HEALTH HAZARD EVALUATION REPORT

HETA 93-1000
ITHACA CITY SCHOOL DISTRICT
TRANSPORTATION DEPARTMENT
ITHACA, NEW YORK

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I. SUMMARY

The National Institute for Occupational Safety and Health (NIOSH) received a union request for a Health Hazard Evaluation (HHE) at the Ithaca City School District Transportation Department. The employees were concerned about exposures to diesel exhaust, paint and lacquer solvents, and asbestos from brake pads. NIOSH investigators conducted a site visit in November 1993. The facility and its operations were observed and several personal breathing zone and general area air samples were collected for elemental carbon and solvents.

Elemental carbon samples were collected as a surrogate for diesel exhaust. Levels in the garage and office area of the building appeared to be higher than the ambient air concentration. Since NIOSH considers diesel exhaust a potential human carcinogen, recommendations for increased ventilation were made to reduce the diesel exhaust levels to as low as feasibly possible.

Neither painting nor brake pad procedures were being performed during the site visit. The organic solvent concentrations suggest that solvents are not a health hazard in the garage or office area when no painting is occurring. The exposures should be characterized during painting, however, and appropriate ventilation, such as a paint booth or local exhaust ventilation (LEV) system, should be considered. NIOSH investigations at other work sites have documented asbestos exposures during brake pad operations.

Environmental tobacco smoke appears to be a health hazard in this facility. Several workers smoke inside the building. There is no smoking policy, nor any ventilation except an intermittently used wall exhaust fan in the garage. Recommendations are made to prohibit smoking in the workplace or to at least provide a separate smoking room with a dedicated ventilation system for the employees.

> The elemental carbon samples suggest that the diesel exhaust concentrations in the garage and office areas of the Transportation Department building are elevated with respect to the ambient levels. Because diesel exhaust is considered a potential occupational carcinogen, and environmental tobacco smoke is a known human carcinogen, their concentrations should be reduced to the lowest feasible levels. Suggestions for reducing exposures are offered in the Recommendations section of this report.

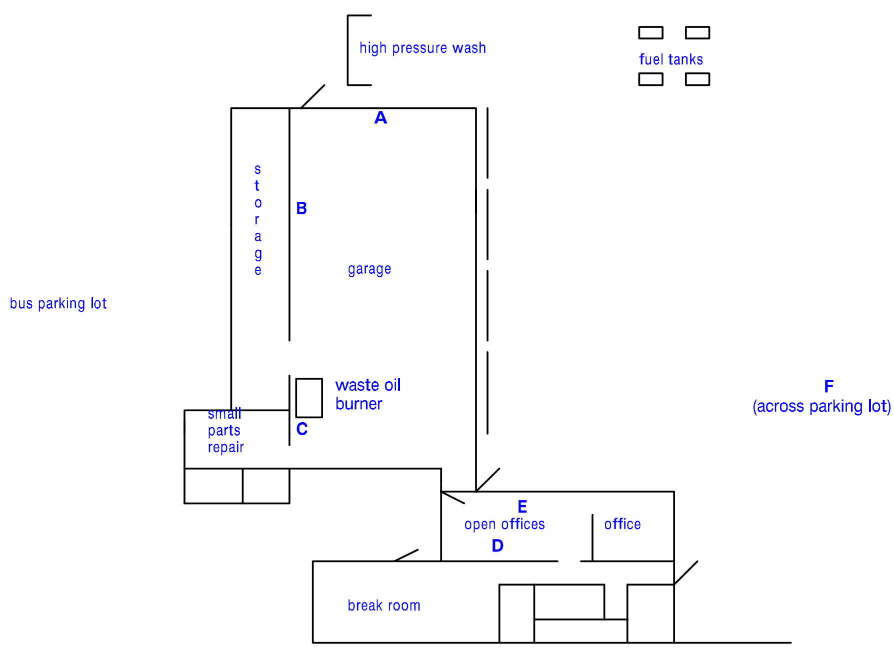
KEYWORDS: SIC 4151 (school buses), diesel exhaust, elemental carbon, paint, organic solvents, transportation department, environmental tobacco smoke (ETS)

II. INTRODUCTION

On November 8 and 9, 1993, the National Institute for Occupational Safety and Health (NIOSH) conducted a Health Hazard Evaluation (HHE) at the Ithaca City School District Transportation Department at the request of the local section of the National Education Association (NEA). There was concern of employee exposures to diesel exhaust, solvents, and asbestos from brake pads. The bus drivers, mechanics, and office workers were exposed to diesel exhaust; the mechanics and office workers were exposed to solvents; and the mechanics were possibly exposed to asbestos during brake repair work. The facility and its operations were observed and several personal breathing zone and general area air samples were collected for elemental carbon (C_e) and solvents. The C_e samples were used to estimate the exposure to diesel exhaust.

III. BACKGROUND

Figure 1. Diagram of the Ithaca City School District Transportation Department. HETA 93-1000 11/9/93



The Ithaca City School District Transportation Department is a single-story brick building situated a few miles west of the southwestern finger of Cayuga Lake. The building is divided equally between office/break rooms and a garage. There is one enclosed office, one room with three open office areas, a break room, and several storage rooms in the main building. The adjoining garage, which is a little larger than the main building, has three bays with bus lifts, a small parts repair shop, and a storage room along the entire back of the garage. One of the repair bays is also the priming and painting area. The building has a furnace heating system, a few relief exhausts, and two smoke-eater air filter units. The garage has a waste oil burner that is used for heat, ducted exhaust that connects to vehicle exhaust pipes when they are running in the garage, and one through-the-wall exhaust fan that is operated during painting activities. Figure 1 shows the layout of the building and garage.

The union request for an HHE was prompted by an individual who is no longer employed with the Ithaca City School District, but the union felt that the present employees could benefit from an evaluation of potential hazards since there had been no previous industrial hygiene monitoring.

IV. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ evaluation criteria for the assessment of a number of chemical (and physical) agents. The primary sources of environmental evaluation criteria for the workplace are the following: (1) NIOSH Criteria Documents and Recommended Exposure Limits (RELs), (2) the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs), and (3) the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs).[1,2,3] The objective of these criteria for chemical agents is to establish levels of exposure to which the vast majority of workers may be exposed without experiencing adverse health effects.

Full-shift and shorter duration criteria are available depending on the specific physiologic properties of the agent. Full-shift limits are based on the time-weighted average (TWA) airborne concentration of a substance that workers may be repeatedly exposed to during an eight or 10 hour work day, up to 40 hours a week for a working lifetime, without adverse health effects. Some substances have short-term exposure limits (STELs) or ceiling limits (CLs) which are intended to supplement the full-shift criteria where there are recognized irritative or toxic effects from brief exposures to high airborne concentrations. STELs are based on 15 minute TWA concentrations, whereas CL concentrations should not be exceeded even momentarily.

Occupational health criteria are established based on the available scientific information provided by industrial experience, animal or human experimental data, or epidemiologic studies. Differences between the NIOSH RELs, OSHA PELs, and ACGIH TLVs may exist because of different philosophies and interpretations of technical information. It should be noted that RELs and TLVs are guidelines, whereas PELs are standards which are legally enforceable. OSHA PELs are required to take into account the technical and economical feasibility of controlling exposures in various industries where the agents are present. The NIOSH RELs are primarily based upon the prevention of occupational disease without assessing the economic feasibility of the affected industries and as such tend to be conservative. A Court of Appeals decision vacated the OSHA 1989 Air Contaminants Standard in *AFL-CIO v OSHA*, 965F.2d 962 (11th cir., 1992); and OSHA is now enforcing the previous 1971 standards (listed as Transitional Limits in 29 CFR 1910.1000, Table Z-1-A).[2] However, some states which have OSHA-approved State Plans will continue to enforce the more protective 1989 limits. NIOSH encourages employers to use the 1989 limits or the RELs, whichever are lower.

ACGIH is not a government agency, it is a professional organization whose members are industrial hygienists or other professionals in related disciplines and are employed in the public or academic sector. TLVs are developed by consensus agreement of the ACGIH TLV committee and are published annually. The documentation supporting the TLVs (and proposed changes) is periodically reviewed and updated if believed necessary by the committee. It is not intended by the ACGIH for TLVs to be applied as the threshold between safe and dangerous exposures.

Not all workers will be protected from adverse health effects if their exposures are maintained below these occupational health exposure criteria. A small percentage may experience adverse effects due to individual susceptibility, a pre-existing medical condition, previous exposures, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, or with medications or personal habits of the worker (such as smoking) to produce health effects even if the occupational exposures are controlled to the limit set by the evaluation criterion. These combined effects are often not considered by the chemical specific evaluation criteria. Furthermore, many substances are appreciably absorbed by direct contact with the skin and thus potentially increase the overall exposure and biologic response beyond that expected from inhalation alone. Finally, evaluation criteria may change over time as new information on the toxic effects of an agent become available. Because of these reasons, it is prudent for an employer to maintain worker exposures well below established occupational health criteria.

Diesel Exhaust

Based on findings of carcinogenic responses in exposed rats and mice, NIOSH recommends that whole diesel exhaust be considered a potential occupational carcinogen and that exposures be reduced to the lowest feasible concentration.[4] In addition to the carcinogenic effects, eye irritation and reversible pulmonary function changes have been experienced by workers exposed to diesel exhaust.[4-7]

Diesel exhaust is a complex mixture that consists of both a gaseous and particulate fraction. The composition will vary greatly with fuel and engine type, maintenance, tuning, and exhaust gas treatment.[4,8] The gaseous constituents include carbon dioxide, carbon monoxide (CO), nitrogen dioxide, oxides of sulfur, and hydrocarbons. The particulate fraction (soot) of diesel exhaust is comprised of solid carbon cores produced during the combustion process. More than 95% of these particles are less than 1 micron diameter (µmd) size. It has been estimated that up to 18,000 different substances from the combustion process can be adsorbed onto diesel exhaust particulates.[4] Up to 65% of the total particulate mass may be these adsorbed substances and includes compounds such as polynuclear aromatic hydrocarbons (PAHs), some of which are carcinogenic.[4] Particles in this size range are considered respirable because when inhaled they reach the deeper, non-ciliated portions of the lungs where they may be retained. In general, particles greater than 7-10 µmd are all removed in the nasal passages and have little probability of penetrating to the lung. Particles smaller than this can reach the air-exchange regions (alveoli, respiratory bronchioles) of the lung, and are considered more hazardous.

As noted, based on the results of laboratory animal and human epidemiology studies, NIOSH considers whole diesel exhaust to be a potential occupational carcinogen.[4] The studies of rats and mice exposed to diesel emissions, especially the particulate portion, confirmed an association with lung tumors.[4] Human epidemiology studies also suggest an association between occupational exposure to whole diesel exhaust and lung cancer.[4,9]

In addition to the carcinogenic potential, many other components of diesel exhaust have known toxic effects. These effects include pulmonary irritation from nitrogen oxides, eye and mucous membrane irritation from sulfur dioxide and aldehyde compounds, and chemical asphyxiation effects from CO. Exposure criteria has been established for some of these compounds; however, there are no exposure limits directly applicable to evaluation of whole diesel exhaust emissions.

Assessing worker exposure to diesel exhaust is difficult because of the complex makeup of emissions, uncertainty about which specific agent(s) may be responsible for the carcinogenic properties, and the effect of other potential sources of similar compounds (e.g., tobacco smoke particles are also primarily < 1 µmd). Measurements of some commonly found components of diesel exhaust have generally shown concentrations to be well below established exposure criteria. Efforts have focused on evaluating the particulate portion because most studies have associated the carcinogenic potential of diesel exhaust with the particulate fraction. NIOSH is currently investigating the use of C_e as a surrogate index of exposure. The use of C_e holds promise because the sampling and analytical method is very sensitive, and a high percentage of diesel particulate (80-90%) is C_e, whereas tobacco smoke particulate is composed primarily of organic carbon.[10] Although exposure criteria has not been established, sampling was conducted for C_e to determine the relative diesel emission levels in different areas, and to provide baseline information that could be useful for assessing the effectiveness of future control measures.

Table 1

Guidelines and Standards Relevant to Air Monitoring at the Ithaca City School District Transportation Department

Substance	NIOSH REL[1]	OSHA PEL[2]	ACGIH TLV[3]	Principle Health Effects[1,14]
EGBE	5 ppm (skin)	50 ppm (skin)	25 ppm (skin)	eye/respiratory irritation; tissue irritation; hematopoietic system effects; CNS depression
Isopropanol	400 ppm STEL 500 ppm	400 ppm	400 ppm	eye/respiratory irritation; possible carcinogenic effects
PGME/PGMEA*	100 ppm STEL 150 ppm	none	100 ppm	eye/respiratory irritation; CNS depression
1,1,1-trichloroethane	CL 350 ppm	350 ppm	350 ppm	eye irritation; dizziness, CNS depression; liver and cardiovascular effects
toluene	100 ppm STEL 150 ppm	200 ppm CL 300 ppm	100 ppm	eye.respiratory irritation; fatigue, headache, CNS depression
xylene	100 ppm STEL 150 ppm	100 ppm	100 ppm	eye/respiratory irritation; headache, CNS depression

EGBE = ethylene glycol monobutyl ether
PGME = propylene glycol monomethyl ether
CL = ceiling limit
STEL = short term exposure limit (15 minute time-weighted average)
ppm = parts per million
mg/m^3 = milligrams per cubic meter

* Propylene glycol monomethyl ether acetate (PGMEA) is rapidly metabolized to PGME in the body, and therefore the exposure criteria for PGME are applied to PGMEA as well.[15]

Organic Solvents

Many industrial solvents are irritants of the eyes, mucous membranes, and upper respiratory tract, and can cause defatting of the skin and dermatitis.[11] Exposure to organic solvents can occur through inhalation of the vapors, skin contact with the liquid, or ingestion. As many organic solvents have relatively high vapor pressures and readily evaporate, inhalation of vapors is considered a primary route of exposure. Overexposure to many organic solvents can result in irritation, central nervous system depression, headache, nausea, and possible effects on the liver, kidney or other organs.[11-13] Biological effects of exposure can range from practically non-toxic (e.g., some freons) to highly toxic (e.g., carbon tetrachloride) or to carcinogenic (e.g., benzene).[13] Table 1 summarizes the principle health effects associated with the solvents evaluated in this survey, and lists the relevant guidelines and standards -- NIOSH RELs, OSHA PELs, and ACGIH TLVs.

V. METHODS OF EVALUATION

The site visit consisted of a walk-through of the facility, observations of work practices, review of Material Safety Data Sheets (MSDSs), and collection of personal breathing zone (PBZ) and general area (GA) air samples. Air samples were collected for solvents and for C_e, which is used to estimate diesel exhaust exposure. Solvents were collected on Thermal Desorption tubes with Gillian® low-flow pumps at 50 milliliters per minute (ml/min) for qualitative analysis, and on charcoal tubes with Gillian® low-flow pumps at 200 ml/min for quantitative analysis, based on the compounds that were identified by the qualitative analysis. All of the solvent samples were GA except for one PBZ on a mechanic during a priming process. Four GA samples were taken in the garage and two in the office area.

Diesel exhaust exposure was estimated by measuring the concentration of C_e. A single-stage personal impactor was used to sample submicrometer-sized diesel particles on quartz fiber filters.[10] The filters were then analyzed by a thermal-optical method to quantitate the elemental carbon concentration. Five PBZ air samples were collected for C_e, two bus drivers and three mechanics. Also, two GA samples were collected in the garage, one in the office area, and one outside approximately 200 yards from the building and bus parking lot.

VI. OBSERVATIONS AND RESULTS

The office workers reported that exhaust and solvent odors often migrate into the office area. Thus, some GA samples were collected in the office area for C_e and solvents, as well as in the garage. When the exhaust fan in the garage is not operating and the smoke-eater in the open office area is off, the office area is at a slightly negative pressure to the garage. Turning on the garage exhaust fan does bring the two areas to about equal pressure, but not if the smoke-eater is operating. When the "smoke-eater" is on, regardless of the garage exhaust fan, air flows into the office area from the garage. Smoking is permitted at this workplace.

On the day of sampling, no buses were left running while in the garage.
Basic maintenance/mechanic work was being performed on the buses, and one section of a bus was primed to prepare it for painting. The priming process occurred at 2:50 pm and lasted only about one minute, thus no significant sampling was conducted during painting or priming. No brake pad work occurred during our site visit.

The painting area does not contain a paint booth or any local exhaust ventilation (LEV). Due to complaints of solvent odors from the office workers, no painting occurs during work hours, only priming. A mechanic returns at night or on weekends to paint. The mechanic wears a 3M® Easicare Dual Cartridge Respirator for Paint Spray Assembly. However, there is no fit-testing or medical surveillance program. Goggles are worn, but no gloves are worn during the priming or painting processes.

The Thermal Desorption tube samples revealed the presence of about 50 different compounds in the air. The results are displayed in Appendix A. Based on the estimated amounts of each compound, which ones appeared consistently, and the analytical methods available for quantitation, seven compounds were selected to be quantified -- isopropanol, 1,1,1-trichloroethane, toluene, xylene, propylene glycol monomethyl ether acetate (PGMEA), and ethylene glycol monobutyl ether (EGBE). The solvent area air sample concentrations were relatively low, approximately three orders of magnitude lower than the standards. Isopropyl alcohol, EGBE, and PGMEA were not detected in any of the samples. In the office area, the levels were either not detected or detected, but below the minimal quantifiable concentrations. In the garage area, the levels for 1,1,1-trichloroethane, toluene, and xylene were all less than 0.60 parts per million (ppm).

The C_e sampling results are displayed in Table 2. Area air sample levels ranged from 2.5 micrograms per cubic meter ($\mu g/m^3$) outside, across the employee parking lot, to 14 $\mu g/m^3$ in the garage. The garage mechanics both had personal sample concentrations of 13 $\mu g/m^3$, and Driver 1 and Driver 2 had concentrations of 7.2 and 5.9 $\mu g/m^3$, respectively. These C_e levels are only 5% to 28% of the total carbon concentrations. The organic carbon (C_o) concentrations on the sampling filters, 72% to 95% of the total carbon, could only in part be from diesel exhaust, which is only usually 10% to 30% C_o.[10] Other sources of C_o are from cigarette smoke (which has submicrometer-sized particles and could thus be collected on the filters), degreasing solvents, grease, and oil. Tobacco smoke has been found contain on the order of less than 2% C_e.[10]

Table 2

Personal and Area Air Sampling Results for Elemental Carbon, 11/9/93
Ithaca City School District Transportation Department
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Sample Site	Sample Volume (L)	Elemental Carbon (C_e) (µg/m^3)	Organic Carbon (C_o) (µg/m^3)	Total Carbon (C_t) (µg/m^3)	C_e/C_t Ratio
GA - office	1852	4.8	86	91	0.05
GA - garage	1848	13	35	49	0.27
GA - garage	2032	14	36	50	0.28
PBZ - mechanic 1	1740	13	87	100	0.13
PBZ - mechanic 2	1952	13	39	52	0.25
PBZ - driver 1	1328	7.2	52	59	0.12
PBZ - driver 2	1284	5.9	42	48	0.12
GA - outside	1420	2.5	18	21	0.12

µg/m^3 = micrograms per cubic meter
GA = general area air sample
PBZ = personal breathing zone air sample

VII. CONCLUSIONS

Environmental tobacco smoke (ETS) is a health hazard at this workplace. Not only is smoking permitted, but also there is no mechanical ventilation system in the building. The exhaust fan in the garage only operates during painting procedures and does not provide any ventilation for the office area.

The C_e levels suggest that diesel exhaust concentrations are elevated in the garage and office building as compared with the ambient concentration, and that the levels in the garage are more than double the levels in the office area. In a study of C_e exposure in the trucking industry, Zaebst *et. al.* found average C_e levels of 23.5 µg/m^3 for dock workers (n = 75), 26.6 µg/m^3 for mechanics (n = 80), 5.4 µg/m^3 for local drivers (n = 56), 5.1 µg/m^3 for road drivers (n = 72), a highway background of 3.4 µg/m^3 (n = 21), and a residential background of 1.4 µg/m^3 (n = 23).[10] Zaebst also mentions that levels ranging from 17 to 134 µg/m^3 have been measured in the railroad industry.[10]

The organic solvents do not appear to be a health hazard when the mechanics are not painting. The painting process, however, should not be occurring in an open room without any ventilation.

VIII. RECOMMENDATIONS

1. To help reduce the migration of exhaust and solvent vapors into the building, the garage should be kept at a pressure that is negative with respect to the building so that air flows from the office area into the garage, not from the garage into the office area. Operating the existing garage exhaust fan when the garage or building is occupied, as well as adding an additional exhaust system to the garage, will further reduce the diesel exhaust exposures. In addition, a second door could be added in the small hallway between the building and the garage.

2. The painting area must be designated and properly controlled. A spray booth can control the accumulation of vapors and particulates that may pose a fire, an explosion, or a health hazard. With appropriate ventilation in the spray booth, workers may not require the use of respiratory protection.

3. Proper personal protective equipment should be worn during the priming and painting processes. Gloves that protect skin from general solvents, such as neoprene or nitrile, and eye protection should always be worn. Respirators, if necessary, must be fit properly to their user. If a paint booth or local exhaust ventilation (LEV) system provides enough ventilation, the painter may not require respiratory protection. Industrial hygiene monitoring can characterize the exposure and determine if it is appropriate.

   If respirator use is necessary, implement a Respiratory Protection Program that provides medical surveillance and fit-testing for employees who use respirators, in accordance with the requirements described in 29 CFR 1910.134.[16] Publications developed by NIOSH which should also be referenced when developing an effective respirator program include NIOSH Respirator Decision Logic and the NIOSH Guide to Industrial Respiratory Protection.[17,18] It is recommended that the written program be revised to designate one individual with the responsibility for administering the respiratory protection program. The written respirator program should also contain information on the following topics: (a) the departments/operations which require respiratory protection; (b) the correct respirators required for each job/operation; (c) specifications that only NIOSH/MSHA approved respiratory devices shall be used; and (d) the criteria used for the proper selection, use, storage and maintenance of respirators, including limitations. The respirator program should also reference the requirements contained in the confined space program to assure that employees are adequately protected when working in these areas. A respiratory protection program should include the following elements:

   a. Written operating procedures.
   b. Appropriate respirator selection.
   c. Employee training.
   d. Effective cleaning of respirators.
   e. Proper storage.
   f. Routine inspection and repair.
   g. Exposure surveillance.
   h. Program review.
   i. Medical approval.
   j. Use of approved respirators.

4. Cigarette smoking should not be permitted in the building or a separate smoking room needs to be established. ETS has been shown to be casually associated with lung cancer and cardiovascular disease in adults, and respiratory infections, asthma, middle ear effusion, and low birth weight in children.[19-21] It is also a cause of annoying odor and sensory irritation. The U.S. Environmental Protection Agency (EPA) has classified ETS

as a known human (Group A) carcinogen.[22] NIOSH considers ETS to be a potential occupational carcinogen and believes that workers should not be involuntarily exposed to tobacco smoke.[23]

ETS consists of exhaled mainstream smoke from the smoker and sidestream smoke which is emitted from the smoldering tobacco. ETS consists of between 70 and 90% sidestream smoke. More than 4000 compounds have been identified in laboratory-based studies, including many known human toxins and carcinogens such as CO, ammonia, formaldehyde, nicotine, tobacco-specific nitrosamines, benzo(a)pyrene, benzene, cadmium, nickel, and aromatic amines.[24,25] Many of these toxic constituents are more concentrated in sidestream than in mainstream smoke.[26] In studies conducted in residences and office buildings with tobacco smoking, ETS was a substantial source of many gas and particulate polycyclic aromatic compounds.[27]

The most direct and effective method of eliminating ETS from the workplace is to prohibit smoking in the workplace. To facilitate elimination of tobacco use, employers should implement smoking cessation programs. Management and labor should work together to develop appropriate nonsmoking policies that include some or all of the following:

- Distribute information about health promotion and the harmful effects of smoking.

- Offer smoking-cessation classes to all workers.

- Establish incentives to encourage workers to stop smoking.

Until this measure can be achieved, employers can designate separate, enclosed areas for smoking, with separate ventilation. Air from this area should be exhausted directly outside and not recirculated within the building or mixed with the general dilution ventilation for the building. Ventilation of the smoking area should meet general ventilation standards, such as ASHRAE Standard 62-1989, which suggests the introduction of 60 cubic feet per minute of outside air per person, and the smoking area should have slight negative pressure to ensure airflow into the area rather than back into the airspace of the workplace.[23]

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X. INVESTIGATORS AND ACKNOWLEDGEMENTS

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Originating Office:	Hazard Evaluations and Technical Assistance Branch Division of Surveillance, Hazard Evaluations and Field Studies

XI. DISTRIBUTION AND POSTING

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Copies of this report have been sent to:

1. Ithaca City School District Employees' Association
2. Ithaca City School District Transportation Department
3. New York State Department of Labor

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

APPENDIX A

QUALITATIVE ANALYSIS OF THERMAL DESORPTION TUBES FOR VOLATILE ORGANIC COMPOUNDS

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 and 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, medical, nursing, and industrial hygiene technical and consultative assistance (TA) 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.

DEPARTMENT OF HEALTH & HUMAN SERVICES

Memorandum

Date December 3, 1993

From Chemist, MDS, MRSB

Subject Sequence 7909B; HETA 93-1000: Qualitative Analysis of Thermal Desorption Tubes for Volatile Organic Compounds.

To D. Tharr, HETAB Lab Coordinator
Attn: B. Donovan
Through: Acting Director, DPSE 12/3/93
Chief, MRSB, DPSE

INTRODUCTION:

Thermal desorption tubes collected at a vehicle maintenance facility for the Ithaca City School District were submitted for qualitative analysis of volatile organic compounds by GC-MS.

EXPERIMENTAL:

Since concentrations of contaminants were expected to be low, thermal tubes were used for sampling. For this study, stainless steel tubes configured for the Perkin-Elmer ATD 400 thermal desorption system were prepared in-house. Each thermal tube contained three beds of sorbent materials--a front layer of Carbotrap C (~350 mg), a middle layer of Carbotrap (~175 mg), and a back section of Carboxen 569 (~150 mg). Prior to field sampling, the thermal desorption tubes were conditioned for 2 hours at 375°C.

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). Samples were analyzed separately by directly inserting each into the thermal desorber unit with no other sample preparation. Each sample tube was desorbed at 350°C for 10 minutes.

A stock solution of CS_2 containing known amounts of several common solvents identified on these samples were analyzed along with the sample set to estimate concentrations. To prepare the spikes, aliquots of 0.1 μL to 2.0 μL of the stock solutions were spiked directly onto thermal desorption tubes as air was drawn through the tubes at 40-50 cc/min for 10 minutes. This stock solution contained the following compounds: hexane, 1,1,1-

trichloroethane, benzene, toluene, butyl cellosolve, decane, and limonene. Concentrations of the spikes ranged from 13 to 540 ng/sample.

RESULTS:

Copies of the reconstructed total ion chromatograms from the TD-GC-MSD analyses of samples and the standard spikes 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. The relative amounts varied among samples. Concentrations for some compounds were much greater than the highest spiked sample (which contained 260-540 ng/tube for 7 compounds).

Compounds detected on each tube also varied among the six field samples. Compounds detected on most samples included toluene, methanol, ethanol, ethylene glycol, various aliphatic hydrocarbons C_4-C_{16}, xylenes, C_9-C_{10} alkyl benzenes (propyl benzenes, tri- and tetramethylbenzenes, etc.), and naphthalene. Only two of the samples contained ethyl acetate, isopropanol, and acetone as major components (CX-37, CX-41); hexanes, dichloroethylene, and 1,1,1-trichloroethane were major compounds on the other samples. Some, but not all, samples contained limonene and other terpenes, butyl cellosolve, p-dichlorobenzene, menthol, methoxypropanol, propylene glycol monomethyl ether acetate (PGMEA), furfural, siloxanes, butanol, propylene glycol, diethyl phthalate, pyridine (CX-28), and vinylpyridine (CX-21).

The six charcoal tubes submitted at the same time as the thermal desorption tubes will be analyzed at a later date for the following specified compounds: isopropanol, 1,1,1-trichloroethane, toluene, xylenes, PGMEA, butyl cellosolve and total hydrocarbons.

Ardith A. Grote

Ardith A. Grote

Donald D. Dollberg

for John L. Holtz
Chief, MDS, MRSB, DPSE

Attachments

SEQ 7909 :
PEAK IDENTIFICATION
THERMAL DESORPTION TUBES

1) Air/CO_2*
2) Formaldehyde*
3) SO_2*
4) Propane
5) Acetaldehyde
6) Methanol
7) C_4H_8/C_4H_{10} aliphatics
8) Ethanol
9) Acetonitrile
10) Acetone*
10A) Trichlorofluoromethane
11) Isopropanol
12) C_5H_{12} aliphatics
13) C_5H_8 pentadiene isomer
14) Dichloroethylene isomer
15) Methylene chloride
16) C_6H_{14}/C_6H_{12} aliphatics
16A) 2-Butanol
17) n-Hexane
18) Ethyl acetate
19) C_6H_{12} methly cyclopentane
20) 1,1,1-trichloroethane
21) Benzene*
22) n-Butanol
22A) 1-Methoxy-2-propanol
23) Ethylene glycol
24) C_7H_{14}/C_7H_{16} aliphatics/trace trichloroethylene
24A) 2-hexanol?
25) Propylene glycol
25A) Pyridine
26A) n-Heptane
26) C_7H_{14} methyl cyclohexane
27) Toluene
28) C_8H_{16}/C_8H_{18} aliphatics
29A) Hexanal*
29) n-Octane
30) Furfural
30A) Hexamethylcyclotrisiloxane*
31) Perchloroethylene/C_8 aliphatic
31A) Propylene glycol monomethyl ether acetate
32) Xylenes/ethyl benzene
33) Styrene
34) 2-Butoxyethanol (butyl cellosolve)
35) n-Nonane
36) C_9-C_{10} aliphatics/C_9H_{12}, M.W.120 alkyl benzenes/trace benzaldehyde and terpenes
36A) 3-Vinylpyridine
37) Octamethylcyclotetrasiloxane*
38) p-Dichlorobenzene plus decane
38A) n-Decane
39) C_{10}-C_{12} aliphatics/$C_{10}H_{14}$, M.W.134 alkyl benzenes
40) Limonene
41) n-Undecane
42) Decamethylcyclopentasiloxane*
43) $C_{10}H_{20}O$ menthol isomer
44) Naphthalene/α-terpineol
44A) Naphthalene
45) n-Dodecane
46) n-Tridecane
47) Methyl naphthalenes
48) Siloxane compound*
49) n-Tetradecane
50) Dimethyl naphthalenes
51) $C_{10}H_{10}N_2$, a dimethylnaphthyridine?
52) n-Pentadecane
53) Diethylphthalate
54) n-Hexadecane
55) Aliphatic ester
56) M.W.210, diethyl biphenyl isomers

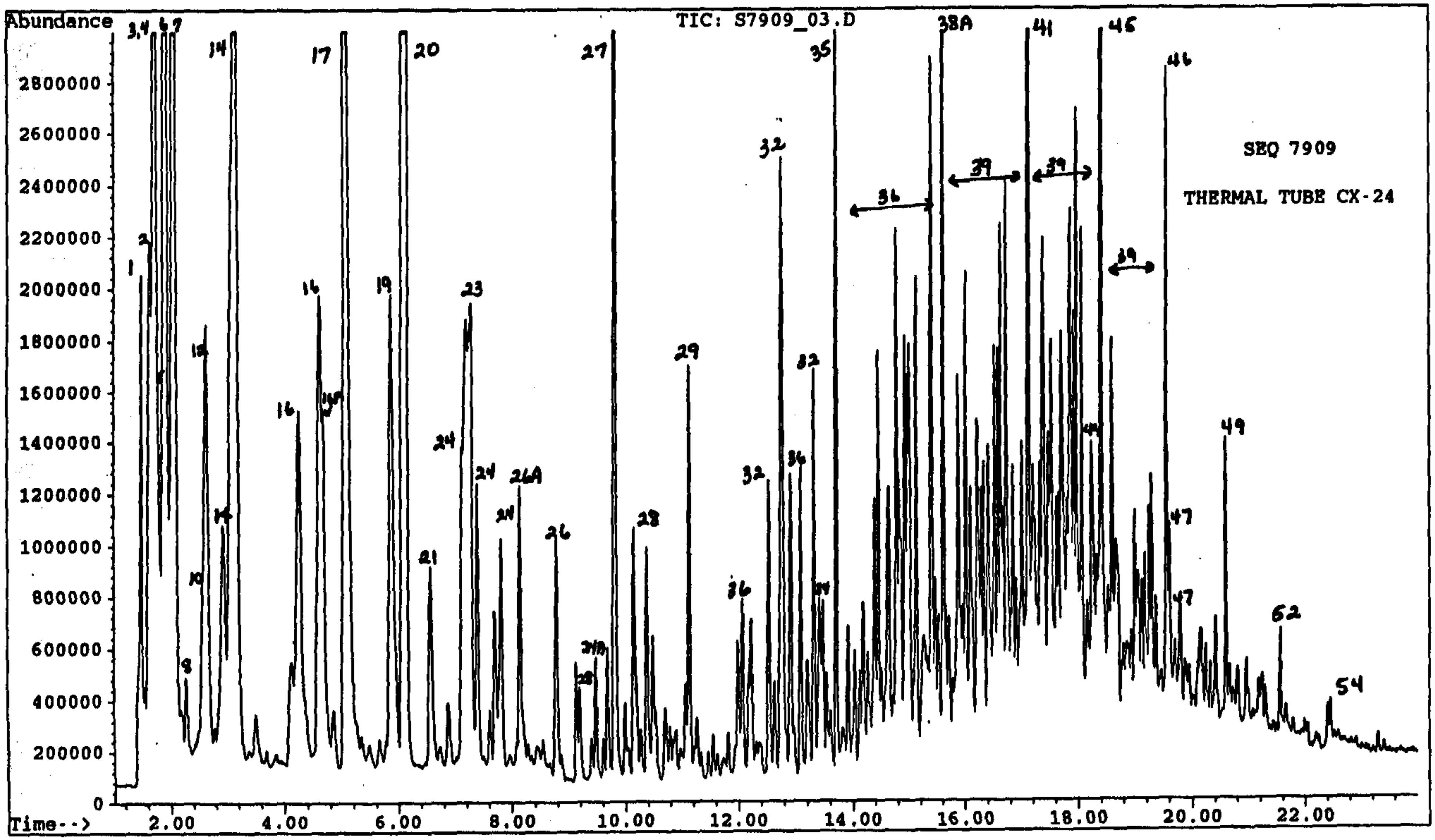
* Also present in some blanks.

SEQ 7909
SPIKED STANDARDS

PEAK NO.	COMPOUND	ng/sample 0.1 SPIKE	ng/sample 1.0 SPIKE	ng/sample 2.0 SPIKE
17	n-Hexane	13	132	264
20	1,1,1-Trichloroethane	27	270	540
21	Benzene	18	176	351
27	Toluene	17	174	346
34	Butyl cellosolve	18	180	360
38A	n-Decane	15	146	292
40	Limonene	17	168	336

GARAGE SAMPLE

File : C:\HPCHEM\1\DATA\S7909\S7909_03.D
Operator : AAG
Acquired : 15 Nov 93 4:11 pm using AcqMethod ATD.M
Instrument : 5970MSD--
Sample Name: SEQ 7909 CX-24 garage
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 3



GARAGE SAMPLE

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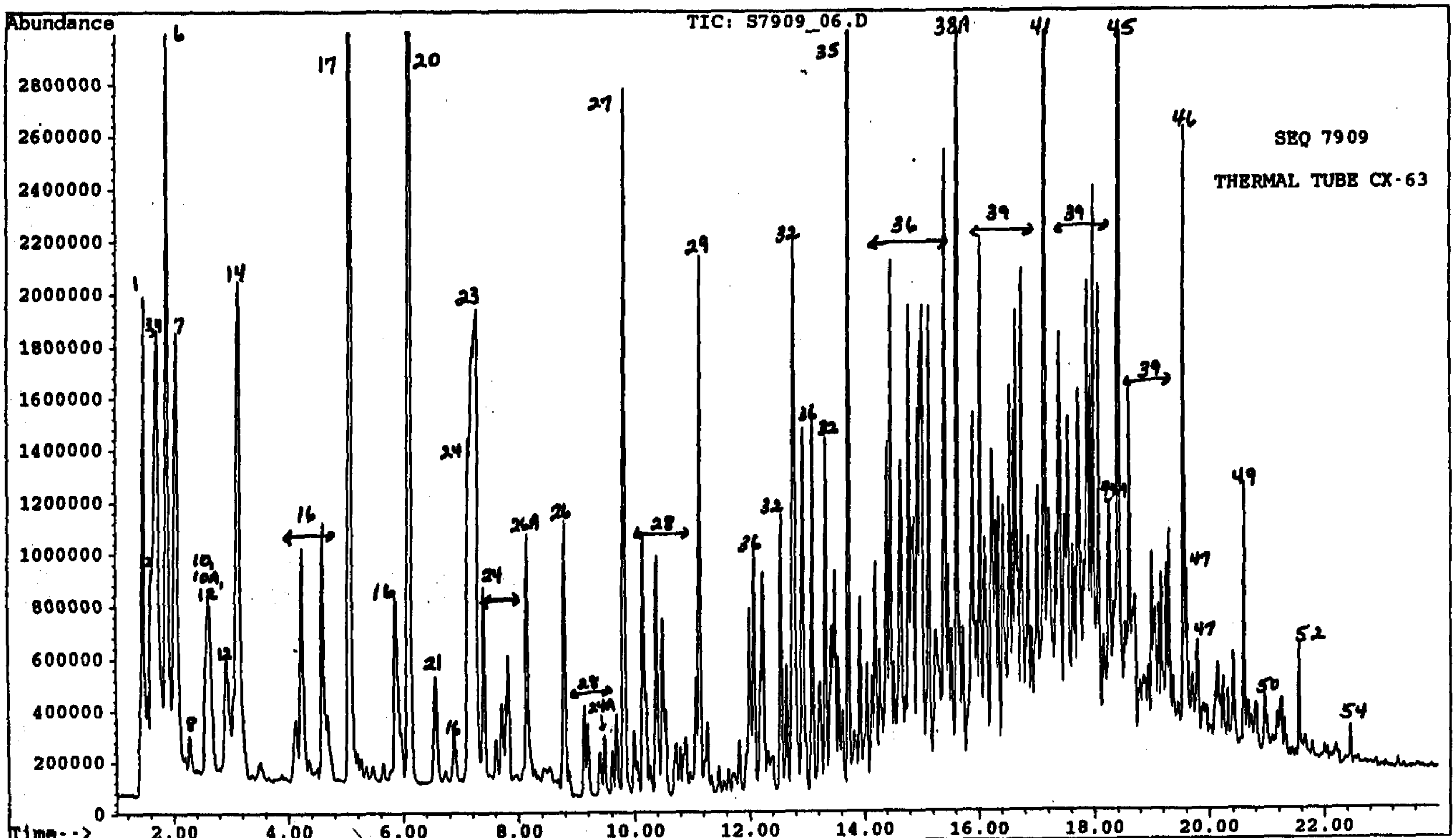
Instrument : 5970MSD--
Sample Name: SEQ 7909 CX-63 garage
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 6



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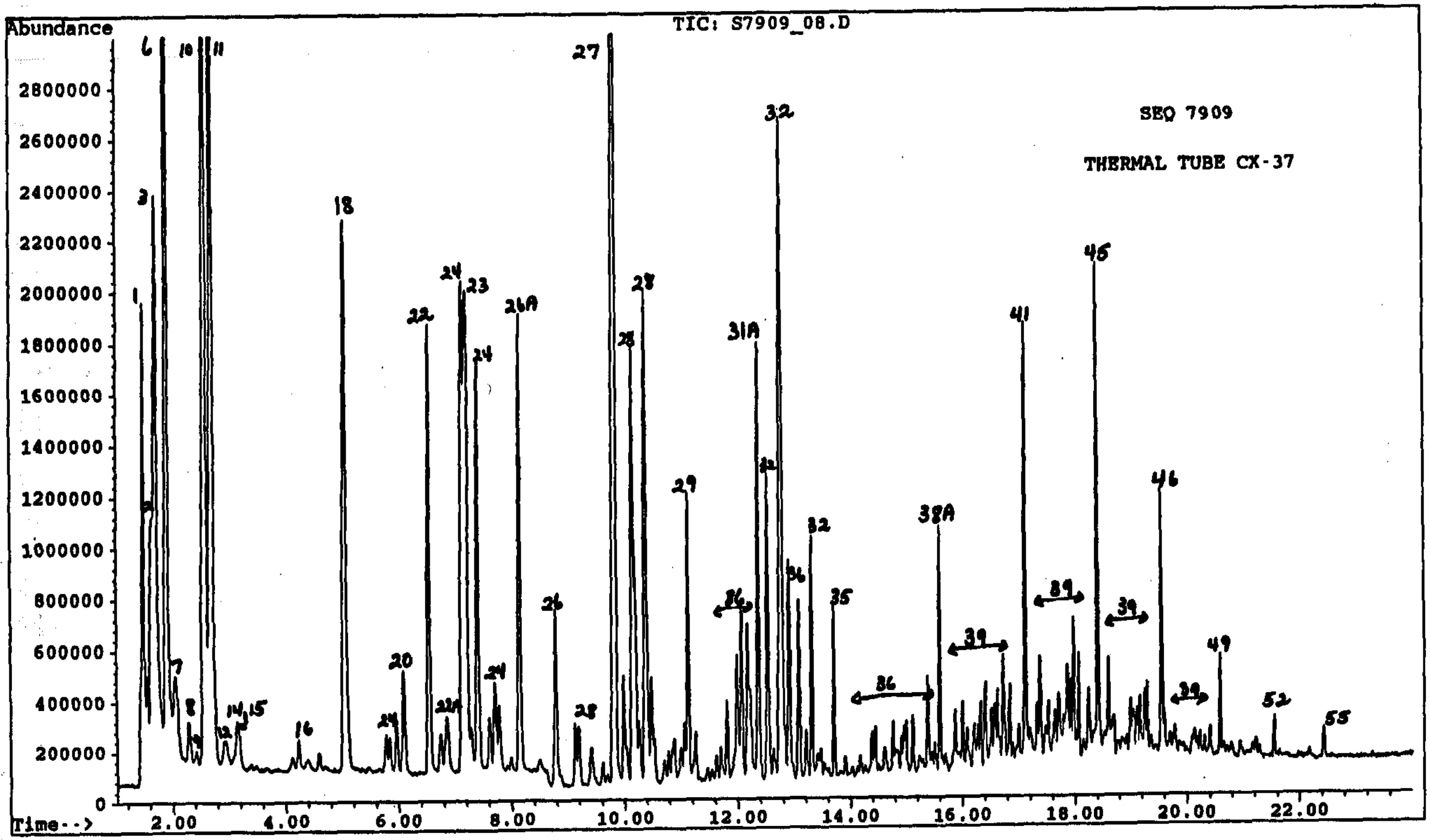
Acquired : 15 Nov 93 9:10 pm using AcqMethod ATD.M
Instrument : 5970MSD--
Sample Name: SEQ 7909 CX-37 garage
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 8

GARAGE SAMPLE



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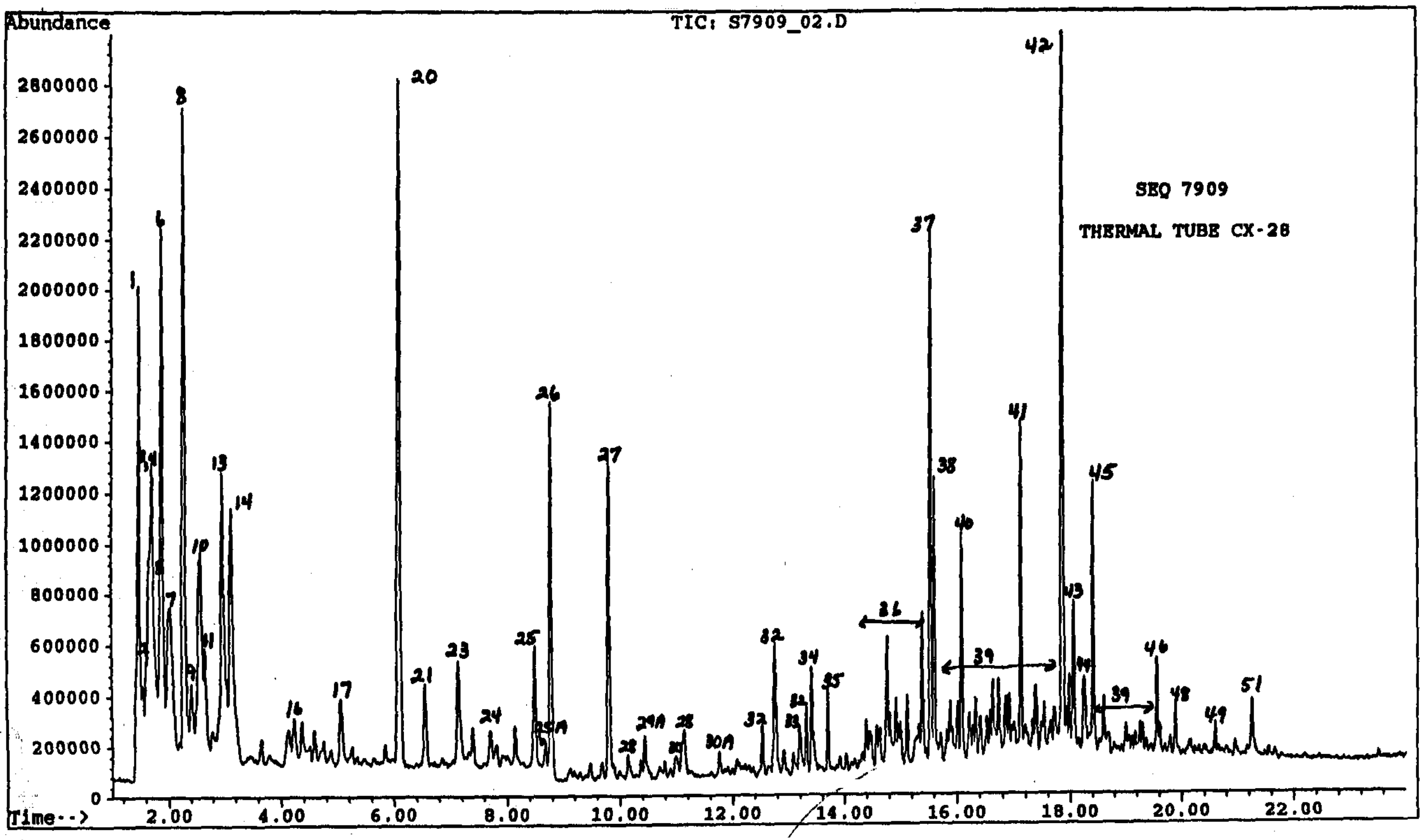
Instrument : 5970MSD--
Sample Name: SEQ 7909 CX-28 office
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 2

OFFICE SAMPLE



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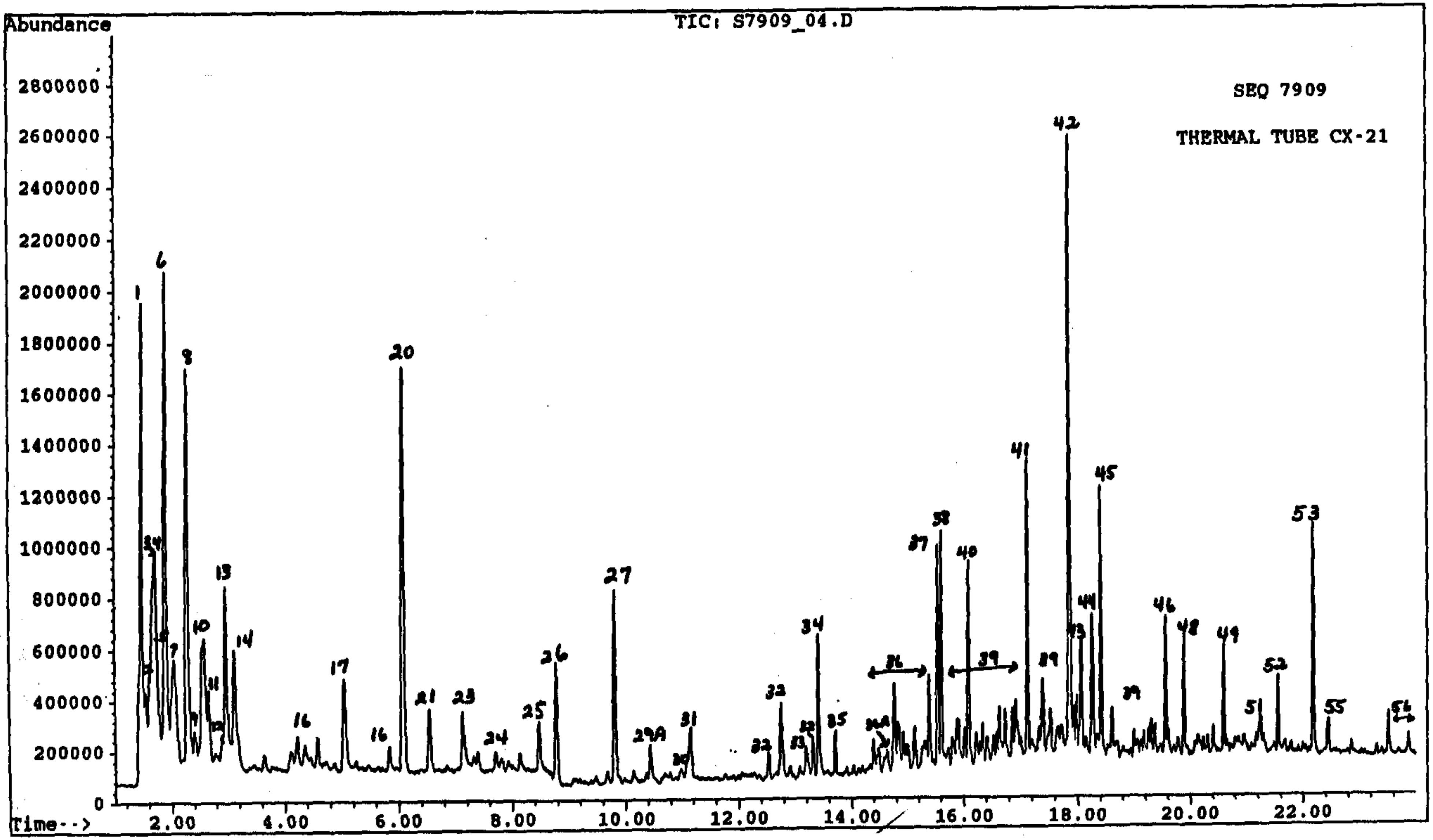
Operator : AAG
Acquired : 15 Nov 93 5:51 pm using AcqMethod ATD.M
Instrument : 5970MSD--
Sample Name: SEQ 7909 CX-21 office
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 4

OFFICE SAMPLE



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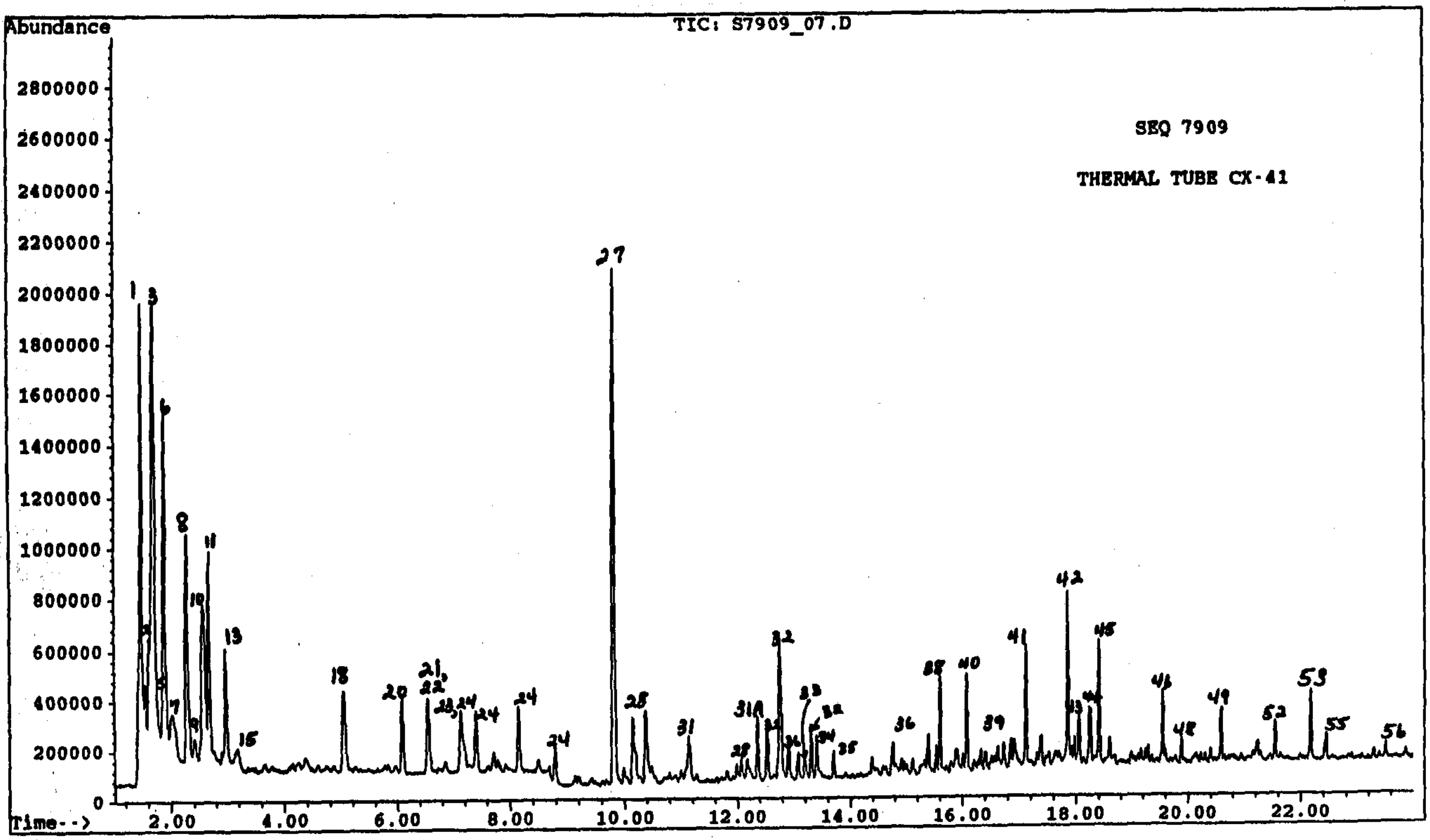
Operator : AAG
Acquired : 15 Nov 93 8:21 pm using AcqMethod ATD.M
Instrument : 5970MSD--
Sample Name: SEQ 7909 CX-41 office
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 7

OFFICE SAMPLE



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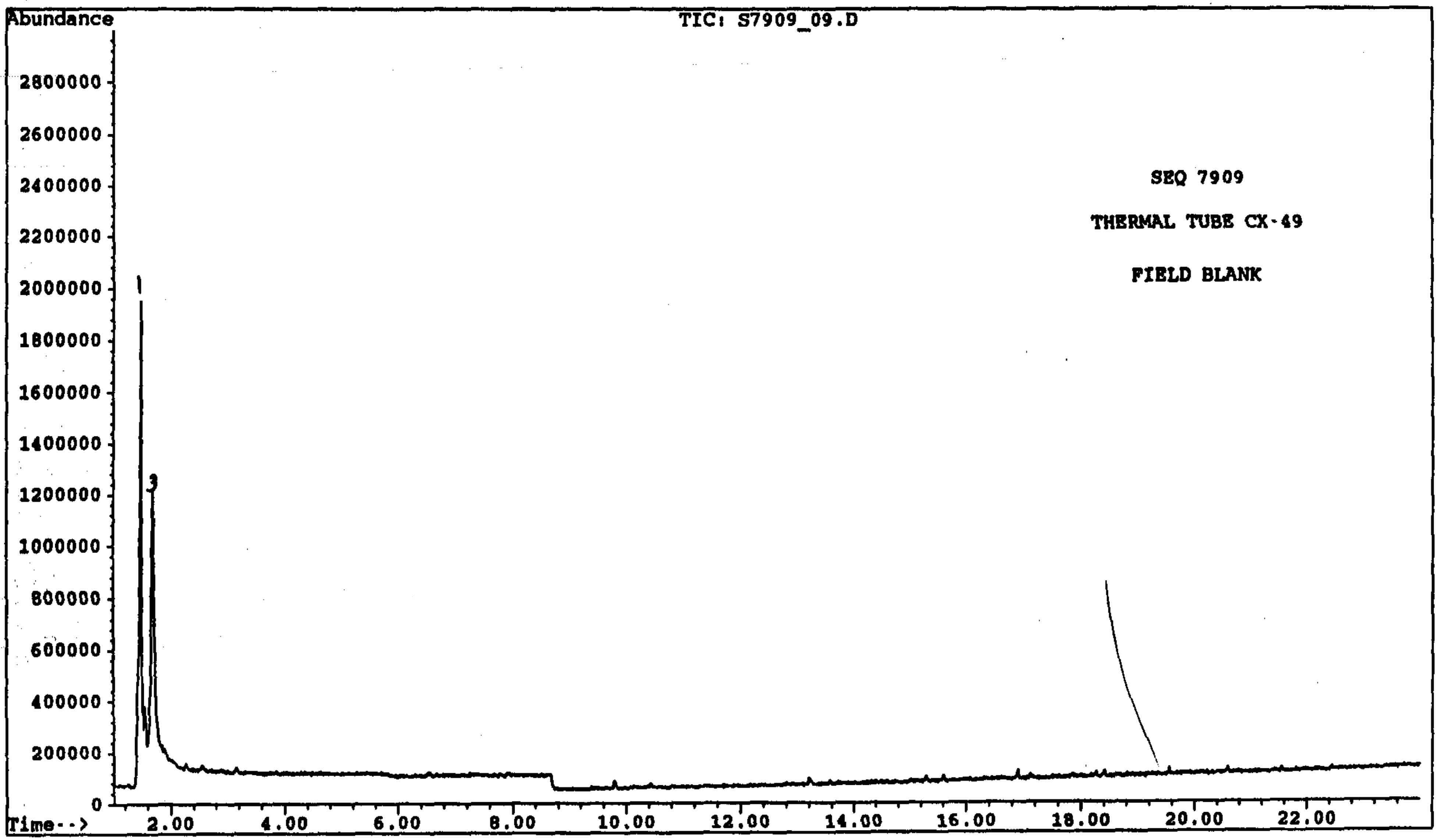
Acquired : 15 Nov 93 10:00 pm using AcqMethod ATD.M
Instrument : 5970MSD--
Sample Name: SEQ 7909 CX-49
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 9



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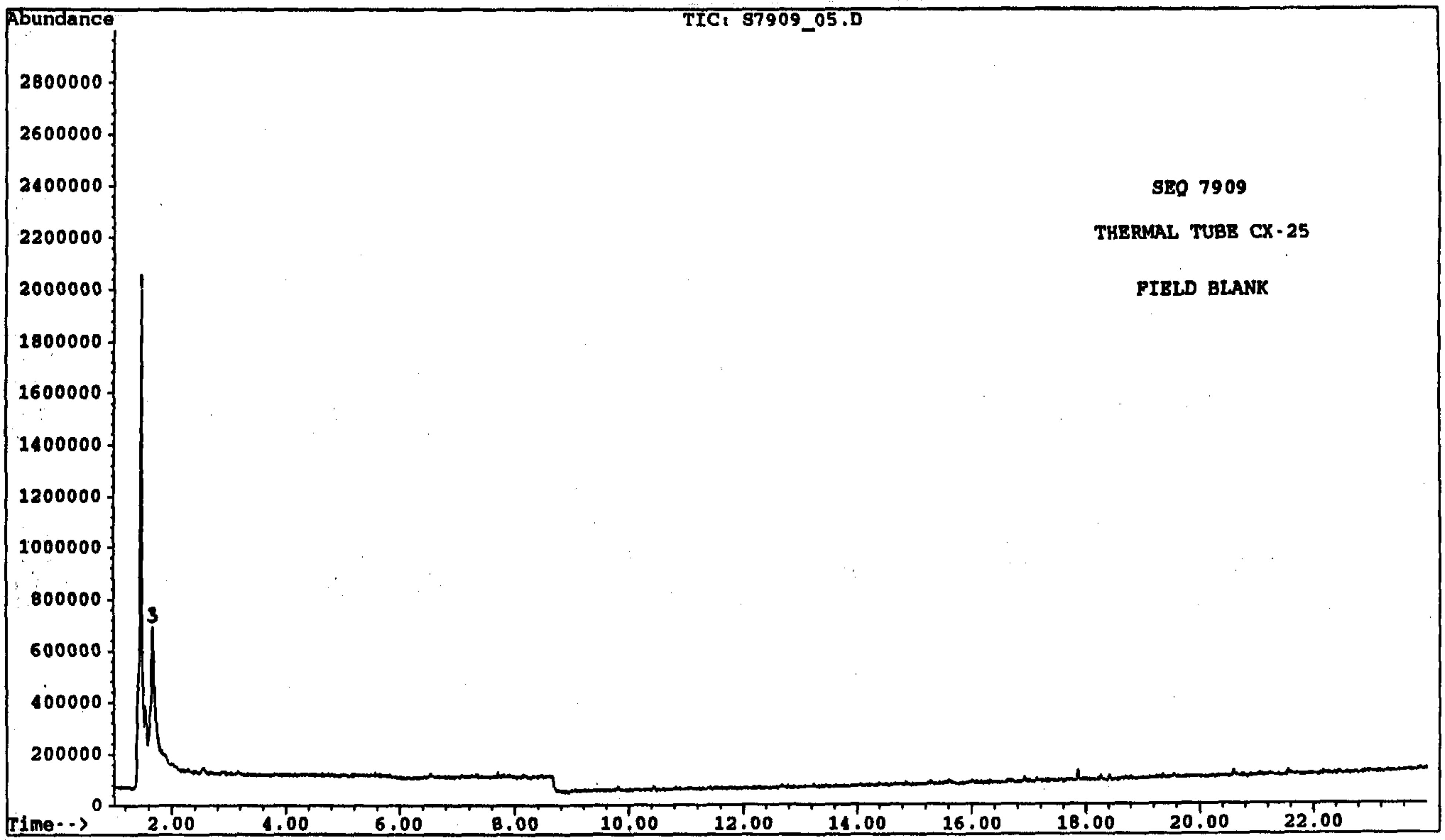
Operator : AAG
Acquired : 15 Nov 93 6:41 pm using AcqMethod ATD.M
Instrument : 5970MSD--
Sample Name: SEQ 7909 CX-25 FIELD BLANK
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 5



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Operator : AAG
Acquired : 15 Nov 93 10:49 pm using AcqMethod ATD.M
Instrument : 5970MSD--
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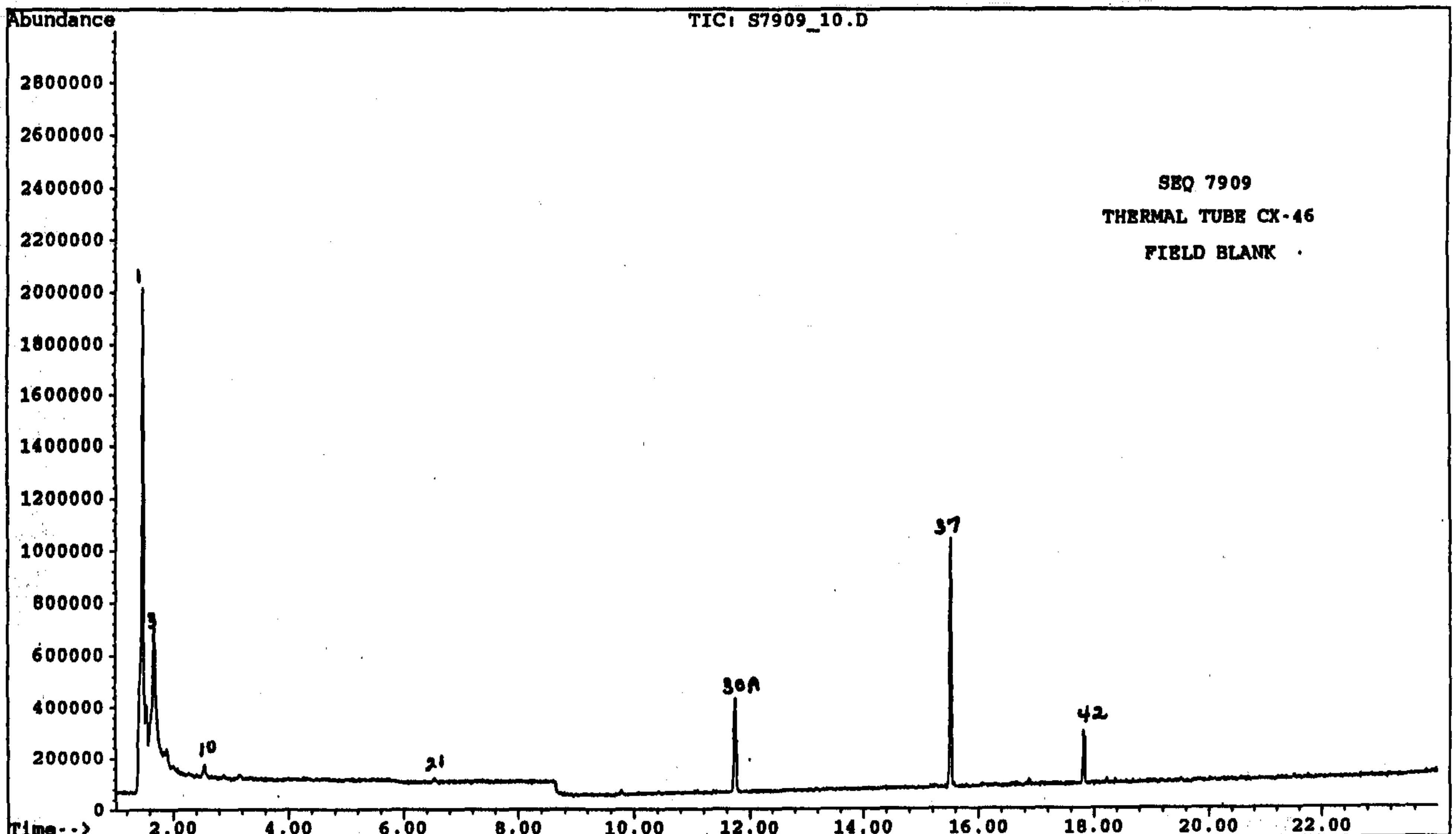
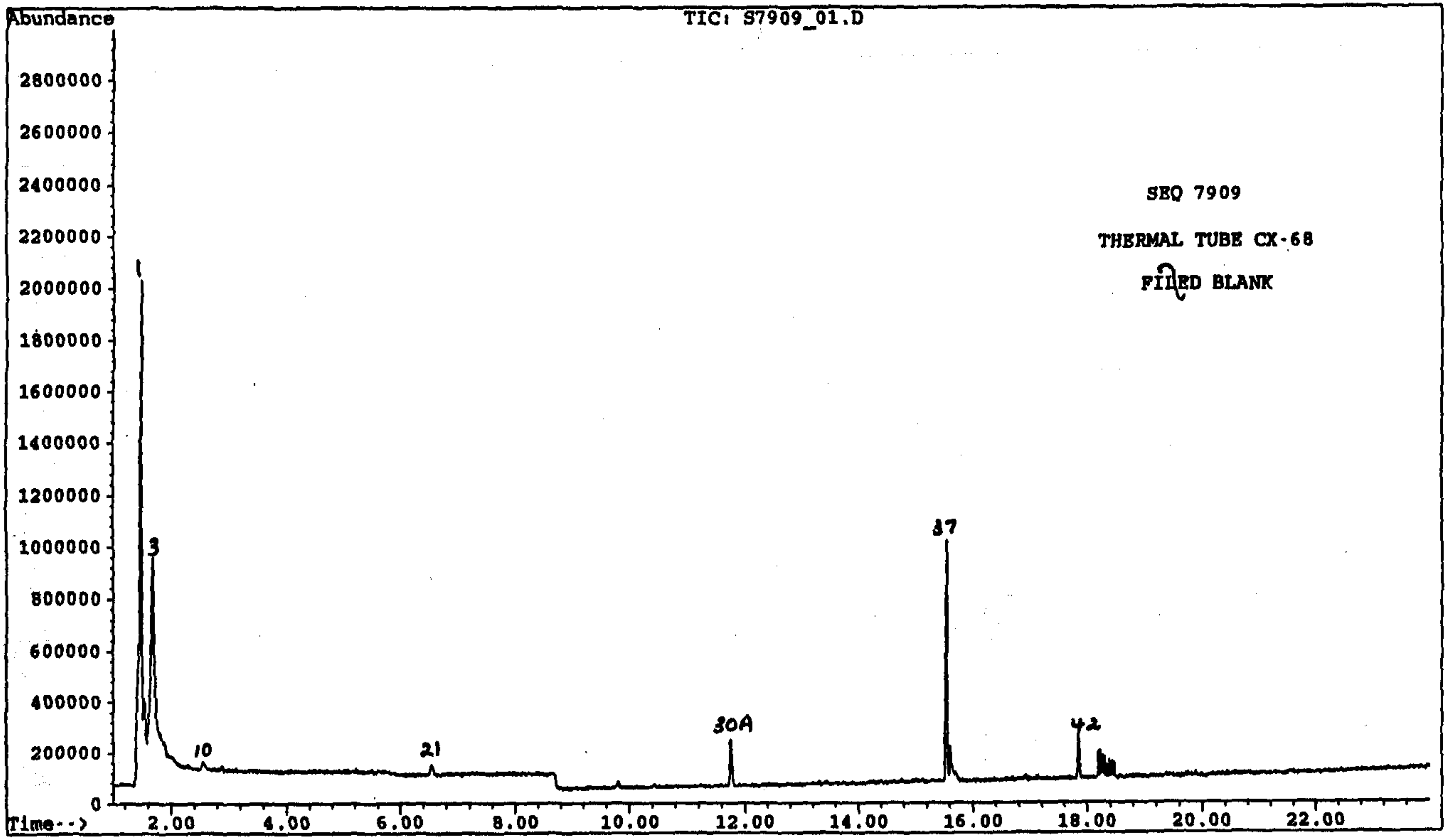
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 10



File : C:\HPCHEM\1\DATA\S7909\S7909_01.D
Operator : AAG
Acquired : 15 Nov 93 2:30 pm using AcqMethod ATD.M
Instrument : 5970MSD--
Sample Name: SEQ 7909 CX-68 BLANK
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 1



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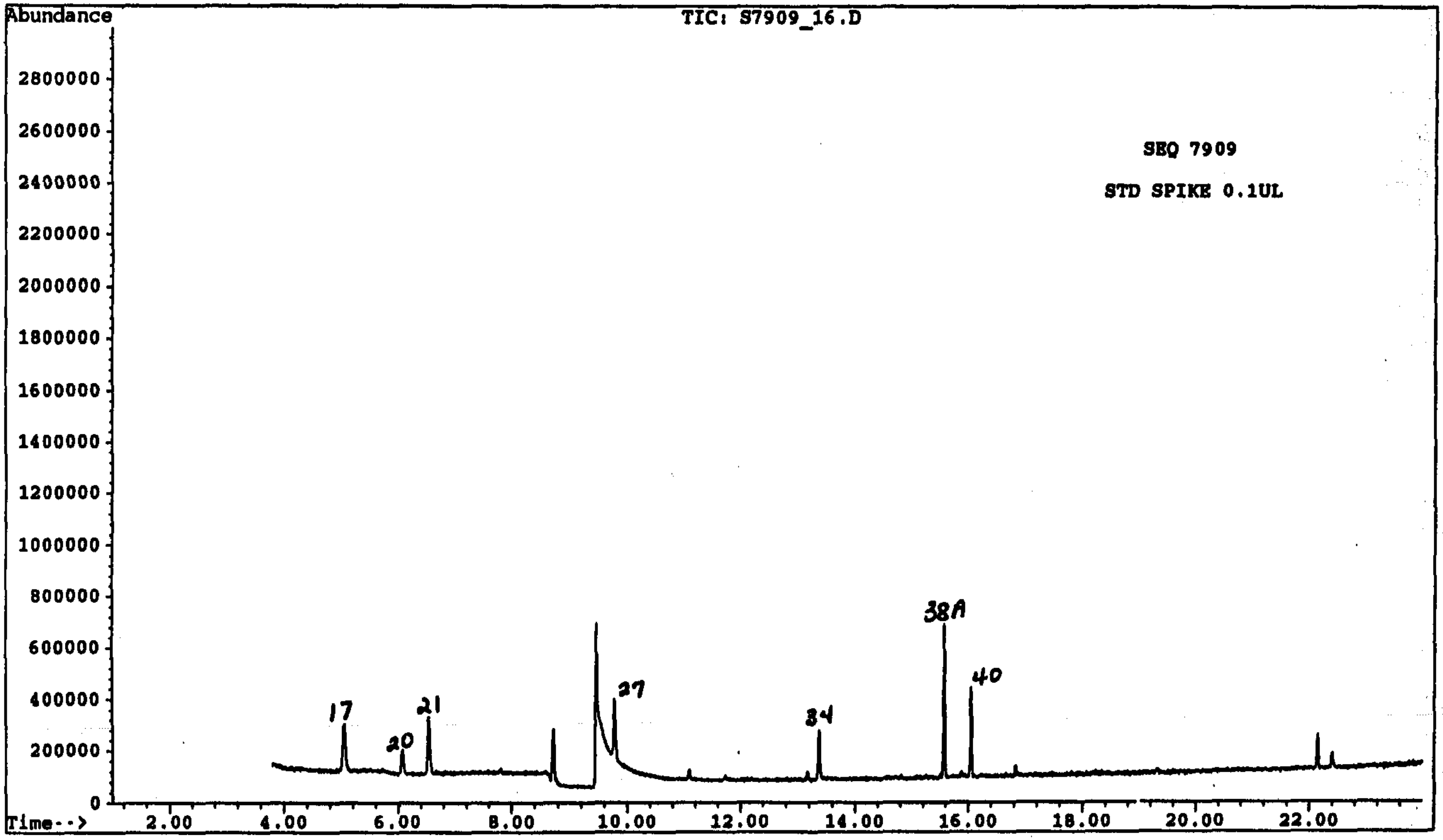
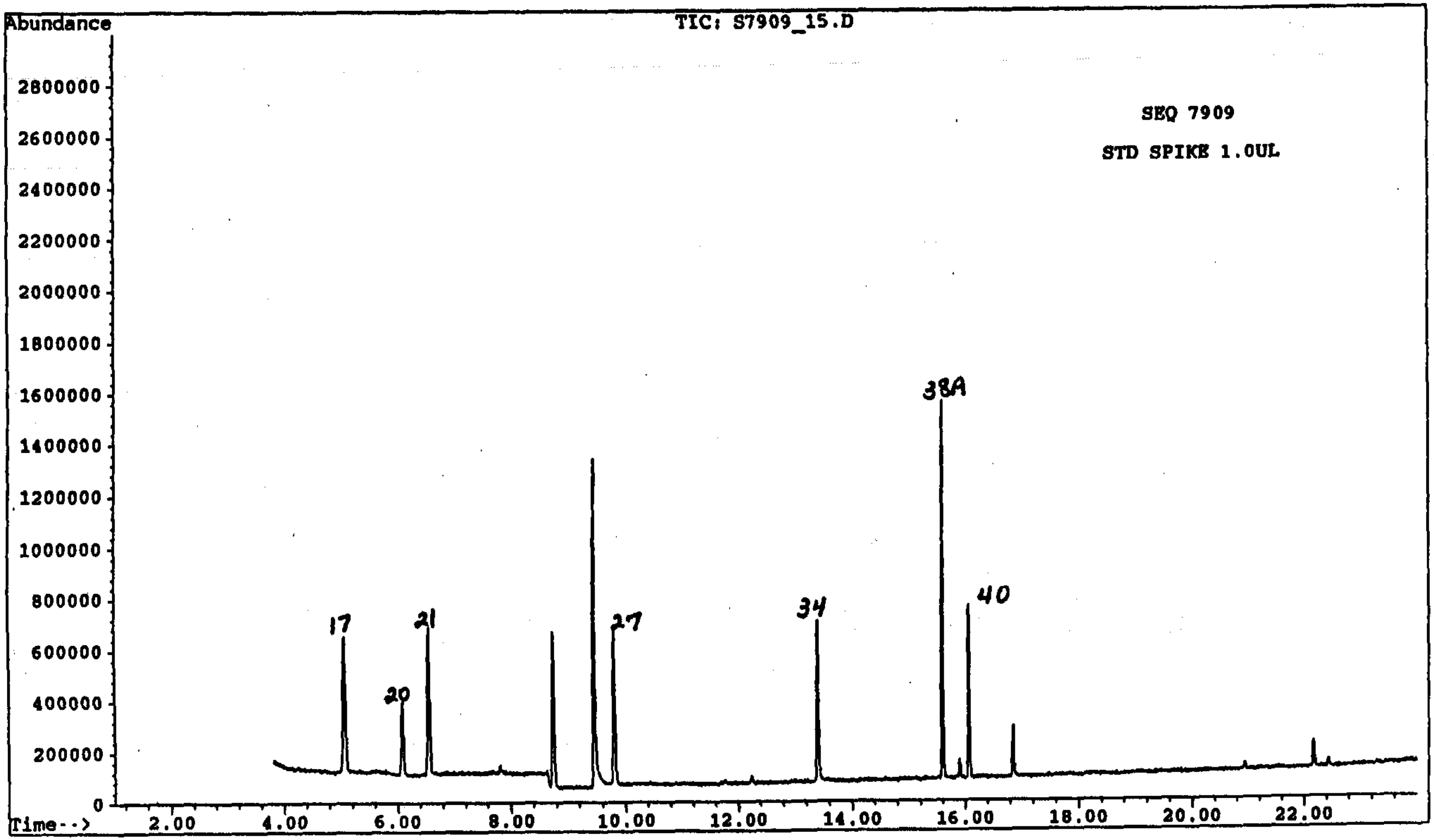
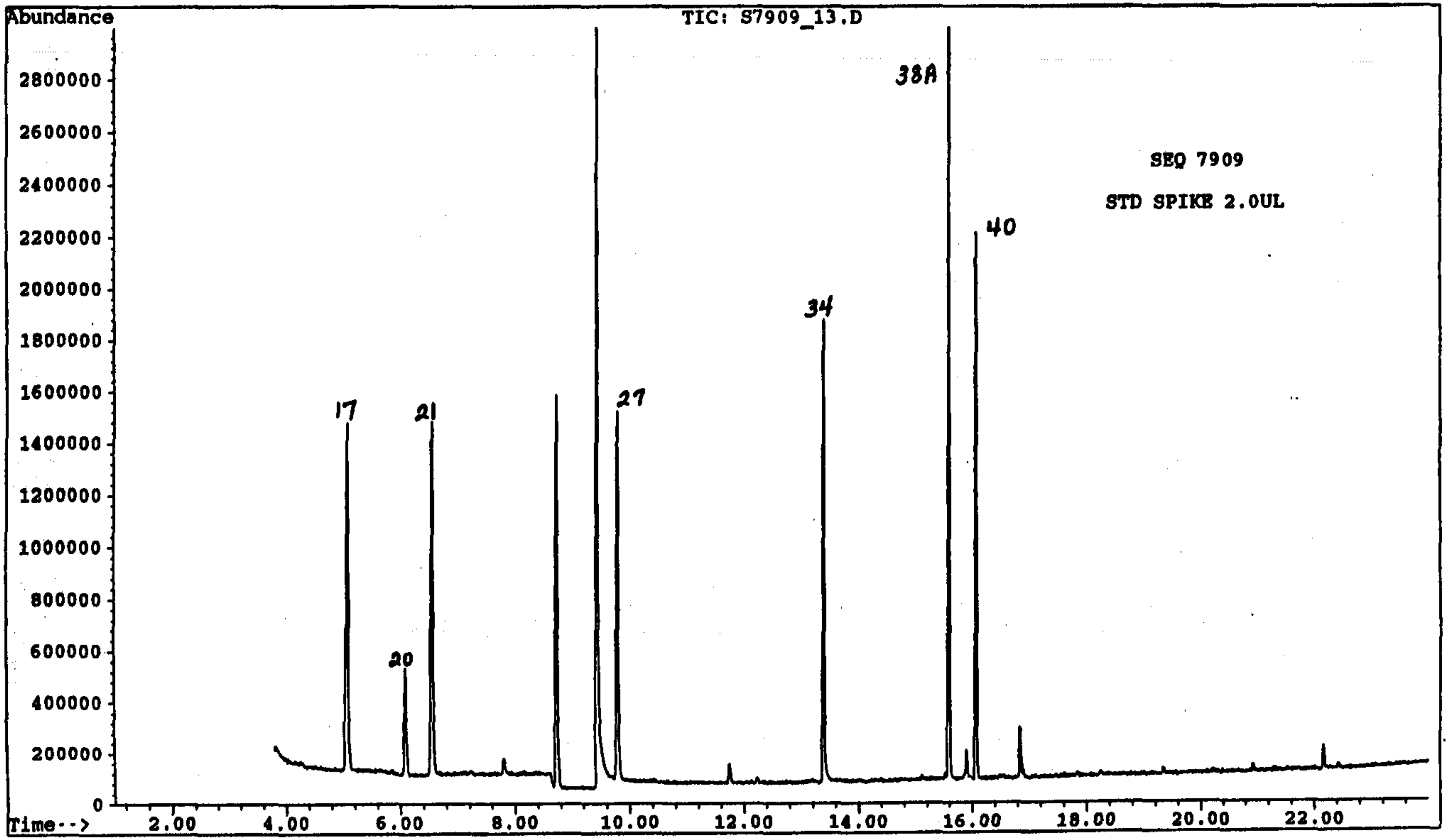
Operator : AAG
Acquired : 16 Nov 93 12:48 pm using AcqMethod CS2.M
Instrument : 5970MSD--
Sample Name: SEQ 7909/7910 SPIKE 0.1UL CX-43
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 16



File : C:\HPCHEM\1\DATA\S7909\S7909_15.D
Operator : AAG
Acquired : 16 Nov 93 11:58 am using AcqMethod CS2.M
Instrument : 5970MSD--
Sample Name: SEQ 7909/7910 SPIKE 1UL CX-16
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 15



File : C:\HPCHEM\1\DATA\S7909\S7909_13.D
Operator : AAG
Acquired : 16 Nov 93 10:18 am using AcqMethod CS2.M
Instrument : 5970MSD--
Sample Name: SEQ 7909/7910 SPIKE 2.0UL
Misc Info : 30 M DB-1 SC20-300 TP35-300
Vial Number: 13



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