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ALTERNATIVE CONCENTRATION TECHNIQUES FOR THE TRACE ANALYSIS OF SEMI-VOLATILE ORGANIC AIR POLLUTANTS BY CAPILLARY GAS CHROMATOGRAPHY

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Alternative Concentration Techniques for the Trace Analysis of Semi-Volatile Organic Air Pollutants by Capillary Gas Chromatography

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by

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the requirements for the degree of

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in the Faculty of Science
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August 1994

There is no end

to Human Potential -

and there's

so much to learn.

-Leo Buscaglia.

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BY

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SYNOPSIS

Standard methods for the determination of semi-volatile organic air pollutants are somewhat outdated and can be improved by utilising new sample concentration techniques. Two techniques, compatible with capillary gas chromatography, were developed in this study that show promise of increased speed, cost-efficiency and ease of automation:

An existing method, involving adsorption of pollutants on XAD resin, followed by liquid dichloromethane extraction, was improved by replacing the subsequent evaporative concentration step with solvent effect concentration.

A technique was developed based on thick film silicone rubber traps, known to effectively accumulate pollutants from air. Novel multichannel traps, consisting of a few silicone rubber tubes positioned in parallel, were made and conditioned to give minimal degradation peaks. Breakthrough volumes were determined with the aid of permeation tube standards. As sample recovery of these traps is by thermal desorption, expensive solvents are not required. Sharp chromatographic peaks were obtained without cryogenic refocusing.

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Semi-Volatile Organic Air Pollutants by
Capillary Gas Chromatography

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SAMEVATTING

Standaardmetodes vir die bepaling van min-vlugtige organiese verbindings wat met lugbesoedeling geassosieer word, is ietwat verouderd en kan verbeter word deur die aanwending van nuwe konsentrasietegnieke. Twee tegnieke, geskik vir kapillêre gaschromatografie, is in hierdie studie ontwikkel met voordele ten opsigte van verhoogde spoed, kostedoeltreffendheid en maklike outomatisasie:

’n Bestaande metode wat besoedelende komponente op XAD-hars adsorbeer, gevolg deur dichloormetaanekstraksie, is verbeter deur die daaropvolgende verdampings-konsentrasiestap met die oplosmiddeleffek te vervang.

’n Konsentrasietegniek is ontwikkel, wat gebaseer is op silikoonrubber-valle. Hierdie buise is bekend vanweë hul vermoë om besoedelende komponente effektief uit lug te versamel. Nuwe veelkanaalkonsentreerders, bestaande uit ’n aantal silikoonrubberbuise, is vervaardig en gekondisioneer om die kleinste afbraakpieke te gee. Permeasiebuisies wat lae-konsentrasie gasstandaarde verskaf, is vervaardig om die nuwe veelkanaalval te karakteriseer. Aangesien herwinning van opgevangde komponente deur termiese desorpsie geskied, word duur oplosmiddels nie benodig nie. Skerp chromatografiese pieke is verkry sonder die gebruik van ’n koueval om herfokussering te bewerkstellig.

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ABBREVIATIONS

AEC = Atomic Energy Corporation of South Africa Limited

PUF = Polyurethane Foam

PCB = Polychlorinated Biphenyl

PAH = Polycyclic Aromatic Hydrocarbons

PTV = Program Temperature Vaporization

CH_2Cl_2 = Dichloromethane

MC-TFT = Multichannel Thick Film Trap

MC3 = Multichannel silicone rubber trap containing 3 silicone rubber tubes inside a glass tube.

MC8 = Multichannel silicone rubber trap containing 8 silicone rubber tubes inside a quartz tube.

US EPA = USA Environmental Protection Agency

CHAPTER 1

INTRODUCTION

1.1 Background

In spite of the ever growing concern over environmental pollution, millions of tons of various ecologically harmful substances are released annually into the atmosphere and oceans. To keep this pollution at a minimum, effective methods for the analysis of pollutant concentrations are required. The concentration of many pollutants in the air is very low, often 10^{-4} - 10^{-3} % [1.1] or lower. Thus complicated trace analysis methods are required to analyze air pollution quantitatively.

Semi-volatile organic compounds contain a significant number of substances that are mutagenic, some are animal carcinogens and still others are linked to a variety of chronic diseases such as emphysema [1.2]. The term 'semi-volatile organic pollutants' was coined by the US EPA to designate compounds that are not sufficiently volatile to be analyzed by purge-and-trap GC. The compounds range in volatility from dichlorobenzenes to benzo-[ghi]-perylene [1.3].

The Atomic Energy Corporation of South African (AEC) uses the US EPA method S008 to analyze semi-volatile organic pollutants in flue gases. This method analyzes for dichloromethane-soluble materials and a series of polynuclear aromatic hydrocarbons (PAH's). The adsorbent used in these analyses to collect the organic pollutants is XAD-2 resin. To recover the pollutants after sampling, the XAD-2 resin is Soxhlet extracted with large volumes of ultra pure dichloromethane for 24 hours. This dichloromethane sample is concentrated using a Kurderna-Danish concentrator and then analyzed by capillary gas chromatography / mass spectrometry.

The AEC experiences many problems with the XAD-2 resin used in these analyses. The XAD-2 resin appears to be temperature sensitive; at high temperatures it breaks up into benzene derivatives which interfere with the pollution analyses. The use of XAD-2 as an adsorbent for pollution sampling is expensive as the XAD-2 cannot be reused after analysis. Also large volumes of pure solvent are required and the analyses are time consuming, with the long Soxhlet extractions and concentration steps.

On the basis of these problems, research was done to determine alternative concentration techniques.

1.2 Approach

The standard methods for the determination of semi-volatile organic air pollutants are somewhat outdated and can be improved by utilising new sample concentration techniques. The objective of the proposed research was to study the latest concentration techniques designed for capillary gas chromatography that show promise of increased speed, cost-effectiveness and ease of automation.

Firstly, the sample analysis time can be reduced by decreasing the time required to concentrate the sample solvent with the Kurderna-Danish concentrator, by replacing this step with the solvent effect. The solvent effect has only been studied with hexane as solvent. As dichloromethane is widely used to extract pollutants from adsorbents [1.1, 1.4] and it is also used in method S008 to extract semi-volatiles from the XAD-2 resin, a study was done to optimize the solvent effect for dichloromethane.

Secondly, research was done to find a new adsorbent which could replace the XAD-2 resin in the analysis of semi-volatile organic air pollutants. Sorbents used as concentrators of air contaminants should fulfil the following requirements [1.1]:

1) They should efficiently trap small concentrations of contaminants and retain them until the analysis can be performed.

2) Their capacity should be sufficiently high; have high breakthrough volumes.
3) They should not react with the contaminants while the sample is stored; nor should they decompose during storage loaded or unloaded.
4) They should selectively adsorb contaminants in the presence of bulk matrix compounds, (eg. water).
5) Convenient quantitative methods of sample recovery should be available.
6) Preferably they should be easy to handle and cheap.

Thick film silicone rubber traps [1.5] show promise of increased speed, acceptable retention, ease of automation and cost-effectiveness as they can be reused and do not require large volumes of pure solvents for sample recovery. In this work the use of multichannel silicone rubber traps for the analysis of semi-volatile organic air pollutants is investigated.

1.3 Arrangement and Presentation

This dissertation firstly (chapter 2) looks at the different techniques to analyze semi-volatile organic air pollutants. It is then divided up into two parts. The first part (chapter 3), concentrates on the optimization of the solvent effect for dichloromethane. The second part looks at the development and characterization of the multichannel thick film trap;

where chapter 4 discusses the making and conditioning of the trap and determines the maximum expected interference of the trap itself due to chemical degradation under air pollution sampling and analysis conditions. Chapter 5 examines the different ways of producing standards which are used to help characterize (Chapter 6) the multichannel thick film trap.

CHAPTER 2

COLLECTION AND PRETREATMENT TECHNIQUES FOR THE ANALYSIS OF ORGANIC AIR POLLUTANTS

2.1 Collection of Organic Pollutants

Sorption on solid sorbents is the principal method for sample collection and the concentration of toxic agents from polluted air. Large volumes of air are passed through a sorbent bed with a large surface area and the concentrated contaminants are recovered by thermal desorption of the trap or by extracting the pollutants from the trap with an appropriate solvent. Porous polymers are most successfully used to trap toxic agents of high molecular weight and non-volatile substances such as pesticides. They are relatively inert, hydrophobic and normally have large surface areas. These non-polar porous polymers retain water and volatile organic compounds poorly, which is an advantage if a sample is collected in an atmosphere with a high moisture and solvent vapour content [1.1].

A literature study was done on two porous polymers, PUF and XAD-2 as adsorbents which collect semi-volatile organic air pollutants. The collected contaminants for both these adsorbents is recovered by solvent extraction. A literature survey of the collection of pollutants on diffusion denuders and thick film silicone rubber traps was undertaken, where recovery of the collected sample is by thermal desorption.

2.1.1 Polyurethane Foam (PUF)

PUF is often used as a vapour-trapping medium for semi-volatile organic compounds in high volume air samplers operated at several hundred cubic meters per day. Some compounds for which PUF has found wide application are pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins and dibenzofurans, and phthalate esters [2.1]. These organic compounds are typically recovered from the PUF sorbent by performing a solvent extraction with the aid of a Soxhlet apparatus or by ultrasonication. Prior to liquid extractions, the PUF cartridges are spiked with a liquid internal standard containing typical target PAHs [2.2, 2.3, 2.4]. The sample extractions generally require several hours to perform, and use relatively large volumes of ultrapure solvent resulting in a diluted sample that must be concentrated before analysis.

It was noted that PUF has the following disadvantages: Prior to sampling PUF is extensively cleaned with large volumes of pure solvent. When using PUF as an adsorbent, samples must be taken at low temperatures, preferably below 20°C. At higher temperatures PUF shows very low breakthrough volumes [2.2, 2.1, 2.3]. PAH species that are prone to degradation during sampling or during sample storage, prior to extraction, exhibit greater losses from PUF than from other adsorbents like XAD-2 resin [2.3]. Semi-volatile organic compounds in the volatility range of chlorobenzenes and two-ring aromatic hydrocarbons are poorly collected by high-volume air samplers using PUF alone as an adsorbent. Collection of these semi-volatile compounds is greatly improved by using granular adsorbents with high specific surface areas such as Tenax [2.1, 2.2, 2.5], XAD-2 [2.1, 2.3] or charcoal [2.4], either alone or sandwiched between two PUF plugs.

Even though PUF has these disadvantages it is widely used due to the fact that it is cheap, is easy to handle, can be produced in any shape and size, has low resistance to air flow as required for rapid sampling and can be reused [2.6].

2.1.2 XAD-2

Amberlite XAD-2 is a styrene-divinylbenzene copolymer of hydrophobic character [2.7]. It is a common adsorbent used in the collection of a wide range of organic compounds from water. In air pollution analyses XAD-2 is most suited for the collection of polar compounds and is used in the sampling of semi-volatile organic pollutants which include PAHs [2.3], PCBs [2.8, 2.9], organothiophosphates and hexachlorobezenes [1.1].

Prior to sampling, the XAD-2 resin goes through an extensive series of Soxhlet extractions to clean the adsorbent from any interfering compounds. After sampling, the XAD-2 resin is spiked with a liquid internal standard and Soxhlet extracted with large amounts of solvent. This solvent sample also has to be concentrated prior to GC injection.

Even though XAD-2 is often used to analyze semi-volatile organic air pollutants and is the chosen adsorbent of the US EPA to analyze semi-volatile organic pollutants in flue gases (method S008), it portrays many problems which include: it is temperature sensitive, ie. brakes up into benzene derivatives at high temperatures, and it is expensive as it cannot be reused and requires large volumes of pure solvent and time for Soxhlet extractions.

2.1.3 Diffusion Denuders

A diffusion denuder consists of an aluminium [2.19], stainless steel [2.17] or pyrex glass [2.18] tube, or a set of tubes through which an atmospheric sample is passed. The inside of the tube is coated with a material which collects the components of interest. Most commonly denuders are used to remove selected vapour phase components from the sample stream while transmitting other vapour components and particles to subsequent stages of the sampling apparatus. Because the diffusion coefficients of particles and vapour-phase molecules differ by 10^3-10^6 [2.10], the particles tend to pass through the tube while the vapour-phase components tend to diffuse to the wall, where they are accumulated. The substitution of packed tubes by annular denuders serves to increase the collection effiency [2.11]. After accumulation the adsorbed species are removed from the denuder either by thermal desorption or solvent extraction.

Diffusion denuders have commonly been used to collect selectively volatile inorganic compounds such as SO_2 [2.12, 2.13], from aerosols. In addition, they have been used to remove NH_3 and HNO_3 [2.14, 2.15, 2.16], in order to determine true atmospheric nitrate concentrations. The technique has also been applied in sampling semi-volatile organic compounds [2.10, 2.17, 2.18, 2.19,] and to determine particle associated organic pollutants by removing vapours such as phenanthrene and octadecane [2.20].

Historically, most denuders consisted of an open cylindrical design. The collection efficiency of these denuders depends on the nature of the sorbent coating the walls, the geometry, flow rate and diffusion coefficients for the materials to be removed. Assuming 100% collection efficiency for the wall coating, and viscous, laminar flow the equation below applies according to Gormely and Kennedy (GK) [2.21]:

$$\frac{C}{C_0}=0.819\exp(-14.6272\Delta)+0.0976\exp(-89.22\Delta)+0.01896\exp(-212\Delta)$$

where $$\Delta = \frac{DL}{\gamma dRe}$$

and C_0 is the gas concentration entering the tube, C is the average gas concentration leaving the tube, L is the length of the coated tube, D is the diffusion coefficient of the gas, γ is the kinematic viscosity of air (0.152 $cm^2.s^{-1}$ at 20°C and 1atm), d is the internal diameter of the tube and Re is the Reynolds number. The efficiency of open cylindrical denuders for a given size and flow rate have been improved by developing annular denuders [2.18, 2.19, 2.21], parallel plate denuders [2.13] and multiple tube denuders [2.14, 2.15, 2.17, 2.10]. The annular denuder is the design used most often. Possanzini [2.21] developed and designed a diffusion denuder made of two concentric short tubes and proved that the annular geometry, based on theoretical considerations is superior in terms of efficiency and absorptive capacity compared with the single cylindrical one. Since then multiple annular denuders bearing as many as 12 concentric tubes have been described, and PC-based programs are available for computing the collection efficiency of such denuders [2.19].

Recently Krieger [2.10] designed a new multiple tube denuder consisting of 120, 25cm gas chromatographic column pieces bonded in parallel with thermally stable epoxy resin. The parallel design of the sampler increases the total sampling flow rate, while keeping the flow rate per tube low. This new denuder shows a lot of scope and promise.

2.1.4 Thick Film Silicone Rubber Traps

In the last few years some studies have been done to analyze organic volatiles using thick film rubber traps [1.5, 2.22, 2.23, 2.24, 2.25, 2.26, 2.27, 2.28]. These traps are used for the analysis of pollutants both in air and water [2.28]. The trap shows acceptable retention, low resistance to air flow, is suitable for repetitive collections of organic air samples and the collected material can be obtained either by thermal desorption or liquid extraction [2.24]. Also, background peaks due to degradation of the trap appear only when desorption is done at 250°C or higher [2.27].

Initially these traps were prepared by a difficult process of coating glass or fused-silica capillary tubing with a 15-100μm film of a cross-linked, apolar stationary phase, [2.22-2.26]. Burger devised a method of inserting a silicone rubber tube into a 0.53mm i.d. fused silica capillary by an innovative stretch and freeze method [1.5]. Commercial polymer tubes thus produce 145μm film thicknesses and a corresponding increase in retention for volatile organics, [2.27, 1.5]. Figure 2.1 shows a single channel silicone rubber trap.

To increase the retention capacity of these traps they are increased in length up to a meter [2.27]. Due to the increased length of these traps two column ovens are required for desorption [2.24, 2.27].

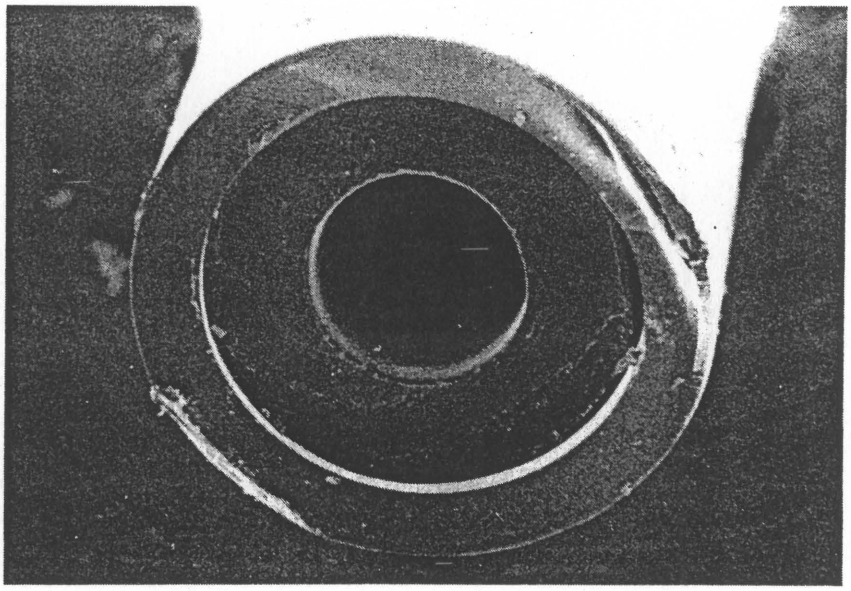


Figure 2.1 Cross section of a single channel ultra-thick film trap with $d_f = 145\mu m$. Reproduced from B.V. Burger, M. Le Roux and W.J.G. Burger, HRC, 13, 1990, p. 778.

2.2 Concentration of Dilute Solutions

Recovery of pollutants from many adsorbents entails liquid extraction. Large solvent volumes are used in these liquid extractions compared to the sample volumes analyzed chromatographically. This dilution of the sample is often too great for direct determination without a preconcentration step. Table 2.1 taken from a review by Poole and Schuette [2.29] shows the different methods used for selective solvent evaporation. An alternative solvent evaporation method not mentioned by Poole and Schuette is the solvent effect.

Table 2.1 Method used for selective solvent evaporation.

METHOD AND PRINCIPLE	COMMENTS
Rotary Evaporation Solvent removed at reduced pressure by mechanically rotating a flask in a controlled temperature water bath. Provision is made for condensing and collecting the evaporated solvent.	Volatile compounds are generally lost. Recovery of less volatile material may be lower than expected due to entrainment of the sample in the solvent vapours. Adsorption on the glass walls of the flask and apparatus may be a problem. Uncontrolled expulsion from the flask due to uneven evaporation.
Kurderna-Danish Evaporation Concentrator Evaporative concentrator is operated at atmospheric pressure under partial reflux conditions using a three-ball Snyder column with an efficiency of about 2.7 theoretical plates. Condensed vapours in the Snyder column are returned to the boiling flask, washing down organics from the sides of the glassware; the returning condensates also contacts the rising vapours and helps to recondense volatile organics. The concentrator is mounted with the boiling flask in a controlled temperature water bath and the final solvent concentrated into a collection tube of small volume compared to the boiling flask.	Provides a slower rate of evaporation than the rotary evaporator but recovery of trace organic compounds is generally higher. Generally not possible to reduce sample volumes of several hundred millilitres to less than 1ml in a single apparatus.
Gas Blow Down A gentle stream of pure gas is passed over the surface of the extract contained in a conical-tipped vessel or culture tube partially immersed in a warm bath. The solvent evaporation is a function of the gas flow rate, the position of the gas inlet tube relative to the evaporating solvent, the water bath temperature, and the solvent surface area.	Generally limited to sample volumes$<$25ml. High gas flow rates may cause sample losses by nebulization. Gas supply may contaminate sample. If sample is reduced to dryness subsequent dissolution may be incomplete. Carryover of aqueous and high boiling solvents difficult to remove by evaporation.

2.2.1 Solvent Effect

The solvent effect is a phenomenon which may be employed as one of the many ways of sample introduction in gas-liquid chromatography. It is an especially effective means of quantitatively and reproducibly transferring solutes from dilute solutions to the column without overloading and under mild conditions.

The solvent effect is divided up into two principle concentration modes. The static solvent effect [2.30] which is an online concentration technique, focusing a 20μl dilute sample as a narrow band onto a capillary column. The dynamic solvent effect [2.31] is an offline concentration technique which focuses volatiles from a larger volume of dilute sample into a porous bed concentrator. Figure 2.2 shows a vertical and horizontal section through a porous bed concentrator used to concentrate samples in the solvent effect [2.31].

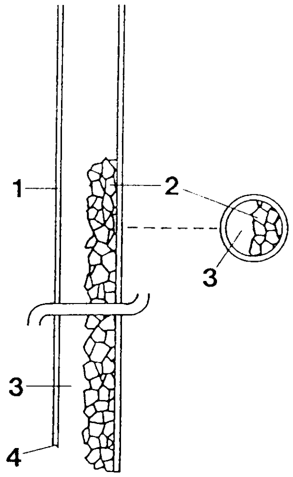


Figure 2.2 Vertical and horizontal section through a solvent effect concentrator. 1) borosilicate glass tube; 2) porous bed; 3)open channel; 4) chamfered lower end of bed to improve solvent and gas flow.

For the transfer of sample from the porous bed concentrator, to a capillary column a solvent effect inlet, that resembles a modern programmed temperature vaporization (PTV) injector, is used. Figure 2.3 is a diagram of such a solvent effect inlet [2.31].

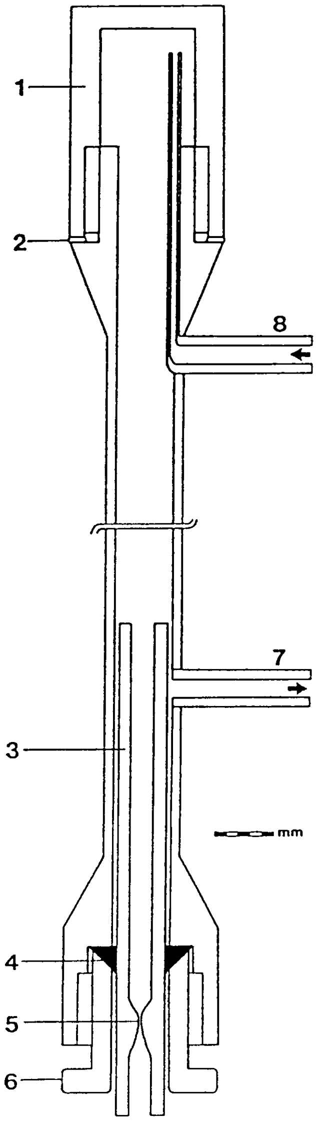


Figure 2.3 Vertical section of inlet for transfer of solute from concentrator to capillary column. 1) screw cap; 2) PTFE seal; 3) silica seat; 4) graphite ferrule; 5) taper for press fit polyimide connection to column; 6) nut; 7) purge outline; 8) carrier gas inlet. A 120W heater element is wound onto the inlet body. The inlet is mounted with the screw cap protruding through the roof of the gas chromatography oven.

2.2.1.1 Static Solvent Effect Focusing [2.32]:

A 20μl liquid sample fills the porous bed of the concentrator by capillary action. The filled concentrator is then transferred to the PTV inlet of a gas chromatograph. At a temperature below the boiling point of the solvent and at inlet pressure, carrier gas is passed over the upstream edge of the sample film, causing solute and solvent to evaporate and the upstream edge to move axially in the direction of the gas flow. As the upstream edge of the liquid film moves downstream, solutes for which the condition for solvent effect focusing is met, accumulate in a short band at the upstream edge of the film. Within the limits imposed by the usual chromatographic band spreading processes, the length of the band of concentrated solutes is small compared to the length of the film, and the solute focusing mechanism continues to operate until nearly all the film has evaporated. At this stage the length of the film has become the same as that of the concentrated band so that the solutes are no longer chromatographically retarded by a film of liquid lying downstream of them. The last traces of the liquid film therefore consist of a concentrated solution of the solutes occupying a short region of the porous layer at the position previously occupied by the downstream end of the liquid film. It is the high concentration and small volume of this solution which makes possible its efficient transfer to a capillary column, and it is in this respect that static solvent effect focusing is useful as a sampling technique for large, dilute, liquid specimens. The focusing process is analogous to that taking place in the "retention gap" after on-column injection in capillary gas chromatography.

2.2.1.2 Dynamic Solvent Effect Focusing [2.31]:

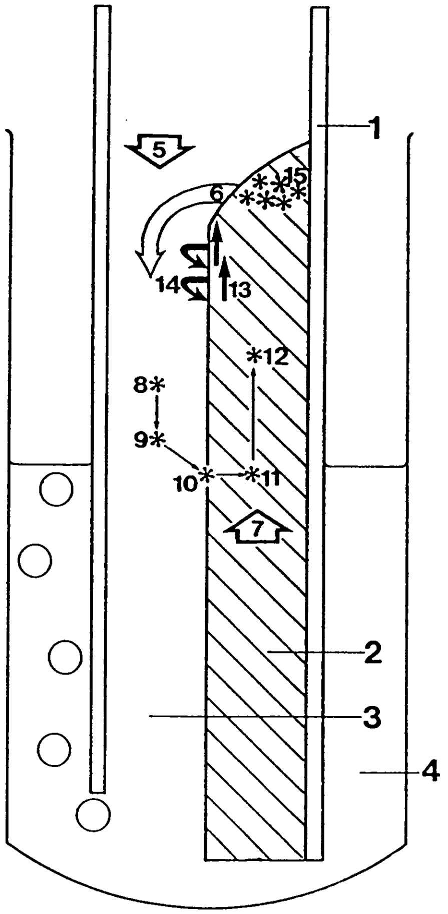


Figure 2.4 Schematic representation of the operation of the dynamic solvent effect. 1) glass tube; 2) sintered porous bed; 3) gas channel; 4) solvent. When gas is passed down the tube (5), evaporation of the solvent at the top edge of the bed (6) causes an upward movement of solvent driven by capillary rise (7), solutes in the gas phase (8) are carried downwards by the gas phase (9), impinge (10) on and dissolve (11) in the solvent and are carried upwards by it (12). Exchange of solute between gas and liquid results in a chromatographic transport of solute. As long as the rate of upward transport (13) is greater than the rate of downward transport (14) solutes accumulate in the evaporation zone (15).

When large amounts (larger than ± 20μl of sample) of dilute sample need to be concentrated the dynamic solvent effect can be used. The dynamic solvent effect is an offline concentration technique that concentrates volatiles at the evaporating, upstream edge of a film of solvent held in dynamic equilibrium between evaporation and capillary rise in a porous bed concentrator. Figure 2.4 shows a schematic representation of the dynamic solvent effect in operation [2.31]. The contents of a loaded concentrator, that consists of preconcentrated volatiles and approximately 20μl of solvent, can be transferred directly to a capillary column by carrying out static solvent effect focusing with the concentrator in a PTV inlet to which the column is connected.

CHAPTER 3

OPTIMIZATION OF THE SOLVENT EFFECT FOR DICHLOROMETHANE

3.1 Introduction

A trace is a constituent which is found in a minor concentration in another material called the 'matrix'. In air pollution sampling the air is the matrix from which the trace quantities of pollutants are collected. During sampling the trace quantities of pollutants are removed from the bulk matrix, the air, onto an adsorbent. These trace quantities of pollutants are now transferred to a new matrix consisting of the solvent which extracts the pollutants from the adsorbents. It is of utmost importance to use high purity solvents especially when large volume injection techniques are employed. The purity of the solvent and the sensitivity of the detector will determine the detection limits achievable for air pollutants. These limits are also effected by the method used to concentrate and transfer samples to the GC column. Thus when optimizing the solvent effect for dichloromethane it is important to ensure that sharp chromatographic peaks, with minimal peak broadening are obtained.

3.2 Analytical Instrumentation

Gas chromatography-flame ionization detector (GC-FID) analyses were performed on a Varian Aerograph Series 2700 gas chromatograph modified for capillary work and fitted with a solvent effect inlet (p 16 fig 2.3). The column used was a glass capillary column (25m x 0.3mm), deactivated and coated with a 0.4μm layer of cross linked polydimethylsilicone, according to the method of Grob [3.1]. Fused silica legs were attached to the column [3.2] to facilitate easy coupling to the injector and flame ionization detector. The column was manufactured in our laboratory. The detector sensitivity was set at 8 x 10^{-12} A.mV^{-1} and a recorder giving a full scale deflection for 1mV was used. The carrier gas was hydrogen with a linear velocity of 50cm.s^{-1}. The flame ionisation detector temperature was 270°C and detector flow rates were as follows; hydrogen 30ml.min^{-1}, nitrogen 20ml.min^{-1} and air 300ml.min^{-1}. Data was collected on a SP4290 integrator.

3.3 Experimental

3.3.1 Samples

Pure dichloromethane (CH_2Cl_2) was obtained from the AEC. The purity of the CH_2Cl_2 is essential as any artifacts in the solvent will influence the detection limits of the air pollution analyses. Four experiments were done to determine the purity of the CH_2Cl_2 solvent. Firstly, a blank run was done following the method in par 3.3.2, except no solvent was placed into the concentrator. The method was repeated with 20μl of CH_2Cl_2 solvent, injected by the solvent effect. Lastly 100μl and 1000μl of CH_2Cl_2 solvent was concentrated separately onto the porous bed concentrator by the dynamic solvent effect (par 2.2.1.2, p 18) with ca. 10ml.min^{-1} of palladium cell purified hydrogen at room temperature and injected by the static solvent effect method.

This CH_2Cl_2 was used to study solvent peak tailing and to make some standard samples. A standard sample was made from a Grob [3.3] mixture. Table 3.1 indicates the concentrations.

Table 3.1 Grob standard mixture

	GROB MIXTURE 1	**CONC. μg.ml^{-1}**
A:	2,3-Butanediol	1.056
B:	n-Decane	0.477
C:	1-Octanol	0.617
D:	Nonanal	0.694
E:	2,6-Dimethylphenol	0.528
F:	2-Ethylhexanoic acid	0.672
G:	2,6-Dimethylaniline	0.567
H:	n-Dodecane	0.489
I:	Methyl decanoate	0.672
J:	Dicyclohexylamine	0.567
K:	Methyl undecanoate	0.655
L:	Methyl dodecanoate	0.639

Hexane was purified in our laboratory by spinning band fractional distillation [3.4], and used in the comparison tests of the solvent effect between CH_2Cl_2 and hexane.

Air pollution samples HGDPW4 and COS1/4 were obtained from the AEC. These samples were real samples adsorbed on XAD-2 from factory stacks, to be analyzed by the US EPA method S008. After extracting the pollutants from the adsorbents with CH_2Cl_2, liquid samples were supplied, before the samples were concentrated with the Kurderna-Danish concentrator. The AEC concentrated the bulk samples with a Kurderna-Danish concentrator and analyzed the samples by gas chromatography/mass spectrometry. The HGDPW4 sample was a very dilute sample. Thus 100μl of the sample was first concentrated to 20μl into a concentrator using the dynamic solvent effect. Whereafter the 20μl was injected by the static solvent effect. The COS1/4 was a more concentrated sample, such that 20μl of the sample could be concentrated and injected by the static solvent effect method as in par 3.3.2.

3.3.2 Basic Method of Sample Injection

CH_2Cl_2 was sampled by dipping the concentrator directly into the solvent, removing it and shaking it once or twice lightly to remove any excess solvent; alternatively by off-line preconcentration of the sample in the same concentrator tube, utilizing the dynamic solvent effect. The loaded concentrator is transferred to the capillary column by carrying out the static solvent effect on the concentrator bed. The following procedure is followed: the carrier gas supply is switched off, the screw cap of the inlet is removed, the loaded concentrator is dropped into the seat, the screw cap is replaced, the carrier gas supply is turned on and the timer is started. The starting temperature of both the inlet and the column is 35°C, 5°C lower than the boiling point of CH_2Cl_2. CH_2Cl_2 has a lower boiling point than hexane, thus instrumental adjustments had to be made to cool the inlet below the boiling point of CH_2Cl_2. The inlet is cooled down to 35°C by placing a cup of liquid nitrogen below the inlet during injection. When 60% of the solvent peak width has eluted the inlet is ballistically heated to 220°C [2.30, p 55]. The column temperature program of 10°C.min^{-1} is started after all of the solvent has eluted from the column. For a 20μl CH_2Cl_2 sample the inlet is heated 7,5 min after injection and the column temperature program is started 12 min after injection.

3.3.3 Comparison between CH_2Cl_2 and Hexane

Using the static solvent effect method, as described in par 3.3.2., 20μl of both pure hexane and pure CH_2Cl_2 was injected.

3.3.4 Comparison between two different volumes of CH_2Cl_2

20μl and 10μl of pure CH_2Cl_2 was injected as in par 3.3.2. For the 10μl CH_2Cl_2 injection the concentrator is not filled by dipping, but by injecting 10μl of the solvent into the concentrator. The inlet is heated after 5 min of injection and the column temperature program is started 8 min after injection due to the smaller sample volume and thus smaller solvent peak.

3.3.5 Influence of FID on solvent peak tailing

A series of tests was done by varying, step by step, the parameters of the FID in order to see the effect of the flame ionisation detector on solvent peak tailing. The flow rate of the air to the detector was systematically varied from 300cm^3.min^{-1} to 500cm^3.min^{-1} and the flow rate of hydrogen to the detector was decreased from 30cm^3.min^{-1} to 16cm^3.min^{-1}. A series of tests was also carried out at different detector temperatures. Lastly the metal flame tip of the FID was replaced with a quartz flame tip and the flow rates of the gases to the detector optimised.

3.3.6 Other Solvents used with the Solvent Effect

CH_2Cl_2 was the first and most important solvent to be tested with the solvent effect. Previous experience was limited to hexane only. A brief investigation of the use of other solvents, specifically polar solvents was done. Other solvents may be used in the extraction of compounds from different adsorbents and thus it is important to know how other solvents behave with the solvent effect.

Studies were done using methanol, acetone and acetonitrile in the solvent effect. A second Grob mixture was made using each of these solvents. The concentration of Grob mixture 2 was double that of Grob mixture 1. 6μl of Grob mixture 2 for each solvent was injected individually by the solvent effect method. The experimental conditions for each solvent are given in table 3.2.

Table 3.2 Experimental conditions for methanol, acetone & acetonitrile

SOLVENT	INITIAL INLET TEMP / °C	INITIAL COLUMN TEMP / °C	TIME INLET HEATED	TIME COL. HEATED
Methanol	65	60	15min	24min
Acetone	50	40	7min	15min
Acetonitrile	70	60	12min	19min

3.4 Results and Discussion

The CH_2Cl_2 obtained from AEC has a reasonable level of purity. From the purity tests done on it, it can be seen that if 20μl of CH_2Cl_2 (Chr.3-2) is injected there are no impurity peaks present. The injection of 1000μl of CH_2Cl_2 (Chr.3-4) by the dynamic solvent effect, however, does indicate some undesirable impurity peaks. A 100μl injection of CH_2Cl_2 (Chr.3-3) shows minimal impurity peaks. Thus depending on the concentration levels of the pollutants extracted from the adsorbent, the matrix effect due to this particular purity grade of CH_2Cl_2 solvent should be minimal.

With the injection of CH_2Cl_2 at the optimum conditions for hexane, it was found that the CH_2Cl_2 solvent peak gave a lot of tailing. This solvent peak tailing was unacceptable and would easily overshadow peaks of early eluting compounds. Thus a series of tests was carried out to determine the origin of this tailing and also to minimize it, enabling successful injections of CH_2Cl_2 samples.

3.4.1 Comparison between CH_2Cl_2 and Hexane

From Chr.3-5 it can be seen that there is no tailing present in the 20μl injection of hexane compared to the large peak tailing observed in the 20μl injection of CH_2Cl_2 (Chr.3-6). This indicates that the tailing is caused by the chemical nature of CH_2Cl_2.

3.4.2 Comparison between two different volumes of CH_2Cl_2

Two different volumes of CH_2Cl_2 were injected to determine what effect the volume of CH_2Cl_2 had on the solvent peak tailing. When the two chromatograms obtained from the 10μl and 20μl CH_2Cl_2 injections are superimposed, it is observed that there is no difference in their peak tailing, (Chrs.3-7,8). This indicates that the solvent peak tailing of CH_2Cl_2 is independent of the volume injected.

It was decided from these results that the solvent peak tailing of CH_2Cl_2 is possibly caused by the following two factors: (i) One of the joints in the instrument is causing a dead volume which is particularly sensitive to CH_2Cl_2 and not hexane. (ii) Combustion of the CH_2Cl_2 solvent is incomplete in the detector, causing soot to form that is continuously being released into the system causing the large solvent peak tail.

From the chromatograms (Chrs.3-(5-8)), a lot of spikes are observed which could indicate a dirty detector and soot formation due to incomplete combustion. Thus it was decided to do a series of tests to investigate the different parameters of the detector to increase combustion.

3.4.3 Influence of FID on solvent peak tailing

3.4.3.1 Effect of varying the gas flow rates to the detector

By varying the flow rates of air and hydrogen to the FID it was observed, that the solvent peak tailing of CH_2Cl_2 is only slightly affected. When the flow rate of air is increased the solvent peak tailing slightly decreases but the baseline takes longer to return to its original position at injection. A decrease in hydrogen flow to the detector decreases the solvent peak tailing. This result correlates with the FID manual [3.5] which suggests that slightly lower hydrogen flow rates to the detector should be used when using chlorinated solvents. When the hydrogen concentration of the gas at the flame is too high with chlorinated solvents, soot and black smoke forms which interferes with normal detection. The decreased flow rate of hydrogen causes the solvent peak tailing to decrease more than when increasing the air flow rate. Chr.3-9 shows how the solvent peak tailing has improved with the new gas flow rates: air $500cm^3.min^{-1}$, H_2 $16cm^3.min^{-1}$ and N_2 $20cm^3.min^{-1}$. Under these conditions $100\mu l$ of the air pollution sample HGDPW4 from the AEC was injected using the solvent effect. Chr.3-10 was obtained and compares well with the chromatogram (Chr.3-11) obtained by the AEC when concentrating the sample with a Kurderna-Danish concentrator. Concentration with the Kurderna-Danish concentrator results in increased losses of the more volatile compounds.

Concentration and injection with the solvent effect gave nice sharp and well shaped peaks except for the slight solvent peak tailing that is still present.

3.4.3.2 Effect of varying detector temperatures

Chr.3-9 indicates that the solvent peak tailing has decreased with a variation in gas flow rates to the detector, however, it has not been eliminated altogether. It was decided to investigate the effect of the detector temperature on the solvent peak tailing. It was presumed that by increasing the detector temperature combustion and desorption of any condensates would improve and thus the solvent peak tailing would decrease.

Surprisingly, however, the tailing worsened at a higher temperature. This result prompted a series of tests at different detector temperatures . It was found that the solvent tailing decreased at lower detector temperatures and disappeared at a detector temperature of 150°C (Chrs.3-12,13). Figure 3.1 & 3.2 and table 3.3 show some calculations that were done to determine the extent of solvent peak tailing due to a decrease in detector temperature. The solvent peak height was measured at the base of the solvent peak, 15 minutes after injection and again 40 minutes after injection (indicated by side and bottom respectively in figure 3.1). The graph in figure 3.2 clearly shows how the solvent peak tailing drastically increases with detector temperature. The short term and long term tailing improved with a decrease in detector temperature.

The FID used had a metal flame tip. It can be concluded that the metal causes a catalytic reaction with the CH_2Cl_2, producing condensation products of low volatility. Slow desorption of the compounds gives rise to the large solvent peak tail.

Under these optimum conditions for dichloromethane, air pollution sample, COS1/4 was run (Chr.3-14) . The chromatogram obtained is very good compared with that obtained by the AEC (Chr.3-15). The more volatile, early eluting compounds, have much smaller peak sizes when concentrated with a Kurderna-Danish concentrator than with the solvent effect. Also the concentration step with the Kurderna-Danish concentrator took the AEC just under a day (± 8 hours) to complete, whereas concentration by the solvent effect took less than a minute.

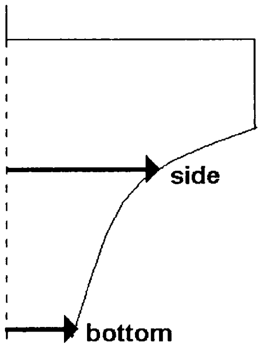


Figure 3.1 Diagram indicating where measurements were taken of the CH_2Cl_2 solvent peak tailing at different detector temperatures.

Table 3.3 Measurements of CH_2Cl_2 solvent peak tailing at different temperatures

TEMPERATURE (°C)	SIDE (mm)	BOTTOM (mm)
300	31.0	14.0
250	12.5	3.0
200	10.0	2.5
150	2.5	0.0

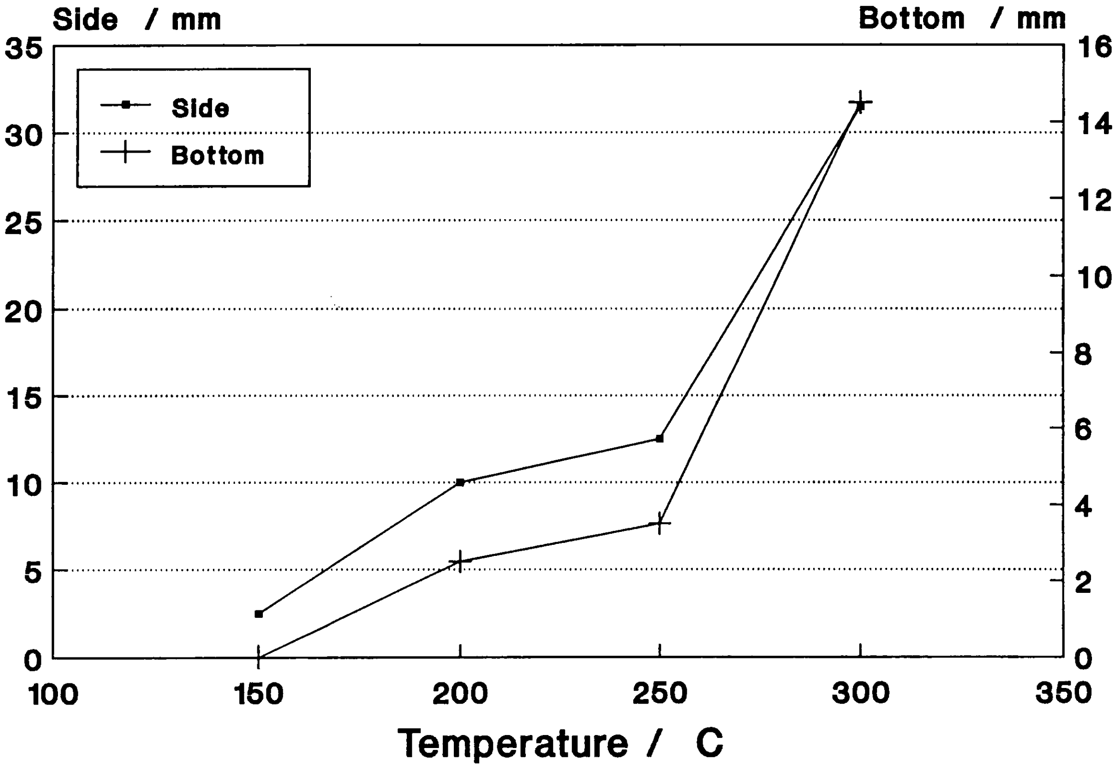


Figure 3.2 Graph showing the effect of FID temperature on the CH_2Cl_2 solvent peak tailing when using a metal flame tip.

This air pollution sample was run at a detector temperature of 200°C which is 50°C lower than the maximum temperature of the column at the end of the sample run. Working at such a low detector temperature could cause that less volatile compounds or column bleed condense in the detector and thus produce inaccurate analyses. For this reason it was decided to replace the metal tip of the detector with a quartz tip, which should give lower catalytic activity and hopefully peak tailing could be suppressed at higher detector temperatures.

3.4.3.3 Quartz FID Flame Tip

The very first runs done with the quartz tip are illustrated in Chrs.3-16,17. Both for hexane (Chr.3-16) and dichloromethane (Chr.3-17) a baseline hump exists after the solvent peak. This indicates a delayed, additional release of solvent after the main peak. As the detector was the last part of the GC that was altered it was assumed that the dead volume was caused by installation of the new tip.

Figure 3.3 shows a section through the detector tip. There are two possible origins of the delayed release of the solvent. (i)The quartz tip was placed directly onto the base of the detector. A space is formed which could trap some solvent and form a dead volume. (ii) The graphite ferrule which holds the tip in place could cause adsorption of the solvent followed by delayed desorption. (The metal tip was held in place by a metal ferrule)

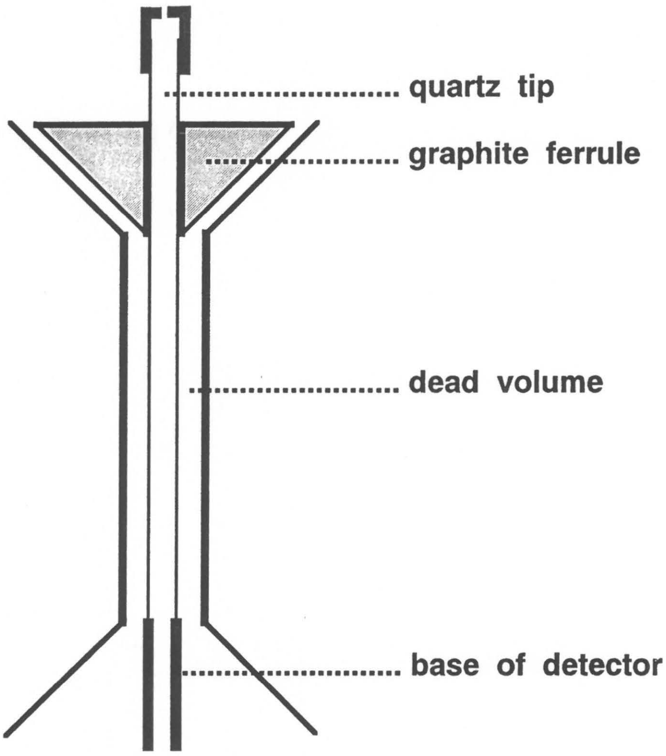


Figure 3.3 Section through a FID flame tip - showing a possible dead volume.

A series of tests was done by moving the quartz tip slightly up from the base of the detector. This reduced the baseline hump slightly, but the main cause of the delayed desorption was the graphite ferrule. After replacing the graphite ferrule with a polyimide ferrule there was no longer a baseline hump present after the hexane solvent peak and only a small baseline hump after the CH_2Cl_2 solvent peak (Chrs.3-18,19). It is very difficult to determine if the hump after the CH_2Cl_2 solvent peak is actually a baseline hump or just a small amount of solvent peak tailing, as the end of the solvent peak goes below the baseline. This latter phenomenon was often seen in the studies done with dichloromethane. As can be seen in

Chr.3-20 the solvent peak goes below the baseline before and after the solvent peak, which is probably an indication of an electron capture property of CH_2Cl_2, that is caused by the formation of stable chloride ions. The electron capture mechanism is the predominating effect decreasing the FID response to compounds that contain halogen atoms [3.6].

When 10μl of the Grob mixture 1 was injected (Chr.3-21), it was obvious that the sensitivity was too low. This was not surprising since the position of the quartz tip was different from that of the metal tip, also the nozzle i.d. of the quartz tip (0.4mm) is a lot smaller than that of the metal tip (0.9mm). After optimizing the flow rates of the gases to the detector the sensitivity of the detector was regained (Chr.3-22). The new optimum flow rates to the detector for the quartz tip are as follows: air 500cm^3.min^{-1}, H_2 30cm^3.min^{-1} and N_2 45cm^3.min^{-1}. An increase in nitrogen (make up gas) flow to the detector, increased the grob mixture 1 peak sizes. The background noise might have increased slightly with an increase in nitrogen flow rate but not to such an extent that it affected the analysis. If the nitrogen flow rate was increased too much it caused the flame to lift off the flame tip while the solvent came out of the column.

Chrs.3-23,24 show the injection of the air pollution sample COS1/4 from the AEC by the method in par 3.3.2, before and after optimization of the detectors gases.

Chrs.3-25,26 illustrate the difference between the air pollution sample COS1/4 injection with the quartz flame tip at a detector temperature of 270°C and the metal flame tip at the detector temperature of 200°C. There is no real difference between the two chromatograms. The peaks just after the solvent peak, of the more volatile compounds, on the chromatogram obtained with the quartz tip are larger than those obtained with the metal tip.

The solvent effect is now optimized to use dichloromethane as a solvent. I believe the solvent effect is a much quicker, cheaper and possibly more accurate way of concentrating air pollution samples than using the Kurderna-Danish concentrator.

3.4.4 Other Solvents used in the Solvent Effect

3.4.4.1 Methanol

The solvent peak has a good shape with very little peak tailing. Chr.3-27 is of the Grob mixture 2 in methanol. Most of the standard peaks have a good shape except for the two non-polar compounds *n*-Decane and *n*-Dodecane. *n*-Decane is much smaller and *n*-Dodecane is not properly focused as can be expected for non-polar compounds in a polar solvent. During the solvent effect concentration (par 2.2.1.1, p 17) non-polar compounds spend more time in the mobile phase and are not focused in a thin band on the column, causing peak broadening. The shape of the peaks of non-polar compounds are a "chair" shape with the "back" of the "chair" being eluted after the "seat". The "seat" represents partially trapped solute material which escaped from the sample layer and started the gas chromatographic process in the normally coated column during the solvent evaporation period. The "back" of the "chair" is due to fully trapped material, accumulated at the rear of the solvent layer and is released at the end of the solvent evaporation period. The ratio of the peak areas comprising the "seat" and the "back" of the "chair" depends on the retention power of the sample layer on the solute. The stronger this retention, the higher the "back" and the lower the "seat" [3.7]. Methanol as a polar solvent can thus be used for selective focusing polar compounds.

3.4.4.2 Acetone

Acetone gives good Grob standard peaks which are well focused (Chr.3-26). Before any further studies can be done with acetone it needs to be distilled as the extra peaks seen in Chr.3-28 are impurities which will interfere with standard analyses and the shape of the solvent peak is difficult to determine.

3.4.4.3 Acetonitrile

Acetonitrile caused the detector flame to go out whilst the solvent was eluting from the column. If the flame did not blow out the acetonitrile solvent peak showed some peak tailing (Chr.3-29). Also a baseline hump appeared after the solvent peak which makes analysis of elements in this area difficult. The baseline hump after the solvent peak could be due to water in the solvent, as the acetonitrile was not distilled, or due to retarded release of acetonitrile in the GC instrument. Grob [3.8] observed that acetonitrile alongside a few other solvents cause baseline humps after the solvent peak if the column oven is rapidly heated after an on column injection. This retarded release of solvent is thought to arise as a result of extra retention by a porous capillary surface acting in a manner analog to that of a molecular sieve. Grob [3.8] proved that the (pre)column is the source of the problem.

Further studies need to be done to purify acetonitrile and determine what is causing the baseline hump when acetonitrile is used in the solvent effect.

From the studies done on CH_2Cl_2 and the above solvents it appears that the solvent effect shows a lot of scope for use with different solvents. Also the diversity of uses of the solvent effect increases with the use of different solvents. Depending on the polarity of the solvent used, specialised techniques can be developed to focus only specific compounds.

CHAPTER 4

PRODUCTION OF MULTICHANNEL SILICONE RUBBER TRAPS

4.1 Introduction

A study was done to replace the long thick film silicone rubber traps found in the literature, by changing their configuration to a shorter more manageable multichannel trap, consisting of a silica tube filled with a few silicone rubber tubes positioned in parallel. In this way, roughly the same internal volume and phase ratio is obtained when compared to the equivalent single channel trap with the identical total length of rubber tube.

The breakthrough volume of a thick film silicone trap is a function of temperature, phase ratio, trap hold up volume V_g, and number of theoretical plates. The linear flow rate affects the number of theoretical plates N, generated by the given trap, which in turn has a direct influence on the breakthrough volume V_b, as indicated by the following two relations: [2.24]

$$V_R = V_g(1+k) \tag{1}$$

$$V_b = V_R\left(1-\frac{2}{\sqrt{N}}\right) \tag{2}$$

where k is the capacity factor. The higher the number of plates, N, the closer the breakthrough approaches the retention volume V_R. In order to achieve acceptable accumulation rates, these traps are generally operated at linear flow rates far beyond the optimum, resulting in fewer plates and unacceptably low breakthrough volumes. Increased length increases both the retention volume (by increased V_g) and the number of theoretical plates.

The lower linear velocity of the multichannel trap, compared to the single channel trap operated at the same volume flow rate, should result in a reduced theoretical plate height and thus provide roughly the same number of theoretical plates as that of the long single channel trap. The trap is also of more manageable dimensions allowing it to fit into conventional GC desorption devices. The lower pressure drop associated with multichannel flow would eliminate the need for gas tight couplings to the GC-column in the inlet [2.22] and would allow for accumulation at very high volume flow rates when sampling from ambient pressures.

This multichannel thick film trap (MC-TFT) should show the same advantages as the PUF adsorbent; having a low resistance to air flow , easy to make and handle, and can be reused. It should also show all the advantages that Kriegers' [2.10] diffusion denuder portrays, with the added advantage that the silicone tubes used in the multichannel trap are all placed inside one quartz tube, thus allowing the whole silicone tube to be exposed to the organic pollutants been sampled. Also the MC-TFT configuration would show greater inertness towards polar compounds due to a decrease in total area of solid support material and possibly less thermal degradation of the stationary phase because of less contact area with catalytically active support.

When introducing a new trap for air pollution studies, easy and reproducible construction is an important criterium. Before any samples can be collected on a new trap, the trap needs to be conditioned and the blank background of the conditioned trap has to be determined. It is important that the artifacts formed from the trap during concentration and desorption are minimal.

In this study the multichannel traps are made of polydimethylsiloxane (PDMS) tubes. Degradation of PDMS have extensively been studied in the literature [4.1, 4.2, 4.3]. Thermal degradation of PDMS under inert conditions gives rise to pure dimethylcyclosiloxanes where neither C-H nor Si-C bonds are broken. The main products of degradation under these conditions are low molecular weight cyclosiloxanes with hexamethylcyclotrisiloxane (D_3) predominating. Trace amounts of hexamethyldisiloxane and octamethyltrisiloxane are also detected. The introduction of branching in linear PDMS makes the characterization of the depolymerization products more difficult, as the decomposition products are more numerous and have more complex molecular structures.

However, the real conditions under which siloxanes are used, e.g. in the presence of residual catalyst from the polymer synthesis, the nature of the degradation atmosphere and the presence or absence of water gives rise to new reactions which compete with the fundamental depolymerization reactions.

If PDMS has been in contact with air and is heated to high temperatures, it degrades by rupture of both Si-C and Si-O bonds. Cleavage of Si-C bonds give rise to volatile organic materials. The organic group is replaced by a new siloxane bond and branching, followed by cross linking occurs.

With this knowledge of PDMS degradation, it was important to determine to what extent the degradation of the silicone rubber tubes, in the multichannel silicone rubber traps, would effect air pollution analyses and if it would even be possible to obtain acceptable blanks with minimal degradation peaks.

4.2 Experimental

4.2.1 Making of Multichannel Traps

The first multichannel silicone rubber trap made (MC3) consisted of a 125mm long glass tube (2mm o.d. x 1.5mm i.d.) filled with three polysiloxane rubber tubes (0.65 mm o.d. x 0.30 mm i.d. , Silastic, medical grade tubing, Dow Corning, Midlands, MI, USA). The general procedure to produce multichannel traps is as follows: An uncut stretch of rubber tube is doubled and threaded through the glass tube by means of a hairpin-shaped wire. The resulting loop ends are then simply cut off against the glass edge with a pair of scissors.

Further multichannel silicone rubber traps were made consisting of a 105mm long quartz tube (4mm o.d. x 2mm i.d.) filled with eight polysiloxane rubber tubes (MC8) as above. Figure 4.1 shows a schematic representation of the cross section through a multichannel trap, in this case one with seven polysiloxane rubber tubes.

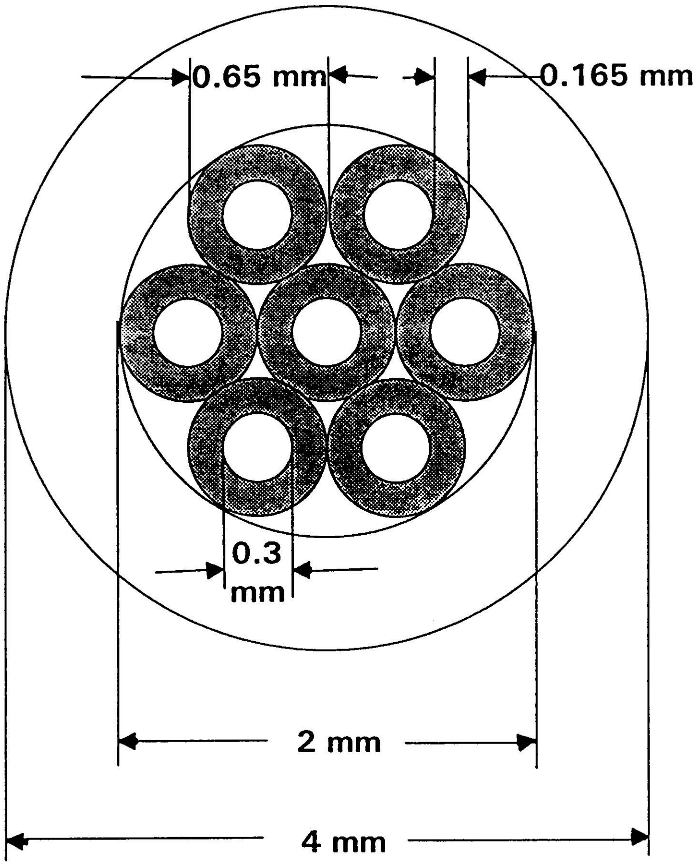


Figure 4.1 Cross section through a seven tube multichannel trap.

4.2.2 Analytical Instrumentation

GC-FID analyses of the MC3 trap were performed on the Varian Aerograph Series 2700 gas chromatograph, described in par 3.2, p 21. GC-FID analyses of the MC8 traps were performed on a Varian 3700 GC, also fitted with a glass capillary column (25m x 0.3mm), coated with a 0.4μm layer of polydimethylsilicone. The Varian 3700 GC is fitted with a PTV inlet which has a slightly larger internal diameter than that of the Varian 2700, which can thus accommodate the wider MC8 trap. The detector sensitivity of the Varian 3700 FID was set at 4 x 10^{-11} A.mV^{-1}

and a recorder giving a full scale deflection for 1mV was used. The carrier gas was hydrogen with a linear velocity of 50 cm.s^{-1}. The flame ionisation detector temperature was 280 °C and detector flow rates were as follows; hydrogen 30cm^3.min^{-1}, nitrogen 20cm^3.min^{-1} and air 300cm^3.min^{-1}. Data was collected on a SP4290 integrator. For mass spectrometry runs the Varian 3700 GC was connected to a Finnigan Mat Ion Trap Detector 700.

4.2.3 Conditioning of Multichannel Traps

Before the multichannel traps can be used in analyses they have to be conditioned to ensure minimal silicone decomposition byproducts being formed by the traps during analyses. The MC3 trap was conditioned at 280 °C for approximately a day with a helium carrier gas flow of ca 10cm^3.min^{-1}. The MC8 traps were conditioned at 280 °C for several days (± 60 hours) with a hydrogen carrier gas flow of ca 2cm^3.min^{-1}. The temperature program used to bring the oven up to 280 °C in order to bake out the multichannel traps is very slow, 2 °C.min^{-1}. After initial baking out of the traps, they are cooled down very slowly from 280 °C to room temperature, 30 °C.

4.2.4 Determining Degradation of Traps

Degradation of the multichannel trap was studied under different conditions. Blank runs done of the trap under inert conditions were tested. The effect of oxygen and temperature on the degradation of the multichannel trap was determined by varying these two parameters.

4.2.4.1 Degradation under Inert Conditions

After the trap has been baked out and cooled down it is not removed from the PTV inlet but is constantly kept under hydrogen. A blank run is carried out: The inlet has a starting temperature of 40°C. It is heated ballistically to either 220°C or 250°C within about two minutes. The temperature of the column is maintained at 30°C for 2 minutes. The column is then temperature programmed at 10°C.min^{-1} up to 250°C and held there until the end of the run.

4.2.4.2 Effect of Temperature on Degradation

The effect of temperature on degradation is studied by varying the maximum inlet temperature, which contains the trap, during blank runs from 220°C to 250°C. Degradation due to temperature is also studied by keeping the column at 30°C for longer periods than 2 minutes, before column temperature programming is started, thus trapping silicone degradation products on the column. Mass spectra of the thermal degradation products were determined.

4.2.4.3 Effect of Oxygen on Degradation

Initially the effect of oxygen on the degradation of the silicone tubes was tested by exposing the trap to the laboratory air for different periods of time or by sucking carbon cleaned air through the trap and then running a blank as in par 4.2.4.1. Later the effect of oxygen was tested by passing carbon-cleaned air over the trap at room temperature and then running a normal blank.

4.3 Results and Discussion

MC3 and MC8 traps were successfully made and baked out in such a way that blank runs of the traps under inert conditions show minor degradation peaks. The MC3 trap made with a glass tube showed larger degradation peaks (Chr.4-1) than the MC8 traps made of quartz (Chr.4-3). Increasing the baking time of the MC3 trap did not decrease the rate of thermal degradation. This indicates that the glass possibly catalyses thermal decomposition of the silicone tubes.

As mentioned by Burger [2.27], the degradation peaks increase appreciably when increasing the desorption temperature from 220°C to 250°C, (Chrs.4-2,3). From figure 4.2 it can be seen that the degradation peaks also increase with increasing desorption time at a constant temperature of 220°C. Desorption time of samples from the multichannel silicone rubber traps is normally not longer than 10 minutes. From the graph in figure 4.2 it can be observed that degradation peaks due to heating is minimal for such a short desorption time. Mass spectra (Chr.4-7) of the degradation products gave results that correlate with those described in the literature[4.1]. Under inert conditions the degradation compounds of these traps were mostly cyclosiloxanes. The pattern of degradation is also very reproducible, thus the degradation peaks of the trap can easily be distinguished and should not interfere with the analysis of air pollution samples.

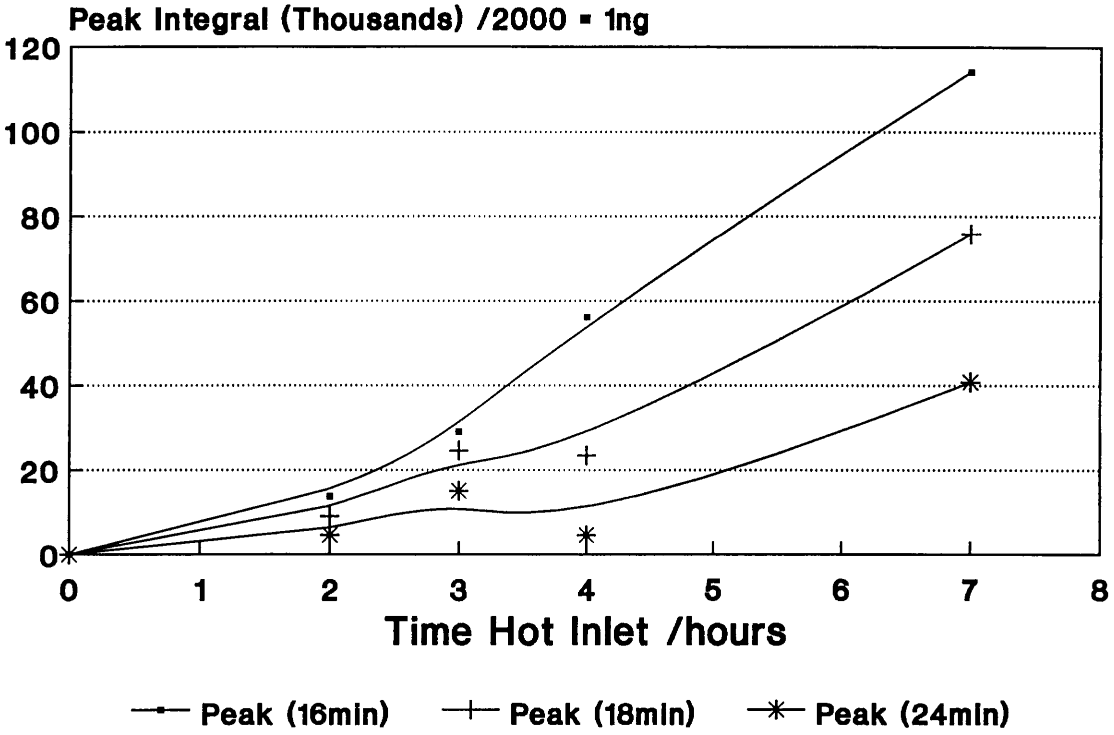


Figure 4.2 Graph indicating the increase in size of three degradation peaks due to prolonged desorption times of the MC8 trap at a temperature of 220°C under inert conditions.

From the initial test done to see the effect of oxygen on the degradation of the silicone rubber tubes, it appeared as if the degradation peaks were constant with very few deviations, neither did they increase with increasing exposure to air (Chrs.4-5,6). The occasional differences in the spectra were also not as expected. The peaks obtained would sometimes be large when the trap had only been exposed for short periods to air and then again smaller when the trap had been exposed for many hours to air. From the mass spectra obtained (Chr.4-8) most of the peaks were identified as organic compounds. When carbon-cleaned air was passed through the trap and a normal desorption run was performed, heating the PTV inlet containing the MC8 trap to 220°C, a perfect blank was obtained with no significant degradation peaks present (Chr.4-4). This indicates that the peaks obtained in the initial blank tests, in determining the effect of oxygen, were due to organic compounds present in the laboratory. The organic compounds were collected by slow diffusion into the trap. For this reason the peaks observed in these blank tests remained constant. When carbon-cleaned air was sucked through the trap, the organic compounds from the laboratory were only collected on the trap whilst moving the trap from the GC to the vacuum pump and back to the GC before injection. This explains why the organic peaks remained the same size, whether the trap was left only for a few minutes in the laboratory air or when carbon cleaned air was sucked through the trap. The occasional deviations were due to pollution deviations in the laboratory air. These results indicate that the trap is very sensitive and adsorbs organic compounds easily. But from the Chrs.4-5,6 the peaks obtained from the laboratory are reasonably small and should not interfere with analyses.

It has been established that multichannel silicone rubber traps can successfully be conditioned. Under analysis conditions of air pollution samples, background peaks due to degradation of the trap should be minimal.

CHAPTER 5

PREPARATION OF STANDARD MIXTURES OF ORGANIC COMPOUNDS

5.1 Gas Standards

The study of air pollution control necessitates the development of methods to prepare known concentrations of target compounds. These gaseous pollutants, which are often reactive and toxic, must be prepared in the ppb range. The standard gaseous mixture obtained must also fulfil a number of practicle requirements [5.1]. Firstly it should be stable, i.e. maintain a definite concentration of the component to be measured for prolonged periods of time. It should also be available in sufficient quantities to permit the completion of the required investigations. The purity of the diluent gas should be such that it does not interfere with the analysis of the trace target compounds.

The preparation of accurate standard mixtures of gases is very difficult as gases cannot easily be weighed, volumes may change during handling, and temperature and pressure effects must be considered [2.29]. In general the preparation of gas standards can be divided into two methods:

static and dynamic.

The static methods [5.1, 5.2, 5.3] involve preparing and storing the standard mixture in a closed vessel, ie. a cylinder, flask or plastic bag. The sample volume is limited to that of the container. Thus static systems are preferred when comparatively small volumes of mixtures are required, containing the component to be measured in the concentration range from less than 1ppm to several tenths of one percent. The advantage of these methods is that they do not require complex instrumentation, but the disadvantages are adsorption and condensation on the walls of a container with the accompanying loss of standard compounds.

Dynamic methods [5.1, 5.2, 5.3] are those where the analyte is continuously added to a flowing stream of the diluent gas. These methods are particularly suitable for preparing standards that are reactive or labile, or where the storage of a large number of standard mixtures is not possible or desirable. Diffusion and permeation are the most widely used methods.

5.1.1 Diffusion Method

Diffusion methods [2.29, 5.1, 5.3, 5.4] depend on the diffusion of the vapour of a liquid through capillary tubing at a constant temperature into a carrier gas of a known constant flow rate. The rate of diffusion is determined by the length and diameter of the capillary tube and by the temperature of the liquid or solid analyte which controls its vapour pressure. The mass flow (r) of vapour diffusing into the stream is given by the equation [5.4]:

$$r = -\frac{D_o P_o M A}{R T^2 L} T Log(1 - p/P) \qquad (1)$$

where D_0 is the NTP diffusion coefficient of the vapour in the carrier gas, M the molecular mass of the vapour, A the cross section area of the diffusion tube, L its length, R the ideal gas constant, T the absolute temperature of the liquid, p its vapour pressure and P the total pressure in the apparatus.

There are many different designs of diffusion vessels [5.1]. Diffusion vessels are such that they should not contain multicompound mixtures. The diffusion method is calibrated by determining the mass loss of the liquid analyte. Diffusion rates are low and calibration may require a long period of time.

5.1.2 Permeation Method

Permeation methods [2.29, 5.1, 5.3] are often used for the preparation of standards for which the analyte is a gas, liquid or solid. A membrane, usually constructed of a silicone or PTFE polymer, acts as a barrier through which the analyte permeates at a fixed and controlled rate. The driving force for the process is the difference in partial pressures of the analyte between the inner and outer walls of the tube. The rate of permeation depends on the dissolution of the vapour in the membrane, the rate of diffusion through the membrane wall, and the rate at which the vapour is removed from the outer surface of the membrane.

All permeation methods are based on Fick's diffusion law. According to this law of diffusion of gases, the permeation rate (R) of any gas through a plastic membrane of thickness L and surface area A can be expressed by the following equation [5.1]:

$$R=DS(p_1-p_2)\frac{A}{L} \qquad (2)$$

where D is the diffusion coefficient, S the solubility constant and p_1 and p_2 the partial pressures on the two sides of the membrane. The diffusion rate can thus be determined by equation (2) if all the parameters of the equation are known or, directly, by measuring the loss in mass of the device over a suitably long time interval. At t = 25°C and P = 760 mmHg the concentration C of the component that passes through the permeable membrane into the stream of diluting gas can be calculated as follows [5.1]:

$$C=\frac{22.45R}{MQ} \qquad (3)$$

where 22.45 is the molar volume of the permeating components at STP, M is its molecular mass and Q the flow rate of diluting gas.

Permeation tubes are used as convenient gas standard sources. However, they have the disadvantage of producing only one concentration of the gas under constant conditions. In addition, they have a limited lifetime and the permeation rate may change with time due to pressure deformation of the plastic membranes [5.5].

5.2 Liquid Standards

Often liquid standards are used to determine the efficiency of organic pollution collection devices. Liquid standards have the advantage that multicompound standards can be formed. Liquid standards are easy to make and transfer of standards to the collection device is normally also easy and accurate. The methods used to transfer the standard to a collection device vary tremendously. The simplest method used, is to inject the standard directly onto the collection device[5.6, 5.7]. Vaporizing known quantities of a liquid standard onto the collection device is also a very popular method [5.8, 5.9, 5.10]. The vaporization method enables a constant known quantity of a variety of standards to be transferred to the collection device in the gaseous form.

5.3 Experimental

Permeation tubes for the compounds toluene, 1,2,4 trimethylbenzene, α-methylstyrene, naphthalene, 2-methylnaphthalene and 2,6-dimethylnaphthalene were made from shrink Teflon tubes (2mm o.d. x 1.5mm i.d.) of varying lengths, typically 4cm or 9cm. These tubes were closed at each end by shrinking onto glass stoppers. To determine permeation rates of the standards, the devices were weighed at weekly intervals on a scale with a readout to the nearest 0.01mg. The permeation tubes were calibrated and used in the laboratory thermostated at 25 °C.

Two liquid standards were made. The first consisted of anthracene and pyrene dissolved in CH_2Cl_2. The second liquid standard (PAH1) was obtained from the AEC. It contained 16 different PAHs (table 5.1) at a concentration of $2000\mu g.cm^{-3}$ each in dichloromethane / benzene solution. Various dilutions of this standard (PAH1) was made with CH_2Cl_2 to characterise the multichannel thick film traps.

Table 5.1 Liquid standard mixture of PAH compounds.

PAH COMPOUNDS	RETENTION INDICES [5.11]
Naphthalene	200.0
Acenaphthylene	246.9
Acenaphthene	253.1
Fluorene	269.7
Phenanthrene	300.0
Anthracene	301.1
Fluoranthene	344.5
Pyrene	351.5
Benz[a]anthracene	398.8
Chrysene	400.0
Benzo[b]fluoranthene	443.1
Benzo[k]fluoranthene	444.0
Benzo[a]pyrene	454.0
Indeno[1,2,3-cd]pyrene	493.2
Dibenz[a,h]anthracene	496.2
Benzo[ghi]perylene	500.3

5.4 Results and Discussion

Gravimetric calibrations of the permeation devices are shown in figure 5.1 and table 5.2. The linear correlation coefficient (r^2), for the mass against time curve indicates constant permeation for all the standards except 2,6-dimethylnaphthalene. This is probably due to the difficulty to accurately weigh such a small mass loss of 2,6-dimethylnaphthalene over weekly periods.

It was attempted to make a permeation tube with anthracene. Anthracene did however not permeate through the teflon at a measurable rate, thus another method had to be used to obtain a gas standard for anthracene. If a diffusion rate of 1ng.min^{-1} were required for anthracene at room temperature, it was calculated from equation (1) that the use of the diffusion method would not be possible. This is due to the low vapour pressure of anthracene at room temperature. With such a low vapour pressure, a 10cm long diffusion tube would have to have a diameter of 1cm. Such a tube could no longer be regarded as a diffusion device as bulk movement of gases in the tube cannot be excluded. Any compounds less volatile than anthracene will portray the same problems. Thus the first liquid standard containing anthracene and pyrene was made. This standard was successfully transferred to the MC8 trap by vaporisation. The standard was injected into a quartz tube and thermally desorbed onto the MC8 trap. Sample transfer proved to be 100%, by thermally

Table 5.2 Permeation of gases through teflon permeation tubes.

COMPOUND	PERMEATION RATE ng.min^{-1}	r^2
Toluene	65.00	0.9997
1,2,4 Trimethylbenzene	4.45	0.9918
α-Methylstyrene	11.16	0.9969
Naphthalene	0.63	0.9665
2-Methylnaphthalene	3.38	0.9657
2,6-Dimethylnaphthalene	0.08	0.0098

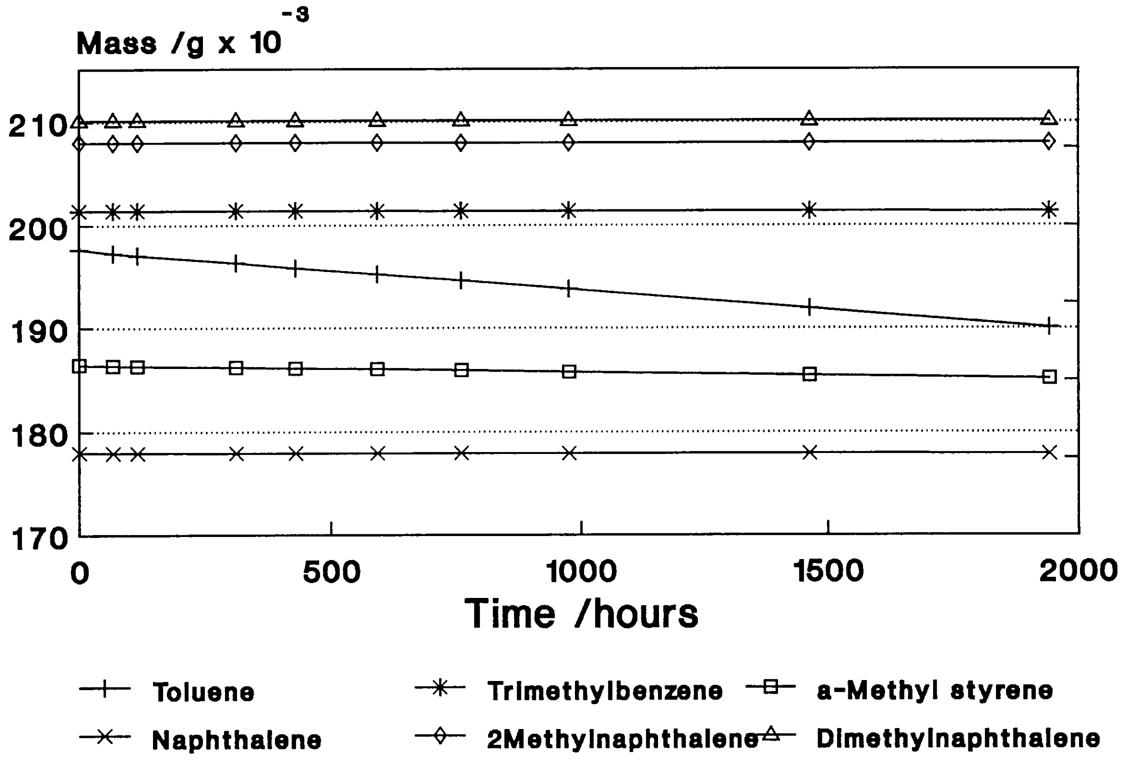


Figure 5.1 Graph showing mass loss of permeation tubes over ca. 3 months.

desorbing and analysing the residual content of the quartz tube.

It was attempted to transfer the PAH liquid standard by the same method. Unfortunately only the standards up to pyrene were successfully transferred to the MC8 trap by thermal desorption off the quartz tube. This was confirmed by testing the contents of the quartz tube after thermal desorption of the standard onto the MC8 trap. It was found that standards after pyrene were still present on the quartz tube.

Due to the multichannel nature of the MC8 trap it was difficult to inject liquid standard directly onto the MC8 trap, because it is very difficult to spread the standard evenly over all of the 8 silicone rubber tubes in the MC8 trap. One is inclined to inject most of the liquid standard into only one or two of the silicone rubber tubes of the trap. Thus the MC8 trap is not fully utilised and incorrectly tested.

It was finally decided to dip the trap into a known quantity of liquid standard. A specially designed container, with an indentation on the side wall, was constructed for this purpose (figure 5.2). When the MC8 trap is dipped into the indentation filled with standard, all 7μl of the liquid is drawn into the trap by capillary action. The CH_2Cl_2 is evaporated off the trap leaving the PAH compounds for analysis.

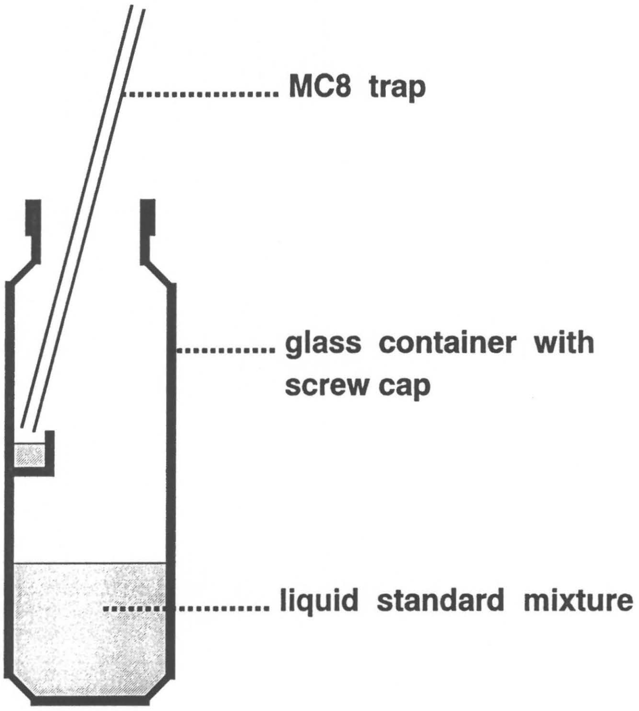


Figure 5.2 Diagram depicting the transfer of liquid PAH standard to the MC8 trap.

CHAPTER 6

CHARACTERIZING MULTICHANNEL SILICONE RUBBER TRAPS

6.1 Introduction

In chapter 4 it was shown that multichannel silicone traps can easily be made and that, after thorough heat treatment, degradation products produce minimal peaks during desorption. Next it was necessary to look at the quantitative efficiency of the multichannel silicone rubber traps. The successful operation of capillary GC systems requires the minimization of extracolumn band broadening. Often, the injection technique is a major source of these extracolumn effects. It is thus very important to study the ability to transfer collected standards from the multichannel silicone rubber traps successfully onto the GC column such that narrow standard peaks are obtained showing good resolution. It must also be determined if standard samples can quantitatively be adsorbed and desorbed from the traps, a prerequisite for accurate quantitation of air pollution samples.

Before any real air pollution samples can be collected it is necessary to determine the breakthrough volumes of some target compounds at different collection flow rates. As multichannel silicone rubber traps are coated with a similar stationary phase as the GC column, a calibration curve of breakthrough volumes against retention time can be constructed. From this calibration curve breakthrough volumes of unknown compounds can be predicted from their position on the chromatogram.

6.2 Experimental

6.2.1 Collection and Analysis of Standards

Gas standards from the permeation tubes were collected on the MC8 trap by drawing laboratory air, precleaned over activated carbon, over the permeation bank and into the trap by means of a vacuum pump (figure 6.1). The air flow rate is measured with a bubble flow meter.

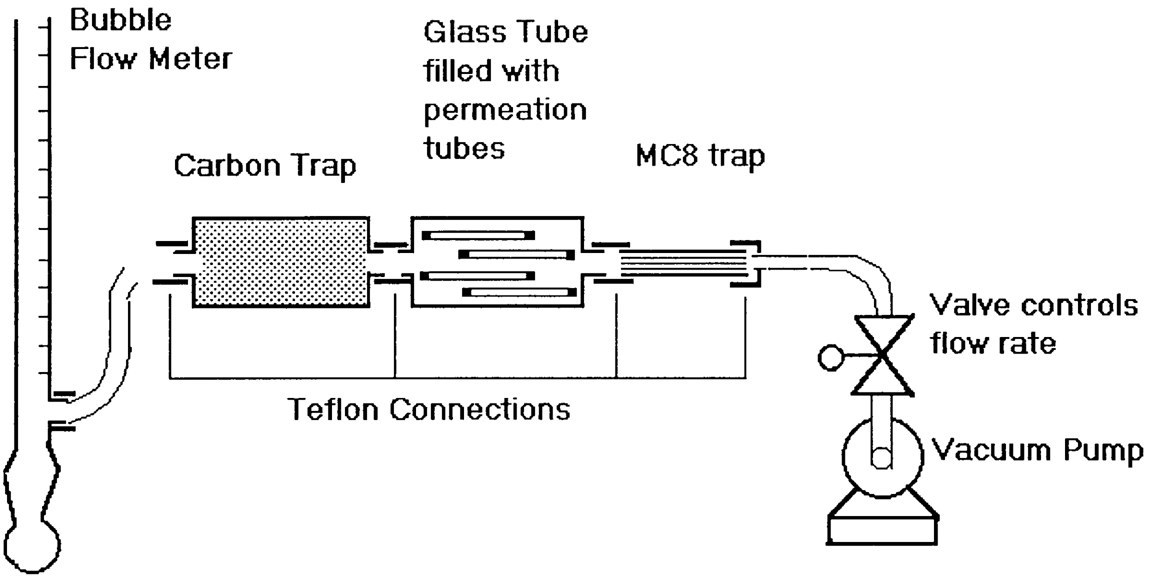


Figure 6.1 Schematic representation of the collection of gas standards from permeation tubes onto a multichannel trap.

The liquid, anthracene and pyrene standard (par 5.3, p 54) was thermally desorbed from a quartz tube onto the MC8 trap, by placing the quartz tube in the collection arrangement between the permeation tubes and the trap.

The liquid PAH standard was transferred to the MC8 trap by the device described in par 5.4 (figure 5.2) p 58. The MC8 trap remained in the laboratory air for 5 minutes to allow most of the CH_2Cl_2 to evaporate before it was placed into the collection train, if further addition of gas phase standards was required.

After collection of the standards, the trap is placed into the PTV inlet for desorption with the hydrogen carrier gas under backflush conditions. The inlet has a starting temperature of 40°C, and is heated to either 220°C or 250°C within about two minutes. The temperature of the column is maintained at 30°C until desorption is complete. The column is then temperature programmed at $10°C.min^{-1}$ to 250°C. Hydrogen is used as a carrier gas at a linear flow rate of $50cm.s^{-1}$. All chromatograms were run at a setting of 4×10^{-11} $A.mV^{-1}$ on a 1mV full scale recorder.

6.2.2 Collection and Analysis of Air Pollution Samples

6.2.2.1 Experiment 6.1

20 L of air was collected in a chemical storage room at the university of Pretoria onto the MC3 trap (glass trap containing 3 silicone rubber tubes)

at a flow rate of 330 $cm^3.min^{-1}$. After sampling, the trap was placed inside the PTV inlet of the Varian 2700 GC. A desorption temperature of 220°C and a desorption time of 2 minutes was used. The attenuation was set at 8×10^{-12} $A.mV^{-1}$ on a 1mV full scale recorder.

6.2.2.2 Experiment 6.2 a & b

Two sets of air pollution studies were done in an organic synthesis laboratory at the University of Pretoria. Two MC8 traps were connected in series to a vacuum pump. The first collection (Experiment 6.2a) was at a flow rate of 800 $cm^3.min^{-1}$ for 40 minutes sampling 32 L of air. The second collection (Experiment 6.2b) was at a flow rate of 190 $cm^3.min^{-1}$ for 60 minutes sampling 11.5 L of air. In each experiment both MC8 traps were analyzed with the Varian 3700 GC. A desorption temperature of 250°C and a desorption time of 10 minutes was used. The attenuation was set at 4×10^{-11} $A.mV^{-1}$ on a 1mV full scale recorder.

6.3 Results and Discussion

Chr.6-1 shows the collection of the five standards from the permeation tubes onto the MC8 trap at 5 $cm^3.min^{-1}$ for 30 minutes. The identification of the standard peaks was confirmed by GC-MS (Chr.6-2). *α*-Methylstyrene was not collected because its retention time is very similar to that of 1,2,4 trimethylbenzene. From Chr.6-1 it can be seen that the toluene peak is very wide, whereas the next peak, 1,2,4 trimethylbenzene, is well focused. From these results it can be concluded that compounds which are less volatile than 1,2,4 trimethylbenzene can be focused without cryotrapping, on a SE30 column of 0.4μm film thickness.

The PAH standards in Chrs.6-3(a-d) were identified by the standards retention indexes and by GC-MS. The peak shapes of the standards are narrow except for the last few standards from benzo[a]pyrene. This is due to the column having reached its maximum temperature of 250 °C long before elution of these peaks. Thus the last few compounds elute at a constant temperature, resulting in wider peaks in time. The reason why the maximum column temperature was not increased, is that the present PTV inlet which contains the MC8 trap is inside the column oven and thus also heats up to the higher temperature causing the MC8 trap to bleed.

6.3.1 Adsorption and Desorption of Standards from MC8 Traps

The degree of quantitative adsorption of standards onto the MC8 traps was determined by comparing the peak areas of the standards with the quantity of standards that was transferred to the traps. The FID response was standardised with Grob standards.

A short test was carried out to investigate desorption of standards from the MC8 trap at room temperature, 25 °C. Toluene, 1,2,4-trimethylbenzene, naphthalene, 2-methylnaphthalene and 2,6-

dimethylnaphthalene was collected onto the MC8 trap at 5 $cm^3.min^{-1}$ for 30 minutes at 25°C. The flow direction was then reversed for a further 30 minutes. A second MC8 trap was connected in series to the first MC8 trap such that any standard leaving the first trap during backflushing would be collected on it. Both traps were analyzed with a thermal desorption time of 5 minutes. This experiment was repeated twice.

Table 6.1 Testing desorption of standards from MC8 trap at 25°C under reverse flow conditions.

COMPOUNDS	PERCENTAGE REMAINING IN FIRST TRAP	PERCENTAGE TRANSFERRED TO SECOND TRAP
Toluene	50	50
1,2,4 Trimethylbenzene	73	27
Naphthalene	48	52
2-Methylnaphthalene	62	38
2,6-Dimethylnaphthalene	80	20

It was expected that by backflushing, [6.1] the compounds will exit the trap in the same time as they were sampled into the trap. The results obtained from these tests are depicted in table 6.1. These results indicate that most of the standards remained inside the first MC8 trap and were not backflushed onto the second trap under reverse flow conditions at room temperature. The probable reason for this is due to peak broadening. When a narrow band of compounds move through a column at a constant temperature, peak broadening occurs. If the flow is now reversed the peak broadening is increased due to the doubled resident time. Thus for the same adsorption and desorption time at constant temperature not all of the standard will leave the trap. In a system like the MC8 trap which has a small number of theoretical plates, peak broadening is more pronounced and the effect more visible. The gas standards collected on the trap were also collected as a frontal band and not as one narrow band which could also increase the effect of peak broadening. From the results it is observed that only a small quantity of the less volatile compounds, 2-methylnaphthalene and 2,6-dimethylnaphthalene were transferred to the second MC8 trap under reverse flow conditions. This is ascribed to irreversible adsorption of these compounds on the trap at room temperature. Thus under frontal collection conditions it should be expected that when the flow direction is reversed at 25 °C , not all of the compound will be backflushed out of the trap.

These problems could be considerably reduced by employing a temperature programming technique which is most frequently used to control solute retention. If the collected standards are desorbed under reverse flow conditions at a desorption temperature equal to the elution temperature of the most retained compound then all the collected standards should elute from the MC8 trap as a single band.

The desorption characteristics of the MC8 traps at an elevated temperature of 220 °C was tested by collecting 1,2,4 trimethylbenzene, naphthalene, 2-methylnaphthalene, 2,6 dimethylnaphthalene and pyrene at a collection rate of $5cm^3.min^{-1}$ for 30 minutes onto the MC8 trap. The desorption time of the trap in the PTV inlet was varied from 0.2 to 6 minutes. The trap was physically removed from the heated inlet after the set desorption time, before the temperature program of the column was started. Desorption was performed in the reverse direction to adsorption. The traps were rerun after the first desorption test, to determine the quantity of standards remaining in the trap, as an independent test on the desorption rate.

Figure 6.2 shows the desorption characteristics of MC8 traps for 1,2,4 trimethylbenzene, naphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene and pyrene. From this graph we can see that all the standards show similar desorption patterns with complete transfer after 3 minutes. This important test confirms the expected desorption behaviour under flow reversal conditions and indicates that even less volatile compounds can be quantitatively desorbed at these higher temperatures. Rerunning the traps that were removed after a 3 minute desorption time, gave no sample peaks, confirming complete desorption during the first run. Table 6.2 illustrates the quantitative recoveries obtained for these gas standards with the MC8 trap at a desorption temperature of 220°C and a desorption time of 4 minutes. 2,6-dimethylnaphthalene appears to have an increased analysis value compared to the quantity injected, this is probably due to the difficulty in determining the exact concentration of 2,6-Dimethylnaphthalene which

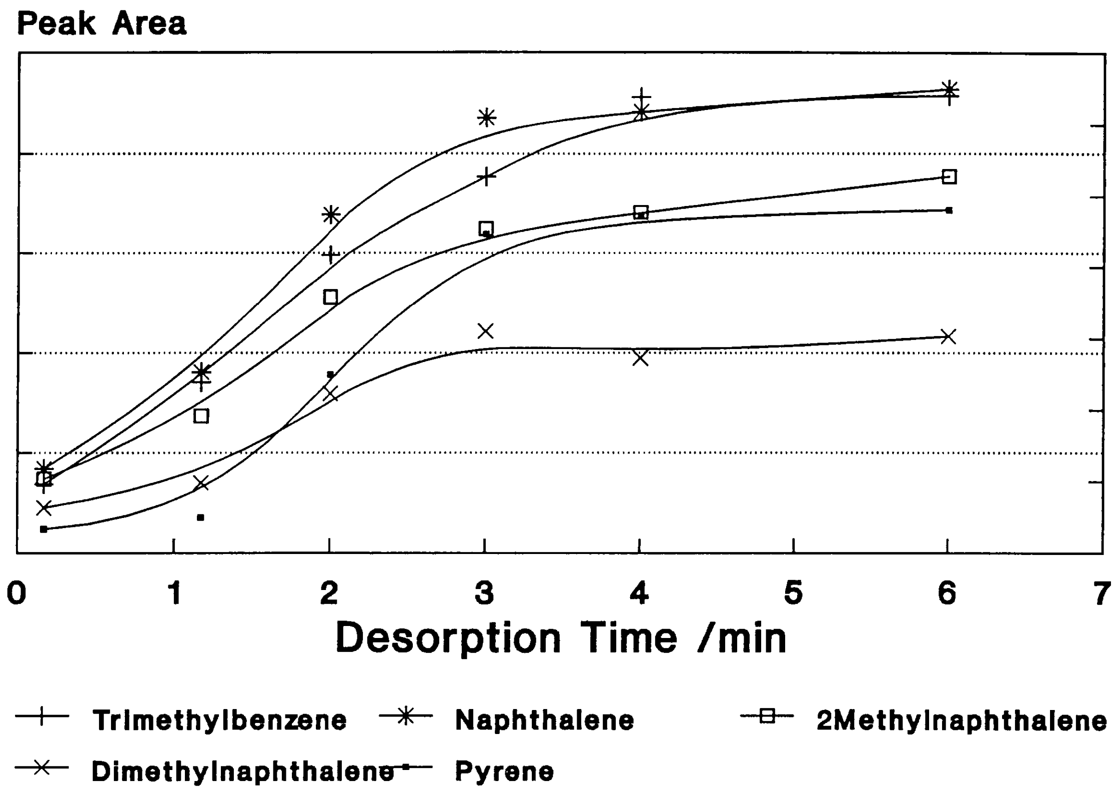


Figure 6.2 Graph representing peak area vs. desorption times for standards from MC8 trap.

Table 6.2 Results obtained when desorbing gas standards from the MC8 trap for 4 minutes under reverse flow conditions at 220°C.

COMPOUNDS	QUANTITY INJECTED ng	QUANTITY ANALYZED ng
1,2,4 Trimethylbenzene	133,5	133,0
Naphthalene	18,9	18,5
2-Methylnaphthalene	101,4	99,4
2,6-Dimethylnaphthalene	2,4	8,0
Pyrene	18,8	14,1

permeates through the permeation tube, thus the calculated injection value of 2,6-dimethylnaphthalene for 30 minutes is incorrect. The slightly lower analysis value of pyrene is due to the method used to transfer pyrene to the MC8 trap. 3μl of a liquid standard of pyrene (6,25 μg.cm^{-3}) is injected into a glass tube which is left to stand in the laboratory for ca. 30 minutes to allow the CH_2Cl_2 to evaporate. The pyrene is then thermally desorbed from the glass tube onto the MC8 trap. It is very possible that a small amount of pyrene also evaporated whilst the glass tube remained in the laboratory during the CH_2Cl_2 evaporation step.

As the trap did not contain the maximum retention volume of each compound for these tests it is expected that the desorption time will be slightly longer than 3 minutes when the trap is totally filled with standards. A series of tests were carried out by desorbing the collected liquid PAH standard onto the GC column in the same flow direction as the adsorption flow direction. This will ensure that the standards which are on the top of the trap, will have to move right through the trap before they are finally desorbed onto the column, thus testing if all standards can successfully be desorbed from the trap if the trap is totally filled with standards. By placing a small band of standard in the top section of the MC8 trap and then desorbing the standards, the standards will not leave the trap simultaneously as expected with reverse flow desorption. The compounds will undergo chromatographic separation such that the compound with the highest k value will leave the trap last. It can thus be assumed that if the compound with the highest retention index is totally analyzed then all of the standards have been desorbed. In the PAH standard the most retained compound is benzo[ghi]perylene.

The first results were surprising as hardly any of the standards came out of the trap at all. Increasing the desorption times up to a maximum of an hour did not result in any standards been desorbed onto the column. Initially it was presumed that possibly the flow of carrier gas through the MC8 trap was minimal and that most of the carrier gas was passing the trap on the outside. The possible reason that all the standards came out of the trap when the band of standards was placed at the bottom of the trap in a reverse flow direction could be due to mass transfer by diffusion. The purge flow in the PTV inlet was closed due to initial tests, which indicated that standard samples were lost via the purge flow line. This is expected in the absence of a gas tight coupling, with the MC8 trap only placed on top of the PTV silica seat and not inside it (See figure 2.3 p16). With the purge closed the desorbed standards are forced out of the inlet onto the column. Resistance to hydrogen flow inside the MC8, however, could be so large that it reduces flow of carrier gas through the trap causing the hydrogen carrier gas to pass between the MC8 trap and the silica inlet seat where the resistance to hydrogen flow is lower. To test this a Teflon connection was made between the silica seat and the MC8 trap such that the carrier gas would be forced through the trap. The Teflon connection, however, showed no improvement in desorbing the standards onto the GC column. This indicates that the assumption of the carrier gas not passing through the trap was incorrect, there had to be another reason why the standards did not desorb off the trap.

The screw cap of the present PTV inlet is unheated and surrounded by room temperature air. This prevents the cap from reaching the indicated 250°C. Approximately 1cm of the MC8 trap extends into the cap and is therefore not appropriately heated. When the standard is placed at the top of the trap and desorbed in the same direction as adsorption, the collected standard at the top of the trap can not be desorbed efficiently. The inlet cap was heated to 250°C with a hot air gun whilst the standard was desorbed from the trap, with a desorption time of 10 minutes, all the compounds of the PAH standard was desorbed from the MC8 trap. Regulating the temperature of the cap when heating it with the hot air gun was very difficult. If the temperature of the cap did not reach 250°C the last seven to eight standards did not desorb from the trap (Chr.6-4). If the trap was then turned around with the remaining standards at the bottom and desorbed again, the remaining standards desorbed quantitatively from the trap (Chr.6-5). This indicates that provided the entire trap reaches 250°C, all the standards up to benzo[ghi]perylene can be quantitatively desorbed from the MC8 trap.

Table 6.3 Results obtained from desorbing approximately 15ng of each PAH compound from a glass tube, from the bottom and from the top of the MC8 Trap, to the GC column.

COMPOUNDS	QUANTITY DESORBED (ng)		
	GLASS TUBE	STD BOTTOM	STD TOP
Naphthalene	0.0	15.5	14.3
Acenaphthylene	5.2	14.1	16.2
Acenaphthene	6.4	15.4	16.5
Fluorene	10.4	15.0	15.2
Phenanthrene	15.5	16.7	16.2
Anthracene	5.8	6.6	10.5
Fluoranthene	16.4	16.5	16.3
Pyrene	16.7	17.3	15.9
Benz[a]anthracene	14.4	14.6	14.3
Chrysene	16.8	16.1	13.8
Benzo[b]fluoranthene	15.6	15.8	10.6
Benzo[k]fluoranthene	16.5	15.6	12.0
Benzo[a]pyrene	11.9	11.9	9.6
Indeno[1,2,3-cd]pyrene	8.9	7.5	4.9
Dibenz[a,h]anthracene	8.3	6.3	4.3
Benzo[ghi]perylene	8.9	8.8	2.7

Table 6.3 shows the degree of quantitative desorption of standards from the MC8 trap. In the case of the glass tube, 7μl of the diluted PAH (2 μg.cm^{-3}) standard was injected into the tube. The glass tube with the liquid PAH standard stood in the laboratory air for 5 minutes to allow the CH_2Cl_2 to evaporate. The standard compounds were then desorbed from the glass tube onto the GC column via the PTV inlet in the same manner as for the MC8 traps. The analysis of the PAH standard from the glass tube enabled one to determine the quantity of standard introduced into the MC8 trap in comparison to the amount actually desorbed from the MC8 trap. The first four PAH compounds desorbed from the glass tube

are less than those desorbed from the MC8 trap. This is due to evaporation of these compounds during the 5 minute CH_2Cl_2 evaporation step. The last few standards desorbed from the MC8 trap, when the standards are placed on top of the trap, are less than expected. This is probably due to the inlet cap not reaching 250°C during desorption.

Table 6.4 depicts the reproducibility of analysis of the PAH liquid standard with the MC8 traps. Approximately 7μl (ca. 15ng per compound) of the liquid PAH standard (2μg.cm^{-3}) was transferred by capillary action to a MC8 trap which was then left in the laboratory air for 5 minutes allowing the CH_2Cl_2 to evaporate. Carbon-cleaned air was sucked through the trap containing the PAH standard at varying flow rates and collection times. The PAH standard was then desorbed from the MC8 trap in the reverse flow direction to adsorption. Most of the percentage random standard deviation (RSD) values are less than 10%, indicating good reproducibility. These variations are probably only due to the transfer method of the liquid standard to the trap. The ability to analyze the last few compounds was also favourable. GC-MS analyses done by direct liquid injection of this PAH standard by the AEC, only allowed for the analysis of compounds up to benzo[a]pyrene. This indicates the severity of adsorption problems normally associated with the transfer of these heavy compounds, even under the best of circumstances.

Table 6.4 Reproducibility of analysis of PAH standards with the MC8 trap.

COMPOUNDS	ANALYSIS EFFICIENCY		
	x,ng	RSD,%	n
Naphthalene	13,4	19	4
Acenaphthylene	14,1	18	4
Acenaphthene	16,1	5	4
Fluorene	14,9	8	4
Phenanthrene	15,7	3	4
Anthracene	13,1	6	4
Fluoranthene	15,1	8	4
Pyrene	15,6	6	4
Benz[a]anthracene	11,2	8	4
Chrysene	16,9	7	4
Benzo[b]fluoranthene	10,1	7	4
Benzo[k]fluoranthene	15,3	10	4
Benzo[a]pyrene	8,6	9	4
Indeno[1,2,3-cd]pyrene	7,0	9	3
Dibenz[a,h]anthracene	4,7	6	4
Benzo[ghi]perylene	6,4	24	3

Chrs.6-3(a-d) indicate the slight variations observed when analysing for standards on the MC8 trap. Different collection flow rates and collection times were used in each analysis. The desorption time was 10 minutes with a desorption temperature of 250 °C for each run. The first large peak observed is toluene and possibly CH_2Cl_2 remaining in the trap from the liquid PAH standard, or a very volatile compound breaking through the carbon trap used to clean the laboratory air during the collection. As mentioned previously these more volatile compounds are not well focused on the GC column resulting in the bad peak shapes observed in the first 10 minutes. Chr.6-3a shows very little background noise. This is probably due to a small leak that was detected between the column and the inlet. The background noise varies slightly in every analysis. The background noise is attributed to two factors: (i) The increased degradation of the MC8 trap due to the high desorption temperature of 250°C and (ii) Impurities from the laboratory air adsorbed onto the trap whilst moving the trap in the laboratory between collection and GC analysis steps. The slight variations in the size of the last three compounds eluted can also be noted as discussed above.

6.3.2 Determining Breakthrough Volumes

Naphthalene and toluene from the permeation tubes were collected on the multichannel silicone rubber trap (MC8) at different flow rates. A series of experiments were done where the collection time was varied for a specific flow rate to determine the breakthrough volumes of naphthalene and toluene at that specific flow rate. At high flow rates the breakthrough volumes of the more volatile compounds, toluene and naphthalene, are too low to determine accurately. A study was done at lower flow rates to determine breakthrough volumes of toluene and naphthalene. The linear flow rate affects the number of theoretical plates generated by the given trap, which in turn has a direct influence on the breakthrough volume, as discussed in par 4.1, p 38. As the multichannel trap is operated in the high flow rate region of the Van Deemter curve where the plate height is dominated by slow mass transfer of the thick stationary phase film [6.2], a lower collection flow rate will increase breakthrough volume.

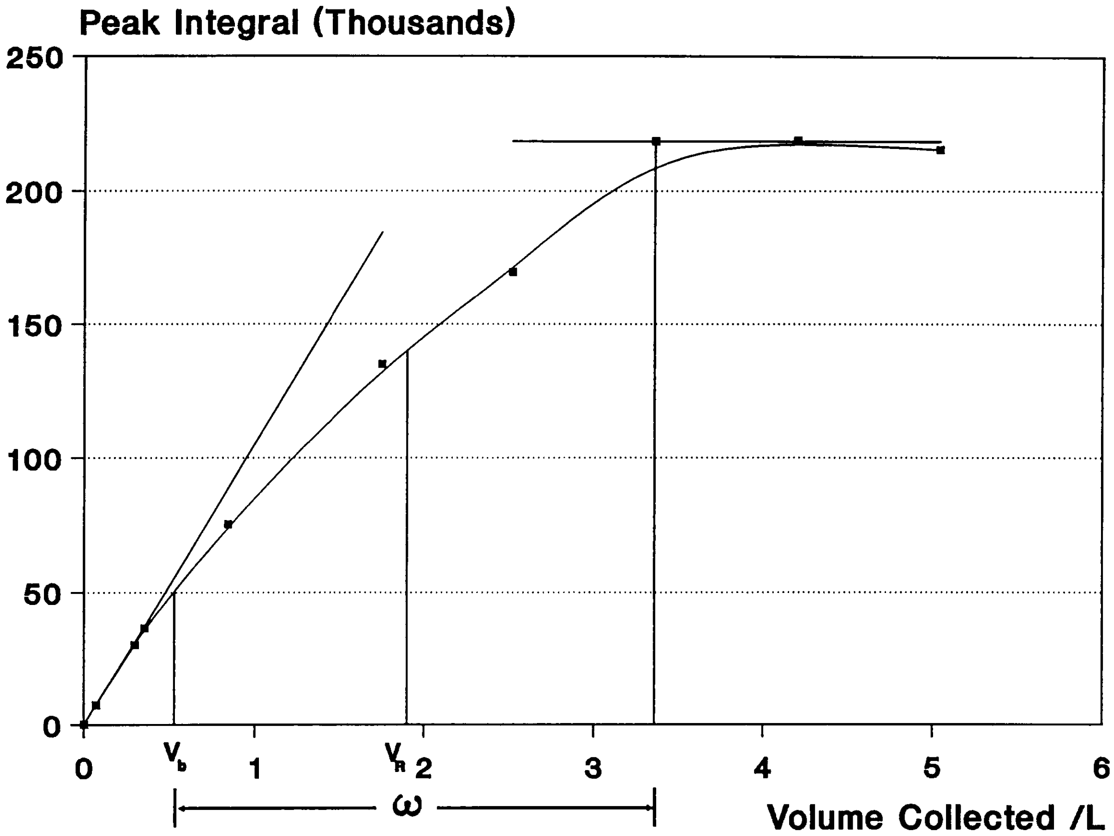


Figure 6.3 Graph representing collection data of naphthalene on mc8 trap at a flow rate of 14cm^3.min^{-1}, Conc 0.05 ng.cm^{-3}. V_b = breakthrough volume, V_R = retention volume, ω = base width of peak.

Figure 6.3 shows the collection data of naphthalene on a MC8 trap at a flow rate of 14 cm^3.min^{-1}, over a range of collection times. A second MC8 trap gave the same results at an accumulation rate of 14 cm^3.min^{-1}. The collection times of the concentration standards are varied before each injection. The accumulated mass of each compound is then determined by GC-peak area and plotted against total amount of gas that passed through the trap. From this graph we can see that the breakthrough volume for naphthalene is ca. 500cm^3. This value is taken at the position on the graph, where the collected naphthalene shows ca. 10% loss. The number of theoretical plates, N, for this MC8 trap for naphthalene at a flow rate of 14cm^3.min^{-1} (linear flow rate of 22.2cm.s^{-1}), is calculated to be 7,3 by using equation (1) [5.4]:

$$N=16\left(\frac{V_R}{\omega}\right)^2 \tag{1}$$

where V_R is the retention volume and ω is the base width of the peak measured in volume units.

As toluene is a lot more volatile than naphthalene, its breakthrough volume at a flow rate of 14 cm^3.min^{-1} is correspondingly lower, ca. 90cm^3 (Figure 6.4). When using the collection data of toluene at this flow rate, equation (1) gives a theoretical plate number of 7,9 for the MC8 trap. Clearly, longer traps would have to be studied to generate more accurate values for plate number and plate height.

From the breakthrough volumes of naphthalene (500cm^3) and toluene (90cm^3) it was calculated that the minimum concentrations detectable are 0.3 and 3 ppb (10^{-9} mol/mol) respectively for this system, based on a minimum detectable amount of 1ng for the GC-FID combination with a signal to noise ratio of ca. 10.

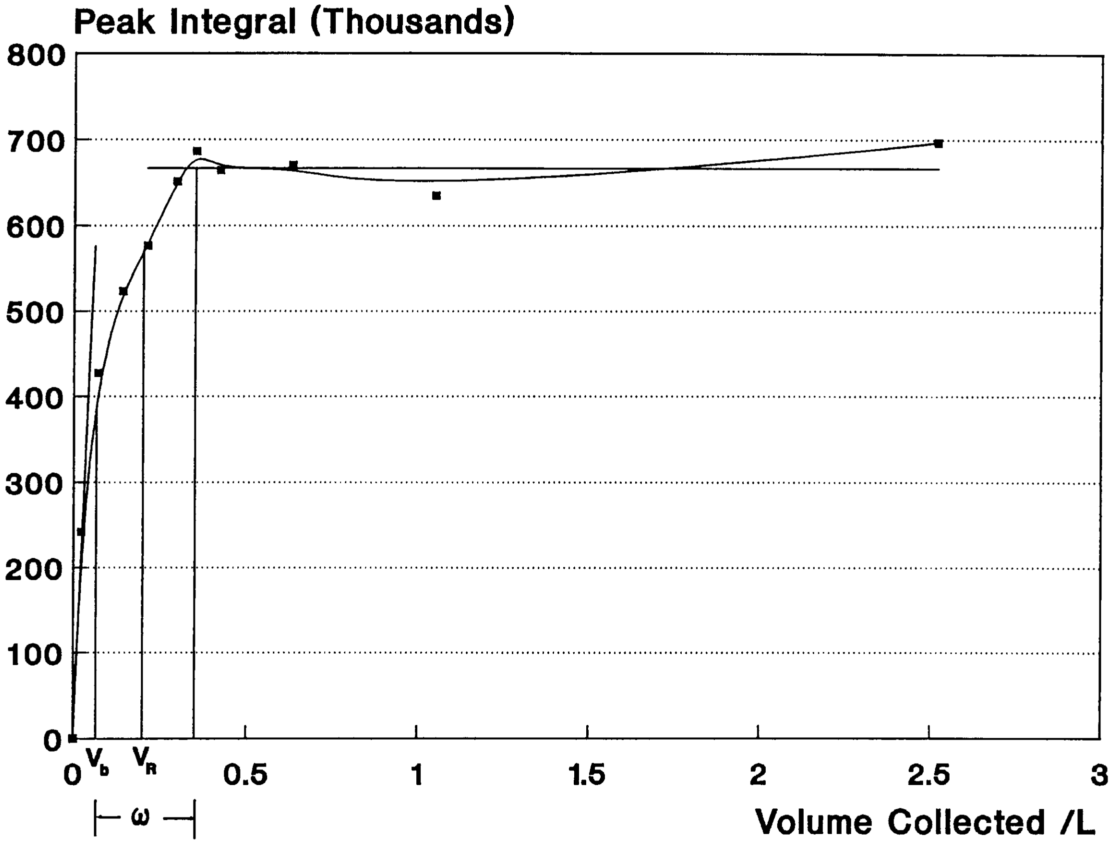


Figure 6.4 Graph representing data of toluene collected on MC8 trap at a flow rate of 14 $cm^3.min^{-1}$, Conc. 4.6 $ng.cm^{-3}$.

The capacity factors k, for naphthalene and toluene for the MC8 trap at 25 °C, were calculated to be 17193 and 1809 respectively, using equation (2) [5.4] :

$$k=\frac{V_R}{V_g}-1 \qquad (2)$$

where V_R is 1900cm^3 and 200cm^3 for naphthalene and toluene respectively, obtained from figures 6.3 & 6.4. The hold-up volume V_g of the trap, was calculated to be 0.1105cm^3. These high capacity factors are the result of the extremely low phase ratio, β=0.50 of the trap. The phase ratio, β was calculated from geometric considerations, using equation (3) [6.2]:

$$\beta = \frac{V_g}{V_s} \qquad (3)$$

where V_s, the volume of stationary phase of the MC8 trap, is $0.2194 cm^3$. The high retention properties compensate, to a large extent, for the limited number of plates generated, and ensure good breakthrough volumes, V_b.

It was attempted to determine theoretically the plate height, H of the MC8 trap at 25°C, at a flow rate of 14 $cm^3.min^{-1}$, by using equation (4) [6.2]:

$$H = \frac{2D_m}{\bar{u}} + \frac{1+6k+11k^2}{24\,(1+k)^2}\,\frac{r_c^2}{D_m}\,\bar{u} + \frac{2}{3}\,\frac{k}{(1+k)^2}\,\frac{d_f^2}{D_s}\,\bar{u} \qquad (4)$$

where D_M is the diffusion coefficient in the mobile phase, D_S the diffusion coefficient in the stationary phase, r_c characteristic diffusion distance (rubber tube i.d.), u the carrier gas velocity and d_f the average film thickness of the stationary phase.

All the parameters of the equation (4) were known except D_S which could not be found anywhere in the literature for the diffusion of any PAHs at 25°C in silicone. Due to the thick film tubes used in the multichannel silicone rubber traps, it is not possible to ignore the diffusion in the stationary phase. For thick films the resistance to mass transfer in the stationary phase becomes very important and can completely govern H_{min}.

It is also very difficult to find V_b, V_R and N data in the literature for direct comparison of the multichannel trap to others utilizing silicones as dissolution media. However, data presented by Blomberg and Roeraade [2.24] for a 2m long capillary coated with 80μm polysiloxane ($\beta = 1{,}44$) seem appropriate. The MC8s' plate number (N = 7.6) and plate height (H = 1.4cm) compares well with their reported value of N = 16 (and H = 12.5cm) at a similar linear flow rate. It is difficult to reconcile these differences, which could conceivably be ascribed to the different methods employed for the determination of these parameters. The multichannel trap has the advantage of higher accumulation flow rates for the same linear flow, lower phase ratio (β), easier construction and handling.

Studying breakthrough volumes of the less volatile compounds was approached slightly differently from the above study. The permeation method provided a continuous source of constant concentration of standards, thus it was possible to determine exactly when compounds were breaking through the MC8 trap. With the liquid PAH standard, only a specific quantity of standard can be transferred to the MC8 trap. Thus the retention capacity of the trap for these less volatile compounds was studied by transferring ca.7μl of the PAH liquid standard (2μg.cm^{-3} per compound) by capillary action onto the MC8 trap, allowing the CH_2Cl_2 to evaporate over a period of 5 minutes and then sucking carbon cleaned air through the MC8 trap. The first study was done by sucking carbon cleaned air through the MC8 trap containing the standards, at a flow rate of 24 $cm^3.min^{-1}$ for 261 hours giving a total air volume of $0.376m^3$. A second trap was placed behind the first trap to collect any standards that escaped from the first trap. From the analysis of both traps it could be seen that phenanthrene and all the compounds less volatile than phenanthrene, were retained quantitatively on the first trap without any breakthrough to the second trap. Most of acenaphthylene and acenaphthene broke through the first trap onto the second trap such that only ca. 5% of these two standards remained on the first trap, whereas with fluorene 70% remained on the first trap and only 30% broke through to the second trap.

Studies were also done at a higher flow rate of 190 $cm^3.min^{-1}$. Tables 6.5 & 6.6 show the results obtained. For a collection volume of $1.3m^3$ at 190 $cm^3.min^{-1}$ all compounds less volatile and including phenanthrene do not show breakthrough from the MC8 trap. This indicates that the minimum calculated concentration detectable by this system is 0.1 ppt (10^{-12} mol/mol) for phenanthrene, based on a minimum detectable amount of 1ng for the GC-FID calibration with a signal to noise ratio of ca. 10 and a breakthrough volume of $1.3m^3$. Thus these low volatility compounds should also show good collection efficiencies in the ppb range at higher flow rates. Naphthalene, acenaphthylene and acenaphthene already show more than 10% breakthrough when $0.2m^3$ of air was passed through the trap, whereas the breakthrough volume for fluorene lies between $0.5m^3$ and $1m^3$.

Table 6.5 PAH standards that remained in the first trap, onto which 7µl (ca. 15ng of each compound) of PAH standard was transferred, after carbon-cleaned air had passed through the trap at 190cm^3.min^{-1}, for the specified times.

COMPOUNDS	PAH STANDARDS REMAINING IN FIRST MC8 TRAP			
	17h(193L) ng/%[a]	43h(490L) ng/%	90h(1000L) ng/%	114h(1300L) ng/%
Naphthalene	0/0	0/0	0/0	0/0
Acenaphthylene	5/35	2/14	0/0	0/0
Acenaphthene	10/62	1/6	0/0	0/0
Fluorene	13/87	14/94	9/60	2/13
Phenanthrene	15/96	16/102	15/96	14/89
Anthracene	11/84	14/107	11/84	12/92
Fluoranthene	15/99	17/113	17/113	18/119
Pyrene	15/96	14/90	16/103	13/83
Benz[a]anthracene	7/62	10/89	11/98	10/89
Chrysene	14/83	17/101	18/107	16/95
Benzo[b]fluoranthene	6/59	10/99	10/99	9/89
Benzo[k]fluoranthene	9/59	14/92	16/105	16/105
Benzo[a]pyrene	5/58	8/93	8/93	8/93
Indeno[1,2,3-cd]pyrene	7/100	6/86	6/86	7/100
Dibenz[a,h]anthracene	3/64	3/64	2/43	3/64
Benzo[ghi]perylene	4/63	4/60	4/63	4/63

a. The percentage is calculated between the ng value remaining in the first trap and the average collection values,ng in table 6.4.

Table 6.6 PAH standards that escaped from the first trap containing 7μl of PAH standard, onto the second trap while carbon-cleaned air had passed through the traps at 190cm^3·min^{-1}, for the specified times.

COMPOUNDS	PERCENTAGE BROKEN THROUGH TO SECOND MC8 TRAP			
	17h(193L) ng/%[a]	43h(490L) ng/%	90h(1000L) ng/%	114h(1300L) ng/%
Naphthalene	0/0	0/0	0/0	0/0
Acenaphthylene	1/7	1/7	0/0	0/0
Acenaphthene	6/37	16/99	6/37	6/37
Fluorene	0/0	1/7	4/27	7/47
Phenanthrene	0/0	0/0	0/0	0/0
Anthracene	0/0	0/0	0/0	0/0
Fluoranthene	0/0	0/0	0/0	0/0
Pyrene	0/0	0/0	0/0	0/0
Benz[a]anthracene	0/0	0/0	0/0	0/0
Chrysene	0/0	0/0	0/0	0/0
Benzo[b]fluoranthene	0/0	0/0	0/0	0/0
Benzo[k]fluoranthene	0/0	0/0	0/0	0/0
Benzo[a]pyrene	0/0	0/0	0/0	0/0
Indeno[1,2,3-cd]pyrene	0/0	0/0	0/0	0/0
Dibenz[a,h]anthracene	0/0	0/0	0/0	0/0
Benzo[ghi]perylene	0/0	0/0	0/0	0/0

a. The percentage is calculated between the ng value remaining in the first trap and the average collection values,ng in table 6.4.

6.3.3 Air Pollution Samples

6.3.3.1 Experiment 6.1

Chr.6-6 shows the collection of 20L of air from a chemical store room onto the MC3 trap. The peaks indicated with * are silicone degradation peaks from the trap. These were easily identified.

6.3.3.2 Experiment 6.2 a & b

Chrs.6-7,8 show the collection and breakthrough of 32 L of air collected in an organic synthesis laboratory, with a MC8 trap. From Chr.6-8 it is observed that a small percentage of volatile compounds broke through the first trap onto the second trap. The less volatile compounds appear to have been collected totally on the first trap. Chr.6-9,10 show similar results where 11.5 L of laboratory air was collected onto the MC8 traps. In Chr.6-10 there appear some small peaks at a later time which appear to indicate breakthrough of less volatile compounds from the first trap onto the second trap. From the studies done on the breakthrough of PAH standards this is not very likely. Also no significant breakthrough of more volatile compounds are observed on Chr.6-10 which indicates that these later eluting compounds are not due to breakthrough of compounds from the first trap. There was no blank run done between the analysis of the first collection trap and the backup trap, thus the presence of these peaks should probably be ascribed to contamination of the inlet used in the experiments due to carry-over from the first trap.

These preliminary studies on the collection of real air pollution samples are very promising. Further mass spectrometry studies still need to be done to identify the pollutants collected.

CHAPTER 7

CONCLUSION

It has been demonstrated that conventional air pollution analysis methods can be improved with the use of the solvent effect concentration technique and the multichannel silicone rubber sampling traps. Both methods depict shorter analysis times, improved cost effectiveness and ease of automation.

The optimum conditions for the solvent effect using dichloromethane have been determined. This method can be utilized to successfully decrease concentration time, labour time and improve analysis quality of semi-volatile organic air pollutants. As the solvent effect replaces the Kurderna-Danish evaporation step, organic air pollutants of greater volatility show better recovery values. Studies on other solvents with the solvent effect look promising but further studies still need to be done on the specific behaviour of each solvent with the solvent effect.

Easy to prepare, multichannel silicone rubber traps, were made and tested for the first time. These concentrators are of conveniently small dimensions for easy handling and on-column transfer of accumulated samples in standard desorption units or PTV inlets. As recovery of thick film traps is by thermal desorption, expensive solvents are not required. After thorough heat treatment, degradation products produce minimal peaks during desorption. These peaks are easily identified and do not interfere with the analysis of air pollution samples. Multichannel thick film traps were shown to produce sharp gas chromatographic peaks for semi-volatile compounds without cryogenic refocusing. The traps were reused over a period of a year without deterioration of performance.

Permeation tubes were successfully made and calibrated to produce reliable primary gas standards in the ppb range. This enabled breakthrough volumes, retention volumes and plate numbers of the trap to be experimentally determined. These basic parameters are important and allow the performance of longer and wider versions to be estimated for comparison with high flow rate devices that have been reported in the literature [2.10, 2.18].

Reliable standards of less volatile compounds, such as chrysene, benzo[a]pyrene and benzo[ghi]perylene were produced, in order to determine breakthrough volumes and desorption characteristics of these compounds. It was experimentally proven that these compounds can successfully be desorbed from the multichannel silicone rubber traps. Breakthrough volumes at high flow rates are indicated for these compounds. Multichannel traps show promising results in the sampling of air pollution at high flow rates of 200 $cm^3.min^{-1}$.

The multichannel traps share the benefits of all polysiloxane concentrators, amongst others, that (a) breakthrough volumes of unknown compounds can be estimated from their retention on GC-columns coated with a similar stationary phase, and (b) they can also be used for concentration of organic compounds from aqueous media [2.28].

REFERENCES

1.1 V.G. Berezkin and Y.S. Drugov, "*Gas Chromatography in Air Pollution Analysis*", Elsevier Science Publishers B.V., 1991.

1.2 O. Hutziger, "*Air Pollution, The Handbook of Environmental Chemistry*", Volume 4, Part B, Springer - Verlag Berlin Heidelberg, 1989.

1.3 S. Lesage, "*Methods for the Analysis of Hazordous Wastes*", J. of Chromatography, 642, 1993, 65-74.

1.4 M.H. Hiatt and T.L. Jones, "*Identification and Quantification of Diesel Fuel Components derived from Off-shore Drilling Operation Discharges*", J. of High Resolution Chromatography & Chromatography Communications, 8, 1985, 4-7.

1.5 B.V. Burger, M. Le Roux and W.J.G. Burger, "*Headspace Analysis: A novel method for the Production of Capillary Traps with Ultra-Thick Stationary Phase Layers*", J. of High Resolution Chromatography, 13, 1990, 777-779.

2.1 M.T. Zaranski, G.W. Patton, L.L. McConnell, T.F. Bildeman and J.D. Mulik, "*Collection of Nonpolar Organic Compounds from Ambient Air using Polyurethane Foam-Granular Adsorbent Sandwich Cartridges*", Analytical Chemistry, 63, 1991, 1228-1232.

2.2 M.P. Ligocki and J.F. Pankow, "*Assessment of Adsorption / Solvent Extraction with Polyurethane Foam and Adsorption / Thermal Desorption with Tenax-GC for the collection and Analysis of Ambient Organic Vapours*", Analytical Chemistry, 57, 1985, 1138-1144.

2.3 J.C. Chung, S.W. Hannan and N.K. Wilson, "*Field Comparison of Polyurethane Foam and XAD-2 resin for Air Sampling for Polynuclear Aromatic Hydrocarbons*", Environmental Science and Technology, 21, 1987, 798-804.

2.4 A. Rosell, J.I. Gomez-Belinchon and J.O. Grimalt, "*Gas Chromatography - Mass Spectrometric Analysis of Urban Related Aquatic and Airborn Volatile Organic Compounds. Study of the Extracts obtained by Water Closed-Loop Stripped and Air Adsorption with Charcoal and Polyurethane Foam*", J. of Chromatography Biomedical Application, 562, 1991, 493-506.

2.5 G.W. Patton, L.L. McConnell, M.T. Zaranski and T.F. Bildeman, "*Laboratory Evaluation of Polyurethane Foam-Granular Adsorbents Sandwich Cartridges for Collecting Chlorophenols from Air*", Analytical Chemistry, 64, 1992, 2858-2861.

2.6 I.D. DeGraff and W.R. Betz, "*Polyurethane Foam as an Effective Adsorbent for Monitoring Pesticides in Indoor Air*", The New Expanded Supelco Reporter, 11, 1992, 20-22.

2.7 M. Dressler, "*Extraction of Trace Amounts of Organic Compounds from Water with Porous Organic Polymers*", J. of Chromatography, 165, 1979, 167-206.

2.8 P.V. Doskey and A.W. Andren, "*High-Volume Sampling of Airborn Polychlorobiphenyls with Amberlite XAD-2 Resin*", Analytica Chimica Acta, 110, 1979, 129-137.

2.9 G.J. Hollod and S.J. Eisenreich, "*Collection of Atmospheric Polychlorinated Biphenyls on Amberlite XAD-2 Resins*", Analytica Chimica

Acta, 124, 1981, 31-38.

2.10 M.S. Krieger and R.A. Hites, "*Diffusion Denuder for the Collection of Semi-Volatile Organic Compounds*", Environmental Science and Technology, 26, 1992, 1551-1555.

2.11 M. Possanzini and V. Di Palo, "*Improved HPLC Determination of Aliphatic Amines in Air by Diffusion and Derivatization Techniques*", Chromatographia, 29, 1990, 151-154.

2.12 J.L. Durham, W.E Wilson and E.B. Bailey, "*Application of an SO_2-Denuder for Continuous Measurement of Sulphur in Submicrometric Aerosols*", Atmospheric Environment, 12, 1978, 883-886.

2.13 P.K. Simon and P.K. Dasgupta, "*Wet Effluent Denuder Coupled Liquid / Ion Chromatography Systems*: Annular and Parallel Plate Denuders", Analytical Chemistry, 65, 1993, 1134-1139.

2.14 R.K. Stevens and T.G. Dzubay, "*Sampling and Analysis of Atmospheric Sulphates and Related Species*", Atmospheric Environment, 12, 1978, 55-68.

2.15 J. Forrest D.J. Spandau, R.L. Tanner and L. Newman, "*Determination of Atmospheric Nitrates and Nitric Acid Employing a Diffusion Denuder with a Filter Pack*", Atmospheric Environment, 16, 1982, 1473-1485.

2.16 R.S. Braman, t.J. Shelley and W.A. McClenny, "*Tungstic Acid for Preconcentration and Determination of Gaseous and Particulate Ammonia and Nitric Acid in Ambient Air*", Analytical Chemistry, 54, 1982, 358-364.

2.17 R.W. Coutant, L. Brown and J.C. Chuang, "*Phase Distribution and Artifacts Formation in Ambient Air Sampling for Polynuclear Aromatic Hydrocarbons*", Atmospheric Environment, 22, 1988, 403-409.

2.18 D.A. Lane, N.D. Johnson, S.C. Barton, G.H.S. Thomas and W.H. Schroeder, "*Development and Evaluation of a Novel Gas and Particle Sampler for Semivolatile Chlorinated Organic Compounds in Ambient Air*", Environmental Science and Technology, 22, 1988, 941-947.

2.19 R.W. Coutant, P.J. Callahan and M.R. Kuhlman, "*Design and Performance of a High-Volume Compound Annular Denuder*", Atmospheric Environment, 23, 1989, 2205-2211.

2.20 B.R. Appel, Y. Tokiwa and E.L. Kothny, "*Sampling of Carbonaceous Particles in the Atmosphere*", Atmospheric Environment, 17, 1983, 1787-1796.

2.21 M. Possanzini, A. Febo and A. Liberti, "*New Design of a High-Performance Denuder for the Sampling of Atmospheric Pollutants*", Atmospheric Environment, 17, 1983, 2605-2610.

2.22 K. Grob and A. Habich, "*Headspace Gas Analysis: The role and design of Concentration Traps specifically suitable for Capillary Gas Chromatography*", J. of Chromatography, 321, 1985, 45-58.

2.23 B.V. Burger and Z. Munro, "*Headspace Gas Analysis. Quantitative Trapping and Thermal Desorption of Volatiles using Fused-Silica Open Tubular Capillary Traps*", J. of Chromatography, 370, 1986, 449-464.

2.24 S. Blomberg and J. Roeraade, "*Preparative Capillary Gas Chromatography. II. Fraction Collection on Traps Coated with a Very Thick Film of*

Immobilized Stationary Phase", J. of Chromatography, 394, 1987, 443-453.

2.25 S. Blomberg and J. Roeraade, "*A Technique for Coating Capillary Columns with a Very Thick Film of Cross-Linked Stationary Phase*", J. of High Resolution Chromatography & Chromatography Communications, 11, 1988, 457-461.

2.26 C. Bicchi, A. D'Amato, F. David and P. Sandra, "*Capturing of Volatiles Emitted by Living Plants by means of Thick Film Open Tubular Traps*", J. of High Resolution Chromatography, 12, 1989, 316-321.

2.27 B.V. Burger, M. Le Roux, Z.M. Munro and M.F. Wilken, "*Production and Use of Capillary Traps for Headspace Gas Chromatography of Airborne Volatile Organic Compounds*", J. of Chromatography, 552, 1991, 137-151.

2.28 B.V. Burger and M. Le Roux, "*Trace Determination of Volatile Organic Compounds in Water by Enrichment in Ultra-Thick-Film Capillary Traps and Gas Chromatography*", J. of Chromatography, 642, 1993, 117-122.

2.29 C.F. Poole and S.A. Schuette, "*Isolation and Concentration Techniques for Capillary Column Gas Chromatographic Analysis*", J. of High Resolution Chromatography & Chromatography Communications, 6, 1983, 526-549.

2.30 P.J. Apps, "*The Quantitative Analysis of Semiochemicals*", Dissertation, Unversity of Pretoria, Pretoria, R.S.A., 1988.

2.31 P.J. Apps, V. Pretorius, K.H. Lawson, E.R. Rohwer M.R. Centner, H.W. Viljoen and G. Hulse, "*Trace Analysis of Complex Organic Mixtures using*

Capillary Gas-Liquid Chromatography and the Dynamic Solvent Effect", J. of High Resolution Chromatography & Chromatography Communications, 10, 1987, 122-127.

2.32 V. Pretorius, C.S.G. Phillips and W. Bertsch, "*Solute Focusing, in GLC, using the Solvent Effect: A General Description*", J. of High Resolution Chromatography & Chromatographic Communication, 6, 1983, 232-235.

3.1 K. Grob, "*Making and Manipulating Capillary Columns for Gas Chromatography*", Huethig, Heidelberg, 1986

3.2 E.R. Rohwer and V. Pretorius, "*Hybrid Fused Silica/Glass Capillary Columns for GLC*", J. of High Resolution Chromatography & Chromatography Communication, 10, 1987, 145-147.

3.3 K. Grob and G. Grob, "*Testing Capillary Gas Chromatography Columns*", J. Of Chromatography, 219, 1981, 13-20.

3.4 G.C. Chen, "*The Preparation an Storage of Ultra High Purity Hexane for Solvent Effect Gas Chromatography Analysis*", Dissertation, University of Pretoria, Pretoria, R.S.A., 1992.

3.5 *Flame Ionization Detector Addendum*, Publication number 85-001139-20, June 1979.

3.6 J. Sevcik, "*Detectors in Gas Chromatography*", Elsevier Scientific Publishing Company, 1976.

3.7 K. Grob, "*On-Column injection in Capillary Gas Chromatography: Basic techniques, retention gaps, solvent effects*", Heidelberg, Hüthig, 1987.

3.8 K. Grob and A. Artho, "*Distorted Solvent Peaks in Capillary GC: A Symptom of Porous Column Surfaces*", J of High Resolution Chromatography, 13, 1990, 803-810.

4.1 S. Patai and Z. Rappoport, "*The Silicone-Heteroatom Bond*", Chapter 3 & 4, JohnWiley & Sons Ltd, 1991.

4.2 W. Blum and R. Aichholz, "*Hochtemperatur Gas-Chromatographie*", Hüthig, Heidelberg, 1991.

4.3 T. Welsch and U. Teichmann, "*The Thermal Immobilization of Hydroxy-Terminated Silicone Phases in High-Temperature-Silyated Glass Capillaries. A Study of Reaction Mechanisms*", J of High Resolution Chromatography, 14, 1991, 153-159.

5.1 J. Namiesnik, "*Generation of Standard Gaseous Mixtures*", J. of Chromatography, 300, 1984, 79-108.

5.2 G.O. Nelson, "*Controlled Test Atmospheres: Principles and Techniques*", Ann Arbor Science Publishers, Inc, 1972.

5.3 R.S. Barratt, "*The Preparation of Standard Gas Mixtures*", The Analyst, 106, 1981, 817-849.

5.4 A. Raymond and G. Guiochon, "*The Use of Graphitized Carbon as a Trapping Material for Organic Compounds in Light Gases Before a Gas Chromatographic Analysis*", J. of Chromatographic Science, 13, 1975, 173-177.

5.5 M.L. Stellmack and K.W. Street, Jr.,"*Permeation Devices for High Pressure Gases*", Analytical Letters, 16(A2), 1983, 77-100.

5.6 E.M. Roper and C.G. Wright, "*Sampling Efficiency of Five Solid Sorbents for Trapping Airborne Pesticides*", Bulletin of Environmental Contamination and Toxicology, 33, 1984, 476-483.

5.7 E.G. Stephanou and N.E. Stratigakis, "*Determination of anthropogenic and biogenic organic compounds on airborne particles: flash chromatographic fractionation and capillary gas chromatographic analysis*", J. of Chromatography, 644, 1993, 141-151.

5.8 J.A. Cucco, "*A method of Determining the Efficiency of Air Sampling Traps to Collect and Release Volatile Organic Compounds*", Analytical Letters, 20, 1987, 223-234.

5.9 R.G. Lewis and M.D. Jackson, "*Modification and Evaluation of a High-Volume Air Sampler for Pesticides and Semivolatile Industrial Organic Chemicals*", Analytical Chemistry, 54, 1982, 592-594.

5.10 R.G. Lewis and K.E. MacLeod, "*Portable Sampler for Pesticides and Semivolatile Industrial Organic Chemicals in Air*", Analytical Chemistry, 54, 1982, 310-315.

5.11 D.L. Vassilaros, R.C. Kong, D.W. Later and M.L. Lee, "*Linear Retention Index System for Polycyclic Aromatic Compounds*", J. of Chromatography, 252, 1982, 1-20.

6.1 H.J. Cortes, "*Multidimensional Chromatography, Techniques and Applications*", Marcel Dekker, INC, New York, 1990.

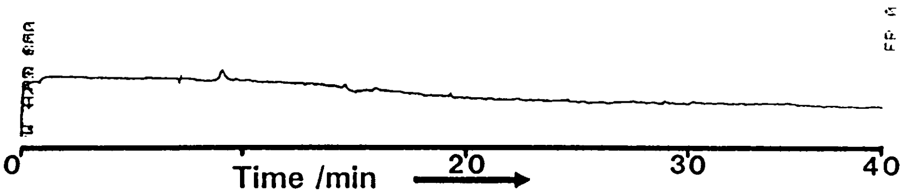
6.2 P.Sandra, "*Fundamentals. Resolution-Column Efficiency*", High Resolution Chromatography, 12, 1989, 273-277.

APPENDIX A

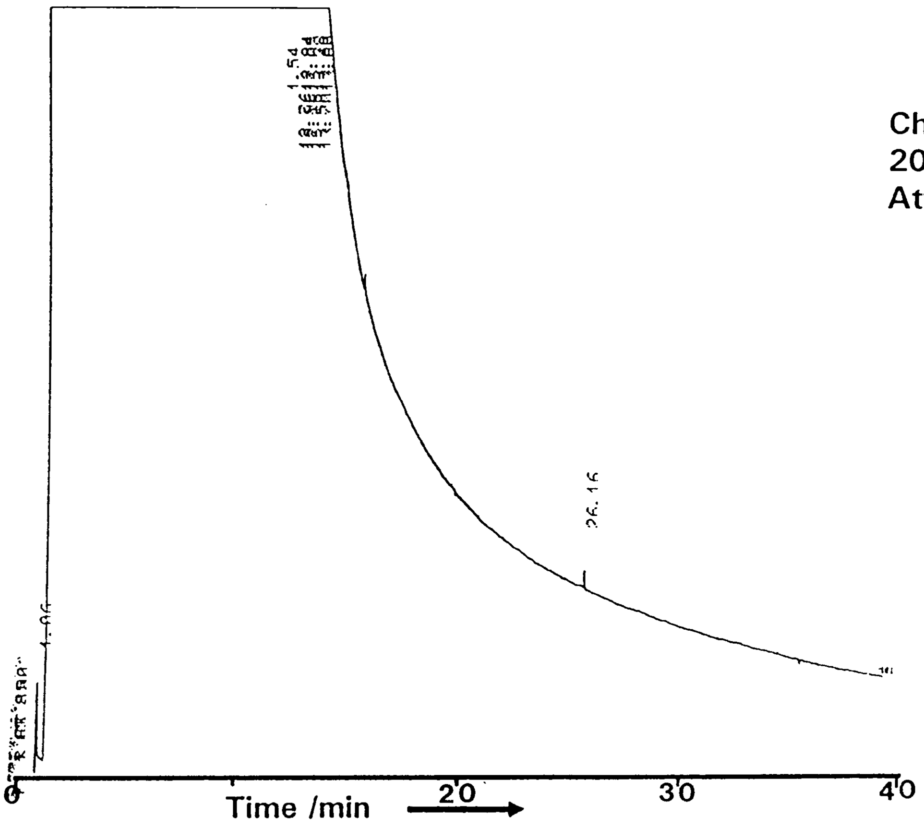
CHROMATOGRAMS

Determining Purity of CH_2Cl_2

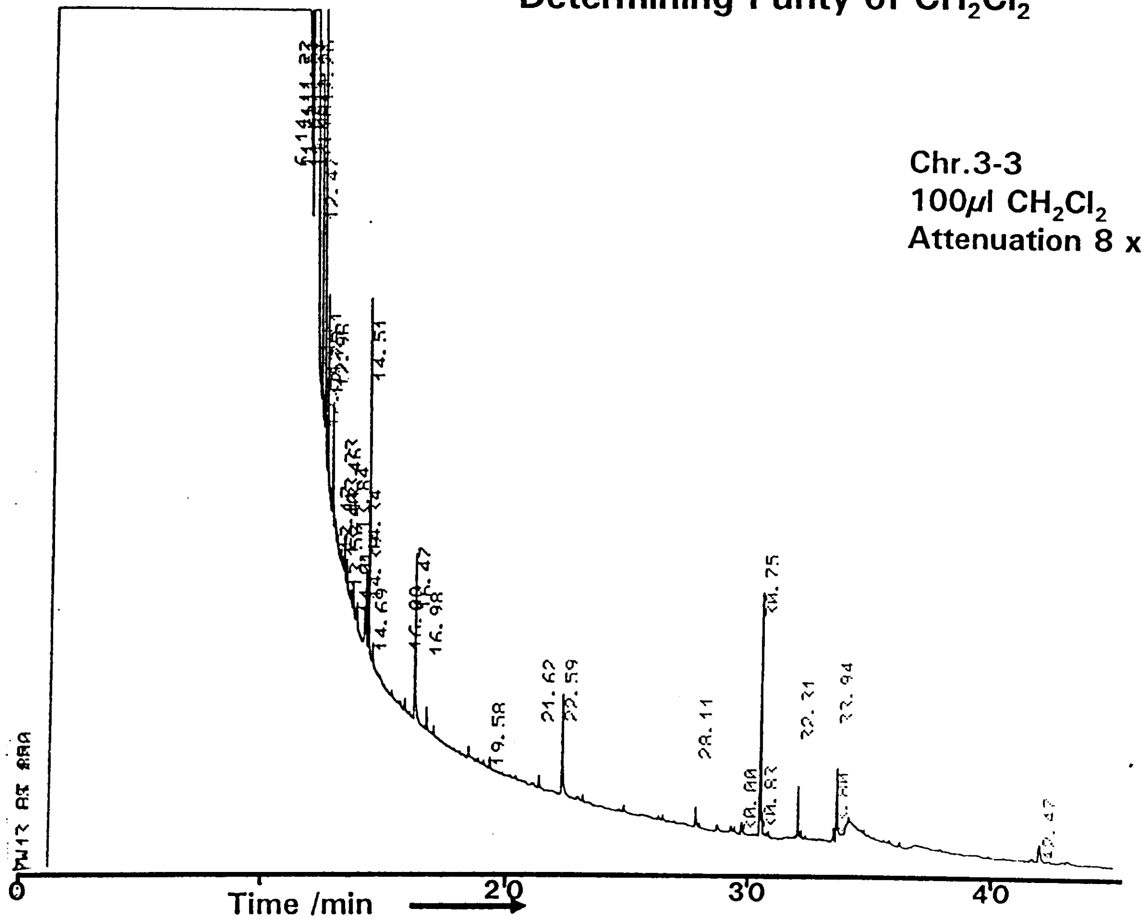
Chr.3-1
Blank Run
Attenuation 8 x 10^{-12}A.mv^{-1}



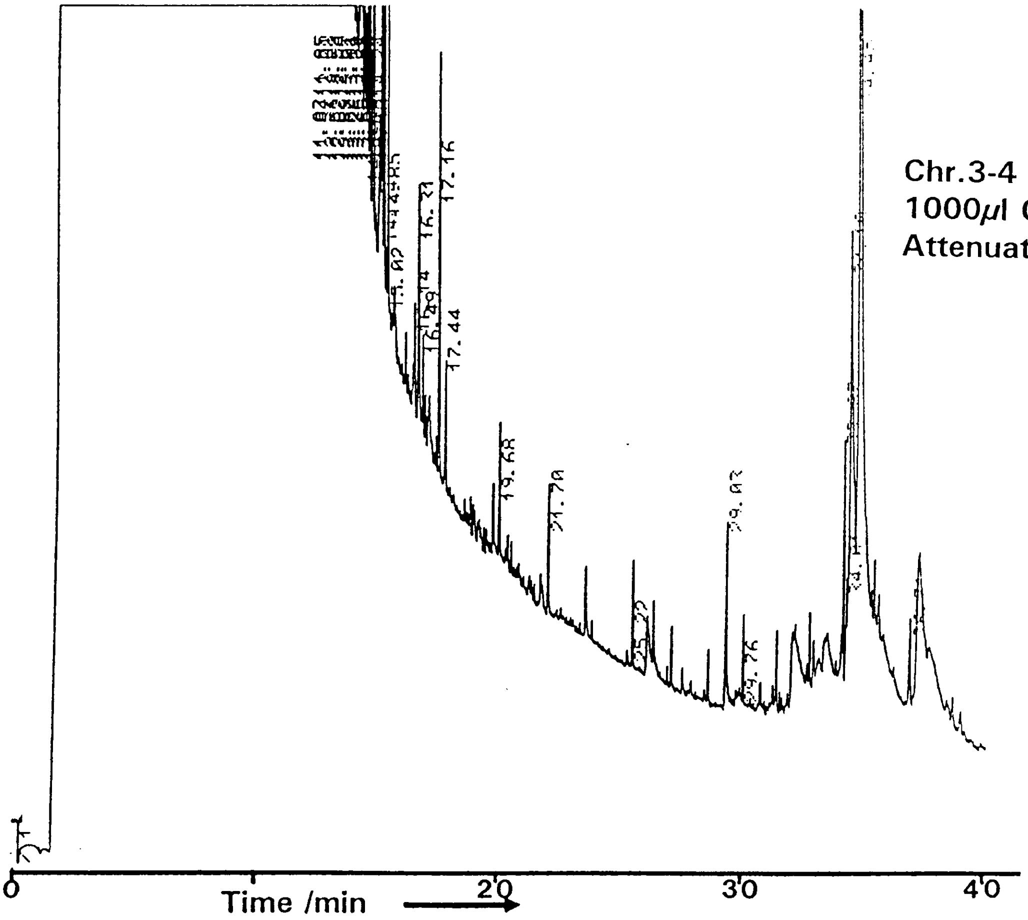
Chr.3-2
20μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}



Determining Purity of CH_2Cl_2

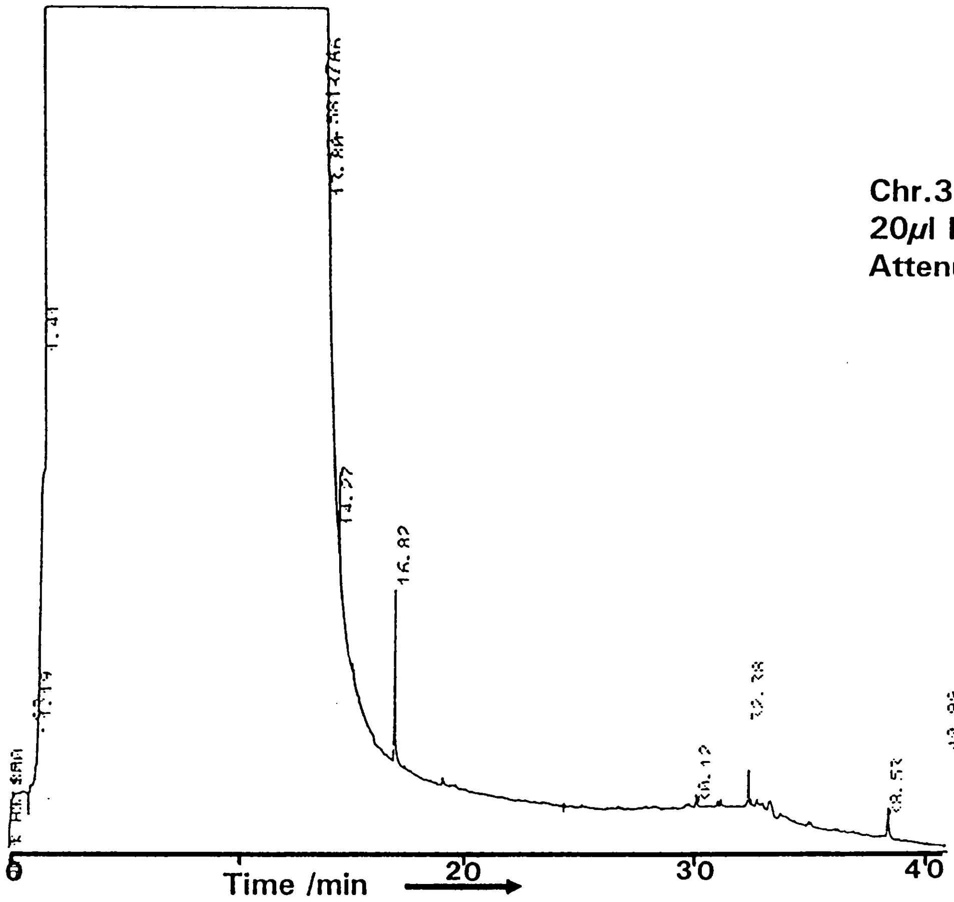


Chr.3-3
100μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}

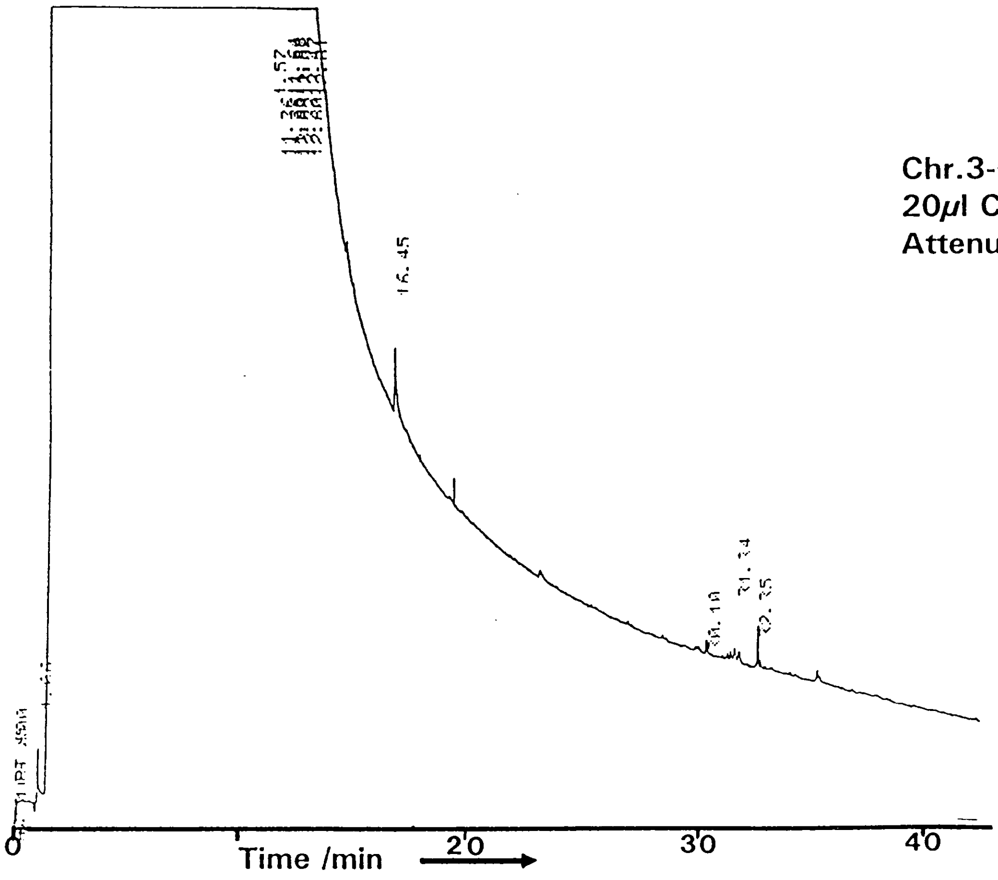


Chr.3-4
1000μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}

Comparison between CH_2Cl_2 and Hexane

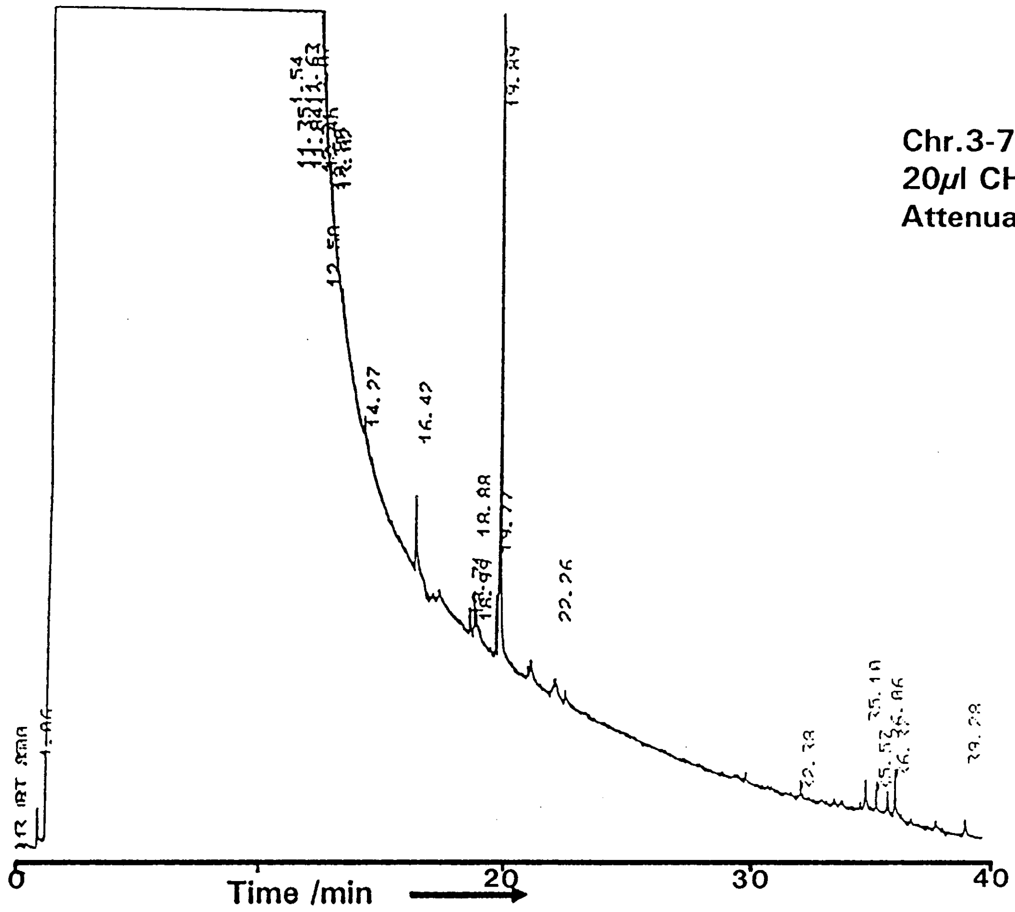


Chr.3-5
20μl Hexane
Attenuation 8 x 10^{-12}A.mv^{-1}

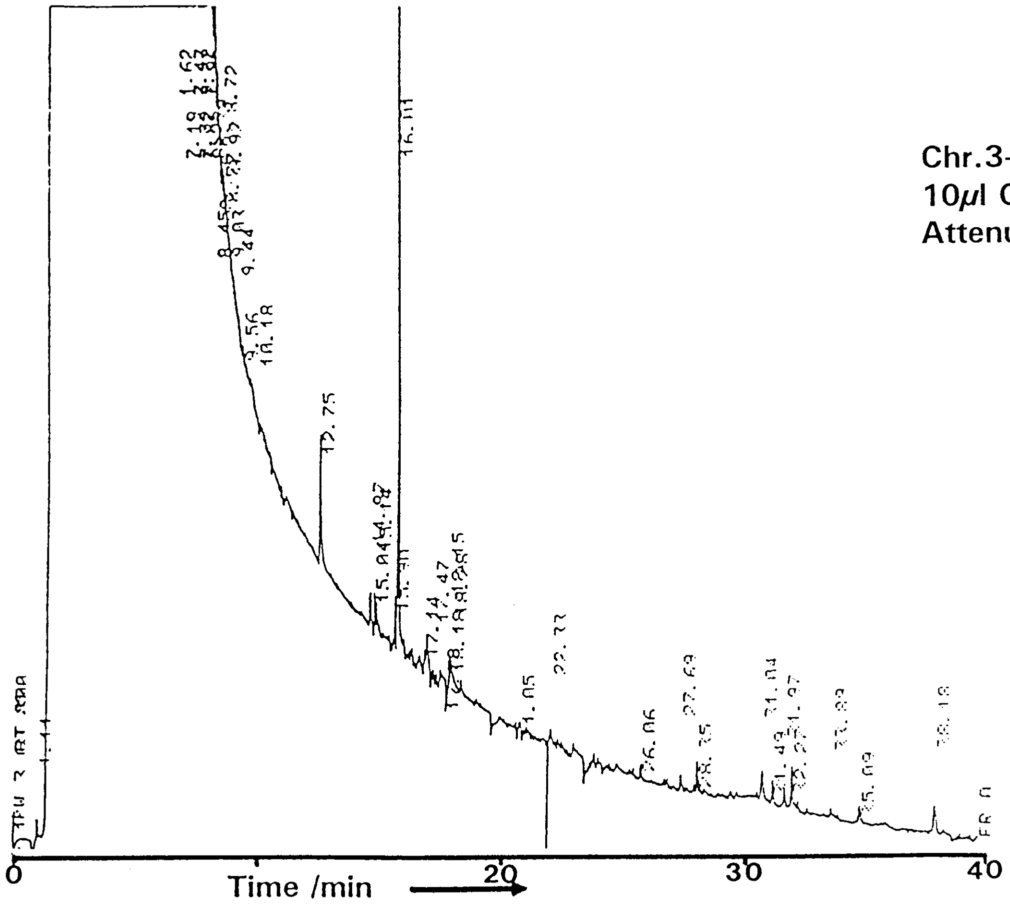


Chr.3-6
20μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}

Comparison between two different injection volumns of CH_2Cl_2



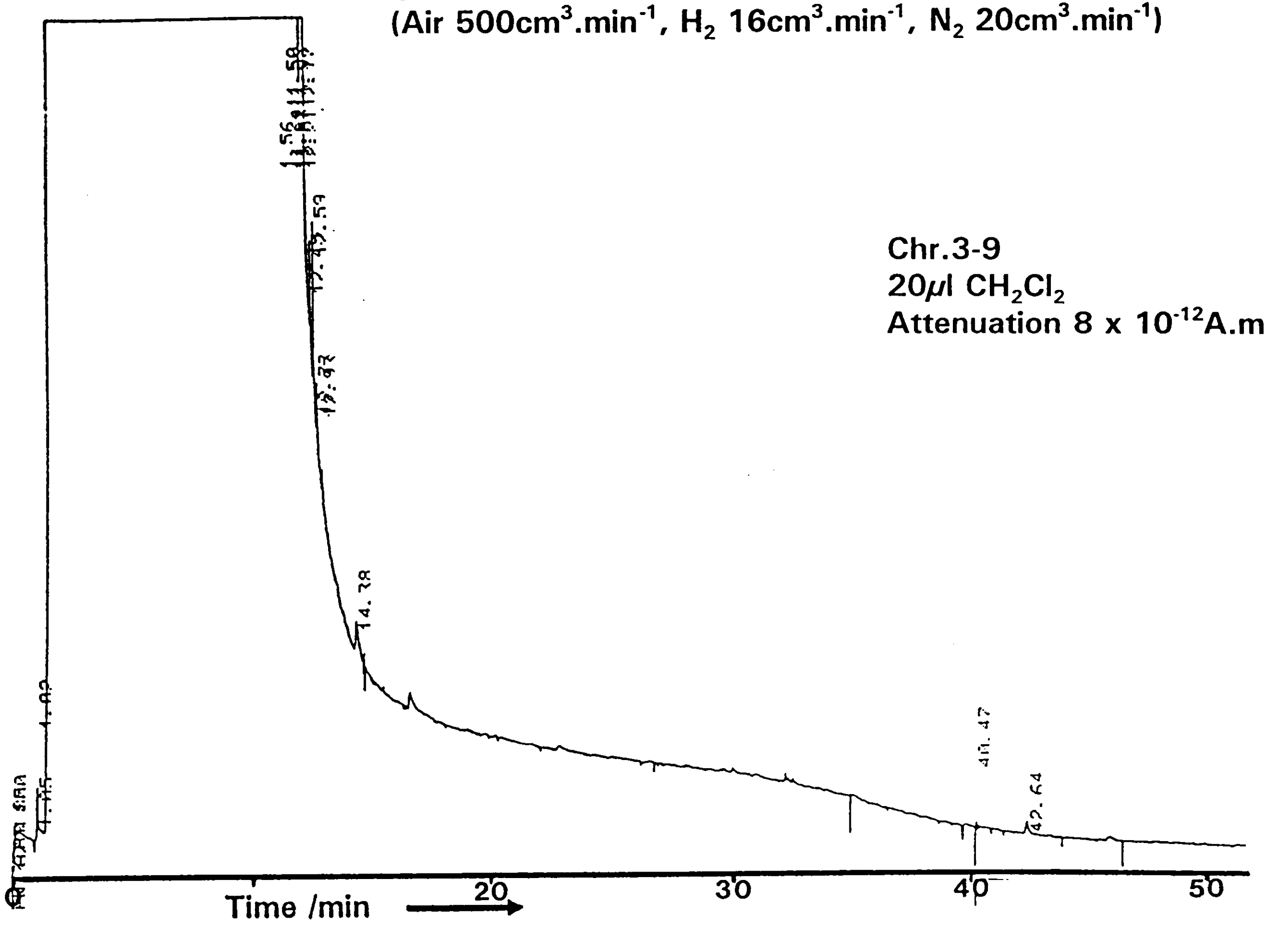
Chr.3-7
20μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}



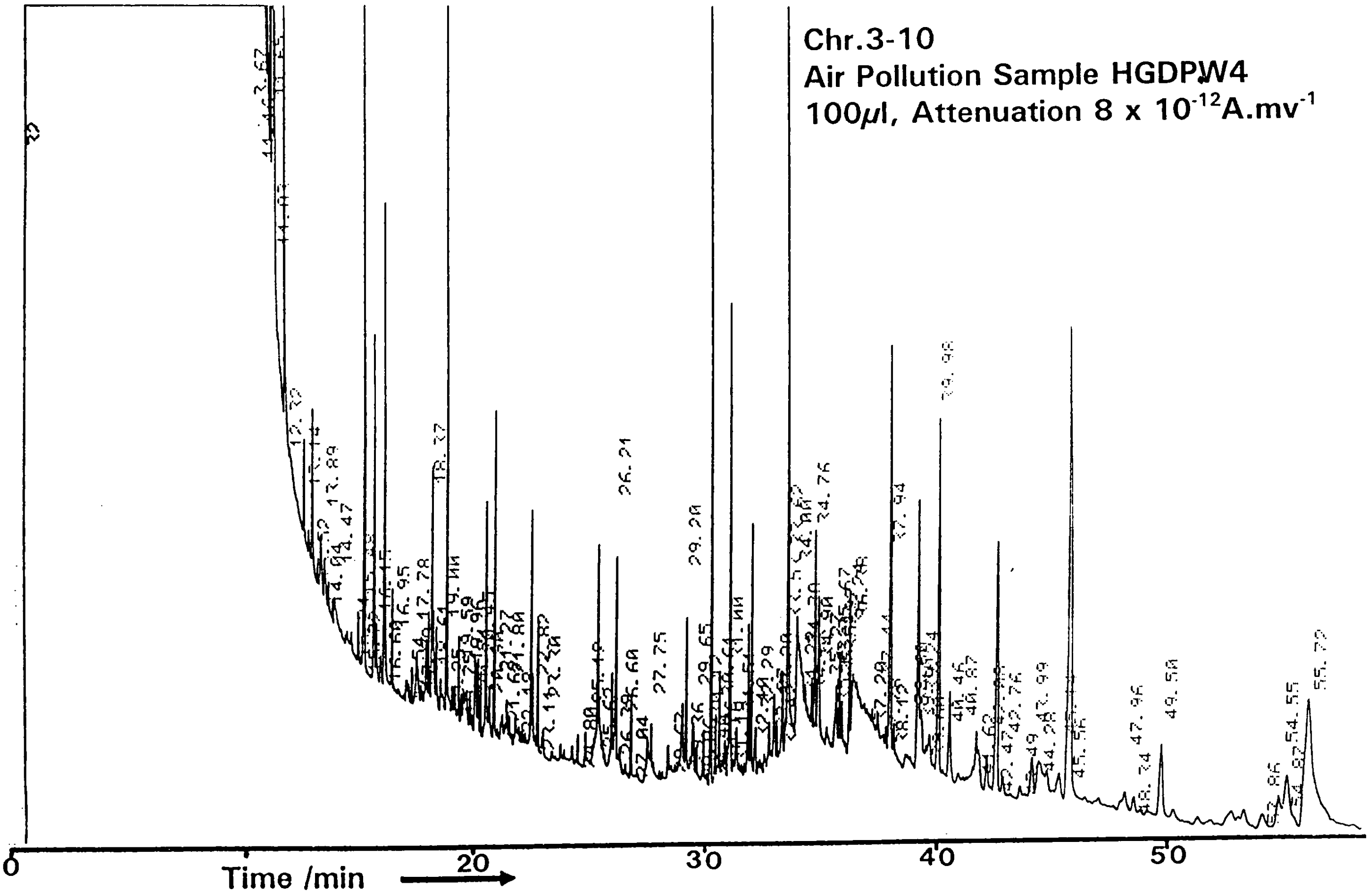
Chr.3-8
10μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}

Optimum flow rate of FID gases with Metal Tip

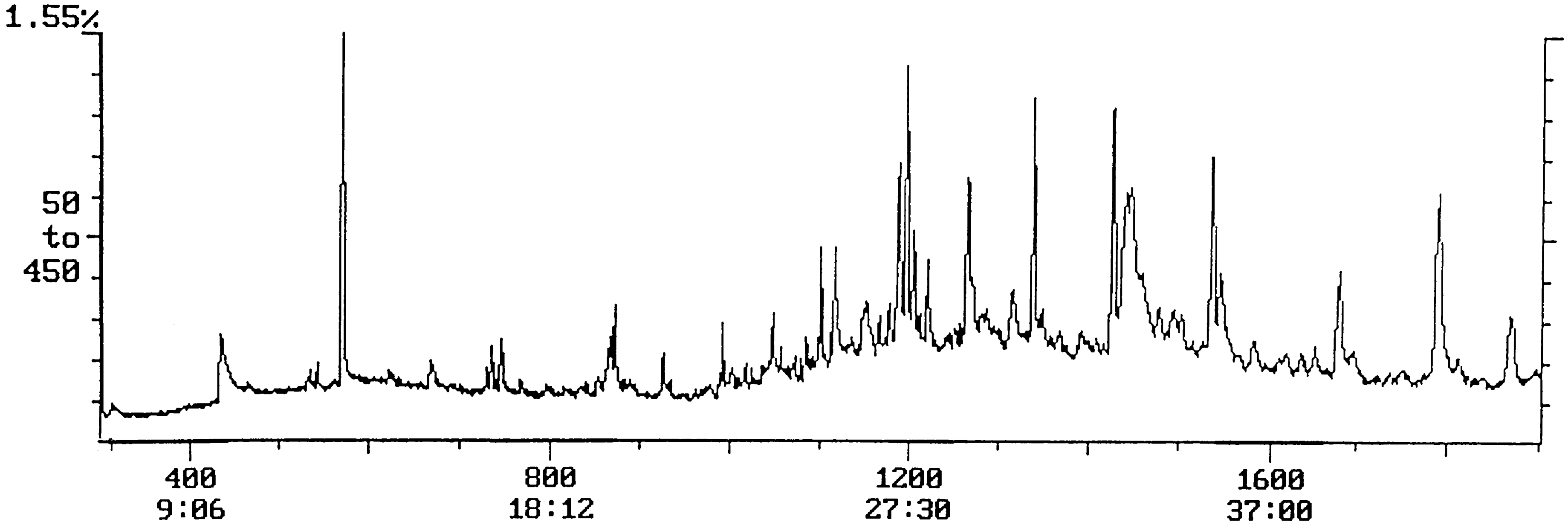
(Air 500cm^3.min^{-1}, H_2 16cm^3.min^{-1}, N_2 20cm^3.min^{-1})



Chr.3-9
20μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}

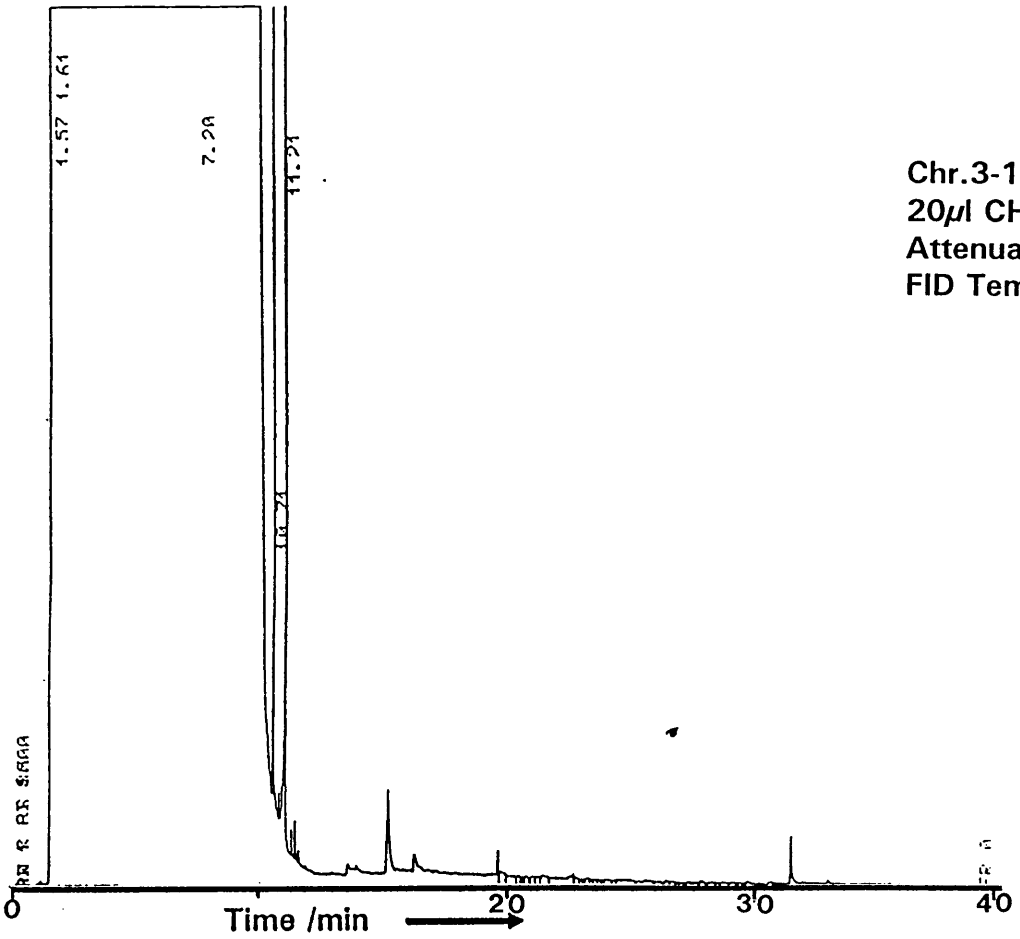


Chr.3-10
Air Pollution Sample HGDPW4
100μl, Attenuation 8 x 10^{-12}A.mv^{-1}

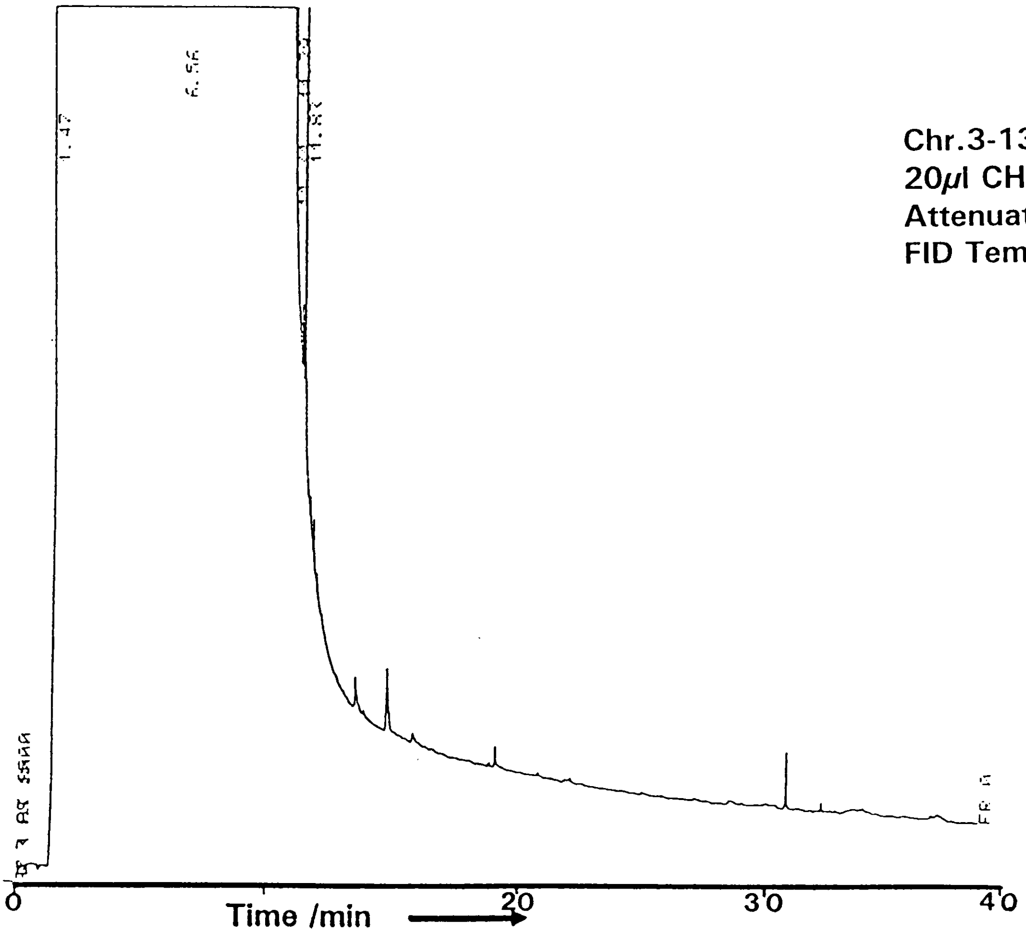


Chr.3-11
Concentration of Air Pollution Sample HGDPW4
using Kurderna-Danish Concentrator

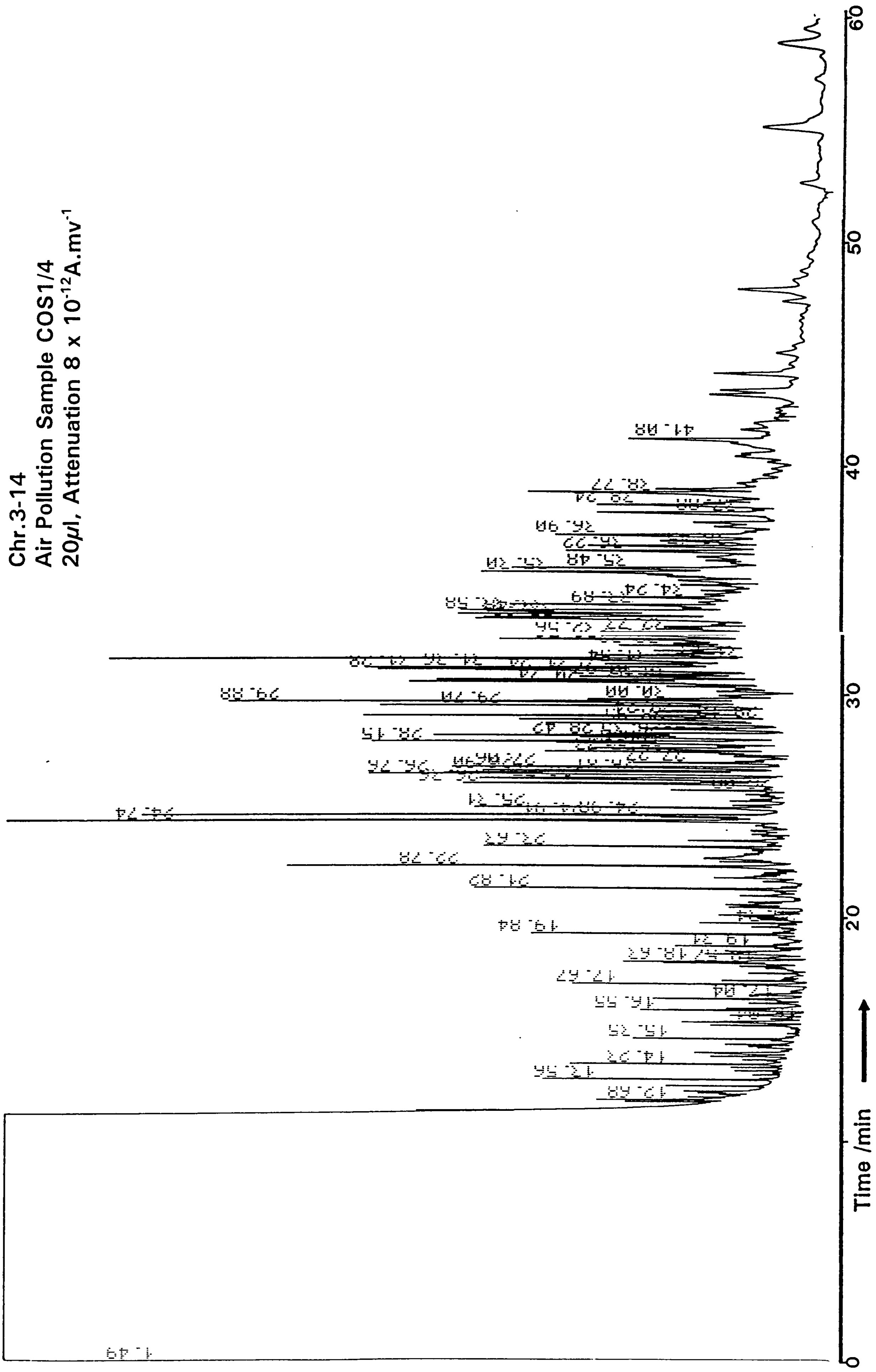
Varying FID Temperature



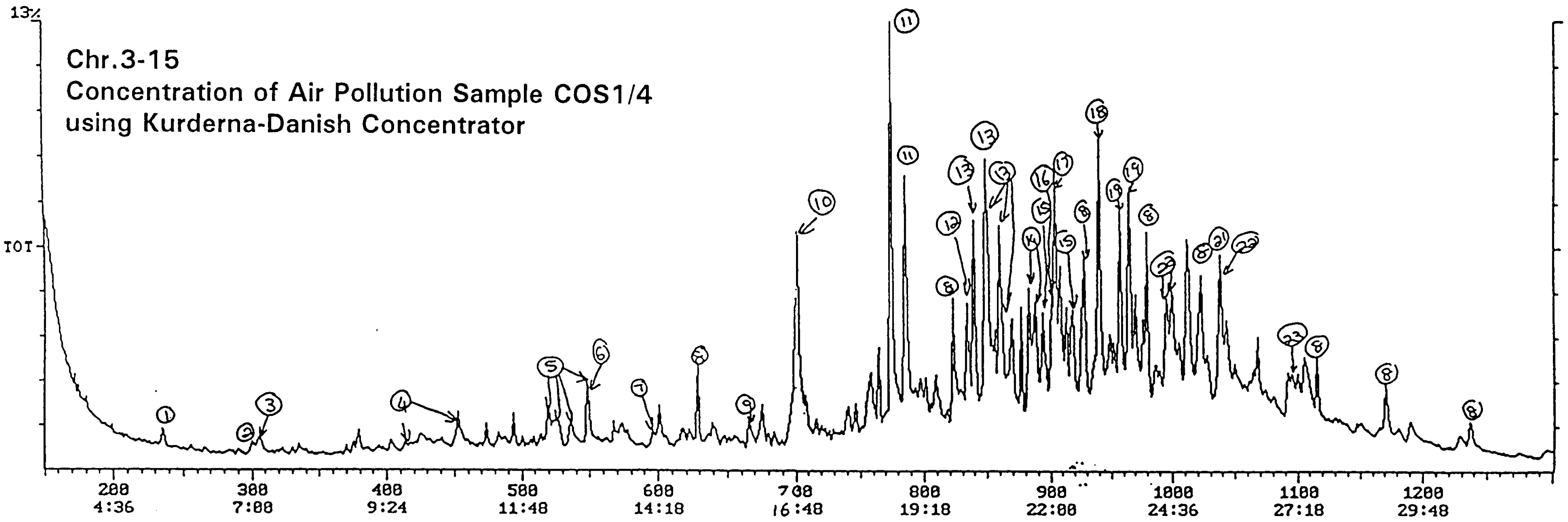
Chr.3-12
20μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}
FID Temp. 150°C



Chr.3-13
20μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}
FID Temp. 300°C



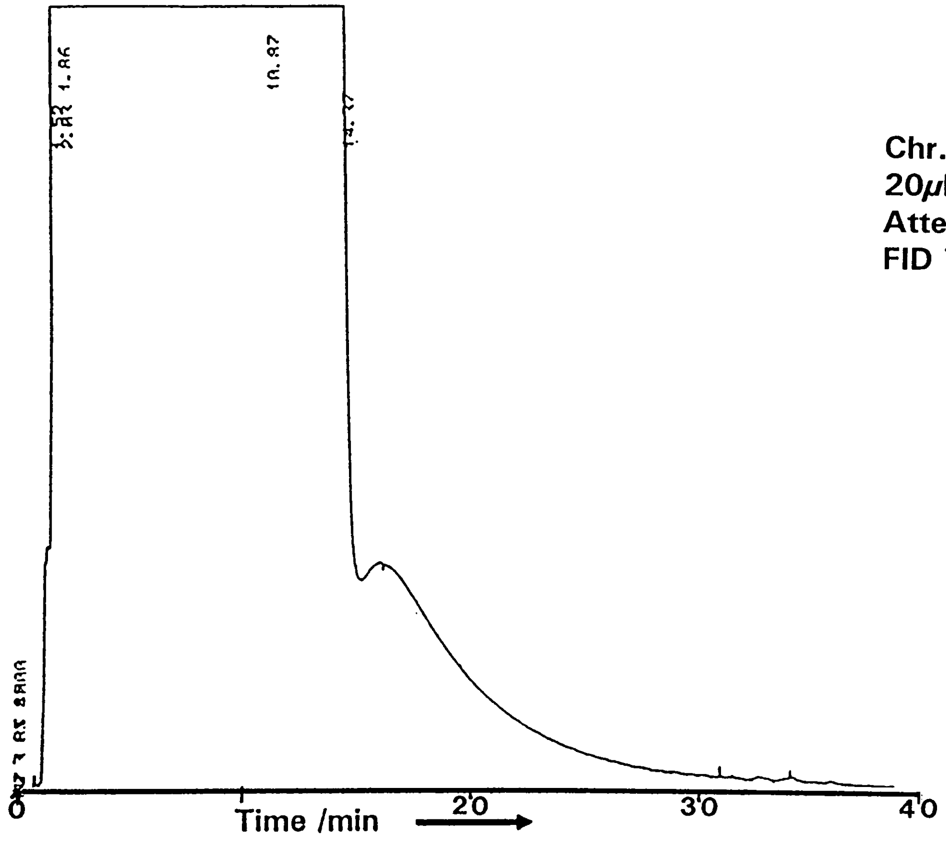
Chr.3-14
Air Pollution Sample COS1/4
20μl, Attenuation 8 x 10^{-12}A.mv^{-1}



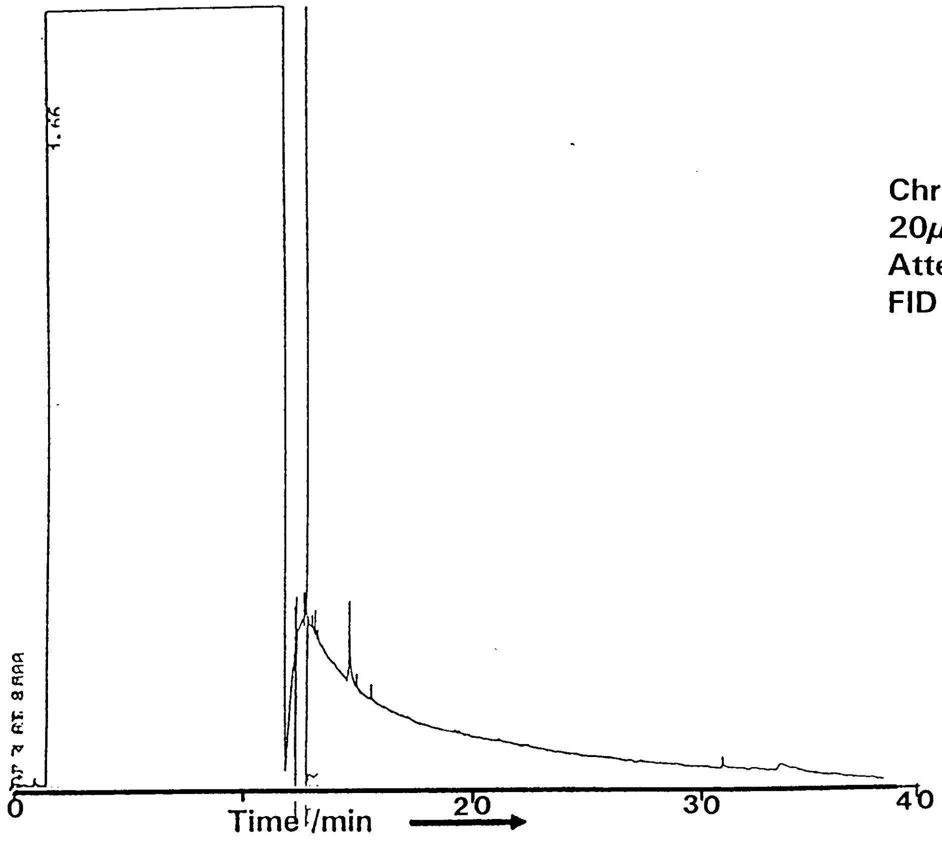
Chr.3-15
Concentration of Air Pollution Sample COS1/4
using Kurderna-Danish Concentrator

1. C_7H_{14}-isomer
2. Toluene C_7H_8
3. C_8H_{16}-isomer
4. Dimethylbenzene C_8H_{10}
5. C_9H_{12}-alkylbenzene isomer
6. $C_{10}H_{22}$-alkane
7. $C_{10}H_{14}$-alkylbenzene isomer
8. $C_x H_y$-hydrocarbon compounds
9. $C_{11}H_{16}$-alkylbenzen isomer
10. Naphthalene $C_{10}H_8$
11. Methylnaphthalene $C_{11}H_{10}$
12. Ethylnaphthalene $C_{12}H_{12}$
13. Dimethylnaphthalene $C_{12}H_{12}$
14. Methylbiphenyl $C_{13}H_{12}$
15. Trimethylnaphthalene $C_{13}H_{14}$
16. Trimethylphenylbutenone $C_{13}H_{16}O$
17. Dibenzofuran $C_{12}H_8O$
18. Fluorene $C_{13}H_{10}$
19. Methyldibenzofuran $C_{13}H_{10}O$
20. Methylfluorene $C_{14}H_{12}$
21. Phenanthrene $C_{14}H_{10}$
22. Internal standard d_{10}-Phenanthrene
23. Methylphenanthrene

First runs taken with Quartz Flame Tip

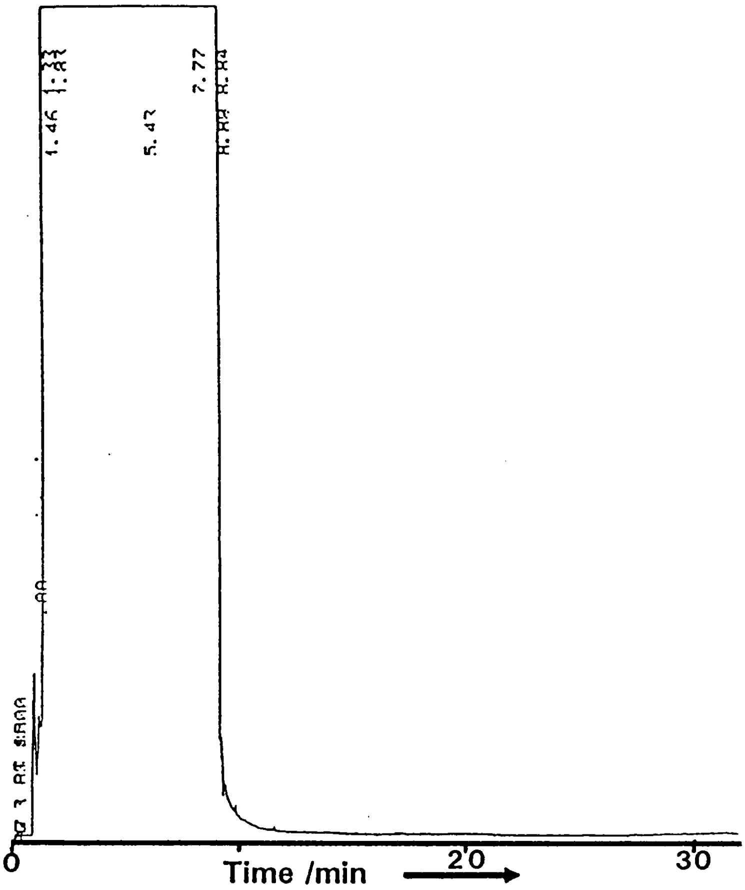


Chr.3-16
20μl Hexane
Attenuation 8 x 10^{-12}A.mv^{-1}
FID Temp. 270°C

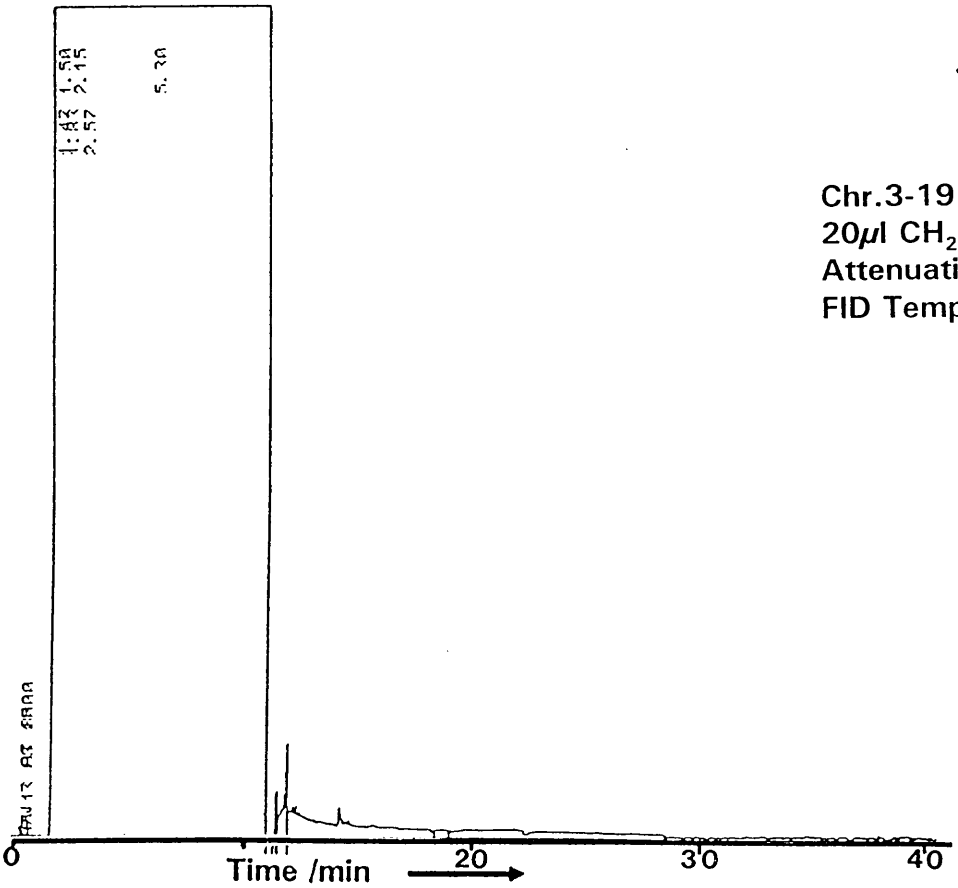


Chr.3-17
20μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}
FID Temp. 270°C

Polyimide ferrule used in place of Graphite ferrule

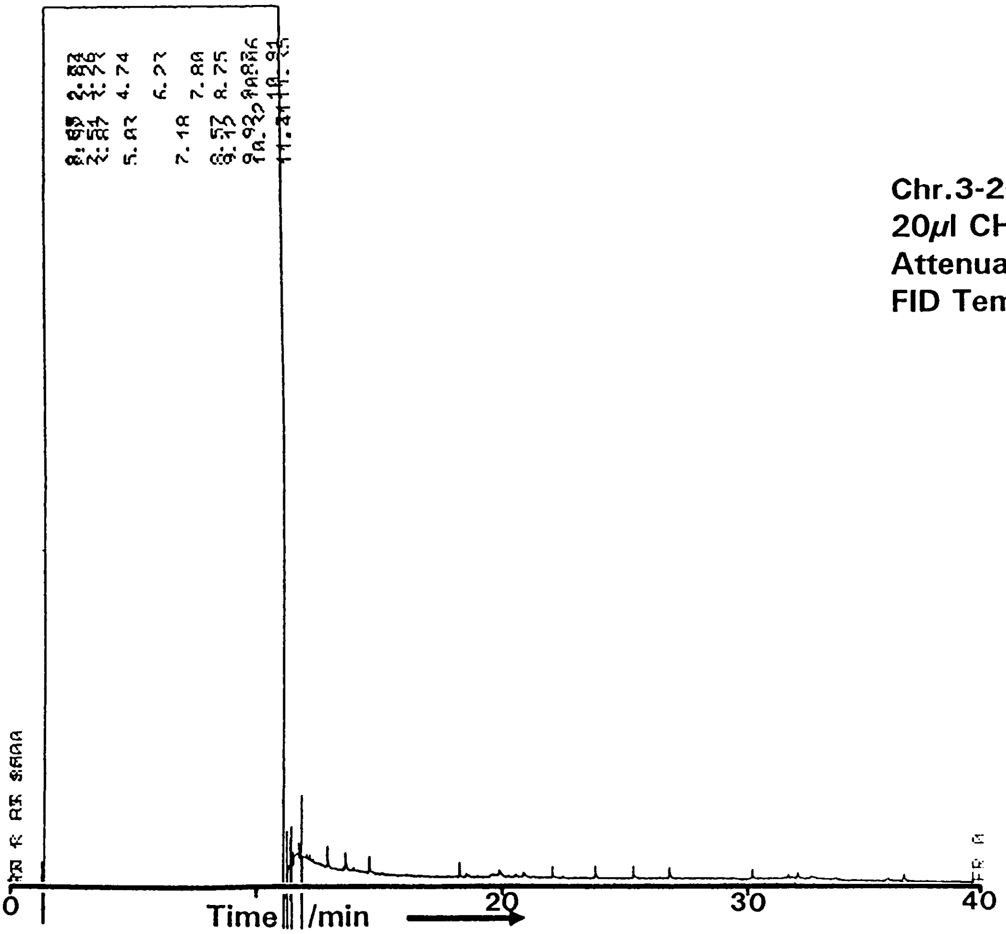


Chr.3-18
20μl Hexane
Attenuation 8 x 10^{-12}A.mv^{-1}
FID Temp. 270°C



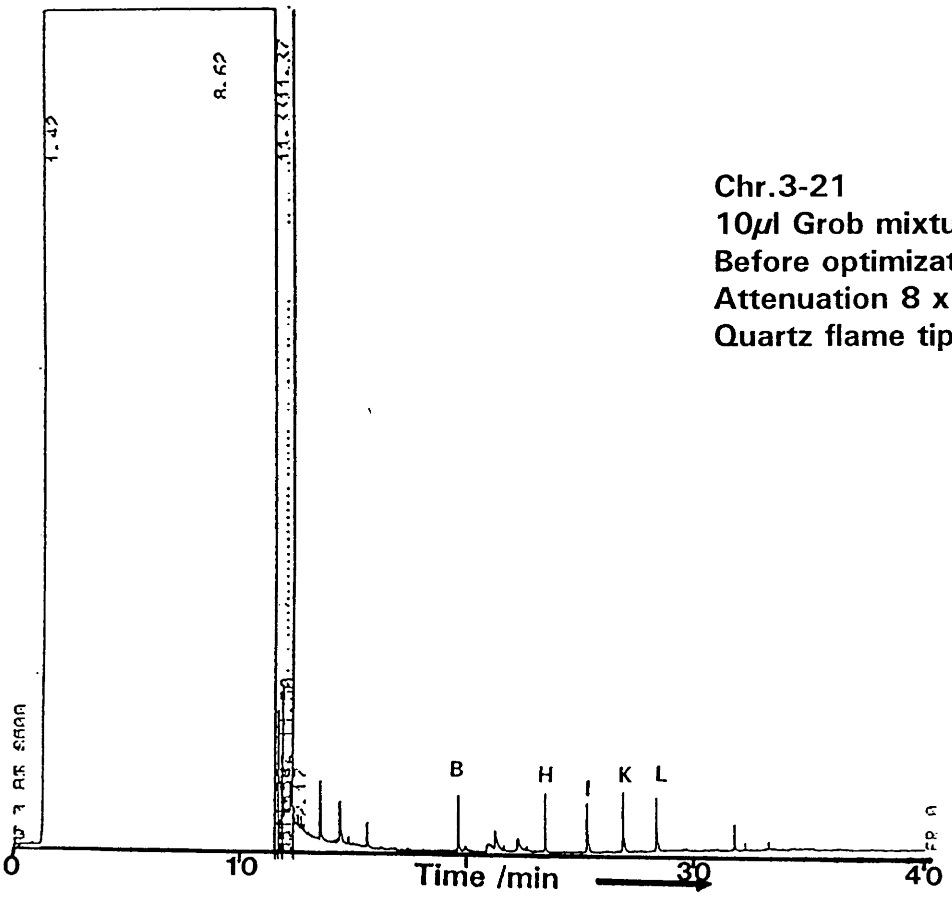
Chr.3-19
20μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}
FID Temp. 270°C

Diagram showing Electron Capture Effect of CH_2Cl_2

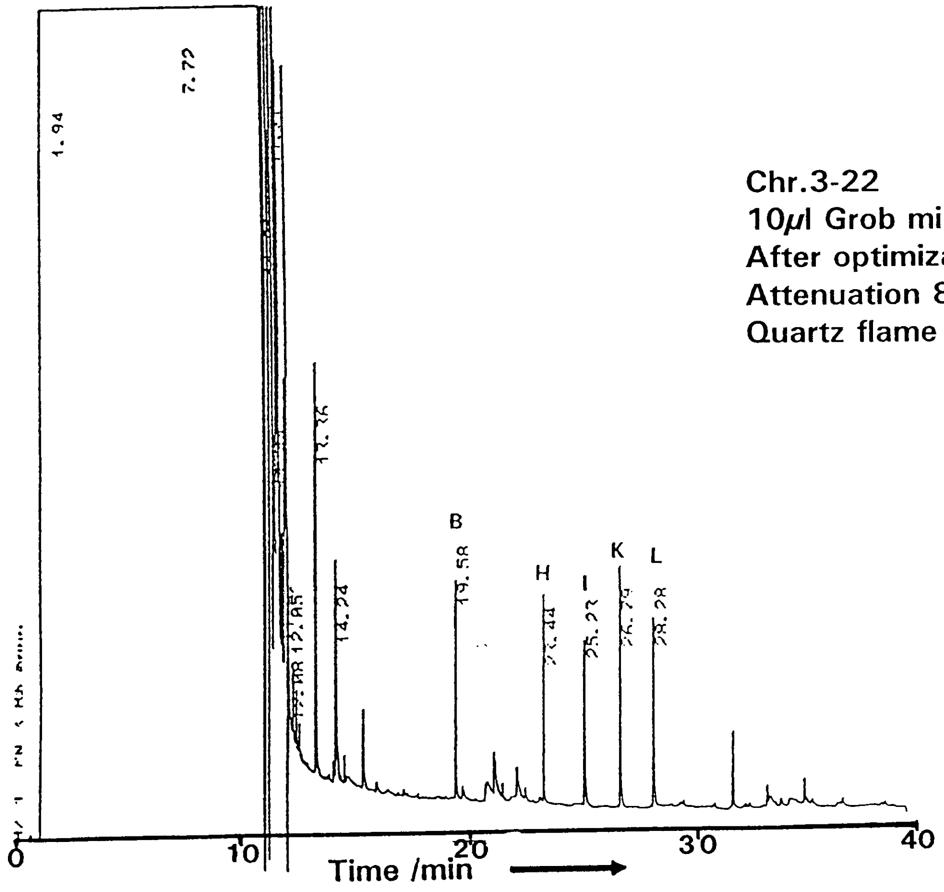


Chr.3-20
20μl CH_2Cl_2
Attenuation 8 x 10^{-12}A.mv^{-1}
FID Temp. 270°C

Grob Tests (±7ng)

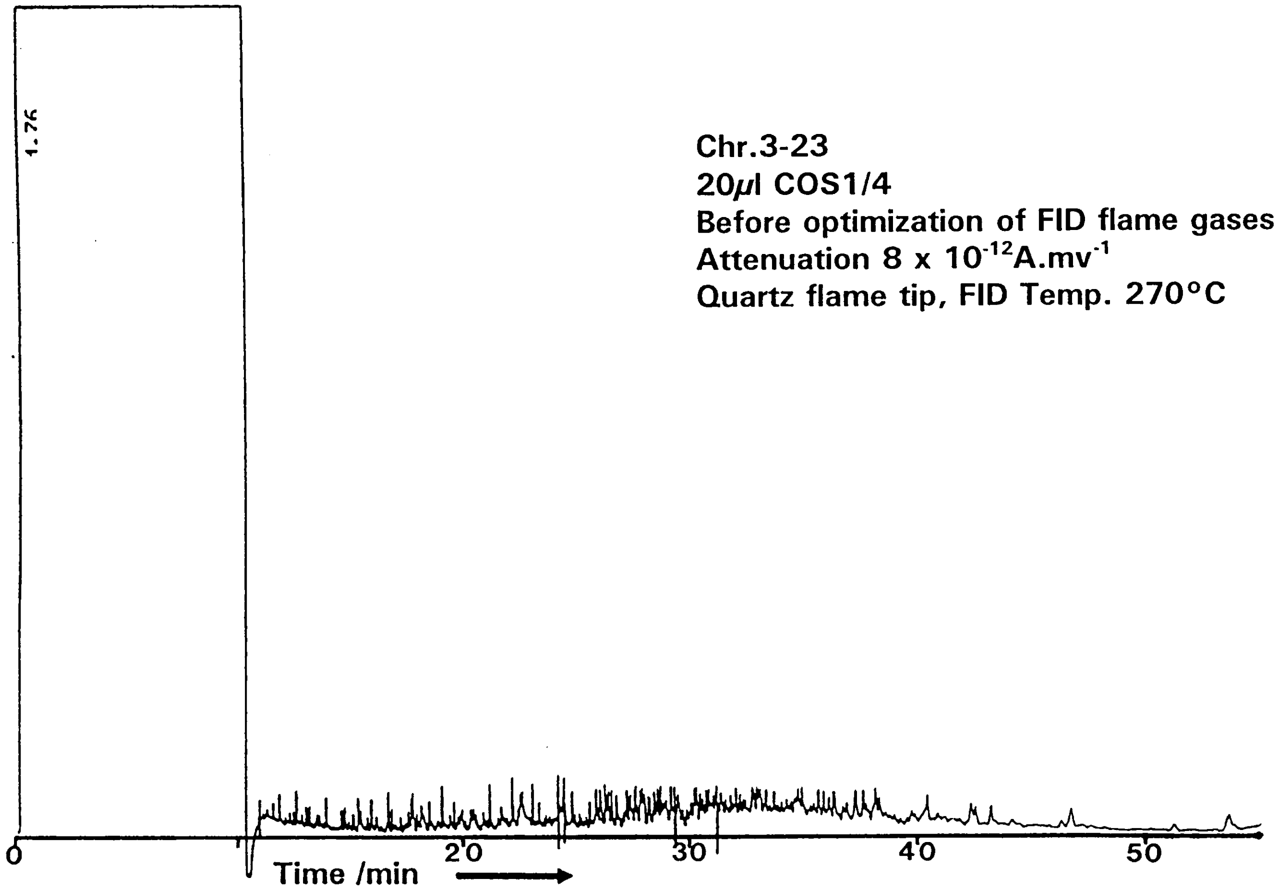


Chr.3-21
10μl Grob mixture1
Before optimization of FID flame gases
Attenuation 8 x 10^{-12}A.mv^{-1}
Quartz flame tip, FID Temp. 270°C

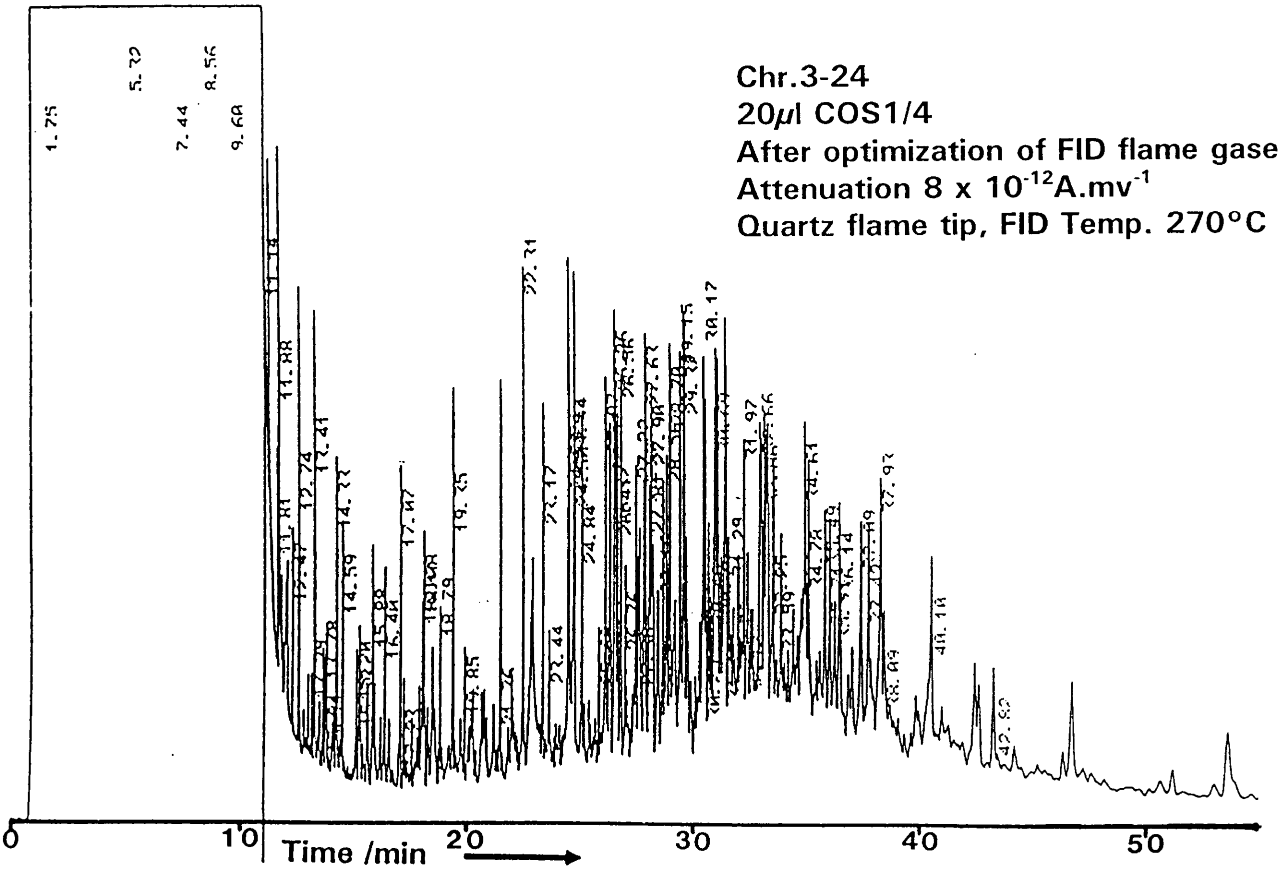


Chr.3-22
10μl Grob mixture1
After optimization of FID flame gases
Attenuation 8 x 10^{-12}A.mv^{-1}
Quartz flame tip, FID Temp. 270°C

Air Pollution Sample COS1/4

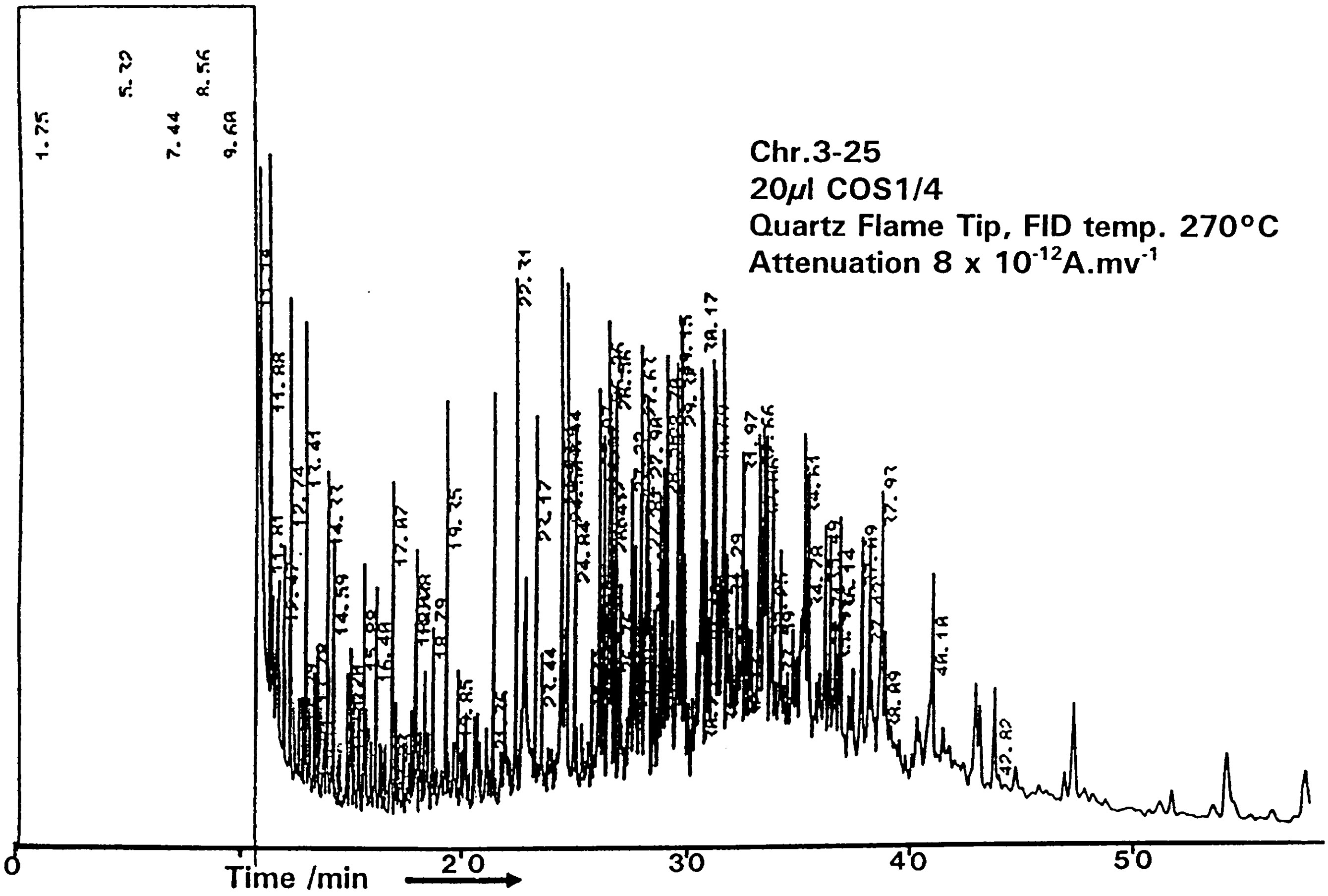


Chr.3-23
20μl COS1/4
Before optimization of FID flame gases
Attenuation 8 x 10^{-12}A.mv^{-1}
Quartz flame tip, FID Temp. 270°C

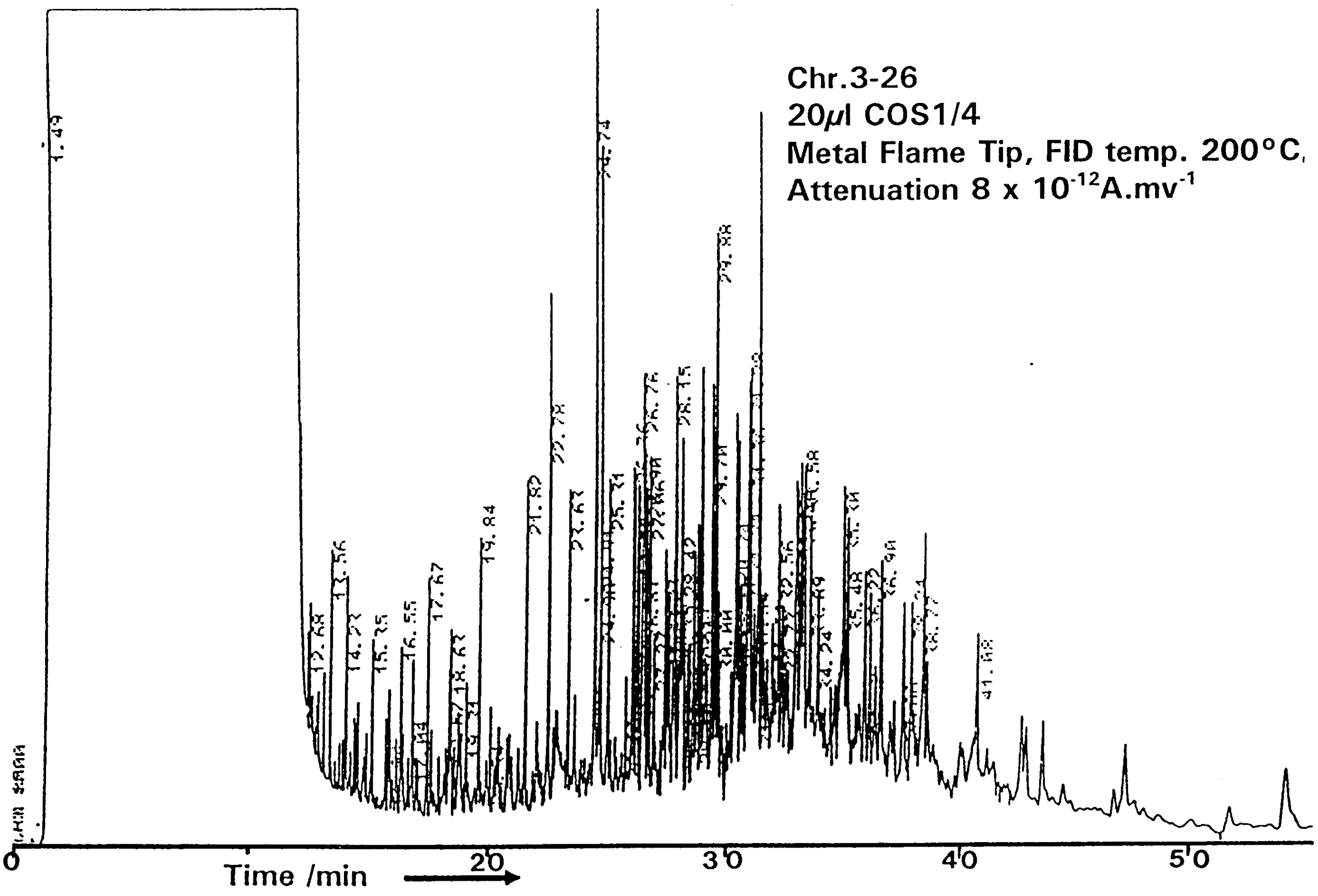


Chr.3-24
20μl COS1/4
After optimization of FID flame gases
Attenuation 8 x 10^{-12}A.mv^{-1}
Quartz flame tip, FID Temp. 270°C

Comparison between Metal and Quartz Flame Tip

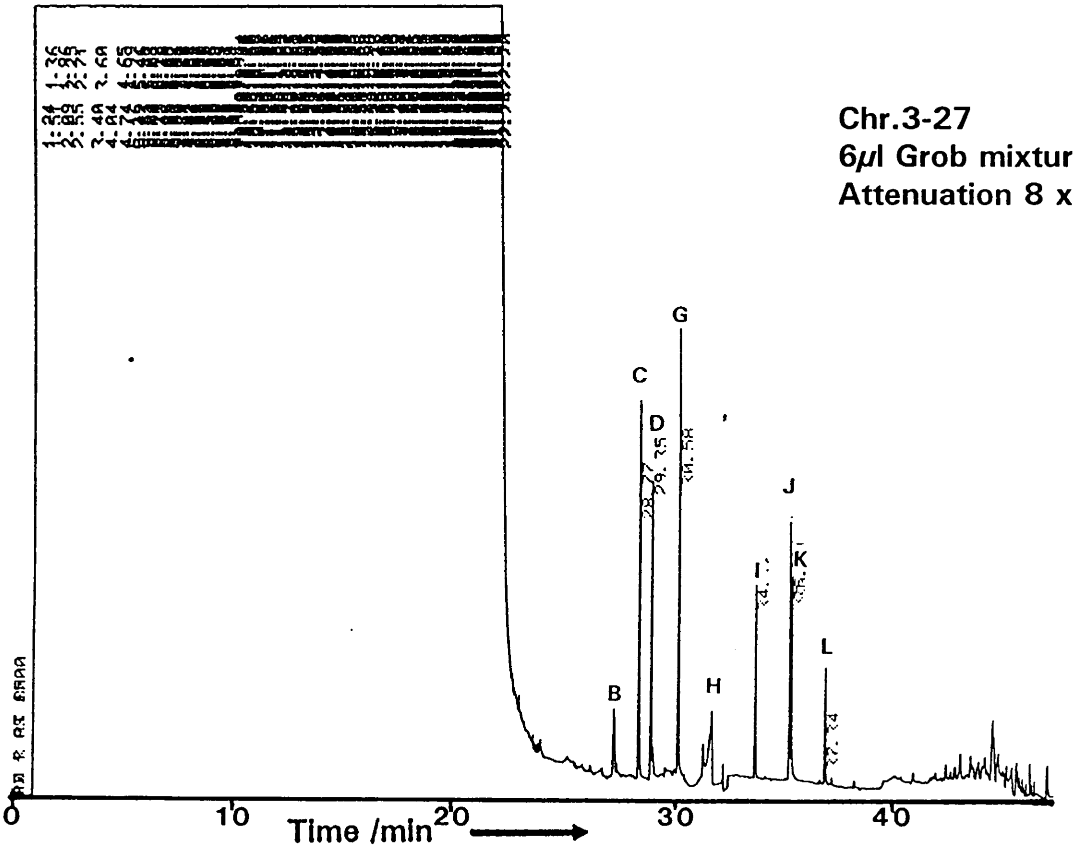


Chr.3-25
$20\mu l$ COS1/4
Quartz Flame Tip, FID temp. 270°C
Attenuation 8 x 10^{-12}A.mv^{-1}

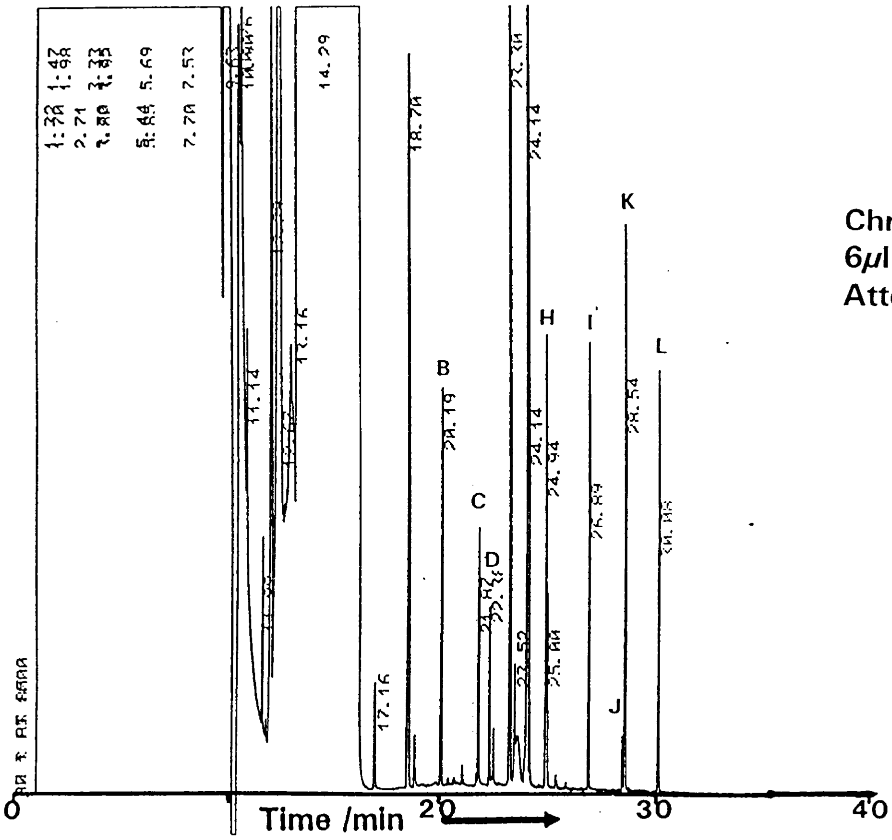


Chr.3-26
$20\mu l$ COS1/4
Metal Flame Tip, FID temp. 200°C,
Attenuation 8 x 10^{-12}A.mv^{-1}

Grob Mixture2 with different solvents (± 10ng)

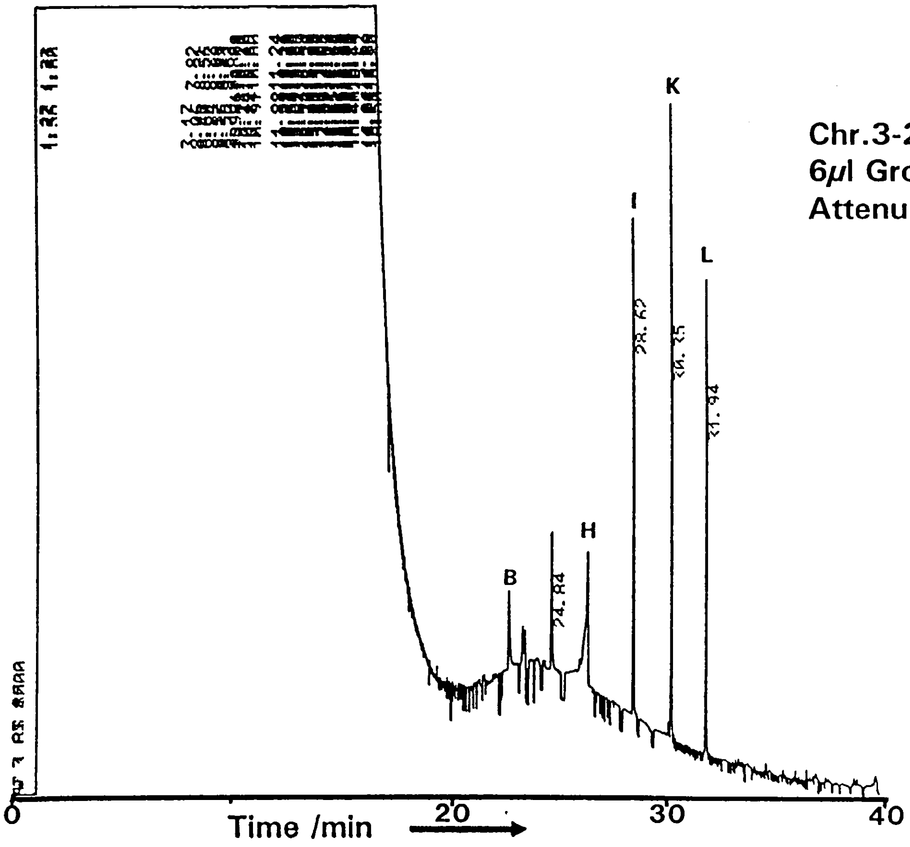


Chr.3-27
6μl Grob mixture2 in Methanol
Attenuation 8 x 10^{-12}A.mv^{-1}

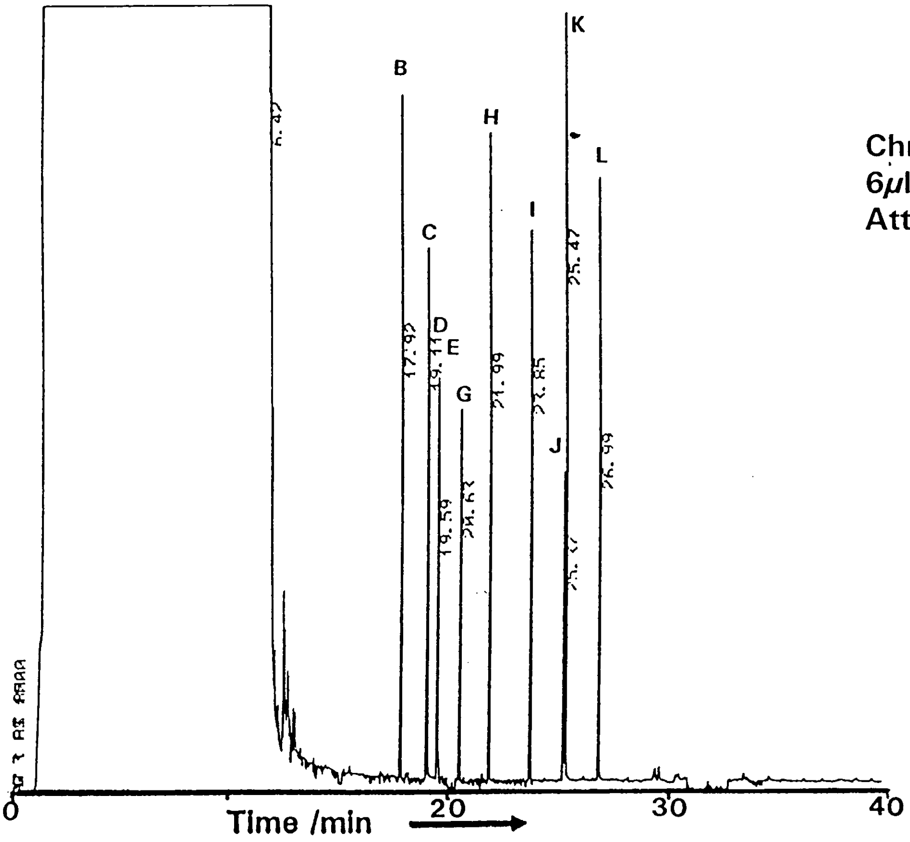


Chr.3-28
6μl Grob mixture2 in Acetone
Attenuation 8 x 10^{-12}A.mv^{-1}

Grob Mixture2 with different solvents (± 10ng)

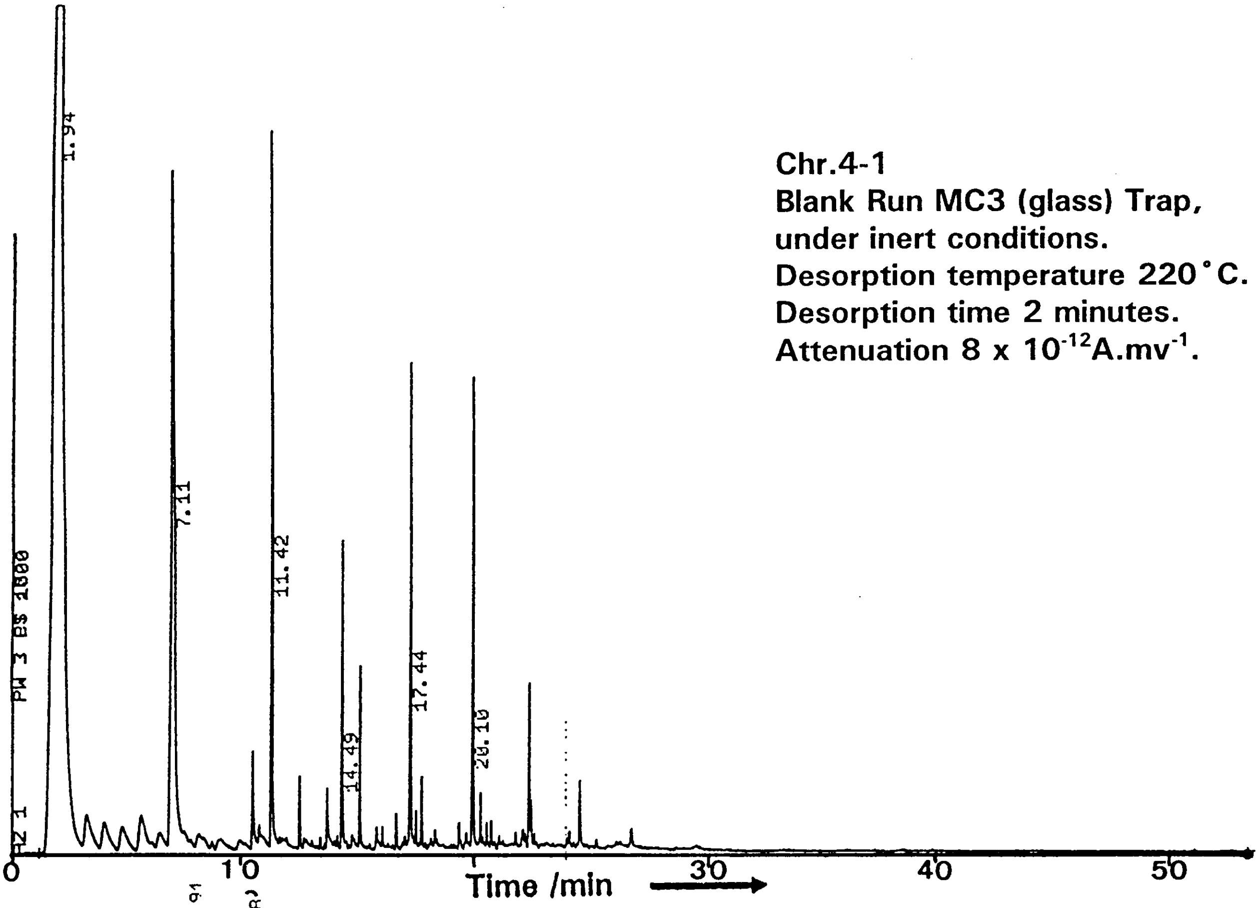


Chr.3-29
6μl Grob mixture2 in Acetonitrile
Attenuation 8 x 10^{-12}A.mv^{-1}

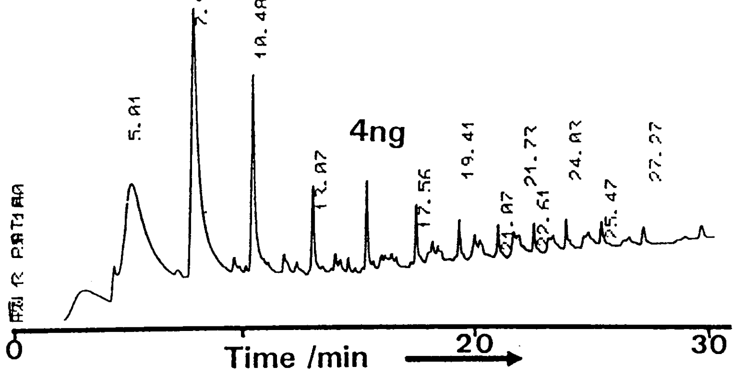


Chr.3-30
6μl Grob mixture2 in Hexane
Attenuation 8 x 10^{-12}A.mv^{-1}

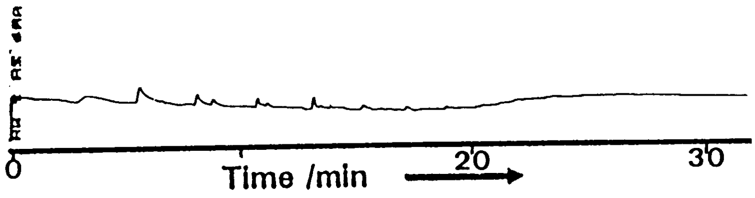
Blank Runs of Multichannel Silicone Rubber Traps



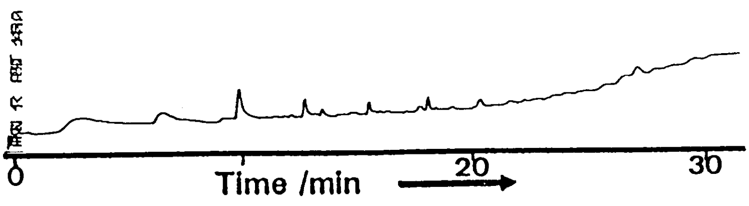
Chr.4-1
Blank Run MC3 (glass) Trap,
under inert conditions.
Desorption temperature 220 °C.
Desorption time 2 minutes.
Attenuation 8 x 10^{-12}A.mv^{-1}.



Chr.4-2
Blank Run MC8 (quartz) Trap,
under inert conditions.
Desorption temperature 250 °C.
Desorption time 2 minutes.
Attenuation 4 x 10^{-11}A.mv^{-1}.

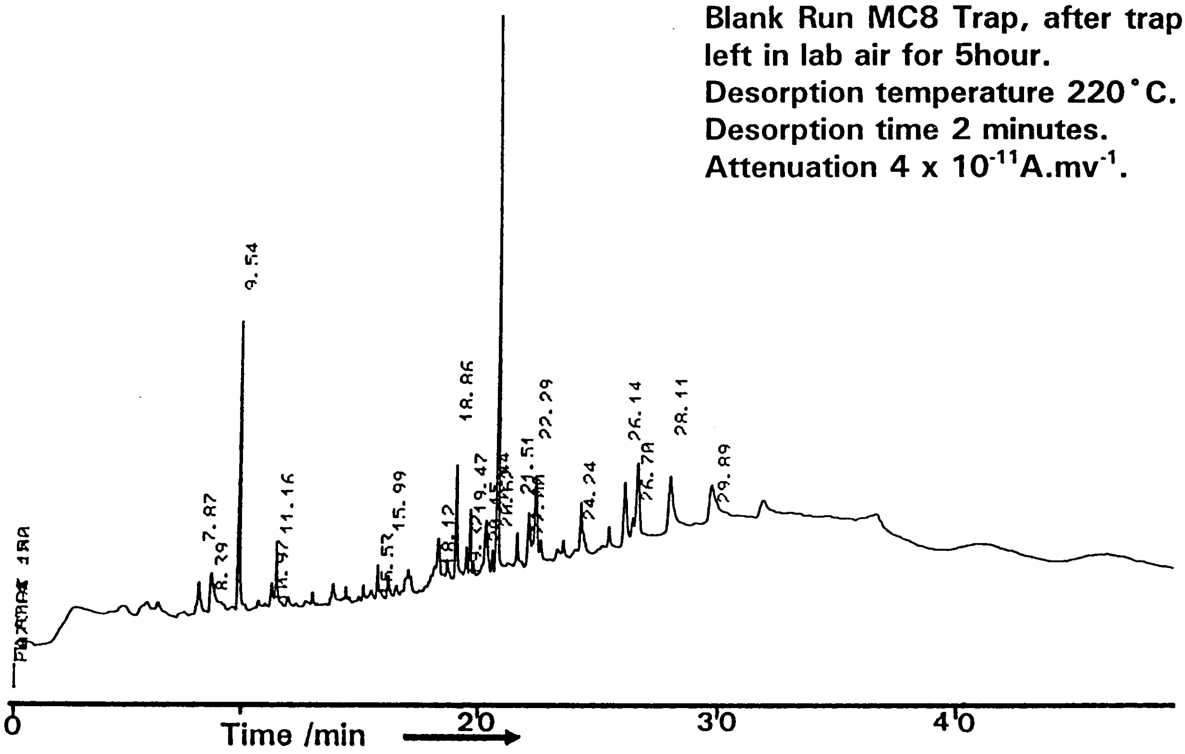


Chr.4-3
Blank Run MC8 Trap,
under inert conditions.
Desorption temperature 220 °C.
Desorption time 2 minutes.
Attenuation 4 x 10^{-11}A.mv^{-1}.

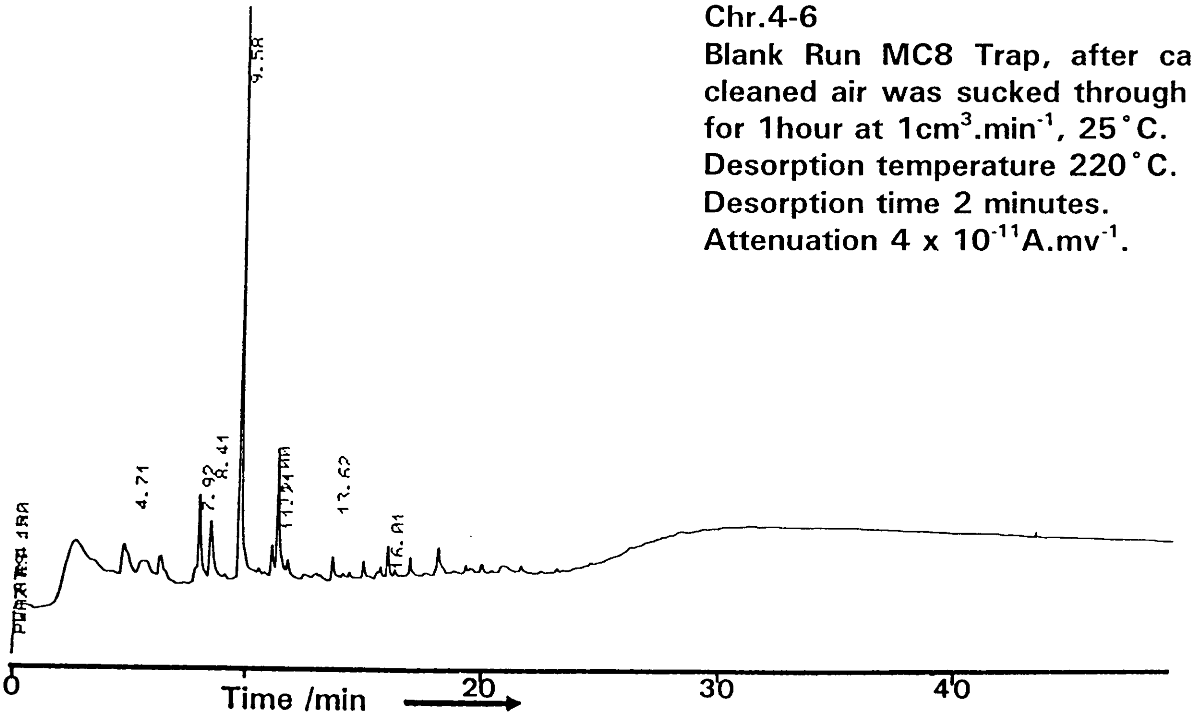


Chr.4-4
Blank Run MC8 Trap, after clean air had passed through trap for 10min at 25 °C.
Desorption temperature 220 °C.
Desorption time 2 minutes.
Attenuation 4 x 10^{-11}A.mv^{-1}.

Chromatograms showing the effect of Laboratory Air on MC8 Trap

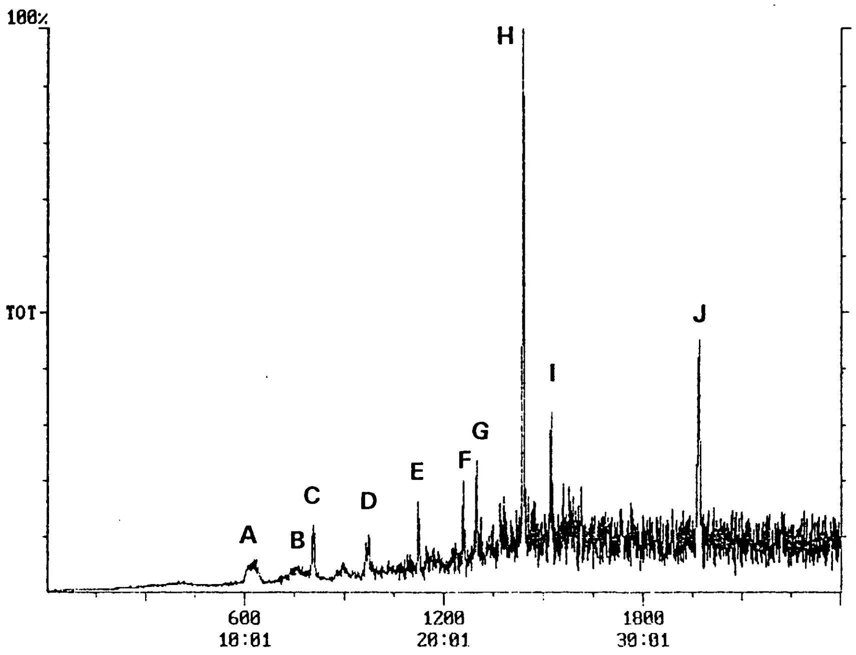


Chr.4-5
Blank Run MC8 Trap, after trap was left in lab air for 5hour.
Desorption temperature 220°C.
Desorption time 2 minutes.
Attenuation 4 x 10^{-11}A.mv^{-1}.



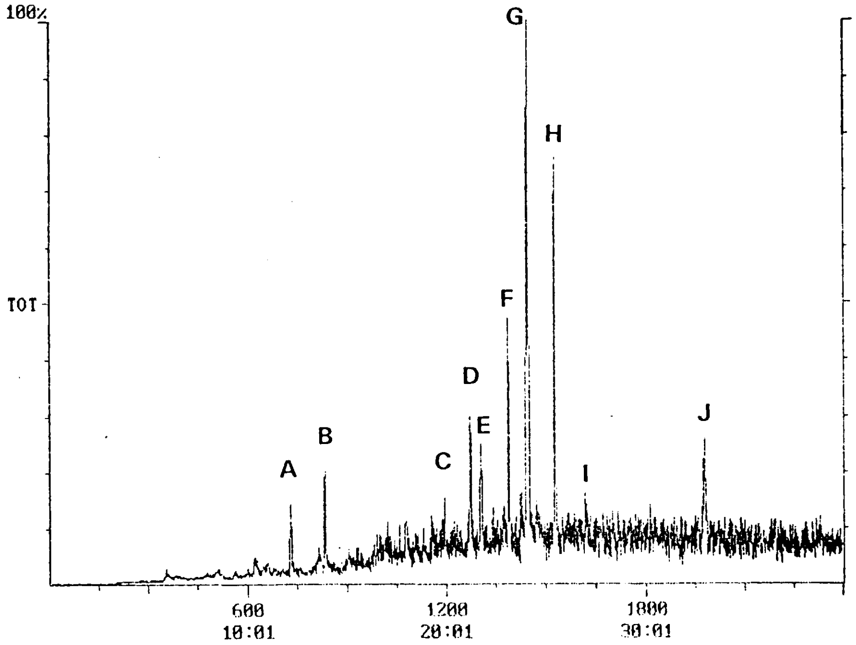
Chr.4-6
Blank Run MC8 Trap, after carbon cleaned air was sucked through trap for 1hour at $1cm^3.min^{-1}$, 25°C.
Desorption temperature 220°C.
Desorption time 2 minutes.
Attenuation 4 x 10^{-11}A.mv^{-1}.

Identification of Degradation of MC8 Trap with ITD/MS



Chr.4-7
Blank Run MC8 Trap, after the trap was kept under helium at 220°C for 2 hours.

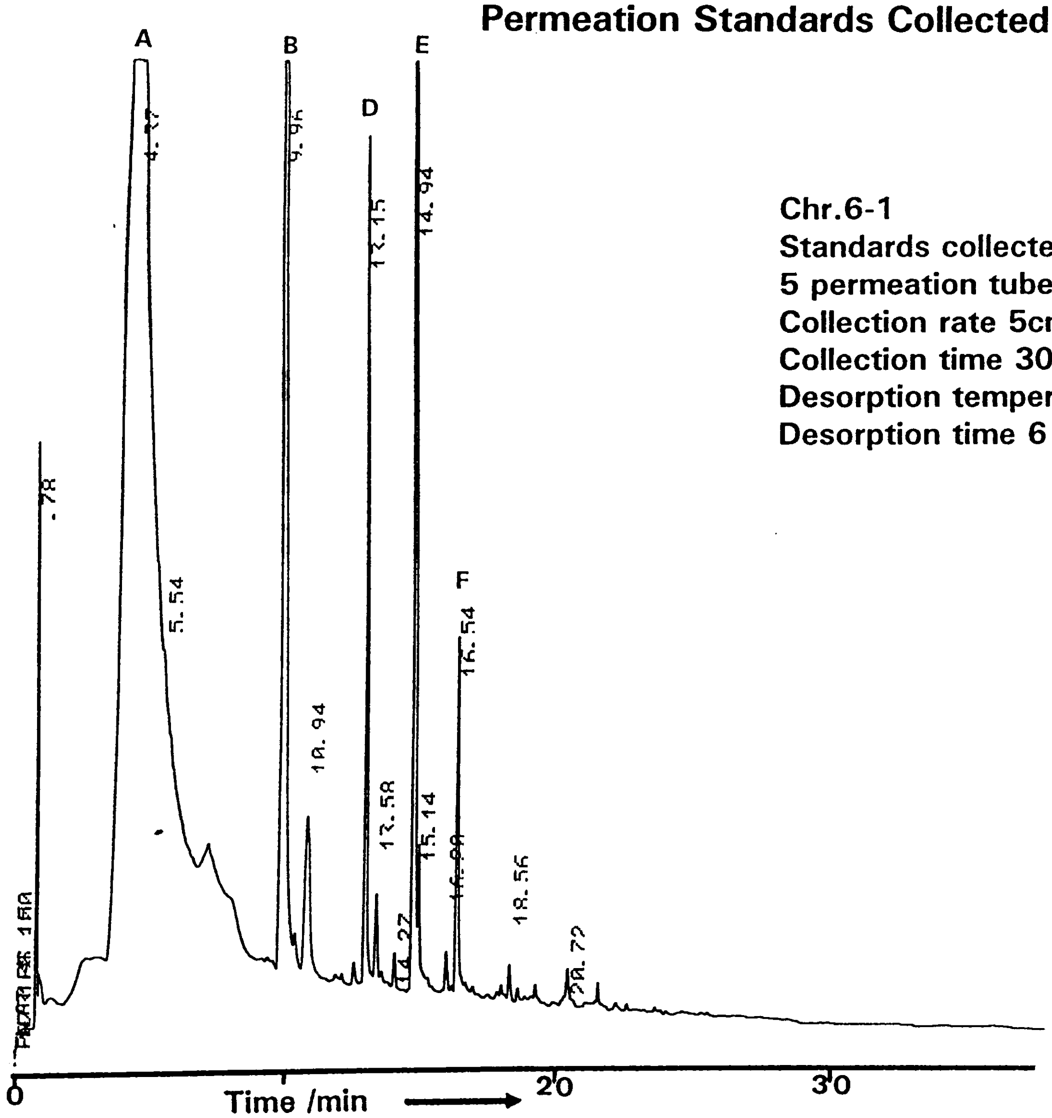
- A. Cyclotetrasiloxane, Octamethyl (D_4)
- B. Cyclopentasiloxane, Decamethyl (D_5)
- C. Cyclopentasiloxane, Decamethyl (D_5)
- D. Cyclohexasiloxane, Dodecamethyl (D_6)
- E. Pentasiloxane, Dodecamethyl
- F. Hexasiloxane, Tetradecamethyl
- G. Silicone
- H,I,J. Organic Compounds



Chr.4-8
Blank Run MC8 Trap, after the trap was kept in the lab air for five days.

- A. Alcohol
- B. Alcohol
- C. Hydrocarbon
- D. Silicone
- E. Silicone
- F. Alkene
- G. Organic Compound
- H. Alkene
- I. Alkene
- J. bis(2-ethyyl-hexyl)ϕnthalate

Permeation Standards Collected on MC8 Trap

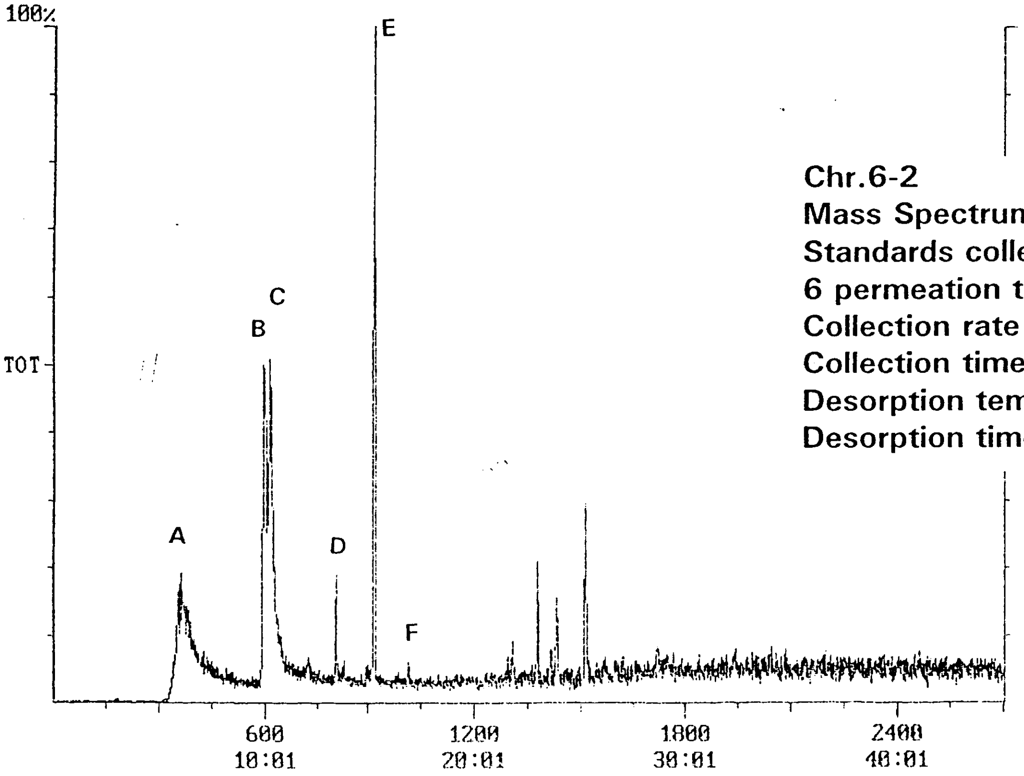


Chr.6-1
Standards collected from
5 permeation tubes on MC8 trap.
Collection rate 5cm^3.min^{-1}.
Collection time 30 minutes.
Desorption temperature 250°C.
Desorption time 6 minutes.

Time /min →

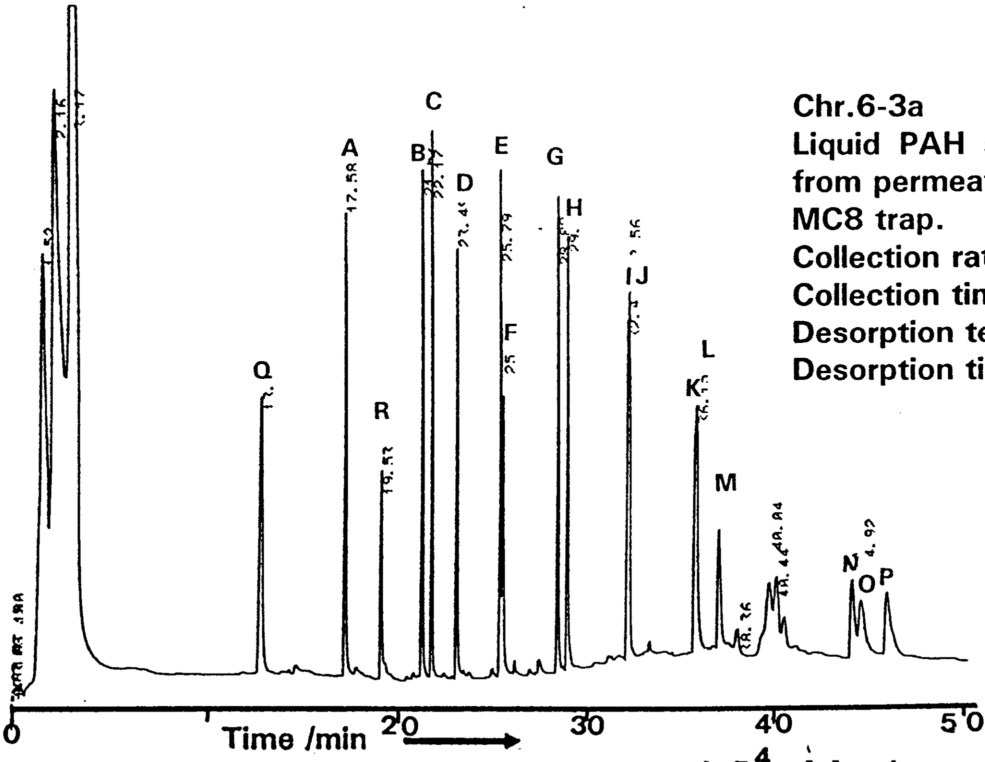
A: Toluene
B: 1,2,4 Trimethyl benzene
C: *α*-Methyl Styrene

D: Naphthalene
E: 2-Methylnaphthalene
F: 2,6-Dimethylnaphthalene



Chr.6-2
Mass Spectrum
Standards collected from
6 permeation tubes on MC8 trap.
Collection rate 5cm^3.min^{-1}.
Collection time 2 hours.
Desorption temperature 250°C.
Desorption time 6 minutes.

PAH Standard Collected on MC8 Trap



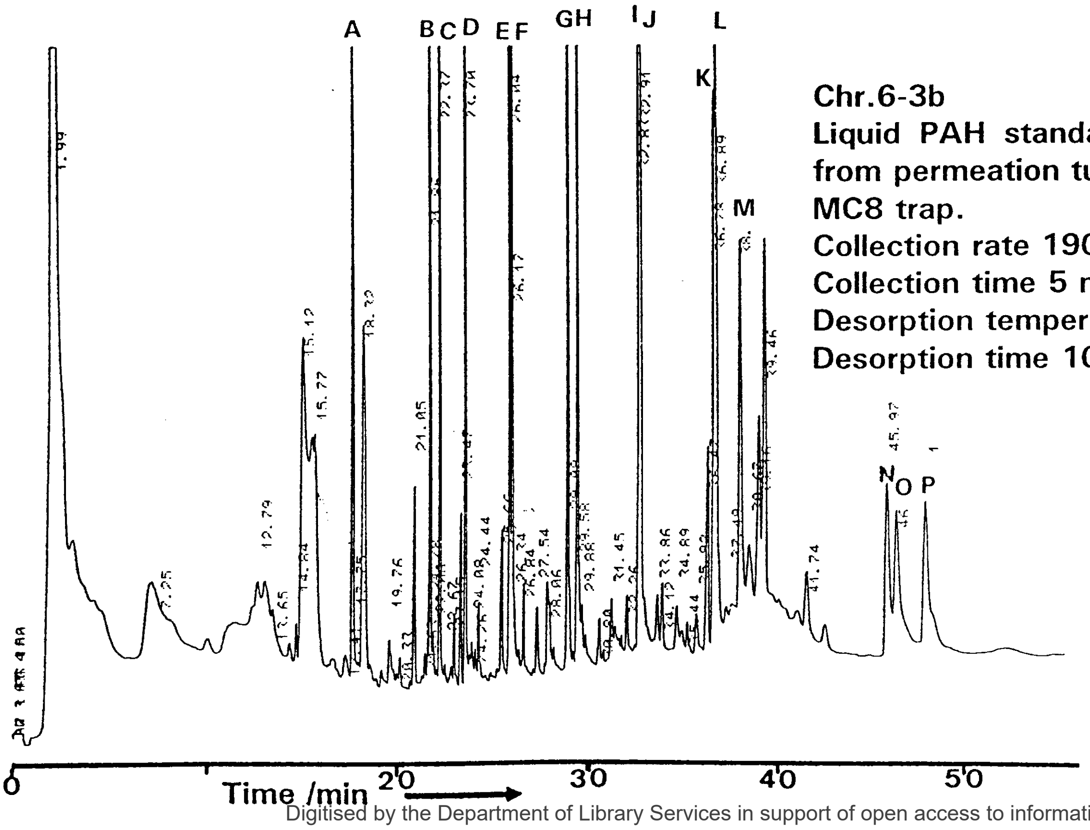
Chr.6-3a
Liquid PAH standard and standards from permeation tubes collected on MC8 trap.
Collection rate 5 $cm^3.min^{-1}$.
Collection time 15 minutes.
Desorption temperature 250°C.
Desorption time 10 minutes.

A: Naphthalene
B: Acenaphthylene
C: Acenaphthene
D: Fluorene
E: Phenanthrene
F: Anthracene
G: Flouranthene
H: Pyrene

Q: 1,2,4 Trimethyl benzene

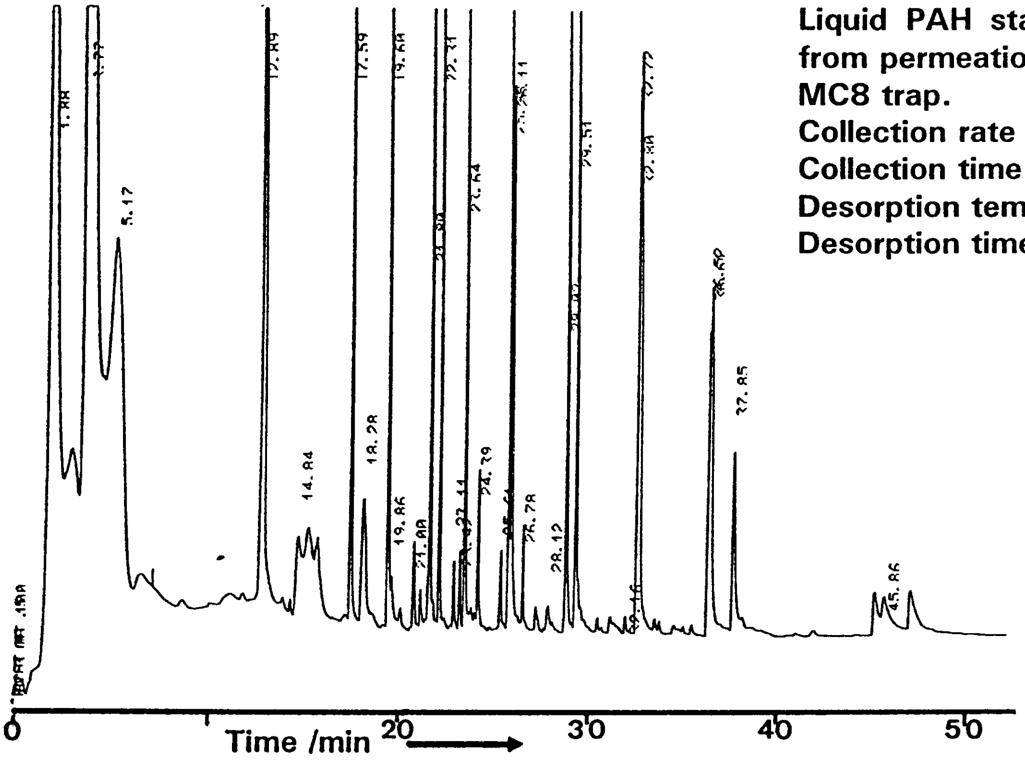
I: Benz[a]anthracene
J: Chrysene
K: Benzo[b]fluoranthene
L: Benzo[k]fluoranthene
M: Benzo[a]pyrene
N: Indeno[1,2,3-cd]pyrene
O: Dibenz[a,h]anthracene
P: Benzo[ghi]perylene

R: 2-Methylnaphthalene

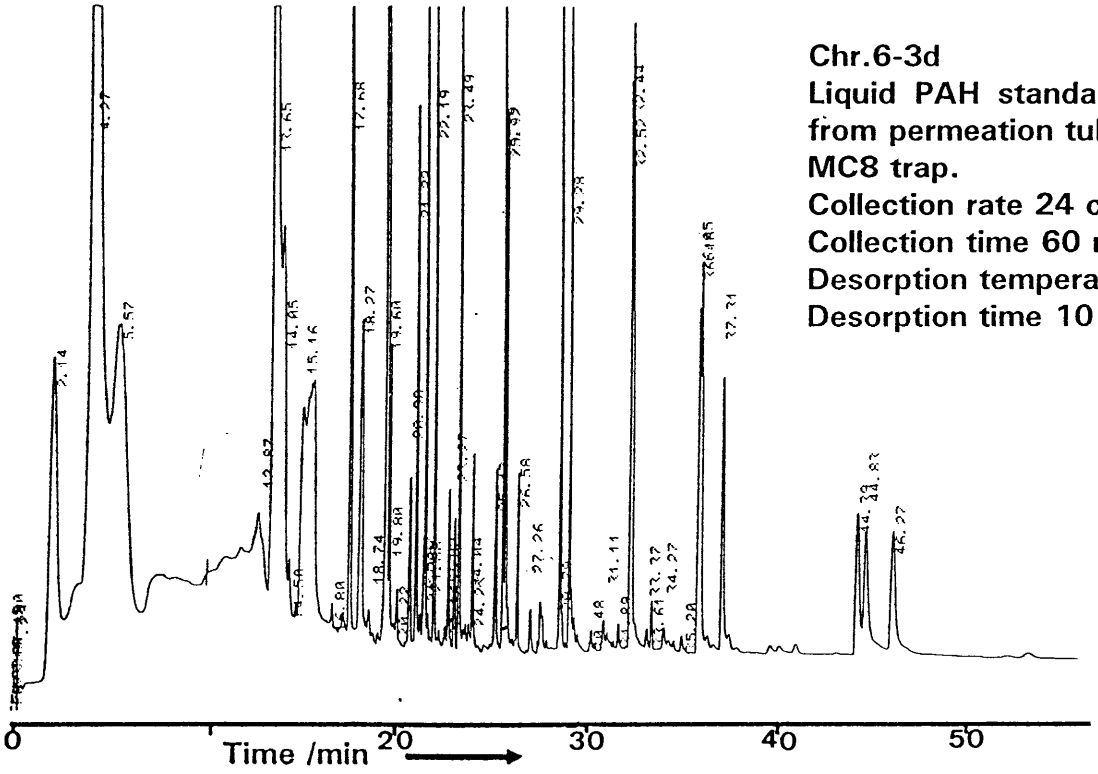


Chr.6-3b
Liquid PAH standard and standards from permeation tubes collected on MC8 trap.
Collection rate 190 $cm^3.min^{-1}$.
Collection time 5 minutes.
Desorption temperature 250°C.
Desorption time 10 minutes.

PAH Standard Collected on MC8 Trap

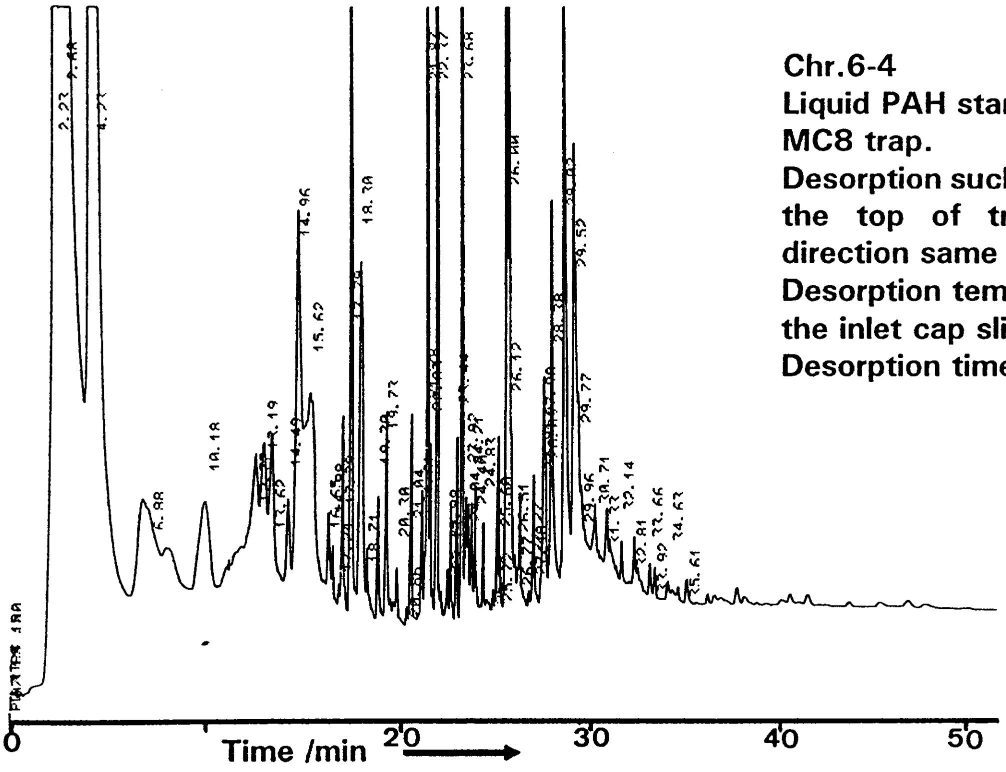


Chr.6-3c
Liquid PAH standard and standards from permeation tubes collected on MC8 trap.
Collection rate 24 cm^3.min^{-1}.
Collection time 15 minutes.
Desorption temperature 250°C.
Desorption time 10 minutes.

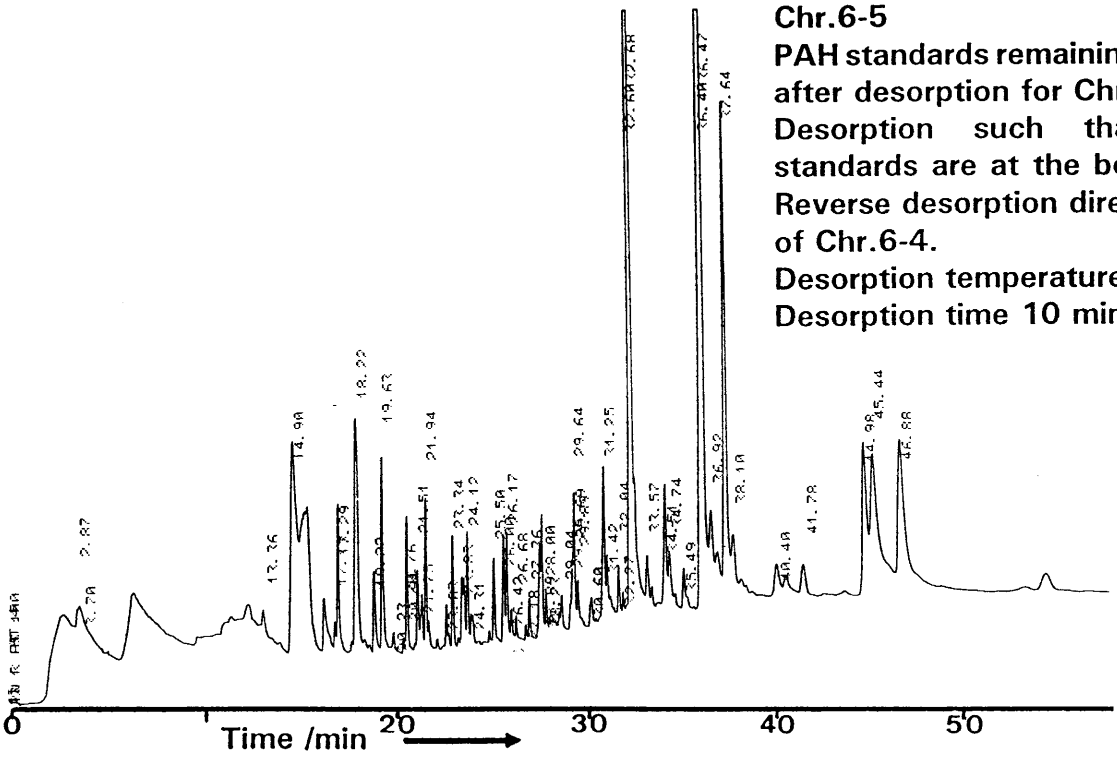


Chr.6-3d
Liquid PAH standard and standards from permeation tubes collected on MC8 trap.
Collection rate 24 cm^3.min^{-1}.
Collection time 60 minutes.
Desorption temperature 250°C.
Desorption time 10 minutes.

Incomplete Desorption due to Cold Inlet Cap

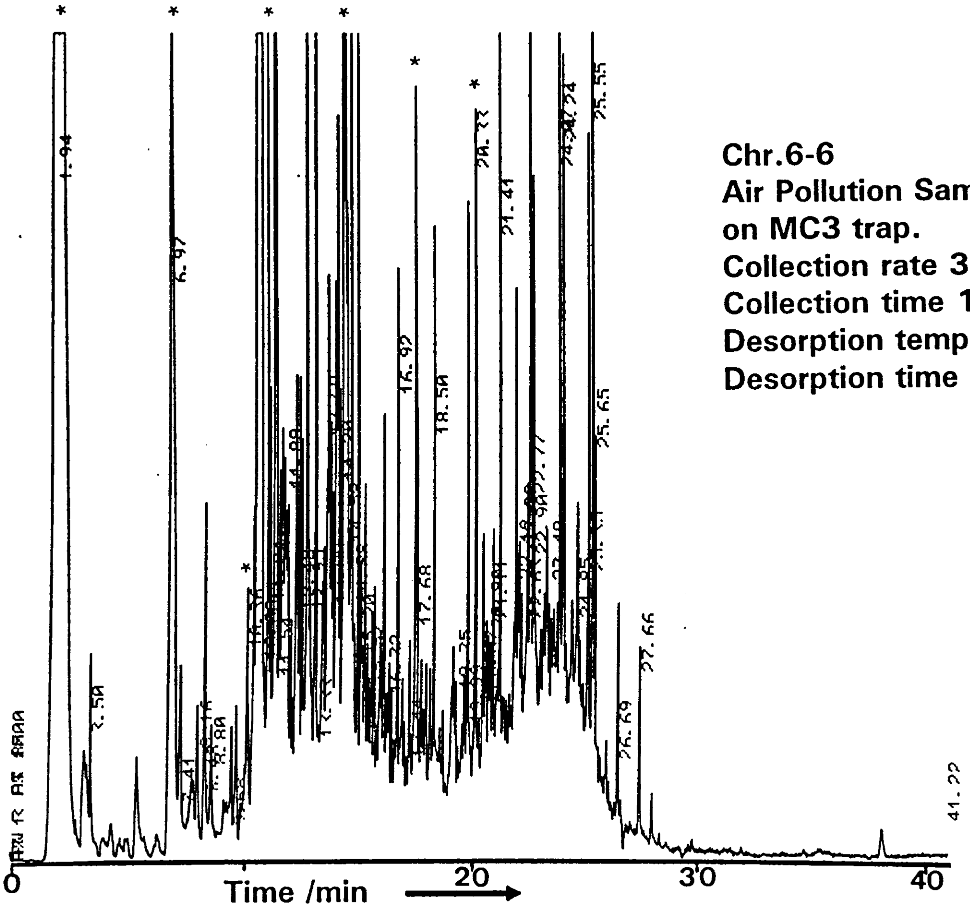


Chr.6-4
Liquid PAH standard collected on MC8 trap.
Desorption such that standards are at the top of trap, flow desorption direction same as adsorption.
Desorption temperature 250°C, with the inlet cap slightly cooler.
Desorption time 10 minutes.



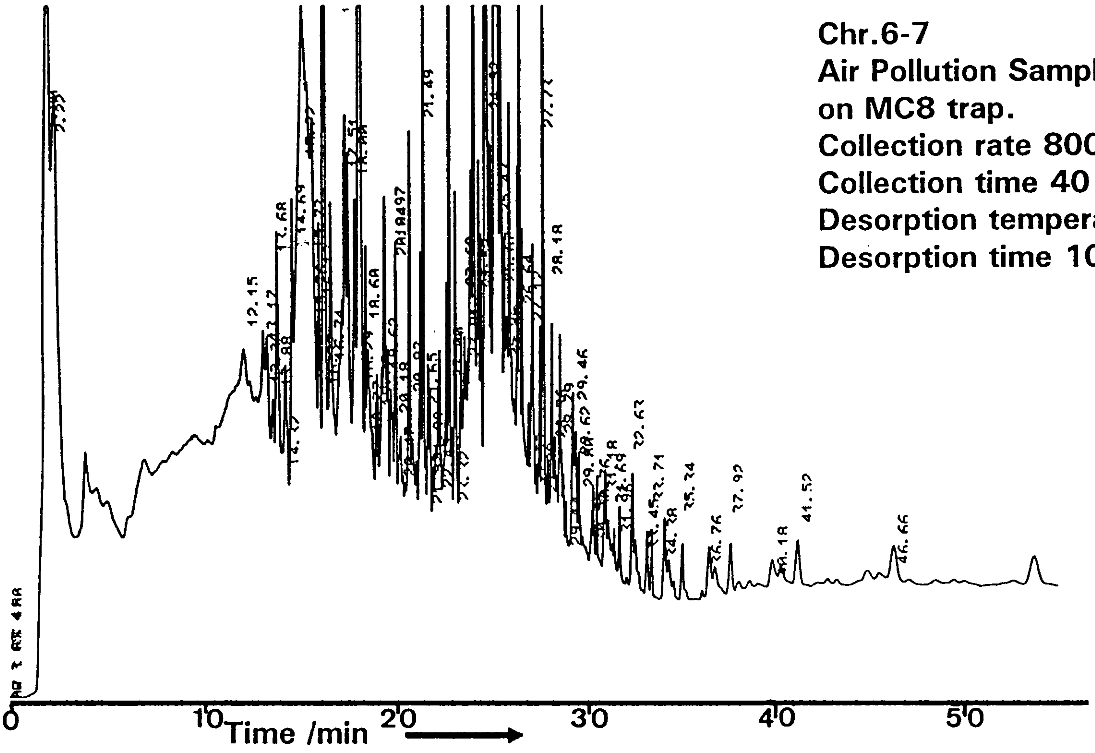
Chr.6-5
PAH standards remaining on MC8 trap after desorption for Chr.6-4.
Desorption such that remaining standards are at the bottom of trap.
Reverse desorption direction to that of Chr.6-4.
Desorption temperature 250°C.
Desorption time 10 minutes.

Air Pollution Sample Collected on MC3 Trap

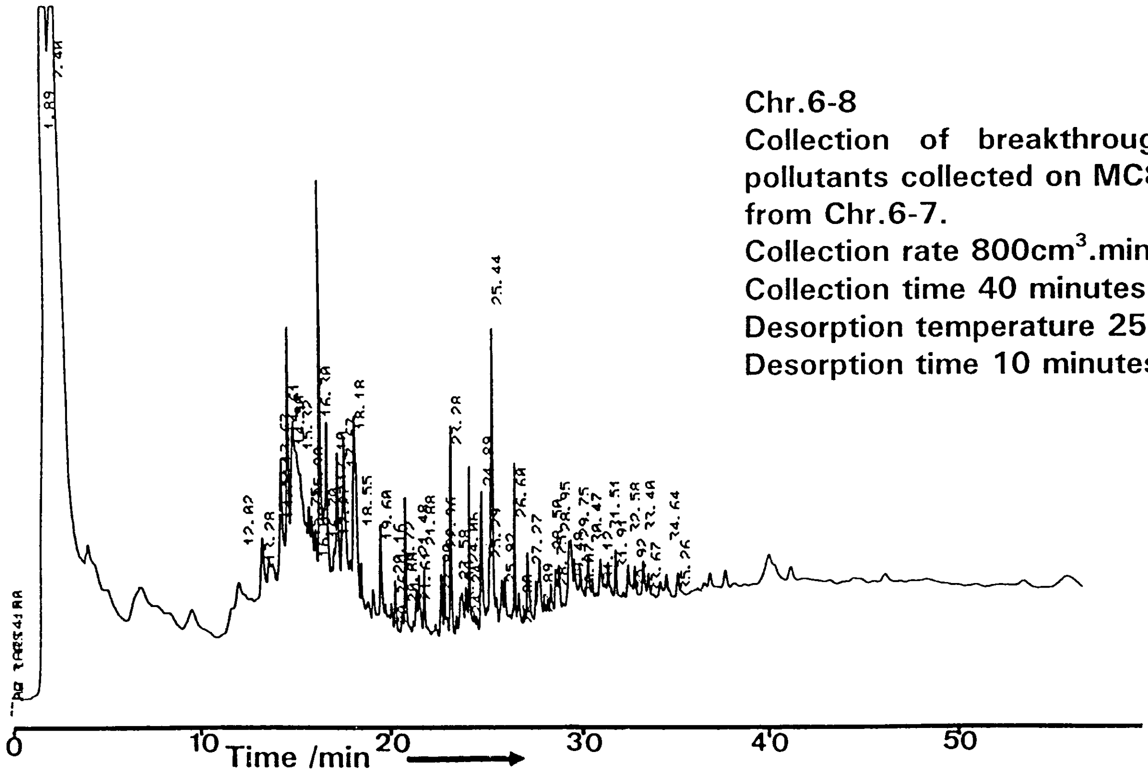


Chr.6-6
Air Pollution Sample collected on MC3 trap.
Collection rate 330cm^3.min^{-1}.
Collection time 1 hours.
Desorption temperature 220°C.
Desorption time 2 minutes.

Air Pollution Samples Collected on MC8 Trap



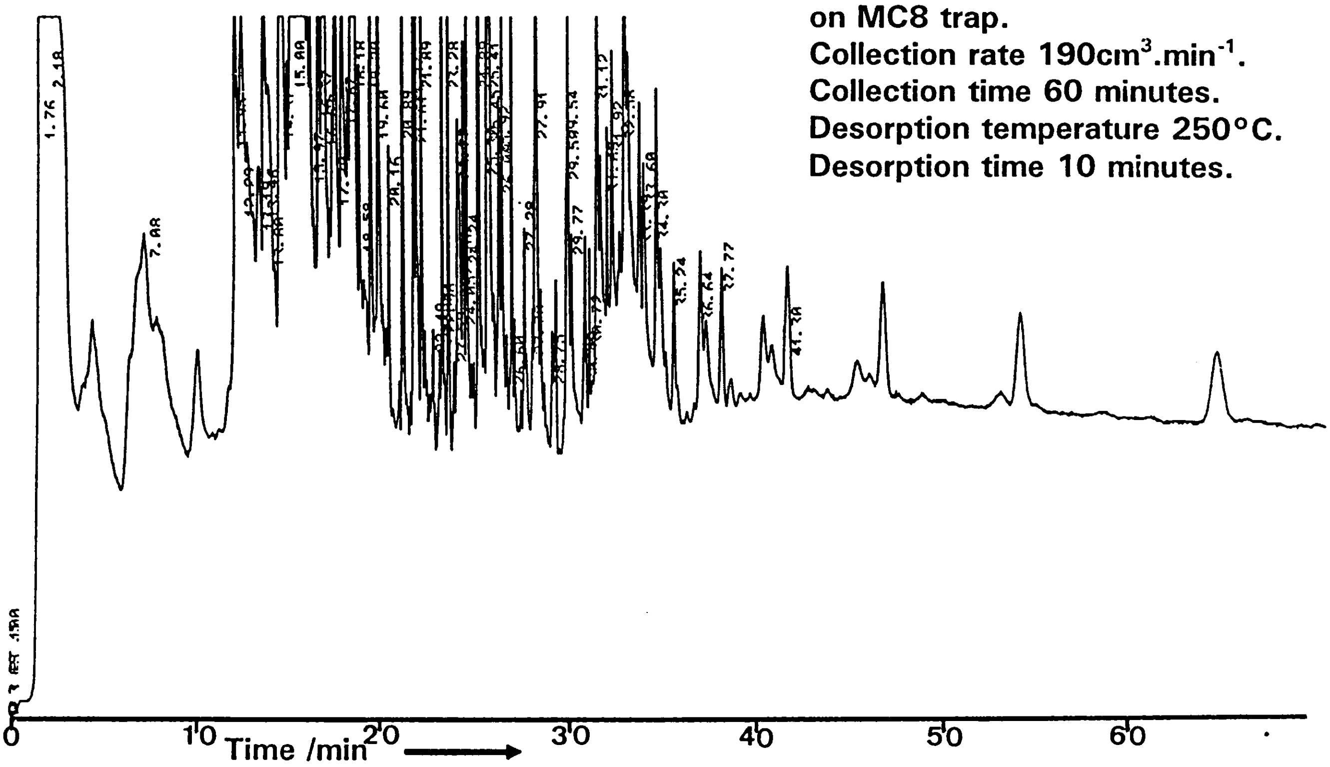
Chr.6-7
Air Pollution Sample collected on MC8 trap.
Collection rate 800cm^3.min^{-1}.
Collection time 40 minutes.
Desorption temperature 250°C.
Desorption time 10 minutes.



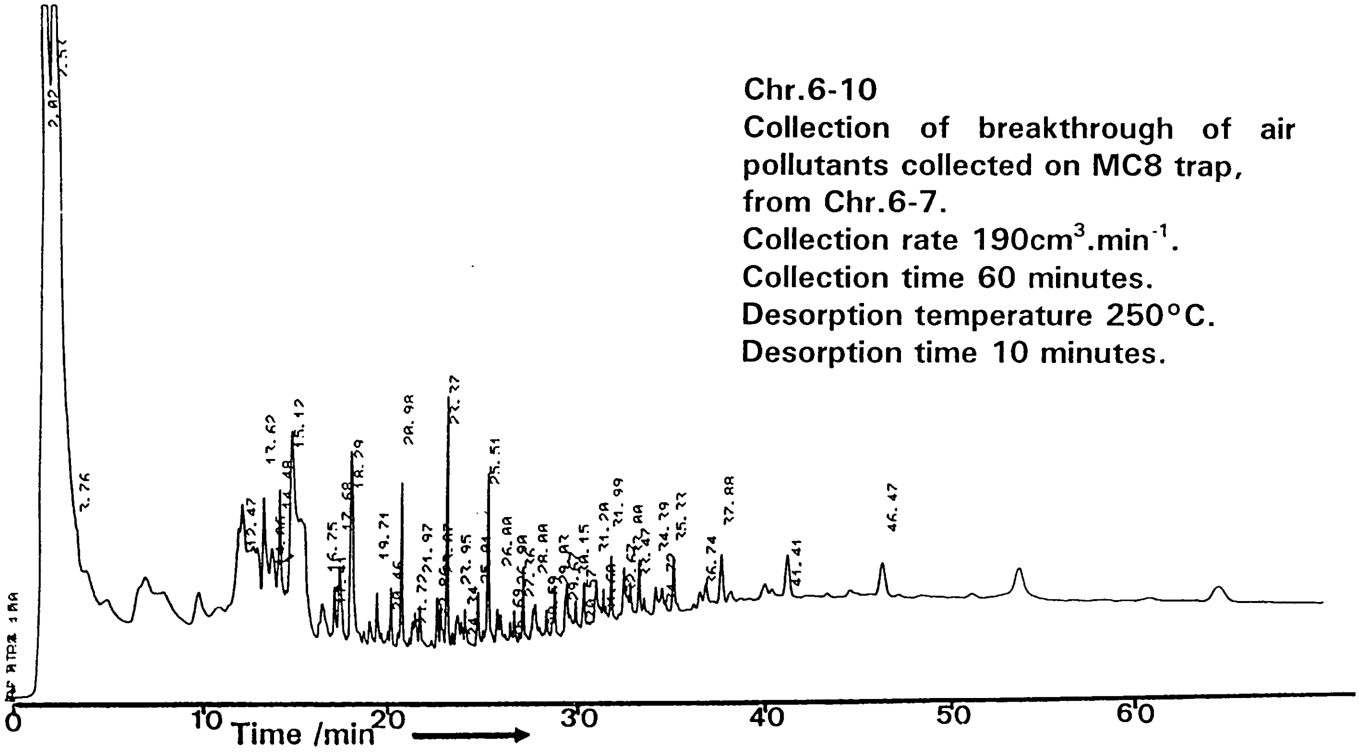
Chr.6-8
Collection of breakthrough of air pollutants collected on MC8 trap, from Chr.6-7.
Collection rate 800cm^3.min^{-1}.
Collection time 40 minutes.
Desorption temperature 250°C.
Desorption time 10 minutes.

Air Pollution Samples Collected on MC8 Trap

Chr.6-9
Air Pollution Sample collected on MC8 trap.
Collection rate 190cm^3.min^{-1}.
Collection time 60 minutes.
Desorption temperature 250°C.
Desorption time 10 minutes.



Chr.6-10
Collection of breakthrough of air pollutants collected on MC8 trap, from Chr.6-7.
Collection rate 190cm^3.min^{-1}.
Collection time 60 minutes.
Desorption temperature 250°C.
Desorption time 10 minutes.



Chr.3-14
Air Pollution Sample COS1/4
20μl, Attenuation 8 x 10^{-12}A.mv^{-1}