Chapter 22
Multidimensional Chromatographic Techniques for Monitoring and Characterization of Environmental Samples

Eduardo P. Mateus, Marco D.R. Gomes da Silva, Alexandra B. Ribeiro, and Philip Marriott

22.1 Introduction

The electrokinetic process (EK) has been applied for removal of inorganic and organic contaminants in polluted soils (Lageman et al. 1989; Pamukcu and Wittle 1992; Probstein and Hicks 1993; Ribeiro and Mexia 1997; Ribeiro 1998; Ribeiro et al. 1998; Virkutyte et al. 2002), Cu-Cr-As impregnated wood waste (Ribeiro et al. 2000), fly ash from straw combustion (Hansen et al. 2001), or municipal solid waste incinerators fly ash (Pedersen et al. 2001). Research on the application of the EK has mainly been performed for heavy metals remediation. EK research aiming organic pollutants remediation can be found on the removal of pesticide/herbicides (Ribeiro and Mateus 2009; Polcaro et al. 2007), pharmaceutical and personal care compounds (Guedes et al. 2014), chlorinated solvents (Rohrs et al. 2002; Rabbi et al. 2002), petroleum hydrocarbons (Murillo-Rivera et al. 2009; Park et al. 2005), phenol (Acar et al. 1995), polycyclic aromatic hydrocarbons (Alcantara et al. 2008; Niqui-Arroyo et al. 2006; Maini et al. 2000), or polychlorinated biphenyls (Gomes et al. 2015). Those studies, conducted with the emphasis on the movement of target contaminants in the EK system, in order to assess whether the method can be applied to remove them from polluted matrices, have been performed by spiking the matrices with the analytes at higher concentrations far from those present in real

E.P. Mateus (✉) • A.B. Ribeiro
CENSE, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica 2829-516, Portugal
e-mail: epm@fct.unl.pt

M.D.R. Gomes da Silva
LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica 2829-516, Portugal

P. Marriott
Australian Centre for Research on Separation Science, School of Chemistry, Monash University, Wellington Road, Clayton, VIC 3800, Australia

A.B. Ribeiro et al. (eds.), *Electrokinetics Across Disciplines and Continents*,
DOI 10.1007/978-3-319-20179-5_22

samples or by means of model matrices (e.g., kaolinite), which are much less complex than real environmental matrices.

The setup of a remediation strategy requires the previous characterization of the polluted matrices in terms of its chemical composition, and the success of the remediation process improves with the level of the characterization and contaminants monitorization.

However, the elucidation of the behavior of organic contaminants present in real environmental matrices, when submitted to the EK remediation, is a hard and challenging task. Environmental matrices produce complex samples, which are composed by a wide array of components, through volatiles and semi-volatiles compounds to more heavy compounds, comprising several polarity and concentration ranges. Thus, the qualitative and quantitative analysis of pollutants in complex environmental matrices requires a technique able to separate the analytes from the other components of the matrix. In the past decades, for environmental characterization, analysis and identification of environmental contaminants one-dimensional gas chromatography (1D-GC), often coupled to a mass spectrometry (GC/MS) as a specific detection method, has been the analytical method of choice. Nevertheless, in spite of its resolution power and the continuous development of equipment and analytical methodologies and techniques, the components from environmental samples may remain difficult or unachievable to separate by 1D-GC. This is specially the case if additional sample fractionation methodologies prior to the final analysis are not used, thus promoting coelutions and difficult or ambiguous compound identification and monitorization (Meyer et al. 1999). This drawback is due to the complexity of the environmental samples with their large number of potential components that are usually present in a wider range of concentrations. Consequently, the trace level analytes, that sometimes are the toxically active components in the matrix under study, may never be detected, if they are co-eluting with high concentration compounds. Another potential problematic issue is related to the existence of possible isomeric configurations of analytes that, due to its structural similarity, promote almost identical mass spectra and retention times. This reality, when using GC/MS, jeopardizes analytes identifications and demands the acquisition of pure mass spectra, a task that makes the identification process very difficult and sometimes even impossible without the full separation of peaks in order to assure clean mass spectra.

Consequently, the 1D-GC approach may not always achieve satisfactory results, although valid, for the chemical composition of environmental matrices, resulting in a considerable amount of information that remains unexploited or hidden.

The development of new analytical techniques, in order to maximize analyte separations, has always been a target that is historically highlighted by the progression of packed column to capillary column chromatography and by the upgrade of one-dimensional (1D) to multidimensional (MD) chromatography systems. Such advances aim to reach a higher chromatographic capacity, in order to achieve the separation for all sample analytes (David and Sandra 1987; Bertsch 1999).

22.2 Some Theoretical Considerations

The pursuit for multidimensional systems is supported by the limitations of the achievable maximum number of theoretical plates for a single column in 1D systems due to inherent physical and statistical constraints (Grushka 1970; Chaves das Neves and Freitas 1996; Bartle 2002).

The physical limitations may be exemplified, using equation (22.1) (Grushka 1970), to calculate the chromatographic capacity of a capillary column with 50 m × 0.25 mm and $d_f = 0.25$ μm, assuming $R = 1$ and t_2/t_1 as 10:

$$n = \frac{\sqrt{N}}{4R} ln\left(\frac{t_2}{t_1}\right) + 1 \tag{22.1}$$

where:

n = peak capacity of a single column chromatographic system
N = number of theoretical plates of a single column
t_1 and t_2 = retention time window, t_1 and t_2 are retention times
R = resolution for the separation of two compounds with retention times t_1 and t_2.

The estimated value will tell us that theoretically the column will be able to separate 260 analytes under ideal conditions (Grob et al. 1978, 1981; Bartle 2002), a number that will be insufficient for some contaminated environmental matrices.

However, when the statistical theory of overlap (STO) is applied (Davis and Giddings 1983; Martin et al. 1986; Bertsch 1999; Bartle 2002) for the same column, the result will give us an even more limited picture of separation power in 1D systems. The maximum number of analytes that the chromatographic column can theoretically separate is, in equation I, expressed by the capacity factor (n). Statistically, this value decreases because the analytes will be on reality randomly and not discretely distributed through the chromatographic separation. The STO points out (22.2) that in a chromatographic analysis the number of separated peaks (S) is related to the capacity factor of the column (n) and with the total number of analytes (m) present in the sample (Davis and Giddings 1983; Bertsch 1999; Bartle 2002).

From (22.2), the probability (P) of observing a peak, consisting of one single component, will be estimated by (22.3).

$$S = m \cdot \exp\left(-\frac{2m}{n}\right) \tag{22.2}$$

$$P = \exp\left(-\frac{2m}{n}\right) \tag{22.3}$$

where:

S = number of separated single peaks
n = peak capacity of a single column chromatographic system
m = number of sample components

The application of equation (22.3) leads to the theoretical conclusion that for a sample with 100 components, a column with a capacity for 290 analytes will be needed in order to guaranty the separation of half of the components (Bartle 2002). This shows the limitation of 1D-GC, in spite of its high separation power, even under ideal separation conditions without the variables, peak tailing, and/or the wide ranges of analytes concentrations that are not considered by the STO (Bertsch 1999).

Due to the potential high complexity of some of the environmental samples, which easily reach 100 components, in a wide range of concentrations, the occurrence of co-elutions became inevitable, even in most efficient columns in 1D-GC.

22.3 Multidimensional Systems

22.3.1 Multidimensional Gas Chromatography with a Flow Switching Device: GC–GC

The potential high complexity of the chromatograms that result from environmental samples forwarded the analysts to new ways of chromatography, such as multidimensional systems, where the analytes are submitted to two or more independent separation steps, on independent columns, in order to achieve separation efficiency.

The classical example came from the "heart-cut" systems using flow switching devices, interfacing two columns (GC–GC), such as the Deans switch (Fig. 22.1),

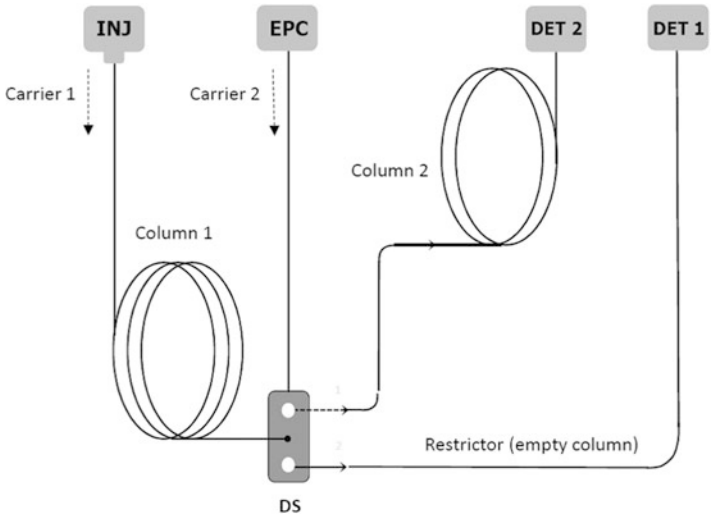

Fig. 22.1 Schematic representation of a multidimensional GC system with a heart-cut configuration, using a Dean switch device (DS), *INJ* injector, *DET* detector, *EPC* electronic pressure control

based on pneumatic pressure balancing. This configuration allows the isolation of target peaks, or packet of compounds, by partial selective transference (online heart-cut), from a primary column to a second column with different selectivity. On the second column/dimension, the transferred target analytes or the components of a retention time window (packet) are submitted to improved chromatographic separation, avoiding the potential co-elution with the transferred interfering peaks and with the non-transferred compounds that will resume on the first dimension (Schomburg et al. 1984; David and Sandra 1987; Bertsch 1999; Poole 2003).

Figure 22.2 shows an example of GC–GC, with flame ionization detection (FID), performed with a Polycyclic Aromatic Hydrocarbons (PAHs) standard mix sample, using the heart-cut system through a Deans switch device, to target the peak of Benzo[a]pyrene (B[a]P) that is eluting on a nonpolar column (5 % phenyl in polydimethylsiloxane) and transferring it to a medium polar column (50 % phenyl in polydimethylsiloxane) for secondary analysis. Figures 22.3 and 22.4 demonstrate the applicability of the same system, using the same columns to isolate B[a]P, on complex chromatograms. In Fig. 22.3, the B[a]P peak is targeted on an atmospheric particulate matter (PM_{10}) extract and sent to the second dimension where it is

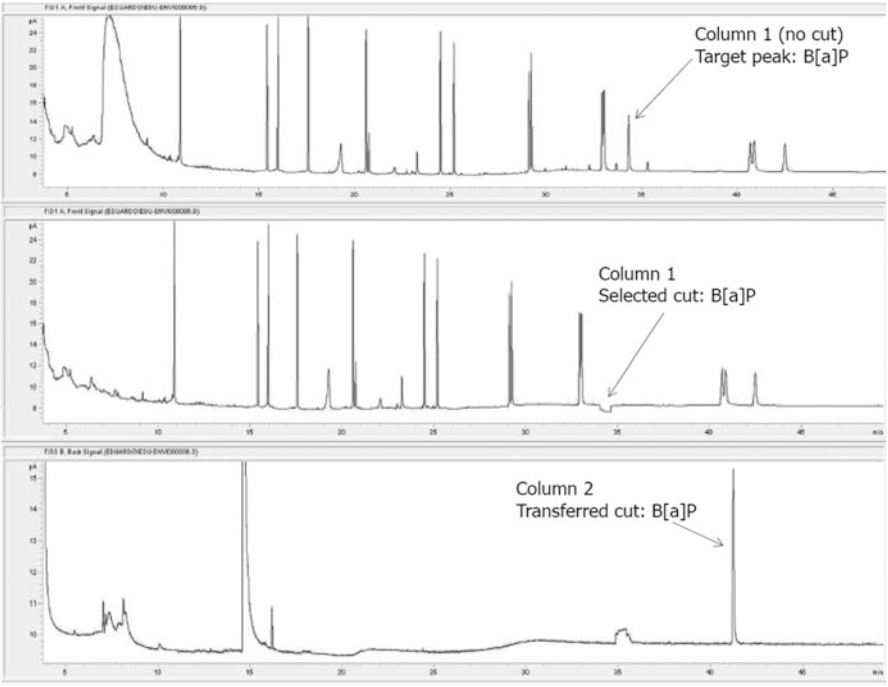

Fig. 22.2 Representation of multidimensional GC–GC analysis from a PAHs mix test sample, using a heart-cut system to transfer Benzo[a]pyrene. The first top chromatograms show the primary separation and the bottom ones the resulting heart-cut chromatograms on both dimensions (Detector: FID, Injection: 1 μL splitless)

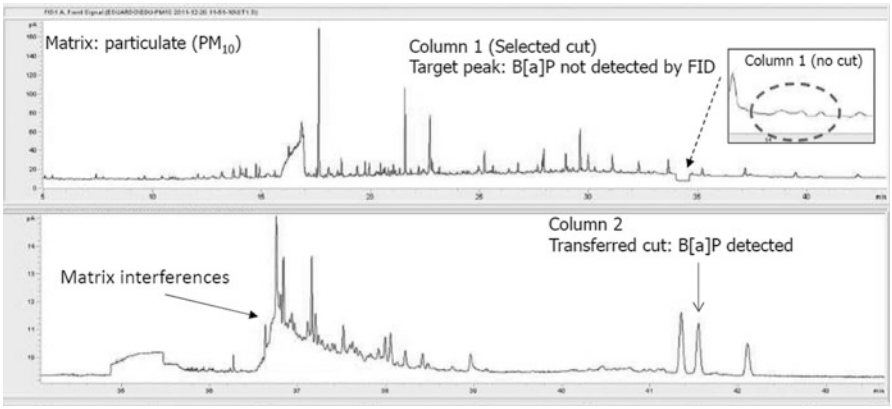

Fig. 22.3 Representation of multidimensional GC–GC analysis from atmospheric particulate matter (PM10), using a heart-cut system, targeting Benzo[a]pyrene. The top chromatogram shows the primary separation, and the bottom one the resulting heart-cut chromatograms on second dimension (Detector: FID, Injection: 1 μL splitless)

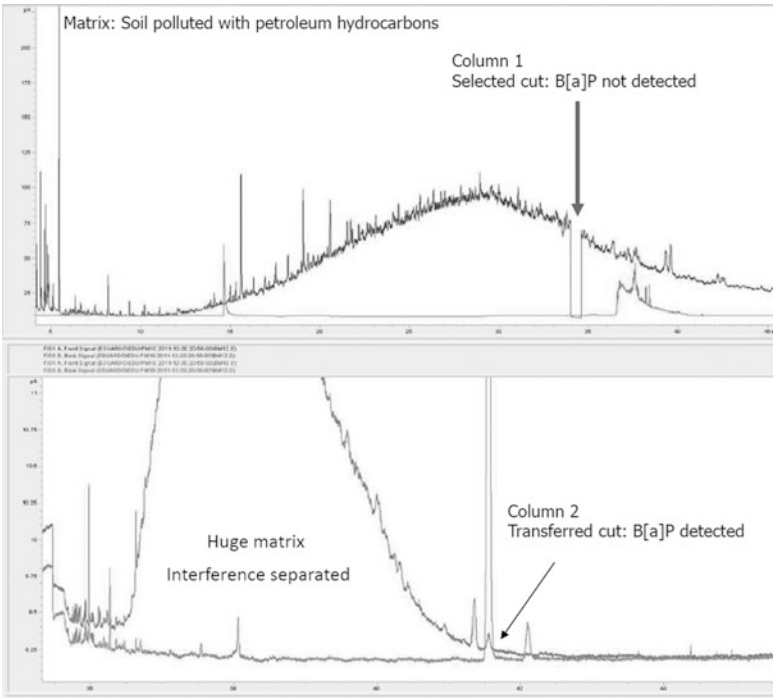

Fig. 22.4 Representation of multidimensional GC–GC analysis from a soil polluted with petroleum hydrocarbons, using a heart-cut system, targeting Benzo[a]pyrene. The top chromatogram shows the primary separation, and the bottom one the resulting heart-cut chromatograms on second dimension. The major peak overlaying B[a]P transferred peak is its standard used for retention time confirmation (Detector: FID, Injection: 1 μL splitless)

separated from the interferences that co-elute with it on the first dimension. Note that on the first dimension the baseline hides the peaks. A more dramatic example is shown in Fig. 22.4, where the B[a]P peak is targeted on a chromatogram from an extract of a soil polluted with petroleum hydrocarbons. The chromatogram is very complex, being impossible to detect B[a]P. After the cut, a large gap is easily observed on the first dimension, a sign of the amount of compounds that are co-eluting. In spite of its trace amount, the B[a]P peak is detected on the second dimension and isolated from other peaks, including a significant amount of matrix interference components. These examples clearly show the power of the technique for target analysis, even using an "almost universal" detector such as the FID, which do not perform structural identifications.

In spite of its efficiency for target analysis, the MDGC is a time-consuming technique, with long analysis times, which may not fit with the demands of routine analysis. Additionally, it may be technically impractical to analyze, on the fly, all the target compounds that elute from the first dimension or carry out sequential transfers in a narrow window of retentions times. The probability of new co-elutions on the second column (Poole 2003) will increase, leading to system inefficiency if large amount of analytes need to be monitored on the same chromatographic run. However, this apparent disadvantage may be compensated by the accessible information content of the data that is processed in the same way as in 1D-GC and by its operational simplicity.

22.3.2 Comprehensive Two-Dimensional Gas Chromatography: GC × GC

In 1991, Liu and Phillips (1991) introduced the comprehensive two-dimensional gas chromatography (GC × GC). The GC × GC system consists of two columns with different selectivities that are serially connected through a suitable interface, which usually is a thermal modulator (Fig. 22.5) (Phillips and Beens 1999; Marriott and Shellie 2002; Dimandja 2003). At the GC × GC technique, the entire sample separated on the first column is transferred to the second one, resulting in an enhanced chromatographic resolution into two independent dimensions, where the analytes are separated by two independent mechanisms (orthogonal separation) (Schoenmakers et al. 2003).

By definition, a chromatographic method is considered comprehensive if (1) the sample transfer from the first to the second column is qualitatively and quantitatively complete; (2) the orthogonality principle is respected, meaning that both separation mechanisms are independent; and (3) the separation on the first column is preserved on the second one (Bertsch 2000; Dallüge et al. 2003; Schoenmakers et al. 2003).

Operationally, the most important component in the GC × GC system is the interface. The common interface comprises usually a thermal modulator, which either performs heating (to accelerate solute into a narrow band in the second column) or cooling (to retard analyte and cause on-column trapping or cryofocusing of the bands) or both, depending on the design.

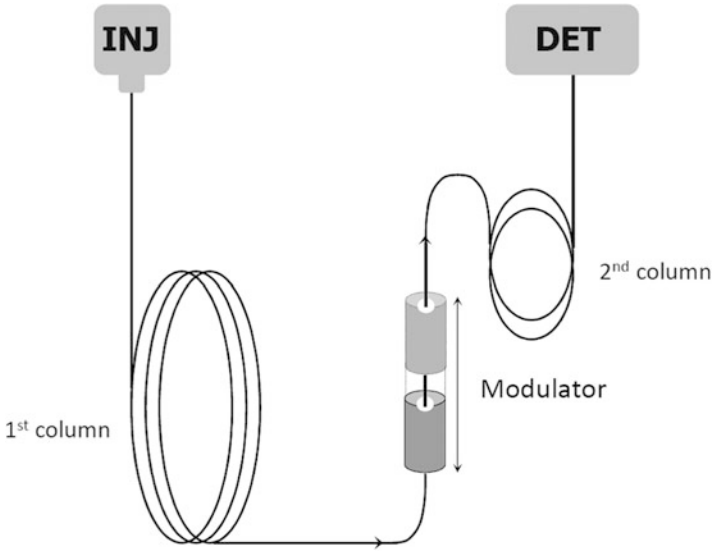

Fig. 22.5 Schematic representation of a GC × GC system (modulator: longitudinally modulated cryogenic system—LMCS)

The modulator collects and cuts the effluent from the first column into small portions, which are refocused and sampled onto the second column, in the form of narrow pulses. The modulation is thus the sequential liberation of the solute from the first column onto the second column, preserving and further fractionating the separation obtained on the first column. Additionally, since the modulated zones of a peak analyte are thermally focused before the separation on the second column, in a mass conservative process, the resulting segments (peaks) of the modulation are now more intense, with higher *S/N* ratios, and much narrower than in conventional GC (Lee et al. 2001; Dallüge et al. 2002b), improving the detection of trace analytes and the chromatographic resolution (Fig. 22.6). An example of the modulation effect, with the promoted increase of analytes *S/N* ratio, and the resulting increase in sensibility, can be observed on Fig. 22.6 for an extract from a soil polluted with hydrocarbons.

In theory, the total peak capacity n in GC × GC is the product of the peak capacities of the two individual columns n_1 (column 1) and n_2 (column 2), which results in separation potential $n_t = n_1 \times n_2$, that theoretically is much higher than in any other chromatographic arrangements (Fig. 22.7) (Venkatramani et al. 1996; Bertsch 2000).

In order to maximize the column peak capacities and the separation power of the GC × GC system, the separation mechanisms in both columns should be based on different and independent physical–chemical interactions (orthogonality) (Venkatramani et al. 1996; Phillips and Beens 1999; Marriott and Shellie 2002; Dallüge et al. 2003; Dimandja 2003; Schoenmakers et al. 2003), meaning that columns with stationary phases with maximum different selectivity should be selected for both dimensions. The first dimension columns have usually nonpolar

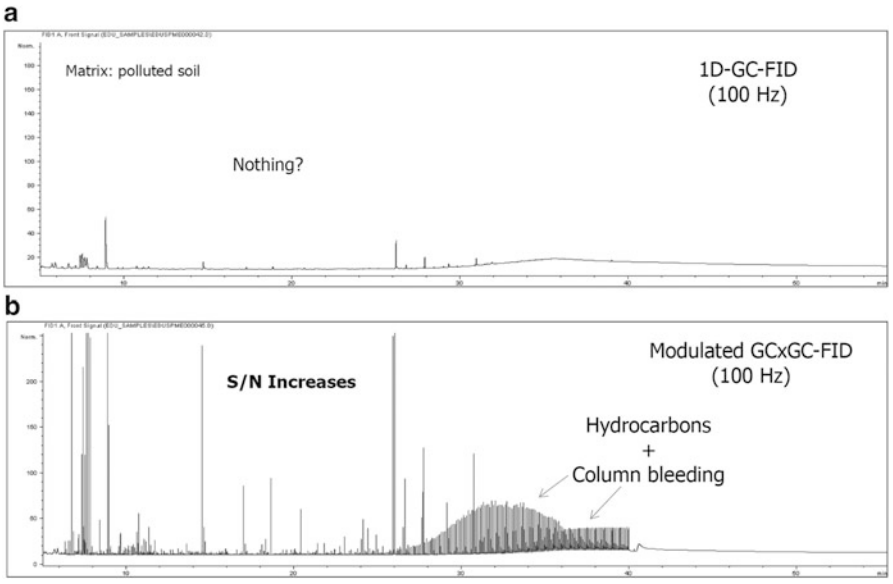

Fig. 22.6 Chromatograms from the same extract of a polluted soil sample obtained by conventional 1D-GC-FID (**a**), and by modulated GC × GC-FID (**b**), showing the peak signal increment (Injection: 1 μL in splitless)

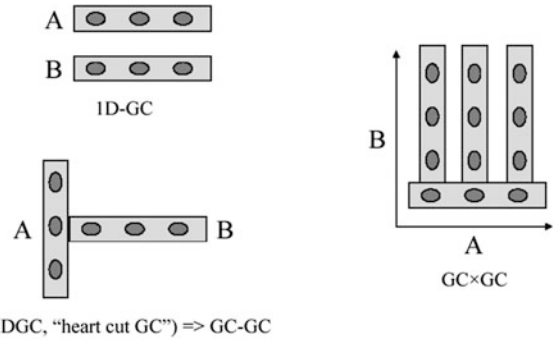

Fig. 22.7 Schematic representation of peak capacity for two individual columns A (column 1) and B (column 2) in 1D-GC and coupled for multidimensional GC using heart cut and GC × GC configurations

stationary phases and promote separation mainly due to the volatility of sample components (boiling point separation) (Phillips and Beens 1999; Marriott and Shellie 2002; Dallüge et al. 2003). The first column is usually of standard dimensions (e.g., 30 m × 0.25 mm; $d_f = 0.25$ μm), and the time scale of the first dimension separation corresponds to a normal GC separation, resulting in peak widths of several seconds. The second-column stationary phase is usually polar, or mid-polar (Beens et al. 2000; de Geus et al. 2001; Dallüge et al. 2002a). Fast GC can be performed in the second dimension column if a short narrow bore column (e.g., 1 m × 0.1 mm × 0.1 μm) is used. This configuration allows that the total time of the chromatographic run on the second column never exceeds more than a few

seconds. This means that the second-column separation is performed essentially under isothermal conditions (Beens et al. 1998) and, therefore, analyte separation is based only on their polarity or on another property independent from the first dimension. Additionally, using the short narrow bore column the actual total run time of both 1D-GC and GC × GC analysis, for the same sample, will be approximately the same (Marriott and Shellie 2002; Dallüge et al. 2003).

The very fast separation in the second column results in very narrow peaks with widths between 0.1 and 0.6 s (Beens et al. 1998; Lee et al. 2000; Marriott et al. 2000), that require high data acquisition rate detectors (50–100 Hz) to obtain sufficient number of data points over a chromatographic peak for its accurate description (Zrostlíková et al. 2003). The use of detectors, such as FID (Frysinger et al. 1999), electron capture detector (ECD) (de Geus et al. 2000; Korytár et al. 2002), nitrogen phosphorous detector (NPD) (Khummueng et al. 2006; Ochiai et al. 2007; Mateus et al. 2008), and mass spectrometer detectors with quadrupoles (qMS) (Song et al. 2004; Adahchour et al. 2005; Mateus et al. 2008) and time-of-flight mass analysers (TOFMS) (Dallüge et al. 2002c; Ma et al. 2007; Mateus et al. 2008), on GC × GC applications, has been described in the literature. However, for mass spectrometry, the fast acquisition TOF mass analysers are the suitable detectors for this technique and have considerably driven and enlarged the application potential of GC × GC.

After data acquisition, suitable software is used to generate a reconstructed two-dimensional chromatogram, or a 3D plot; which is the representation of the linear modulated chromatograms projected on the second dimension for each modulation. The independent second dimension chromatograms are aligned in a bidimensional plane, the GC × GC data contour plots representing the "bird's-eye view" of the chromatogram, where the *X*-axis represents the separation on the first column, the *Y*-axis the separation achieved on the second column and, for the 3D plots, the *Z*-axis the intensity of detector response (Marriott and Shellie 2002; Dallüge et al. 2003; Dimandja 2003). Figure 22.8 shows a representation of a one-dimensional chromatogram versus the two-dimensional contour plot GC × GC chromatogram for the same chromatographic window. It must be pointed that any peaks that are vertically aligned are co-eluting on the first column, and thus preventing 1D-GC-FID to be used for their monitorization purposes, a situation that is overtaken for GC × GC-FID since the peaks are adequately resolved on the 2D plot.

In Fig. 22.9, one can observe the separation obtained for a creosote sample, where the compounds show a very good resolution between themselves and from the matrix interferences.

Due to the orthogonal separation occurring in both columns, the chromatograms resulting from GC × GC are ordered, producing structured chromatograms, where the analytes have their spatial location, in the contour plot, based on their structures and thus physical–chemical nature (Phillips and Beens 1999). In the reconstructed 2D contour plots, characteristic patterns are obtained, in which the members of homological series with different volatilities are ordered along the first dimension axis, and the compounds are scattered along the second dimension axis according to their polarity (for a nonpolar–polar column set). This cluster representation of

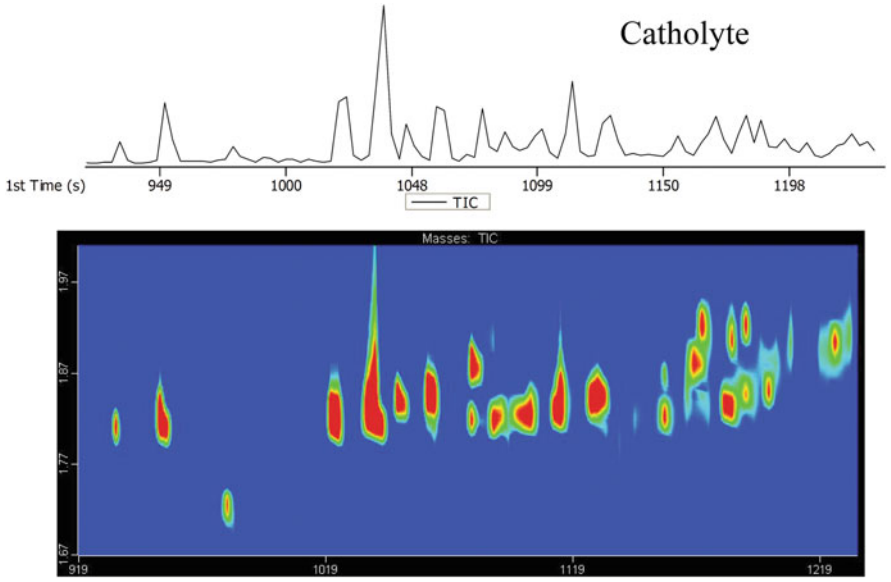

Fig. 22.8 Representation of the process of a GC × GC chromatogram: (*Top*) raw linear chromatogram showing the elution profile in 1D-GC; (*Bottom*) the software processed GC × GC chromatogram visualized as a two-dimensional contour plot (Electrokinetic remediation of wood treated with creosote: Catholyte sample)

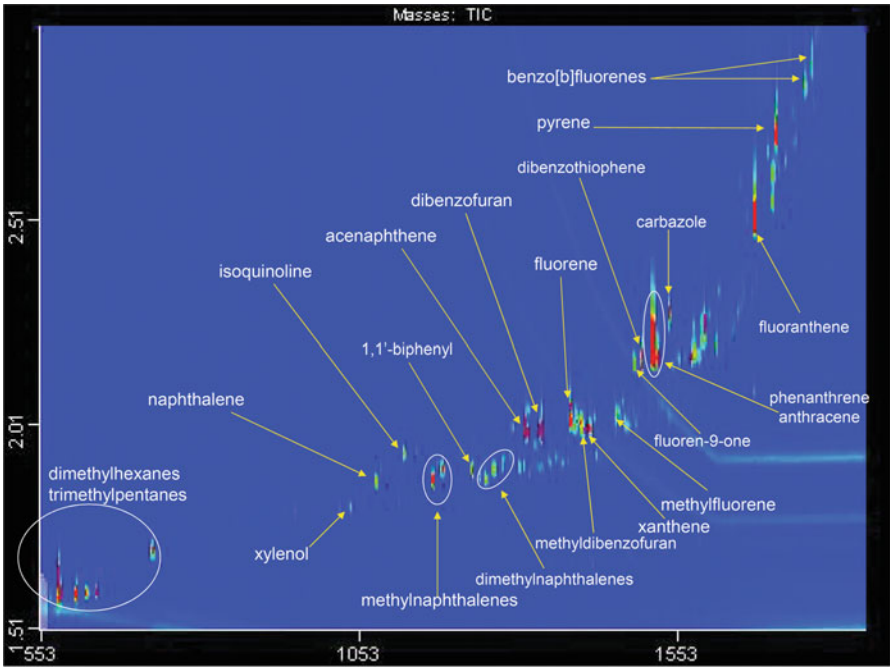

Fig. 22.9 Comprehensive two-dimensional separation space for a creosote sample GC × GC analysis

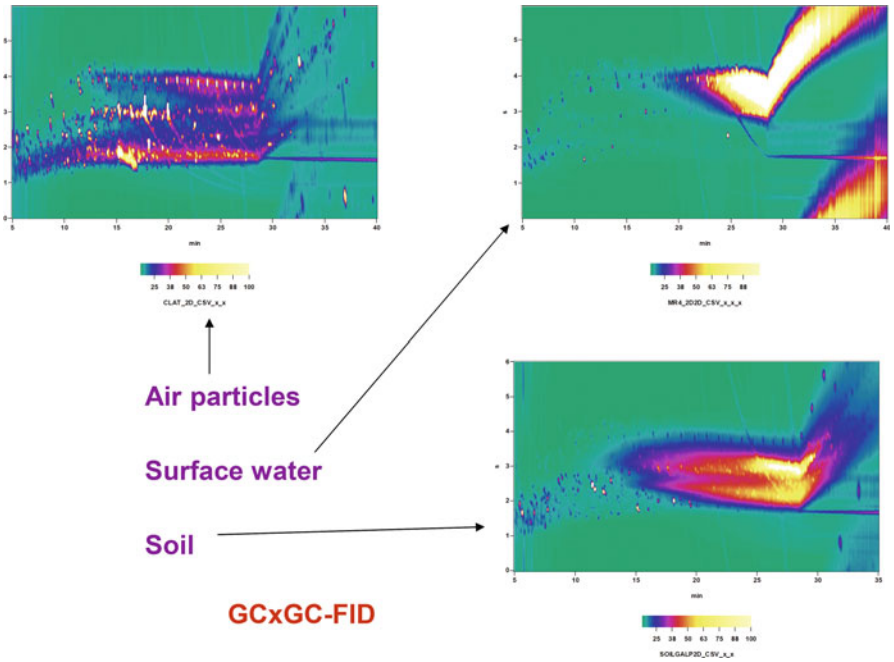

Fig. 22.10 GC × GC-FID contour plots for three different environmental matrices: atmospheric particulate matter (PM10), surface water, and polluted soil. The column set was mid-polar × nonpolar (Injection: 1 μL in splitless)

various subgroups of analytes in the GC × GC contour plots, that turn in some way the 2D space in chromatographic maps of chemical properties, may be used as a tool for compound class analysis, tentative identification/detection of analytes (Frysinger et al. 1999; Korytár et al. 2002), and matrix characterization (Fig. 22.10) with the use of any detector.

Acknowledgments Financial support for the work was provided by project FP7-PEOPLE-2010-IRSES-269289-*ELECTROACROSS—Electrokinetics across disciplines and continents*: *an integrated approach to finding new strategies for sustainable development*.

Very special thanks are due to Dr. Blagoj Mitrevski for his valuable technical support and advice.

References

Acar YB, Gale RJ, Alshawabkeh AN, Marks RE, Puppula S, Bricka M, Parker RJ (1995) Electrokinetic remediation: basics and technology status. J Hazard Mater 40(2):117–137

Adahchour M, Brandt M, Baier H-U, Vreuls RJJ, Batenburg AM, Brinkman UAT (2005) Comprehensive two-dimensional gas chromatography coupled to a rapid-scanning quadrupole mass spectrometer: principles and applications. J Chromatogr A 1067(1–2):245–254

Alcantara T, Pazos M, Cameselle C, Sanroman MA (2008) Electrochemical remediation of phenanthrene from contaminated kaolinite. Environ Geochem Health 30(2):89–94
Bartle KD (2002) Introduction. In: Mondello L, Lewis AC, Bartle KD (eds) Multidimensional chromatography. Wiley, Chichester, pp 3–15
Beens J, Boelens H, Tijssen R, Blomberg J (1998) Quantitative aspects of comprehensive two-dimensional gas chromatography (GC × GC). J High Resolut Chromatogr 21:47–54
Beens J, Blomberg J, Schoenmakers PJ (2000) Proper tuning of comprehensive two-dimensional gas chromatography (GC × GC) to optimize the separation of complex oil fractions. J High Resolut Chromatogr 23:182–188
Bertsch WJ (1999) Two-Dimensional gas chromatography. Concepts, instrumentation, and applications—part 1: fundamentals, conventional two-dimensional gas chromatography, selected applications. J High Resolut Chromatogr 22(12):647–665
Bertsch WJ (2000) Two-dimensional gas chromatography. Concepts, instrumentation and applications—part 2: comprehensive two-dimensional gas chromatography. J High Resolut Chromatogr 23:167–181
Dallüge J, van Rijn M, Beens J, Vreuls RJJ, Brinkmann UAT (2002a) Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection applied to the determination of pesticides in food extracts. J Chromatogr A 965:207–217
Dallüge J, Vreuls RJJ, Beens J, Brinkmann UAT (2002b) Optimisation and characterisation of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection. J Sep Sci 25:201–214
Dallüge J, van Stee LLP, Xu X, Williams J, Beens J, Vreuls RJJ, Brinkman UAT (2002c) Unravelling the composition of very complex samples by comprehensive gas chromatography coupled to time-of-flight mass spectrometry: cigarette smoke. J Chromatogr A 974(1–2):169–184
Dallüge J, Beens J, Brinkman UAT (2003) Comprehensive two-dimensional gas chromatography: a powerful and versatile analytical tool. J Chromatogr A 1000(1–2):69–108
David F, Sandra P (1987) In: Sandra P, Bicchi C (eds) Capillary gas chromatography in essential oil analysis. Huething, Heidelberg, p 387
Davis JM, Giddings JC (1983) Statistical theory of component overlap in multicomponent chromatograms. Anal Chem 55:418–424
de Geus H-J, Schelvis A, de Boehr J, Brinkman UAT (2000) Comprehensive two-dimensional gas chromatography with a rotating thermal desorption modulator and independently temperature programmable columns. J High Resolut Chromatogr 23:189–196
de Geus H-J, Aidos I, de Boer J, Luten JB, Brinkman UAT (2001) Characterisation of fatty acids in biological oil samples using comprehensive multidimensional gas chromatography. J Chromatogr A 910:95–103
Dimandja JMD (2003) A new tool for the optimized analysis of complex volatile mixtures: comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry. Am Lab 25(3):42–53
Frysinger GS, Gaines RB, Ledford EB Jr (1999) Quantitative determination of BTEX and total aromatic compounds by comprehensive two-dimensional gas chromatography. J High Resolut Chromatogr 22:195–200
Gomes HI, Ottosen LM, Ribeiro AB, Dias-Ferreira C (2015) Treatment of a suspension of PCB contaminated soil using iron nanoparticles and electric current. J Environ Manage 151:550–555. doi:10.1016/j.jenvman.2015.01.015
Grob K Jr, Grob G, Grob K (1978) Comprehensive, standardized quality test for glass capillary columns. J Chromatogr A 156(1):1–20
Grob K, Grob G, Grob K Jr (1981) Testing capillary gas chromatographic columns. J Chromatogr A 219(1):13–20
Grushka E (1970) Chromatographic peak capacity and the factors influencing it. Anal Chem 42 (11):1142–1147
Guedes P, Mateus EP, Couto N, Rodríguez Y, Ribeiro AB (2014) Electrokinetic remediation of six emerging organic contaminants from soil. Chemosphere 117:124–131

Hansen HK, Ottosen LM, Pedersen AJ, Villumsen A (2001) Speciation and mobility of cadmium in straw and wood combustion fly ash. Chemosphere 45:123–128

Khummueng W, Trenerry C, Rose G, Marriott PJ (2006) Application of comprehensive two-dimensional gas chromatography with nitrogen-selective detection for the analysis of fungicide residues in vegetable samples. J Chromatogr A 1131(1–2):203–214

Korytár P, Leonards PEG, de Boer J, Brinkman UAT (2002) High-resolution separation of polychlorinated biphenyls by comprehensive two-dimensional gas chromatography. J Chromatogr A 958:203–218

Lageman R, Pool W, Seffinga G (1989) Electro-reclamation: theory and practice. Chem Ind 18:585–590

Lee AL, Lewis AC, Bartle KD, McQuaid JB, Marriott PJ (2000) A comparison of modulating interface technologies in comprehensive two-dimensional gas chromatography (GC × GC). J Microcolumn Sep 12:187–193

Lee AL, Bartle KL, Lewis AC (2001) A model of peak amplitude enhancement in orthogonal two dimensional gas chromatography. Anal Chem 73:1330–1335

Liu Z, Phillips JB (1991) Comprehensive two-dimensional gas chromatography using an on-column thermal modulator interface. J Chromatogr Sci 29:227–231

Ma C, Wang H, Lu X, Li H, Liu B, Xu G (2007) Analysis of Artemisia annua L. volatile oil by comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry. J Chromatogr A 1150(1–2):50–53

Maini G, Sharman AK, Knowles CJ, Sunderland G, Jackman SA (2000) Electrokinetic remediation of metals and organics from historically contaminated soil. J Chem Technol Biotechnol 75(8):657–664

Marriott PJ, Ong RCY, Kinghorn RM, Morrison PD (2000) Time-resolved cryogenic modulation for targeted multidimensional capillary gas chromatography analysis. J Chromatogr A 892 (1–2):15–28

Marriott P, Shellie R (2002) Principles and applications of comprehensive two-dimensional gas chromatography. Trends Anal Chem 21(9–10):573–583

Martin M, Herman DP, Guiochon G (1986) Probability distributions of the number of chromatographically resolved peaks and resolvable components in mixtures. Anal Chem 58:2200–2207

Mateus EP, Gomes da Silva MDR, Ribeiro AB, Marriott PJ (2008) Qualitative mass spectrometric analysis of the volatile fraction of creosote-treated railway wood sleepers by using comprehensive two-dimensional gas chromatography. J Chromatogr A 1178(1–2):215–222

Meyer S, Cartellieri S, Steinhart H (1999) Simultaneous determination of PAHs, hetero-PAHs (N, S, O), and their degradation products in creosote-contaminated soils. Method development, validation, and application to hazardous waste sites. Anal Chem 71(18):4023–4029

Murillo-Rivera LI, Barrón J, Oropeza-Guzman MT, González I, Teutli-Leon MMM (2009) Influence of anolyte and catholyte composition on TPHs removal from low permeability soil by electrokinetic reclamation. Electrochim Acta 54(7):2119–2124

Chaves das Neves HJ, Freitas AMC (1996) Introdução à Cromatografia Gás-Líquido de Alta Resolução. Dias de Sousa, Ltd

Niqui-Arroyo JL, Bueno-Montes M, Posada-Baquero R, Ortega-Calvo JJ (2006) Electrokinetic enhancement of phenanthrene biodegradation in creosote-polluted clay soil. Environ Pollut 142(2):326–332

Ochiai N, Ieda T, Sasamoto K, Fushimi A, Hasegawa S, Tanabe K, Kobayashi S (2007) Comprehensive two-dimensional gas chromatography coupled to high-resolution time-of-flight mass spectrometry and simultaneous nitrogen phosphorous and mass spectrometric detection for characterization of nanoparticles in roadside atmosphere. J Chromatogr A 1150(1–2):13–20

Pamukcu S, Wittle JK (1992) Electrokinetic removal of selected heavy metals from soil. Environ Prog 11(3):241–250

Park JY, Kim SJ, Lee YJ, Baek K, Yang JW (2005) EK-Fenton process for removal of phenanthrene in a two-dimensional soil system. Eng Geol 77(3–4):217–224

Pedersen AJ, Ottosen LM, Villumsen A (2001) Electrodialytic removal of heavy metals from MSWI fly ashes. In: Proceedings of the 3rd symposium and status report on electrokinetic remediation, Karlsruhe

Phillips JB, Beens J (1999) Comprehensive two-dimensional gas chromatography: a hyphenated method with strong coupling between the two dimensions. J Chromatogr A 856:331–347

Polcaro AM, Vacca A, Mascia M, Palmas S (2007) Electrokinetic removal of 2,6-dichlorophenol and diuron from kaolinite and humic acid-clay system. J Hazard Mater 148(3):505–512

Poole CF (2003) The essence of chromatography. Elsevier, Boston

Probstein RF, Hicks R (1993) Removal of contaminants from soils by electric fields. Science 260:498–503

Rabbi MF, Clark B, Galeb RJ, Ozsu-Acar E, Pardue J, Jackson A (2002) In situ TCE bioremediation study using electrokinetic cometabolite injection. Waste Manag 20(4):279–286

Ribeiro AB (1998) Use of electrodialytic remediation technique for removal of selected heavy metals and metalloids from soils. Ph.D. Thesis, Technical University of Denmark, Denmark

Ribeiro AB, Mateus EP (2009) In: Krishna RR, Cameselle C (eds) Electrochemical remediation technologies for polluted soils, sediments and groundwater, 1st edn. Wiley, New York

Ribeiro AB, Mexia JT (1997) A dynamic model for the electrokinetic removal of copper from a polluted soil. J Hazard Mater 56(3):257–271

Ribeiro AB, Villumsen A, Bech-Nielsen G, Réffega A, Vieira e Silva JM (1998) Electrodialytic remediation of a soil from a wood preservation industry polluted by CCA. In: Proceedings of the 4th international symposium the challenge safety and environment in wood preservation. Cannes-Mandelieu

Ribeiro AB, Mateus EP, Ottosen LM, Bech-Nielsen G (2000) Electrodialytic removal of Cu, Cr, and As from chromated copper arsenate-treated timber waste. Environ Sci Technol 34 (5):784–788

Rohrs J, Ludwig G, Rahner D (2002) Electrochemically induced reactions in soils—a new approach to the in-situ remediation of contaminated soils? Part 2: remediation experiments with a natural soil containing highly chlorinated hydrocarbons. Electrochim Acta 47 (9):1405–1414

Schoenmakers P, Marriott P, Beens J (2003) Nomenclature and conventions in comprehensive multidimensional chromatography. LCGC Europe 16:335–339

Schomburg G, Husmann H, Hübinger E, König W (1984) Multidimensional capillary gas chromatography-enantiomeric separations of selected cuts using a chiral second column. J High Resolut Chromatogr 7:404–410

Song SM, Marriott P, Wynne P (2004) Comprehensive two-dimensional gas chromatography-quadrupole mass spectrometric analysis of drugs. J Chromatogr A 1058(1–2):223–232

Venkatramani CJ, Xu J, Phillips JB (1996) Separation orthogonality in temperature-programmed comprehensive two-dimensional gas chromatography. Anal Chem 68:1486–1492

Virkutyte J, Sillanpaa M, Latostenmaa P (2002) Electrokinetic soil remediation—critical overview. Sci Total Environ 289(1–3):97–121

Zrostlíková J, Hajslová J, Cajka T (2003) Evaluation of two-dimensional gas chromatography–time-of-flight mass spectrometry for the determination of multiple pesticide residues in fruit. J Chromatogr A 1019(1–2):173–186