CHROMATOGRAPHY OF XENOBIOTICS IN BIOLOGICAL AND ENVIRONMENTAL MATRICES

Gyula Oros[a], Tibor Cserháti[b]* and Mária Szőgyi[b]

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The newest results in the chromatographic analysis of xenobiotics present in biological and environmental matrices are compiled and the results are critically evaluated. Examples for the employment of preconcentration and prepurification technologies, gas chromatography using electron capture detection (ECD), nitrogen phosphor detector (NPD), various mass spectrometric detection methods (MS, MS/MS, etc), liquid chromatographic methodologies such as thin-layer chromatography (TLC), high performance liquid chromatographic methods (HPLC) as well as electrically driven systems are presented. The advantages and disadvantages of the various chromatographic technologies are shortly discussed and the efficacies of the methodologies are compared. Xenobiotics included in the review are volatile organic compounds (VOC), hydrocarbons and hydrocarbon-based pollutants, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenols (PCB), other polyhalogenated compounds, pesticides, etc. The application of various chromatographic methods for the determination of xenobiotics in a wide variety of biological and environmental matrices is discussed in detail.

* Corresponding Authors
Fax: +36-1-3257554
E-Mail: szogyim@t-online.hu
[a] Plant Protection Institute, Hungarian Academy of Sciences, H-1029, Nagykovácsi út 26-30, Budapest, Hungary
[b] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1025, Pusztaszeri u. 59-67, Budapest, Hungary

Introduction

Chromatography has been developed as a powerful separation technique suitable for the separation and quantitative determination of organic and inorganic compounds with very similar chemical structure. Various chromatographic techniques such as gas chromatography (GC), liquid chromatographic procedures (thin layer chromatography (TLC), high performance liquid chromatography (HPLC), ultra performance liquid chromatography (UPLC) and electrically driven systems found application in biology, medicine, chemical technology and in the analysis of natural products contributing to the isolation and identification of new molecules. These methodologies were successfully employed in analytical quality control and environmental sciences. Moreover, chromatography has been applied for the residue analysis of xenobiotics in air, ground and surface water, sludge, soil matrices, foods and food products and in human and veterinary health care.

The objectives of the recent review are the compilation and concise evaluation of the newest results obtained in the chromatographic analysis of xenobiotics present in biological and environmental matrices and the critical evaluation of the results.

Prepurification and preconcentration methodologies

The application of magnetic nanomaterials for the preconcentration and prepurification of pollutants has been previously reviewed. It was stated that the advances of the use of magnetic nanomaterials are the high surface-to-volume ratio, easy surface modification and strong magnetism. The efficacy of the extraction is influenced by hydrophobic interactive forces, electrostatic attraction, and/or on the formation of covalent bonding between the analytes and the surface of nanomaterials. Pollutants can be desorbed by modifying ligands, changing pH, or adding organic solvent to the mobile phase. The desorbed pollutants can be separated and quantitatively determined by GC and/or HPLC.[1]

Gas chromatography

Gas chromatographic (GC) methods are suitable for the separation and quantitative determination of compounds which are volatile or semi-volatile and thermally stable at the temperature of the measurement. Unfortunately, the considerable numbers of xenobiotics are not volatile, consequently, the application of GC methods for the separation and quantitative determination of xenobiotics in biological and environmental matrices is limited.

Volatile organic compounds (VOC)

Because of their considerable impact on human health many analytical methods have been developed and successfully applied for the separation and quantitative determination of VOCs in atmospheric air.

The application of various on-line gas analyzers used for the monitoring of VOC in air has been earlier discussed in detail. [2] The newest methods employed for the determination of VOCs in atmospheric air, housing air, office air, occupational air and exhaled air have also been reviewed.[3]

The large volume injection-programmable temperature vaporization-GC-MS analysis (LVI-PTV-GC-MS) has been optimized for the determination of estrogenic compounds in environmental matrices. Analytes investigated included estrone, 17-β estradiol, 17-α-ethynyl estradiol, mestranol and estriol. The concentration of xenobiotics was analysed in estuarine water, wastewater, fish bile and fish homogenate. Optimized conditions of the measurements were: 45 µL volume of n-hexane extract injected at 60 ^{0}C, 6 µL/s with a went flow and vent pressure of 50 mL/min during 5 min. Limit of detection varied between 0.04 – 0.1n ng/L for water samples, 0.04 – 0.67 ng/g for fish bileang 0.1-0.75 ng for fish homogenate. It was established that the sensitivity of the method was higher than that of common split/splitless inlet.[4]

GC coupled with time-of-flight MS (GC-TOF-MS) was applied for the investigation of the composition of VOCs emitted from historical books. Contact head-space solid-phase extraction was employed for the preconcentration of target compounds. Linear hydrocarbons, linear aldehydes, 2-furfural and isopropyl were identified in the samples.[5]

Solid phase extraction of water samples was carried out by using C18 SPE column. Toluene, xylene, and cumene were extracted with dichloromethane and analyzed by GC/MS. It was found that the amount of target compounds varied between 2.34 and 52.12 ppm. It was established that the type of SPE stationary phase and that of the desorption sorbent influences markedly the efficacy of the prepurification.[6]

Solid-phase microextraction and GC/MS were employed for the measurement of the volatile compositions of mouse urine. The aim of the measurements was the elucidation of the relationship between the composition and concentration of VOCs and age, sex, social and reproductive status, physiologic state and genotype. Investigations indicated the presence of 49 new predictive compounds. Multivariate mathematical-statistical calculations proved that the data are suitable for the determination of the maturation state, stress level, and diet of mice. [7] Thermal desorption aerosol gas chromatography was employed for the study to determine gas-to-particle transitioning for polar and nonpolar VOCs found in the ambient atmosphere. It was suggested that the method is suitable for the study of the gas/particle-phase transitions for atmospheric semivolatile organic compounds.[8]

The volatile organic compound emissions from subarctic tundra was investigated by GC/MS. The measurements indicated that the emission of monoterpenes and sesquiterpenes increase markedly with increasing air temperature. [9] A new GC/MS was developed for the analysis of volatile organic compounds present in the urine of exposed volunteer workers. Samples were acidified, extracted by SPE, and derivatized with trimethylsilyl group. Accuracy was over 82.4%, precision was less than 28.4%. After the clean-up the level of mandelic acid and trans,trans-muconic acid considerably increased.[10]

GC/MS combined with solid-phase microextraction has been applied for the determination of the chromatographic profile of microbial volatile organic compounds in the headspace of cultures of filamentous fungi. Fungus (*Trichoderma atroviride*) was grown on a solid culture medium directly in headspace vials. GC/MS found various classes of compounds such as alcohols, ketones, alkanes, furanes, pyrones (mainly the bioactive 6-pentyl-α-pyrone), mono- and sesquiterpenes.[11]

A method based on thermal desorption followed by GC was developed for the measurement of five carbon compounds (acetaldehyde, propionaldehyde, butyraldehyde, isovaleraldehyde, and valeraldehyde). The results indicated that the mode of calibration exerts a considerable effect on the reliability of the analytical process.[12] The influence of the processing conditions on the VOC emission of larch particleboard has been investigated by GC/MS. The measurements indicated that the emission concentration and the amount of VOCs increased with increasing hot-pressing temperature and time. It was further established that the processing conditions influenced the composition of VOCs (variety of terpene, benzene, and derivatives). [13] A HS-GC-MS method was developed for the analysis of biogenic VOCs emitted by plants (monoterpenes, sesquiterpenes, and other related compounds). It was stated that the procedure is suitable for the simultaneous analysis of isoprene, and mono- and sesquiterpenes from plant emissions.[14]

Solid-phase microextraction followed by GC/MS and olfactometry were employed for the analysis of p-cresol, acetic, propionic, isobutyric, butyric, isovaleric, valeric and hexanoic acid in emissions at agricultural facilities. Samples were collected in polyvinyl fluoride bags. Recoveries of the target compounds ranged from 2 to 40% after 1 h and 0 to 14% after 7 d. The investigation indicated that the method of sampling exerts a marked influence of the concentration and composition of target compounds.[15]

An SPME method employing pencil-lead fibre was coupled with GC/MS. The concentration of organic volatile compounds of the roots, leaves and gum of *Astralagus compactus* was measured. Only one volatile organochlorine compound was detected in the samples (1-chlorotetradecane,). [16] Volatile organic compounds emitted from painting application and printing processes have been analyzed by GC/MS/FID. It was established that the toluene and C_8 aromatics were the most abundant compounds emitted from paint application while emissions from printing emission contained mainly heavier alkanes such as n-nonane, n-decane, n-undecane, toluene, and m/p xylene.[17]

An Y-tube experiment was employed for the investigation of house dust mite pheromones. American house dust mite (*Dermatophagoides farinae Hughes*) and

European house dust mite (*Dermatophagoides pteronyssinus Trouessart*) were included in the investigation. The experiments were motivated by the fact that mites can cause atopic diseases such as asthma, rhinitis, and dermatitis. The hexane extract of *D. farinae* was fractionated by microscale liquid chromatography using Florisil as stationary phase and the biological activity of the fractions was assessed. GC/MS measurements indicated that neryl or geranyl isomers are responsible for the biological activity. It was stated that neryl formate can be applied as a part of novel lure-and-kill system for house dust mite control.[18]

The efficacy of a novel in-tube extraction device for headspace sampling of waters was investigated by GC/MS. The method allowed the separation and quantitative determination of halogenated hydrocarbons, benzene, toluene, ethylbenzene, xylenes, fuel oxygenates, geosmin, and 2-methyl isoborneol. The measurements indicated that the highest extraction efficacy can be achieved by using mixed bed trap. The average relative standard deviations were lower than 10%. It was stated that the procedure can be employed for the analysis of tap, pond, and reservoir water and soft drinks.[19] GC/MS has also been employed for the separation and identification of the volatiles of *Streptomyces globisporus JK-1*. The measurements were motivated by the fact that some of the volatiles showed marked fumigant activity against *Penicillium italicum* on *Citrus microcarpa*. GC results indicated that the concentration of geosmin (trans-1,10-dimethyl-trans-9-decalol). It was further established that phenylethyl alcohol and caryophyllene showed weak inhibitory activity. Dimethyl disulfide and dimethyl trisulfide showed antifungal activity. It was concluded from the results that these class of volatiles have potential to control of blue mold of citrus species through fumigant activity.[20]

A GC method was employed for the study of the adsorption characteristics of the mesoporous silicate MCM 48 as enrichment medium. VOCs were applied as model compounds. The investigations indicated that the preconcentration efficacy of the sorbent markedly depended on the character of the enrichment medium and the conditions of desorption.[21] GC/MS technology was employed for the separation and quantitative determination of VOCs present in natural spoiled pork and *Salmonella typhimurium*-contaminated pork. The similarities and dissimilarities between the samples were elucidated by using multivariate mathematical-statistical methods such as principal component analysis (PCA) and multi-block PCA. The calculations proved that the method can be applied for the differentiation between natural spoiled pork and those contaminated with *S. typhimurium.*[22]

Hydrocarbons and hydrocarbon-based pollutants

Hydrocarbons were separated and quantitatively determined in geological chert samples. Analytes were extracted with focused ultrasound extraction (FUSE) and microwave-assisted extraction (MAE). Traditional Soxhlet extraction was employed as reference method. Both methods were optimized for solvent mixture composition (dichloromethane/hexane/acetone) and for process variables (sonication time and cycles and extraction temperature and time). The optimal conditions for FUSE were DCM/hexane 60:40, sonication time of 30 min and 9 cycles. The optimal extraction conditions for MAE were DCM/hexane/acetone 60:30:10, irradiation time of 15 min at 110 ^{0}C. Hydrocarbons C16-C40 were analysed by GC-MS.[23]

Another GC procedure was applied for the measurement of light hydrocarbons in Brazilian coal mines. It was established that the concentration of methane ranged from 3 ppm to 27% in the atmosphere of underground mines. Methane concentration in the air of surface mines varied between 3 and 470 pp.[24] GC/MS has been used for the investigation of the residual oil contamination of sediments. It was proposed that the method can be employed for the identification of oil in soils taking into consideration the transfer and weathering of oils in sediment.[25]

Aromatic and polyaromatic pollutants

A headspace-GC-MS method was developed for the analysis of monoaromatic volatile compounds (benzene, toluene, ethylbenzene, o-, m- and p-xylenes, and styrene) in olives and olive oil. Samples were put in the HS vial without any pretreatment and clean-up. Samples were automatically processed and injected in the GC column. Analytes were detected in SIM mode. The relative standard deviation (RDS, %) varied between 1.6-5.2% and 10.3-14.2% for olive oil and olives, respectively. The concentrations of the pollutants ranged between 23-332 μg/kg and 4.2-87 μg/kg for olive oil and olives, respectively.[26] Phenols and chlorophenols were separated and quantitatively determined in water using in situ derivatization headspace solid phase microextraction followed by GC/MS. It was established that fiber coating, extraction time and temperature, amount of derivatizating agent and ionic strength influenced markedly the efficacy of the extraction. The optimal conditions of the extraction were 4.0 g NaCl, 0.10 g of Na_2HPO_4 in 10 ml of sample solution, extraction temperature 60 ^{0}C, 600 r/min for 30 min. LOD values varied between 0.014 – 0.044 μg/L. Precision (RSD) was about 13.7%. Because of its precisity the method was proposed for the determination of phenols in wastewater samples.[27] The application parameters of silica gel modified with ketoimine groups was investigated as SPE stationary phase. It was established that the new sorbent is suitable for the preconcentration of benzene, phenol and o-chlorophenol before GC analysis.[28]

The oxidative degradation of chlorophenol derivatives was followed by GC/MS. Samples were treated power ultrasound (US), microwave (MW) irradiation It was established that these technologies promoted the decomposition of chlorophenol derivatives and can be successfully applied for the acceleration of the decomposition of chlorophenol derivatives.[29]

Polycyclic aromatic hydrocarbons

PAHs have been determined in surface waters using GC-MS. It was found that the PAH profiles were dominated by low molecular weight PAHs (two- and three ring

components). The data indicated that the PAH contamination has the origin in petrogenic input.[30] The concentration of polycyclic aromatic hydrocarbon (PAHs) in higher plants grown on an oil exploration site was measured by GC-MS. It was established that the amount of PAHs in the leaves ranged from 365 to 2870 µg/kg the average being 1430 µg/kg. Dibenzo[a,h]anthracene and 9,10-diphenylanthracene were not detected in the samples. It was further found that the concentration of 2- and 3-ring PAHs was higher than those of 4-, 5- and 6-ring PAHs.[31]

GC has been employed for the determination of 14 PCBs and 13 organochlorine pesticides in human plasma and the chromatographic data were correlated with plasma organochlorine levels. The calculations suggested that neither the amount of PCBs nor that of organochlorine pesticides are related to the occurrence of prostate cancer. It was further established that long-term low level exposure to organochlorine pesticides and PCBs in the general population does not contribute to increased prostate cancer risk.[32]

The occurrence and distribution of PAH in two soil size fractions have also been investigated by GC/MS. Particle size fractions included in the experiments were: < 250 µm (fraction A) and >250 µm to 2 mm (fraction B). Analytes were preconcentrated by pressurized fluid extraction (PFE) and analyzed by GC/MS. The concentration of PAHs varied from 9.0 to 1.404 mg/kg (soil fraction A) and from 6.6 to 872 mg/kg (soil fraction B). In the majority of cases significant differences were found between the concentration of PAHs in soil fractions A and B.[33] The occurrence of PAHs in dairy milk samples was assessed by using liquid-liquid extraction and solid-phase extraction followed by GC/MS. The results were evaluated by factor analysis. Calculations indicated that the main source of PAHs in milk may be the exhaust emitted from vehicles.[34]

The transport of semivolatile organic compound to the Tibetian Plateu was investigated in detail. The separation and quantification of the target compounds was achieved by GC/MS. The measurements indicated that the concentration of hexachlorobenzene was the highest followed by hexachlorocyclohexanes, DDT-related compounds and PCB congeners. It was further established that the amount of pollutants in the air was higher than in winter.[35]

Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are extensively used in many up-to date technological processes. Besides of the manyfold benefits as adjuvants in a considerable number of modern industrial methods they show considerable undesirable toxicological effect. These side effects make necessary the development and application of reliable analytical methods for the separation and quantitation of PCB congeners. The application of GC methods employed for the analysis of PCB has been previously reviewed.[36]

Many investigations indicated that the low-level PCB exposures can be associated with immune system disfunction, cardiovascular disease, and impairement of the developing nervous system. The possible mechanism of PCB toxicity has been recently reviewed.[37]

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), PAHs, polybrominated diphenyl ethers (PBDEs), organochlorine pesticides (OCPs) and heavy metals were determined in adipose tissues of patients with *uterine leiomyomas* using GC/MS and inductively coupled plasma-optical emission spectrometry. It was assumed that the concentration of POPs can be correlated with the occurrence of *uterine leiomyomas*. [38] 145 PCB congeners and OCPs were determined in fur seal (*Callorhinus ursinus*) population (blubber, heart, liver, kidney, muscle, reproductive tissues, brain and lung were investigated). The concentration of POP sin various organs was measured by GC/ion trap mass spectrometry. It was concluded from the data that PCB can exert an effect on the fur seal population.[39]

The concentration of PAHs and PCBs were determined from the combustion of biomass pellets. It was established that the total concentration of PAHs varied between 6.4 and 154 µg/m^3 . Target compounds were analysed by GC/MS. Significant relationship was found between the amount of inorganic gases and the concentration of organic pollutants as well as between the concentration of PAHs and PCBs. It was suggested that the method can be employed for prediction purposes.[40]

Serum concentrations of PCBs were measured by high resolution gas chromatography using microelectron capture detection. It was established that PCBs can deteriorate the outer hair cells of the cochlea.[41] The enantiomeric composition of chiral PCB congeners and their biotransformation in a stream food web has also been investigated. The enantiomeric fractions of six PCB atropisomers (PCBs 84, 91, 95, 136, 149 and 174) were determined in fine benthic organic matter, coarse particulate organic matter, periphyton, Asian clam, mayflies, yellowfin shiner. The concentration and composition of PCBs were analyzed by GC-ECD. The measurements indicated that biotransformation of PCBs considerably depended on the type and composition of the microbial communities.[42] PCB levels in human adipose tissue was investigated by GC/tandem mass spectrometry (GC-MS/MS). The total mean PCB concentration were 27.2 µg/kg fat (Anhui Province) and 17.2 µg/kg fat (Jiangsu Province). A significant correlation was found between the age and PCB levels but the gender and PCB concentration was not correlated.[43]

GC/ECD measurements were applied for the determination of several PCB congeners in maternal, cord, and 6-month infant sera. The concentration of IG-specific anti-haemophilus influenzae type b, tetanus toxoid and diphteria toxoid were measured in 6-month infant sera using ELISA technologies. Multiple linear regression method was applied for the elucidation of the relationships between the measured biological and biochemical characteristics. It was concluded from the data that significant correlations cannot be assessed among parameters investigated.[44]

GC/MS measurements were performed for the study of the direct assessment of cumulative aryl hydrocarbon receptor agonist activity in sera from experimentally exposed mice and environmentally exposed humans.[45]

Solid-phase microextraction followed by GC-ECD was employed for the determination of PCBs in Brazilian breast milk samples. The relationship between detector response and analyte concentration was linear up till 16 µg/L (*r* over 0.9884). Precision (RSD) was <12%, (n = 5), recovery varied between 71 and 127%. The limit of quantitation varied from 0.45 to 2.42 µg/mL. The measurements indicated that there is a strong correlation between the level of contamination of the breast milk samples and the industrialization of the region.[46] GC-ECD and GC-MS negative chemical ionization detection (NCI) were employed for the determination of PCBs and polybrominated diphenyl ethers (PBDEs) in the tissues of the migrating salmon species *Oncorhynchus*, tshawytscha (Chinook salmon). It was established that the concentration of PCBs and PBDEs ranged from 78-25.5 ng/l wet weight and 272-1046 pg/gl wet weight, respectively.[47]

PCBs and OCPs were determined in biota and in sediments too. Ultrasonic extraction combined with silica gel with 45% sulphuric acid and florisil with 5% waster were employed for the preconcentration of analytes in biota. Samples of sediments were treated with metallic mercury and florisil column. Analytes were separated by GC/electron capture detection (ECD). The similarities and dissimilarities between the samples was assessed by principal component analysis (PCA).[48] The concentration of PCBs, p,p'-dichlorodiphenyldichloroethene (DDE) and methylmercury was assessed in human serum by using GC/ECD, cold vapor atomic absorption and atomic fluorescence spectroscopy. It was established that the total PCB concentration ranged from 8.7 to 3.091 ng/g. The amount of DDE varied between 0.3 to 7.083 ng/g. It was established that the serum concentrations of PCBs correlated linearly with fish consumption (r = 0.43, $p<0.0001$) but not with the DDDE concentration.[49] GC coupled with low-resolution mass spectrometry was employed for the analysis of PCBs and OCPs in serum samples. It was found that age and residence exert a significant influence on the amount of pollutants while the effect of gender was not significant. It was suggested that long-banned substances can occur in the general population.[50]

A new GC method was developed for the determination of polychlorinated and polybrominated dibenzo-p-dioxins (PCDDs/PBDDs), dibenzofurans (PCDFsPBDFs), biphenyls (PCBs/PBBs) and diphenyl ethers (PBDEs). The method applied various columns (silica, alumina and active carbon) and high resolution mass spectrometry. Samples were taken from the atmosphere near to a municipial solid waste incinerator.[51]

GC/MS has also been applied for the measurement of the concentration of PCDD/F and PCBs in food from animal origin. Samples of subcutaneous adipose tissue and blood as well as from muscle and liver after slaughtering. It was found that the results obtained in vivo and ex vivo samples showed good correlation. It was concluded from the measurements that the weakly invasive biopsy of subcutaneous adipose tissue performed on living animal can be used for the prediction of pollutants in muscle and liver.[52]

The efficacy of extraction technique suitable for the preconcentration of pollutants PCBs and OCBs has been compared. Extraction methods were Soxhlet extraction, accelerated solvent extraction (ASE) and supercritical fluid extraction (SFE). Ultrasonic extraction was applied for the determination of analytes in marine samples. Separation and quantitative analysis of target compounds was achieved by GC/ECD. It was established that the ultrasonic extraction was more efficient, more easily to carry out using smaller quantity of solvent and shorter analysis time.[53] The efficacy of various extraction technologies such as Soxhlet extraction (SE), accelerated solvent extraction (ASE), and microwave-assisted extraction (MAE) was compared using PCB and polybrominated diphenyl esters (PDBEs) as model compounds. Both soil and fish samples were investigated. It was established that the extraction efficacy of ASE and MAE was comparable with that of SE, and higher temperature and pressure increases the efficacy of the procedure.[54]

The fate of PCBs in soils amended with biosolids was investigated using incubation and leaching columns. Analytes were separated from the solid matrix by ultrasound-assisted pressurized solvent extraction (US-PSE). Samples were analysed by GC/MS. It was observed that the extractability of PCBs increased with increasing incubation time . It was further found that $CaCl_2$ cannot mobilize PCBs while linear alkylbenzene sulfonate (LAS) mobilized these target compounds.[55] The occurrence of inadvertent PCBs in commercial paint pigments were assessed by GC-tandem mass spectrometry (GC/MS/MS). The measurements revealed that PCB congeners can be detected in azo and phthalocyanine pigments, inks, textiles, paper, cosmetics, leather, plastics, food and other materials.[56]

GC followed by low-resolution tandem mass spectrometry (MS/MS) was employed for the measurement of co-eluting unlabeled and ^{13}C-labeled PCB congeners. It was concluded from the results that MS/MS can be applied for the determination of co-eluting unlabeled and ^{13}C-labeled PCBs.[57] A GC-ECD method was developed and applied for the determination of PCBs in the sediments. Target compounds were extracted by the Soxhlet method. Concentration of PCBs ranged from 15.3 to 997 ng/g (dry weight in < 2 mm fraction and from 29.9 to 952 ng/g in <200 µm fraction. The investigations indicated that the highest concentration of PCBs occurred below the discharge of municipal wastewater treatment plant.[58]

The efficacy of the serially coupled GC columns for the separation of PCBs has been investigated. The columns included in the experiments were a non-polar poly(5%-phenyl-95% methyl) siloxane column (40 m x 100 µm x 0.1 µm) and a polar 70%-cyanopropyl-polysilphenylene-siloxane column (4 m x 0.1 mm x 0.1 µm). The retention data were employed for the construction of the 2D and 3D images.[59]

GC followed with ECD detection was employed for the analysis of organochlorine compounds (OCs). The measurements were motivated by the supposition that diet and serum concentration of OCs may influence the K-ras

mutations in exocrine pancreatic cancer. The investigations suggested that dairy products may be source of OCPs.[60]

A GC technique was applied for the measurement of PCB congener profiles in clapper rails (*Rallus longirostris*) and the results were compared with those obtained by ELISA. It was concluded from the data the ELISA is more suitable for the qualitative exposure assessment while GC method is more reliable for detection.[61] The concentration of dioxins, furans and PCBs were measured in blood samples collected from 446 mothers in the city of Chapaevsk, Russia using high-resolution GC/MS. It was established that the concentration of target compounds increased with age, with the proximity to a local chemical plant, duration of local farming and consumption of local beef. Pollution decreased with longer breastfeeding, increase of body mass index and later blood draw date.[62]

The decomposition of PCBs in microcosm experiments was followed and the change of the composition of PCB congeners was followed by GC/MS. The measurements indicated that the biodegradation rates decreased with the degree of chlorination (from 75% to 22%). The bacterial abundance was also lower in soil microcosms exposed to the higher-chlorinated congeners. It was further established that the amount of biphenyl dioxygenase (BPH) genes increased in the presence of various PCB congeners.[63]

GC-ECD technology was employed for the analysis of PCBs, organochlorine pesticides (OCP), dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorobenzene (HCB), and hexachlorocyclohexane isomers (HCHs) in maternal serum. The results indicated that the concentration of DDTs is prevalent in the samples.[64] The concentration of PCBs was measured in butter available on the Polish retail market. Analytes were detected with a ion-trap mass spectrometer. The recoveries of the individual PCBs varied from 58% to 105%, RSDs were between 3-16%.[65] The effect of analytical artefacts on the determination of organochlorine pesticides and PCBs by GC/ECD and GC/MS was investigated in detail. The measurements indicated that artefacts can potentially render interferences difficult, confounded and erroneous. The use of an appropriate reference material considerably increases the reliability of the measurements.[66]

GC/MS has also been employed for the measurement of the amount of PCB 153, PCB 180 and PCB 138 in adult adipose tissue. PCB residues were found in 92% (PCB 153), 90% (PCB 180) and 86% (PCB 138) of the population. The mean concentration of the PCBs in the samples were 161.65±4.41. ng/g lipid for PCB 153, 111.62±6.27 ng/g lipid for PCB 180, and 38.41±8.61 ng/g lipid for PCB 138. Multivariate mathematical statistical methods indicated that age and body mass index correlated with PCB concentration. It was further established that occupation and diet predicted exposure in males while only dietary predictors influenced the exposure in females.[67]

GC method was employed for the determination of PAHs, PCBs, organochlorine pesticides and organotin compounds in the sediment of the Sava river. It was established that PAHs were present in moderate concentrations and their concentrations increased downstream. The concentrations of PCBs were low, the amount of hexachlorobenzene was relatively high. Organotin compounds were not detected.[68] GC/MS has also found application in the investigation of the fate of PCBs in a plant of high-temperature plasma melting of ash residues after municipal waste incineration. The results indicated the high the composition level of the incineration process [69] The relationship between the concentration of PCBs and the development of central-nervous system was investigated in detail. PCBs were separated by high-resolution GC. The measurements indicated that mono-ortho-substituted PCBs influenced unfavourably the psychomotor and mental development indices. It was further established that children with higher prenatal mono-ortho-substituted PCB exposures performed more poorly on the Bayley scale of infant development. It was further assumed that that dioxine-like PCBs may interfere with brain development in utero.[70]

Another GC/MS method was employed for the separation and identification of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated diphenyls (dl-PCBs). On the base of the results a new screening approach was developed. [71] GC/ECD analytical technique was also employed for the analysis of PCBs in the serum of pregnant women. The investigations suggested that higher PCB concentrations result in decrements of fetal and infant growth and development. [72] A GC-MS/MS technique was employed for the measurement of 83 PCBs, 23 OCPs and 19 PBDEs in the blood, eggs, and hatchling blood in the green sea turtle *Chelonia midas*. Significant correlations were found between the maternal transfer of persistent organic pollutants (POPs) and the amount of PCBs, PBDEs, gamma HCH, trans cordane and mirex. It was concluded from the data that POPs influence the development of *C. midas* eggs.[73]

Semi-empirical topological indexes was developed for the prediction of the relative retention time of of PCBs on 18 different high resolution GC columns. Calculations proved that the calculated molecular volume, molecular surface area, and the position and number of substituents are linearly correlated with the relative retention.[74]

A novel SPE-GC/MS method was developed for the analysis of 23 polychlorinated PCBs in sewage water using pyrenebutyric acid-bonded silica as sorbent. The recoveries of the method ranged from 69.44% to 111.91%. The results indicated that the novel sorbent can be successfully applied as SPE sorbent for the preconcentration of PCBs in sewage water. The LOD varied between 0.06-0.22 ng/L.[75] The separation capacity of three GC columns coupled in two series was investigated using PCBs as model compounds. A non-polar capillary column coated with poly(5%-phenyl-95%-methyl)siloxane was employed as the first column. The second columns were a polar capillary column coated with 70% cyanopropyl-polysilphenylene-siloxane and a

capillary column coated with ionic liquid 1,12-di(tripropylphosphonium)dodecane bis(trifluoromethane-sulfonyl)imide. The results indicated that the separation capacity of the apolar + ionic liquid column was better than that of non-polar – polar column coupling.[76] A GC-MS technology was applied for the measurement of POPs in adults from Guinea-Bassau. The following POPs were included in the investigation: 1,1,1-trichloro-2-2-bis(4-chlorophenyl)ethane and its metabolites, PCBs, PBDEs and HCHs. The investigations revealed that the concentration of 4,4'-DDE was the highest in the samples followed by other DDT metabolites, PCBs and HCHs and their concentrations decrease with time.[77]

Pyrethroids in apple juice were analysed by isotope dilution GC/MS method. The concentration of cypermethrin, permethrin, and bifentrin was determined. It was found that the intraday and interday reproducibilities of the method was lower then 0.5%. The expanded relative uncertainty was between 3 – 6%.

An other GC/ECD procedure was employed to control the validity of the data obtained by GC/MS.[78] The amount of PCBs, hexachlorobenzene (HCB), pentachlorobenzene (PeCB), hexachlorocyclohexane compounds (α–, β–, γ– and δ–HCH), and dichlorodiphenyltrichloroethane (DDT) derivatives (p,p'-DDE, p,p'-DDD, p,p'-DDT, o,p'-DDD, and o,p'-DDT) were determined in air and soil using passive sampling procedure followed GC/ECD analysis. The chromatographic retention data indicated the the pollution caused by the target compounds investigated was relatively low.[79]

Pesticides such as coumaphos, diazinon, amitraz or fluvalinate were introduced in bee hives and the pesticide concentration in bee workers, larvae and royal jelly was analysed by GC/ECD. Amitraz was determined by HPLC and GC-MS/MS was employed for the determination of diazinon. Amiraz and diazinon were not found in the samples while coumaphos and fluvalinate occurred in royal jelly and bee heads. The additional potential sub-lethal effects of the pesticides on the honey bees was discussed in detail.[80]

Another study employed HPLC-UV and HPLC-MS-MS for the determination of amitraz and its degradation product 2,4-dimethylaniline (2,4-DMA) in honey. Target compounds were purified by liquid-liquid extraction using hexane and isopropyl alcohol as solvents. Analytes were separated on a C-18 column using gradient elution. Acetonitrile and 0.02 M ammonium acetate were the components of the mobile phase. Recoveries varied between 83.4 and 103.4% for amitraz and 89.2 and 104.7% for 2,4-DMA. RSD values were lower than 11.6% for both HPLC-UV and LC-MS/MS measurements. LOD values were 6 μg/kg for amitraz and 8 μg/kg for 2,4-DMA. LOQ values were 20 μg/kg for amitraz and 25 μg/kg for 2,4-DMA. The validation parameters of LC-MS/MS method were: LOD, 1 μg/kg for amitraz; 2 μg/kg for 2,4-DMA; LOQ, 5 μg/kg for amitraz and 10 μg/kg for 2,4-DMA.[81]

The concentration of PAHs, PCBs and DDT adsorbed on microplastics was determined by GC/MS. Plastics were identified by Fourier transformed infra-red spectroscopy. The measurements indicated that the concentration of pyrene, phenanthrene, chrysene and fluoranthene, as well as those of PCB congeners 18, 31, 138, and 187 were the highest in the samples.[82]

Organic pollutants such as PAH, PCB, and OCP were analyzed in two different types of forest soil. The investigations were motivated by the strong adsorption of pollutants to soil organic matter. Cyclohexane, ethyl acetate and acetone were applied as extracting agents. Target compounds were preconcentrated with different techniques and the efficacy of various extraction procedures (pressurized liquid extraction, Soxhlet extraction, fluidized bed extraction, sonication, shaking and one-step extraction) was compared. Samples were further purified by gel permeation chromatography (GPC) and SPE. Concentrations of analytes in the samples were determined by GC/MS using two-different injection systems: split/splitless injection and programmable temperature vaporizer (PTV) injection. The measurements indicated that the highest extraction efficiency was achieved by using acetone/cyclohexane (2:1, v/v). It was further established that a two-step preconcentration procedure employing GPC followed by SPE can be successfully used for the separation of humic materials. It was found that the recovery rates varied between 89% and 106%. Because of the highest efficacy the application of PTV injection system was proposed. It was further stated that the method is suitable for the separation and quantitative determination of these classes of analytes in the trace level of 1-2 μg/kg humic soil.[83]

GC-MS-MS technology was employed for the determination of benzo[a]pyrene (BaP) on particulate matter less or equal to 10 μ (PM 10). The investigations were motivated by the carcinogenic character on BaP. Multivariate linear regression method was applied for the elucidation of the correlation between the concentration of BaP and the environmental conditions taking into consideration the various meteorological conditions such as solar radiation and wind speed.[84]

Similar GC-MS technique was employed for the analysis of particle-associated 16 PAHs near power plants. Samples PM10 and PM2,5 were collected on poly-tetra-fluorinated-ethylene (PTFE) filters. Target analytes were extracted by reflux followed by ultrasonication. GC-MS system used programmable temperature vaporizers (PTV) injector and large volume injection (LVI) method. It was foud that the average daily concentration of B[a]Py was 0.57 – 0.58 ng/m^3. It was assumed that the main sources of PAH pollution was oil and coal burning.[85]

Isotope dilution GC-MS was successfully applied for the analysis of 16 PAHs in edible oils. Target compounds were extracted by sonication using acetonitrile as solvent. Samples were further purificated using narrow gel permeation chromatography. LOQs were below 0.5 ng/g the recoveries being 81 – 96%. RSDs were lower than 20%. It was concluded from the results that the method can be employed for the measurement of PAHs in edible oils.[86]

Other pollutants

GC-ECD and GC-MS were simultaneously employed for the determination of the antiparasitic drug amitraz and its main metabolite, 2,4-dimethylaniline in food animal tissues. Analytes were preconcentrated by accelerated solvent extraction (ASE). Target compounds were extracted with n-hexane/methanol then further cleaned on a C18 silica bonded cartridge, hydrolyzed and derivatized to 2,4-dimethyl-7-F-butyramide for GC-ECD measurements. Samples were not hydrolyzed and derivatized before GC-MS analysis. Recoveries ranged from 72.4 to 101.3%, RSD being lower than 11.5% for GC-ECD. Recoveries for GC-MS measurements were between 77.4 and 107.1% RSD being lower than 11.6%. LOD and LOQ values were 5 and 10 µg/kg. For GC-MS LOD and LOQ were 2 and 5 µg/kg. It was stated that the method is rapid, reliable and can be used for the measurement of amitraz and 2,4-dimethylamine in liver and kidney of swine, sheep and bovine [2,4-dimethylamine in liver and kidney of swine, sheep and bovine.[87]

A highly sensitive GC-MS method was developed and successfully applied for the determination of dithiocarbamates (DTCs) and milneb in foods. Analytes were extracted with cysteine EDTA and methylated with methyl iodide. The methyl derivatives were cleaned-up on a neutral alumina mini column. The main recoveries were between 72 and 120% except for methiram. LOQ was 0.01 mg/kg. The procedure was successfully applied for the analysis of dimethyldithiocarbamates, ethylene-bisdithiocarbamates, polycarbamate, propineb and milneb. [88] GC-MS has also been employed for the determination of various pesticide residues in lettuce. Analytes were extracted with the matrix solid-phase dispersion technique. The optimal conditions were: 4.0 g of lettuce, 2 g of silica as dispersant sorbent, 0.1 g of activated carbon as clean up sorbent and acetonitrile as eluting sorbent. Pirimicarb, methyl parathion, procymidone, α-endosulfan, β-endosulfan were included in the experiments. Recoveries varied between 50 -120% RSD ranging from 0.6 to 8.0%. LOD and LOQ varied 0.01 to 0.02 mg/kg and 0.04 to 0.10 mg/kg.[89]

The relationship between the concentrations of persistent organochlorine pestides (OCPs) and endometriosis has been investigated in detail. The amount of target molecules (ng/g serum) was measured by GC-ECD. Calculations revealed a strong linear correlation between the concentration of OCPs and the occurrence of endometriosis.[90] The uptake, distribution and degradation of the fungicide propiconazole in red oaks (*Quercus rubra*) were assessed by GC-MS measurements. The data indicated the basipetal movement and degradation of the fungicide, and the survival of the pathogen *Ceratocytis fagaecearun* in roots. [91] The preconcentration method matrix solid-phase dispersion followed by GC-MS-SIM (selected ion monitoring) was applied for the determination of eight multi-class pesticides such as vinclozolin, dichlofuanid, penconazol, captan, quiboxyfen, fluquinconazol, boscalid and pyraclostrobin in grapes. The optimal conditions of preconcentration technology were: 0.5 g of grapes, 1.0 g of silica as clean-up sorbent, 1.50 g of C18 as bonded phase and 10 ml of dichloromethane/ethyl acetate (1:1, v/v). Because of the considerable matrix effects GC measurements used matrix-matched standards. Recoveries were better than 80% except captan. LOQ values ranged from 3.4 to 8.7 µg/kg. This values were lower than the maximum residue limit (MRLs) officially established.[92]

Liquid chromatographic technologies

Aromatic hydrocarbons

Not only GC methods but also HPLC technologies have been employed for the quantitative determination of phenols and related compounds in various accompanying matrices. The overwhelming majority of methods employ reversed phase stationary phases but other supports such as porous graphitized carbon has also found application in the HPLC analysis of xenobiotics.[93] Thus, the application of SPE followed with HPLC-UV for the quantitative determination of phenols in water was reported. Phenol and 10 phenol derivatives served as target compounds. The parameters of the method such as pH, solvent ratio, column temperature, sample volume, run time and flow rate were optimized. It was found that the run time was 20 min, the coefficient of determination (r^2) was over 0.99, the recovery ranged from between 67.9±7.28 and 99.6±4.26. LOD varied 0.51 – 13.79 µg/mL.[94]

Not only GC but also various high-performance liquid chromatographic technologies (HPLC) has also been employed for the separation and quantitative determination of PAHs in different matrices. Thus, the HPLC analysis of PAHs in water and soil has been reported. It was found that water, sediment and soil contain PAHs representing potential risk to human health.[95]

Ultrasonic abstraction followed by HPLC was employed for the investigation of the generation of PAHs during cooking. The measurements indicated that the majority of PAHs are generated during the first 1-4 h of cooking. [96] A new procedure was developed and successfully applied for the HPLC separation of nitrated-polycyclic aromatic hydrocarbons (nitro-PAHs) and PAHs. Analytes were analysed using normal-phase HPLC. The stationary phase was a phenyl column, mobile phase was hexane, the flow rate being very low (0.05 mL/min). It was established that pollutants were separated according to their polarity.[97]

SPE followed by HPLC and fluorimetric was applied for the separation and quntitative determination of PAHs in drinking water. Acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]-anthracene, benzo[g,h,i]-perylene, indenol[1,2,3-c,d]pyrene were the target compounds. Some parameters of the SPE procedure such as solvent volume for cartridge conditioning, sample volume, and the methanol concentration in the sample were optimized. It was stated that the LOQ of the method ranged from 0.04 – 1 ng/L. It was further found the solvent consumption of the technique is low, the analysis time short, therefore, it can be applied for legislation purposes.[98]

HPLC has also been employed for the determination of PAHs (benzo[a]anthracene, chrysene, benzo[h]-fluoranthrene, benzo[h]fluoranthrene, benzo[a]pyrene, dibenzo[a]anthracene, benzo[g,h,i]perylene) in roasted coffee beans. Samples were saponified with potassium hydroxide then the pollutants were preconcentrated by liquid-liquid extraction (LLE) followed by solid-phase extraction (SPE). The regression coefficients of the linear correlation between the concentration of analytes and the detector response ranged form 0.9938 to 0.9995. The limit of detection (LOD) and limit of quantification (LOQ) varied between 0.016 and 0.497 and between 0.054 and 1.656 μg/kg, respectively.[99]

Polychlorinated biphenyls (PCBs)

PCBs were separated and quantitatively determined by HPLC technologies, too. The application of three types of RP sub-2-μm stationary phases has been previously reported. The correlations between the detector responses and the concentration of analytes were linear in the range of 0.5 – 50.0 μg/mL. LOD values varied from 0.1 to 5 ppm. It was concluded from the measurements that ultra high-performance liquid chromatography with UV detection can be applied for the analysis of various PCBs. The results were compared with those obtained by GC/MS. [100] The concentration of pollutants (mercury, methylmercury, and persistent organic compounds) was measured in marine fish oil; capsules; and canned cod liver. Analyses were carried out by vapour atomic absorption spectroscopy and GC/MS. The results indicated that the consumption of fish oil in capsules, and canned liver is safe, healthy and can be encouraged.[101]

A new extraction vessel was developed and successfully applied for the preconcentration of PCBs in avian blood. The method included pressurized solvent extraction (PSE). Florisil was employed for the elimination of lipids. Extraction volume was reduced from 30 to 10 cm^3. The recoveries achieved with the new method were between 70-130%. Target compounds were separated and determined by GC coupled with large volume injection ion-trap mass spectrometry (GC-LVI-ITMS-MS). LOD values ranged from 0.05 to 0.5 ng/g. RSD was in each case lower than 5%.[102]

The enantiomers of the organophosphorous insecticide O-ethyl O-4-nitrophenyl phenylphosphonothioate (EPN) were separated on two different chiral HPLC columns and the aquatic toxicity of the enantiomers was assessed using *Daphnia magna* and zebrafish (*Danio rerio*) embrio test . It was established that the separation capacity of the HPLC system was higher at lower temperature and at lower concentration of organic modifier in the mobile phase. The investigations indicated that the biological activity of enantiomers shows marked differences. [103] Although the majority of chromatographic technologies employs GC, HPLC methods have also found application in the chromatographic analysis of PCBs. The concentration of persistent organic pollutant (POP) in farmed Atlantic salmon was investigated in detail. The concentration of dioxin-like PCBs, non-dioxin-like PCBs, dioxins, polybrominated diphenyl ethers (PBDE), organochlorine pesticides, and very long chain marine ω-3 (VLC-n3) were determined in Atlantic salmon. Fish oils were decontaminated using active carbon and short path distillation. The measurements indicated that the decontamination process reduces by 68-85% the amount of POPs while the concentration of VLC-n3 was decreased only with 4-7%.[104]

Other pollutants

The concentration of acaricides frequently used in apiculture (fluvalinate, coumaphos, bromopropylate and its metabolite 4,4'-dibromobenzophenone) was determined in beeswax using HPLC followed by DAD detection. Samples were prepurified by SPE using Florisil cartridge. It was established that fluvalinate residues were present in 36.3% of samples, concentration ranging from 1.2 to 6.6 μg/g wax. Other acaricide residues were not detected.[105]

Malachite green (MG) has been frequently used in aquaculture as a parasiticide and fungicide. As MG shows marked carcinogenecity and mutagenicity the determination of its concentration in foods and food products is of paramount importance. The application of isotope dilution liquid chromatography/MS for the separation of MG and its principal metabolite leucomalachite green (LMG) has been previously reported. Fat content of the samples was removed by using an additional saponification step. This step increased considerably the efficacy of SPE columns. MS detection was carried out in selected ion monitoring (SIM) mode (m/z 329 and 334 for MG and d(5)-MG; 331 and 337 m/z for LMG and $^{13}C(6)$-LMG). It was established that the accuracy of the method was the same as other generally accepted methods.[106]

The ecotoxicologic effect of herbicides (oxadiazon, benzofenap, clomazone, and benzosulfuron-methyl) and fungicides (carbendazim, tricyclazole, and flusilazole) was monitored by various biological, microbiological and analytical (SPE-LC-electrospray-tandem MS). The measurements indicated that herbicides and fungicides exert a negative impact to planctonic organisms but the effect seem to be short lived.[107] A new enzyme-linked immunosorbent assay was developed for the determination of the fungicide fenhexamid and the results were compared with those obtained by HPLC. An excellent correlation was found between the methods.[108]

Both GC-MS and LC-Q-TOF were applied for the study of the degradation of the fungicide prochloraz by pathogen microorganisms. LC measurements indicated that the main degradation product of prochloraz was N-(2-(2,4,6-trichlorophenoxy)ethyl)propan-1-amine. [109] Ultra-sound-assisted emulsification (method A) and single-drop liquid-liquid microextraction (method B) were employed for the preconcentration of seven strobilurin and six oxazole fungicides in fruits and juice samples before GC-MS-SIM analysis. Enrichment factors ranged from 140 to 1140 for method A and from 80 to 1600 for method B. The procedure has been successfully applied for the determination of this class of fungicides in various fruit and juices.[110]

GC-MS and LC-MS-MS were employed for the investigation of the fate of pesticides in grapes and vinification process. It was found that multiresidue GC-

MS method was suitable for the detection of 71 pesticides, LC-MS-MS for the measurement of 45 pesticides, GC-MS was sued for the analysis of dithiocarbamates. It was established that boscalid and phosalone were the most persistent pesticides in grapes during ripening. The pesticides detected during the vinification process were: boscalid, cyprodinil, dimethomorph, fenhexamid, metalaxyl and procymidone their average concentration was 0.01-0.02; 0.04; 0.01-0.08; 0.12-0.13; 0.09-0.11 and 0.07-0.13 mg/L.[111]

LC-MS-MS procedure was applied for the analysis of methyldinocap in mango and soil. Target compound was extracted with acetone:methanol:4 N HCl (100:10:5, v/v/v) than hydrolyzed to 2,4-DNOPC. Analytes were cleaned up by liquid-liquid partition using ethyl acetate. LOQ of methyldinocap in soil and mango was 0.025 µg/g, RSDs ranged from 93 to 98%. The method has been employed for the study of the dissipation of methyldinocap in mango.[112]

The photocatalytic degradation of boscalid in aqueous titanium dioxide suspension was followed by using SPE prepurification step, HPLC-DAD and total organic carbon (TOC) analysis. The measurements indicated that the photodecomposition of boscalid follows pseudo-first-order reaction kinetics. This combined analytical technology allowed the separation and identification of 17 degradation products.[113]

HPLC-UV/Vis, fluorometric detection, ion chromatography and LC-MS were employed for the investigation of the radiolytic removal of carbendazim and chlorphenvinphos. It was concluded from the measurements that irradiation influences considerably the biological activity.[114]

A combined method employing GC and LC both hyphenated with tandem MS with quadruple-analyzer was used for the determination of organic contaminants in wastewater. GC-MS-MS technique applied C-18 cartridges for the prepurification of the target compounds. The method allows the detection of about 60 analytes (PAHs, octyl/nonylphenols, PCBs, organochlorine compounds, insecticides, herbicides and PBDEs. The UHPLC-MS-MS procedure made possible the analysis of 37 (more polar) pesticides. The most frequently detected pollutants were herbicides (simazine, terbutylazine, terbutryn, terbumeton, terbacyl, and diuron), fungicides (thiabendazole and carbendazim) and 4-t-octylphenol. The presence of insecticide diazinon, fungicide diphenylamide, UV filter benzophenone, N-butylbenzenesulfonamide, the insect repellent diethyltoluamide, caffeine, the pharmaceuticals erythromycin, benzenesulfonanilide, ibuprofen, atenolol, and paracetamol was also verified.[115]

Abbreviations

ASE	accelerated solvent extraction
BaP	benzo[a]pyrene
DCM	dichloromethane
DDTs	dichlorodiphenyltrichloroethane and its metabolites
ECD	electron capture detection
FID	flame ionisation detector
FUSE	focused ultrasound extraction
GC-MS	gas chromatography-mass spectrometry
GPC	gel permeation chromatography;
HCB	hexachlorobenzene;
HCHs	hexachlorocyclohexane isomers;
HS	head-space
LLE	liquid-liquid extraction;
LOD	limit of detection;
LOQ	limit of quantification;
LVI	large volume injection;
MAE	microwave-assisted extraction;
MSDP	matrix solid-phase dispersion;
MW	microwave;
NCI	negative chemical ionization;
OCPs	organochlorine pesticides;
PAHs	polycylic aromatic hydrocarbons;
PBBs	polybrominated biphenyls;
PBDDs	polybrominated dibenzo-p-dioxins;
PBDEs	polybrominated diphenyl ethers;
PBDFs	polybrominated dibenzofurans;
PCA	principal component analysis;
PCBs	polychlorinated biphenyls;
DL	dioxin-like polychlorinated biphenyls
PCDD/Fs	polychlorinated dibenzofurans
PFE	pressurized fluid extraction
PLE	pressurized liquid extraction
POPs	persistent organic pollutants
PSE	pressurized solvent extraction
PTFE	poly-tetra-fluorinated-ethylene
PTV	programmable temperature vaporizer
SIM	selected ion monitoring
SPE	solid-phase extraction
SPME	solid phase microextraction
SFE	supercritical fluid extraction
UPLC	ultra high-performance liquid chromatography
TEQ	toxic equivalent quotient
US	ultrasound
US-PSE	ultrasound-assisted pressurized solvent extraction

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