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Review

# Modern developments in gas chromatography–mass spectrometry-based environmental analysis

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**Abstract**

Gas chromatography coupled with mass spectrometry (GC–MS) continues to play an important role in the identification and quantification of organic contaminants in environmental samples. GC–MS is one of the most attractive and powerful techniques for routine analysis of some ubiquitous organic pollutants due to its good sensitivity and high selectivity and versatility. This paper presents an overview of recent developments and applications of the GC–MS technique in relation to the analysis in environmental samples of known persistent pollutants and some emerging contaminants. The use of different mass analysers such as linear quadrupole, quadrupole ion-trap, double-focusing sectors and time-of-flight analysers is examined. The advantages and limitations of GC–MS methods for selected applications in the field of environmental analysis are discussed. Recent developments in field-portable GC–MS are also examined.


*Keywords:* Reviews; Environmental analysis; Gas chromatography–mass spectrometry; Mass spectrometry

## Contents



## 1. Introduction

Gas chromatography coupled to mass spectrometry (GC–MS) is the technique most commonly employed today for the analysis of volatile organic

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pollutants in environmental samples. The very high number of applications is the result of the efficiency of gas chromatography separation and the good qualitative information and high sensitivity provided by mass spectrometry (MS). The MS fragmentation pattern can often provide unambiguous component identification by comparison with library spectra. When gas chromatography (GC) and MS are combined, the GC separation usually provides isomer selectivity, while the MS shows compound class and homologue specificity. GC–MS was born in 1959, when Gohlke [1] first described the direct introduction of GC effluent into a time-of-flight (TOF) mass spectrometer equipped with an oscilloscope. In the mid-1960s the analysis of different volatile organic mixtures with the new technique was reported [2,3]. These procedures mainly involved using TOF and high-resolution mass spectrometers. Nevertheless, to couple packed columns to MS, a reduction of pressure was needed to meet the vacuum requirements of the mass spectrometer. At present, direct coupling of capillary columns to the ion source of the mass spectrometer is by far the most common interfacing method in use. High-resolution GC directly coupled to low cost bench-top MS instruments has made GC–MS one of the most attractive techniques for routine analysis of volatile organic pollutants.

Several ionisation techniques are used in GC–MS. Among them, electron ionisation (EI) is the most popular because it often produces both molecular and fragment ions. In EI, gas analyte molecules are bombarded by energetic electrons (typically 70 eV), which leads to the generation of a molecular radical ion ($M^{+\cdot}$) that can subsequently generate ionised fragments. This technique generally allows for the determination of both relative molecular mass and the structure of the molecule. One important feature of electron ionisation spectra is that they are highly reproducible, which means that mass spectral libraries can be used for identification of unknowns. However, in some cases, EI does not provide the sensitivity required for the analysis of very small amounts of compounds in environmental samples. This is mainly due to extensive fragmentation. To solve this problem, softer ionisation techniques such as chemical ionisation (CI) are applied. In CI, ion–molecule reactions take place between reagent gas ions and sample molecules. As a result, molecular ions, adduct ions and fragment ions can be generated. However, the degree of fragmentation is much less than in EI and can be controlled by varying the nature of the reagent gas. CI reagents vary from application to application, but the most popular are methane, isobutane and ammonia. The major reaction in positive-ion chemical ionisation (PCI) is proton transfer, which takes place in sample molecules with a higher proton affinity (PA) than the reagent ions. Other reactions that can also occur include charge exchange, if the reagent gas does not contain available hydrogen, electrophilic addition and anion abstraction. In CI, negative ions can also be produced (NCI). These negative ions are formed by ion–molecule reactions between sample and reagent gas ions. Such reactions include proton transfer, charge exchange, nucleophilic addition or nucleophilic displacement. Moreover, the capture of the thermal electrons generated under CI conditions allows for the formation of molecular anions from compounds with a positive electron affinity (i.e. electron-capturing compounds). Chemical ionisation provides better sensitivity and selectivity than EI, but, given the special requirements of CI work, the number of applications is relatively low compared to EI. Nevertheless, CI is the technique of choice for the analysis of isomers in environmental samples, because different isomers have different reactivities towards the reagent gas, resulting in different spectra. In contrast, with EI, very similar spectra are obtained for different isomer compounds. Some examples of the applicability of CI in the analysis of isomers will be discussed in the next sections of this paper.

Compound identification is currently performed by comparing an unknown electron ionisation MS spectrum with collections of reference spectra. Huge electron ionisation mass spectral libraries are commercially available, such as the NIST Library, which contains 230 000 spectra, and the Wiley Library, with 275 000 spectra. The identification process is based on search algorithms that compare the obtained spectra with those of a library, which are generally implemented in the GC–MS instrument. A spectral match and fit factor defines the certainty of the identification. Although the library search is a powerful tool for the identification of unknowns, for

identification a series of conditions must be satisfied: the compound must be included in the library; the MS conditions at which both spectra have been obtained must be similar; and the GC separation must be sufficiently efficient to obtain a clean mass spectrum. In order to guarantee correct identification and prevent false positives, different strategies can be adopted. For instance, the U.S. Environmental Protection Agency (U.S. EPA) proposes the use of at least two different $m/z$ for each analyte, and the relative abundance of both ions must be kept within the 15–20% range. Even if the spectrum is not in the library, the search procedure can yield valuable information that can be complemented with additional MS experiments. Such complementary procedures may include CI, to provide molecular mass, high-resolution MS (HRMS), for accurate mass determination, or tandem mass spectrometry (MS–MS), for structure elucidation.

A large number of publications have resulted from research on environmental applications of GC–MS. This technique is frequently used to study the behavior of environmental pollutants and to monitor their presence in the environment. GC–MS is currently a mature technique applied in the analysis of a significant number of pollutants in samples of different origin, such as air, atmospheric aerosols, water, soils, sludges, biological samples and others. The compounds most commonly analysed include alkanes, polycyclic aromatic hydrocarbons (PAHs), pesticides, off-flavor compounds, water disinfection by-products, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), as well as other endocrine disrupting chemicals such as phthalates and short ethoxy alkylphenol etoxilates. GC–MS is also the technique of choice for the analysis of emerging pollutants such as polybrominated diphenyl ethers (PBDEs) or polychlorinated alkanes. In addition to the above-mentioned compounds, GC–MS has also been applied in the analysis of polar and non-thermal stable compounds after derivatisation. Derivatisation converts the analyte into a product with greater stability and superior chromatographic properties, such as improved peak shape. Moreover, in MS, derivatisation may result in improved ionisation efficiency, enhanced response and the production of fragmentation patterns related to the introduced organic group, which can help in the identification of families of compounds.

Instruments with different mass analysers, e.g. magnetic sectors, linear quadrupoles, quadrupole ion traps and time-of-flight analysers have been used for coupling to GC. The great majority of GC–MS applications utilise bench-top instruments with linear quadrupoles and electron ionisation. There are, however, new and interesting applications using other mass analysers and ionisation techniques. As the number of GC–MS applications in environmental analysis is very large, only some selected examples of recent research are included in the following sections. These sections are organised according to mass analyser type, the characteristics of which, obtained from specifications of commercial instruments, are summarised in Table 1.

## 2. Gas chromatography–quadrupole mass spectrometry

The popularity of quadrupole mass spectrometers arises from their relatively low cost, compactness, the ease with which their resolution can be electronically controlled and the simplicity of operation. The linear quadrupole mass analyser can be considered as a mass filter and it consists of four hyperbolic rods placed parallel in a radial array. An appropriate combination of DC and RF electric field applied to the four rods induces an oscillatory motion in a beam of ions injected approximately axially into the assembly by means of a low accelerating potential. The oscillating trajectories are mass dependent and ions with one particular $m/z$ can be transmitted toward the detector when a stable trajectory through the rods is obtained. Ions of different $m/z$ can be consecutively transmitted by the linear quadrupole filter toward the detector when the DC and RF potentials are swept at a constant ratio and oscillation frequencies.

Linear quadrupoles are the mass analysers most widely used for the analysis of environmental pollutants by GC–MS, mainly because they make it possible to obtain high sensitivity, good qualitative information and adequate quantitative results with relatively low maintenance. Moreover, the ready availability of reliable commercial instruments has promoted the widespread use of this type of equip-

Table 1
General specifications and features for linear quadrupole, ion-trap, double-focusing magnetic sector and TOF analysers

| Criteria | Linear quadrupole | Ion-trap | Double-focusing magnetic sector | Time-of-flight |
|---|---|---|---|---|
| Mass range | 2–1000 Da | 10–1000 Da | 2–4000 Da | 5–1500 Da |
| Mass accuracy | | ±0.1–0.2 *m*/*z* | <5 ppm (<2 mDa)) | To within 5 ppm (±10 mDa) for GCT™-Micromass |
| Speed | 5200–10 000 a.m.u./s | 5600–10 000 a.m.u./s | 0.15 s/decade | 5000–40 000 transients/s |
| Monitoring mode | Full-scan, SIM and simultaneous full-scan/SIM | Full-scan, SIM, full-scan of product ions | Full-scan, SIM | Full range spectrum |
| Sensitivity | EI full-scan: 1–10 pg OFN *S*/*N* 20:1, *m*/*z* 272<br>EI-SIM: 20–100 fg OFN *S*/*N* 25:1, *m*/*z* 272 | EI full-scan: 1–10 pg OFN *S*/*N* 50:1 for *m*/*z* 272 | 100 fg of 2,3,7,8-TCDD, *S*/*N* 125:1 *m*/*z* 321.8936 (SIM mode at 10 000 of resolution) | 1–2 pg HCB *S*/*N* 10:1 for *m*/*z* 284 |
| Dynamic range | 4–7 Orders of magnitude | 4–5 Orders of magnitude | >5 Orders of magnitude | 2.5–5 Orders of magnitude |
| Versatility | EI, PCI, NCI | EI, PCI, NCI (only PolarisQ) | EI, PCI, NCI, field ionisation | EI, PCI, NCI, Field ionisation |
| Mass resolution | Unit mass resolution | Unit mass resolution | >10 000 (10% valley definition) | 1000–10 000 FWHM (≤7000, 10% valley definition) |
| MS–MS | None[a] | $MS^n$, *n*=5–10 | Only with EBEqQ configuration | None |
| Performance/cost | Low | Low | Very high | High |

BzPh, benzophenone; DFBZ, decafluorobenzophenone; HCB, hexachlorobenzence; OFN, octafluoronaphthalene.
[a] Only triple-step quadrupole MS.

ment. Generally, these instruments are characterised by a bench-top configuration with mass unit resolution and both electron and chemical ionisation techniques (Table 1). A survey of the literature over the last 5 years shows that the number of papers describing GC–MS applications using linear quadrupole instruments is on the order of several thousand and the ongoing trends indicate a constant and impressive improvement in sensitivity and detection limits. Recently, some new developments have been implemented in GC–MS instrumentation based on quadrupole technology and related to the stability of mass calibration and higher scan-speed and sensitivity similar to ion-trap analyser (Table 1). This has led to a significant improvement in GC–linear quadrupole MS capabilities and it is now possible to work simultaneously with full-scan and selected ion monitoring (SIM) modes in a single run (Table 1).

One of the main areas of interest to environmental chemists is the identification and quantification of polycyclic aromatic hydrocarbons and pesticides in water, air and sediments. These compounds represent an important class of hazardous organic chemicals that are ubiquitous in the environment due to their high persistence and bioaccumulation. Different analytical methods have been proposed in the literature for their determination, but GC with selective detectors and coupled to MS are the most widely used techniques. GC–MS has proved to be an advantageous and powerful technique compared with other selective detection systems due to its good sensitivity, high versatility and selectivity. Confirmation capabilities are an additional advantage. For this reason, selective detectors have progressively been replaced by MS using both electron and chemical ionisation modes. A large number of applications related to the analysis of different families of pesticides in water, soil and sediment samples can be found in the literature [4–7]. Most applications are based on the combination off-line or on-line sample preparation techniques such as SPE and SPME with GC–MS in order to obtain less time- and labor-consuming procedures [5,6,8].

In recent years, a great deal of research has focused on disinfection by-products (DBPs) in drinking water [9], following the finding that several DBPs are carcinogenic and may have adverse reproductive consequences [10]. In addition to volatile chlorinated compounds such as trihalomethanes (THMs), attention has been directed to other semi-volatile compounds such as haloacetic acids (HAAs), haloacetonitriles, haloketones and haloaldehydes. Most of the methods used to determine these compounds involve gas chromatography, with electron-capture detection, or coupled with EI low-resolution mass spectrometry with quadrupole mass analysers [11,12]. Due to the regulation of HAAs in drinking water [13], these compounds continue to be the subject of new analytical methods [14]. For their analysis by GC, a prior derivatisation step is necessary because of their low volatility and high polarity. For instance, recently, Xie developed a method for the analysis of HAAs using liquid–liquid microextraction, acidic methanol derivatisation and GC–EI-MS determination [15]. Limits of detection were in the microgram per liter range, and in comparison to EPA Method 552.2 [16], which uses GC with electron capture detection (GC–ECD), cleaner baselines and fewer interfering peaks were evident. Another problem of major concern for many water utilities around the world is the presence of off-flavour compounds that produce an unpleasant taste and odor in water. The most obvious taste and odor compounds, such as hydrocarbons, solvents, iodoforms and various chloro- and bromophenols, which have odor thresholds in the microgram per liter range, are currently analysed by GC–EI-MS using linear quadrupole bench-top instruments. In addition, the implementation of extraction and preconcentration techniques such as closed-loop-stripping analysis (CLSA) and solid-phase microextraction (SPME), coupled to GC–MS instruments, has allowed for the identification and quantification of algal metabolites (geosmin and methylisoborneol), which, at their ng/l odor thresholds, are responsible for most earthy-musty odor episodes around the world [17–20].

Endocrine-disrupting chemicals (EDCs) have also received special attention in recent years. In wildlife, these compounds are suspected of being responsible for the decline of certain species and change of sex in fish and shellfish. Chemicals suspected of being estrogenic include synthetic estrogens, steroids, pesticides, phthalates, alkylphenol ethoxylate surfactants, dioxins, PCBs, PBDEs and natural estrogens

such as phytoestrogens [9]. GC–MS and LC–MS are the most commonly used techniques for the environmental analysis of EDCs. Generally, GC–MS is used for apolar (e.g. PCDD/Fs, PCBs, PBDEs) or moderate polar compounds (e.g. alkylphenols, phthalates), while for polar compounds such as alkylphenol carboxylates, LC–MS is the preferred technique. Other compounds such as steroid sex hormones are analysed using both techniques. Among these compounds, nonylphenol ethoxylates (NP*n*EOs, $n$ = number of ethoxy units) have recently been studied as a result of the fact that persistent degradation products (nonylphenols and carboxylic derivatives) generated during wastewater treatment and in sewage treatment plants are regarded as endocrine-disrupting compounds [21]. Recently, nonylphenol (NP) and NP*n*EOs ($n \leq 2$) have been analysed in water from a sewage treatment plant and in fish by GC–EI-MS, and detection limits were 4–2100 ng/l [22] and 17 ng/g [23], respectively. For the analysis of nonylphenoxy carboxylic acids (NP*n*ECs), a derivatisation step is required to overcome the problem posed by their low volatility. Díaz et al. [24] recently proposed the use of dimethyl sulfate/NaOH for the derivatisation of NP*n*EOs and NP*n*ECs ($n \leq 2$) to their corresponding methyl esters. The analysis of these compounds was performed by headspace solid-phase microextraction and GC–MS in SIM mode. As an example, Fig. 1 shows GC–EI-MS single-ion chromatograms of derivatised NP, NP*n*EOs and NP*n*ECs for a water sample taken from a river where they had been detected. PCI-MS with ammonia as the reagent gas has also been used for the analysis of NP*n*ECs in paper mill and municipal sewage treatment plant effluents and river water. All NP*n*ECs produced molecular ion adducts with ammonia to give base peaks corresponding to $[M+NH_4]^+$. Using this ionisation mode, limits of de-

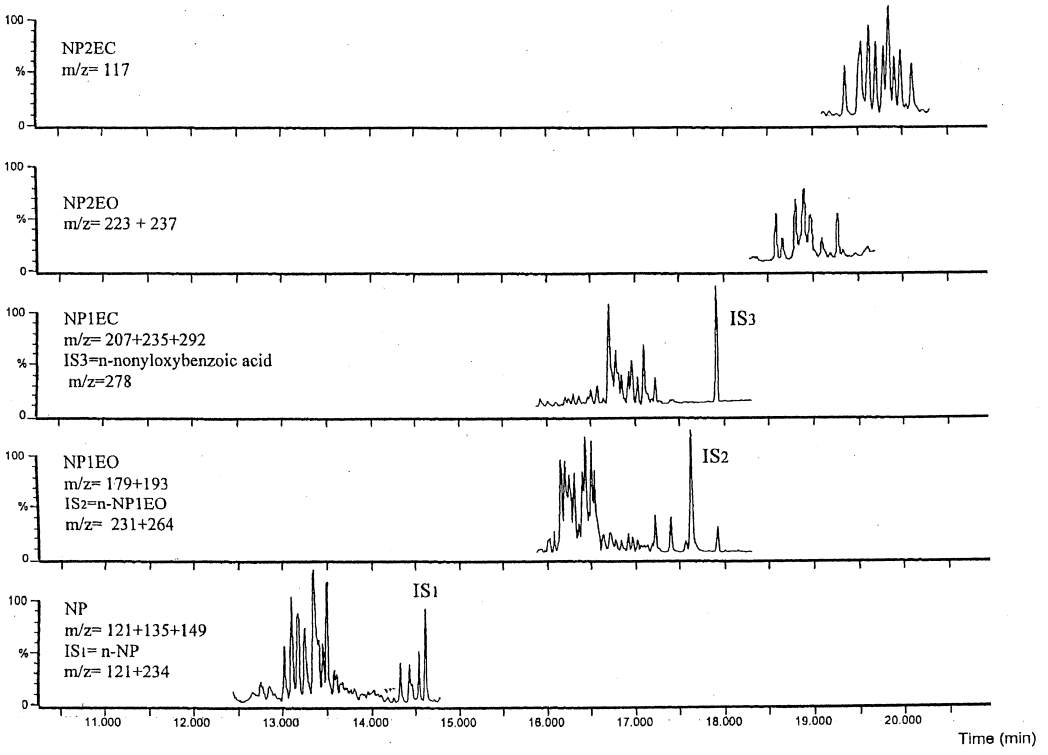


Fig. 1. Headspace-SPME–GC–MS single-ion chromatograms of derivatized compounds from river water entering water treatment plant. NP, nonylphenol; NP1EO, nonylphenol monoethoxylate; NP2EO, nonylphenol diethoxylate; NP1EC, nonylphenoxyacetic acid; NP2EC, nonylphenoxyethoxyacetic acid. Experimental conditions: GC column: DB-5MS, 30 m×0.25 mm I.D., 0.25 μm film thickness. MS analyser: quadrupole, operating in SIM mode. (Reprinted with permission from Ref. [24], Copyright 2002, American Chemical Society)

tection lower (4–8-fold) than those with EI-MS were achieved for NP*n*ECs (*n*: 1–4) [25,26].

Several papers have recently been published concerning the analysis of phthalates, another estrogenic family of compounds. GC–MS with EI and CI, using methane or isobutane as reagent gas, has been used for the analysis of these compounds in water, soil and sewage sludge samples [27]. PCI with methane was found to be very useful in obtaining molecular mass information, but EI-MS is the most sensitive mode. The ion at *m/z* 149 is the most abundant in the EI mass spectra for all phthalates except dimethylphthalate, which gives a base peak at *m/z* 163. These ions and other ions at higher mass range are currently selected for quantification purposes and for the identification of isomeric mixtures. Using GC–MS in EI mode, limits of detection of 2–30 ng/l in river and sea water, 125–250 ng/kg in sediments, and 10–600 ng/g in sewage sludge have been reported [27–29]. The main problem to be solved when analysing phthalates is contamination by laboratory materials during the different steps of the analysis. To solve the background contamination problem, simple and rapid analytical procedures have been proposed, based on SPME. These involve applying both direct immersion and headspace techniques, and subsequent GC–MS analysis [29–31]. Another endocrine disrupting compound of recent interest is bisphenol A, which has also been analysed by GC–MS, although its high polarity often requires a derivatisation step prior GC analysis. Derivatisation to silyl bisphenol A [32,33] or pentafluorobenzoylate ester [34] are the most commonly used procedures for the analysis of this compound. GC–NCI-MS with methane as reagent gas allowed for a very high detectability of BPA in water (0.02 ng/l) after derivatisation to pentafluorobenzoylate [35], which is greater than that obtained using GC–EI-MS for underivatised BPA (0.1 μg/l) [36,37].

Polybrominated diphenyl ethers (PBDEs), which are used as flame retardants, are being determined in a growing number of environmental samples around the world because they have been shown to be significant endocrine disrupting compounds [38]. Up until recently, quantification of PBDEs had been carried out using technical PBDE products due to the lack of pure reference standards, but more than 30 individual congeners are now commercially available and are used for congener-specific determination. In addition, the availability of various $^{13}$C-labeled standards allows for quantification using the isotopic dilution method. GC–low-resolution MS with negative chemical ionisation is commonly employed for the analysis of PBDEs in environmental samples, although in some cases GC–HRMS is preferred. The high selectivity of HRMS prevents interferences produced by other halogenated compounds, although it has not been demonstrated that in practice this technique is superior to LRMS [39]. GC–NCI-LRMS offers higher sensitivity than EI-LRMS, especially for compounds with more than four bromine atoms. Nevertheless, a drawback of the NCI technique is that for most PBDEs only the ions due to bromine can be monitored (*m/z* 79 and 81), although, occasionally, some higher mass fragments can be used for quantification, such as *m/z* 487 and 489 for BDE-209. EI-LRMS would offer higher selectivity and the capability of confirming the identity of compounds from the full mass spectrum, but at the cost of lower sensitivity. Eljarrat et al. [40], who have compared the two ionisation methods, indicate that for EI-MS limits of detection were 15 times higher than those for NCI-MS. In contrast, Covaci et al. [41], using large volume injection and narrow bore columns, obtained comparable results with both ionisation modes. However, EI provides better structure information than NCI, and interference problems between the penta-BDE-126 and hexa-BDE-155 in NCI mode can be overcome when using EI mode by monitoring the molecular ions of each homologue group. In spite of these considerations, as a result of its higher sensitivity, GC–NCI-MS has been the most frequently used technique for the analysis of PBDEs in air [42], sediment [39,43] and biota samples [39,44–50]. As an example, Fig. 2 shows the chromatograms of a PBDE standard solution containing 14 BDE congeners, and cormorant liver and porpoise blubber samples where various BDE congeners were detected by GC–NCI-MS in SIM mode [44].

## 3. Gas chromatography–ion-trap mass spectrometry (GC–ITMS)

The ion-trap mass spectrometer is a member of the

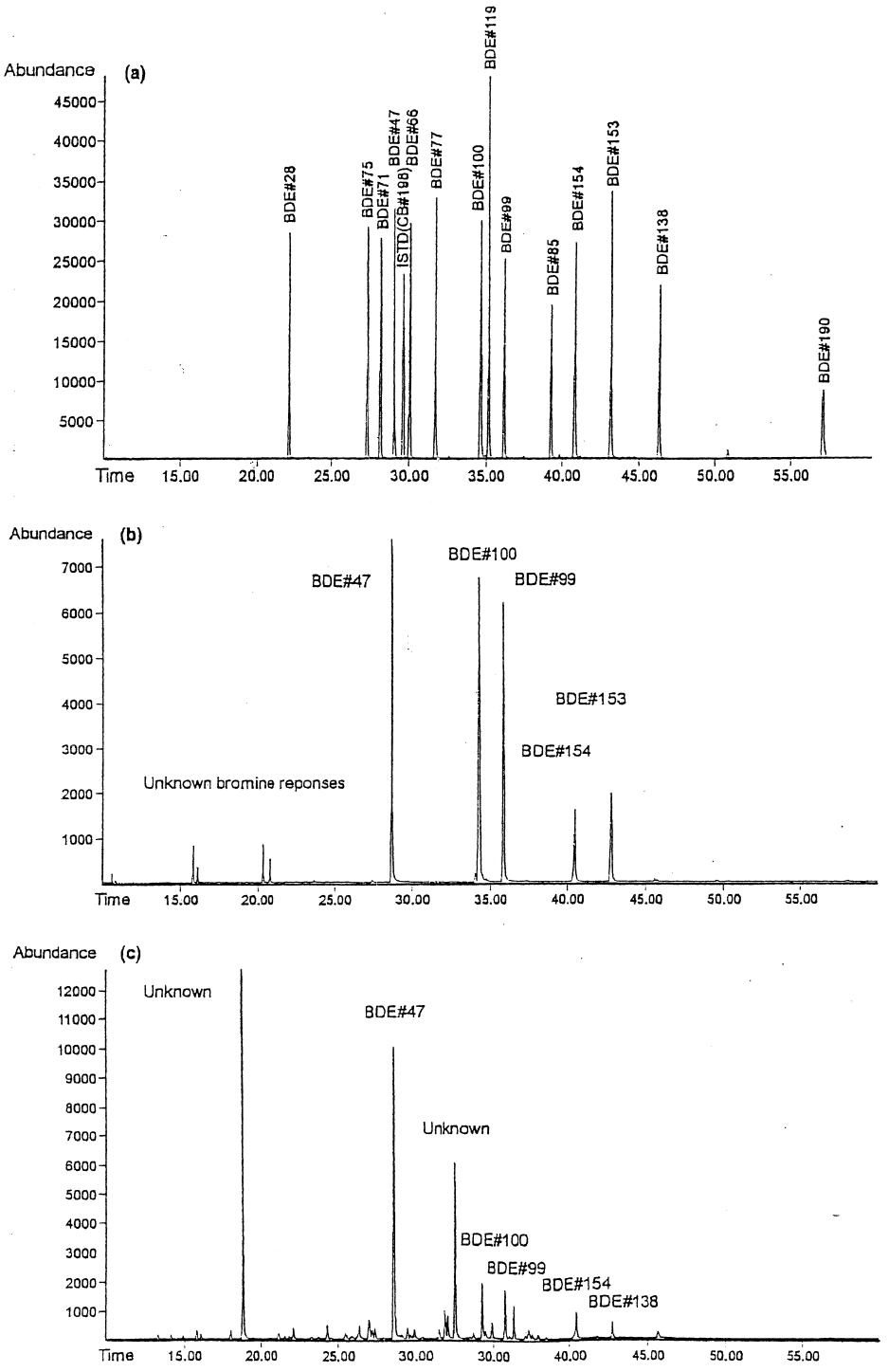


Fig. 2. GC–NCI-MS chromatograms for the sum of two bromine ions monitoring (79 and 81 Da) for (a) a standard solution containing the 14 BDE congeners determined, (b) a cormorant liver sample, and (c) a porpoise blubber sample. Experimental conditions: GC column: CP-Sil 8, 50 m×0.21 mm I.D., 0.25 μm film thickness. MS analyser: quadrupole, operating in NCI mode, monitoring bromine at 79 and 81 Da. (Reprinted from Ref. [44], Copyright 2002, with permission from Elsevier Science)

quadrupole family of instruments, first described by Paul and Steinwedel [51], who developed a method for mass analysis by trapping a range of ion masses in the quadrupole ion trap and detecting and measuring the ions while stored. From 1960 to 1980, modifications in the operating system were made in order to store only a single mass at a time, but the impetus for the widespread implementation of the ion trap in mass spectrometry was the invention in the early 1980s of a mode of ion trap operation termed mass-selective ejection [52]. Using this technique, trapped ions are sequentially ejected from the trapping volume towards an external detector in increasing mass/charge order. Prior to this development, the acquisition of an entire mass spectrum using an ion trap was a complex and time-consuming process and the linear quadrupole, invented concurrently with the quadrupole ion trap, became the dominant bench-top mass spectrometer. At present, the ion trap is challenging this position, with thousands of GC–MS instruments installed in research and routine laboratories worldwide.

Coupled to gas chromatography, quadrupole ion-trap mass spectrometry offers good sensitivity, the ability to manipulate ions during storage, relatively high mass range, low cost and reduced size. Currently, two ion-trap instruments coupled to GC are commercially available: ThermoFinnigan's PolarisQ uses external source ionisation, and Varian's Saturn 2000, internal source ionisation. Both commercial instruments offer electron and positive chemical ionisation modes as well as an MS–MS option, but only PolarisQ can function in negative chemical ionisation mode. All these instruments offer unit mass resolution, a mass range up to 1000 a.m.u. and high sensitivity (Table 1). Moreover, enhanced selectivity can be obtained in MS–MS mode, with the additional advantage of confirmation capabilities as the full-scan spectra of product ions is collected. A drawback of ion-trap instruments is that sensitivity depends on the quantity of ions present in the trap, which affects the response in real samples. As a consequence, additional requirements for either calibration or clean-up procedures are needed.

The quadrupole ion trap is the three-dimensional analogue of the conventional quadrupole mass filter. It consists of three cylindrically symmetric electrodes (two end-caps and a ring). In the normal mode of use, an auxiliary oscillating potential of low amplitude is applied across the end-cap electrodes while a radio-frequency (RF) oscillating drive potential of ~1 MHz is applied to the ring electrode. Ions are created within the ion trap by injection of electrons, or may be injected from an external source. A range of $m/z$ values can be held in stable orbits by virtue of the RF potential and become focused as a cloud at the ion trap center. As the amplitude of RF potential is increased, the motion of the ions becomes progressively more energetic and they develop unstable trajectories. Ions then exit the ion trap to a detector in order of increasing $m/z$ value, generating a mass spectrum. Usually, several such mass spectra, termed micro-scans, are obtained in succession and summed prior to being displayed as a scan.

An important breakthrough in GC–MS analysis was achieved with the advent of the ion-trap detector because of its capability of performing MS–MS by means of collision-induced dissociation (CID). The theoretical aspects of ion-trap tandem mass spectrometry can be found in the comprehensive paper published by Plomley et al. [53]. The most common way to perform CID is to apply a radio-frequency (RF) voltage to the end-cap electrodes of the ion trap to isolate ions with a selected $m/z$ value or a small range of $m/z$ values. After isolation, an excitation voltage, resonant or non-resonant, is applied over the trap, and collisions with helium buffer gas lead to the formation of product ions. Compared with the triple-stage quadrupole, the ion trap offers some advantages. First, it operates in a pulsed mode, so that ions are accumulated mass selectively over time. In this way, a target ion number can be selected so as to ensure constant signal-to-noise ratio over a wide range of eluent concentrations. This results in an enhancement in sensitivity at low concentrations (Table 1). A second advantage is that collision-induced dissociation in the ion trap is produced by several hundred collisions of a mass-selected ion with helium buffer gas atoms. Under these conditions, it is possible to dissociate the accumulated mass-selected ions completely, and, moreover, practically 90% of fragment ions are confined within the ion trap in favorable cases. In such cases, the efficiency of formation, storage and transmission of product ions to the detector is high, and more product ions are therefore obtained. An additional

advantage of ion-trap instruments is the capability of performing $MS^n$. Environmental applications have exploited this advantage only to a limited extent, despite its usefulness, as for instance for the identification of metabolites of environmental contaminants. In comparison with triple-stage quadrupole or hybrid sector instruments, one limitation of the ion trap in MS–MS mode is the fact that only helium can be used as the collision gas.

In recent years, some interesting applications of GC–ion trap mass spectrometry in environmental analysis have been published. These have focused mainly on the determination of halogenated compounds, such as PCDDs/Fs, PCBs, toxaphene and polybrominated diphenyl ethers, steroids, pesticides and PAHs and their derivatives. Generally, EI is the chosen ionisation technique, and full-scan acquisition mode is currently used because it provides qualitative information for unequivocal identification. One of the advantages of ion-trap analysers compared to linear quadrupoles is their high sensitivity in full scan mode, which means reliable spectra can be produced at low concentration levels. Different authors have taken advantage of this capability to identify and quantify environment contaminants at ppt levels. Typical recent applications include the use of full-scan ITMS for the analysis of PBDEs in sediments and biota by Allchin et al. [54], and an SPME–GC–ITMS method for the determination of haloacetic acids in water, proposed by Sarrión et al. [55]. In contrast with what happens in linear quadrupole analysers, the selected ion monitoring mode is not frequently used in ion traps because no improvement in sensitivity is obtained with respect to the full-scan mode. Nevertheless, an enhancement of selectivity is achieved, which can be used to prevent MS interferences.

GC–ITMS combined with chemical ionisation (CI) and full-scan operation mode has not been frequently applied in the analysis of organic pollutants in the environment. Nevertheless, several papers that compare CI and EI modes have been published. Methane is the most widely used chemical ionisation reagent, although other compounds have also been proposed. For instance, Mosi et al. [56] utilised 1,1-difluoethane as a reagent gas to differentiate PAH isomers through the formation of specific adducts by ion–molecule reaction between the cations $CH_3CHF^+$ and $CH_3CF_2^+$ and PAHs. This method allowed for the separation and determination of co-eluting isomers. Another example of chemical ionisation and full-scan IT is the analysis of linear alkylbenzenesulfonates (LAS) and their degradation products, sulfophenylcarboxylic acids, in sewage effluents and river water [57]. Since the abundance of LAS molecular ions in EI mass spectra is low and sometimes they are not detected, the use of positive chemical ionisation has been proposed. This allows for a 10- to 50-fold enhancement of sensitivity in relation to the EI mode. An interesting characteristic of ion-trap mass spectrometry is the ability of the system to change the ionisation mode from positive to negative during the analysis. Sequential positive and negative chemical ionisation combined with GC–ITMS has been used as a selective and sensitive method for the analysis of organochlorine and organophosphorus pesticides in vegetable samples [58] with good reproducibility, $<25\%$, and low detection limits, 2–2000 times below EU regulatory levels (0.01 mg/kg).

Tandem mass spectrometry is the ITMS mode most widely used for the analysis of environmental contaminants because it provides very high selectivity. The potential of ion-trap tandem mass spectrometry (ITMS–MS) using EI mode for the analysis of polychlorodibenzo-*p*-dioxins and dibenzofurans, dioxin-like PCBs, toxaphene and polybrominated diphenyl ethers has recently been evaluated. These compounds are often analysed by GC–HRMS, but this technique involves high investment and maintenance costs. Alternative methods such as GC–ITMS–MS have been studied to replace the reference method (GC–HRMS), or at least decrease analysis costs by using such methods for preliminary screening. Only suspect samples are then kept for analysis by the reference method. A recent estimate of the total time required for instrumental analysis revealed that HRMS requires at least 50% more time per sample than does ITMS–MS, considering the analysis time as the time required for instrument tuning, calibration, maintenance and repair [59]. Several papers related to the evaluation of the GC–ITMS–MS technique for the analysis of these compounds have recently been published. For instance, the technique has been successfully applied to the analysis of PCDD/Fs in fly ash [60,61], soil extracts

[62], sewage effluents [63], foods [59,64], fish tissues [65] and waste mineral oils [66]. Non-ortho PCBs (77, 81, 126 and 169) and mono- and di-ortho substituted PCBs (105, 118, 128, 156 and 157), also known as dioxin-like PCBs, have also been determined using GC–ITMS–MS in EI mode [53,67–69]. The predominant transitions $[M+2]^{+\cdot} \rightarrow [M+2-COCl^{\cdot}]^{+}$ from tetra- to octa-chlorinated dioxins and furans and $[M+2]^{+\cdot} \rightarrow [M+2-Cl_2]^{+}$ for each chlorination degree of dioxin-like PCBs have been commonly used in EI-MS–MS mode. High selectivity and specificity have been obtained using these product ions for these families of compounds. As an example, Fig. 3 shows the GC–ITMS–MS chromatograms corresponding to tetrachlorodibenzo-*p*-dioxins (product ion *m*/*z* 259) from a ball clay containing chicken feed, a reference toxic fat and fly ash, where different elution profiles and abundance of 2,3,7,8-TCDD were detected [70]. Generally, GC–ITMS–MS provides good repeatability and reproducibility (RSD% <15%) with low limits of detection. Typical LODs are 60–300 fg injected for non-ortho PCBs [67,68] and 150–500 fg for the 17 toxic PCDD/Fs congeners [59], although values from 1 to 3 pg have also been reported [60,65]. These values are slightly higher than those obtained by GC–HRMS, but in all cases they are enough to obtain reliable results at low concentration levels. One interesting approach to improve the sensitivity of GC–ITMS for the analysis of these compounds is to replace the standard stainless steel electrodes of the ion trap with fused-silica-coated electrodes (silchrom electrodes) [59]. These electrodes have been found to produce a 30–50% increase in response for all PCDD/Fs congeners. GC–ITMS–MS has generally produced results comparable to those obtained with high-resolution mass spectrometry for PCDD and PCDFs in different environmental matrices. Nevertheless, the quality of the clean-up procedures and the presence of interfering compounds in the final extracts can significantly affect the sensitivity and reproducibility of the method. For instance, Kemmochi et al. [62] indicate that low ionisation conditions (electron energy 30 eV and emission current 150 A) are enough to obtain a reproducible quantification, but if interfering ions are present higher ionisation conditions (electron energy 90 eV and emission current 350 A) must be used.

A further example of the applicability of GC–ITMS–MS with EI mode is the analysis of tox-

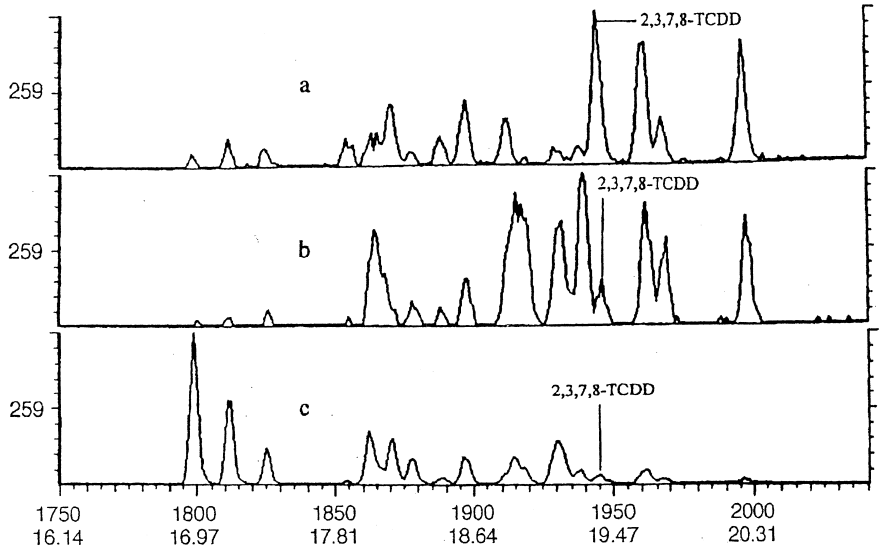


Fig. 3. GC–ITMS–MS product ion chromatograms (*m*/*z* 259) for tetrachlorodibenzo-*p*-dioxins from (a) a ball clay containing chicken feed, (b) a reference toxic fat, and (c) a fly ash from a waste cogeneration incinerator. Experimental conditions: GC column: DB-5MS, 40 m×0.18 mm I.D., MS analyser: ion-trap MS, working in MS–MS mode. (Reprinted from Ref. [70], Copyright 1999, with permission from Elsevier Science)

aphene in biological samples. Currently, negative chemical ionisation mass spectrometry (NCI-MS) in SIM mode has been used for quantification of total toxaphene and selected polychlorobornane congeners in environmental matrixes. However, differences of at least 1 order of magnitude in the response factors between isomers have been obtained using NCI-MS. Although EI shows more similar response factors for toxaphene congeners, low-resolution MS with linear quadrupole analysers is not sensitive enough for the analysis of these compounds in environmental samples. The high sensitivity and selectivity of the EI-ITMS–MS prompted some authors [71,72] to propose the use of this technique as an alternative to NCI-MS. For the analysis of these compounds, the ion at $m/z$ 125, which corresponds to a chlorinated monochlorotropolium structure, and the ions at $m/z$ 303/305 were selected as precursor ions. As an example, Fig. 4 shows the GC–EI-ITMS and GC–EI-ITMS–MS chromatograms ($m/z$ 125→$m/z$ 89+99) obtained from cod liver oil NIST SRM 1588 and beluga skin samples. As can be seen, the gain in selectivity and sensitivity was considerable when switching from EI-MS mode to EI-MS–MS mode [72], and the chromatograms were virtually undisturbed by the sample matrix and other polychlorinated compounds. Instrumental detection limits of 1–2 pg for the individual congeners and 130 pg for the total toxaphene have been achieved [72]. These detection limits are lower than those obtained by NCI-MS or by EI-HRMS in SIM mode.

## 4. Gas chromatography–high resolution mass spectrometry (GC–HRMS)

For many years, a high level of concern about the presence of different pollutants at low levels (part per trillion) in the environment has led scientists to develop sensitive analytical methods. Although in most applications of GC–MS a linear quadrupole or a quadrupole ion trap is used for mass analysis, higher mass resolution is sometimes needed in order to avoid some interferences detected in the environmental analysis. Due to its high specificity and sensitivity, gas chromatography coupled with high-resolution mass spectrometry (GC–HRMS) has been employed for many years and is still being used to solve some specific environmental problems in different GC–MS application areas. An example of these applications is the analysis of polychlorinated compounds such as polychlorodibenzo-*p*-dioxins and furans. Highly sophisticated and dedicated equipment is used for this purpose, generally based on double-focusing sector instruments. The characteristics of this instrumentation are summarised in Table 1.

Environmental applications of HRMS in GC–MS are based on enhancing the selectivity of the MS as a detector by increasing resolution. There are two main types of applications of HRMS in environmental analysis. The first is based on a very high capacity to remove the contribution of matrix interfering compounds in the determination of the analytes. This capacity is exploited, for example, in the analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs) and furans (PCDFs), dioxin-like PCBs and polybrominated diphenyl ethers. Using selected ion monitoring (SIM) at a mass resolution of 10 000, the presence of matrix components in the extracts does not interfere and detection at a high level of mass accuracy can be performed. The second type of application is related to the determination of complex mixtures of contaminants such as polychlorinated terphenyls, toxaphene and polychlorinated alkanes, where, in addition to the matrix interferences, some problems arise due to interferences between fragment ions of congeners with different degrees of chlorination. In order to remove these specific interferences, HRMS at a resolving power higher than 10 000 is required.

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like PCBs (non-ortho and mono-ortho PCBs) are examples of polyhalogenated compounds whose determination is mainly performed by gas chromatography coupled to high-resolution mass spectrometry (GC–HRMS) using the EI mode to provide the required sensitivity and selectivity for analysis. Negative chemical ionisation with methane as reagent gas has also been used as an alternative technique to electron ionisation, but lower sensitivities have been reported [73,74]. A complete picture of the state-of-the-art for PCDD and PCDF analysis was given by Liem [75]. Improvements in the sensitivity of mass spectrometers, the use of high-resolution capillary GC columns

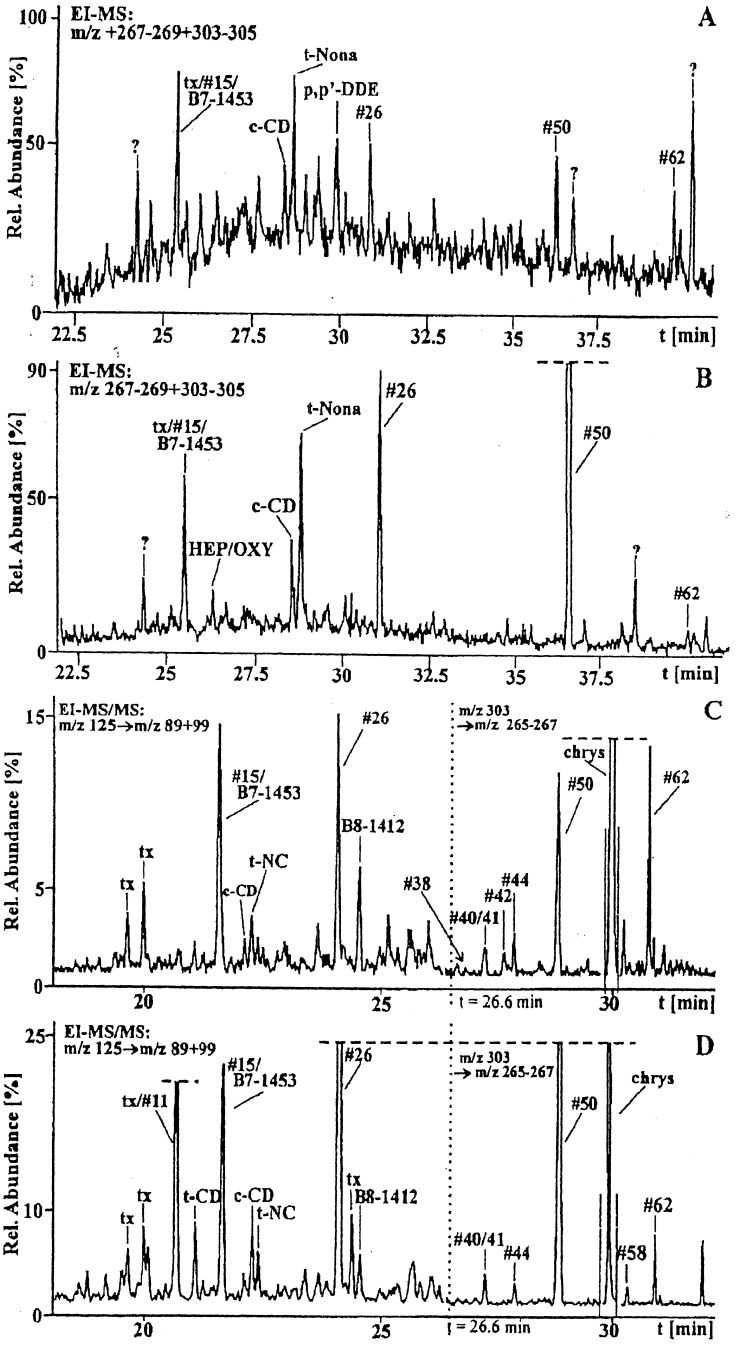


Fig. 4. GC–EI-MS and GC–EI-MS–MS mass chromatograms of a NIST SRM 1588 (A and C) and a beluga ''muktuk'' (skin) sample (B and D), respectively. Toxaphene congeners (Parlar and Andrews-Vetter nomenclature) and other chlorinated pesticides are assigned as well as the time where the product ion was changed (dotted line). Signals exceeding the abundance scale are marked with a dashed line: c-CD, cis-chlordane; chrys, chrysene-d12; HEP, heptachlorepoxide; OXY, oxychlordane; t-CD, trans-nonachlor; tx, probably unknown toxaphene congeners; ?, unknown. Experimental conditions: GC column: DB-5MS, 30 m×0.25 mm I.D., 0.25 μm film thickness. MS analyser: ion-trap MS, working in full-scan mode and full-scan product mode. (Reprinted with permission from Ref. [72], Copyright 2002, American Chemical Society)

and the availability of high-purity chemical standards have allowed the quantification of all PCDD/Fs in the sub-ppt range. GC–HRMS with EI (electron energy ~38 eV) at a resolving power of 10 000 is the reference method for the analysis of PCDD/Fs and non-ortho PCBs. This method is described in U.S. EPA Methods 1613 and 1668, and the European Standard EN1948-1/2/3 [76–78]. Quantification is performed by selected ion monitoring (SIM) and isotopic dilution using stable isotope-labelled $^{13}C_{12}$ analogues of PCDD/Fs and dioxin-like PCBs. Although the signal due to the polychlorinated compounds decreases as a result of increasing mass spectral resolution, detection limits improve, because noise decreases even further. Limits of detection as low as 10–200 fg have been obtained using GC–HRMS systems [79]. Over the last 2 years, a large number of papers (almost 200) have been published describing GC–HRMS applications for routine analysis of PCDD/Fs and dioxin-like PCBs in environmental samples. These papers focus primarily on the analysis of soils [80], sediments [81–83], sludges [84], municipal solid wastes [85], incinerator emissions [86] and biota [87,88]. Typical limits of detection for PCDD/Fs using GC–EI-HRMS are 0.05–0.3 ppt for animal tissues, $<0.02$ ppt for feeds, and $<0.03$ ppt for biota [89].

Another important example of the application of GC–MS in environmental analysis is the determination of two families of brominated compounds, polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs). Although GC–low resolution MS in NCI mode provides sufficiently high sensitivity, magnetic-sector-based GC–MS systems operating at high resolution (10 000) are the ideal instruments for analysis of compounds of this type, because they remove the contribution of other halogenated contaminants present in the matrix. Given the commercial availability of individual congeners, quantification based on congener-specific method is currently a routine practice. In recent years, some applications of GC–HRMS to the analysis of these compounds in different environmental matrices such as biota [90,91], fish [92] and vegetables [93] have been reported. Using the two most abundant ions of the molecular cluster for mono-, di-, tri- and tetrabromo-DEs, and the $[M-2Br]^+$ for tetra- to hepta-bromosubstituted congeners, high sensitivity and selectivity can be achieved. Typically, LODs ranging from 0.1 to 5 pg have been obtained.

GC–HRMS is also applied to the environmental analysis of complex mixtures such as toxaphene (chlorobornanes), polychlorinated terphenyls (PCTs), and polychlorinated alkanes (PCAs). In these applications, the interferences produced by matrix components and between congeners with different degrees of chlorination can be overcome by using HRMS at a resolving power higher than 10 000. The analysis of chlorobornanes (CHBs) in environmental and biological samples is difficult, mainly due to the substantial difference in peak profiles between samples and industrial formulations and to the lack of individual isotopically labelled internal standards for quantification. The use of GC–HRMS allows for higher selectivity than low-resolution mass spectrometry, and unambiguous determination of the individual congeners in environmental samples has been achieved. Three different approaches using GC–EI-HRMS have been applied. The first is based on monitoring of the $m/z$ 158.9768 and the isotope peaks at $m/z$ 160.9739 and 162.9709, which correspond to the dichlorotropylium ion structure ($C_7H_5Cl_2^+$). The use of these characteristic ions in combination with HRMS at a resolving power higher than 10 000 allows good selectivity, but only the concentration of total toxaphene can be determined and the presence of the different homologue groups cannot be distinguished [94–96]. This method has been successfully applied to the analysis of toxaphene in biota samples [94,95], providing limits of detection lower than 10 μg/g. The second approach is based on the determination of homologue composition. Due to the interferences of homologues with an additional chlorine atom over each homologue group, GC–EI-HRMS at resolving power of 20 000 is needed. A scheme of the contribution of the nonachlorobornane $[M-Cl-HCl]^+$ ions on the selected octachlorobornane $[M-Cl]^+$ ions is given in Fig. 5, as an example of the high resolution needed. In practice, when using a resolution of 10 000, most of the interferences can be eliminated [97]. Finally, the third approach is based on specific-congener analysis using GC–EI-HRMS in SIM mode [98]. Negative chemical ionisation-HRMS at resolving power higher than 10 000 has also been used for the analysis of CHBs in environmental samples [99,100].

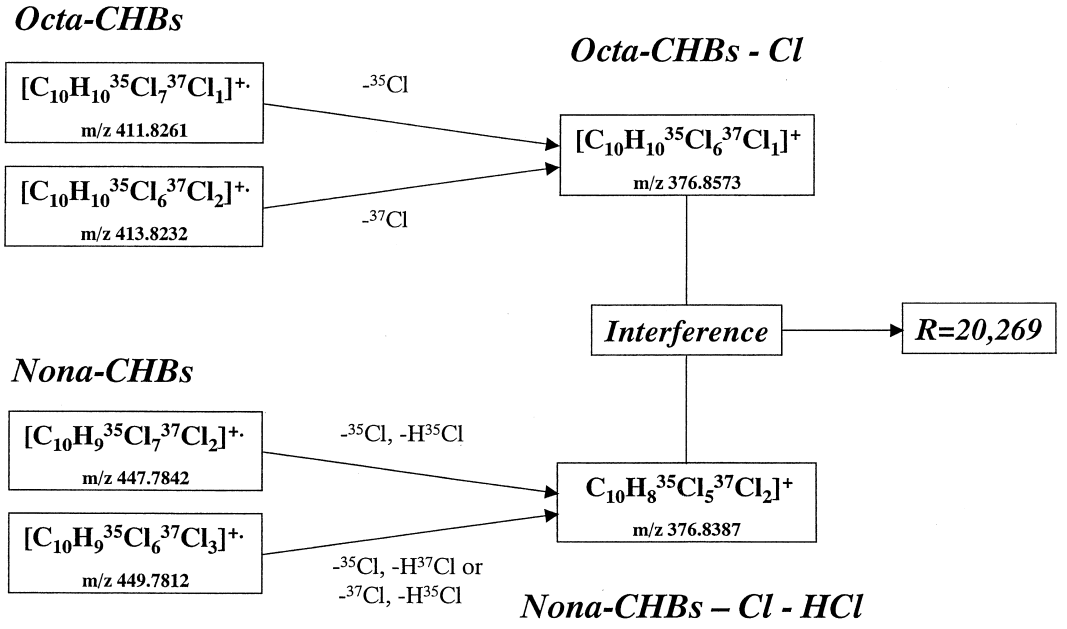


Fig. 5. Interfering mass from nonachlorobornane $[M–Cl–HCl]^+$ fragment ion at the monitored $[M–Cl]^+$ fragment ions for octachlorobornanes.

This technique provides good selectivity and very high sensitivity, while avoiding interferences by other organochlorine compounds such as polychlorinated diphenyl ethers or organochlorine pesticides. In all cases, methane has been used as the moderating gas for NCI mode. Using this technique, low detection limits have been obtained for individual CHB congeners, ranging from 0.3 to 7 pg as amount injected.

GC–EI-HRMS operating in SIM mode has also been used for the analysis of complex mixtures such as PCTs and polychlorinated alkanes (PCAs) in environmental samples. Analysis of PCTs has proven to be difficult because of the complexity of the mixtures, the high boiling points of the heavily chlorinated congeners, and the co-elution of the lower chlorinated PCTs with some PCBs. The analysis of these compounds using EI-LRMS presents some interferences due to the contribution of $[M–Cl_2]^+$ fragment ions of homologues with two additional chlorine atoms over the molecular ions of each homologue group. In general, for the complete elimination of all internal interferences, a resolution of 35 000 is recommended to avoid errors in quantification due to interfering fragments [79,101]. For quantification purposes, homologue distributions of some PCT standard mixtures and environmental samples have been determined using HRMS [101,102], making it possible to determine the source of PCT sample contamination. The analysis of PCAs is very difficult because of the complexity of mixtures (more than 10 000 congeners), and only semi-quantitative analysis is currently performed [79]. PCA chromatograms are characterised by a large hump where all congeners coelute. The determination of PCAs in environmental samples has mainly been performed by GC–ECD and GC–NCI-low resolution MS, but some authors have proposed the use of GC–NCI-high resolution MS at a resolving power of 10 000–12 000, because with this technique it is possible to determine the contribution of each homologue group in the samples and avoid interferences from other organochlorine compounds [79,103–105]. This method, which involves using methane as moderating gas and selecting the $[M–Cl]^-$ ions of each homologue group, has been successfully used for the determination of PCA in sediments and biota [103,104]. As an example, Fig. 6 shows the GC–NCI-HRMS elution profiles obtained for each degree of chlorination and carbon chain

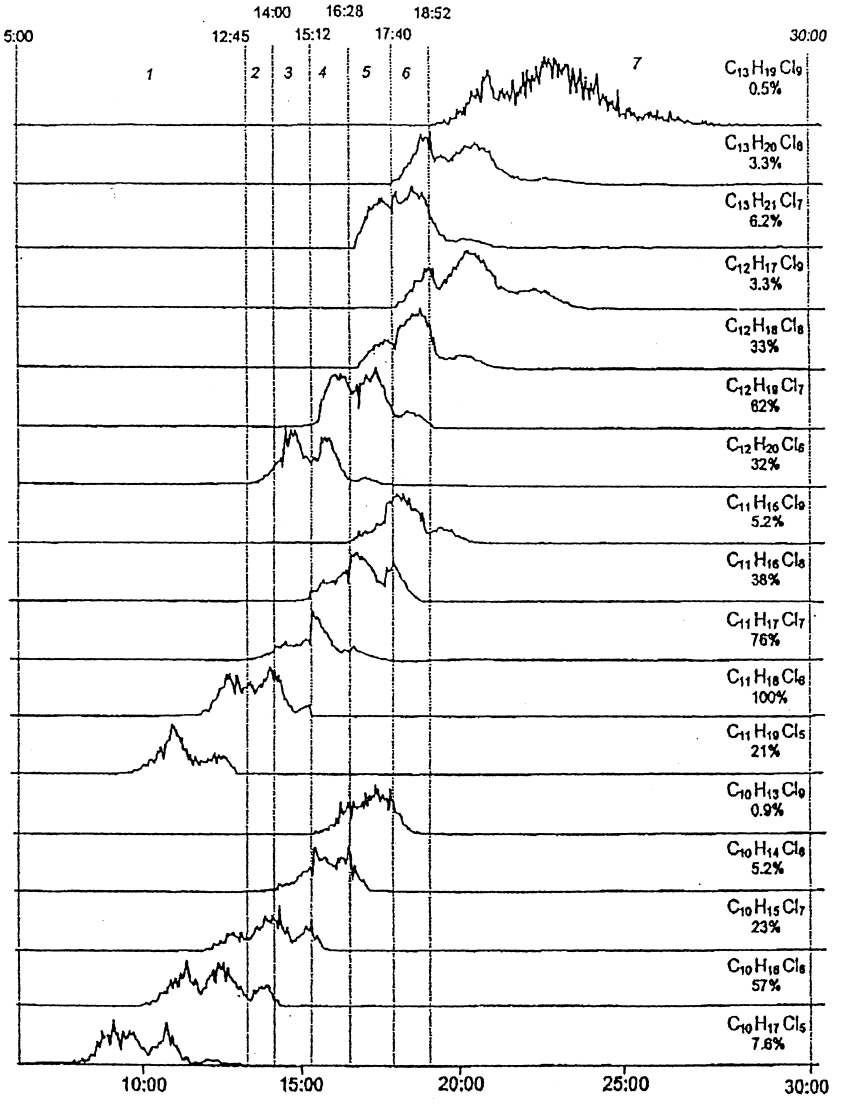


Fig. 6. GC–NCI-HRMS elution profiles of monitoring ions in a commercial PCA mixture of $C_{10}$–$C_{13}$ chain length and ~60% chlorine by mass (PCA-60). Experimental conditions: GC column: DB-5MS, 30 m×0.25 mm I.D., 0.25 μm film thickness. MS analyser: double-focusing magnetic sector (EBE, geometry), operating in NCI at a resolving power of 12 000 and SIM mode. (Reprinted with permission from Ref. [103], Copyright 1997, American Chemical Society)

length of the commercial PCA product PCA-60 ($C_{10}$–$C_{13}$ carbon chain length and ~60% chlorine).

## 5. GC–time-of-flight mass spectrometry (GC–TOF-MS)

In recent years, time-of-flight mass spectrometry (TOF-MS) has gained considerable acceptance as a mass analyser for different applications. In fact, the renaissance of TOF-MS, a technique that was established more than 50 years ago, is largely due to biological applications that require a large mass range ($>10^5$ a.m.u./charge). Recently, however, the advantages of the high speed of the technique (a few milliseconds) are being exploited in other research

fields, and TOF-MS is being coupled to GC. From a conceptual point of view, time-of-flight instruments are very simple: ions are formed or sampled on bushes, which are accelerated within a linear electric field into a field-free flight tube. Ions travel some distance in the field and gain kinetic energy which is related to their velocity. Since velocity is inversely proportional to the square root of $m/z$, the ions will separate so that lighter ions traverse the acceleration and drift regions before the heavier ones. A planar detector is used to convert the ion arrival event into an electrical signal whose time relative to the start event is recorded.

The mass resolving power in TOF-MS instruments is independent of ion mass but for a given uncertainty in time ($\Delta t$) it increases with $(m/z)^2$. Mass resolving power can be improved by increasing the flight time, which can be achieved by using lower accelerating voltages or longer flight distances. Moreover, a decrease in the uncertainty in time will also produce an improvement in mass resolving power. In spite of the simplicity of the method, there are a number of factors that can have a significant effect on flight time: differences in the initial position at which ions are formed (spatial spread), in the times over which they are formed (temporal spread), in initial velocity (kinetic energy spread), and in direction of motion (angular spread). The dispersion in ion arrival time due to differences in initial position of ionisation may be corrected by spatial focusing. The ions are generated in an electric field such that those formed further from the detector experience the force due to the field for longer and reach a higher velocity. As a result, time-focusing of ions of the same mass occurs at the detector. For velocity focusing, the best device is the reflectron, which is placed at the end of the drift region and consists of a series of lens plates with different voltages that act as a retarding field. Ions with the same mass that have greater kinetic energy will penetrate more deeply into the retarding field and take longer to emerge. So they will catch up with the ions with lower kinetic energy at the detector. Additional refocusing is often achieved by lenses or by ion reflectors.

In TOF instruments, ions must be sampled in bushes. If they are produced continuously, they can be stored for a very short time, extracted using a voltage push and bunched in time. In most GC–TOF-MS instruments, an appropriate voltage pulse is applied to accelerate the ions in the direction orthogonal to their initial flight direction. In orthogonal acceleration (oa-TOF-MS) a nearly parallel ion beam ideally has no velocity spread, and the finite spatial spread is corrected with a linear or reflecting instrument geometry. In GC–TOF-MS, the predominant method of data collection is integrating transient recording (ITR), in which the successive ion pulses that arrive at short time intervals (10 000 pulses per second) are collected and stored in the consecutive recording channels of a multichannel analyser. Relatively noise-free mass spectra can be obtained by the addition of several spectra. When signals are very weak, the flight times of individual ions can be determined from their start and stop signals by using a multistep time-to-digital (TDC) converter.

The key strengths of TOF-MS are summarised in Table 1. In relation to the coupling to gas chromatography, the most important features are the capability of producing mass spectra of good quality within a very short time (a few milliseconds) and high sensitivity (higher efficiency than scanning MS). High speed has made it possible to use TOF mass analysers as detectors in high-speed GC. Moreover, the good mass accuracy (low ppm errors) of the oa-TOF mass analyser has provided an alternative to accurate mass GC–MS with sector instruments. Different commercial TOF instruments have appeared offering high speed (Pegasus-LECO and Tempus-ThermoQuest) or high mass accuracy (GCT™-Micromass) as their main feature. Some environmental applications of GC–TOF-MS are described in the following sections.

### *5.1. Fast GC and GC×GC*

Fast separations have represented a major trend in gas chromatography in recent years. These techniques can dramatically reduce analysis time for the determination of volatile and semi-volatile organic compounds, and should result in increased sample throughput and reduced analysis costs for many environmental applications. In high-speed gas chromatography (HSGC) the timescale has shifted 1 to 2 orders of magnitude and separations that required 20 min or longer by conventional capillary GC can be

obtained in 20 s by HSGC. Different terms such as fast GC, very fast GC and ultra fast GC are often used in the literature; separation is performed in the minute range in fast GC, and in seconds or subseconds in very fast GC and in ultra fast GC, respectively.

High-speed separations are currently obtained using capillary short columns (length $<10$ m) operated at higher than usual carrier gas flow rates. Under these conditions peak widths are very small. For instance, van Deursen el al. [106] have calculated peak widths at half-height for a narrow bore column (10 m$\times$50 μm I.D.) for fast GC, and two very short columns (1 m and 0.3 m$\times$50 μm I.D.) for very fast GC and ultra fast GC. The values obtained were 0.2 s for the narrow bore column and 30 ms and 10 ms, respectively, for the short columns. So, in order to couple high-speed GC to MS for the characterisation of complex environmental mixtures, an extremely fast acquisition rate is needed. With TOF instruments complete mass spectra can be obtained at rates as high as 500 spectra per second, which can allow for accurate treatment of the very narrow chromatographic peaks produced by HSGC. An additional advantage of TOF instruments with time-array detection is the complete absence of concentration biasing, given that all the ion fragments of the spectrum represent the same point on the chromatographic peak. This is not the case with scanning instruments, where, in addition to their relatively low scan rate (a few spectra per second), the concentration for each mass changes in the ion source during a scan and the spectra would be distorted as ion currents are simply sampled with no regard for their intensity between points.

An important consequence of the absence of concentration biasing in TOF instruments is the possibility of performing spectral deconvolution of partially overlapping chromatographic peaks if the fragmentation patterns for the overlapping components are significantly different. Up to now, most of the papers published in the literature related to environmental applications of HSGC–TOF-MS deal with the compromise between the need for fast separation and the resolution requirements for the identification of unknown peaks using spectral deconvolution. The acquisition rate of the TOF analyser is highly significant. For instance, Fig. 7 shows the deconvoluted chromatogram of nine pesticides eluting in a 3-s window obtained at a relatively low acquisition rate (40 spectra/s) [107]. This was sufficient to separate nine of the ten compounds tested. As an example of the influence of acquisition rate on peak resolution and deconvolution performance, Fig. 8 shows the chromatograms of a mixture of hydrocarbons recorded at 500 and 50 spectra per second, respectively [106]. At 500 spectra per second, the first three peaks are baseline separated and quantitation can be performed. In contrast, at 50 spectra per second it is not possible to deconvolute the overlapping peaks. The greater the peak overlap, the higher the spectral acquisition rate required to ensure a sufficient number of spectra (at least four) between peaks. However, an increase in spectral acquisition rate results in a reduction in the intensity of the peaks (Fig. 8) so the optimum scan rate must be a compromise between sufficient resolution and high sensitivity.

Currently, chromatographic separations obtained in fast GC are sufficient for peak finding and for applying deconvolution algorithms to recognise the presence of two or more components in a single chromatographic feature and some applications to environmental contaminants such as pesticides, herbicides, aromatic hydrocarbons, PCBs and pharmaceutical compounds in water and sediments, have been published [107–111]. The fragmentation patterns of isomers, however, are often too similar for deconvolution and spectral identification based on comparisons with library spectra. For instance, congener-specific PCB identification is difficult because the lack of separation in the short columns used in very fast GC results in coelution of isomers that cannot be differentiated on the basis of their mass spectra [107]. In these cases, greater peak separation is required. This can be achieved by a combination of GC columns of different selectivity. Various approaches have been proposed to increase separation capacity in order to obtain sufficient resolution to solve the coelution problem and allow for the use of the TOF-MS additional separation dimension to produce library-searchable mass spectra. One possibility is the combination in series of two GC columns by means of an electronic pressure control at the junction point between the columns. Leonard and Sacks [112] have proposed the use of this

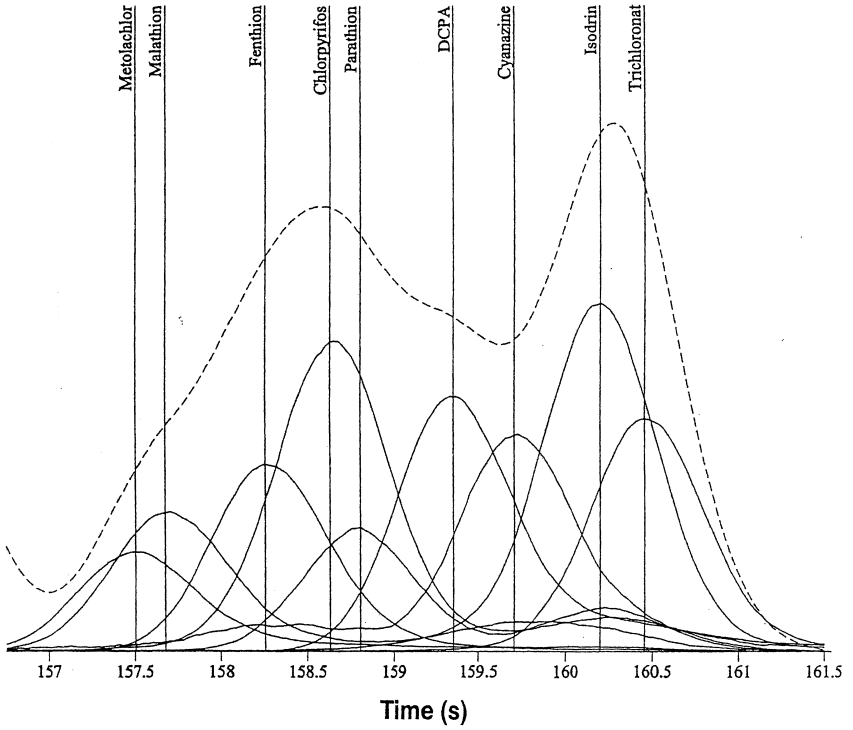


Fig. 7. Chromatogram of pesticides using vacuum-outlet GC–TOF-MS at 40 spectra/s. Unique ions and TIC (dashed line) are plotted. A faster acquisition rate allowed automatic peak location for nine of the ten compounds. Experimental conditions: GC column: CP-Sil 8 CB, 5 m×0.53 mm I.D., 0.5 μm film thickness with a 3 m×0.18 mm I.D. deactivated fused-silica column as retention gap. MS analyser: TOF, operating at $m/z$ range 120–520. (Reproduced from Ref. [107], Copyright 2002, by permission of Preston Publications)

procedure for the separation of a mixture of compounds with different polarities and a wide range of boiling points. Results show that pressure-tuneable column ensembles can be useful for the high-speed analysis of moderately complex mixtures. Another highly promising possibility for the separation of very complex mixtures is comprehensive two-dimensional gas chromatography.

Comprehensive two-dimensional gas chromatography (GC×GC) involves the direct coupling of two columns with different separation mechanisms in order to separate in the second column unresolved compounds that eluted from the first. Thus GC×GC can be considered a special case of multidimensional gas chromatography, where every component of the mixture is subjected to an orthogonal two-dimension separation. The instrumental design involves a modulator interface that couples the two columns. The first column generally is a conventional non-polar GC column, and the second one is a short polar column. Since separation in the second column is very fast and peaks are on the order of 200 ms wide at half width, only TOF-MS instruments have the rapid spectrum acquisition capability required for the reconstruction of the chromatograms and for quantification. Data from GC×GC–TOF-MS shows groups of pulsed peaks with the same spectra, corresponding to the series of pulses of a single component. The pulsed peaks are separated by a time interval depending on the modulation frequency. For overlapping peaks eluted from the first column, interleaved pulses of peaks appear if the compounds are resolved in the second dimension. The compounds can be identified by their retention time and mass spectra and quantified by combining all the second-dimension peaks that belong to the same analyte.

Thus far, very few papers have been published dealing with the use of GC×GC–TOF-MS for the analysis of contaminants in environmental samples.

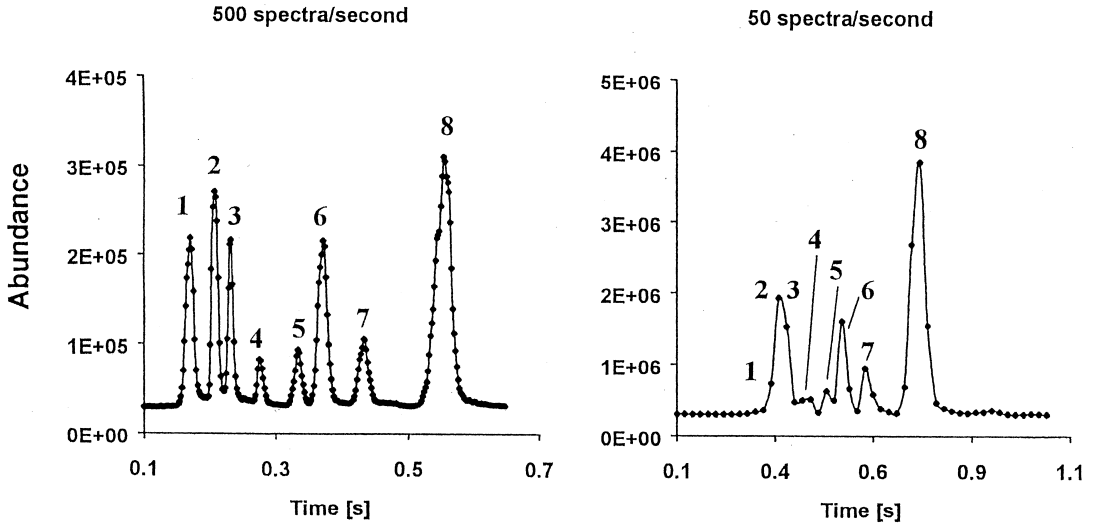


Fig. 8. Comparison of chromatograms recorded at 500 and 50 spectra per second, respectively. Experimental conditions: capillary column: OV-1, 0.3 m×50 μm I.D, 0.17 μm film thickness. MS analyser: TOF, operating at $m/z$ range 40–200. Compounds: (1) pentane, (2) 2,3-dimethylbutane, (3) hexane, (4) benzene, (5) heptane, (6) methylcyclohexane, (7) toluene and (8) octane. (Reprinted from Ref. [106], Copyright 2000, with permission from Elsevier Science)

Nevertheless studies that demonstrate the power of the method have been performed using phenols and PAHs [113], PCBs [114] and pesticides [115,116]. In a recent publication, Dallüge et al. [115] give interesting information about GC×GC–TOF-MS quality parameters, demonstrating that for pesticides good linearity and repeatability of peak areas (RSD 5–11%) can be obtained. The paper includes a thorough discussion of data processing procedures to obtain analytical information such as identification and quantification of target analytes, screening for unknowns and group type analysis.

### *5.2. Accurate mass instruments*

The very good mass accuracy of the oa-TOF mass analyser has provided an alternative to accurate GC–MS with sector instruments. For peaks with sufficient intensity and using internal reference mass, a mass accuracy of 0.001 Da can be obtained (5 ppm for measurements at $m/z$ 200). Mass accuracy, however, depends on signal intensity and decreases at both very low and very high signal intensities. Low mass accuracy at low mass intensities can result in an underestimation of the peak area. Consequently, a broader mass window must be used for quantification at trace levels [117]. The decrease in mass accuracy at high signal intensities is due to the time-to-digital converter (TDC) used for data collection. TDC is only able to distinguish between events separated by sufficient time (dead time). At high ion currents, multiple ion arrivals cause counts to be missed, resulting in mass spectral peaks with lower intensity than expected and inaccurate mass assignment. A dead time correction algorithm and a device that reduces the transmission of the ion beam into the sample region are used to increase the dynamic range and exact mass capability. Very few papers have been published concerning the application of these instruments to environmental problems [117,118], but Dalüge et al. have demonstrated that very good detection limits can be obtained for PCBs and pesticides, at low pg range. In addition, the use of narrow mass windows provides a good separation of coeluting compounds. As an example, Fig. 9 shows the GC–TOF-MS [117] chromatogram of a PCB congener (CB-118) in an eel extract using two different mass windows, 1 Da (B) and 0.02 Da (C). In this case, the use of a mass window of 0.02 Da prevented a false-positive identification.

An interesting development in GC–TOF-MS is the use of the field ionisation ion source (FI). Many

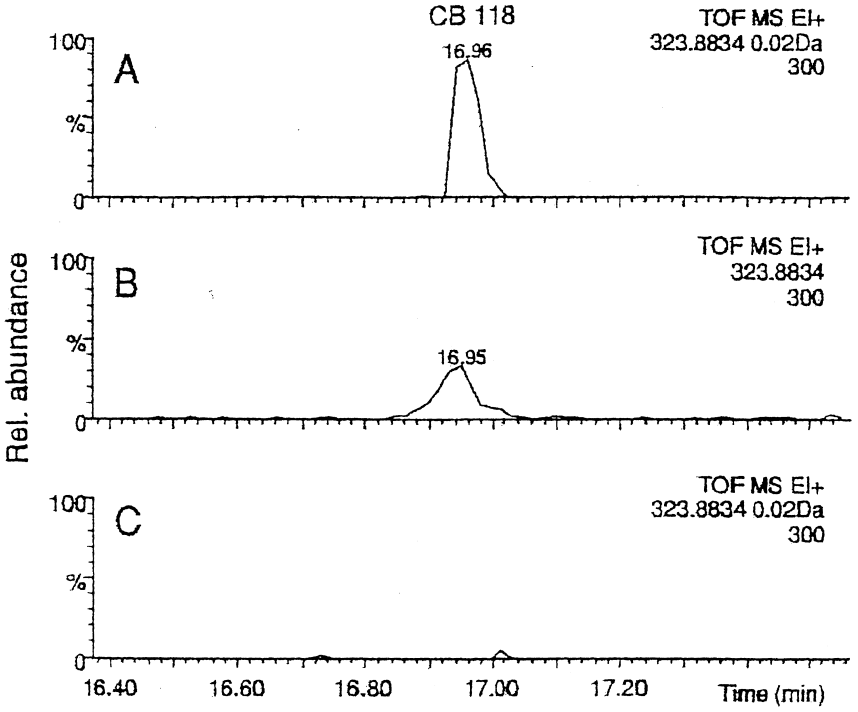


Fig. 9. GC–TOF-MS chromatograms of the $m/z$ 323.8834 ion traces of (A) a PCB standard (10 pg) and (B,C) an eel extract. (A,C) Extracted using a window of 0.02 Da, and (B) using a mass window of 1 Da. Signal intensities are the same in all three frames. Experimental conditions: GC column: DB-5, 40 m×0.18 mm I.D., 0.18 μm film thickness. MS analyser: TOF equipped with 1-GHz time-to-digital converter and operating at a pusher interval of 40 μs and at $m/z$ range 50–500. (Reprinted from Ref. [117], Copyright 2002, with permission from Elsevier Science)

compounds of interest do not provide good molecular weight information by electron impact methods, whereas FI yields simple spectra with intense molecular ions and very little or no fragmentation. The mass and full spectrum sensitivity of oa-TOF-MS combines well with FI and the high mass accuracy obtained can greatly simplify the interpretation of chromatograms from complex mixtures such as coal-based fuels [119].

### *5.3. Laser and plasma sources*

Laser-induced resonance-enhanced multiphoton ionisation time-of-flight mass spectrometry (REMPI–TOF) is a highly selective and sensitive technique that has been used as a detector for gas chromatography. This technique combines UV spectroscopy and mass spectrometry. Intermediate stages of target molecules are selectively excited by absorption of a laser photon when the wavelength of the laser is in resonance with a UV transition. The excited molecules are subsequently ionised by absorption of an additional laser photon. The method has been proposed for the determination of PAHs and chlorinated benzenes in environmental samples [120,121].

Plasma source mass spectrometry (PS-MS), which employs plasma sources such as microwave induced plasma (MIP), inductively coupled plasma (ICP), and glow discharge (GD), have been coupled to gas chromatography for speciation analysis in environmental samples. Some recent publications in GC–ICP-TOF-MS have shown the potential of this technique for the separation and speciation of organotin [122] and organolead compounds [123]. The important characteristics that make TOF-MS well suited for coupling to ICP are the high sampling rate, which prevents peak distortions, and the possibility

of simultaneously measuring different isotopes during a single chromatographic run. Limits of detection in the fg level and reproducibilities lower than 10% have been obtained. As an example, Fig. 10 shows the chromatogram obtained from an alpine snow sample where dimethyllead (DML) and trimethyllead (TML) were identified [123]. The coupling of TOF-MS to a helium microwave plasma torch and gas chromatography has been explored for the element-selective detection of halogens [124]. Recently, gas chromatography has been coupled to a helium-supported gas sampling glow discharge (GSGD) ionisation source for mass spectrometry with a TOF instrument [122,125]. Both atomic and molecular spectra can be generated sequentially in the helium-supported plasma. Thus far, experiments have been conducted with chlorinated hydrocarbons and results show that low detection limits (1–5 pg/s in the atomic mode and 10–20 pg/s at the molecular mode) can be obtained. Moreover, elemental ratios, for instance, $^{35}Cl^{+}/^{12}C^{+}$ can be used to differentiate chlorinated compounds. Additional work needs to be done in order to determine how this source can be used in environmental applications.

## 6. Portable GC–MS instruments

Field-portable GC–MS instruments and applications have evolved and grown considerably over the last decade. The concept of mobile GC–MS began to be developed more than 30 years ago for use on board planetary and interplanetary space probes, and its possibilities prompted researchers to consider other applications. Several instruments have been developed and successfully used for environmental applications including in situ analysis and remediation, emissions monitoring and control, site characterisation, emergency response, chemical weapons detection and mapping of air pollutants. Other field analytical techniques are also used to provide information about environmental problems, but many lack the high level of certainty provided by GC–MS analysis. Field-portable GC–MS systems are widely used in situations that require rapid identification of the analytes and a high degree of certainty in data. Current environmental sampling and analysis methods are time-consuming, costly and present potential exposure hazards to the personnel involved. In situ measurements of environmental contaminants are

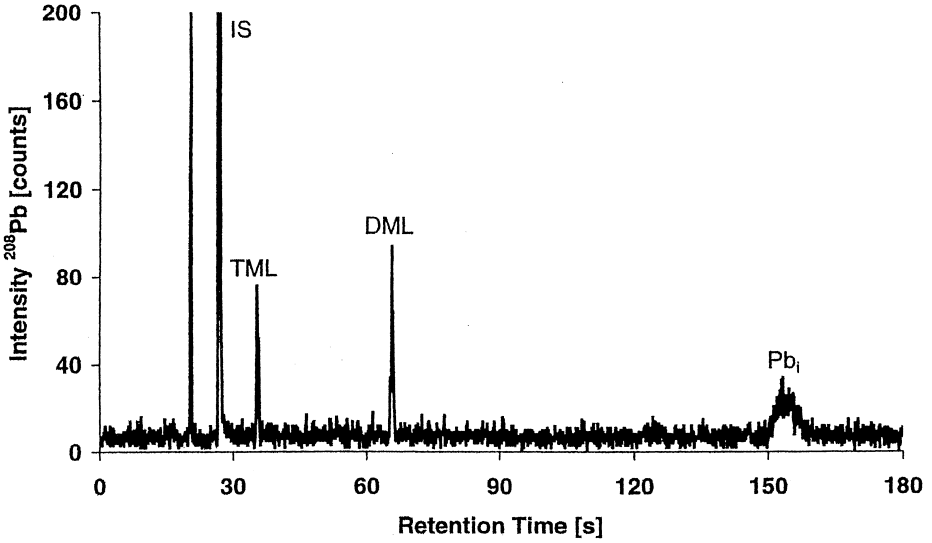


Fig. 10. GC–ICP-TOF-MS chromatogram obtained from an alpine snow sample. Compounds: DML, dimethyllead; I.S., internal standard, trimethylethyllead; $Pb_i$, tetrapropyllead originated from inorganic lead; TML, trimethyllead. Experimental conditions: GC column: HP-1, 25×0.32 mm I.D., 0.17 μm film thickness. (Reprinted from Ref. [123], Copyright 2001, with permission from Springer-Verlag)

preferable to laboratory analysis, but they must meet data quality objectives and be cost competitive.

Commercial transportable GC–MS instruments have been used for several years, although limitations are imposed by power, weight and analytical capability issues. Nevertheless, recent advances in design and miniaturisation of components have led to reductions in size, weight and power consumption. The essential features of these instruments are sample capabilities, robust detection, autonomy for sufficiently long periods of time, and flexible and easy-to-use software systems. In environmental applications, different types of field-portable GC–MS instruments are used, which can be grouped in two main categories: vehicle-portable and man-portable systems [126]. Vehicle-portable instruments involve the use of a car, a boat or a helicopter to transport the mobile GC–MS instrument to the location where the system performs the analysis. The latest generation of these systems are the so-called roving GC–MS, which are capable of taking measurements on the fly, and are used for monitoring and mapping trends and gradients in space and time. Man-portable GC–MS systems require miniaturised fast capillary GC, simple and compact small mass spectrometers, small vacuum pumps and battery-operated instrumentation.

One of the advantages of using field-portable GC–MS systems is that analysis can be performed at or near the sampling point. Sampling must, however, be representative and sample integrity must be maintained. The sampling system in a field-portable GC–MS unit should be compact, stable, capable of remote operation and versatile for use with multiple media sampling. Direct injection, thermal desorption, gas sampling/thermal desorption and membrane inlets are currently used. For instance, Eckenrode [127] has demonstrated the capability of a valving and control system using absorbing tubes to successfully trap and desorb volatile organic compounds (VOCs) in air, with low detection limits (reaching single-digit ppb levels) and good reproducibilities. In situ analysis of these highly volatile compounds in air is a good option because it can solve the problems related with sampling, evaporative loss and transport. Direct vapor sampling that introduces the sample to the head of the GC column without valves or seals and reduces the potential sites for analyte condensation and sample loss has also been applied for monitoring of air pollutants. For instance, this sample system coupled to a GC-MS instrument has been used in a roving instrument for the analysis of benzene, toluene and xylenes (BTX) in urban outdoor environments. As an example, Fig. 11 shows the temporal fluctuations of toluene and benzene in a street near a gas station [128].

The mass analyser most frequently used in GC–MS field instruments is the linear quadrupole because of its inherent simplicity, small size, durability and compactness. Most of the commercial transportable GC–MS instruments incorporate this type of mass analyser. For instance, the mobile Bruker EM 640 consists of a quadrupole mass spectrometer (mass range $m/z$ 1–640) with a membrane separator inlet, a 70-eV electron ionisation ion source, a membrane pump and a turbomolecular pump (70 l/s). This instrument features several sampling accessories that allow a wide range of applications, and has been used for the analysis of gaseous samples, volatiles and semivolatiles in water and soils [129]. The Agilent 5973 mass selective detector, which also belongs to the linear quadrupole family, has been incorporated in the products of Viking Instruments, recently acquired by Bruker. The last instrument of the series, the Viking 573, is a small, compact, robust and lightweight portable instrument (39 kg) that also provides a multifunction inlet system, including purge and trap, thermal desorption, direct air sampling and direct injection. These instruments have been used for different applications, such as on-site analysis and remediation [130], and identification of hazardous compounds after chemical accidents or fires [131,132]. Quality control through inter-laboratory comparisons shows good results and demonstrates the good quality of the data obtained with this instrumentation [130]. The HAPSITE (Inficon) GC–MS system is a man-portable instrument (16 kg) especially designed for on-site analysis of volatile organic compounds. The U.S. Environmental Protection Agency has recently evaluated this instrument for the measurement of VOC levels in ground water, and results show that it can provide useful and cost-effective data for on-site and real-time monitoring. Moreover, accurate and precise analytical results directly comparable with those from an off-site laboratory were obtained [133].

Given its relative simplicity and performance

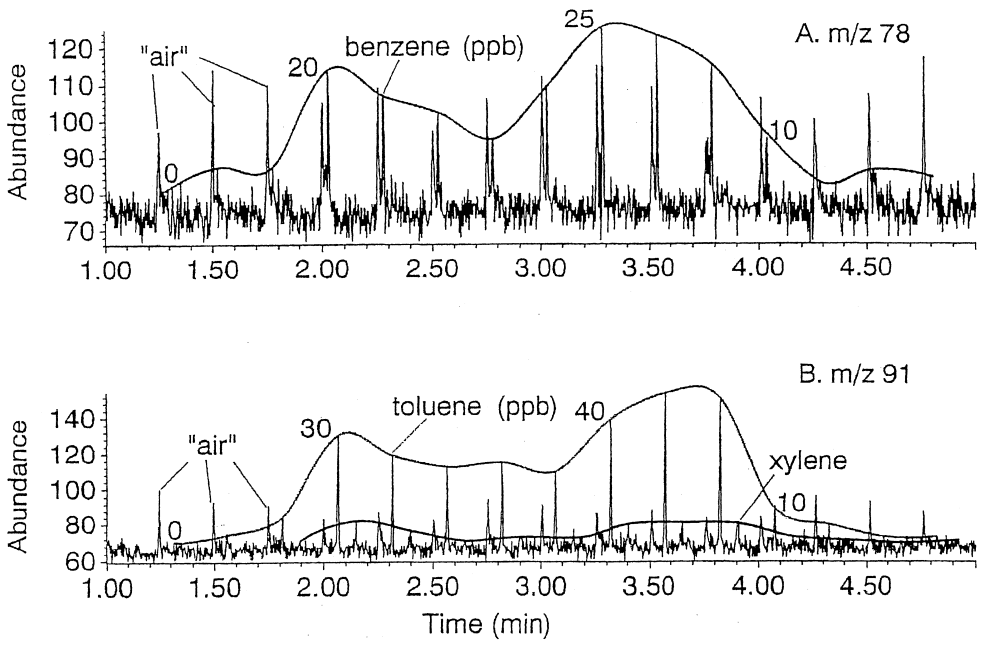


Fig. 11. Roving GC–MS data showing temporal fluctuations in ambient BTX concentration with the selected ion chromatograms for: (A) benzene ($m/z$ 78) and (B) toluene and xylene ($m/z$ 91) obtained while standing ~10 m downwind from a gas station. Experimental conditions: GC column: DB-5 1.85 m×0.1 mm I.D., 0.1 μm film thickness. MS analyser: quadrupole, operating in SIM mode. (Reprinted from Ref. [128], Copyright 1996, by permission of John Wiley and Sons, Inc.)

characteristics, TOF-MS has considerable potential to address the needs of field-portable GC–MS instrumentation. Although various field-portable TOF-MS instruments have been designed, very few papers have been published about the coupling of these instruments to GC. Syage, for example, has developed a GC–TOF-MS for man-portable field-use [134], which uses a photoionisation source and a quadrupole ion trap-TOF mass analyser. The principal purpose of the ion trap is to accumulate ions that are continuously generated from the source and inject them to the TOF-MS. Preliminary results show that fast chromatography with reasonable separation and responses can be obtained.

Miniature instrumentation and field portability is an area of increasing interest in mass spectrometry. The commercial introduction of small vacuum pumps, battery power supplies, and other off-the-shelf components makes it possible to build small and hand-portable GC–MS instruments for environmental applications. In a recent review on miniature mass analysers, Badman and Cooks [135] indicated that the limiting factor for cost, power, size and mass of miniature mass spectrometers is not the mass analyser itself but the associated vacuum and electronic components. The trend to miniaturisation is now being applied to sector analysers [136], linear quadrupoles [137], ion traps and TOF mass spectrometers [135], and it is likely that in a few years these instruments will be coupled to GC for in situ analysis.

## 7. Conclusions and future perspectives

GC combined with MS provides reliable and conclusive analytical information for the identification and quantification of a wide range of organic contaminants in environmental samples. The GC–MS instruments used range from simple linear quadrupoles to multi-sector analysers with EI and positive/negative CI capabilities that allow for the achievement of low detection limits. At present, the linear quadrupole is still the most widely used MS

analyser for GC–MS analysis of environmental samples because it offers high sensitivity and good qualitative information at low cost. However, HRMS is recommended when an enhancement of the selectivity of MS detection is required, because this technique has the capacity to remove the contribution of matrix-interfering compounds. In recent years, the use of MS instruments with quadrupole ion-trap or time-of-flight mass analysers has come to play an important role in environmental analysis. The use of these instruments is bound to increase in coming years due to their ease of operation, selectivity and detection limits down to parts per trillion (ppt). GC–ion trap tandem mass spectrometry (GC–ITMS–MS) has proved to be an attractive method for the analysis of some persistent organic contaminants, e.g. PCDDs and PCDFs, allowing high selectivity and low analyte detectability. Recent GC–ITMS–MS applications have shown that this technique can successfully be used as an alternative to GC–HRMS for the analysis of complex environmental samples, but further studies need to be carried out in order to determine the reliability of quantitative results and to ensure sufficient selectivity to prevent matrix interferences.

The new generation of fast-scanning time-of-flight mass spectrometers are capable of working at high scan rates (500 scan/s). These are sensitive detection instruments that are ideal for combining with high-speed GC or comprehensive two-dimensional gas chromatography (GC×GC), the two most promising recent developments in GC. This coupling will provide a powerful technique for the identification and quantification of complex environmental samples which require an extremely fast acquisition rate. Moreover, the capability of TOF-MS to increase MS resolving power and perform accurate mass measurements using a relatively high resolution makes this technique attractive to solve some analytical problems in environmental analysis. It is expected that in the near future some GC–TOF-MS instruments will replace GC–HRMS instruments given that the former are easier to operate and less costly.

The use of portable GC–MS is increasing in situations where an incident has occurred and rapid identification of chemicals with a high degree of certainty is required. As a consequence, portable GC–MS based on linear quadrupoles and on the new generation of time-of-flight analysers is expected to add to the capabilities and performance features of field-portable GC–MS instrumentation over the next few years.

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