

CHROM. 12,532

SOFTWARE IMPROVEMENTS FOR GAS CHROMATOGRAPHY-MASS SPECTROMETRY-CALCULATOR SYSTEM USED IN THE ANALYSIS OF TRACE ORGANIC COMPOUNDS FROM ENVIRONMENTAL SAMPLES

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(Received October 22nd, 1979)

SUMMARY

Computer programs are described which have significantly increased the capabilities of a low-cost gas chromatography-mass spectrometry (GC-MS)-calculator system. These programs allow storage on floppy disk of ion abundance and retention time data for the total ion current and as many as six mass chromatograms in addition to mass spectra taken at the top of eluting GC peaks. Manufacturer-supplied software was only capable of storing the mass spectra. Ion abundance data may be displayed by means of a flexible, interactive program which uses an x - y plotter. Both qualitative and quantitative analyses may be performed for selected compounds in a single GC-MS run. Examples of the use of this software in the analysis of benzene extracts of incinerator fly-ash samples are presented.

INTRODUCTION

The combination of the techniques of gas chromatography (GC) and mass spectrometry (MS) presents a valuable tool for the analysis of complex mixtures of organic compounds. Addition of a computer to GC-MS instrumentation has substantially increased the capabilities of the GC-MS technique, since instrument operation, data acquisition and data manipulation functions can all be controlled by the computer with speed, precision, and minimal operator intervention. By as early as 1972, nineteen different commercial GC-MS-computer units were available¹. Due to the large amounts of data that can be quickly generated by the GC-MS-computer system, the trend has been towards powerful minicomputers with large data storage capabilities. Some GC-MS-computer systems are capable of performing repetitive mass spectral scans and storing each scan taken during a GC run². Such systems can generate reconstructed gas chromatograms (RGC) and mass chromatograms (MC) from the stored mass spectral data.

The ability to display the RGC after or during a GC-MS run is a valuable asset for the analysis of complex mixtures such as those which arise from samples of environmental origin. This is especially true when comparing different runs, since

many components at low levels or components not well resolved chromatographically may be observed in the RGC, even though mass spectra for such components are not obtained. Therefore characterizing the overall chromatographic pattern can be an important part of the analytical procedure^{3,4}.

Generation of MC is one of the most useful analytical features of systems that store every mass spectrum taken during a GC-MS run⁵. By judicious choice of ions that are plotted compounds present at very low concentrations may be detected that otherwise would have been missed. A MC, which is a plot of the unnormalized intensity of one specific ionic mass *versus* spectrum scan number, does not provide the high sensitivity of selected ion monitoring (SIM) in which only the chosen ionic mass values are monitored by the mass spectrometer. However, for SIM analysis no mass spectra are obtained.

The trend towards larger GC-MS-computer systems was reversed with the introduction of the Hewlett-Packard 5992A GC-MS system for which operation and data handling are controlled by a sophisticated calculator⁶. Unfortunately, the limited data storage media with which this low-cost system is equipped (tape cassette and floppy disk) make the feasibility of storing every mass spectrum taken during a GC-MS run impractical. The RGC and one MC are output in real-time on a thermal printer, but comparison between runs is difficult, particularly since timing marks are printed on the output and not actual times.

To approach the capabilities of the more expensive GC-MS systems, a series of computer programs were written which enable the acquisition and storing of the RGC as well as six MCs in real-time on a single floppy disk. Mass spectra taken at the top of eluting GC peaks are also saved. Stored ion abundance data may be plotted at the end of the run on an *x-y* plotter as ion abundance *versus* retention time. The software improvements are presented here, as well as an example of the use of the improved system for the analysis of organic compounds which have been extracted from municipal incinerator fly-ash samples.

EXPERIMENTAL

Instrumentation

The GC-MS system used was a Hewlett-Packard (HP) 5992A GC-MS-calculator system, equipped with an HP 9862A X-Y plotter and HP 9885M single floppy disk drive. The HP 5992A consists of an HP 5990A GC-MS, HP 9825A calculator and HP 9866B thermal printer-plotter.

Tape cartridges are used to store programs which can be input into the calculator memory from a tape drive located on the calculator. Calculator storage consists of 24 K bytes RAM plus 280 K bytes on one tape cartridge. A single floppy disk contains 457.5 K bytes of useable storage.

Program description

Computer programs were written in a high level interactive language called HPL, which is similar to Basic⁷. Initial software supplied by Hewlett-Packard was extensively modified to allow storage of MCs, the RGC as well as mass spectra taken at the top of an eluting GC peak. The modified data acquisition software is referred to as dual-mode (DM).

Acquisition, storage and output of data required the development of several programs, including a disk file marking program, DMDISKMARK, and plotting program, DMXYPLOT. The acquisition software was too large for the calculator's memory and was consequently split into two smaller programs, DM startup (DMSTART) and DM data acquisition (DMDATAC).

(i) DMDISKMARK: This program marks two types of data storage areas on a flexible disk. One area is used to store mass spectra and the second area is reserved for total ion abundance (TIA) and MC data. In effect, some mass spectral data is sacrificed in favour of having the TIA and MC data stored. An option in the program allows the ratio of mass spectral data storage space to TIA and MC storage space to be set by the user. Typically, a disk marked only for mass spectral storage can store about 450 mass spectra, each containing a maximum of 250 peaks. By marking the disk for 350 spectra, the remaining storage is sufficient to save six MCs and the TIA for four 50-min long GC-MS runs. DMDISKMARK occupies 2600 bytes of calculator memory.

(ii) DMSTART: GC-MS parameters are input and stored by this program which must be executed before the data acquisition program. Although it occupies only 2752 bytes of calculator memory, DMSTART was necessary since sufficient useable calculator memory was not available to hold both DMSTART and DMDATAC. Run parameters are stored on disk and tape, where they can be accessed by DMDATAC.

(iii) DMDATAC: This program controls the actual data acquisition and storage on floppy disk. A simplified flow chart for the procedure is given in Fig. 1. Before the start of the run, ion masses to be monitored are input in the initialization step. During the GC-MS run, mass spectra are continually produced and those taken at the top of eluting GC peaks are stored on floppy disk. A background spectrum is also stored at the point of lowest abundance between detected peaks for later background subtraction.

For each mass scan made, the retention time, TIA for that scan, and selected ion abundances are stored in a buffer in the calculator memory. The retention time and TIA are printed on heat-sensitive paper, as well as one MC, as the run progresses. When the calculator buffer (1024 bytes) is full, the retention time and ion abundance data are written onto floppy disk, and this process is repeated until the run time expires or the run is terminated by the user from the calculator keyboard.

The location on floppy disk of each run is stored in a disk file directory which includes initial and final disk storage locations, sample run number, date of the run, number of ions monitored and amount of data stored for the run. If the disk storage area becomes filled before completion of a run, a message is printed for the operator and DMDATAC will save only mass spectral data from this time until the end of the run.

At the end of a GC-MS run, several functions are available to the user. Background spectra may be subtracted from corresponding peak spectra; a new run may be started using the same run parameters (reinject), or different parameters (restart); mass spectra stored on disk may be plotted (plot-tabulate); mass spectra may be matched with reference spectra from a tape library; or the tape manager may be accessed. From the tape manager, a program to plot the stored total ion and MC data using the x - y plotter (DMXYPLOT) can be run.

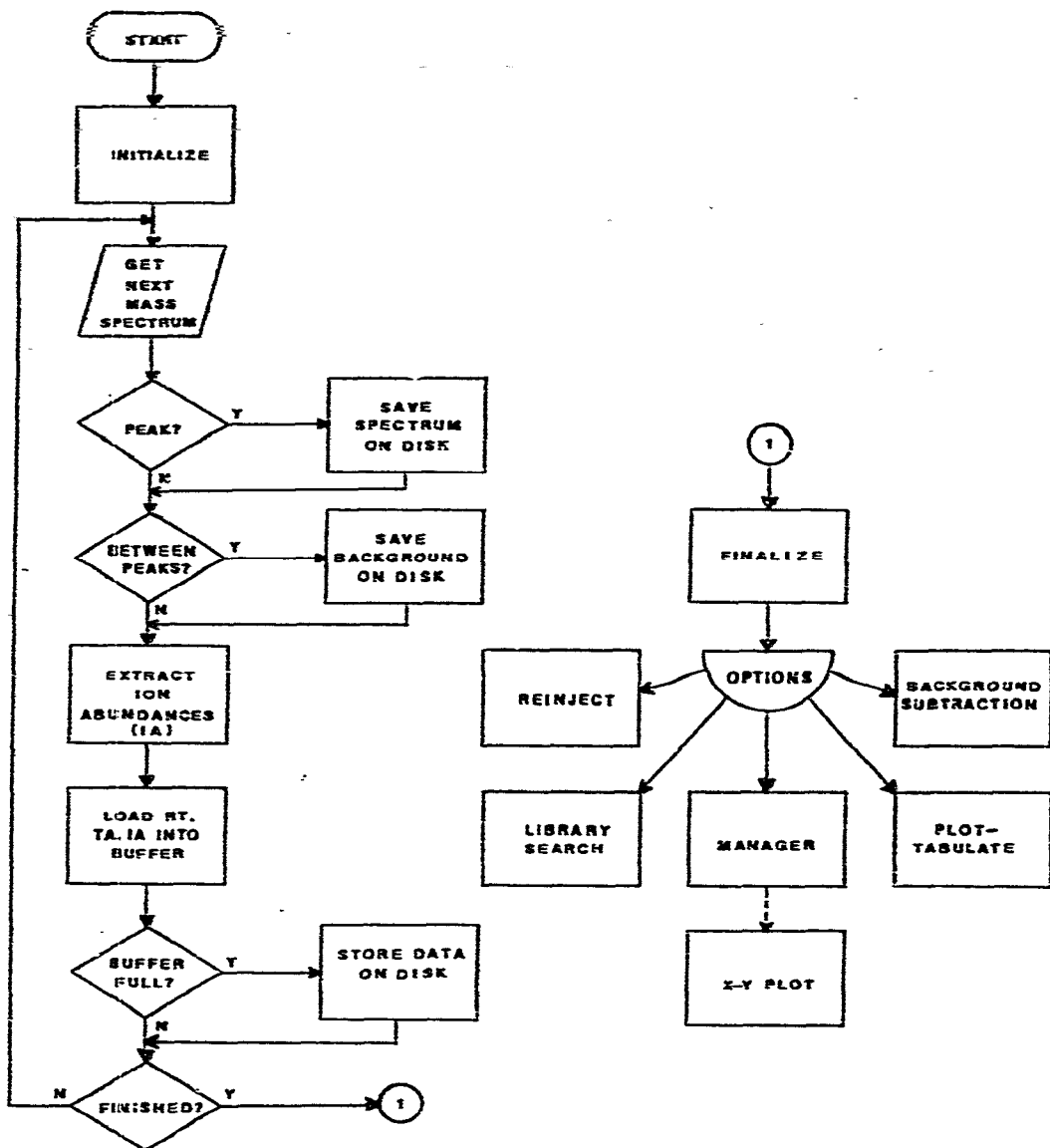


Fig. 1. Simplified flow chart of DMDATAC.

A safety feature has been incorporated into DMDATAC for the protection of the mass spectrometer electron multiplier detector, which can be damaged by very large sample peaks. When the total abundance of a mass scan exceeds 32760 counts, the mass analyzer is put on standby. The run may be restarted from the calculator keyboard after allowing sufficient time for the large peak to elute. In the standby state, the retention time clock is not stopped.

During a GC-MS run it is often necessary to change the electron multiplier sensitivity. Although the change in sensitivity will result in a large change in ion

abundances this may not be apparent in the plotted data, since the data is smoothed before plotting. Therefore DMDATAC stores the total abundance and ion abundance values that have been extracted from the next mass scan made after the change in sensitivity, as negative numbers. Negative abundance data are detected by the plotting program, which will mark the location of the sensitivity change. DMDATAC occupies 12922 bytes of calculator memory.

(iv) DMXPLOT: RGC and MC plots are produced on x-y plotter from data stored on disk by this program. DMXPLOT fills 5382 bytes of calculator memory.

Analysis of environmental samples

To illustrate the use of these programs for the analysis of samples of environmental origin, benzene extractions of municipal incinerator fly-ash samples were analyzed. Extractions were performed using Soxhlet extraction apparatus, and were followed by a 2000-fold concentration of the extracted material by rotary evaporation under aspirator vacuum. Chromatographic conditions were; column, 1.8 m \times 2 mm I.D. glass packed with Aue packing⁸; helium carrier gas flow-rate, 40 ml/min; injection port, 250°; temperature programmed from 70° to 250° at 4°/min and held for 15 min. The quadrupole mass spectrometer was scanned from 500 a.m.u. to 40 a.m.u. at a rate of 330 a.m.u./sec. A silicone rubber membrane was employed as the GC-MS interface. Details of the analysis of organic material extracted from incinerator fly-ash samples are reported elsewhere⁹.

RESULTS AND DISCUSSION

Fig. 2 shows the type of data display obtained in real-time from DM. This is the same type of data output as is given by the manufacturer-supplied software. Only the interval between retention times 7 and 23 min is shown. The top is a MC of the m/e 85.1 ion and the bottom trace represents the total ion current (TIC). The darker (shaded) areas for both traces is a 10 \times scale. Full-scale values for either the MC or TIC may be changed at any time during the run, but the original software could not re-plot a run for which the chosen full-scale values were too high or too low. The MC being monitored also can be changed during the run, but only one may be monitored at a time. Small tic-marks are displayed every minute during the run, larger marks for every 5 min, and a double tic-mark is given every 10 min. The marks appearing as upside-down exclamation marks show where the GC-MS system has saved a mass spectrum on floppy disk.

The chromatogram shown in Fig. 2 is for a concentrated benzene extract of an incinerator fly-ash sample. Analysis of such complex mixtures is facilitated by the type of data output which can be generated by DM, shown in Fig. 3. This TIC was plotted from ion abundance and retention time information which was stored on floppy disk for the run shown in Fig. 2. Times that are plotted on the abscissa simplify the task of matching retention times of saved mass spectra to particular peaks in the GC-MS run. The run number and full-scale abundance values are given in the lower right-hand corner of the plot. Since plot and label sizing, and the full-scale abundance value to be plotted are controlled through interactive dialogue between the user and DMXPLOT, comparisons between runs can easily be made.

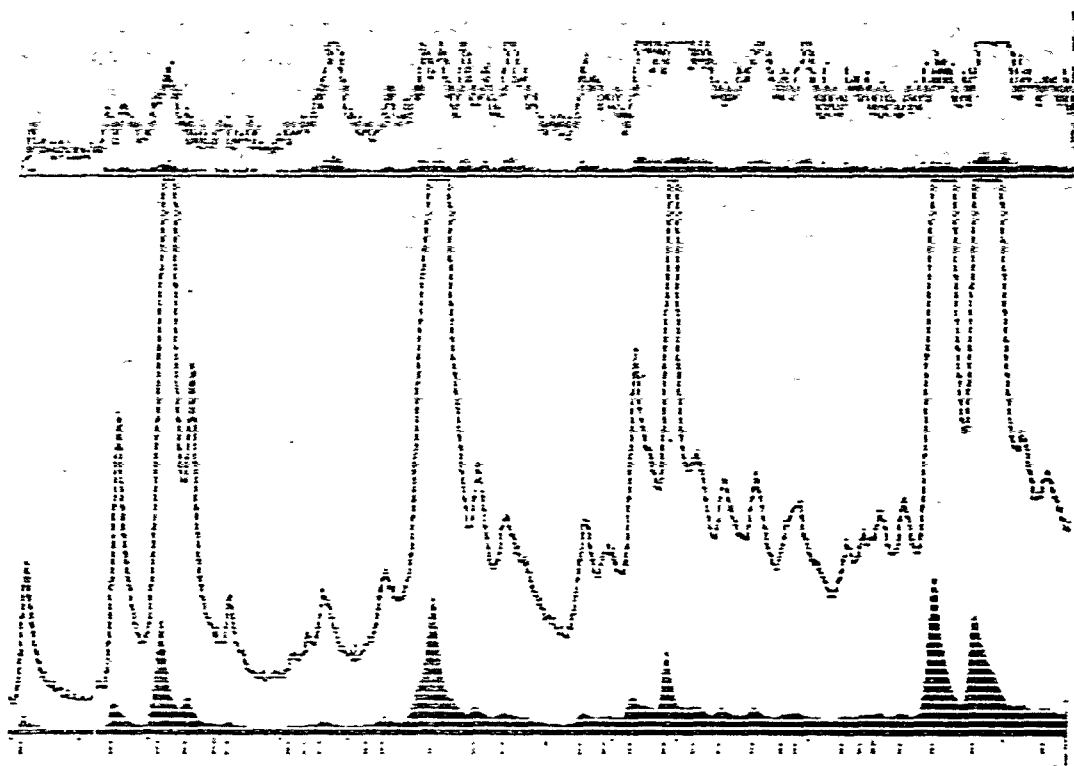


Fig. 2. Real-time data output obtained from manufacturer-supplied software. DM gives the same output, however ion abundance data is stored on floppy disk and can be plotted later.

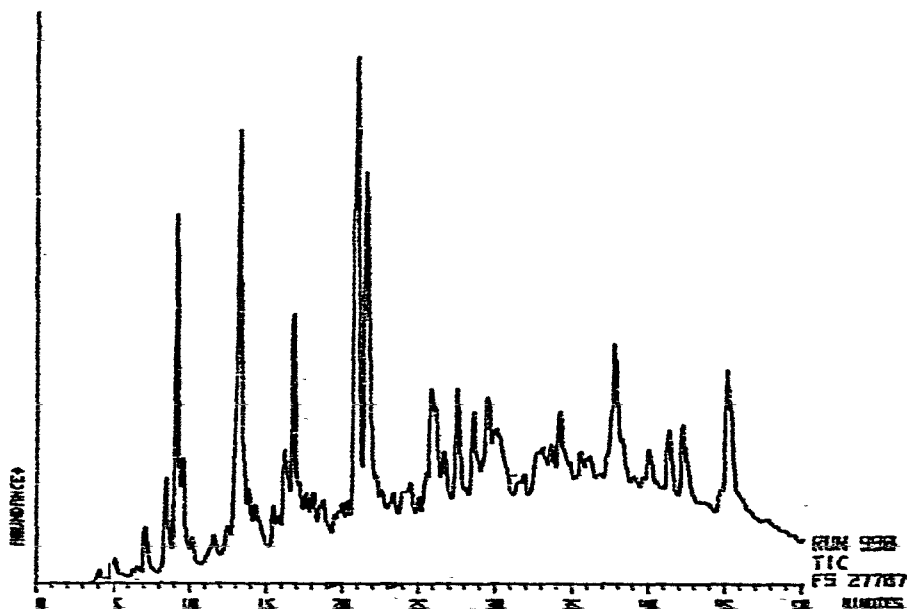


Fig. 3. Ion abundance data from a GC-MS run of an incinerator fly-ash sample extract stored on floppy disk by DM and plotted by DMXPLOT. These data are from the same GC-MS run as shown in Fig. 2.

Fig. 4 is a comparison between four different fly-ash sample extracts, including the sample shown in Fig. 3. Major differences and similarities in the four samples can be quickly ascertained. Such comparisons are virtually impossible with the real-time generated output due to the physically unwieldy nature of the data and the decreased user control over plotting dimensions. Also, full-scale values for the real-time generated TIC are changeable only in set increments.

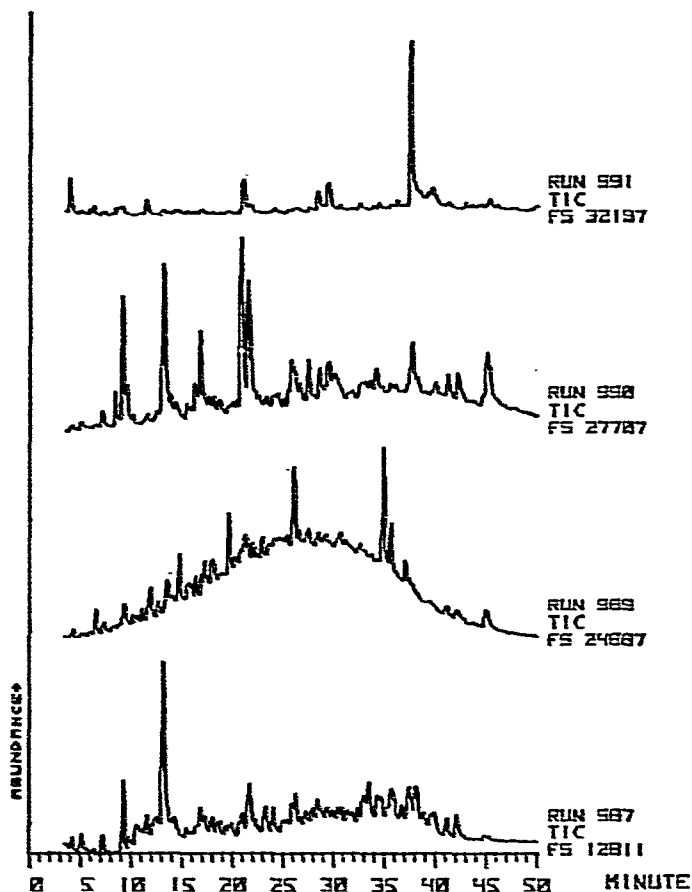


Fig. 4. Comparison of the TIA from GC-MS runs of four different fly-ash samples.

Fig. 5 shows the TIC of a fly-ash sample extract plotted with its corresponding mass chromatograms which were obtained during a single DM run. The MCs of the m/e 149.1, 154.1, 166.1, 178.1, 202.1 and 252.1 ions which are shown are indicative of the presence of phthalates, biphenyl, fluorene, anthracene, fluoranthene and pyrene and benzopyrenes, respectively, in the fly-ash extract. For qualitative analysis the ions to be monitored must be carefully chosen to avoid interferences. The peak observed at a retention time of five minutes in the MC of m/e 252.1 ion, for example, results from the presence of that ion in the mass spectrum of an interfering compound.

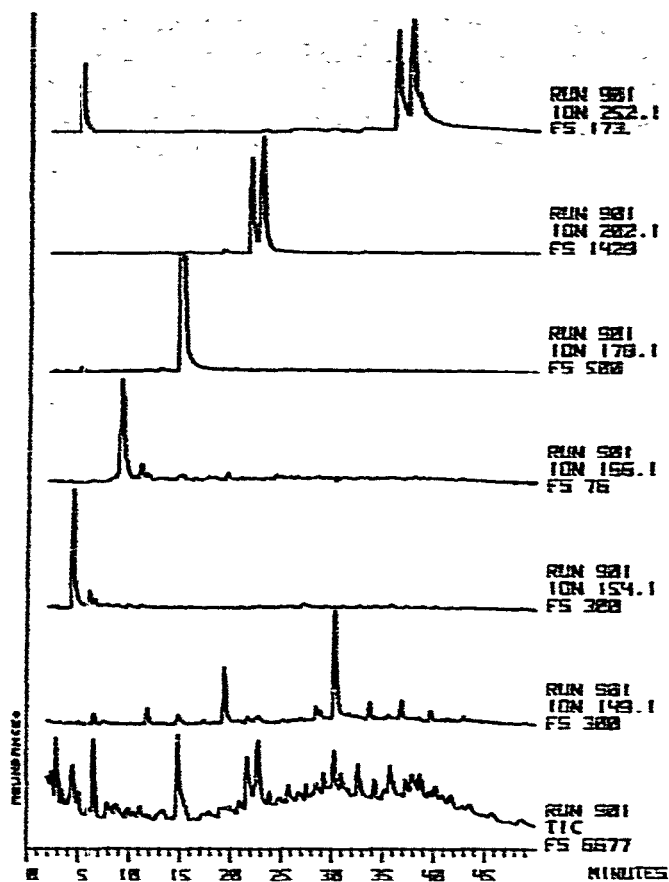


Fig. 5. TIAs and six MCs obtained from a single GC-MS run of a fly-ash sample extract.

When combined with retention time data for known compounds, use of MCs provides a selective and sensitive method of identification.

It is possible to detect particular compounds using MC data, even in sample runs for which the compounds co-elute with other sample components having much greater abundance, or where a compound of interest is barely detectable above the background level of unresolved components. The MC of ion 166.1 clearly indicates the presence of fluorene in the fly-ash sample extracts, although only very minor peaks are observed in the TIC at a corresponding retention time.

Since the MC full-scale values are directly proportional to concentrations of the various compounds which have been detected, MCs that have been generated by DM can be used for quantitation. DM also saves mass spectra taken at the top of eluting GC peaks, therefore both qualitative and quantitative analyses for selected components can be performed from a single GC-MS run. Use of these programs for the rapid analysis of chlorinated dioxins extracted from incinerator fly-ash samples has been reported¹⁰.

Development of the software described here was necessary to improve the

capabilities of our instrumentation for the analysis of trace levels of organic compounds extracted from environmental samples. The ability to generate MCs and compare data from different runs using an x - y plotter is an important step in the overall analytical procedure.

ACKNOWLEDGEMENT

This work was supported by the Ontario Ministry of the Environment, Air Resources Branch.

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