



Evaluation of the HP 6890/5973 bench-top gas chromatograph/mass selective detector for use in mobile laboratories

Ken Li*, Merv Fingas

*Emergencies Science Division, Environmental Technology Centre, Environment Canada,
River Road, Ottawa, Ont., Canada, K1A 0H3*

Abstract

Introduced in 1996, the Agilent (Hewlett Packard) HP 6890/5973 GC/MSD system is the latest of the bench-top GC/mass spectrometry (MS) family. Started with the HP 5970 MSD, introduced in the mid-1980s, has provided small/medium size laboratories with the power of a true MS that provides selectively and library-searchable capability. This paper presents study results on instrumental sensitivity achieved with the new MSD, with examples illustrating trace-level analysis of semi-volatile compounds such as PCB and Dioxins. Investigations were carried out to study the effect of some operational parameters such as ionisation energy, dynode voltages and dwell time. In the standard electron impact selected ion monitoring (SIM) mode, the new MSD can provide sub-picogram level sensitivity for chlorinated hydrocarbons. In scan mode, under optimal condition, the system can generate library-searchable spectra from sub-nanogram quantity of analytes. This sensitivity level rivals traditional GC with selective detectors such as electron capture detector but at the same time possesses the advantage of computerised library search against a database of over 100 thousand spectra. The relatively compact size makes the system practical in a mobile laboratory, providing qualitative as well as quantitative data in spill emergencies analyses.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Bench-top gas chromatograph; Selected ion monitoring; MSD; Mobile laboratory

1. Introduction

Gas chromatography/mass spectrometry (GC/MS) has generally been recognised as one of the most powerful analytical tool for separation, identification and quantitation of organic compounds in a complex mixture. In this respect, GC/MS has been a mainstay of

* Corresponding author. Tel.: +1-613-991-9485; fax: +1-613-990-3219.

E-mail address: li.ken@etc.ec.gc.ca (K. Li).

analytical tool for environmental analysis, where detection and quantitation of trace level of contaminants are often sought after in the presence of a myriad of background materials.

One of the most significant developments in the GC/MS instrumentation field in recent years is the introduction of relatively low-cost bench-top GC/MS systems. Part of the impetus came from the space exploratory programme in the 1960s, plus the advent of inexpensive personal computer technology. Bench-top MS is characterised by a relatively compact manifold, which houses the ion source, analyser and detector assembly. For cost consideration, the majority of them operate by electron impact ionisation mode only. The analyser is the active component that separates the fragment ions by mass/charge ratio. This is achieved inexpensively by quadrupole or ion cyclotron. Detector technology is invariably the electron photo multiplier type. Because of the relatively small manifold volume, vacuum is readily achieved by low-cost air-cooled diffusion or a small turbo pumps and backed by rotary pump. In contrast, a traditional research grade standalone GC/MS system requires ancillary equipment for operation. For instance, cooling water is required in a large diffusion pump to condense the pump fluid or the bearing in the case of a high capacity turbo pump. Such MS also has relatively high initial purchase price and requires more to service, but does offer a more flexible sample introductory device such as liquid chromatography interface or solid probe. In addition, it also provides a more comprehensive sample ionisation technique such as chemical ionisation, which might be particularly sensitive to some compounds with high electron affinity.

The mass selective detector (MSD), first introduced by Hewlett Packard (HP) in the early 1980s as the HP 5970, was one of the first generation of legitimate low-cost MS used as dedicated GC detectors (the other one being Varian's ion trap detector). To keep the cost down, the MSD did not have other sample introduction devices. Electron impact was the standard mode of ionisation. No interface other than a simple direct interface was available, and column flow was restricted to 1 ml/min or less. Higher column flow rate was possible through an open-split interface, which bled off excess column flow via a three-way union open to the atmosphere, with a restrictor limiting the flow to a nominal 0.7 ml/min. No enrichment or other separation device was available to keep the design simple. Used solely with an attached GC, it was attractive to a lot of small labs, providing them with the unique power of mass spectral identification.

The MSD has evolved through three model changes to the present 5973, bringing improvements in sensitivity and capability with each update. The current MSD has an optional chemical ionisation. In addition, there is an increase in mass range to 800 amu, a high capacity turbo pump which provides a cleaner background and faster pump down, plus ability to handle flow up to 4 ml/min from a 0.32 mm wide bore column. The ion source and analyser are now independently heated, an improvement over the previous designs, which rely on conductive heat from the interface heater and thus require a 4 h stabilising time. The vacuum manifold can now be heated up faster and to a higher temperature, which provides a cleaner ion source in the presence of matrix-rich sample.

In this work, we will present our experience with the new MSD. We have carried out studies of some of the parameters affecting sensitivity. Examples include the analyses of semi-volatiles such as PCBs, pesticides and dioxin/furans in environmental samples. Results of past performance evaluation exercise, conducted by Canadian Association of Environmental Laboratories (CAEL) were used to illustrate the performance of the system. We

also demonstrate, using the existing configuration, effective VOC screening of water samples can be carried out via headspace (HS) sampling using the auto-liquid sampler (ALS). Though not as sensitive as traditional high temperature HS analysis, it can be easily carried out using low-cost consumable items without any other ancillary instrumentation.

2. Instrumentation and methodology

The system consists of the HP 6890 GC/5973 MSD with a HP 7683 ALS. High vacuum is provided by the upgraded 250-l turbo pump. System control is by a HP ChemStation with a Kayak Pentium-based PC running under Windows-NT. The software includes autotune programmes for EI, as well as programmes for data acquisition, data editing, reporting, quantitation and library searching. Several columns were used in the course of this study. Due to the restriction of the vacuum system, columns less than 0.32 mm i.d. were used.

All semi-volatile analyses were carried out using a 30 m HP-5 MS capillary column (0.25 mm i.d., 0.25 μm film) was used. Experimental parameters were: injector temperature, 270 °C; capillary interface temperature: 300 °C; automated injection of 1 μl ; MSD operated in selected ion monitoring (SIM) mode. Tuning was performed by autotuning and the electron multiplier (EM) was at a nominal value of 1400 V. The GC column flow was a constant 1 ml/min controlled via the electronic pressure programming (EPP) constant flow mode. The oven temperature programme for PCB analysis was: 120 °C for 1 min heated to a final temperature of 310 °C at 10 °C/min, and held at this temperature for 5 min. Prior to injection, an internal standard of d14-Terphenyl was added to give a final concentration of 1 $\mu\text{g}/\text{ml}$. In actual analysis, quantitation was based on the internal standard method.

For dioxin/furan analysis, the oven temperature was 100 °C for 1 min and heated to 200 °C at the rate of 35 °C/min, then to 280 °C at the rate of 2.5 °C/min and held at the final temperature for 3 min. One microlitre was injected via an auto-sampler using the splitless mode. Injector and detector temperature was 270 and 280 °C, respectively. For the purpose of evaluation, a simplified one-step SIM acquisition programme was carried out. Ion source was held at 220 °C.

2.1. Performance evaluation (CAEL): PCB in water

2.1.1. Liquid–liquid extraction

Liquid–liquid extraction was performed on a 1:1 aliquot of the received water sample, fortified with known amounts of Aroclor mixtures by a contract lab of CAEL. A mixture of isotopically labelled surrogates (C-13 tetrachlorobiphenyl to heptachlorobiphenyl) was added to the sample in the separatory funnel just before extraction. Extraction was carried out with a 50 ml aliquot of dichloromethane and the process was repeated two more times with fresh solvent. The extracts were combined, filtered and dried over Na_2SO_4 . After the addition of 1 ml of iso-octane, the volume was reduced by evaporation to ~ 1 ml using a roto-evaporator. The extract was transferred quantitatively to a calibrated test tube and blown down to less than 1 ml under UHP-grade nitrogen. The extract was finally made up to 1 ml in iso-octane and an internal standard of d14-Terphenyl added at 1 $\text{ng}/\mu\text{l}$. One microlitre of the extracts was injected in the GC/MSD for analysis.

2.2. HS by ALS

A 1 ml aliquot of water was pipetted into a 2 ml screw-cap ALS vial with 0.2 g sodium sulphate. A 100 μ l gas-tight syringe was installed into the ALS injector, with depth of needle set to 20 mm. A narrow bore (2 mm i.d.) injector liner was installed into the inlet. A 20 μ l aliquot of the HS was injected in splitless mode. Oven temperature was 30 °C for 5 min and heated to 170 °C at the rate of 7 °C/min.

3. Results and discussions

3.1. Analysis of dioxin/furan (PCDD/PCDF)

Within a family of 75 congeners of PCDD and 135 PCDF, TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) and the corresponding furan are among the most toxic substances known to man. Their presence in the environment, even at trace levels of parts-per-billion or trillion, is of great concern due to its propensity to bio-accumulate, similar to most persistent chlorinated substances. Mass spectrometry techniques play a key role in monitoring environmental samples for this substance and its isomers because of the sensitivity and unique conformational power of GC/MS, important because in actual samples, trace levels of TCDD/F is often present in a myriad of background organic compounds. Traditionally, trace analysis of PCDD/F are mostly carried out on research grade high-resolution GC/MS for its high sensitivity and specificity. MSD, however, can have a role in routine monitoring exercise such as air quality survey, in which target analytes at picogram level need to be detected. The MSD can provide reliable and consistent data quality, important in trend analysis. In episodes of chemical spillage or fires, relatively high levels of contaminants are usually encountered; the analytical requirement is easily met with bench-top MS such as the MSD. Within the last 10 years, such instrumentation has made great strides in terms of sensitivity and ease of operation such that it has become a common GC detector in most labs. The following presents the finding of the new MSD in this application.

A stock solution of EPA 1613 PCDD/F standard solutions (0.4–4 ppm) obtained from Wellington Lab, Guelph, was serially diluted to give mixtures down to 0.4–4 ppb. This mixture contains all of the 2, 3, 7, 8-substituted chlorinated dioxins/furans, noted for their enhanced toxicity due to the coplanar nature of the molecule.

3.1.1. Investigation of operational parameters

There are several ways to improve the detection limit, one can introduce more samples onto the column, or set up the MS to increase analyte response. To inject more samples onto the column, one can make use of EPP on the HP 6890 GC in the pulse splitless mode. The column pressure prior to injection was programmed to step up to a high value, thereby reducing the larger vapour cloud contained in the injection port liner and minimise peak broadening. A series of injections (1–5 μ l) were made in a EPP pulse mode three times the normal value (45 psi) during the initial 0.5 min. There was a more or less linear increase in analyte response with increasing injection volume. However, the peak shape was extremely

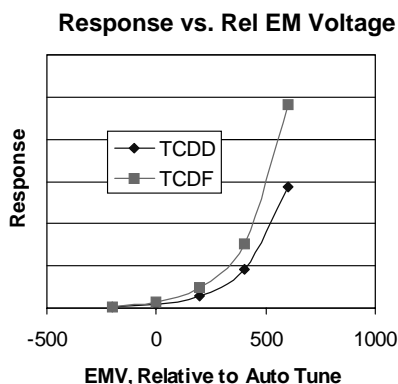


Fig. 1. Response vs. EM voltage, dioxin analysis.

poor with broad base, indicating there was band broadening for high injection volume even at the high inlet pressure.

Since detection of column effluent starts with an ionisation process at the source, it was thought that an obvious path of improving the sensitivity lies with improving the ionisation process. The electron energy is the amount of energy carried by the ionising electrons and determined by the bias voltage; -70 V dc bias on the filament causes emitted electrons to possess -70 eV. Normal operation sets this parameter to 70, which generates classical mass spectrum for library searches. As known to PCDD/F analysts, reducing the electron energy from the normal 70 eV causes less fragmentation, thereby increasing the abundance of the parent ion and improving the detection limit. A series of runs were made to lower the ionisation energy by 10 eV steps from 70 to 40 eV. No changes in the resulting chromatograms were noted. In fact, at 40 eV, baseline noise became excessive and significantly degraded the signal-to-noise ratio. Emission current was also lowered by 50% of the tune value to reduce the extent of ionisation, but again no improvement was observed.

To study the effect of dynode voltage, the EM was varied by steps of 200 V relative to the autotune value. Started with a tune value of 1000 V (nominal), a series of injections were made at -200 , $+200$, $+400$ and $+600$ V. Results are shown in Fig. 1. The log function characteristic of the EM was closely reflected in the observed response curve. While greatly increasing the analyte response, the life of EM is shortened by operating the EM in high voltages.

Dwell time was also varied from 25 to 200 ms for each monitored ion in the SIM mode. There were no significant difference in response but 100 ms appears to give a slight enhancement in OCDF (Fig. 2). Longer dwell time usually improves the signal-to-noise ratio, but this is offset by inadequate re-construction of the profile of narrow capillary peaks. In general, a minimum 15–20 points are required to construct a peak accurately (HP 5970A Workstation Operation Manual).

3.1.2. Calibration

Fig. 3 shows a calibration curve created by using various amounts of 2,3,7,8-TCDD congeners and a fixed amount (40 pg) of a carbon-13 2,3,7,8-congener. The ordinate of

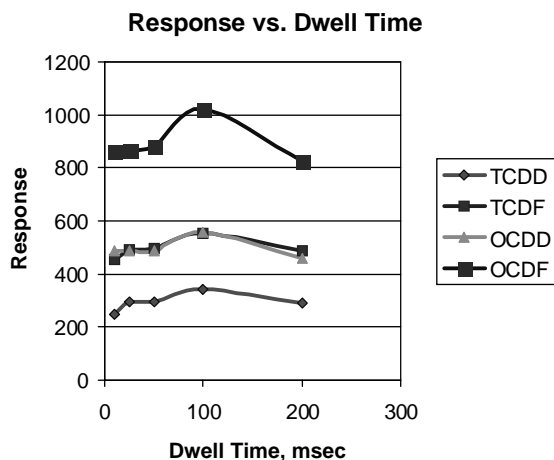


Fig. 2. Response vs. dwell time, dioxin analysis.

the curve is the ratio of the measured area of the 322 m/z ion to the measured area of the 334 m/z ion from the carbon-13-enriched congener. The areas of these two-ion fragments were measured in SIM mode, each ratio was calculated from a single area measurement for each of the two m/z ions. The abscissa is the ratio of the amount of the 2,3,7,8-congener (0.4, 4, 40, 100 and 400 pg) to the fixed amount of the carbon-13-enriched 2,3,7,8-congener internal standard. The calibration curve is linear up to 400 pg of TCDD/F injected.

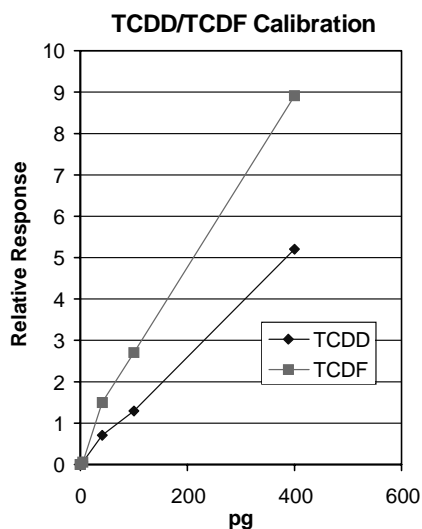


Fig. 3. Trace-level dioxin/furan calibration, SIM mode.

3.1.3. Detection limit and repeatability for quantitative analysis of TCDD

Five replicate injections of a 0.4–4 ppb mixture were made at an EM voltage of 1600 V (+600 V over tune value). At 0.4 pg TCDD/F injected on the column, we obtained RSD of 4.7 and 9.8%, respectively. For qualitative analysis, using a criteria of the presence of 320/322 ion pair at a ratio of 0.7($\pm 25\%$):1, an instrument detection limit down to 0.4 pg is readily achievable. For a 1:1 water sample extracted and concentrated to a final volume of 0.1 ml, a total of 40 pg is detectable in the final extract. This translated to a method detection limit of 40 pg/l or 40 ppt, which is sufficient for screening purpose, thus reducing the number of samples needed to be taken for confirmation on a more powerful MS. The high sensitivity means that for screening purpose, a micro-scale extraction can be carried out conveniently in the field using small volumes of water and solvent, and inject the raw extract directly into the GC/MSD, thereby reducing solvent usage and faster sample turnaround time. Fig. 4 illustrates a total ion chromatogram (TIC) of a 4–40 ppb standard at the normal tune values.

3.2. Pesticide analysis

The dwell-time study was repeated using a mixture of chlorinated pesticides at 1 ppm. Again, there appears to be no significant difference in response from a dwell time of 25–200 ms. A calibration curve was generated by injecting a series of solutions ranging from 0.2 to 50 ppm and shown to be linear (Fig. 5).

3.3. PCB analysis

Performance evaluation was carried out using Aroclor mixtures of 1242, 1254 and 1260. Calibration standards ranging from 0.01 to 0.2 ppm of each Aroclor were run and found to be linear at this extreme low level (Fig. 6). It was interesting to note that the performance of the new MSD actually surpassed the sensitivity of the specific electron capture detector, which is around 0.05 ppm. In general, the sensitivity improvement over the previous generation of MSD is at least 10 times. In the extraction of PCB from soil, a 0.4 ppm carbon-13 surrogate mixtures were routinely used to monitor PCB sample workup loss, thus accurate determination of the surrogate standards affects the quality of data. Five replicate injections of a raw water extract were made and RSD was found to be from 11 to 14%.

3.3.1. CAEL performance evaluation

As part of the accreditation programme, ESD has joined this performance evaluation exercise conducted twice a year. The analysis of PCB in water is among a number of environmental analytical protocols ESD has been accredited. In each round, four 1:1 aliquots of water sample fortified with Aroclor mixtures were received. They were extracted in accordance to established protocol. Analysis was carried out on the MSD, using a multi-stepped SIM programme. Results of the past two rounds are shown in Fig. 7. In each of the two rounds, PCB was measured in the ppb level. ESD were credited with the maximum points assigned in each sample with a score of 100%.

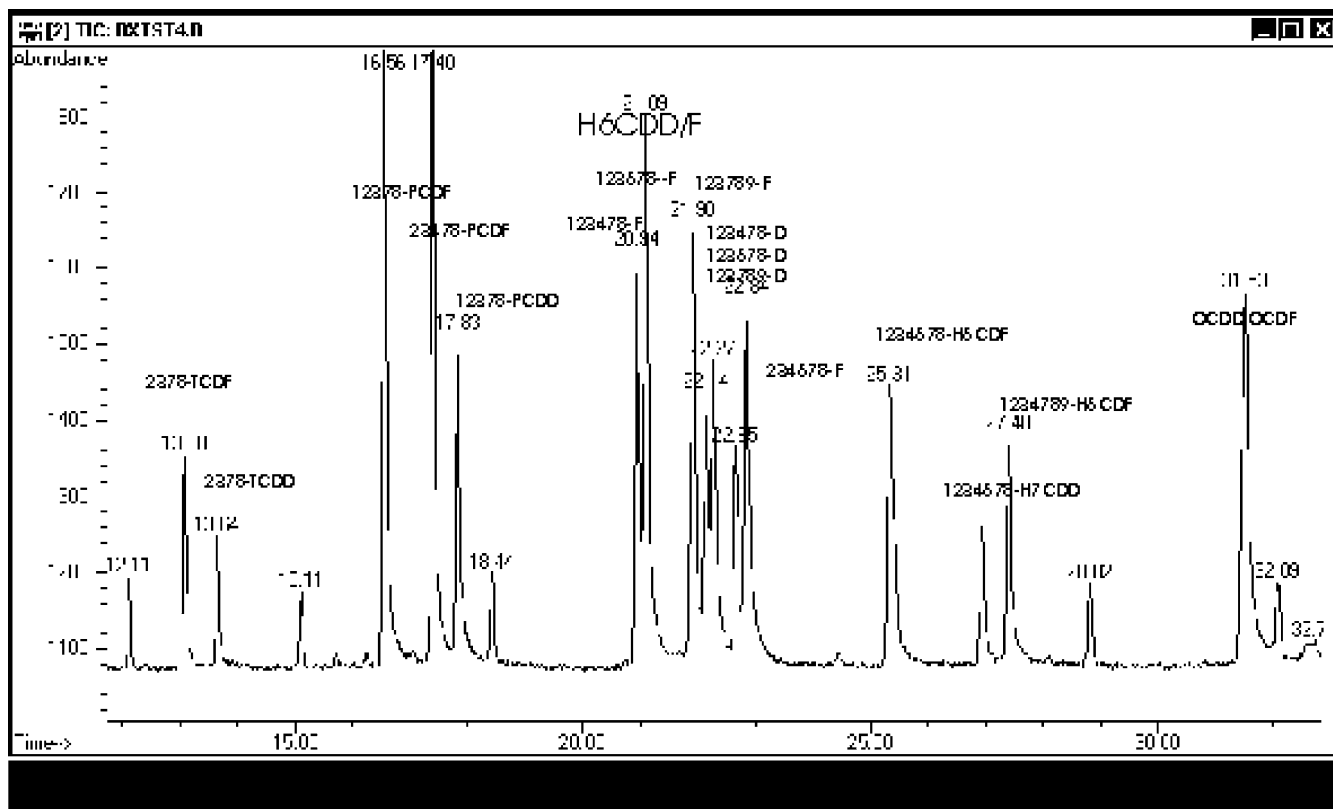


Fig. 4. Total ion chromatogram of PCDD/PCDF, 4–40 ppb.

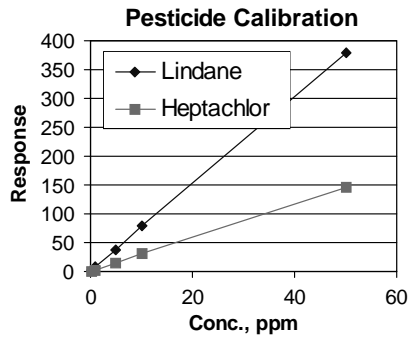


Fig. 5. Pesticide calibration, SIM mode.

Low Conc. PCB Calibration

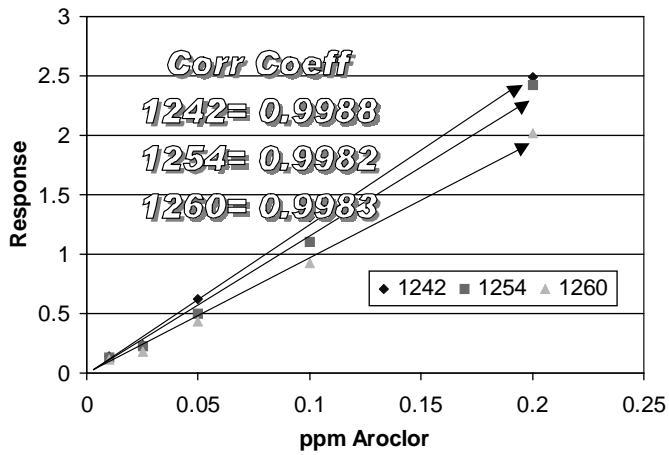


Fig. 6. Low-level PCB calibration, SIM mode.

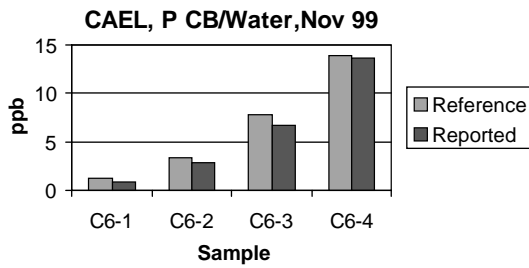


Fig. 7. CAEL performance evaluation PCB in water samples.

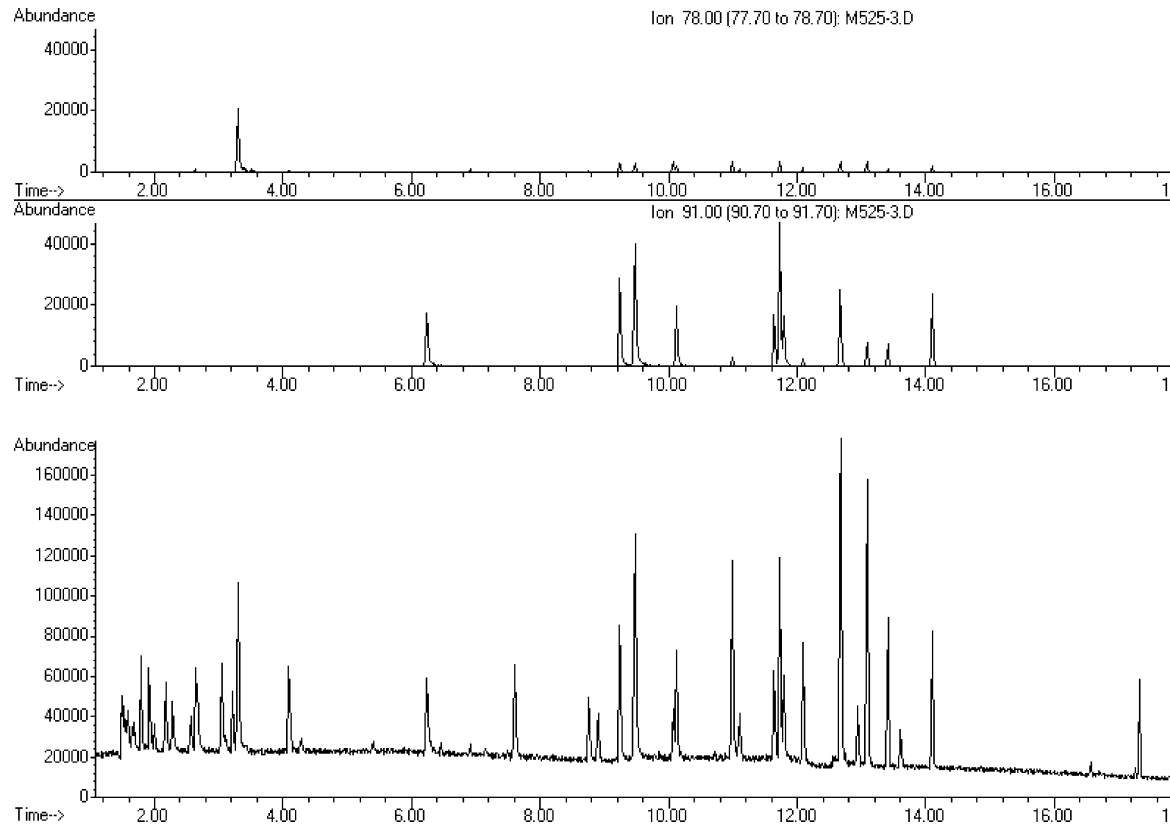


Fig. 8. M524 mix, 0.2 ppm by HS-ALS.

3.4. VOC analysis

Because of the sheer volume of fuels and industrial solvents consumed and transported annually, spills or accidents often involve volatile analyses. A GC/MSD system is invaluable by nature of its versatility. While VOC is usually carried out by an ancillary technique such as purge and trap (P&T) or HS analysis, a GC/MSD configured for semi-volatile analysis having an ALS can also be used for screening purpose [1].

In that application, a gas-tight syringe of 50 or 100 μl is substituted in place of the usual 10 μl , liquid sample of less than 1 ml is placed in the ALS vial and the depth of syringe is reduced to 20 mm for the syringe to sample the HS above the liquid. To improve the peak shape, a narrow bore injector liner (2 mm i.d.) is used. Since HS concentration depends on temperature, ambient HS does not have the sensitivity of conventional heated HS. Salt can also be added to the aqueous phase to enhance the HS concentration of some VOC. The practicality of ambient HS via ALS is illustrated with a water solution spiked with a VOC mixture (EPA method 524, containing about 60 compounds; 0.2 ppm final concentration). On a column used for semi-volatile analysis (DB-5, 30 M, 0.25 mm and 0.25 μm film), the early eluting peaks cannot be resolved at an oven temperature of 30 °C but de-convolution of the peaks can be performed by extracted ion chromatograms. BTEX can clearly be analysed at a detection limit of 0.05 ppm (Fig. 8), which is adequate for field analysis. The cost of consumables is also far less expensive: the screw cap ALS vial costs \$0.32 versus \$1.99 (Canadian) for the 20 ml HS vial. In the minimal working environment of on-site analysis, there is clear advantage of using one instrument for volatile and semi-volatile analysis, since instrument set up and maintenance is greatly reduced.

4. Conclusions

The HP MSD has been a mainstay in ESD's analytical instrumentation and the new 5973 MSD proves to be a very capable performer. A number of new features have brought increased performance to an already versatile analytical system. In this study, we have investigated a few of the operation parameters of the system for analysing a variety of semi-volatile and volatile contaminants. In general, the system was shown to perform admirably well in all aspects of environmental testing.

Reference

- [1] M. Szelewski, B. Quimby, Ambient Headspace GC and GC-MSD Analysis of Non-Polar Volatiles in Water, Agilent Application Note, Feb 2000.