

**DESENVOLUPAMENT DE METODOLOGIES ANALÍTIQUES PER
A LA DETERMINACIÓ DE COMPOSTOS ORGÀNICS EN
MATRIUS COMPLEXES.
APLICACIÓ A L'ESTUARI DEL RIU EBRE**

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6. Conclusions generals

- En el decurs d'aquesta Tesi Doctoral, s'han desenvolupat diferents metodologies analítiques per a la caracterització de mostres complexes de lípids, utilitzant com a matriu de referència la lanolina. Les metodologies emprades s'han basat tant en tècniques monodimensionals com multidimensionals:
 - o Les tècniques monodimensionals, desenvolupades s'han emprat per analitzar les famílies químiques següents:
 - VFAs per SPME en espai de cap i GC-MS, analitzant l'interval C₂-C₇.
 - FFAs, FALs, hidroxiàcids i diols amb GC-MS.
 - Èsters alifàtics emprant HTGC-MS, arribant a analitzar l'interval C₃₇-C₅₄.
 - Èsters esteroidals amb GC a pressió sub-ambient acoblada a un MS treballant tant en mode EIMS com en mode CIMS evitant la degradació dels compostos termolàbils.
 - Malgrat les potencialitats de les tècniques d'espectrometria de masses, la utilització d'índexs de retenció cromatogràfics continua sent imprescindible per la determinació dels isòmers posicionals.
 - Gràcies a les tècniques desenvolupades, s'han caracteritzat els lípids de la lanolina podent extreure conclusions de la distribució isomèrica dels diferents compostos. Es proposa un sistema de dos enzims per a la síntesi dels FAs, l'un responsable de la síntesi *de novo* i l'altra de l'allargament de la cadena. Els FFAs provenen de la hidròlisi dels èsters ja que tenen la mateixa distribució i finalment els diols i hidroxiàcids tenen un origen comú.
 - o S'ha posat al punt, una tècnica multidimensional GC×GC-ToF MS per a la determinació simultània de les diferents famílies de lípids; demostrant la relació que existeix entre les propietats fisicoquímiques dels compostos, com per exemple el Log P, i el seu comportament en GC×GC (temps de retenció segona dimensió).

- S'han aplicat les tècniques desenvolupades a la caracterització dels traçadors moleculars lípidics a l'estuari del riu Ebre tot aconseguint així:
 - o conèixer l'origen de la matèria orgànica present a l'estuari, sent terrestre el de l'aigua superficial i marí el de l'aigua profunda.
 - o conèixer la composició planctònica de l'estuari posant especial èmfasi en les diferències existents entre la capa superior (aigua dolça) i la capa inferior (aigua salada) de la falca salina. En l'aigua dolça el fitoplàncton és més abundant amb una elevada proporció de dinoflagelats. En el cas de l'aigua salada, que conté més zooplàncton, el fitoplàncton està majoritàriament format per diatomees.
 - o identificar marcadors moleculars de processos biogeoquímics específics (foto-oxidació) en l'aigua superficial majoritàriament. Així doncs, els processos biogeoquímics que es produeixen són diferents per les dues capes d'aigua.

- S'han desenvolupat metodologies analítiques per a la determinació de contaminants orgànics en matrius ambientals i lipídiques mitjançant la cromatografia de gasos dual GC-ECD/NPD.

- S'ha demostrat el potencial d'aquesta tècnica per a confirmar la identificació dels diferents compostos d'interès, basant-se amb el quocient de les respostes dels dos detectors emprats.

- S'ha modelitzat, gràcies a un experiment en microcosmos, el comportament dels contaminants orgànics en un estuari de règim de falca salina. Els processos de difusió que s'han correlacionat amb el volum molar dels anàlits han demostrat ser els principals responsables del transport vertical dels compostos d'interès. Pel que fa la seva eliminació, l'evaporació ha estat identificada com la via principal. En aquest sentit s'ha correlacionat l'eliminació amb la constant de Henry dels anàlits.

- S'han determinat diferents contaminants orgànics a l'estuari del riu Ebre i s'ha estudiat el seu comportament.
 - o La gran variabilitat temporal de les concentracions dels contaminants s'ha atribuït amb una doble estacionalitat natural i antropogènica.

- S'han aproximat els fluxos d'emissió de contaminants i matèria en suspensió al Mediterrani, gràcies a un regim de campanyes de mostratge que integra la variabilitat estacional del riu.
- S'ha posat de manifest la gran influència de la falca salina en la distribució vertical dels contaminants orgànics, concentrant-se majoritàriament a la capa superior i no observant-se un enriquiment a l'interfase.
- S'ha descrit la distribució geogràfica dels contaminants a l'estuari associant-se les diferències a aportos locals o difusos, més que a processos de transformació que tindrien lloc en el curt tram de riu estudiat.

7-Bibliografia

Cold Spring Harbor Laboratory and European Bioinformatics Institute, 2006; Vol. 2006.

Confederación Hidrografica del Ebro, 2005; <http://www.che.es>.

European Union, On the quality of water intended for human consumption. European Council *Directive 98/83/EC*, 1998.

EPA, Tetra- through Octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS, EPA, *Method 1613*, 2004.

EPA, Drinking Water Candidate list 2, 2005; http://www.epa.gov/OGWDW/ccl/ccl2_list.html.

Ministerio de Consumo y Sanidad, "European Pharmacopeia," 2002.

NASA, 2006; <http://www.nasa.gov>.

Syracuse Research Corporation, 2006, <http://www.syrres.com/esc/kowdemo.htm>.

UNEP/MAP "Riverine transport of water, sediment and pollutants to the Mediterranean Sea.," UNEP/MAP, 2003.

Abad, E.; Caixach, J.; Rivera, J.; Gustems, L.; Massague, G.; Puig, O. Temporal trends of PCDDs/PCDFs in ambient air in Catalonia (Spain). *Sci. Total Environ.* **2004**, *334*, 279-285.

Abalos, M.; Pawliszyn, J.; Bayona, J. M. Development of a headspace solid-phase microextraction procedure for the determination of free volatile fatty acids in waste waters. *J. Chromatogr. A* **2000**, *873*, 107-115.

Ackman, R. G. The gas chromatograph in practical analyses of common and uncommon fatty acids for the 21st century. *Anal. Chim. Acta* **2002**, *465*, 175-192.

Adahchour, M.; Beens, J.; Vreuls, R. J. J.; Batenburg, A. M.; Brinkman, U. A. T. Comprehensive two-dimensional gas chromatography of complex samples by using a 'reversed-type' column combination: application to food analysis. *J. Chromatogr. A* **2004**, *1054*, 47-55.

Adahchour, M.; Brandt, M.; Baier, H. U.; Vreuls, R. J. J.; Batenburg, A. M.; Brinkman, U. A. T. Comprehensive two-dimensional gas chromatography coupled to a rapid-scanning quadrupole mass spectrometer: principles and applications. *J. Chromatogr. A* **2005**, *1067*, 245-254.

Adahchour, M.; Stee, L. L. P. v.; Beens, J.; Vreuls, R. J. J.; Batenburg, M. A.; Brinkman, U. A. T. Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection for the trace analysis of flavour compounds in food. *J. Chromatogr. A* **2003**, *1019*, 157-172.

Adahchour, M.; Taso, A.; Beens, J.; Vreuls, R. J. J.; Batenburg, A. M.; Brinkman, U. A. T. Fast comprehensive two-dimensional gas chromatography (GC×GC) using 50- μ m ID second-dimension columns *J. Sep. Sci.* **2003**, *26*, 753-760.

Adahchour, M.; Wievel, J.; Verdel, R.; Vreuls, R. J. J.; Brinkman, U. A. T. Improved determination of flavour compounds in butter by solid-phase (micro)extraction and comprehensive two-dimensional gas chromatography. *J. Chromatogr. A* **2005**, *1086*, 99-106.

Amaral, J. S.; Cunha, S. C.; Santos, A.; Alves, M. R.; Seabra, R. M.; Oliveira, B. P. P. Influence of cultivar and environmental conditions on the triacylglycerol profile of hazelnut (*Corylus avellana* L.). *J. Agr. Food Chem.* **2006**, *54*, 449-456.

Amirav, A.; Gordin, A.; Tzanani, N. Supersonic gas chromatography/mass spectrometry *Rapid Commun. Mass. Spectrom.* **2001**, *15*.

Amon, R. M. W.; Meon, B. The biogeochemistry of dissolved organic matter and nutrients in two large Arctic estuaries and potential implications for our understanding of the Arctic Ocean system. *Mar. Chem.* **2004**, *92*, 311-330.

Archer, N. E.; Charles, Y.; Elliott, J. A.; Jickells, S. Changes in the lipid composition of latent fingerprint residue with time after deposition on a surface. *Forensic Sci. Int.* **2005**, *154*.

Balinova, A. Strategies for chromatographic analysis of pesticide residues in water *J. Chromatogr. A* **1996**, *754*, 125-135.

Barcelo, D.; Sole, M.; Durand, G.; Albaiges, J. Analysis and behavior of organophosphorus pesticides in a rice crop field. *Fresen. j. Anal. Chem.* **1991**, *339*, 676-683.

Barnett, G. *Cosm. Toiletr.* **1986**, *101*, 23.

Barry, E. F. *Modern practice of gas chromatography*; Fourth Edition ed.; John Wiley & Sons: Hoboken, New Jersey, 2004.

Bartle, K. D.; Myers, P. History of gas chromatography *Trends Anal. Chem.* **2002**, *21*, 547-557.

Beens, J.; Janssen, H. G.; Adahchour, M.; Brinkman, U. A. T. Flow regime at ambient outlet pressure and its influence in comprehensive two-dimensional gas chromatography. *J. Chromatogr. A* **2005**, *1086*, 141-150.

Bicchi, C.; D'Amato, A.; Binello, A. Identification of pesticide residues in real matrices by combining retention indices and specific multidetection responses *J. High Res. Chromatogr.* **1996**, *19*, 80-84.

Bodineau, L.; Thoumelin, G.; Beghin, V.; Wartel, M. Tidal time-scale changes in the composition of particulate organic matter within the estuarine turbidity maximum zone in the macrotidal Seine estuary, France: the use of fatty acid and sterol biomarkers. *Estuar. Coast. Shelf Sci.* **1998**, *47*, 37-49.

Brody, S. S.; Chaney, J. E. Flame photometric detector - Application of a specific detector for phosphorus and for sulfur compounds - sensitive to subnanogram quantities *J. Gas Chromatogr.* **1966**, *4*, 42.

Cauwet, G. Carbon inputs and biogeochemical processes at the halocline in a stratified estuary: Krka River, Yugoslavia. *Mar. Res.* **1991**, *32*, 269-283.

Centre, 2006; <http://www.jic.bbsrc.ac.uk/services/proteomics/tof.htm>.

Christie, W. W. Equivalent chain-lengths of methyl ester derivatives of fatty acids on gas chromatography. A reappraisal. *J. Chromatogr.* **1988**, *447*, 305-314.

Coderch, L.; Maza, A. d. l.; Pinazo, A.; Parra, J. L. Physicochemical characteristics of liposomes formed with internal wool lipids. *J. Am. Oil Chem. Soc.* **1996**, *73*, 1713-1718.

Cramers, C. A.; Janssen, H. G.; Deursen, M. M. v.; Leclercq, P. A. High-speed gas chromatography: an overview of various concepts. *J. Chromatogr. A* **1999**, *856*, 315-329.

Cremer, E.; Prior, F. Z. *Elektrochem* **1951**, *55*, 66.

Cruzado, A.; Velasquez, Z.; Perez, M. D.; Bahamon, N.; Grimaldo, N. S.; Ridolfi, F. Nutrient fluxes from the Ebro River and subsequent across-shelf dispersion. *Cont Shelf Res.* **2002**, *22*, 349-360.

Dalluge, J.; Beens, J.; Brinkman, U. A. T. Comprehensive two-dimensional gas chromatography: a powerful and versatile analytical tool. *J. Chromatogr. A* **2003**, *1000*, 69-108.

Dalluge, J.; Rijn, M. v.; Beens, J.; Vreuls, R. J. J.; Brinkman, U. A. T. Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection applied to the determination of pesticides in food extracts. *J. Chromatogr. A* **2002**, *965*, 207-217.

Dalluge, J.; Stee, L. L. P. v.; Xu, X. B.; Williams, J.; Beens, J.; Vreuls, R. J. J.; Brinkman, U. A. T. Unravelling the composition of very complex samples by comprehensive gas chromatography coupled to time-of-flight mass spectrometry - cigarette smoke. *J. Chromatogr. A* **2002**, *974*, 169-184.

Dalluge, J.; Vreuls, R. J. J.; Beens, J.; Brinkman, U. A. T. Optimization and characterization of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection (GCXGC-TOFMS). *J. Sep. Sci.* **2002**, *25*, 201-214.

Dandeneau, R. D.; Zerenner, E. H. An investigation of glasses for capillary chromatography *J. High Res. Chromatogr.* **1979**, *2*.

Deans, D. R. *Chromatographia* **1968**, *1*, 18-22.

Deans, D. R. Use of heart cutting in gas chromatography a review *J. Chromatogr.* **1981**, *203*, 19-28.

Desty, D. H.; Goldup, A.; Whyman, B. H. F. *J. Inst. Petrol* **1959**, *45*, 287-298.

Deursen, M. v.; Beens, J.; Reijenga, J.; Lipman, P.; Cramers, C.; Blomberg, J. Group-type identification of oil samples using comprehensive two-dimensional gas chromatography coupled to a time-of-flight mass spectrometer (GCXGC-TOF) *J. High Res. Chromatogr.* **2000**, *23*, 507-510.

Deursen, M. v.; Janssen, H. G.; Beens, J.; Lipman, P.; Reinierkens, R.; Rutten, G.; Cramers, C. Fast gas chromatography using vacuum outlet conditions. *J. Microcolumn Sep.* **2000**, *12*, 613-622.

Dimandja, J. M. D. A new tool for the optimized analysis of complex volatile mixtures: comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry *Am. Lab.* **2003**, *35*, 42-53.

Ding, J.; Welton, T.; Armstrong, D. W. Chiral ionic liquids as stationary phases in gas chromatography. *Anal. Chem.* **2004**, *76*, 6819-6822.

Domínguez, C.; Jover, E.; Bayona, J. M.; Erra, P. Effect of the carbon dioxide modifier on the lipid composition of wool wax extracted from raw wool. *Anal. Chim. Acta* **2003**, *477*, 233-242.

Eglinton, G.; Calvin, M. Chemical Fossils *Sci. Am.* **1967**, *216*, 32.

Eiceman, G. A.; Gardea-Torresdey, J.; Overton, E.; Carney, K.; Dorman, F. Gas chromatography. *Anal. Chem.* **2004**, *76*, 3387-3394.

Focant, J. F.; Eppe, G.; Scippo, M. L.; Massart, A. C.; Pirard, C.; Maghuin-Rogister, G.; Pauw, E. d. Comprehensive two-dimensional gas chromatography with isotope dilution time-of-flight mass spectrometry for the measurement of dioxins and polychlorinated biphenyls in foodstuffs. Comparison with other methods. *J. Chromatogr. A* **2005**, *1086*, 45-60.

Fonollosa, J.; Martí, M.; Maza, A. d. l.; Parra, J. L.; Coderch, L. Analysis of the ceramide content of internal wool lipids. *J. Plan. Chromatogr.* **2000**, *13*, 119-122.

Gammon, D. W.; Silva, M.; Aldous, C.; Sanborn, J. R.; Carr, W. C.; Pfeifer, K.; Schreider, J. P. "Atrazine risk characterisation document," Medical Toxicology Branch,

California Department of Pesticide Regulation, California Environmental Protection Agency, 2001.

Gere, D. R. Supercritical fluid chromatography *Science* **1983**, 222, 253-259.

Geus, H. J. d.; Aidos, I.; Boer, J. d.; Luten, J. B.; Brinkman, U. A. T. Characterisation of fatty acids in biological oil samples using comprehensive multidimensional gas chromatography. *J. Chromatogr. A* **2001**, 910, 95-103.

Gogus, F.; Ozel, M. Z.; Lewis, A. C. Extraction of essential oils of leaves and flowers of *Achillea monocephala* by superheated water. *Flavour Frag. J.* **2006**, 21, 122-128.

Gohlke, R. S. Time-of-Flight Mass Spectrometry and Gas-liquid Partition Chromatography. *Anal. Chem.* **1959**, 31, 535-541.

Golay, M. J. E. *Gas chromatography (Lansing Symposium)*; Academic Press: New York (USA), 1957.

Golay, M. J. E. *Gas chromatography*; Butterworths: London, 1958.

Gomes, R. L.; Avcioglu, E.; Scrimshaw, M. D.; Lester, J. N. Steroid estrogen determination in sediment and sewage sludge: a critique of sample preparation and chromatographic/mass spectrometry considerations, incorporating a case study in method development *Trends Anal. Chem.* **2004**, 23, p737-744.

Gómez-Gutiérrez, A. I.; Jover, E.; Bodineau, L.; Albaiges, J.; Bayona, J. M. Organic contaminant loads into the Western Mediterranean Sea: Estimate of Ebro River inputs. *Chemosphere* **2006**, *in press*.

Grimalt, J. O.; Drooge, B. L. v. Polychlorinated biphenyls in mountain pine (*Pinus uncinata*) needles from Central Pyrenean high mountains. *Ecotox. Environ. Safe* **2006**, 63, 61-67.

Grimalt, J. O.; Fernandez, P.; Bayona, J. M.; Albaiges, J. Assessment of fecal sterols and ketones as indicators of urban sewage inputs to coastal waters. *Environ. Sci. Technol.* **1990**, 24, 357-363.

Grob, K.; Grob, G. Splitless injection on capillary columns, I. Basic technique-steroid analysis as an example *J. Chromatogr. Sci.* **1969**, 7, 584.

Guillén, J.; Palanques, A. Sediment dynamics and hydrodynamics in the lower course of a river highly regulated by dams: the Ebro River. *Sedimentology* **1992**, 39, 567-579.

Halket, J. M. *Handbook of derivatives for chromatography*; John Wiley & Sons: London, UK, 1993.

Hamilton, J. F.; Webb, P. J.; Lewis, A. C.; Hopkins, J. R.; Smith, S.; Davy, P. Partially oxidised organic components in urban aerosol using GCXGC-TOF/MS. *Atmos. Chem. Phys.* **2004**, *4*, 1279-1290.

Hamilton, J. F.; Webb, P. J.; Lewis, A. C.; Reviejo, M. M. Quantifying small molecules in secondary organic aerosol formed during the photo-oxidation of toluene with hydroxyl radicals. *Atmos. Environ.* **2005**, *39*, 7263-7275.

Hao, C.; Headley, J. V.; Peru, K. M.; Frank, R.; Yang, P.; Solomon, K. R. Characterization and pattern recognition of oil-sand naphthenic acids using comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry. *J. Chromatogr. A* **2005**, *1067*, 277-284.

Harju, M.; Bergman, A.; Olsson, M.; Roos, A.; Haglund, P. Determination of atropisomeric and planar polychlorinated biphenyls, their enantiomeric fractions and tissue distribution in grey seals using comprehensive 2D gas chromatography. *J. Chromatogr. A* **2003**, *1019*, 127-142.

Harju, M.; Danielsson, C.; Haglund, P. Comprehensive two-dimensional gas chromatography of the 209 polychlorinated biphenyls *J. Chromatogr. A* **2003**, *1019*, 111-126.

Hart, S. R.; Gaskell, S. J. LC-tandem MS in proteome characterization. *Trends Anal. Chem.* **2005**, *24*, 566-575.

Hellings, L.; Dehairs, F.; Tackx, M.; Keppens, E.; Baeyens, W. Origin and fate of organic carbon in the fresh water part of the Scheldt estuary as traced by stable carbon isotope composition. *Biogeochemistry* **1999**, *47*, 167-186.

Hinshaw, J. V. Comprehensive two-dimensional gas chromatography *LCGC North America* **2004**, *22*, 32-40.

James, A. T.; Martin, A. J. P. Gas-Liquid partition chromatography - The separation and micro-estimation of volatile fatty acids from formic acid to dodecanoic acid. *Biochem. J.* **1952**, *50*, 679-690.

Jeffries, H. P. Seasonal composition of temperate plankton communities - fatty acids. *Limnol. Oceanogr.* **1970**, *15*, 419.

Jennings, W. Use of glass-capillary columns for food and essential oil analysis *J. Chromatogr. Sci.* **1979**, *17*, 636-639.

Jitaru, P.; Birzu, A.; Mocanu, R.; Adams, F. C. Effect of the interface on separation in multicapillary gas chromatography-based hyphenated techniques for speciation analysis of organometallic compounds. *Anal. Bioanal. Chem.* **2005**, *382*, 1993-1998.

Jover, E.; Àbalos, M.; Ortiz, L.; Bayona, J. M. Volatile fatty acids as malodorous compounds in wool scouring water and lanolin. Origin and characterisation. *Environ. Technol.*, **2003**, *24*, p1465-1470.

Jover, E.; Adahchour, M.; Bayona, J. M.; Vreuls, R. J. J.; Brinkman, U. A. T. Characterization of lipids in complex samples using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. *J. Chromatogr. A* **2005**, *1086*, 2-11.

Jover, E.; Domínguez, C.; Erra, P.; Bayona, J. M. Comparative characterization of a wool-wax extract by two complementary chromatographic techniques. *J. Cosmet. Sci.* **2006**, *57*, 23-35.

Kamm, W.; Dionisi, F.; Hischenhuber, C.; Schmarr, H. G.; Engel, K. H. Rapid detection of vegetable oils in milk fat by on-line LC-GC analysis of B-sitosterol as marker. *Eur. J. Lipid Sci. Technol.* **2002**, *104*, 756-761.

Klesper, E.; Corwin, A. H.; Turner, D. A. High pressure gas chromatography above critical temperatures *J. Org. Chem.* **1962**, *27*, 700.

Kolattukudy, P. E. *Chemistry and biochemistry of natural waxes.*; Elsevier: Amsterdam, The Netherlands, 1976.

Kolb, B.; Bischoff, J. New design of a thermionic nitrogen and phosphorus detector for GC *J. Chromatogr. Sci.* **1974**, *12*, 625-629.

Korytar, P.; Parera, J.; Leonards, P. E. G.; Santos, F. J.; Boer, J. d.; Brinkman, U. A. T. Characterization of polychlorinated n-alkanes using comprehensive two-dimensional gas chromatography-electron-capture negative ionisation time-of-flight mass spectrometry. *J. Chromatogr. A* **2005**, *1086*, 71-82.

Korytar, P.; Stee, L. L. P. v.; Leonards, P. E. G.; Boer, J. d.; Brinkman, U. A. T. Attempt to unravel the composition of toxaphene by comprehensive two-dimensional gas chromatography with selective detection *J. Chromatogr. A* **2003**, *994*, 179-189.

Kovats, E. Gas-chromatographische charakterisierung organischer verbindungen. 1. retentionsindices aliphatischer halogenide, alkohole, aldehyde und ketone. *Helv. Chim. Acta* **1958**, *41*, 1915-1932.

Krock, K. A.; Ragunathan, N.; Wilkins, C. L. Parallel cryogenic trapping multidimensional gas chromatography with directly linked infrared and mass spectral detection. *J. Chromatogr.* **1993**, *645*, 153-159.

Lachenmeier, D. W.; Kroener, L.; Musshoff, F.; Madea, B. Application of tandem mass spectrometry combined with gas chromatography and headspace solid-phase dynamic extraction for the determination of drugs of abuse in hair samples. *Rapid Commun. Mass. Spectrom.* **2003**, *17*, 472-478.

Lambertus, G. R.; Fix, C. S.; Reidy, S. M.; Miller, R. A.; Wheeler, D.; Nazarov, E.; Sacks, R. Silicon microfabricated column with microfabricated differential mobility spectrometer for GC analysis of volatile organic compounds. *Anal. Chem.* **2005**, *77*, 7563-7571.

Leathard, D. A.; Shurlock, B. C. *Identification techniques in gas chromatography*; John Wiley & Sons: London, 1970.

Leaver, I. H.; Lewis, D. M.; westmoreland, D. J. Analysis of wool lipids using thin-layer chromatography with flame ionization detection. *Text. Res. J.* **1988**, *58*, 593-600.

Lieshout, M. v.; Derks, R.; Janssen, H. G.; Cramers, C. A. Fast capillary gas chromatography: Comparison of different approaches. *J. High Res. Chromatogr.* **1998**, *21*, 583-586.

Loconto, P. R.; Gains, A. K. Isolation and recovery of organophosphorus pesticides from water by solid-phase extraction with dual wide-bore capillary gas chromatography. *J. Chromatogr. Sci.* **1989**, *27*, 569-573.

Lovelock, J. E.; Lipsky, S. R. Electron affinity spectroscopy, a new method for the identification of functional groups in chemical compounds separated by gas chromatography. *J. Amer. Chem. Soc.* **1960**, *82*, 431-433.

Lu, X.; Cai, J. L.; Kong, H. W.; Wu, M.; Hua, R. X.; Zhao, M. Y.; Liu, J. F.; Xu, G. W. Analysis of cigarette smoke condensates by comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry 1 acidic fraction. *Anal. Chem.* **2003**, *75*, 4441-4451.

Lu, X.; Zhao, M. Y.; Kong, H. W.; Cai, J. L.; Wu, J. F.; Wu, M.; Hua, R. X.; Liu, J. F.; Xu, G. W. Characterization of cigarette smoke condensates by comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry (GC×GC/TOFMS) - Part 2: Basic fraction. *J. Sep. Sci.* **2004**, *27*, 101-109.

Marklund, A.; Andersson, B.; Haglund, P. Traffic as a source of organophosphorus flame retardants and plasticizers in snow. *Environ. Sci. Technol.* **2005**, *39*, 3555-3562.

Marriott, P. J.; Morrison, P. D.; Shellie, R. A.; Dunn, M. S.; Sari, E.; Ryan, D. Multidimensional and comprehensive two-dimensional gas chromatography. *LCGC Europe* **2003**, *16*, 23-34.

McWilliam, I. G.; Dewar, R. A. Flame ionization detector for gas chromatography. *Nature* **1958**, *181*, 760.

Melchert, H.-U.; Pabel, E. Reliable identification and quantification of trichothecenes and other mycotoxins by electron impact and chemical ionization-gas chromatography-mass spectrometry, using an ion-trap system in the multiple mass spectrometry mode. Candidate reference method for complex matrices. *J. Chromatogr. A* **2004**, *1056*, 195-199.

Miwa, N.; Nakamura, S.; Nagao, N.; Naruse, S.; Ito, H.; Takada, Y.; Kageyama, K. Wool grease-derived alpha-monohydric fatty alcohols are carcinostatic depending on their branched alkyl moiety bulkiness. *Anticancer Res.* **1996**, *16*, 2479-2484.

Moldovan, Z.; Jover, E.; Bayona, J. M. Gas chromatographic and mass spectrometric methods for the characterisation of long chain fatty acids. Application to wool wax extracts. *Anal. Chim. Acta* **2002**, *465*, 359-378.

Moldovan, Z.; Jover, E.; Bayona, J. M. Systematic characterisation of long-chain aliphatic esters of wool wax by gas chromatography-electron impact ionisation mass spectrometry. *J. Chromatogr. A* **2002**, *952*, 193-204.

Mondello, L.; Casilli, A.; Tranchida, P. Q.; Dugo, G.; Dugo, P. Comprehensive two-dimensional gas chromatography in combination with rapid scanning quadrupole mass spectrometry in perfume analysis. *J. Chromatogr. A* **2005**, *1067*, 235-243.

Morales-Muñoz, S.; Vreuls, R. J. J.; Castro, M. D. L. d. Dynamic ultrasound-assisted extraction of environmental pollutants from marine sediments for comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection. *J. Chromatogr. A* **2005**, *1086*.

Motiuk, K. Wool wax acids - Review *J. Am. Oil Chem. Soc* **1979**, *56*, 91-97.

Motiuk, K. Wool wax alcohols - Review *J. Am. Oil Chem. Soc* **1979**, *56*, 651-658.

Nakano, Y.; Miyazaki, A.; Yoshida, T.; Ono, K.; Inoue, T. A study on pesticide runoff from paddy fields to a river in rural region-1: Field survey of pesticide runoff in the Kozakura River, Japan. *Wat. Res.* **2004**, *38*, 3017-3022.

Oaks, D. M.; Dimick, K. P.; Hartmann, H. Analysis of sulfur compounds with electron apture/ hydrogen flame dual channel gas chromatography *Anal. Chem.* **1964**, *36*, 1560.

Oh-Shin, Y. S.; Ko, M.; Shin, H. S. Simultaneous quantification of insecticides including carbaryl in drinking water by gas chromatography using dual electron-capture and nitrogen-phosphorus detection. *J. Chromatogr. A* **1997**, *769*, 285-291.

Ong, R.; Marriott, P.; Morrison, P.; Haglund, P. Influence of chromatographic conditions on separation in comprehensive gas chromatography. *J. Chromatogr. A* **2002**, *962*, 135-152.

Ozel, M. Z.; Gogus, F.; Hamilton, J. F.; Lewis, A. C. The essential oil of *Pistacia, vera L.* at various temperatures of direct thermal desorption using comprehensive gas chromatography coupled with time-of-flight mass spectrometry *Chromatographia* **2004**, *60*, 79-83.

Paustenbach, D. J. The practice of exposure assessment: A state-of-the-art review (Reprinted from principles and methods of toxicology, 4th edition, 2001) *J. Toxicol. Environ. Health* **2000**, *3*, 179-291.

Petrisor, I. G. Emerging contaminants- The growing problem. *Environ. Forensics* **2004**, *5*, 183-184.

Philp, R. P. High temperature gas chromatography for the analysis of fossil fuels: a review. *J. High Res. Chromatogr.* **1994**, *17*, 398-406.

Prat, N.; Ibañez, C. Effects of water transfers projected in the Spanish Hydrological Plan on the ecology of the lower river Ebro (N.E. Spain) and its delta. *Wat. Sci. Technol.* **1995**, *31*, 79-86.

Quigley, W. W. C.; Dovichi, N. J. Capillary electrophoresis for the analysis of biopolymers. *Anal. Chem.* **2004**, *76*, 4645-4658.

Ray, N. H. Gas chromatography. 1. The separation and estimation of volatile organic compounds by gas-liquid partition chromatography. *J. Appl. Chem.* **1954**, *4*, 21-25.

Richardson, S. D.; Ternes, T. A. Water analysis: Emerging contaminants and current issues. *Anal. Chem.* **2005**, *77*, 3807-3838.

Rontani, J. F.; Volkman, J. K. Phytol degradation products as biogeochemical tracers in aquatic environments. *Org. Geochem.* **2003**, *34*, 1-35.

Rose, R. L.; Hodgson, E.; Roe, R. M. *Pesticides*; Academic Press: Nova York, 1999.

Runge, F. F. *Farbenchemie I and II*, 1834.

Saliot, A.; Parrish, C. C.; Sadouni, N.; Bouloubassi, L.; Fillaux, J.; Cauwet, G. Transport and fate of Danube delta terrestrial organic matter in the Northwest Black Sea mixing zone. *Mar. Chem.* **2002**, *79*, 243-259.

Santos, F. J.; Galceran, M. T. The application of gas chromatography to environmental analysis. *Trends Anal. Chem.* **2002**, *21*, 672-685.

Schnelle-Kreis, J.; Welthagen, W.; Sklorz, M.; Zimmermann, R. Application of direct thermal desorption gas chromatography and comprehensive two-dimensional gas chromatography coupled to time of flight mass spectrometry for analysis of organic compounds in ambient aerosol particles. *J. Sep. Sci.* **2005**, *28*, 1648-1657.

Schoenmakers, P.; Marriott, P.; Beens, J. Nomenclature and conventions in comprehensive multidimensional chromatography *LCGC Europe* **2003**, *June*, 1-4.

Schomburg, G. 2-dimensional gas-chromatography - principles, instrumentation, methods *J. Chromatogr. A* **1996**, *703*, 309-325.

Schurig, V. Contributions to the theory and practice of the chromatographic separation of enantiomers. *Chirality* **2005**, *17*, S205-S226.

Shellie, R.; Marriott, P.; Morrison, P. Concepts and preliminary observations on the triple-dimensional analysis of complex volatile samples by using GC×GC-TOFMS. *Anal. Chem.* **2001**, *73*, 1336-1344.

Shellie, R.; Marriott, P.; Morrison, P. Comprehensive two-dimensional gas chromatography with flame ionization and time-of-flight mass spectrometry detection: Qualitative and quantitative analysis of west Australian sandalwood oil. *J. Chromatogr. Sci.* **2004**, *42*, 417-422.

Shellie, R. A.; Welthagen, W.; Zrostlikova, J.; Spranger, J.; Ristow, M.; Fiehn, O.; Zimmermann, R. Statistical methods for comparing comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry results: Metabolomic analysis of mouse tissue extracts. *J. Chromatogr. A* **2005**, *1086*, 83-90.

Shende, C.; Kabir, A.; Townsend, E.; Malik, A. Sol-gel poly(ethylene glycol) stationary phase for high-resolution capillary gas chromatography. *Anal. Chem.* **2003**, *75*, 3518-3530.

Sierra, J. P.; Sánchez-Arcilla, A.; Figueras, P. A.; Rio, J. G. d.; Kassmussen, E. K.; Mösso, C. Effects of discharge reductions on salt wedge dynamics of the Ebro River. *Riv. Res. Appl.* **2004**, *20*, 61-77.

Sinha, A. E.; Hope, J. L.; Prazen, B. J.; Nilsson, E. J.; Jack, R. M.; Synovec, R. E. Algorithm for locating analytes of interest based on mass spectral similarity in GCXGC-TOF-MS data: analysis of metabolites in human infant urine. *J. Chromatogr. A* **2004**, *1058*, 209-215.

Southwick, L. M.; Grigg, B. C.; Fouss, J. L.; Kornecki, T. S. Atrazine and metolachlor in surface runoff under typical rainfall conditions in southern Louisiana. *J. Agr. Food Chem.* **2003**, *51*.

Stenson, A. C.; Landing, W. M.; Marshall, A. G.; Cooper, W. T. Ionization and fragmentation of humic substances in electrospray ionization Fourier transform-ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2002**, *74*, 4397-4409.

Stephens, W. E. A pulsed mass spectrometer with time dispersion. *Phys. Rev.* **1946**, *69*, 691.

Thewlis, J. *Cosm. News* **1996**, *106*, 27.

Thewlis, J. Lanolin for cosmetics application. *Agro Food Ind. Hi. Technol.* **1997**, *8*, 10-15.

Tiselius, A. *Ark. Kemi. Mineral. Geol.* **1941**, *15B*.

Tomlinson, M. J.; Sasaki, T. A.; Wilkins, C. L. Applications of multidimensional-gas chromatography-mass spectrometry and gas chromatography-fourier transform infrared-mass spectrometry *Mass Spectrom. Rev.* **1996**, *15*, 1-14.

Vendeuvre, C.; Bertoncini, F.; Duval, L.; Duplan, J. L.; Thiébaud, D.; Hennion, M. C. Comparison of conventional gas chromatography and comprehensive two-dimensional gas chromatography for the detailed analysis of petrochemical samples. *J. Chromatogr. A* **2004**, *1056*, 155-162.

Volkman, J. K. *Marine organic matter. Biomarkers, isotopes and DNA.*; Springer-Verlag: Berlin, 2006.

Welthagen, W.; Schnelle-Kreis, J.; Zimmermann, R. Search criteria and rules for comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry analysis of airborne particulate matter. *J. Chromatogr. A* **2003**, *1019*, 233-249.

Wu, J. F.; Lu, X.; Tang, W. Y.; Kong, H. W.; Zhou, S. F.; Xu, G. W. Application of comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry in the analysis of volatile oil of traditional chinese medicines *J. Chromatogr. A* **2004**, *1034*, 199-205.

Zhu, S.; Lu, X.; Dong, L.; Xing, J.; Su, X.; Kong, H.; Xu, G.; Wu, C. Quantitative determination of compounds in tobacco essential oils by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry. *J. Chromatogr. A* **2005**, *1086*, 107-114.

Zhukova, N. V.; Kharlamenko, V. I. Sources of essential fatty acids in the marine microbial loop. *Aquat. Microb. Ecol.* **1999**, *17*, 153-157.

Zlatkis, A.; Walker, J. Q. Direct sample introduction for large bore capillary columns in gas chromatography. *J. Gas Chromatogr.* **1963**, *1*, 9-11.

Zrostlikova, J.; Hajslova, J.; Cajka, T. Evaluation of two-dimensional gas chromatography-time-of-flight mass spectrometry for the determination of multiple pesticide residues in fruit. *J. Chromatogr. A* **2003**, *1019*, 173-186.

Zuin, V. G.; Yariwake, J. H.; Bicchi, C. Fast supercritical fluid extraction and high-resolution gas chromatography with electron-capture and flame photometric detection for multiresidue screening of organochlorine and organophosphorus pesticides in Brazil's medicinal plants. *J. Chromatogr. A* **2003**, *985*, 159-166.

Zutic, V.; Legovic, T. A film of organic-matter at the fresh-water sea-water interface of an estuary. *Nature* **1987**, *328*, 612-614.

8. Annex

En el decurs d'aquesta Tesi Doctoral s'han realitzat d'altres publicacions científiques que al tenir una temàtica diferent a la de la Tesi Doctoral no s'han introduït en el text d'aquesta memòria.

C. Domínguez, E. Jover, J.M. Bayona i P. Erra "Effect of the carbon dioxide modifier on the lipid composition of wool wax extracted from raw wool.", *Anal. Chim. Acta*, **2003**, 477, p233-242.

C. Domínguez, E. Jover, F. Garde, P. Erra, J.M. Bayona "Characterization of supercritical fluid extracts from raw wool by TLC-FID and GC-MS." C., *J. Am. Oil Chem. Soc.*, **2003**, 80, p717-724.

P. Montuori, E. Jover, R. Alzaga, S. Díez, J.M. Bayona "Improvements in the methylmercury extraction from human hair by headspace solid-phase microextraction followed by gas chromatography cold vapour atomic fluorescence spectrometry determination", *J. Chromatogr. A*, **2004**, 1025, p71-75.

R. Alzaga, C. Salgado-Petinal, E. Jover, J.M. Bayona "Development of a procedure for the determination of perfluorocarboxylic acids in sediment by pressurised fluid extraction, headspace solid-phase microextraction followed by gas chromatographic-mass spectrometric determination." *J. Chromatogr. A*, **2005**, 1083, p1-6.

C. Domínguez, E. Jover, J.M. Bayona, P. Erra "Caracterización de cera de lana mediante las técnicas TLC preparativa, TLC-FID y CG-MS.", *Revista de Química Textil*, **2006**, 176, p64-68.

E. Jover, C. Domínguez, P. Erra, J.M. Bayona "Comparative characterization of a wool wax lipid extract by thin-layer chromatography flame ionization detection and by thin-layer chromatography-gas chromatography-mass-spectrometry detection." *J. Cosmet. Sci.*, **2006**, 57, 23-35.

P. Montuori, E. Jover, S. Díez, N. Ribas-Fitó, J. Sunyer, M. Triassi, J.M. Bayona "Mercury speciation in the hair of pre-school children living near a chlor-alkali plant" *Sci Total Environ*, acceptat

A.I. Gómez, E. Jover, J. Albaigès, J.M. Bayona "Filtration influence on the dissolved/particulate phase partitioning in the determination of low levels 53 organic contaminants" *submitted to Chemosphere*.

C. J. Houtman, P. Booij, E. Jover, D. Pascual del Rio, K. Swart, M. van Velzen, R. Vreuls, M.H. Lamoree, J. Legler, A. Brouwer "Estrogenic and dioxin-like compounds in sediment from Zierikzee harbor identified using CALUX assay-directed fractionation and several GC techniques." *submitted to Chemosphere*.