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# Continuous Water Monitoring System

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November 1990

Final Report for Period September 1989 through February 1990

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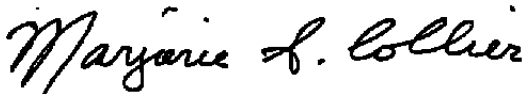
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## PREFACE

The work reported herein was conducted by EXTREL Corporation, 240 Alpha Drive, Pittsburgh, Pennsylvania 15238 for Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Base, TN, under Phase I of Small Business Innovation Research (SBIR) contract number F40600-89-C-0013, during the period September 1989 to February 1990. The Air Force Project Manager was Ms. Marjorie S. Collier. The principal investigator was Dr. Seksan Dheandhanoo of EXTREL Corporation. The reproducibles used in this report were supplied by the author.

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## INTRODUCTION

Contract No. F40600-89-C-0013, which was a Phase I contract under the Air Force Small Business Innovation Research program, was awarded to Extrel Corporation in September, 1989. The work undertaken was the design, prototype construction and testing of membrane interfaces (MI) which will be used in conjunction with quadrupole mass spectrometers (QMS) for continuous water monitoring.

Shortly after the Phase I work commenced, EXTREL personnel (Dr. Seksan Dheandhanoo and Dr. Stephen M. Penn) visited Arnold Air Force Base technical personnel (Marjorie Collier and Judy McLean) to discuss the details of the project. Ms. Collier and Ms. McLean described the water demands and the distribution system at AEDC. The discussions included compounds of interest, detection levels, response times and alarm capabilities. A list of organic compounds that are of special interest to Arnold AFB was also given to EXTREL personnel.

During the first three months of the project, the primary focus of the work was to design and construct the interfaces. Samples of permeable membranes were ordered from two vendors. We faced a few problems during the testing. One major problem was the existence of background gas in the vacuum chamber which housed the QMS. Since a detection limit in the low parts per billion (ppb) range is required, the signal from the background gas has a significant effect on the detection limit.

We were able to eliminate most of the problems and conduct the experimental work in the last three months of the project. The MI's were tested with aqueous solutions of the recommended organic compounds.

The results of the experiments lead us to conclude that the MI/QMS is capable of detecting most of the recommended compounds in water at levels as low as 15 ppb with a response time of less than 2 minutes. We plan to submit a Phase II SBIR proposal which involves construction of the instrument for optimization of these types of measurements.



## BACKGROUND

The permeation mechanism of gas or vapor through a membrane is basically simple. It was found that the flow rate of the permeating gas through a membrane depends on the membrane thickness, partial pressure difference across the membrane, surface area of the membrane and permeability.<sup>(1)</sup> The permeability is also an intrinsic function of the solubility and diffusion rate of the permeating gases and temperature of the membrane.

Several types of permeability-selective membranes, such as Teflon™, silicone rubber membranes and polyvinyl chloride have been used previously for the separation of gases and volatile compounds from liquid matrices. The pioneer work of Westover and co-workers<sup>(2)</sup> indicated that silicone-rubber membranes were superior to other types of membranes with respect to their permeability. Furthermore, silicone-rubber membranes are particularly suitable for measuring non-polar volatile compounds in aqueous solutions because they are almost impermeable to polar molecules, such as water. Previous experimental studies indicated the MI's capability of analyzing organic volatile compounds and dissolved gas in water.<sup>(3,4)</sup>

## INSTRUMENTATION

Two forms of permeable membranes are commercially available: tubing and sheet. Extrel designed two types of membrane interfaces to accommodate both forms of the membranes: 1) an interface for membrane tubing and 2) an interface for sheet membranes.

### Interface for Membrane Tubing

A schematic of this type of interface is shown in Fig. 1. This interface is quite simple and easy to assemble. The interface consists of Dow Corning Silastic™ tubing membrane, which is a silicone membrane. The membrane tubing was of 0.037" OD and 1.5" long. The wall thickness of the membrane tubing was 0.008". The membrane tubing was located inside an 1/8" stainless steel (SS) tube. The SS tube was wrapped with heating tape so that the temperature of the interface could be elevated.

Aqueous solution is introduced into one end of the interface and flows out at the other end, without prior preparation. If the solution contains some large particulates, a filter should be used to prevent clogging. Analytes that pass through the membrane will be transferred into the QMS via the SS tube. The temperature of the SS tubing was raised to about 80 °C to avoid the condensation of the analytes. The actual temperature of the membrane was not measured. However, the temperature of the membrane should be lower than that of SS tube due to the continuous flow of solutions. Increasing the temperature of the membrane results in higher diffusivities and decreases the response time of the membrane.<sup>(5)</sup>

### Interface for Sheet Membranes

An interface for sheet membranes was designed for use with the GE MEM 213™ membrane. This type of membrane is different from the silicone membrane and is not available in tubing form. Although the permeability of the MEM 213™ membrane is not as good as silicone-rubber membranes, it is stronger than the silicone membrane. The MEM-213™ membrane can also be used at higher temperatures. We planned to experiment with this type of the membrane only in cases where chemicals do not permeate the silicone-rubber membrane.

A diagram of the interface is shown in Fig. 2. The interface is composed of two identical stainless steel pieces. The sheet membrane is sandwiched between these two pieces. The seal between the top and the bottom pieces depends on the elasticity of the membrane itself. The temperature of the interface can be raised by a pair of heaters which are located in both the top and the bottom pieces.

Aqueous solution is introduced in the bottom piece. The analytes that permeate the membrane will be transmitted through circular channels, in the top piece, into the QMS. The operating temperature of this interface was ~ 80 °C.

This type of MI was used only in cases where the Silastic™ membrane tubing is not applicable. In this project, this type of MI was used only for ethylene glycol.

The MI interfaces were integrated to an Extrel QMS. The QMS control and data analysis were done by a 286 personal computer and a Teknivent data system. Aqueous solutions of recommended chemicals of various concentrations were used to test the MI/QMS instrument.

#### Quadrupole Mass Spectrometer (QMS) and Ionizer

An EXTREL QMS was used during the course of this experiment. The diameter of the quadrupole rods was 3/8". The QMS has the capability to analyze ions of mass as high as 2000 amu and can be controlled manually or operated by the computer. Manual control mode is very useful during the set up of the experiment. Once an optimal operational condition was obtained, the QMS was switched to computer controlled mode.

For reasons discussed in the next section, an electron impact ionization source was placed in front of the QMS. The analytes that entered the ionizer underwent electron impact ionization by 70 eV electrons. The electron impact ionization technique was chosen for generating analyte ions because of its simplicity. This ionization technique is suitable for process applications, such as continuous water monitoring. The energy of the electrons was set at 70 eV so that standard mass spectra can be used as a reference. A diagram of the QMS and the ionizer is shown in Fig. 3.

Ions that are selected by the QMS are detected by an analog channeltron multiplier which is mounted behind the QMS. The gain of the analog multiplier can be controlled by adjusting the multiplier high voltage. The analog signals from the multiplier are fed to the computer.

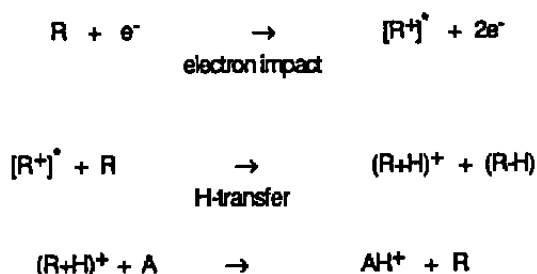
## EXPERIMENTAL

Comparison of Ionization Techniques

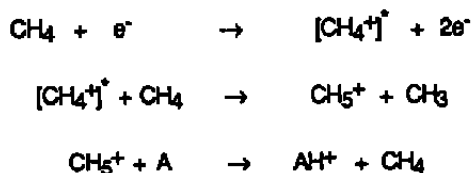
The purpose of this portion of work is to find the most suitable ionization technique for continuous water monitoring application. The technique should be simple, easy to operate and provide high sensitivity.

Two common ionization techniques, which were considered for this application, were electron impact ionization (EI) and chemical ionization (CI). The EI is actually simpler than the CI in term of operations.

CI is a softer ionization technique. The principle of CI can be described by the following reactions:



A reactant gas molecule R, such as CH<sub>4</sub>, is ionized by normal electron impact ionization. The excited molecular ion [R<sup>+</sup>]<sup>•</sup> then undergoes H-transfer reaction to form a protonated ions (R+H)<sup>+</sup>, such as CH<sub>5</sub><sup>+</sup>, and then the primary protonated ion (R+H)<sup>+</sup> reacts further with the analyte molecule, which results in protonated analyte ion AH<sup>+</sup>, see the following example:



In the CI technique, most of the analyte molecules form protonated molecular ions and generate very few fragment ions. Most analyte molecules have sufficient time for the H-transfer reaction with primary protonated ions. Therefore, CI is can be more sensitive than EI.

The comparison experiments were performed using an EXTREL GC/MS Instrument. The methane positive CI spectrum and the EI spectrum of 10 ng of benzene is shown in Figs. 4(a) and 4(b), respectively. The dominant ion in the CI spectrum is the ion of mass 79 which is protonated benzene. The dominant ion in the EI spectrum is an ion of mass 78 which is a molecular ion. The intensity of mass 79 in CI spectrum is 12917 and the intensity of mass 78 in EI spectrum is 21321.

This indicates that EI is more efficient than CI in the EXTREL source that was used in this experiment.

The same experiment was repeated for toluene. The CI and EI spectrum of toluene is shown in Figs. 5(a) and 5(b), respectively. The ion intensity of protonated toluene (mass 93 in the CI spectrum) is lower than that of mass 91 in the EI spectrum.

The negative methane CI technique was tested with chlorinated compounds, such as methylene chloride. Negative methane CI is not a true negative CI in this case. It is actually an electron capture technique used to form negative ions. The negative ions of the chlorinated compounds are mostly negative chlorine ions. Fig. 6(a) and 6(b) show the EI spectrum and negative ion spectrum of methylene chloride, respectively.

The results of this portion of the experiment shows that EI is more suitable for a water monitoring application than CI. Therefore, EI was chosen as the ionization technique for this application.

#### Sample Preparation

Studies of the sensitivity and response of the MI/QMS to volatile organic compounds in water require standard solutions of known concentrations. Many of these compounds did not dissolve well in water. In such cases, the chemicals were dissolved in a small amount of methanol and then diluted with distilled water to obtain stock solutions. The mass concentration of the stock solutions was 1 ng of the chemical in 1  $\mu$ l of distilled water, which corresponds to 1 part per million (ppm). For the same solution, mass concentration is usually higher than molar concentration. The difference in the value between mass concentration and molar concentration depends on the molecular weight of the chemical. For example, 1 ppm of mass concentration of benzene solution is equivalent to 0.23 ppm of molar concentration.

The names of chemicals which were used in this experiment are listed below:

1. Benzene
2. Carbon tetrachloride
3. Chlorobenzene
4. 1,3-Dichlorobenzene
5. 1,4-Dichlorobenzene
6. 1,2-Dichloroethane
7. 1,1-Dichloroethane
8. Ethylbenzene
9. Methylene Chloride
10. 1,1,2,2-Tetrachloroethane
11. Toluene
12. 1,1,1-Trichloroethane
13. Trichloroethene
14. Trichlorofluoromethane (Freon III)
15. Xylenes

16. Ethylene glycol
17. Oil

In order to obtain solutions of concentrations lower than 1 ppm, we diluted the stock solution with distilled water. Two dilution methods were used during the course of this experiment:

1. In the first method, standard solutions of lower concentrations were prepared by a 50% dilution of the next higher concentration. For example, we mixed equal amounts of the stock solution of 1 ppm and distilled water, which resulted in a 500 parts per billion (ppb) solution. Again, equal amounts of the 500 ppb solution and distilled water were mixed to obtain a 250 ppb solution.

We discovered later that this is not an accurate method for preparing standard solutions of low concentrations, especially for highly volatile compounds. Although this mixing technique is relatively easy and fast, the solutions were exposed to air and were transferred many times during the preparation. The loss of the chemicals due to evaporation was significant and caused an error in the concentrations of the solutions. We suspect that chemicals also adhered to the wall of glass containers.

2. The second method provided higher accuracy but it was time consuming. To minimize the evaporation of the chemicals, all the standard solutions of lower concentrations were prepared directly from the stock solution of 1 ppm. For example, a 25 ppb solution was prepared by adding 5 ml of 1 ppm stock solution to 195 ml of distilled water. This technique was used to make solutions of 15, 25, 50, 100, 250, 500, and 1000 ppb for all of the chemicals.

In addition, all the standard solution bottles were silanized, in order to prevent the adherence of chemicals to the walls of the glass bottles.

### Sample Introduction

Aqueous solutions were introduced into the MI by means of a syphoning technique. It was discovered from previous experiments that the response of the membrane depended on the sample flow rate.<sup>(6)</sup> The optimum flow rate for volatile organic compounds was between 0.3-0.5 ml/min. In this experiment the flow rate of the sample was controlled by adjusting the height of the sample reservoir. A flow rate of 0.5 ml/min was used throughout the experiment.

### Data Analysis

An Everex 286/12 PC and a Teknivent data system, model Vector/One, were used to control the QMS and analyze the data.

Once analytes entered the ionizer, they were ionized by 70 eV electrons. The mass spectra that were generated from each chemical can be found in standard references. Each chemical produced several fragment ions of various intensities. To analyze any chemical, one can monitor all the fragment ions simultaneously and compare the ion spectrum with the reference

spectrum. However, this is not practical for process applications. A better technique would be to monitor only one or two selected fragment ions. The criteria for selections are as follows:

1. Ion intensity. We prefer the fragment ions that have high intensities. High ion intensity will improve the signal to noise ratio which results in lower detection limit.
2. Background intensity. Low background intensity will increase the sensitivity of the instrument. For example, the fragment ion of mass 32 amu is not desirable because ions of mass 32 are also  $O_2^+$ . There are always some oxygen molecules present in the vacuum system even at the pressure as low as  $1 \times 10^{-7}$  torr. Therefore, background ion intensity at mass 32 is always high.

The computer was set to monitor ions in the mass range of interest. Ion intensities of all the ions in that mass range are recorded as a function of time and stored in the memory. The quantities of the analytes were determined by observing the ion intensities of the selected ions.

The background ion intensity was established by introducing distilled water into the interface and monitoring that ion for about 10 minutes or until the ion signal was stable.

For example, the intensity of benzene ions (78 amu) as a function of time is shown in Fig. 7a. Distilled water was introduced into the MI for 12 minutes and then replaced by 25 ppb aqueous solution of benzene. The solution flowed through the MI for 8 minutes, after which it was replaced with distilled water. Measurements of background intensity were taken before each introduction of aqueous solutions of a different concentration.

In this experiment, response time is defined as the time between the introduction of the solution and the time when the ion signal reaches the maximum level. As shown in Fig. 7a, a 100 ppb solution of benzene was introduced into the MI at the 43<sup>rd</sup> minute, the ion signal of mass 78 started to increase immediately and reached the maximum level at the 45<sup>th</sup> minute. Therefore, the response time for benzene is about two minutes when the temperature of the SS tube is about 80 °C. Changes in temperature should result in changes in response time.

The entire ion spectrum in the mass range of interest was stored in the computer. For example, the ion spectrum between masses 45 and 90 amu during the 40<sup>th</sup> minute of the experiment is shown in Fig. 7b. At this time only distilled water was introduced into the interface. Therefore, this is a background spectrum. Fig. 7c shows the spectrum of the same mass range during the 50<sup>th</sup> min. At this time the distilled water was replaced by an aqueous solution of benzene. Therefore, this spectrum is composed of the benzene spectrum and the background spectrum. By doing background subtraction of the mass spectrum in Fig. 7c, the benzene mass spectrum can be obtained (see Fig. 8). The ion spectrum is very useful in the identification of chemical species in the solution.

In order to show the response of the MI/QMS instrument to the different concentrations of the chemicals, the ion intensities in arbitrary units were plotted as a function of concentration. The response of the MI to different chemicals depends on the nature of the chemicals. In favorable cases such as benzene, the ion intensity of ions of mass 78 is very high even at 25 ppb solution. Therefore, the gain of the multiplier was reduced so that the ion intensity at 1,000 ppb would not exceed the dynamic range of the computer. In cases where the response was poor, such as

carbon tetrachloride, the gain of the multiplier was increased so that we could analyze the chemicals at very low concentrations.

The QMS that was used in this experiment showed a slight mass discrimination between ions of different masses. For example, the concentrations of methylene chloride were determined by monitoring ions of mass 49, and trichloroethene was determined by monitoring ions of mass 130. The resolution of the QMS was reduced when the ions of mass 130 were monitored. This problem can be significantly alleviated if a larger size quadrupole mass spectrometer (with a diameter of the quadrupole rod larger than 3/8") is used. A quadrupole of 3/4" is proposed for the phase II instrument.

The goals of this experiment also include the study of the response of the MI/QMS to the chemicals of concentrations between 15 and 1000 ppb and to determine the detection limit of the instrument. Therefore, the multiplier gain and the resolution of the QMS were optimized for each compound or for a certain group of compounds. Due to differences in operating conditions, the ion intensities are expressed in the arbitrary units.



## RESULTS

The MI/QMS was tested by using two types of aqueous solutions: 1) solutions composed of one chemical and 2) mixtures of two or three compounds in the same solution. To avoid difficulties in analyzing the data, the dominant fragment ions of the chemicals in the mixtures do not have the same mass. The mixture solutions were used to study the interference effects of one compound on other compounds in the solutions.

### Trichloroethene

The molecular weight of trichloroethene is 130 amu. According to the standard mass spectrum, ions of mass 95 and 130 have almost the same intensities. The ion of mass 130 amu was selected for monitoring this chemical because the background ion intensity at mass 130 was much lower than at mass 95.

Standard solutions at concentrations of 31, 62, 125, 250, 500 and 1000 ppb were prepared by preparation method #1. Fig. 9 shows the ion intensity as a function of solution concentration. The results were obtained from two consecutive runs. The response is not linear. The ion intensities from both runs were reproducible, except at 1000 ppb. The difference between the 2 sets of experiments is that the 1000 ppb solution in run #1 came directly from the stock solution immediately before introducing it into the MI. In run #2, the 1000 ppb solution was transferred into a glass container like other solutions of lower concentrations. The glass container was not silanized in this case. The ion intensity at 1000 ppb in run #1 was 9000 counts higher than in run #2.

This effect suggested that the loss of chemicals due to evaporation during preparation and due to adherence to the glass container is significant. The change in concentration is the most likely cause of the non-linearity, not the response of the membrane.

The same effect was also observed in dichloroethane experiments. Standard solutions of both trichloroethene and dichloroethane were prepared by method 1.

Another set of standard solutions was prepared by method #2. The results obtained from the latter set of solutions shows a linear response of the MI to this chemical, (see Fig. 10).

### 1.1-Dichloroethane

The molecular ion of this compound mass can not generated in significant amount by electron impact ionization with 70-eV electrons. The dominant fragment ion is the ion of mass 63. Fig. 7 shows the results obtained from the set of solutions which were prepared by method #1. The reason for non-linearity in the response of the membrane was explained above.

Once we discovered that dilution method #1 caused a significant error in the standard solutions, another set of standard solutions was prepared by using dilution method #2. The concentration of the solutions varied from 15 to 1000 ppb. The experimental results, which were obtained from the latter set of stock solutions, showed the linear response of MI/QMS Instrument

to this chemical (see Fig. 11). The response of the MI/QMS to various concentrations of this chemical is shown in Fig. 12.

After we realized that dilution method No. 1 was not suitable for preparation of the solutions of volatile compounds, dilution method No. 2 was chosen for preparing all of the solutions used in this experiment.

#### 1,1,1-Trichloroethane

Ions of mass 97 and 99 were monitored for this chemical. Although ions of mass 97 have a higher intensity, the background at mass 97 is much higher than at mass 99. Fig. 13 shows the intensities of ions of mass 99 at the concentrations between 25 ppb to 1 ppm. The plot of ion intensity as a function of concentration is shown in Fig. 14.

#### Carbon tetrachloride

The dominant fragment ions of carbon tetrachloride are ions of mass 117 amu. Ions of mass 117 amu were monitored as a function of the concentration of this compound in aqueous solutions. The MI responded linearly to this chemical (see Fig. 14).

#### Methylene Chloride

Determination of this chemical in aqueous solutions is done by monitoring ions of mass 49 and 84. The response of the membrane to six concentrations of methylene chloride is shown in Fig. 15. The concentration of methylene chloride in water varied from 25 ppb to 1 ppm. The linear response of the MI is shown in Fig. 16a. Due to the strong response to this compound, the detection limit can be expected to be in the range of ten ppb.

#### Benzene

The molecular ion of mass 78 was observed as a function of concentration from 25 ppb to 1 ppm. The MI responded linearly to benzene (see Fig. 16a). Due to the high signal to noise ratio at 25 ppb, the detection limit of benzene can be expected to be lower than 10 ppb.

#### Methylene Chloride and Benzene

A set of mixture solutions of methylene chloride and benzene of the concentrations between 15 ppb to 500 ppb were prepared and were introduced into the MI. The response of the MI/QMS instrument to the mixtures are similar to the single solution for both chemicals. The linear response of the instrument to these chemicals is shown in Fig. 16b. This suggests that the interference from the existence of other chemicals in the solution is nil or insignificant. However, comparing the response lines in Figs. 16a and 16b, there are slight changes in the slopes of the lines. The standard solutions of the mixtures were freshly prepared. As mentioned earlier, slight errors in sample preparation can cause a significant change in ion intensities. One should realize that these chemicals are highly volatile and we are dealing with very low concentrations of the chemicals in water. Therefore, a slight error in the concentrations of the mixture will contribute to a noticeable change in the ion intensities.

## Xylenes

Trace concentrations of xylenes in water were determined by observing the ions of mass 91 and mass 106. The lowest concentration of the solution was 25 ppb. The MI responds strongly to xylenes, therefore, we expect the detection limit to be lower than 25 ppb. Fig. 17 shows the linear response of the MI to xylenes at various concentrations.

## 1,2-Dichloroethane, Toluene and 1,4-Dichlorobenzene

Mixtures of 1,2-dichloroethane, toluene and 1,4-dichlorobenzene of various concentrations from 15 ppb to 200 ppb were used in this experiment. Trace concentrations of 1,2 dichloroethane, toluene and 1,4-dichlorobenzene in the mixtures were determined by monitoring ions of mass 62, 91 and 146, respectively. Plots of the ion intensities versus concentrations are shown in Fig. 18.

## 1,1,2,2-Tetrachloroethane and Ethylbenzene

Mixtures of 1,1,2,2-tetrachloroethane and ethylbenzene were analyzed by monitoring ions of mass 83 and 91, respectively. The MI responded linearly to both chemicals, as shown in Fig. 19. The lowest concentration of standard solution was 15 ppb.

## Chlorobenzene and 1,3-Dichlorobenzene

Mixtures of chlorobenzene and 1,3-dichlorobenzene of concentrations of 15, 25, 50, 100, 250 and 500 ppb were used in the experiment. Ions of mass 112 and 146 were used to identify chlorobenzene and 1,3-dichlorobenzene, respectively. A plot of ion intensities as a function of the concentrations of both chemicals is shown in Fig. 20.

## Trichlorofluoromethane (Freon III)

We detected Freon III in water by monitoring the ions of mass 101 which are the dominant fragment ions of this chemical. Because Freon III is a gas, we purchased a stock solution containing 200 ppb in water. Fig. 21 shows linear response of the membrane to Freon III from 15 to 200 ppb.

## Ethylene Glycol

The Silastic™ membrane tubing responded poorly to ethylene glycol. Fig. 22 shows the response of the membrane to 10 parts per million (ppm) of ethylene glycol. This chemical is a somewhat polar molecule. Therefore, the degree of permeability of this chemical is very low. Its low volatility may also contribute to the poor response.

We also replaced the Silastic membrane with the GE MEM-213™ membrane. The results of the experiment showed that ethylene glycol did not permeate the membrane. At present, we have not found a most suitable membrane for ethylene glycol. However, Dow Corning membrane can be used to detect ethylene glycol at a few ppm range.

## Oil

Two types of oil were sent to us by Arnold AFB: 7808 oil and Texaco Cappella WF68. Neither oil dissolves in water and it was therefore not possible to prepare standard solutions of known concentrations. Instead, emulsions were prepared by mixing 3 ml of oil in 50 ml of water, and stirring produced small oil droplets in the emulsions. The oil emulsions were then introduced into the MI.

The mass spectra of the two oils permeating the membrane are shown in Figs. 23 (a) and 23 (b). It should be noted that oils in general are mixtures of hundreds to thousands of hydrocarbon compounds. The interesting feature of the spectra of these oils is that there are relatively few large mass peaks and that the large peak spectra are different, reflecting the fact that the two oils are different mixtures of hydrocarbons. It is seen that the ion at 55 amu ( $C_4H_9^+$ ) and ions at increments of 14 amu are present in both spectra (as is generally true in hydrocarbon oils). Of particular interest, however, is the presence of an ion at 55 amu in the 7808 oil and at 69 amu in the Texaco Capella WF 68 oil, neither of which is a major ion in the spectrum of the other, and which can be used as characteristic ions for single-ion monitoring. Of particular significance, neither of these ion masses coincide with the masses used in the measurements of the volatile organic compounds which were on the list of contaminants given to us by Arnold AF Base and which are of interest to the EPA. This implies that single-ion monitoring may be capable of concurrently monitoring for both oils and the volatile organics. (Of course, after an alarm sounds in single-ion monitoring, one would probably always want to take full mass spectra in order to positively confirm the contaminant material's identity, which in many cases could identify the location of the spill within a given facility.)

The experimental method employed in these exploratory experiments, as noted above, was to stir the oil to produce small emulsion droplets and then introduce the emulsion into the MI. Figs. 24 and 25 shown the time response of the instrument. The abrupt time dependence and the large size of the signals (the amplitude in Fig. 25 actually saturated the data system) suggests that the compounds permeating the membrane came from a single large droplet.

Because we received the oil samples late in the project, there was neither sufficient time nor funds to investigate better ways to emulsify the oils in water. We believe, however, that emulsions with sufficiently small droplet size can be made, either through magnetic or ultrasonic emulsification methods, that the droplets would present an effectively continuous source of exposure of the membrane surface to the oil droplets and allow quantitative determination of the MI/QMS technique for oil in water, in a manner analogous to quantitation of the volatile organics.

## CONCLUSIONS

The main concerns of these experiments were the sensitivity, response time and memory effects of the MI/QMS instrument.

From the ionization comparison studies, we believe that EI technique is more suitable for the continuous water monitoring, due to its simplicity and the fact that EI is also more sensitive than CI for the chemicals that we are interested in. Therefore, the EI technique was selected as a means of ionization in this experiment.

The results of the experiments show that the detection limit of a simple MI/QMS to several volatile organic compounds can be lower than 20 ppb with a response time of a few minutes. The QMS that was used throughout the experiment was EXTREL's quadrupole which consists of four 3/8" OD rods. The sensitivity of the MI/QMS can be increased by 2-4 times by replacing the 3/8" OD rods with 3/4" OD rods. This means using a bigger quadrupole would result in higher overall sensitivity. Use of a membrane arrangement with a greater surface area should improve sensitivity even further.

The MI/QMS responded linearly to all the chemicals used in this experiment. The variation in the slope of the response curve for each compound is caused by the differences in permeability of the chemicals.

The response time and memory effects depend on the nature of the chemicals. According to the experimental results (see Fig. 26), the response time of the MI to volatile organic compounds is less than 2 minutes, at ~80 °C, in all cases except 1,3-dichlorobenzene. Response time and decay time of most of the chemicals were approximately equal. In most cases, the memory effects are not a serious problem.

It is important to realize that this instrument, like other process mass spectrometers, provides a means of real time analysis of liquid samples, provided that all the chemicals in the liquid matrix are known. Once the chemicals in the matrices are identified, a unique fragment ion of each compound of interest will be chosen as a monitoring ion.

If there are more than two chemicals in a matrix that provide the same fragment ions, this can cause problems in the determination of the quantities of the chemicals. For example, considering a mixture of toluene and o-xylenes, the fragment ions of both chemicals and their intensities are listed in Table 1. The major fragment ion of both chemicals is an ion of mass 91. The second most dominant ions of o-xylene and toluene are ions of mass 106 and 92, respectively. Since toluene does not produce fragment ions of mass 106, these ions are unique for o-xylenes and will be chosen for monitoring xylenes.

The second most dominant ions of toluene are ions of mass 92 whose intensity is 62% with respect to the major dominant ion of mass 91, (see Table 1). However, there is some contribution of ions of mass 92 from o-xylenes. The intensity of ions of mass 92 from o-xylene is 7% of the major dominant ions of xylenes, which are ions of mass 91. The second most dominant

TABLE 1 Eight peak Spectra of o-xylene and toluene.

| COMPOUND NAME | MW  | MASS TO CHARGE RATIOS |             |             |            |            |           |           |           |
|---------------|-----|-----------------------|-------------|-------------|------------|------------|-----------|-----------|-----------|
|               |     | 91                    | 106         | 105         | 77         | 51         | 92        | 39        | 79        |
| O-xylene      | 106 | 91<br>[100]           | 106<br>[58] | 105<br>[27] | 77<br>[11] | 51<br>[10] | 92<br>[8] | 39<br>[7] | 79<br>[7] |
| Toluene       | 92  | 91<br>[100]           | 92<br>[68]  | 65<br>[12]  | 39<br>[9]  | 51<br>[6]  | 63<br>[6] | 93<br>[5] | 45<br>[4] |

Note: [X] = ion intensity, MW = molecular weight

ions of xylenes are ions of mass 106 which are about 60% of ion of mass 91. To determine the concentration of toluene in the matrix, ions of mass 92 will be monitored. Due to small contribution of ions of mass 92 from xylenes, some data manipulation is required. This is a problem that is routinely encountered in process mass spectrometry and can be solved by simple calculation. The calculation procedures will be handle by a computer. In this case, we need to calculate the intensity of ions of mass 92 which come from xylenes. According to the Table 1<sup>(7)</sup>,

$$I_{106}(X) = I_{91}(X) \times 0.6$$

$$I_{92}(X) = I_{91}(X) \times 0.07$$

where  $I_{106}(X)$  and  $I_{92}(X)$  are intensities of ions of mass 106 and 92 from xylenes, respectively.

Therefore, 
$$\frac{I_{106}(X)}{I_{92}(X)} = \frac{0.6}{0.07}$$

$$I_{92}(X) = I_{106}(X) \times \frac{0.07}{0.6} = I_{106}(X) \times 0.116$$

Since  $I_{106}(X)$  is a value measured by using a mass spectrometer, the  $I_{92}(X)$  can be evaluated from the above equation. The concentration of toluene in the matrix can then be determined by subtracting the calculated value of  $I_{92}(X)$  from the total measured intensity of ion of mass 92,  $I_{92}(\text{TOTAL})$ . For instance, the total intensity of ions of mass 106,  $I_{106}(\text{TOTAL})$  is 100 count and the total intensity of ions of mass 92,  $I_{92}(\text{TOTAL})$  is 50 counts. Since the only chemical that generates ions of mass 106 are xylenes,

$$I_{106}(\text{TOTAL}) = I_{106}(X) = 100 \text{ counts}$$

$$I_{92}(X) = I_{106}(X) \times 0.116 = 100 \times 0.116 = 11.6 \text{ counts}$$

The intensity of the ions of mass 92 from toluene,  $I_{92}(T)$ , can be expressed as:

$$I_{92}(T) = I_{92}(\text{TOTAL}) - I_{92}(X) = 50 - 11.6 = 38.4 \text{ counts/s}$$

Using this calculation, one can extract the needed information from the mass spectrometry data. If there are more than two compounds that provide the same fragment ions, the simple calculation becomes lengthy. This type of calculation can be easily handled by a computer, so, we do not foresee any problem with the calculation.

If two chemicals have the same ion fragment pattern, a mass spectrometer can not distinguish these compounds. This situation occurs when the matrix consists of two isomers such as 1,3 dichlorobenzene and 1,4 dichlorobenzene .

The advantages of the membrane interface technique are its simplicity, fast response time and low detection limit. Water samples from several sample locations can be analyzed simultaneously. The water samples can be introduced directly to the MI/QMS without prior preparation. The MI/QMS instrument is very rugged and needs only minimum maintenance. Only one tubing membrane interface was used throughout the course of this project.

It is clear that, based on the Phase I experimental results, a fully automated MI/QMS instrument can be built right now for Arnold Air Force Base to operate on the non-polar compounds of interest at the 15 ppb level and a 2 minute response time. The only two compounds in which the detection limit is higher than expected are ethylene glycol and oil compounds. The instrument is able to detect ethylene glycol in the low ppm level. As stated earlier, oil forms emulsion in water rather than solution; therefore it is difficult to determine the detection limit for oil compounds. We will however, be able to detect oil with this instrument.

Due to the low volatility and polarity nature of ethylene glycol, the detection limit of this chemical was in the low ppm range. We believe that the detection limit of this chemical at the level of a few ppm can be achieved if a larger QMS is used. The quantity of this chemical is determined by monitoring ions of mass 31, which is only one mass unit less than molecular ion of oxygen of mass 32 amu. A minute amount of oxygen is always present in the vacuum chamber as a background gas. Therefore, it is usually difficult to monitor ions of low intensity, such as mass 31, when it is present next to a intensity peak of mass 32 which comes from background oxygen. We may be able to separate the oxygen background ions from the ethylene glycol by using a supersonic molecular beam (SMB) technique. Therefore, if the SMB technique is applicable, it may be possible to reduce the detection limit of ethylene glycol to a ppb level.

## RECOMMENDATIONS

During the course of this project, we have learned that there are several features that can be incorporated to the instrument to improve the response time and the sensitivity. We suggest that these modifications should be included in the Phase II of this SBIR project. Some of these modifications are:

1) Replacing the analog multiplier with a counting multiplier. The counting multiplier operates at a higher gain and is more stable than the analog multiplier. An analog/counting multiplier should also be considered for this instrument. This type of multiplier can be operated in either the analog or the counting mode. Using the counting mode for multiplier operation will increase the overall sensitivity of the instrument.

2) Operating the MI at the optimum temperature. In order to optimize the operating temperature, the effects of the membrane temperature on the response time and sensitivity should be investigated systematically.

3) Using a quadrupole mass spectrometer with larger diameter rods would definitely increase the ion signal.

4) The use of the "hyperthermal supersonic molecular beam" (HSMB) technique would reduce the signal from the background gases and result in higher sensitivity. This technique is based on the co-expansion of a supersonic beam of the analyte molecule and carrier gas such as hydrogen or helium. As a result of supersonic expansion, the kinetic energy of the analyte molecules is higher than thermal energy. The kinetic energy of the analyte molecules can be as high as several electron volts (eV) depending on their molecular weight. In contrast, the background gas molecules have thermal energy (~0.1 eV). Due to the difference in their kinetic energies, background ions can be separated from analyte ions by adjusting the retarding potential at an exit lens of the ionizer. The retarding potential will be set high enough to stop the background ions but not enough to prevent the analyte ions from entering the QMS.

5) Due to the fact that we received oil sample from the Arnold Air Force Base at the end of the project, we were not able to study oil extensively. Furthermore, we have had some difficulty in preparing standard mixture of oil in water. Because oil is a mixture of many hydrocarbon compounds and each oil is different in the mixture, we should be able to identify each type of oil by monitoring a unique mass of the oil. We suggest further study of the mass spectra of all types of oil that are used at the Arnold Air Force Base in order to find a unique ion for each type of oil. The technique of homogenize oil emulsion also needs investigation. With sufficient time and funding, we believe that the identification and quantification of oil in water can be accomplished. The extensive study of oil can be done as a part of phase II project.



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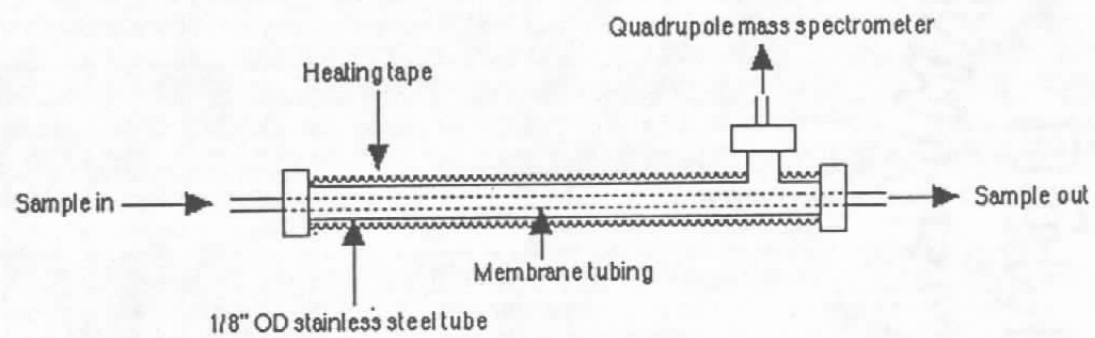


Fig. 1 Diagram of the interface for membrane tubing

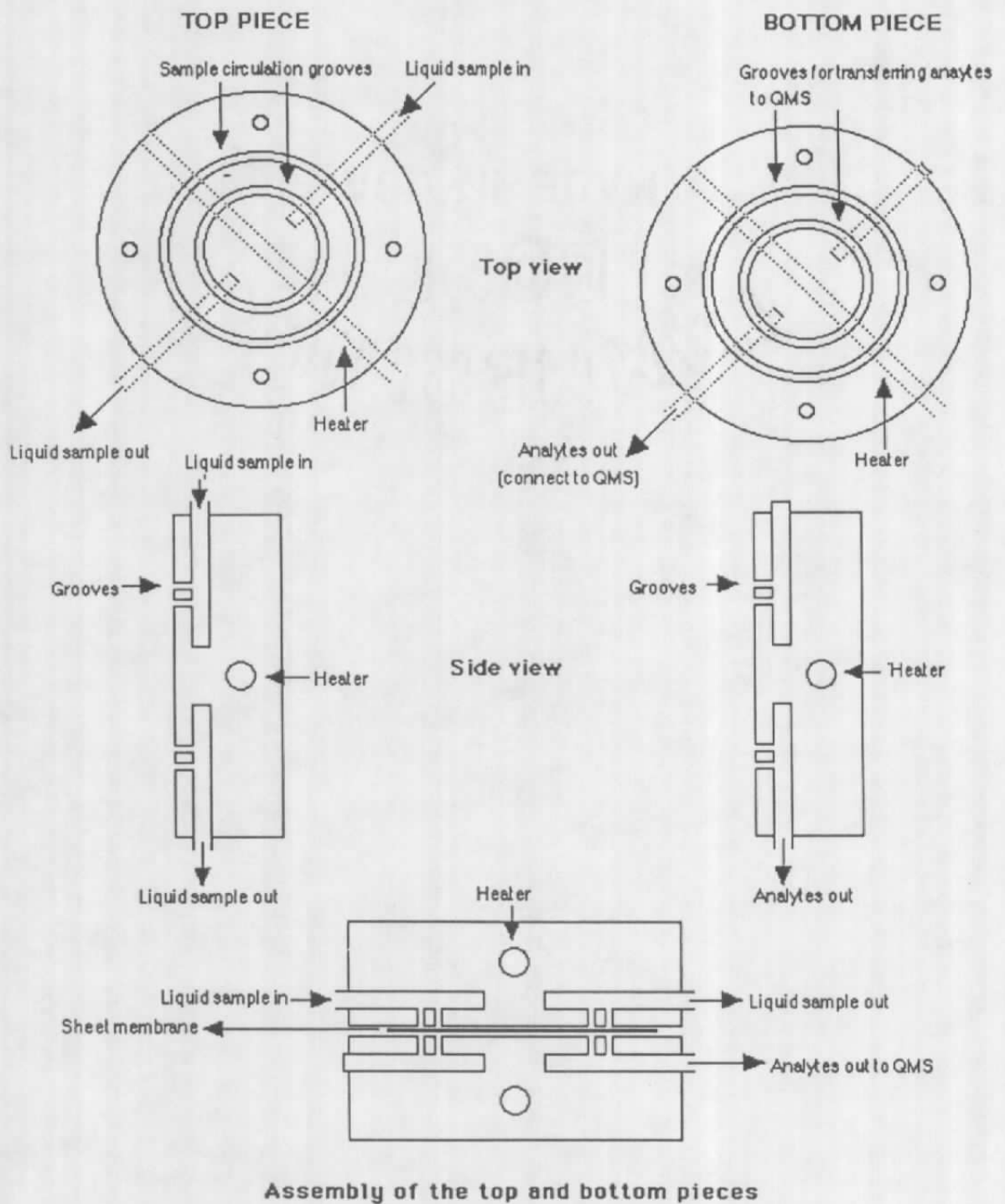


Fig. 2 Diagram of membrane interface for sheet membranes

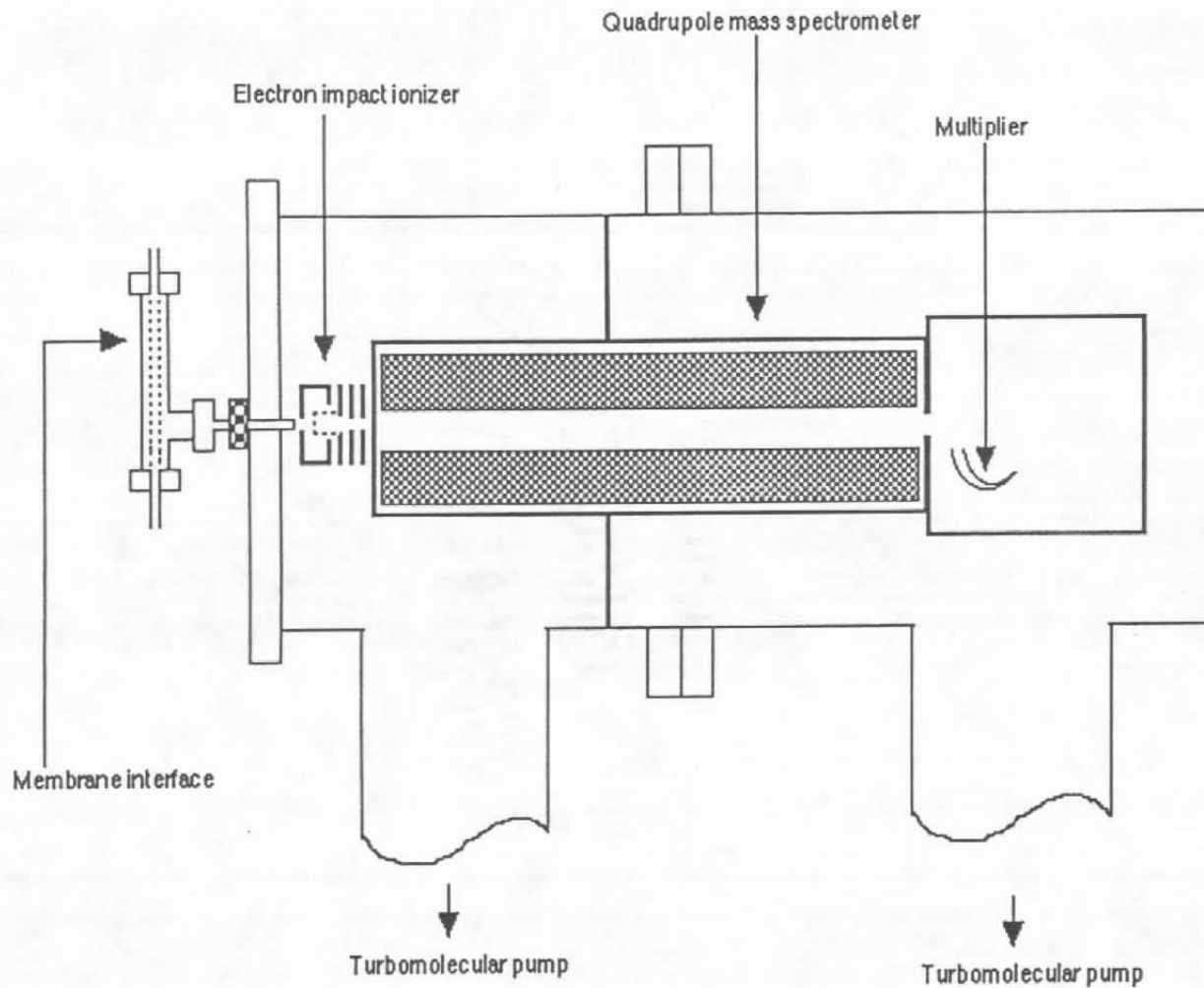
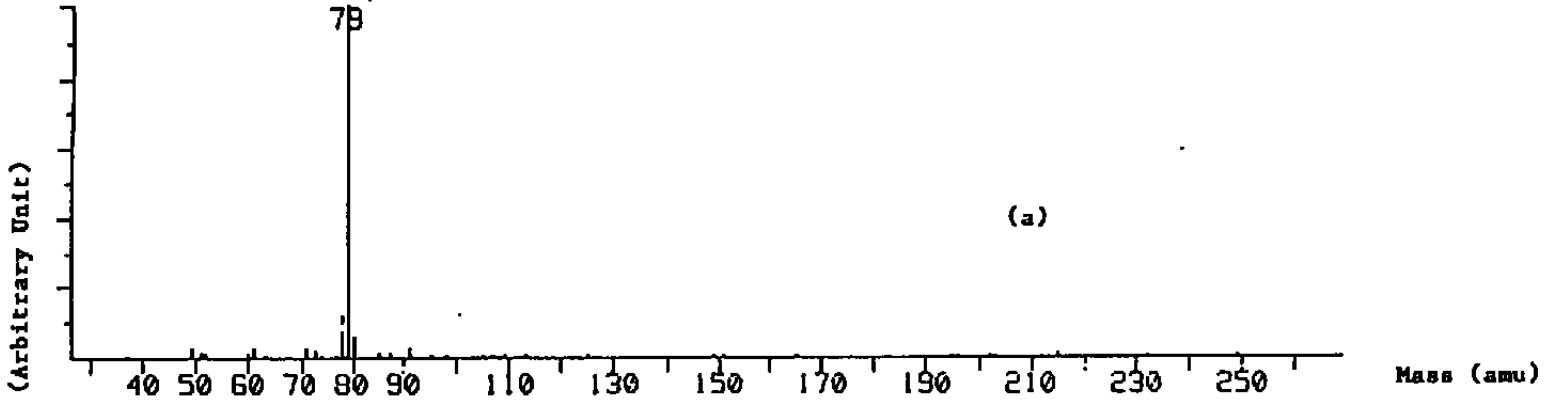
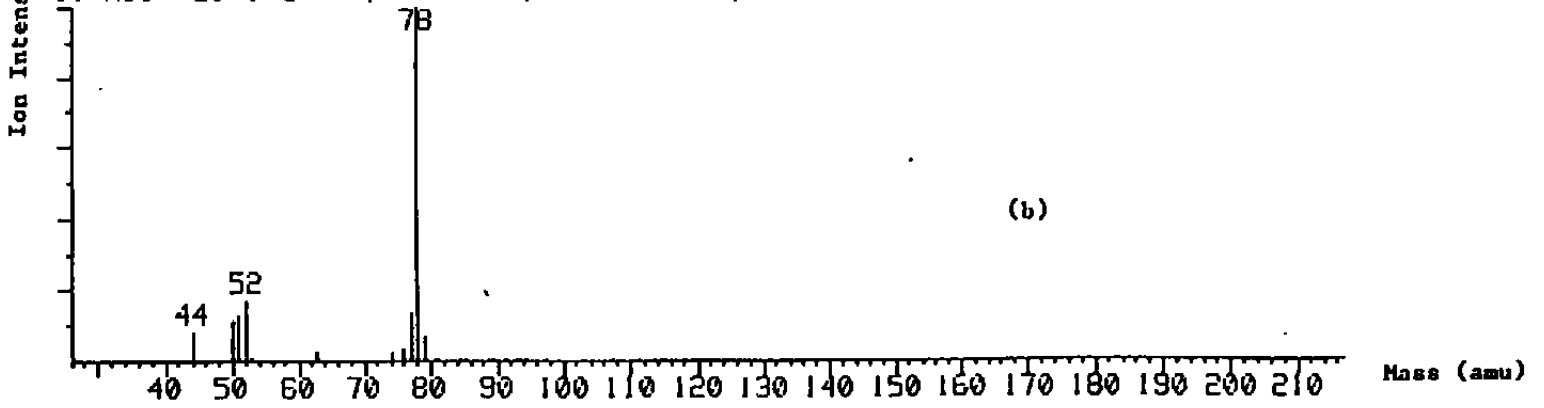


Fig. 3 Diagram of quadrupole mass spectrometer and electron impact ionizer

DU0: [301,1]10NGCI, 10ng ON COLUMN CI+ (METHANE) FOR R, 01-DEC-89, 15:09:26  
Q1 Mss: 26.0-269.0, Sn: 486, B: 1.0 440, Max: 12917, ART: 7.3



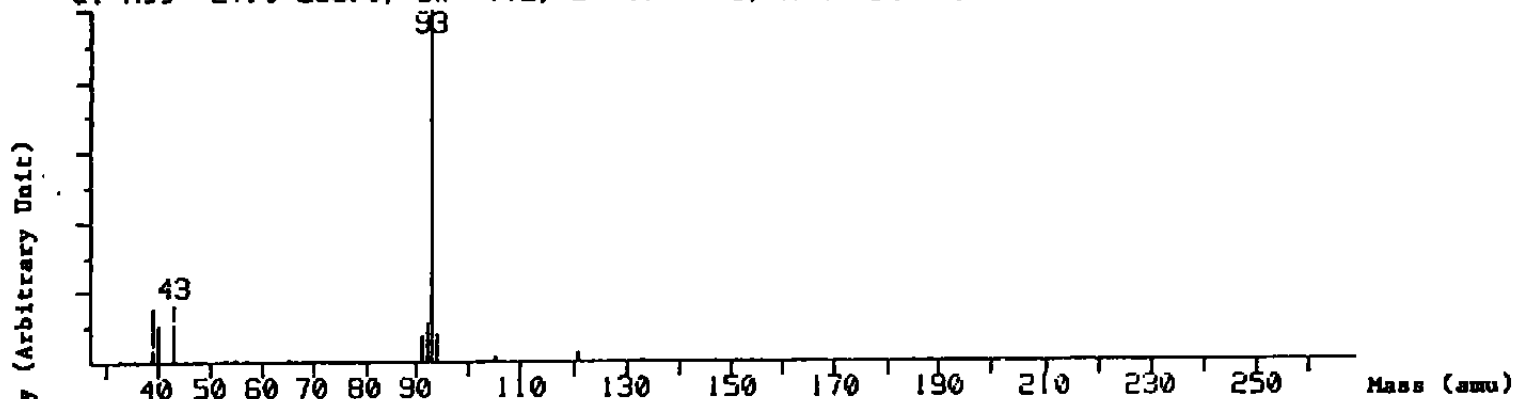
DU0: [301,1]10NGEI, 10ng ON COLUMN EI FOR RESEARCH, 01-DEC-89, 13:14:05  
Q1 Mss: 26.0-217.0, Sn: 486, B: 1.0 452, Max: 21321, ART: 7.3



30

Fig. 4 (a) CI spectrum of benzene  
(b) EI spectrum of benzene

DUO: [301.1110]NGCI, 10ng ON COLUMN CI+ (METHANE) FOR R, 01-DEC-89, 15:09:26  
Q1 M<sub>s</sub>: 27.0-269.0, S<sub>n</sub>: 772, B: 1.0 703, Max: 82602, ART: 11.7



DUO: [301.1110]NGEI, 10NG ON COLUMN EI FOR RESEARCH, 01-DEC-89, 13:14:05  
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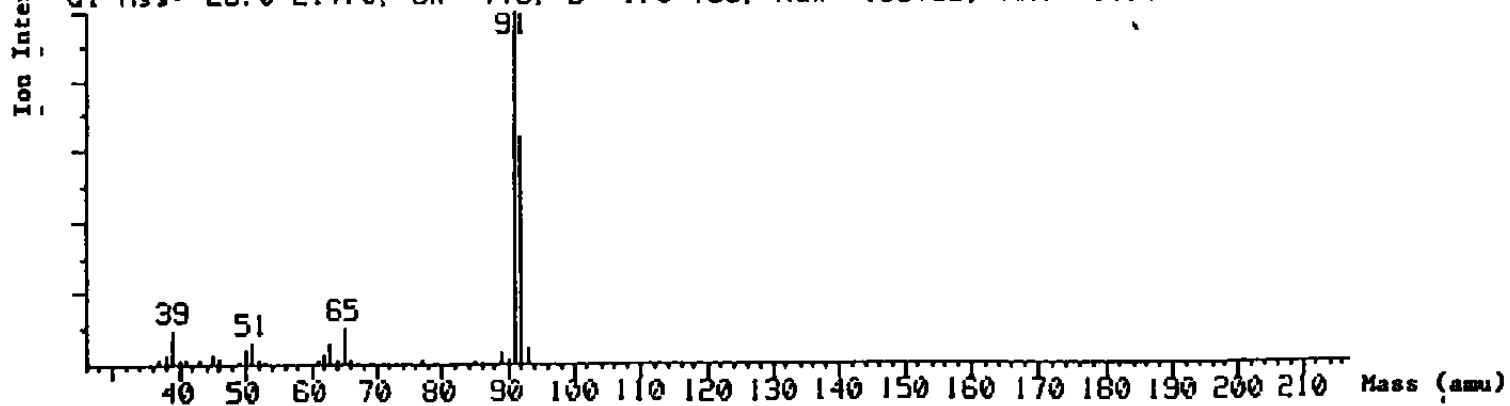


Fig. 5 (a) CI spectrum of toluene  
(b) EI spectrum of Toluene

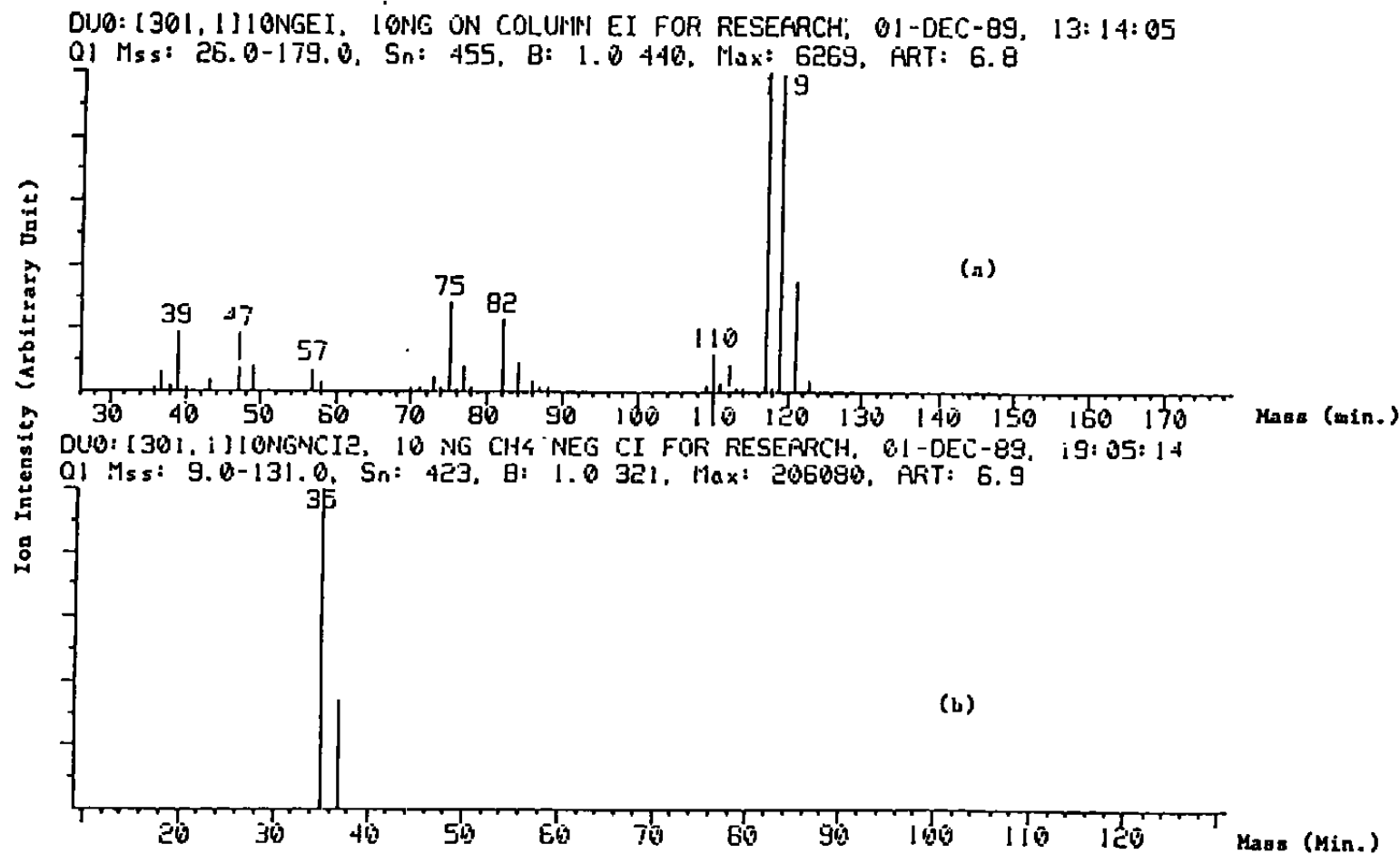


Fig. 6 (a) EI spectrum of carbon tetrachloride  
(b) Negative ion spectrum of carbon tetrachloride



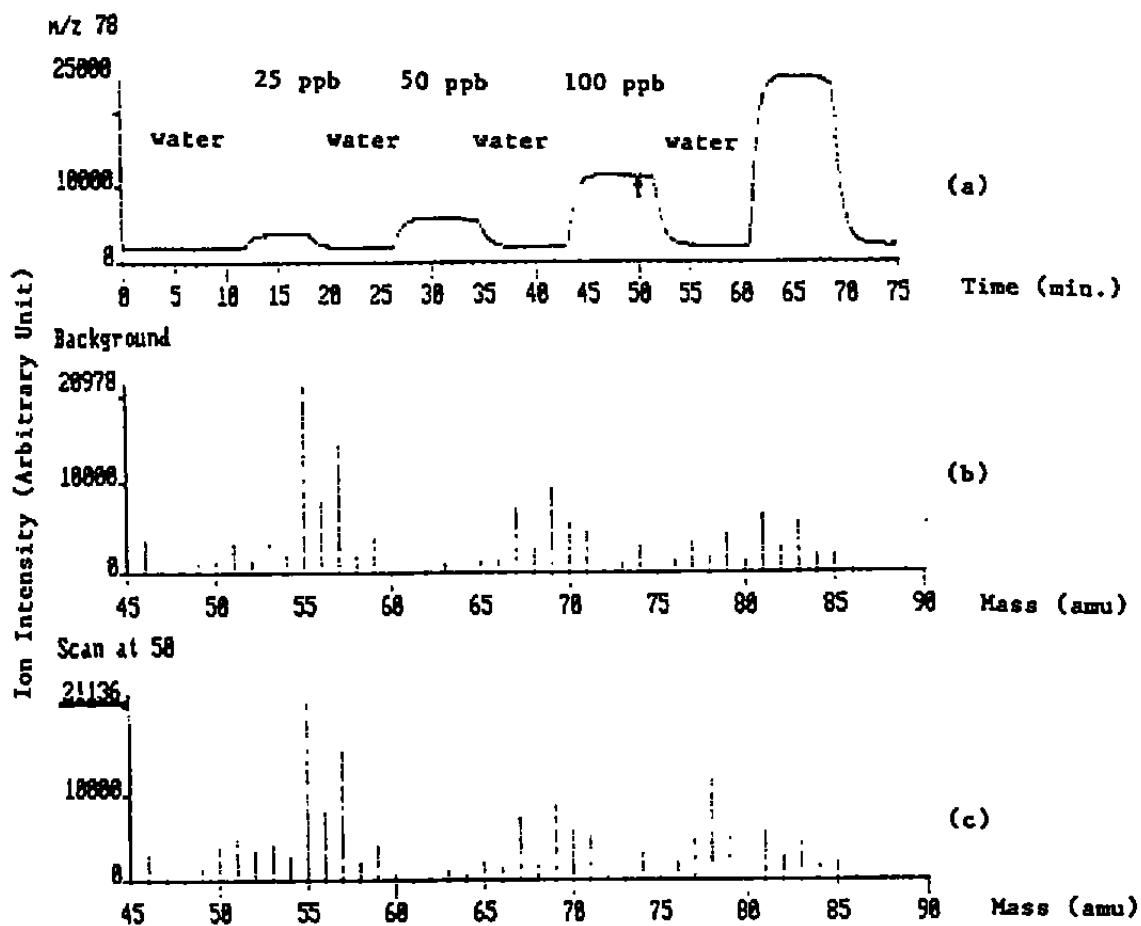


Fig. 7 a) Response of the MI/QMS to various concentration of benzene.  
 b) Background spectrum during the 40<sup>th</sup> minute.  
 c) Mass spectrum during the 50<sup>th</sup> minute of the experiment.

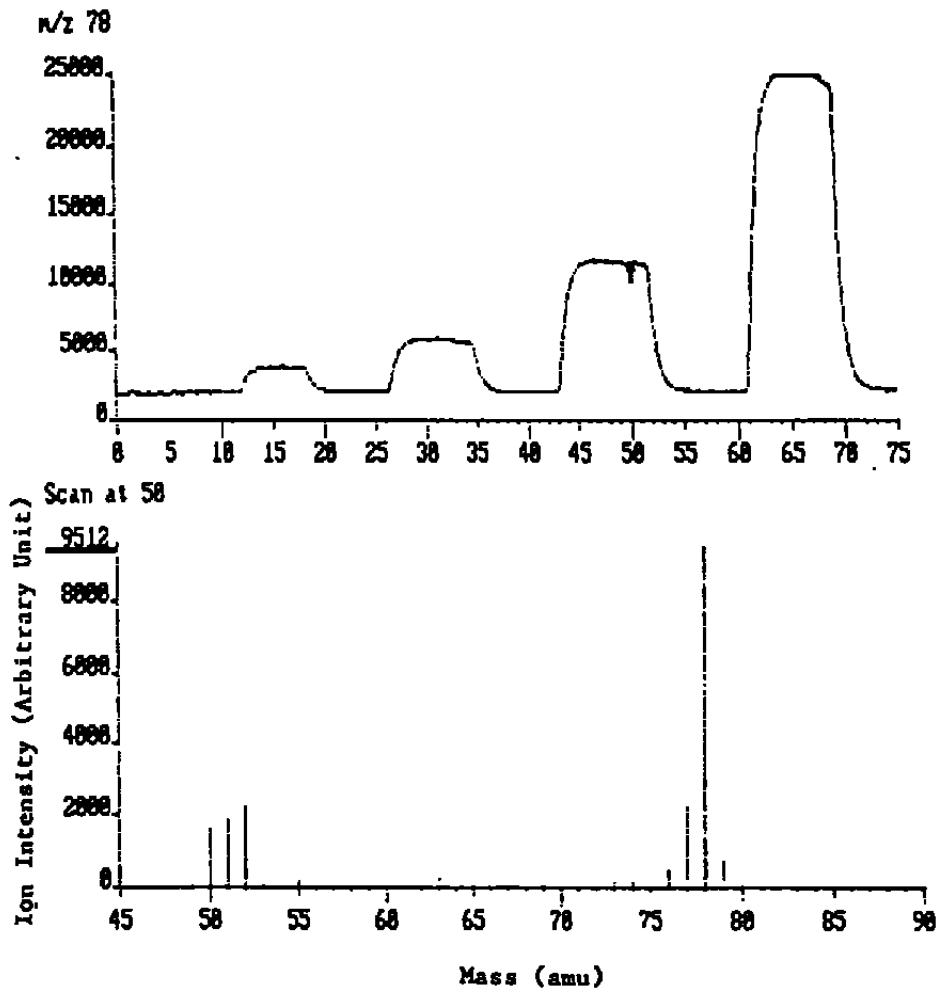


Fig. 8 Mass spectrum of benzene in the mass range of 45 to 90 amu.

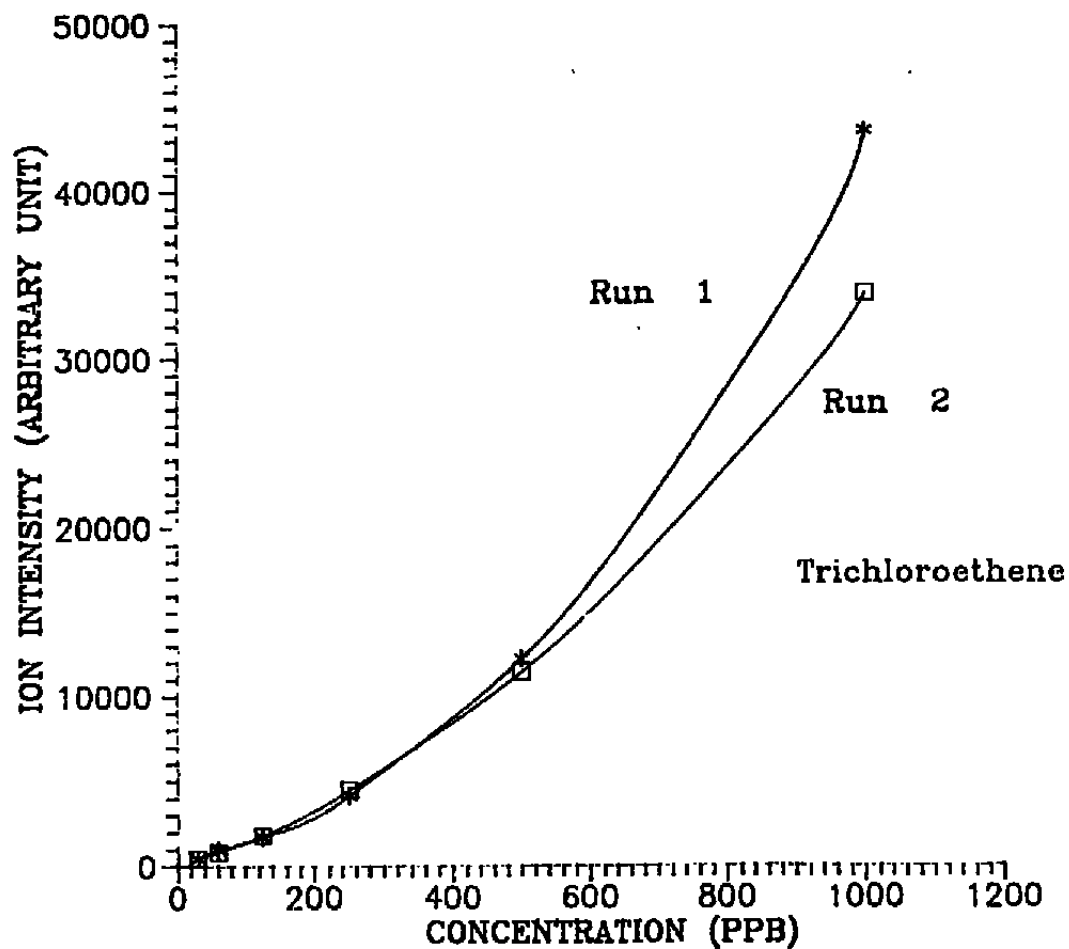


Fig. 9 Plot of dominant fragment ion intensities of trichloroethene as a function of concentration between 30 ppb and 1000 ppb. Solutions were prepared by dilution method No. 1.

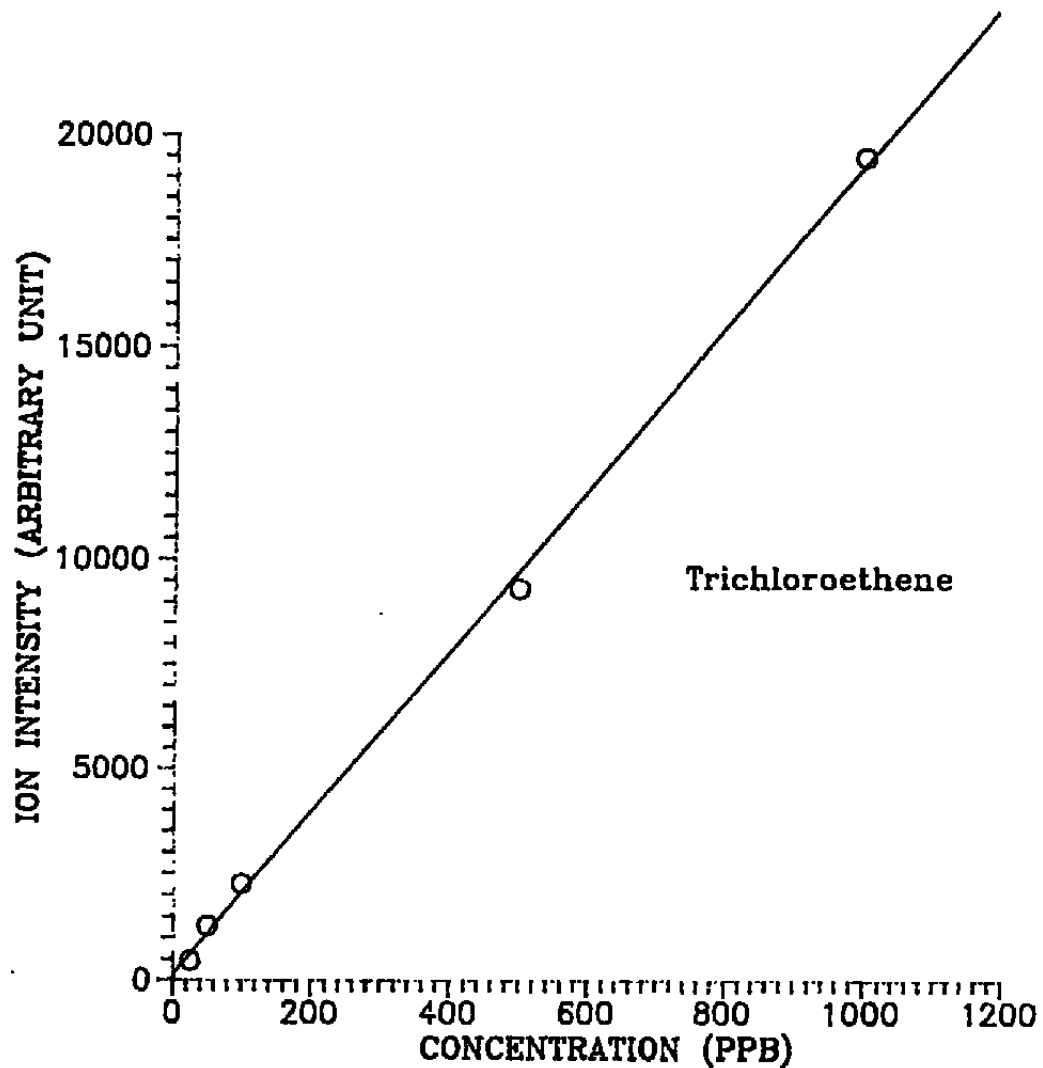


Fig. 10 Plot of dominant fragment ion intensities of trichloroethene as a function of concentration between 25 ppb and 1000 ppb. Solutions were prepared by dilution method No. 2.

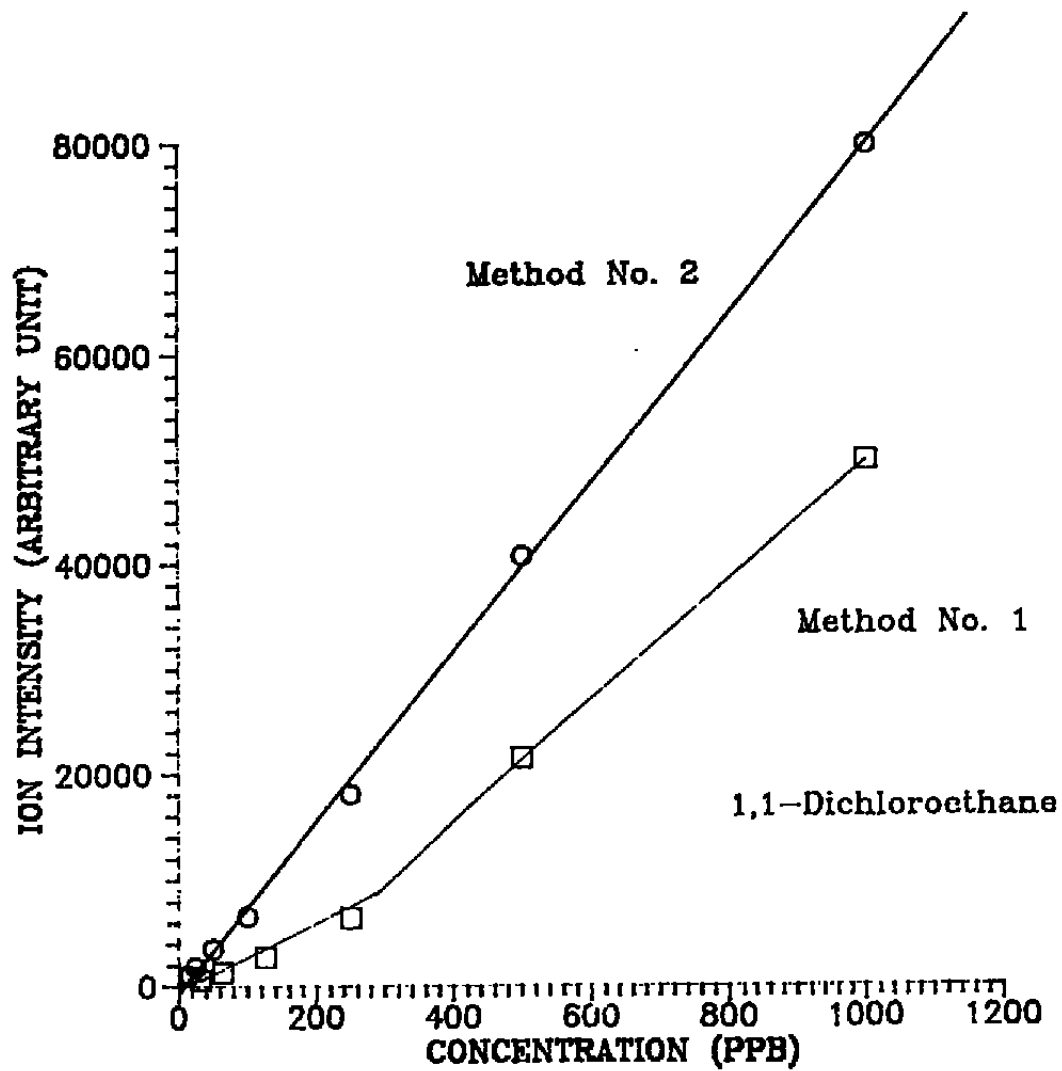


Fig. 11 Plot of dominant fragment ion intensities of 1,1-dichloroethane as a function of concentration. Comparison of two dilution methods.

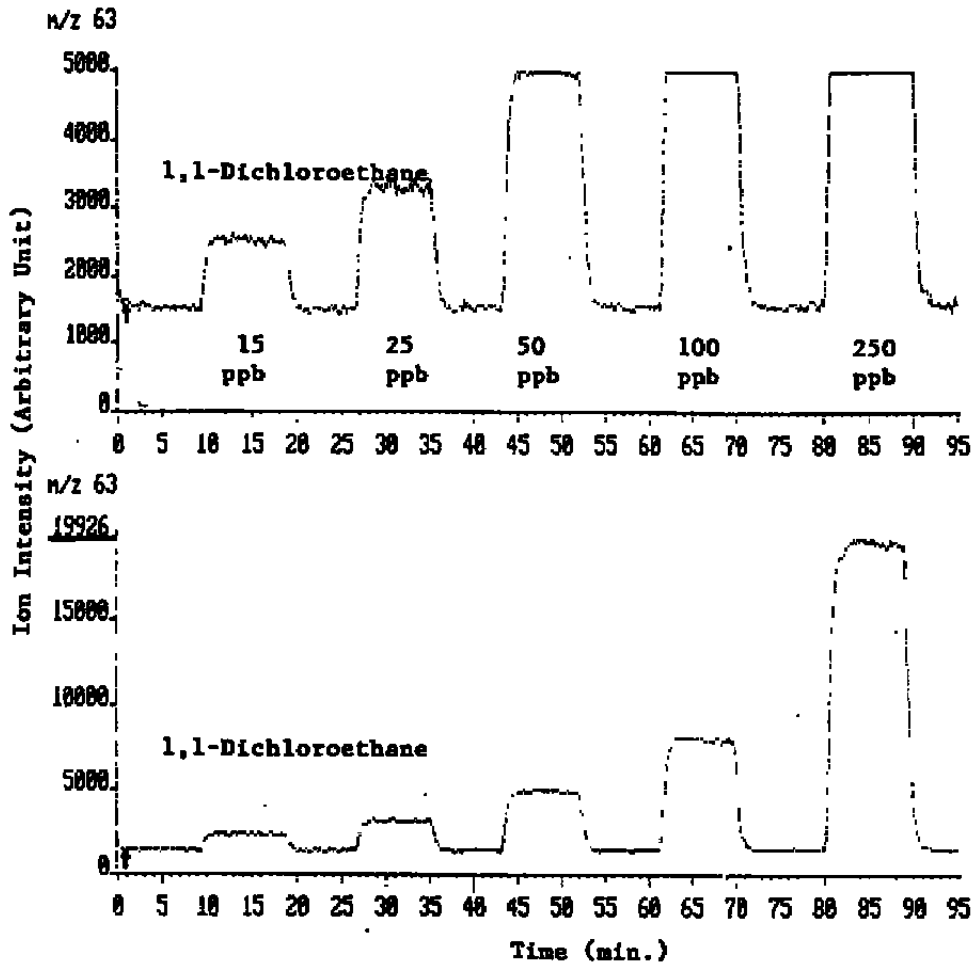


Fig. 12 Response of the MI/QMS to various concentrations of 1,1-dichloroethane.

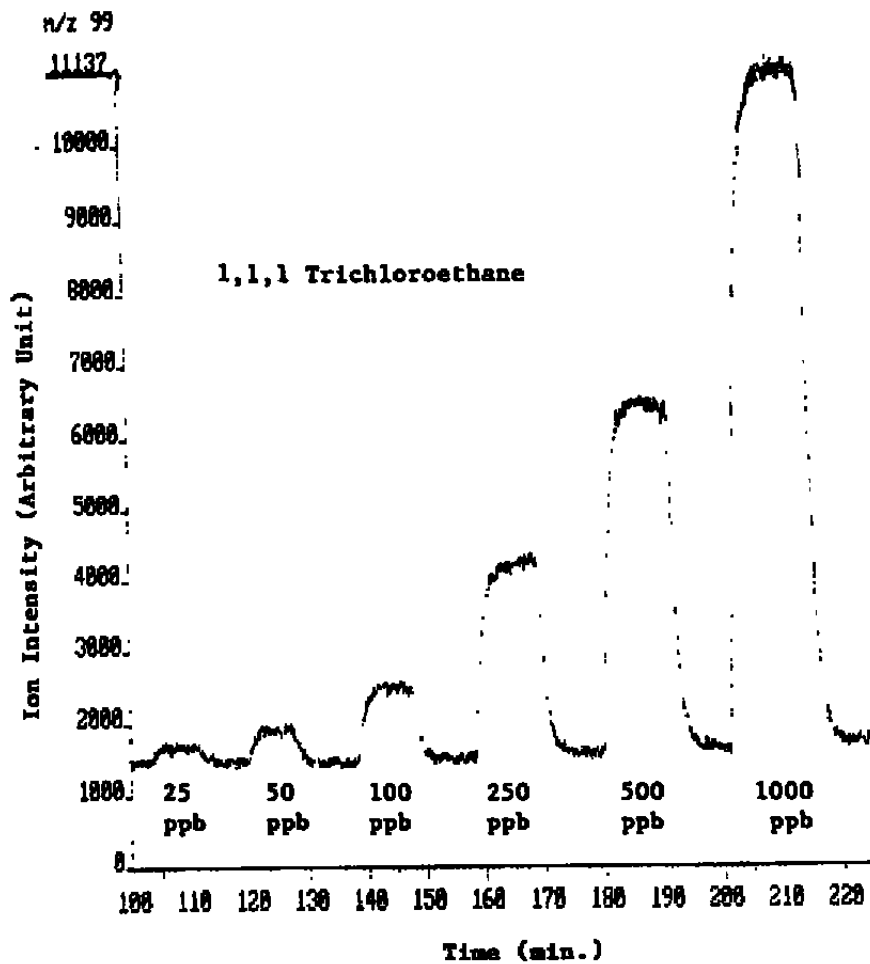


Fig. 13 Response of the MI/QMS to various concentrations of 1,1,1-trichloroethane.

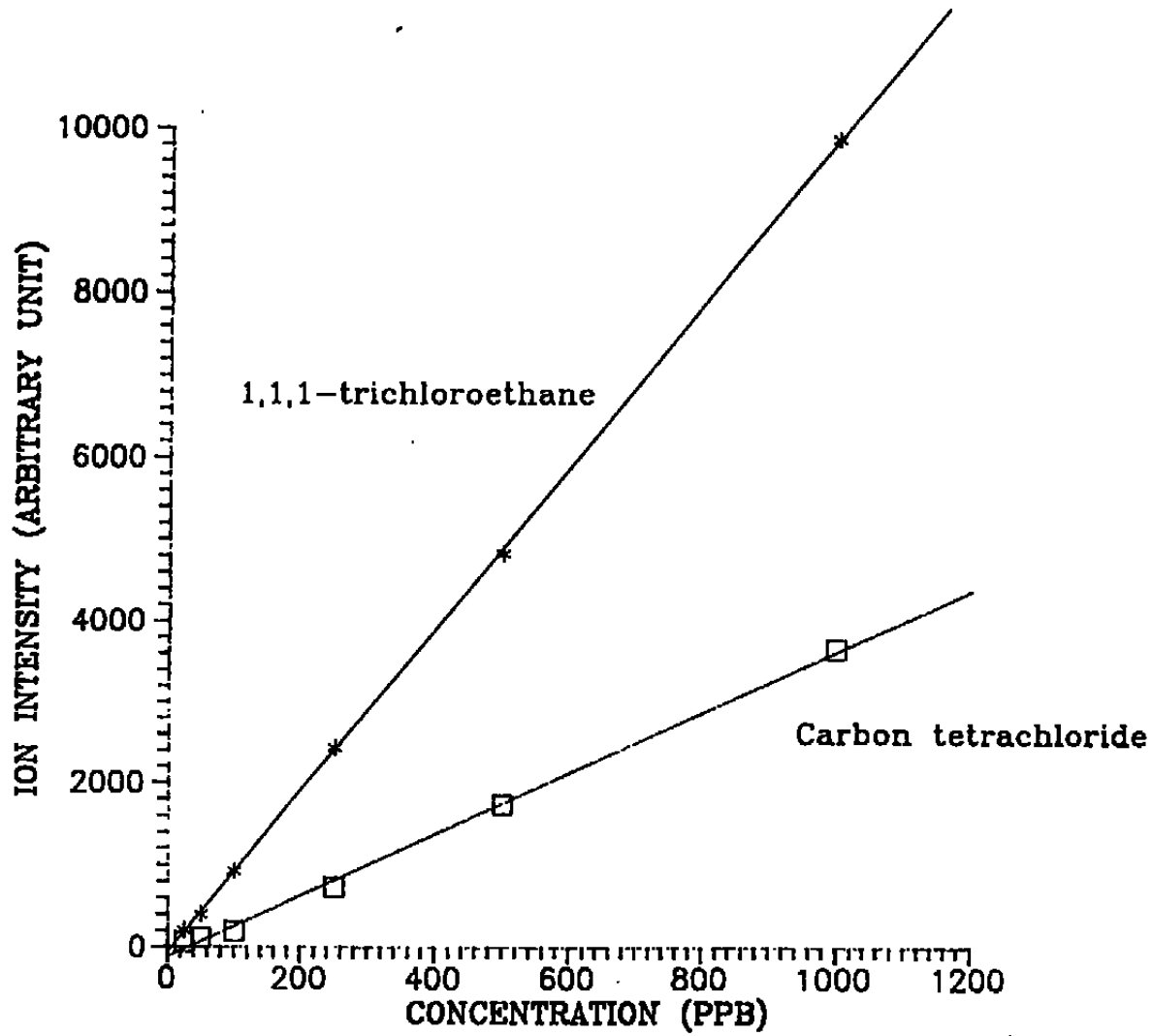


Fig. 14 Plot of dominant fragment ion intensities of 1,1,1-trichloroethane and carbon tetrachloride as a function of concentration.



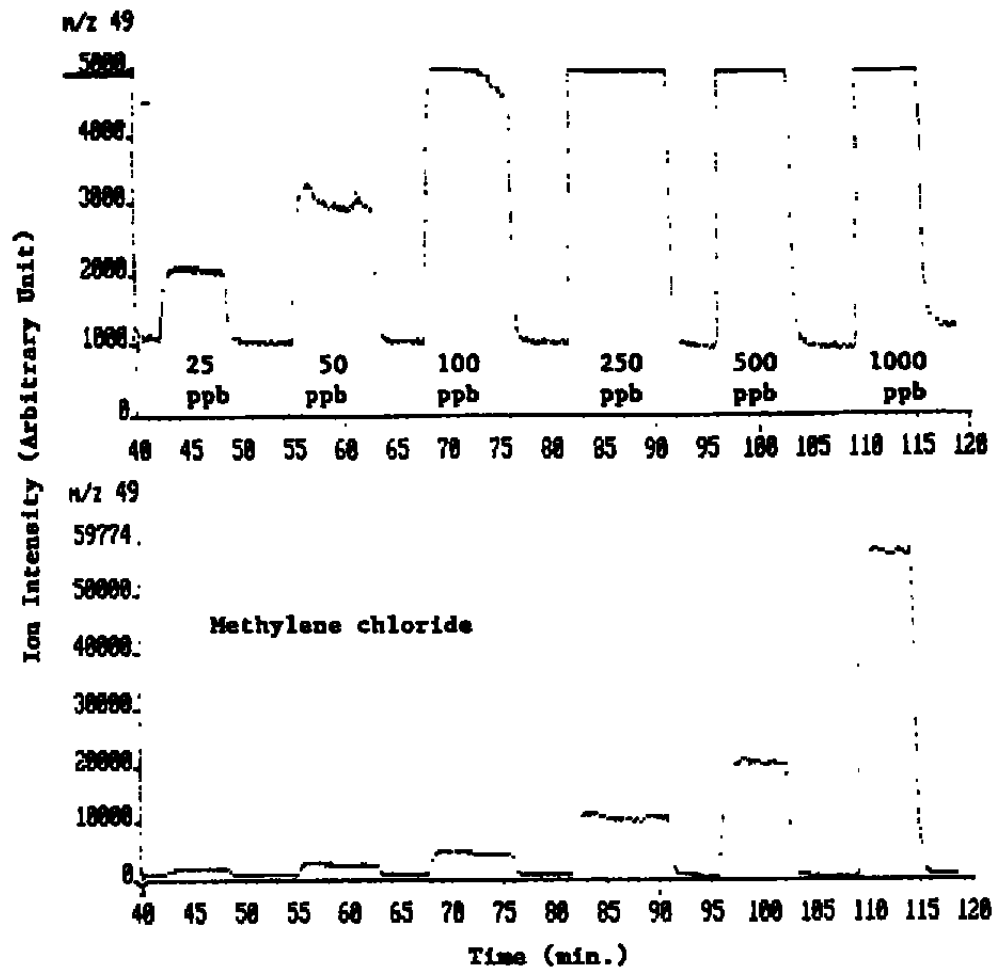


Fig-15 Response of the MI/QMS to various concentrations of methylene chloride.

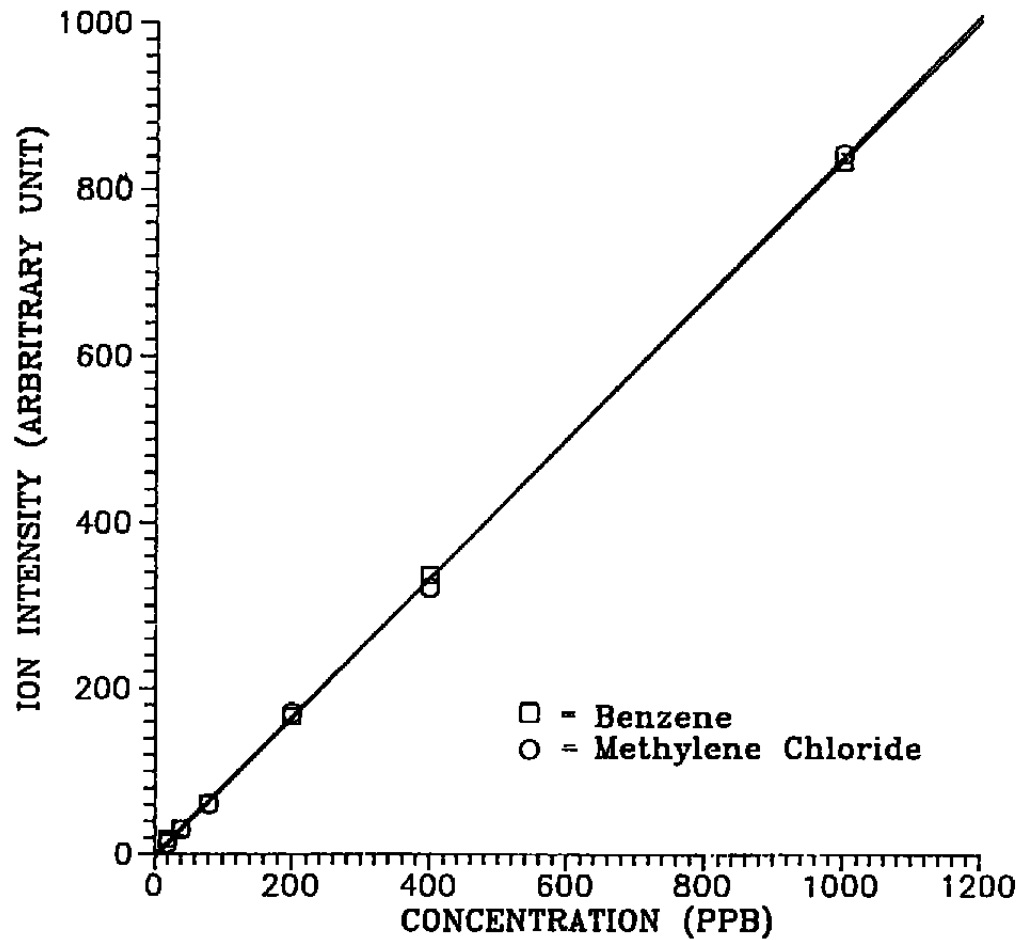


Fig.16a Plot of dominant fragment ion intensities of benzene and methylene chloride as a function of concentration. Data obtained from chemical solutions of individual chemicals.

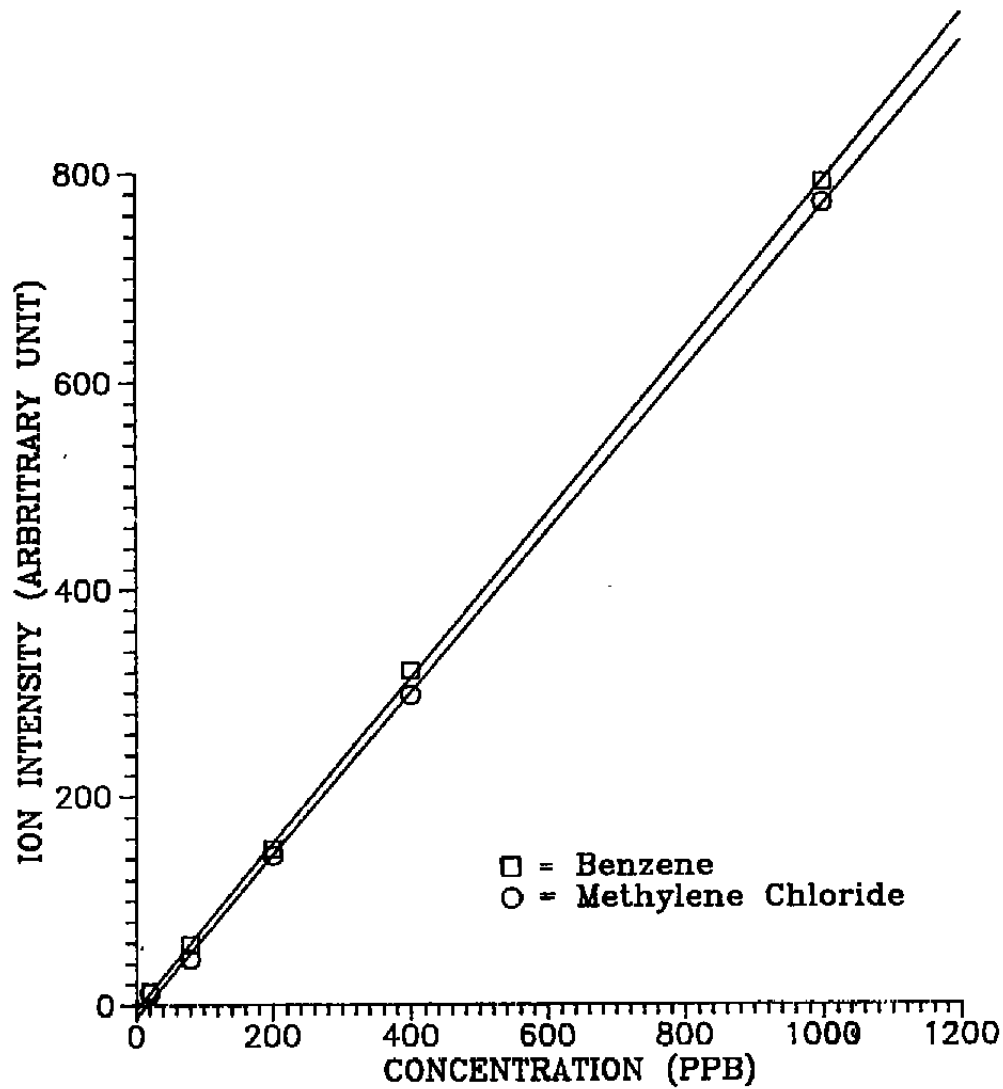


Fig.16b Plot of dominant fragment ion intensities of benzene and methylene chloride as a function of concentration. Data obtained from a mixture of benzene and methylene chloride.

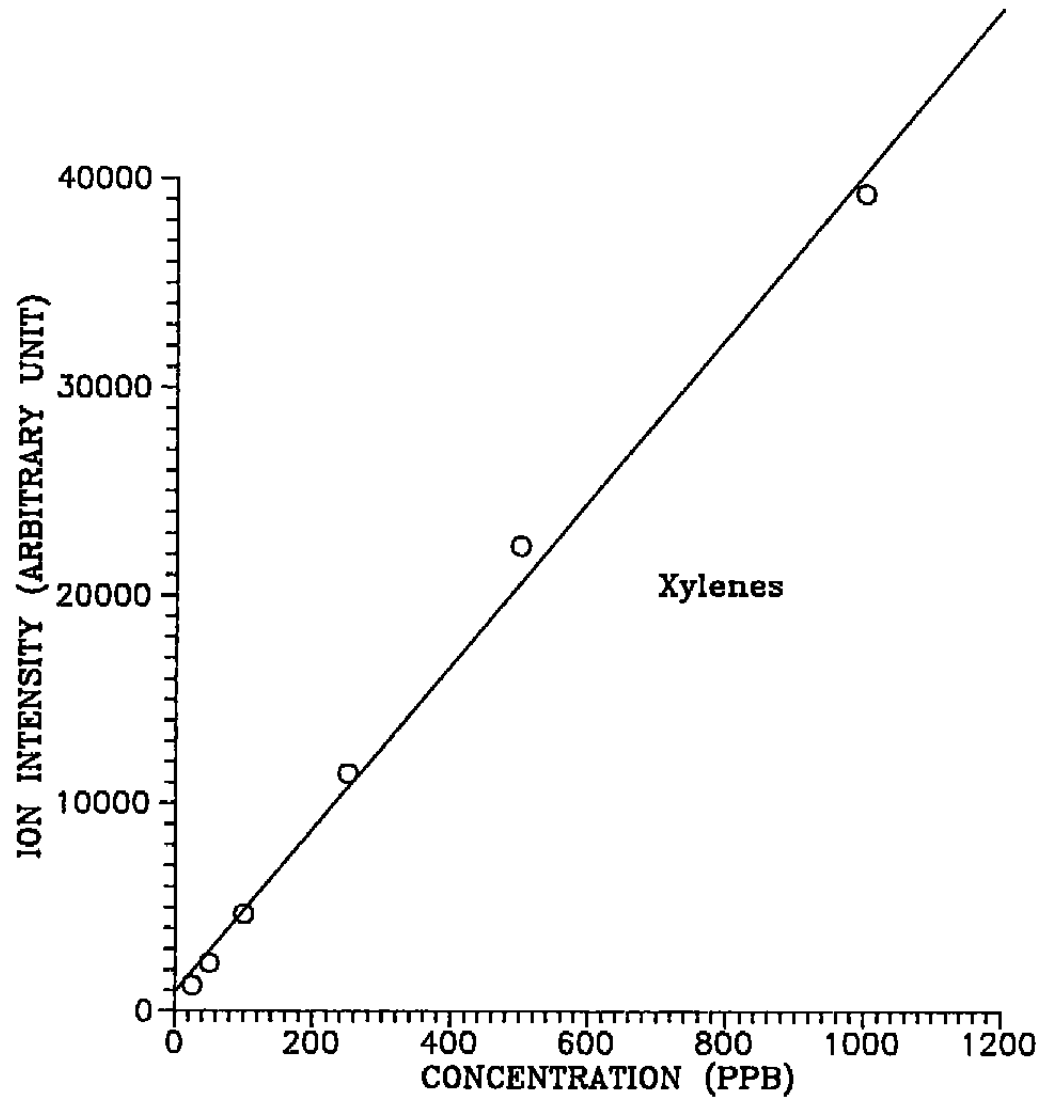


Fig. 17 Plot of dominant fragment ion intensities of xylenes as a function of concentration.

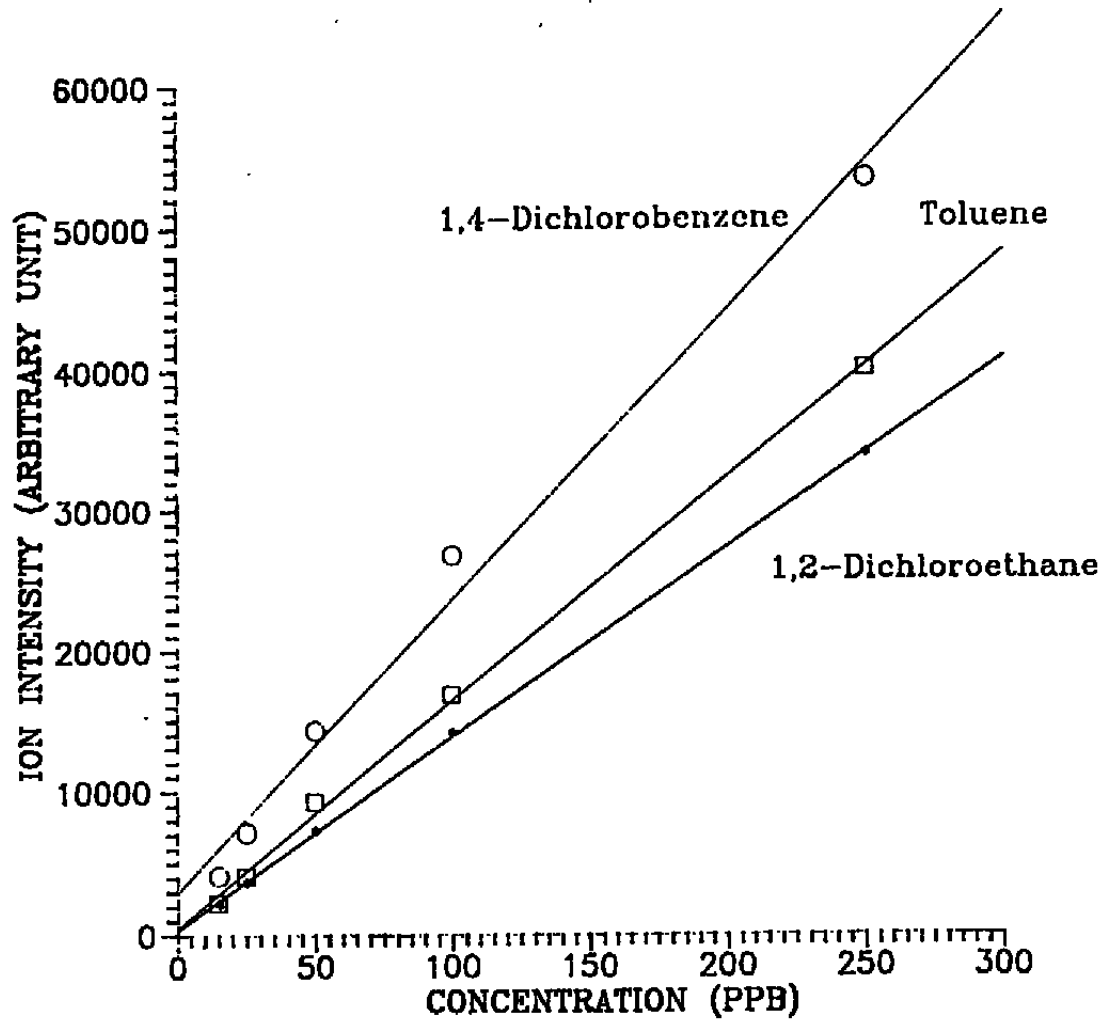


Fig. 18 Plot of dominant fragment ion intensities of 1,2-dichloroethane, toluene and 1,4-dichlorobenzene as a function of concentration.

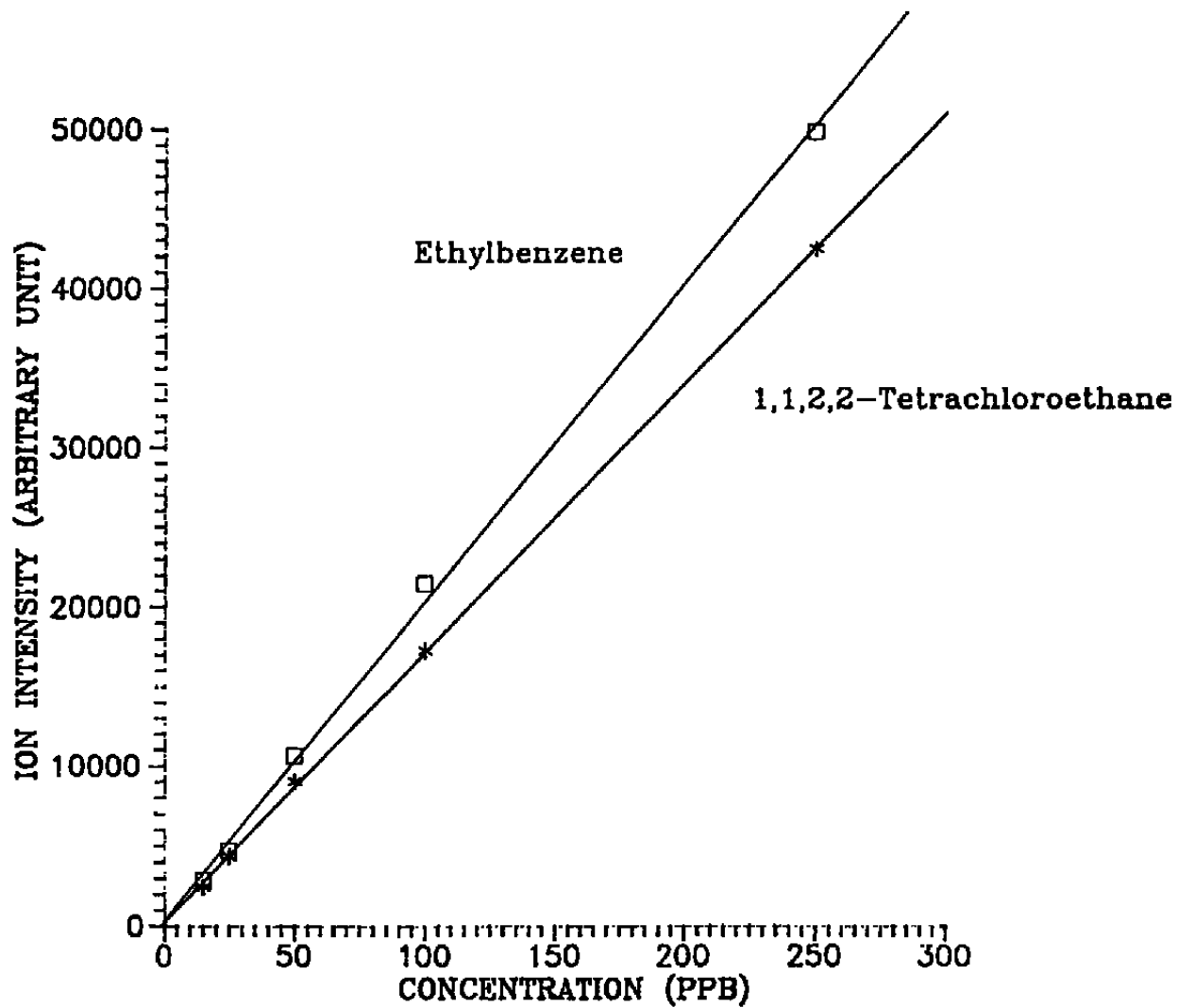


Fig. 19 Plot of dominant fragment ion intensities of 1,1,2,2-tetrachloroethane and ethylbenzene as a function of concentration.

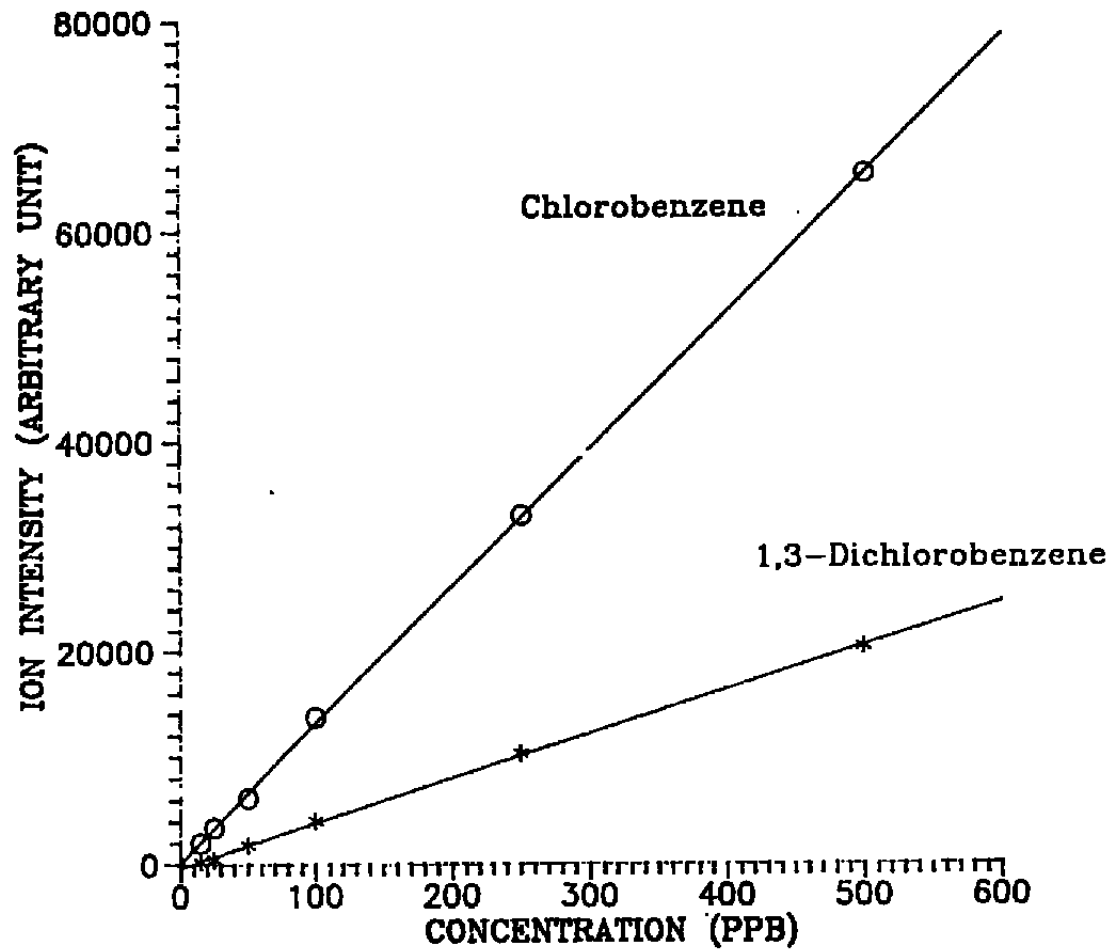


Fig. 20 Plot of dominant fragment ion intensities of chlorobenzene and 1,3-dichlorobenzene as a function of concentration.

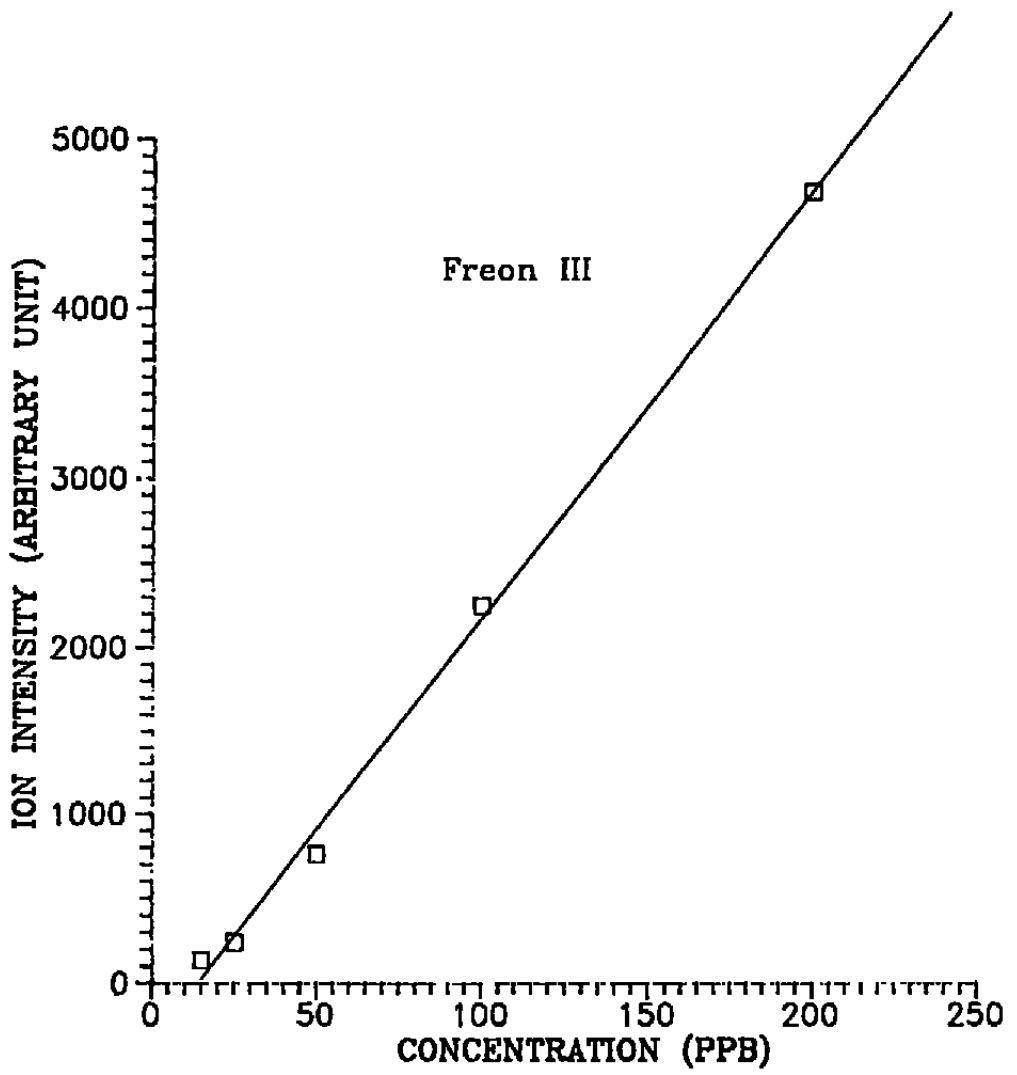


Fig. 21 Plot of dominant fragment ion intensities of freon III as a function of concentration.



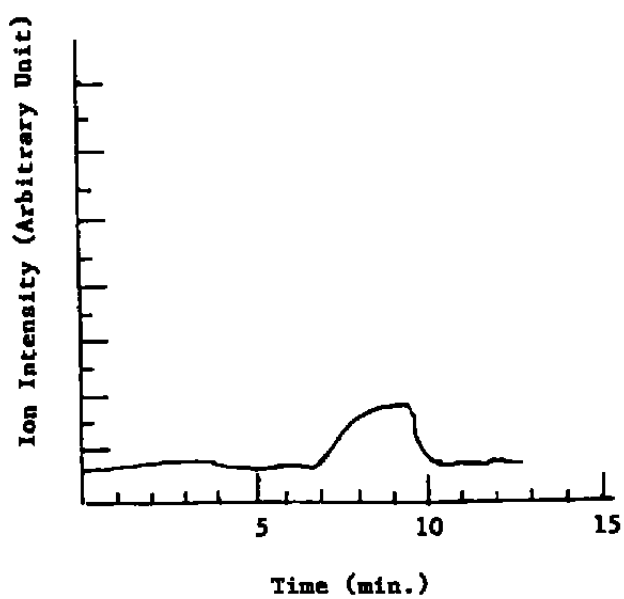


Fig. 22. Response of the MI/QMS instrument to 10 ppm of ethylene glycol.

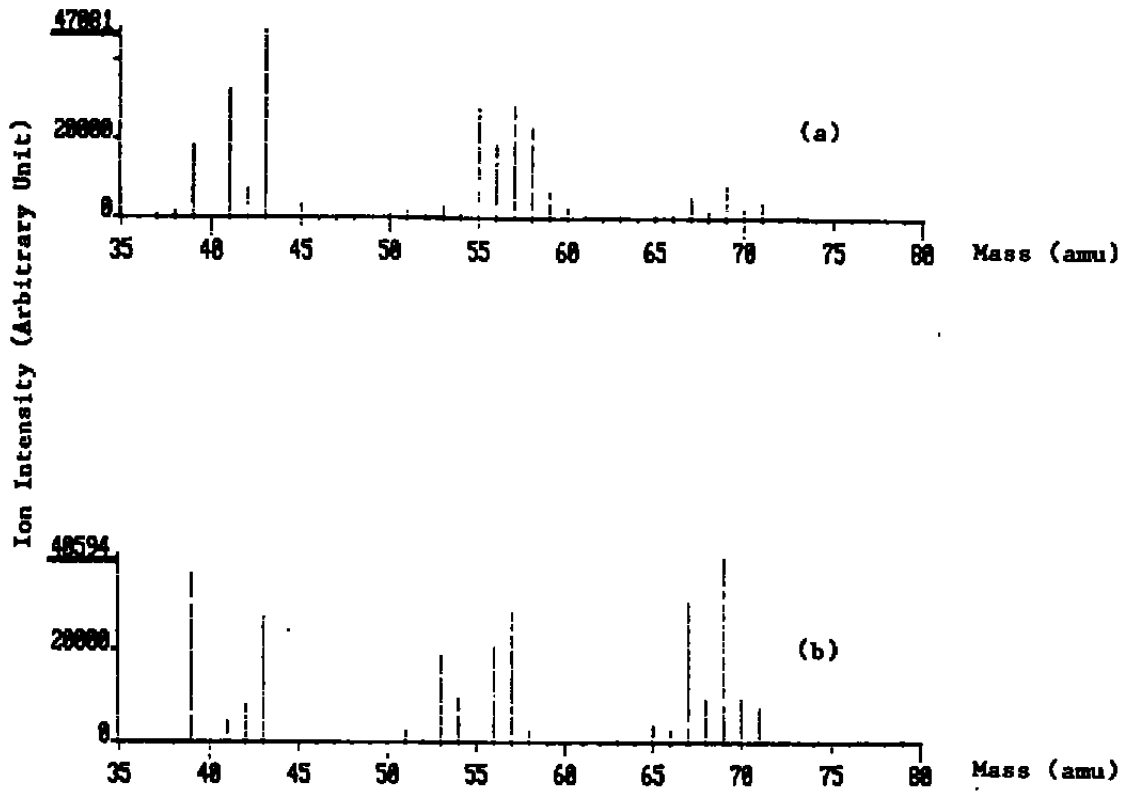


Fig. 23 (a) EI spectrum of 7808 oil  
(b) EI spectrum of Texaco Capella WF 68

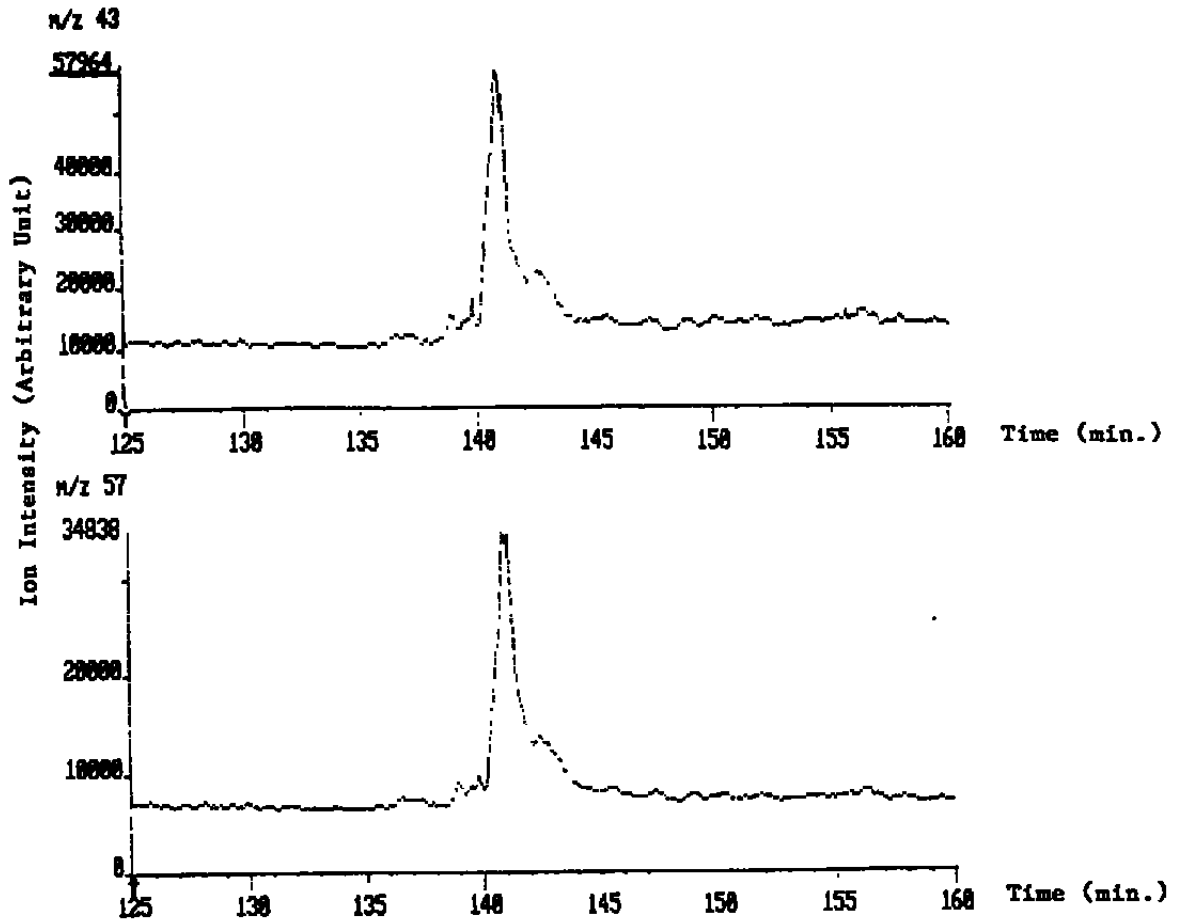


Fig. 24 Response of the MI/QMS to 7808 oil.

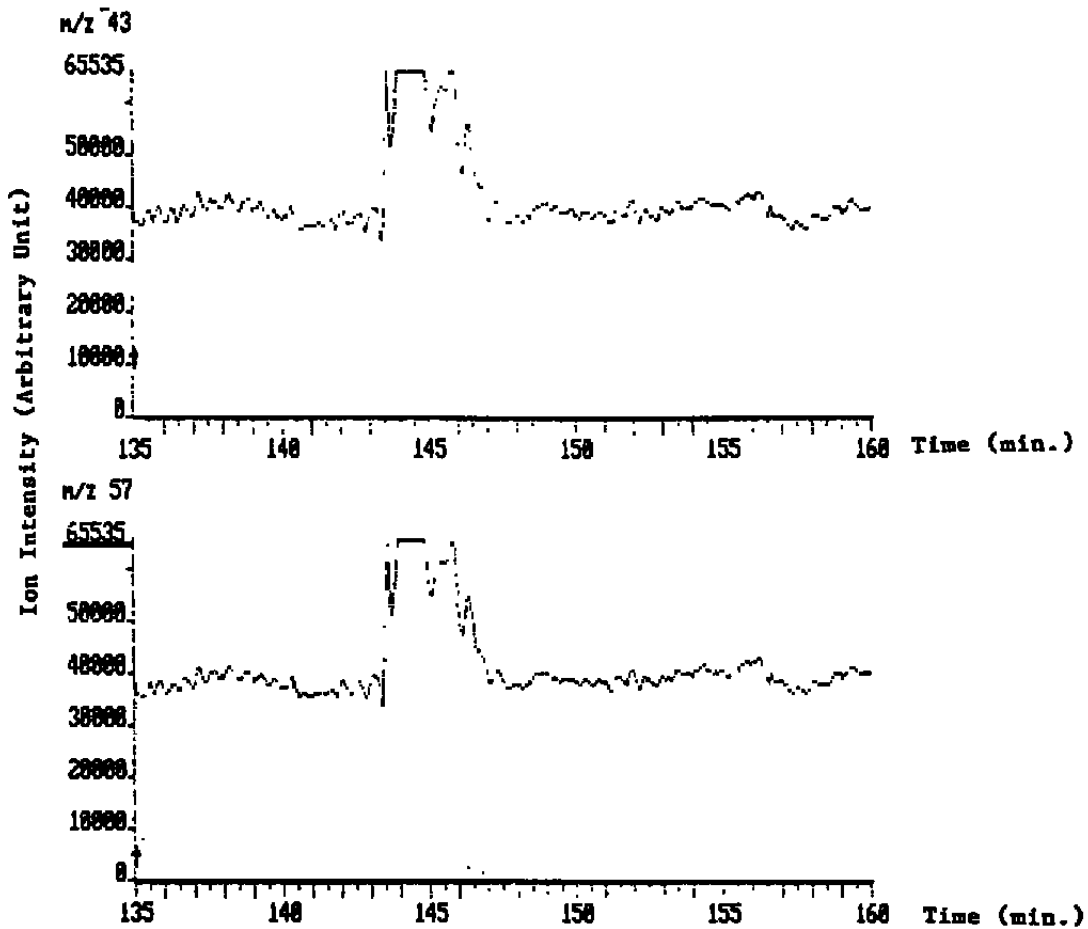


Fig. 25 Response of the MI/QMS to Texaco Capella WF68