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NIOSH HEALTH HAZARD EVALUATION REPORT

HETA 95-0092-2545
Kaiser Aluminum
Mead, Washington

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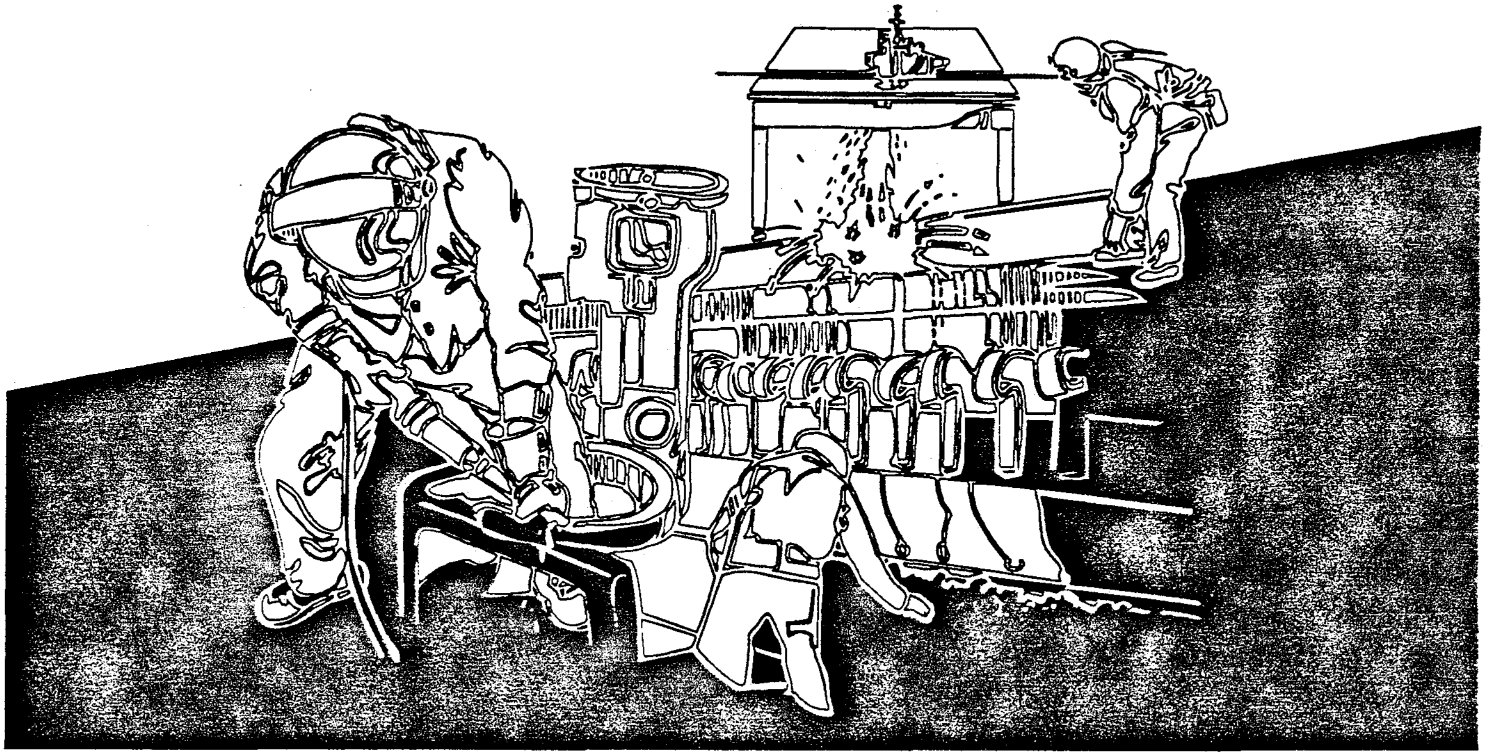

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PREFACE

The Hazard Evaluations and Technical Assistance Branch of the National Institute for Occupational Safety and Health 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 an employer or authorized representative of the employees, to determine whether any substance normally found in the place of employment has potential toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance to Federal, State, local agencies, labor, industry, and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

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I. SUMMARY

On December 16, 1994, NIOSH received a request to evaluate occupational exposures associated with the use of spent activated alumina (RALF) at Kaiser Aluminum, Mead, Washington. The request was submitted by a representative of the United Steelworkers of America, Local 329. The requestor felt that since the introduction of RALF, employees had experienced increased skin rash and nasal bleeding.

In February 1995, a NIOSH representative conducted an initial visit to the facility during which bulk samples of RALF were collected for analysis. In May 1995, a combined environmental/medical survey was conducted during which air samples were collected, records were reviewed, and employees were interviewed regarding the presence of any work-related health problems.

Of six bulk RALF samples analyzed, aluminum was found to be the major metallic component, ranging from 27.4% to 33.4% by weight, with a mean of 30.2%. Other substances detected at lesser concentrations included sodium (< 5%), calcium (< 0.3%), and trace concentrations of iron, molybdenum, magnesium, and zirconium (< 0.1%). The results of the bulk sample headspace analysis for qualitative identification of volatile organic compounds by gas chromatography-mass spectrophotometry (GC-MS) revealed only low levels of any volatile organic compounds in the samples.

In the long-term personal breathing zone (PBZ) samples, time-weighted average (TWA) concentrations of gaseous fluoride ranged from 0.21 to 1.5 milligrams per cubic meter of air (mg/m^3), with a mean concentration of 0.78 mg/m^3, concentrations of particulate fluorides ranged from 0.01 to 1.94 mg/m^3, with a mean of 0.78 mg/m^3, and concentrations of total fluorides ranged from 0.43 to 3.18 mg/m^3, with a mean of 1.56 mg/m^3. Two samples (3.13 and 3.18 mg/m^3) exceeded the evaluation criteria for total fluoride of 2.5 mg/m^3 as a TWA. Short-term concentrations of gaseous fluorides ranged from 2.0 to 15 mg/m^3, with a mean of 7.6 mg/m^3. Nine of these 11 samples exceeded the evaluation criteria of 5.0 mg/m^3 as a ceiling concentration for hydrogen fluoride. TWA concentrations of sulfur dioxide in long-term PBZ samples ranged from 1.37 to 2.43 mg/m^3, with a mean of 1.83 mg/m^3, and concentrations of particulate sulfate ranged from 0.12 to 0.46 mg/m^3, with a mean of 0.22 mg/m^3. Concentrations of sulfur dioxide in short-term PBZ samples ranged from 4.0 to 31 mg/m^3, with a mean of 12 mg/m^3. One sample exceeded the short-term evaluation criteria of 10 mg/m^3. Concentrations of trace metals and inorganic acids were found to be well below their respective evaluation criteria. Qualitative analysis of air samples for volatile organic compounds revealed only trace contaminant concentrations. No substantial difference was noted in contaminant concentrations with RALF use in long-term personal and area samples. Some variation was noted in the short-term samples, but this would be expected based on the nature of the specific tasks being monitored.

Meaningful comparisons of the prevalence rates of skin problems between employee groups who had and who had not used RALF were not possible in this investigation since there were only four employees working in the area where RALF had not been used. Interview results (74% of employees had experienced skin problems for two years) suggest that RALF use may cause skin problems because its introduction was followed by an increase of skin problems. However, the number of recorded skin disorders on the company injury report declined after RALF was introduced, even though no change in reporting practices was apparent. These findings showed conflicting evidence of a temporal relationship that would support an association between the use of RALF and skin problems.

On the basis of this evaluation, no substantial difference was noted in airborne potroom emissions with the use of RALF. The results of the medical survey were not conclusive regarding any increase in skin problems experienced by employees using RALF. In order to reduce the potential for adverse health effects from exposure to the potroom emissions, ongoing environmental and medical monitoring are recommended.

KEYWORDS: SIC 3334 (Primary Production of Aluminum), RALF, spent activated alumina, aluminum fluoride substitute, skin problems, dermatitis, nosebleeds, hydrogen fluoride, gaseous fluoride, particulate fluorides, sulfur dioxide, potrooms.

II. INTRODUCTION

On December 16, 1994, NIOSH received a request to evaluate occupational exposures associated with the use of spent activated alumina (RALF) at Kaiser Aluminum, Mead, Washington. The request was submitted by a representative of the United Steelworkers of America, Local 329. The requestor felt that since the introduction of RALF, employees had experienced increased skin rash and nasal bleeding.

On February 7, 1995, a NIOSH representative conducted an initial visit to the facility. Background information on the process of concern was obtained, and bulk samples of the RALF material were collected for analysis. On May 11 and 12, 1995, a combined environmental/medical survey was conducted by NIOSH representatives. Personal and area air samples were collected, records were reviewed, and employees were interviewed regarding the presence of any work-related health problems.

III. BACKGROUND

A. General Description of Aluminum Reduction Operations

Kaiser Aluminum, located in Mead, Washington, is a primary aluminum production facility which began operations in 1942. The Kaiser Aluminum Mead Works produces aluminum through the electrolytic reduction of aluminum oxide (alumina) by the Hall-Heroult process. In this process, alumina (Al_2O_3) is added to an electrolytic bath composed of cryolite (Na_3AlF_6), aluminum fluoride (AlF_3), and fluorospar (CaF_2). The bath is contained in a reduction cell or "pot" which is composed of an outer rectangular steel shell lined with insulating refractory material and an inner lining of a baked carbon material which serves as the cathode. Banks of 71 cells are connected in series and referred to as a "potline." The anodes used in these cells consist of copper conducting rods attached to a prebaked carbon electrode. Electricity is passed through the cell to break down the alumina into metallic aluminum and oxygen, which combines with the carbon from the carbon anode. The basic equation for the production of aluminum is as follows:

$$\underset{\text{(Alumina)}}{2\,Al_2O_3} + \underset{\text{(Carbon)}}{3\,C} \text{ ------> } \underset{\text{(Aluminum)}}{4\,Al} + \underset{\text{(Carbon Dioxide)}}{3\,CO_2}$$

The molten aluminum formed by this reaction is more dense then the electrolyte and sinks to the bottom of the pot from where it is periodically vacuum-tapped into a crucible. The alumina, which is used up as aluminum is produced, is replaced in the bath through hoppers located at the top of the cells. As the carbon from the anodes is consumed, they are replaced with new anodes, and the spent carbon anode "butts" are sent back to the carbon plant for recycling.[1,2]

During the aluminum reduction process, gaseous and particulate fluorides may be liberated. The equation for this reaction is as follows:

$$\underset{\text{(Cryolite)}}{2\,Na_3AlF_6} + \underset{\text{(Water)}}{3\,H_2O} \text{-------->} \underset{\text{(Alumina)}}{Al_2O_3} + \underset{\text{(Sodium Fluoride)}}{6\,NaF} + \underset{\text{(Hydrogen Fluoride gas)}}{6\,HF}$$

In order to replace the fluoride lost in this process and to maintain the bath ratio at the correct acidic conditions, aluminum fluoride is periodically added to the baths. The use of aluminum fluoride is critical to the efficiency and stability of the process, and it is the bath ingredient used in the second greatest quantity next to alumina.[1]

B. The Chemistry of RALF

Spent activated alumina (RALF) is a byproduct of the hydrogen fluoride alkylation process used in the gasoline refining industry. With the elimination of tetraethyl lead, alkylation has become increasingly important as a means of increasing the octane rating of gasoline. Alkylation is a chemical process that can be used in gasoline refining to combine small hydrocarbon molecules into larger molecules to produce high boiling fuel components which can then be blended to increase the octane content of fuels. The following formula illustrates this reaction:

$$\underset{\text{(Isobutane)}}{I\text{-}C_4H_{10}} + \underset{\text{(Butylene)}}{C_4H_8} \text{-------->} \underset{\text{(Isooctane)}}{C_8H_{18}}$$

The alkylation process utilized in this reaction requires a catalyst such as hydrofluoric acid. Following alkylation, propane and n-butane, which are byproducts of the reaction, leave the alkylation unit contaminated with free hydrofluoric acid and organic fluorides. The fluoride components must then be removed to allow these alkane gases to be suitable for consumer use. In order to accomplish this, the gas process stream is passed through defluorinators which contain beds of activated alumina (Al_2O_3). The hydrofluoric acid in the heated gas reacts with the alumina to produce alumina fluoride (AlF_3) and water. When the activated alumina in a defluorinator bed is no longer effective in removing the fluoride components from the gas, it is replaced. At this point, the waste absorber material, which is in the form of small gray spherical-shaped pellets, is classified as spent activated alumina or RALF.[3]

C. The Use of RALF at Kaiser Aluminum

As a result of its use as a fluoride scavenger in the defluorination process, RALF contains an appreciable content of aluminum fluoride. In 1990, Kaiser Mead Works began using RALF as a partial substitute for aluminum fluoride as a source of fluoride in the electrolytic baths. While limited use of RALF was begun on one of the pot lines (Line 2) in 1992, due to limited supplies, the material had to be stockpiled prior to more widespread use which began around mid-1993. Since that time, RALF has been used on 5 different lines (Lines 1, 2, 3, 6, and 8) .

Currently, there are several different refineries supplying Kaiser Aluminum Mead Works with RALF. Prior to obtaining the material from the refinery, Kaiser Aluminum requires that three samples from each batch of RALF be tested for fluoride and arsenic content. A minimum of 30% fluorine is required, with maximum specifications for carbon (5%), silicon (0.5%), iron (0.5%), potassium (0.2%), phosphorus (0.02%) and arsenic (0.05%). However, based on analysis conducted by the company on several batches, concentrations of fluorine were reported to typically range from 45 to 55%, with concentrations of arsenic less than 0.01%. When it has been determined by the company that the RALF meets the required specifications, it is shipped to the plant by rail. The bags containing the RALF are stored in a warehouse.

D. Description of Potroom Operations

Because the use of aluminum fluoride is critical to the efficiency and stability of the reduction process, additions of RALF are carefully controlled based on the individual chemistry of the pots. Weekly samples are taken to determine the amount of RALF and aluminum fluoride to be added to each pot. When needed, RALF is added, along with the other ore, to the hoppers above each pot by overhead crane. The hoppers then release approximately 12 lbs of ore into each pot every three to five minutes.

Each pot is equipped with local exhaust ventilation which normally captures the majority of the pot emissions. However, periodic tasks require personnel to remove some of the anode covers, which causes the employee to be in close proximity to the pot emissions. One such task is the replacement of spent anodes. In this task, "anode setters" are required to enter the potline, remove the covers from three anodes, and attach the anodes by chain to the overhead cranes which then remove the anodes from the line. The crane then returns with new anodes and the anode setter guides them into place and replaces the covers on the pots. Each pot may take anywhere from a few minutes to several minutes depending on whether any difficulties are encountered, such as a broken anode which requires the anode butt to be pulled out manually.

Another task that presents a potential for employee exposure to pot emissions is "crust" breaking. During this task, employees are required to break the "crust" around the electrodes to enable them to be removed. This task was in the process of being converted from a manual task to a more automated task. A mechanical crust breaker, which is a jackhammer assembly attached to an overhead crane, is now being used on most of the lines. In this process, the anode setters remove the anode covers and uses the jackhammer to break the crust around the anodes. However, metal bars are required when mechanical crust breaking is not used, or when the anode is not totally free from the crust during anode setting.

Like anode setters, the tappers and pot operators can also be potentially exposed to pot emissions. During the tapping process, the tapper uses a large vacuum spout to tap the aluminum metal from the side of the pot into a large crucible. Each pot may take several minutes to tap. The crucible and tapping spout are moved around the room by overhead crane. The pot operators travel through the line making adjustments on the pots to maintain optimal conditions.

Six pot lines were operational during the NIOSH survey, with two rooms per line. At the time of the environmental survey, there were 3 anode setters per room working 12-hour shifts. At the time of the survey Lines 1 and 2 were in the process of being converted from a 2-anode to a 3-anode setting schedule. This required a fourth anode setter because of the extra number of pots which needed to be set during the transition. A crane driver was present in each room and worked a 12-hour shift. Each line had a pot operator and tapper working 12-hour shifts.

E. Respiratory Protection

During crust breaking, anode setting, and tapping, the employees wear half-face respirators with cartridges designed for protection against dust, mists, and hydrogen fluoride (TC 23C-1116). Prior to 1992, the workers wore a single use disposable type respirator. A few of the workers with facial hair were allowed to wear positive-pressure air-purifying respirators. A written respiratory protection program was in place for these areas.

F. Environmental and Medical Monitoring

Environmental monitoring was conducted annually in the potroom. The various jobs were all monitored on a full-shift and short-term basis for hydrogen fluoride, particulate fluorides, and sulfur dioxide. Specific testing had also been conducted on bulk samples of the RALF since its introduction.

A medical monitoring program was also in place. For anode setters this included yearly audiograms, pulmonary function testing, and a respiratory symptom questionnaire. Urinary fluoride testing was conducted periodically (last time - 2 years prior to the NIOSH survey). At the time of the survey the company had hired a new occupational physician who was in the process of restructuring the medical surveillance program.

IV. MATERIALS AND METHODS

A. Initial Survey

During the initial survey of February 7, 1995, bulk samples were collected from six different batches of RALF. These samples were analyzed for trace metals using an inductively coupled plasma atomic emission spectrometer (ICP-AES) by a modified version of NIOSH Method 7300.[4] In addition, headspace analysis of the bulk samples was conducted for volatile organic compounds using gas chromatography-mass spectrophotometry (GC-MS). For this procedure, portions of each bulk sample were placed in glass tubes and held in place by salinized glass wool or cleaned quartz filters. Samples were analyzed using a thermal desorption system interfaced directly to a gas chromatograph and mass selective detector (TD-GC-MSD). The mass spectrometer was operated in the full scan mode (20-300 amu). A thirty-meter fused-silica capillary column was used for analysis. Samples were desorbed at 300°C for 10 minutes prior to each analysis. A blank tube was analyzed between each sample to minimize the possibility of carryover.

B. Environmental Survey

The environmental survey conducted on May 11 & 12, 1995, consisted of the collection of personal and area samples in the potroom to compare emissions from lines using RALF with emissions from lines where RALF was not in use. Sampling was limited to the potroom because this was determined to be the area where the highest RALF emissions would be expected. Samples were collected using battery-powered sampling pumps attached with Tygon tubing to a collection device which was located in the employees breathing zone. These were collected for durations that allowed a determination of both full-shift and short-term exposures. Area samples were collected in the same manner as the personal samples, except that the sampling devices were placed in a basket located in the middle of a pot line using RALF and at a similar location on a potline not using RALF. The following table contains a listing of the compounds which were sampled for, the sampling media used, the corresponding pump flow rates in liters per minute (LPM), and the analytical technique and NIOSH analytical method number.

Analyte	Sampling Media	Flow Rate	Analytical Technique	NIOSH Method #[4]
Particulate Fluoride	0.8-um cellulose ester membrane filter	2.0 LPM	Ion Chromatography/ Conductivity	7906
Gaseous Fluoride	Alkaline-impregnated backup pad	2.0 LPM	Ion Chromatography/ Conductivity	7906
Particulate Sulfate	0.8-um cellulose ester membrane filter	1.5 LPM	Ion Chromatography	6004
Sulfur Dioxide	Alkaline-impregnated cellulose filter	1.5 LPM	Ion Chromatography	6004
Trace Metals	0.8-um cellulose ester membrane filter	3.0 LPM	ICP-AES	7300
Inorganic Acids	Washed silica gel sorbent tube	0.3 LPM	Ion Chromatography	7903
Particulate Weight	Pre-weighed polyvinyl chloride filter	3.0 LPM	Gravimetric Weight	0500
Arsenic	0.8-um cellulose ester membrane filter	3.0 LPM	Atomic Absorption, Graphite Furnace	7901
Volatile Organics	Thermal desorption tubes	0.05 LPM	Thermal Desorption, GC-MS	No Method #

C. Medical Survey

The NIOSH medical evaluation consisted of employee interviews, a review of the company injury report, and a review of the proposed medical surveillance and existing respiratory protection program.

During site visits on May 10-12, 1995, the NIOSH medical officer interviewed 27 employees working in the potroom and later interviewed an additional three potroom workers over the phone. Total employment at the potroom in Kaiser Mead Works, during the survey was about 300 people. Employees were conveniently selected for interviews from six of eight lines in the potroom; the other two lines (Line 4 and Line 5) were not operating when site visits were made. Thirty-seven percent (11/30) of employees were selected from the list of employees who had notified an employee representative of their medical problems. Only four employees from Line 7, where RALF has not been used, were available for interview as a comparison group during the survey.

Interviews focused on employee skin problems (e.g., presence of current rash, location, duration, work-relatedness, medical evaluation, treatment, etc.) and included job history, past medical history about allergy and skin disease, presence of pulmonary symptoms (e.g., physician diagnosed asthma, cough, chest tightness, shortness of breath, wheezing, upper respiratory symptoms, etc.), and other medical symptoms (e.g., nose bleed, difficulty in concentration, peripheral neuropathy, musculoskeletal symptoms, etc.). The same questions were asked of every worker interviewed.

The NIOSH medical officer evaluated the temporal relationship between exposure to RALF and signs and symptoms, and compared symptom prevalence among employees working in the line where RALF has not been used with those among employees working in the lines where RALF has been used.

V. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs)[5], (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs)[6], and (3) the U.S. Department of Labor, OSHA Permissible Exposure Limits (PELs)[7]. In July 1992, the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air

Contaminants Standard. OSHA is currently enforcing the 1971 standards which are listed as transitional values in the current Code of Federal Regulations; however, some states operating their own OSHA approved job safety and health programs continue to enforce the 1989 limits. NIOSH encourages employers to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard and that the OSHA PELs included in this report reflect the 1971 values.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8-to-10-hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

Following is a discussion of the toxicity and evaluation criteria for the major substances evaluated in this survey.

A. Particulate and Gaseous Fluorides, Inorganic

Short-term exposure to particulate fluorides may cause irritation of the eyes and respiratory tract. Irritation of the eyes and nose has been reported when fluoride concentration has reached 5 milligrams per cubic meter of air (mg/m^3).[8] Nose bleeds and sinus trouble may develop on chronic exposure to low concentrations of fluorides in air.[9] Repeated exposure to fluorides can cause calcification of the bone and ligaments that may result in stiffness and limitation of motion, a condition known as fluorosis. Fluorides can also cause dermatitis on repeated exposure.[8] The NIOSH REL, OSHA PEL and ACGIH TLV for inorganic fluorides, all are 2.5 mg/m^3 as a TWA, and are intended to prevent skeletal fluorosis.

In addition to particulate fluorides, gaseous fluorides (primarily hydrogen fluoride) also are emitted from the aluminum reduction process. Short-term exposure to hydrogen fluoride (HF) can cause severe irritation of the nose, throat, and lungs. Exposure to low concentration of vapors of hydrogen fluoride on a long-term basis can cause chronic irritation and congestion of the nose, throat, and bronchial tubes. Hydrogen fluoride has been reported to cause dermatitis on prolonged exposures to concentrations ranging from 1.8 to 8.1 mg/m^3.[8] The NIOSH REL and OSHA PEL for hydrogen fluoride are 2.5 mg/m^3 as a TWA, while the ACGIH TLV is a ceiling concentration of 2.3 mg/m^3.

B. Sulfur Dioxide and Particulate Sulfates

Sulfur dioxide is intensely irritating to the eyes, mucous membranes, and respiratory tract. It can cause burning of the eyes, coughing, and chest tightness. Exposure may cause severe breathing difficulties. It forms sulfurous acid on contact with moist membranes.[9] NIOSH and ACGIH have set an exposure limit for sulfur dioxide of 5 mg/m^3 as a TWA, and, OSHA, and ACGIH have set limits of 13 mg/m^3 as a STEL; the NIOSH STEL REL is 10 mg/m^3.

Particulate sulfate may be present in aluminum reduction emissions as the salts of metals, such as aluminum sulfate. Aluminum sulfate is water soluble and, as such, can be hydrolyzed to form sulfuric acid.[10] The ACGIH TLV for soluble salts, as aluminum, is 2 mg/m^3 as a TWA.

C. Other Miscellaneous Compounds

The following table lists additional substances which were evaluated during the environmental survey. For each substance the evaluation criteria are listed (in mg/m^3), along with a brief summary of the primary health effects. All criteria listed are for TWA exposures, unless followed by a "C," which denotes a ceiling concentration.

Substance	NIOSH REL	OSHA PEL	ACGIH TLV	Primary Health Effects[8,9]
Aluminum	5		10	Irritation of skin, eyes, and respiratory tract
Arsenic	0.002 C	0.01	0.01	Dermatitis, mucous membrane irritation, cancer
Hydrochloric Acid	7	7	7.5 C	Dermatitis, respiratory tract irritatation, laryngitis, and bronchitis
Nickel	0.015	1	1	Skin sensitization, chronic eczema, cancer
Phosphoric Acid	1	1	1	Irritation of the skin, eyes, and upper respiratory tract
Sulfuric Acid	1	1	1	Irritation of the eyes and respiratory tract, bronchitis, dental enamel etching

VI. RESULTS

A. Initial Survey

The following table presents the results of the bulk RALF sample analysis for trace metals. Each element is listed as a percentage of its weight in the bulk sample.

Substance	Bulk 1	Bulk 2	Bulk 3	Bulk 4	Bulk 5	Bulk 6
Aluminum	30.9%	29.7%	31.1%	33.4%	28.7%	27.4%
Calcium	0.153%	0.165%	0.206%	0.171%	0.123%	0.133%
Iron	0.012%	0.012%	0.012%	0.017%	0.011%	0.012%
Magnesium	0.065%	0.091%	0.074%	0.080%	0.054%	0.055%
Molybdenum	0.079%	0.068%	0.070%	0.080%	0.064%	0.064%
Sodium	3.45%	3.74%	3.77%	4.12%	3.23%	3.19%
Zirconium	0.020%	0.022%	0.022%	0.032%	0.025%	0.024%

There was very little variability in the elemental content of the six bulk RALF samples. Aluminum was found to be the major metallic component in the samples, ranging from 27.4% to 33.4% by weight, with a mean of 30.2%. Other substances detected at lesser concentrations included sodium (< 5%), calcium (< 0.3%), and trace concentrations of iron, molybdenum, magnesium, and zirconium (< 0.1%). The following metals were not detected in the bulk samples (< than the limit of detection of 0.005% by weight); arsenic, barium, beryllium, cadmium, cobalt, chromium, copper, lanthanum, lithium, manganese, nickel, phosphorus, lead, selenium, silver, strontium, tellurium, titanium, thallium, vanadium, yttrium, and zinc.

The results of the bulk sample headspace analysis for qualitative identification of volatile organic compounds by GC-MS are presented in Attachments 1 - 7. These attachments are copies of the reconstructed total ion chromatograms from the sample analysis. The chromatograms are all scaled the same for comparison, and spread out into two sections to improve the visual separation among peaks. A separate table, Attachment 8, is enclosed which lists each peak number with its corresponding identification.

All samples except B-1 had very low levels of any volatile compounds. Compounds detected in B-1 included tetrafluorosilane, numerous C_3-C_{16} aliphatic hydrocarbons, alkyl benzenes, methyl ethyl ketone, and a few sulfide compounds. Tetrafluorosilane may be a reaction product formed between the hydrofluoric acid (known to be present) and various silicon compounds present in the analytical system (silanized glass wool, SI-based GC column). Hydrofluoric acid (HF) itself would not have been detected under these analytical conditions since the scan range was too high to detect HF, which has a molecular weight of 20. Hydrochloric acid and alkyl phenols were also detected in some of the other heated samples.

B. Environmental Survey

The following table presents the results of the long-term personal samples collected for gaseous and particulate fluorides during the environmental survey.

Sample Date	Job and Location Sampled	Sample Time (minutes)	Sample Volume (Liters)	Gaseous Fluoride (mg/m^3)	Particulate Fluoride (mg/m^3)	Total Fluoride (mg/m^3)	RALF Use
5/11/95	Anode Setter Line 2 Room 8	400	800	1.50	1.63	3.13	Partial
5/11/95	Anode Setter Line 2 Room 8	348	696	0.91	0.66	1.57	Partial
5/11/95	Anode Setter Line 1 Room 4	466	932	1.07	0.02	1.09	Partial
5/11/95	Anode Setter Line 1 Room 4	471	942	0.86	1.06	1.92	Partial
5/11/95	Craneman Line 1 Room 4	465	930	0.35	0.41	0.76	Partial
5/11/95	Anode Setter Line 7 Room 28	430	860	0.81	0.98	1.79	No
5/11/95	Anode Setter Line 7 Room 28	433	866	1.04	1.27	2.31	No
5/11/95	Anode Setter Line 7 Room 28	431	862	0.21	0.22	0.43	No
5/12/95	Craneman Line 8 Room 32	382	764	0.22	0.22	0.45	No
5/12/95	Anode Setter Line 8 Room 32	375	750	1.05	1.27	2.32	No
5/12/95	Craneman Line 3 Room 12	364	728	0.30	0.63	0.93	Yes
5/12/95	Anode Setter Line 3 Room 12	365	730	0.85	0.54	1.38	Yes
5/12/95	Anode Setter Line 3 Room 12	367	734	1.24	1.94	3.18	Yes
5/12/95	Anode Setter Line 2 Room 8	338	676	0.47	0.33	0.80	Yes
5/12/95	Anode Setter Line 2 Room 8	319	638	0.77	1.27	2.04	Yes
5/12/95	Anode Setter Line 2 Room 8	332	664	0.78	0.01	0.80	Yes

TWA concentrations of gaseous fluoride ranged from 0.21 to 1.5 mg/m^3, with a mean of 0.78 mg/m^3. These concentrations were all below the evaluation criteria of 2.5 mg/m^3 for hydrogen fluoride. TWA concentrations of particulate fluorides ranged from 0.01 to 1.94 mg/m^3, with a mean of 0.78 mg/m^3. These concentrations were below the evaluation criteria of 2.5 mg/m^3. TWA concentrations of total fluorides (arrived at by calculating a concentration from the combined weights of particulate and gaseous fluoride in the samples) ranged from 0.43 to 3.18 mg/m^3, with a mean of 1.56 mg/m^3. Two samples (3.13 and 3.18 mg/m^3) exceeded the evaluation criteria for total fluoride of 2.5 mg/m^3 as a TWA.

In order to illustrate the effect that the use of RALF would have on employee exposures, the following table classifies the sample results as to whether or not RALF was used on the potline during the period of sample collection. The samples listed as "partial" were collected on a day when RALF was not used until approximately half-way through the period of sample collection. The following table presents comparative data on the long-term fluoride exposures when classified by the use of RALF. The range of exposures are presented, followed by the mean exposure in parenthesis ( ).

	No RALF Use	RALF Use	Partial RALF Use
Gaseous Fluorides	0.30 to 1.24 mg/m³ (0.74 mg/m³)	0.21 to 1.05 mg/m³ (0.67 mg/m³)	0.35 to 1.50 mg/m³ (0.94 mg/m³)
Particulate Fluorides	0.01 to 1.94 mg/m³ (0.78 mg/m³)	0.22 to 1.27 mg/m³ (0.79 mg/m³)	0.02 to 1.63 mg/m³ (0.76 mg/m³)
Total Fluorides	0.80 to 2.04 mg/m³ (1.52 mg/m³)	0.43 to 2.32 mg/m³ (1.46 mg/m³)	0.76 to 3.13 mg/m³ (1.69 mg/m³)

As evidenced by these data, the concentrations of gaseous, particulate, and total fluorides did not appear to differ substantially with the use of RALF.

The following table presents the results of the short-term samples collected for fluorides. Each sample reflects an employee exposure during anode setting on a single pot, which is the time when the highest exposures would be expected.

Sample Date	Job and Location Sampled	Sample Time (minutes)	Sample Volume (liters)	Gaseous Fluoride (mg/m³)	Particulate Fluoride (mg/m³)	Total Fluoride (mg/m³)	RALF Used
5/12/95	Anode Setter Line 8 Room 32	5	10	4.10	5.30	9.40	No
5/12/95	Anode Setter Line 8 Room 32	10	20	2.00	1.00	3.00	No
5/12/95	Anode Setter Line 8 Room 32	13	26	3.30	1.58	4.88	No
5/12/95	Anode Setter Line 8 Room 32	6	12	10.00	4.83	14.83	No
5/12/95	Anode Setter Line 8 Room 32	10	20	10.00	4.10	14.10	No
5/12/95	Anode Setter Line 3 Room 12	6	12	6.17	8.33	14.50	Yes
5/12/95	Anode Setter Line 3 Room 12	5	10	5.30	4.60	9.90	Yes
5/12/95	Anode Setter Line 3 Room 12	4	8	15.00	10.88	25.88	Yes
5/12/95	Anode Setter Line 3 Room 12	6	12	11.67	4.92	16.58	Yes
5/12/95	Anode Setter Line 3 Room 12	8	16	8.13	3.81	11.94	Yes
5/12/95	Anode Setter Line 3 Room 12	5	10	7.70	9.00	16.70	Yes

Short-term concentrations of gaseous fluorides ranged from 2.0 to 15 mg/m^3, with a mean of 7.6 mg/m^3. Nine of the 11 samples exceeded the NIOSH REL of 5.0 mg/m^3 as a ceiling concentration for hydrogen fluoride. There are no ceiling or STEL criteria for particulate or total fluorides.

When these data are examined in light of the use of RALF, a difference is evident (a mean of 9.0 for short-term samples where RALF was used and a mean of 6.0 where RALF was not used). However, the average sample period on the non-RALF lines was approximately 9 minutes vs. 6 minutes for the samples where RALF was used. The longer sampling period for the non-RALF line, which likely included time spent waiting for the crane when the employee would stand away from the pots, would have been expected to have a dilution effect on the exposures.

The following table presents the results of the long-term personal samples collected for sulfur dioxide and particulate sulfate.

Sample Date	Job and Location Sampled	Sample Time (minutes)	Sample Volume (liters)	Sulfur Dioxide (mg/m^3)	Particulate Sulfate (mg/m^3)	RALF Use
5/11/95	Anode Setter Line 7 Room 28	431	646.5	2.43	0.12	No
5/11/95	Anode Setter Line 2 Room 8	187	280.5	1.78	0.15	Yes
5/11/95	Anode Setter Line 1 Room 4	452	678	1.47	0.16	Yes
5/12/95	Anode Setter Line 8 Room 32	371	556.5	1.37	0.25	No
5/12/95	Anode Setter Line 2 Room 8	335	502.5	1.95	0.19	Yes
5/12/95	Anode Setter Line 3 Room 12	302	453	1.98	0.46	Yes

TWA concentrations of sulfur dioxide in the personal samples ranged from 1.37 to 2.43 mg/m^3, with a mean of 1.83 mg/m^3. These concentrations were below the NIOSH REL of 5 mg/m^3 as a TWA. TWA concentrations of particulate sulfate ranged from 0.12 to 0.46 mg/m^3, with a mean of 0.22 mg/m^3. Although the exact form of sulfate was not determined by this analytical method, these concentrations would be below the ACGIH TLV of 2 mg/m^3 for aluminum sulfate, a compound which would be expected to be present.

Although a limited number of samples were collected, there did not appear to be a substantial difference in the concentrations of sulfur dioxide and particulate sulfate between lines using RALF and lines not using RALF. The average concentrations of sulfur dioxide were 1.8 mg/m^3 for the lines where RALF was being used, and 1.9 mg/m^3 for the non-RALF lines. Average particulate sulfate concentrations for lines using RALF was 0.24 mg/m^3, and 0.18 for non-RALF lines.

The following table presents the data for the short-term personal samples collected for sulfur dioxide and particulate sulfate.

Sample Date	Job and Location Sampled	Sample Time (minutes)	Sample Volume (liters)	Sulfur Dioxide (mg/m³)	Particulate Sulfate (mg/m³)	RALF Use
5/12/95	Anode Setter line 8 Room 32	5	10	31.00	0.60	No
5/12/95	Anode Setter line 8 Room 32	12	24	6.25	0.50	No
5/12/95	Anode Setter line 8 Room 32	10	20	4.00	0.20	No
5/12/95	Anode Setter Line 3 Room 12	16	24	6.25	1.25	Yes

Concentrations of sulfur dioxide ranged from 4.0 to 31 mg/m^3, with a mean concentration of 12 mg/m^3. One sample exceeded the NIOSH REL of 10 mg/m^3 as a STEL. Concentrations of particulate sulfate ranged from 0.20 to 1.25 mg/m^3, with a mean of 0.64 mg/m^3. There are no short-term evaluation criteria for particulate sulfates.

Average concentrations for sulfur dioxide were highest on the non-RALF lines, but due to the wide variability in the results and the limited number of samples, comparisons of these results would not be meaningful.

The results of the personal samples collected for inorganic arsenic are included in the following table.

Sample Date	Job and Location Sampled	Sample Time (minutes)	Sample Volume (liters)	Inorganic Arsenic (mg/m³)	RALF Use
5/12/95	Tapper Line 3 Room 14	295	590	0.00068	Yes
5/12/95	Tapper Line 2 Room 10	165	495	0.00042	Yes
5/12/95	Tapper Line 8 Room 34	155	465	0.0010	No

TWA concentrations of inorganic arsenic ranged from 0.00068 mg/m^3 to 0.0010 mg/m^3, with a mean concentration of 0.00071 mg/m^3. These results are below the NIOSH REL of 0.002 mg/m^3 as a ceiling concentration, and the OSHA PEL of 0.01 mg/m^3 as an 8-hour TWA. Based on the limited number of samples, a comparison between RALF and non-RALF lines would not be meaningful.

The following table shows the results of the area samples collected on the RALF and non- RALF lines for fluorides, sulfur dioxide, sulfates, and total particulate. The samples were collected at similar locations on the two lines to allow for comparison of the results.

Sample Location	RALF Use	Gaseous Fluoride (mg/m³)	Particulate Fluoride (mg/m³)	Total Fluoride (mg/m³)	Sulfur Dioxide (mg/m³)	Particulate Sulfate (mg/m³)	Total Particulate (mg/m³)
Line 8 Room 32	No	0.32	0.15	0.47	0.51	0.32	0.45
Line 3 Room 12	Yes	0.27	0.12	0.39	0.42	0.33	0.50

As evidenced by these data, there was little difference in these results between the RALF and non-RALF lines. Since these were area samples located on the potlines, and are not personal samples, comparison to exposure criteria would not be appropriate.

The following table shows the results of the area samples collected on the RALF and non- RALF lines for various inorganic acids. The samples were collected in the manner described above to allow for comparison of the results.

Sample Location	RALF Use	Hydrofluoric Acid (mg/m³)	Hydrochloric Acid (mg/m³)	Sulfuric Acid (mg/m³)	Phosphoric Acid (mg/m³)	Nitric Acid (mg/m³)
Line 8 Room 32	No	0.43	0.02*	0.56	0.06*	<LOD
Line 3 Room 12	Yes	0.49	0.02*	0.05*	<LOD	<LOD

Little difference is noted in contaminant concentrations between the RALF and non-RALF lines with the exception of sulfuric acid, where a higher concentration was measured on the line where RALF was not in use. However, wide variability in sample results for other sulfur containing compounds (SO_2 and particulate sulfate) were also found in the personal samples. It should be noted that the methodology used to collect these acid mist samples (NIOSH Method #7903) is subject to interference by particulate salts of the acids listed. Since the particulate salts of many of these acids are known to be present, these results would be expected to overstate the actual airborne acid concentrations. Since these are area samples, comparison to evaluation criteria would not be appropriate.

Area samples were also collected on each of the two lines for trace metals analysis. However, during the analytical process, the sample from the line using RALF was lost in preparation due to a faulty microwave vessel. Therefore, comparative data from the area samples for trace metals is not available. The results of the trace metal analysis for the sample for the line where RALF was not used revealed aluminum to be the metallic substance found at the highest concentration, 0.14 mg/m³, with nickel found at a concentration of 0.003 mg/m³. Arsenic and beryllium were detected, but at concentrations below the limit of quantitation of the analytical method used. Since these were area samples, comparison to exposure criteria would not be appropriate.

The results of the air samples collected for qualitative determination of volatile organic compounds are provided in Attachments 9 - 16. These attachments are copies of the reconstructed total ion chromatograms, and are scaled the same for comparison. The location of sample collection is noted on each chromatogram. A separate table, Attachment 17, is enclosed which lists each peak number with its corresponding identification. As noted from these attachments, only trace levels of any contaminants were detected. Compounds detected above blank levels on some samples were sulfur dioxide, p-dichlorobenzene, and a couple of unknown, possibly sulfur containing compounds.

C. Medical

Interviews

The mean age of the 30 employees interviewed was 34.6 years old. All were male, and all but one were white. Thirty percent (9 of 30) were current smokers. Seventy percent (21/30) of the interviewed employees were carbon setters. Twenty-three percent (7/30) were mechanized cell operators, and the remaining two were a crane operator and a laborer. The mean length of time in the current job was 5 years, and the mean tenure at the Kaiser aluminum plant was 7.3 years.

Seventy-seven percent (23/30) of all interviewed employees had experienced skin problems (e.g., rash, itch, burning, bump, flaky, dry, hair loss, etc.) during the past year. However, only 17% (5/30) of the interviewed employees were observed to have skin rash during the survey. Thirteen percent (4/30) of all employees interviewed had a history of eczema, and 27% (8/30) had a history of allergy. Fifty percent (2/4)of employees working in Line 7, where RALF has not been used, also had experienced skin problems. The facial area (e.g., cheek, forehead, scalp, neck, etc.) was the most frequently affected location, with 17 of the 23 people who had skin problems reporting that their face was involved. Four employees had experienced skin problems in multiple locations (e.g., face, hands, groins, legs, etc.). Seventy-four percent of employees (17/23) who had skin problems reported that they had experienced skin problems for two years. Seventy percent of these employees (16/23) reported that their skin problems were relieved when they were no longer exposed to RALF, such as during weekends or on vacation.

More than half of interviewed employees had experienced respiratory symptoms during the past year (cough-62%; chest tightness-54%; and shortness of breath-50%). Three employees (10%) had physician-diagnosed adult onset asthma. Sixty percent (18/30) of all interviewed workers had musculoskeletal symptoms (e.g., low back pain, shoulder pain, carpal tunnel syndrome, etc.). Thirty-seven percent (11/30) of all interviewed employees had experienced nose bleeding. Thirty percent (9/30) had experienced difficulty in concentration/memory loss. Seventeen percent (5/30) had experienced peripheral nervous system symptoms (e.g., numbness, tingling).

Injury reports

The company injury report relating to skin disorders was reviewed. There were 45 cases in 1989, 21 in 1990, 16 in 1991, 20 in 1992, 11 in 1993, and 10 in 1994. Although the injury report data may not reflect all skin disorders during these periods, it indicates that the number of skin disorders decreased after RALF was first used in the potroom in 1992.

Review of medical surveillance and respiratory protection programs

At the time of the survey, the company was in the process of restructuring the medical surveillance program and the NIOSH medical officer reviewed the proposed program. The proposed program has three major components, including pre-placement screening, industrial hygiene monitoring, and medical monitoring. It also contained department-specific recommendations. Included were data on potential toxic exposures and job specific recommendations to minimize them. Information included industrial hygiene monitoring for particulate, total fluoride exposure, gaseous hydrogen fluoride, sulfur dioxide, coal tar pitch volatile, trace metals, carbon monoxide, and refractory ceramic fibers in the potroom section, respiratory protection, general medical monitoring recommendations, physical exposures with potential for injury or illness in the potroom (e.g., heat stress, noise exposures, non-ionizing electromagnetic fields, and physical injury hazards), and job-specific medical monitoring recommendations for all job titles in the potroom.

The respiratory protection program has four major components: purpose, objectives, scope, and procedures. The section for program requirements contains several important topics, including administration issues, respirator selection, respirator sealing requirements, fit test, physiological and psychological limitations for respirator wearers, individual wearer's responsibility, monitoring and training, respirator program evaluation, and audit mechanisms. The program also contains jobs/tasks and area specific respirator requirements.

VII. DISCUSSION

A. Environmental

The environmental survey focused on the assessment of contaminant concentrations that might be affected by the use of RALF. Since RALF is used as an alternative source of aluminum fluoride in the potroom, and fluorides are known to cause many of the health effects reported by the employees, fluoride exposures were a major focus of the evaluation. Based on the data collected, no major differences were noted in the exposures with RALF use in the long-term personal samples. Some differences were noted in the short-term personal samples, but this may be attributable to the relatively small number of samples collected and the differences in the manner in which the tasks which were monitored (setting one anode pot) were conducted. Employee exposure during the anode changing on a single pot can be affected by many factors, including difficulty removing spent anodes (the number of burn offs), difficulty replacing new anodes (improper crust breaking), the amount of time spent waiting for a crane, and the efficiency of the local exhaust ventilation for that pot. Therefore, the long-term or TWA exposures, which include several anode changes over a number of different pots, would be expected to be more valid for comparative purposes. However, the short-term samples do indicate the potential for exposures above the NIOSH REL for hydrogen fluoride as a ceiling concentration. The company was aware of this potential and had implemented a respiratory protection program for protection against fluorides during these tasks. If properly used and maintained, adequate protection should have been provided to substantially reduce the employees' actual exposures.

TWA exposures to SO_2 and particulate sulfate in the personal samples did not show substantial differences in the environmental samples between the RALF and non-RALF lines. Once again, there was some variability in the short-term samples (a higher average concentration was found on the non-RALF line); however, for the reasons previously discussed, and in particular the very small number of samples, the TWA exposures would be considered a better representation of exposures. However, the short-term samples did indicate that there was a potential for SO_2 concentrations to exceed the STEL evaluation criteria.

The area samples, which were collected to examine a number of different contaminants at similar locations on RALF and non-RALF lines, did not reveal any marked differences in airborne concentrations for most of the contaminants. The total particulate levels were in close agreement indicating the two area sample locations were very comparable from the standpoint of overall particulate emissions. Concentrations of gaseous and particulate fluoride, particulate sulfate, SO_2, and the inorganic acids did not substantially differ. There was a difference in the sulfuric acid concentration (a higher concentration was found on the non-RALF line), but the method used also would detect the particulate sulfate salts. Some variability was previously noted in the personal samples for the sulfur containing compounds. The reason for this variability is not readily explainable; however, based on the nature and use of RALF, it would not normally be expected to contain significant amounts of sulfur-containing compounds.

Due to the loss of a sample during analysis, no comparative data is available for trace metals between the RALF and non-RALF lines. However, the analysis of the six bulk samples which were collected from different batches of RALF did not indicate any significant quantities of trace metals other than aluminum. Therefore, under normal circumstances, the RALF would not be expected to contribute to trace metals in the environment. The area sample from the non-RALF line showed very low but detectable concentrations of some metals with appreciable toxicity (i.e., arsenic, beryllium, and nickel). Since no data was supplied by the company regarding exposures to trace metals on the potlines, it would be prudent to conduct baseline personal monitoring for trace metals to ensure that these exposures are within their respective evaluation criteria.

A limited number of samples were collected for arsenic in response to an employee concern with potential arsenic exposure during pot tapping. The airborne concentrations detected in these samples were below the evaluation criteria. As previously discussed, the bulk sample analysis did not show the RALF to contain any detectable concentrations of arsenic. In addition, each batch of RALF is tested by the company for arsenic content. Therefore, the RALF would not be expected to contribute to the arsenic levels in the environment under normal conditions. However, since a small number of samples were collected, unless already present, baseline monitoring of these employees (tappers) would be prudent to ensure they are not exposed to arsenic or other trace metals.

The possible contribution of the RALF to volatile organic emissions in the work environment was also a major focus of the evaluation. This was due to the fact that RALF is a byproduct of a petroleum process. The bulk sample analysis showed very low levels of volatile organic compounds. One of the bulk samples showed a higher contaminant concentration than the others, but when considering the extreme sensitivity of this method, this would not be expected to contribute substantial concentrations during actual use in the potroom. The environmental monitoring for volatile organics in the workplace also revealed very low contaminant concentrations. Previous monitoring conducted by the company on bulk samples and on RALF dumps on the potlines had also shown very low or non-detectable concentrations of volatile organics. Therefore, under normal conditions, RALF would not be expected to contribute significantly to volatile organics in the workplace.

B. Medical

Meaningful comparisons of the prevalence rates of skin problems between the two groups who have and who have not used RALF were not possible in this investigation since there were only four employees working in the area where RALF had not been used. Interview results (74% of employees had experienced skin problems for two years) suggest that RALF use may cause skin problems because its introduction was followed by an increase in reports of skin problems. 70% of employees reported that their symptoms went away when they were not exposed to RALF (during weekends or on vacation). However, because they were also not exposed to other chemicals which can cause skin problems (e.g., hydrogen fluoride, particulate fluorides, etc.) during weekends or on vacation, it was not possible to prove that the disappearance of skin problems was due to the interruption of RALF exposure.

Although a majority of the employees reported rashes over the preceding two years, only 5 (17%) reported a current skin rash, even though RALF was still being used. Furthermore, the number of recorded skin disorders declined after RALF was introduced, even though no change in reporting practices was apparent. In summary, these findings show a lack of consistency and conflicting evidence of a temporal relationship that would support an association between the use of RALF and skin problems.

VIII. CONCLUSIONS

The results of the environmental survey did not appear to indicate a marked difference in personal breathing zone TWA exposures between employees working on lines using RALF and those on lines not using RALF. Furthermore, the results of the area samples collected at similar locations on lines with and without RALF also did not reveal substantial differences in concentrations for the majority of the contaminants. An attempt was made to sample for the major contaminants which might be expected to be produced by the use of RALF. It should be noted that there is a potential for some variability due to individual factors which may occur in the refinery where the RALF is obtained. Continued vigilance to ensure continuity between RALF batches would therefore be prudent.

While the data from the medical survey were not sufficient to determine if symptoms were due to the use of RALF, they did report health problems which they attributed to the workplace. As evidenced by the personal sample results, the employees work in an environment which contains airborne contaminants at concentrations sufficient to cause many of the symptoms the employees reported. The company is aware of these exposures and conducts environmental and medical monitoring and has implemented engineering controls and personal protection measures. The fact that employees continue to report health problems would seemingly indicate some failure of the controls which are in place. Therefore, employees should make an effort to report any adverse health effects they experience, regardless of whether they are related to the use of RALF. Management, in turn, should quickly attempt to determine the cause of the problem, (i.e., inadequate pot ventilation, improper respirator fit, etc.). Maintaining a log of such occurrences would also assist in determining if problems are more prevalent among employees exposed to RALF. It would also indicate if symptoms are clustered during the use of a particular batch of RALF.

IX. RECOMMENDATIONS

1. The proposed medical surveillance program should be implemented as soon as possible. Particular attention should be given to the respiratory and musculoskeletal systems (e.g., ergonomic job analysis, symptom questionnaire) since significant numbers of employees have experienced respiratory and musculoskeletal problems. The NIOSH criteria document for inorganic fluorides should be consulted for more specific medical recommendations.[11]

2. Employees should promptly report any adverse health effects experienced in the workplace. Such reports should be logged and all reports should be promptly investigated to attempt to determine the cause. Where appropriate, engineering controls should be examined and the personal protection used by the employee should be reviewed. Periodically, these complaints should be examined in light of RALF use.

3. Ongoing monitoring for fluorides and SO_2 should continue. These data should continue to be evaluated in light of RALF use. Additionally, personal monitoring should be conducted for trace metals to obtain baseline data and ensure concentrations are within the appropriate evaluation criteria. Also, the ambient conditions during the NIOSH evaluation were such that the building was opened up to allow for maximum outside air circulation. It would be prudent to conduct additional monitoring during any periods when the building might be more closed up and the exposures higher.

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2. United Steel Workers of America, Local 329
3. Occupational Safety and Health Administration - Region X

For the purpose of informing affected employees, copies of the report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

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Vial Number: 10      Sample Identifier: Cenex  10/26/94
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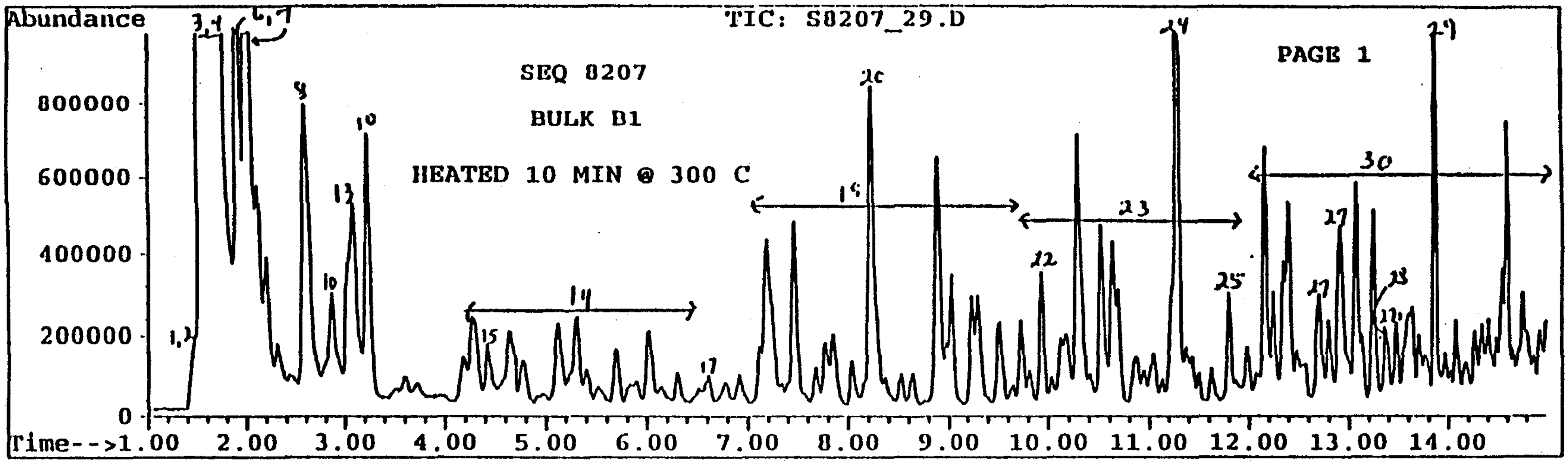

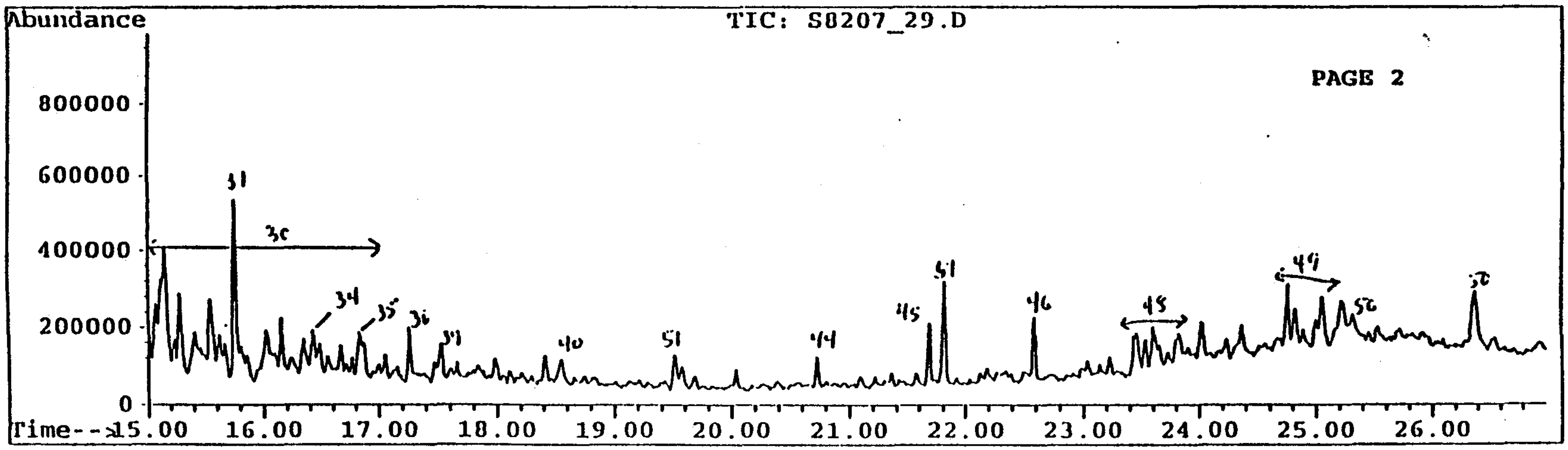

ATTACHMENT 1

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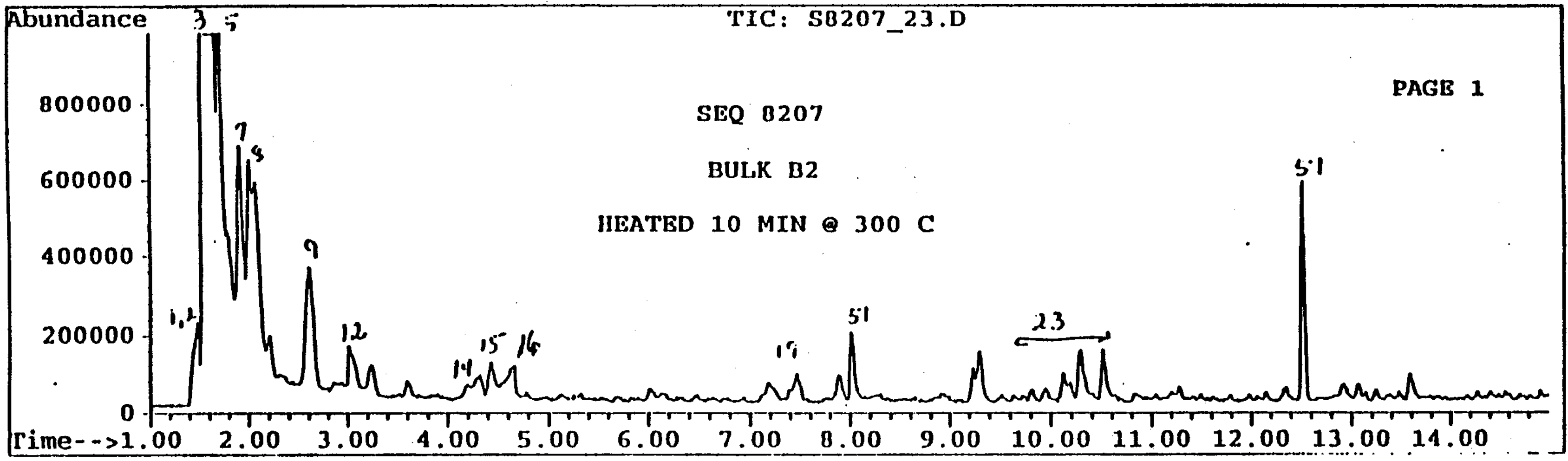
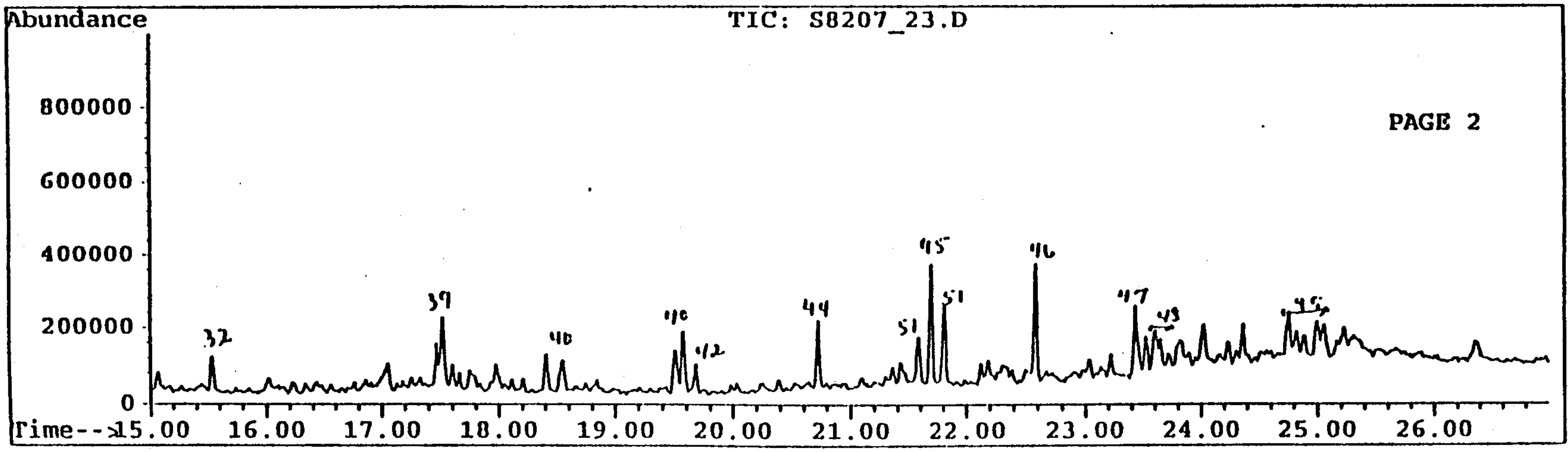
Sample Identifier: Total Petroleum 2/7/95





ATTACHMENT 2

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Instrument  :    5970 - In
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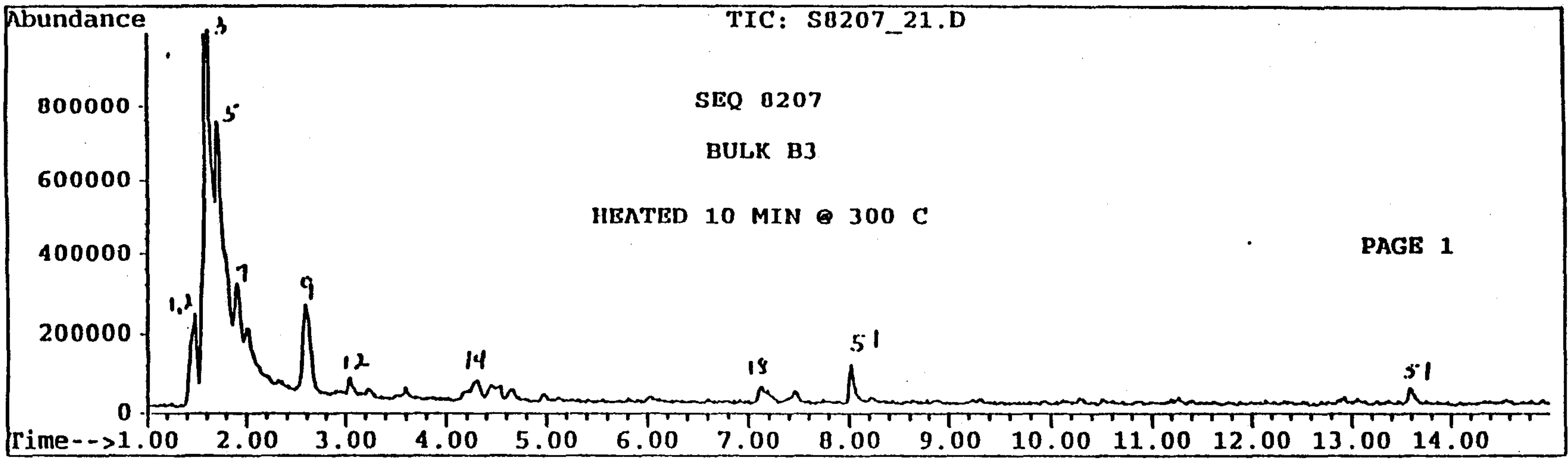
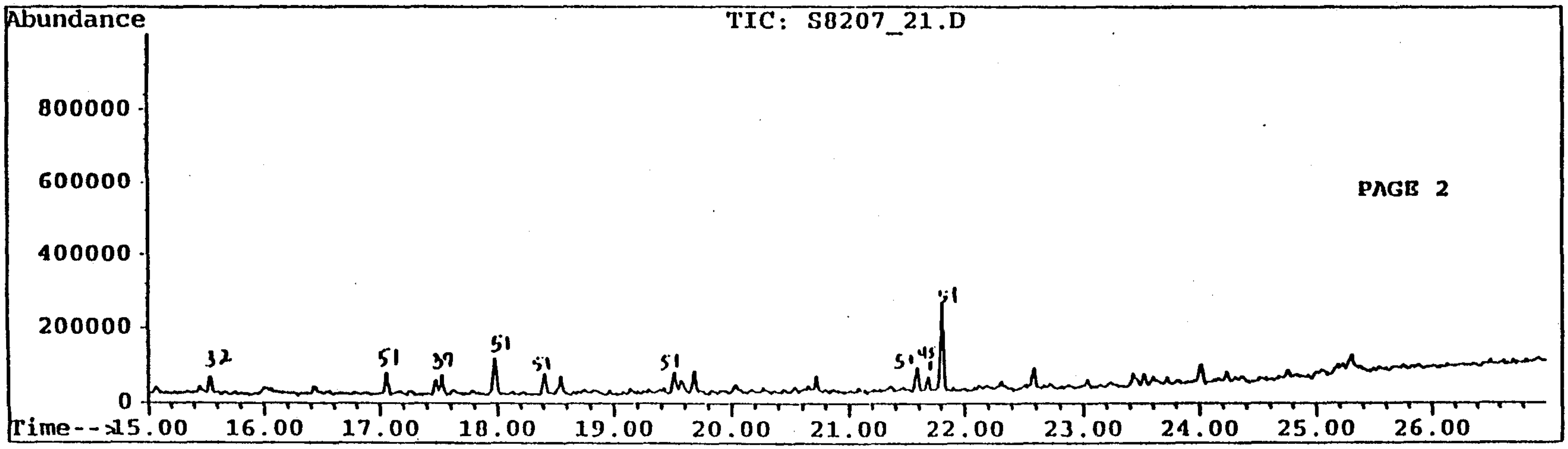
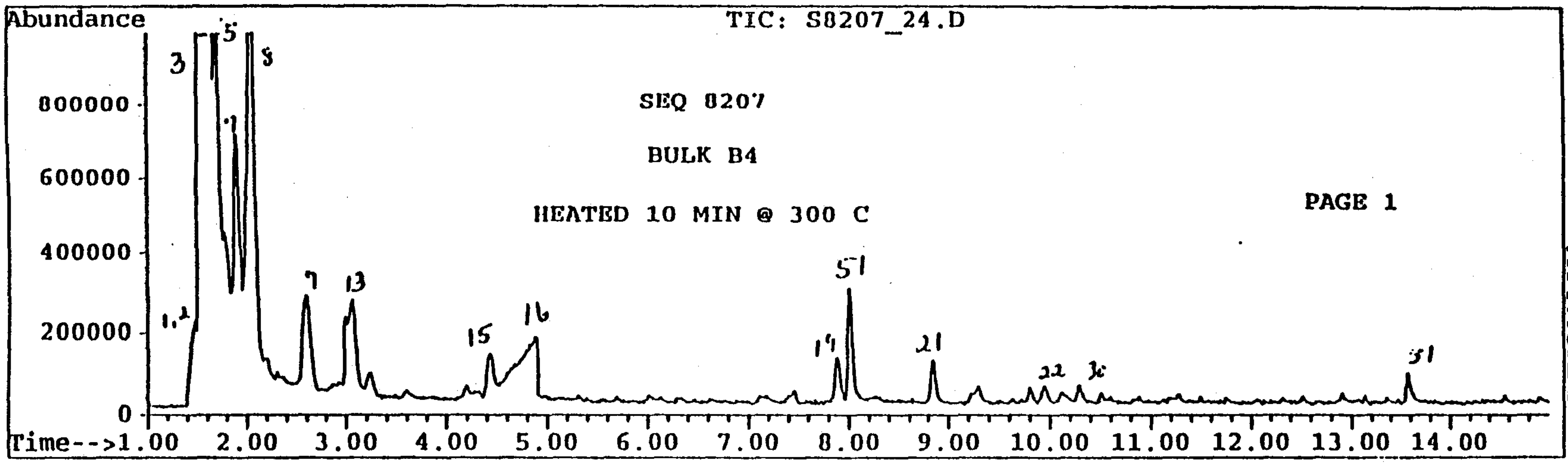
Misc Info   : 30 M DB-1   SC20-400    TP35-300
Vial Number: 2        Sample Identifier: Mobil Torrence   6/29/94
```

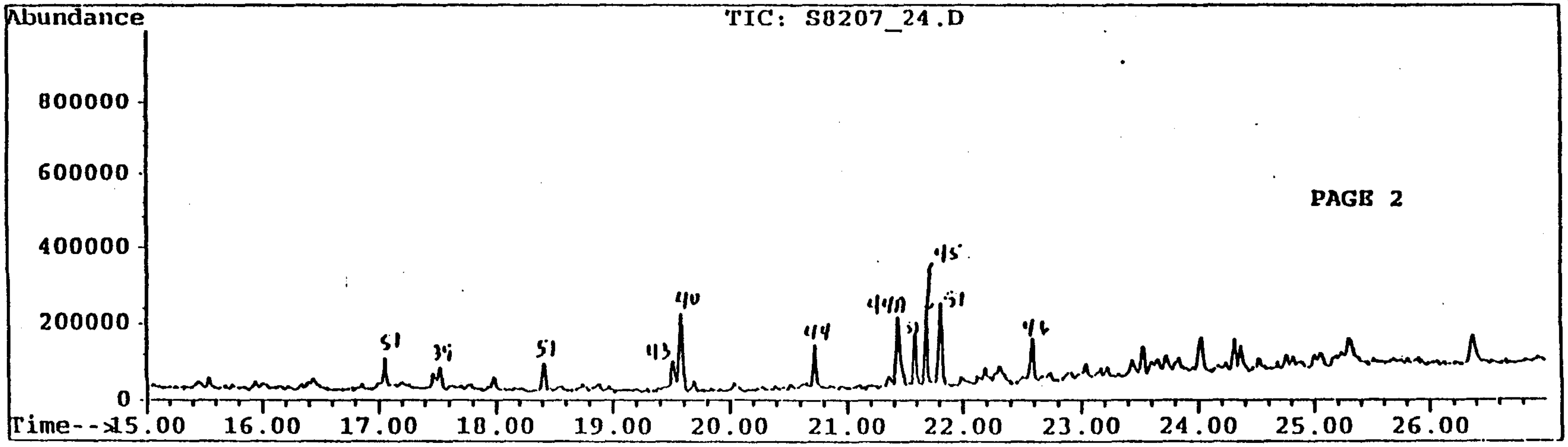




ATTACHMENT 3

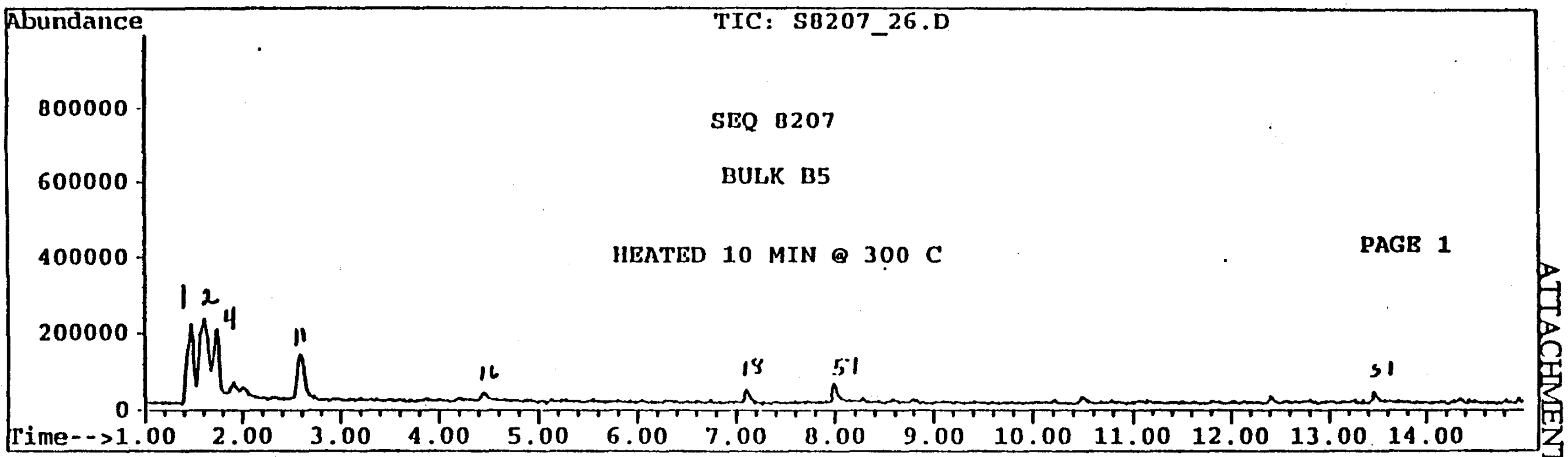
File : C:\HPCHEM\1\DATA\S8207\S8207_24.D
Operator : AAG
Acquired : 17 Apr 95 1:25 pm using AcqMethod PLASTIC
Instrument : 5970 - In
Sample Name: BULK B4/ QUARTZ FILTER 300C VALVE 190C
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 5 Sample Identifier: Phillips Sweeney 9/21/94

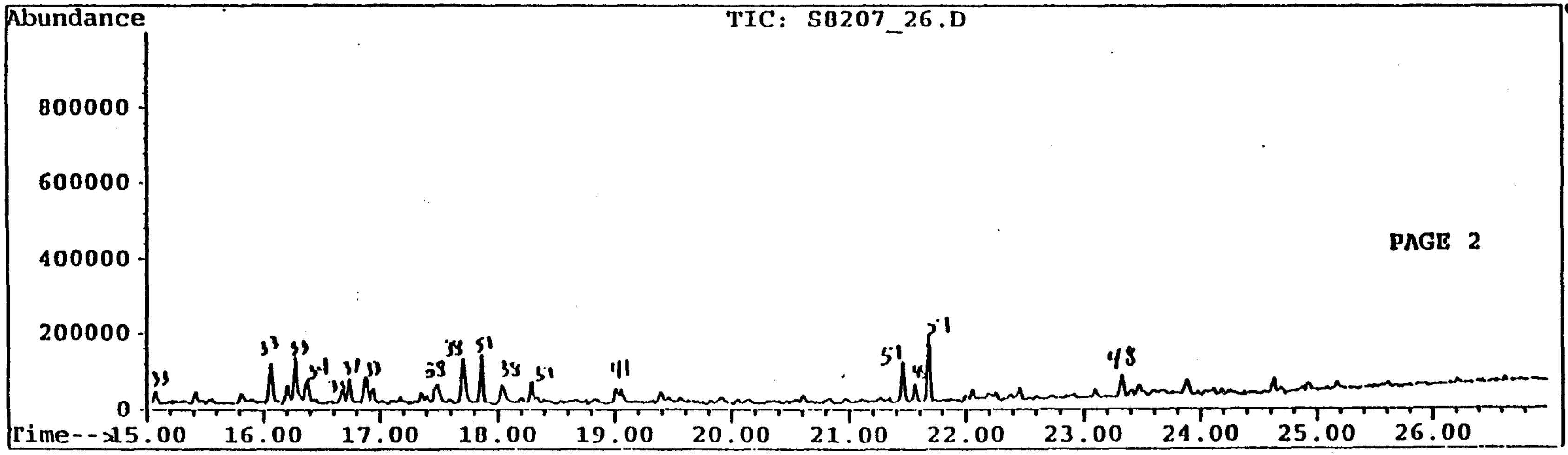




ATTACHMENT 4

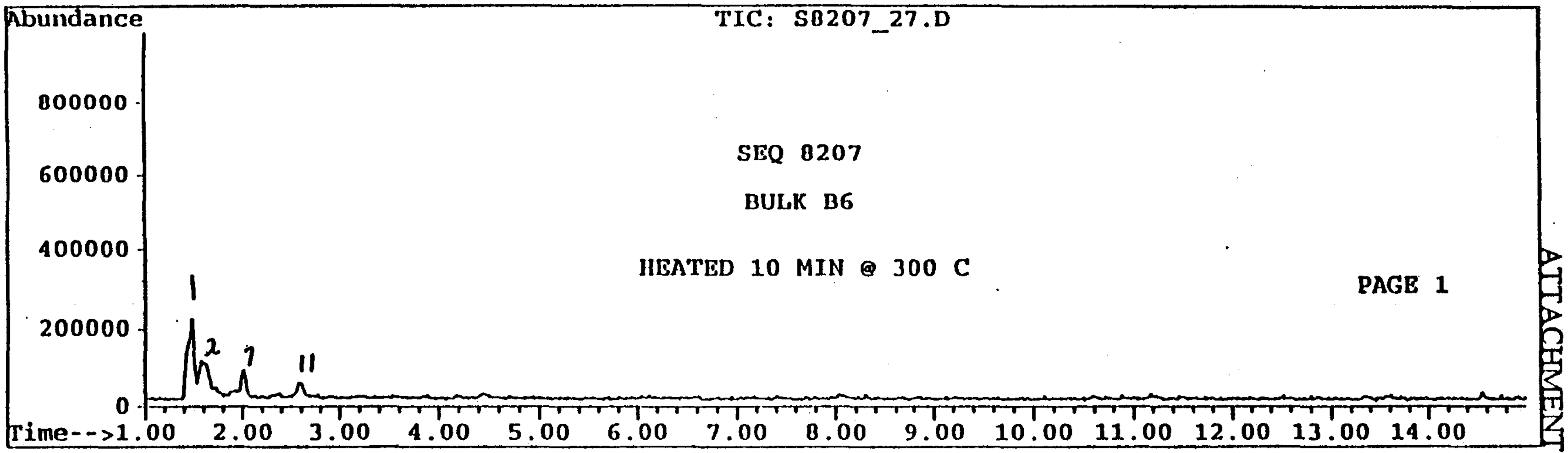
File : C:\HPCHEM\1\DATA\S8207\S8207_26.D
Operator : AAG
Acquired : 17 Apr 95 3:24 pm using AcqMethod PLASTIC
Instrument : 5970 - In
Sample Name: BULK B5/QUARTZ FILTER 300C VALVE 190C
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 7 Sample Identifier: Marathon Garysville 5/19/94



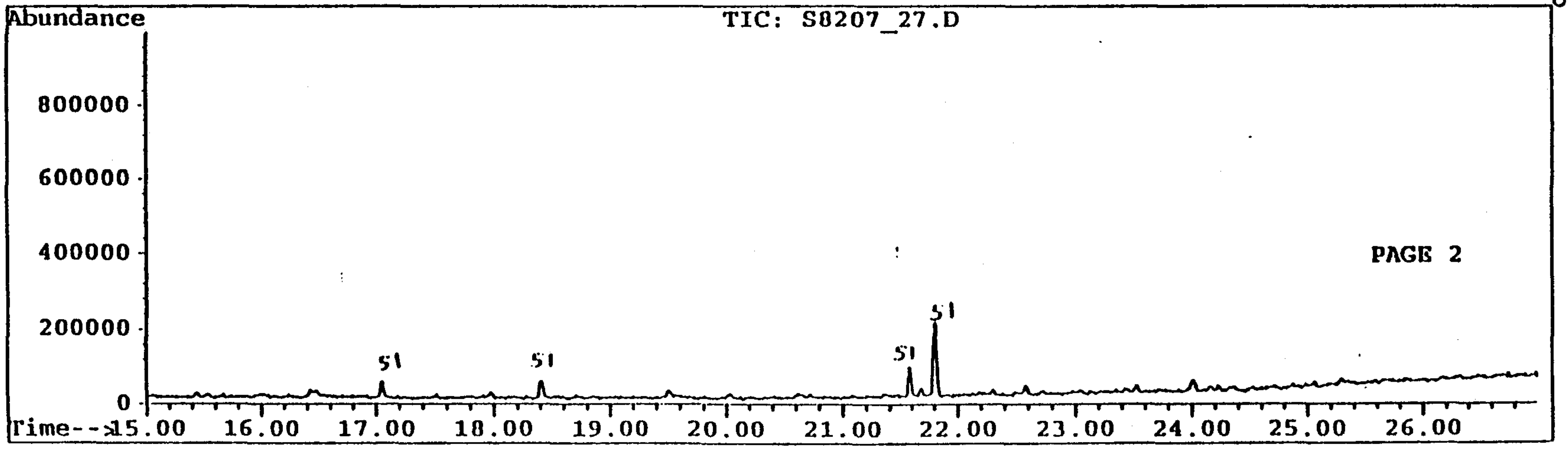


ATTACHMENT 5

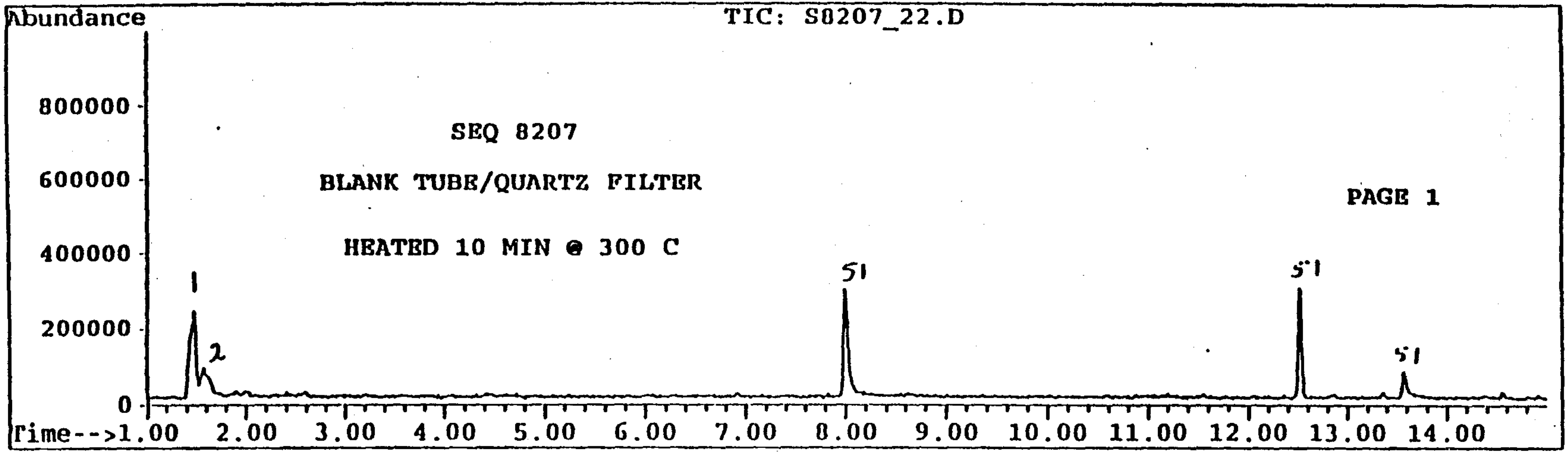
File : C:\HPCHEM\1\DATA\S8207\S8207_27.D
Operator : AAG
Acquired : 17 Apr 95 4:23 pm using AcqMethod PLASTIC
Instrument : 5970 - In
Sample Name: BULK B6/QUARTZ FILTER 300C VALVE 190C
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 8 Sample Identifier: Conoco Billings Date Unknown

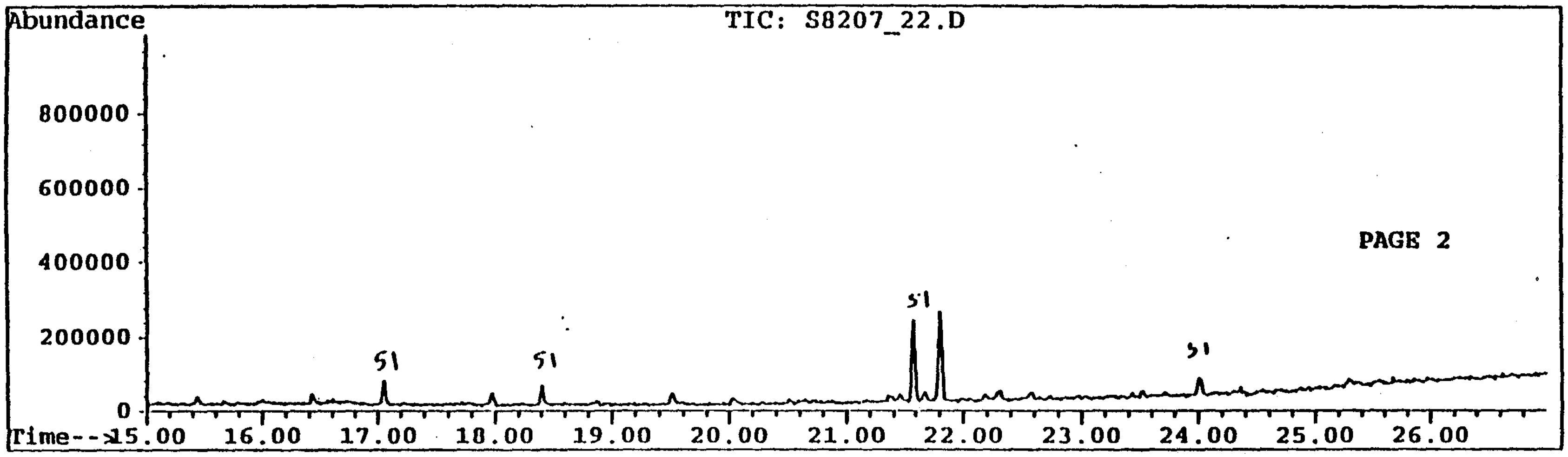


ATTACHMENT 6



File : C:\HPCHEM\1\DATA\S8207\S8207_22.D
Operator : AAG
Acquired : 17 Apr 95 11:22 am using AcqMethod PLASTIC
Instrument : 5970 - In
Sample Name: BLANK QUARTZ FILTER 300C VALVE 190C
Misc Info : 30 M DB-1 SC20-400 TP35-300
Vial Number: 3





ATTACHMENT 7

ATTACHMENT 8

SEQ 8207
BULK MATERIALS, HEATED HEADSPACE AT 300°C
PEAK IDENTIFICATION

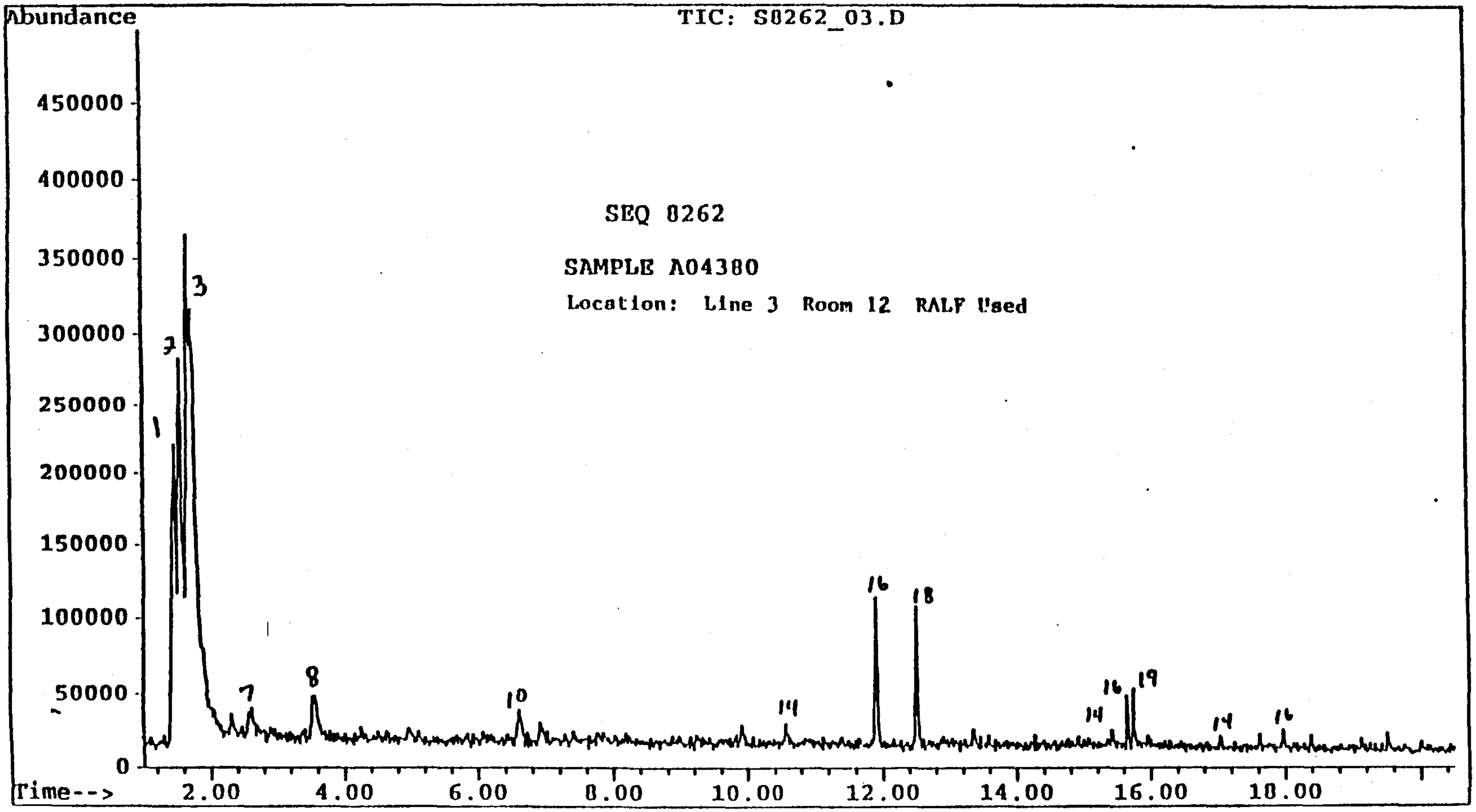
1) Air*
2) CO_2*
3) Tetrafluorosilane (F_4Si)**
4) Propene/propane
5) Hydrochloric acid (HCl)
6) Methanol
7) Butenes/isobutane
8) Butane
9) Pentane
10) Pentene/methyl butenes
11) Acetone
12) Formic acid
13) Dimethyl sulfide
14) C_6H_{14}/C_6H_{12} aliphatics
15) Methyl ethyl ketone (MEK)
16) Acetic acid
17) Benzene
18) 2-Pentanone
19) C_7H_{16}/C_7H_{14} aliphatics
20) n-Heptane
21) Methyl isobutyl ketone (MIBK)
22) Toluene
23) C_8H_{18}/C_8H_{16} aliphatics
24) n-Octane
25) Methyl ethyl disulfide
26) C_9H_{20}/C_9H_{18} aliphatics
27) Ethyl benzene/xylene isomers
28) Methylisopropyl sulfide
29) n-Nonane
30) C_9-C_{12} aliphatics plus C_9-C_{10} alkyl benzenes (trimethyl-, tetramethyl benzenes, etc.)
31) n-Decane
32) C_9H_{12} alkyl benzenes (trimethyl-, dimethylethyl benzene, etc.)
33) M.W. 124, $C_8H_{12}O$ compounds
34) Methyl phenol isomer (cresol)
35) Furanmethanol
36) n-Undecane
37) Methoxy methyl phenol
38) Dimethyl phenols
39) $C_{10}H_{14}$ alkyl benzenes (tetramethyl-, dimethylethyl benzenes, etc.)
40) $C_{11}H_{16}$ alkyl benzenes (methyl-butyl-, pentamethyl benzenes)
41) Trimethyl phenols
42) n-Tridecane
43) Dibutylformamide/phthalic anhydride*
44A) $C_{12}H_{18}$, hexamethylbenzene
44) n-Tetradecane
45) n-Pentadecane
46) n-Hexadecane
47) n-Heptadecane
48) $C_{14}H_{16}$, M.W.184 alkyl benzenes
49) $C_{15}H_{18}$, M.W.198 alkyl benzenes
50) M.W. 212, phenyl-oxygen compound $C_{14}H_{12}O_2/C_{15}H_{16}O$ compounds?
51) Blank contaminants*

*Also present on media (empty glass tubes with glass wool/quartz filter plugs) blanks.

**F_4Si may be present as a reaction product formed between HF (known to be in the samples) and silicon compounds present in the analytical system (silanized glass wool, GC column).

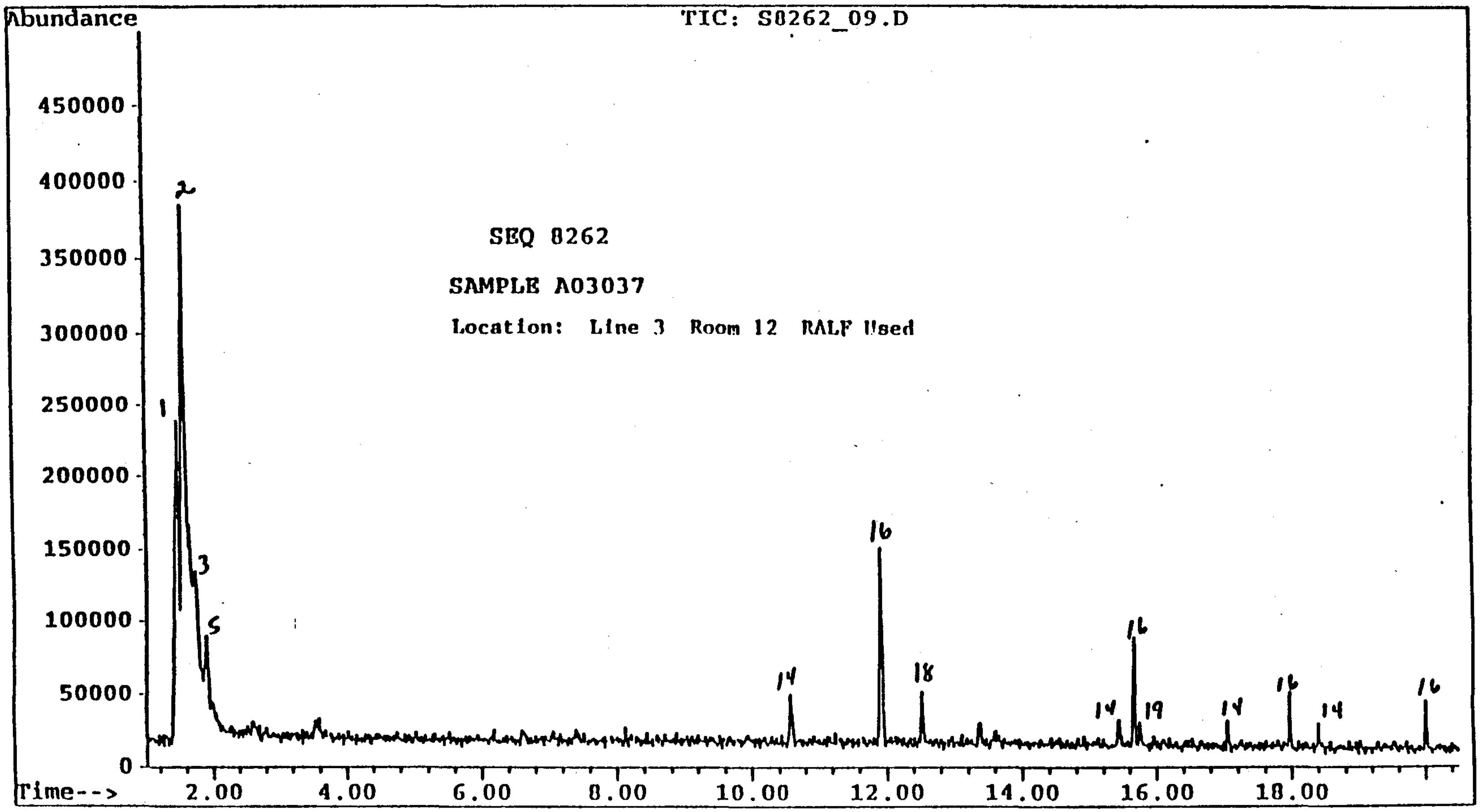
ATTACHMENT 9

```
File        : C:\HPCHEM\1\DATA\S8262\S8262_03.D
Operator    : AAG
Acquired    : 15 May 95  11:53 am using AcqMethod PLASTIC
Instrument  :   5970 - In
Sample Name: A04380       375 TRAP/OVEN
Misc Info   : 30 M DB-1    SC20-400    TP35-300
Vial Number: 3
```



ATTACHMENT 10

```
File        : C:\HPCHEM\1\DATA\S8262\S8262_09.D
Operator    : AAG
Acquired    : 15 May 95   5:52 pm using AcqMethod PLASTIC
Instrument  :   5970 - In
Sample Name: A03037       375 TRAP/OVEN
Misc Info   : 30 M DB-1   SC20-400    TP35-300
Vial Number: 9
```

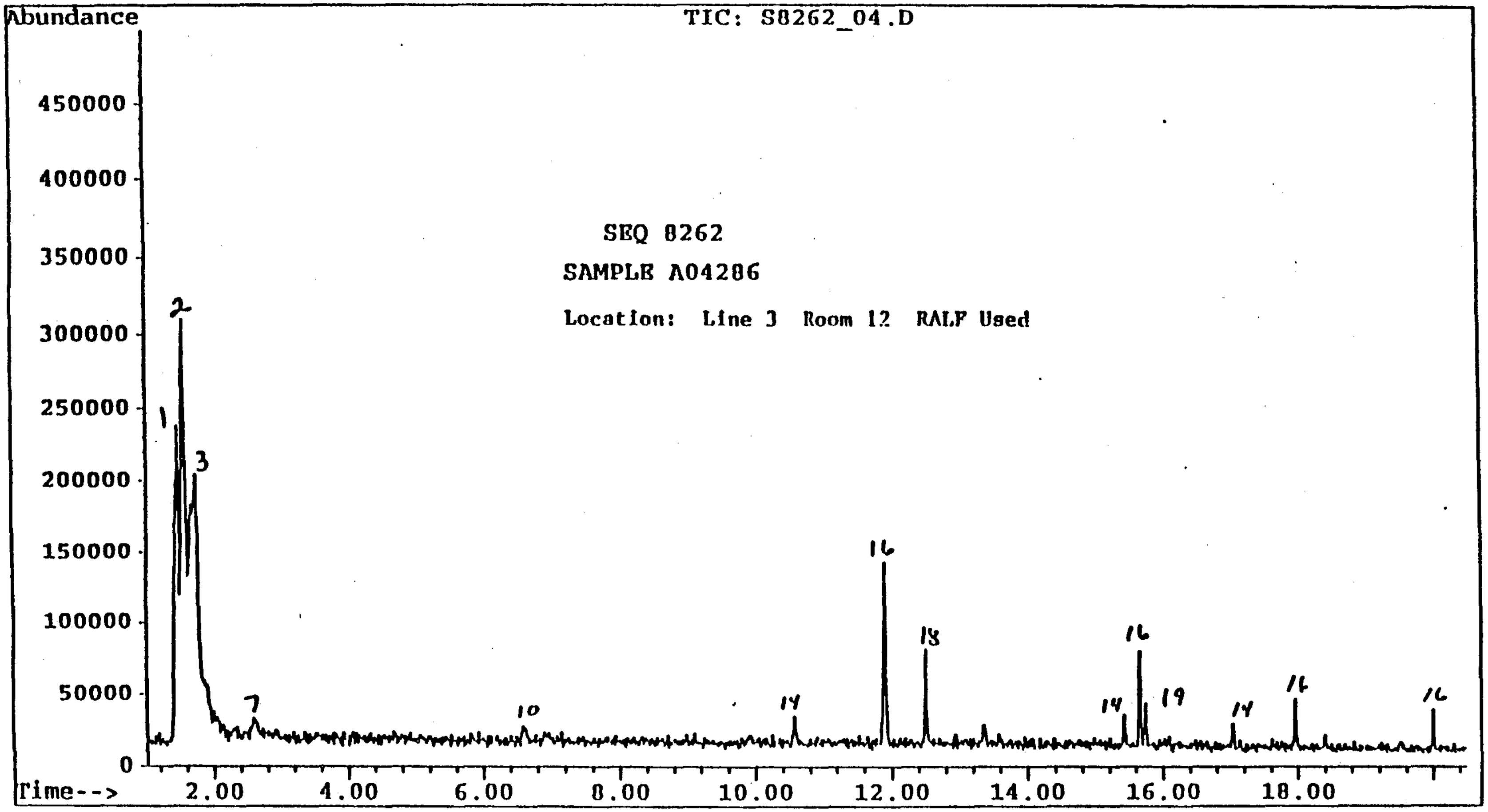


SEQ 8262

SAMPLE A03037

Location: Line 3 Room 12 RALF Used

```
File        : C:\HPCHEM\1\DATA\S8262\S8262_04.D
Operator    : AAG
Acquired    : 15 May 95  12:53 pm using AcqMethod PLASTIC
Instrument :   5970 - In
Sample Name: A04286      375 TRAP/OVEN
Misc Info   : 30 M DB-1   SC20-400   TP35-300
Vial Number: 4
```



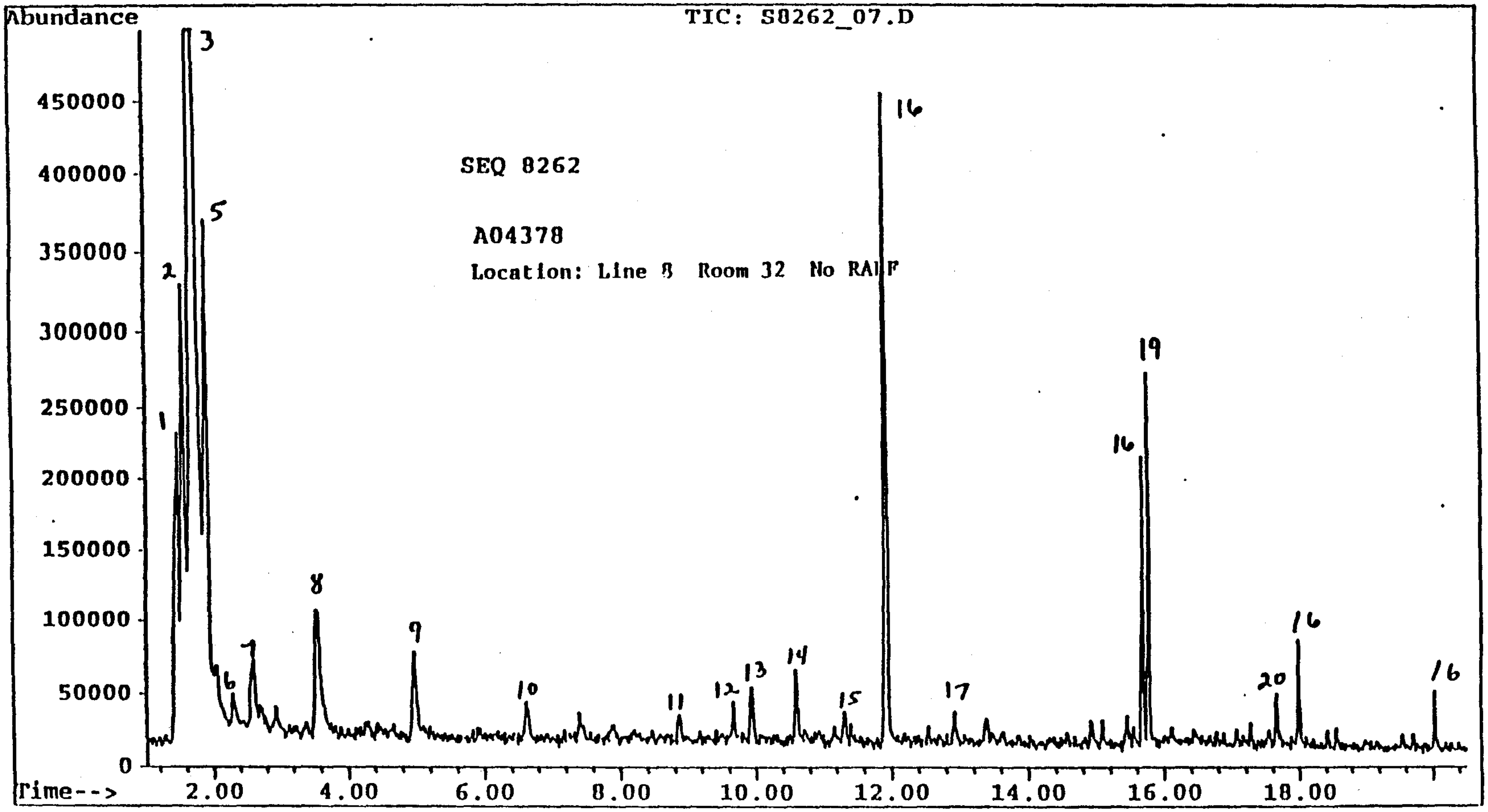
SEQ 8262

SAMPLE A04286

Location: Line 3 Room 12 RALF Used

ATTACHMENT 11

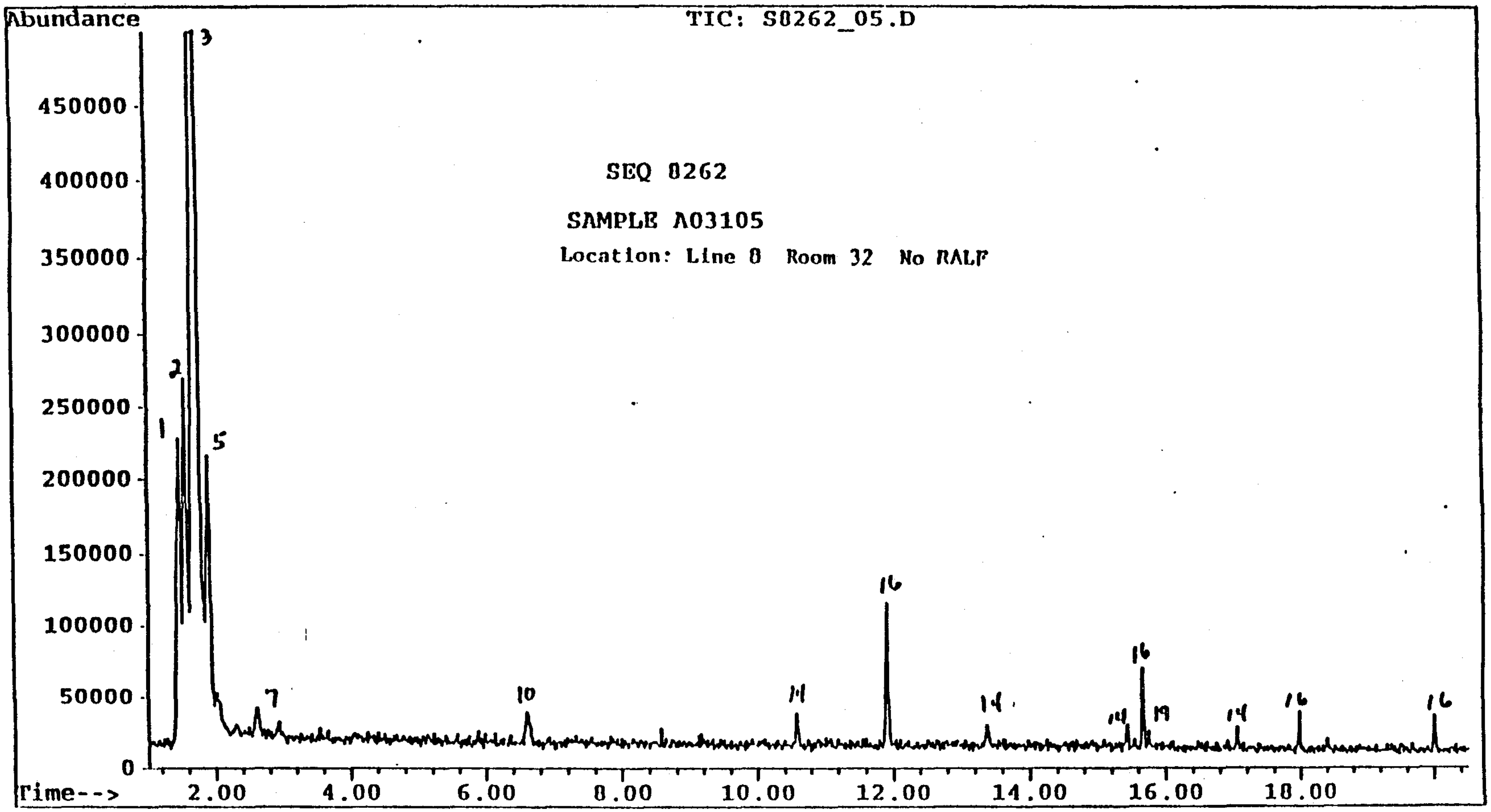
```
File        : C:\HPCHEM\1\DATA\S8262\S8262_07.D
Operator    : AAG
Acquired    : 15 May 95   3:52 pm using AcqMethod PLASTIC
Instrument  :   5970 - In
Sample Name: A04378       375 TRAP/OVEN
Misc Info   : 30 M DB-1    SC20-400    TP35-300
Vial Number: 7
```



ATTACHMENT 12

ATTACHMENT 13

```
File        : C:\HPCHEM\1\DATA\S8262\S8262_05.D
Operator    : AAG
Acquired    : 15 May 95   1:53 pm using AcqMethod PLASTIC
Instrument  :   5970 - In
Sample Name: A03105      375 TRAP/OVEN
Misc Info  : 30 M DB-1    SC20-400    TP35-300
Vial Number: 5
```



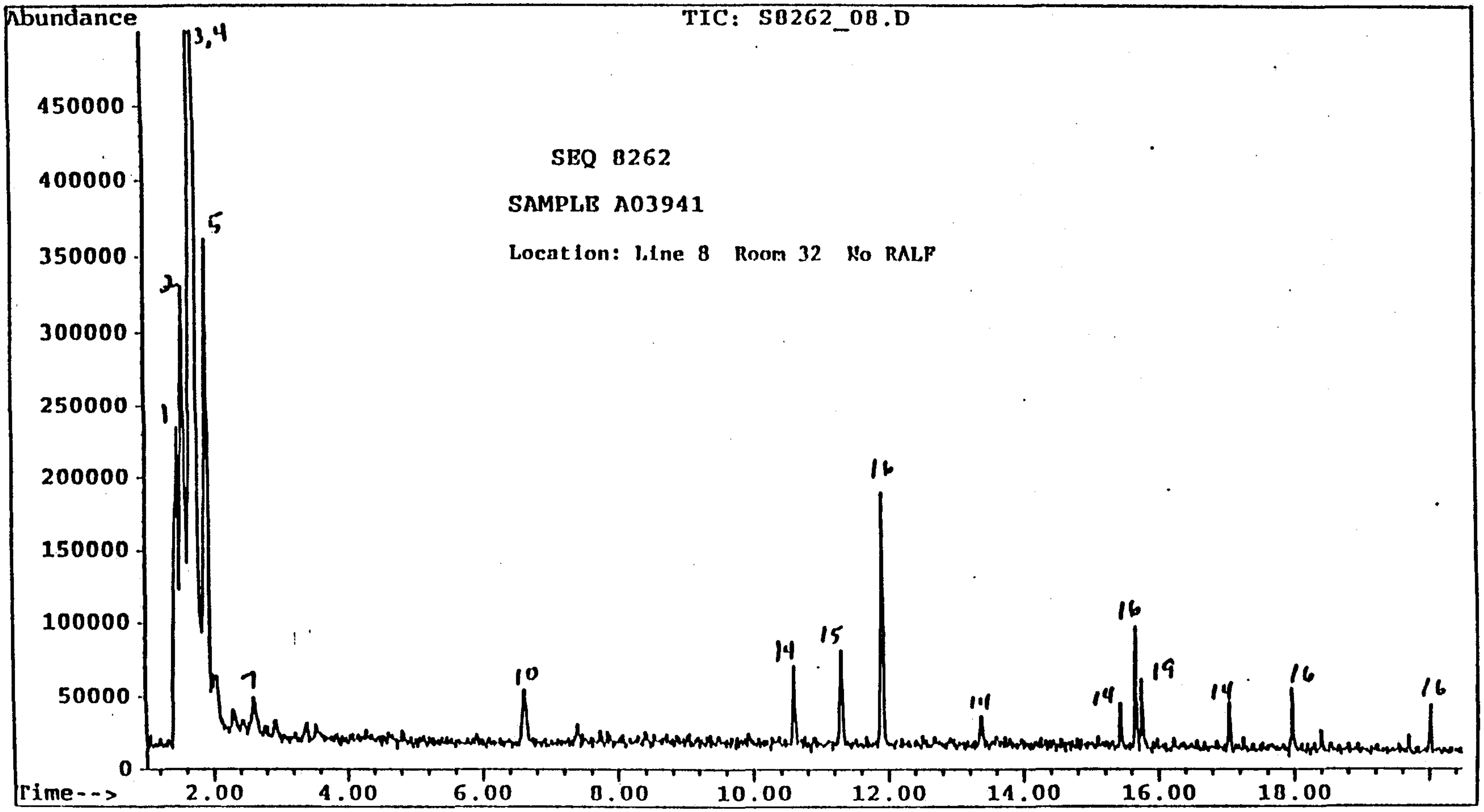
SEQ 8262

SAMPLE A03105

Location: Line 8 Room 32 No RALF

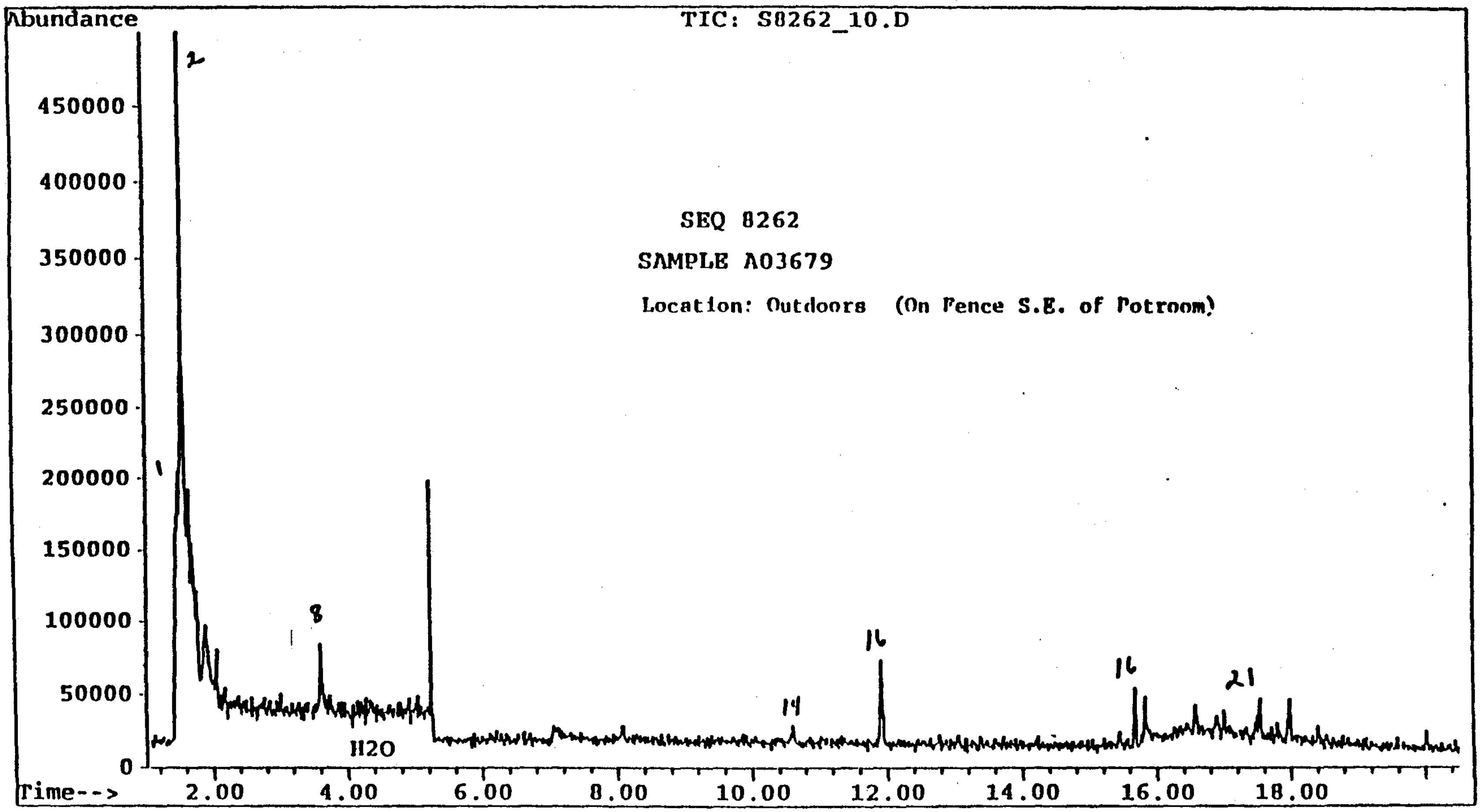
ATTACHMENT 14

```
File         : C:\HPCHEM\1\DATA\S8262\S8262_08.D
Operator     : AAG
Acquired     : 15 May 95   4:52 pm using AcqMethod PLASTIC
Instrument :   5970 - In
Sample Name: A03941        375 TRAP/OVEN
Misc Info  : 30 M DB-1    SC20-400    TP35-300
Vial Number: 8
```



ATTACHMENT 15

```
File        : C:\HPCHEM\1\DATA\S8262\S8262_10.D
Operator    : AAG
Acquired    : 15 May 95   6:52 pm using AcqMethod PLASTIC
Instrument :    5970 - In
Sample Name: A03679       375 TRAP/OVEN
Misc Info   : 30 M DB-1    SC20-400    TP35-300
Vial Number: 10
```



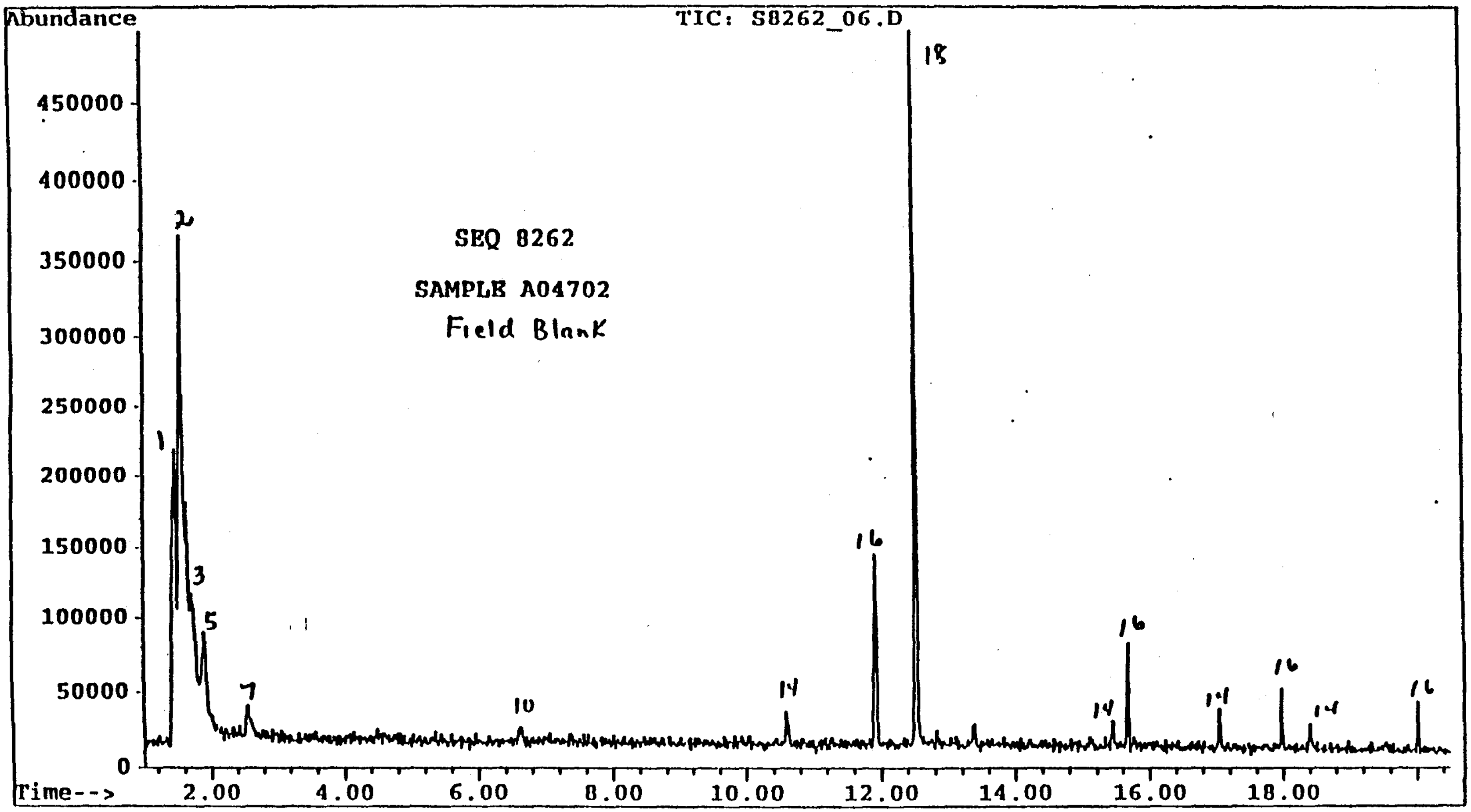
SEQ 8262

SAMPLE A03679

Location: Outdoors (On Fence S.E. of Potroom)

ATTACHMENT 16

File   : C:\HPCHEM\1\DATA\S8262\S8262_06.D
Operator   : AAG
Acquired   : 15 May 95   2:52 pm using AcqMethod PLASTIC
Instrument :   5970 - In
Sample Name: A04702   375 TRAP/OVEN
Misc Info   : 30 M DB-1   SC20-400   TP35-300
Vial Number: 6



ATTACHMENT 17

SEQ 8262
THERMAL DESORPTION TUBES
PEAK IDENTIFICATION

1) Air*
2) CO_2*
3) Sulfur dioxide (SO_2)*
4) Propane
5) Isobutane*
6) Ethanol
7) Pentane
8) Unknown, possible sulfur-oxygen compound, M.W.94?
9) Unknown, possible sulfur compound, M.W.155?
10) Benzene
11) Methyl isobutyl ketone (MIBK)
12) Unknown, possible nitrogen-sulfur-oxygen compound, M.W.153?
13) Toluene
14) Aliphatic aldehydes*
15) Perchloroethylene
16) Siloxane compounds*
17) Xylene
18) Propylene glycol methyl ether acetate**
19) p-Dichlorobenzene
20) Benzoic acid
21) $C_{10}H_{14}$ alkyl benzenes

*Also present on some field/media blanks.
**Present on field blank. Possibly a tube contaminant from previous field use.

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Through research and prevention

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