REL) is greater than 1, then overexposure to the mixture				0.05

µg/sample – micrograms per sample

mg/m³ – milligrams per cubic meter

NIOSH REL – National Institute for Occupational Safety and Health recommended exposure limit

**Table 10. Microbial Bulk Sampling Results. Harley-Davidson. Tomahawk, Wisconsin
HETA 96-0100, 8/14/96.**

Location	Bacteria		Fungi	
	Count (CFU/mL)*	Identification (Gram sign, +/-)‡	Count (CFU/mL)*	Identification
East line water pit	2,000,000 1,000,000	<i>Flavobacterium meningosepticum</i> (G-) <i>Comomonas testosteroni</i> (G-)	500 100	<i>Paecilomyces</i> <i>Acremonium</i>
North line water pit	1,500,000 100,000	<i>Comomonas testosteroni</i> (G-) <i>Comomonas acidovorans</i> (G-)	2,700 300	<i>Paecilomyces</i> <i>Acremonium</i>
South line water pit	6,000 5,000	<i>Comomonas testosteroni</i> (G-) <i>Methylobacterium extorquens</i> (G-)	800 100	<i>Paecilomyces</i> <i>Acremonium</i>
Clear line water pit	less than 10	not applicable	12,000 30	<i>Paecilomyces</i> <i>Acremonium</i>
East paint room AHU	30,000 10,000 10,000	<i>Micrococcus</i> species† (G+) <i>Hydrogenophagi flava</i> CDC group E	less than 10	not applicable
	(CFU/gram)			
Debris from north line AHU	81,600,000 81,600,000 40,800,000 8,160,000	<i>Corynebacterium pilosum</i> (G+) <i>Rhizobium loti B</i> (G-) <i>Psychrobacter immobilis</i> (G-) <i>Rhodococcus luteus</i> (G+)	21,000,000 3,000,000	<i>Cladosporium</i> <i>Phoma</i>

* CFU/mL – colony forming units per milliliter

‡ Gram (+) and gram (-) are terms assigned to bacteria based on their color after a certain staining procedure. The color difference is because of differences in the cell walls of the bacteria. The significance to this study is that gram (-) bacteria have endotoxins in their cell walls.

† Insufficient growth for speciation.

NOTE: No *Thermoactinomyces* were detected in these samples.

**Table 11. Endotoxin General Area Air Sampling Results. Harley-Davidson.
Tomahawk, Wisconsin, HETA 96-0100, 8/13-15/96.**

Location	Date	Sample Volume (Liters)	Endotoxin Concentration (EU/m ³ , blank adjusted)
East line water pit	8/13/96	970	208.8
East line water pit	8/14/96	910	122.9
East line area	8/13/96	968	21.0
North line water pit	8/13/96	966	1359.1
North line water pit	8/14/96	914	465.1
North line water pit	8/15/96	664	1074.7
South line water pit	8/13/96	966	less than average of blanks
South line water pit	8/14/96	908	2.9
North/south line area	8/13/96	968	less than average of blanks
Clear line water pit	8/13/96	960	0.1
Clear line water pit	8/14/96	904	less than average of blanks
Clear line water pit	8/15/96	558	10.0
Clear line area	8/13/96	956	18.5
Clear line area	8/14/96	904	less than average of blanks
Clear line area	8/15/96	660	30.0
Outside	8/13/96	950	12.7
Outside	8/14/96	618	less than average of blanks
Outside	8/15/96	660	less than average of blanks
North line water pit	11/18/96	632	3.8
North line water pit	11/19/96	826	0.4
North line area	11/18/96	632	less than average of blanks
North line area	11/19/96	824	less than average of blanks
Clear line water pit	11/18/96	634	less than average of blanks
Clear line water pit	11/19/96	822	12.0
Clear line area	11/18/96	624	less than average of blanks
Clear line area	11/19/96	820	12.2
Outside	11/18/96	500	1.8
Outside	11/19/96	838	less than average of blanks

EU/m³ – endotoxin units per cubic meter; 1 EU = 1 nanogram

Note: Average of blank samples was 0.90 EUs per milliliter (mL).

**Table 12. Endotoxin General Area Air Sampling Results. Harley-Davidson.
Tomahawk, Wisconsin, HETA 96-0100, 11/18-20/96.**

Location	Date	Sample Volume (Liters)	Endotoxin Concentration (EU/m³, blank adjusted)
North line water pit	11/18/96	632	3.8
North line water pit	11/19/96	826	0.4
North line area	11/18/96	632	less than average of blanks
North line area	11/19/96	824	less than average of blanks
Clear line water pit	11/18/96	634	less than average of blanks
Clear line water pit	11/19/96	822	12.0
Clear line area	11/18/96	624	less than average of blanks
Clear line area	11/19/96	820	12.2
Outside	11/18/96	500	1.8
Outside	11/19/96	838	less than average of blanks

EU/m³ – endotoxin units per cubic meter; 1 EU = 1 nanogram
 Note: Average of blank samples was 0.90 EUs per milliliter (mL).

Table 13 Comparison of Respondent Characteristics for Survey 1 and Survey 2 Harley-Davidson, Tomahawk, Wisconsin HETA 96-0100		
Characteristic	Survey 1 n=72	Survey 2 n=85
Age	38 years	40 years
Gender	58% Male 42% Female	61% Male 39% Female
Shift	51% First Shift 49% Second Shift	60% First Shift 40% Second Shift
Years Employed at Harley Davidson	7 years	8 years
Years working current job	3 years	4 years

Table 14 Symptoms Reported by Workers Harley-Davidson, Tomahawk, Wisconsin HETA 96-0100				
	Survey 1 No Heat n=72		Survey 2 Heat n=85	
Symptoms	Number Reporting	Percent	Number Reporting	Percent
Unusual Fatigue	39	54%	41	48%
Itchy Watery Eyes	36	50%	29	34%
Chest tightness	31	43%	34	40%
Cough with Phlegm	29	40%	30	35%
Shortness of Breath	26	36%	26	31%
Dry Cough	23	32%	34	40%
Muscle Aches	24	33%	29	34%
Wheezing	22	31%	23	27%
Chills	11	15%	5	6%

Table 15
Number of Persons Indicating Symptoms by Department
Harley-Davidson, Tomahawk, Wisconsin
HETA 96-0100

Symptoms	Dept 452		Dept 453		Dept 456	
	Survey 1 n=9	Survey 2 n=16	Survey 1 n=33	Survey 2 n=23	Survey 1 n=21	Survey 2 n=32
Dry Cough	1 (11%)	6 (38%)	10 (30%)	6 (27%)	10 (47%)	16 (50%)
Cough with Phlegm	2 (22%)	3 (19%)	17 (52%)	8 (35%)	8 (42%)	13 (41%)
Wheezing	3 (33%)	2 (13%)	10 (30%)	3 (13%)	7 (33%)	15 (47%)
Chest Tightness	2 (22%)	1 (6%)	12 (36%)	9 (39%)	15 (71%)	17 (53%)
Short of Breath	2 (22%)	2 (13%)	10 (30%)	6 (26%)	12 (54%)	13 (41%)
Fever	3 (33%)	1 (6%)	3 (9%)	4 (17%)	7 (33%)	7 (22%)
Chills	1 (11%)	0	4 (12%)	1 (4%)	5 (23%)	3 (9%)
Aches	2 (22%)	2 (13%)	9 (27%)	7 (30%)	9 (47%)	16 (50%)
Unusual Fatigue	1 (11%)	4 (25%)	18 (55%)	7 (30%)	16 (76%)	24 (75%)
Itchy Watery Eyes	5 (56%)	4 (25%)	16 (48%)	3 (13%)	13 (62%)	18 (56%)

Table 16
Prevalence of Symptoms by Work Area
Harley-Davidson, Tomahawk, Wisconsin
HETA 96-0100

Symptoms	East line n=10	North Line n=7	South Line n=7	Masking (not East Line) n=5	Pin-stripe n=11	Clear Line n=10	Assembly n=12	Rough Sanding n=8
Dry Cough	5 (50%)	2 (29%)	2 (29%)	3 (60%)	6 (55%)	2 (20%)	5 (42%)	2 (25%)
Cough with Phlegm	3 (30%)	1 (14%)	4 (57%)	3 (60%)	5 (45%)	3 (30%)	6 (50%)	1 (13%)
Wheezing	2 (20%)	1 (14%)	2 (29%)	4 (80%)	6 (55%)	1 (10%)	2 (17%)	0
Chest Tightness	1 (10%)	4 (57%)	5 (71%)	2 (40%)	8 (73%)	4 (40%)	5 (42%)	1 (13%)
Short of Breath	3 (30%)	3 (43%)	2 (29%)	1 (20%)	7 (64%)	3 (30%)	3 (25%)	0
Fever	1 (10%)	0	0	3 (60%)	3 (27%)	3 (30%)	0	0
Chills	1 (10%)	0	0	2 (40%)	1 (9%)	0	1 (8.3%)	0
Muscle Aches	3 (30%)	2 (29%)	2 (29%)	3 (60%)	6 (55%)	3 (30%)	3 (25%)	1 (13%)
Unusual Fatigue	7 (70%)	3 (43%)	5 (71%)	4 (80%)	9 (82%)	2 (20%)	4 (33%)	1 (13%)
Itchy Watery Eyes	5 (50%)	3 (43%)	1 (14%)	3 (60%)	6 (55%)	2 (20%)	4 (33%)	3 (38%)
Head Aches	4 (40%)	5 (71%)	2 (29%)	4 (80%)	7 (64%)	5 (50%)	5 (42%)	2 (25%)
Chest Pain	1 (10%)	1 (14%)	1 (14%)	1 (20%)	5 (45%)	1 (10%)	2 (17%)	0
Nausea	4 (40%)	1 (14%)	0	3 (60%)	1 (9%)	1 (10%)	1 (8%)	0
Dizzy	5 (50%)	2 (29%)	2 (29%)	2 (40%)	5 (45%)	3 (30%)	4 (33%)	0

Figure 1
Diagram of Plant and Locations of Thermal Desorption Tube Sampling
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

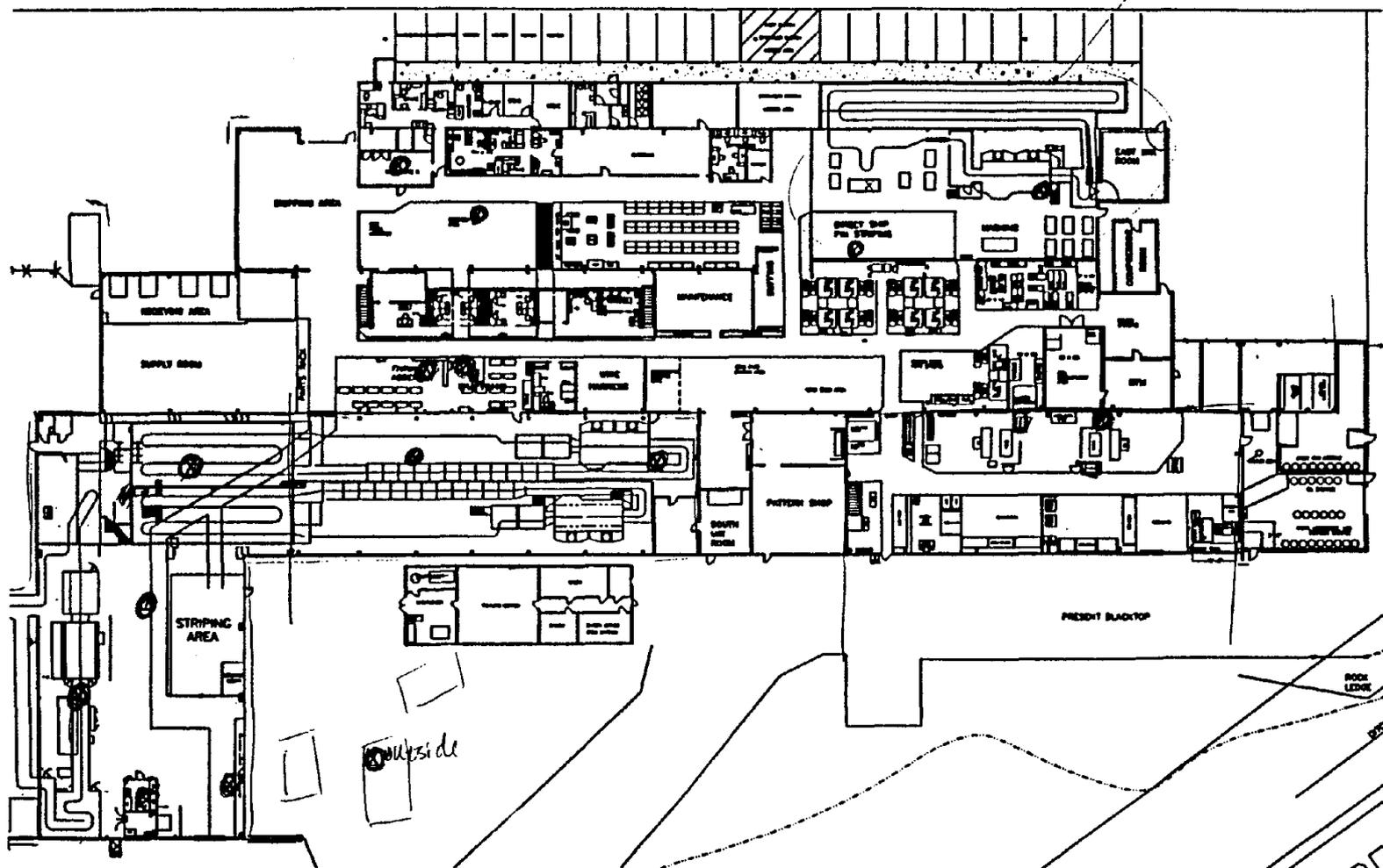


Figure 2
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

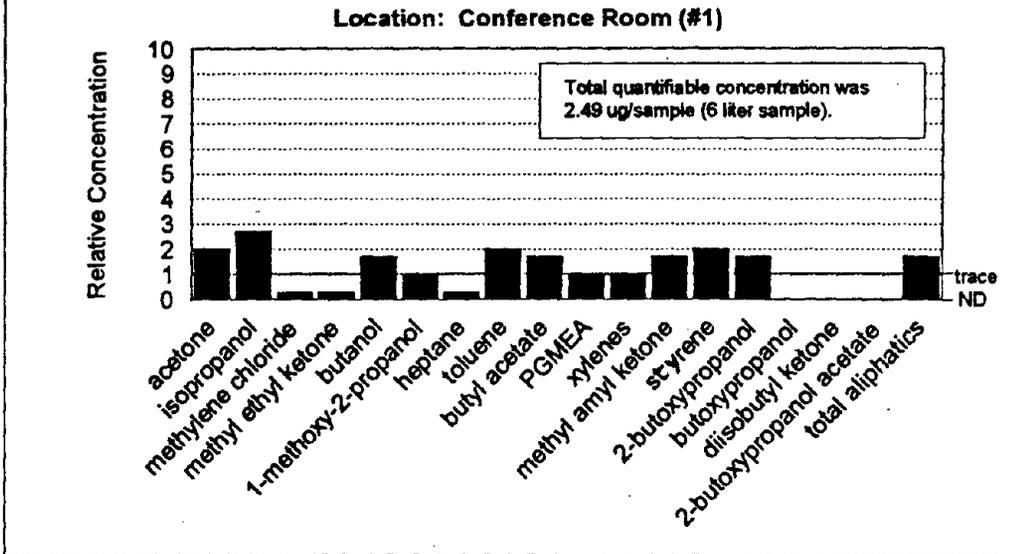


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

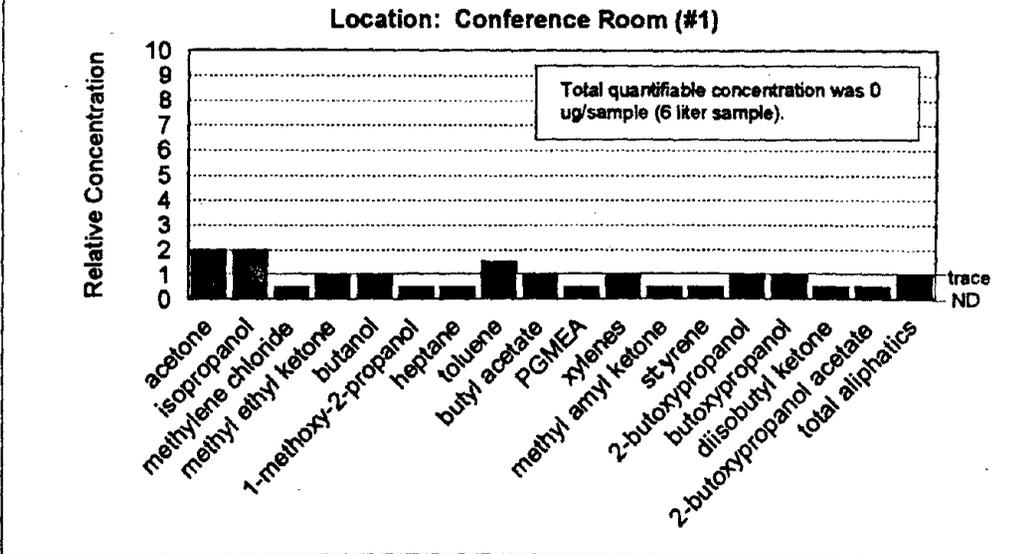


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

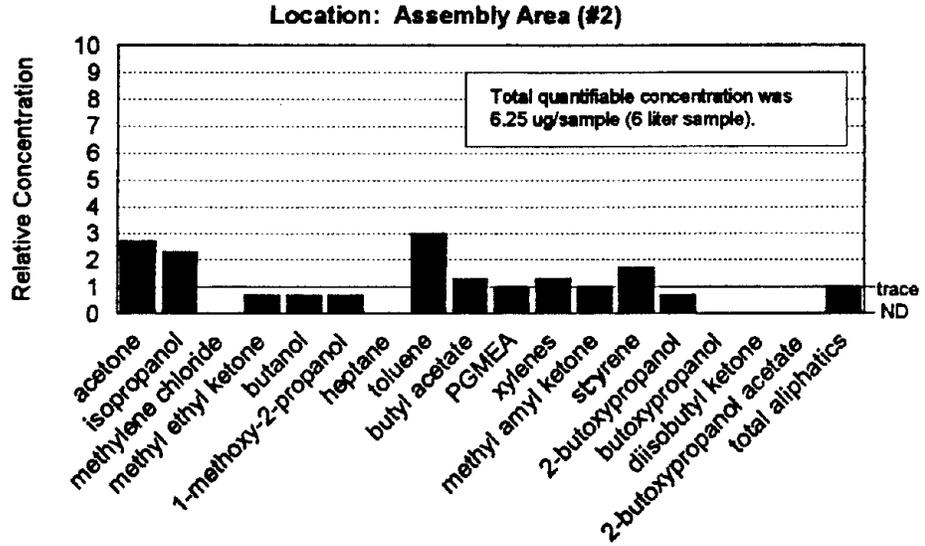


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

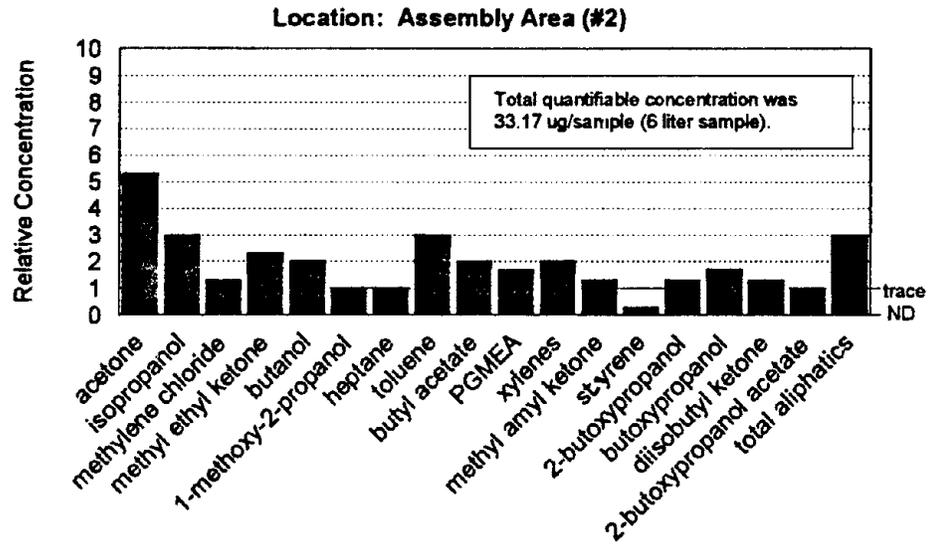
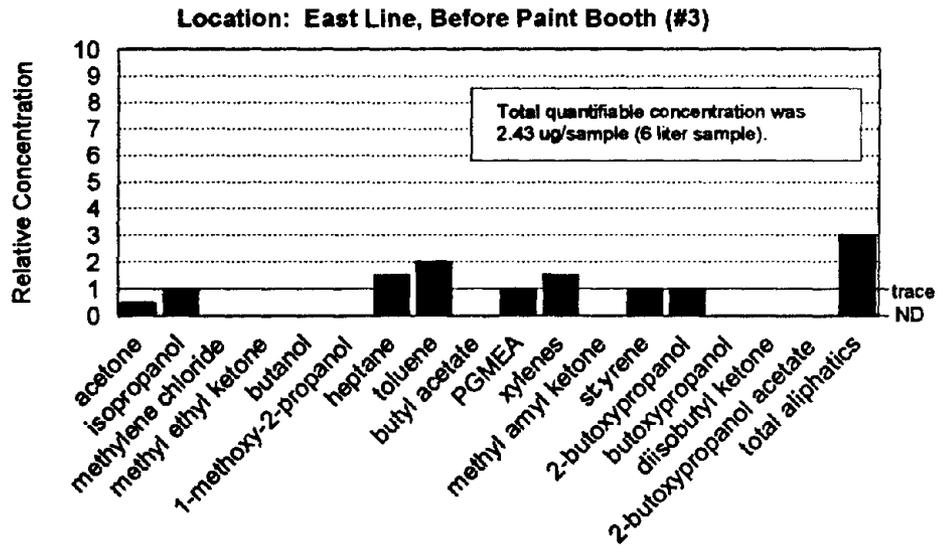


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100



No sample collected at this site during the November site visit.

Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

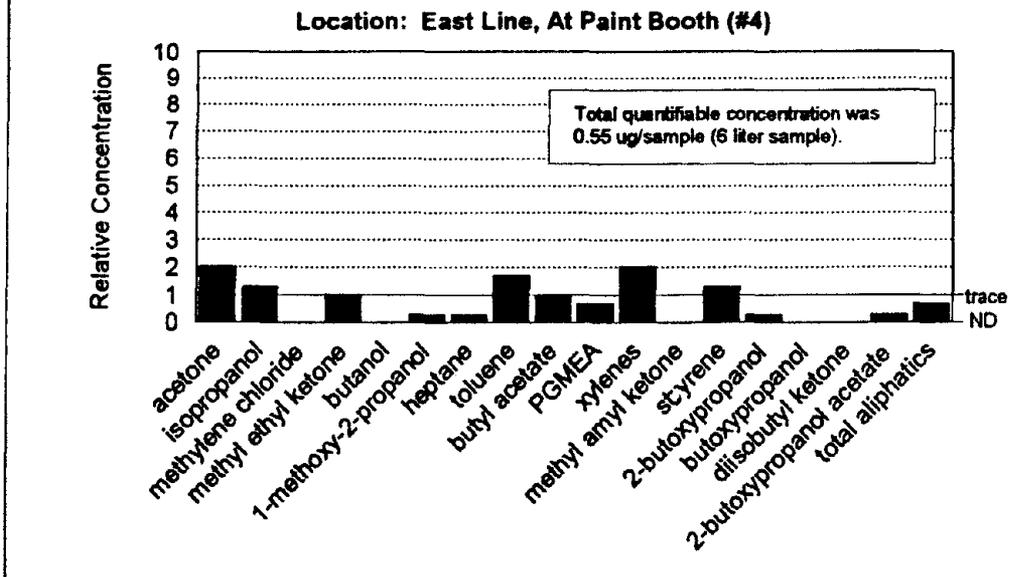


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

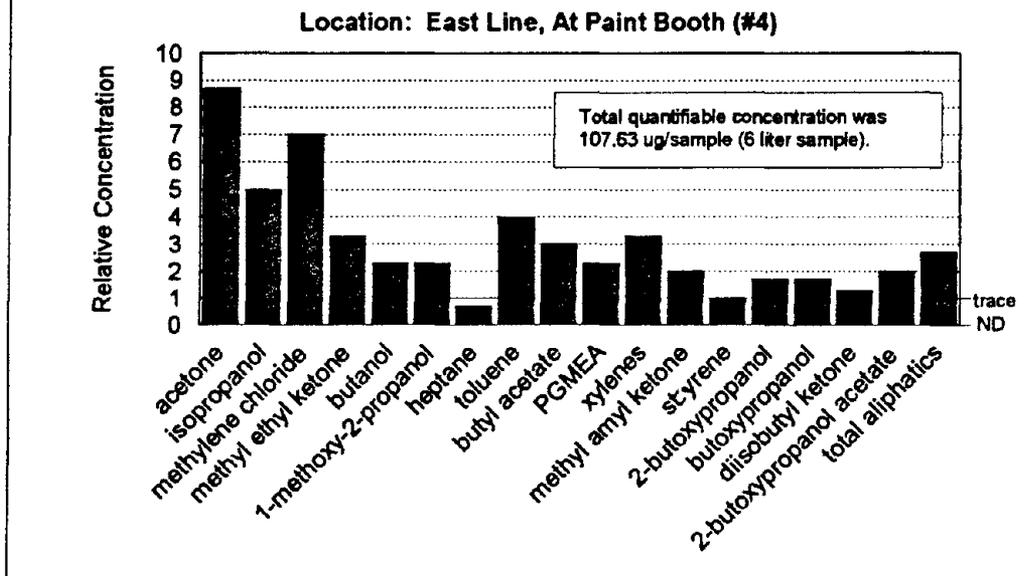
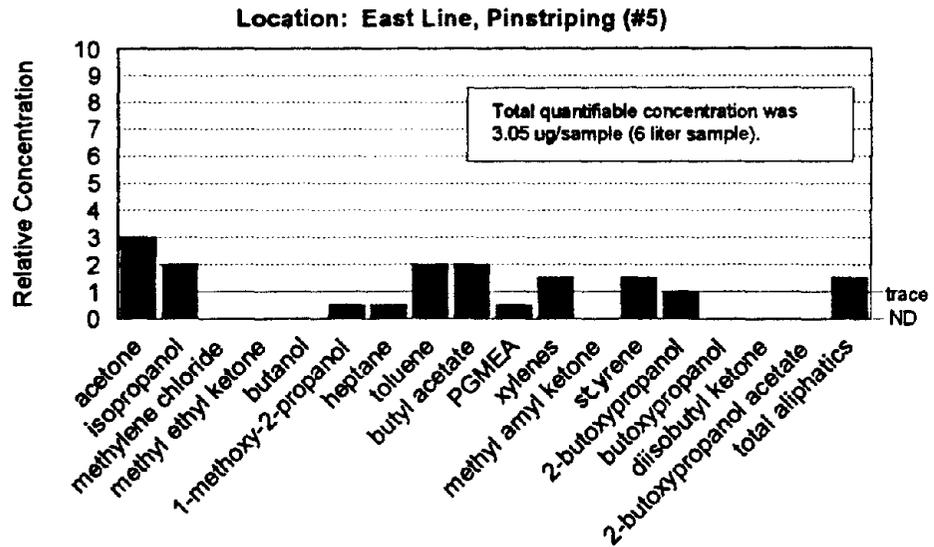


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100



No sample collected at this site during the November site visit.

Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

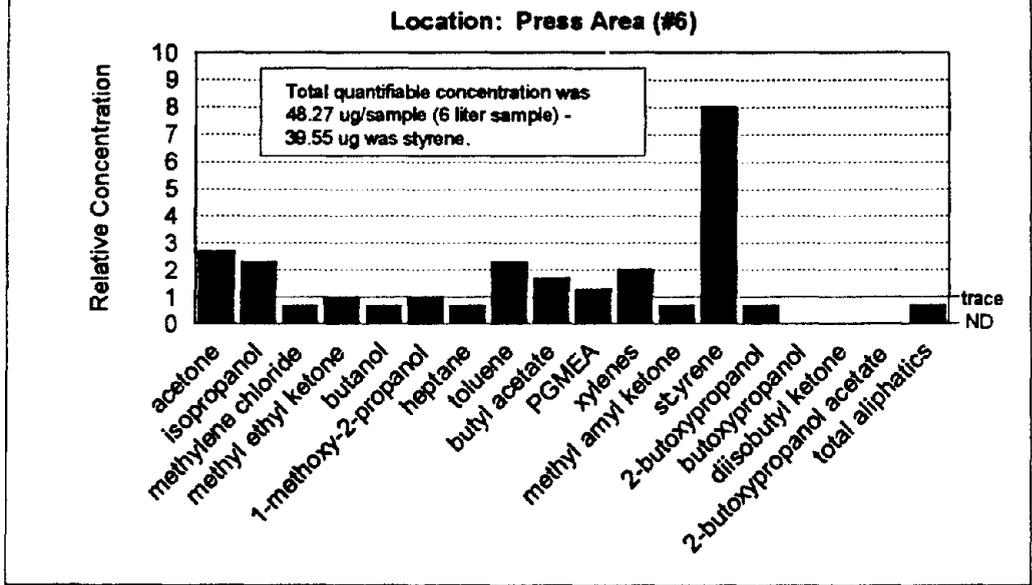


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

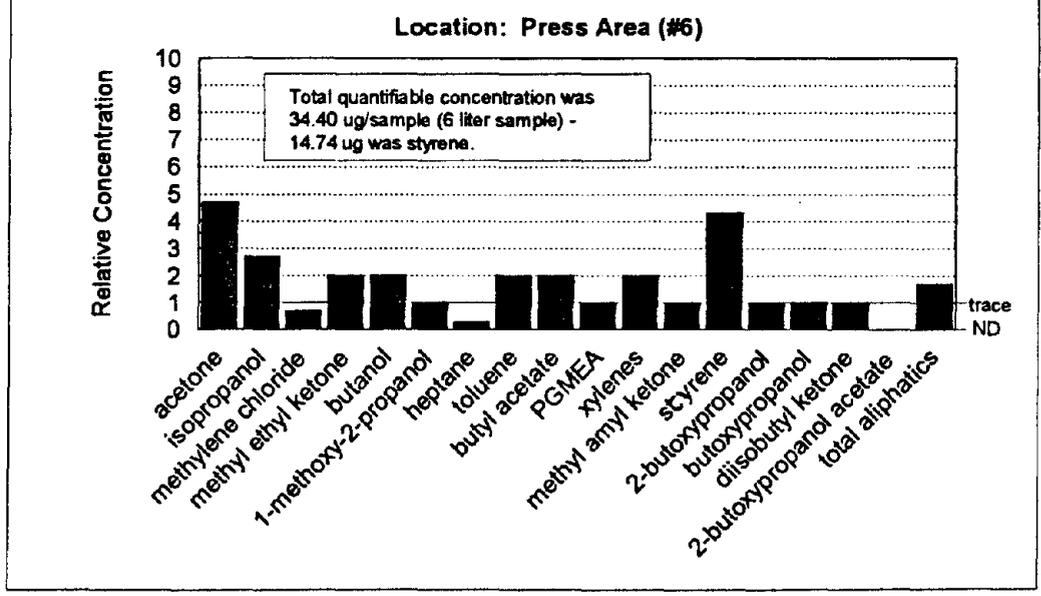


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

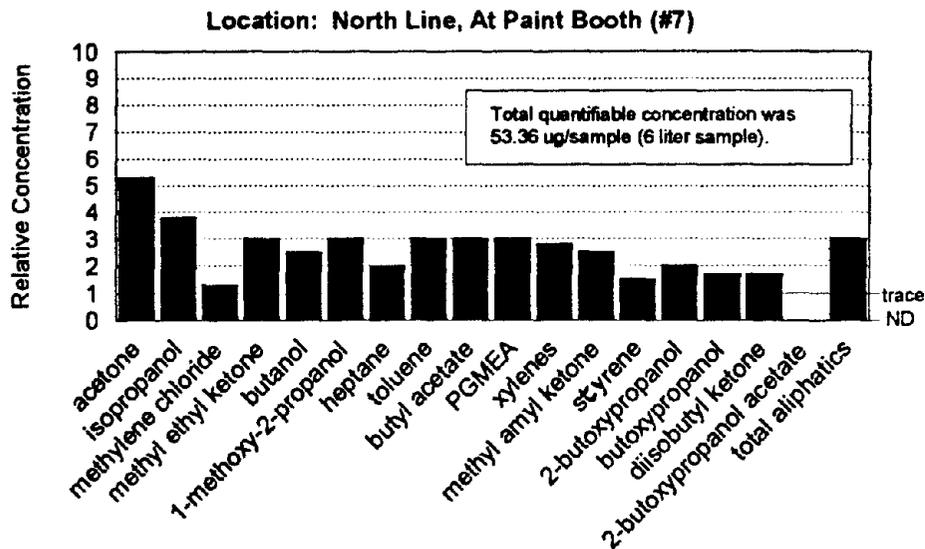


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

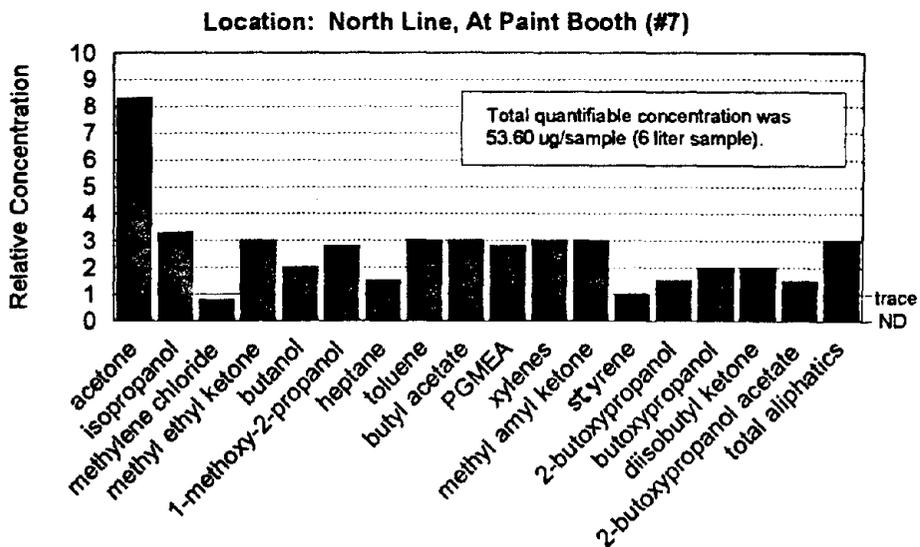


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

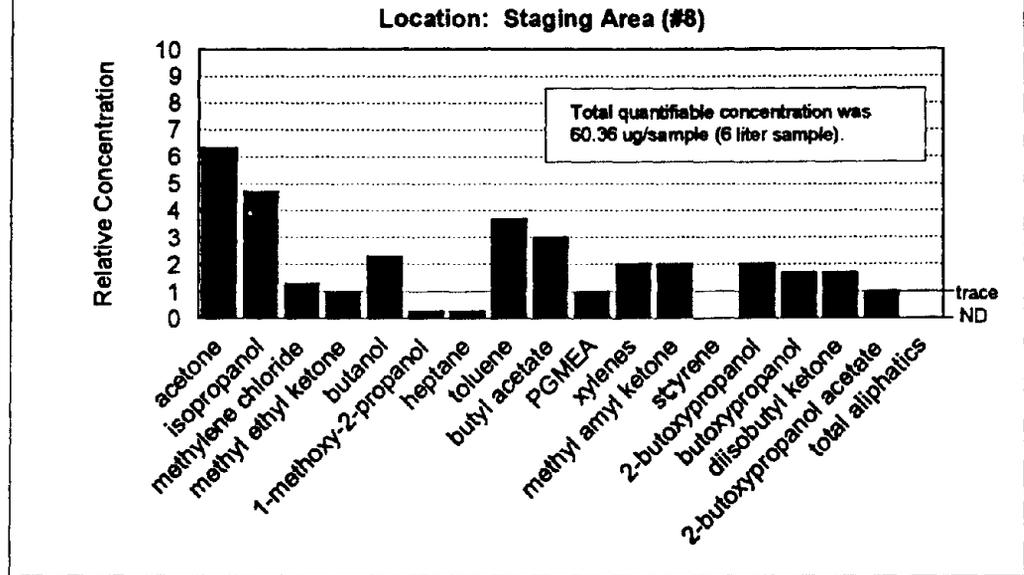


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

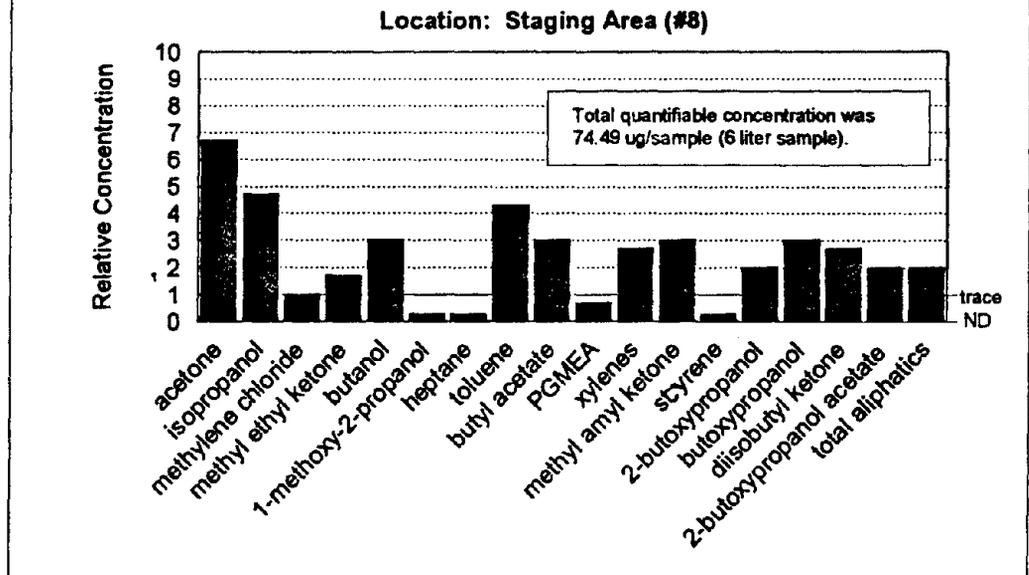


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

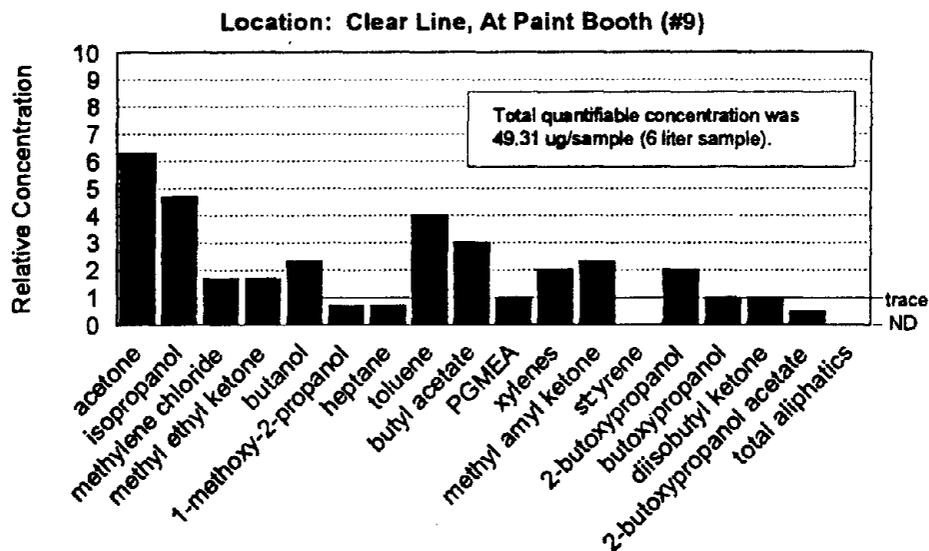


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

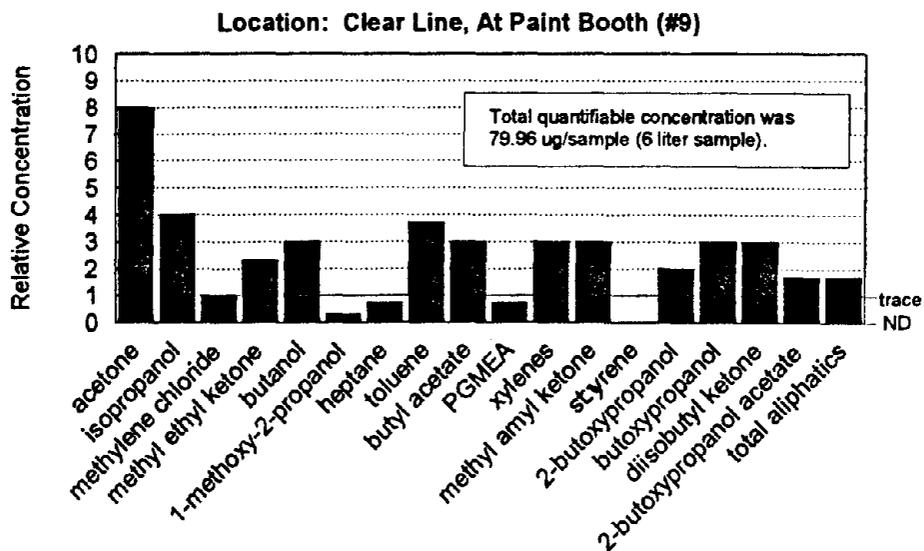


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

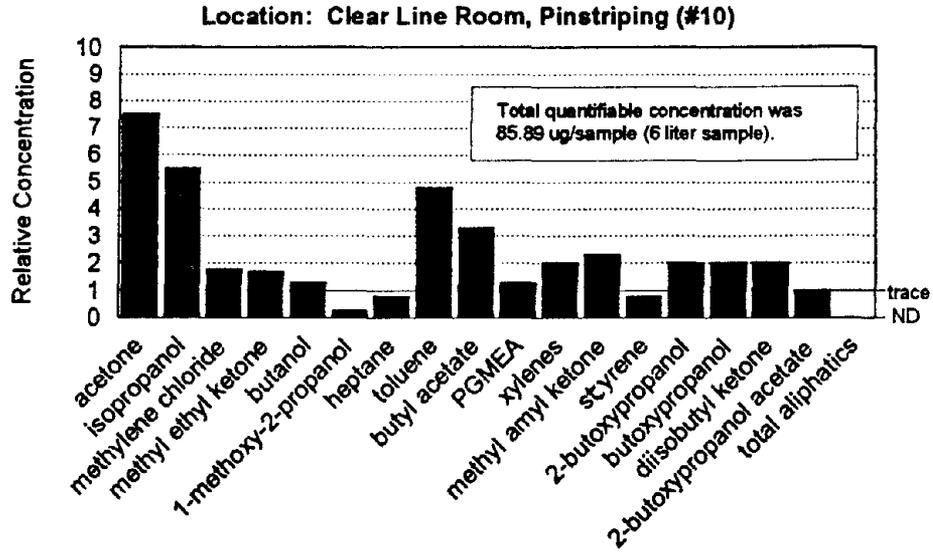


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

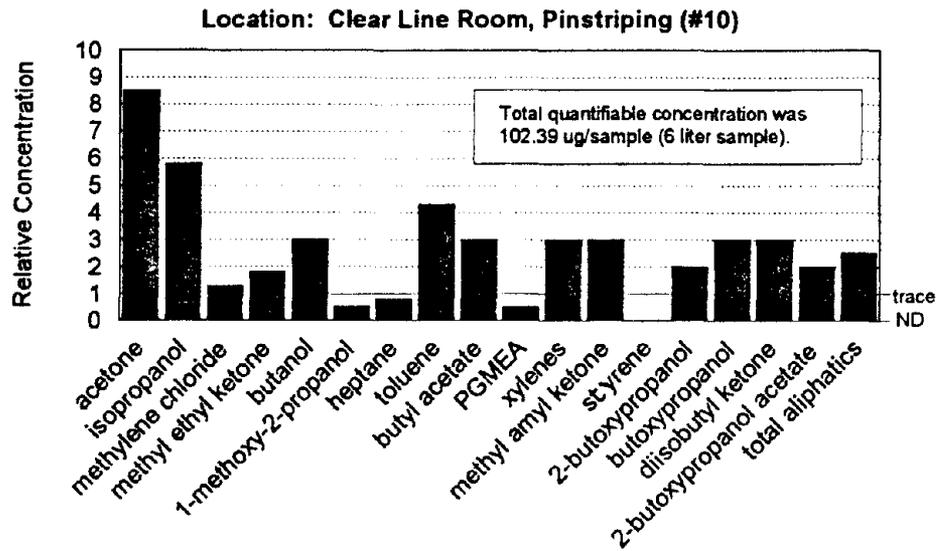


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

Location: Masking Area (#11)

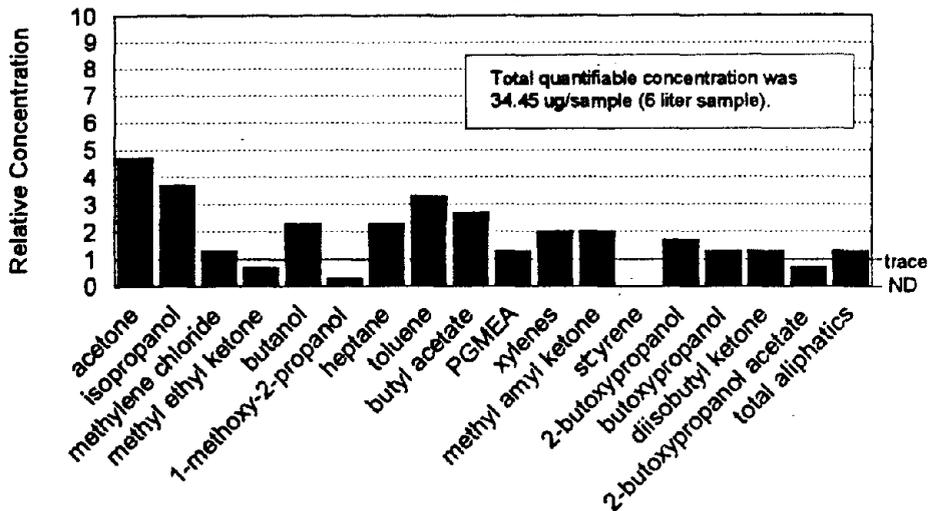


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

Location: Masking Area (#11)

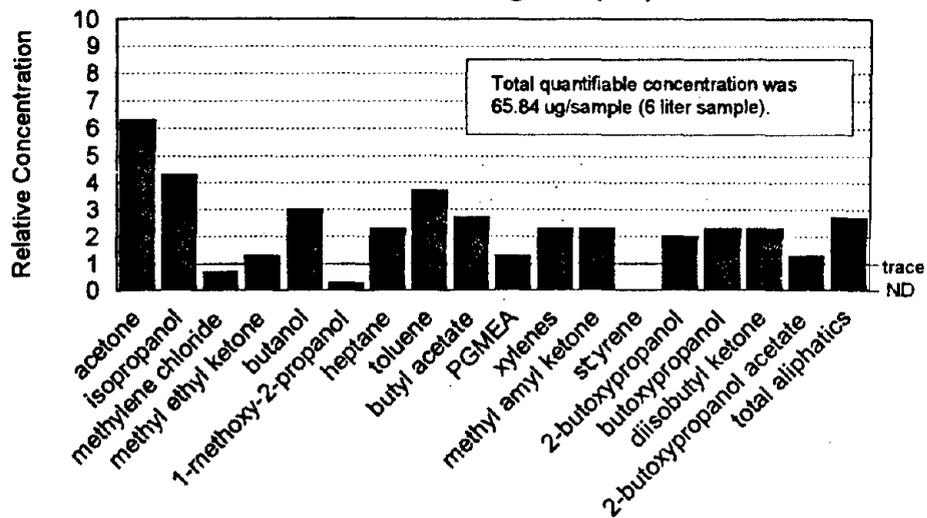


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

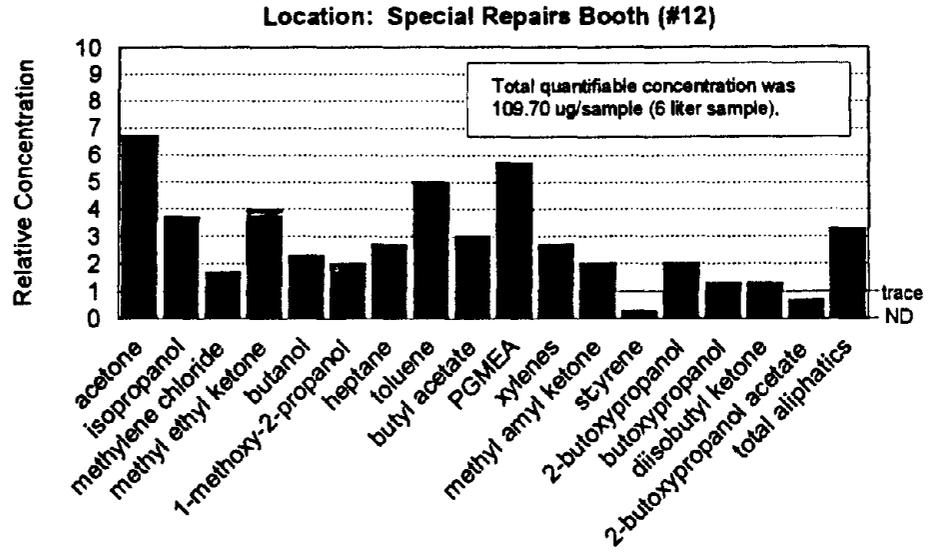


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

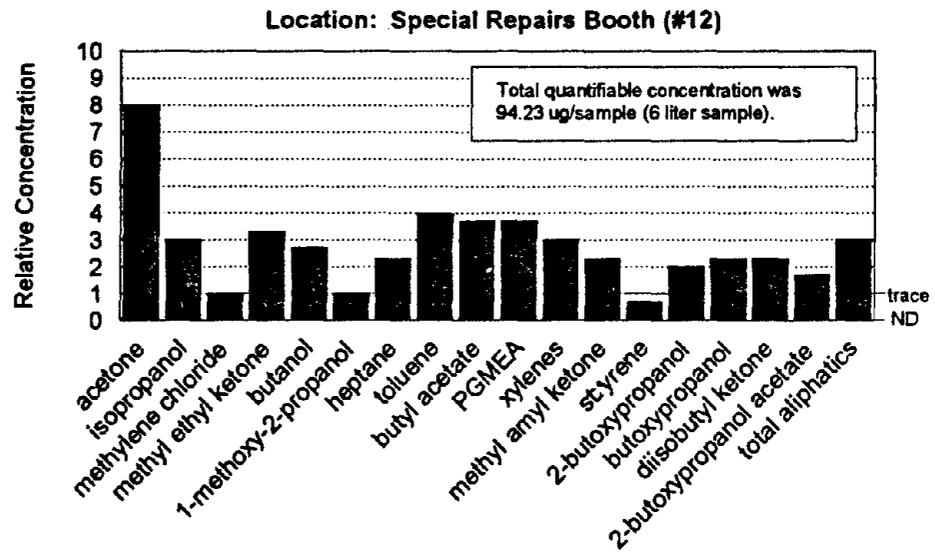


Figure 2 (continued)
 Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
 Harley-Davidson Plant, Tomahawk, Wisconsin
 HETA 96-0100

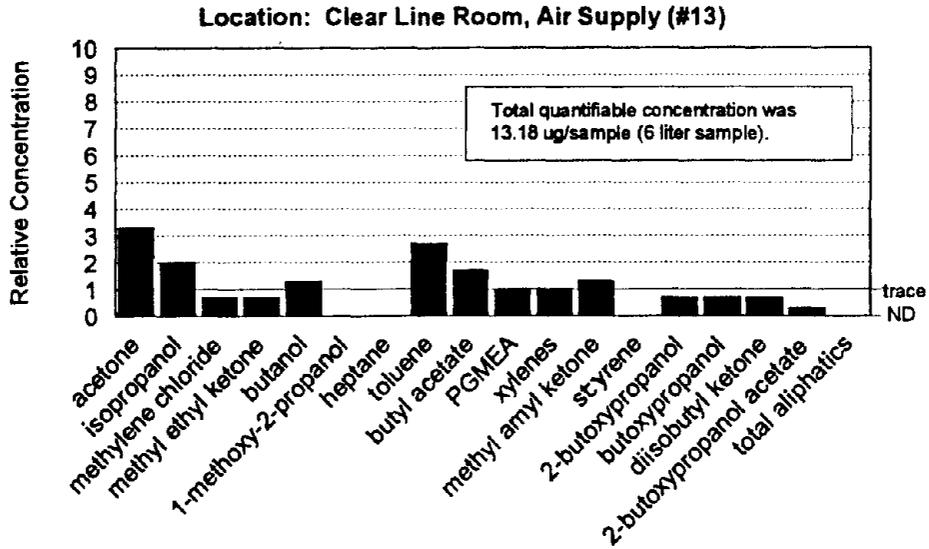


Figure 2 (continued)
 Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
 Harley-Davidson Plant, Tomahawk, Wisconsin
 HETA 96-0100

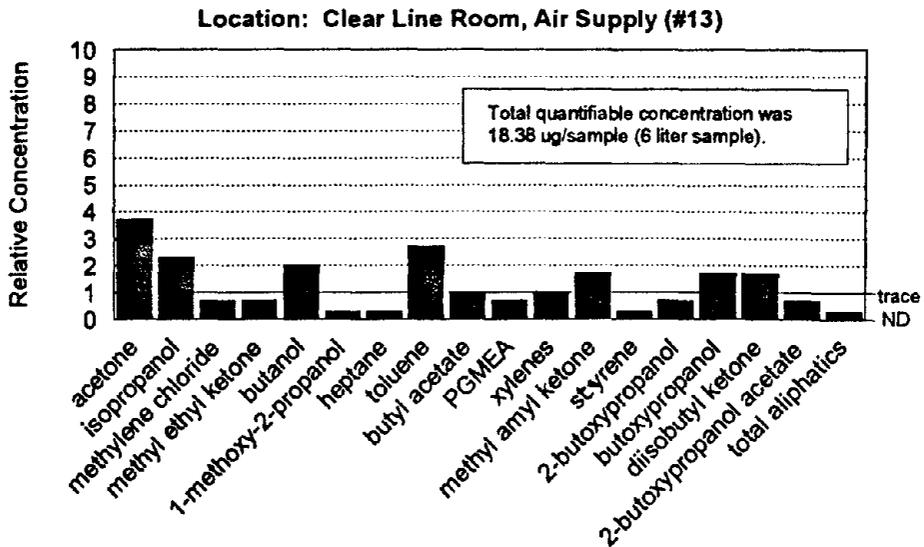
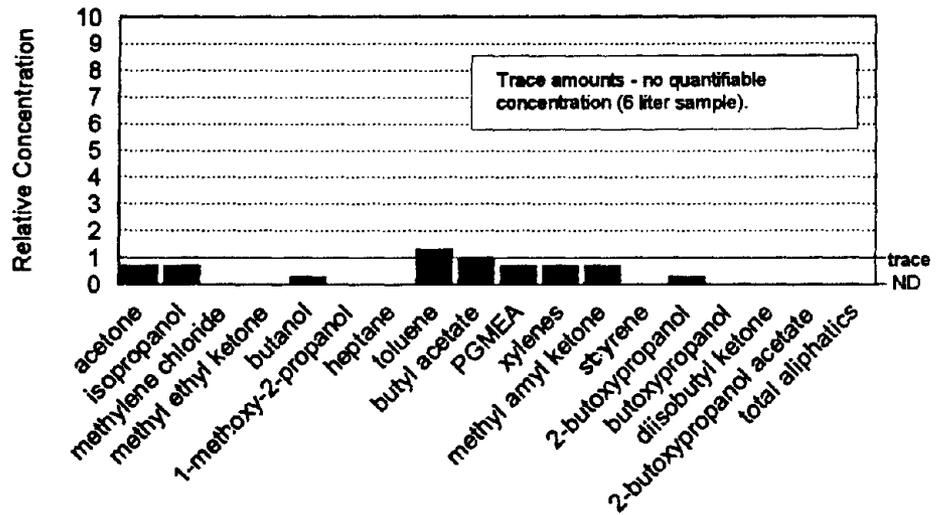


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

Location: Clear Line Room, Outside Air Intake (#14)



No sample collected at this site during the November site visit.

Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

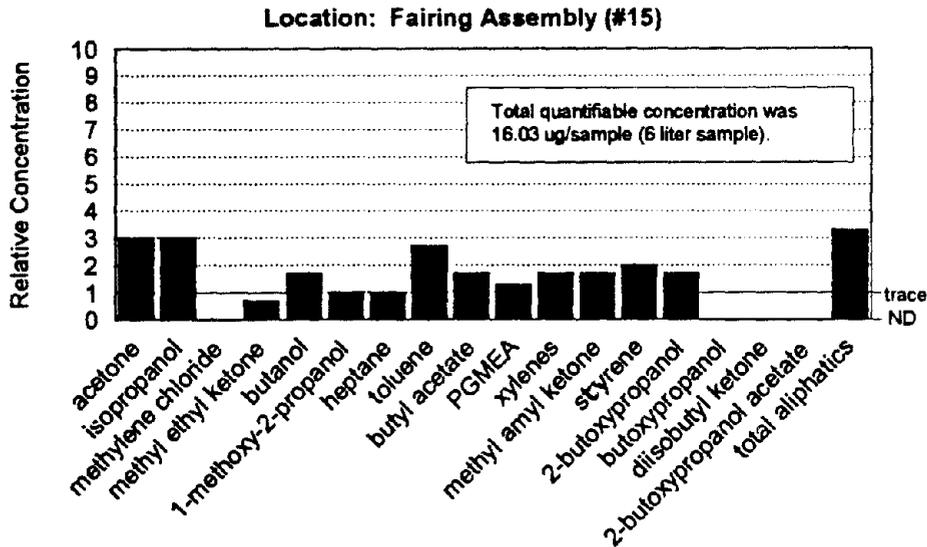


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

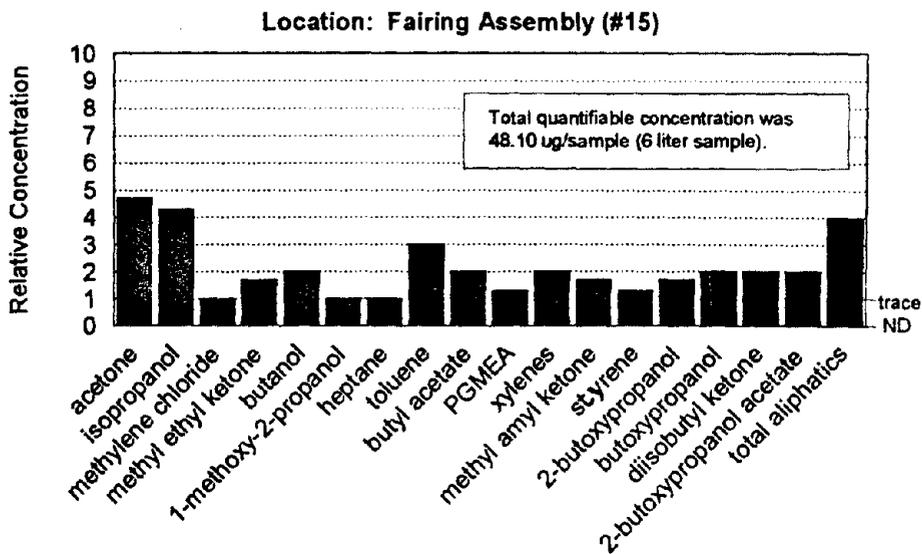
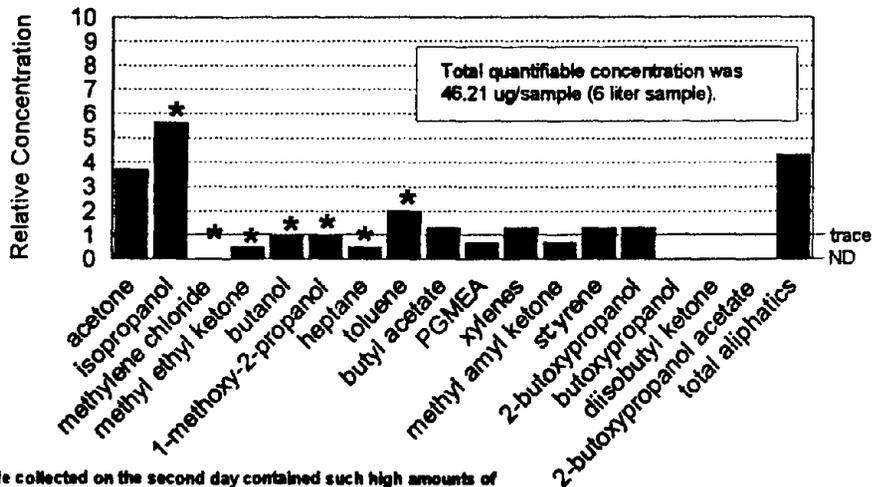


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

Location: Buffing Area (#16)



* Sample collected on the second day contained such high amounts of isopropanol that the system was overloaded and shut-down. The system restarted but the peaks that eluted near isopropanol were lost. See raw data for further clarification.

Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

Location: Buffing Area (#16)

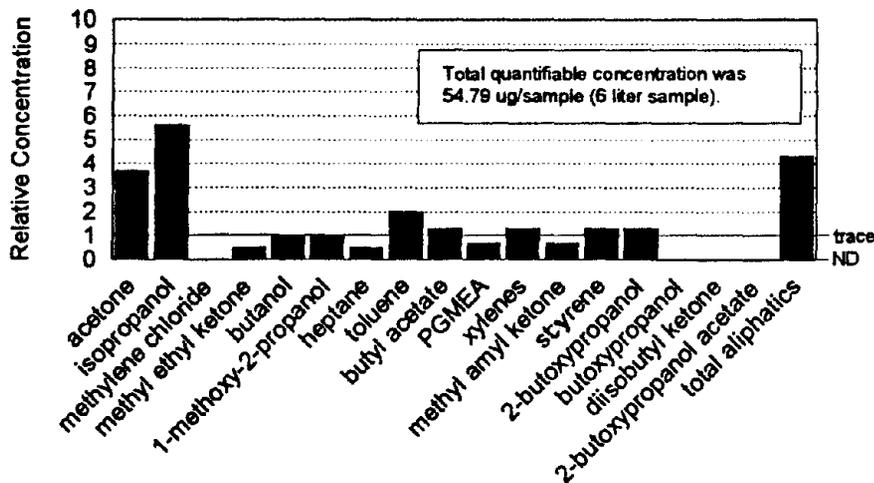
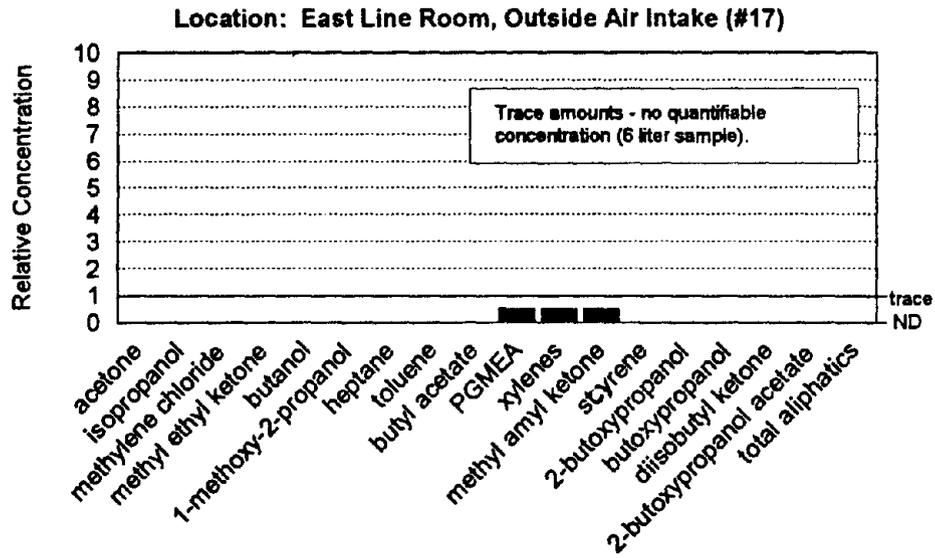


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100



No sample collected at this site during the November site visit.

Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 8/13-15/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

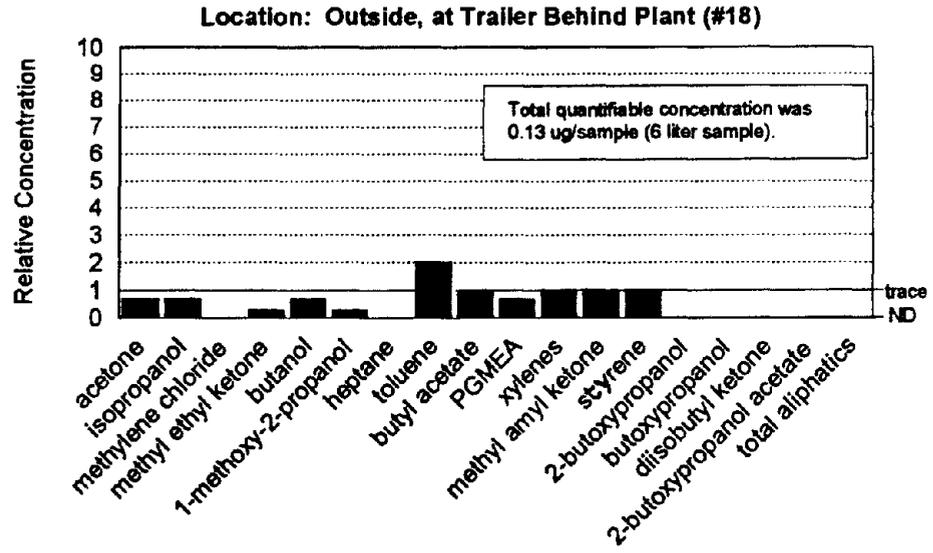


Figure 2 (continued)
Average Relative Estimates of Analyte Concentrations Detected on 11/18-20/96
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100

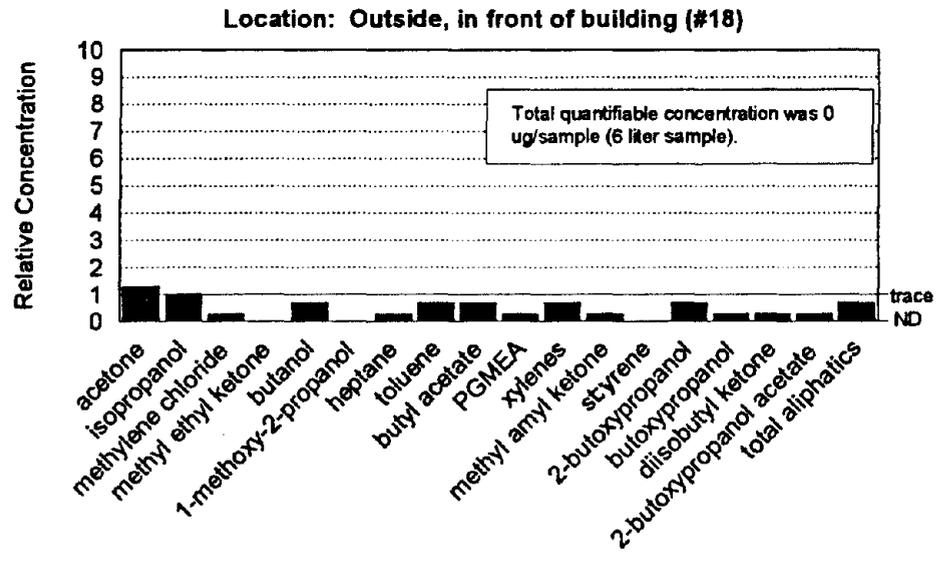


Figure 3
Totals of Average Quantifiable Concentrations by Location, 8/13-15/96
 (micrograms/sample, each sample 6 liters)
 Harley-Davidson Plant, Tomahawk, Wisconsin
 HETA 96-0100

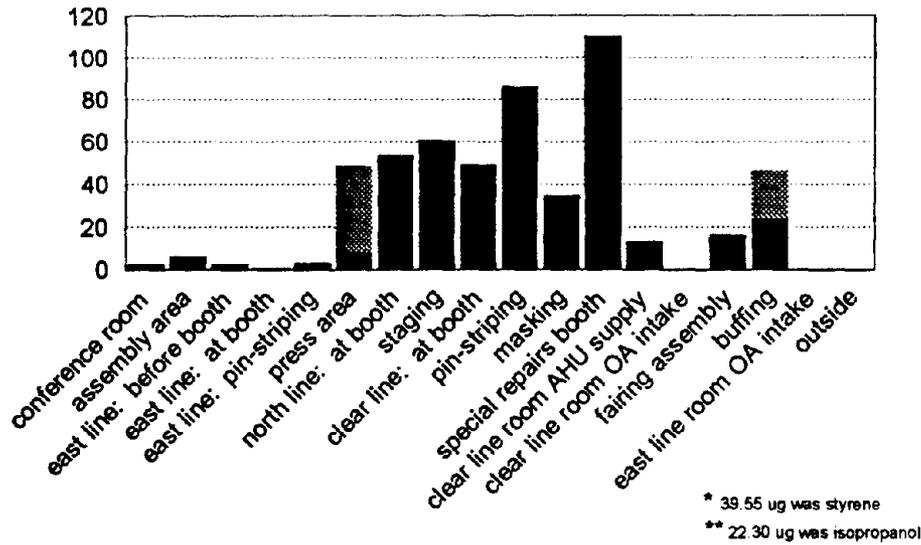


Figure 3 (continued)
Totals of Average Quantifiable Concentrations by Location, 11/18-20/96
 (micrograms/sample, each sample 6 liters)
 Harley-Davidson Plant, Tomahawk, Wisconsin
 HETA 96-0100

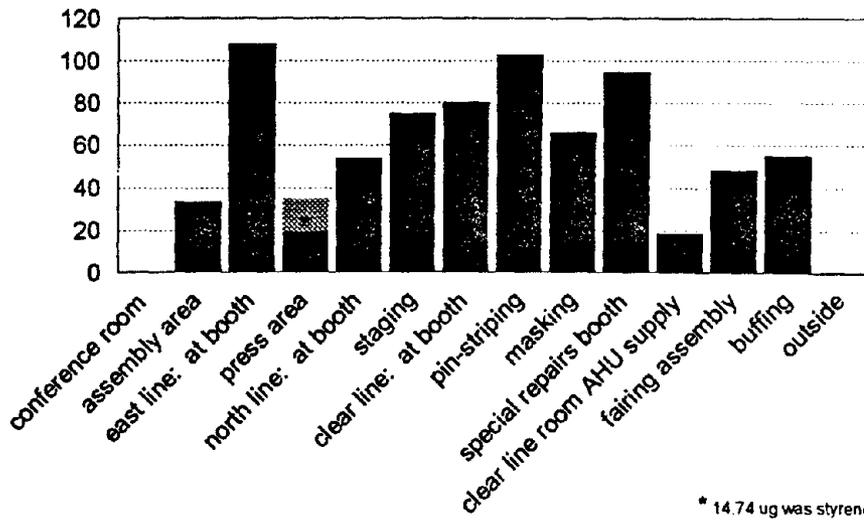
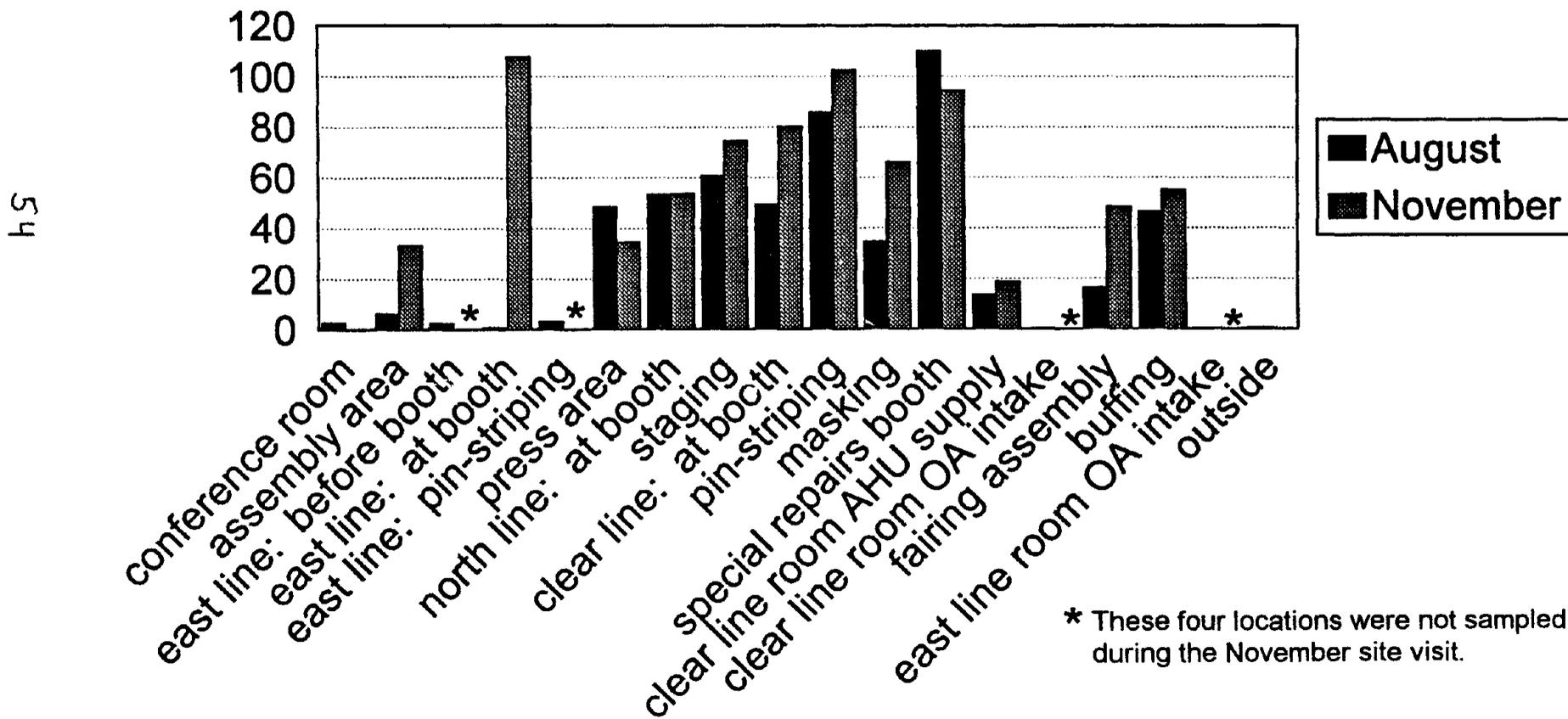


Figure 4
Average Relative Estimates of Analyte Concentrations Detected
Comparison by Season
Harley-Davidson Plant, Tomahawk, Wisconsin
HETA 96-0100



Appendix A
Thermal Desorption Tube Sampling



COPY

Memorandum

Date October 2, 1996

From Chemist, MDS, MRSB

Subject Sequence 8507A,B; HETA 96-0100: Qualitative Analysis of Thermal Desorption Tubes for Volatile Organic Compounds.

To D. Tharr, HETAB Lab Coordinator
Attn: B. Reh
Through: Chief, MRSB, DPSE *RLL*

INTRODUCTION:

Fifty four thermal desorption tubes plus blanks collected at Harley-Davidson were submitted for analysis of volatile organic compounds by GC-MS. Sets of samples collected at the same locations over a three day period were submitted. Air volumes were approximately 6 liters for all samples so a visual comparison of the results could be made. Operations involved molding and painting accessories. MSDS were supplied with the samples.

EXPERIMENTAL:

Since the types of contaminants were expected to be widely varied, thermal desorption tubes were used for sampling. Stainless steel tubes configured for the Perkin-Elmer ATD 400 thermal desorption system were used. Each thermal desorption tube contained three beds of sorbent materials--a front layer of Carbopack Y (≈ 90 mg), a middle layer of Carbopack B (≈ 115 mg), and a back section of Carboxen 1003 (≈ 150 mg). Prior to field use, each tube was cleaned by conditioning at 375°C for 2 hours.

Samples were analyzed using the ATD 400 automatic thermal desorption system containing an internal focusing trap packed with Carbopack B/Carboxen 1000 sorbents. The thermal unit was interfaced directly to a HP5890A gas chromatograph and HP5970 mass selective detector (TD-GC-MSD). The mass spectrometer was operated under EI conditions in full scan mode (20-300 amu). A thirty meter DB-1 fused silica capillary column was used for analyses. Sorbent tubes were desorbed in the ATD at 300°C for 10 minutes prior to analyses.

An initial set of four thermal desorption tubes were sent to the laboratory from the field to be analyzed first. Based on the qualitative findings from this initial set, standards and spikes were then prepared so the remaining samples could be quantified for specific compounds. This initial set of samples were also used to check out the potential water background on future samples. Some of these samples indicated that amounts of water

on the collected samples could be significant. Therefore, all remaining sample tubes were dry purged with helium for 30-45 minutes at 100 cc/min. prior to analyses. This procedure has been shown to be effective in removing excess water collected on the tubes without causing any significant loss of compounds.

Stock solutions in CS₂ containing known amounts of various solvents identified on the initial set of tubes were used to prepare spikes. These solutions contained acetone, isopropanol (IPA), methylene chloride, methyl ethyl ketone (MEK), butanol, 1-methoxy-2-propanol (propylene glycol monomethyl ether), heptane, toluene, butyl acetate, propylene glycol monomethyl ether acetate (PGMEA), xylenes, methyl amyl ketone (MAK), styrene, butyl cellosolve, and Stoddard solvent. To prepare the spikes, blank thermal desorption tubes were inserted into a GC injector (120°C). Aliquots of 0.1 µL to 0.5 µL of the stock solutions were injected into the GC and onto the thermal desorption tubes with helium flowing through the tubes at 40-50 cc/min for 10 minutes.

RESULTS:

The first samples analyzed were initially dry purged with helium for only 15 minutes. Some of these samples contained significant amounts of water which may have caused a loss of early eluting and polar compounds. These samples are marked with an asterisk in the enclosed tables. Sample A04085 (noted by the IH to be wet after sampling) was dry purged for an extended time, 45 minutes, prior to analysis. However, even with additional drying time, sample A04085 still contained enough water to shut down the mass spectrometer when analyzed. The system was restarted but some compounds may have been lost. One other sample, A04718, shut down the GC-MS system due to the huge amount of isopropanol on it. Again, the system was restarted, but some compounds eluting after the IPA were lost.

All thermal desorption tubes were quantified by GC-MS for the 15 compounds listed above by comparing samples to spiked tubes and the results are reported in the enclosed Table 1. Characteristic ions for each analyte were used for quantitation. Since the method has not been fully validated (no capacity/desorption studies, etc.), results are estimates. In addition, estimated results for 1-butoxy-2-propanol, diisobutyl ketone, and butyl cellosolve acetate were calculated using butyl cellosolve as the standard; total aliphatics were estimated using Stoddard solvent for standards. These latter results are reported on the enclosed Table 2. All results are reported in terms of µg/sample.

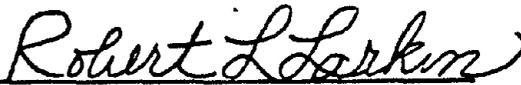
Copies of the reconstructed total ion chromatograms from the initial four test samples plus a few representative samples are

enclosed. Chromatograms are all scaled the same for comparison (same time and abundance axes). A separate table is enclosed listing each peak number with its corresponding identification.

Since samples were collected at the same locations over a three day period, sets of three samples plotted by location are also enclosed and major peaks identified. Samples contained various compounds depending on location. Several samples contained none or only very low levels of any contaminants. Others, in comparison, contained quite high concentrations. Major components on several sample sets were isopropanol, acetone, MEK, butanol, 1-methoxy-2-propanol, toluene, butyl acetate, PGMEA, MAK, xylenes, butyl cellosolve, butoxy propanol, and diisobutyl ketone. Also present on some of these samples were ethyl acetate, isobutyl acetate, methylene chloride, and several higher molecular weight esters (dimethyl succinate, dimethyl glutarate, dimethyl adipate). Some samples had a predominant hydrocarbon pattern, mostly aliphatic hydrocarbons in the C₉-C₁₃ range. A few contained a VM&P type naphtha pattern, mostly C₇-C₈ aliphatics. Styrene was the major compound at another location. Samples with high styrene concentrations also contained benzaldehyde, N,N-dimethylformamide, and benzoic acid. One sample, A04128, was different from all others. It was the only sample to have major peaks of 1,1,1-trichloroethane, 1,1,2,2-tetrafluoroethane, trichloroethylene, and dichloroethylene.

The tables of results are available electronically as Excel 5.0 spreadsheets.


Ardith A. Grote


Robert L. Larkin
Acting Chief, MDS, MRSB,
DPSE

Attachments

SEQ 8507
TABLE 1--PAGE 1 OF 2
UG/SAMPLE

Field No.	methylene		1-methoxy-				butyl		PGMEA	xylenes	MAK	styrene	butyl cellosolve	
	acetone	isopropanol	chloride	MEK	butanol	2-propanol	heptane	toluene						
A03791	23.72	8.67	0.36	3.25	0.59	1.50	0.18	3.43	2.60	1.22	0.88	0.96	(0.02)	0.32
A05078*	6.75	1.34	N.D.	N.D.	(0.11)	(0.08)	N.D.	2.34	0.11	N.D.	(0.04)	(0.06)	N.D.	(0.04)
A03074*	N.D.	N.D.	N.D.	0.14	N.D.	N.D.	(0.03)	0.22	N.D.	N.D.	0.31	N.D.	(0.04)	N.D.
A03879	36.18	19.38	0.29	(0.06)	0.84	N.D.	(0.04)	18.48	2.68	(0.09)	0.46	0.61	(0.02)	0.56
A05366	2.38	4.51	N.D.	(0.04)	0.04	(0.05)	N.D.	0.16	(0.04)	(0.04)	(0.06)	(0.02)	0.07	0.14
A04210	23.26	11.77	N.D.	(0.08)	0.50	(0.05)	N.D.	7.11	2.43	(0.08)	0.42	0.34	N.D.	0.32
A04468*	1.26	0.73	N.D.	N.D.	N.D.	N.D.	N.D.	0.09	0.22	N.D.	(0.07)	N.D.	0.07	(0.04)
A03659*	2.47	0.60	N.D.	(0.10)	N.D.	N.D.	N.D.	(0.05)	(0.04)	N.D.	0.26	N.D.	(0.05)	N.D.
A04215*	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	0.07	N.D.	0.03	0.05	N.D.	N.D.	(0.11)
A05924	23.97	7.50	0.32	2.42	0.58	1.82	0.22	5.39	3.45	1.64	1.12	0.99	(0.03)	0.35
A03974	35.80	22.37	0.28	(0.08)	0.87	(0.05)	(0.03)	16.90	2.41	(0.08)	0.62	0.84	N.D.	0.54
A05389	3.87	24.39	N.D.	(0.06)	(0.06)	(0.06)	N.D.	0.19	0.06	(0.05)	0.09	(0.02)	0.10	0.61
A03777	21.77	9.97	(0.07)	0.14	0.44	N.D.	(0.02)	5.03	1.88	(0.08)	0.54	0.33	N.D.	0.30
A03938*	(0.17)	0.04	N.D.	N.D.	N.D.	N.D.	(0.02)	0.17	N.D.	N.D.	(0.05)	N.D.	0.07	(0.09)
A04130	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
A04620	5.45	1.73	N.D.	N.D.	0.12	N.D.	1.07	1.90	0.54	(0.08)	0.11	(0.06)	N.D.	(0.11)
A03534	0.57	0.14	N.D.	N.D.	N.D.	(0.05)	N.D.	0.14	(0.08)	(0.05)	0.09	N.D.	33.11	N.D.
A04286 OUTSIDE	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.09	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
A04085 (WET) ¹	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
A04128	0.42	2.06	(0.06)	N.D.	0.07	(0.05)	N.D.	0.25	0.07	(0.07)	(0.08)	0.07	0.10	0.30
A03700	13.28	1.89	N.D.	0.24	N.D.	N.D.	N.D.	0.26	0.10	(0.06)	0.33	(0.02)	(0.05)	N.D.
A03328	39.54	23.24	0.37	(0.06)	1.01	N.D.	(0.06)	21.56	3.39	(0.10)	0.56	0.77	(0.02)	0.77
A03722	0.48	0.61	N.D.	N.D.	(0.04)	(0.05)	N.D.	0.27	(0.08)	(0.08)	0.13	0.10	0.18	(0.04)
A05534	9.27	1.24	0.06	0.18	(0.09)	(0.08)	(0.03)	1.11	0.27	(0.07)	0.21	(0.05)	30.33	(0.05)
A04409	0.24	0.08	N.D.	N.D.	(0.07)	N.D.	N.D.	0.76	(0.08)	(0.04)	N.D.	(0.06)	N.D.	N.D.
A04828	1.29	1.11	N.D.	(0.05)	(0.05)	(0.06)	N.D.	0.35	0.10	(0.05)	(0.08)	(0.03)	0.10	0.21
A04174	14.99	11.56	N.D.	6.26	1.05	3.68	0.14	2.71	5.93	2.98	2.21	1.78	0.06	0.40
A04448	33.27	6.86	(0.06)	25.67	0.34	0.21	2.54	15.83	5.37	10.98	3.84	0.21	N.D.	0.59
A03072	29.98	17.73	0.20	(0.05)	0.55	N.D.	(0.02)	13.97	1.73	(0.08)	0.40	0.58	N.D.	0.42
A03428	1.12	0.19	N.D.	N.D.	N.D.	(0.05)	N.D.	0.18	0.11	0.11	0.63	N.D.	0.08	(0.07)
A05090	(0.17)	(0.12)	N.D.	N.D.	N.D.	N.D.	N.D.	0.43	0.24	(0.06)	(0.05)	(0.03)	N.D.	(0.05)
A04197	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(0.03)	(0.03)	(0.02)	N.D.	N.D.
A05120	23.48	13.25	0.23	N.D.	0.68	N.D.	0.72	12.00	1.39	(0.10)	0.37	0.61	N.D.	0.80
A04069	28.67	13.65	0.27	0.13	0.68	N.D.	N.D.	9.45	2.95	(0.09)	0.58	0.56	N.D.	0.60
A05428	17.38	10.63	(0.07)	4.44	1.03	2.83	0.11	6.61	3.48	2.33	1.44	2.27	0.08	0.24
A04869	4.76	0.73	N.D.	(0.05)	(0.04)	(0.08)	(0.03)	0.98	0.28	0.15	0.28	(0.03)	55.21	(0.05)
A03798 OUTSIDE	N.D.	N.D.	N.D.	N.D.	(0.07)	N.D.	N.D.	0.16	(0.03)	(0.05)	(0.06)	0.11	0.06	N.D.

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SEQ 8507
TABLE 1--PAGE 2 OF 2
UG/SAMPLE

Field No.	acetone	isopropanol	methylene chloride	MEK	butanol	1-methoxy- 2-propanol	heptane	toluene	butyl acetate	PGMEA	xylene	MAK	styrene	butyl cellosolve
A05008	35.61	17.85	(0.16)	0.15	1.18	(0.05)	N.D.	11.62	7.51	(0.10)	0.77	0.35	(0.02)	0.42
A04150	2.14	0.42	N.D.	N.D.	N.D.	(0.07)	0.15	1.08	0.14	(0.04)	0.19	N.D.	(0.03)	(0.08)
A05487 OUTSIDE	0.18	0.14	N.D.	(0.10)	(0.04)	(0.11)	N.D.	0.14	0.13	(0.10)	0.09	(0.07)	(0.05)	N.D.
A05054	0.07	N.D.	N.D.	N.D.	(0.09)	N.D.	N.D.	0.34	(0.06)	(0.06)	(0.04)	(0.07)	N.D.	N.D.
A05635 BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
A04718 (PARTIAL) ²	18.12	EXCESS ²	___ ²	___ ²	___ ²	___ ²	___ ²	___ ²	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
A04801 BLANK ³	N.D.	1.92 ³	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
A05000	33.42	17.46	0.28	(0.10)	1.00	N.D.	N.D.	12.22	1.87	(0.08)	0.51	0.82	N.D.	0.22
A03645	20.73	8.33	0.22	0.15	1.10	(0.05)	0.20	5.22	1.20	0.16	0.53	1.01	N.D.	0.69
A04725	(0.09)	0.27	N.D.	N.D.	0.06	(0.06)	(0.03)	0.30	(0.08)	(0.05)	(0.08)	(0.02)	0.14	(0.04)
A03679	33.90	15.91	0.31	0.29	1.56	(0.05)	N.D.	10.02	2.01	(0.10)	0.85	1.27	N.D.	0.28
A0 3893	25.26	6.18	0.25	0.49	0.76	(0.07)	0.18	6.85	2.63	1.29	0.75	0.97	N.D.	0.54
A03181 BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(0.02)	N.D.	N.D.
A03763	(0.10)	(0.12)	N.D.	N.D.	(0.05)	N.D.	N.D.	0.36	(0.05)	(0.05)	(0.03)	(0.05)	N.D.	N.D.
A05422 BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(0.03)	N.D.	N.D.	N.D.	N.D.
A03026	43.69	23.99	0.56	(0.09)	1.23	N.D.	(0.03)	17.55	3.82	0.15	0.86	1.36	N.D.	0.39
A04958	0.28	0.54	N.D.	N.D.	(0.05)	(0.05)	N.D.	0.22	(0.05)	(0.04)	(0.07)	N.D.	0.08	(0.05)
A04202 BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
A05518 BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
A04378	34.69	17.07	0.36	14.93	1.16	1.65	1.78	33.87	3.84	59.62	6.19	0.99	(0.02)	0.98
A03231	2.49	5.41	N.D.	(0.05)	(0.11)	(0.07)	(0.04)	1.65	0.17	(0.09)	0.12	0.07	0.34	(0.06)
A03730	2.85	4.17	N.D.	N.D.	0.17	(0.12)	0.07	1.88	0.23	0.11	0.19	0.16	0.57	0.28
A04575	4.55	20.11	N.D.	N.D.	(0.11)	(0.06)	(0.03)	0.69	0.10	(0.06)	0.11	(0.06)	0.37	0.45
LOD	0.05	0.04	0.05	0.04	0.04	0.05	0.02	0.02	0.03	0.03	0.03	0.02	0.02	0.04
LOQ	0.18	0.13	0.17	0.12	0.12	0.16	0.07	0.07	0.10	0.11	0.09	0.07	0.06	0.12

*Sample contained high water background which may have affected results; values for compounds may be low
Values in parenthesis fall between the LOD and LOQ.

1-methoxy-2-propanol = propylene glycol methyl ether

MEK = methyl ethyl ketone

PGMEA = propylene glycol monomethyl ether acetate

MAK = methyl amyl ketone (2-heptanone)

¹Sample (reported to be "wet" after sampling in the field) contained excess water even after purging and shut system off; restarted but no peaks present.

²Sample contained such high amounts of isopropanol that the MS system was overloaded and shut down and no value can be reported for isopropanol.
System restarted and later peaks detected but any compounds eluting around isopropanol were lost.

³Tube analyzed after sample with excess isopropanol; value reported was due to carryover from previous sample.

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SEQ 8507
TABLE 2-PAGE 1 OF 2
ug/sample

Field No.	Butoxypropanol ¹	Diisobutyl ketone ¹	Butyl cellosolve acetate ¹	Total aliphatics ²
A03791	(0.17)	0.26	N.D.	1.57
A05078*	N.D.	N.D.	N.D.	N.D.
A03074*	N.D.	N.D.	N.D.	N.D.
A03879	0.41	0.37	(0.08)	N.D.
A05366	N.D.	N.D.	N.D.	4.09
A04210	(0.13)	(0.17)	(0.07)	N.D.
A04468*	N.D.	N.D.	N.D.	N.D.
A03659*	N.D.	N.D.	N.D.	N.D.
A04215*	N.D.	N.D.	N.D.	2.33
A05924	(0.15)	0.23	N.D.	2.27
A03974	0.47	0.43	(0.08)	N.D.
A05389	N.D.	N.D.	N.D.	19.98
A03777	N.D.	N.D.	N.D.	N.D.
A03938*	N.D.	N.D.	N.D.	2.11
A04130	N.D.	N.D.	N.D.	N.D.
A0 4620	N.D.	N.D.	N.D.	6.15
A03534	N.D.	N.D.	N.D.	N.D.
A04286 OUTSIDE	N.D.	N.D.	N.D.	N.D.
A04085 WET*	N.D.	N.D.	N.D.	N.D.
A04128	N.D.	N.D.	N.D.	0.90
A03700	N.D.	N.D.	N.D.	(0.58)
A03328	0.53	0.45	(0.11)	N.D.
A03722	N.D.	N.D.	N.D.	N.D.
A05534	N.D.	N.D.	N.D.	(0.73)
A04409	N.D.	N.D.	N.D.	N.D.
A04828	N.D.	N.D.	N.D.	N.D.
A04174	0.24	(0.19)	N.D.	2.28
A04448	N.D.	N.D.	N.D.	18.71
A03072	0.36	0.33	(0.07)	N.D.
A03428	N.D.	N.D.	(0.11)	0.48
A05090	N.D.	N.D.	N.D.	N.D.
A04197	N.D.	N.D.	N.D.	N.D.
A05120	0.41	0.37	(0.07)	(0.62)
A04069	0.22	0.28	(0.07)	N.D.

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SEQ 8507
TABLE 2—PAGE 2 OF 2
ug/sample

Field No.	Butoxypropanol ¹	Diisobutyl ketone ¹	Butyl cellosolve acetate ¹	Total aliphatics ²
A05428	0.24	0.53	N.D.	1.91
A04869	N.D.	N.D.	N.D.	(0.32)
A03798 OUTSIDE	N.D.	N.D.	N.D.	N.D.
A05008	0.25	0.24	(0.18)	N.D.
A04150	N.D.	N.D.	N.D.	1.63
A05487 OUTSIDE	N.D.	N.D.	N.D.	N.D.
A05054	N.D.	N.D.	N.D.	N.D.
A05635 BLANK	N.D.	N.D.	N.D.	N.D.
A04718	N.D.	N.D.	N.D.	9.63
A04801 BLANK	N.D.	N.D.	N.D.	N.D.
A05000	0.53	0.52	(0.09)	N.D.
A03645	0.58	0.54	(0.08)	N.D.
A04725	N.D.	N.D.	N.D.	1.36
A03679	0.55	0.70	(0.09)	N.D.
A0 3893	0.55	0.51	(0.07)	N.D.
A03181 BLANK	N.D.	N.D.	N.D.	N.D.
A03763	N.D.	N.D.	N.D.	N.D.
A05422 BLANK	N.D.	N.D.	N.D.	N.D.
A03026	0.88	0.84	(0.17)	N.D.
A04958	N.D.	N.D.	N.D.	0.95
A04202 BLANK	N.D.	N.D.	N.D.	N.D.
A05518 BLANK	N.D.	N.D.	N.D.	N.D.
A04378	0.71	0.47	(0.14)	16.47
A03231	N.D.	N.D.	N.D.	7.20
A03730	N.D.	N.D.	N.D.	8.80
A04575	N.D.	N.D.	N.D.	14.28
LOD	0.07	0.07	0.07	0.25
LOQ	0.22	0.22	0.22	0.83

*Sample contained high water background which may have affected results; values for compounds may be low
Values in parenthesis fall between the LOD and LOQ.

¹Reported values are estimates since butyl cellosolve was used for standards

²Reported values are estimates since Stoddard solvent was used for standards

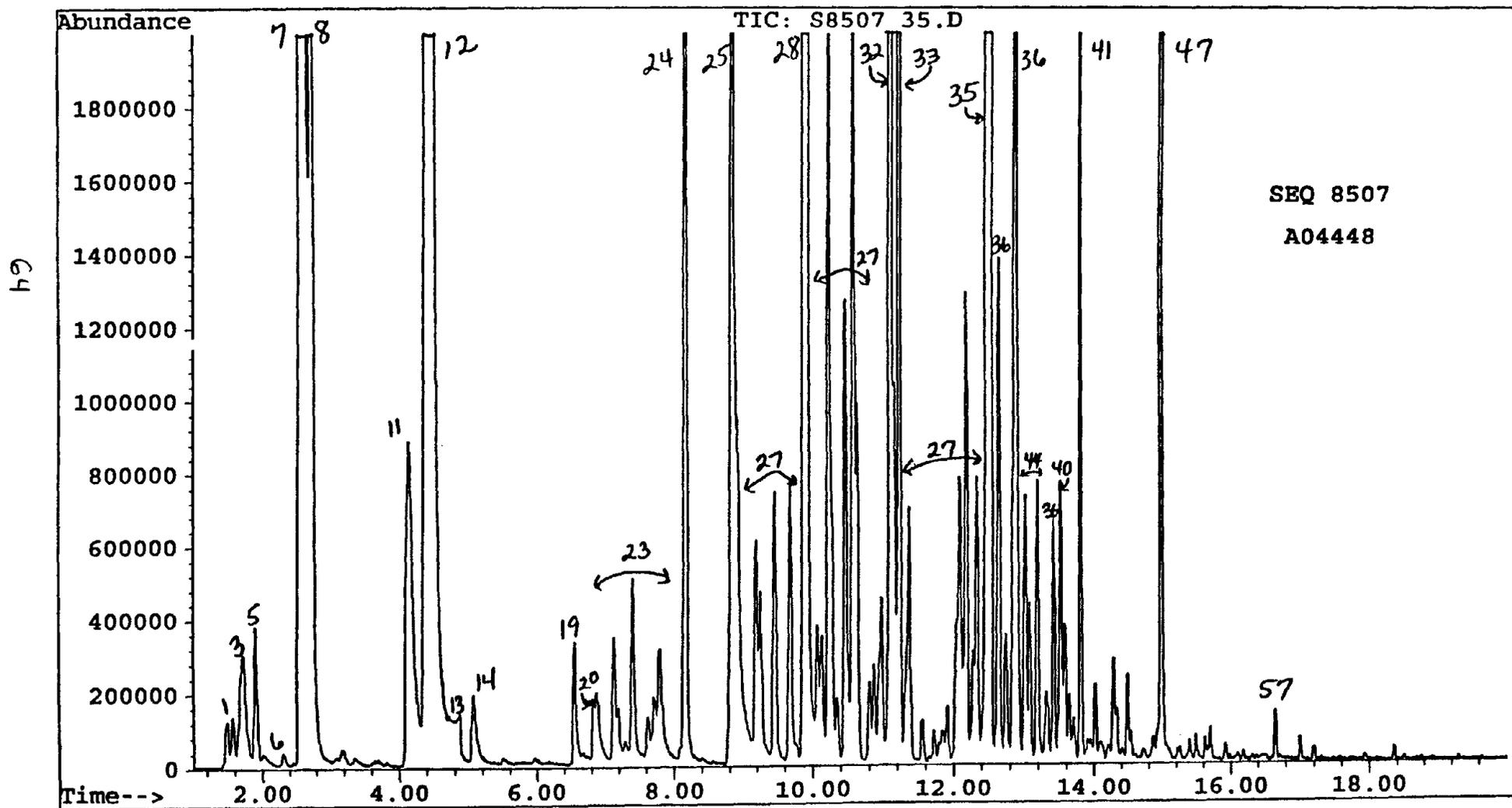
SEQ 8507
THERMAL DESORPTION TUBES
PEAK IDENTIFICATION

- | | |
|---|---|
| 1) Air*/CO ₂ * | 37) Methyl amyl ketone (MAK) |
| 2) Formaldehyde | 38) Styrene |
| 3) Propene/propane | 39) Cellosolve acetate* |
| 4) 1,1,2,2-Tetrafluoroethane | 40) Butyl cellosolve
(2-butoxyethanol) |
| 5) Methanol/acetaldehyde | 41) n-Nonane |
| 6) Ethanol | 42) 1-Butoxy-2-propanol |
| 7) Acetone | 43) Benzaldehyde |
| 8) Isopropanol | 44) C ₉ -C ₁₂ aliphatics |
| 9) Dichloroethylene isomer | 45) C ₉ H ₁₂ alkyl benzenes
(trimethyl-, propyl-,
methylethybenzenes, etc.) |
| 10) Methylene chloride | 46) Diisobutyl ketone
(2,6-dimethyl-4-heptanone) |
| 11) 2-Buten-one? | 47) Ethyl-3-ethoxy propionate |
| 12) Methyl ethyl ketone (MEK) | 48) Aliphatic ketone |
| 13) Acetic acid* | 49) Butanedioic acid, methyl
ester (dimethyl succinate) |
| 14) Ethyl acetate | 50) n-Decane |
| 15) 2-Methyl-1-propanol | 51) 2-Ethyl-1-hexanol |
| 16) Isopropyl acetate | 52) Acetophenone |
| 17) Formamide | 53) Limonene |
| 18) 1,1,1-Trichloroethane | 54) Terpene, C ₁₀ H ₁₆ |
| 19) Butanol | 55) Aliphatic aldehydes, C ₇ -C ₁₀ * |
| 20) 1-Methoxy-2-propanol
(Propylene glycol methyl
ether) | 56) n-Undecane |
| 21) Trichloroethylene | 57) Butyl cellosolve acetate
(butyl glycol acetate) |
| 22) Pentanal* | 58) Aliphatic acetates
(heptyl, decyl?) |
| 23) C ₇ H ₁₆ /C ₇ H ₁₄ aliphatics | 59) Decamethylcyclopenta-
siloxane* |
| 24) n-Heptane | 60) n-Dodecane |
| 25) Methylcyclohexane | 61) Pentanedioic acid,
dimethyl ester
(dimethyl glutarate) |
| 26) N,N-Dimethylformamide | 62) Benzoic acid |
| 27) C ₈ H ₁₈ /C ₈ H ₁₆ aliphatics | 63) Hexanedioic acid, dimethyl
ester (dimethyl adipate) |
| 28) Toluene | 64) n-Tridecane |
| 29) Isobutyl acetate | 65) Aliphatic esters? |
| 30) Hexanal* | |
| 31) 2-Propoxyethanol | |
| 32) n-Butyl acetate | |
| 33) n-Octane | |
| 34) Hexamethylcyclotri-
siloxane* | |
| 35) Propylene glycol mono-
methyl ether acetate | |
| 36) Xylenes/ethyl benzene | |

*Also present on some media/field blanks.

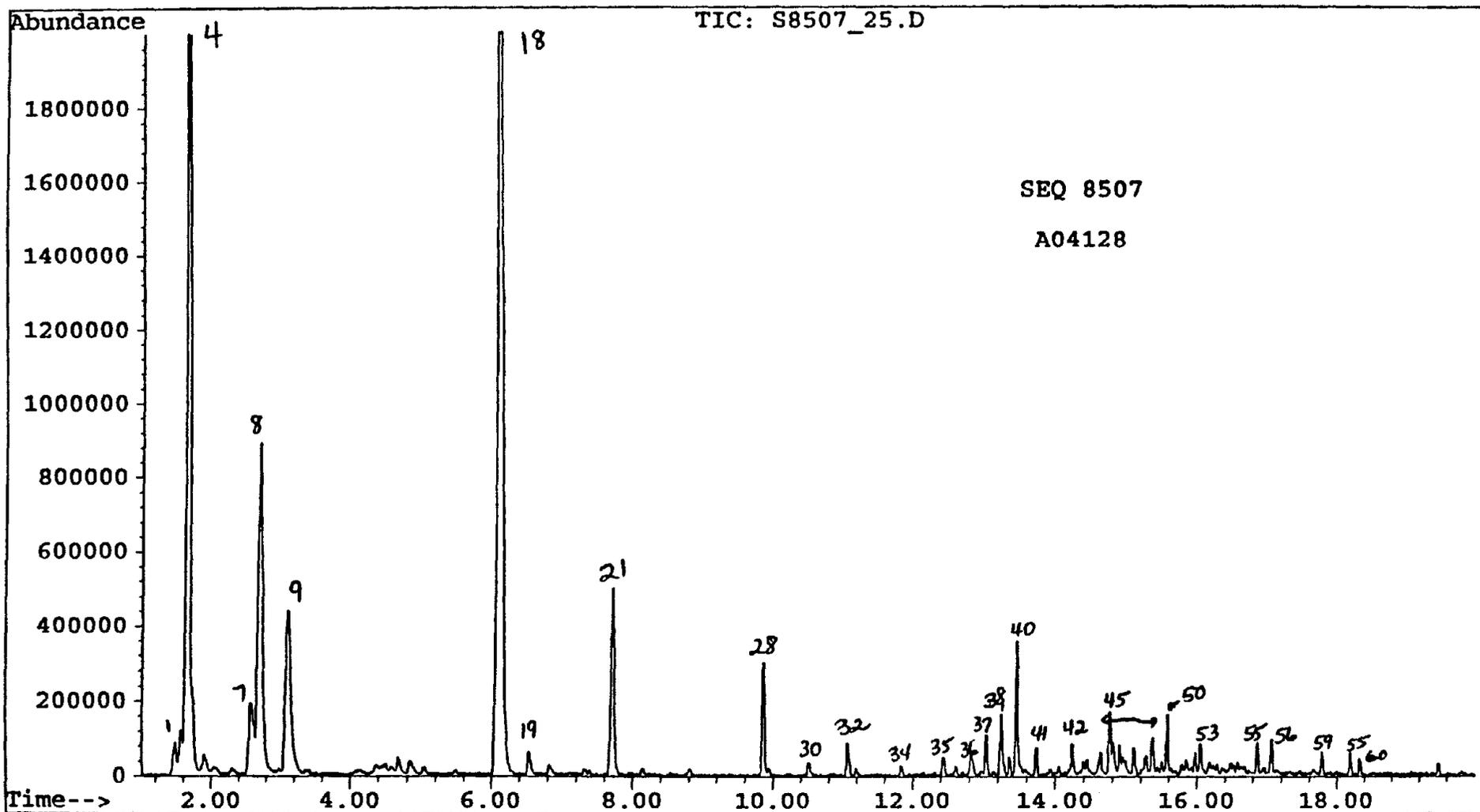
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Operator : AAG
Acquired : 20 Aug 96 8:45 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A04448 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 31

Touch-up Spray, day 3



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Operator : AAG
Acquired : 20 Aug 96 12:22 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A04128 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 21

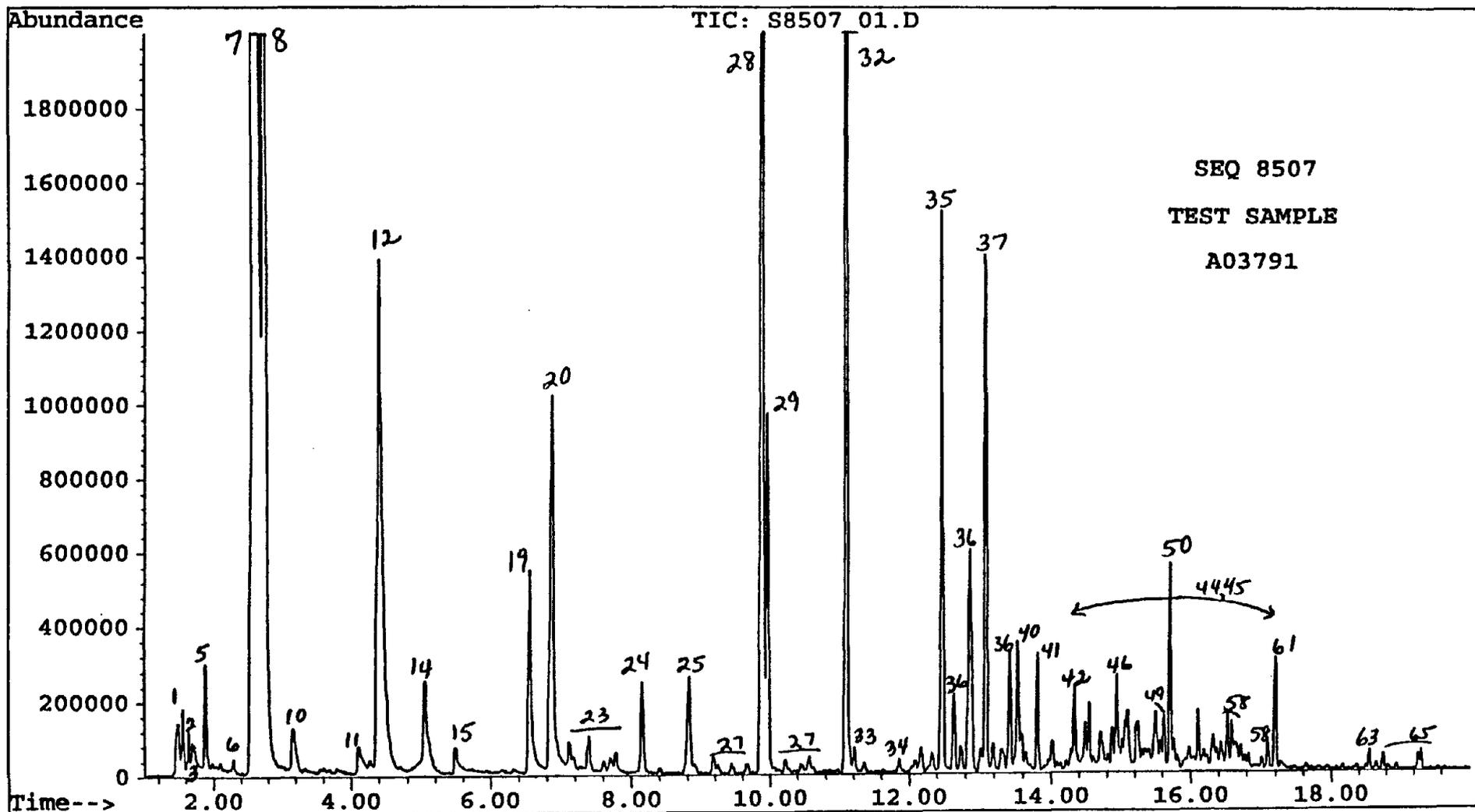
conf room, day 1



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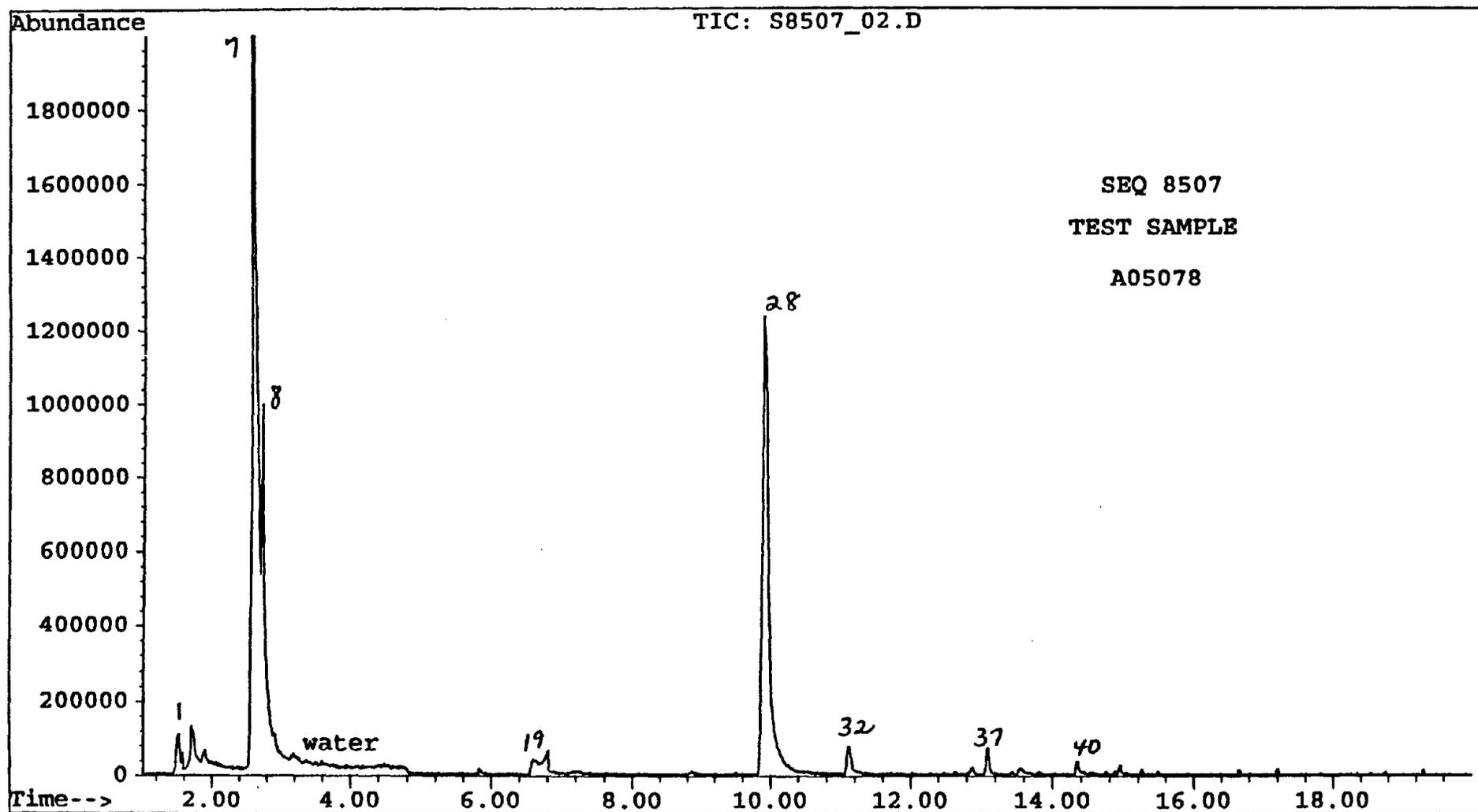
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Instrument : 5970 - In
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Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 1

north line , day 1
(duplicate)



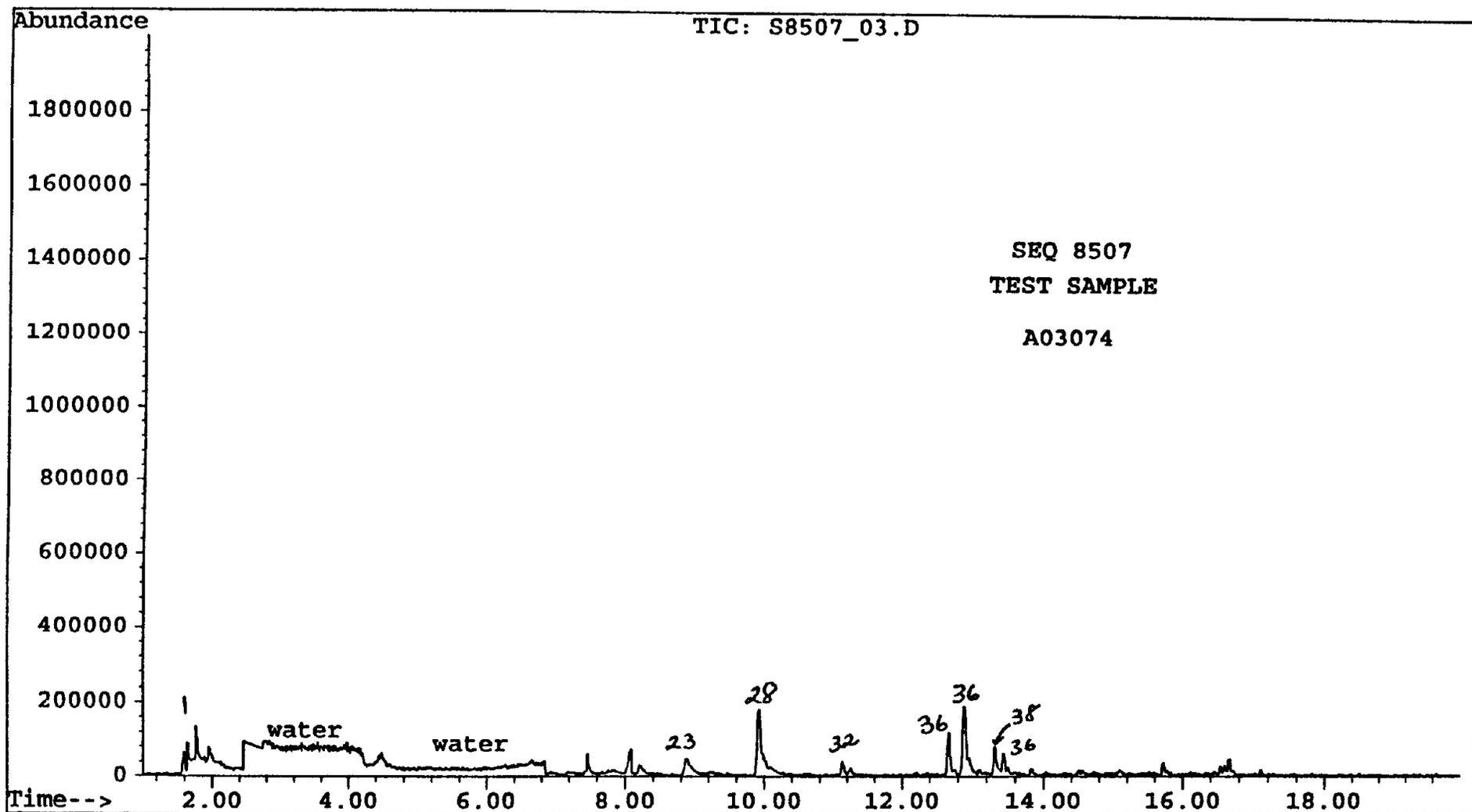
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Instrument : 5970 - In
Sample Name: SAMPLE A05078
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 2

clear line, day 1
(duplicate)



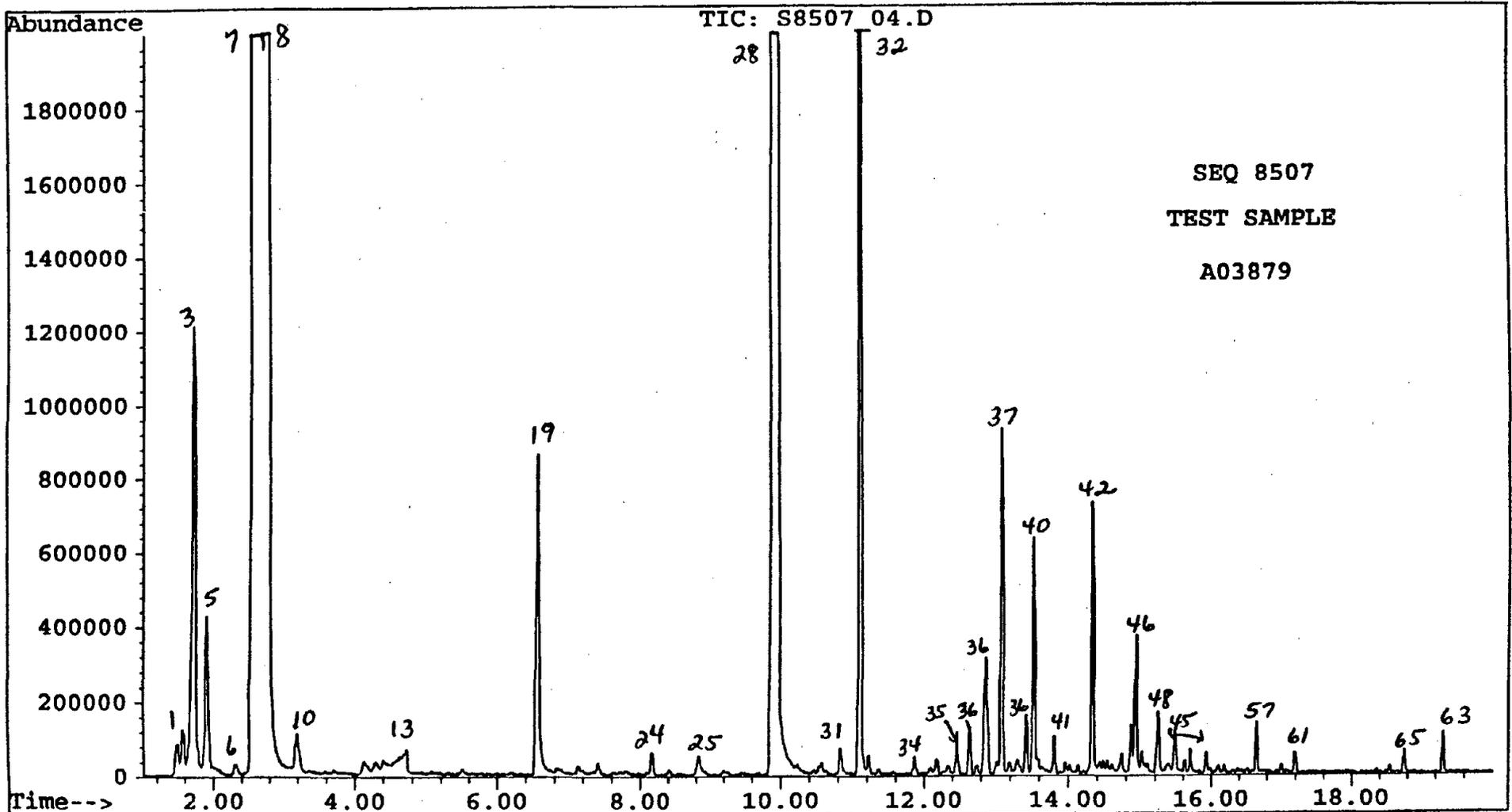
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Instrument : 5970 - In
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Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 4

east line, day 1
(duplicate)



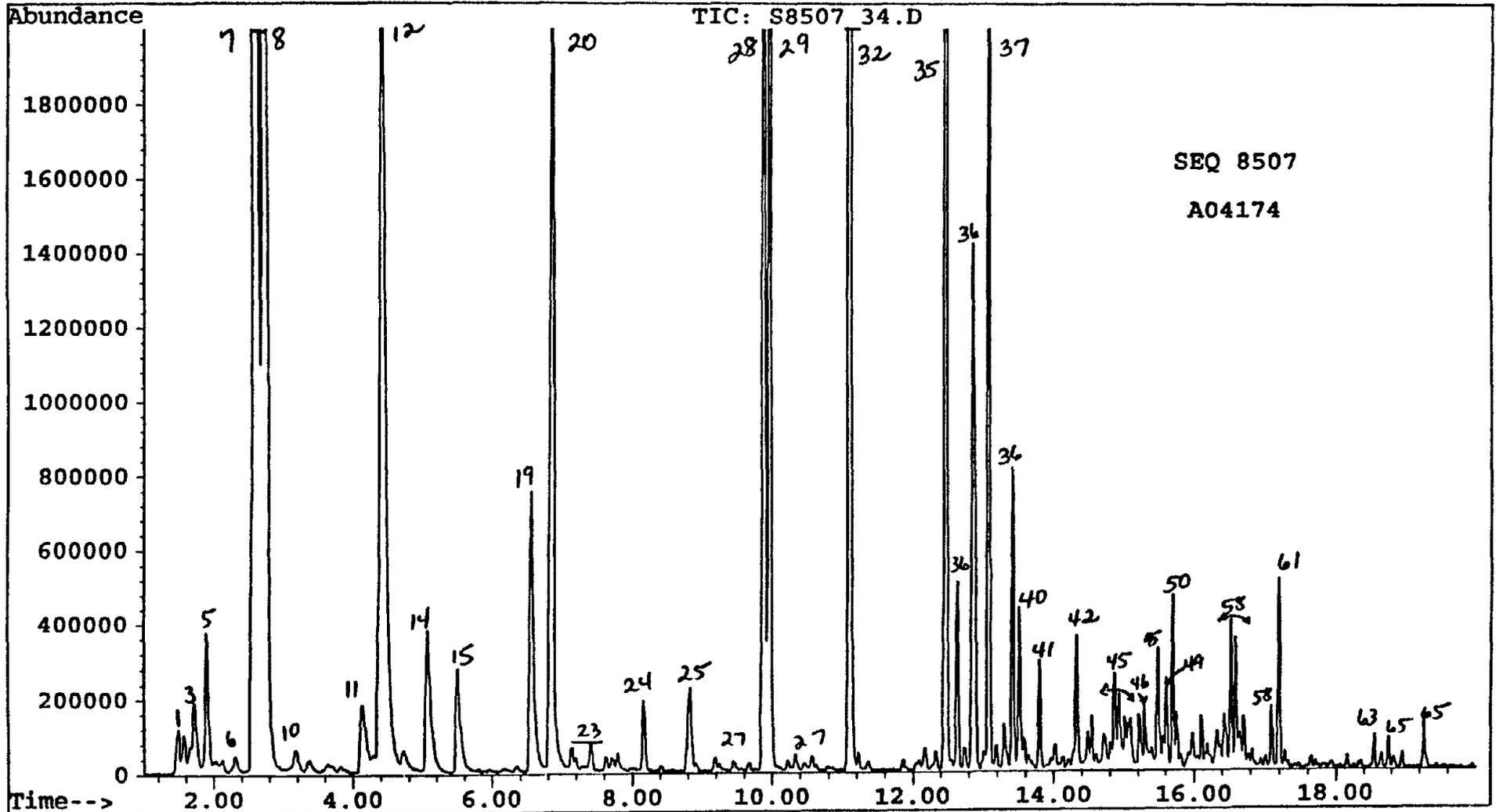
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Acquired : 15 Aug 96 3:18 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A03879 PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 5

pinstriping, day 1
(duplicate)



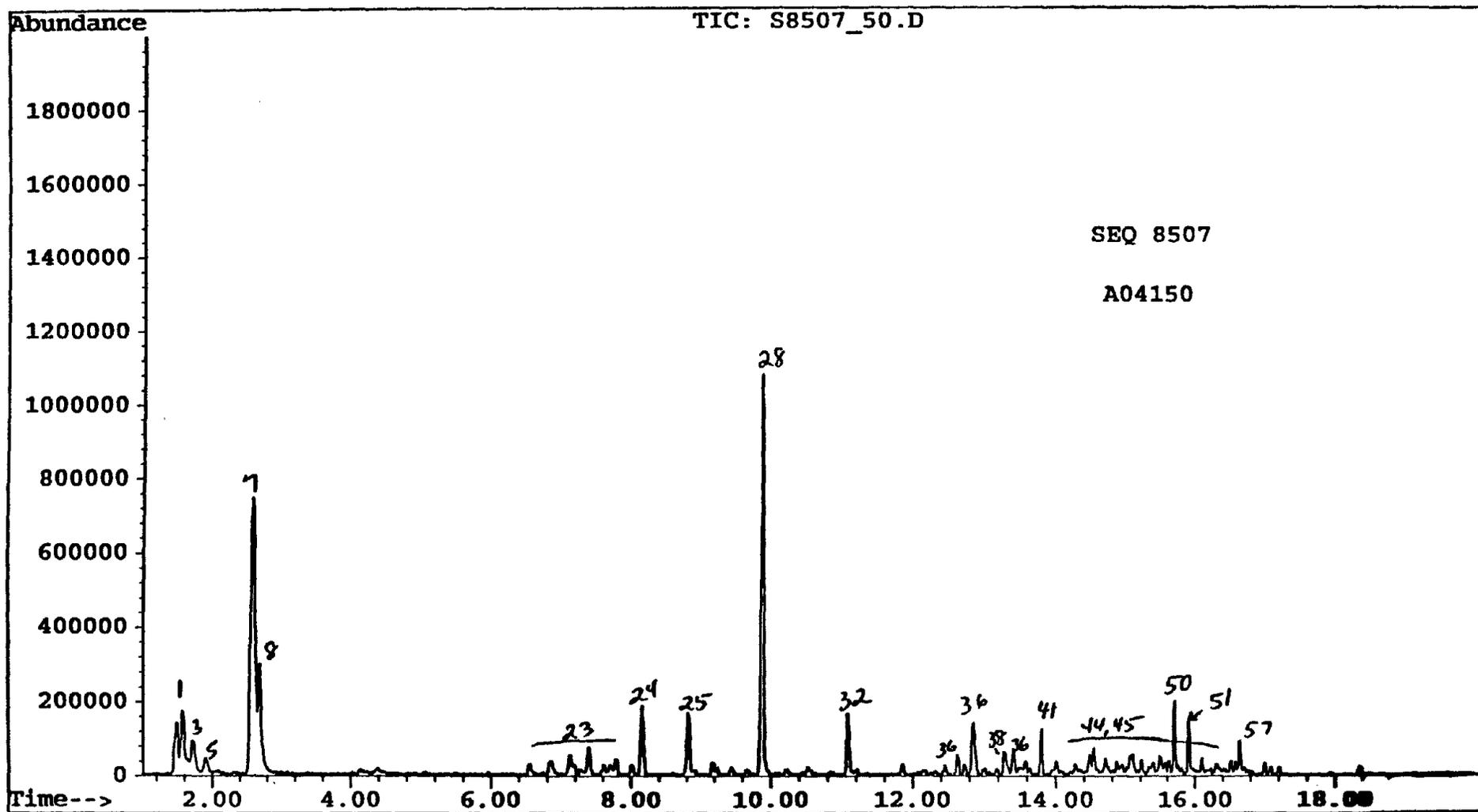
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Instrument : 5970 - In
Sample Name: SAMPLE A04174 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 30

north line, day 3



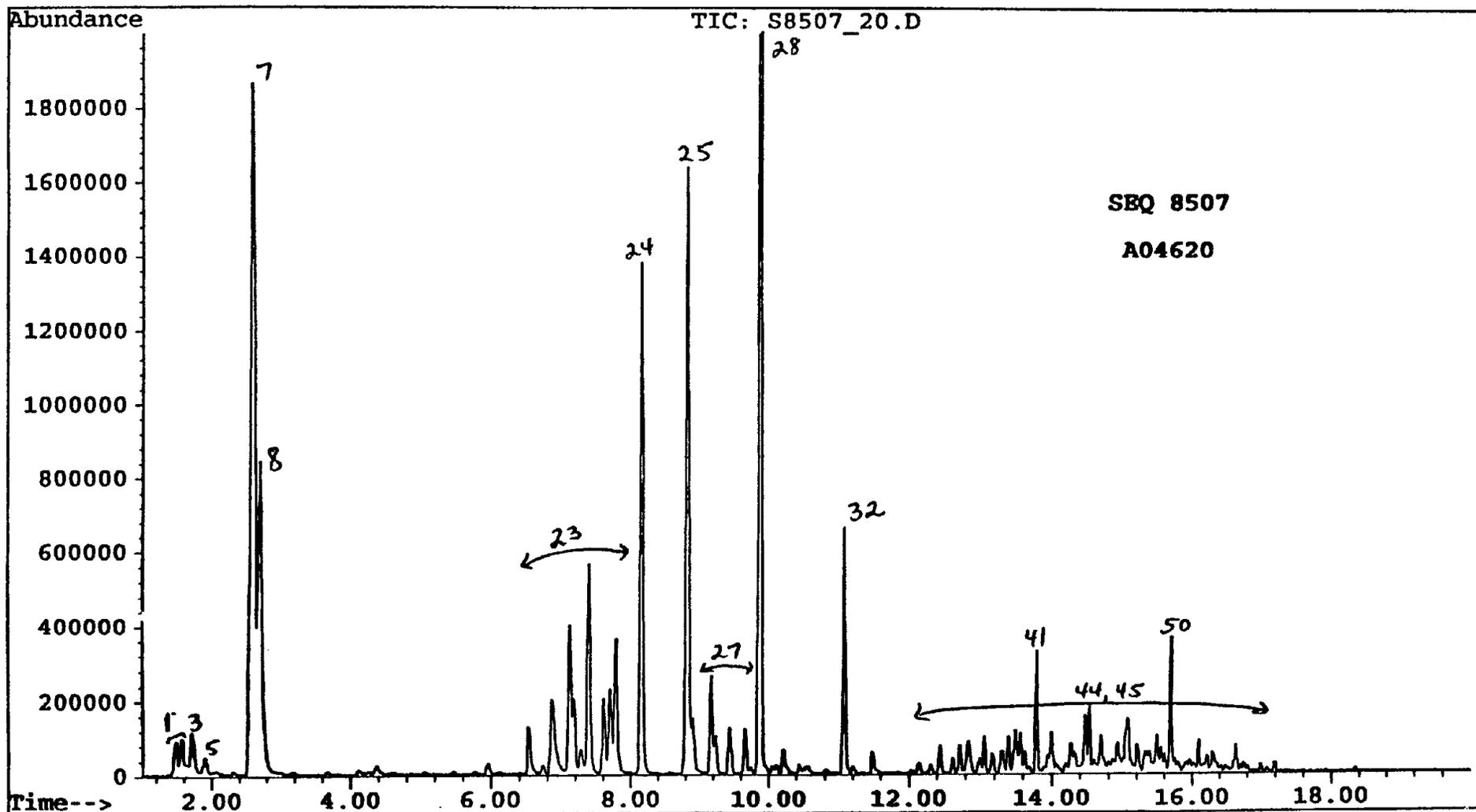
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Sample Name: SAMPLE A04150 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 46

east line pin-striping, day 2



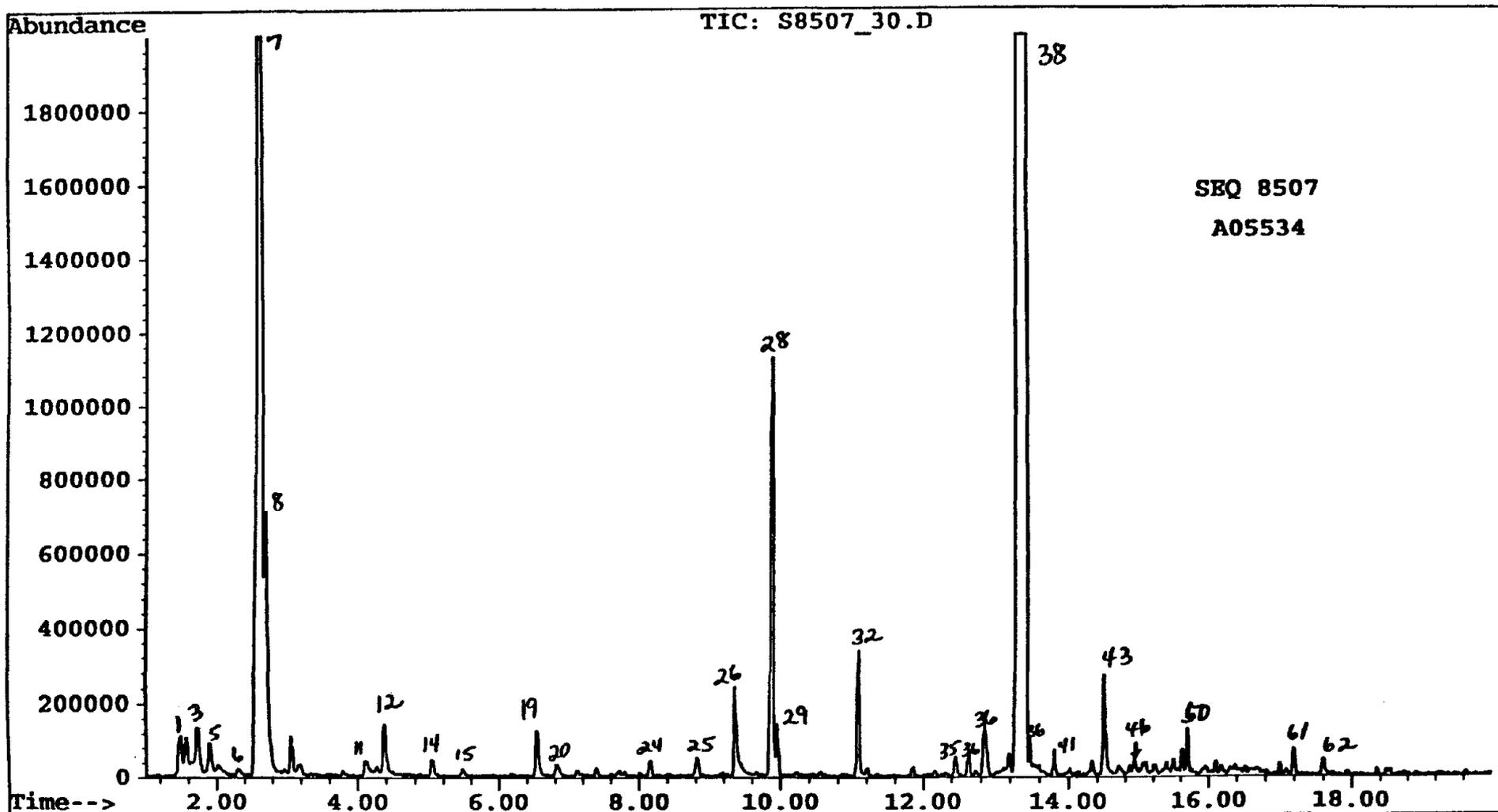
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Acquired : 20 Aug 96 8:02 am using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A0 4620
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 17

masking, day 3



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Acquired : 20 Aug 96 4:37 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A05534 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 26

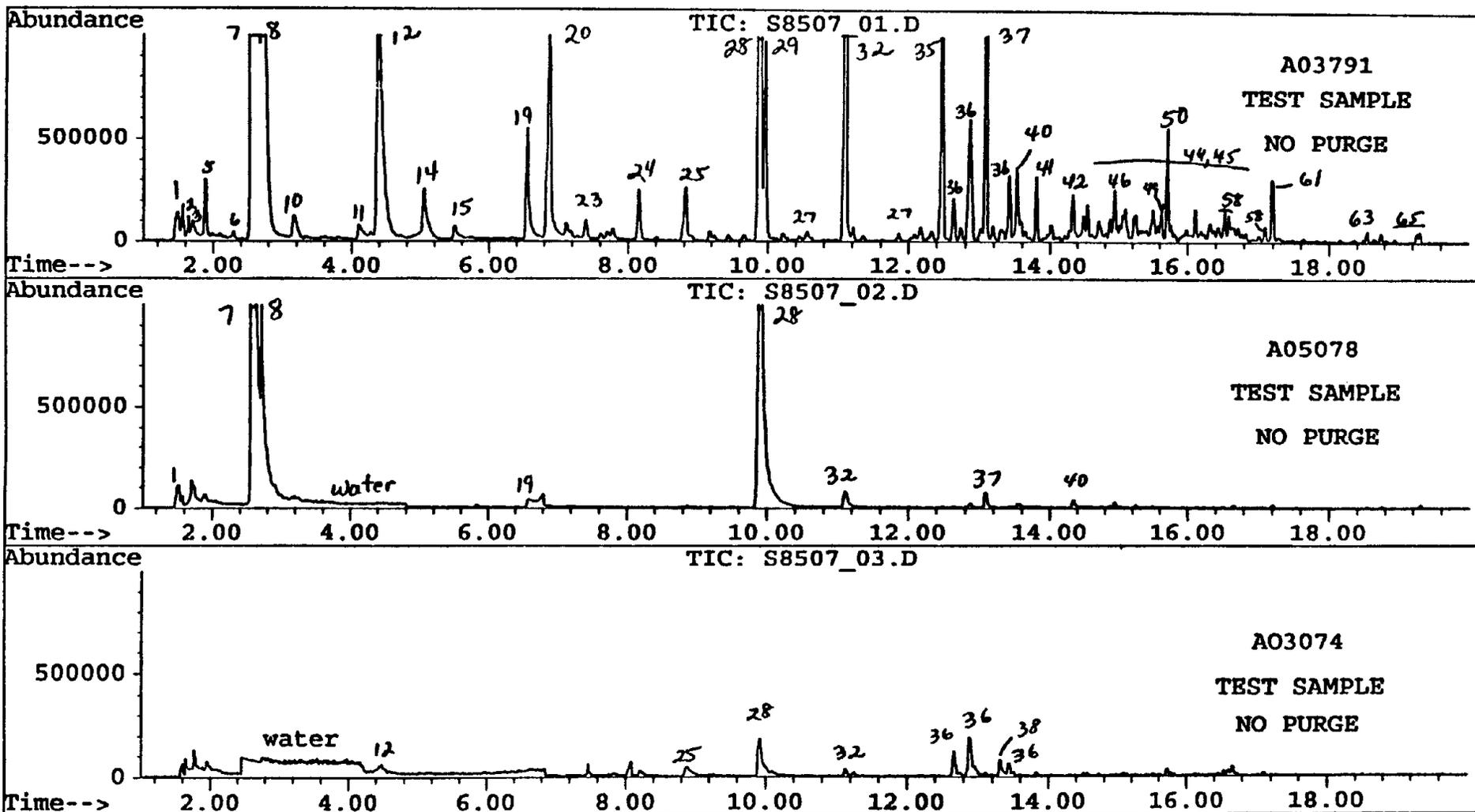
press, day 1



73

File : C:\HPCHEM\1\DATA\S8507\S8507_01.D
Operator : AAG
Acquired : 15 Aug 96 12:40 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A03791 NO PURGE
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 1

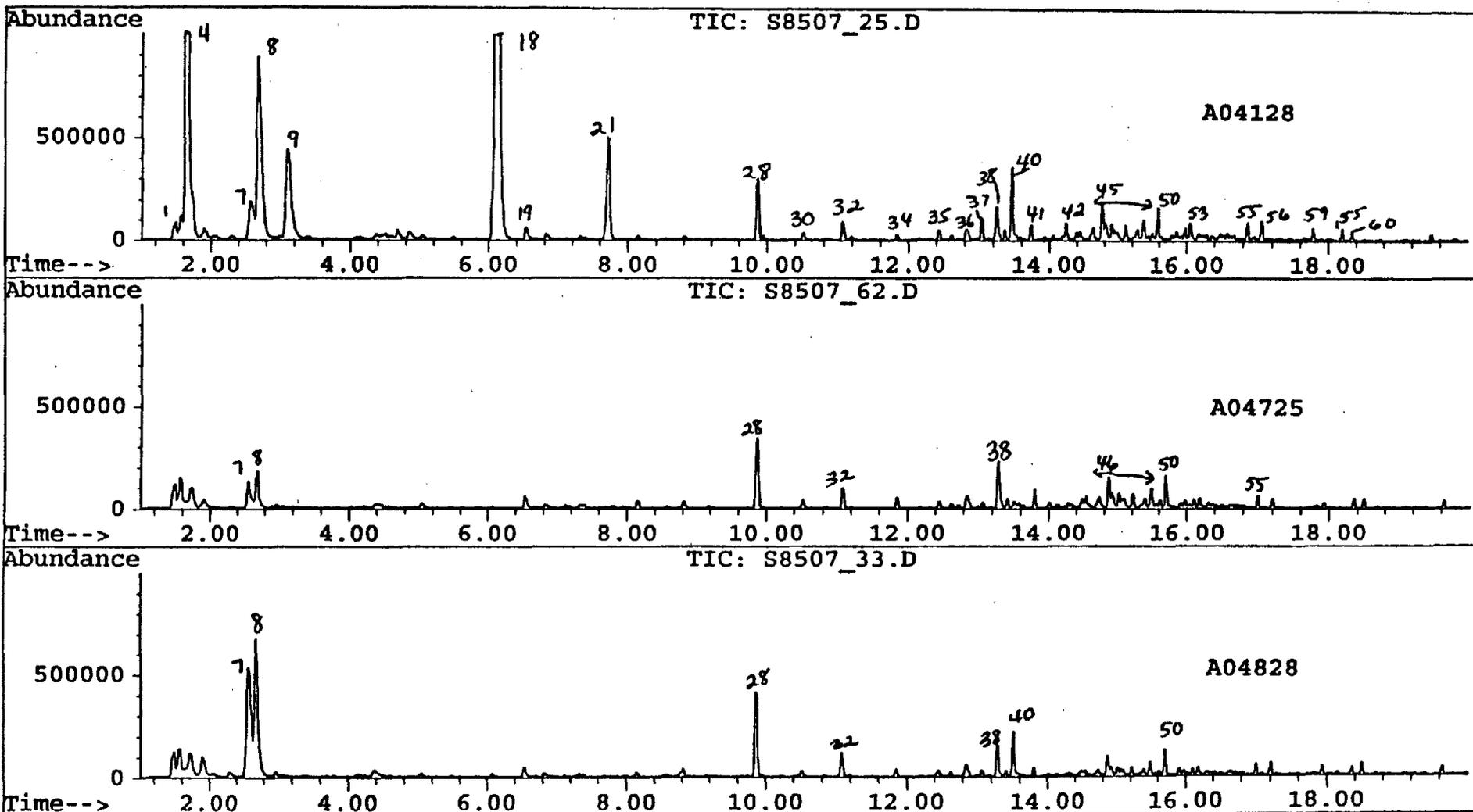
74



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Operator : AAG
Acquired : 20 Aug 96 7:06 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A04828 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 29

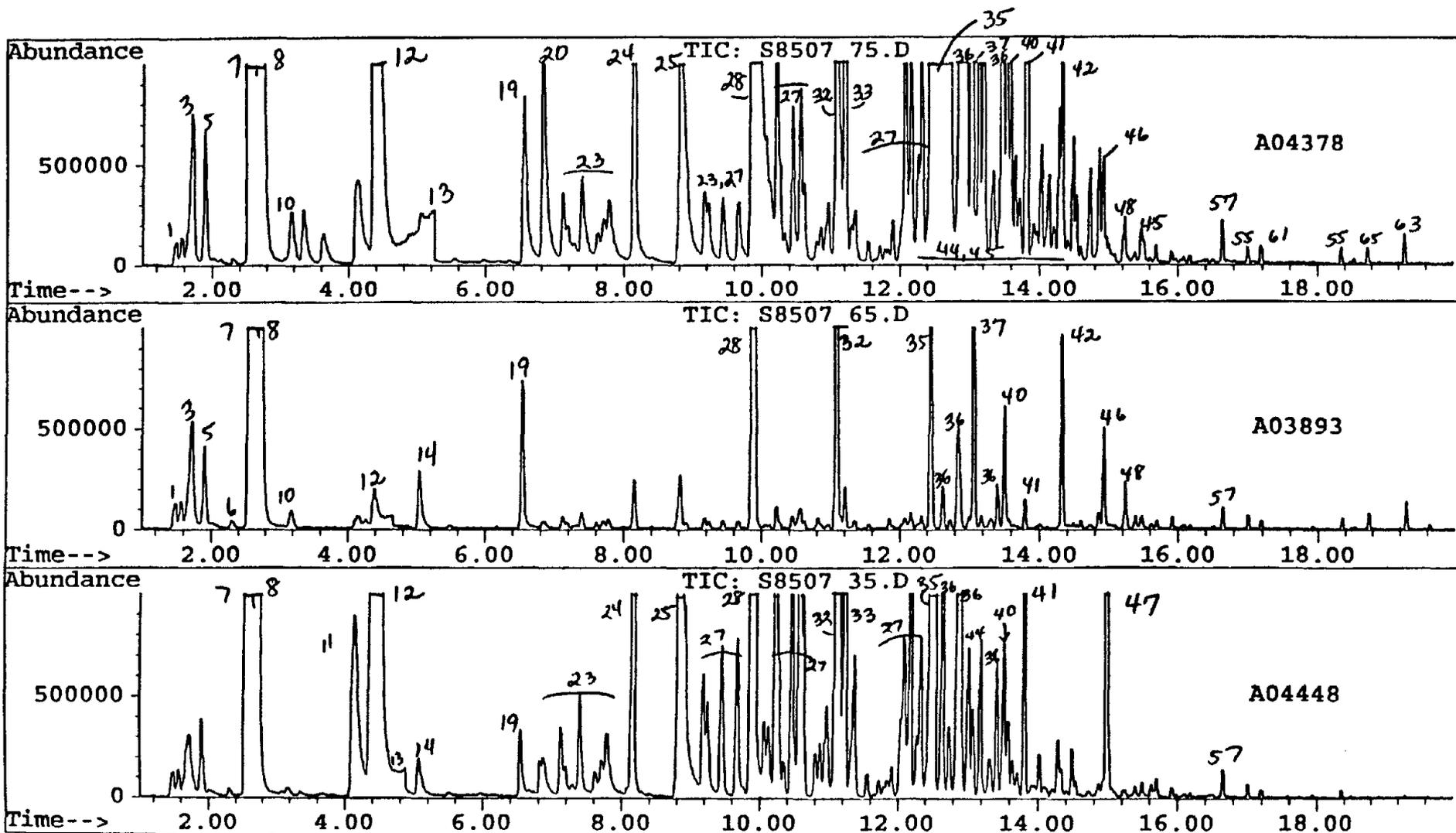
conference room

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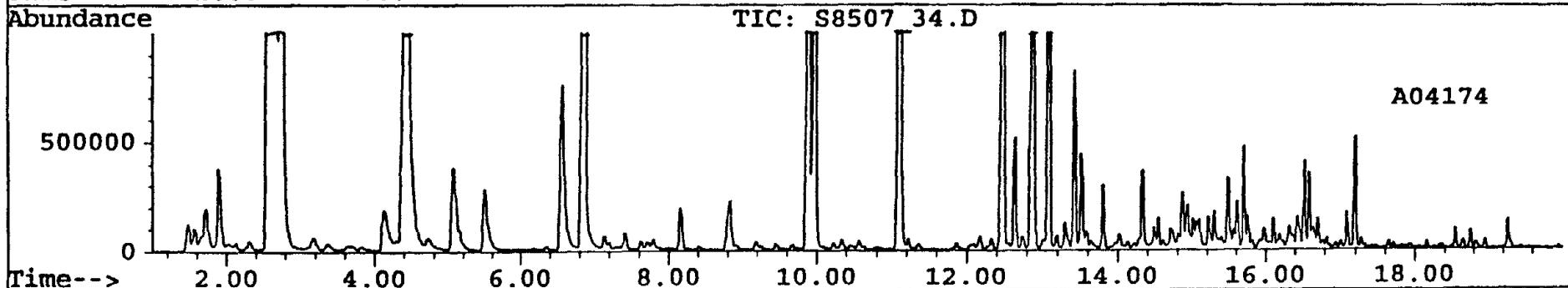
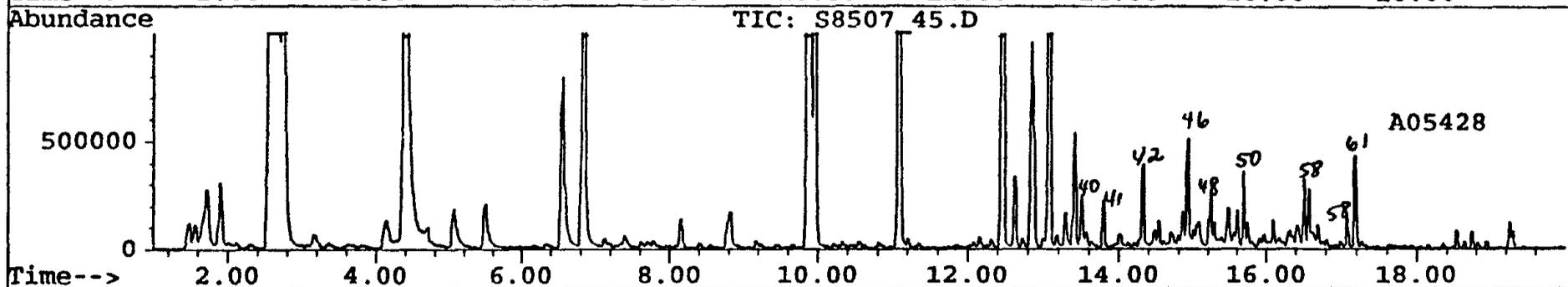
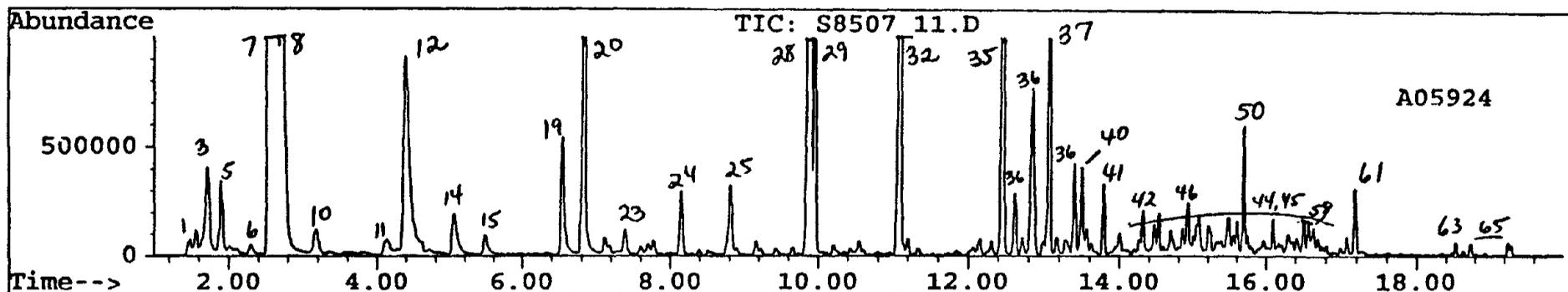
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Acquired : 22 Aug 96 5:56 am using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A04378 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 71

touch-up spray booth



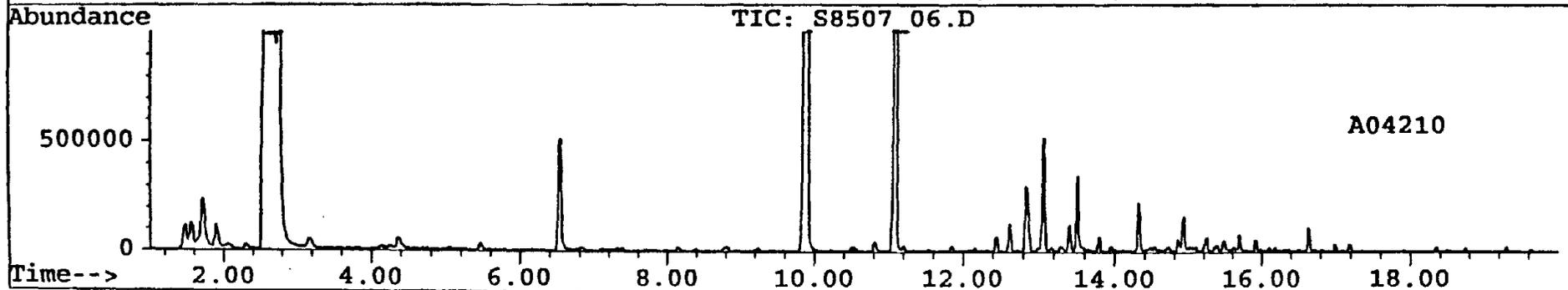
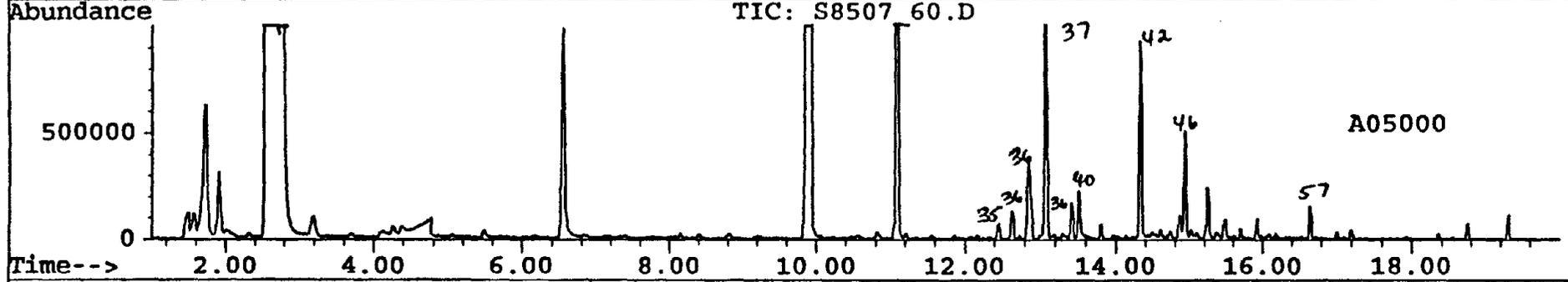
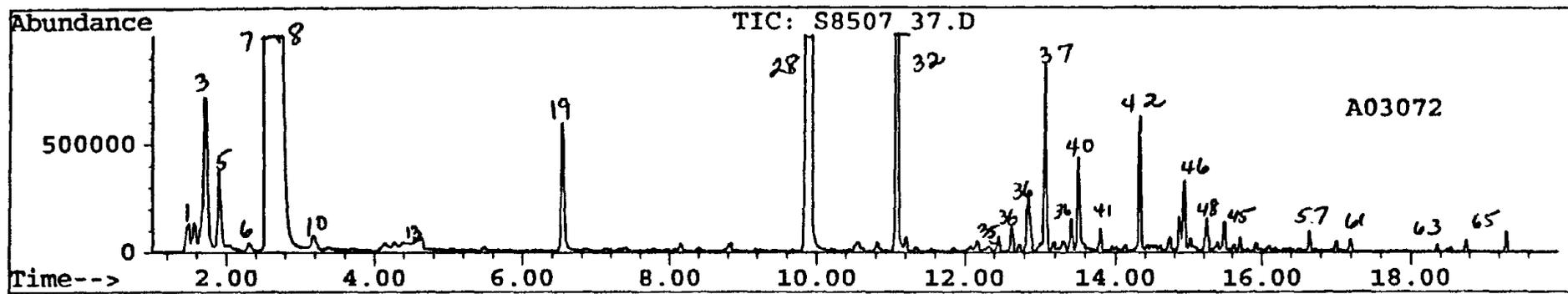
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Instrument : 5970 - In
Sample Name: SAMPLE A05924
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 7

north line



File : C:\HPCHEM\1\DATA\S8507\S8507_37.D
Operator : AAG
Acquired : 20 Aug 96 10:24 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A03072 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 33

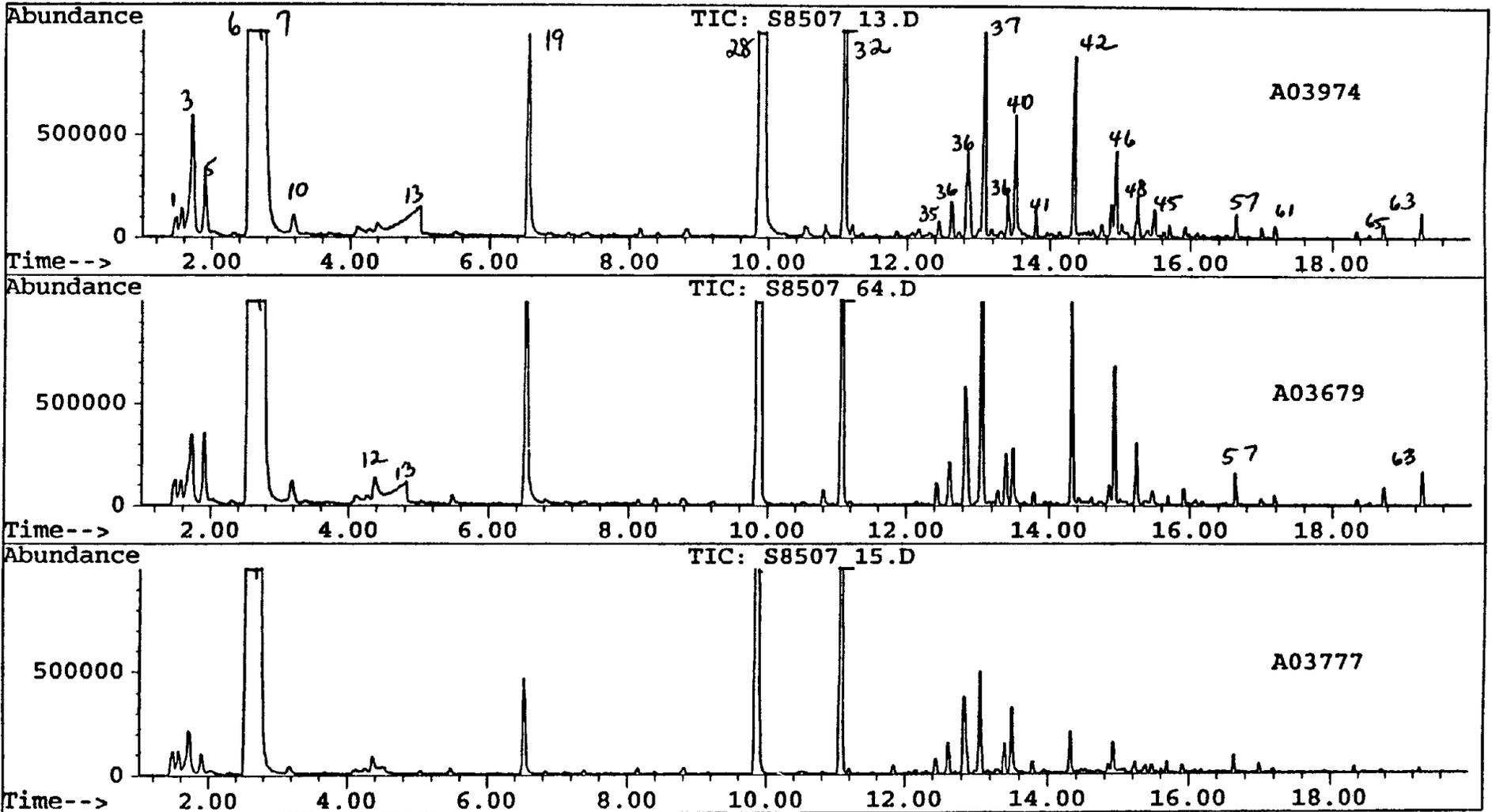
staging



69

File : C:\HPCHEM\1\DATA\S8507\S8507_13.D
Operator : AAG
Acquired : 19 Aug 96 9:44 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A03974
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 9

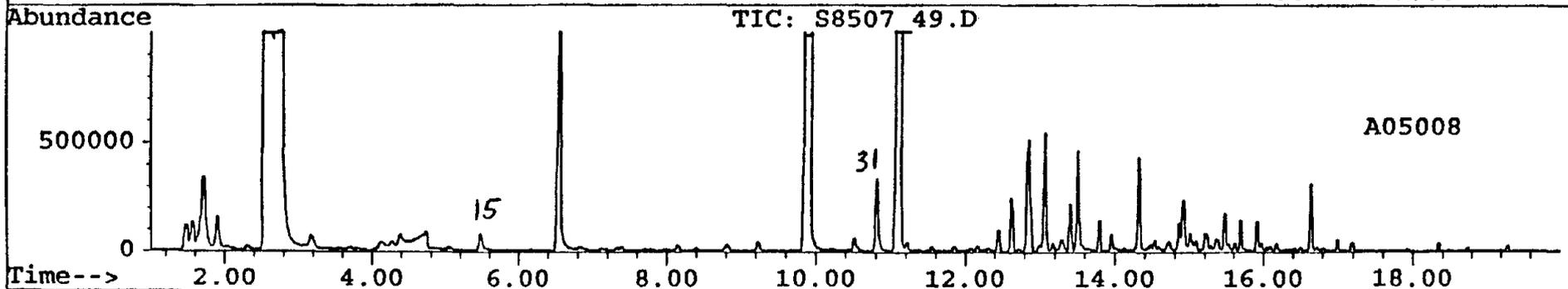
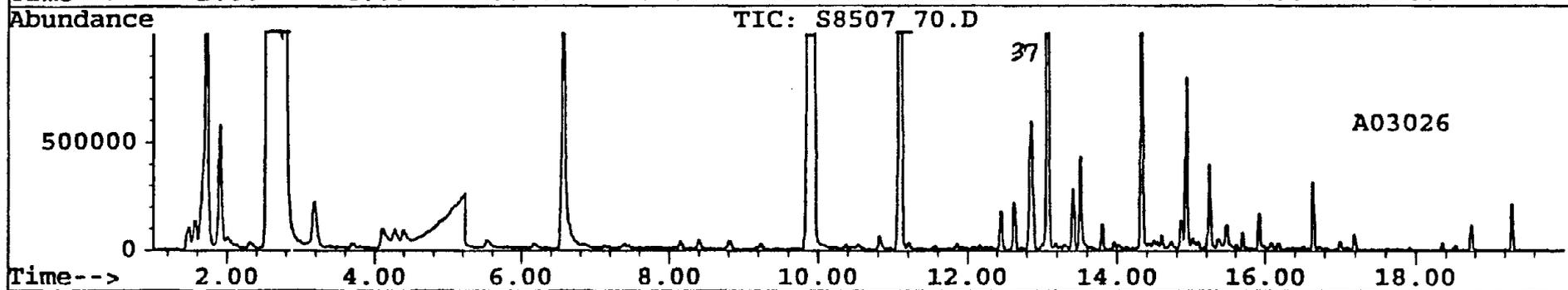
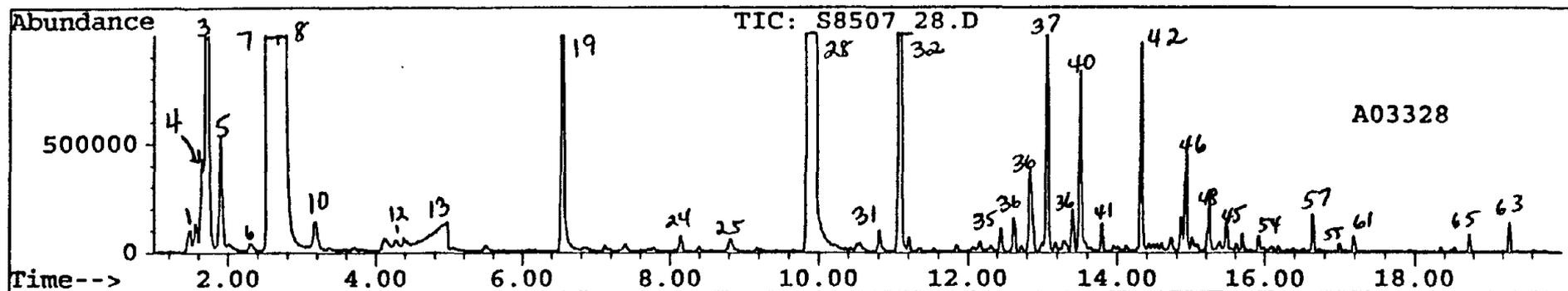
clear line



08

File : C:\HPCHEM\1\DATA\S8507\S8507_28.D
Operator : AAG
Acquired : 20 Aug 96 2:51 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A03328 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 24

pin-stripping

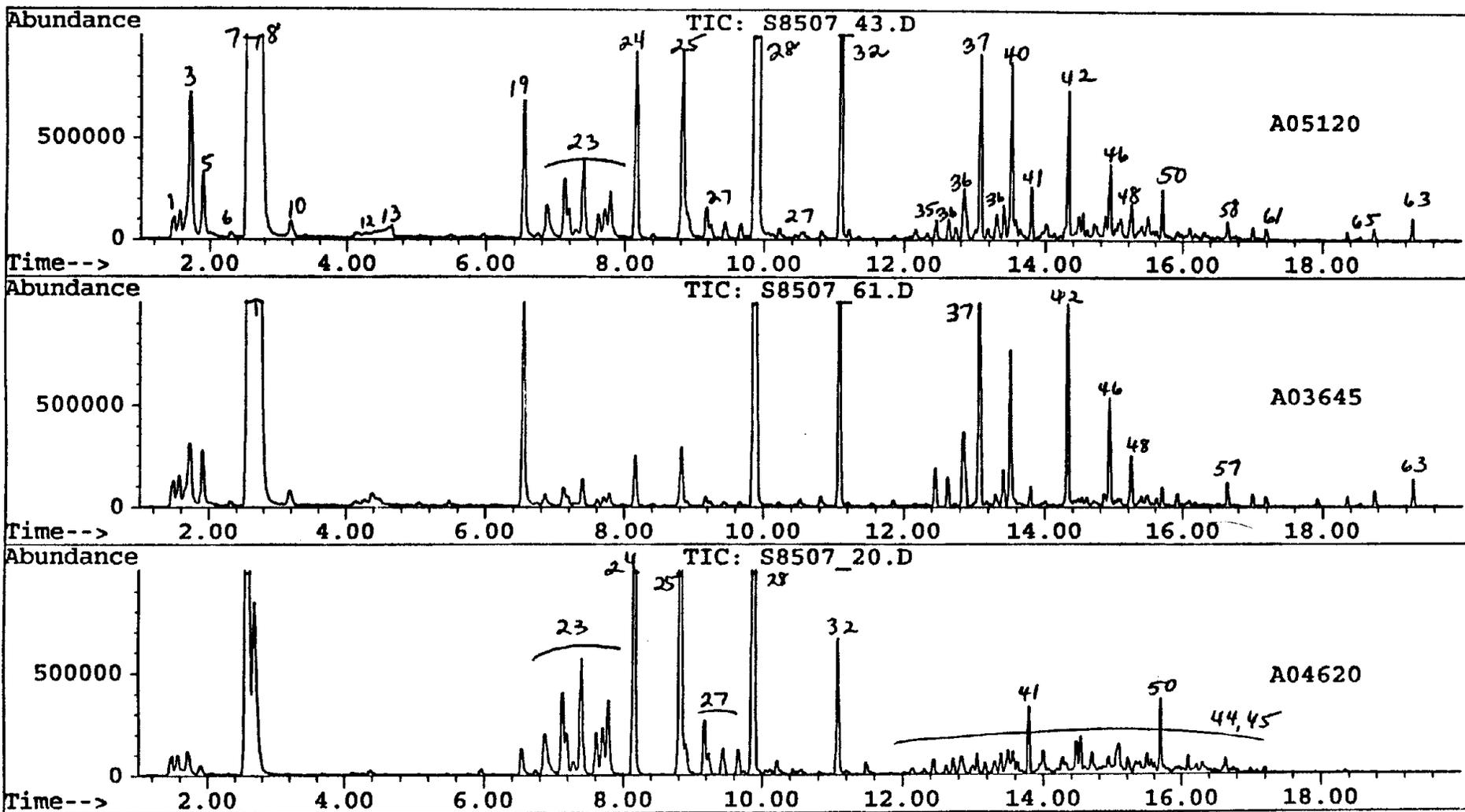


18

File : C:\HPCHEM\1\DATA\S8507\S8507_43.D
Operator : AAG
Acquired : 21 Aug 96 3:21 am using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A05120 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 39

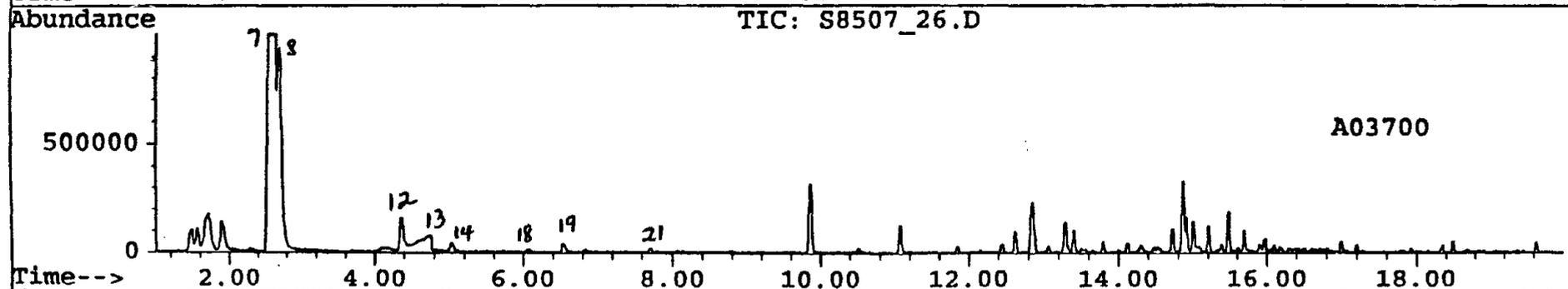
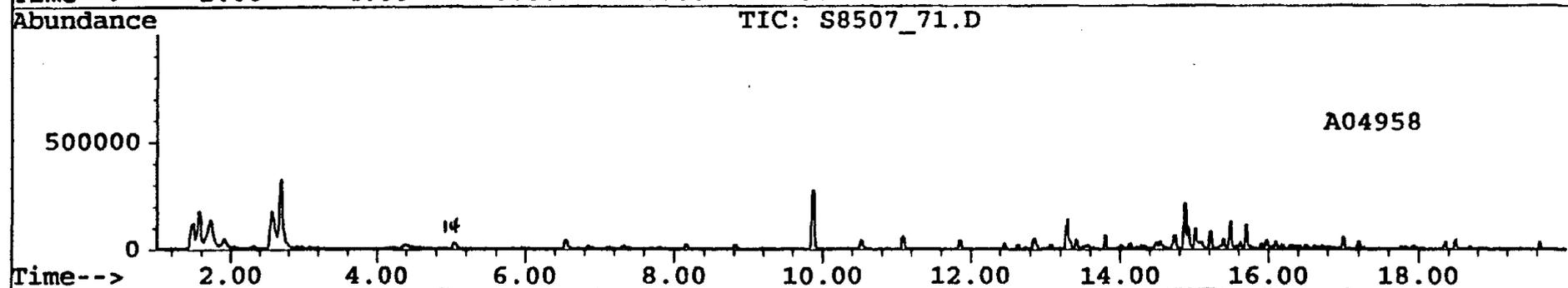
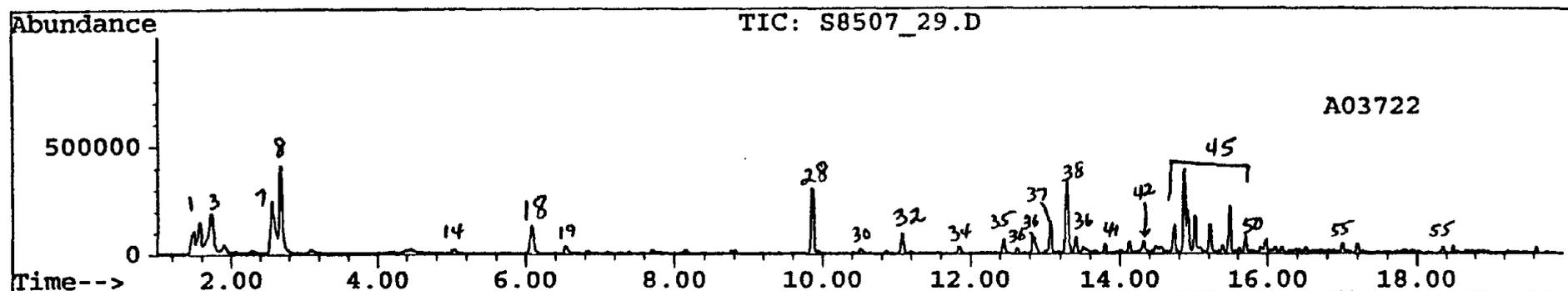
Masking

88



File : C:\HPCHEM\1\DATA\S8507\S8507_29.D
Operator : AAG
Acquired : 20 Aug 96 3:47 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A03722 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 25

Assembly

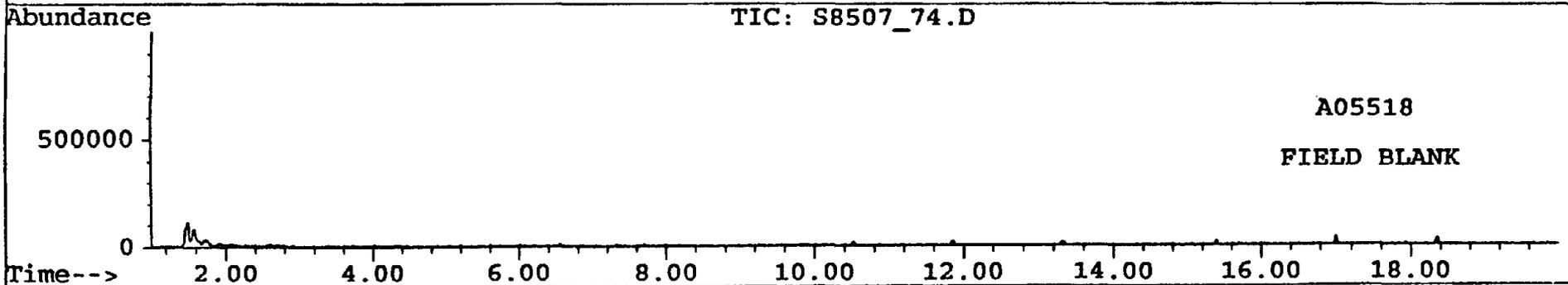
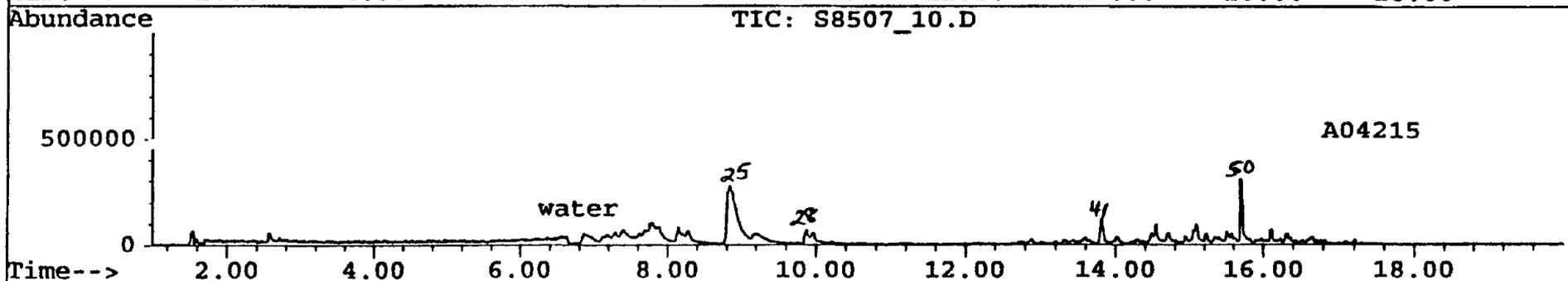
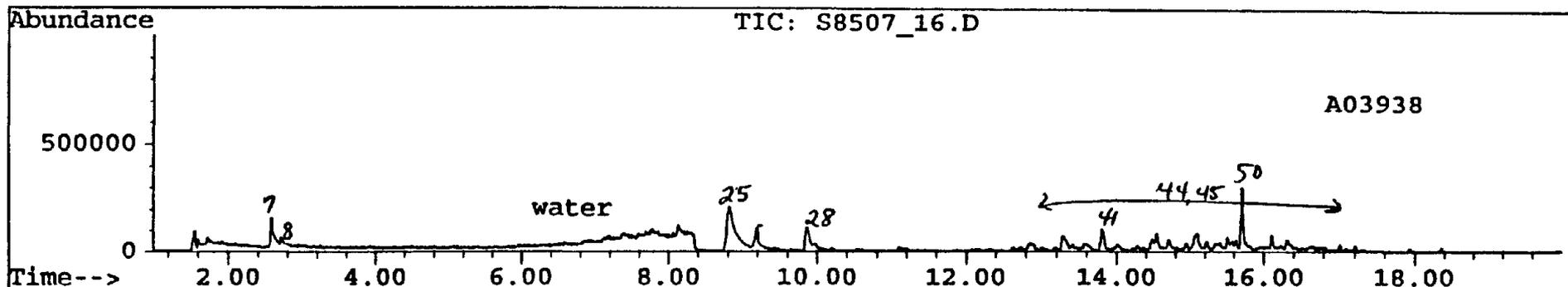


83

File : C:\HPCHEM\1\DATA\S8507\S8507_16.D
Operator : AAG
Acquired : 20 Aug 96 12:12 am using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A03938
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 12

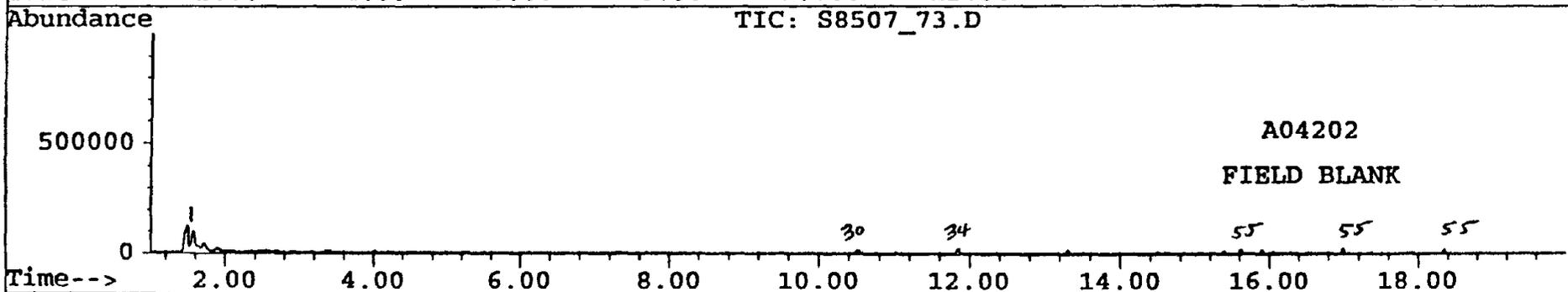
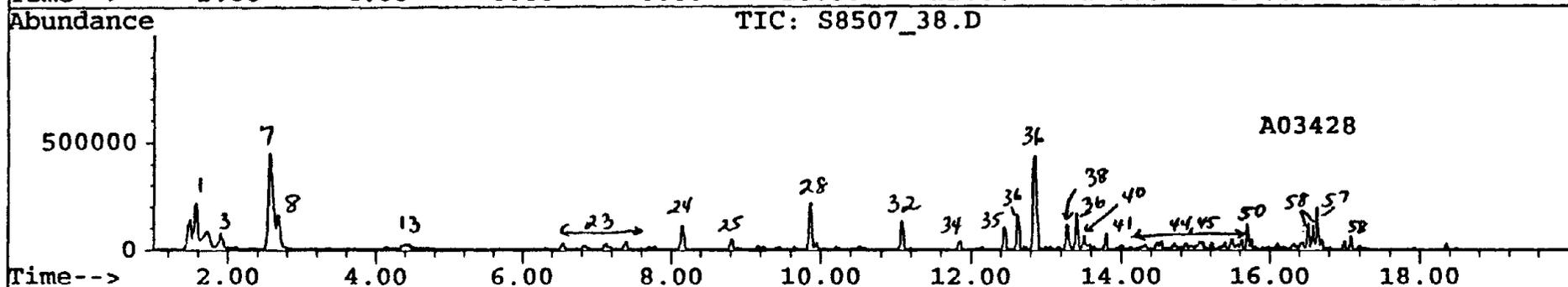
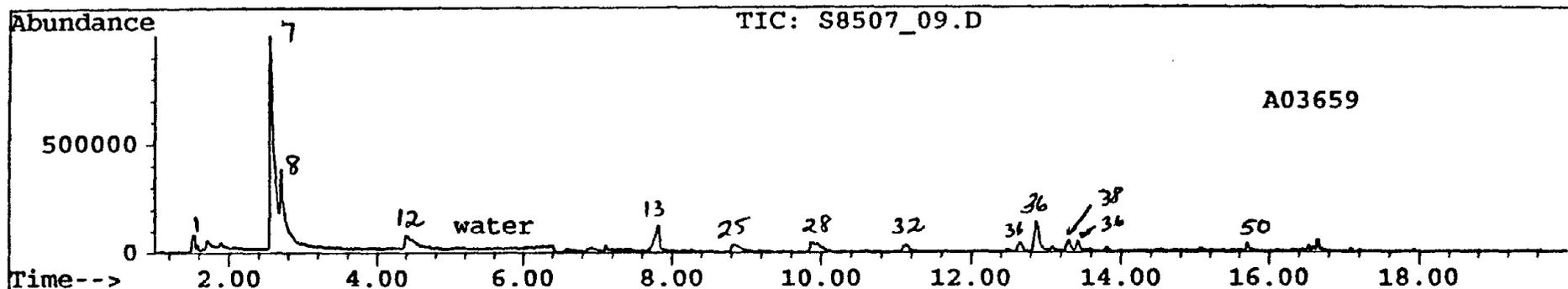
east line, before booth

78



File : C:\HPCHEM\1\DATA\S8507\S8507_09.D
Operator : AAG
Acquired : 19 Aug 96 6:26 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A03659
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 5

east line, at booth

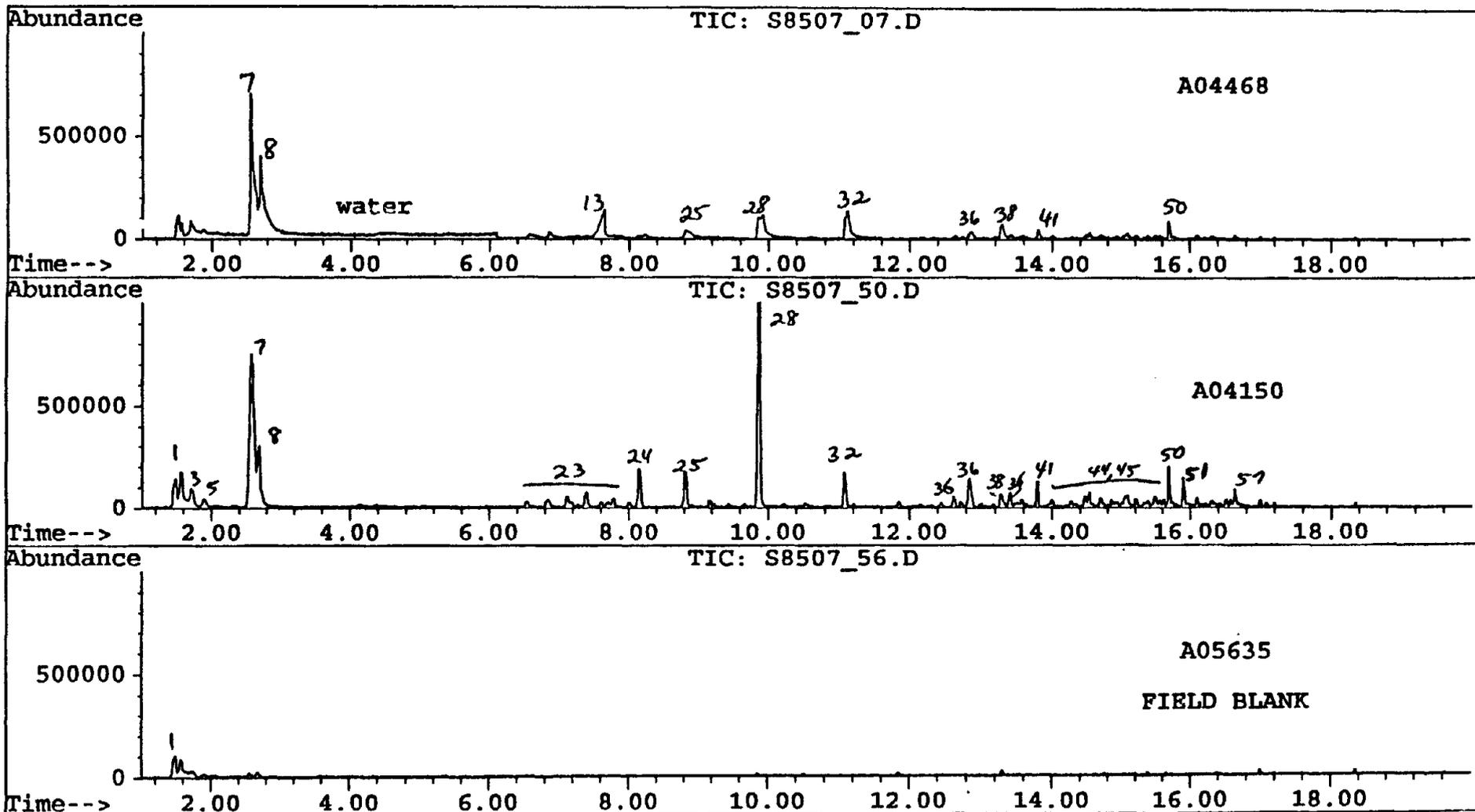


85

File : C:\HPCHEM\1\DATA\S8507\S8507_07.D
Operator : AAG
Acquired : 19 Aug 96 4:46 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A04468
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 3

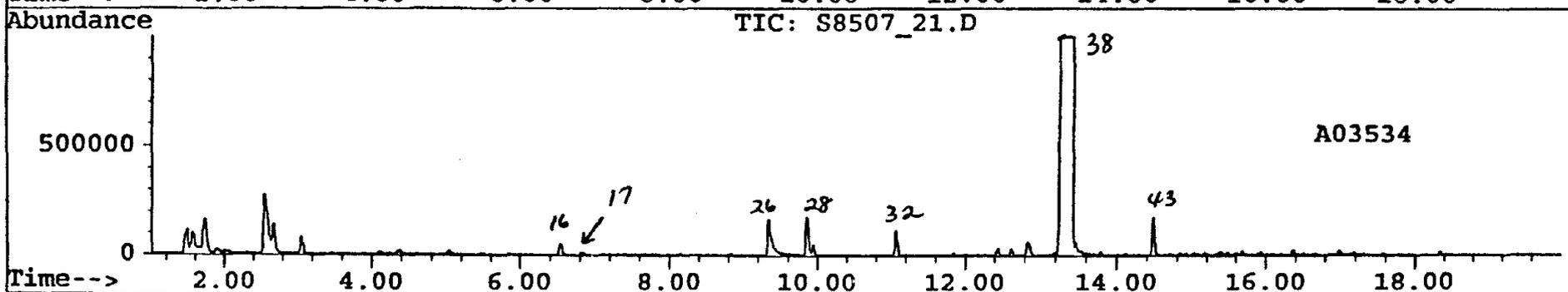
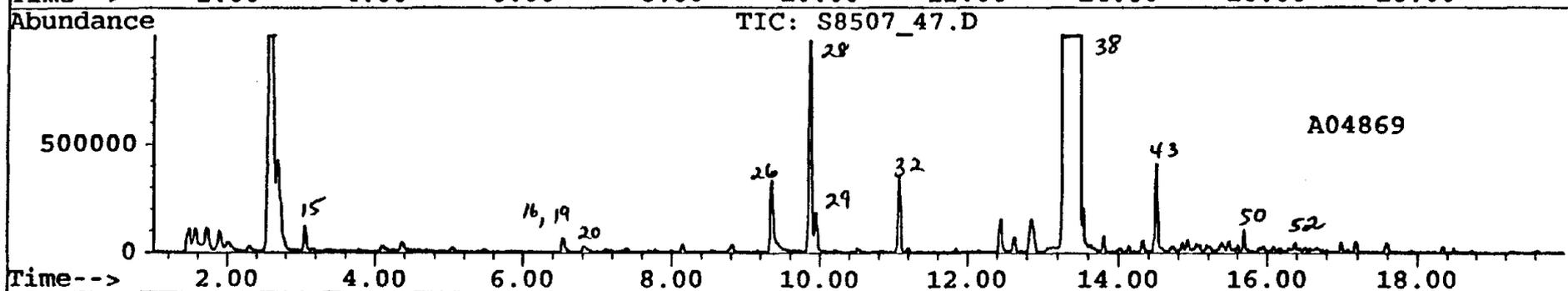
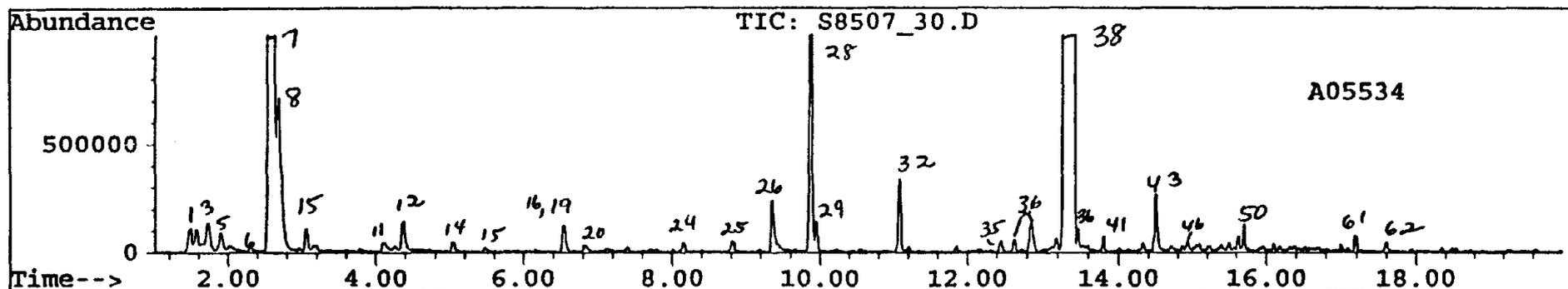
east line pin-striping

98



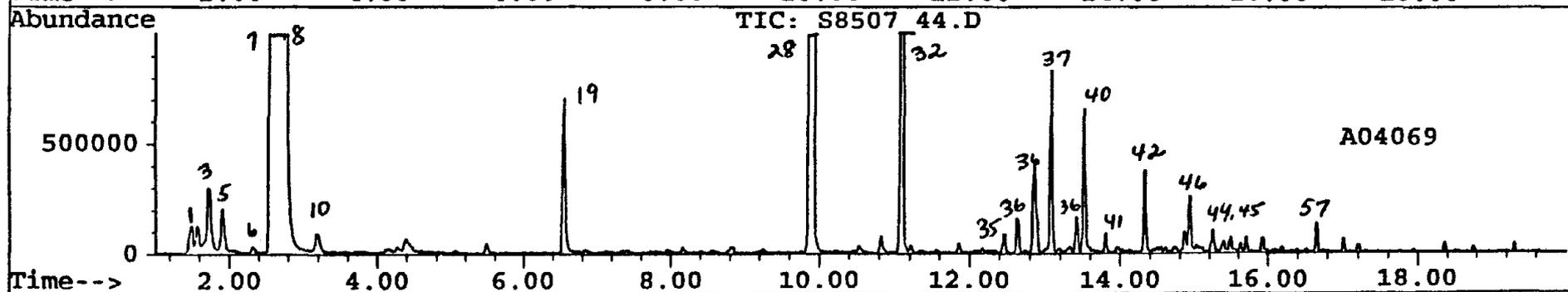
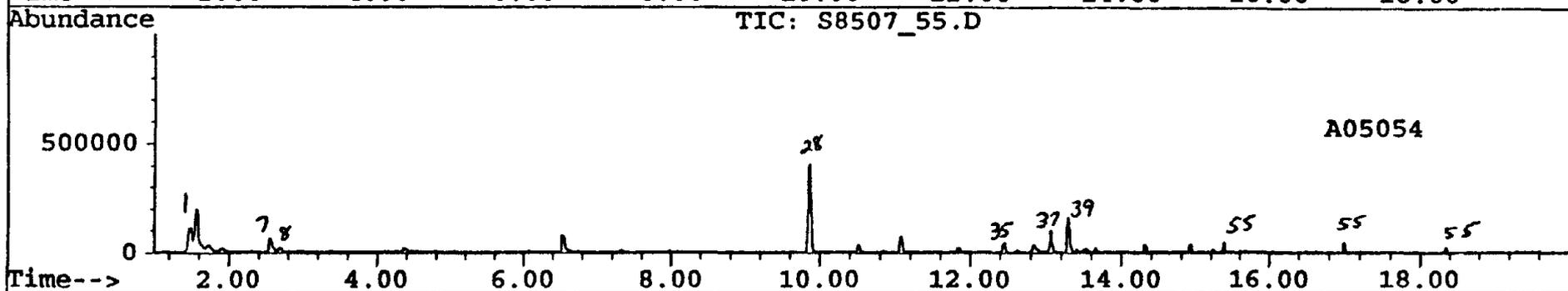
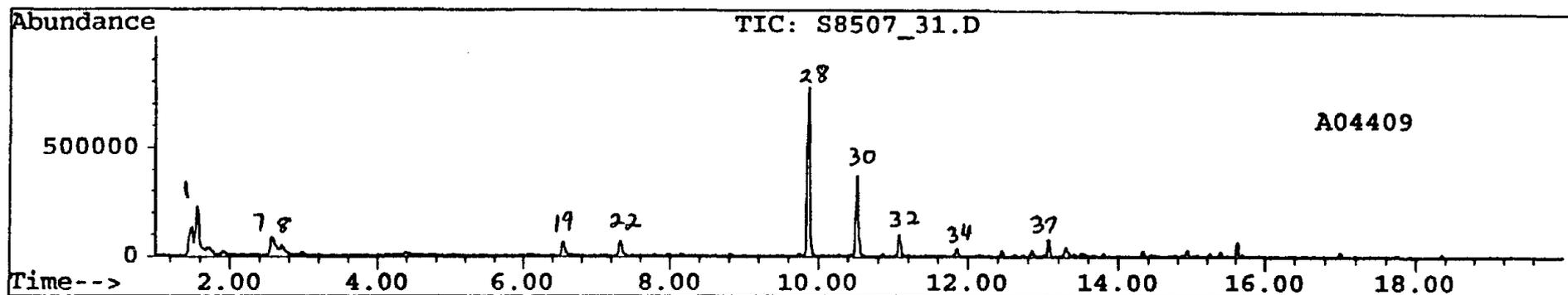
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Operator : AAG
Acquired : 20 Aug 96 4:37 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A05534 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 26

press area



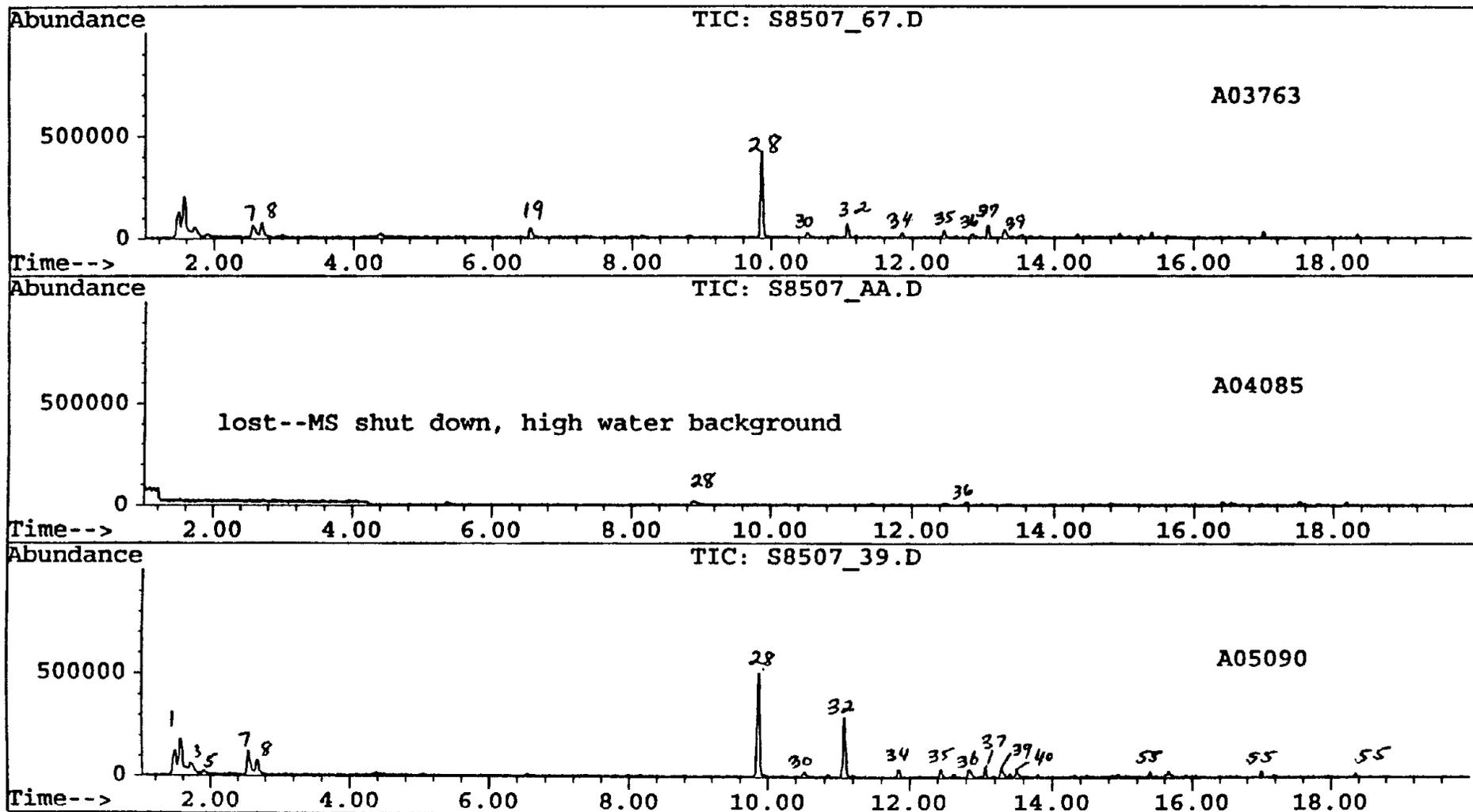
File : C:\HPCHEM\1\DATA\S8507\S8507_31.D
Operator : AAG
Acquired : 20 Aug 96 5:27 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A04409 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 27

main paint room AHU supply



File : C:\HPCHEM\1\DATA\S8507\S8507_67.D
Operator : AAG
Acquired : 21 Aug 96 11:20 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A03763 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 63

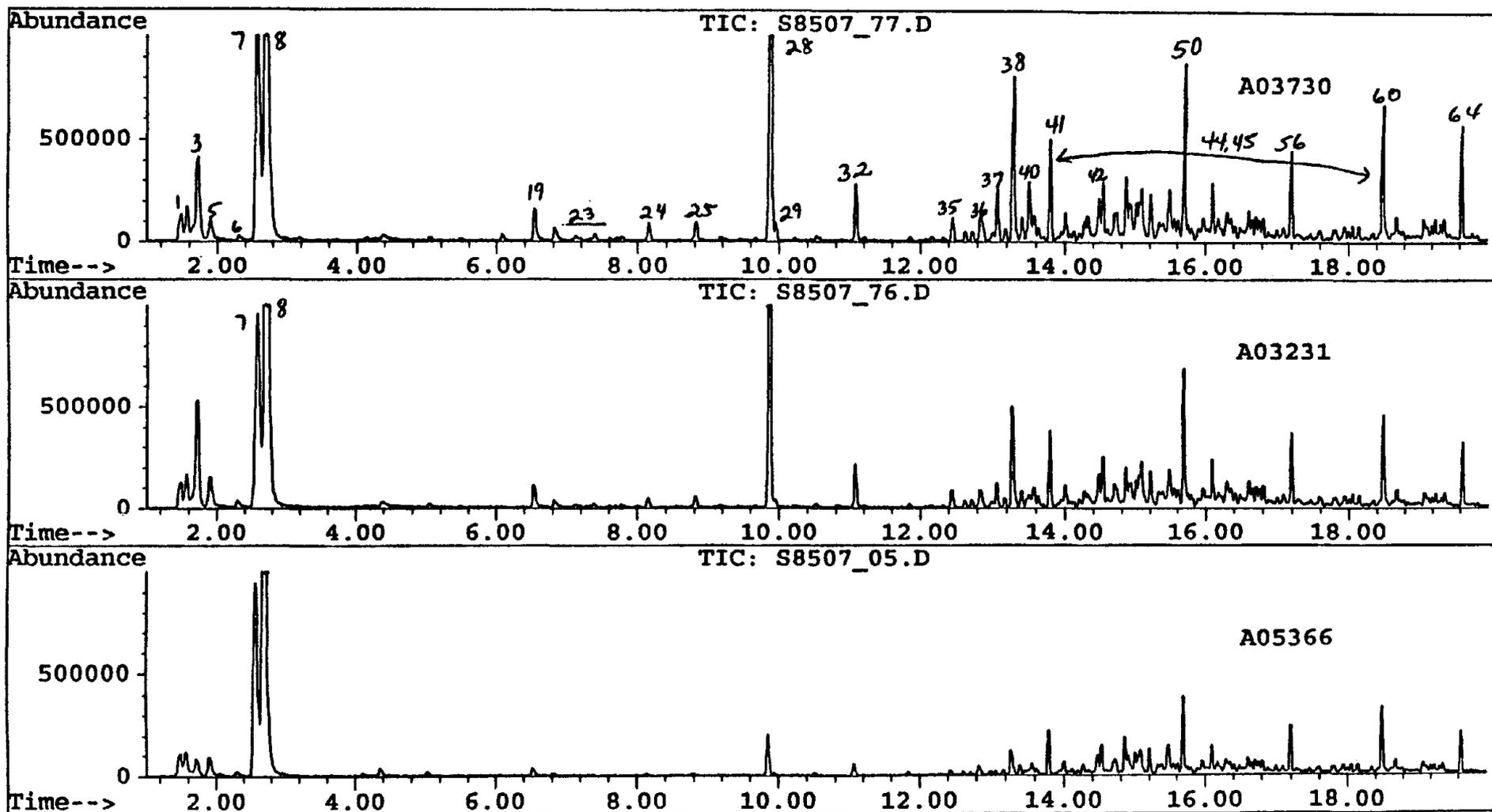
main paint room OA Intake



68

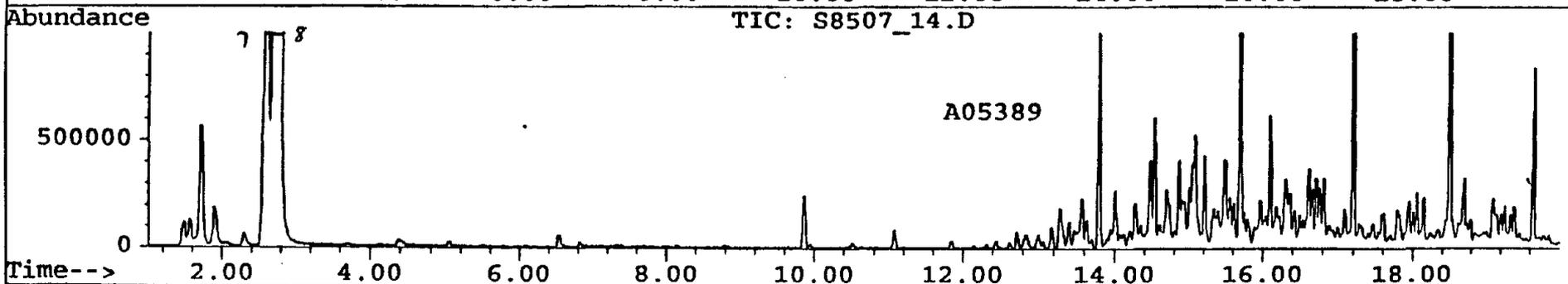
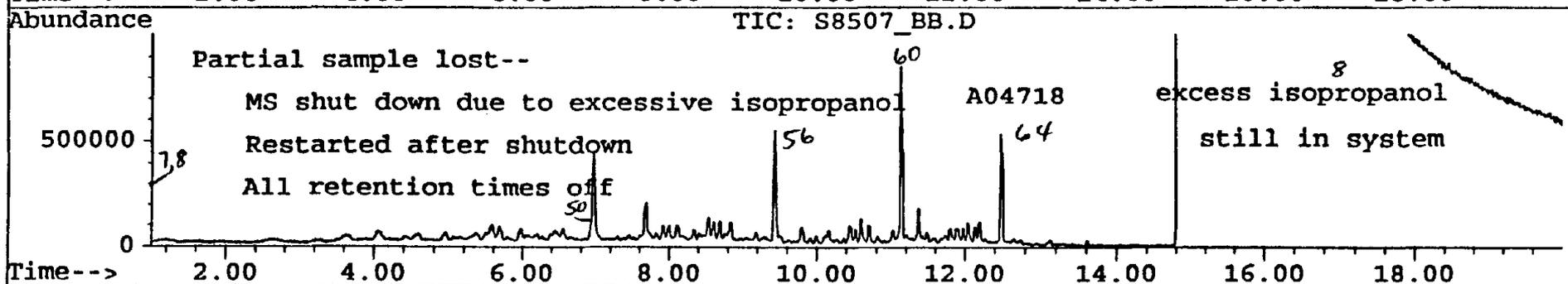
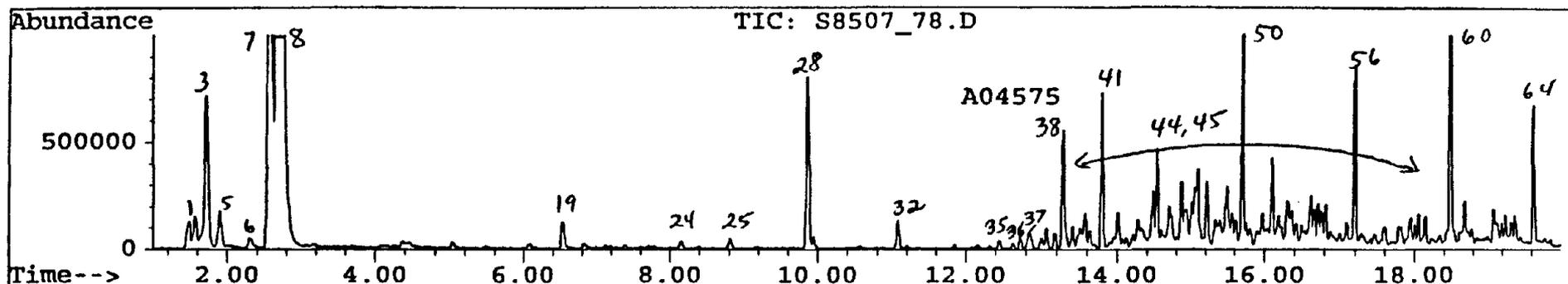
File : C:\HPCHEM\1\DATA\S8507\S8507_77.D
Operator : AAG
Acquired : 22 Aug 96 7:35 am using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A03730 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 73

Fairing Assembly



File : C:\HPCHEM\1\DATA\S8507\S8507_78.D
Operator : AAG
Acquired : 22 Aug 96 8:25 am using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A04575 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 74

Buffing

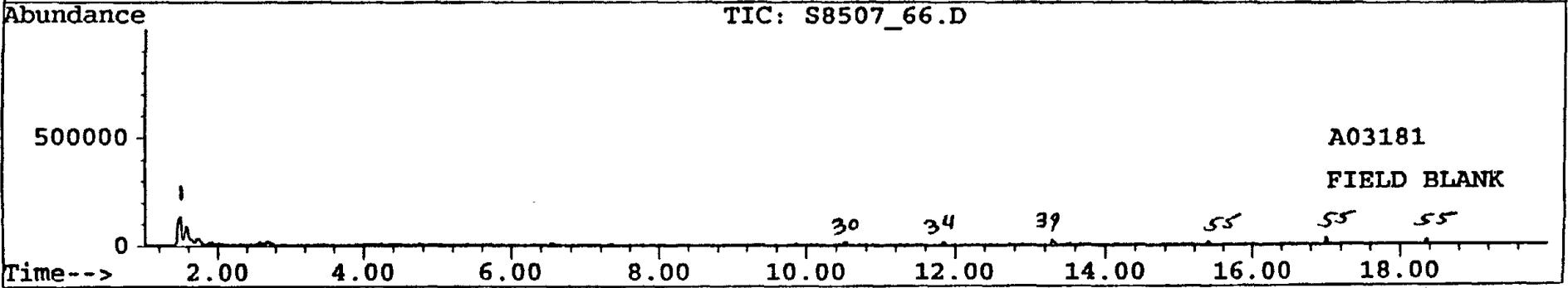
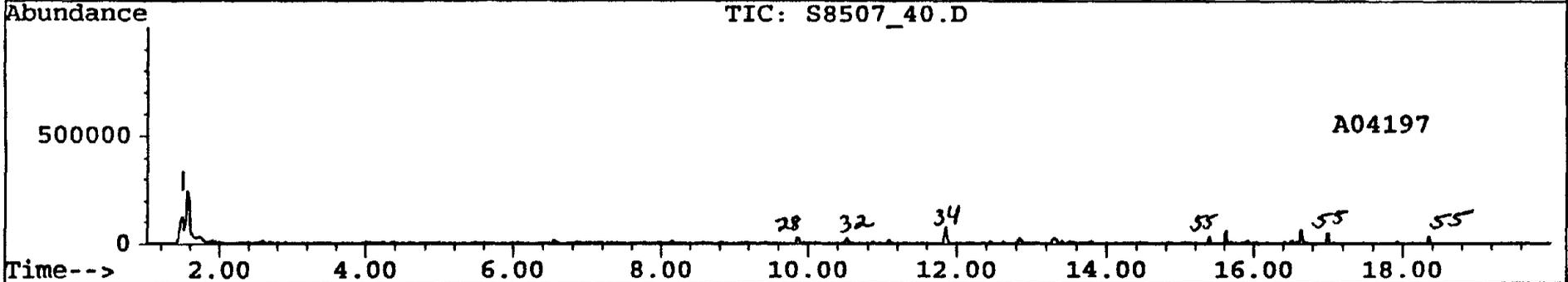
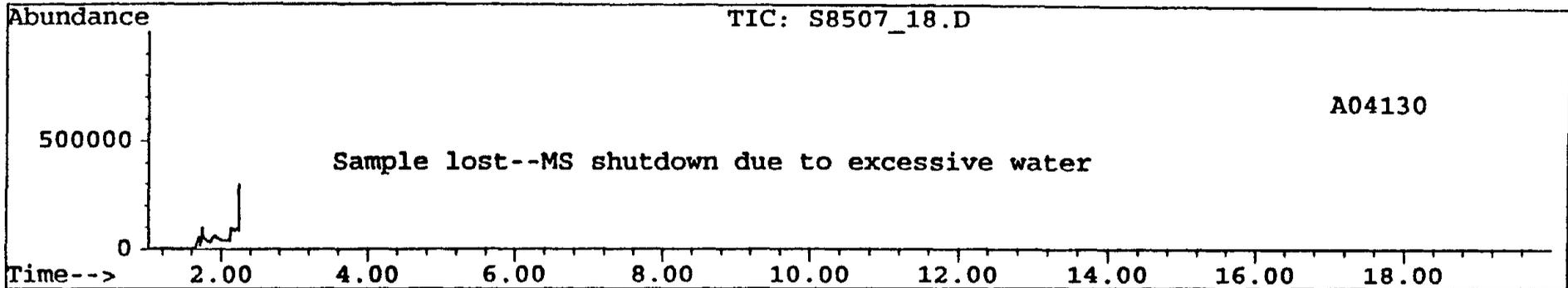


16

File : C:\HPCHEM\1\DATA\S8507\S8507_18.D
Operator : AAG
Acquired : 20 Aug 96 1:51 am using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A04130
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 14

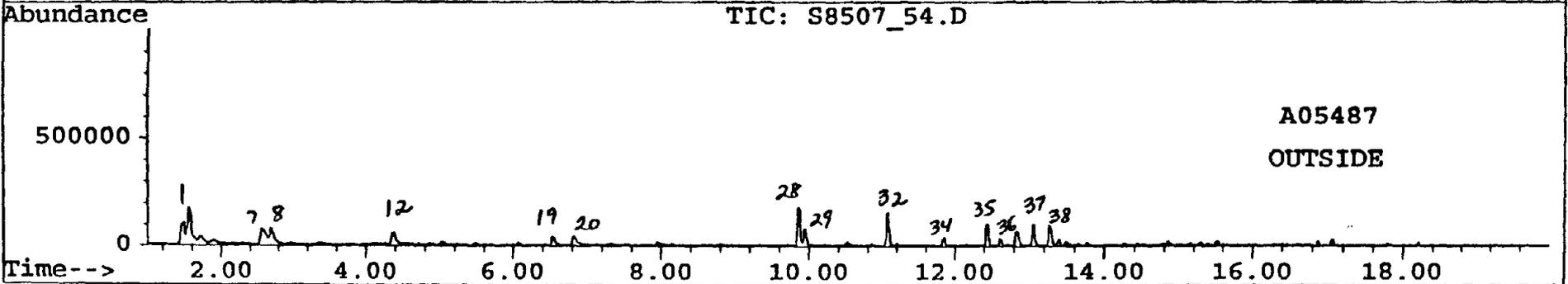
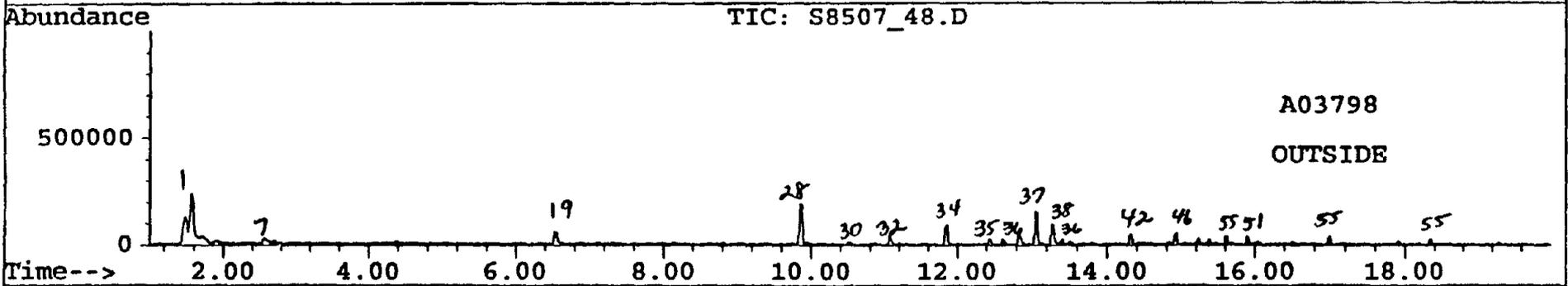
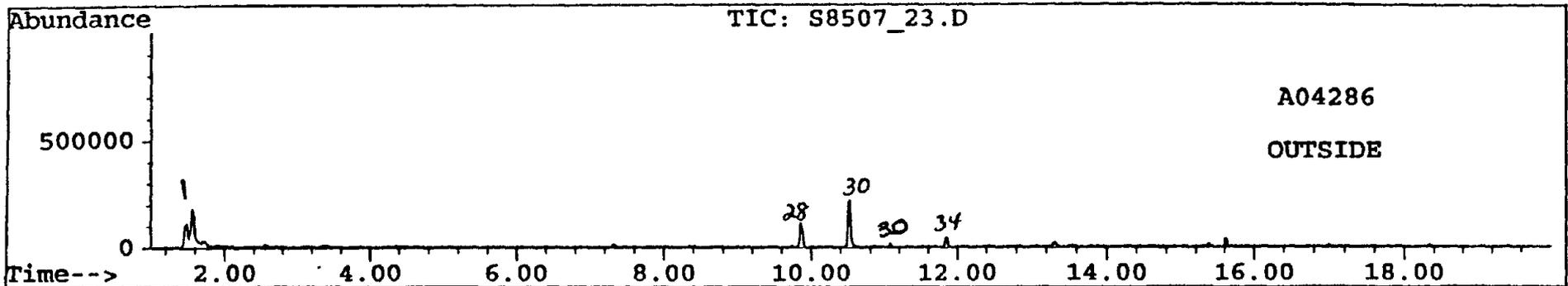
East Line Room OA Intake

9a



File : C:\HPCHEM\1\DATA\S8507\S8507_23.D
Operator : AAG
Acquired : 20 Aug 96 10:39 am using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: SAMPLE A04286 OUTSIDE 100CC/45MIN
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 19

Outside



93



Memorandum

Date January 28, 1997

From Chemist, MDS, MRSB

Subject Sequence 8566A, B, C; HETA 96-0100: Qualitative Analysis of Thermal Desorption Tubes for Volatile Organic Compounds.

To D. Tharr, HETAB Lab Coordinator .
Attn: B. Reh
Through: Chief, MRSB, DPSE _____

INTRODUCTION:

Fifty thermal desorption tubes collected at Harley-Davidson were submitted for analysis of volatile organic compounds by GC-MS. Three sets of samples collected at the same locations over a three day period were submitted. Volumes were approximately 6 liters for all samples so a visual comparison of the results could also be made. Operations involved molding and painting accessories. MSDS were supplied with the samples.

EXPERIMENTAL:

Since the types of contaminants were expected to be widely varied, thermal desorption tubes were used for sampling. Stainless steel tubes configured for the Perkin-Elmer ATD 400 thermal desorption system were used. Each thermal desorption tube contained three beds of sorbent materials--a front layer of Carbopack Y (≈ 90 mg), a middle layer of Carbopack B (≈ 115 mg), and a back section of Carboxen 1003 (≈ 150 mg). Prior to field use, each tube was cleaned by conditioning at 375°C for 2 hours.

Samples were analyzed using the ATD 400 automatic thermal desorption system containing an internal focusing trap packed with Carbopack B/Carboxen 1000 sorbents. The thermal unit was interfaced directly to a HP5890A gas chromatograph and HP5970 mass selective detector (TD-GC-MSD). The mass spectrometer was operated under EI conditions in full scan mode (20-300 amu). A thirty meter DB-1 fused silica capillary column was used for analyses. Sorbent tubes were desorbed in the ATD at 300°C for 10 minutes prior to analyses.

During an initial survey at this plant (Seq 8507), eighteen compounds were identified for quantitation. Therefore, the same compounds were also quantified for this set. Since humidity was a problem on the first set, as a precaution, all samples for this survey were dry purged with helium for 30 minutes at 100 cc/min. prior to analyses. This procedure has been shown to be effective in removing excess water collected on the tubes without causing any significant loss of compounds.

Stock solutions in carbon disulfide (CS_2) containing known amounts of various solvents identified on the initial set of tubes were used to prepare spikes. These solutions contained acetone, isopropanol (IPA), methylene chloride, methyl ethyl ketone (MEK), butanol, 1-methoxy-2-propanol (propylene glycol monomethyl ether), heptane, toluene, butyl acetate, propylene glycol monomethyl ether acetate (PGMEA), xylenes, methyl amyl ketone (MAK), styrene, butyl cellosolve, and Stoddard solvent. To prepare the spikes, blank thermal desorption tubes were inserted into a GC injector ($120^\circ C$). Aliquots of $0.1 \mu L$ to $0.5 \mu L$ of the stock solutions were injected into the GC and onto the thermal desorption tubes with helium flowing through the tubes at 40-50 cc/min for 10 minutes.

RESULTS:

One sample, A03763, was lost due to a mass spectrometer malfunction. The remaining thermal desorption tubes were quantified for the 15 compounds listed above by comparing samples to spiked tubes and the results are reported on the enclosed Table 1. Since the sampling and analytical techniques used in this analysis have not been validated, all results should be considered as estimated values. In addition, estimated results for 1-butoxy-2-propanol, diisobutyl ketone, and butyl cellosolve acetate were calculated using butyl cellosolve as the standard; total aliphatics were estimated using Stoddard solvent for standards. These latter results are reported on the enclosed Table 2. All results are reported in terms of μg /sample.

Copies of the reconstructed total ion chromatograms from the thermal desorption tube samples are enclosed. Since samples were collected at the same locations over a three day period, samples from the same location are plotted on the same sheet. Major peaks for each page of chromatograms are numbered on at least one plot. Chromatograms are all scaled the same for comparison (same time and abundance axes). A separate table is enclosed listing each peak number with its corresponding identification.

Samples contained various compounds depending on location. Several samples contained none or only very low levels of any contaminants. Others, in comparison, contained quite high concentrations. Major components on several sample sets were isopropanol, acetone, MEK, butanol, 1-methoxy-2-propanol, toluene, butyl acetate, PGMEA, MAK, xylenes, butyl cellosolve, butoxy propanol, and diisobutyl ketone. Also present on some of these samples were ethyl acetate, isobutyl acetate, methylene chloride, methyl isobutyl ketone (MIBK), propylene glycol, hydroxy methyl pentanone, methyl propanol, acetic acid, propoxy ethanol, and several higher molecular weight esters (dimethyl succinate, dimethyl glutarate, dimethyl adipate). Some samples

had a predominant hydrocarbon pattern, mostly aliphatic hydrocarbons in the C₉-C₁₃ range. Styrene was the major compound at another location. Samples with high styrene concentrations also contained benzaldehyde, N,N-dimethylformamide, and benzoic acid.

Ardith A. Grote

Robert L. Larkin
Acting Chief, MDS, MRSB,
DPSE

Attachments

DPSE:MRSB:MDS:AAGROTE:bjj\sequence\s8566abc.aag\1-28-97

SEQ 8566
TABLE 1--PAGE 1 OF 2
UG/SAMPLE

Field No.	methylene		MEK	1-methoxy-			butyl			MAK	styrene	cellosolve		
	acetone	isopropanol		chloride	butanol	2-propanol	heptane	toluene	acetate				PGMEA	xylenes
SAMPLE A04702 OUTSIDE	8.82	3.81	(0.09)	N.D.	0.08	N.D.	(0.06)	0.90	0.23	(0.08)	0.22	(0.15)	N.D.	0.15
SAMPLE A05428	45.23	24.44	0.32	0.72	4.96	(0.10)	(0.09)	14.13	7.31	(0.21)	1.92	3.31	N.D.	0.15
SAMPLE A04667	25.08	5.78	(0.08)	2.49	0.85	1.26	(0.12)	2.21	1.59	0.94	1.01	1.37	0.60	(0.09)
SAMPLE A03798	8.62	0.63	N.D.	0.35	0.16	(0.18)	N.D.	0.48	0.25	(0.10)	0.26	0.24	6.02	(0.04)
SAMPLE A03026	26.95	6.50	(0.10)	2.98	0.73	0.89	(0.12)	2.22	1.67	1.03	1.07	1.41	0.63	(0.09)
SAMPLE A05534	17.72	4.83	(0.13)	(0.17)	0.22	N.D.	(0.11)	1.39	0.36	(0.08)	0.35	0.25	N.D.	(0.07)
SAMPLE A03534	54.84	31.38	17.21	14.27	1.86	5.63	0.17	19.96	4.33	4.99	10.49	0.50	0.23	0.54
SAMPLE A03941	38.41	19.32	0.34	0.59	4.90	(0.14)	(0.13)	10.56	3.51	(0.18)	1.69	3.72	(0.09)	0.17
SAMPLE A04448	46.25	24.73	0.35	0.43	4.92	(0.11)	(0.12)	14.72	7.26	(0.21)	1.92	3.63	N.D.	0.20
SAMPLE A04215 FIELD BLANK	N.D.	N.D.	N.D.	N.D.	(0.02)	(0.05)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SAMPLE A04575	35.65	18.14	0.21	0.43	2.33	(0.09)	(0.09)	9.87	2.68	(0.12)	1.09	2.00	(0.07)	0.17
SAMPLE A03974	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SAMPLE A05370	43.03	21.33	0.28	0.62	3.90	(0.10)	(0.10)	12.62	4.15	(0.19)	2.38	3.95	N.D.	0.49
SAMPLE A03730	46.82	25.43	0.33	0.40	4.38	(0.09)	1.14	16.85	5.33	(0.16)	1.63	3.50	N.D.	0.17
SAMPLE A05120	60.67	0.52	0.31	6.91	3.75	(0.14)	0.73	15.11	11.77	9.45	2.61	0.19	(0.08)	0.24
SAMPLE A05054 FIELD BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SAMPLE A05518	12.27	6.74	(0.10)	(0.17)	0.48	(0.11)	(0.14)	1.92	0.53	(0.08)	0.33	0.35	N.D.	(0.11)
SAMPLE A04676	(0.12)	(0.19)	N.D.	N.D.	(0.03)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(0.04)
SAMPLE A04801	26.27	6.65	0.22	1.01	0.08	(0.10)	(0.08)	1.68	0.46	0.61	0.69	(0.06)	N.D.	(0.05)
SAMPLE A03659	29.05	21.28	2.78	2.57	0.38	0.64	N.D.	8.53	2.03	0.83	3.30	0.20	N.D.	(0.08)
SAMPLE A03037	20.02	1.47	(0.06)	0.64	0.08	(0.12)	N.D.	0.67	0.40	(0.15)	0.41	N.D.	22.11	(0.04)
SAMPLE A04202 OUTSIDE	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SAMPLE A03364	17.80	11.88	(0.13)	0.50	0.12	(0.13)	(0.05)	1.24	0.31	0.35	0.53	(0.08)	0.32	1.71
SAMPLE A03722	21.25	21.44	(0.16)	0.80	0.15	(0.10)	(0.09)	1.70	0.36	(0.27)	0.56	(0.10)	0.22	0.49
SAMPLE A05078	0.37	(0.18)	N.D.	N.D.	0.08	N.D.	N.D.	0.28	N.D.	N.D.	N.D.	(0.08)	N.D.	N.D.
SAMPLE A03074 FIELD BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	(0.06)	N.D.	N.D.
SAMPLE A05417	39.12	5.93	(0.06)	4.65	0.81	2.92	0.23	3.56	5.67	3.12	2.76	1.85	N.D.	0.39
SAMPLE A03929	36.54	19.16	(0.12)	0.36	2.27	N.D.	N.D.	16.60	2.12	(0.08)	1.32	1.90	N.D.	0.49
SAMPLE A04286	57.96	1.55	(0.16)	1.52	2.11	N.D.	N.D.	9.27	1.32	(0.15)	3.66	2.76	N.D.	0.33
SAMPLE A03791	44.61	24.81	(0.15)	0.34	2.53	N.D.	N.D.	20.77	3.80	N.D.	1.25	1.71	N.D.	0.42

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SEQ 8566
TABLE 1—PAGE 2 OF 2
UG/SAMPLE

Field No.	acetone		methylene		1-methoxy-			butyl			butyl			
	isopropanol	chloride	MEK	butanol	2-propanol	heptane	toluene	acetate	PGMEA	xylenes	MAK	styrene	cellosolve	
SAMPLE A05368	17.04	6.26	N.D.	(0.15)	1.10	N.D.	0.48	3.39	0.49	N.D.	0.51	0.78	N.D.	(0.10)
SAMPLE A04378	35.89	7.56	(0.08)	4.47	1.10	(0.09)	0.30	7.54	6.18	5.22	1.34	0.84	N.D.	0.15
SAMPLE A03938 FIELD BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SAMPLE A05422	19.24	7.96	N.D.	(0.11)	1.02	N.D.	0.63	3.47	1.01	N.D.	0.40	0.75	N.D.	3.48
SAMPLE A05635	15.57	23.70	(0.08)	0.63	0.36	(0.14)	(0.13)	2.04	0.54	0.32	0.47	0.29	0.24	0.20
SAMPLE A03231	18.44	6.73	(0.16)	1.22	0.15	(0.15)	(0.14)	1.94	0.51	0.75	0.58	(0.13)	(0.15)	0.14
SAMPLE A04715	56.04	2.53	3.41	1.85	0.24	0.40	N.D.	4.14	1.40	0.87	3.62	0.21	(0.18)	0.12
SAMPLE A03886	15.75	28.81	(0.08)	0.74	0.35	(0.22)	(0.10)	1.68	0.52	0.38	0.55	(0.08)	0.30	0.36
SAMPLE A03998	37.76	19.70	N.D.	(0.24)	2.41	N.D.	(0.06)	11.50	4.77	N.D.	1.02	1.56	N.D.	0.55
SAMPLE A05000	12.20	10.14	(0.06)	0.63	0.15	(0.09)	(0.10)	1.39	0.32	(0.25)	0.35	(0.13)	(0.10)	0.29
SAMPLE A03428 OUTSIDE	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SAMPLE A03181	16.43	7.63	N.D.	3.01	0.70	1.75	0.24	3.09	2.15	2.34	1.07	1.21	N.D.	0.22
SAMPLE A04328	19.66	2.14	(0.05)	0.75	0.11	(0.13)	(0.07)	1.10	0.40	(0.25)	0.38	(0.14)	16.08	(0.09)
SAMPLE A05487	29.33	14.86	N.D.	(0.20)	1.83	N.D.	N.D.	(7.62)	2.27	N.D.	0.80	1.44	N.D.	0.50
SAMPLE A04359 FIELD BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SAMPLE A03075 FIELD BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SAMPLE A03679	29.36	12.10	N.D.	0.75	2.12	N.D.	(0.09)	4.28	1.99	N.D.	1.55	1.84	N.D.	0.84
SAMPLE A04509	23.95	1.35	N.D.	12.96	0.96	(0.16)	1.22	13.76	11.37	10.54	3.05	1.20	(0.15)	0.79
SAMPLE A04958	(0.27)	(0.14)	N.D.	N.D.	(0.07)	N.D.	N.D.	0.26	N.D.	N.D.	N.D.	(0.09)	N.D.	N.D.
SAMPLE A04069 FIELD BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SAMPLE A03072 FIELD BLANK	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
SAMPLE A03763 ¹	—	—	—	—	—	—	—	—	—	—	—	—	—	—
LOD	0.09	0.10	0.05	0.09	0.02	0.09	0.05	0.06	0.06	0.08	0.05	0.05	0.07	0.03
LOQ	0.29	0.34	0.18	0.29	0.07	0.29	0.15	0.19	0.20	0.28	0.17	0.18	0.22	0.12

Values in parenthesis fall between the LOD and LOQ.

¹Sample lost due to mass spectrometer malfunction.

1-methoxy-2-propanol = propylene glycol methyl ether

MEK = methyl ethyl ketone

PGMEA = propylene glycol monomethyl ether acetate

MAK = methyl amyl ketone (2-heptanone)

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SEQ 8566
TABLE 2--PAGE 1 OF 2
ug/sample

Field No.	Butoxypropanol ¹	Diisobutyl ketone ¹	Butyl cellosolve acetate ¹	Total aliphatics ²
SAMPLE A04702 OUTSIDE	(0.10)	(0.11)	(0.04)	3.23
SAMPLE A05428	3.60	2.19	0.44	1.29
SAMPLE A04667	0.38	0.42	(0.05)	2.11
SAMPLE A03798	(0.10)	(0.11)	N.D.	(0.52)
SAMPLE A03026	0.40	0.45	(0.06)	2.13
SAMPLE A05534	0.20	0.19	(0.07)	2.78
SAMPLE A03534	0.98	0.19	1.52	5.81
SAMPLE A03941	3.85	2.22	0.19	(0.58)
SAMPLE A04448	3.76	2.18	0.41	1.18
SAMPLE A04215 FIELD BLANK	N.D.	N.D.	N.D.	N.D.
SAMPLE A04575	2.06	1.29	0.22	1.34
SAMPLE A03974	N.D.	N.D.	N.D.	N.D.
SAMPLE A05370	3.40	2.09	0.23	0.76
SAMPLE A03730	3.62	2.16	0.39	4.39
SAMPLE A05120	3.42	1.99	0.20	3.45
SAMPLE A05054 FIELD BLANK	N.D.	N.D.	N.D.	N.D.
SAMPLE A05518	0.29	0.30	0.12	7.81
SAMPLE A04676	N.D.	N.D.	N.D.	(0.53)
SAMPLE A04801	(0.04)	(0.04)	(0.04)	1.27
SAMPLE A03659	(0.08)	(0.05)	0.14	0.74
SAMPLE A03037	(0.05)	(0.06)	N.D.	(0.48)
SAMPLE A04202 OUTSIDE	N.D.	N.D.	N.D.	N.D.
SAMPLE A03364	(0.08)	0.44	0.49	35.58
SAMPLE A03722	0.12	0.19	0.14	10.14
SAMPLE A05078	(0.07)	(0.05)	N.D.	N.D.
SAMPLE A03074 FIELD BLANK	N.D.	N.D.	N.D.	N.D.
SAMPLE A05417	0.37	0.45	0.14	3.17
SAMPLE A03929	1.74	1.12	0.13	(0.33)
SAMPLE A04286	2.22	1.60	(0.09)	N.D.
SAMPLE A03791	2.06	1.23	0.19	(0.51)

bb

SEQ 8566
TABLE 2--PAGE 2 OF 2
ug/sample

Field No.	Butoxypropanol ¹	Diisobutyl ketone ¹	Butyl cellosolve acetate ¹	Total aliphatics ²
SAMPLE A05366	0.94	0.60	(0.10)	(0.51)
SAMPLE A04378	0.74	0.50	(0.07)	1.95
SAMPLE A03938 FIELD BLANK	N.D.	N.D.	N.D.	N.D.
SAMPLE A05422	0.84	0.71	0.17	9.70
SAMPLE A05635	0.28	0.29	0.16	10.90
SAMPLE A03231	0.12	(0.10)	(0.05)	2.16
SAMPLE A04715	0.12	(0.07)	(0.09)	0.91
SAMPLE A03886	0.24	0.65	0.80	50.88
SAMPLE A03998	1.80	1.11	0.30	1.34
SAMPLE A05000	0.25	(0.11)	(0.05)	2.22
SAMPLE A03428 OUTSIDE	N.D.	N.D.	N.D.	N.D.
SAMPLE A03181	0.39	0.33	0.13	3.88
SAMPLE A04328	(0.09)	(0.09)	N.D.	1.04
SAMPLE A05487	1.43	0.88	0.15	0.80
SAMPLE A04359 FIELD BLANK	N.D.	N.D.	N.D.	N.D.
SAMPLE A03075 FIELD BLANK	N.D.	N.D.	N.D.	N.D.
SAMPLE A03679	1.20	1.09	0.17	1.60
SAMPLE A04509	0.42	0.31	0.19	5.76
SAMPLE A04958	(0.08)	(0.05)	N.D.	N.D.
SAMPLE A04069 FIELD BLANK	N.D.	N.D.	N.D.	N.D.
SAMPLE A03072 FIELD BLANK	N.D.	N.D.	N.D.	N.D.
SAMPLE A03763 ³	—	—	—	—
LOD	0.03	0.03	0.03	0.22
LOQ	0.12	0.12	0.12	0.73

Values in parenthesis fall between the LOD and LOQ.

¹Reported values are estimates since butyl cellosolve was used for standards

²Reported values are estimates since Stoddard solvent was used for standards

³Sample lost due to mass spectrometer malfunction.

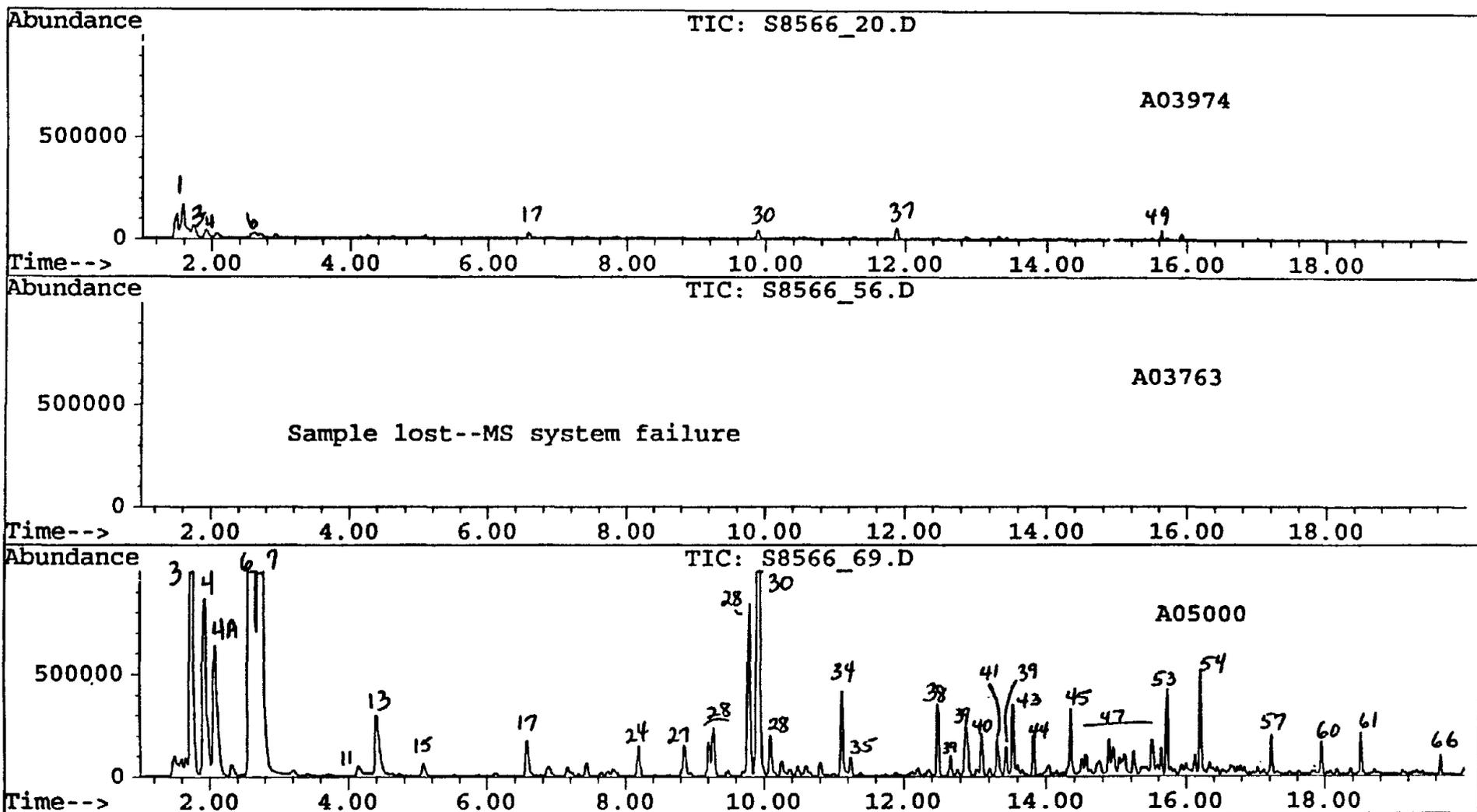
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SEQ 8566
THERMAL DESORPTION TUBES
PEAK IDENTIFICATION

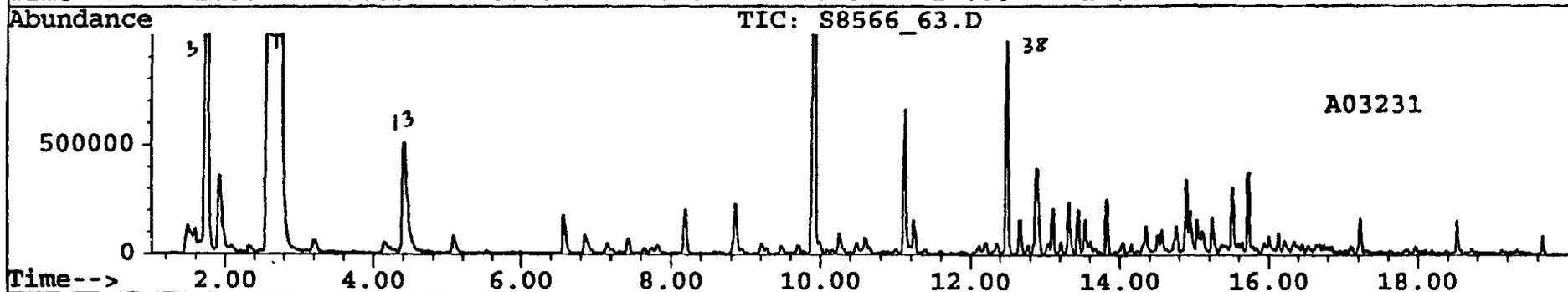
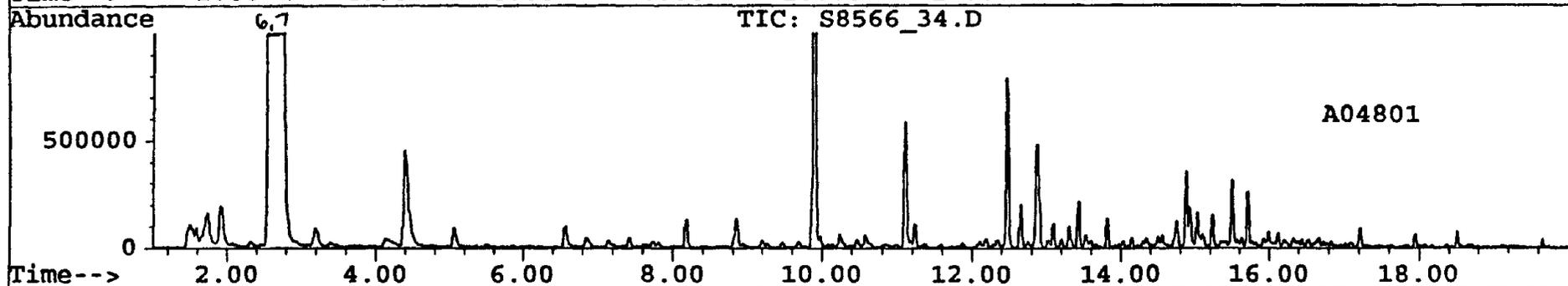
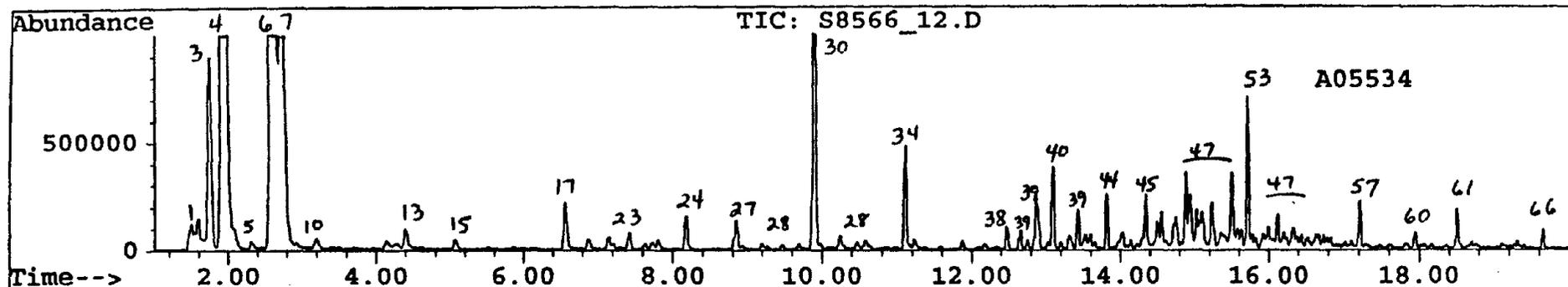
- | | |
|---|---|
| 1) Air*/CO ₂ * | 39) Xylenes/ethyl benzene |
| 2) Formaldehyde | 40) Methyl amyl ketone (MAK) |
| 3) Propane and/or propene | 41) Styrene |
| 4A) Butane | 42) Cellosolve acetate* |
| 4) Methanol and/or isobutane | 43) Butyl cellosolve
(2-butoxyethanol) |
| 5) Ethanol | 44) n-Nonane |
| 6) Acetone | 45) 1-Butoxy-2-propanol |
| 7) Isopropanol | 46) Benzaldehyde |
| 8) 2-Methyl-2-propanol | 47) C ₉ -C ₁₂ aliphatics plus some
C ₉ H ₁₂ alkyl benzenes
(trimethyl-, propyl-,
methylethybenzenes, etc.) |
| 9) Nitromethane | 48) Phenol |
| 10) Methylene chloride | 49) Octamethylcyclotetra-
siloxane |
| 11) 2-Buten-one? | 50) Diisobutyl ketone
(2,6-dimethyl-4-heptanone) |
| 12) Butanal | 51) Aliphatic ketone |
| 13) Methyl ethyl ketone (MEK) | 52) Butanedioic acid, methyl
ester (dimethyl succinate) |
| 14) Acetic acid | 53) n-Decane |
| 15) Ethyl acetate | 54) Limonene |
| 15A) Hexane | 55) Terpene (carene?), C ₁₀ H ₁₆ |
| 16) 2-Methyl-1-propanol | 56) Aliphatic aldehydes, C ₇ -C ₁₀ * |
| 17) Butanol/trace benzene* | 57) n-Undecane |
| 18) 1-Methoxy-2-propanol
(propylene glycol methyl
ether) | 58) Butyl cellosolve acetate
(butyl glycol acetate) |
| 19) Trichloroethylene | 60) Decamethylcyclopenta-
siloxane* |
| 20) Pentanal | 61) n-Dodecane |
| 22) Trichloroethylene | 62) Pentanedioic acid,
dimethyl ester
(dimethyl glutarate) |
| 23) C ₇ H ₁₆ /C ₈ H ₁₄ aliphatics | 63) 2-Nitrophenol? |
| 24) n-Heptane | 64) Benzoic acid |
| 25) Propylene glycol | 65) Hexanedioic acid, dimethyl
ester (dimethyl adipate) |
| 26) Butyl formate | 66) n-Tridecane |
| 27) Methylcyclohexane/methyl
isobutyl ketone (MIBK) | 67) A diethyl-dimethylsuccinic
acid dinitrile (possible
intermittent system
contaminant) |
| 27A) N,N-Dimethylformamide | 68) Aliphatic, acid esters |
| 28) C ₈ H ₁₈ /C ₉ H ₁₆ aliphatics | |
| 29) N,N-Dimethylformamide | |
| 30) Toluene | |
| 31) Isobutyl acetate | |
| 32) 4-Methyl morpholine | |
| 33) 2-Propoxyethanol | |
| 34) n-Butyl acetate | |
| 35) n-Octane | |
| 36) 4-Methyl-4-hydroxy-
2-pentanone | |
| 37) Hexamethylcyclotri-
siloxane* | |
| 38) Propylene glycol mono-
methyl ether acetate | |

*Also present on some media/field blanks.

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Operator : AAG
Acquired : 22 Nov 96 8:45 am using AcqMethod STD8566
Instrument : 5970 - In
Sample Name: OLD SPIKE A03763 0.1UL STD A
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 56

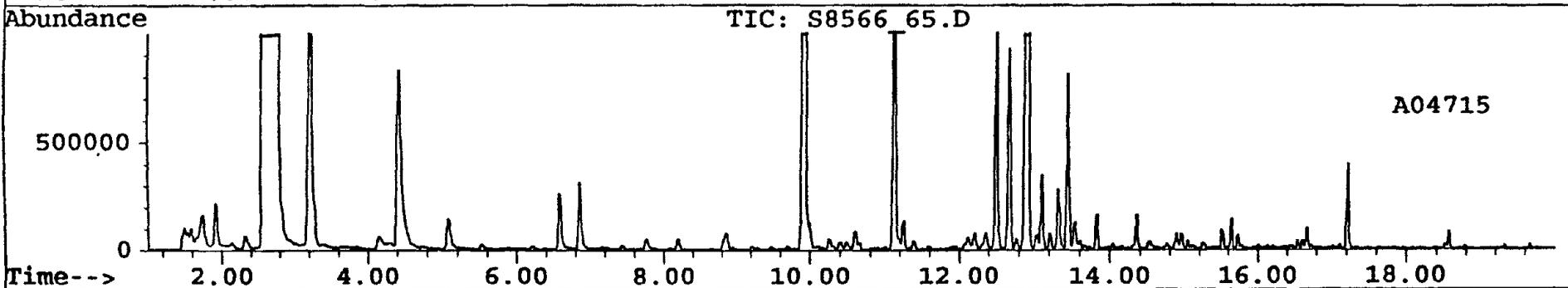
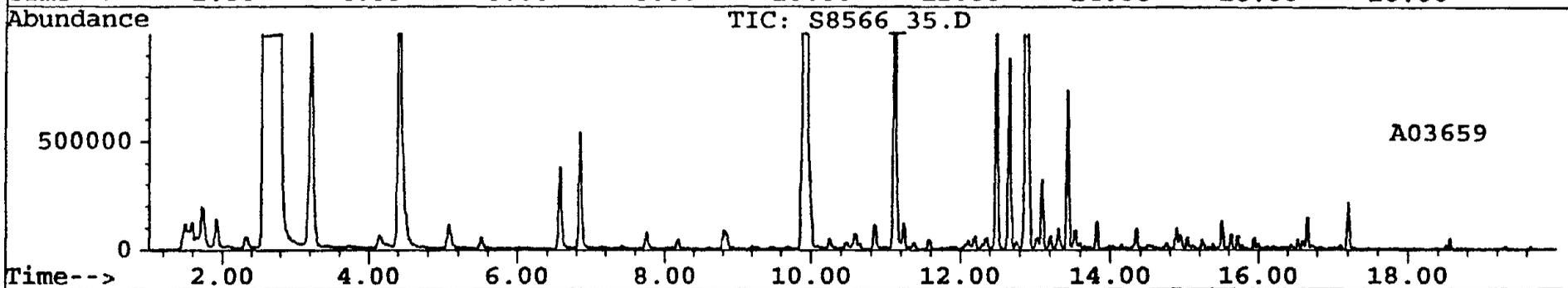
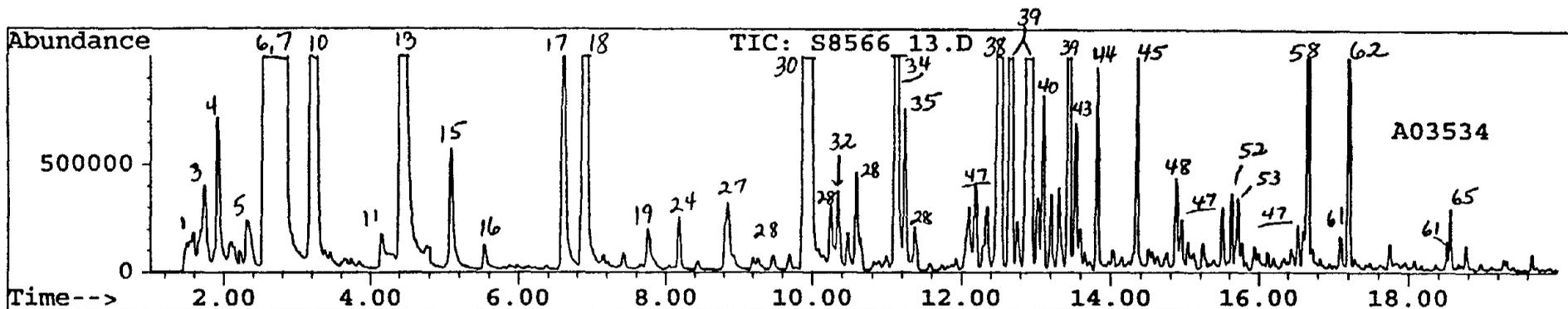


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Acquired : 21 Nov 96 2:51 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: A04801
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 34



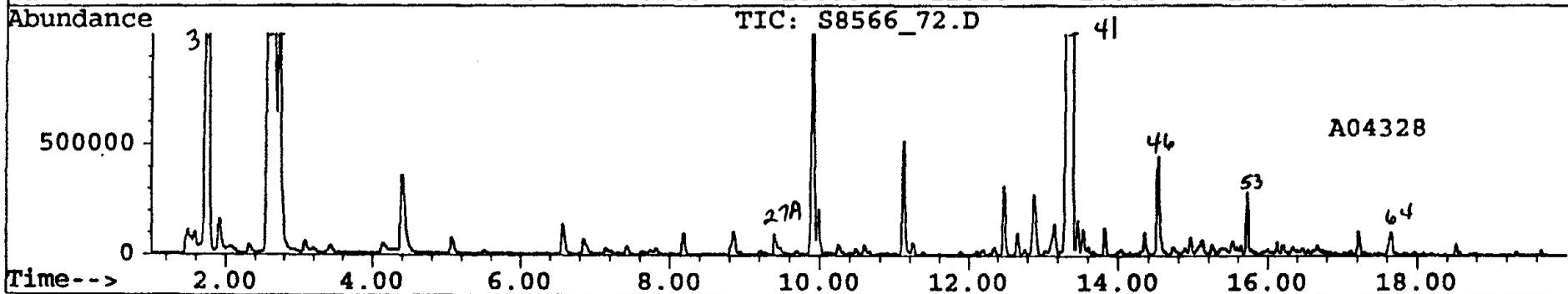
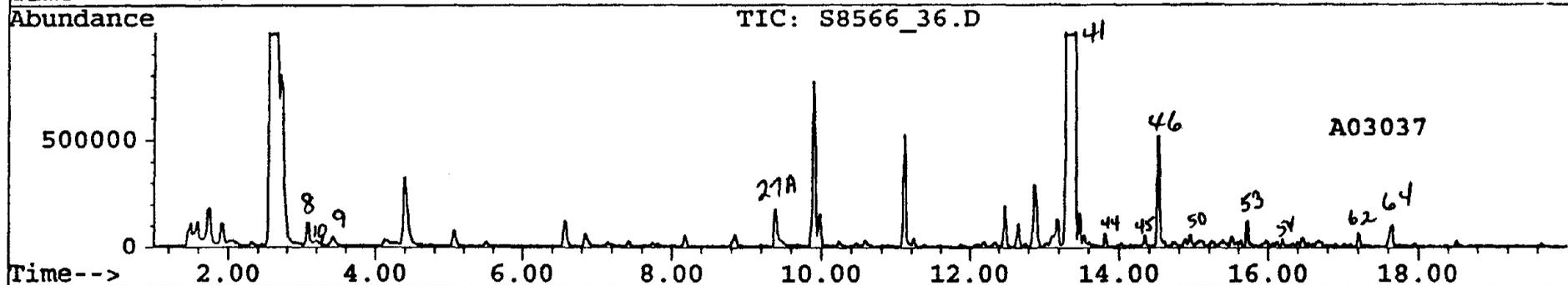
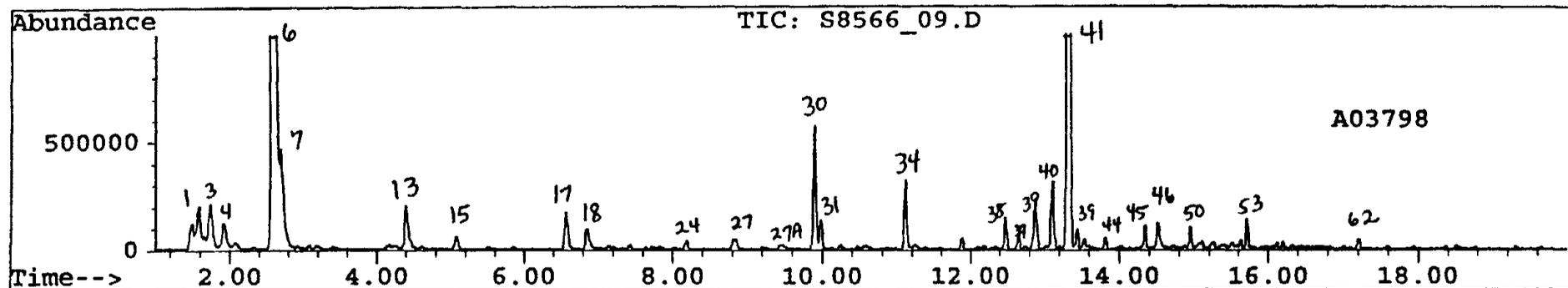
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Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 12

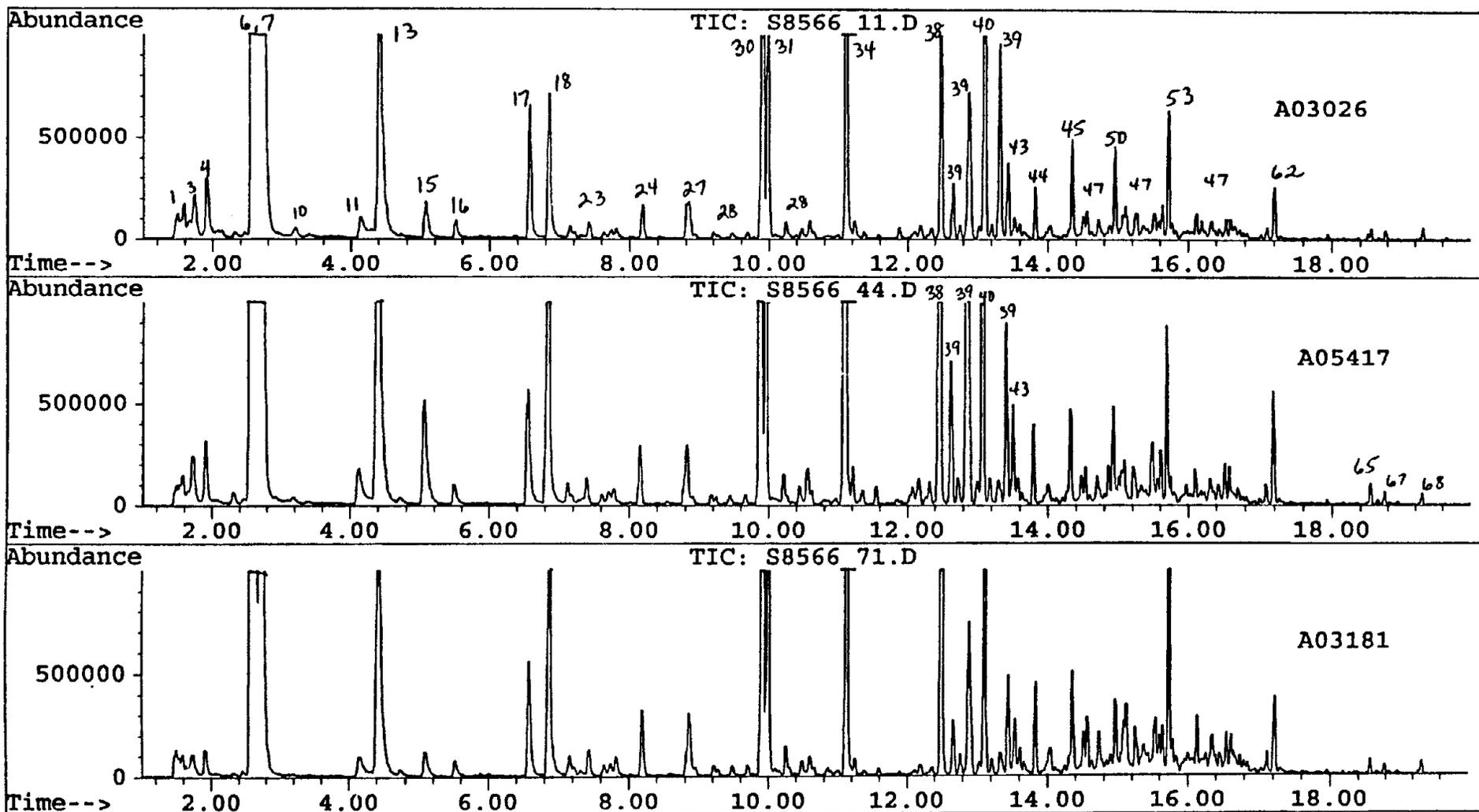


hcl

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Instrument : 5970 - In
Sample Name: A04328 PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 19

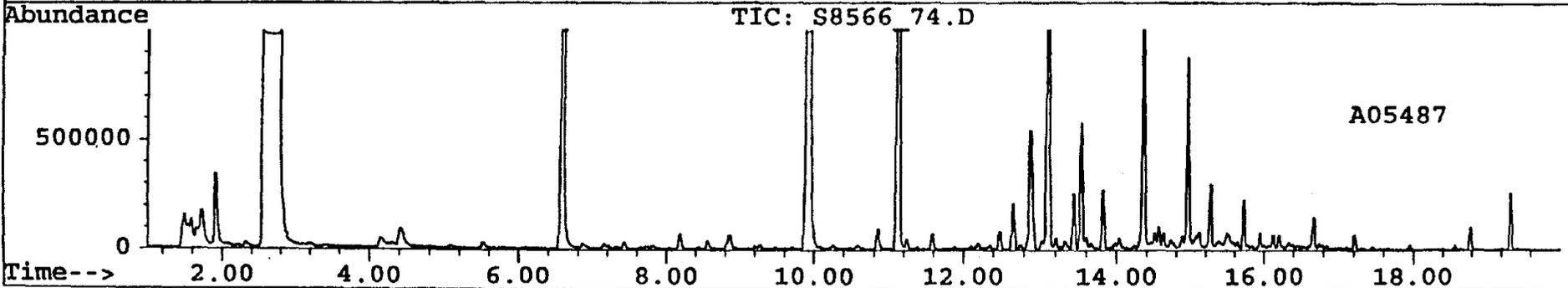
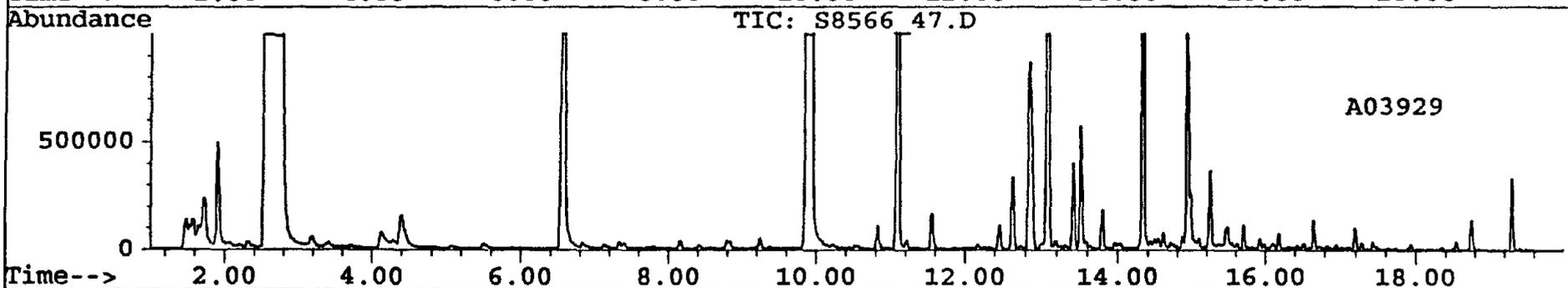
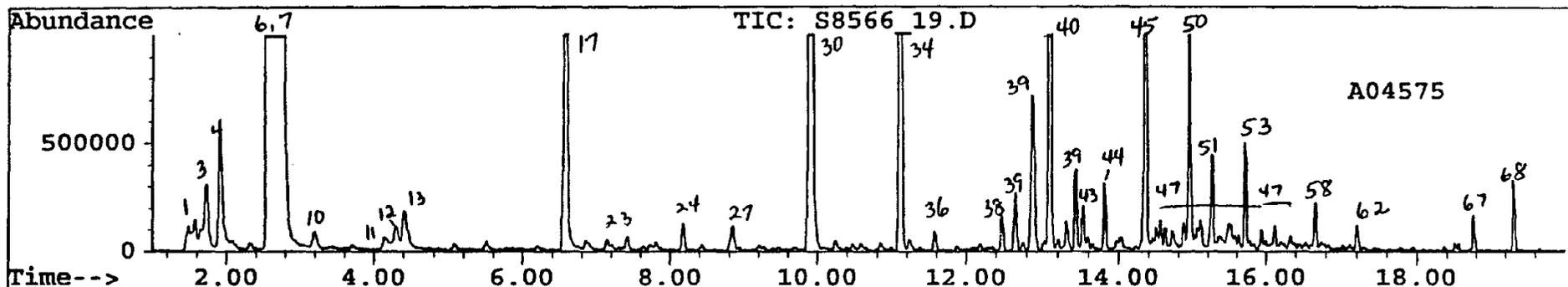


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Acquired : 26 Nov 96 12:53 am using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: A03181 PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 18



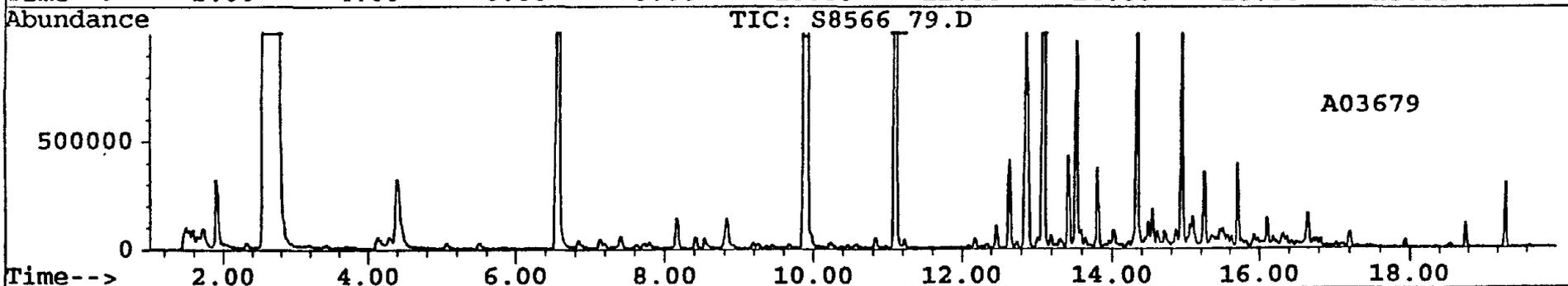
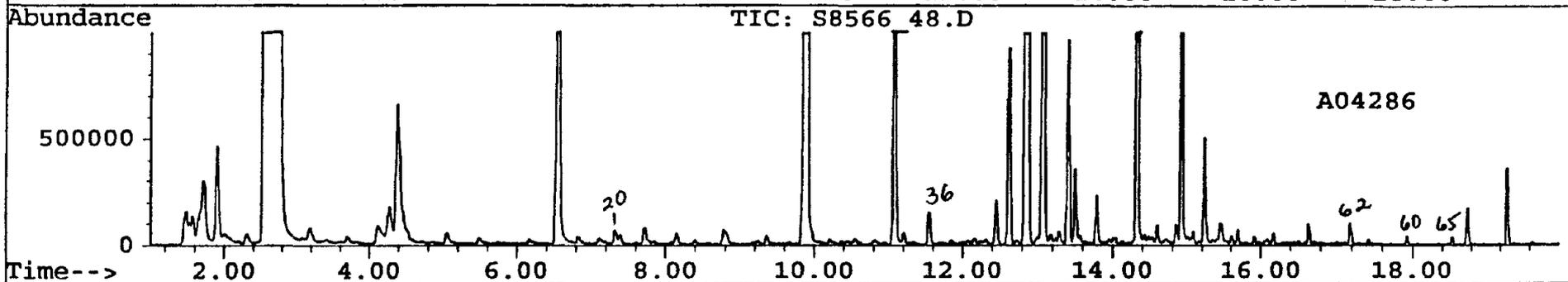
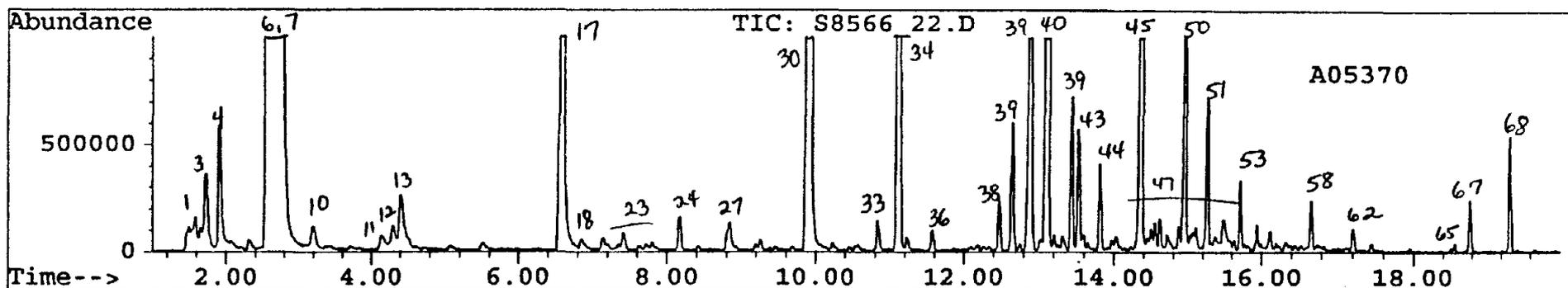
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Sample Name: A03929
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Vial Number: 47

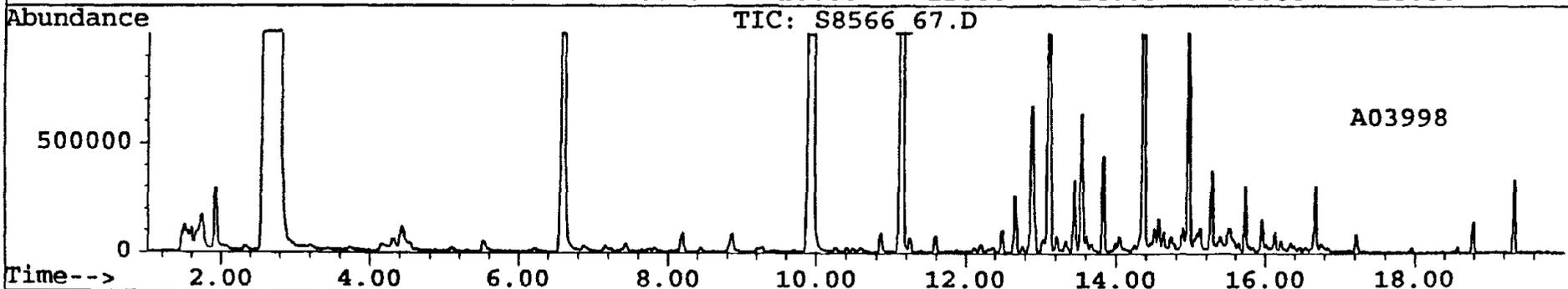
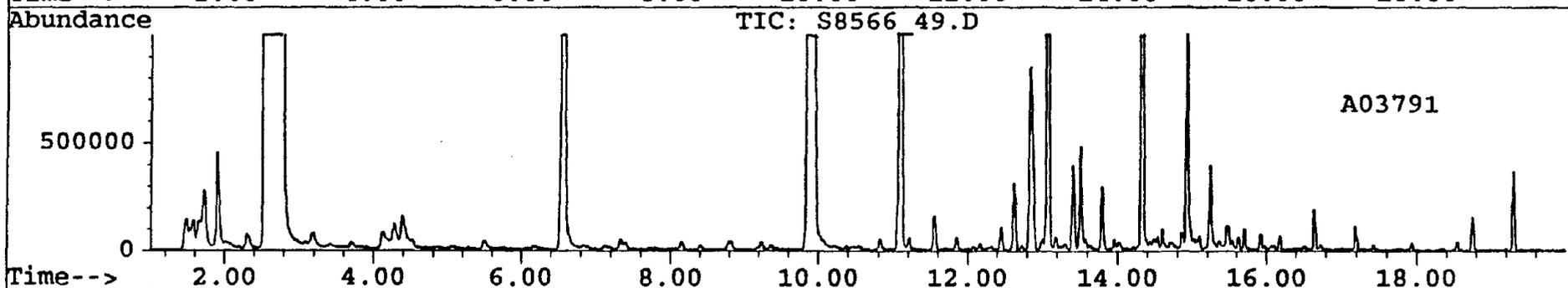
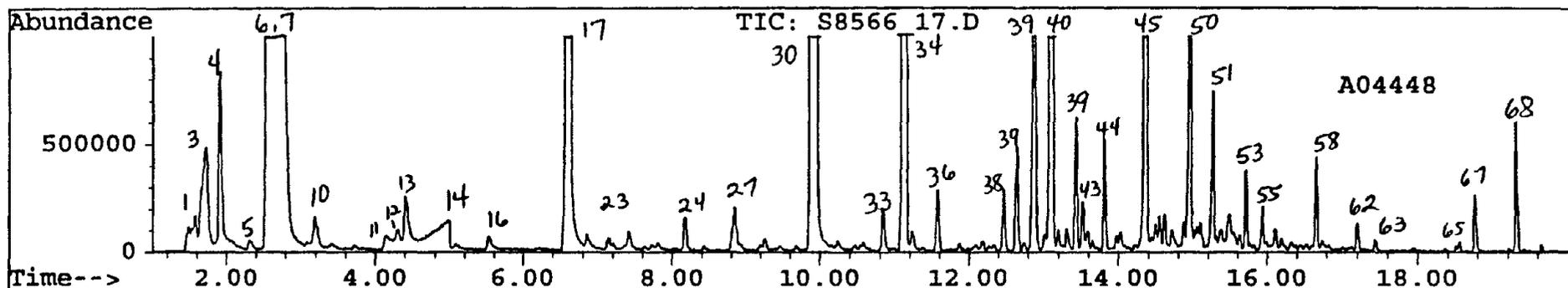


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Acquired : 26 Nov 96 7:24 am using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: A03679 PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 26

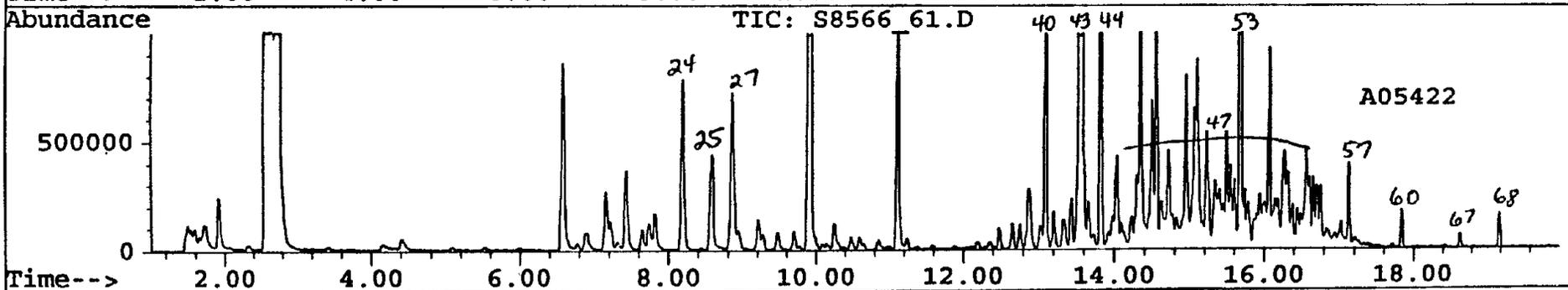
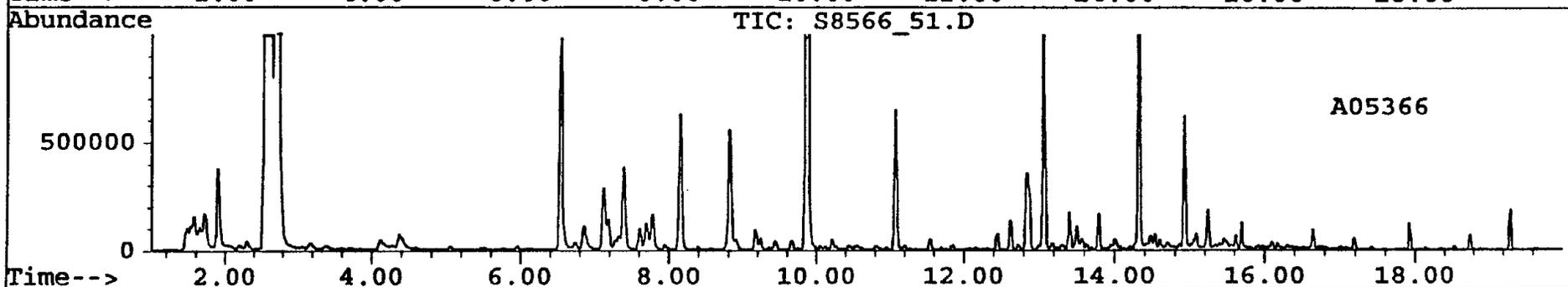
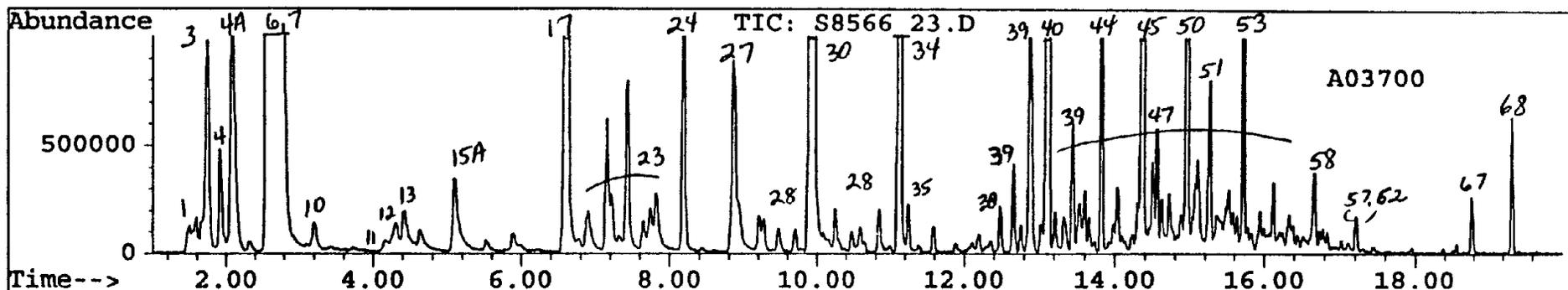


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Instrument : 5970 - In
Sample Name: A03998 PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 14

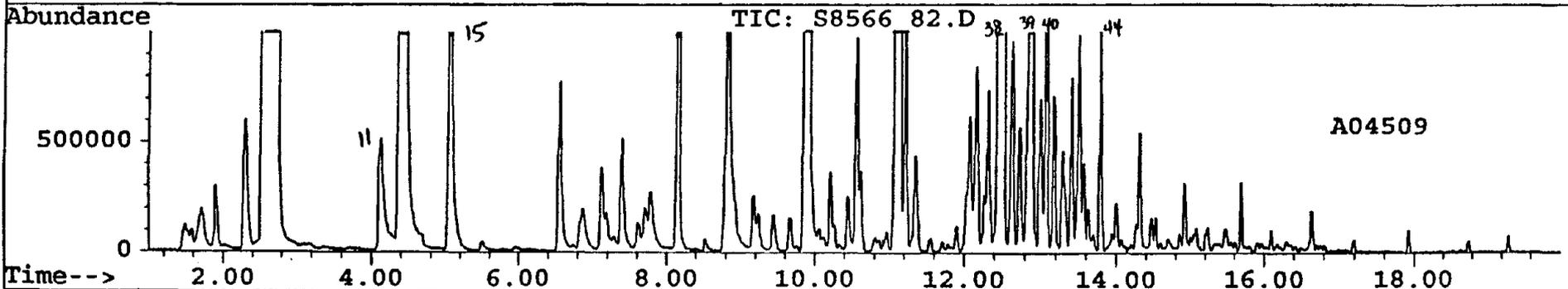
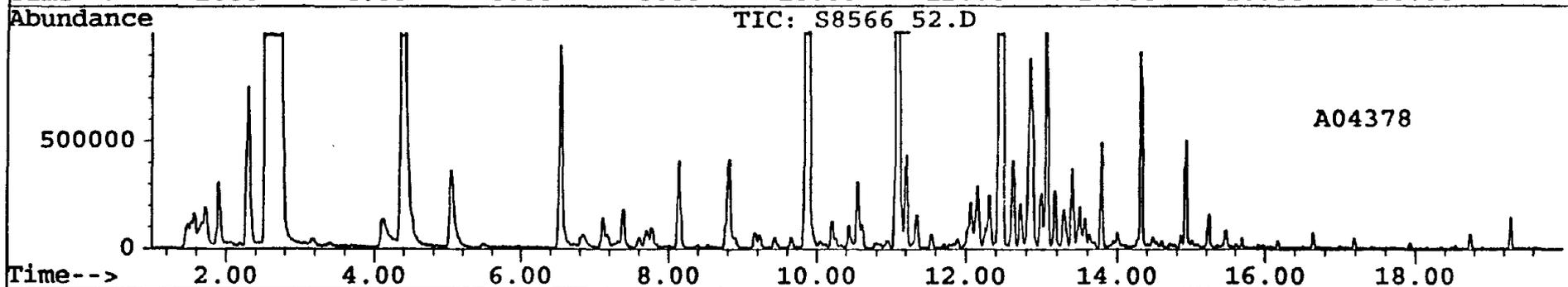
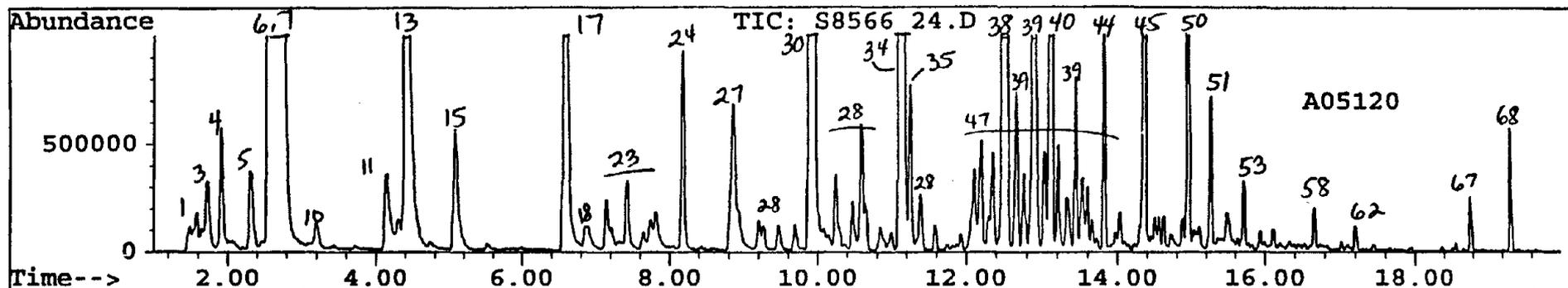


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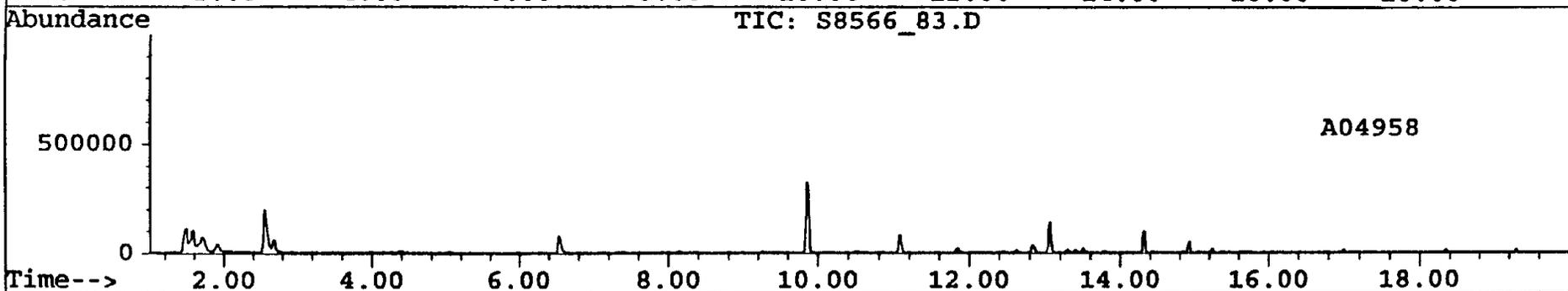
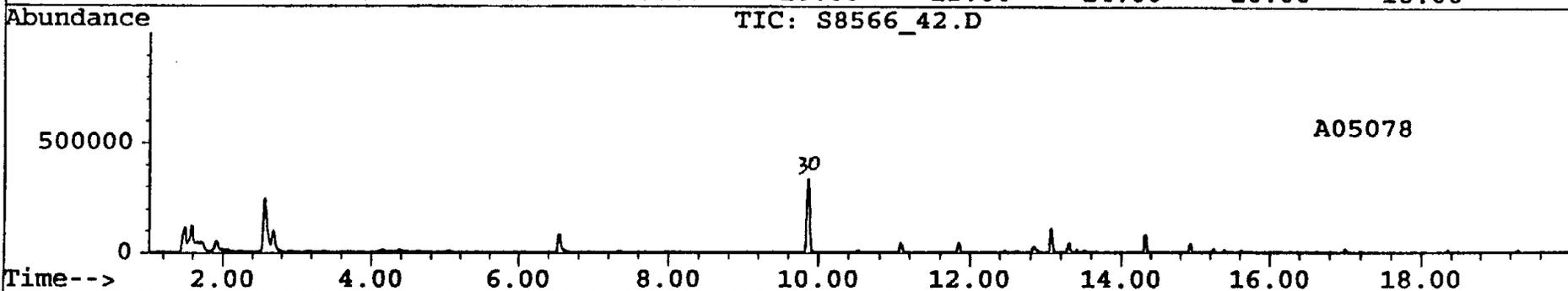
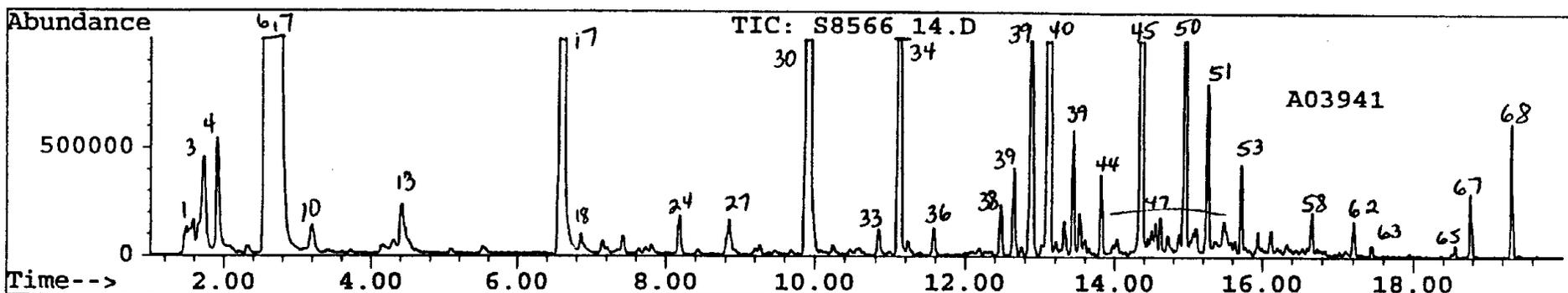
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Instrument : 5970 - In
Sample Name: A05422 PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 8



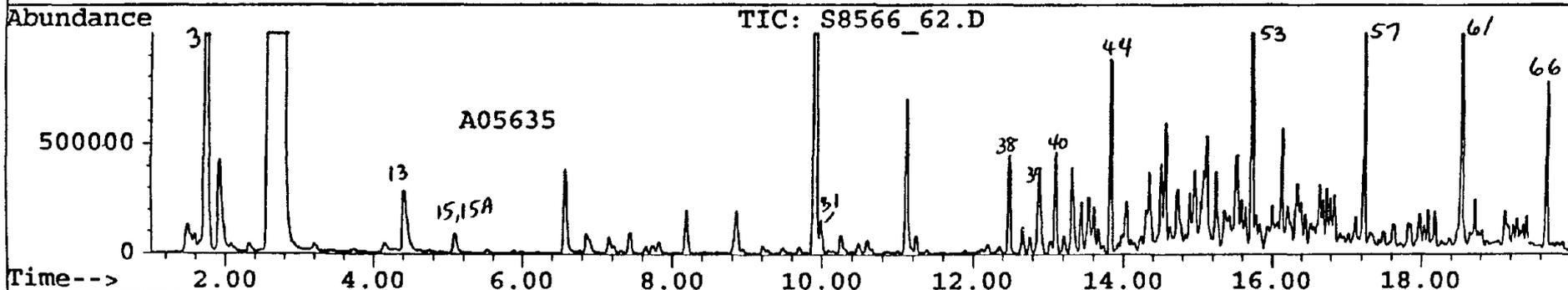
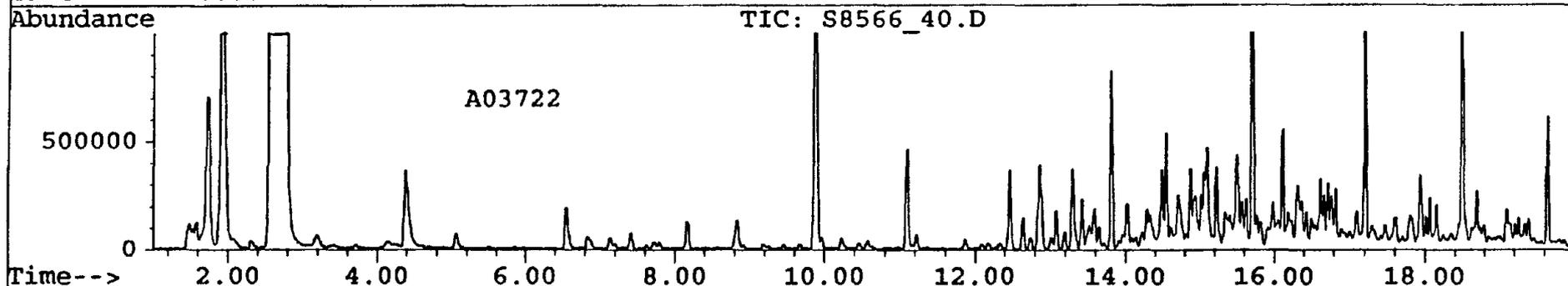
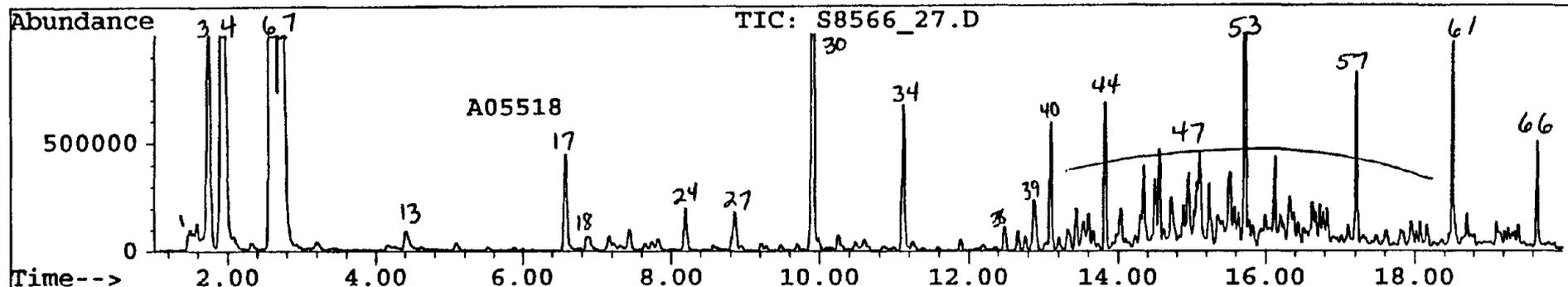
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Instrument : 5970 - In
Sample Name: A04509 PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 29



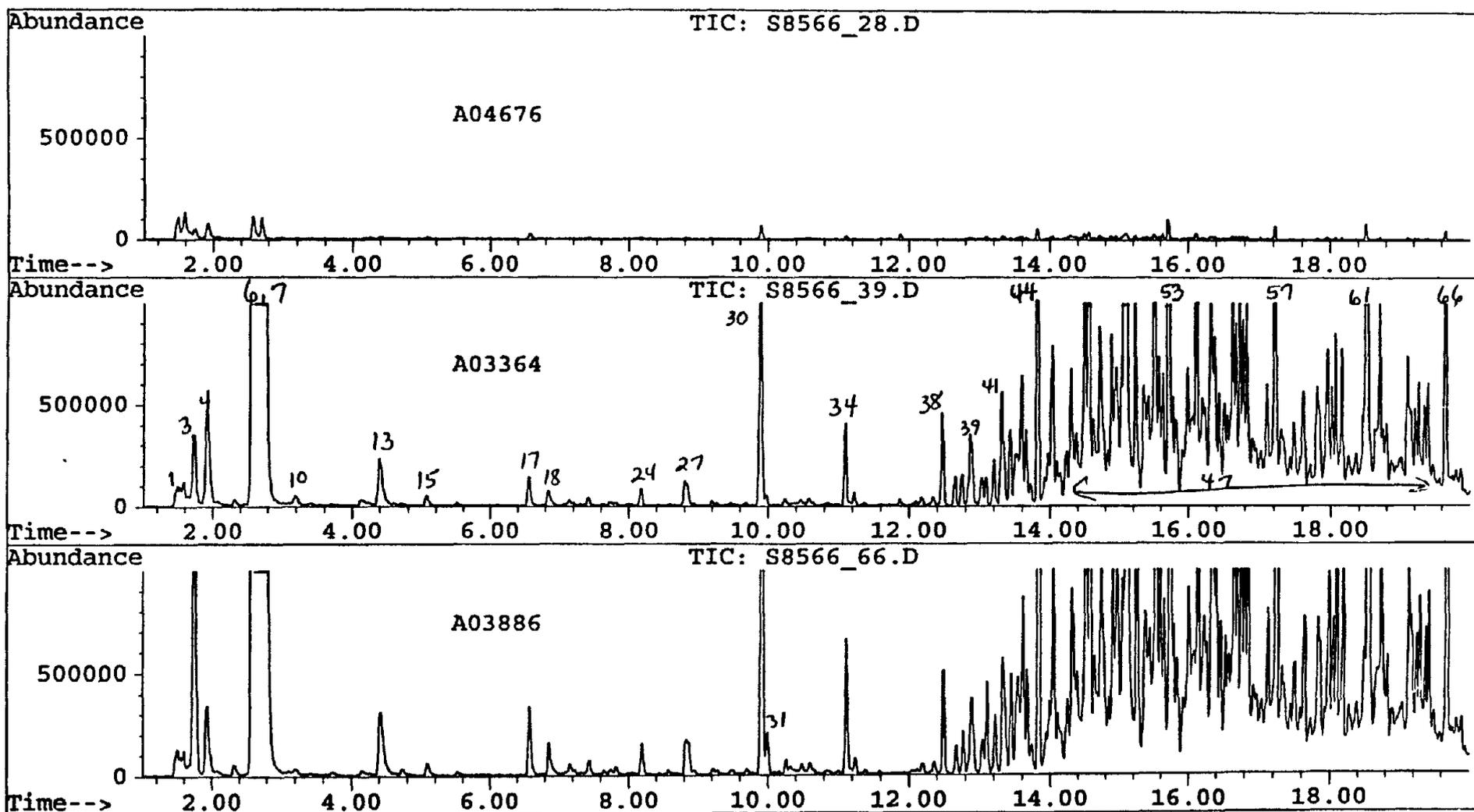
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Vial Number: 30



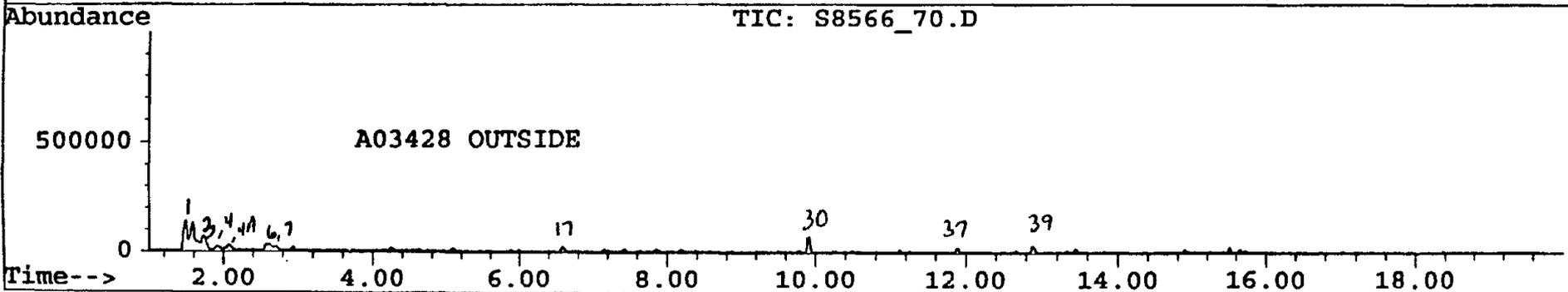
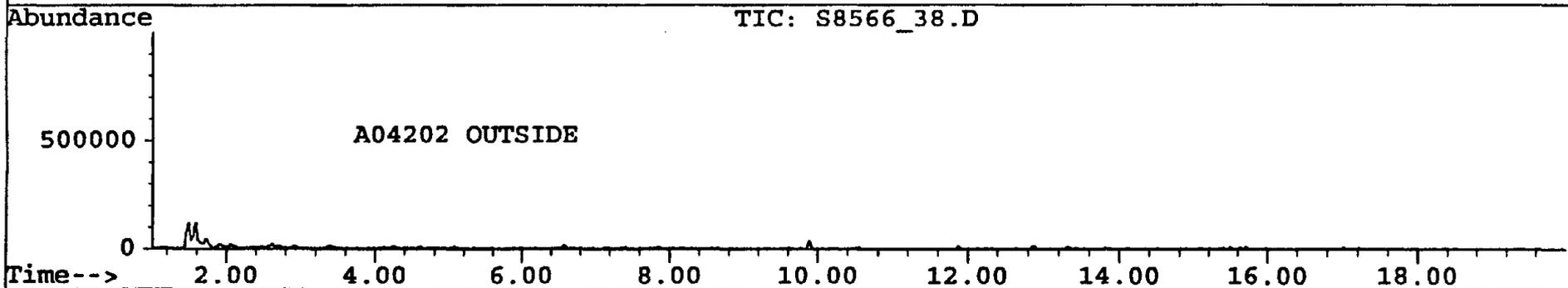
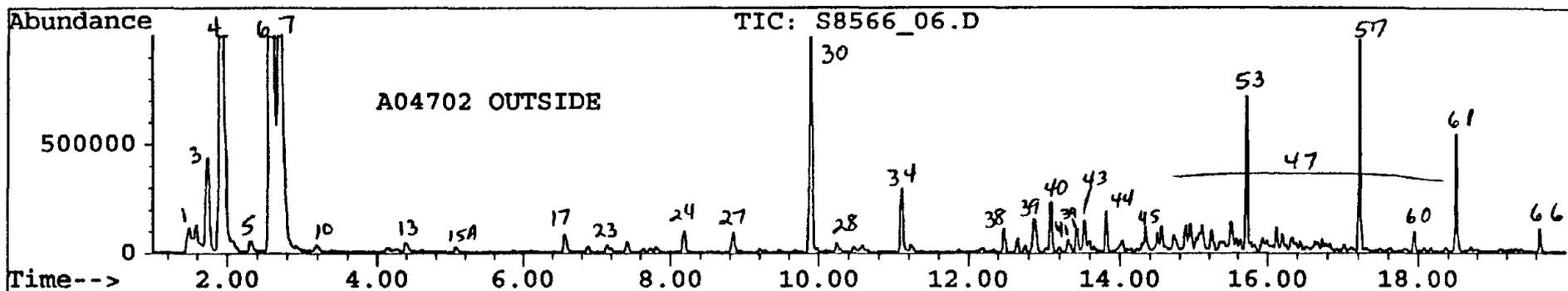
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Instrument : 5970 - In
Sample Name: A05635 PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 9



File : C:\HPCHEM\1\DATA\S8566\S8566_66.D
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Instrument : 5970 - In
Sample Name: A03886 PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 13

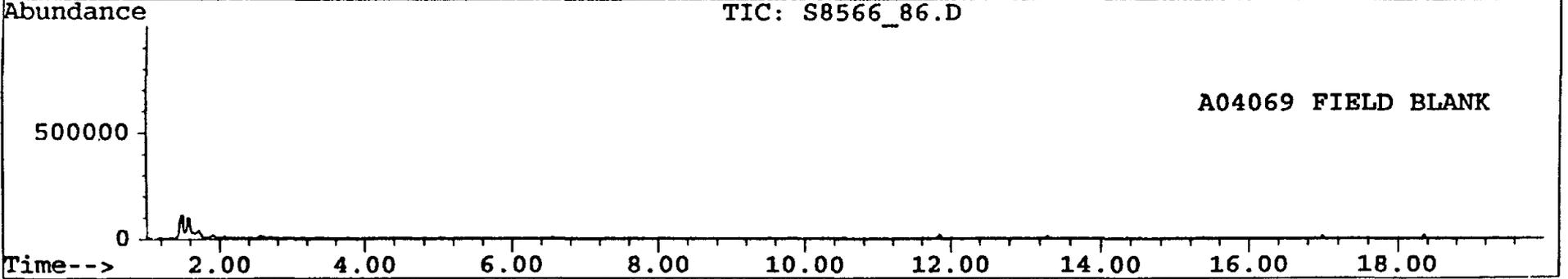
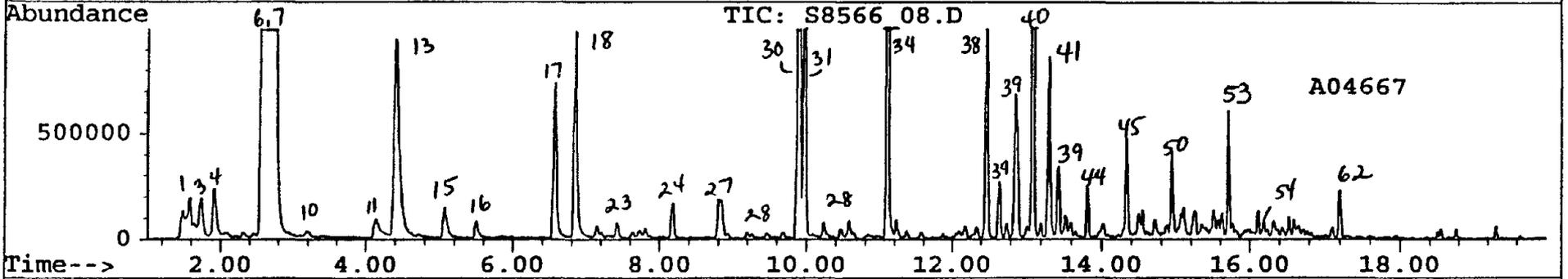
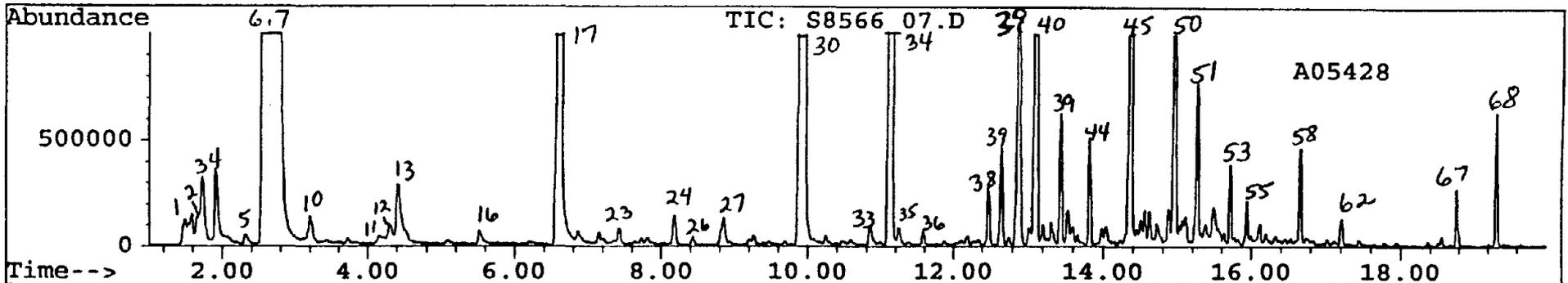


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Instrument : 5970 - In
Sample Name: A03428 OUTSIDE PURGED
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 17



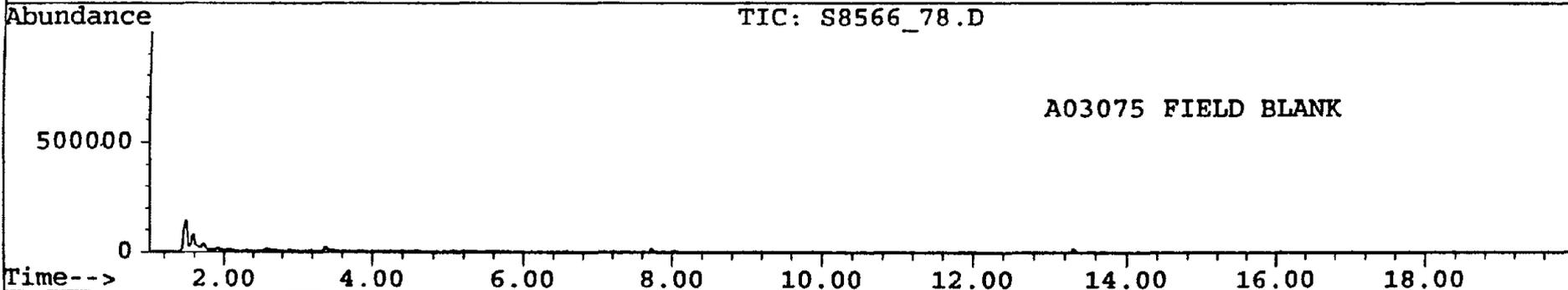
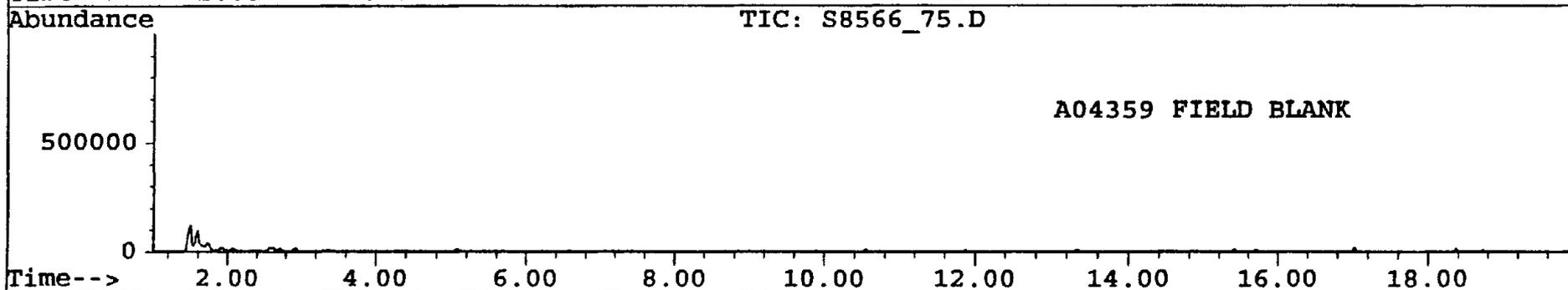
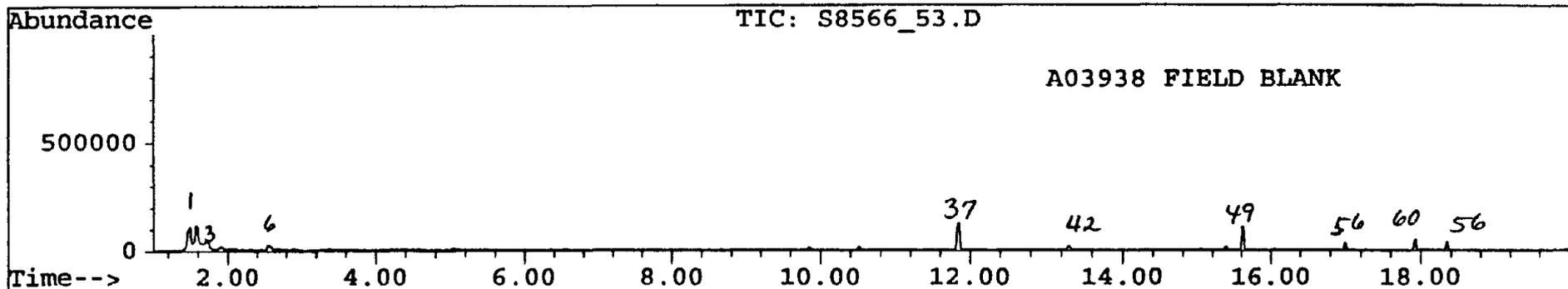
115

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Sample Name: A04069 PURGED FIELD BLANK
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 33



116

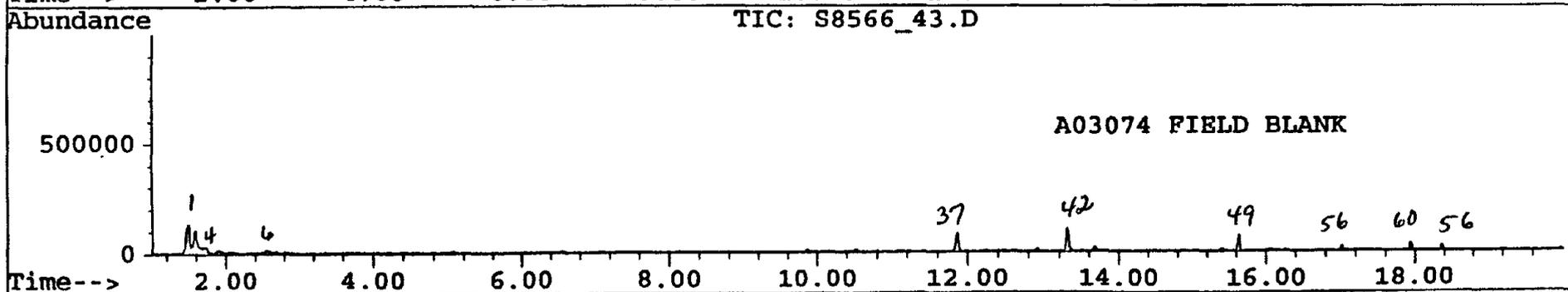
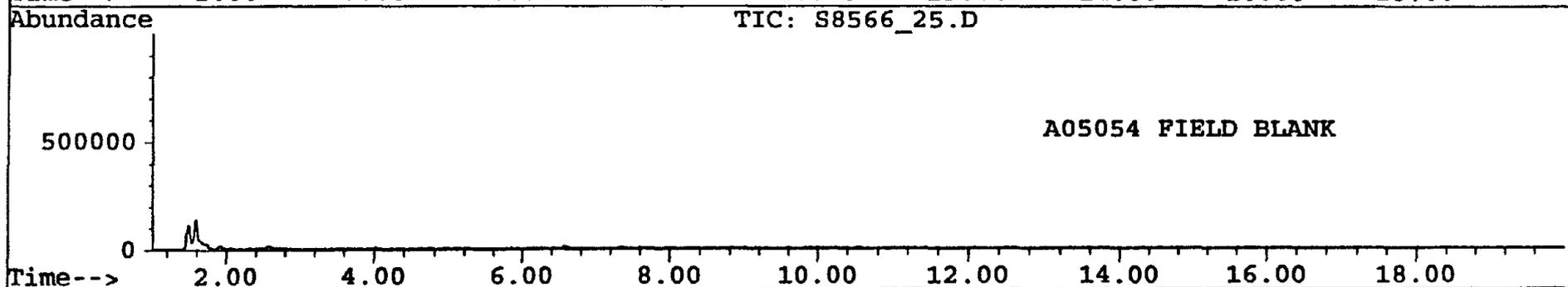
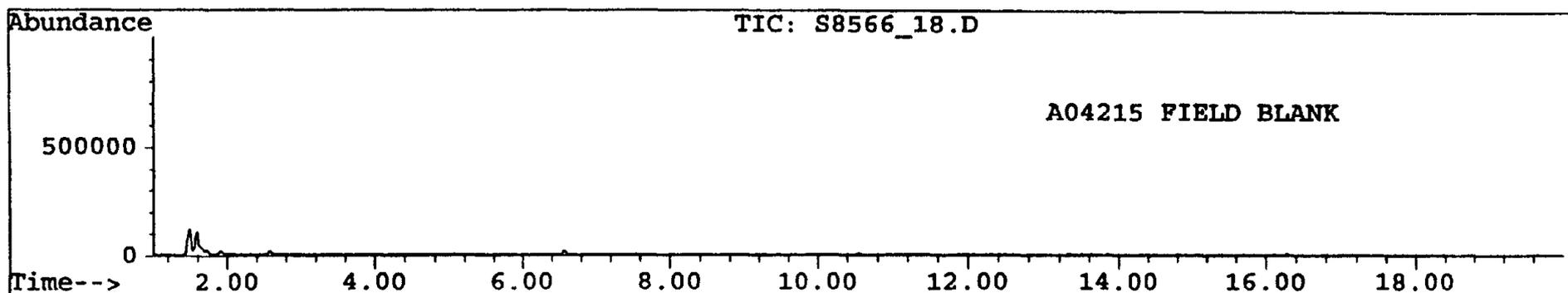
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Instrument : 5970 - In
Sample Name: A03075 PURGED FIELD BLANK
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 25



117

File : C:\HPCHEM\1\DATA\S8566\S8566_43.D
Operator : AAG
Acquired : 21 Nov 96 10:11 pm using AcqMethod TOTAL
Instrument : 5970 - In
Sample Name: A03074 FIELD BLANK
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 43

811



Appendix B
Hexahydrophthalic Anhydride Analysis





COPY

Memorandum

Date October 7, 1996

From Chemist, MSS, MRSB

Subject Sequence 8507-C; HHE #96-0100: Determination of Hexahydrophthalic Anhydride in Air Samples from Harley-Davidson Plant, Tomahawk, MI.

To Dawn Tharr, HETAB Laboratory Coordinator
Attn: Beth D. Reh
Through: Chief, MRSB, DPSE *RLL*

INTRODUCTION:

Two air samples, as PVC filters in cassettes, were submitted for the determination of hexahydrophthalic anhydride. These samples were taken at the Harley-Davidson production plant in Tomahawk, Michigan. Sampling was performed during molding and painting of accessories for the company's line of motorcycles.

Hexahydrophthalic anhydride exists as both the *cis* and *trans* isomers, is more correctly known as 1,2-cyclohexanedicarboxylic anhydride (CHDA), and is the saturated analog of phthalic anhydride. The determination of CHDA is not a standard NMAM analysis. Therefore, development of a method to determine CHDA had to be implemented prior to samples being analyzed. Expectations were that the response of the analyte would be linear over a concentration range that would incorporate the submitted samples.

EXPERIMENTAL:

Development of a method for the analysis of CHDA was based on an OSHA method for the determination of phthalic anhydride. One major concern for this work was the fact that the CHDA moiety does not have a strong chromophore in the UV range and therefore the lower limits of detection and quantitation could be abnormally restricted. Standards were prepared of both the *cis* and *trans* isomers to make certain that there was no difference in their retention times in the chromatographic analysis. Since there was no difference, the *cis* standard was used throughout this analysis for the preparation of standard solutions and the calibration curve.

The submitted samples were prepared for analysis by removing the PVC filter from the filter cassettes and placing the filter in a sample vial. One mL of ethanol was added to the sample, the vial capped and placed in an ultrasonic bath for 30 minutes. An aliquot of the ethanol solution was subsequently removed for injection into the LC instrument.

Chromatographic Analysis:

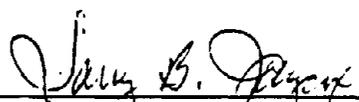
Mobile Phase: 27%/73%/0.1% MeCN/H₂O/H₃PO₄
Flow Rate: 0.4 mL/min
Column: Alltech Alltima C-18, 5 μm, 150 X 2.1 mm
Detector: UV @ 208 nm, sensitivity = 0.010 AUFS
Injector: Rheodyne 8125 valve, 50 μL sample loop

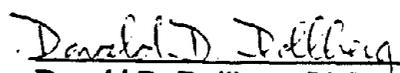
RESULTS:

Analysis results for the two air samples indicate that there was no hexahydrophthalic anhydride present. The LOD and LOQ that resulted from the limited method development work was 11 and 37 μg/sample respectively. Although these figures are relatively high compared to other methods, the limiting factor was the lack of response of the analyte in the UV range.

A verification analysis was performed on a peak in the air sample chromatogram which eluted near the CHDA peak. Verification was done by spiking the prepared air sample with an aliquot of the stock analytical solution. Figure 1 shows the five to ten minute scan portion of three chromatograms used in the verification process. The lower chromatogram shows the peak for the CHDA standard of 50 μg/sample. A chromatogram of the air sample labeled A-1 is shown in the center and shows the peak which elutes near the standard CHDA peak. The upper chromatogram shows the results of mixing the stock analytical solution and a portion of sample A-1. As shown in these scans, the unknown peak and the standard peak are well resolved from each other and that the unknown peak is not CHDA.

No further work is planned at this time.


Larry B. Jaycox, Ph.D.
Research Chemist


Donald D. Dollberg, Ph.D.
Chief, MSS, MRSB, DPSE

Attachment

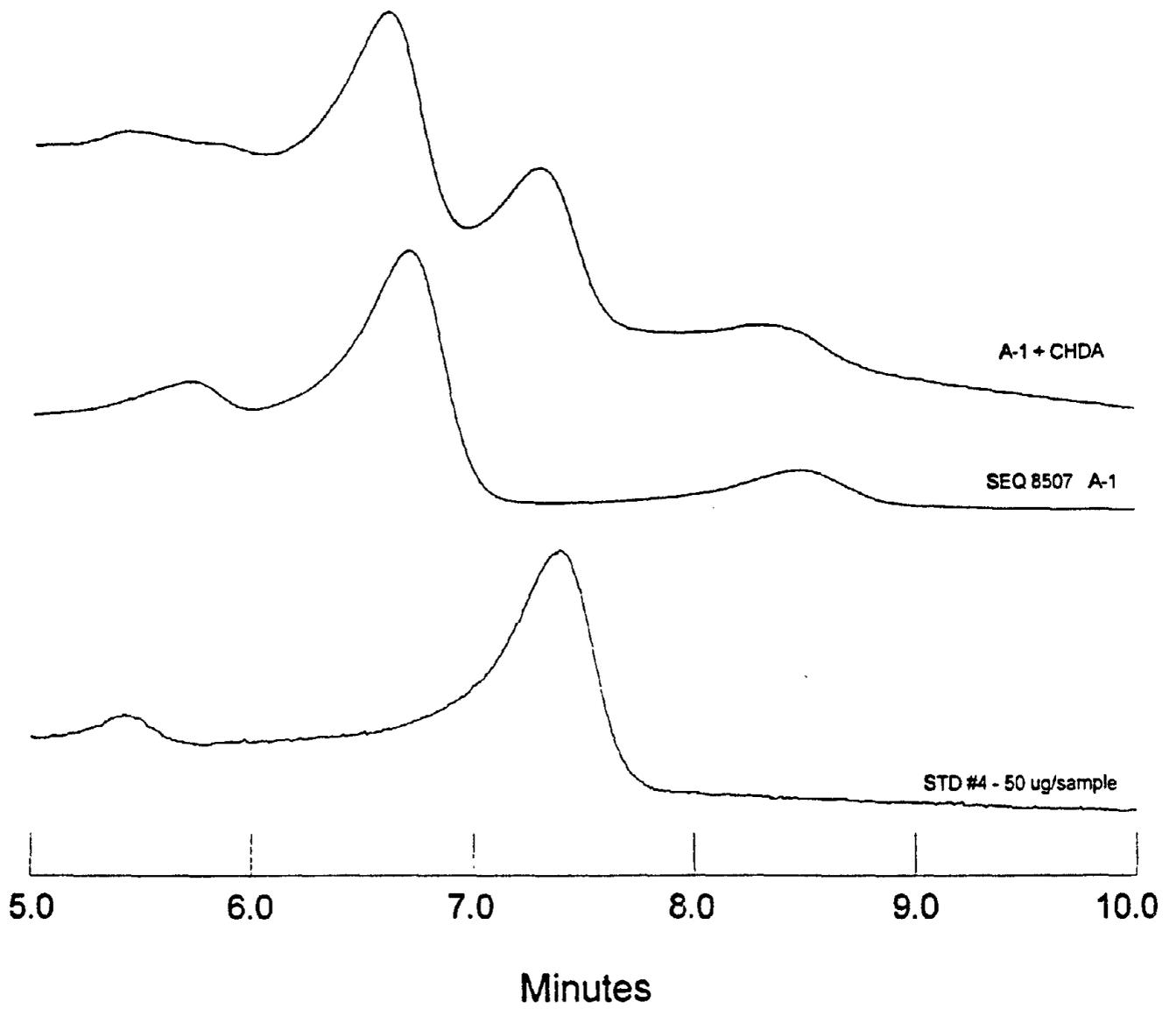


Figure 1