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## CAPILLARY COLUMN GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC–COMPUTER ANALYSIS OF ENVIRONMENTAL SPILLS

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### SUMMARY

Two samples taken from the sites of environmental spills were analyzed by computerized gas chromatography–mass spectrometry utilizing packed and capillary chromatographic columns.

An oil spill sample was compared with a sample from a possible source by examining specific ion profiles from both. A sample from a spill involving an industrial discharge was examined for the presence of specific types of compounds by examining characteristic ion profiles.

The capillary columns provided greatly improved chromatographic separations compared to packed columns.

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### INTRODUCTION

Packed column gas chromatograms have been useful in the matching of oil spills and oil samples from suspect sources; however, it has not always been possible to differentiate samples of similar oil types. Capillary column gas chromatography (GC) of complex hydrocarbon mixtures has been shown by Grob and Grob<sup>1</sup> to provide greater resolution than packed column GC. Previous work in this laboratory<sup>2</sup> has shown the ability of computerized GC–mass spectrometry (MS) to serve as retrospective specific GC detectors in detecting low level components of complex mixtures.

The present work was undertaken to determine the utility of capillary column GC combined with computer-controlled low-resolution MS in matching suspects with spills. Two environmental spills that had previously been analyzed utilizing packed GC columns were selected as candidates for this examination.

### EXPERIMENTAL\*

The GC–MS–computer system utilized was a Finnigan 9500 GC, 3200 EI/CI

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\* Mention of commercial products does not constitute endorsement or recommendation for use by the Environmental Protection Agency.

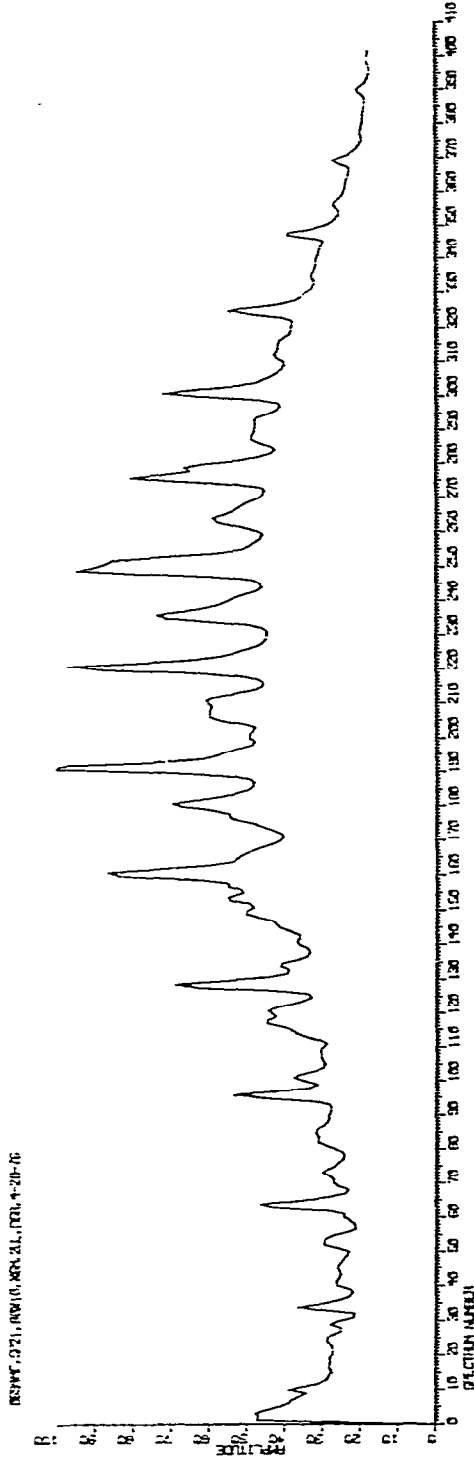


Fig. 1. TICP of an oil spill analyzed on a packed column with EI-MS.

chemical ionization (CI) mass spectrometer interfaced to a System Industries System 150 data system. The gas chromatograph was equipped with a Grob type injector<sup>1</sup> and was interfaced to the mass spectrometer with a 45-cm platinum capillary coaxial inside a 0.3175 cm O.D., glass-lined stainless-steel tube. (The use of noble metal interfaces can lead to chromatographic problems in certain circumstances<sup>3</sup>; however, the liquid phases utilized and the type compounds examined in this work do not appear to be affected.) The CI reagent gas was introduced into the ion source through the stainless-steel tube surrounding the platinum capillary. A 34-m glass capillary column coated with SE-30 fabricated at the Athens Laboratory and a 33-m glass support-coated open tubular (SCOT) column with OV-17 liquid phase supplied by Scientific Glass Engineering (Austin, TX, U.S.A.) were used in the study.

The system used for packed column analysis was a Finnigan 1015 gas chromatograph-mass spectrometer interfaced to a System 150 data system. The column used was a 250 cm × 2 mm I.D. glass column packed with 3% Supelco SP-2100 on Supelcoport (80-100 mesh). The gas chromatograph to mass spectrometer interface was a glass jet separator.

For the oil spill samples, the capillary column system was run in CI mode with methane as the reagent gas and helium as the carrier gas. The CI mode was selected because it gives better molecular weight information than electron impact (EI) for aliphatic hydrocarbons; the  $M - 1^+$  ion in CI is stronger than the  $M^+$  in EI. Indicated source pressure was 800  $\mu$ m; scan range was  $m/z$  66-420 with an integration time of 4 msec per mass and a settling time of 2.3 msec per mass. A 1.5- $\mu$ l injection was made with the septum wash valve of the Grob injector closed and the column oven at ambient temperature (approximately 25°C). The valve was opened 30 sec after injection and left open. The oven was heated rapidly to 50°C one minute after injection and programmed to 230°C at a rate of 4°C/min; the injection port pressure was 30 p.s.i.g.

The MS data acquisition parameters resulted in the acquisition of mass spectra at the rate of approximately one spectrum every 2.2 sec. Because the GC peaks were approximately 9 sec wide at the beginning of the GC run, this scan rate was not fast enough to utilize all the resolution offered by the helium carrier and tuning the source at low pressure. The scan range was from  $m/z$  41 to 430 with an integration time of 4 msec per mass and a settling time of 2.3 msec per mass. Spectra were acquired at the rate of approximately 24 per minute. The GC program and injection procedure was the same as with the oil spill samples.

## RESULTS

### *Oil spill*

An MS total ion current profile (TICP) of an oil spill sample obtained on a packed column in the EI mode by the Surveillance and Analysis Division of EPA Region IV is shown in Fig. 1. This oil spill sample and a sample from a possible source were then run on the capillary system in order to obtain fingerprints having more points of comparison than the packed column analysis. Fig. 2 shows the TICPs in the CI mode of the spill and the possible source.

The spectra acquired on the packed column system were scanned at a slower rate because the chromatographic peaks were wider. The total analysis times were

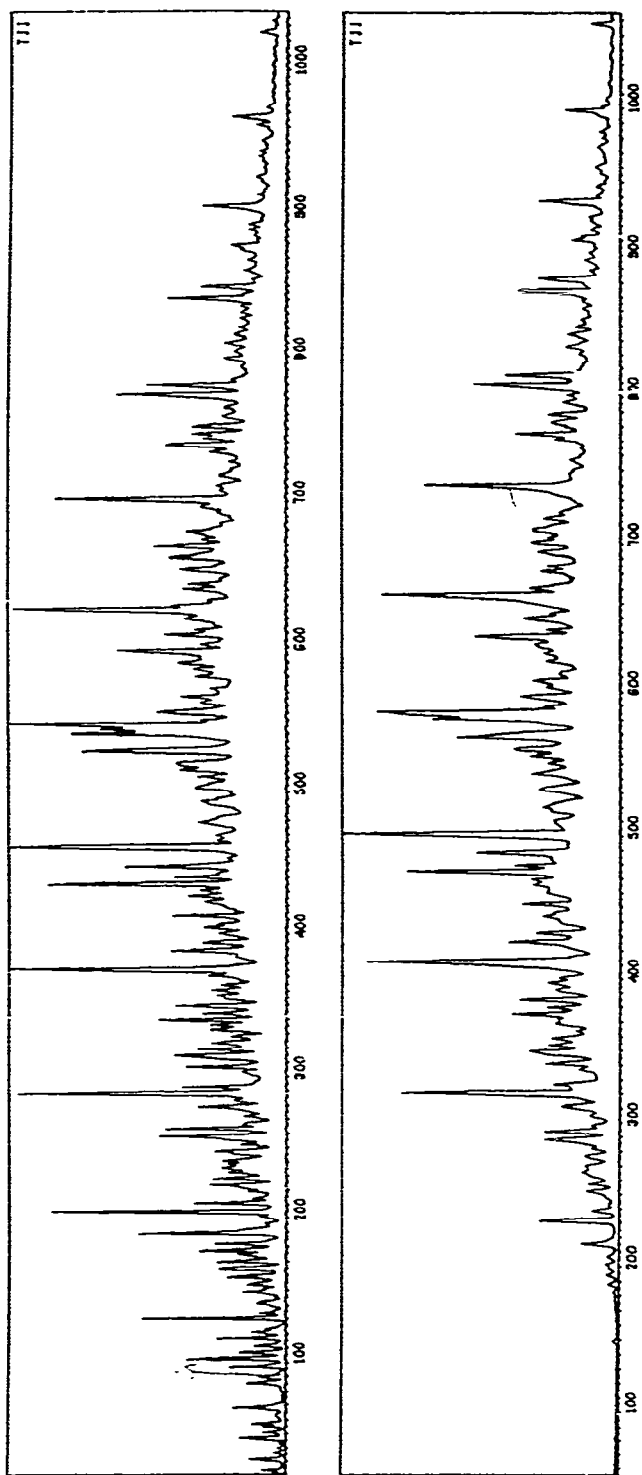


Fig. 2. TICs of an oil spill (bottom) and a possible source analyzed on a capillary column with CI-MS.

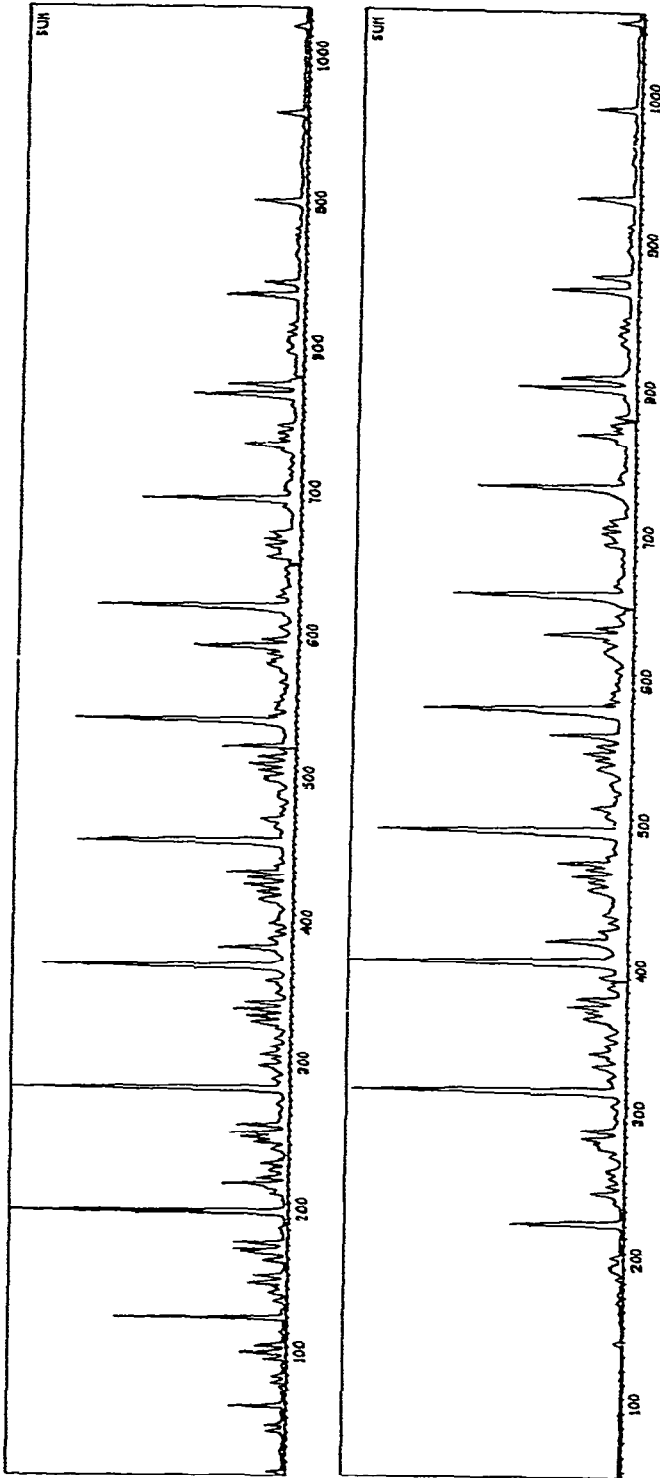


Fig. 3. Summation of  $m/z$  71 and 85 for an oil spill (bottom) and a possible source analyzed on a capillary column with CI-MS.

comparable in all three TICPs. A comparison of the TICPs in Fig. 1 and 2 shows that the capillary column resolved many more peaks than the packed column.

The traces in Fig. 2 have many similarities. The one major difference—the lack of chromatographic peaks before spectrum number 160 in the spill sample—was attributed to weathering and evaporation losses. The large number of peaks in these two TICPs made visual comparison rather difficult, so extracted ion current profiles (EICPs) of masses characteristic of certain classes of compounds were plotted. EICPs are plots of the intensity of individual masses by spectrum number. Peaks indicate compounds that may be members of the class of interest. If the intensities of two or more characteristic ions are summed and plotted by spectrum number, peaks are more likely to indicate compounds of the class of interest than are single ion peaks.

Fig. 3 shows profiles generated by summing the intensities of  $m/z$  71 and 85. These masses are characteristic of the methane CI spectra of aliphatic hydrocarbons<sup>4</sup>. Compared with Fig. 2, the specificity of the profiles is increased, the number of peaks is reduced, and comparison of the spill with the possible source is simplified.

Similarly, Fig. 4 shows a portion of the profiles generated by summing the intensities of  $m/z$  129, 143, and 157. These masses are characteristic of the methane CI spectra of naphthalene, methylnaphthalene, and dimethyl- or ethylnaphthalene<sup>5</sup>. These profiles provide a further basis of comparison.

#### *Industrial spill*

The second spill analyzed was an industrial discharge involving chlorinated compounds in addition to hydrocarbons. The TICP of the spill and an EICP for  $m/z$

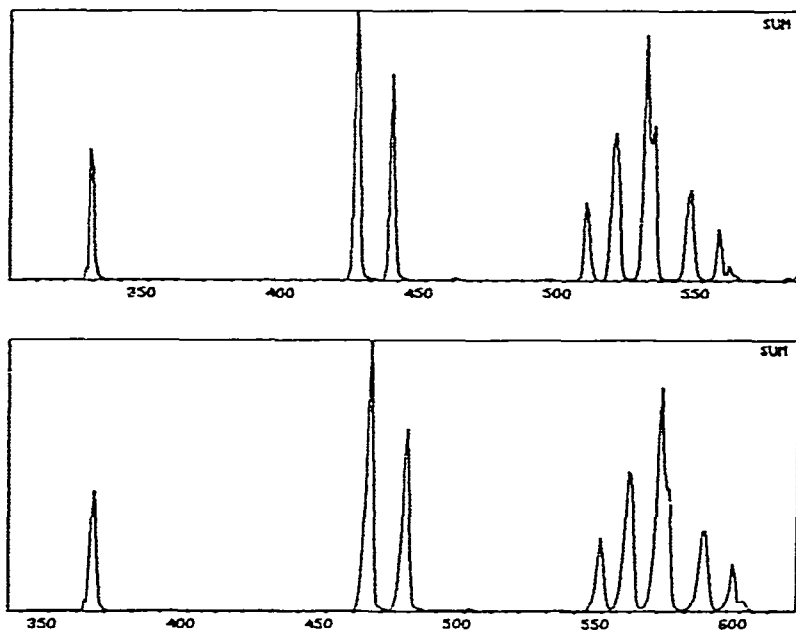


Fig. 4. Summation of  $m/z$  129, 143, and 157 for an oil spill (bottom) and a possible source analyzed on a capillary column with CI-MS.

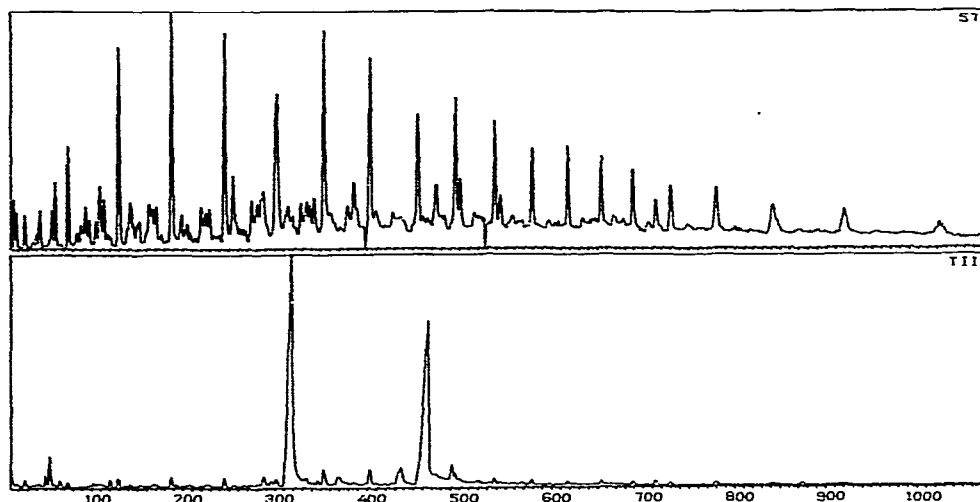


Fig. 5. TICP and EICP for  $m/z$  57 for an industrial spill and analyzed on a capillary column with EI-MS.

57 are shown in Fig. 5. The large chromatographic peaks at spectrum numbers 310 and 450 in the TICP reflect the presence of chlorinated compounds at much higher concentrations than the other components in the sample.

Since the TICP is dominated by two large chromatographic peaks, other characteristics of the sample are not apparent. The ion at  $m/z$  57 is characteristic of the EI mass spectra of aliphatic hydrocarbons<sup>6</sup>; therefore, that EICP was obtained to

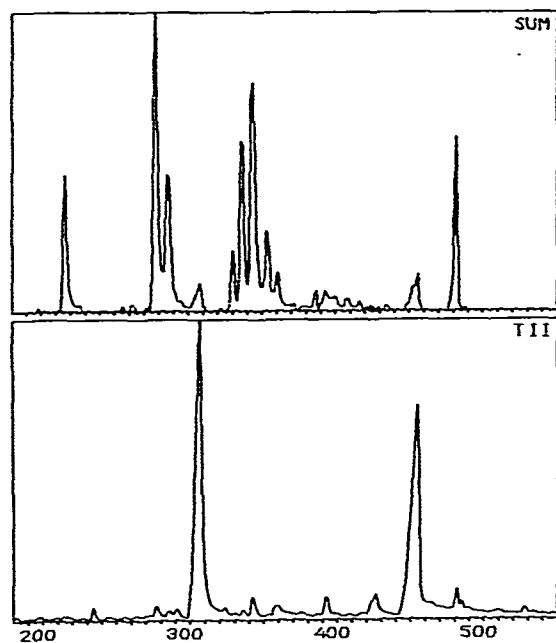


Fig. 6. TICP and summation of  $m/z$  128, 142, and 156 for industrial spill analyzed on a capillary column with EI-MS.

check for the presence of petroleum products. The mass spectra of the chlorinated compounds have no significant intensity at  $m/z$  51, so there is minimal response to them in this trace. The  $m/z$  57 profile in Fig. 5, therefore, suggests the presence of oil, which is not evident in the TICP.

Similarly, Fig. 6 shows a comparison of a portion of the TICP to the same portion of the profile as a result of the summation of  $m/z$  128, 142, and 156. These masses are characteristic of the EI mass spectra of naphthalene, methylnaphthalene, and dimethyl- or ethylnaphthalene<sup>7</sup>. These components are indistinguishable in the TICP, but clearly defined in the summation profile and further suggest the presence of oil in the sample.

#### CONCLUSIONS

These examples illustrate the power of computerized MS as a detector in capillary column gas chromatography. From stored data, characteristic profiles can be generated for the comparison of different samples or the examination of individual samples to identify specific classes of compounds. Mass spectra of each chromatographic peak are available for more exact identification of the peak, and archival storage of the data permits future examination if additional information is required.

#### ACKNOWLEDGEMENTS

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