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Recent Applications of Comprehensive Two-Dimensional Gas Chromatography to Environmental Matrices

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1. Introduction

Anthropological pressure on environment combined with continuous progress of analytical techniques allows the detection of more micro-pollutants in environmental matrices. Analysis of Persistent Organic Pollutants (POPs) remains a real challenge due to the large number of compounds and the complexity of environmental matrices. Conventional Gas Chromatography (GC) coupled with mass spectrometry (MS) is the reference technique for the analysis and the quantification of volatile and semi-volatile pollutants. Comprehensive two-dimensional gas chromatography (GC×GC) is a relatively new technique, developed in 1991 by Liu and Phillips (Liu & Phillips, 1991). This technique provides high separation power and sensitivity. The principles of multidimensional chromatography were described by Giddings (Giddings, 1984). When a fraction or few fractions of the effluent from a first column, is subsequently injected into a second column with a different selectivity, the multidimensional chromatographic separation techniques are called ‘heart cutting’. These methods have proved to be very effective only in target compounds analysis. A two-dimensional separation can be called comprehensive if the three following conditions are established (Schoenmakers et al., 2003). First, every part of the sample is subjected to two different separations. Secondly, equal percentages (either 100% or lower) of all sample components pass through both columns and eventually reach the detector. Finally, the separation (resolution) obtained in the first dimension is essentially maintained. This latter point could be reached if the transfer of the effluent from the first column to the second one was successfully performed by a modulator or column interface. So, the modulator could be considered as the ‘heart’ of the system and is currently in development. A maximum of retention space could be used especially if compounds are subjected to two independent separations. Orthogonal separation occurs when the two columns use different separation mechanisms, operating independently in the two dimensions. In practice, columns containing chemically different stationary phases are chosen. In normal orthogonality, the first apolar column is coupled to a column containing a stationary phase of equivalent or higher polarity. For reversed orthogonality, the more polar stationary phase is used in first dimension and a less polar one in second dimension. Due to the low peak width, some constraints are imposed for the choice of detector. An ideal data acquisition rate for GC×GC...
detector is equal or more than 100 Hz to maintain its large separation power. Numerous
detectors, conventionally used in GC like Flame Ionization Detector (FID), Electron Capture
Detector (ECD) and microECD (µECD), have been widely employed. Concerning the MS,
the high speed time-of-flight (TOFMS) with a unit-mass resolution has proved to be the best
candidate for GC×GC. Moderate acquisition rate instruments, such as quadrupole mass
spectrometer qMS (e.g. 20 Hz) were also used with a limited mass range. Several GC×GC
instruments with various modulators have been developed (Semard et al., 2009) and are
now commercially available. GC×GC has now demonstrated its capacity of resolution in the
field of complex matrices like petroleum products, fragrance (Dallüge et al., 2003). GC×GC
is currently one of the most effective techniques for the separation and analysis of
environmental samples, offering significantly greater peak capacities than conventional
chromatographic methods. GC×GC provides three major benefits, namely, enhanced
chromatographic separation, improved sensitivity by effect of cryofocusing with the thermal
modulator, and chemical class ordering in the contour plot (Ballesteros-Gomez & Rubio,
2011). Research in GC×GC has recently shifted from instrumental development to
application to real samples over the last four years especially with the coupling to MS.
Nearly 83% of the over 110 research articles published (specify the type or classification of
articles) in 2010 were devoted to applications of GC×GC (Edwards et al., 2011). Moreover,
some software improvements have also facilitated GC×GC quantitative analyses.

A few reviews were already published about applications of comprehensive GC in relation
to environmental analyses. The most recent review was proposed by Wang et al. (Wang et
al., 2010) that covered the works published between 2007 and the beginning of 2009. This
chapter focuses on the most important developments in environmental applications of
GC×GC, salient advances in GC×GC instrumentation and theoretical aspects reported over
the period 2009 to July 2011. Recent applications using GC×GC methods for analysis of
environmental toxicants such as PolyChlorinatedDibenzo-p-Dioxins (PCDDs),
PolyChlorinatedDibenzoFurans (PCDFs), PolyChlorinatedBiphenyls (PCBs), Polycyclic
Aromatic Hydrocarbons (PAHs), pesticides, alkylphenols etc... are reviewed. Moreover, this
technique appeared especially suitable for the development of multiresidue analytical
methods which was the most important trend in GC×GC-MS environmental analysis over
the last period. The recent works demonstrated that this technique provides interesting
alternative methods in terms of sensitivity and mapping of pollutants and minimizes
sample preparation steps. A part of this chapter will be dedicated to the recent screening of
emerging contaminants such as pharmaceuticals, plasticizers, personal care products, ...
Various matrices (water, soils and sediments) will be considered including river and
wastewater. Analysis of air sample were not reported according to the publication of recent
reviews dealing with the analysis of Volatile and semivolatile Organic Compounds (VOCs)
found in the atmosphere (Arsene et al., 2011; Hamilton, 2010). All aspects of GC×GC will be
presented including instrumentation, theoretical considerations and applications. Moreover,
novel tools used for optimization of retention space or orthogonality estimation will be
discussed.

2. GC×GC and environmental analysis reviews

A non exhaustive review (Ballesteros-Gomez & Rubio, 2011) was focused on main
developments and advances in environmental analysis reported over the period 2009-2010.
Recent Applications of Comprehensive Two-Dimensional Gas Chromatography to Environmental Matrices

Numerous aspects of environmental analysis, based on more than 200 articles, were reported including sampling, sample preparation, separation and detection. Emerging contaminants and atomic spectrometry for the determination of trace metals and metalloids topics were excluded due to the publication of other reviews. Few applications of GC×GC were shortly reported (Eganhouse et al., 2009; Matamoros et al., 2010a; Hilton et al., 2010) and will be discussed in the present chapter. Recently, GC×GC applications devoted to measurement of volatile and semivolatile organic compounds in air and aerosol were reviewed and discussed (Arsene et al., 2011, Hamilton, 2010).

Wang et al. (Wang et al., 2010) have reviewed technological advances and applications of GC×GC between 2007 and July 2009. For example, separations of eight persistent organohalogenated classes of pollutants including OrganochlorinatedPesticides (OCPs), PCBs, PolyBrominatedDiphenylEthers (PBDEs), PolyChlorinatedNaphthalenes (PCNs), PCDDs, PCDFs, PolyChlorinatedTerphenyls (PCTs), and toxaphene (CTT) in environmental samples were reported by Bordajandi et al. (Bordajandi et al., 2008). Nine column combinations in normal and reversed orthogonality (ZB-5, HT-8, DB-17 and BP-10, as first dimension column and HT-8, BPX-50 and Carbowax as second dimension one) were tested. The feasibility of the proposed approach for the fast screening of the target classes of pollutants was illustrated by the analysis of food and marine fat samples. A method of quantification of PAHs in air particulates based on a GC×GC isotope dilution mass spectrometry method was also reported by Amador-Munoz et al. (Amador-Munoz et al., 2009) with favorable resolution and sensitivity over conventional one dimensional GC. GC×GC-TOFMS method was successfully developed by Skoczynska et al. (Skoczynska et al., 2008) to identify 400 compounds in highly polluted sediment sample from the River Elbe (Czech Republic). Several older reviews dealing with the development of GC×GC and its applications including environmental matrices could be mentioned (Ramos et al., 2009; Cortes et al., 2009; Adahchour et al., 2006; Adahchour et al., 2008; Pani & Gorecki., 2006).

3. PCBs

PCBs are composed of 209 distinct congeners and are found in complex mixtures (Aroclors). They were commercially used in a variety of applications, including heat transfer and hydraulic fluids, dielectric fluids for capacitors, and as additives in pesticides, sealants, and plastics (Osemwengie & Sovocool, 2011). The World Health Organization (WHO) has designated twelve PCBs as “dioxin-like”, coplanar PCB congeners that exhibited high toxicity.

Recently, a routine accredited method (Muscalu et al., 2011) was presented for analysis of PCBs, chlorobenzenes and other halogenated compounds in soil, sediment and sludge by GC×GC-µECD. A column combination DB1×Rtx-PCB was used to minimize coelution of analytes. The method was developed to analyze these pollutants in a single analytical run and no fractionation of sample extracts prior to instrument analysis, with enhanced selectivity and sensitivity over one dimensional GC method. The method can also be used to perform analytical triage to screen for additional compounds, for additional extract processing and testing or for identification and monitoring of new and emerging halogenated compounds present in sample extracts and to screen other halogenated organics. The optimized method provided quantification of Aroclors and Aroclors mixtures to within 15% of targets values and sub-nanograms per gram detection limits. The authors
claimed that GC×GC requires minimal additional training to be used as a routine analytical method for the analysis of halogenated compounds.

Separation of 209 PCB congeners, using a sequence of 1D and 2D chromatographic modes was evaluated (Osemwengie et al., 2011). The authors used a RTX-PCB column as the first column and a DB-17 as the second one. In two consecutive chromatographic runs, 196 PCB congeners were distinguished, including 43 of the 46 pentachlorobiphenyl isomers. PCBs congeners that were not resolved chromatographically were resolved with the deconvolution program (ChromaTOFSoftware). Nevertheless, the 209 congeners have not been successfully separated.

New capillary columns coated with Ionic Liquids (ILs) were used as second columns for the separation of 209 PCBs congeners (Zapadlo et al., 2010; Zapadlo et al., 2011). In the first paper (Zapadlo et al., 2010), the orthogonality of three columns coupled in two series was studied. A non-polar capillary column coated with poly(5%-phenyl-95%-methyl)siloxane was used as the first column in both series. A polar capillary column coated with 70% cyanopropyl-polyisilphenylene-siloxane or a capillary column coated with the ionic liquid 1,12-di(tripropylphosphonium)-dodecanebis(trifluoromethanesulfonylimide (IL36) was used as the second columns. The authors concluded that column coated with IL was more polar and more selective for the separation of PCBs than BPX-70 column (Figure 1).

![Fig. 1. 2D images for the separation of toxic, dioxin-like PCBs 81 and 105 on DB-5×BPX-70 and DB-5×IL-36 column series. Reprinted from Journal of Chromatography, A, (Zapadlo et al., 2010). Copyright (2010), with permission from Elsevier.](www.intechopen.com)
All “dioxin-like” PCBs, with the exception of PCB 118 and PCB 106, were resolved by this set of columns. In the second study (Zapadlo et al., 2011), the separation of 209 PCBs congeners was investigated using GC×GC-TOF-MS with a non-polar/IL column series consisting of poly(50%-n-octyl-50%-methyl)siloxane and (1,12-di(tripropylphosphonium)-dodecanes(trifluoromethansulfonyl)amide) (SLB-IL59) in the first and second dimensions, respectively. A total of 196 out of 209 PCBs congeners were resolved by separation and/or mass spectral deconvolution using the ChromaTOF software. All “dioxin-like” congeners were separated with no interferences from any PCB congener. The 109 PCBs present in Aroclor 1242 and the 82 PCBs present in Aroclor 1260 were resolved on this column set.

A Quantitative Structure–Retention Relationship (QSRR) method (D’Archivio et al., 2011) was applied to predict the retention times of 209 PCBs in GC×GC. Predicted data were compared to GC×GC retention data taken from the literature. Authors demonstrated that the experimental GC×GC chromatogram of PCBs can be accurately predicted using a QSRR model calibrated with retention data of about 1/3 of the congeners collected under the same separation conditions. The effect of structure on retention time in both dimensions can be successfully encoded by theoretical molecular descriptors quickly available by means of various computational methods.

4. PCDDs and PCDFs

PCDDs and PCDFs constitute two classes of structurally related chlorinated aromatic hydrocarbons that are both highly toxic and produced as by-products during a variety of chemical and combustion processes. Due to their hydrophobic character and resistance to metabolic degradation, these substances exist as complex congener mixtures in the environment and are considered as POPs.

De Vos et al. (de Vos et al., 2011a) developed an alternative method of GC coupled with High Resolution Mass Spectrometry (HRMS) for analysis of PCDDs and PCDFs using GC×GC-TOFMS in different matrices. Three GC column combinations (Rtx-Dioxin 2×Rtx-PCB, Rxi-5 SilMS×Rtx-200 and Rxi-XLB×Rtx-200) were evaluated to quantify PCDDs and PCDFs in numerous soil and sediment samples taken from various strategic sites in South Africa with a highest result obtained of 76 ng Toxic Equivalent Quantity/kg. Results were also compared with those obtained using GC–HRMS and a good agreement was observed. The limit of detection (LOD) for the method (300 fg on column for spiked soil samples) was determined using the combination Rxi-XLB×Rtx-200 which provided excellent separation of the compounds mandated for analysis by United States Environmental Protection Agency (US EPA) Method (Figure 2).

Using a multi-step temperature program, all seventeen PCDDs and PCDFs components mandated by EPA Method 1613 were separated. GC×GC-TOFMS appeared to be a viable tool for dioxin screening and quantitation, especially in cases where PCDDs/PCDFs levels are greater than 1 ng.kg\(^{-1}\). The technique proved to be ideal for application in developing countries where GC-HRMS is not available, and can be used to minimize costs by selecting only positive samples for further analysis by GC–HRMS. GC×GC-TOFMS additionally provides full range mass spectra for all sample components, thus allowing for identification of non-target analytes e.g. the brominated dioxins.
GC×GC–TOFMS was also applied to investigate (de Vos et al., 2011b) toxic waste. This technique has allowed both comprehensive screening of samples obtained from a hazardous waste treatment facility for numerous classes of POPs and also quantitative analysis for the individual compounds. Various column combinations have been investigated for handling very complex waste samples. The close correlation between values obtained using the GC×GC-TOFMS approach and the GC-HRMS method has confirmed the validity of this technique to quantify PCDDs, PCDFs and four dioxin-like non-ortho substituted PCBs at levels required by regulatory bodies. The authors have obtained consistently higher values with the GC×GC-TOFMS method than those obtained with GC-HRMS. Nevertheless, they considered that the differences were certainly within permissible levels considering that the analyses have been performed in different laboratories.

An original application of the high sensitivity obtained using cryogenic zone compression (CZC) has been described by Patterson et al. (Patterson et al., 2011). The use of a GC×GC cryogenic loop modulator to perform CZC-GC coupled with Isotopic Dilution (ID) HRMS has been shown to be the most sensitive method available for the measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) (less than approximately 586,000 2,3,7,8-TCDD molecules) in human samples.

5. PAHs and hydrocarbons

PAHs are organic pollutants generated during the incomplete combustion of different natural and anthropogenic sources. They could enter the environment via
municipal/industrial effluents. Exposure to PAHs represents a risk for human health due to their genotoxic and carcinogenic effects. The International Agency for Research on Cancer has classified them as possible and probable carcinogens for humans. The US EPA has included sixteen of them in the list of priority pollutants and establishes a maximum contaminant level for benzo[a]pyrene in drinking water at 0.2 µg.L\(^{-1}\). In the European Union (EU), eight PAHs have been identified as priority hazardous substances in the field of water policy.

Chlorinated or brominated PAHs (Cl-PAHs and Br-PAHs) have been already detected in environmental samples such as fly ash (Horii et al., 2008) and sediment (Ishaq et al., 2003; Horii et al. 2009). Moreover, toxicities of Cl-PAHs have been investigated and reported (Horii et al., 2009). A method (Ieda et al. 2011) using GC×GC coupled with HRTOFMS was developed for the analysis of Cl-PAHs and Br-PAHs congeners in environmental samples. The GC×GC-HRTOFMS method allowed highly selective group type analysis with a very narrow mass window (e.g. 0.02 Da), accurate mass measurements for the full mass range (m/z 35–600) in GC×GC mode, and the calculation of the elemental composition for the detected congeners in the real-world sample. The authors reported, for the first time, the detection of highly chlorinated PAHs, such as C\(_{14}\)H\(_{3}\)Cl\(_{7}\) and C\(_{16}\)H\(_{3}\)Cl\(_{7}\), and ClBr-PAHs, such as C\(_{14}\)H\(_{7}\)Cl\(_{2}\)Br and C\(_{16}\)H\(_{8}\)ClBr in the environmental samples (Figure 3).

Fig. 3. The difference of isotope patterns between two peaks in the soil extract; (a)-1 C\(_{14}\)H\(_{6}\)Cl\(_{4}\) and (b)-1 C\(_{16}\)H\(_{8}\)ClBr and GC×GC–HRTOFMS 2D exact mass chromatogram of a 0.02 Da wide windows (a)-2 C\(_{14}\)H\(_{6}\)Cl\(_{4}\); m/z 337.9224 and (b)-2 C\(_{16}\)H\(_{8}\)ClBr; m/z 313.9498. Reprinted from Publication, Journal of Chromatography, A, (Ieda et al., 2011). Copyright (2011), with permission from Elsevier.
Other organohalogen compounds; e.g. PCBs, PCNs, and PCDFs were also detected. This technique provided exhaustive analysis and powerful identification for the unknown and unconfirmed Cl-/Br-PAH congeners in environmental samples.

GC×GC-FID and GC×GC-TOFMS methods (Wardlaw et al., 2011) were used to study the biodegradation of alkylated naphthalenes and benzothiophenes isomers in marine sediment contaminated with crude oil. Their power resolution enabled separation and quantification of multiple structural isomers to determine their first order rate constants for aerobic biodegradation. Rate constants were used as proxies for microbial preference. A strong isomeric biodegradation preference was noted within each of these compound classes, with rate constants varying as much as a factor of 2 for structural isomers of the same compound class.

HPLC-GC×GC-FID and GC×GC-TOFMS were used to study the biodegradation of petroleum hydrocarbons in soil microcosms during 20 weeks (Mao et al., 2009). Aromatic hydrocarbons and n-alkanes were better biodegradable (>60% degraded) than iso-alkanes and cycloalkanes (<40%). GC×GC chromatograms showed that more polar and heavier compounds were formed as biodegradation proceeded.

6. Alkyl phenol isomers

AlkylPhenol EthOxylates (APEOs) are surfactants that have been widely used as detergents, emulsifier and dispersing agents in industrial or household cleaning products including laundry detergents. These compounds are degraded in wastewater treatment plants (WWTPs) in more toxic compounds, such as nonylphenols (NPs) and octylphenols (OPs). NPs and OPs, used for industrial production of APEOs surfactants, are complex mixtures of C₃-10-phenols where the main isomers are para-substituted. The interest in NPs and OPs analysis has increased during the last decades due to their capacity to disrupt the endocrine system which varies according to the structure of the branched alkyl group. They have been included in the water framework directive (WFD) as priority hazardous substances.

GC×GC was applied by Eganhouse et al. (Eganhouse et al., 2009) to enhance the chromatographic resolution of highly similar compounds such as 4-nonylphenol isomers and facilitate identification of a number of previously unrecognized components. Among the 153-204 peaks attributed to alkylphenol, 59-664-NPs were identified (Figure 4). Seven technical NPs products were analyzed using eight synthetic 4-NP isomers, with significant differences among the products and between two samples from a single supplier. This technique was also applied to environmental samples (wastewater, contaminated groundwater and municipal wastewater). The authors demonstrated that alteration of NP's composition through degradation results in enrichment of the more persistent isomers and removal or reduction of less persistent isomers. So, the estrogenicity may be increased or decreased depending on which 4-NP isomers are removed most rapidly.

The optimization of the separation of complex NPs technical mixtures (Vallejo et al., 2011) has been performed by means of experimental designs using GC×GC-FID and GC×GC-qMS equipped with valve-based modulator. Up to 79 OPs and NPs isomers have been separated using the FID detector and 39 have been undoubtedly identified using the mass spectra obtained from the qMS detector. The 22 OP, 33 OP, 363 NP and 22 NP isomers have been synthesized and quantified in two different technical mixtures from Fluka and Aldrich.
The values obtained for NP isomers were in good agreement with the literature and the values calculated for OP were for the first time reported.

Fig. 4. Total ion chromatograms of technical NP (Fluka) showing (a) reconstructed 1-dimensional plot, and (b) 2-dimensional plot with alkylphenol regions indicated. Cx) C_xH_{2x+1}, OPs) octylphenols, DPs) decylphenols. x-axis represents the separation in the column with the nonpolar stationary phase (DB-5 ms), whereas the y-axis represents the separation in the column with the polar stationary phase (Supelcowax 10); retention time is given in seconds. Reprinted with permission from Environmental Science & Technology (Eganhouse et al., 2009). Copyright 2011 American Chemical Society.
7. Pesticides

Recently, a study (Macedo da Silva et al., 2011) demonstrated the potential of the application of GC×GC-µECD to the analysis of seven pesticide residues (propanil, fipronil, propiconazole, trifloxystrobin, permethrin, difenoconazole and azoxystrobin) in sediments. GC×GC-ECD method improved the separation between analytes and matrix interferences, minimizing the possibility of co-elutions. Its resolution capacity allowed the use of a selective detector instead of the use of a more expensive mass spectrometry detector. Best results were obtained with the set of columns DB-5×DB-17ms. The LODs for GC×GC method were about 36% lower than those obtained for the one dimensional GC method (in the range from 0.08 to 1.07 g.L\(^{-1}\)). Accuracy also indicated better results for GC×GC, possibly due to its higher sensitivity and lower contribution of co-eluting matrix components, which was minimized by increased peak capacity.

A GC×GC-qMS method (Purcaro et al., 2011) was developed for the multiresidue analysis of 28 pesticides contained in water. Pesticides extraction was performed by using direct Solid-Phase MicroExtraction (SPME). The rapid-scanning (20000 amu/s) qMS system was operated using a rather wide \(m/z\) 50–450 mass range and a 33 Hz spectral production rate. The qMS performances were evaluated in terms of number of data points per peak, mass spectral quality, extent of peak skewing, and consistency of retention times.

A method for the determination of ultra-trace amounts of OCPs in river water was developed by Ochiai et al. using GC×GC–HR TOFMS (Ochiai & Sasamoto, 2011). Stir Bar Sorptive Extraction (SBSE) followed by thermal desorption (TD) was used for sample preparation. SBSE conditions including extraction time profiles, phase ratio (sample volume/PolyDiMethylSiloxane (PDMS) volume), and modifier addition were studied. The SBSE–TD–GC×GC–HR TOFMS method was solvent-free and highly selective and sensitive (LOD: 10–44 pg.L\(^{-1}\)). The method was successfully applied to the determination of 16 OCPs in river water sample. Authors showed that the results for 8 OCPs were in good accordance with the values obtained by a conventional Liquid–Liquid Extraction (LLE)–GC–HRMS (Selected Ion Monitoring) SIM method. The method also allowed the identification of 20 non-target compounds, e.g. pesticides and their degradation products, PAHs, PCBs and pharmaceuticals and personal care products and metabolites in the same river water sample, by using full spectrum acquisition.

A review dedicated to determination of pyrethroid insecticides in environmental samples was recently published by Feo et al. (Feo et al., 2010). The authors discussed the advantages and the disadvantages of the different instrumental techniques including GC×GC.

8. VOCs and other compounds

Benzothiazoles, benzotriazoles and benzosulfonamides are high-production-volume chemicals that are used in industrial and household applications. These compounds were detected in various environmental aqueous samples and were usually quantified by LC-MS/MS. Jover et al. (Jover et al., 2009) developed a Solid Phase Extraction (SPE)-GC×GC–TOFMS method for the characterization of benzothiazoles, benzotriazoles and benzosulfonamides in aqueous matrices. Columns combination was optimized to ensure a good separation between target analytes and interfering compounds of the matrix. 12 target analytes were characterized in river water and in wastewater from both the influent and the
Recent Applications of Comprehensive Two-Dimensional Gas Chromatography to Environmental Matrices

The methods for the determination of polycyclic and nitro-aromatic musk compounds as well as those for the respective metabolites are reviewed by Bester (Bester, 2009). The power of GC×GC approaches was demonstrated considering the various production impurities (isomers) of the two polycyclic musks with the highest usage rates.

A methodology to characterize VOCs and semi-volatile compounds from marine salt using Headspace (HS)-SPME and GC×GC-TOFMS was developed by Silva et al. (Silva et al., 2010). 157 VOCs distributed over the chemical groups of hydrocarbons, aldehydes, esters, furans, haloalkanes, ketones, ethers, alcohols, terpenoids, C_{13} norisoprenoids, and lactones were detected. Furans, haloalkanes and ethers were identified for the first time in marine salt. Contour plot analysis revealed the complexity of marine salt volatile composition and confirmed the importance of a high resolution, sensitive analytical procedure (GC×GC-TOFMS) for this type of analysis. The structured 2D chromatographic profile arising from 1D volatility and 2D polarity was demonstrated, allowing more reliable identifications. Results obtained for analysis of salt from two diverse locations and harvests over three years have suggested loss of volatile compounds according to storage duration of the salt, with environmental factors surrounding the salt pans influencing the volatile composition of the salt. At present the relative contributions of these factors have not been quantified. Origins of newly identified compounds in marine salt were in accordance with previous propositions, with algae, surrounding bacterial community, and environmental pollution being obvious sources.

9. Screening

In environmental monitoring, pollutants lists are periodically updated by regulatory agencies. Both the European Union (EU) and US EPA issued dangerous and hazardous contaminant lists, the so-called priority substances, whose concentration and occurrence in waters were strictly regulated (Directive 2000/60/EC; Decision No.2455/2001/EC and Clean Water Act) (Matamoros et al., 2010a). As the number of environmental regulated pollutants increases, it is necessary to develop global detection methods which can be used to screen a large number of substances simultaneously. This kind of method could reduce cost and time necessary for their detection and quantification. Moreover, there is a diverse group of unregulated pollutants called “emerging” contaminants, including pharmaceuticals and personal care products which were interesting to identify and monitor due to their high mass discharge into the environment. Some emerging contaminants have been recently included in candidate contaminant lists either from US EPA and the EU commission.

Semard et al. (Semard et al., 2008a; Semard et al., 2008b) reported a GC×GC-TOFMS method to search 58 target compounds and screen hazardous contaminants including PBDEs, PAHs and pesticides in urban wastewater. A variety of drugs (antidepressants, antibiotics, anticoagulants, etc...), personal care products (sunscreens, antiseptics, cosmetics etc.) and carcinogenic compounds, pesticides and compounds toxic for reproduction were identified in the raw wastewater. Most of these compounds were removed or decreased by the WWTP. Four priority substances (1,2,3-trichlorobenzene, 4-tert-butylphenol, benzothiazole...
and naphthalene) were present with concentrations in the range of 0.05 to 1.5 mg.L\(^{-1}\) in the raw wastewater and 0.01 to 0.1 mg.L\(^{-1}\) in the treated wastewater.

Household dusts were investigated using GC×GC-TOFMS as efficient screening method (Hilton et al., 2010). PAHs, phthalates, and compounds containing chlorine, bromine, or nitro groups were located on the chromatogram. Household dust (SRM-2585) was extracted with hexane using accelerated solvent extraction (ASE). Large molecules, such as triglycerides and fatty acids were removed with gel permeation chromatography. The resulting peak table was automatically filtered to identify compound classes such as phthalates, PAHs (Figure 5) and their heterocyclic analogs, PCBs, PBDEs, chloroalkyl phosphates, pesticides, and pesticides degradation products... By comparison with concentrations determined by National Institute of Standards and Technology, the technique was able to identify analytes at concentrations as low as 10-20 ng.g\(^{-1}\) dust for compounds quantified by NIST (National Institute of Standards and Technology).

Fig. 5. Location of peaks matching the PAH spectral pattern with those identified by library searching. PAHs can be expected to fall into a band, shown starting at about 2 seconds in the second dimension and, as the chromatogram proceeds, falling later in the second dimension. Reprinted from Journal of Chromatography, A, (Hilton et al., 2010). Copyright (2010), with permission from Elsevier.

A SPE-GC×GC-TOFMS screening method for 97 priority and emerging contaminants in river was developed by Matamoros et al. (Matamoros et al., 2010a). The SPE was followed by in GC-port methylation using trimethylsulfonium hydroxide. The target analytes included 13 pharmaceuticals, 18 plasticizers, 8 personal care products, 9 acid herbicides, 8 triazines, 10 organophosphorous compounds, 5 phenylureas, 12 organochlorine biocides, 9
PAHs, 5 benzothiazoles and benzotriazoles. Best resolution between matrix constituents and target analytes was observed with TRB-5MS×TRB-50HT (apolar – polar) columns combination. Moreover, using polar-nonpolar columns combination, a strong correlation between the second dimension retention time and log $K_{ow}$ for the target compounds was observed and was proposed as an additional identification criterion. The method was successfully applied to the analysis of four river water samples with LOD ranging from 0.5 to 100 ng.L$^{-1}$ (Figure 6). Plasticizers (e.g., phthalates and bisphenol A), pharmaceuticals (e.g., naproxen, ibuprofen), and personal care products (e.g., tonalide and methyl dihydrojasmonate) were the most abundant in concentration and detection frequency.

Fig. 6. 3D contour plots of four rivers sampled in this study in which the total ion chromatogram is shown: Ebro (A), Llobregat (B), Ter (C), and Beso’s (D). Reprinted with permission from Analytical Chemistry, (Matamoros et al., 2010a). Copyright 2011 American Chemical Society.

Gomez et al. (Gomez et al., 2011) developed a GC×GC–TOFMS method for the automatic searching and evaluation of nonpolar or semipolar contaminants (13 personal care products, 15 PAHs and 27 pesticides) in wastewater and river water. SBSE was selected for sample preparation step. Good results have been obtained in terms of separation efficiency and detection limits at or below 1 ng.L$^{-1}$ for most of the compounds in the MS full scan mode, using only 100 mL of river water sample and 25 mL of wastewater effluent sample. The authors mentioned the possibility to screen for non-target compounds or unknowns. New contaminants have been identified in the wastewater effluents and river water samples, such as cholesterol and its degradation products, pharmaceuticals, illegal drugs, industrial
products as well as other pesticides and personal care products. Moreover, GC×GC features were proposed to compare the fingerprinting of different water samples giving valuable information about the contamination status of rivers and wastewaters (Figure 7).

Fig. 7. Contamination status. Automatic searching of temporal and spatial contamination variation of organic contaminants. Reprinted with permission from Analytical Chemistry, (Gómez et al., 2011). Copyright 2011 American Chemical Society.

The most frequently detected contaminants and the contaminants detected at higher concentrations were the personal care products (musk fragrances galaxolide and tonalide). The pesticides and PAHs were detected at much lower concentration.

Halogenated compounds were successfully detected (Hashimoto et al., 2011) from several kinds of environmental samples by using a GC×GC chromatograph coupled with a tandem mass spectrometer (GC×GC–MS/MS). The global and selective detection of halogenated compounds was achieved by neutral loss scans of chlorine, bromine and/or fluorine using an MS/MS which was especially effective for compounds with more than two halogen substituents (Figure 8).

Screening and identification of pollutants was performed with GC×GC–HRTOFMS under the same conditions as those used for GC×GC–MS/MS. A lot of dioxins and PCBs congeners and many other compounds were identified in fly ash extract without any cleanup process and in sediment samples. In the future, the authors expect to achieve the complete global detection of any compound in one measurement of a crude sample simply with a GC×GC–HR TOFMS if it becomes possible to extract the desired information from the GC×GC-HR TOFMS data.
Fig. 8. Two-dimensional TICs of fly ash extract (NIES CRM17) measured with a $^{35}$Cl-NLS (upper) and a conventional scan (lower) obtained with the GC×GC-MS/MS. The red translucent shape in the upper chromatogram shows the area where organohalogens are expected to appear. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.). Reprinted from Journal of Chromatography, A, (Hashimoto et al., 2011). Copyright (2011), with permission from Elsevier.

10. GC×GC instrumentation and optimization of operating conditions

Publications and reviews were dedicated to specific aspect of GC×GC. Major innovations in GC×GC modulator development were recently reviewed (Edwards et al., 2011). Cryogenic modulators remain very popular because of their ability to produce very small peak widths at half height and minimize breakthrough. Their commercial availability from several...
suppliers, has also contributed to their popularity. The use of valve-based modulators is increasing because of their less operating cost and easier maintenance than cryogenic modulator. Nevertheless, their coupling to MS remains problematic due to the large carrier gas flows in the second column and these modulators are not able to produce peaks of the same quality. Thermal modulation with the use of thermoelectric cooling could be a promising alternative if temperatures can be lowered enough to trap VOCs. Tranchida et al. (Tranchida et al., 2011a) have also published a review focused on the history (1991–2010) and present trends and future prospects for GC×GC modulation. Authors provided detailed descriptions and discussed the advantages and the disadvantages of the most significant thermal and pneumatic modulators. The authors have concluded that if at the moment, dual stage liquid N\textsubscript{2} systems can still be considered as the most effective modulators, in the next 10 years, the popularity of pneumatic modulators will gradually increase. The authors have included the description of their simple flow modulator, a seven port metallic disc published in 2011 (Tranchida et al., 2011b). A rotary and diaphragm 6-port 2-position valves have been also evaluated as modulators for GC×GC (Lidster et al., 2011).

Fig. 9. Chromatogram illustrating the retention space used (white) and the space used calculated with Delaunay’s triangulation algorithms (yellow) obtained on HP5-Mega225. Reprinted from Journal of Chromatography, A, (Semard et al., 2010). Copyright (2010), with permission from Elsevier.

In 2011, Panic et al. (Panic et al., 2011) developed a new consumable-free thermal modulator for GC×GC. The modulator was constructed from a trapping capillary, installed outside the GC oven, and coated inside with PDMS stationary phase. Dual-stage modulation was accomplished by resistively heating alternate segments of the trap with a custom-designed
Recent Applications of Comprehensive Two-Dimensional Gas Chromatography to Environmental Matrices

Recent applications of comprehensive two-dimensional gas chromatography to environmental matrices involve capacitive discharge power supply. The two unique inventions presented, flattening of the trap and selective removal of the stationary phase, have successfully eliminated the traditional drawbacks of resistively heated modulators.

The identification of compounds by using GC is based on peak retention times and mass spectra which generates uncertainty for the analyst for complex samples containing isomeric species. Retention index procedures were introduced to minimize misidentification of compounds in conventional chromatography. Various approaches to use of the retention index in GC×GC were reviewed and discussed (von Muhlen & Marriott, 2011).

A new method for the calculation of the percentage of separation space used was developed by Semard et al. (Semard et al., 2010) using Delaunay’s triangulation algorithms (convex hull).

This approach was compared with an existing method and showed better precision and accuracy. It was successfully applied to the selection of the most convenient column set (HP5-Mega225) for the analysis of 49 target compounds including pesticides, HAPs, PCBs, PBDE etc… in wastewater. The diameter and length of the second column were optimized to improve the percentage of separation space used up to 40%.

Recently, Omais et al. (Omais et al., 2011) have shown that the general notion of orthogonality combining retention mechanisms independence and two dimensional space occupation must be decoupled. They have demonstrated that a non-orthogonal system can offer a good separation and a great space occupation. Moreover, orthogonality is intimately linked to the sample properties and cannot be considered as a sine qua non condition to achieve a good separation.

Table 1 summarizes the acronyms used in this review.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>APEOs</td>
<td>AlkylPhenol EthOxylates</td>
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<tr>
<td>CTT</td>
<td>Toxaphene</td>
</tr>
<tr>
<td>CZC</td>
<td>Cryogenic Zone Compression</td>
</tr>
<tr>
<td>ECD, µECD</td>
<td>Electron Capture Detector, Micro Electron Capture Detector</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
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<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
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<tr>
<td>GC×GC</td>
<td>Comprehensive two-dimensional gas chromatography</td>
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<tr>
<td>HS</td>
<td>HeadSpace</td>
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<tr>
<td>HRMS</td>
<td>High Resolution Mass Spectrometry</td>
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<tr>
<td>HRTOF</td>
<td>High resolution time-of-flight</td>
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<tr>
<td>ID</td>
<td>Isotope Dilution</td>
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<tr>
<td>ILs</td>
<td>Ionic Liquids</td>
</tr>
<tr>
<td>LLE</td>
<td>Liquid Liquid Extraction</td>
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<tr>
<td>LOD</td>
<td>Limit of detection</td>
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<tr>
<td>MS</td>
<td>Mass Spectrometer</td>
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<tr>
<td>MS/MS</td>
<td>Tandem mass spectrometer</td>
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<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
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<tr>
<td>NPs</td>
<td>NonylPhenols</td>
</tr>
</tbody>
</table>
Table 1. List of acronyms

11. Conclusion

This work reviews about 40 publications over the period 2009-2011 dealing with GC×GC and more especially on environmental applications. This technique coupled to mass spectrometry is an excellent choice for analyzing complex environmental samples and is suitable for multiresidue and non target analyses. As the number of environmental regulated pollutants increases, GC×GC appears ideal for the development of global detection method which can be used to screen a large number of compounds simultaneously. This kind of method could reduce cost and time necessary for their detection and quantification. GC×GC provides the analytical chemist with a new tool for a better separations of organohalogen congeners and, potentially, for more accurate human and environmental exposure data for risk assessments. Moreover, the authors highlighted the improved resolution and sensitivity offered by GC×GC over conventional one dimensional GC. The high selectivity of GC×GC-TOFMS has also facilitated the development of a wide range of analytical methods with minimal sample preparation and allowed the screening of emerging contaminants. Table 2 summarizes the main technical characteristics of methods applied to the various classes of pollutants reviewed in this chapter.
Recent Applications of Comprehensive Two-Dimensional Gas Chromatography to Environmental Matrices

Table 2. Characteristics of methods applied to the various classes of pollutants based on compounds, sample preparation techniques, GC×GC method and set of columns used.
12. References


Progress in agricultural, biomedical and industrial applications’ is a compilation of recent advances and developments in gas chromatography and its applications. The chapters cover various aspects of applications ranging from basic biological, biomedical applications to industrial applications. Book chapters analyze new developments in chromatographic columns, microextraction techniques, derivatisation techniques and pyrolysis techniques. The book also includes several aspects of basic chromatography techniques and is suitable for both young and advanced chromatographers. It includes some new developments in chromatography such as multidimensional chromatography, inverse chromatography and some discussions on two-dimensional chromatography. The topics covered include analysis of volatiles, toxicants, indoor air, petroleum hydrocarbons, organometallic compounds and natural products. The chapters were written by experts from various fields and clearly assisted by simple diagrams and tables. This book is highly recommended for chemists as well as non-chemists working in gas chromatography.

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