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SELECTED-ION MONITORING ANALYSES OF ENVIRONMENTAL SAMPLES USING IMPROVED SOFTWARE

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SUMMARY

Computer programs have been written which significantly increase the storage capabilities of a low-cost gas chromatography-mass spectrometry (GC-MS)-calculator system. These programs convert raw selected ion monitoring (SIM) data to a more compact form and allow the storage of fourteen 60-min GC-MS analyses on disks which were previously limited to four analyses. SIM data can be displayed by means of an interactive program which uses an x - y plotter. The total ion current and mass chromatograms generated during operation of the GC-MS system in scanning mode can be displayed on the same plot as SIM analyses with this versatile program. In addition, the sum of SIM ion abundances, analogous to a scan run total ion current trace can be displayed or integrated. The software was used in a GC-MS analysis of organic compounds extracted from a ground water leachate sample taken at a municipal dumpsite.

INTRODUCTION

The selected ion monitor (SIM) mode of operation of a gas chromatograph-mass spectrometer-computer system is a valuable tool for the analysis of complex mixtures of trace organic compounds. In this mode, a mass spectrometer is consecutively tuned to each of several pre-selected ions for a specified dwell time. A survey of compounds present in a sample can be made by selecting ions indicative of various compound classes. Detection limits at the parts-per-trillion (ppt)* level can be achieved for specific compounds in the types of complex organic mixtures generally found in the environment.

The large amount of data produced by a gas chromatography-mass spectrometry (GC-MS) instrument has been handled by data systems which have generally

* Throughout this article the American trillion (10^{12}) is meant.

been based on powerful minicomputers and hard disk data storage¹. The Hewlett-Packard (HP) 5992A GC-MS/calculator system is different in that it was designed to be a low-cost compact unit without sacrificing essential functions². The data system consists of a calculator with data storage on floppy disk. Although these disks are inexpensive and have found widespread use on many small GC-MS systems, they are slower than hard disks and have limited storage capacity. Typically, floppy disks can store from 100 to 1000 kilobytes (Kbytes) of data as compared to 10 to 100 Megabytes (Mb) for hard disks.

Analysis of environmental samples which contain many unidentified compounds generate large amounts of data. Using manufacturer-supplied software only four 60-min selected ion monitoring (SIM) analyses could be stored on one disk. There was a need to increase this number to reduce the large number of disks used to store the data accumulated from many analyses and to determine quickly which classes of compounds are present as well as identifying and quantifying particular components. New data display techniques were necessary to make detection of compound classes and correlations between SIM and scan analyses more apparent.

Large-disk storage can alleviate the storage problem. However, the cost of these devices is high, which defeats the purpose of the lower priced system. An alternative is for users to develop their own specialized data storage and retrieval software³. The usefulness of user-developed software has been demonstrated with an algorithm which automatically identified compound classes from GC-MS data⁴. A program called Dual Mode (DM), which allows the storage of six mass chromatograms (MC) and total ion current (TIC) for subsequent display on an X-Y plotter in addition to mass spectra of eluting peaks, has also been demonstrated⁵. A versatile plotting program was an important feature of DM since it allowed comparison of TIC's and MC's from different analyses on a single plot.

Programs are presented which store SIM data in one-quarter the space previously required. Repetitive scan and SIM data can be displayed on the same plot using a flexible iterative program driving an X-Y plotter. The sum of the ion abundances monitored can be plotted *versus* retention time or integrated. This software was used for the analysis of organic compounds which have been extracted from ground water leachate from a municipal dump site.

EXPERIMENTAL

Instrumentation

The HP 5992A GC-MS-calculator system was equipped with an HP 9826A X-Y plotter and two HP 9885 floppy disk drives. The 5992A consists of an HP 5990A gas chromatograph-mass spectrometer, HP 9825B calculator and an HP 9866B thermal printer-plotter.

Floppy disks were used to store programs and data. Calculator storage consists of 64 Kbytes random access memory (RAM). A single floppy disk contains 457.5 Kbytes of usable storage.

Program description

Computer programs were written in a high-level language called HPL, which is similar to BASIC⁶. Original SIM data acquisition and processing software was

supplied by the manufacturer. Compression and output of data required the development of five programs.

Packed SIM data acquisition software. The HP SIM data acquisition program uses a full-precision binary-coded-decimal (BCD) word (8 bytes) for ion abundance values. However, when performing trace analysis abundances seldom reach the maximum integer value, 32,768, which can be stored on this system. The acquisition program was modified to convert BCD SIM data to a signed-binary-integer (packed) format in which each value occupies two bytes of memory. Retention times are multiplied by fifty before conversion to retain 0.02-min precision. Abundance values below 300 counts are multiplied by negative one hundred before conversion to avoid introduction of quantizing noise. This noise arises from the loss of the fractional part of the abundance value upon truncation to integer precision.

SIM DM plotting software. Plotting software had previously been developed to display data obtained with the DM scan software on an X-Y plotter⁵. This program was modified to plot full-precision SIM and/or packed SIM data in addition to the TIC and MC's on the same plot. One additional feature is the ability to sum ion abundances from a SIM run and plot the SIM total ions (STI) as a function of retention time. Manufacturer-supplied software could only plot the abundances of individual ions. The program will also subtract a constant value from each abundance before plotting. This option is used when plotting a vertical expansion of a portion of a trace where the baseline abundance is high. The baseline can be dropped to the time axis, allowing more useful information to be displayed.

Packed SIM processor. The SIM integration and plotting software supplied by the manufacturer was modified to read data stored in packed format.

Total ion SIM processor. The SIM single ion integration and plotting software supplied by the manufacturer was modified to integrate the STI trace.

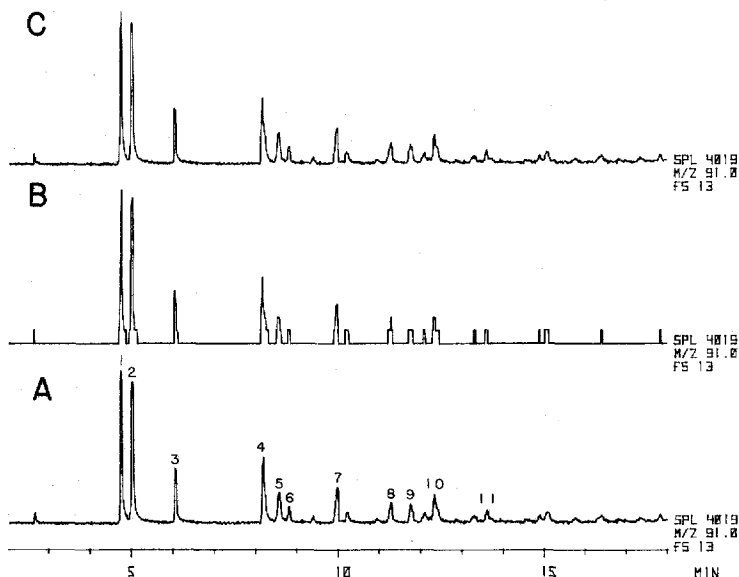


Fig. 1. Data from the SIM analysis of a leachate extract for alkylbenzenes showing the effect of quantizing noise introduced during conversion to packed format. This noise was reduced using an improved algorithm. Numbered peaks are identified in Table I.

TABLE I
COMPARISON OF INTEGRATED PEAK AREAS

NI = Not integrated.

Peak No.	Retention time (min)	Integrated peak areas			Component
		BCD	Packed	Improved	
1	4.8	661	517	661	Ethylbenzene
2	5.1	587	465	586	Xylene
3	6.1	232	258	231	Xylene
4	8.2	407	194	393	Propylbenzene
5	8.6	189	NI	189	Ethyltoluene
6	8.8	78	NI	79	Trimethylbenzene
7	10.0	241	NI	239	Trimethylbenzene
8	11.3	127	NI	137	Trimethylbenzene
9	11.8	98	NI	98	Methylstyrene
10	12.3	210	NI	212	Methylpropylbenzene
11	13.6	52	NI	94	Dimethyldiethylbenzene

SIM packed data compression software. A large amount of data had been collected using manufacturer-supplied software. A program was written to read BCD SIM data, convert it to packed format and write it to a data file residing on a disk in the second disk drive.

Analysis of samples

A dichloromethane extract of ground water leachate from a municipal dumpsite was analysed using this software. Chromatographic conditions were: column, 30 m × 0.30 mm I.D. DB-1701 fused silica (J. & W. Scientific, Rancho Cordova, CA, U.S.A.); helium carrier-gas flow 3 ml/min; injection port, 30°C; GC oven held isothermal at 40°C for five min then programmed to 250°C at 4°C/min. In scan mode the quadrupole mass spectrometer was scanned from 400 a.m.u. to 40 a.m.u. at a rate of 630 a.m.u./sec; at this rate spectra were taken every 0.84 seconds. In SIM mode, dwell times were 50 msec, giving a cycle time of 0.79 seconds. For both SIM and DM analyses the ions of m/z values 69, 83 (cyclic aliphatics), 91, 105, 119 (alkylbenzenes) and 128 (naphthalene) were selected. A glass-lined restrictor with a flow of 0.5 ml/min, was employed as the gas chromatograph-mass spectrometer interface.

RESULTS AND DISCUSSION

SIM data which are converted to packed format can be stored in 25% of the space required by the BCD data. A full four-fold increase in available disk space was not obtained because a file header for each analysis consisting of dwell times, ion m/z values and maximum abundances is required, and these data were left in BCD format. This header is stored in the first 512 bytes of each SIM file. Typically, one floppy disk can store data from four 60-min analyses, using the original manufacturer-supplied software. After converting data to packed format, data from fourteen 60-min analyses can be stored.

In packed format, abundances are limited numerically to values below 32,768

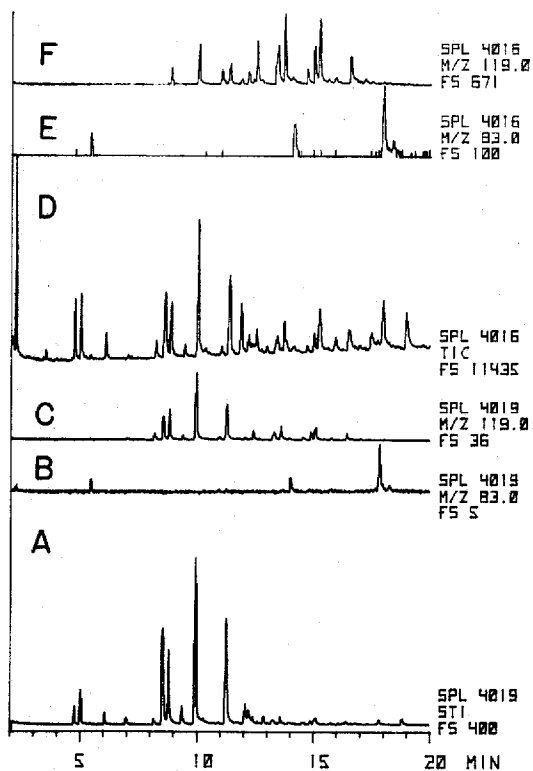


Fig. 2. Illustration of the flexibility of the plotting program in combining both scan and SIM-derived data on the same plot. The presence of alkylbenzenes and aliphatic compounds in a leachate extract are indicated by peaks in the SICP's, traces B and C, and in the MC's, traces E and F.

counts, since this is the largest integer that can be manipulated by the Hewlett-Packard 9825A calculator. However, with proper prescreening SIM abundances seldom reach this value. Gas chromatographic peaks which exhibit ion abundances of this magnitude during SIM operations are evidence of capillary column overloading or indicate the detector is being operated at a sensitivity which is higher than necessary. Therefore limiting SIM abundances to a maximum of 32,768 counts was not a limitation of the new software.

Truncating data to integer precision can introduce quantizing noise. This noise can cause both false early peak detection and a failure to detect the end of a peak when integrating the data. Quantizing noise was reduced by an improved algorithm in which all ion abundances below 300 counts are multiplied by a factor of negative one hundred before packing. The negative sign indicates that the stored value is to be divided by the factor before plotting or integration. Fig. 1 illustrates the effects of quantizing noise on the appearance of selected-ion current profiles (SICP) from the analysis of the leachate extract. The abundances of the ion of m/z 91, indicative of alkyl benzenes, are plotted against retention time. Numbered peaks are identified in Table I. Trace A was plotted using BCD data acquired with manufacturer-supplied software while trace B presents the same data after conversion to integer precision. Only unit changes can be observed in trace B giving a step-like appearance to peaks.

Small peaks appear as spikes. Trace C is from data stored using the improved algorithm. A summary of the results obtained by integrating the data in Fig. 1 is presented in Table I. Peaks numbered 5-11 were not detected in the integer precision data due to the additional noise. Integration of BCD and improved packed data yield nearly identical peak areas. The improved software gives greater flexibility for data display. Fig. 2 presents scan and SIM data from the analysis of the ground water leachate extract. Trace A, labelled STI, is the sum of the abundances of the six ions monitored. Manufacturer-supplied software only gave this trace in real time on a thermal printer-plotter. Traces B and C are SICIP's of ions of m/z 83 and 119, which are indicative of cyclic aliphatics and alkyl benzenes respectively. The results from a DM analysis of the sample are presented for comparison where trace D is the TIC and MC's for ions 83 and 119 are plotted as traces E and F. Relative amounts of the various peaks can be approximated by the full-scale (FS) abundance values for each trace shown on the right-hand side of the plot. The maximum abundance of the largest peak is used by the plotting program as a default value, although any value may be selected by the user. If desired, the time axis can be included in each trace. A sample run number assigned by the user at the time of the analysis is displayed on the right-hand side of the trace.

There are several qualitative differences between SIM and DM data which become apparent when plotted together. The STI, being more selective than a TIC, will generally show fewer peaks. This selectivity is at the expense of not detecting some compounds. The major TIC peak in Fig. 2 at 11.8 minutes is very small in the STI. This compound methylstyrene, does not contain ions of m/z 69 or 83 and contains ion m/z 119 as the base peak. Therefore ions to be monitored must be carefully chosen based on prior knowledge of the sample or a survey run in scan mode.

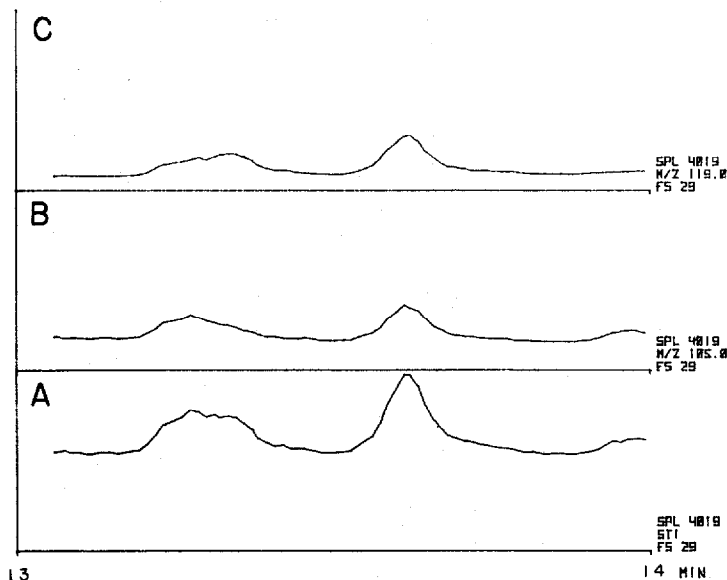


Fig. 3. A higher response is achieved by integrating the sum of the abundances of the ions monitored during a SIM analysis than by integrating each SICIP separately.

Plots derived from scan data may contain more noise than those plotted from SIM data. Noise can arise from the loss of low masses when the spectrum data buffer is filled, integer precision in mass peak abundances, changes in background ion composition and from the detector and amplifier electronics. An increase of electron-multiplier voltage to improve detection limit increases high-frequency electrical noise. Electronic filtering to remove this component can cause clipping of the mass peak and cause peak shape distortions⁷. In Fig. 2, traces B and E are derived from SIM and scan data respectively. The peak shapes in trace E are distorted by noise, mainly arising from integer precision abundances which is not present in trace B. The plot program allows the SICP to be displayed in place of the MC to aid in the classification of peaks in a TIC.

The MC and SIM traces for the m/z 119 ion exhibit some differences in relative peak heights and peak shapes. These differences are due to bias in repetitive scanning. Both methods have nearly equal cycle times but in scan mode a one-a.m.u. mass range is sampled for only 1.5 msec compared to 50 msec for SIM. Only if the mass analyser is tuned to the desired ion exactly at the peak maximum will the true peak height be measured. A SIM analysis has a much better chance of producing true concentration profiles.

Sensitivity in GC-MS-SIM analyses depends on the time taken to accumulate counts, known as dwell time, and the relative abundance of the chosen ion in a compound's spectrum. Greatest sensitivity is achieved when the base ion alone is monitored with a dwell time chosen to give six to ten readings across a chromatographic peak. The identity of an eluting compound is confirmed by monitoring several characteristic ions of the compound. However, sensitivity is lowered since the total dwell time is partitioned among several ions. Some sensitivity can be regained by integrating the sum of the abundances of the characteristic ions. Fig. 3 illustrates the technique for isomers of dimethyldiethylbenzene eluting between 13 and 14 min. The STI, trace A, has a higher response for the component at 13.6 minutes than either of the SICP's, traces B and C. Therefore an analysis using the STI would be more sensitive than one using either of the SICP traces.

Development of the programs here increased the capabilities of a GC-MS-calculator system past those supplied by the manufacturer. Storage capacity for GC-MS-SIM data was increased almost four-fold with no loss in analytical capability. Scan and SIM data from different analyses can be displayed together and compared. Because of the increasing emphasis on computerized equipment, enhancements such as described here are of growing importance to the analytical chemist. These programs may be obtained from the authors on request⁸.

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REFERENCES

- 1 F. W. Karasck, *Res. Develop.*, 25 (9) (1974) 42-48.

- 2 F. W. Karasek, *Res. Develop.*, 27 (11) (1976) 42-48.
- 3 A. L. Burlingame, C. H. L. Shackleton, I. Howe and O. S. Chizhov, *Anal. Chem.*, 50 (1978) 346R-384R.
- 4 J. T. Clerc, M. Kutter, M. Reinhard and R. Schwarzenbach, *J. Chromatogr.*, 123 (1976) 271-278.
- 5 L. C. Dickson, R. E. Clement, K. R. Betty and F. W. Karasek, *J. Chromatogr.*, 190 (1980) 311-319.
- 6 *HP 9825A Calculator Operating and Programming Manual (No. 09825-90000)*, Hewlett-Packard, Palo Alto, CA, 1976.
- 7 B. S. Middleditch and D. M. Desidero, *Anal. Chem.*, 45 (1973) 806-808.
- 8 L. C. Dickson, *M.Sc. Thesis*, Department of Chemistry, University of Waterloo, September, 1983.