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Gas Chromatography–Mass Spectrometry

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Introduction

Increasing public concern over environmental pollution reflects the heightened awareness of the toxicity of a large number of chemicals that find extensive application in wide-ranging fields. The consequent impetus to reduce chemical contamination of the environment has generated a growing body of legislation and mechanisms for enforcement via specific regulatory agencies. For example, following the discovery of trihalomethanes in chlorinated drinking water in the 1970s the Safe Drinking Water Act (SDWA) was passed that directed the United States Environmental Protection Agency (US EPA) to undertake a comprehensive study of the contaminants present in drinking water. The pre-eminent technique employed in these investigations was gas chromatography with mass spectrometric detection (GC-MS). The distinctiveness of the mass spectra of the target analytes and their volatility were two vital characteristics required for GC-MS. As the studies initiated by the SWDA yielded results, GC-MS has been recommended for analysis of many environmental contaminants.

Since many pollutants occurring at trace levels in complex matrices are either volatile or amenable to derivatization to volatile products, GC-MS has proved to be an effective means for verification of compliance with environmental regulations. GC and MS play complementary roles in the analysis of mixtures. Volatile constituents of complex mixtures may be conveniently separated by GC but not identified unambiguously with conventional detectors. MS provides much more definitive structural information that permits identification. The sample sizes necessary for GC and MS are also comparable and sample volatility is necessary for both.

The utility of GC-MS for environmental analysis has been further enhanced by the development of relatively inexpensive table-top instruments that has brought the technique within the reach of most laboratories. Computer-assisted operation of these instruments, including automated sample injection, data acquisition, online searches of mass spectral libraries and quantification by selected ion monitoring (SIM) has led to rapid, efficient and convenient analytical systems. These advances have made compact, rugged, portable GC-MS instruments available for field applications, thereby rendering GC-MS a vital technique in environmental analysis.

Sample Pre-Treatment

The low concentrations of pollutants and the complex matrices in which they frequently occur generally preclude direct injection of environmental samples into a chromatograph. Sample pretreatment is then necessary to remove components that would interfere in the analysis and to concentrate target analytes that are present at extremely low levels. Pretreatment varies considerably with the nature of the sample and the information sought. Pollutants are dispersed in air, water and soil.

Atmospheric samples may contain numerous species ranging from gaseous to nonvolatile substances adsorbed on particles. They are usually collected in highly polished SUMMA® canisters and Tedlar® bags or on sorbents or in an impinger solution. Specifically, the EPA Compendium Method TO-14 mandates SUMMA passivated canister sampling. Particles are commonly retained on membrane filters or impactors. Gaseous components and volatile organic compounds (VOCs) are collected by trapping, either cryogenically for the most volatile or on sorbents of increasing retentivity for the less volatile.

The constituents of particulates are separated into approximately organic and inorganic substances by Soxhlet extraction or ultrasonication with an appropriate organic solvent (methanol, dichloromethane, cyclohexane, etc.) or by supercritical fluid extraction (SFE) with CO_2. SFE is becoming increasingly accepted for the extraction of analytes because it is more rapid, reliable and efficient for a variety of matrices than the older techniques and is environmentally friendly in reducing the need for organic solvents.

The soluble fraction comprises a complex mixture of various organic compounds that may require further fractionation prior to GC-MS analysis. This has entailed separation into fractions of different polarities by such techniques as liquid–liquid extraction or column chromatography following preliminary removal of the acidic and basic components. Solid-phase extraction (SPE) has become a popular alternative because of its simplicity, speed, improved sample clean-up, easy automation and the capacity to handle multiple samples simultaneously. More recently filter discs have been introduced to perform the same functions more conveniently.

VOCs are generally preconcentrated on adsorbent traps. Different traps are often necessary as no single sorbent performs satisfactorily over the entire range of organic volatilities and polarities encountered. Two (or more) sorbents are used in tandem, first a weak one to adsorb the heavier organics, followed by strong one to retain all the remaining. The analytes are desorbed by flash-heating from weak adsorbents (primarily graphitized carbon black and Tenax); by solvent extraction from strong ones (activated charcoals), using carbon disulfide, dichloromethane, etc. (**Figure 1**).

For aqueous samples preconcentration and clean-up are often achieved concurrently. In the purge-and-trap (dynamic headspace sampling) technique, the volatile species that are present in water are swept out of solution by a stream of nitrogen or helium into a sorbent trap consisting of activated carbon, Tenax or silica gel. The analytes are desorbed thermally and transferred along with the carrier gas to the GC-MS instrument. If the number of volatile compounds is few, analysis of the headspace gases is possible directly but with the drawback that water vapour is likely to be injected into the instrument.

Semi-volatile species present in water must be first extracted into a suitable organic solvent or retained

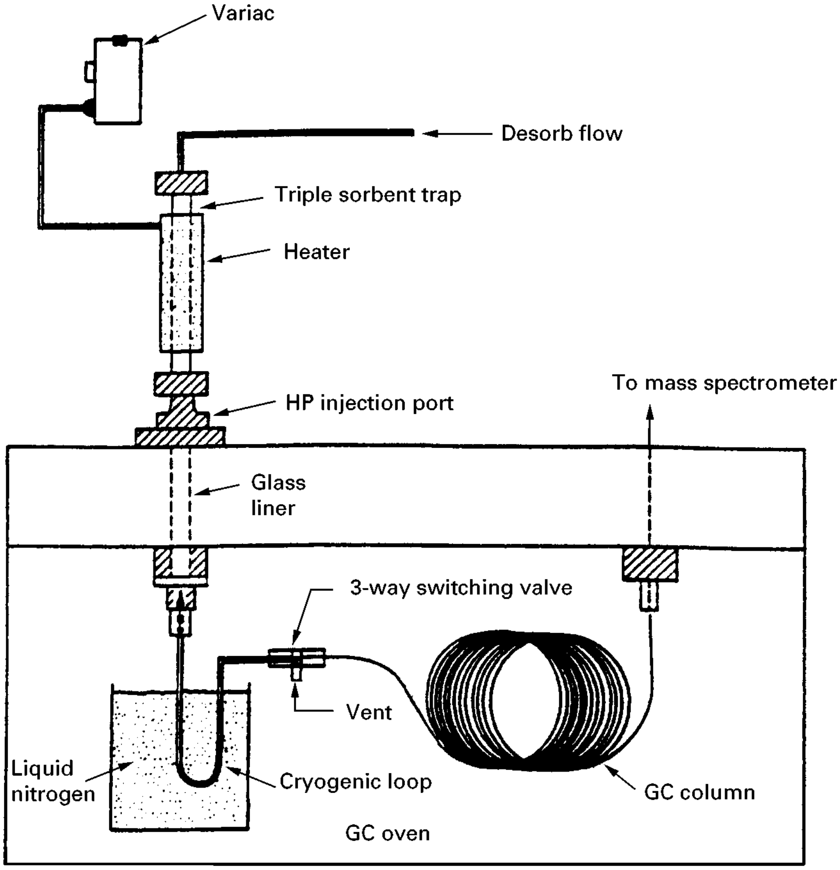

Figure 1 Schematic diagram for thermal desorption–gas chromatography–mass spectrometry system. (Reproduced from Ma C (1997) Performance evaluation of a thermal desorption/gas chromatographic/mass spectrometric method for the characterization of waste tank headspace samples. *Environmental Science and Technology* 31(3): 853–859, with permission from the American Chemical Society.)

on an SPE cartridge and then eluted for injection. The polarity of the organic stationary phase, which is bonded to a silica support, determines the retention selectivity.

For solid samples, VOCs are first extracted into methanol, which is then added to water for purge-and-trap. For extraction of semivolatiles from solid samples SCF is particularly advantageous. The extracted analytes collect in an appropriate solvent on reducing the pressure to atmospheric level.

Sample pretreatment is beset with a serious problem – the potential loss of analytes – which necessitates monitoring solute recovery by employing internal standards with similar properties. Also accumulation of water during preconcentration can affect the GC-MS instrument, especially the pumps necessary to maintain the vacuum. A remedy that has been attempted is the use of Nafion diffusion dryers, but this may cause the loss of small, polar organic compounds.

Instrumentation

Capillary columns (0.32 mm i.d.) of appropriate polarity are routinely used in view of their greater efficiency. However, for relatively high concentrations megabore capillary columns (0.53 mm i.d.) are preferred with connection to the mass spectrometer ion source being achieved via a glass jet separator for whose optimum functioning a stream of make-up gas is provided. This approach has been widely used for the analysis of ambient air samples; waste and solid samples; purge-and-trap analysis; as well as thermal desorption analysis of sorbent tubes.

The mass spectrometer of a GC-MS system must be capable of rapid response to monitor the solutes that are eluted from the chromatographic column in quick succession. Hence ion trap and quadrupole instruments are the most widely used mass analysers. The compact ion trap detector (ITD) also enhances the portability of GC-MS instruments for field analysis.

Calibration of a mass spectrometer is usually based on the diagnostic ions of either perfluorotributylamine (PFTBA) or perfluorokerosene (PFK). However the US EPA has introduced m/z abundance calibration for checking the performance of the entire GC-MS system, not merely of the mass spectrometer. Two compounds mandated for this purpose are bromofluorobenzene (BFB) for volatile analytes and decafluorotriphenylphosphine (DFTPP) for semivolatiles.

Electron impact (EI) ionization is the most widely used mode of ionization mainly because the databases available for mass spectral library searches (such as those provided by the National Institute of Science and Technology and John Wiley & Sons) are compilations of EI-mass spectra. However, negative chemical ionization mass spectrometry (NCIMS) is used sometimes, e.g. for the analysis of positional isomers of nitropolycyclic aromatic hydrocarbons via high resolution mass spectrometry (HRMS). Organophosphates can be analysed by either EI or CI.

Quantification of very low concentrations necessitates operating in the SIM mode. SIM involves acquiring ion currents only at a few specified m/z values that are characteristic of the analyte(s). Data acquisition in this mode avoids sampling the barren regions of a full scan spectrum, thereby improving the ion counting and the sensitivity of detection. Internal standards are usually isotopically labelled compounds that may be purchased individually or as mixtures from agencies such as the National Institute of Science and Technology (NIST) or the EPA.

Despite enhanced sensitivity, SIM limits the detectable analytes to those producing ions of the specified m/z values. Hence, for identification, scanning the entire mass spectrum of each compound may be necessary. But this compromises the detection sensitivity. Therefore one strategy is to use GC with a multidetector system (GC/MD) in conjunction with GC-MS. The multidetector system enables sensitive quantification while the mass spectrometer operated in the full-scan mode enables identification of some of the unknown pollutants. The primary quantification system is thus the GC/MD system that comprises conventional GC detectors such as FID, PID (photoionization detector) and ECD (electron-capture detector).

Applications

Environmental analysis serves different objectives, including routine monitoring, quality assurance, litigation and research. The list of target pollutants and the desired detection limits undergo continual revision in light of toxicological research. For the determination of a particular pollutant at the desired level of sensitivity, the same analytical technique is not adopted by all environmental agencies. GC-MS is sometimes mandated, sometimes suggested as an alternative method. Hence some examples that are presented in this article may not (yet) be approved by regulatory agencies but are nevertheless acceptable to environmental chemists as representing the wide applicability of GC-MS in this field.

The US EPA classifies organic pollutants into two classes: volatiles (compounds that exist as gases at room temperature and are easily removed from the sample matrix); and semivolatiles (compounds that can also exist as gases but need some form of extraction to be removed from the matrix). Both classes of compounds occur in outdoor, indoor and workplace atmospheres as well as in soil and water, and their concentrations may range from 100 ppm in the vicinity of emission points to a few parts per trillion (ppt) in pristine environments. The components of a particular mixture are likely to occur at different concentrations, with the more toxic target compounds being at times at much lower levels than the less hazardous ones.

VOCs for which US EPA approved GC-MS methods of analysis exist cover a broad range of compounds, including highly volatile organics (carbon tetrachloride, chloroform, acrylonitrile, allyl chloride, etc.); semivolatile organics (benzene, nitrobenzene, chlorobenzenes, toluene, trichloroethane, etc.); *N*-nitrosodimethylamines; polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated biphenyls (PCBs); and a variety of miscellaneous compounds including chlorinated compounds and aromatics.

A major fraction of VOCs are hydrocarbons, especially by roadsides where traffic is heavy. For example, in West Los Angeles, petroleum residues are the main solvent-soluble organic fraction of carbonaceous aerosols. For analysis, these particles are collected on quartz filters and extracted by ultrasonication first with hexane and then with benzene/isopropanol. The extracted constituents are determined by high resolution gas chromatography-MS. A bonded OV-1701 (86% dimethyl/14% cyanopropylphenyl polysiloxane) column and a quadrupole mass spectrometer operated in the EI mode have been employed in such studies.

Hydrocarbon contamination of ground water and soil often occurs through leaking fuel tanks. In the California Leaking Underground Fuel Tank (LUFT) method GC-MS is preferred to GC-FID for monitoring such leakage without interference by other semivolatile species. The most abundant ions in the mass spectra result from the fragmentation of C_{10}–C_{23} *n*-alkanes and occur at *m*/*z* values of 43 and 57. They correspond to $C_3H_7^+$ and $C_4H_9^+$, respectively, and are regarded as qualifier and target ions for monitoring purposes.

GC-MS is an invaluable technique for chemical fingerprinting of crude oil spills in land or marine environments. Initial screening by fluorescence spectroscopy and GC is followed by GC-MS identification of specific compounds such as steranes, triterpanes, phytanes, pristanes, etc., that are most resistant to weathering. Similar analysis of tarballs, which are formed by highly weathered oils, may enable identification of the petroleum source (**Figure 2**). When considerably more components are monitored, multivariate and pattern recognition statistical analysis methods become necessary for data interpretation.

In order to avoid the cumbersome process of determining individual compounds, more convenient methods have been accepted as regulatory benchmarks. These include the GC-MS or GC-FID analysis of total petroleum hydrocarbons (TPH) or mixtures of benzene, toluene, ethylbenzene and xylene isomers (BTEX). In the TPH method the total area of unresolved and resolved chromatographic peaks is measured.

Interest in monitoring the indoor environment has been prompted by the well-known 'sick building syndrome'. The environment indoors can be worse than that outdoors because of the accumulation of volatile pollutants owing to poor air circulation. These pollutants not only enter from the air outdoors but are also released from building materials and furnishings, cleaners, air fresheners, gas-burning stoves, etc. GC-MS has been invaluable for their analysis following preconcentraton on Tenax and thermal desorption. Separation has been achieved on a bonded SE-54 capillary column with temperature programming (**Figure 3**).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants with carcinogenic properties and present an analytical challenge because of the complexity of the mixtures in which they exist as many different isomers of the parent compounds. Hence a separation step is indispensable but volatility requirements restrict the applicability of GC to compounds of low and moderate molecular mass, the heavier ones being analysed by HPLC with fluorescence detection. PAHs are isolated from airborne samples by a combination of a Teflon filter and polyurethane foam sampling; from solid matrices either by extraction with SCF employing carbon dioxide, or by microwave-assisted extraction (MAE) into an organic solvent. For concentration and sample clean-up SPE with combined C_{18} amino (NH_2) or cyano (CN) solid phases can be employed with subsequent elution being carried out with CH_2Cl_2. Deuterated PAHs are available from US EPA to serve as internal standards. More than 60 compounds encompassing parent PAHs, their alkylated derivatives and heterocyclic analogues have been analysed at 5–100 ppb levels with a DB-5 capillary column employing both the scanning and SIM modes. Of even greater toxicological interest are the nitro-PAHs that have been ranked by the International Agency for Research on Cancer (IARC) as probable human carcinogens. Their analysis is even more difficult because of the much lower concentrations and the presence of many positional isomers. Moreover, unlike the parent PAHs, nitro-PAHs are not fluorescent, thereby limiting the sensitivity attainable by HPLC. Hence GC-NCI-MS is the technique of choice for the

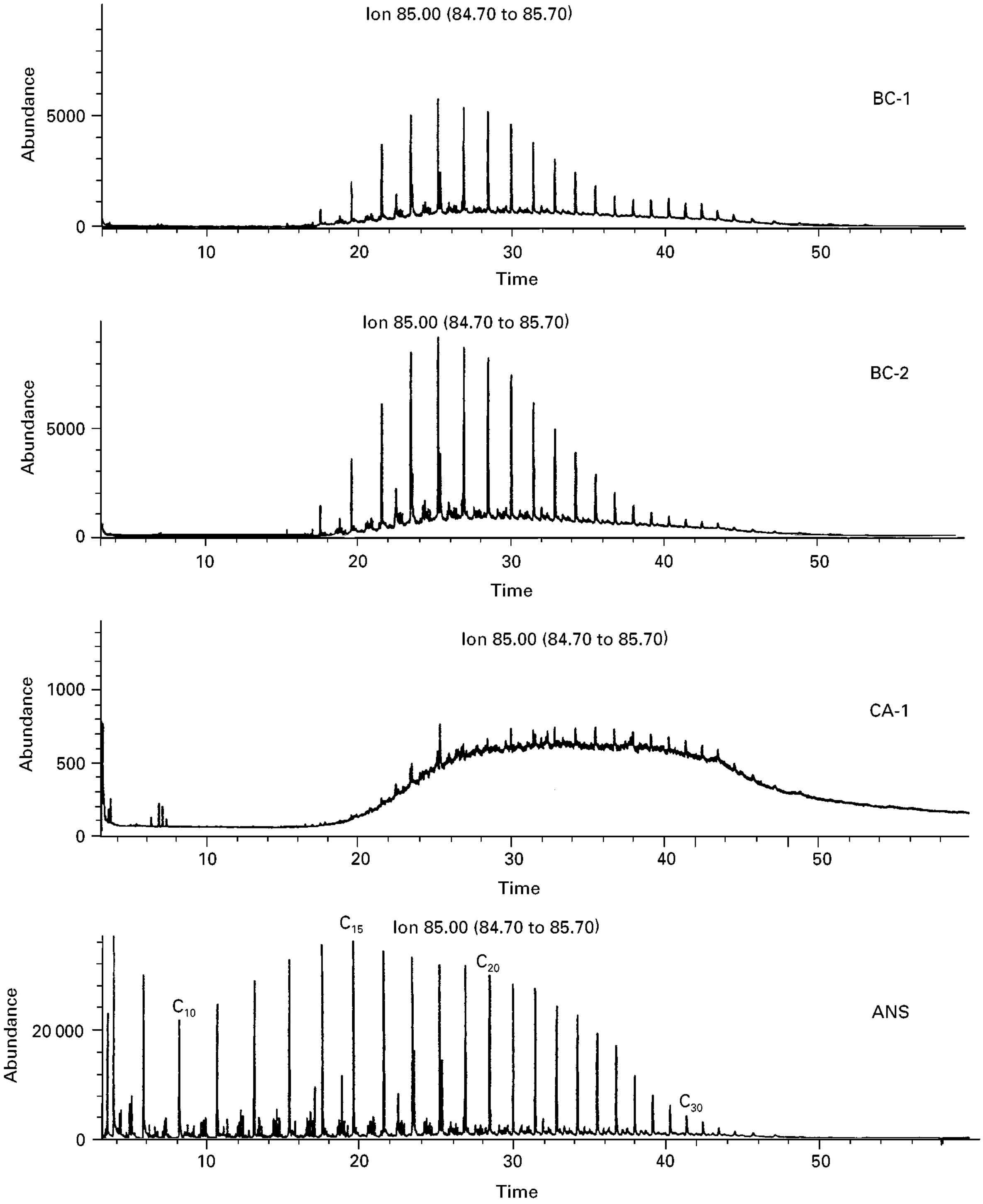

Figure 2 GC-MS *n*-alkane distribution patterns (*m*/*z* 85) for tarball samples BC-1, BC-2, CA-1 and ANS reference oil. (Reproduced from Wang Z *et al.*, 1998, with permission from Wiley–VCH.)

determination of nitro-PAHs. Polar or moderately polar capillary columns have been utilized for their separation with d_9-1-nitopyrene or d_5-dinitropyrene serving as internal standards for quantification.

Organochloro and organophosphate pesticides constitute another major category of toxic pollutants. Chlorinated herbicides and pesticides are routinely analysed by capillary GC with MS or ECD. In view of the volatility of organophosphates GC is the technique of choice for analysis via phosphorus-specific detectors. However, MS detectors operated in the SIM mode are gaining popularity, especially with

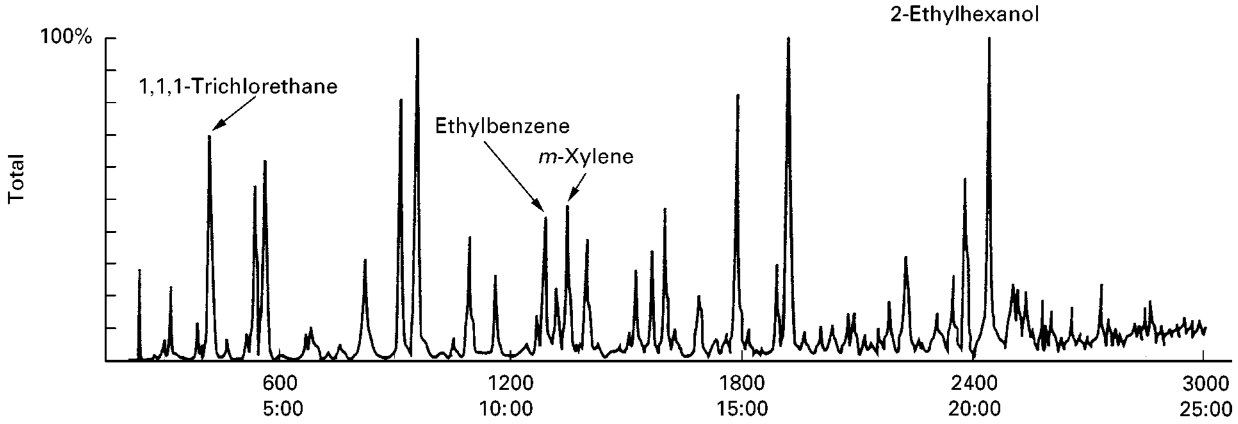

Figure 3 Indoor air at a Swedish preschool. (Reproduced from Subramanian, 1995, with permission from Wiley–VCH.)

electron impact (EI) or chemical (CI) ionization for detection at low ppb. For characterization, CI is preferred because when CH_2Cl_2 is used as reagent gas the $(M + Cl)^-$ ion is formed that gives a peak at a higher m/z value, thereby enhancing selectivity.

Insecticidal carbamates readily undergo thermal degradation and hence must be derivatized with heptafluorobutyric anhydride (HFBA) prior to GC-MS analysis. Ethylenethiourea, an environmental metabolite of carbamate fungicides and an accelerator used in synthetic rubber production, has been classified by the IARC as a potential human carcinogen. Its high polarity and water solubility require derivatization to a volatile compound and extraction into an organic solvent. This has been achieved by conversion to an *S*-alkyl derivative with *m*-trifluoromethylbenzyl chloride or 3,5-bis(trifluoromethyl)benzyl bromide. GC-NCI-MS on a D-1701 capillary column and the SIM mode has permitted sub-ppb detection limits to be realized.

Other organochloro compounds of great interest include the highly toxic, and environmentally persistent, polychloro-dibenzo-*p*-dioxins (PCDDs), -furans (PCDFs) and -biphenyls (PCBs), which are generated mainly during various combustion and manufacturing processes. They usually occur as very complex mixtures of a large number of compounds. For example, there are 22 isomers of tetrachlorodibenzo-*p*-dioxin (TCDD) alone, the 2,3,7,8-isomer being the most toxic. The very similar masses of these compounds demand high mass spectrometric resolving powers for peak separation. Hence much attention has been focused on simplifying the composition of the mixtures by appropriate sample extraction and clean-up prior to GC-MS. They are extracted from solids such as soil, sediments, dust, etc., into an organic solvent and the extracts are cleaned up via column chromatography on silica gel or alumina. Analysis is invariably carried out by GC-MS. A non-polar column such as DB-5 enables determination of homologous groups of the dioxins but a polar column such as SP-2331 is necessary for separation of most of the 2,3,7,8-congeners. EI is the usual method of ionization and ^{13}C-2,3,7,8-TCDD is widely used as an internal standard in quantification. A mass spectrometer resolving power of even 10 000 is insufficient to separate a TCDD ($m/z = 321.8936$) that is coeluted with heptachlorobiphenyl ($m/z = 321.8678$). This difficulty underscores the importance of high resolution GC-high resolution MS. Despite this difficulty, by the mid-1980s GC-MS analytical methods had been developed for the separation of all TCDD isomers and quantification at the 10^{-15} level (**Figure 4**).

PCBs and polychloroterphenyls, which number over 200, are stable compounds that can cause serious toxicity through bioaccumulation. PCBs have been used in transformers, hydraulic fluids, etc. The method of choice for their analysis is GC-MS. In the EI mode, a PCB molecule can lose an ortho- chlorine atom giving a $(M - 35)^+$ ion, which facilitates distinguishing between two coeluted PCBs one of which lacks an ortho-chlorine atom. NCI, with methane as reagent gas, has improved detection sensitivities 10 to 100-fold not only for PCBs, but also for other organochlorine compounds such as toxaphene, chlordane, etc. In NCI, the base peak is usually either M^- or $(M-H)^-$.

Large volume (100 μL) on-column injection capillary GC-MS has been applied to the determination of aliphatic and aromatic organochlorine compounds present in process water at low ppt levels. In the extraction of these solutes into hexane, the tedium of manual operation has been obviated by an automated procedure involving a laboratory robot. This has led to significant savings in extracting solvent, sample size, labour and time of analysis.

In recent years concern over the possible use of chemical warfare agents has generated interest in

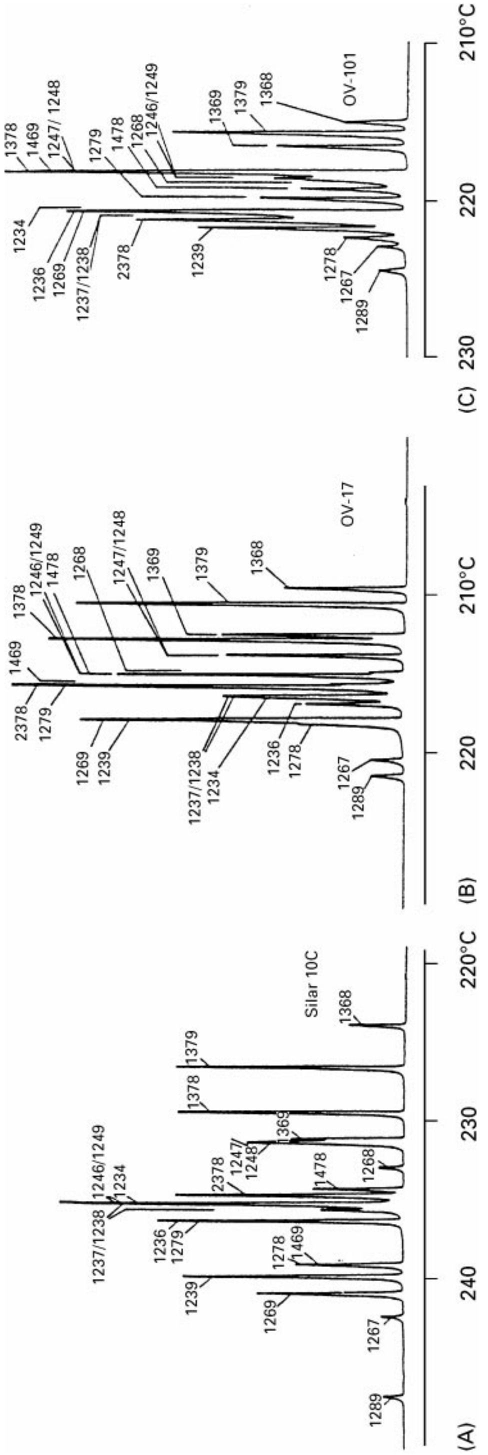

Figure 4 Mass fragmentogram (*m/z* 320) of a composite sampling showing elution of all 22 TCDD isomers on (A) 55 m Silar 10C, (B) 50 m OV-17, and (C) 50 m OV-101 HRGC columns. (Reproduced from Buser HR (1980) High resolution gas chromatography of the 22 tetrachlorodibenzo-p-dioxin isomers. *Analytical Chemistry* 52: 2257–2262, with permission from the American Chemical Society.)

their sensitive and reliable determination. The most common include 1,1-thiobis(2-chloroethane) (sulfur-mustard gas); *O*-ethyl-*N*,*N*-dimethylphosphoroamidocyanidate (tabun); isopropylmethylphosphonofluoridate (sarin) and pinacolyl methylphosphonofluoridate (soman). Their degradation products include methylphosphoric acid (MPA); iP MPA; pinacolyl MPA; cyclohexyl MPA and dithioglycol (DTG). GC-MS is advantageous for their analysis since their mass spectra are well known and available for comparison. From samples such as clothing, soil, exhumed skeletons, etc., the parent compounds are extracted into CH_2Cl_2; the degradation products are extracted into water and converted to *t*-butyldimethylsilyl (TBDMS) derivatives. After preliminary screening by low resolution EI GC-MS, confirmatory evidence is obtained by one of two methods: (1) GC-MS with EI or CI with NH_3 as reagent gas or (2) GC-tandem mass spectrometry (GC-MS/MS), where a precursor ion further fragments in a collisional deactivation chamber. For confirming the presence of sarin at low ppb to ppm level, GC-MS/MS using both EI and NH_3 CI has been carried out, employing two columns of different polarity (**Figure 5**).

GC-MS has been extended to the analysis of highly polar compounds such as aliphatic glycols that are used as antifreeze in automobiles and in aircraft deicing. Interest in their determination stems from the

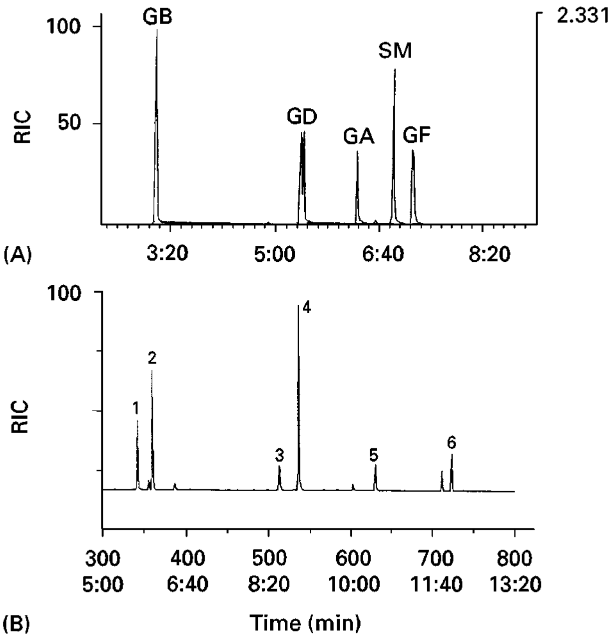

Figure 5 Reconstructed ion chromatograms for (A) nerve agents GA, GB, GD, GF and sulfur mustard (SM) (1 ng injected) and (B) TBDMS derivatives of: 1, ethyl MPA; 2, iPMPA; 3, pinacolyl MPA; 4, cyclohexyl MPA; 5, 5-cyclohexyl MPA; and 6,TDG (500 pg injected). (Reproduced from Black *et al.*, 1994, with permission from Elsevier Science.)

acute toxicity of their metabolic products. Glycols form volatile *n*-butylboronate derivatives with the characteristic ^{10}B : ^{11}B isotopic ratio (1 : 4) assisting in identification. Employing a DB-1 column and an ion trap detector operated in the SIM mode, sub-ppm detection limits have been attained. Haloacids that are formed during disinfection of drinking water constitute another group of polar compounds that have been analysed by GC-MS. These acids are readily derivatized to their methyl esters with diazomethane.

GC-MS interfaced to inductively coupled plasma–mass spectrometry (ICP-MS) enables speciation of elements at trace levels and has been applied, in conjunction with isotope dilution, to the analysis of some environmentally significant inorganic species. A knowledge of the total content of an element is of limited toxicological value since the toxicity is species dependent. Organometallic compounds of lead and tin have been reduced to their hydrides and sorbed on the GC column of a GC-ICP-MS unit and detection limits of 0.3–2 ng mL^{-1} for tin have been attained. Developing a convenient method for the analysis of mixtures of arsenic(III), arsenic(V), monomethylarsonic and dimethylarsinic acids continues to be a formidable analytical challenge. In a recent low resolution EI GC-MS method, which has employed hexachlorobenzene as internal standard, ppb detection limits have been attained following derivatization to methyl thioglycolates. However, arsenic(III) and arsenic(V) have been left unresolved (**Figure 6**).

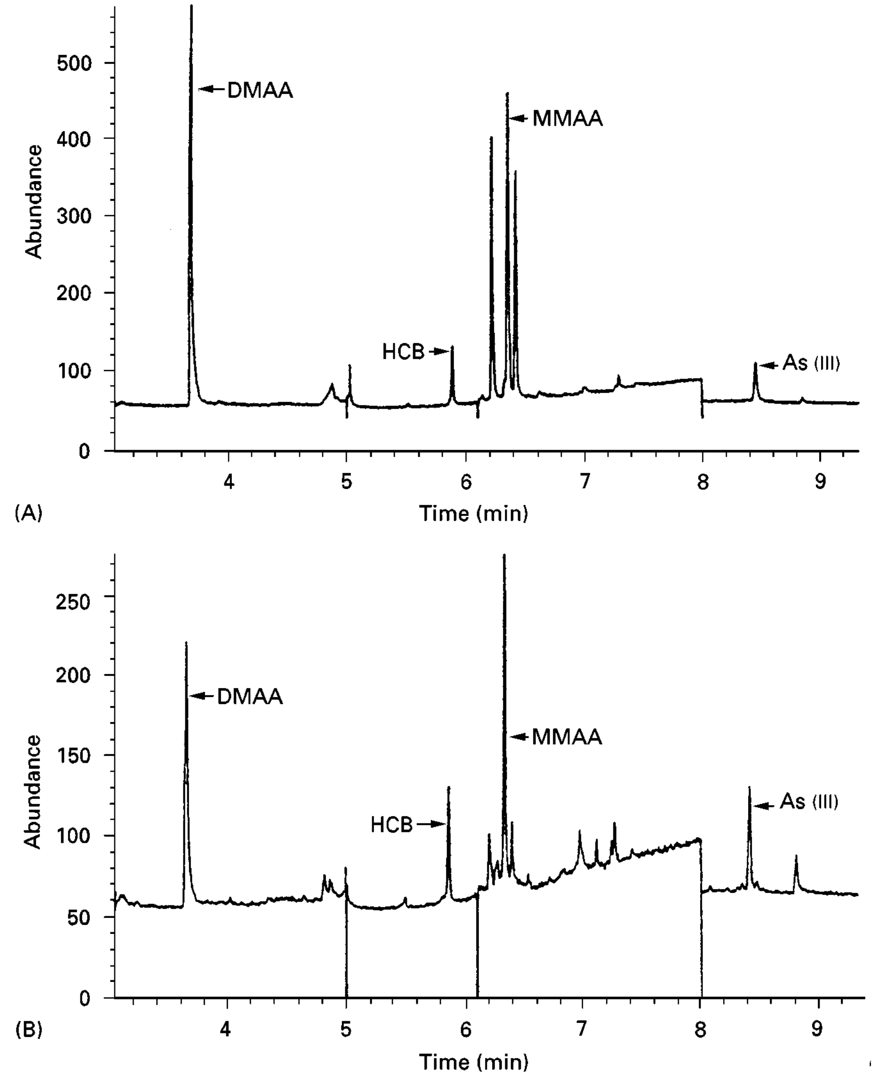

Figure 6 Representative chromatograms of HCB and the TGM derivatives of DMAA, MMAA and As(III). (A) Calibration standard containing 10 ppb DMAA and MMAA and 20 ppb As(III). (B) River water spiked with 5 ppb DMAA and MMAA and 40 ppb total inorganic arsenic (As(III) and As(V)). SIM program: *m*/*z* 195 from 3.0 to 5.0 min, *m*/*z* 282 from 5.0 to 6.1 min, *m*/*z* 195 from 6.1 to 8.0 min, and *m*/*z* 285 from 8.0 to 9.3 min. (Reproduced from Claussen, 1997, with permission from Elsevier Science.)

Conclusion

Future developments of GC-MS in environmental analysis will encompass both sampling and instrumentation. Environmentally friendly extraction methods such as SFE and MAE that reduce or eliminate the need for organic solvents are likely to gain greater acceptance. A striking development in this trend is the solventless extraction technique of solid-phase microextraction (SPME), which concentrates the analytes on a stationary phase that is bonded or coated onto a fused silica fibre. Subsequent thermal desorption introduces the analytes into the injection port of the GC-MS unit. This method has been applied to the analysis of volatile organic solvents, organochlorine and organophosphate compounds and sub-ppb to ppt detection levels have been attained with ion trap mass spectrometry.

There is tremendous interest in developing miniaturized, field-portable GC-MS units to facilitate on-site, real-time monitoring. For unattended operation and reduced labour, the sampling, extraction and injection steps should be carried out by a robot, the entire system being under computer control. A paramount consideration is the ability of the system to withstand shocks and vibrations during transport to and from the site(s). The greater speed, sensitivity and resolution needed for analysis of toxic pollutants produced in fast processes such as fires are continually the focus of developments in HRGC/HRMS. For faster analysis, short (1 m) capillary columns called 'transfer lines' and supersonic molecular beams for sampling and ionization have been employed. The low sample capacity associated with very short columns has been overcome via multicapillary columns. For monitoring solutes that are rapidly eluted from columns, mass spectrometer scan speeds must be increased significantly without compromising resolution. Alternatively, all masses must be scanned at the same time as is done in Fourier transform-MS (FTMS) and ITD. However, both these techniques operate in the pulse mode, making sample utilization inefficient. Hence other modes of array detection have been attempted, an interesting example being the development of an electro-optical ion detector (EOID) for microbore capillary column chromatography. In

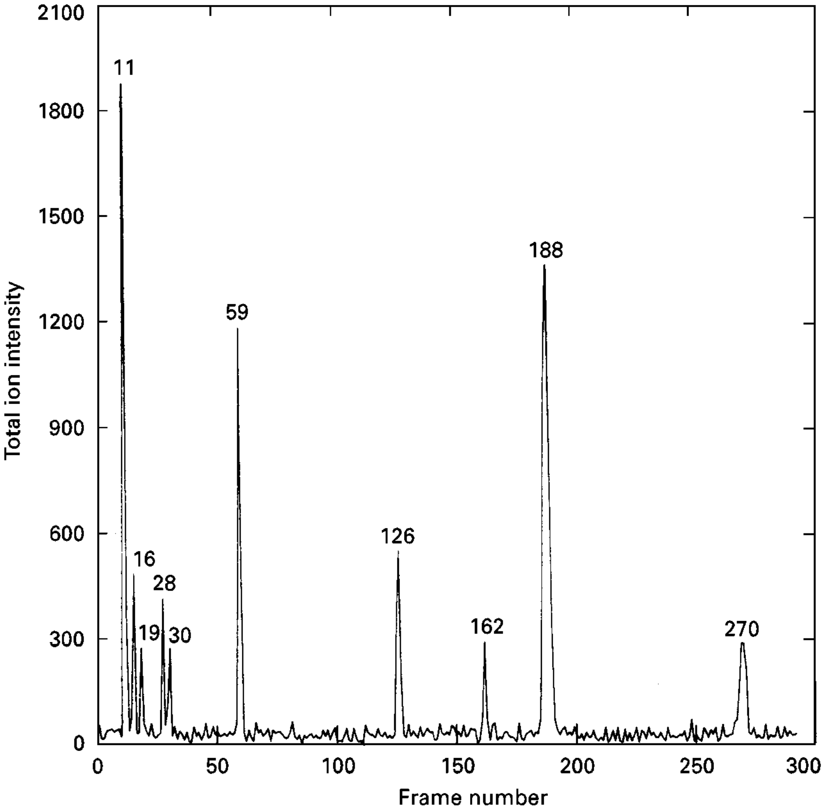

Figure 7 Total ion chromatogram obtained from a mixture of compounds consisting of air (11), dichlorofluoromethane (16), chloromethane (19), bromoethane (28), chloroethane (30), dichloromethane (59), 1,1,1-trichloroethane (126), chloroform (162), benzene (188), and trichloroethylene (270). Each compound in the mixture has a concentration of 1 ppmv. A sample volume of 0.5 μL was injected, and a signal integration time of 250 ms was used for each frame. (Reproduced from Gutnikov G. (1991) Development of a miniaturized gas chromatograph-mass spectrometer with a microbore column and an array detector. *Analytical Chemistry* 63(18): 2012–2016, with permission from the American Chemical Society.)

EOID the electrons generated by a microchannel electron multiplier array are converted to photons by a phosphor screen and detected via an array of photodiodes (**Figure 7**). Very high sensitivites have been reported, with benzene being detected at 7.5×10^{-14} g levels.

Multidimensional gas chromatography (MDGC) is another technique that seeks to overcome the problems involved in the analysis of multicomponent mixtures of volatile constituents. It is based on the separation of the constituents via one column and isolating the coeluted species in one or more cryotraps to be separated by a second column of different selectivity. MDGC is usually coupled with detectors such as IR and MS for increased specificity.

GC-MS has emerged as one of the premier methods for the rapid, convenient and sensitive analysis of pollutants. This development is partly a result of the public concern and legislative pressure for reliable monitoring of environmental quality. The commercial availability of relatively inexpensive, computer-interfaced, bench-top instruments has rendered the technique almost routine for cost-effective analysis. Even greater speeds and resolving powers of the future generations of instruments will augment the significance of GC-MS in the environmental field.

See also: **II/Chromatography: Gas:** Detectors: Mass Spectrometry. **Extraction:** Solid-Phase Extraction. **III/ Fungicides:** Gas Chromatography. **Herbicides:** Gas Chromatography. **Pesticides:** Gas Chromatography. **Polychlorinated Biphenyls: Gas Chromatography. Polycylic Aromatic Hydrocarbons:** Gas Chromatography.

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Pressurized Fluid Extraction

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Introduction

Pressurized fluid extraction (PFE) is used to extract a wide variety of compounds from solid and semi-solid environmental samples. Soil is the predominant environmental solid extracted. Sediment samples are also frequently extracted. Sludge, chimney brick, fly ash and urban dust comprise other materials that are extracted using PFE. There are several reasons to use pressurized fluid extraction for environmental samples. PFE methods are:

- automated
- easy to transfer
- environmentally friendly, consuming little solvent
- relatively fast