DEVELOPMENT OF A MICROBORE CAPILLARY COLUMN GC-FOCAL PLANE MASS SPECTROGRAPH WITH AN ARRAY DETECTOR FOR FIELD MEASUREMENTS

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A gas chromatograph-mass spectrograph (GC-MS) system using a microbore capillary column (50 μm i.d.), and a miniaturized focal plane mass spectrograph (Mattauch-Herzog type) with an array detector has been developed. The extremely small carrier gas flow rate (0.05 atm $cm^3 min^{-1}$ of helium) through the column permits its direct coupling to the ion source, and reduces the pumping needs of the MS. The mass spectrograph with an array detector measures the intensities of all masses simultaneously. Analysis of mixtures of compounds, each at a concentration of 1 ppmv has been performed with high signal-to-noise ratio. The minimum detectable quantity of benzene is determined to be 7.5×10^{-14} g which corresponds to a concentration of 40 ppb for an injected sample volume of 0.5 μl. Lower analyte concentration can be determined by increasing the sample volume and/or the signal integration time. The system is found to have a linear dynamic range of $>10^3$. Because of its low weight, power, and high sensitivity, the combination of a microbore GC column and a miniaturized plane mass spectrograph is uniquely suited for field analysis.

INTRODUCTION

The combination of a gas chromatograph with a mass spectrometer (GC-MS) is one of the most powerful instruments for the analysis for complex mixtures. GC-MS is eminently suited for the measurement of environmental pollutants. However, in its present form it has remained largely confined to the laboratory because of its mass and power requirements. Our own interest lies in the development of a field-portable GC-MS instrument. Such an instrument is much needed for the real-time, on-site measurement of pollutants, e.g., at toxic waste dump sites and for fugitive emissions from various sources. This instrument should also be fast and possess high efficiency and sensitivity in order to analyze compounds present at low concentration levels. In the hyphenated technique of GC-MS, the speed of analysis is determined by the GC separation time. Fast separation with high efficiency can be achieved by the use of a narrow-bore capillary column (e.g., 50 μm i.d.) of short length.[1-3] Also, the carrier gas flow rate through such a column is very low which offer the advantage of reducing the pump-size (often requiring large mass and power) needed to maintain the proper operating vacuum conditions in the MS.

Such microbore columns, however, put important restrictions on the sample size for analysis, and on the detector used for measuring the eluted compounds.[4,5] Extremely narrow and closed spaced peaks are produced from the use of microbore columns, particularly in the early part of the chromatogram. The detector must, therefore, have a high sensitivity and a low-time constant for signal measurement. To maintain the column efficiency, the dead volume needs to be minimized. These considerations have prohibited the application of columns of <100 μm i.d. in commercial GCs. The fast rate of data acquisitions needed to measure peaks from a microbore column makes it incompatible with a scanning type mass spectrometer.[4]

The aforementioned problems in exploiting the advantages of a microbore column can be overcome by the use of a mass spectrograph (non-scanning). The capability of a mass spectrograph for measuring the intensities of all masses at the same time confers on it an almost unlimited speed for obtaining mass

spectra. Its sensitivity also is inherently greater that of a scanning-type MS because the latter measures the signal at a given mass peak only for a short dwell time. However, in the past, the lack of a sensitive ion detector has been an important reason for not using a nonscanning MS for measurements that required high sensitivity. Recently, an array detector known as an electro-optical ion detector (EOID) has been developed in our laboratory for a focal plane mass spectrograph (Mattauch-Herzog type).[6,7] The EOID possesses the simultaneity of a photoplate (used in focal plane MS) and the high gain of an electron-multiplier. The EOID can integrate signals continuously for a wide range of time (25 ms - 30 s) and, by an appropriate selection of integration time, multiple mass spectra from transient samples (like a narrow GC peak) can be obtained without sacrificing sensitivity.

Our approach towards the development of a high performance field-portable GC-MS instrument consists of combining a short microbore column and a miniaturized focal plane mass spectrograph. In this paper, the new GC-MS system developed in our laboratory is described. Some of the results obtained on this system for the analysis of a mixture of priority pollutants are also reported.

II. EXPERIMENTAL

A. Gas Chromatograph

The experimental arrangement is shown schematically in Fig. 1. The fused silica microbore GC column (3.0 m, 50 μm i.d.) with a 0.2 μm bonded DB-5 stationary phase (J. & W. Scientific, Folsom, Ca.) was housed in a temperature programmable oven. The outlet end of the column was directly led into the ion source of that mass spectrograph. A sample injector valve (Valco Instruments) with an internal volume of 0.5 μl was used to inject the sample onto the column. A pneumatic actuator along with pilot valves and a digital valve interface[8] was incorporated into the sample injector for fast injection. Samples could thus be injected reproducibly in less than 14 ms. GC-grade helium was used as a carrier gas at a flow rate of 40 cm s^{-1}. Because of the small volume flow rate of the carrier gas (0.05 atm cm^3 min^{-1}), it was possible to connect the GC column and the MS without any interface. The direct inlet of the column effluents into the ion source eliminated the dead volume that usually arise from GC-MS interfaces and allowed for the complete utilization of the analyte sample.

B. Mass Spectrograph

Two miniaturized focal plane mass spectrographs, one with 2.0" long focal plane and the other with a 5.0" long focal plane have been designed and fabricated at JPL. The 2.0" focal plane covering a mass range of 40-250 amu is destined to be used for field measurements. A photograph of this MS is shown in Fig. 2a. The magnetic sector of this analyzer was fabricated from new magnetic materials having high energy product value, and high magnetic flux permeability for reducing the mass of this sector. The 5.0" focal plane MS covers a mass range of 28-500 amu.

C. Array Ion Detector

The details of the EOID have been reported previously.[6,7] In short, it consists of a microchannel electron multiplier array, a phosphor-coated (P-31) fiber optic window, and a photodiode array (PDA). In the EOID, an ion exiting the magnet impinges on the microchannel array and initiates an electron cascading process along the channel length. The electrons coming out at the other end of the channels produce photon images of their parent ions on the phosphor window (shown in Fig. 2b). The intensities of these images are then measured by the photodiode array (2.0" long active region) having a center-to-center distance of 25 μm between its two adjacent diodes.

The photodiodes are integrating detectors and accumulate the photon signal (proportional to the ion signal) for the desired period of integration. The position of the photodiode along the focal plane determines the mass of the ions producing the ion image at that location. The signal stored in the photodiodes are read (at a rate of 220 kHz) serially by a computer after a predetermined integration time. Each readout, called a frame, provides a mass spectrum of all the ions accumulated during the integration period. Each diode accumulates the signal continuously except for its read-out time (~4 μs) when it is reset and resumes signal integration. This allows for the complete mass spectral measurement of GC effluents at a high frequency without any loss of sensitivity in the process.

Both of the mass spectrographs described above are equipped with their own array detectors. The computer interface electronics for the small MS has not been completed at this time and, therefore, the results reported in the paper were obtained on the 5.0 in. focal plane MS. For laboratory measurements, this did not create any complications and demonstrated the analytical capability of the MS-EOID system.

Moreover, it is expected that the new 2.0-in. array detector will have better performance because of the minimization of the signal losses at the PDA-fiber-optic window interface in this design.

A mixture having a concentration of 1 ppmv in air of each of the compounds listed in Table 1 was prepared. The internal volume of the injector valve was filled with this mixture and injected on the GC column for analysis.

RESULTS AND DISCUSSIONS

The mass chromatogram of a mixture of the compounds listed in Table 1 is shown in Fig. 3. Each component in the mixture had a concentration of 1 ppmv in air. The GC column was maintained at the room temperature and a signal integration time of 250 ms for the array detector was used in the measurement. Complete mass spectra of the components eluting into the ions were recorded every 250 ms. In obtaining the mass chromatograph, the sum of the intensities of all masses (>45 amu) in each record (frame) is plotted against the corresponding frame member (time).
The chromatogram shows that the components (dichlorodifluoromethane, chloromethane, bromomethane and chloromethane) correspond to peaks 2-5 are narrow and closed spaced. For example, the peak-to-peak separation between 2 and 3 is less than 700 ms and the full width of peak 2 is about 300 ms. Quantitative measurement of such GC peaks are made possible by the simultaneous measurement of all ions and by the proper selection of the signal integration time.

The continuous measurement by the EOID with a short integration time (>25 ms) can be used to perform time-resolved mass spectral measurement and can be applied to resolve otherwise overlapping GC peaks. Figure 4 demonstrates the effect of measurement time on resolution of compounds by the microbore column. It is seen in Fig. 4a that bromomethane and chloromethane corresponding to frame numbers 89 and 95, respectively, are well separated when an integration time of 100 ms is used for their mass spectral measurement. For 250 ms integration time, the chromatographic separation is barely adequate (Fig. 4b) but the separation is lost when spectral measurements are made every 500 ms (Fig. 4c). The time resolution capabilities of the MS-EOID make it particularly useful for short columns of moderate resolving power. Their combination reduces the analysis time and renders it suitable for a field-portable GC-MS analyzer.

It should be noted that the quantitative nature of measurement is not compromised by the number of mass spectra (frames) obtained from a GC peak because of the continuous and simultaneous measurements of ion intensities. Figure 5 shows that some of the intensities contained in all the frames of a GC peak (corresponding to dichlorodifluoromethane) is independent of the integration time used in recording these frames. The sum of intensities determines the amount of the compound.

The mass chromatogram (Fig. 3) demonstrates that this GC-MS system can readily analyze mixtures of compounds present at the 1 ppmv level without preconcentration of the analytical sample. From these data, the minimum detectable quantity (MDQ) was calculated for each compounds. For benzene this amounts to 7.5×10^{-14} g, which corresponds to a concentration of 40 ppb for an injected volume of 0.5 μl (results of 100 ppb mixtures of benzene and chloroform are included in Fig. 6). Lower analyte concentrations (<40 ppb) can be determined by increasing the sample volume and/or the signal integration time. However, larger volumes (>2 μl) cannot be injected without degrading column resolution. The problem can be overcome by sweeping the sample from an injector valve and cryofocusing the volatile organic compounds at the head of the column, thus, removing the air. The temperature of the column can then be programmed for subsequent analysis.

A series of mixtures of chloroform and benzene of various concentrations (0.1 - 100 ppmv) in air was prepared to study the dependence of mass spectral intensity on concentration. These mixtures were injected onto the GC column and their mass spectra were measured. In Fig. 6, the sum of the intensities of a single mass (m/z = 83, characteristics of chloroform) and also of a group of masses (76-78 amu characteristics of benzene) contained in frames of the respective GC peaks have been plotted. The intensity is found to increase linearly with concentration showing a linear dynamic range of $>10^3$. This is the range with a constant integration time of 250 ms. It is possible to further extend the dynamic range by suitably adjusting the signal integration time. The straight lines in Fig. 6 are the least square fit through the data points. A linear-correlation coefficient equal to 0.99 is found for mass spectral measurement of benzene showing an excellent correlation between concentration and intensity.

CONCLUSIONS

A GC-MS system using a microbore column (50 μm i.d.) and a miniaturized mass spectrograph

with an array detector has been developed. The performance of this system in the analysis of mixture of priority pollutants has been demonstrated. A short microbore column (50 μm i.d., 3.0 in. long), when combined with the MS-EOID, resolves the early eluted gases satisfactorily. The GC-MS system described above possesses high sensitivity and a linear dynamic range of $>10^3$. The minimum detectable quantity (MDQ) for benzene is found to be 7.5×10^{-14}g which corresponds to a concentration of 40 ppmv in a sample volume of 0.5 μl. Larger sample volume can allow measurement of lower concentrations. The combination of a microbore column and a miniaturized focal plane MS is eminently suited for field measurements. The extremely small carrier gas flow rate drastically reduces the mass and power needs of the mass spectrograph.

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TABLE 1

Compounds	Peak No. (Fig. 3)
air	1
dichlorodifluoromethane	2
chloromethane	3
bromomethane	4
chloroethane	5
dichloromethane	6
1, 1, 1 - trichloroethane	7
chloroform	8
benzene	9
trichloroethylene	10

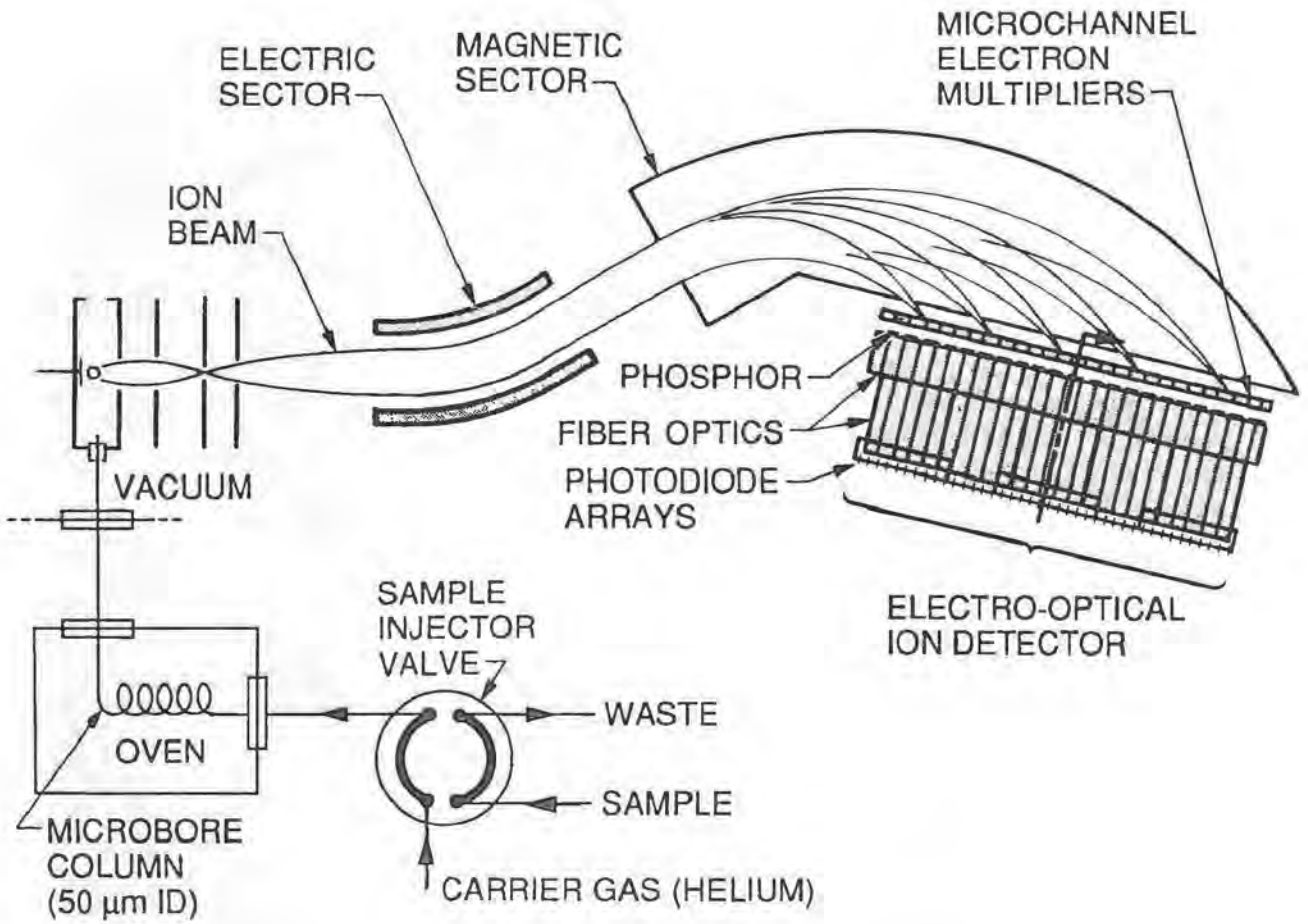

Fig. 1 Schematic of the microbore capillary column gas chromatorgraph and the focal plane mass spectrograph assembly. The sample injector is pneumatically actuated and is provided with pilot valves and a digital valve interface for fast sample injection.

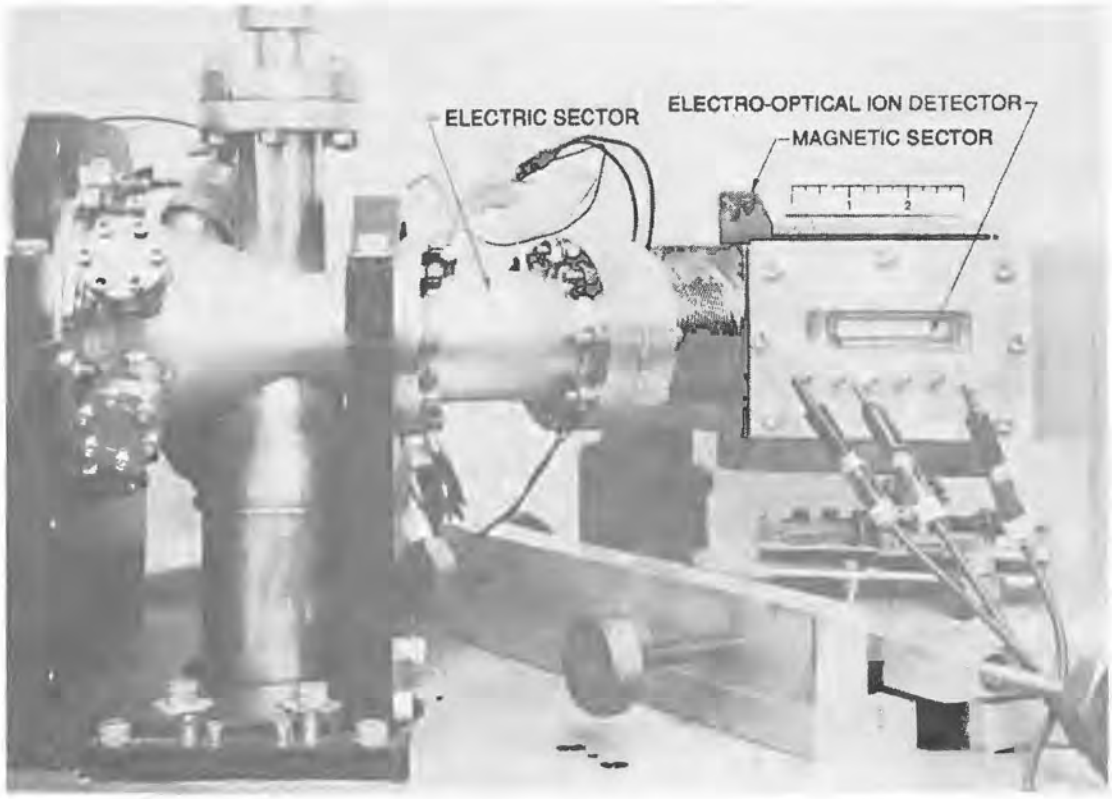

Fig. 2a: Photograph of the focal plane (2.0-in) mass spectrograph with an electro-optical ion detector.

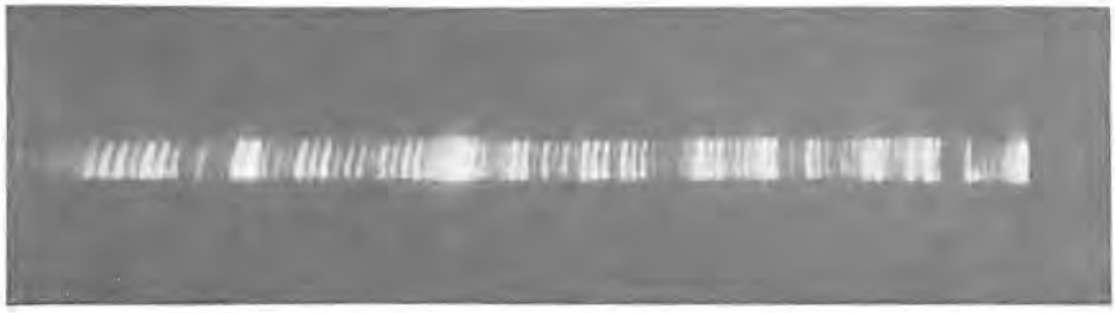

Fig. 2b: Photograph of ion images

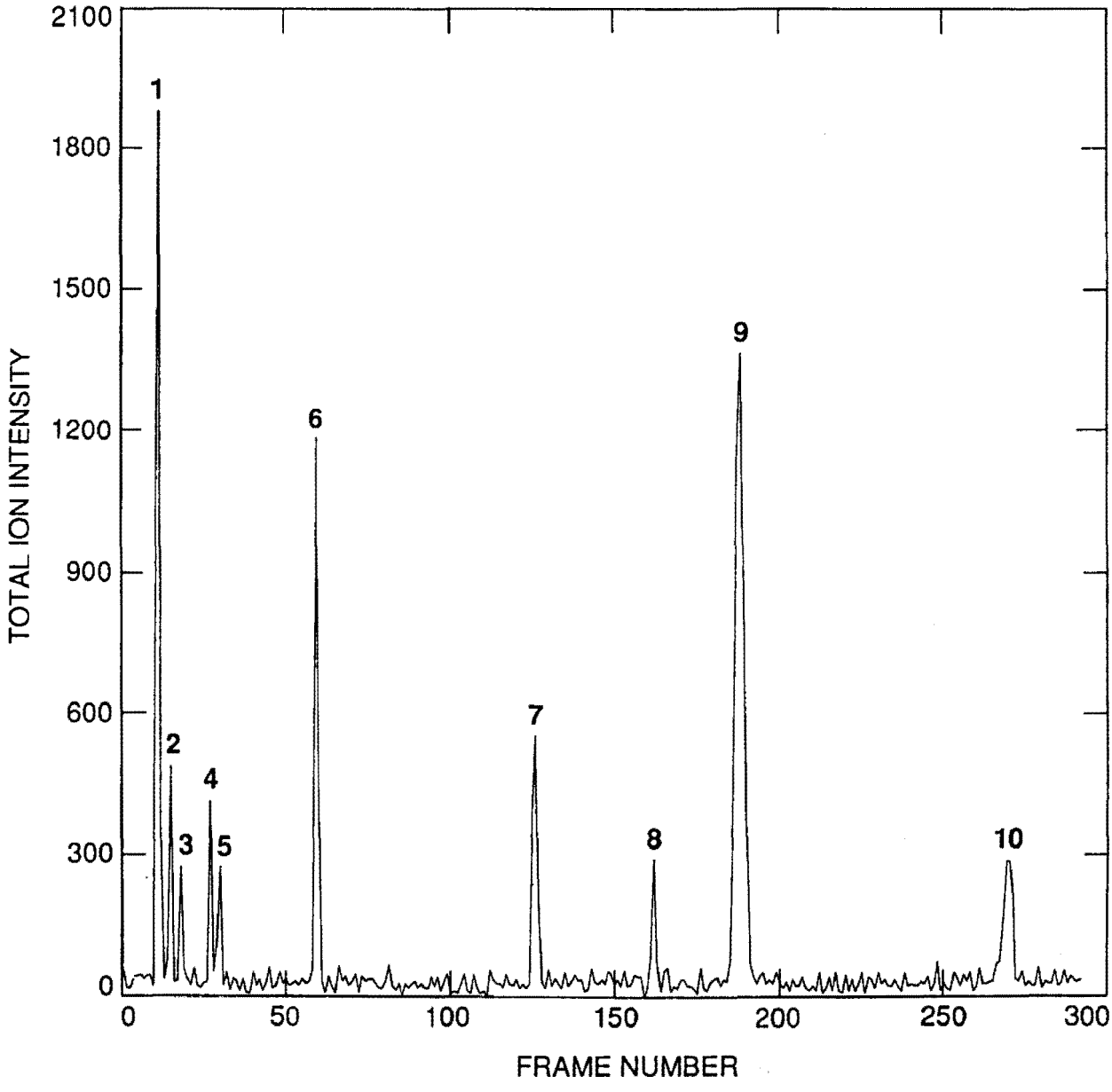

Fig. 3: Total ion chromatogram obtained from a mixture of compounds listed in Table 1. Each component in the mixture has a concentration of 1ppmv. A sample volume of 0.5 µ l was injected, and a signal integration time of 250 µs was used for each frame.

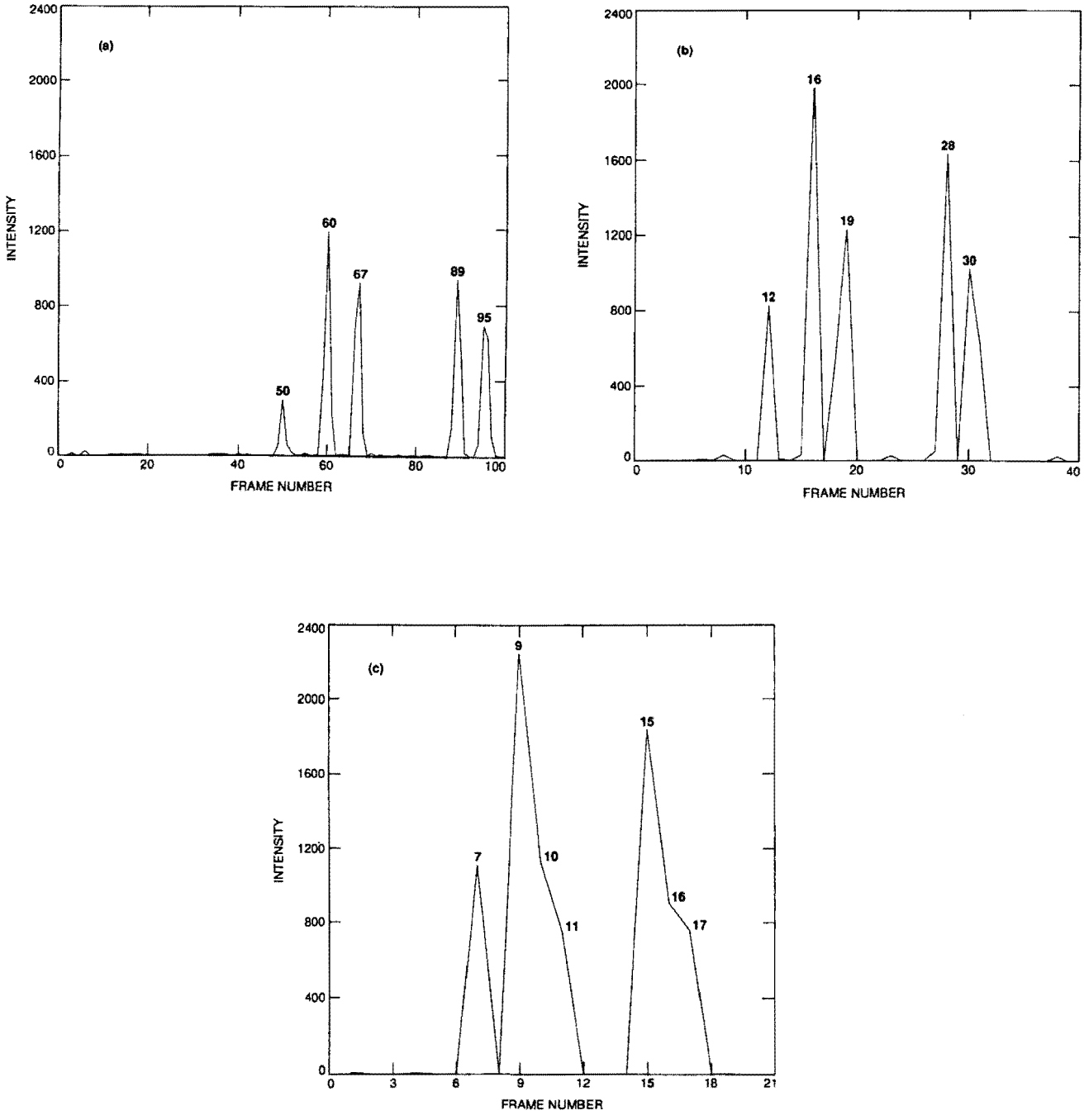

Fig. 4 Effect of signal integration time on resolution of GC peaks. Integration times of 100, 250, and 500 μs were used for a frame in (a), (b), and (c), respectively. The peaks corresponding to dichlorodifluoromethane and chloromethane, and bromomethane and chloroethane are not resolved with 500 μs integration time.

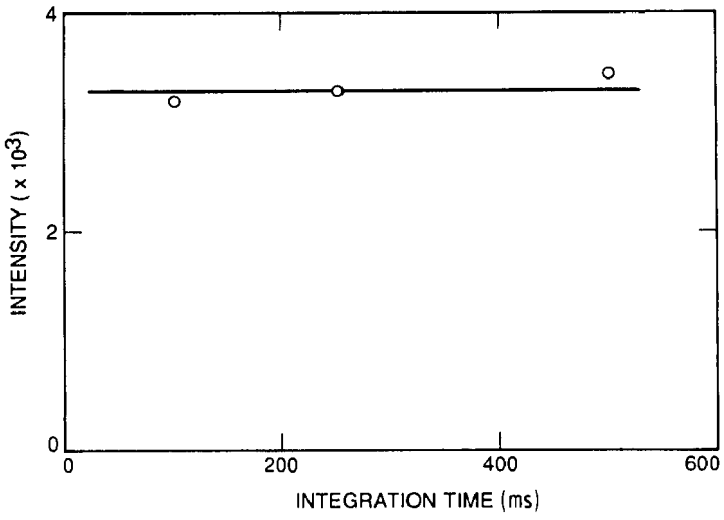

Fig. 5 Sum of the intensities of the frame comprising the last two peaks in Figs. 4 a, b, c are plotted against their frame integration time. The sum is found to be independent of the integration time.

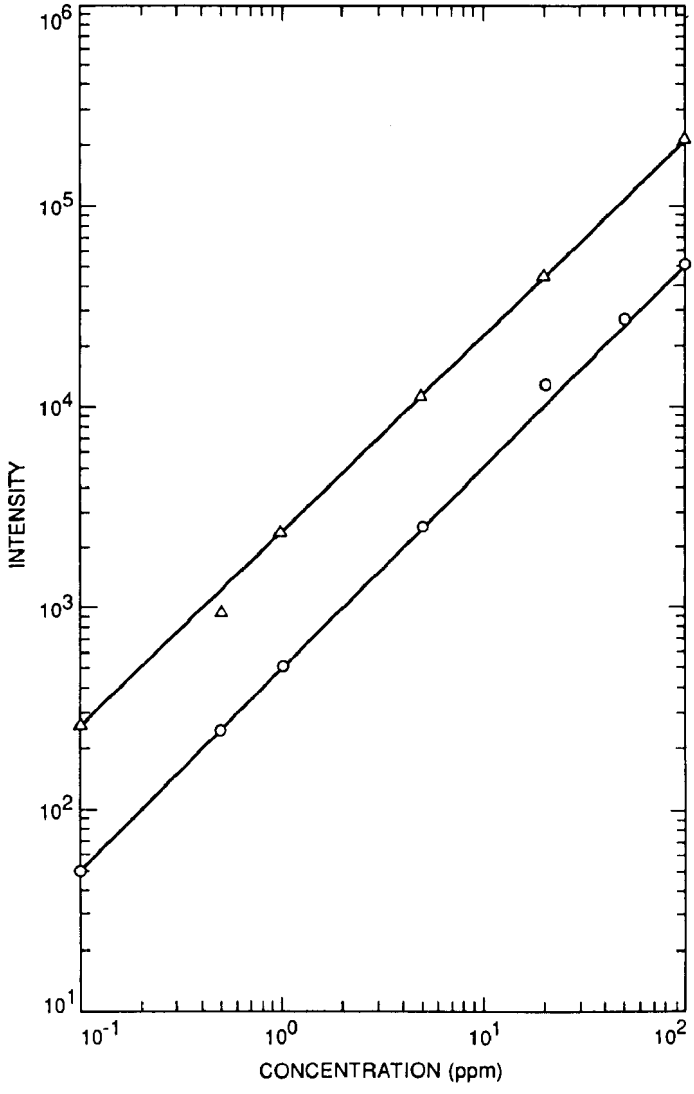

Fig. 6 The straight line plots show a linear dynamic range of $>10^3$ Os represent the sum of intensities in various frame of mass 83 (characteristic of chloroform) where as Δs represent the sum of intensities for a group of masses 76-78 (characteristic of benzene).

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