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# Preface

The presence of emerging pollutants (EPs)—pharmaceuticals, personal care products, industrial and household products, surfactants, industrial additives, and solvents, etc.—and their fate in the environment are especially worrisome because they cannot be completely degraded by conventional treatment technologies. The necessity of a book addressed to professional audience (e.g., environmental scientists, chemists, and engineers) to provide advice in real situations is paramount to mitigating the effects of EPs.

EPs' determination is relatively recent when compared to conventional pollutants (toxic metals, pesticides, oil derivatives, etc.), probably because EPs as pharmaceuticals and personal care products are consumed in large quantities and without concern for the environment. Then, analytical chemistry is paramount to understand EPs' presence, fate, and effects. From this development, the trend is to expand EPs' determination and their number and species in few years.

Technological advances in analytical techniques related to miniaturization and automatization are at the frontiers of knowledge in order to reduce costs and time, as probes and sensors.

Aquatic environment is the most impacted medium due to EPs' use and their discards, and legislation is incipient to regulate their presence and management in the environment. However, the generated knowledge supports the increasing of the regulation.

This book deals with the understanding of EPs and their sources and fate in the environment (Chap. 1), the fundamentals of analytical chemistry for analyses of EPs (Chap. 2), the main analytical technologies to be applied (Chap. 3), the description of most representative environmental matrices (air, soil, and water), and the most adequate analytical methods for those matrices (Chap. 4), the degradation processes and treatments of EPs (Chap. 5), and the general remarks and conclusions (Chap. 6). Furthermore, aspects of toxicology, chemometrics, QA&QC, sample preparation, and green analytical chemistry, among others, are considered in the text. In this way, the reader can have a broad vision of the analytical approaches to be used for the monitoring and control of EPs in the environment.

From these observations, the analysis of EPs in environmental matrices is a topic that generates opportunities for analytical services, research, technology, and improvement of environment and health conditions.

Good lecture!

Brasília, Brazil Sílvio Vaz Jr.

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# About the Author

**Sílvio Vaz Jr.** is currently a research scientist at the Brazilian Agricultural Research Corporation (Embrapa) working on the development of renewable chemicals from biomass, the application of analytical chemistry to bioenergy, and environmental chemistry.

He holds a DSc in analytical chemistry from the University of São Paulo and a PhD in chemistry from the University of Coimbra.

# Chapter 1
# What Are Emerging Pollutants (EPs) and Their Fate on the Environment


## 1.1 Introduction

Chemicals are present in our day in every materials that we handle in our house and work, in our food, etc. There is a huge amount of chemicals introduced in our society during the last 200 years without taking into account toxicological aspects for the human and animal health and for the environment. However, we can observe in the last decades—from the 1970s to the current days—the establishment of legislation and monitoring of hazardous substances in the environment (e.g., pesticides, oil derivatives, metals, and ions) and most recently a concern with emerging pollutants (EPs).

EPs can be understood in a broad sense as any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored or regulated in the environment with potentially known or suspected adverse ecological and human health effects. These pollutants include mainly chemicals found in *pharmaceuticals, personal care products, pesticides, industrial and household products, metals, surfactants, industrial additives, and solvents*. Many of them are used and released continuously into the environment even in very low quantities and some may cause chronic toxicity, endocrine disruption in humans and aquatic wildlife, and development of bacterial pathogen resistance (United Nations Educational, Scientific and Cultural Organization (UNESCO) 2017).

Scientific knowledge and understanding on potential human and ecosystem health risks posed by emerging pollutants are still very scarce as well as on their presence in water resources and wastewater and their pathways and accumulation in the environment—what limits the best strategies to avoid or to remedy their presence. Most emerging pollutants are not regulated in environmental, water quality, and wastewater discharge regulations. Hence, there is an urgent need to strengthen scientific knowledge and adopt appropriate technological and policy approaches to monitor emerging pollutants in the environmental matrixes, assess their potential human health and environmental risks, and prevent and control their disposal to



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water resources and the environment (United Nations Educational, Scientific and Cultural Organization (UNESCO) 2017).

## 1.2 Classes of Emerging Pollutants

From UNESCO's orientation (United Nations Educational, Scientific and Cultural Organization (UNESCO) 2017), we can consider the following EP classes:

- *Pharmaceuticals*: antibiotics, anti-inflammatories, analgesics, psychiatric drugs, lipid regulators, β-blockers, X-ray contrasts, steroids, and hormones.
- *Personal care products*: fragrances, sunscreen agents, insect repellents, antiseptics, soaps, toothpaste, shampoos, creams, deodorants, hair color, etc.
- *Pesticides*: biopesticides, insecticides, fungicides, herbicides, and antibiotics.
- *Industrial and household products*: cleaning formulations, degreasers, aerosols, lubricating oils, coatings, paints, sealants, germicides, wood treatments, thinner, etc.
- *Metals*: Pb, Cd, Cr, Cu, Hg, Ni, and Zn.
- *Surfactants*: nonionics, anionics, and cationics.
- *Industrial additives and solvents*: dispersing agents, wetting agents and surface modifiers, defoamers, rheology modifiers and film-forming agents, BTEX, and halogenated solvents.

We can include in this relation products in nanoscale (paints, coatings, catalysts, delivery drugs, etc.) due to their probable action under environment, animal, and human bodies (Ribeiro et al. 2017). Additionally, we can consider asbestos, a mineral fiber, released into the air by the disturbance of asbestos-containing material during product use, demolition work, building or home maintenance, repair, and remodeling; this material is well recognized as a health hazard (US Occupational Safety and Health Administration (OSHA) 2017). Microplastics deserve attention due to their toxic effect to the marine environment that include loss of nutritional value of diet, physical damages, exposure to pathogens, and transport of alien species besides exposure to chemical additives (Avio et al. 2017).

Table 1.1 presents examples of EPs according to their classes. We can see a huge diversification of molecular structure (Fig. 1.1) that suggests different interaction mechanisms and different effects on health and environment.

## 1.3 Sources and Fate on the Environment

From item 1.2 we can establish the main sources and fate on the environment for large EP classes, according to the data in Table 1.2.

From Table 1.2 it is possible to understand that EPs are very commercially available and easy to purchase that increase their environmental risk. Several sources

**Table 1.1** Classes and molecules of EPs

| Classes | Examples of EPs |
|---|---|
| *Pharmaceuticals* | |
| Veterinary and human antibiotics | Trimethoprim, erythromycin, lincomycin, sulfamethoxazole |
| Analgesics, anti-inflammatory drugs | Codeine, ibuprofen, acetaminophen, acetylsalicylic acid, diclofenac, fenoprofen |
| Psychiatric drugs | Diazepam |
| Lipid regulators | Bezafibrate, clofibric acid, fenofibric acid |
| β-Blockers | Metoprolol, propranolol, timolol |
| X-ray contrasts | Iopromide, iopamidol, diatrizoate |
| Steroids and hormones | Estradiol, estrone, estriol, diethylstilbestrol |
| *Personal care products* | |
| Flagrances | Nitro, polycyclic and macrocyclic musks |
| Sunscreen agents | Benzophenone, methylbenzylidene camphor |
| Insect repellents | N, N-diethyl-*m*-toluamide (DEET) |
| Antiseptics | Triclosan, chlorophene |
| *Surfactants and surfactant metabolite* | Alkylphenol ethoxylates, 4-nonylphenol, 4-octylphenol, alkylphenol carboxylates |
| *Flame retardants* | Polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A, $C_{10}$–$C_{13}$ chloroalkanes, tris (2-chloroethyl)phosphate |
| *Industrial additives and agents* | Chelating agents (e.g., ethylenediaminetetraacetic acid, EDTA), aromatic sulfonates |
| *Gasoline additives* | Dialkyl ethers, methyl-*tert*-butyl ether (MTBE) |

Adapted from Eugris (2017)

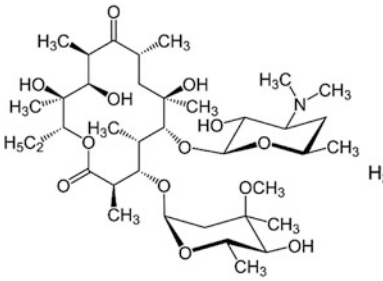
imply in a high pollutant input onto environmental matrices (more details in Chap. 4). Water and wastewater are the main fates of EPs on the environment—due to the large use of pharmaceuticals, personal care products, and surfactants—although soil, groundwater, and air have a strong contribution. Seawater is the fate for microplastics besides receiving pharmaceuticals, personal care products, and surfactants from sewage of the cities.

Table 1.3 summarizes additional data regarding EP presence and concentration on the environment.

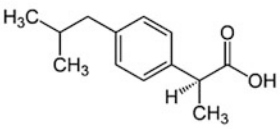
## 1.4 Physicochemical Properties and Behaviors

The fate, availability, and influence of the EPs on environment depend on their physicochemical properties, as we can see in Table 1.4. Some highlights from these properties are given below:

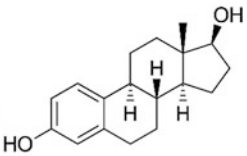
- Organic chemicals are the most representative molecules despite inorganic and organometallic compounds having a strong contribution, mainly metals.
- Organic EP molecules have a molecular weight from medium to large values.



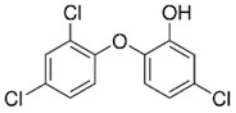
Erythromycin (antibiotic)



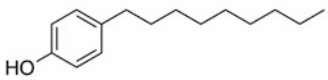
Ibuprofene (anti-inflamatory)



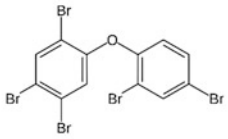
Estradiol (sexual hormone)



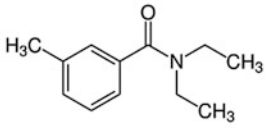
Triclosan (antiseptic)



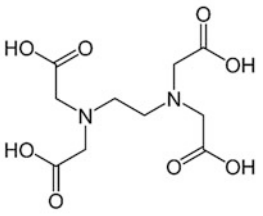
4-Nonylphenol (surfactant)



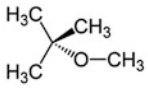
PBDE (flame retardant)



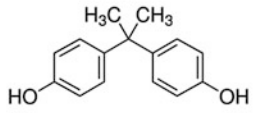
DEET (insect repellent)



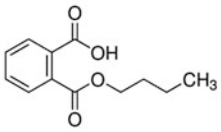
EDTA (industrial agent)



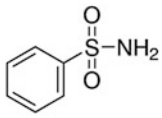
MTBE (gasoline additive)



Bisphenol A (monomer)



Butyl phthalate (monomer)



Benzenesulfonamide (plasticizer, pharmaceutical)

**Fig. 1.1** Some examples of EP molecules according to their classification. *PBDE* Polybrominated diphenyl ether, *DEET N*,*N*-diethyl-*m*-toluamide, *EDTA* Ethylenediaminetetraacetic acid, *MTBE* Methyl-*t*-butyl ether, *TCDF* 2,3,7,8-Tetrachlorodibenzofuran

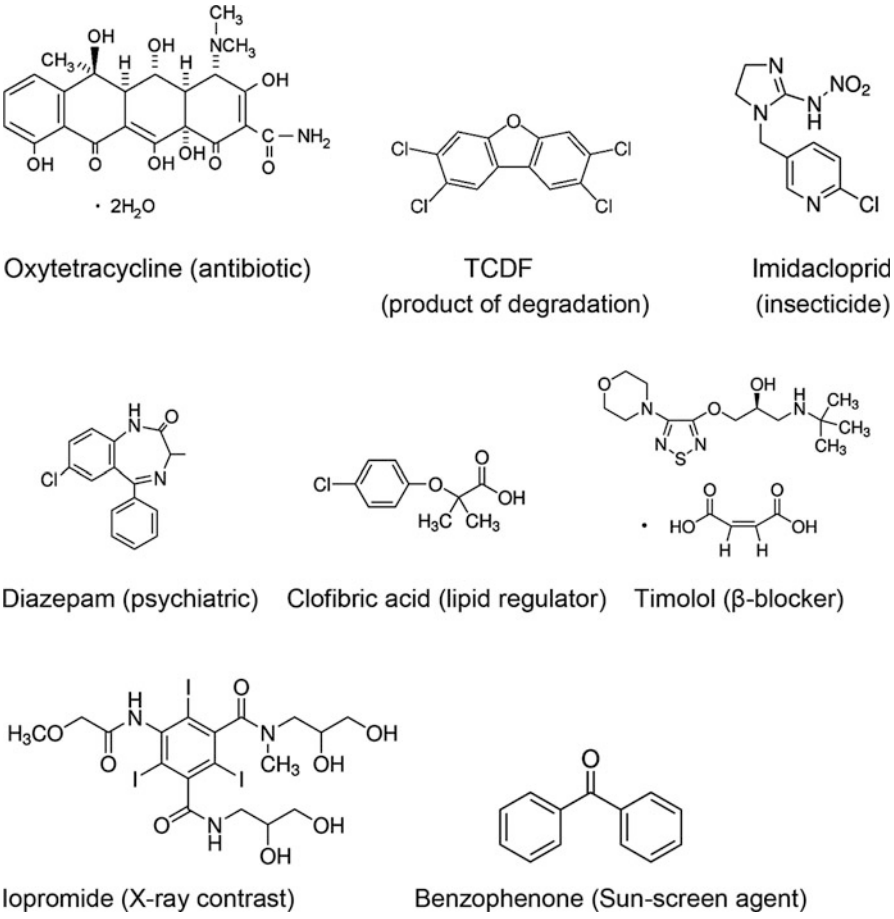



**Fig. 1.1** (continued)

- Hydrogen bonds are the main interaction possibility among EPs with environmental matrices due to the high donor and acceptor hydrogen capacity of the EP molecules.
- Polar surfaces are available for sorption processes.
- EPs are present in vapor and liquid phases, according to their vapor pressure and Henry's constant values. Some molecules are present, preferably, in vapor phase (e.g., MTBE), others in liquid phase (e.g., estradiol), and some others in both phases (e.g., benzophenone).

**Table 1.2** Sources and fate of EP classes on the environment

| EP classes | Source(s) | Main fate on the environment |
|---|---|---|
| Pharmaceuticals | Pharma industry (production)<br>Retailors as drugstores (intermediation)<br>Patient (end use) | Surface water and wastewater |
| Personal care products | Chemical industry (production)<br>Retailors as drugstores and markets (intermediation)<br>Ordinary people (end use) | Surface water and wastewater |
| Pesticides | Chemical industry (production)<br>Retailors (intermediation)<br>Agriculture (end use) | Soil<br>Groundwater<br>Air |
| Industrial and household products | Chemical industry (production)<br>Retailors (intermediation)<br>Ordinary people (end use) | Soil<br>Surface water<br>Air |
| Metals | Extraction (extractive industry)<br>Metallurgical industry/steel industry/chemical industry (processing industry)<br>Automotive industry/construction/etc. (intermediary industry)<br>Ordinary people (end use)<br>Recycling industry (processing industry) | Soil<br>Groundwater<br>Surface water<br>Air |
| Surfactants and their metabolites | Chemical industry (production)<br>Retailors as markets (intermediation)<br>Ordinary people (end use) | Surface water and wastewater |
| Industrial additives and solvents | Chemical industry (production)<br>Retailors (intermediation)<br>Chemical industry/construction/petrochemical/etc. (end use) | Surface water and wastewater<br>Air |
| Nanoproducts | Chemical industry (production)<br>Retailors (intermediation)<br>Chemical industry/construction/pharmaceutical industry/etc. (end use) | Not clear |
| Asbestos | Extraction | Air |
| Microplastics | End products | Seawater |

- Some EPs have a tendency of immobilization on organic particles (e.g., erythromycin) while others have a tendency of transference between these particles (e.g., imidacloprid) determining their fate, according to the $K_{OC}$ values.

## 1.5 Toxicological and Ecotoxicological Aspects

Table 1.5 presents toxicological and ecotoxicological parameters and values for EP molecules.

**Table 1.3** Summary data for selected EPs. Adapted from Eugris (2017)

| Compound | Origin | Persistence or bioaccumulation | Observed in environment | Concentration level |
|---|---|---|---|---|
| 4-Nonylphenol | Degradation product of nonionic surfactants | Medium persistent. Bioaccumulative | Soil<br>Sediment<br>Sludge<br>Water | Low mg $kg^{-1a}$<br>Low mg $kg^{-1}$<br>Low-high mg $kg^{-1}$<br>Low μg $L^{-1}$ |
| Bisphenol A | Plastics | Not bioaccumulative | Surface water<br>Groundwater | Low-high ng $L^{-1}$<br>Low-high ng $L^{-1}$ |
| Phthalates | Plastics | Low-to-medium persistent<br>Atmospheric deposition | Water<br>Sediment<br>Sludge | Low-medium μg $L^{-1}$<br>Low μg $kg^{-1}$<br>Low-medium μg $kg^{-1}$ |
| PBDE | Flame retardant | Persistent/highly accumulative<br>Atmospheric deposition | Sediment<br>Soil<br>Sludge | Low-medium μg $kg^{-1}$<br>Low-high ng $kg^{-1a}$<br>Low-medium μg $kg^{-1}$ |
| $C_{10}$–$C_{13}$ chloroalkanes | Flame retardant | Persistent and bioaccumulative | Surface water | Low-medium μg $L^{-1}$ |
| Sulfonamides | Human and veterinary drug | Slightly-very persistent | Groundwater | – |
| Tetracyclines | Human and veterinary drug | Moderately-very persistent | Groundwater<br>Soil<br>Sludge | – |
| Steroid sex hormones | Contraceptives | Moderately persistent | Water<br>Sediment<br>Sludge | Low ng $L^{-1}$<br>Low μg $kg^{-1}$<br>Low-medium μg $kg^{-1}$ |
| MTBE | Gasoline additive | Persistent<br>Not bioaccumulative—but ubiquitous in the atmosphere | Groundwater | – |

[a]Sludge-amended soil. *PBDE* 1,2,3-Tribromo-4-(2, 4-dibromophenoxy)benzene, *MTBE Tert*-butyl methyl ether

We can observe that EPs' presence has an influence on the environment and human health, especially when considering water resources because it is the main fate for EPs related to the daily use (see Table 1.2). The aquatic environment may contain pharmaceuticals, hormones, perfluorinated compounds, by-products of drinking water disinfection, sunscreens or UV filters, benzotriazoles, and naphthalenic acids, all of those with toxicological/ecotoxicological implications (La Farré et al. 2008).

**Table 1.4** Physicochemical properties of representative EP molecules

| Property | Erythromycin | Ibuprofen | Diazepan | Clofibric acid | Timolol | Iopromide | Estradiol | Benzophenone |
|---|---|---|---|---|---|---|---|---|
| Molecular formula | $C_{37}H_{67}NO_{13}$ | $C_{13}H_{18}O_2$ | $C_{16}H_{13}ClN_2O$ | $C_{10}H_{11}ClO_3$ | $C_{13}H_{24}N_4O_3S$ | $C_{12}H_{24}I_3N_3O_8$ | $C_{18}H_{24}O_2$ | $C_{13}H_{10}O$ |
| Molecular weight (g $mol^{-1}$) | 733.937 | 206.285 | 284.743 | 214.645 | 316.42 | 791.116 | 272.388 | 182.222 |
| Hydrogen bond donor count | 5 | 1 | 0 | 1 | 2 | 6 | 2 | 0 |
| Hydrogen bond acceptor count | 14 | 2 | 2 | 3 | 8 | 8 | 2 | 1 |
| Topological polar surface area ($A^2$) | 194 | 37.3 | 32.7 | 46.5 | 108 | 169 | 40.5 | 17.1 |
| Formal charge | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $K_{OC}$ (L $g^{-1}$) | 85,000 | 3400 | 192–630 | – | 240 | – | 30,000 | 430–517 |
| $V_p$ (mmHg at 25 °C) | $1.5 \times 10^{-6}$ | $7.74 \times 10^{-5}$ | $2.8 \times 10^{-8}$ | – | $1.4 \times 10^{-8}$ | – | $6.4 \times 10^{-9}$ | $1.93 \times 10^{-3}$ |
| $K_H$ (atm mol $L^{-1}$) | $1.5 \times 10^{-5}$ | $1.5 \times 10^{-7}$ | $3.6 \times 10^{-9}$ | – | $4.3 \times 10^{-17}$ | – | $3.5 \times 10^{-11}$ | $1.9 \times 10^{-6}$ |
| log$K_{OW}$ | 6.53 | 3.97 | 2.82 | – | 1.83 | – | 4.01 | 3.13 |
| pKa | 8.88 | 4.91 | 3.4 | – | 9.21 | – | – | – |
| Property | DEET | Triclosan | 4-Nonylphenol | PBDE | MTBE | Imidacloprid | Bisphenol A | TCDF |
| Molecular formula | $C_{12}H_{17}NO$ | $C_{12}H_7C_{13}O_2$ | $C_{15}H_{24}O$ | $C_{12}H_5Br_5O$ | $(CH_3)_3COCH_3$ | $C_9H_{10}ClN_5O_2$ | $C_5H_{16}O_2$ | $C_{12}H_4Cl_4O$ |
| Molecular weight (g $mol^{-1}$) | 191.274 | 289.536 | 220.356 | 564.691 | 88.15 | 255.662 | 228.291 | 305.963 |
| Hydrogen bond donor count | 0 | 1 | 1 | 0 | 0 | 1 | 2 | 0 |
| Hydrogen bond acceptor count | 1 | 2 | 1 | 2 | 1 | 4 | 2 | 1 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Topological polar surface area ($A^2$) | 20.3 | 29.5 | 20.2 | 9.2 | 9.2 | 86.3 | 40.5 | 13.1 |
| Formal charge | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $K_{OC}$ (L $g^{-1}$) | 115 | 2400–15,892 | 32,400 | – | 11–12 | 156–800 | 115–3886 | 85,000 |
| $V_p$ (mmHg at 25 °C) | 0.002 | $4.6 \times 10^{-6}$ | $8.175 \times 10^{-4}$ | – | 250 | $3.0 \times 10^{-12}$ | $4.0 \times 10^{-8}$ | $1.5 \times 10^{-6}$ |
| $K_H$ (atm mol $L^{-1}$) | $2.1 \times 10^{-8}$ | $2.1 \times 10^{-8}$ | $3.4 \times 10^{-5}$ | – | $5.87 \times 10^{-4}$ | – | $4.0 \times 10^{-11}$ | $1.5 \times 10^{-5}$ |
| log$K_{OW}$ | 2.02 | 7.76 | 5.76 | – | 0.94 | 0.57 | 3.32 | 6.53 |
| pKa | – | 7.9 | – | – | - 3.70 | $pKa_1 = 1.56$<br>$pKa_2 = 11.12$ | 9.6 | – |

Adapted from PubChem (2017)

$K_{OC}$ organic carbon-water partition coefficient ($C_{solid}/C_{water}$ × organic carbon concentration); $V_p$ vapor pressure; $K_H$ Henry's constant ($V_p$/solubility); log$K_{OW}$ logarithm form of the *n*-octanol-water partition coefficient; pKa negative logarithm of the dissociation constant of a weak acid or weak base; *DEET N*, *N*-diethyl-*m*-toluamide; *PBDE* 1, 2, 3-tribromo-4-(2, 4-dibromophenoxy)benzene; *MTBE tert*-butyl methyl ether; *TCDF* 2,3,7,8-tetrachlorodibenzofuran

**Table 1.5** Toxicological and ecotoxicological data for some EPs

| Parameter | Erythromycin | Ibuprofen | Diazepan | Clofibric acid | Timolol | Iopromide | Estradiol | Benzophenone |
|---|---|---|---|---|---|---|---|---|
| Toxicity | | | | | | | | |
| LD50 rat oral (mg $kg^{-1}$) | 9272 | 636 | 710 | – | 900 | – | – | 1900 |
| LD50 mouse intraperitoneal (mg $kg^{-1}$) | 463 | 320 | 220 | – | – | – | – | 634–833 |
| LD50 mouse subcutaneous (mg $kg^{-1}$) | 1800 | 395 | 300 | – | – | – | – | – |
| Ecotoxicity | | | | | | | | |
| LC50 *Daphinia magna* (μg $L^{-1}$) | – | – | 49.4 | – | – | – | 648 | – |
| Parameter | DEET | Triclosan | 4-Nonylphenol | PBDE | MTBE | Imidacloprid | Bisphenol A | TCDF |
| Toxicity | | | | | | | | |
| LD50 rat oral (mg $kg^{-1}$) | – | 3700 | – | – | 400 | 424 | 3250 | – |
| LD50 mouse intraperitoneal (mg $kg^{-1}$) | – | 84 | – | – | – | 7–24 | 150 | – |
| LD50 mouse subcutaneous (mg $kg^{-1}$) | – | – | – | – | – | – | – | – |
| Ecotoxicity | | | | | | | | |
| LC50 *Daphnia magna* (μg $L^{-1}$) | 26,000 | – | – | – | – | 26,890–35,980 | 806 | – |

Adapted from PubChem (2017)

*LD50* The dose of the compound that causes mortality in 50% of a treated population, *LC50* the concentration of the compound to which the organisms were exposed that causes mortality in 50% of an exposed population

*DEET N,N*-diethyl-*m*-toluamide, *PBDE* 1,2,3-tribromo-4-(2,4-dibromophenoxy)benzene, *MTBE tert*-butyl methyl ether, *TCDF* 2,3,7,8-tetrachlorodibenzofuran

**Table 1.6** Toxicological and ecotoxicological aspects of EPs

| EP | Toxicological or ecotoxicological aspects |
|---|---|
| Benzophenone | Hepatotoxicity |
| Bisphenol A | Estrogenic activity (endocrine disruption); mutation |
| DEET | Dermal and neurological effects |
| Erythromycin | Dermal and neurological effects |
| Estradiol | Carcinogen; impairment of fertility |
| Ibuprofen | Respiratory and neurological effects |
| Imidacloprid | Negative effects on reproductive system and neurological effects |
| MTBE | Carcinogen for animal (limited evidence); nervous system disturbance |
| 4-Nonylphenol | Negative effects on reproductive system |
| PBDE | Recalcitrant and bioaccumulative; associated with tumors, neurodevelopmental toxicity, thyroid hormone imbalance |
| TCDF | Poisonings |
| Timolol | Neurological effects |
| Triclosan | Bioaccumulation; precursor of dioxins by photodegradation |

Adapted from PubChem (2017)
*DEET* *N*,*N*-diethyl-*m*-toluamide, *PBDE* 1,2,3-tribromo-4-(2, 4-dibromophenoxy)benzene, *MTBE* *tert*-butyl methyl ether, *TCDF* 2,3,7,8-tetrachlorodibenzofuran

Table 1.6 describes main toxicological and ecotoxicological aspects of those compounds in Table 1.5.

Nowadays, the use of mathematical tools allied to experimental data, as quantitative structure-activity relationship (QSAR), to predict the toxicological behavior of the EPs could provide a better understanding about the interaction of the pollutants with a human hormone carrier; an example is the case of poly/perfluorinated compounds (PFCs) and brominated flame retardants (BFRs) and their interaction with transthyretin (TTR) molecule that is the carrier for the thyroid hormone thyroxin (T4) (Papa et al. 2013).

## 1.6 Human and Biota Exposure

Generally, humans are exposed to EPs by means of their use whereas biota (animals, plants, microorganisms) by means of their discard. This is not an immutable rule but serves as the start point to understand exposure pathways and routes.

Yusa et al. (2012) proposed pathways and routes for human exposure to some EPs and these are presented in Table 1.7.

From its diversity of organisms, biota is the most complex to determine pathway and routes of exposure compared to human specimens. Figure 1.2 presents exposure pathways in the environment for the antibiotic oxytetracycline (OTC).

According to Vaz (2010), soil can receive OTC from animal feces and urine, application in plants and animal manure. The antibiotic can suffer interaction with

**Table 1.7** Examples of pathways and routes for human exposure to EPs

| EP | Pathway | Route | Observed analytical matrix |
|---|---|---|---|
| Phthalates | Food | Ingestion | Urine |
| Perfluorinated compounds | Food, water | Ingestion | Blood, serum, plasma, human milk |
| Organophosphated flame retardants | Air, food | Inhalation | Urine |
| Personal care products | Skin | Dermal | – |
| DEET | Skin, air | Dermal, inhalation | Urine |

Adapted from Yusa et al. (2012)
*DEET N*,*N*-diethyl-*m*-toluamide

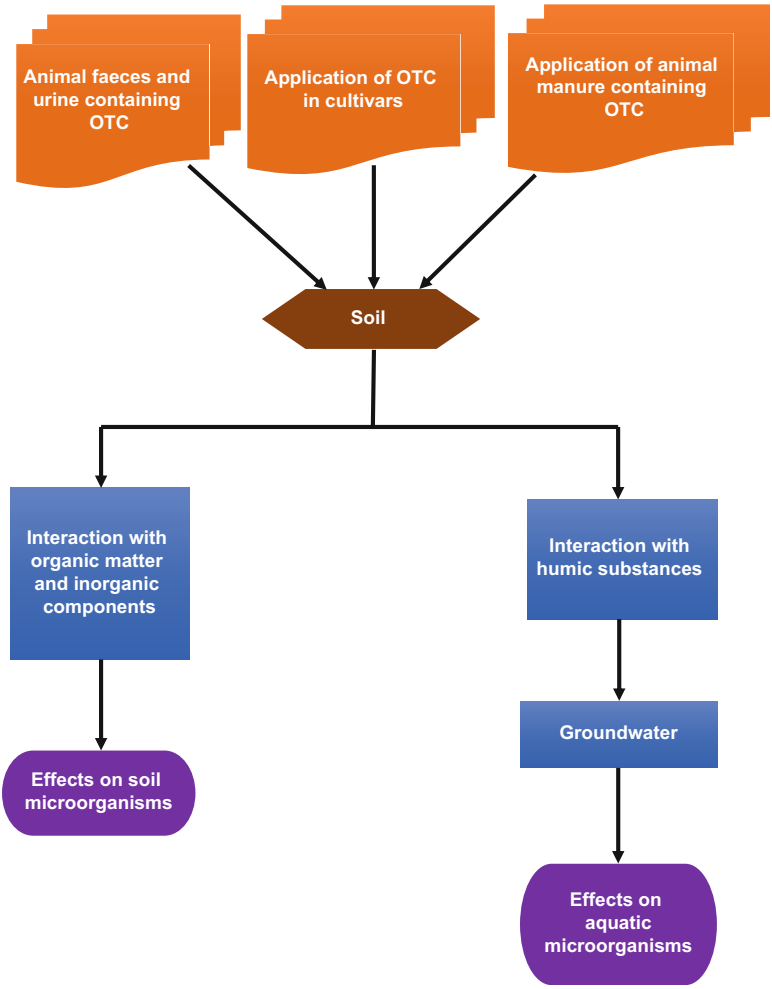



**Fig. 1.2** Pathways for biota exposure to the oxytetracycline (OTC) antibiotic

organic and inorganic components with its retention and effects on soil microorganism; on the other hand, humic substances (e.g., humic acids) can transport the antibiotic to the groundwater with possible effects on aquatic microorganisms (Vaz et al. 2015).

## 1.7 Conclusions

EPs are a large class of pollutants from very different sources—include mainly chemicals found in pharmaceuticals, personal care products, pesticides, industrial and household products, metals, surfactants, industrial additives, and solvents—without concise information about their presence and effects on environment and human health. Hence, there is an urgent need to strengthen scientific knowledge and adopt appropriate technological and policy approaches to monitor and control EPs in the environment.

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# Chapter 2
# Fundamental Aspects of Analytical Chemistry for Environmental Analysis


## 2.1 Fundaments

The role of the analytical chemistry in the analysis and understanding of the emerging pollutant (EP) effects on environment is paramount. The effect of a certain compound just is possible to define if analytical techniques and methods are applied, comprising among others pollutant identification, exposure assessment, risk characterization, and legal regulation aspects (Pierzynski et al. 2005). Figure 2.1 illustrates this approach.

Generally, chemical analysis can be considered as the use of concepts of analytical chemistry and its techniques and methods in the investigation and solution of real problems of variable complexity in different scientific or technological areas. The chemical analysis can generate information of both qualitative and quantitative character.

In order to understand the application of analytical techniques for the analysis of environmental pollutants, especially those emerging pollutants (EPs), it is of fundamental importance to introduce some basic terms of analytical chemistry.

Initially, it should be taken into account that chemical analysis can be applied in three different or complementary situations:

- *Characterization*: Observation of some physical property attributed to the *analyte*—the species of interest in the analytical process. For example, the absorption of visible radiation in the wavelength range of 400–450 nm or the behavior of the molecule against the incidence of radiation of other wavelengths—this is the typical application of certain spectroscopic techniques (infrared, nuclear magnetic resonance) and microscopic techniques.
- *Identification*: Qualitative information on the presence or absence of the analyte—a good example is mass spectrometry, which identifies the compounds from the fractionation of their molecular structure.



S. Vaz Jr., *Analytical Chemistry Applied to Emerging Pollutants*,
https://doi.org/10.1007/978-3-319-74403-2_2

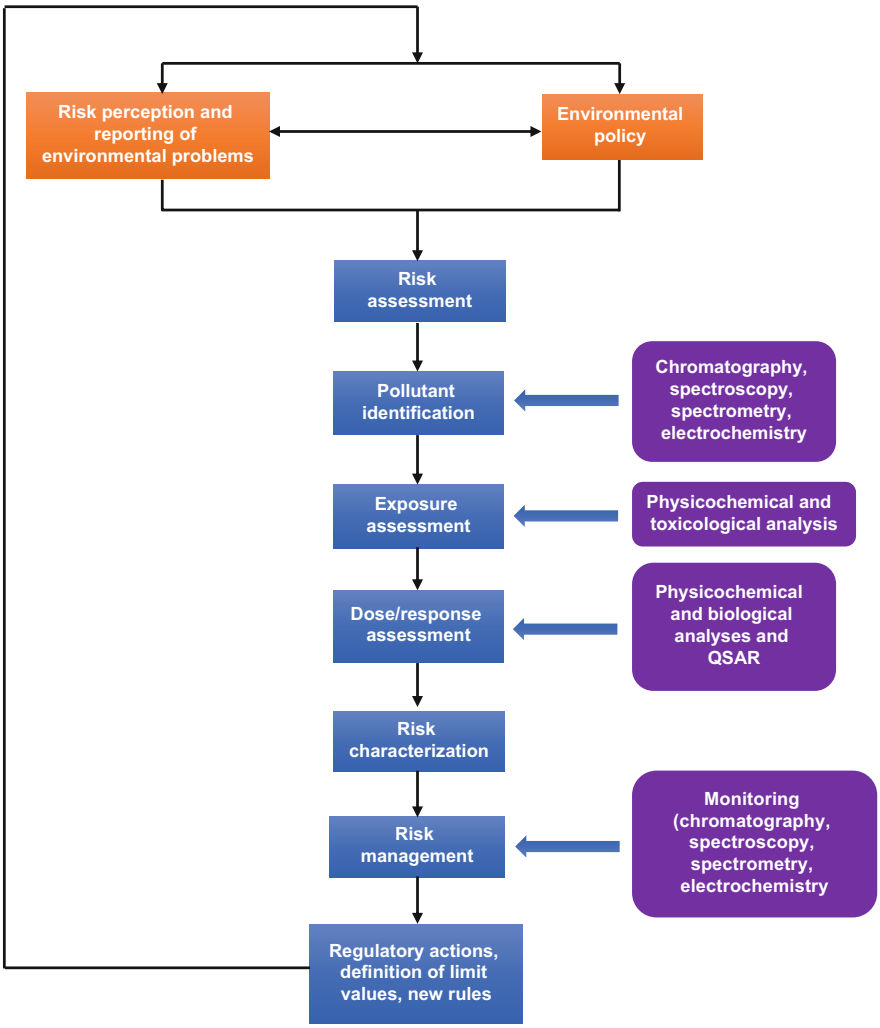


**Fig. 2.1** Flowchart of an environmental risk assessment process where the magenta boxes illustrate some indispensable applications of analytical chemistry. *QSAR* Quantitative structure-activity relationship

- *Determination*: Quantitative information on the analyte concentration in the sample—an example is the elemental analysis of the composition and the chromatographic analyses coupled to the detection techniques.

These terms will be applied in this chapter.

## 2.2 Figures of Merit

Figures of merit are validation parameters used in analytical chemistry for the application of a certain analytical method. The most representative figures are *accuracy*, *linearity*, *limit of detection*, *limit of quantification*, *precision, selectivity*, *sensitivity*, and *robustness* (International Conference on Harmonization of Technical Requirements for Registration of Pharmaceuticals for Human Use (ICH) 2005). Before validating the analytical method, these parameters must be defined, as well as the limits at which results can be accepted.

### *2.2.1 Accuracy*

This represents the degree of agreement between a measured value and a value taken as a "true value." The accuracy expresses the relative error of the measure, from the following equation:

$$\mathrm{AC} = (V_\mathrm{D} - V_\mathrm{T}/V_\mathrm{D}) \times 100 \tag{2.1}$$

where $V_\mathrm{T}$ is the true value and $V_\mathrm{D}$ is the determined value.

### *2.2.2 Linearity*

This expresses the agreement between the results obtained by a given analytical method for a given parameter, such as the absorbance, and the analyte concentration, in a given concentration range. The linear correlation coefficient ($r$), calculated by the linear regression equation (Eq. 2.2), is used to indicate if the mathematical model is adequate. Alternatively, one can use the coefficient of determination $r^2$ that the closer to 1 (one) the greater the linearity represented by the equation below:

$$y_i = a + bx_i \tag{2.2}$$

where $a$ is the line intercept and $b$ is its slope coefficient.

### *2.2.3 Limit of Detection and Limit of Quantification*

The limit of detection (LOD) for an analytical method may vary depending on the type of sample and is defined as the minimum concentration of a measured and declared substance with 95 or 99% of confidence that the analyte concentration is greater than zero.

There are several ways to calculate LOD, but the recommendation is that at least seven replicates of the blank are made in the calculation. The quantification limit (LOQ) is the lowest analyte concentration that can be determined with an acceptable level of accuracy; it can be considered as the mean value of the blank readings by adding 5, 6, or 10 times the standard deviation (shown below). The equations commonly used to determine LOD and LOQ are

$$\mathrm{LOD} = 3.3s/S \tag{2.3}$$
$$\mathrm{LOQ} = 10s/S \tag{2.4}$$

where $s$ is the standard deviation of the mean and $S$ is the slope of the calibration curve (or $b$ in Eq. 2.2).

### 2.2.4 Precision

This is the degree of agreement between indications or measured values, obtained by repeated measurements, on the same object or similar objects, under specified conditions. It is generally expressed in numerical form by means of dispersion measures such as standard deviation, variance, or coefficient of variation, under specified measurement conditions (*recovery*, *repeatability*, or *reproducibility*).

The importance of precision and its modes of measurement in analytical chemistry must be highlighted, which the main measurement form is the *standard deviation*. A measure of the data precision can be obtained by the population standard deviation ($\sigma$) or, more commonly, by the *standard deviation of the mean* ($s$) (International Standard Organization (ISO) 1993):

$$s = \sqrt{\frac{\sum \left(x_i - \bar{x}\right)}{n-1}} \tag{2.5}$$

where $x_i$ is the value of a given measure; $\bar{x}$ is the arithmetic mean of the values of the measures ($\bar{x} = \sum x_i/n$); and $n$ is the number of measurements taken.

The coefficient of variation, or *relative standard deviation*, is useful to observe the relative accuracy of the measurements:

$$\mathrm{CV}\ (\%) = \frac{s}{\bar{x}} \times 100 \tag{2.6}$$

The confidence interval for the mean ($\mathrm{CI_M}$) is very useful when expressing the *confidence interval of a measure*, a relevant aspect in the elaboration of an analytical report:

$$\mathrm{CI_M} = \bar{x} \pm t_{n-1}\frac{s}{\sqrt{n}} \tag{2.7}$$

where $\bar{x}$ is the arithmetic mean of the values of the measures ($\bar{x} = \sum x_i/n$); $n$ is the number of measurements performed; $s$ is the standard deviation of the mean (Eq. 2.5); $t_{n-1}$ is the tabulated critical value of the Student's distribution (see ahead).

### 2.2.5 Sensitivity or Sensibility

It is the measure of the ability to discriminate between small differences in the concentration of an analyte. Two factors limit sensitivity: the slope of the analytical curve and reproducibility. For two methods having the same precision, the one with the most inclined analytical curve will be the most sensitive; if the analytical curves are equal, the one that exhibits greater precision will be more sensitive:

$$\Delta CA = \Delta S_A/k_A \tag{2.8}$$

where $\Delta S_A$ is the smallest increase in the signal that can be measured (the smallest difference is the analyte concentration that can be detected) and $k_A$ is the proportionality constant to be measured.

### 2.2.6 Selectivity

It is the property of a measurement system, whereby the system provides measured values for one or several measurands (magnitude to be measured), such that the values of each measurand are independent of each other. If the chosen method does not exhibit selectivity, the matrix components will interfere with the measurement performance. The evaluation of the selectivity of a method involves assays with reference standards or materials, samples with and without the analyte, and evaluation of the efficiency in determining the analyte in the presence of interferents—if $S$ is equal to unity it means that the method is selective for the analyte:

$$S = K_A(C_A + K_{A,I}C_I) \tag{2.9}$$

where $K_A$ is the analyte's sensitivity coefficient (calculated from Eq. 2.8), $C_A$ is the analyte concentration, $K_{A,I}$ is the selectivity coefficient, and $C_I$ is the interfering concentration.

### 2.2.7 Robustness

This measures the sensitivity of a method to small variations in the conditions of analysis. A method is said to be robust when it is practically insensitive to such

variations. Therefore, the greater the robustness, the greater the confidence of the method related to the precision—the coefficient of variation, treated in the Eq. 2.6, can express this parameter.

### 2.2.8 Recovery

A figure of merit to be treated separately is the recovery percentage, which is important for determining the efficiency of an extraction method, with its value varying between 70 and 120%:

$$\%R = (C_i - C_f / C_i) \times 100 \tag{2.10}$$

where $C_i$ is the initial added concentration of the standard to the matrix, with no traces of the analyte, and $C_f$ is the final concentration determined in the sample (matrix + standard) after the addition of a known concentration of the standard, and after the application of an extraction method.

In any measure we carry out there are errors or uncertainties associated with it. The word *error* can be understood in two distinct ways: it can refer to the difference between a measured value and a known value, or be related to the estimated uncertainty associated with a measurement or an experiment. Thus, the error can be classified as *random or indeterminate*, *systematic or determinate*, and *rough*:

- Random errors exist in every measure, and cannot be totally eliminated, because they are caused by uncontrollable variables in the measurement process—these errors affect the precision of the results.
- Systematic errors have a defined cause, being of the same order of magnitude for replicates of a measure made in a similar way. They can be caused, for example, due to the lack of calibration of an equipment—these errors affect the accuracy of the results.
- Rough errors are usually of great magnitude, caused by human failure. These errors lead to anomalous values that differ significantly from the other replicated values, and there are several statistical tests to identify this type of error, such as the coefficient of variation.

## 2.3 Developing an Analytical Method

The stages of development and validation make up the *modus operandi* of any analytical method. As an example of the importance of these steps, we can mention the constant evaluation of the figures of merit (already seen) for the correct obtaining

of an analytical result, a fundamental procedure in an accreditation process of an environmental analysis laboratory.

The development of a method for environmental analysis requires previously:

- Survey of the historic of the area and the pollution process—involves consulting documents such as construction and production plans, maps, soil, water or air data, and reports of previous analyses.
- Toxicity of the analyte(s)—involves the understanding of the effect of the presence of the analyte(s) on the environment and, in some cases, mathematical models of partition coefficients and mass transport estimation are used. For EPs, generally it is not available.
- Survey of the legal implication of the analyte(s) presence—search for knowledge about the maximum values allowed by the environmental legislation for the analyte(s) in the matrix to be analyzed, in order to know what should be the LOD and LOQ to be reached by the method.
- Survey of information in the technical-scientific literature—compilation of scientific and technical aspects obtained in articles, books, and norms on the method to be developed.
- Survey of other information that is important, such as costs, logistics, and more adequate sampling.

For the development, adaptation, or implementation of a known method, an assessment process that evaluates the method efficiency in the routine of the laboratory should be applied. An essential step is to plan the activities to be performed so that the final result of the analysis performed is as reliable and representative as possible. In this sense, some observations are important:

- Calibrated equipment: The equipment and materials used in the analytical process should be properly calibrated.
- Quality of the analytical reagents: The laboratory needs reagents of high purity for analysis to avoid contaminant effects on the results. It is very critical when analyzing analytes in very small quantities or trace concentrations.
- Certified standards: Whenever possible, we must work with certified standards, which contain uncertainty, and which are traceable.
- Calibrated glassware: Glassware to be used in quantitative analyses, such as pipettes and test tubes, should be checked, observing the calibration temperature, in the case of the calibration process, and estimated at a given temperature.
- Representative sampling: Establish the correct way of sampling, according to the physicochemical characteristics of the material to be analyzed—a correct sampling ensures the reliability of the result.
- Statistical tools: Check for correct data interpretation.
- Qualified personnel: Analysts and technicians must be trained and qualified to perform the procedures, respecting their level of training.

In addition to these points addressed, it is essential that the method chosen attends in a satisfactory form to the analytical goal. In this respect, it is necessary to consider the sensitivity of the method, concentration, and matrix in which the analyte is

present and a presence of chemical interferers, which may mask the result obtained—it is of great importance to know the effect of the matrix on the result. Finally, once the method has been developed, it must be optimized so that it is then validated.

### 2.3.1 Calibration

It is often necessary for the analyst to provide references so that it is possible to correlate the data obtained in an apparatus with the real analyte concentration in the sample—this is done by means of the construction of a *calibration curve*. This procedure is called *calibration of the method*, which is nothing more than determining the relationship between the analytical response and the analyte concentration. The main methods used in the construction of the calibration curves are the following:

- *Standard addition*: Addition of known concentrations of the analyte to known quantities of the sample to be analyzed, generating plots for the construction of the calibration curve from peak area and concentration values. By means of the extrapolation of the curve on the abscissa axis the actual concentration of analyte in the sample is obtained; the difference between the results of the sample without addition and with addition of analyte must be equal to the added concentration. The method can also be used with multiple additions of standard, which allows to verify if there is a linear relationship between the response and the concentration of the analyte. Normally, standard addition is used when the matrix has complex composition that affects the analytical signal, or when an analyte pattern cannot be found—see Fig. 2.2a.
- *External standard*: When it is known that the constituents of the sample do not cause interference in the analyte signal, the external standard method can be used. The method consists in the construction of an analytical curve from the areas obtained with standard solutions of the analyte in known concentrations; special care must be taken with the preparation of the standard solutions, since any contamination will imply an erroneous determination of the analyte concentration—see Fig. 2.2b.
- *Internal standard*: Addition of a standard, which is a compound with a composition different from the analyte and of known concentration, but with a similar chemical structure allowing a behavior close to that of the analyte in relation to the analytical response to a series of analyte standards with known analyte concentrations for the construction of a calibration curve. This curve is constructed not with the analyte response, but with the ratio of the internal standard signal to the analyte signal. Any analyte of unknown concentration can then be determined with addition of the internal standard by projection of the ratio of the responses in the analytical curve. This method is especially used

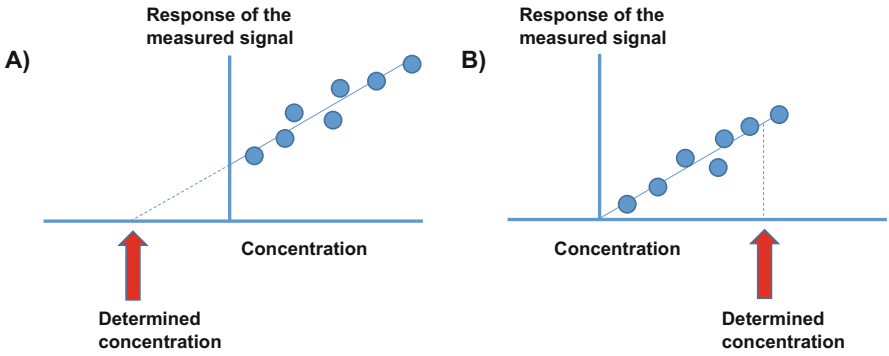


**Fig. 2.2** Calibration curves: (**a**) standard addition, (**b**) external standard

when small variations in the response of the equipment to each analysis performed, as in chromatographic analysis, usually occur.

## 2.4 Validating an Analytical Method

Validation is the proof by an objective evidence that the requirements for a particular application or use of a method have been attended.

According to International Standard Organization (ISO) (2005) the laboratory shall validate nonstandard methods, which are methods developed by the laboratory itself, or standard methods used outside the scope for which they were designed, such as extensions or modifications. The latter refer to methods developed by a standardization body or other segment whose methods are accepted by the technical sector concerned.

There are several definitions for validation in the literature. However, according to Ribani et al. (2004) the validation can proceed in two ways: validation in the laboratory and complete validation. It is considered validation in the laboratory when it is used to verify the suitability of a method or when a method has been developed in the laboratory and all parameters are related to the measurements in that laboratory. Thus, validation in the laboratory is a preliminary step to full validation, which is performed considering all performance characteristics and interlaboratory tests. Figure 2.3 illustrates the generic validation process of an analytical method.

### *2.4.1 Interlaboratory Studies*

The participation of an environmental analytical laboratory in interlaboratorial studies can verify if its adopted methodology is consolidated for a certain type of analysis, with a well-developed and -defined control system.

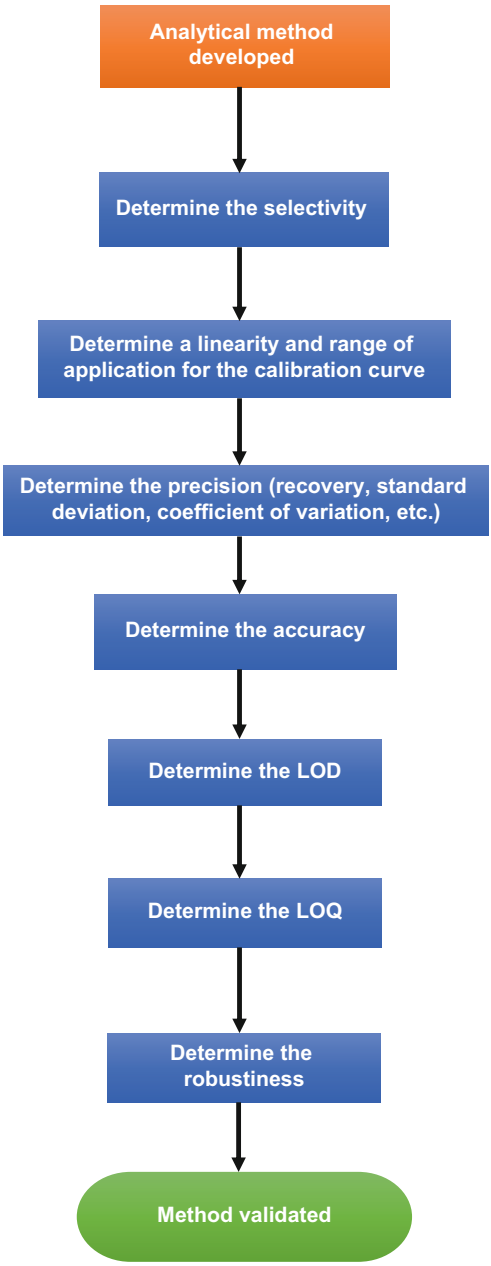


**Fig. 2.3** Validation steps for a certain analytical method

The International Standard Organization (ISO) (2005) recommends that a technique used to determine the interlaboratory performance of a method is as follows—or a combination of them:

- *Calibration with the use of materials or reference standards*: The reference material is a sufficiently homogeneous and stable material with respect to certain physical or chemical properties and is prepared to suit an intended use in a measurement or examination of qualitative properties and shall be accompanied by documentation issued by a notified body authority, a qualification, or more property values specified as uncertainties and as associated traces, called in this case a certified reference material. Already the reference standard is used for the calibration of other standards of magnitude of the same type in a laboratory.
- *Comparisons with results obtained by other methods*: The efficiency of the developing method can be verified by comparing its results with the results of a standardized method, through statistical tests (International Standard Organization (ISO) 1994).

The most utilized test for the comparisons with results obtained by other methods is the Student's—or *t*-test—used to compare a mean of a series of results with a reference value, as means of two sets of results, within a confidence interval. The value found is compared with the tabulated value of *t*, and the first one should be as close as possible to the validation of the proposed method, according to Eq. 2.11:

$$t_{\text{calc}} = \frac{|\mu - \bar{x}|\sqrt{n}}{s} \tag{2.11}$$

where $\bar{x}$ is the arithmetic mean for the set values; $\mu$ is the reference value that can be substituted by the mean from another data set; $n$ is the number of measurements; and $s$ is the standard deviation of the mean. Table 2.1 presents $t$ values according to the measurement number and the correctness probability for those measurements.

Comparing the results of two different methods or comparing the results of two different laboratories can be done by means of the *F*-test, according to Eq. 2.12:

$$F = \frac{Sx^2}{Sy^2} \tag{2.12}$$

where $s$ is the mean standard deviation for each measurement set ($x$ or $y$).

The largest value of $s$ is always used in the numerator, so the value of $F$ will always be greater than the unit. The value found is then compared with the tabulated value of $F$, considering the degrees of freedom of each set of data. To be considered equally efficient the value found has to be less than the tabulated value. Table 2.2 presents $F$ values for an exception probability of 5% of the cases.

**Table 2.1** Tabulated value of $t$, according to the measurement number for 95 and 99% of confidence interval

| Degrees of freedom $(n-1)$ | Critical value of $t$ for 95% of confidence interval | Critical value of $t$ for 95% of confidence interval |
|---|---|---|
| 1 | 12.71 | 63.66 |
| 2 | 4.30 | 9.93 |
| 3 | 3.18 | 5.84 |
| 4 | 2.78 | 4.60 |
| 5 | 2.57 | 4.03 |
| 6 | 2.45 | 3.71 |
| 7 | 2.37 | 3.50 |
| 8 | 2.31 | 3.36 |
| 9 | 2.26 | 3.25 |
| 10 | 2.23 | 3.17 |
| $\infty$ | 1.96 | 2.58 |

Adapted from Harvey (2000)

**Table 2.2** Tabulated values of $F$ for 5% of probability of significance ($P = 0.05$)[a] according to the degrees of freedom of the numerator and denominator

| | Degrees of freedom (numerator) | | | | | | |
|---|---|---|---|---|---|---|---|
| Degrees of freedom (denominator) | 3 | 4 | 5 | 6 | 12 | 20 | $\infty$ |
| 3 | 9.28 | 9.12 | 9.01 | 8.94 | 8.74 | 8.64 | 8.53 |
| 4 | 6.59 | 6.39 | 6.26 | 6.16 | 5.91 | 5.80 | 5.63 |
| 5 | 5.41 | 5.19 | 5.05 | 4.95 | 4.68 | 4.56 | 4.36 |
| 6 | 4.76 | 4.53 | 4.39 | 4.28 | 4.00 | 3.87 | 3.67 |
| 12 | 3.49 | 3.26 | 3.11 | 3.00 | 2.69 | 2.54 | 2.30 |
| 20 | 3.10 | 2.87 | 2.71 | 2.60 | 2.28 | 2.12 | 1.84 |
| $\infty$ | 2.60 | 2.37 | 2.21 | 2.10 | 1.75 | 1.57 | 1.00 |

Adapted from Miller and Miller (2005)

[a]The $p$-value is defined as the probability of the results of an experiment deviating from the null by as much as they did or greater if the null hypothesis is true. Traditionally, the cutoff value to reject the null hypothesis is 0.05, which means that, when there is no difference, a value as high as test statistic is expected to be less than 5% of the time

### *2.4.2 Interlaboratory Comparisons*

The analysis of the same type of sample is carried out by several laboratories, whose objective is to verify if the result obtained by the laboratory that is developing the method is reproducible.

### 2.4.3 Systematic Evaluation of Factors Influencing Results

It is important that you have a good knowledge of the measurement process to evaluate the possible sources of interference in the final result and it should ideally be done continuously.

### 2.4.4 Evaluation of Uncertainty of Results Generated

According to the International Vocabulary of Metrology, the uncertainty of a measurement is a parameter associated with the result that characterizes the dispersion of the values obtained around the mean, since there are associated uncertainties in each measurement process (Bureau International des Poids et Mesures (BIPM) 2012). The combined total uncertainty or standard uncertainty, $u$, is the sum of the uncertainties generated by the various components of the measurement process, each expressed as a standard deviation. Having established a confidence level, the expanded combined uncertainty, $U$, is determined by the confidence interval criterion, using a coverage factor, $k$. Most of the time, we use $k = 2$, corresponding to the confidence level of approximately 95% (Olivieri et al. 2006). The measurement of uncertainty should not be confused with the error. The error is defined as the difference between the measured value and the true value.

$$u = U/k \tag{2.13}$$

### 2.4.5 Repeatability and Reproducibility

These two terms are frequently observed in metrology and in analytical chemistry when we need to evaluate the reliability of analytical results for intra- or interlaboratory studies for quality control and quality assurance (Sect. 2.6 ahead).

According to the International Union of Pure and Applied Chemistry (IUPAC) (2017), we can define as follows:

- *Repeatability*: The closeness of agreement between independent results obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory, and after short intervals of time). The measure of repeatability is the standard deviation qualified as *repeatability standard deviation*.
- *Reproducibility*: The closeness of agreement between independent results obtained with the same method on identical test material but under different conditions (different operators, different apparatus, different laboratories, and/or

after different intervals of time). The measure of reproducibility is the standard deviation qualified as *reproducibility standard deviation*.

### 2.4.6 *Accreditation of an Analytical Laboratory for Environmental Analysis*

Accreditation provides independent confirmation of competence. For an environmental analytical laboratory, it aims to guarantee the reliability of its results issued against quality parameters established and evaluated by a recognized accrediting body. It is required for an agency or a official body to accept its results.

At present, accreditation is one of the main requirements for the performance of an environmental analytical laboratory, taking into account the fact that it accredits the quality, since the accredited laboratory complies with the norm ISO/IEC 17025 (International Standard Organization (ISO) 2005). There are cases that Good Laboratory Practices (GLPs) (Organisation for Economic Co-operation and Development (OECD) 1998) should also be considered in the accreditation process—such as for studies on the registration of pesticides; however, this is not the main focus of environmental analyses. Therefore, accreditation according to ISO/IEC 17025 (International Standard Organization (ISO) 2005) should be the motto of the quality of laboratories carrying out environmental analyses.

Figure 2.4 describes, in a simplified way, an accreditation process that can be applied, among other types of analysis, to the environmental ones. Note that accreditation takes place for a predefined analytical scope. That is, the fact that the laboratory is accredited in polyaromatic hydrocarbon (PAHs) analyses in water does not mean that, for example, it is accredited to perform analyses of organophosphorus pesticides in the same matrix; if not, it should request new accreditation to attend the second case. More information about accreditation process can be obtained on the website of the International Accreditation Forum (International Accreditation Forum (IAF) 2017).

## 2.5 Chemometrics

In some applications, an analytical methodology alone is not sufficient to provide qualitative or quantitative information of the sample, using only data such as the intensity of absorption or emission, and/or the region of absorption of the electromagnetic spectrum—called *univariate analysis*. Often, the analysis is associated with chemometric tools to provide the best information.

Chemometrics can be understood as an area of knowledge of chemistry that uses mathematic models, along with formal logic to interpret and predict data, thus extracting the maximum of relevant information. It is largely used for spectroscopic

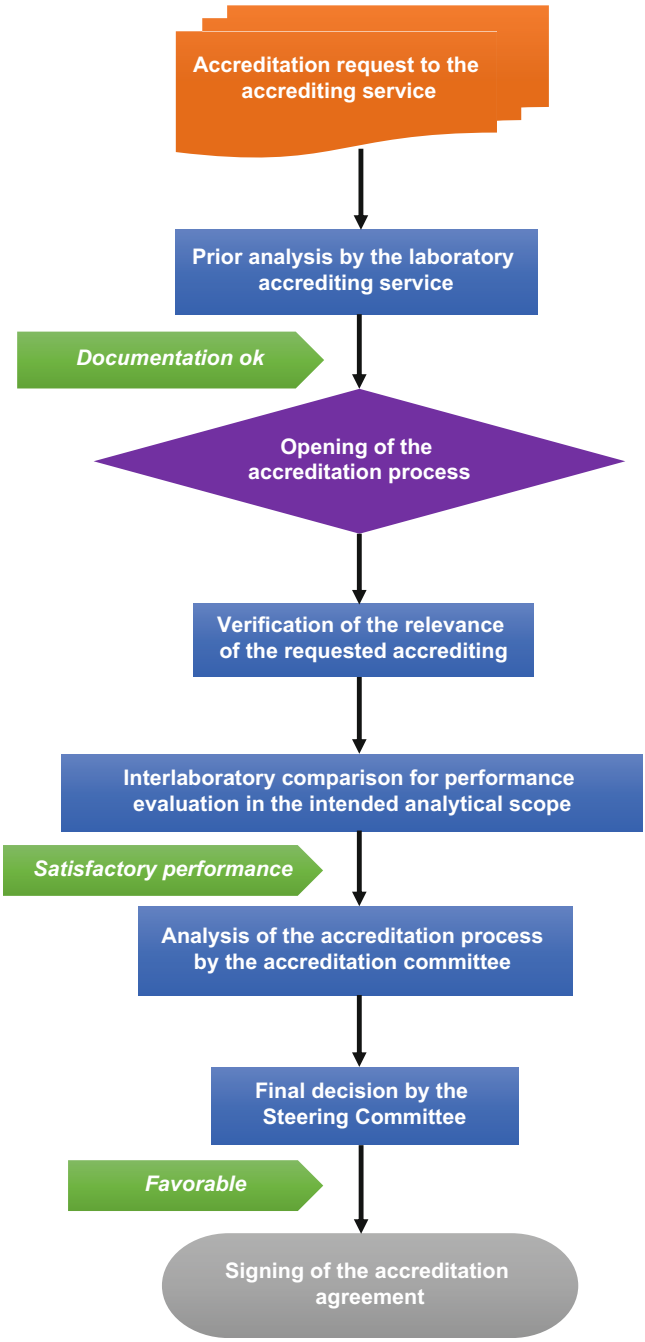


**Fig. 2.4** Simplified flowchart of an accreditation process for an environmental analytical laboratory. Adapted from National Institute of Metrology, Quality and Technology (INMETRO) (2017)

and chromatographic data—in the case of spectroscopic data, each wavelength is a variable. Spectra or complete chromatograms, parts of them, or selection of variables can be used. Since several variables are treated at the same time, the data analysis is called *multivariate analysis*. In order to carry out the multivariate analysis, the data are first organized in matrix form, called matrix $X$ of original data, where the columns correspond to the predictor variables (such as absorbance) and the lines correspond, for example, to the concentration of an analyte (Martens and Naes 1989).

After organizing the data in the matrix, sometimes it is necessary to pre-process, eliminating irrelevant information or standardizing the data. The objective of the multivariate analysis can be from an exploratory analysis to the quantification of an analyte (Brereton 2003). The exploratory analysis is performed with the objective of obtaining initial information from a set of samples, such as the formation of clusters according to a certain chemical property. The main chemometric tool used in the exploratory analysis is the principal component analysis (PCA). When it is desired to verify similarities between samples of a certain class, samples are classified, with the most common methods being *k*-nearest neighbor (KNN), linear discriminant analysis (LDA), hierarchical cluster analysis (HCA), and soft independent modeling of class analogy (SIMCA). When it is intended to predict analyte concentration, calibration models are constructed, with patterns of known concentration and working range that contemplate the analyte concentration. The most widely used method for this purpose is partial least squares (PLS). For instance, Tables 2.3 and 2.4 illustrate the application of PCA on analytical data. Initially, Table 2.3 presents data for a fluorescence hypothetical analysis.

From the data of Table 2.3 we obtain the *covariance matrix*—a joint variance[1] of two variables—, in Table 2.4.

This shows that, for example, the covariance for the fluorescence intensities at 350 and 400 nm is −1.15909. The table also gives the variances of the fluorescence intensities at each wavelength along the leading diagonal of the matrix. For example, for the fluorescence intensities at 350 nm the variance is 2.75. We can consider this kind of information in a practical way to understand the propagation of errors, and consequent reliability, for a certain analysis.

Chemometrics application for quantitative and qualitative purposes can be used (Szymánka et al. 2015):

- *For qualitative results*: compound identification, compound classification, and sample classification
- *For quantitative results*: sample calibration and quantitative structure—activity relationship (QSAR).

Hurtado-Sánchez et al. (2015) applied multivariate calibration in the analysis of EPs (carbamazepine, ofloxacin, piroxicam, ibuprofen, diclofenac, salicylic acid, and

[1]Variance is the square of the standard deviation ($s$); covariance is the sum of variance for a certain measurement.

**Table 2.3** Relative intensities of fluorescence emission at four different wavelengths (300, 350, 400, and 450 nm) for 12 compounds, A–L

| | Wavelength (nm) | | | |
|---|---|---|---|---|
| Compound | 300 | 350 | 400 | 450 |
| A | 16 | 62 | 67 | 27 |
| B | 15 | 60 | 69 | 31 |
| C | 14 | 59 | 68 | 31 |
| D | 15 | 61 | 71 | 31 |
| E | 14 | 60 | 70 | 30 |
| F | 14 | 59 | 69 | 30 |
| G | 17 | 63 | 68 | 29 |
| H | 16 | 62 | 69 | 28 |
| I | 15 | 60 | 72 | 30 |
| J | 17 | 63 | 69 | 27 |
| K | 18 | 62 | 68 | 28 |
| L | 18 | 64 | 67 | 29 |
| Mean | 15.75 | 61.25 | 68.92 | 29.25 |
| Standard deviation | 1.485 | 1.658 | 1.505 | 1.485 |

Adapted from Miller and Miller (2005)

**Table 2.4** Covariance matrix for the data from Table 2.3

| | $\lambda$ (nm) | | | |
|---|---|---|---|---|
| $\lambda$ (nm) | 300 | 350 | 400 | 450 |
| 300 | 2.20455 | | | |
| 350 | 2.25000 | 2.75000 | | |
| 400 | −1.11364 | −1.15909 | 2.26515 | |
| 450 | −1.47727 | −1.70455 | 1.02273 | 2.20455 |

Adapted from Miller and Miller (2005)

flufenamic acid) in waters using excitation–emission photoinduced fluorescence. They proved that the proposed analytical strategy was simpler and greener than chromatographic methods, with the required quality of the results.

Chemometrics does apply not only to measurements, but also to extractions. Because it is based on multiparametric analyses, it allows to evaluate the effect of the variation of the operational parameters on the recovery percentage values of the extraction method. It is possible, for example, to verify among several extraction methods the most suitable for a group of analytes, or the effect of the environmental matrices on the analyte group against more than one extraction method—it is very useful in environmental analysis. Becerra-Herrera et al. (2018) applied chemometrics to optimize the extraction of parabens in water samples resulting in a fast and lower volume-dependent methods by means of the use of rotating-disk sorptive extraction.

## 2.6 Quality Control and Quality Assurance (QA/QC)

After development and validation, the analytical method requires permanent control. It is of extreme relevance, since it allows verifying the need for a revalidation. In general, a revalidation must be carried out, with one of the following situations (International Standard Organization (ISO) 1994):

- Introduction of a new analytical method in place of the previously validated one
- Exchange of a particular reagent for another of different brand that has lower purity and quality specifications
- Preventive or corrective maintenance in an instrument used in the methodology, altering the original technical configurations of the manufacturer
- Changes in work concentration of the analytical method, and changes not predicted in parameters of the analytical method in the original robustness test

The use of the previously described figures of merit (Sect. 2.2) is essential for such methodological control.

According to the US Environmental Protection Agency (EPA) (2017), quality assurance/quality control measures are those activities that are undertaken to demonstrate the *accuracy* (how close to the real result) and *precision* (how reproducible results are)—these figures of merit were seen in Sect. 2.2. Quality assurance (QA) generally refers to a broad plan for maintaining quality in all aspects of a program. This plan comprises proper documentation of all procedures, training of staff, study design, data management and analysis, and specific quality control measures. Quality control (QC) consists of the steps to determine the validity of specific sampling and analytical procedures with internal (e.g., field blank, lab replicates, spike samples, calibration blank, and calibration standards) and external (e.g., internal field duplicates, split samples) checks. The assessment of the overall precision and accuracy of the generated data, after the analyses, is the *quality assessment*.

A quality management system is constituted by the followed components (Prichard and Barwick 2007):

- Management structure and responsibility
- Third-party assessment
- Annual review (by senior management)
- Auditing (internal and external)
- Training (internal and external)
- Records (validation, calibration, quality control, complaints)
- Documentation (central and local)

It is relevant to highlight the GLPs (Organisation for Economic Co-operation and Development (OECD) 1998) as the reference of QA in studies involving environmental pollutants and the norm ISO/IEC 17025 (International Standard Organization (ISO) 2005) as the reference of competency requirements, according to a quality management system, for analytical laboratories.

## 2.7 Green Analytical Chemistry

The 12 fundamental principles of green chemistry (GC) are as follows (ACS Green Chemistry Institute 2017):

1. *Prevention*: It is better to prevent waste than to treat or clean up after it has been created.
2. *Atom economy*: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. *Less hazardous chemical syntheses*: Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. *Designing safer chemicals*: Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. *Safer solvents and auxiliaries*: The use of auxiliary substances (e.g., solvents, separation agents) should be made unnecessary wherever possible and innocuous when used.
6. *Design for energy efficiency*: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. *Use of renewable feedstocks*: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. *Reduce derivatives*: Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. *Catalysis*: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. *Design for degradation*: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. *Real-time analysis for pollution prevention*: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. *Inherently safer chemistry for accident prevention*: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Armenta et al. (2008) have discussed the term *green analytical chemistry*, its milestones, and examples of application, namely:

- Sample treatment
- Oriented scanning methodologies
- Alternatives to toxic reagents
- Waste minimization

- Recovery of reagents
- The online decontamination of wastes
- Reagent-free methodologies

The EP analyses should be based on the 12 principles of green chemistry (Anastas and Werner 1998) as the context of their application is reflected in the sustainability of the raw materials and processes. For instance, the application of seven of the most representative principles for analytical chemistry will contribute to achieving a more sustainable analytical methodology.

Waste prevention, safe solvents and auxiliaries, energy efficiency, and inherently safer chemistry for accident prevention are obvious requirements for all chemical operations. Safer chemicals, reduction of derivatives, and use of catalysts should be taken into account for each analysis because each analytical process has its own technical particularities. For example, the use of real-time analysis for pollution control is a good opportunity for technological development in analytical chemistry in the use of an in situ system for effluent analyses (gaseous and liquids). In a large number of cases it is not possible to apply all of these principles due to the particularities of either the sample or the matrix, but it is very important to consider these individually in an analytical process. This exercise will ensure the "greening" of the analysis.

As a practical guidance, De la Guardia and Garrigues (2011) established the main objectives to be considered in green analytical chemistry:

- Simplification
- The selection of reagents to be avoided based on toxicity, renewability, or degradability data
- The maximization of information
- The minimization of consumables, taking into consideration the number of samples, volumes or masses of reagents, and energy consumption
- The detoxification of wastes

These objectives will define the best strategy to be applied as a result of the principles of green chemistry. Furthermore, the application of green chemistry principles already permeates toxicology for the studies of environmental pollutants, as demonstrated by Crawford et al. (2017), which can promote the reduction of animal testing.

## 2.8 Conclusions

Developing and validating are required steps to assure the correct application of an analytical method for EP analyses.

On the other hand, mathematic methods, especially statistics, offer the basis for data treatment and interpretation.

Furthermore, QA/QC and green chemistry should be both considered for a best analytical approach.

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# Chapter 3
# Analytical Techniques


## 3.1 Concepts of Classical and Instrumental Techniques

The analytical techniques applied in the quantification of the analytes—the main objective of this book—can be divided into two classes: the *classical techniques* based on the measurement of mass, moles, and charge—which provide absolute values—and the *instrumental techniques*, which work with values expressed as mg $L^{-1}$, mg $kg^{-1}$, μg $m^{-3}$, and so on.

Until the beginning of the twentieth century, chemists used the separation of analytes by techniques such as extraction, precipitation, or distillation. For qualitative analysis, these separated analytes were treated with appropriate reagents, yielding compounds which could be identified by properties such as solubility, color, melting points, and boiling. The quantitative analysis was done using reasonably simple and good precision techniques that are used up to the present day, such as volumetry (volume measurement) and gravimetry (mass measurement)—these are typical examples of classical techniques.

Since then, different aspects from those observed by the classical techniques have begun to be investigated and several experiments have been carried out to measure the analytes from some particular physicochemical properties, usually associated with phenomena such as the absorption and emission of radiation, which are the principles of instrumental techniques such as atomic spectrometry and molecular spectroscopy. These findings have boosted the development of a great diversity of instruments that are employed in this class of techniques. Instrumental techniques are generally faster than classical techniques and are employed in the determination of low concentrations of analyte as trace concentrations at or below ng $L^{-1}$/ng $kg^{-1}$ values.

The following equations express the fundamentals of these two sets of techniques:



S. Vaz Jr., *Analytical Chemistry Applied to Emerging Pollutants*,
https://doi.org/10.1007/978-3-319-74403-2_3

**Table 3.1** Physical properties employed in the most commonly used analytical techniques in chemical analysis of environmental matrixes

| Properties | Instrumental techniques |
|---|---|
| Absorption of radiation | Spectrophotometry and photometry (ultraviolet and visible)<br>Atomic spectrometry<br>Infrared spectroscopy (near, medium, and far) |
| Electric current | Voltammetries (cyclic, square wave, anodic, cathodic, polarography) |
| Emission of radiation | Emission spectroscopy (X-ray, ultraviolet, and visible)<br>Optical emission spectrometry<br>Fluorescence (X-ray, ultraviolet, and visible) |
| Mass | Gravimetry |
| Electric potential | Potentiometry |
| Mass/charge ratio | Mass spectrometry |
| Refraction of radiation | Refractometry and interferometry |
| Electrical resistance | Conductometry |

Modified from Skoog et al. (2014)

$$A_S = kn_A \tag{3.1}$$
$$A_S = kC_A \tag{3.2}$$

Equation (3.1) applies to classical techniques, where $A_S$ is the measured signal—or response—of the analyte, $k$ is the proportionality constant to be standardized, and $n_A$ is the number of moles, charge, or grams obtained for the measurement. Equation (3.2) applies to instrumental techniques, where $A_S$ is also the measured signal (or response) of the analyte, $k$ is again the proportionality constant to be standardized, and $C_A$ is the relative concentration of the measured analyte. However, some spectroscopic techniques treated in this chapter do not obey these two concepts, since they provide information about the structural characteristics of the sample.

In Table 3.1 are listed some physical properties explored by the analytical techniques in order to provide the response of the measurement.

Instrumental techniques measure a physical phenomenon resulting from a molecular or an atomic property that will be qualitatively or quantitatively related to the analyte; that is, the physical phenomenon will produce a signal that will be directly correlated to the presence or concentration of the analyte in the sample.

Those techniques from Table 3.1—commonly considered *detection techniques*—can be hyphenated with *separation techniques*, as chromatography or electrophoresis. It will:

- Minimize or eliminate matrix effects on the final result
- Improve the analyte signal
- Decrease the amount of sample and residues generated during the analytical process
- Decrease time

This chapter describes detection, separation, and hyphenated techniques. Furthermore, other techniques and technologies of highlighted importance for EP analysis are treated, as sensors, probes, high-throughput, bioassays, extraction, and cleanup.

## 3.2 Spectroscopic, Spectrophotometric, and Spectrometric Techniques

This diverse set of analysis techniques is functionally based on the extent of absorption or emission of electromagnetic radiation by the analyte (Fig. 3.1). The techniques are classified according to the wavelength or wave number of the spectral region. Table 3.2 shows the main regions of the electromagnetic spectrum as a function of wavelength ($\lambda$), indicating which types of energy transitions are produced when the radiation reaches the sample. According to the spectral region, we have different interactions of incident radiation with matter and from there different techniques can be developed and applied.

Electromagnetic radiation exhibits wave and particle properties, while wave has characteristics like speed, wave number, and frequency. It is quite common to use the wave number in $cm^{-1}$ to describe the radiation. The wave number of the electromagnetic radiation ($k$) is directly proportional to its energy and, consequently, to its frequency ($\nu$), as can be evidenced by Eqs. (3.3) and (3.4):

$$E = h\nu \tag{3.3}$$

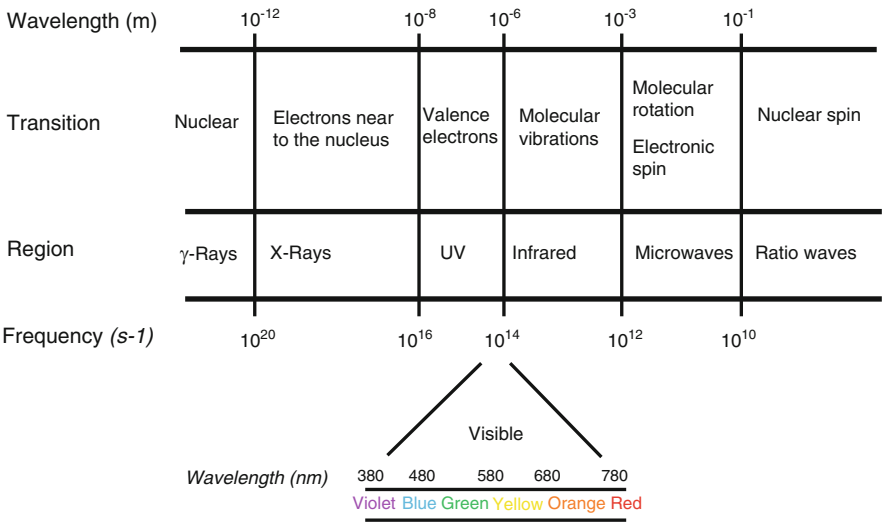


**Fig. 3.1** The electromagnetic spectrum of radiation

**Table 3.2** Approximate regions of the electromagnetic radiation spectrum and the types of energy transitions produced

| Wavelength range ($\lambda$) | Region of the electromagnetic radiation | Associated transitions | Derived techniques for analysis of EPs |
|---|---|---|---|
| $10^{-14}$–$10^{-12}$ m | Gamma ray | Nuclear, in the nucleus of the atom | – |
| $10^{-12}$–$10^{-8}$ m | X-rays | Electronic, in the inner layer of the atom | X-ray fluorescence |
| 200–380 nm | Ultraviolet | Electronic, in the valence layer | Spectrophotometry of absorption or emission (fluorescence) |
| 380 nm (violet)<br>480 nm (blue)<br>530 nm (green)<br>580 nm (yellow)<br>630 nm (orange)<br>730 nm (red) | Visible | Electronic, in the valence layer | Spectrophotometry of absorption or emission (fluorescence) |
| 730–1000 nm | Infrared | Molecular vibration | Fourier-transformed infrared spectroscopy |
| $10^{-3}$–$10^{-1}$ m | Microwaves | Rotation of the electronic spin of the molecule | Nuclear magnetic resonance and electron paramagnetic resonance spectroscopies[a] |
| $10^{-1}$ m–10 km | Radio waves | Nuclear spin of the atom | – |

Adapted from Basset et al. (1989) and Harvey (2000)
[a]For very specific applications. It is not usual for study of pollutants in environmental matrices

$$E = h\,c/\lambda = hck \tag{3.4}$$

where $E$ is the energy (J), $h$ is Planck's constant ($6.626 \times 10^{-34}$ J s), $\nu$ is the frequency (Hz), $c$ is the speed of light ($2998 \times 10$ m s$^{-1}$), $\lambda$ is the wavelength (nm), and $k$ is the wave number (cm$^{-1}$).

It should be remembered that the frequency $\nu$ is directly proportional to $c/\lambda$, while the wave number $k$ is proportional to $1/\lambda$.

The following are the main techniques used for electromagnetic radiation, which can be applied to the EP analyses in environmental matrixes.

### 3.2.1 Absorption of UV-Vis Radiation, or Molecular Spectrophotometry

This technique is widely used for the identification and determination of organic, inorganic, and biological species. Usually, molecular absorption spectra are more complex than atomic absorption spectra due to the higher number of energy states of the molecule compared to the isolated atoms (see ahead in the atomic spectrometry item).

As can be seen in Table 3.1, the UV region of the electromagnetic spectrum is approximately 200–400 nm and the region of the visible is between 400 and 750 nm. The absorption of radiation by molecules in these regions results from the interactions between photons and electrons that participate in a chemical bond, or between electrons that are not bound in atoms like oxygen, sulfur, nitrogen, and halogens. The wavelength where absorption occurs depends on the type of bond that these electrons participate. Electrons shared in single carbon–carbon or hydrogen–hydrogen bonds are so tightly bound that they require high energy at wavelengths below 180 nm and are not observed by the most common methods of analysis. Due to experimental difficulties in working in this region, single-bond spectra are poorly explored. The electrons involved in double and triple bonds are not so strongly trapped and, consequently, they are excited more easily and produce more useful absorption peaks.

Absorption spectroscopy in UV-vis is mainly used in quantitative analysis of several organic compounds containing mainly C=O and C=C bonds, as the intensity of the absorption peaks can be directly correlated to the concentration of the analyte, now called spectrophotometry—it is widely used as a detector after separation by liquid chromatography, to be seen later.

The Lambert-Beer law (Eq. 3.5) correlates the signal intensity at a given wavelength value directly with the analyte concentration, which allows quantitative data to be obtained—it is worth noting that it is necessary to have the respective curve with linear behavior. Figure 3.2 shows a widely used spectrophotometer in aqueous analyses, and in Fig. 3.3 the block diagram for the same system:

$$A = \varepsilon bc \tag{3.5}$$

where $A$ is the absorbed radiation (arbitrary units), $\varepsilon$ is the molar absorptivity of the medium ($cm^{-1}$ L $mol^{-1}$), $b$ is the cell length (cm), and $c$ is the concentration ($mol^{-1}$ L).

The electron transitions give rise to the absorption spectrum as the electron passes from a lower energy state to a higher energy state. In Table 3.3 is described information on electronic transitions and wavelengths of UV absorption of some chemical groups present in the molecules of EPs.

**Fig. 3.2** UV-vis spectrophotometer. Courtesy of Agilent

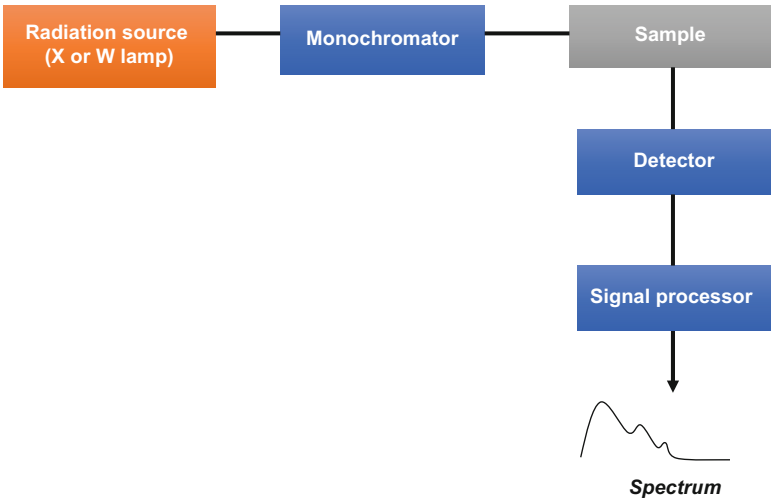


**Fig. 3.3** Simplified block diagram for a UV-vis spectrophotometer

Figure 3.4 shows absorption spectra for organic matter present in the soil. Advantages of UV-vis spectrophotometry are as follows (EAG Laboratories 2017):

- Fast sample analysis
- Suitable for a wide variety of analytes
- Much simpler than chromatographic techniques
- User-friendly interface
- Little maintenance required

Limitations are as follows:

- Subject to fluctuations from scattered light and temperature changes
- Relatively low sensitivity
- Other sample components may cause interferences
- Not as specific as chromatography, for instance
- Requires a relatively large sample volume, >0.2 mL

**Table 3.3** Examples of chemical groups present in EP molecules, which absorb UV radiation, and their associated electronic transitions

| Chemical group | Structure | Electronic transitions | $\lambda_{max}$ (nm), nearly |
|---|---|---|---|
| Carbonyl (ketone) | RR′C=O | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$ | 180<br>271 |
| Carbonyl (aldehyde) | RHC=O | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$ | 190<br>293 |
| Carboxyl | RCOOH | $n \rightarrow \pi^*$ | 204 |
| Amide | $RC{=}ONH_2$ | $\pi \rightarrow \pi^*$<br>$n \rightarrow \pi^*$ | 208<br>210 |
| Conjugated diene | RCH–CH=CH–CHR | $\pi \rightarrow \pi^*$ | 250 |
| Aromatic | $C_6H_6$ | $\pi \rightarrow \pi^*$ | 256 |

Adapted from Settle (1997) and from Pavia et al. (2001)

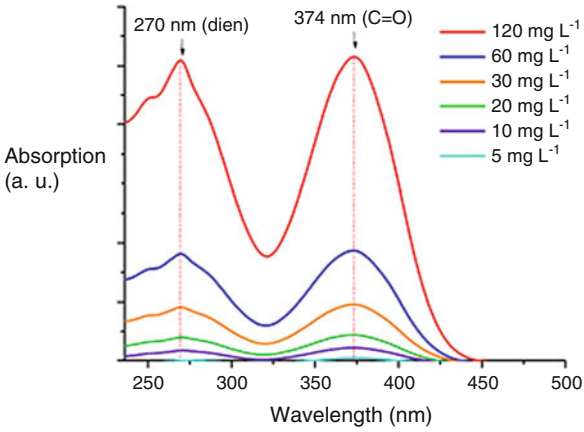


**Fig. 3.4** Absorption spectra in the UV-vis region of organic matter in basic aqueous medium, with absorption bands for conjugated diene (–C=C–C=C–) and carbonyl (C=O). Adapted from Vaz (2010)

### *3.2.2 Emission of UV-Vis Radiation, or Fluorescence*

The process of UV-vis emission, commonly known as fluorescence, occurs when molecules are excited by absorption of electromagnetic radiation, upon returning to the ground state and releasing the excess of energy as photons.

The sample is excited at a given wavelength, called the excitation wavelength, and its emission is measured at a higher wavelength, called the fluorescence wavelength. This phenomenon is usually associated with systems with electrons $\pi$, that is, systems commonly with double bond. Fluorescence usually has a sensitivity and range of work greater than those of UV-vis spectrophotometry. However, it has limited application due to the limited number of systems that fluoresce. It is a technique widely used in the analysis of molecules with aromatic rings, and it is used as a detector after a separation by liquid chromatography. Figure 3.5 shows a fluorescence spectrometer and Fig. 3.6 shows a block diagram. Figure 3.7 shows emission and excitation spectra.


**Fig. 3.5** UV-vis spectrofluorophotometer. Courtesy of Shimadzu

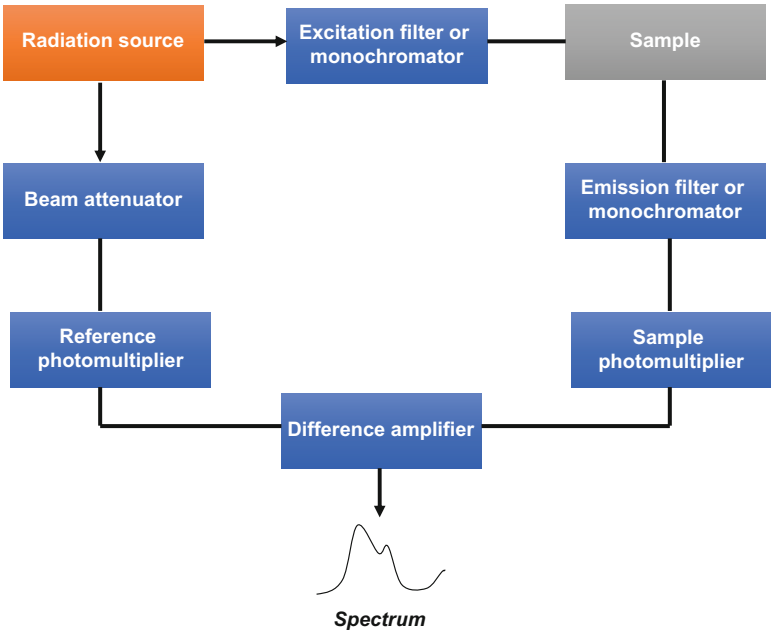


**Fig. 3.6** Block diagram for a UV-vis spectrofluorophotometer

### *3.2.3 Infrared Molecular Spectroscopy*

Vibrational spectroscopy refers to a type of interaction of the radiation with vibrational states of the chemical bonds. Therefore, there is no electronic transition. Here we can highlight infrared (IR) absorption spectroscopy in its three wavelength

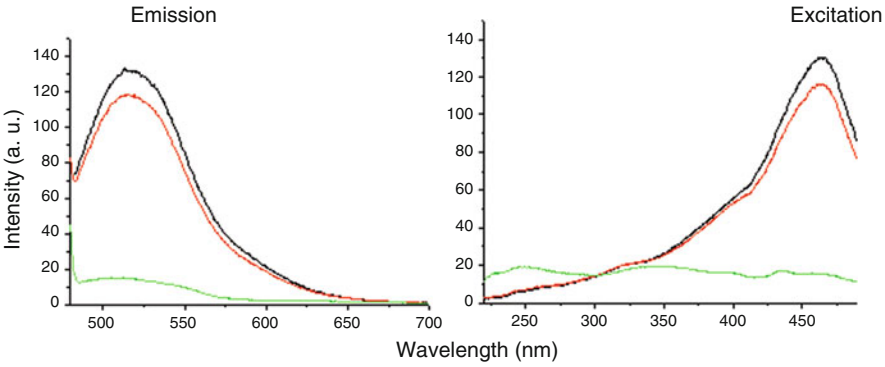


**Fig. 3.7** Fluorescence spectra (emission–excitation modes) of oxytetracycline (OTC, green), humic acid from soil (black), and the product of molecular interaction between both molecules (red). Adapted from Vaz (2010)

ranges: near, medium, and far. Polarity has a direct influence on the IR spectrum, modifying its form.

The electromagnetic region of the IR is located between the visible region and the microwaves, that is, from 12,800 to 10 $cm^{-1}$, remembering that the unit $cm^{-1}$ refers to the wave number. As discussed above, the IR spectrum is subdivided into three regions: near infrared (NIR), medium (MIR, mid-infrared), and far (FIR, far-infrared). The mid-infrared (MIR), which is the most used technique in organic analysis, is divided into two regions: frequency groups, from 4000 up to 1300 $cm^{-1}$, and absorption of functional groups of two atoms, or vibration, of 1300 to approximately 700 $cm^{-1}$, also called *fingerprint*—equipment shown in Fig. 3.8 and its block diagram in Fig. 3.9. In the near infrared (NIR) the radiation is comprised between 12,800 and 4000 $cm^{-1}$. The absorption bands in this region are harmonic or combinations of fundamental stretching bands, often associated with hydrogen atoms—this has been a technique in growing, due to the ease of handling of the sample.

IR spectra are typically employed to identify pure organic compounds or impurities, interactions, and binding formation.

Table 3.4 describes the main possible correlations for the assignment of the absorption bands in the MIR as a function of the type of bound. Figure 3.10 shows an absorption spectrum in this region.

Advantages of FTIR are as follows (EAG Laboratories 2017):

- Capable of identifying organic functional groups and often specific organic compounds.
- Extensive spectral libraries for compound and mixture identifications.
- Ambient conditions (vacuum is not necessary; applicable for semi-volatile compounds).
- Minimum (limit of detection) analysis area: ~15 μm. *Rule of thumb: If you can see the sample by eye, it most likely can be analyzed.*
- Can be quantitative with appropriate standards and uniform sample thicknesses.

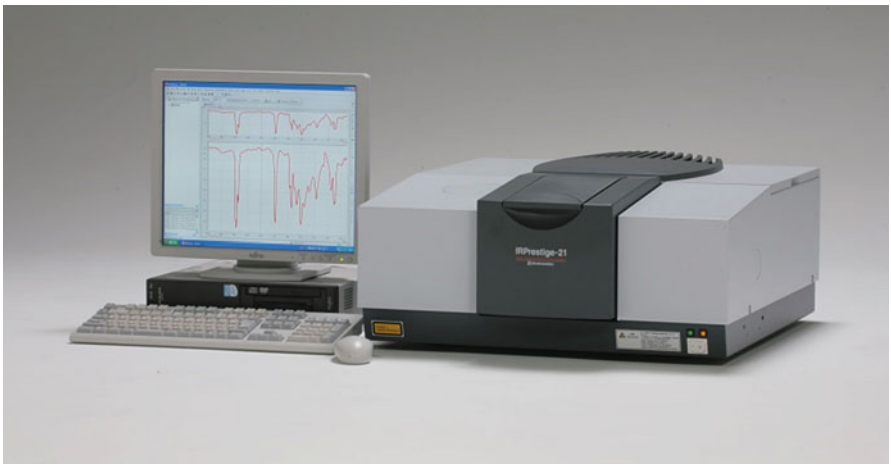

**Fig. 3.8** Medium infrared spectrometer with Fourier transform (FTIR). Courtesy of Shimadzu

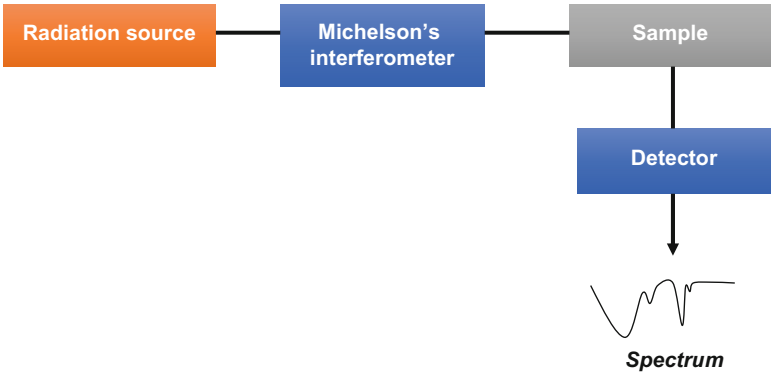


**Fig. 3.9** Simplified block diagram of a medium infrared spectrometer with Fourier transform (FTIR)

Limitations are as follows:

- Limited surface sensitivity (typical limit of detection is a film thickness of 25 nm).
- Only specific inorganic species exhibit an FTIR spectrum (for example silicates, carbonates, nitrates, and sulfates).
- Sample quantitation requires the use of standards.
- Glass absorbs infrared light and is not an appropriate substrate for FTIR analysis.
- Water also strongly absorbs infrared light and may interfere with the analysis of dissolved, suspended, or wet samples.

**Table 3.4** Characteristic bands of deformations and vibrational stretches, which may be present in EPs' organic molecules (e.g., pharmaceuticals, pesticides, personal care)

| Band position ($cm^{-1}$) | Assignment | Intensity |
|---|---|---|
| 3500–3000 | Intramolecular stretching of O–H and N–H | Medium absorption |
| 2940–2900 | Asymmetric stretching of aliphatic C–H | Strong absorption |
| 1725–1720 | Stretching of C=O in COOH and ketones | Strong absorption |
| 1660–1630 | Stretching of amide groups (amide band I) and quinone; C=O stretching of hydrogen bonded to conjugated ketones; stretching of $COO^-$ | Strong absorption |
| 1620–1600 | Stretching of aromatic C=C; stretching of $COO^-$ | Medium-to-weak absorption |
| 1460–1450 | Stretching of aromatic C–H | Medium absorption |
| 1400–1390 | Deformation of O–H and stretching of C–O and OH phenolic; deformation of C–H in $CH_2$ and $CH_3$; asymmetric stretching of $COO^-$ | Medium absorption |
| 1170–950 | Stretching of C–O in polysaccharides or polysaccharide-like compounds | Strong absorption |

Adapted from Stevenson (1994) and Engel et al. (2011)

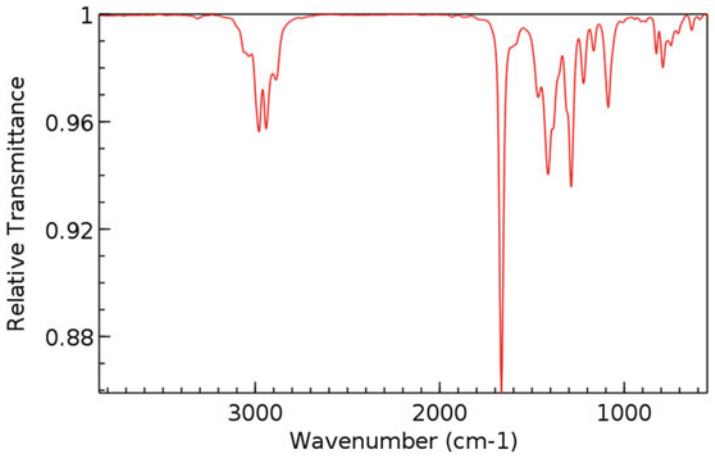


**Fig. 3.10** FTIR absorption spectra of *N*,*N*-diethyl-*m*-toluamide (DEET) molecule, with the sample prepared in KBr pellet; resolution of 4 $cm^{-1}$. Band assignments: 3000 $cm^{-1}$ = intramolecular stretching of N–H; 1600 $cm^{-1}$ = stretching of $–NH_3^+$; 1540 $cm^{-1}$ = stretching of aromatic C–H; 1300 $cm^{-1}$ = deformation of C–H in $CH_2$ and $CH_3$; 1100 $cm^{-1}$ = stretching of C=C–H. Adapted from National Institute of Standard and Technology (2017)

- Simple cations and anions, e.g., $Na^+$ and $Cl^-$, do not absorb FTIR light and hence cannot be detected by FTIR; identification of mixtures/multiple sample components may require additional laboratory preparations and analyses.
- Metals reflect light and cannot be analyzed by FTIR.

Cincinelli et al. (2017) applied FTIR to study the occurrence and extent of microplastics in the surface waters of the Ross Sea (Antarctica). The presence of different types of microplastics was confirmed, with predominant abundance of polyethylene and polypropylene.

### *3.2.4 Atomic Absorption Spectrometry*

When electromagnetic radiation is applied to atoms in the gaseous state, some of these atoms can be brought to a level of energy that allows the emission of the characteristic radiation of that atom. However, most can remain in the ground state and absorb energy, which in general would correspond to the energy in the gaseous state at the wavelength they would emit if they were excited from the ground state. Thus, when atoms absorb energy, an attenuation of the intensity of the radiation beam occurs. Thus, atomic absorption spectrometry (AAS) is based on the absorption of the electromagnetic radiation by gaseous atoms in the ground state.

AAS is widely used in the analysis of metals, semimetals, and nonmetals in all environmental matrices. There are three different types of atomizer: combustion flame of different gases (hydrogen, acetylene, or natural gas), graphite furnace (or electrothermal), and cold mercury vapor (for determination of the mercury present by reduction to elemental mercury), with the application of each of them depending mainly on the analyte to be determined and the LOD required by the method—the flame AAS is the most common technique. The radiation absorbed has a direct relation with the analyte concentration that turns this technique very useful in quantitative analyses of metals, especially for environmental analysis.

In general, the spectra obtained by AAS are simpler than those obtained by atomic or optical emission (see ahead). A particular chemical element absorbs energy at certain wavelengths. Typically, for analysis of an element, the highest absorption wavelength is chosen if there is no interference due to the absorption of the radiation by another element at that wavelength. Due to its simplicity and cost, AAS is the most widely used atomic method. Figure 3.11 shows a spectrometer and Fig. 3.12 its block diagram: source—needed to provide specific radiation (e.g., hollow cathode lamp); atomizer—used to generate gaseous atoms (flame atomization and electrothermal); monochromator—used to select the desired wavelength; the detection system, and, finally, the data recording system.

In Fig. 3.13 are highlighted those elements that are detectable by AAS.


**Fig. 3.11** AAS spectrometer. Courtesy of Shimadzu

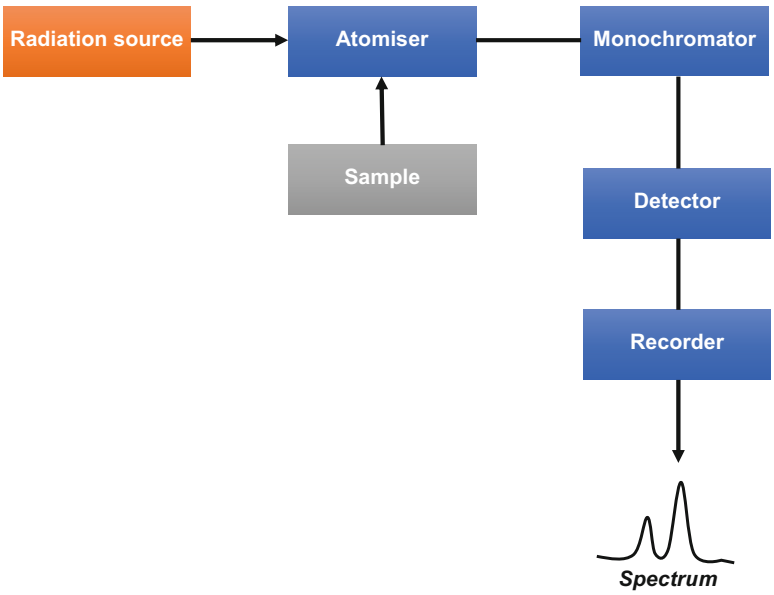


**Fig. 3.12** Block diagram for an AAS equipment

### *3.2.5 Atomic Emission Spectrometry or Optical Emission Spectrometry*

Atomic emission spectrometry (AES), or optical emission spectrometry (OES), is based on the measurement of the emission of the electromagnetic radiation in the UV-visible region by neutral and ionized atoms, not in excited state, being widely

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mb | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

**Fig. 3.13** Elements detectable by AAS are highlighted in pink in this periodic table. Adapted from New Mexico State University (2017)

**Fig. 3.14** ICP-OES spectrometer. Courtesy of Shimadzu

used in elemental analysis. The most common OES system uses an argon plasma torch that can reach up to 9000 K (inductively coupled plasma, ICP) for the electron excitation in gaseous state—the equipment shown in Fig. 3.14. ICP can also be coupled to a quadrupole mass analyzer (ICP-MS); it offers extremely high sensitivity to a wide range of elements.

The technique has high stability, sensitivity, low noise, and low background emission intensity. However, because it involves relatively expensive methods that require extensive operator training, it is not as applied as AAS. All metals or nonmetals of environmental interest, determined by AAS, can be determined by OES—the latter can favor, for some elements, the achievement of lower values of LOD and LOQ.

Advantages of OES are as follows (EAG Laboratories 2017):

- Bulk chemical analysis technique that can determine simultaneously up to 70 elements in a single-sample analysis.
- The linear dynamic range is over several orders of magnitude.
- Instrumentation is suitable to automation, thus enhancing accuracy, precision, and throughput.

Limitations are as follows:

- The emission spectra are complex and inter-element interferences are possible if the wavelength of the element of interest is very close to that of another element.
- In mass spectrometry, determination and quantification of certain elements can be affected by interference from polyatomic species, matrix elements, and atmospheric elements.
- The sample to be analyzed must be completely digested or dissolved prior to analysis in order to determine the element(s) of interest.

### *3.2.6 X-Ray Emission Spectrometry*

This technique allows a rapid and nondestructive multielement analysis for solid and liquid samples (identification and quantification). When an atom is excited by the removal of an electron from its inner layer, it emits X-rays when it returns to its ground state; such radiation has a typical signal intensity for each element, which is used in the analysis (Fig. 3.15). Figure 3.16 shows an X-ray fluorescence (XRF) spectrometer.

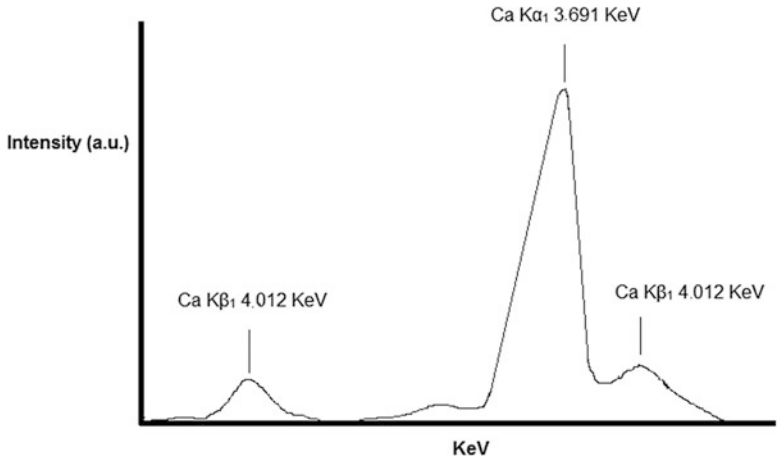


**Fig. 3.15** X-ray emission spectra of calcium in a sample


**Fig. 3.16** X-ray fluorescence spectrometer. Source: Internet

There are two XRF systems available: the wavelength-dispersive spectrometer (WDXRF) and the energy-dispersive spectrometer (EDXRF); the latter has higher signal throughput, which enables small area analysis or mapping.

Figure 3.17 presents a block diagram for an XRF equipment.

Advantages of XRF are as follows (EAG Laboratories 2017):

- Nondestructive technique
- Can analyze areas as small as ~150 μm
- Can analyze any solid material
- Sampling depth ranging from a few micrometers to several millimeters depending on the material

Limitations are as follows:

- Cannot detect elements lighter than Al using small spot EDXRF
- Highest accuracy measurements require reference standards similar in composition and/or thickness to the test sample

Miller et al. (2005) used micro X-ray fluorescence to study heterogeneous soil particle samples. Both single particle and bulk analyses must be performed on the

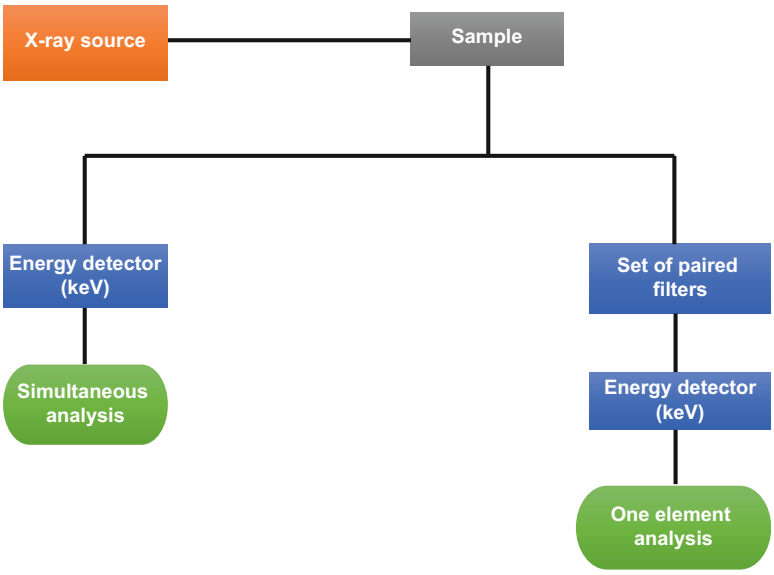


**Fig. 3.17** Simplified block diagram of an XRF system

sample to insure full elemental characterization due to the heterogeneous chemical constitution of soil particles.

## 3.3 Mass Spectrometry

Mass spectrometry (MS) is essentially a technique for detecting molecular components having the mass/charge ratio ($m/z$) as the unit of measurement. Depending on the ionization technique used, analytes may present with one or multiple charges. In single-charge components, the $m/z$ ratio corresponds to the total mass of the ion in Daltons. In cases where ions with two or more charges are more frequent, the calculation of the original ion mass will depend on deconvolutions of the original signal.

The direct analysis of the sample in the mass spectrometer seldom generates results that can be considered quantitatively, even if the sample is pure. This is a consequence of the high sensitivity of the technique and the efficiency of the ionization process, besides the intrinsic characteristics of each sample that allow greater or lesser easiness of ionization.

MS is often associated with a separation technique; usually gas chromatography or liquid chromatography is the hyphenated technique where a separation technique coupled to a detection and quantification technique is used. In this case, the mass spectrometer functions as a detector. Such hyphenated techniques make it possible to separate complex mixtures, identify the components, and quantify them in a single


**Fig. 3.18** Mass spectrometer with *time-of-flight mode*. Courtesy of Brüker

operation. Almost all measurements of MS are done under high vacuum, as this allows the conversion of most of the molecules into ions, with a lifetime enough to allow their measurement. The mass spectrometer (Fig. 3.18) consists essentially of three components: ionization source, mass analyzer, and ion detector, according to the block diagram of Fig. 3.19.

There are several commercially available ionization systems: electron impact ionization (EI), chemical ionization (CI), fast atom bombardment (FAB), particle beam bombardment (PBB), matrix-assisted laser desorption ionization (MALDI), electrospray ionization (ESI), atmospheric pressure photoionization (API), and atmospheric pressure chemical ionization (APCI). For high-molecular-weight, non-volatile, and heat-sensitive materials, such as some EP molecules, MALDI, APCI, and FAB techniques are used. The most common analyzers are quadrupole, quadrupole ion trap, and time-of-flight tube. The detection is done by electron multiplier tube.

Figure 3.20 presents a fragmentogram for an EP molecule.

Advantages of high-resolution MS are as follows (EAG Laboratories 2017):

- Provides comprehensive accurate mass information in a single analysis by $MS^n$ technology

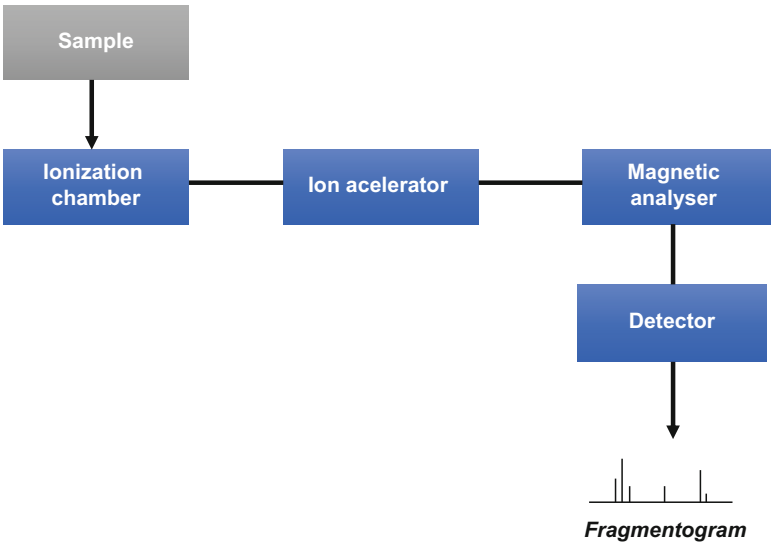


**Fig. 3.19** Block diagram of a mass spectrometer

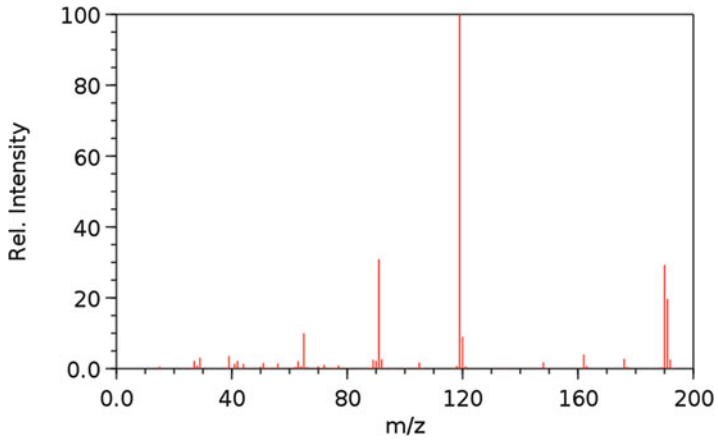


**Fig. 3.20** Fragmentogram of the *N*,*N*-diethyl-*m*-toluamide (DEET) molecule obtained by electron ionization (EI) technique. National Institute of Standard and Technology (2017)

- Detects more low-level components in complex samples
- Designed and well suited for large-molecule analysis

Main limitation is that a large volume of data to process requires experienced mass spectrometrist to operate.

## 3.4 Chromatographic Techniques

Chromatography is, conceptually, a technique of separating components from a sample according to their *retention time*, for further identification and determination/quantification; an instrumental approach is used. The following equations conceptually define the chromatography and its application.

Firstly, resolution is the quantitative measure of the degree of separation between two peaks A and B, referring to two different molecules, and is defined as

$$R = t_{R(B)} - t_{R(A)}/0.5\ (W_B + W_A) \tag{3.6}$$

where $t_{R(A)}$ is the retention time for the peak A, $t_{R(B)}$ is the retention time for the peak B, $W_A$ is the baseline width for the peak A, and $W_B$ is the baseline width for the peak B.

In Fig. 3.21 we have a conceptual chromatogram, with the representations of the terms used in Eq. (3.6).

Separation between peaks A and B is governed by the *partition coefficient*, $K_D$, which measures the solute distribution, or analyte, from its concentration in the *mobile phase* ($S_m$) and in the *stationary phase* ($S_s$), in a condition of equilibrium:

$$K_D = [S_m]/[S_e] \tag{3.7}$$

Thus, the higher the $K_D$ value the lower the $t_R$ of the analyte, and vice versa.

The efficiency of a separation column for the chromatographic analysis can be verified by the number of *theoretical plates* of the column:

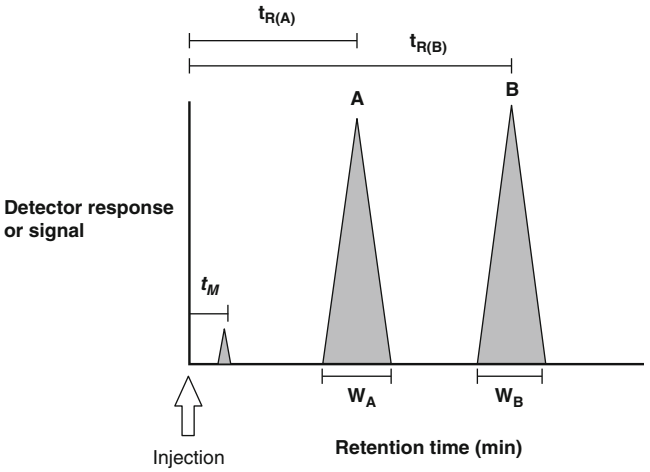


**Fig. 3.21** Description of the components of a chromatogram, with the presence of two peaks corresponding to two different molecules (A and B). The dead time ($t_M$) is the time required for the solute not retained in the column to move from the injection point to the detector, not being considered in the quantitative interpretation of the chromatographic analysis

$$N = 16(t_R/W)^2 \tag{3.8}$$

The column efficiency increases with the increase in the value of $N$, which also leads to an increase in the peak resolution.

In the vast majority of cases, chromatographic techniques are coupled with *detection techniques*—which is known as *hyphenated techniques*—which require an instrumental approach to their understanding and application. As forms of hyphenation, we can mention the following:

- Coupling of solid-phase extraction systems, known as SPE and SPME (solid-phase microextraction)—these systems allow increased extraction performance from equilibrium phenomena, or thermal sorption–desorption or with organic solvents, which may help to reduce LOD and LOQ values.
- Liquid chromatography (LC) coupling with gas chromatography (GC), or vice versa, promoting the so-called multidimensional separation techniques that allow to work with complex mixtures, such as LC-GC, LC-GC×GC, and LC×LC; however, the use of chemometrics for the treatment of the generated data is required for this type of hyphenation.

One way to classify the chromatographic techniques is by the physical form of the mobile and stationary phases. Thus, the first classification would be planar or column—from planar originates the *thin-layer chromatography* and from column *liquid-* and *gas-phase chromatographies*. Table 3.5 provides a description of the functional division categories for gas- and liquid-phase chromatographs.

The division presented above is due to physicochemical equilibrium phenomena, which are those that govern the transfer of analyte mass between the mobile and stationary phases. Partitioning is emphasized here, through the chemisorption (involving covalent bonds) and physiosorption (involving intra- or intermolecular interactions, usually van der Waals forces).

**Table 3.5** Description of categories of chromatographic techniques according to the stationary phase, considering only the case where the separation takes place in chromatographic columns, which is the type of separation most applied in environmental analyses

| General classification | Category | Stationary phase | Equilibrium type |
|---|---|---|---|
| Gas chromatography | Gas–liquid | Liquid bound to solid | Gas–liquid partition |
| | Gas–solid | Solid | Adsorption |
| Liquid chromatography | Liquid–liquid partition | Liquid bound or adsorbed to solid | Liquid–liquid partition (immiscible) |
| | Liquid–solid or adsorption | Solid | Adsorption |
| | Ion exchange | Resin for ion exchange | Ion exchange |
| | Size exclusion | Liquid in the interstices of polymeric solid | Partition or penetration |
| | Affinity | Liquid bound to solid surface | Liquid–liquid partition |

Adapted from Skoog (2014)

### 3.4.1 Gas Chromatography

In gas chromatography (GC) the components of a sample are separated as a function of their partition between a gaseous mobile phase, usually the helium gas, and a liquid or solid phase contained within the column. One limitation of GC is when the analyte to be analyzed is not volatile, or thermally stable, an alternative is the *derivatization*, when the formation of another molecule is from the analyte with lower boiling values. The elution of the components is done by an inert mobile-phase (carrier gas) flow; that is, the mobile phase does not interact with the molecule of analyte.

The modernization of the equipment, through the development of new stationary phases and data processing software, also led to an investment in systems that provide higher speed during the chromatographic analysis. The shortest analysis time has the direct consequence of reducing the cost of the analytical process and increasing the analytical capacity of the laboratory. The increase in the speed of the chromatographic analysis can be related to the reduction of the size of the column, and reduction of its internal diameter, which compensates the loss of resolution in the determinations.

Regarding the choice of the most suitable detector to be used, the nature of the sample (matrix + analyte) should be taken into account. Several detectors are commercially available for use in GC, with thermal conductivity, flame ionization, electron capture, and mass spectrometer detectors being most commonly used. An ideal detector should meet the following characteristics:

- Adequate sensitivity
- Good stability and reproducibility
- Linear response to analytes, extending to several orders of magnitude
- Temperature range from ambient to at least 400 °C
- Ease of use
- Similarity of response to all analytes in the sample

In practice, the detectors do not group all of the features described above. Table 3.6 shows the most common detectors used in GC for environmental analysis and their characteristics.

**Table 3.6** Most common GC detectors for environmental analysis

| Detector | Application | LOD |
|---|---|---|
| Flame ionization detector (FID) | For analysis of carbon compounds | 0.2 pg |
| Thermal conductivity detector (TCD) | Gas analysis | 500 pg |
| Electron capture detector (ECD) | Analysis of halogenated compounds | 5 fg |
| Thermal-ionic detector (TID) or nitrogen-phosphorus detector (NPD) | Analysis of nitrogen and phosphorus compounds | 0.1 pg |
| Mass spectrometer (MS) | Selective for analysis of diverse organic compounds, both polar and nonpolar | <100 pg |

Adapted from Harvey (2000) and Rouessac and Rouessac (2007))
1 pg = $10^{-12}$ g; 1 fg = $10^{-15}$ g

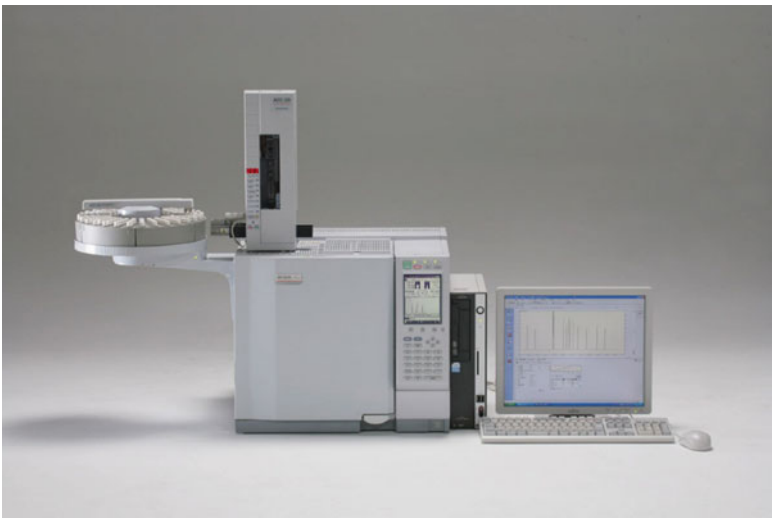

**Fig. 3.22** A GC equipment with automatic injector and a FID detector. Courtesy of Shimadzu

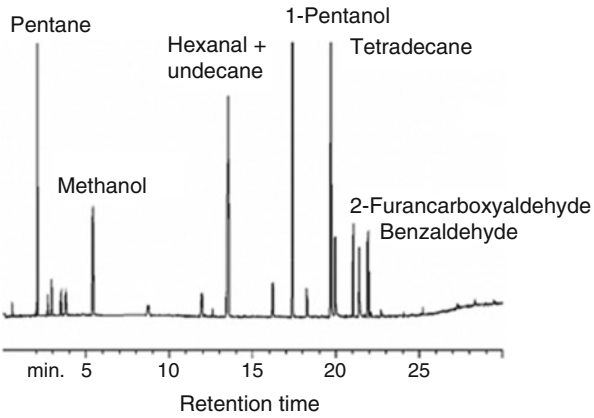


**Fig. 3.23** Chromatogram of a mixture of hydrocarbons, alcohols, and aldehydes from a GC analysis with a FID detector. Courtesy of Shimadzu

Figure 3.22 shows a gas chromatographer with a coupled FID detector, while Fig. 3.23 presents an example of a chromatogram and Fig. 3.24 shows the block diagram of the equipment.

### *3.4.2 Liquid Chromatography*

Liquid chromatography (LC) can be applied in a variety of operating modes, with the best mode depending on the structural characteristics of the analyte to be separated by the chosen analytical method. As shown in Table 3.5, the most commonly used

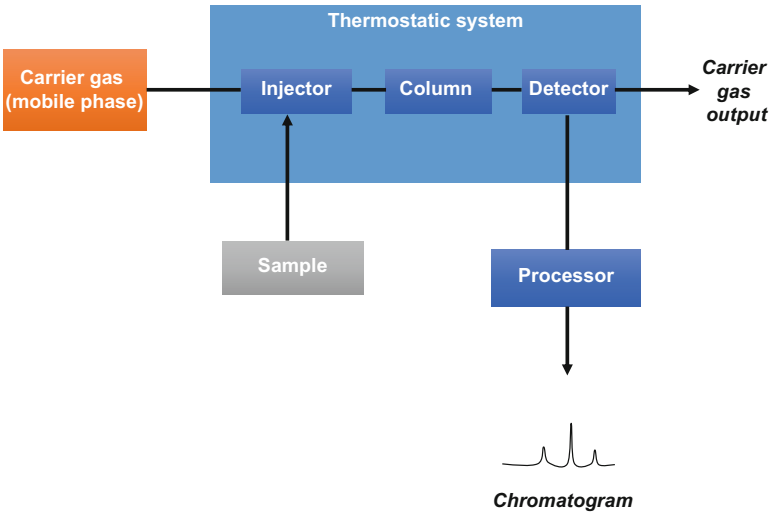


**Fig. 3.24** Block diagram for a GC equipment

modes or categories are partition chromatography, adsorption chromatography, ion-exchange chromatography, size-exclusion chromatography, and affinity chromatography.

### 3.4.2.1 High-Performance Liquid Chromatography

The use of low-pressure and high-pressure columns, called high-performance liquid chromatography (HPLC), outperforms GC in the analysis of semi-volatile and nonvolatile organic compounds. In its many variants, it allows the study of complex mixtures, difficult to separate by other techniques, especially mixtures of biomolecules.

Typically, the HPLC equipment is equipped with two or more solvent reservoirs. Elution with a single solvent or a mixture of solvents of constant composition is called *isocratic elution*, while the use of a mixture of solvents at different polarity, with composition varying in a programmed manner, is a *gradient elution*. Generally, gradient elution improves the efficiency of the separation process. The pumping system is an important component whose function is to ensure a constant and reproducible flow from the mobile phase to the column. They have a pressure of 0.1–350 bar. The columns are generally stainless steel with lengths ranging from 10 to 30 cm and internal diameters between 2 and 5 mm. The column fillings (or stationary phase) typically have particles with diameters between 3 and 10 μm. Systems with particles smaller than 2 μm and pressures in the range of 1000 bar are called ultrahigh-performance liquid chromatography (UHPLC) or ultra-performance liquid chromatography (UPLC)—this mode of liquid chromatography can provide a

higher resolution in a shorter retention time. Stationary phases for most chromatography modes consist of a silica material, or a polymer such as a polysaccharide or polystyrene, with functional groups of interest attached to the surface of this substrate—they may be either *normal phase* (polar stationary phase) type or *reverse phase* (nonpolar stationary phase) type.

Selection of the mobile phase is critical for partitioning, adsorption, and ion-exchange chromatography, and less critical for the other modes. For the solvents used to form this phase, properties such as the UV-vis cutoff wavelength and the refractive index are important parameters when working with UV-vis and/or refractive index detectors. The polarity index (P′) and the eluent force ($\varepsilon^0$) are polarity parameters that aid in choosing the phase for partitioning and adsorption chromatography, respectively.

As for GC, there are several types of detectors available commercially, and the choice usually depends on the type of analyte and the number of analyses required. Detectors may be concentration sensitive, when the analytical signal produced is proportional to the analyte concentration in the effluent or eluted, or mass sensitive, when the signal produced is proportional to the mass flow rate. Table 3.7 lists the main detection systems for HPLC.

Figure 3.25 shows a HPLC equipment, while Fig. 3.26 shows an example of a chromatogram and Fig. 3.27 the block diagram of an HPLC equipment.

### 3.4.2.2 Ion Chromatography

The principle of separation of the ion chromatography (IC) is based on the ion exchange, from the electrostatic attraction between opposing charges—positive and negative. The stationary phase is a polymer resin, such as divinylbenzene bound to polystyrene by cross-linking, with ionic functional groups covalently attached to the resin. The counterion of this ionic grouping, which may be positive or negative, should be displaced by competition with other ions of the same charge, which have greater affinity for the binding site of the functional group attached to the resin. Thus, the exchange resin can be both cationic and anionic. Retention time values will depend on the intensity of the electrostatic attraction of the analyte charge by the binding site present on the resin—higher attraction intensity leads to a longer

**Table 3.7** Characteristics of the main HPLC detectors, which can be used for environmental analysis

| Detector | Application | LOD |
|---|---|---|
| UV-vis absorption or diode array detector (DAD) | Selective for chromophore groups (e.g., C=O and C=C) | 10 pg |
| Mass spectrometer (MS) | Selective for organic and inorganic species | 1 pg |
| Fluorescence detector (FD) | Selective for polyaromatic hydrocarbons | 1 ng |

1 pg = $10^{-12}$ g; 1 ng = $10^{-9}$ g

**Fig. 3.25** Bidimensional HPLC equipment. There are here two LC systems coupled with an increasing separation efficiency. Courtesy of Agilent

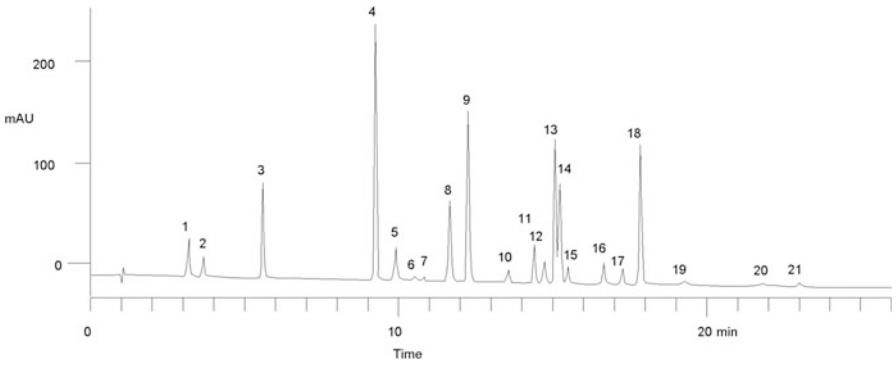


**Fig. 3.26** Chromatogram of carbamate and urea pesticides obtained with an UV-vis detector at 250 nm. Reverse phase; gradient elution: water (solvent A) and acetonitrile (solvent B). Peaks: (1) aminocarb, (2) barban, (3) carbaryl, (4) carbofuran, (5) chlorpropham, (6) diuran, (7) fenuron, (8) fenuron-TCA, (9) fluometuron, (10) linuron, (11) methiocarb, (12) methomyl, (13) mexacarbate, (14) monuron, (15) monuron-TCA, (16) neburon, (17) oxamyl, (18) propham, (19) propoxur, (20) siduron, (21) swep. Courtesy of Phenomenex

retention time. IC and HPLC have common operational characteristics (see Fig. 3.30).

The types of resins available are strongly acidic cation exchange (sulfonic acid as functional group), weakly acidic cation exchange (carboxylic acid), strongly basic anion exchange (quaternary amine), and weakly basic anion exchange (amine). The choice will depend on the analyte superficial charge and the pH value of the medium.

IC is widely used in the analysis of anions and inorganic cations in aqueous medium, such as $Cl^-$, $Br^-$, $NO^{3-}$, $SO_4^{2-}$, $CO_3^{2-}$, $K^+$, and $Na^+$, as well as organic

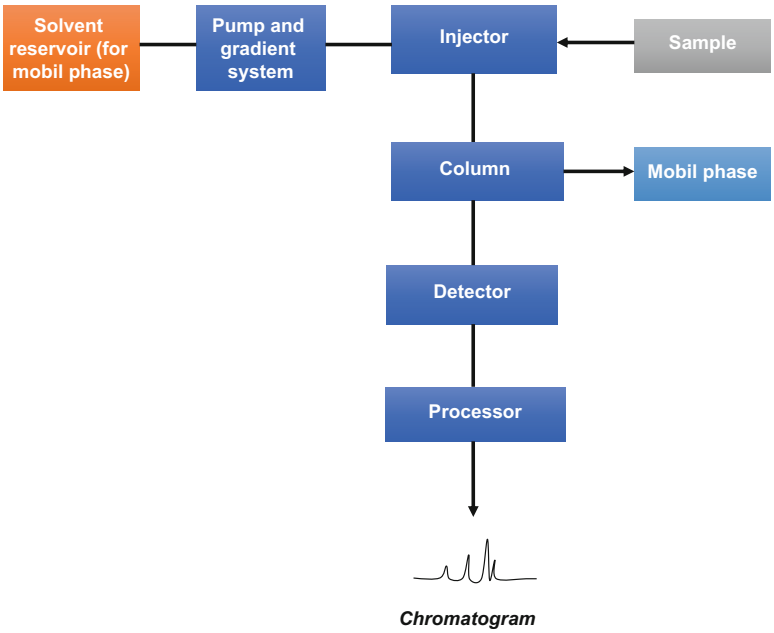


**Fig. 3.27** Block diagram for a HPLC equipment

**Fig. 3.28** IC equipment. Courtesy of Metrohm

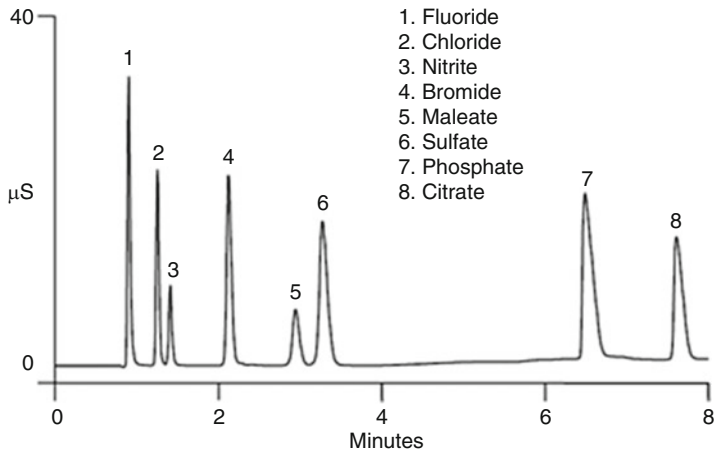


**Fig. 3.29** Chromatogram of an ion mixture from pharmaceuticals. Detector of electrical conductivity suppression; gradient elution: NaOH aqueous solution at 10 and 35 mmol $L^{-1}$. Courtesy of Thermo Fisher Scientific

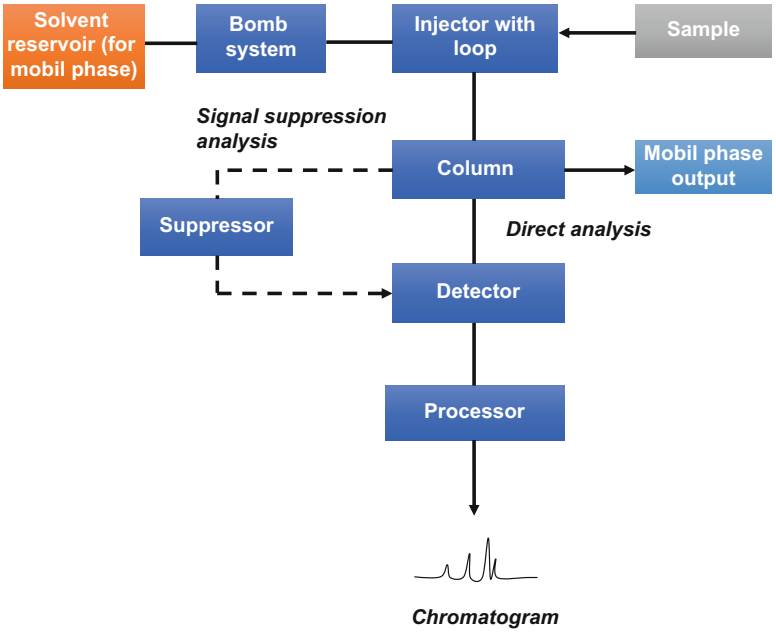


**Fig. 3.30** Block diagram of an IC equipment

compounds such as carboxylic acids, amines, and amides. Detector is usually electrochemical. An equipment is shown in Fig. 3.28, while an example of a chromatogram is shown in Figs. 3.29 and 3.30 shows the block diagram of the equipment.

## 3.5 Electrochemical Techniques

Electrochemistry studies the conversion of electrical energy into chemical energy, and vice versa, considering the transport of charges of ionic species. Some electrochemical techniques are based on oxidation-reduction reactions, such as potentiometry, coulometry, electrogravimetry, and voltammetries. Other electrochemical techniques in faradaic processes, as in the case of conductometry.

### *3.5.1 Potentiometry*

Potentiometry is a technique based on measuring the potential of electrochemical cells without appreciable current consumption. The potentiometric measurements are perhaps the most accomplished in the instrumental chemical analysis, with that of the hydrogenation potential being the best known and applied.

The basic structure of a potentiometer is composed of reference electrode, indicating electrode (or work electrode), and a potential measuring device. Ideally, the reference electrode is a half-cell that has a known and constant electrode potential at a given temperature, independent of the composition of the analyte solution. Potentiometric methods were initially developed to determine the end point of a titration; later, they were used to determine the concentration of ionic species through the so-called *direct potentiometry*. The technique requires only the comparison of the potential developed in the cell, after immersion of the indicator electrode in the analyte solution, with its potential when immersed in standard solutions of known concentrations of the analyte.

One of the applications of direct potentiometry is the determination of the hydrogen ionic potential (pH) of aqueous media using, for this purpose, a glass electrode and a pH meter. This potentiometric method is possibly the most common analytical method ever created. In infinitely diluted solutions the *activity* of an ionic species is approximately equal to its concentration. Thus, the concentration of the species to be determined is related to the potential of the electrode, according to the Nernst equation. For example, when using an electrode of a metal M to determine its $Mn^+$ ion in solution, the Nernst equation will be

$$E = E^{\circ} + (\mathrm{RT}/\mathrm{nF}) \ln a_M^{n+} \tag{3.9}$$

where $E$ is the potential determined by the indicator electrode, or work, with another electrode as reference; $E^{\circ}$ is the standard electrode potential of the metal (it is characteristic for each semi-reaction); $R$ is the ideal gas constant (8.314 J $K^{-1}$ mol $^{-1}$); $T$ is the temperature in Kelvin; $n$ is the number of moles of electrons in the half reaction; $F$ is Faraday's constant (96.649 $\times$ $10^4$ C $mol^{-1}$); ln is the natural logarithm (2.303 log); and $a$ is the activity of the ionic species.

### 3.5.2 *Voltammetry*

Voltammetry is a technique that involves the determination of substances in solution that can be oxidized or reduced on the surface of an electrode. For these determinations the relationships between current, voltage, and time during electrolysis in a cell are studied. The equipment for voltammetry employs three electrodes immersed in the solution containing the analyte and an excess of nonreactive electrolyte, called support electrolyte—Fig. 3.31.

The current of analytical interest is the faradaic current, which arises due to the oxidation or reduction of the analyte in the working electrode. The current due to the migration of ions under the influence of an electric field is called the *capacitive current*. The voltage at the working electrode varies systematically as the current response is measured (Fig. 3.32). Various voltage-time functions called excitation signals can be applied to the working electrode; in function of these signals of excitation is that one has the type of voltammetry: *square wave*, *linear sweep in anodic or cathodic direction*, *cyclic*, and *polarography*. The simplest type is linear sweep voltammetry, where the potential in the electrode of work increases or decreases linearly while the current is recorded. With the development of differential pulse and square wave voltammetries analyte determinations of the order of $10^{-7}$–$10^{-8}$ mol $L^{-1}$ became possible—measurements of lower concentrations are affected by the residual current.

Analytical pre-concentration processes have been used for trace analysis in order to increase the faradaic current. One of the techniques used is the anodic dissolution voltammetry, which can be used in the determination of toxic metals in soil and water.


**Fig. 3.31** Cyclic voltammetry system. Courtesy of Metrohm

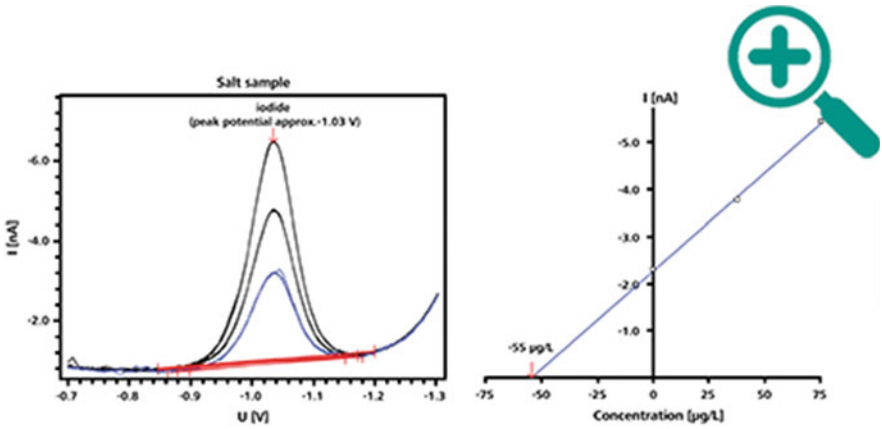


**Fig. 3.32** A voltammogram for a trace-level analysis. Courtesy of Metrohm

### *3.5.3 Electrophoresis*

Electrophoresis is an electrochemical separation technique based on the separation of species of different electric charges after the application of an electric field in a conductive liquid known, the electrolyte. The cations should migrate to the cathode—negatively charged—while the anions will migrate to the positively charged anode; ions of higher electric charge (e.g., $M^{4+}$) will migrate faster than those of lower charge (e.g., $M^{2+}$). Electrophoresis can achieve better resolutions than LC for some chemical species.

In capillary electrophoresis (CE), which is the most widely used mode for environmental analysis, the electrolyte is kept inside a capillary tube of internal diameter between 25 and 75 µm, with the sample being injected into one end of this tube. As the sample migrates through the capillary from the application of the external electric field, its components are separated and eluted at different time values, which results in an *electropherogram*, providing qualitative and quantitative information.

The electrophoretic velocity, or migration of the solute (or analyte), can be described from Eq. (3.10):

$$\nu = \mu E \tag{3.10}$$

where $\nu$ is the electrophoretic velocity of the solute in the medium, $\mu$ is the electrophoretic mobility of the solute, and $E$ is the magnitude of the applied electric field. The electrophoretic mobility of the solute ($\mu$), or analyte, can be described from Eq. (3.11):

$$\mu = q/6\pi\eta r \tag{3.11}$$

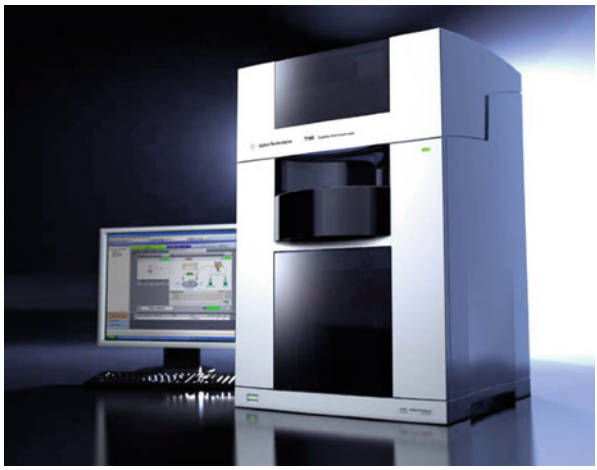

**Fig. 3.33** Equipment for CE. Courtesy of Agilent

where $q$ is the analyte charge, $\eta$ is the viscosity of the medium, and $r$ is the analyte radius. Thus, neutral species whose value of $q$ is zero will have a zero electrophoretic mobility and will not be separated from the other electrically charged ones.

In general, the following observations can be taken into account for the application of electrophoresis:

- Solutes with high electrophoretic mobility will have high separation efficiency.
- Selectivity can often be improved by adjusting the pH values of the conducting medium (electrolyte).
- Resolution is improved by increasing the applied voltage.

Detectors commonly used in capillary electrophoresis are amperometric, mass spectrometry, fluorescence, and UV-vis absorption. Figure 3.33 shows capillary electrophoresis equipment and Fig. 3.34 shows the block diagram of the equipment.

## 3.6 Sensors and Miniaturized Probes

In the broadest definition, a sensor is an electronic component, module, or subsystem whose purpose is to detect events or changes in its environment and send the information to other electronics, frequently a computer processor. A sensor is always used with other electronics, whether as simple as a light or as complex as a computer.

A chemical sensor is a self-contained analytical device that can provide information about the chemical composition of its environment, that is, a liquid or a gas phase (mainly) (Banica 2012). The information is provided in the form of a measurable physical signal that is correlated with the concentration of a certain chemical species (analyte). Two main steps are involved in the functioning of a chemical sensor, namely, *recognition* and *transduction*. In the recognition step, analyte

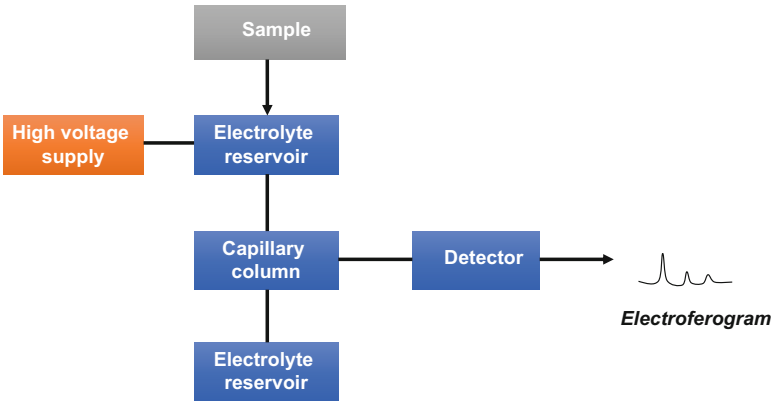


**Fig. 3.34** Block diagram of a CE equipment

molecules interact selectively with receptor molecules or sites included in the structure of the recognition element of the sensor. Consequently, a characteristic physical parameter varies and this variation is reported by means of an integrated transducer that generates the output signal (the transduction step). A chemical sensor based on recognition material of biological nature is a *biosensor*. Nowadays, the development of new materials for sensors, as molecularly imprinted polymers and aptamers, has eliminated the differentiation of chemical/biochemical sensors.

Electrochemical sensors are well recognized as easy-to-handle and fast devices for environmental analyses. For instance, gold nanomaterial-based electrochemical sensor systems have a strong potential for environmental monitoring—organic and inorganic pollutants—through enhanced and stable analytical capabilities (Jin and Maduraiveeran 2017). As traditional techniques (e.g., spectroscopies and chromatographies) require either lengthy sample preparation events or complicate instrumentation and hence are time-consuming techniques, electrochemical sensors present as a good alternative, since they are rapid and have stable response, with a high sensitivity and selectivity, and ease of miniaturization.

Carbon nanomaterials (e.g., nanotubes) and graphene can be used in electrochemical sensors by means of the modification of the electrode. These devices can be used to determine phenolic estrogens, BPA (bisphenol A), 2, 4-dichlorophenol, and octylphenol in waters (Liu et al. 2014).

The development of paper-based sensors using microfluidic (*lab on paper*) for environmental analysis has brought the promise of cheap, simple, and accessible devices for quick, easy, and in-field detection of pollutants. According to Meredith et al. (2016), this technique can be applied to metals (e.g., Cu, Cd, Pb, Hg, and Cr), nonmetals (e.g., $P_{PO_4^{3-}}$, $N_{NO_3^-}$, $N_{NO_2^-}$, $N_{NH_3}$, arsenic, and cyanide), phenolic compounds (e.g., phenol, BPA, *m*-cresol, *p*-cresol, catechol, and dopamine), and pesticides (e.g., organophosphate insecticides). For the analyte detection we can use colorimetry (quantitative/semiquantitative), electrochemical (quantitative), electrochemical conductivity (semiquantitative/quantitative), chemiluminescence

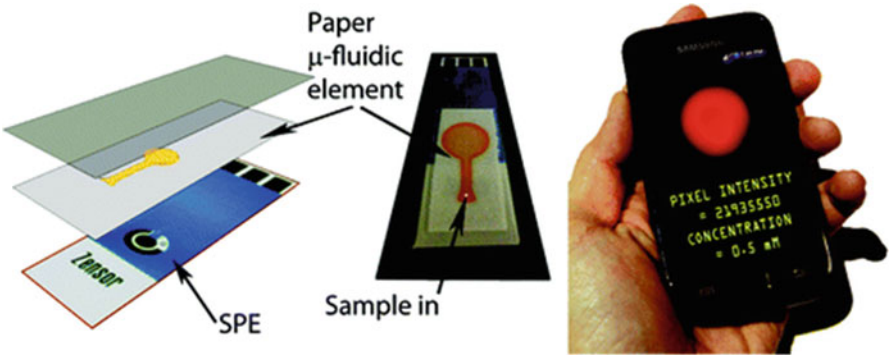


**Fig. 3.35** Fabrication and analysis process of paper-based microfluidic electrochemiluminescence sensor. The hydrophilic region of the paper (in yellow) was spotted with $Ru(bpy)_3^{2+}$ solution and then aligned onto the screen-printed electrode (SPE) by laminating with a transparent plastic. A small amount of sample was introduced through a small hole in the plastic at the base of the channel and the camera phone was placed close to the paper sensor, upon which a potential of 1.25 V was applied, and the emission was captured and analyzed (reprinted with permission from Delaney et al. (2011)). Copyright© 2011 American Chemical Society

(quantitative), and electrochemiluminescence (quantitative) (Liana et al. 2012). However, the commercial availability of paper-based sensors remains limited with an expectation of increasing for the next years. Figure 3.35 describes a paper-based sensor.

Miniaturized probes for environmental analysis and monitoring are frequently based on spectroscopic and electrochemical technologies. For instance, colorimetry can be applied for luminescent probe for field screening of $Pb^{2+}$ in water, being simple, fast, cost effective, and highly selective, without requirements for additional instrumentation (Zeng et al. 2017). Quantum dot-graphene oxide nanocomposite can be applied as fluorescence quenching probe for polycyclic aromatic hydrocarbons (PAHs) (Adegoke et al. 2017), and could be extended to other $\pi$ aromatic systems. Fluorographene can be used as a mass spectrometry probe in high-throughput identification and screening for 28 quaternary ammonium halides in sewage sludge samples collected from municipal wastewater treatment plants with LOD at ppt and sub-ppt levels (Huang et al. 2017). Figure 3.36 presents an example of portable probe.

A practical example of chromatographic technique replacement by probe for pharmaceutical EP analysis is the use of photochemically induced fluorescence matrix data combined with second-order chemometric analysis for the determination of carbamazepine, ofloxacin, and piroxicam in water samples of different complexity without the need of chromatographic separation. It was verified that the proposed strategy was simpler and greener than LC-MS methodologies, without compromising the quality of results (del Carmen Hurtado-Sánchez et al. 2015).

On the other hand, probes for high-throughput analysis of nontarget and suspect analytes are very useful because they can minimize costs and time related to the

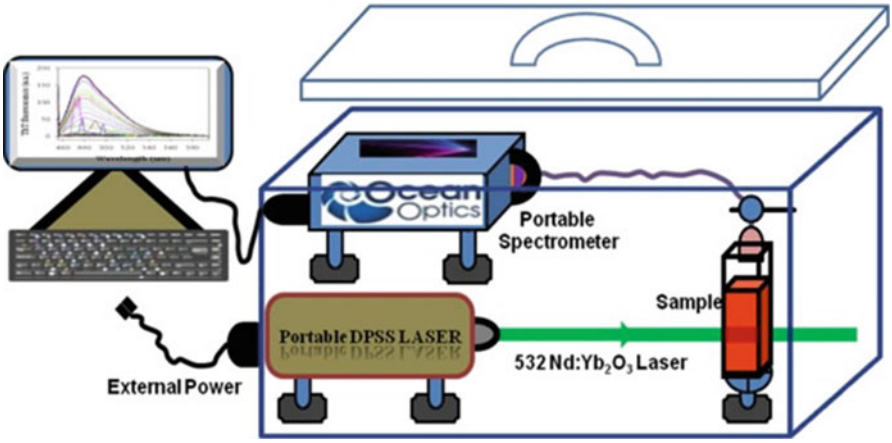


**Fig. 3.36** Schematic design of the portable fluorescence probe for detection of picric acid—or 2,4,6-trinitrophenol—in environmental samples (reprinted with permission from Dassary et al. (2018)). Copyright© 2017 Elsevier

analytical process, besides decreasing the response time to combat negative effects on the environment and public health from pollutants. Ouyang et al. (2017) developed miniaturized fluorescent probe for high-throughput screening of thyroid hormone-disrupting compounds in a 96-well microplate and tested for eight classes of EPs—hydroxylated polychlorinated biphenyls (OH-PCBs), perfluoroalkyl and polyfluoroalkyl substances (PFASs), hydroxylated polybrominated diphenyl ethers (OH-PBDEs), brominated flame retardants (BFRs), bromophenols, phthalates, and antibacterial agents—in herring gull egg extracts (*Larus argentatus*), demonstrating its applicability in the screening of biological samples.

## 3.7 Bioassays

Bioassays could provide an alternative to conventional classical analytical techniques (Sect. 3.1 of this chapter), according to green chemistry principles (Sect. 2.7 of Chap. 2), with a minimization of the negative environmental impacts from analytical chemistry. Furthermore, this kind of analysis provides information about the effect of EPs on the organism and ecosystems that are strongly relevant for the toxicity determination and understanding. Commonly, bioassays are treated as *ecotoxicological assessment*.

Wieczerzak et al. (2016) observed this opportunity by means of the application of commercially available certified bioassays using single-celled organisms (e.g., cell lines, yeast, bacteria) and multicellular organisms (e.g., invertebrate and vertebrate animals and plants). The main advantages for these bioassays are as follows:

- It is possible to conduct tests in situ.
- It is not necessary to purchase high-purity reagents and reference materials.
- Relatively low cost per analysis.

As main disadvantages: (1) experience required to select battery of bioassays; (2) more difficult to maintain reproducibility and repeatability; and (3) necessity to keep clean cultures up. Besides, the use of microorganisms and organisms for bioassays is the object of regulatory surveillance.

Table 3.8 presents an overview of bioassays available for environmental analysis.

## 3.8 Sample Preparation: Extraction, Concentration, and Cleanup Techniques

Extraction, distribution, or partition is the apportionment of a solute—the analyte — between two phases. It takes into account equilibrium phenomena summarized in the partition ratio, $K_D$. The ratio of the concentration of a substance in a single definite form, $A$, in the extract to its concentration in the same form in the other phase at equilibrium, e.g., for an aqueous/organic system (International Union of Pure and Applied Chemistry 2017), is defined as

$$(K_D)_A = \frac{[A]_{org}}{[A]_{aq}} \tag{3.12}$$

$K_D$ is sometimes called the distribution constant. The use of the inverse ratio (aqueous/organic) may be appropriate in certain cases, e.g., where the organic phase forms the feed, but its use in such cases should be clearly specified. The ratio of the concentration in the denser phase to the less dense phase is not recommended as it can be ambiguous.

Extraction is a paramount step of the analytical process, specially in the sample preparation, and the use of solvent extraction is the more recurrent in the environmental analysis of organic molecules. According to the International Union of Pure and Applied Chemistry (2017), the solvent extraction can be defined as the process of transferring a substance from any matrix (e.g., water or soil) to an appropriate liquid phase (e.g., a mobile phase for HPLC). If the substance is initially present as a solute in an immiscible liquid phase the process is synonymous with liquid–liquid extraction. Notes: If the extractable material is present in a solid (such as a soil) the term *leaching* may be more appropriate. The extractable material may also be a liquid entrapped within or adsorbed in a solid phase.

However, there are other extraction techniques to be used for the EP analysis, which their choice depends on the analyte and matrix physicochemical properties, number of samples, time, and costs. Table 3.9 describes these techniques and their main characteristics to take into account for the choice. Take into account that the recovery of the extraction method must be in the *range of 70–120%* (see Chap. 2).

**Table 3.8** Some bioassays commercially available for environmental quality assessment

| Bioassay—company | Species used | Measure of toxicity effects | Application | In accordance with |
|---|---|---|---|---|
| *Plant-based bioassays* | | | | |
| Lemna Test—LemnaTec GmbH, Germany | *Lemna minor*, *Lemna gibba* (duckweed) | Acute and subchronic by means of growth inhibition in 7 days | Pesticides and other chemicals soluble in water (aquatic samples) | ASTM, US-EPA, OECD |
| AlgalToxiit F™—MicroBioTests Inc., Belgium | *Raphidocelis subcapitata* (microalgae) | Short-chronic, by means of inhibition of growth in 72 h | Pure compounds, effluents, sediments, surface and groundwater, wastewaters | ISO, OECD |
| AlgalToxiit F™—MicroBioTests Inc., Belgium | *Phaeodactylum tricornutum* (diatom) | Short-chronic, by means of inhibition of growth in 72 h | Chemicals released in aquatic as well as terrestrial environments | ISO, OECD |
| *Animal-based bioassays* | | | | |
| DaphtoxKit F™ magna—MicroBioTests Inc., Belgium | *Daphnia magna* (crustaceans) | Acute and chronic toxicity screening test in 24–48 h by means of immobilization or mortality, inhibition of reproduction, inhibition of reproduction, inhibition of growth population | Chemicals released in aquatic as well as terrestrial environments | OECD, ISO, US-EPA, ASTM |
| Rotoxkit F™ short-chronic—MicroBioTests Inc., Belgium | *Brachinus calyciflorus* (conifers) | Acute and chronic toxicity in 24–48 h by means of mortality or reduction of reproduction | Testing toxicity of all chemicals and wastes released in aquatic as well as terrestrial environments | OECD, ISO, US-EPA |
| DaphtoxKit F™ pulex—MicroBioTests Inc., Belgium | *Daphnia pulex* (crustaceans) | Acute toxicity in 48 h by means of immobilization or mortality, with calculation of the EC50 or LC50 | Chemicals in wastewater, surface and deep seawaters | OECD, ISO |
| *Single-cell organism-based bioassays* | | | | |
| Microtox® M500—Modern Water, UK | *Photobacterium phosphoreum* | Acute toxicity in 5–30 min by means of the decrease in the bioluminescence | Monitoring toxicity of chemicals in water, sediments, soil, etc. | ISO |
| UmuC Easy AQ—Xenometrix AG, Switzerland | Mutant strains of *Salmonella typhimurium* TA1535/pSK10002 | Mutagenicity/genotoxicity in 30 h | Aqueous and concentrated samples of pure compound, wastewater, drinking water | ISO |

(continued)

**Table 3.8** (continued)

| Bioassay—company | Species used | Measure of toxicity effects | Application | In accordance with |
|---|---|---|---|---|
| Ames MPF™—Xenometrix AG, Switzerland | Mutant strains of *Salmonella typhimurium* TA98 | Mutagenicity/genotoxicity in 48 h | Chemicals in surface water, sediments, sewage, sludge, soils | OECD |

Adapted from Wieczerzak et al. (2016)
*ASTM* American Society for Testing and Materials, *ISO* International Standard Organization, *OECD* Organisation for Economic Co-operation Development, *U.S. EPA* United States Environmental Protection Agency

After the extraction step, we can concentrate the analyte present in the extraction medium to promote a better analytical response. It can be made by means of the following (Mitra 2003):

- Stream of nitrogen gas flow, for nonvolatile analyte and small volume to reduce
- Rotary vacuum evaporator, for large volume to reduce
- Kuderna-Danish concentrator using air-cooled condenser, for smaller volume to be reduced to less than 1 mL

After the extractive concentration, a cleanup step is desirable to remove interfering species prior to the chromatographic or electrophoretic separation. These interfering species are very common in environmental analysis, mainly for soil samples due to the matrix heterogenic composition. The main cleanup techniques for EP analysis are the following (Mitra 2003):

- Gel-permeation chromatography (GPC), for the elimination of lipids, proteins, polymers, copolymers, natural resins, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds from the sample: This method is appropriate for both polar and nonpolar analytes.
- Solid-phase extraction cartridges (SPE), for steroids, esters, ketones, glycerides, alkaloids, and carbohydrates: Cations, anions, metals, and inorganic compounds are also candidates for this technique.

## 3.9 Conclusions

Modern instrumentation and techniques boosted considerable advances on identification and determination of analytes, especially for environmental pollutants in trace concentrations.

Sensors, probes, and bioassays can reduce times, costs, and waste generation.

However, sample preparation is the basis of a reliable analytical process, with techniques of extraction and cleanup providing suitable and representative samples.

**Table 3.9** Extraction techniques available for EP analysis in several environmental matrixes

| Technique | Principle | Classes of EPs | Advantage | References |
|---|---|---|---|---|
| Liquid–liquid extraction | Partition between an aqueous and an organic phase | Pentachlorophenol, bisphenol A, UV filters, endocrine disruptors, antibiotics (fluoroquinolones), etc., in water | Simplicity. Use of greener reagents (e.g., ethanol and ionic liquids) | Primel et al. (2017) |
| Microwave-assisted extraction | Microwave energy is a nonionizing radiation (frequency of 0.3–300 GHz) that causes molecular motion by migration of ions and rotation of dipoles | Personal care products and household products, pharmaceuticals, flame retardants, phthalates, linear alkylbenzene sulfonates, alkylphenol ethoxylates, and phenolic derivatives from solid and liquid matrixes | Great reductions in extraction time and solvent consumption, as well as the possibility of performing multiple extractions, thereby increasing sample throughput | Sanchez-Padro et al. (2015) |
| Stir-bar sorptive extraction | A microextraction technique based on a coating on the bar, as polydimethylsiloxane (PDMS). PDMS is a nonpolar phase so it is not suitable for the extraction of polar compounds, especially those with $\log K_{ow}$ values lower than 3 | Water and oil repellents, preservatives, plasticizers, surfactants, flame retardant, hormones, pharmaceuticals, UV-filter, pesticides in water | Simplification, strong reduction, or even removal of the use of toxic organic solvents and the reduction of required sample volumes | Aparicio et al. (2017) |
| Solid–liquid extraction | Partition between solid and liquid phases based on solvent extraction | Perfluoroalkyl compounds, estrogens, parabens, benzophenones, plasticizers, surfactants, brominated flame retardants, and alkylphenols in marine organisms and marine sediments | Rapid and robust | Martín et al. (2017) |
| Selective pressurized liquid extraction | Exhaustive extraction technique based on solvent extraction and pressure application capable of extracting organic compounds from solid and semisolid matrices | Carbamates, and pyrethroids pesticides, parabens, triclosan, estrogens, bisphenol A in soil, sediments, sludge and organisms | Reduction in the costs intrinsic to sample preparation (i.e., time, solvents, labor, laboratory space, training, and potential loss of analytes) | Subedi et al. (2015) |

(continued)

**Table 3.9** (continued)

| Technique | Principle | Classes of EPs | Advantage | References |
|---|---|---|---|---|
| Ultrasound-assisted extraction | The mechanical effect of ultrasound induces a greater penetration of solvent into solid matrices and mechanical erosion of solids, including particle rupture, which improves mass transfer, leading to enhanced sample extraction efficiency | Personal care products, pharmaceutical drugs, flame retardants, nanoparticles in water, soil, sediment, and sludge | Decreasing in the amount of solvent required and in the extraction time for solid samples; coupling to microextraction techniques for the analysis of liquid samples | Albero et al. (2015) |
| Solid-phase extraction (SPE) | Exhaustive extraction technique based on partition between liquid and solid phases | Pharmaceutical and personal care products in surface water samples and effluent wastewater samples | Faster, less labor intensive and requires smaller volumes of reagents than liquid–liquid extraction. Achieves high extraction efficiency for organic compounds | Andrade-Eiroa et al. (2016) |
| Solid-phase microextraction (SPME) | Non-exhaustive technique based on the partition equilibrium of the analytes between the sample matrix and the extraction phase. In SPME, the extraction phase (fiber coating) can be exposed directly to the sample media (direct immersion, DI) or to its headspace (HS) | Brominated flame retardants and tetracycline antibiotic residues in soil and sediments. Pharmaceuticals and personal care products, polybrominated diphenyl ethers (PBDEs), BPA and analogues, halogenated flame retardants, and estradiol (radiolabeled) in wastewater | Enhanced extraction efficiency and selectivity for the target analytes. Facilitates implementation of on-site sampling and analysis when coupled to portable analytical instruments, with the substantial reduction of errors associated with sample transportation and possible alterations during storage | Souza-Silva et al. (2015) |
| QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) | | Personal care products (UV filters) in marine mussels | As the name said, it will be quick, easy, cheap, effective, rugged, and safe | Groz et al. (2014) |

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# Chapter 4
# The Main Environmental Matrices: Air, Soil, and Water


## 4.1 Air Composition and Properties

Air, as an analytical matrix, presents itself as a vehicle of rapid dispersion of pollutants, much more than water, due to the high fugacity, or tendency to escape, of its gaseous constituents. The average composition of the atmosphere, which includes the air we breathe, is shown in Table 4.1.

The nitrogen and oxygen gases are the main constituents in volume, 78.1% and 20.9%, respectively. However, water vapor, carbon dioxide ($CO_2$), and argon can also be observed in a more representative proportion in relation to the other gases present in much reduced concentrations. Carbon dioxide and methane ($CH_4$) have attracted attention because of global warming—mainly the emission of carbon dioxide in the atmosphere via the burning of fossil fuel leading to an increase in temperature due to the absorption of infrared radiation (wavelength between $10^{-6}$ and $10^{-3}$ m). Methane from biochemical processes of biomass degradation can also produce this heating, due to the absorption of the same radiation.

Ozone ($O_3$), as a constituent of the Earth's protective layer against ultraviolet radiation (wavelength between $10^{-8}$ and $10^{-6}$ m), also raises concern, since the decrease in its atmospheric concentration allows a higher incidence of this radiation, which can lead to skin cancer.

According to the World Health Organization (2006), some listed air pollutants raise greater care due to their toxic effects:

- Volatile organic compounds (VOCs): from the distribution of fuels, industries, vehicles, among others, are precursors of tropospheric $O_3$.
- Particulate matter: suspended particles, inhalable particles (diameter $\leq$10 μm, called $PM_{10}$), and combustion smoke cause respiratory complications.
- Carbon monoxide (CO): from vehicles and incinerators reduce the oxygen exchange capacity of the blood.
- Sulfur oxides ($SO_X$): from combustion and incineration of coal and diesel oil cause acid rain.



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**Table 4.1** Average composition of the atmosphere, according to Mirtov (1964)

| Gaseous constituent | Percentage of volume (%) | Partial pressure (atm) |
|---|---|---|
| $N_2$ | 78.1 | 0.781 |
| $O_2$ | 20.9 | 0.209 |
| Ar | 0.93 | 0.0093 |
| $H_2O$ | 0.1–2.8 | 0.028 |
| $CO_2$ | 0.03 | 0.0003 |
| Ne | $1.8 \times 10^{-3}$ | $1.8 \times 10^{-5}$ |
| He | $5.2 \times 10^{-4}$ | $5.2 \times 10^{-6}$ |
| $CH_4$ | $1.5 \times 10^{-4}$ | $1.5 \times 10^{-6}$ |
| Kr | $1.1 \times 10^{-4}$ | $1.1 \times 10^{-6}$ |
| CO | $0.06–1 \times 10^{-4}$ | $0.6–1 \times 10^{-6}$ |
| $SO_2$ | $1 \times 10^{-5}$ | $1 \times 10^{-6}$ |
| $N_2O$ | $5 \times 10^{-5}$ | $5 \times 10^{-7}$ |
| $H_2$ | $5 \times 10^{-5}$ | $5 \times 10^{-7}$ |
| $O_3$ | $0.1–1 \times 10^{-5}$ | $0.01–1 \times 10^{-7}$ |
| Xe | $8.7 \times 10^{-6}$ | $8.7 \times 10^{-8}$ |
| $NO_2$ | $0.05–2 \times 10^{-5}$ | $0.05–2 \times 10^{-8}$ |
| Rn | $6 \times 10^{-18}$ | $6 \times 10^{-20}$ |

- Nitrogen oxides ($NO_X$): from industrial combustion processes and vehicles—$NO_2$ is the precursor of tropospheric ozone and acid rain.
- Tropospheric ozone ($O_3$): formed when $NO_X$ and VOCs undergo photochemical reactions in the atmosphere in the presence of solar radiation; causes damage to the lungs, materials, and vegetation—not to be confused with the $O_3$ layer of protection against UV radiation.

Those compounds above cited are related to the outdoor pollution. When we consider the indoor pollution, we can observe the following (World Health Organization 2010):

- Benzene: originates from outdoor air and also from sources indoors such as building materials and furniture, attached garages, heating and cooking systems, stored solvents, and various human activities.
- Carbon monoxide: anthropogenic emissions are responsible for about two-thirds of the carbon monoxide in the atmosphere and natural emissions account for the remaining one-third. Small amounts are also produced endogenously in the human body. Exposure to low levels of carbon monoxide can occur outdoors near roads, as it is also produced by the exhaust of petrol- and diesel-powered motor vehicles. Parking areas can also be a source of carbon monoxide.
- Formaldehyde: combustion processes such as smoking, heating, cooking, or candle or incense burning. However, major sources in nonsmoking environments appear to be building materials and consumer products that emit formaldehyde.

This applies to new materials and products but can last several months, particularly in conditions with high relative humidity and high indoor temperatures.

- Naphthalene: it is used as feedstock in the manufacture of phthalic anhydride for the synthesis of phthalate plasticizers and synthetic resins. It is also used as feedstock for naphthalene sulfonic acids often used in the production of plasticizers for concrete, as ingredients for plasterboards, as dispersants in synthetic and natural rubbers, and as tanning agents in the leather industry. Naphthalene is also used in paints and in the production of the insecticide carbaryl, used in home yards and gardens. Still predominant in the exposure of consumers worldwide is the production and use of crystalline (pure) naphthalene as a moth repellent and disinfectant. Its use as a solid block deodorizer for toilets is also reported. Wood smoke, fuel oil, and gasoline also contain naphthalene. The major constituent of creosote, used for timber impregnation, is naphthalene and its alkyl homologues.
- Nitrogen dioxide: formed by various combinations of oxygen and nitrogen at high temperatures during the combustion process. The higher the combustion temperature, the more nitric oxide is generated. Indeed, 90–95% of the nitrogen oxides are usually emitted as nitric oxide and only 5–10% as nitrogen dioxide, although substantial variations from one source type to another have been observed. In ambient conditions, nitric oxide is rapidly oxidized in air to form nitrogen dioxide by available oxidants (such as oxygen, ozone, and VOCs) and this rapid oxidation velocity is such that it is nitrogen dioxide that is usually considered as a primary pollutant.
- Polycyclic aromatic hydrocarbons: PAHs are widespread environmental pollutants that are formed in the combustion process of carbonaceous materials at high temperature. Indoor air is contaminated by PAHs, which come not only from infiltration or intrusion of outdoor air but also from indoor emission sources such as smoking, cooking, domestic heating with fuel stoves and open fireplaces, as well as incense and candle emissions.
- Radon (Rn): all rocks contain some uranium, typically at concentrations of 1–3 ppm. The uranium content of a soil will be about the same as the uranium content of the rock from which the soil was derived. As radium-226, the immediate parent of radon, is a decay product of uranium, the higher the uranium content of the soil the greater the radium concentration and the higher the chance that houses built on such soil will have high levels of indoor radon. The main source of indoor radon is the radon produced by the decay of radium in the soil subjacent to a house. Soil gas containing radon enters a house through cracks and fractures in the foundations by pressure-driven flow, as the air in a house is generally warmer and therefore at a lower pressure than the subjacent soil gas.
- Trichloroethylene: consumers may be exposed to TCE through the use of wood stains, varnishes, finishes, lubricants, adhesives, typewriter correction fluid, paint removers, and certain cleaners, where TCE is used as a solvent.

Furthermore, some compounds have current evidence uncertain or not sufficient for indoor guidelines (World Health Organization 2010):

- Acetaldehyde
- Asbestos
- Biocides, pesticides
- Flame retardants
- Glycol ethers
- Hexane
- Nitric oxide
- Ozone
- Phthalates
- Styrene
- Toluene
- Xylenes

Asbestos, biocides and pesticides, flame retardants, and phthalates can be classified as EPs. On the other hand, Boor et al. (2017) listed indoor air pollutants in sleep microenvironments as house dust, animal allergens, fungi, bacteria, plasticizers, flame retardants, VOCs (e.g., polyurethane or polyester foam, formaldehyde), and unreacted isocyanates.

### *4.1.1 Sampling and Sample Preparation for Indoor Environment*

The indoor environment is just like a concentrator of EPs from various commercial and industrial products (Wang et al. 2016). Then, it needs a correct sampling to achieve the reliable result, taking into account the heterogeneity of the analytical matrix.

We can consider two classes of sampling techniques for indoor air: *active air sampling* and *passive air sampling*. In the first case, we need a pump that is used to force the flow of the air sample through the trap filled with a sorbent material. In the second case, sampling operates without the aid of a pump and consists of a sorbent with a high retention capacity for the target compounds. For EP analysis, active air sampling is more useful and Table 4.2 presents several techniques according to the analyte.

Figures 4.1 and 4.2 show some technologies cited in Table 4.2. Figure 4.3 shows a device based on air sampling pump.

Generally, after the sampling the sample will be forwarded to the laboratory for a chromatographic analysis by GC or LC. For this, the analyte needs to be desorbed from the sorbent material by means of a thermal desorption—commonly used for GC—or using a solvent for solid–liquid extraction for LC.

**Table 4.2** Sampling techniques for EPs in indoor air

| Compound | Phase | Sampling technique (active sampling) | Flow rate (L $min^{-1}$) |
|---|---|---|---|
| Nine synthetic musks, four parabens, and one insect repellent | Gaseous | Tenax® TA | 0.12 |
| Eight synthetic musks | Gaseous + particulate | PUF + GFF | 10 |
| Two synthetic musks, bisphenol A | Gaseous + particulate | PUF + QFF | 2 |
| Liner and cyclic siloxanes | Gaseous | Isolute ENV® + SPE cartridge | 1.5 |
| Liner and cyclic siloxanes | Gaseous | Tenax® GR/graphitized carbon black | 0.12 |
| Bisphenol A | Gaseous + particulate | PUF + QFF | 5 |
| Parabens, bisphenol A | Gaseous + particulate | QFF + Amberlite® XAD-2® resin | <13.3 |
| Benzophenone | Gaseous + particulate | PUF + QFF | 5 |
| Synthetic musks, bisphenol A, parabens, triclosan | Gaseous + particulate | Amberlite® XAD-2® resin + QMA™ filter | – |
| Nine synthetic musks | Gaseous | Tenax® TA | 100 |
| Liner and cyclic siloxanes | Gaseous + particulate | PUF + QFF | 5 |
| Eight synthetic musks | Gaseous | PUF | 5 |
| Bisphenol A | Gaseous + particulate | XAD-2 resin + QFF | 4 |
| Parabens | Gaseous + particulate | XAD-2 resin/ PUF + QFF | 8–9 |
| Parabens | Gaseous + particulate | XAD-2 resin/ PUF + QFF | 8–9 |
| Cyclic siloxanes | Gaseous | Isolute ENV® + SPE cartridge | 3–6 |
| Liner and cyclic methyl siloxanes | Gaseous | Isolute ENV® + SPE cartridge | 0.5 |
| Five synthetic musks | Gaseous | PUF + GFF | – |

Adapted from Wang et al. (2016)
*PUF* Polyurethane foam, *QFF* quarter fiber filter, *GFF* glass fiber filter, *SPE* solid-phase extraction

Particulates (e.g., $MP_{10}$) for metal analysis will be retained under a PVC membrane in a trap cassette (Fig. 4.4) followed by a dissolution and analysis by atomic absorption spectrometry or optical emission spectrometry (Chap. 3).

### *4.1.2 Methods for EP Analyses in Air*

The sample analysis is composed of a sequence of steps illustrated below in Fig. 4.5 for the case of organic EPs.

Table 4.3 describes a compendium of analytical methods dedicated to the EP analysis in indoor air.


**Fig. 4.1** Isolute ENV® solid phase for active sampling. Courtesy of Biotage


**Fig. 4.2** Tenax® TA porous polymer in a glass tube for active sampling. Courtesy of Sigma-Aldrich


**Fig. 4.3** Air sampling pump. Courtesy of Sigma-Aldrich

**Fig. 4.4** Cassette for particulate sampling. Courtesy of Sigma-Aldrich

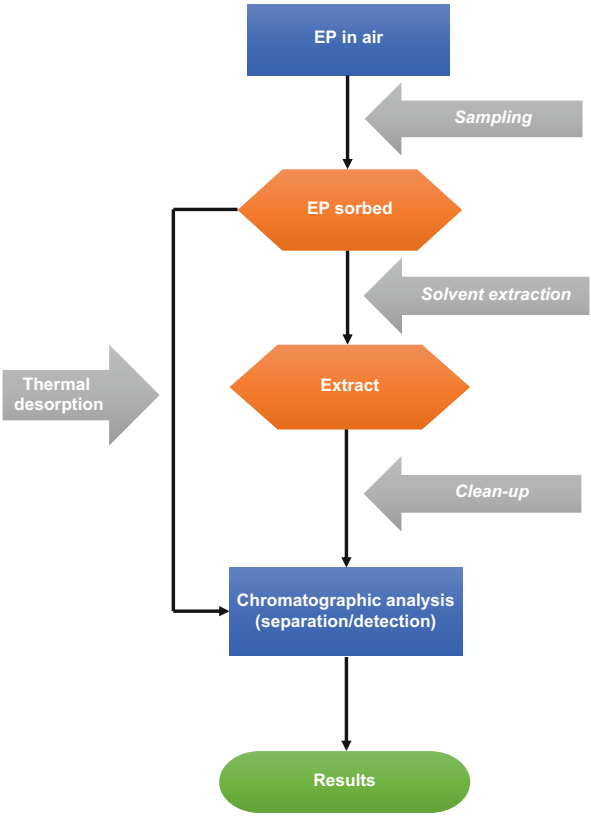


**Fig. 4.5** The analytical approach for organic EP analysis in air

**Table 4.3** Analytical methods for EP analysis in indoor air

| Analyte(s) | Brief method description | LOD | References |
|---|---|---|---|
| VOCs | Method for the determination of VOCs in ambient air using Tenax® adsorption and GC-MS | 0.01–100 $ppb_{v/v}$ | Method TO-1, U.S. Environmental Protection Agency (1999) |
| Phenolic compounds | Method for the determination of phenol and methylphenols (cresols) in ambient air using HPLC-UV | 1–250 $ppb_{v/v}$ | Method TO-8, U.S. Environmental Protection Agency (1999) |
| Flame retardants (DBE-DBCH, PBT, HBB, DDC-CO, and DBDPE) | Methods for the determination of flame retardants using GC-MS-ECNI | 0.41–20 pg $m^{-3}$ | Newton et al. (2016) |
| Polyfluorinated alkyl compounds (nonylphenol, BPA, etc.) | Methods for the determination of polyfluorinated alkyl compounds using GC-MS-PCI, GC-MS-EI/NCI and HPLC–MS | 0.15–20 pg $m^{-3}$ | Xie and Ebinghaus (2008) |

1 ppb v/v = 1 nL of analyte in 1 L of sample. *VOCs* Volatile organic compounds (generally, aromatic compounds as benzene, ethylbenzene, toluene, xylenes, and fluorinated, bromated and chlorinated related compounds with a high vapor pressure), *GC* Gas chromatography, *HPLC* High-performance liquid chromatography, *PCI* Positive chemical ionization, *NCI* Negative chemical ionization, *EI* Electron ionization, *ECNI* Electron capture negative ionization, *UV* Ultraviolet, *DBE-DBCH* Mixture of dimethyl glutarate and dimethyl adipate, *PBT* 10-Hydroxy-10-(2-(2Z)-2-octen-1-ylcyclopropyl)-5,8-decadienoic acid, *HBB* 2-Hydroxybenzylbenzimidazole, *DDC-CO* Dicarbethoxydihydrocollidine, *DBDPE* Decabromodiphenyl oxide

## 4.2 Soil Composition and Properties

Soil is a matrix of the most complex due to the chemical constitution of its organic and inorganic components, and the physical states of the soil—the soil is formed by chemical substances in the solid, liquid, and gaseous states. Then, soils have a natural tendency to interact with different pollutants.

Tables 4.4 and 4.5, and 4.6 present the chemical composition of soil samples of the red latosol type, common in the south-west region in Brazil.

The results presented are typical for red latosol, which were formed under strong weather conditions in hot and humid regions containing low concentrations of silicate minerals and high concentration of FeO, $Fe_2O_3$, and $Al_2O_3$. According to Weber et al. (2005), this type of soil presents variable electric charges on the surface. The largest contents of the sand fraction (Table 4.6) are due to a proximity of the collection points at the river bank. Iron was the natural element determined in higher concentration (Table 4.6). The distribution of organic matter (OM) and the mineral fraction in layers in the soil is as follows:

**Table 4.4** Results of physicochemical analysis of samples of red latosol, collected at different depths

| ID | pH $CaCl_2$ | OM (g $dm^{-3}$) | P resin (mg $dm^{-3}$) | K (mmolc $dm^{-3}$) | Ca (mmolc $dm^{-3}$) | Mg (mmolc $dm^{-3}$) | $H^+ + Al^{3+}$ (mmolc $dm^{-3}$) | Al (mmolc $dm^{-3}$) | CTC (mmolc $dm^{-3}$) | S (mmolc $dm^{-3}$) | V (%) | (Ca + Mg)/ K | $S.SO_4^{2-}$ (mg $dm^{-3}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ST01-0.3m | 6 | 23 | 5 | 0.4 | 45 | 15 | 27 | – | 87 | 60 | 69 | 163 | 7 |
| ST01-0.6m | 5.9 | 24 | 43 | 0.2 | 35 | 15 | 29 | – | 79 | 50 | 63 | 233 | 12 |
| ST01-1.4m | 6.1 | 12 | 3 | 0.7 | 47 | 18 | 21 | – | 87 | 66 | 76 | 96 | 16 |
| ST02-0.3m | 4.4 | 7 | 0 | 2.4 | 6 | 2 | 16 | 8 | 56 | 10 | 19 | 3 | 15 |
| ST02-0.6m | 4.6 | 2 | 0 | 0.1 | 7 | 2 | 33 | 10 | 42 | 9 | 21 | 148 | 1 |
| ST03-0.3m | 5.2 | 19 | 3 | 0.1 | 11 | 4 | 34 | 2 | 49 | 15 | 31 | 246 | 1 |
| ST03-0.6m | 5 | 4 | 1 | 0.1 | 10 | 3 | 33 | 2 | 46 | 13 | 29 | 213 | 4 |
| ST04-0.3m | 5.5 | 10 | 1 | 1.5 | 18 | 6 | 28 | – | 54 | 26 | 48 | 16 | 16 |
| ST04-0.6m | 5.6 | 9 | 1 | 1.7 | 22 | 7 | 27 | – | 57 | 31 | 54 | 17 | 23 |
| ST05-0.3m | 6.1 | 19 | 2 | 0.6 | 30 | 10 | 22 | – | 62 | 41 | 65 | 67 | 1 |
| ST05-0.6m | 5.7 | 5 | 1 | 0.1 | 21 | 8 | 21 | – | 50 | 29 | 58 | 210 | 21 |
| ST06-0.3m | 5.6 | 15 | 15 | 0.8 | 22 | 9 | 34 | – | 66 | 32 | 48 | 41 | 88 |
| ST06-0.6m | 4.3 | 16 | 16 | 1.2 | 5 | 1 | 95 | 18 | 102 | 7 | 7 | 5 | 139 |
| ST07-0.3m | 5.4 | 30 | 35 | 1.1 | 22 | 7 | 36 | 1 | 66 | 30 | 46 | 25 | 9 |
| ST07-0.6m | 5.8 | 25 | 8 | 1 | 42 | 15 | 25 | – | 83 | 58 | 70 | 58 | 8 |
| ST08-0.3m | 6 | 27 | 63 | 1.2 | 60 | 22 | 22 | – | 106 | 83 | 79 | 67 | 7 |
| ST08-0.6m | 6 | 30 | 39 | 1.1 | 58 | 19 | 24 | – | 102 | 78 | 76 | 68 | 8 |

*OM* Organic matter, *CEC* Cation-exchange capacity, *S* Sum of bases saturated with Na, *V* Saturation of bases
Analyses carried out according to methods from the Brazilian Agricultural Research Corporation (1997)

**Table 4.5** Results of granulometric analysis (g $kg^{-1}$) of red latosol samples, collected at different depths

| ID | Sand | Clay | Silt |
|---|---|---|---|
| ST01-0.3m | 655 | 282 | 63 |
| ST01-0.6m | 641 | 278 | 81 |
| ST01-1.4m | 661 | 247 | 92 |
| ST02-0.3m | 662 | 230 | 108 |
| ST02-0.6m | 267 | 555 | 178 |
| ST03-0.3m | 235 | 560 | 205 |
| ST03-0.6m | 398 | 276 | 326 |
| ST04-0.3m | 404 | 192 | 404 |
| ST04-0.6m | 289 | 463 | 248 |
| ST05-0.3m | 377 | 270 | 353 |
| ST05-0.6m | 369 | 140 | 491 |
| ST06-0.3m | 202 | 559 | 239 |
| ST06-0.6m | 187 | 609 | 204 |
| ST07-0.3m | 289 | 442 | 269 |
| ST07-0.6m | 405 | 359 | 236 |
| ST08-0.3m | 233 | 578 | 189 |
| ST08-0.6m | 260 | 511 | 229 |

Analyses carried out according to methods from the Brazilian Agricultural Research Corporation (1997)

**Table 4.6** Results of analysis of chemical elements (mg $kg^{-1}$) in samples of red latosol, collected at different depths

| ID | B | Cu | Fe | Mn | Zn |
|---|---|---|---|---|---|
| ST01-0.3m | 10.8 | 6.2 | 28 | 33 | 2.4 |
| ST01-0.6m | 11.5 | 4.6 | 44 | 34.2 | 1.7 |
| ST01-1.4m | 11.6 | 5.3 | 30 | 18.9 | 3.5 |
| ST02-0.3m | 3.7 | 6.9 | 56 | 8.5 | 1.2 |
| ST02-0.6m | 0.2 | 2.2 | 6 | 6 | 1.7 |
| ST03-0.3m | 4.4 | 6.3 | 64 | 37.1 | 1.8 |
| ST03-0.6m | 1.8 | 4.2 | 29 | 4.7 | 0.5 |
| ST04-0.3m | 1.1 | 3.7 | 8 | 9.3 | 0.3 |
| ST04-0.6m | 0.4 | 2.5 | 5 | 3.6 | 0.3 |
| ST05-0.3m | 3.5 | 5.4 | 24 | 25.4 | 3.2 |
| ST05-0.6m | 5.3 | 2.5 | 9 | 1.3 | 0.3 |
| ST06-0.3m | 11.6 | 3.7 | 22 | 1.7 | 1.1 |
| ST06-0.6m | 11.6 | 3.5 | 19 | 19.5 | 1.8 |
| ST07-0.3m | 1.1 | 2.9 | 24 | 32.7 | 2.2 |
| ST07-0.6m | 1.8 | 4.3 | 18 | 26.3 | 6.4 |
| ST08-0.3m | 1.6 | 4.9 | 32 | 32 | 4.4 |
| ST08-0.6m | 1.9 | 3.1 | 31 | 34.5 | 3.6 |

Analyses carried out according to methods from the Brazilian Agricultural Research Corporation (1997)

- Horizon O (surface): OM in decomposition (0.3 m of depth)
- Horizon A: OM accumulated mixed with the mineral fraction (0.6 m of depth)
- Horizon B: clay accumulation, $Fe^{3+}$, $Al^{3+}$, and low OM content (approximately 1 m of depth)
- Horizon C: materials from rock mother

Thus, it is expected that the higher the concentration of OM, especially of humic acids present in it, the greater the retention capacity of metallic cations in soils, especially in Horizon O, which leads to a reduction in the transport of metallic pollutants in the soil, as the humic substances act as strong complexing agents due to the presence of biding sites formed by carboxylic and phenolic groups (Clapp et al. 2001). Therefore, a higher concentration, for example, of bivalent metal cations in the samples of Horizons O and A of the soil is expected, considering the effect of the presence of silicate compounds in the metal retention, where a greater cation-exchange capacity (CEC) of the soil denotes a higher availability of binding sites for the metal after the exit of cations or protons associated with these silicates, due to the negative surface charge of the latter.

Figure 4.6 shows a soil with a high content of clay.

**Fig. 4.6** Soil with a high content of clay

According to the University of the West of England (2013), the main pollutants observed in European soil are:

- Asbestos
- Dioxin and dioxin-like chemicals
- Metals: cadmium, lead, mercury
- Nonmetal: arsenic
- Persistent organic pollutants (POP): polychlorinated biphenyls (PCBs), polybrominated biphenyls, polychlorinated dibenzofurans (PCDFs), polycyclic aromatic hydrocarbons (PAHs), organophosphorus and carbamate insecticides (pesticides), herbicides, organic fuels (gasoline, diesel), and pharmaceuticals and their metabolites

### *4.2.1 Sampling and Sample Preparation*

Soil samples are collected using the following procedure (U.S. Environmental Protection Agency 1997):

(a) Carefully remove the top layer of soil to the desired sample depth with a precleaned spade.
(b) Using a precleaned, stainless steel scoop, spoon, trowel, or plastic spoon, remove and discard the thin layer of soil from the area that came into contact with the shovel.
(c) Transfer the sample into an appropriate container using a stainless steel or plastic lab spoon or equivalent. If composite samples are to be collected, place the soil sample in a stainless steel or plastic bucket and mix thoroughly to obtain a homogeneous sample representative of the entire sampling interval. Place the soil samples into labeled containers. [Caution: Never composite volatile organic analysis (VOA) samples.]
(d) VOA samples should be collected directly from the bottom of the hole before mixing the sample to minimize volatilization of contaminants.
(e) Check to ensure that the VOA vial Teflon liner is present in the cap, if required. Fill the VOA vial fully to the top to reduce headspace. Secure the cap tightly. The chemical preservation of solids is generally not recommended. Refrigeration is usually the best approach, supplemented by a minimal holding time.
(f) Ensure that a sufficient sample size has been collected for the desired analysis, as specified in the sampling plan[1].

[1] A plan containing, basically, amount of samples, location, methods, QA/QC, and logistic of sampling. Steps related to the sample plan are (National Institute of Standards and Technology 2017) the following: (1) identify the parameters to be measured, the range of possible values, and the required resolution; (2) design a sampling scheme that details how and when samples will be taken; (3) select sample sizes; (4) design data storage formats; and (5) assign roles and responsibilities.

(g) Decontaminate equipment between samples.
(h) Fill in the hole and replace grass turf, if necessary.

After the sampling, samples should obey the follow requirements:

- Holding time: 14 days from sampled
- Minimum volume: 100 g
- Container type: two 40 mL vials and no air space (for volatile compounds); glass jar with Teflon-lined cap (for other compounds)
- Preservation: cool to 4 °C (ice in cooler)

The sample preparation for the analysis step comprises:

(a) Extraction by means solvent (solid–liquid, Soxhlet, accelerated solvent extraction, etc.), according to the analyte and matrix physicochemical properties.
(b) Cleanup by means of the use of solid-phase extraction (SPE) or another technique (see Chap. 3).
(c) Injection for the chromatographic analysis.

For analysis of metals, samples need a digestion in mineral acid, as nitric acidic, or a microwave-assisted digestion.

Figure 4.7 shows a soil sampling.

**Fig. 4.7** Soil sampling with an auger device. Courtesy of U.S. EPA

### 4.2.2 Methods for EP Analyses in Soil

Table 4.7 describes a compendium of analytical methods dedicated to the EP analyses in soil.

## 4.3 Water Composition and Properties

When we talk about water as an environmental matrix, we must consider it in the plural, since we are dealing with two distinct types, the *surface water* and the *groundwater*. The surface water is that found in rivers, lakes, seas, and oceans, while groundwater is that found in the aquifers. Drinking water and wastewater are classifications related to surface and groundwater according to their use. Table 4.8 shows the main characteristics of each of them.

A variation in the water composition is expected according to climate and environmental conditions.

It may be noted that for most of the ions listed in the Table 4.8 there is an increase in their concentration when considering groundwater relative to surface water (except for $Cl^-$ ion). As observed by Snoeyink and Jenkins (1996), groundwater, which has a higher concentration of $CO_2$ gas, is in greater contact with rocks and soil, which leads to a longer dissolution time. The carbonic acid ($H_2CO_3$) produced by the solubilization of $CO_2$ when in contact with these materials leads to the solubilization of the minerals, releasing their constituent ions.

A large amount of suspended material can be found mainly in surface waters. Clay, sand, and organic matter are examples of particles in suspension. There is also a large amount of microorganisms present in water, highlighting bacteria such as

**Table 4.7** Analytical methods for analyses of EPs in soils

| Analyte(s) | Brief method description | LOD | References |
|---|---|---|---|
| Alprostadil (vasodilator) and ethinyl estradiol (semisynthetic alkylated estradiol) | Methods for the determination of steroidal estrogen using GC-MS | 300–570 ng $g^{-1}$ | Gunatilake et al. (2016) |
| Melamine (used in the manufacture of plastics, flame retardants, coatings, and other products) | Method for the determination of melamine using HPLC-DAD | 0.01 mg $kg^{-1}$ | Nong et al. (2014) |
| Antibiotics (sulfadiazine, roxithromycin) | Method for the determination of antibiotics using LC-MS-MS | – | Sun et al. (2015) |
| Antibiotic (OTC) | Method for the determination of OTC antibiotic in soils using HPLC-UV | <1 mg $L^{-1}$ | Vaz Jr. (2016) |

*GC* Gas chromatography, *HPLC* High-performance liquid chromatography, *LC* Liquid chromatography, *MS* Mass spectrometry, *DAD* Diode array detector, *UV* Ultraviolet

**Table 4.8** Typical surface water and groundwater composition in the United States, according to Snoeyink and Jenkins (1996)

| Chemical species | Concentration in surface water (mg $L^{-1}$) | Concentration in groundwater (mg $L^{-1}$) |
|---|---|---|
| $SiO_2$ | 1.2 | 10 |
| $Fe^{3+}$ | 0.02 | 0.09 |
| $Ca^{2+}$ | 36 | 92 |
| $Mg^{2+}$ | 8.1 | 34 |
| $Na^{+}$ | 6.5 | 8.2 |
| $K^{+}$ | 1.2 | 1.4 |
| $HCO_3^-$ | 119 | 339 |
| $SO_4^{2-}$ | 22 | 84 |
| $Cl^-$ | 13 | 9.6 |
| $NO_3^-$ | 0.1 | 13 |
| Total dissolved solids | 165 | 434 |
| Total hardness as $CaCO_3$ | 123 | 369 |

coliforms and cyanobacteria, which often compromise the quality of water, especially surface water.

Important analytical parameters for the monitoring of water quality are the following:

- Electrical conductivity (EC): It provides information on the distribution of ionic species in the medium, with the conductivity being directly proportional to the concentration of these species.
- Dissolved oxygen (DO): $O_2$ gas has a low solubility in water, with a reduction of its concentration indicating its consumption by the chemical oxygen demand (COD) for the formation of oxidized species, as well as consumption by biochemical demand (BOD) due to the activity of the metabolism of present microorganisms—groundwater has DO values much smaller than surface waters.
- pH: Its value indicates the concentration of $H^+$ in the medium—a pH value around 6 is the most common in drinking waters; however, there are variations due to the presence of organic or inorganic species.
- Redox potential ($E_h$): It indicates the oxidizing or reducing characteristic of the medium, having a direct correlation with the pH values.
- Presence of organic compounds: Determination of petroleum derivatives, agrochemicals, and organochlorine compounds produced by treatment processes, which are the main *xenobiotics* observed in waters, among others, as the EPs.
- Presence of toxic metals: Cadmium, mercury, chromium, etc., are also, in most cases, xenobiotic species.

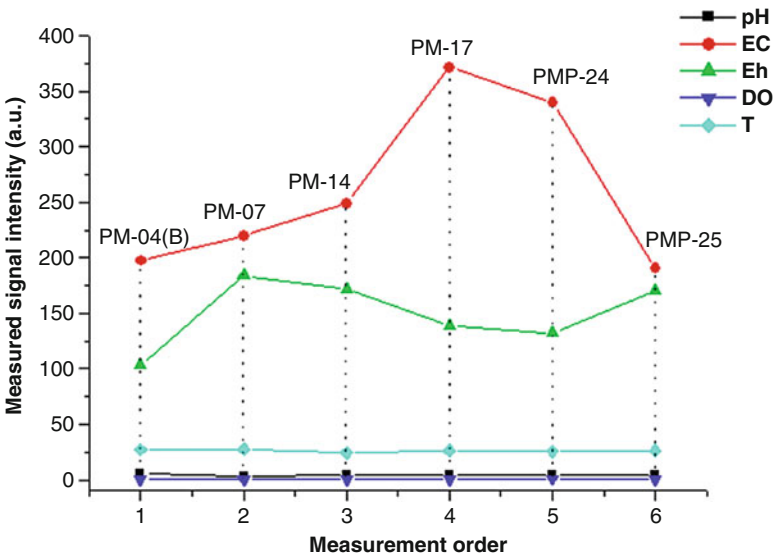


**Fig. 4.8** Behavior of physicochemical parameters measured in situ with the use of multiparameter probe in groundwater located in the southeast region of Brazil. *PM* Monitoring well, *PMP* Deep monitoring well. EC in μS $m^{-1}$, $E_h$ in mV, DO in mg $L^{-1}$, and T in °C

Figure 4.8 shows an example of in situ measurements for the physicochemical parameters mentioned above. We can observe that EC and $E_h$ presented the main variation in their values, probably due to the variability in the concentration of ionic species presented in each monitoring well.

Figure 4.9 shows a water body (surface water) that can also be monitored using the analytical parameters in Fig. 4.8.

Unfortunately, water bodies—especially surface water—are the main route of exposition to EPs due to the fact that these bodies receive a large amount of pharmaceuticals and healthcare products from the human use and excretion.

Other water-related matrices are the following:

- Sediments: naturally occurring material, as rocks, sand, and silt, in contact with water bodies, as rivers
- Sewage or municipal wastewater
- Sludge: a residual semisolid material from industrial, water, or wastewater treatment processes
- Wastewater: result of a domestic, industrial, commercial, or agricultural activities, with negative impacts to the human health and environment

**Fig. 4.9** Small creek (surface water)

The World Health Organization (2017) established the occurrence of chemicals in drinking waters (Table 4.9).

### *4.3.1 Sampling and Sample Preparation*

The sampling of surface water takes into account the following (U.S. Environmental Protection Agency 2016):

(a) Surface water samples will typically be collected either by directly filling the container from the surface water body being sampled or by decanting the water from a collection device such as a stainless steel scoop or other device.
(b) During sample collection, if transferring the sample from a collection device, make sure that the device does not come in contact with the sample containers.

**Table 4.9** Categorization of sources of chemicals in drinking water, according to the World Health Organization (2017)

| Source | Examples |
|---|---|
| Naturally occurring chemicals (including naturally occurring algal toxins) | Rocks and soils (e.g., calcium, magnesium but also arsenic and fluoride, cyanobacteria in surface water) |
| Chemicals from agricultural activities (including pesticides) | Application of manure, fertilizer, and pesticides; intensive animal practices |
| Chemicals from human settlements (including those used for public health purposes, e.g., vector control) | Sewage and waste disposal, urban runoff, fuel leakage |
| Chemicals from industrial activities | Manufacturing, processing, and mining |
| Chemicals from water treatment and distribution | Water treatment chemicals; corrosion of and leaching from storage tanks and pipes, by-products of chemical treatment |

(c) Place the sample into appropriate, labeled containers. Samples collected for volatile organic compounds (VOCs) analysis must not have any headspace. All other sample containers must be filled with an allowance for ullage.
(d) All samples requiring preservation must be preserved as soon as practically possible, ideally immediately at the time of sample collection. If preserved VOC vials are used, these will be preserved with concentrated hydrochloric acid prior to departure for the field investigation. For all other chemical preservatives, use the appropriate chemical preservative generally stored in an individual single-use vial. The adequacy of sample preservation will be checked after the addition of the preservative for all samples, except for the samples collected for VOC analysis. If it is determined that a sample is not adequately preserved, additional preservative should be added to achieve adequate preservation.
(e) All samples preserved using a pH adjustment (except VOCs) must be checked, using pH strips, to ensure that they were adequately preserved. This is done by pouring a small volume of sample over the strip. Do not place the strip in the sample. Samples requiring reduced temperature storage should be placed on ice immediately.

These recommendations can be extended to wastewater and sewage.

For groundwater, sampling recommendation comprises the following (U.S. Environmental Protection Agency 2013):

(a) Groundwater samples will typically be collected from the discharge line of a pump or from a bailer, either from the pour stream of an upturned bailer or from the stream from a bottom-emptying device. Efforts should be made to reduce the flow from either the pump discharge line or the bailer during sample collection to minimize sample agitation.
(b) During sample collection, make sure that the pump discharge line or the bailer does not contact the sample container.

(c) Place the sample into appropriate labeled containers. Samples collected for VOC, acidity, and alkalinity analysis must not have any headspace. All other sample containers must be filled with an allowance for ullage.
(d) All samples requiring preservation must be preserved as soon as practically possible, ideally immediately at the time of sample collection. If preserved VOC vials are used, these will be preserved with concentrated hydrochloric acid prior to departure for the field investigation. For all other chemical preservatives, use the appropriate chemical preservative generally stored in an individual single-use vial. The adequacy of sample preservation will be checked after the addition of the preservative for all samples except for the samples collected for VOC analysis. If additional preservative is needed, it should be added to achieve adequate preservation.

Furthermore, according to the U.S. Environmental Protection Agency (2013) special sample-handling procedures should be instituted when trace pollutant samples are being collected. All sampling equipment, including pumps, bailers, water-level and measurement equipment, which come into contact with the water in the well must be cleaned in accordance with cleaning procedures. Pumps should not be used for sampling unless the interior and exterior portions of the pump and the discharge hoses are thoroughly cleaned. Blank samples should be collected to determine the adequacy of cleaning prior to collection of any sample using a pump other than a peristaltic pump.

For organic EPs, the best preservation method is cool to 4 °C, and add sulfuric acid to pH value below 2, using a glass container. The holding time is 28 days.

In the case of metals, generally filter samples on-site, and add nitric acid to pH value below 2, using a glass or plastic container. The holding time is 6 months.

After the sampling, samples will pass by the following steps:

(a) Analyte extraction, using liquid–liquid extraction with a solvent, solid-phase extraction (SPE), or solid-phase microextraction (SPME).
(b) Cleanup before the extract injection in the chromatographic system, by means of a SPE.

Figure 4.10 shows a surface water sampling.

### *4.3.2 Methods for EP Analyses in Water*

Table 4.10 describes a compendium of analytical methods dedicated to the EP analysis in water.

**Fig. 4.10** Surface water sampling in a lagoon. Courtesy of U.S. EPA

## 4.4 Conclusions

Air, soil, and water have a heterogenic chemical composition, which promotes a large variation in their properties, functionality, and interaction with pollutants.

Nowadays, there is a large variety of technologies of sampling and analysis available for environmental analytical laboratories, which can reduce significantly the time consumed to generate the analytical result.

Despite the availability of advanced techniques as separation and detection, sampling and sample preparation are steps that require attention for the analyses of EPs in environmental matrices. The right choice of both methods will lead to the efficiency of the analytical approach applied.

**Table 4.10** Analytical methods for EP analysis in water

| Analyte (s) | Brief method description | LOD | References |
|---|---|---|---|
| Pharmaceuticals (naproxen, ketoprofen, diclofenac, ibuprofen, mefenamic acid), perfluorinated compounds (PFOA, PFOS) and caffeine | Method for the determination of pharmaceuticals, perfluorinated compounds, and caffeine by LC-MS/MS | 0.15 ng $mL^{-1}$ | Magi et al. (2018) |
| Polar pesticides (atrazine, carbendazim, desethylatrazine, desethylterbutylazine, diuron, S-metolachlor, terbuthylazine; pharmaceuticals (alprazolam, atenolol, carbamazepine, diazepam, diclofenac, ibuprofen, naproxen); steroid hormones (17-α-estradiol, 17-α-ethinylestradiol, 17-β-estradiol, estriol, estrone); brominated diphenyl ethers (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154); fluorinated surfactants (PFOA, PFOS); bisphenol A; triclosan | Method for the determination of polar pesticides, pharmaceuticals, steroid hormones, brominated diphenyl ethers, fluorinated surfactants, bisphenol A, and triclosan by LC-MS (ESI) | 0.3–75 ng $L^{-1}$ | Vrana et al. (2016) |
| Phthalate esters (bis(2-*n*-butoxyethyl) phthalate, bis (2-ethoxyethyl) phthalate, bis(2-methoxyethyl) phthalate, bis(4-methyl-2-pentyl) phthalate, diamyl phthalate, dicyclohexyl phthalate, dihexyl phthalate, diisobutyl phthalate, dinonyl phthalate, hexyl 2-ethylhexyl phthalate) | Method for the determination of phthalate esters by GC-ECD | 22–640 ng $L^{-1}$ | U.S. Environmental Protection (1996) |
| Multiclass pharmaceuticals (analgesics/anti-inflammatories, antibiotics, lipid regulators, β-blockers, antiepileptic/psychiatrics ulcer healings, diuretics, hormones and bronchodilators), lifestyle products (caffeine, nicotine), drugs of abuse and their metabolites, pesticides and some of their more relevant metabolites, nitrosamines, flame retardants, plasticizers, and perfluorinated compounds | Multi-residue method of determination of over 400 priority and emerging pollutants by rapid-resolution LC-TOFMS | <10 ng $L^{-1}$ | Robles-Molina et al. (2014) |

(continued)

**Table 4.10** (continued)

| Analyte (s) | Brief method description | LOD | References |
|---|---|---|---|
| Pharmaceuticals (carbamazepine, ofloxacin, and piroxicam) | Method for the determination of carbamazepine, ofloxacin, and piroxicam in waters using excitation–emission photoinduced fluorescence data and multivariate calibration, without the necessity of chromatographic separation | 2–7 ng $mL^{-1}$ | del Carmen Hurtado-Sánchez et al. (2015) |
| Pharmaceuticals (ibuprofen, diclofenac, bezafibrate, ketoprofen, and mefenamic acid) | Method for screening of pharmaceuticals in waters by means of CE-$C^4D$ | 0.20–0.81 mg $L^{-1}$ | Le et al. (2016) |

*GC* Gas chromatography, *HPLC* High-performance liquid chromatography, *LC* Liquid chromatography, *ECD* Electron capture detector, *MS* Mass spectrometry, *TOFMS* Time-of-flight mass spectrometry, *ESI* Electrospray ionization, *PFOA* Pentadecafluorooctanoic acid, *PFOS* Perfluorooctanesulfonic acid, *CE* Capillary electrophoresis, *$C^4D$* Coupled contactless conductivity detection

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# Chapter 5
# Degradation Processes of EPs


## 5.1 Degradation Under Environmental Conditions

From their chemical structures and their environmental fate, the reactions suffered by EPs are *hydrolysis*, *photolysis*, *oxidation*, *and reduction*. Hydrolysis is defined as the solvolysis by the water, or a reaction with a solvent (water) involving the rupture of one or more bonds in the reacting solute (e.g., EP molecule) (International Union of Pure and Applied Chemistry 2017). Photolysis is the cleavage of one or more covalent bonds in a molecular entity (as EP molecule) resulting from absorption of light, or a photochemical process in which such cleavage is an essential part (International Union of Pure and Applied Chemistry 2017). Oxidation involves the loss of one or more electrons to an oxidative species whereas reduction involves the gain of one or more electrons from a reductive species—these are common processes for metallic species because of their electroactive property.

Hydrolysis (Scheme 5.1) occurs when the EP molecule is in aqueous and vapor phase—with or without the presence of an acid—and photolysis (Scheme 5.2) when the molecule is exposed to the electromagnetic radiation ($h\nu$), as UV and visible radiation. These are the main reactions associated with the degradation of pollutants in the environmental matrixes (Don et al. 2017; Balmer et al. 2000). Redox processes for water treatment, as Fenton reaction (Scheme 5.3), are applied combining photolysis with oxidation reaction by a hydroxyl radical (•OH) formation (Mirzaei et al. 2017); this radical will attack and degrade the organic molecule, as an EP.

Regarding the kinetic of these reactions, Carlos et al. (2012) observed a pseudo-first order for EPs (e.g., clofibric acid) photolysis. Pseudo-first and first order were observed by Sasi et al. (2015) for the methylparaben degradation involving hydrolysis. Zúñiga-Benítez et al. (2016) observed a pseudo-first order for benzophenone-3 and methylparaben using Fenton reaction.

Degradation of a certain molecule under environmental condition—e.g., a pollutant in soil or air—is a frequent process that involves, mainly, *biodegradation* and



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$$(CH_3)_3N + H_2O \rightarrow (CH3)_3NH^+ + OH^-$$

**Scheme 5.1** The hydrolysis reaction of the trimethylamine, a basic nitrogen compound

$$HNO_2 + h\nu \rightarrow {}^{\cdot}OH + NO$$

**Scheme 5.2** The photolysis reaction of the nitrous acid in the indoor atmosphere

**Scheme 5.3** The Fenton reaction to generate the hydroxyl radical and further reactions of degradations of organic molecules

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-$$

$$RX + {}^{\cdot}OH \rightarrow {}^{\cdot}RX^+ + OH^-$$

$$RH + {}^{\cdot}OH \rightarrow {}^{\cdot}R + H_2O$$

$$RHX + {}^{\cdot}OH \rightarrow RHX(OH)$$

*photodegradation*. In the first case, the International Union of Pure and Applied Chemistry (2017) defines it as the breakdown of a substance catalyzed by enzymes in vitro or in vivo. This may be characterized for purposes of hazard assessment as follows:

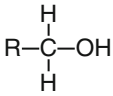
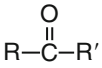
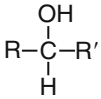
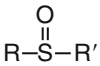
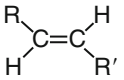
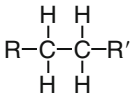
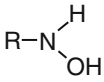
1. Primary: Alteration of the chemical structure of a substance resulting in loss of a specific property of that substance.
2. Environmentally acceptable: Biodegradation to such an extent as to remove undesirable properties of the compound. This often corresponds to primary biodegradation but it depends on the circumstances under which the products are discharged into the environment.
3. Ultimate: Complete breakdown of a compound to either fully oxidized or reduced simple molecules (such as carbon dioxide/methane, nitrate/ammonium, and water). It should be noted that the products of biodegradation can be more harmful than the substance degraded.

Photodegradation is defined by the International Union of Pure and Applied Chemistry (2017) as the photochemical transformation of a molecule into lower molecular weight fragments, usually in an oxidation process. This term is widely used in the destruction (oxidation) of pollutants by UV-based processes.

Biodegradation is most common for soil and water and related matrices (e.g., sewage, wastewater) while photodegradation for air or atmosphere.

The photodegradation of EPs (nonsteroidal anti-inflammatory drugs and endocrine-disrupting chemicals) in surface water at $\lambda > 290$ nm depends on season, pH value, humic acids, and nitrate ion (Koumaki et al. 2015)—humic substances and/or nitrate/nitrite ions can serve as photosensitizers. Apart from photodegradation, the fate of such chemicals in the aquatic environment may be influenced by hydrolysis reactions in an unclear mode (Koumaki et al. 2015). The following photodegradation products were observed:

**Table 5.1** Functional groups that undergo microbial reduction

| Reactant | Process | Product |
|---|---|---|
|  | Aldehyde reduction |  |
|  | Ketone reduction |  |
|  | Sulfoxide reduction | R–S–R′ |
| R–SS–R′ | Disulfide reduction | R–SH, R′–SH |
|  | Alkene reduction |  |
| $R–NO_2$ | Nitro group reduction | R–NO, $R–NH_2$,  |

Adapted from Manahan (2000)

- From ketoprofen ($C_{16}H_{14}O_3$): 3-hydroxyethyl benzophenone, 1-(3-benzoylphenyl)ethane-1-peroxol, 3-acetylbenzophenone, and 3-ethylbenzophenone.
- From diclofenac ($C_{14}H_{10}ClNO_2$): 2-(8-chloro-9H-carbazol-1-yl) acetic acid, 2-(8-hydroxy-9H-carbazol-1-yl) acetic acid, 2-(9H-carbazol-1-yl) acetic acid, and 2-{9-[4-(carboxymethyl)-5-hydroxy-9H-carbazol-9-yl]-8-hydroxy-9H-carbazol-1-yl}acetic acid.

Regarding the biodegradation products, Table 5.1 describes examples of them.

These reactant groups are very common in EP molecules. Then, biodegradation is a class of processes of treatment to be considered, for instance, in wastewater treatment (to be seen ahead).

## 5.2 Degradation by Means of Processes of Treatment

The processes of treatment for EPs are still under evolution because of their physicochemical properties and the lack of mature technologies to degrade these type of pollutants, which are organic compounds in their majority.

We keep in mind that EPs need a complete degradation to avoid their effect on environmental matrices and human health. Table 5.2 shows technologies for EP treatments in water.

**Table 5.2** Water treatment for EPs

| Technology | | Advantages | Disadvantages | Annual cost for a 20 MGD plant (millions of dollars) |
|---|---|---|---|---|
| Oxidation | Ozone | Selective oxidant; good disinfection capacity for bacteria, viruses, and protozoa; good removal of bisphenol A, naproxen, carbamazepine, diclofenac, sulfamethoxazole, triclosan, and trimethoprim; moderate removal of gemfibrozil and atenolol | Large ozone contactors might be needed (>20 min HRT); bromate formation; poor removal of DEET, ibuprofen, *para*-chlorobenzoic acid (*p*CBA), phenytoin, primidone, 1,4-dioxane, atrazine, meprobamate, TCEP, musk ketone, and X-ray contrast | 0.525 |
| | Chlorine | Selective oxidant; provides good disinfection for bacteria and viruses; good removal of 17-α-ethinylestradiol, sulfamethoxazole, and ciprofloxacin | Reacts with amines to form chloramines; can form chlorinated by-products; poor removal of carbamazepine, atenolol, ibuprofen, and X-ray contrast | 0.099 |
| | Chlorine dioxide | Selective oxidant; does not form chloramines; reacts with compounds with high electron density (tertiary amines and phenoxides); more potent oxidant than chlorine; good removal of estrogens (estrone, 17-β-estradiol, 17-α-ethinylestradiol) and sulfonamides (sulfamethoxazole) | Less potent oxidant than ozone; poor removal of bezafibrate, carbamazepine, diazepam, atenolol, ibuprofen, and iopromide | 0.102 |
| | Ferrate (VI) | Selective oxidant; reactive to electron rich moieties including estrogens (estrone, 17-β-estradiol, 17-α-ethinylestradiol, diethylstilbestrol), triclosan, carbamazepine, progesterones (19-norethindrone, norgestrel, medroxyprogesterone), select androgens, glucocorticoids, secondary amines of acidic pharmaceuticals, and antibiotics (sulfonamides, | Poor removal of atenolol, ibuprofen, clofibric acid, gemfibrozil, ketoprofen, erythromycin, select androgens | Not available |

(continued)

**Table 5.2** (continued)

| Technology | | Advantages | Disadvantages | Annual cost for a 20 MGD plant (millions of dollars) |
|---|---|---|---|---|
| | | fluoroquinolones, tetracyclines, sulfamethoxazole) | | |
| | Potassium permanganate | Selective oxidant; good removal of phenolic compounds (estrone, 17-β-estradiol, 17-α-ethinylestradiol, and 4-nonylphenol) at lower doses than chlorine and ferrate, but slower kinetics; moderate removal of ciprofloxacin, lincomycin, and trimethoprim | Slower reaction kinetics with phenolic compounds than chlorine and ferrate; high cost | 1.626 |
| AOPs | $UV/H_2O_2$ | UV alone is effective for microbial inactivation and NDMA mitigation; $UV/H_2O_2$ can oxidize recalcitrant compounds including diclofenac and triclosan; moderate removal of phenytoin, ibuprofen, atenolol, gemfibrozil, naproxen, trimethoprim, carbamazepine, bisphenol A | For effective oxidation high doses of UV and $H_2O_2$ are often needed; poor removal of TCEP, atrazine, meprobamate, primidone, DEET | 0.494 |
| | $O_3/H_2O_2$ | Highly reactive; reduced bromate formation compared to using ozone alone; $H_2O_2$ can be applied to reduce ozone footprint and achieve oxidation; good removal of bisphenol A, naproxen, carbamazepine, gemfibrozil, atenolol, diclofenac, sulfamethoxazole, triclosan, trimethoprim, DEET, ibuprofen, *p*CBA, phytoin, primidone; moderate removal of 1,4-dioxane, atrazine, meprobamate | Nonselective, organic matter can compete for •OH radicals and might reduce removal of target compounds, inefficient for spore-forming microbes, poor removal of TCEP and musk ketone | 0.535 |
| Adsorption | GAC or BAC | Good adsorbent for organic compounds; GAC can be combined with ozone for $O_3$/BAC | Performance is severely impacted by the presence of natural organic matter | 1.192 |

(continued)

**Table 5.2** (continued)

| Technology | | Advantages | Disadvantages | Annual cost for a 20 MGD plant (millions of dollars) |
|---|---|---|---|---|
| Physical | RO or NF | High rejection of large organic compounds | High cost, membrane fouling, small compounds can pass through (NDMA) | 4.611 |
| | MF or UF | Removal of large particles and TOC; some removal of persistent organic compounds | Lower rejection of organic compounds compared to RO or NF | 2.151 |

Advantages, disadvantages, and estimated costs. Adapted from Richardson and Kimura (2017)
*MGD* Millions gallons per day, *HRT* Hydraulic retention time, *DEET* *N*,*N*-diethyl-3-methylbenzamide, *TCEP* Tris(2-carboxyethyl)phosphine, *AOPs* Advanced oxidation processes, *NDMA* *N*-nitrosodimethylanime, *UV* Ultraviolet, *GAC* Granular activated carbon, *BAC* Biological activated carbon, *RO* Reverse osmosis, *NF* Nanofiltration, *MF* Microfiltration, *UF* Ultrafiltration, *TOC* Total organic carbon

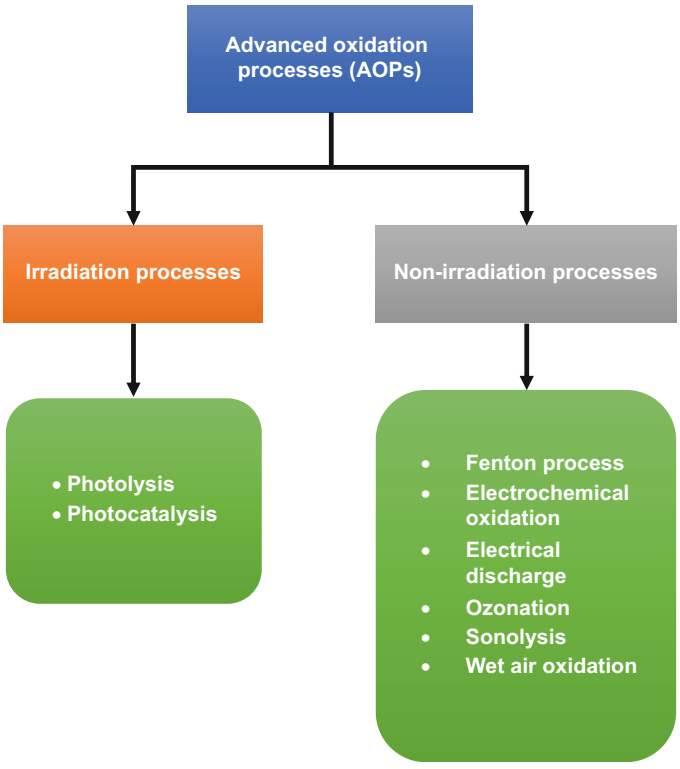



**Fig. 5.1** Classes of advanced oxidation processes (AOPs). Adapted from Hisaindee et al. (2013)


**Fig. 5.2** An AOP plant for groundwater treatment for photolysis of volatile organic compounds (VOCs) by UV radiation. Courtesy of TrojanUV

From the advantages, disadvantages, and costs presented in Table 5.2 we can infer that the better choice is a combination of technologies taking into account the diversity of EPs in wastewater from the large human use of pharmaceuticals and personal care products.

Figure 5.1 illustrates the classes of the advanced oxidation processes (AOPs), the large family of treatment processes for EPs. In Fig. 5.2 we can see an AOP treatment plant.

## 5.3 Analytical

The analytical techniques and methods are very similar to those presented in Chaps. 3 and 4, except a more intensive use of UV-vis spectrophotometer for the observation of the photolysis process. Table 5.3 describes appropriate techniques for the analysis of degradation products from EPs.

**Table 5.3** Analytical techniques applied to the analysis of degradation products

| EPs | Degradation process | Analytical matrix | Analytical technique | Reference |
|---|---|---|---|---|
| 2-QCA, acetaminophen, antipyrine, carbamazepine, ceftiofur, chlortetracycline, clarithromycin, clenbuterol, crotamiton, cyclophosphamide, DEET, diclofenac, disopyramide, ethenzamide, fenoprofen, ifenprodil, indomethacin, isopropylantipyrine, ketoprofen, mefenamic acid, metoprolol, naproxen, oxytetracycline, propranolol, sulfadimethoxine, sulfadimidine, sulfamethoxazole, sulfamonomethoxine, tetracycline, theophylline. | UV photodegradation ($\lambda = 254$ and 185 nm) | Pure water | LC-MS/MS (ESI positive mode) | Kim and Tanaka (2009) |
| Salicylic acid, 4-chlorophenol, benzoic acid and oxalic acid | Photodegradation ($\lambda = 200$–400 nm) using N-titanium oxide catalyst and involving electrochemical oxidation | Ultrapure water | UV-vis spectrophotometer for the observation of the extinction of absorption bands | Shinde et al. (2014) |
| Diclofenac and fluoxetine | Photodegradation ($\lambda = 365$ nm) using hydroxyapatite, $Ca_{10}(PO_4)(OH)_2$, as photocatalyst | Wastewater | HPLC-UV | Brazón et al. (2016) |
| Acetaminophen, caffeine, acetamiprid, clofibric acid, carbamazepine and amoxicillin | Photodegradation using Fenton process ($\lambda = 205$, 225 and 245 nm) | Wastewater | UPLC-UV-vis | Gomis et al. (2014) |
| Benzene, toluene, chlorobenzene, chlorobenzoic acid, chlorinated ethylenes, and psychopharmaceuticals (amitriptyline, dosulepin, chlorprothixene). | Stimulated bacterial biodegradation by means psychrophilic bacteria | Groundwater | GC-FID-MS | Lhotský et al. (2017) |

| | | | | |
|---|---|---|---|---|
| Fluoroquinolones and cephalosporins (veterinary antibiotics) | Combined biodegradation (biotic and abiotic) with the use of rhizosediment of plants as microbial inocula | Livestock wastewater | HPLC-DAD | Alexandrino et al. (2017) |
| Phenolic compounds, DEHP, alkylphenols, PBDEs, chloroalkanes $C_{10}$–$C_{13}$, tributylphosphate and hexachlorocyclopentadiene, and other priority organic compounds | Anaerobic digestion | Treated sludge from wastewater treatment plants | GC-MS | Mailler et al. (2014) |

*2-QCA* Clarithromycin, *DEET N,N*-diethyl-3-methylbenzamide, *UV* Ultraviolet, *LC* Liquid chromatography, *HPLC* High-performance liquid chromatography, *UPLC* Ultra-performance liquid chromatography, *GC* Gas chromatography, *FID* Flame ionization detector, *MS* Mass spectrometry, *ESI* Electrospray ionization, *DAD* Diode array detector, *DEHP* Di(2-ethylhexyl) phthalate, *PBDEs* Polybromodiphenyl ethers

## 5.4 Conclusions

Organic molecules, as EPs, undergo several reactions under environmental conditions, as hydrolysis, oxidation-reduction, and photolysis.

Most representative degradation processes with direct application for depollution are related to biodegradation and photodegradation, becoming both the basis of processes of treatment, highlighting the photodegradation due to its efficiency for aquatic pollutants. However, these processes of treatment are not well established with opportunities to develop remediation technologies.

Regarding the analytical techniques, these are very similar to those applied to EPs in Chap. 4, except a more intensive use of spectrophotometry to observe photodegradation and its products.

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# Chapter 6
# General Remarks and Conclusions


The control and monitoring of EPs are paramount to maintain a good quality of the environment and public health. Unfortunately, the use in large scale without control of EPs as pharmaceuticals and personal care products—probably, the main class—has contributed to the spread of this class of pollutant around the world, mainly in the aquatic environment.

EPs have a behavior, in certain cases, different from the ones of conventional organic and inorganic pollutants (e.g., pesticides, toxic metals, and hydrocarbon derivatives). It comes from the fact that the determination of EPs is relatively recently and we can see a lack of regulatory aspects well defined. For example, the first directive in Europe for the monitoring of this pollutant class in surface water was published in the year of 2013 (European Union 2013). Furthermore, the available information about their presence in environmental matrices is dispersed despite the considerable number of information in the scientific literature. Nevertheless, the presence and fate of EPs can vary according to countries due to climate conditions, economy, legislation, etc.

The United Nations Educational, Scientific and Cultural Organization (2017) recognizes the risk of EPs in water and wastewater with potentially serious threats to human health and ecosystems. Furthermore, the International Initiative on Water Quality (International Initiative on Water Quality 2015) considers EPs a new water quality challenge, with still unknown long-term impacts on human health and ecosystems. The United States Environmental Protection Agency (2017) states that EPs are increasingly being detected at low levels in surface water, and there is concern that these compounds may have an impact on aquatic life, highlighting the presence of pharmaceuticals and personal care products.



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## 6.1 Remarks

We saw in Chap. 1 that UNESCO established the following EP classes (United Nations Educational, Scientific and Cultural Organization 2017): pharmaceuticals, personal care products, pesticides, industrial and household products, metals, surfactants, and industrial additives and solvents. However, pharmaceuticals and personal care products are the most used EPs and deserve a special attention for their determination in environmental matrices to understand their fate and effects on the environment and public health.

In Chap. 2 the fundamentals of analytical chemistry were introduced. Figures of merit, as accuracy, linearity, limits of detection and quantification, precision, sensitivity, selectivity, robustness, and recovery were defined and their uses in chemical analysis were explained. Furthermore, the steps for the development and validating of an analytical method were detailed. Chemometrics, quality assurance/quality control, and green chemistry were treated also in order to allow the best application of analytical chemistry for EP determination.

In Chap. 3 the analytical techniques applied in the EP analysis were detailed, as spectroscopic, spectrophotometric, and spectrometric techniques, mass spectrometry, chromatographic techniques, electrochemical techniques, sensors and miniaturized probes, bioassays, and sample preparation (extraction, concentration, and cleanup techniques). We saw a large variety of techniques and their uses depends on the analyte and matrix physicochemical properties.

Chapter 4 presented the main environmental matrices (air, soil, and water), their chemical composition and functionality, and examples of analytical methods to determine EPs in these matrices. Furthermore, sampling and sample preparation were considered. It was possible to note a large variety of sampling technologies to assure the reliability of the analytical results.

In Chap. 5 the analysis of EP degradation was treated by understanding the degradation processes under environmental conditions and the processes of treatment of wastewater, groundwater, and sewage. The main technologies of treatment are based on advanced oxidation processes and biodegradation, as anaerobic digestion. Despite the need of more development, these technologies are effective to degrade EPs, mainly in aquatic environment—the most impacted medium. Furthermore, analytical techniques for degradation products were presented.

## 6.2 Conclusions

We can conclude that:

(a) EP determination is relatively recent when compared against conventional pollutants, probably, because EPs as pharmaceuticals and personal care products are consumed in large quantities and without a concern with their effect on the environment.

(b) Analytical chemistry is paramount to understand EP presence, fate, and effects. Identification and determination give basis for strategic decisions.
(c) Chromatographic techniques (GC and LC) stand out as the most used set of techniques for analyses of EPs, with a large variety of available detectors.
(d) Technological advances in analytical techniques related to miniaturization and automatization are in the frontier of knowledge in order to reduce costs and time, as probes and sensors.
(e) Aquatic environment is the most impacted medium due to the EP uses and discards.
(f) Legislation is incipient to regulate the EP presence and management in the environment. It is a fragile point to be improved.

Then, the analysis of EPs in environmental matrices is a topic that generates opportunities for analytical services, research, technology, and improvement of environment and health conditions. Furthermore, it can generate scientific understandings for environmental chemistry and related environmental sciences and technology.

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# Index

**Abiotic** A process or a substance not associated with living organisms.

**Abiotic transformation** Process in which a substance in the environment is modified by nonbiological mechanisms.

**Analytical approach** Purpose of a chemical analysis that defines technique and analytical method to be applied.

**Analytical matrix** Physical medium in which the analyte is to be sampled and analyzed. A given environmental matrix to be analyzed becomes an analytical matrix.

**Analytical method** Application of an analytical technique for the determination of an analyte in a specific medium or analytical matrix.

**Analytical monitoring** Chemical analysis or set of chemical analyses performed to monitor a given process in the environment, be it chemical, physical, or biological.

**Analytical procedure** Set of technical details for the application of an analytical method in a given sample, considering the sampling stage, the elimination of interferents, and the data validation.

**Analytical process** Set of operations leading to an analytical result.

**Analytical protocol** Set of guidelines detailing the procedures that must be followed in order for the results to be accepted by an agency or regulatory body.

**Analytical technique** Technological strategy for the use of a physical or chemical phenomenon for the identification or quantification of an analyte.

**Analyte** A chemical species of interest in a chemical analysis, which may be organic or inorganic.

**Anthropic activities** Activities developed by the man, as agriculture, industry, commerce, and traffic, among others, with direct effects on the environment.

**Blank of method** Material of known composition, such as distilled water, without the presence of the analyte, handled in the same way as the sample, and used to observe possible contamination resulting from the application of the analytical method.



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**Blank of sample** Material of known composition, such as distilled water, without the presence of the analyte, handled in the same way as the sample, and used to observe possible contaminations arising from the sampling step.

**Calibration curve or analytical curve** Graphical display of an analyte against the change in the behavior of a property, such as absorption, depending on the variation of its concentration.

**Carcinogenic** Property of a compound, which produces cancer through biochemical changes in cells.

**Chemical analysis** Experimental procedure for the identification or quantification of one or more analytes.

**Chemical species** Chemical entity or particle, as a radical, ion, molecule, or atom.

**Chemometrics** A set of statistical tools to be used in experimental planning and in the treatment of analytical data.

**Chemisorption** Adsorption resulting from the formation of chemical bond between the adsorbent and the adsorbate in a monolayer on the surface of the matrix.

**Chemical substance** Matter of constant composition best characterized by entities (molecules, structural formulas, and atoms). Physical properties such as density, refractive index, electrical conductivity, melting points, and boiling characterize such substances.

**Compound** Chemical substance whose molecule is formed by different atoms, which can only be separated by means of a chemical reaction.

**Contamination** Influence on an analytical result due to the presence of a certain chemical species, which may be the analyte itself from a source other than that from the sample, or any other chemical species.

**Effect** Event resulting from the presence of a chemical (e.g., molecules, ions) or biological (e.g., bacteria, virus) species in the medium; its extent can be considered on the environment or on human or animal health.

**Effluent** Any liquor or waste material discarded, which are emitted by a source, such as chemical production plants and sewage treatment plants, among others.

**Environmental matrix** Medium where a chemical, physical, or biological process occurs that produces a given effect on the environment. Soil, water (groundwater, surface water, wastewater), air, sediment, and sludge are examples of environmental matrix.

**Environmental impact** Effect caused by the presence of a xenobiotic in the environment. May be positive or negative.

**Exposure** Process by which a substance becomes available for absorption by the target population, organism, organ, tissue or cell, by any route.

**Groundwater** Water contained in the aquifer reservoir.

**Genotoxic** Property of a compound, which produces genetic changes through damage to the structure of deoxyribonucleic acid (DNA).

**Green chemistry** Set of 12 guiding principles, which seek, among other objectives, the reduction of waste generation, the atomic and energy economy, and the use of renewable raw materials.

**Hazardous waste or residue** Property of a particular waste or residue, which may cause potential harm to human and animal health or to the environment.

**Humic substances** Chemical substances of complex structure formed through chemical and biological processes of degradation of organic matter; are classified as humic acids (soluble in basic medium), fulvic acids (soluble under any condition of the medium), and humin (insoluble under any condition of the medium).

**In loco** Analysis of a chemical species, organic or inorganic, at its site of origin.

**In situ** Analysis of a chemical species, organic or inorganic, at the time of its formation in the environmental matrix.

**Isotherm** Mathematical model that expresses the relation of equilibrium between the concentration of a component of the sample in the stationary phase ($C_s$) and its concentration present in the mobile phase ($C_M$), expressed as $C_s = kC_M$. The partition constant is $k$.

**Limit of detection (LOD)** It is the lowest concentration or amount that can be detected with reasonable certainty for a given analytical procedure.

**Limit of quantification (LOQ)** It is the lowest concentration or quantity that can be quantified with reasonable certainty for a given analytical procedure.

**Mutagenic** Property of a particular compound, which produces physical defects through changes in the structure of deoxyribonucleic acid (DNA).

**Operation** Technical procedure component of an analytical process or chemical analysis.

**Organic matter** Compositional fraction of an environmental matrix formed by residues of biological origin (plants and animals) under physical, chemical, or biological decomposition processes. It is rich in carbon, nitrogen, hydrogen, oxygen, and sulfur.

**Physiosorption** Adsorption in which the forces involved are intermolecular (van der Walls forces), similar to those responsible for the imperfection of the real gases and the condensation of the vapors. Does not cause changes in the electronic orbital involved.

**Pollutant** A gaseous, liquid, or solid chemical, which has been introduced into the environment by human activity or by natural processes in sufficient concentration to produce measurable effects on humans, animals, vegetation, or materials.

**Pollution** Presence of chemical species in the atmosphere, water, or soil, resulting from human activity or natural processes, in a concentration sufficient to interfere with the comfort, health, or well-being of people or the environment.

**Quantitative structure–activity relationships (QSAR)** The building of structure–biological activity mathematical models by using regression analysis applying physicochemical constants. Activity should be understood as reactivity or molecular interaction.

**Reliability** Confidence level expressed by an analytical result.

**Residue** Any substance or mixture of chemicals present in an environmental matrix resulting from the use of a given chemical substance including its derivatives from degradation and conversion processes.

**Risk** Probability of occurrence of adverse effects caused under specific circumstances by an agent (chemical, physical, or biological) in an organism, population, or ecological system.

**Risk assessment**[1] Identification and quantification of the risk resulting from a specific use or occurrence of an agent (i.e., chemical, physical, or biological), taking into account possible harmful effects on individuals exposed to the agent in the amount and manner proposed and all the possible routes of exposure.

**Routes of Exposure** Routes by which a substance can enter the body. There are four routes: inhalation, skin (or eye) absorption, ingestion, and injection.

**Sample** Representative physical portion to be analyzed, formed by matrix and analyte. May be solid, liquid, or gaseous, or a combination thereof.

**Sampling plan** A detailed outline of which measurements will be taken at what times, on which material, in what manner, and by whom.

**Surface water** Water contained in lakes, rivers, seas, and oceans.

**Surrogate** A compound similar in chemical composition to the analyte of interest and spiked into environmental samples prior to preparation and analysis. They are used to evaluate extraction efficiency and matrix interference.

**Sustainability** Measurement of the environmental, social, and economic impacts of a given process or product.

**Toxicity** Ability to cause internal damage to a living organism, defined by reference to the amount of the substance administered or absorbed. Can also be considered as the measure of the incompatibility of a substance with life.

**Traceability** Property of a result or measure by which it can be reported to an appropriate national or international standard through an uninterrupted chain of comparisons.

**Xenobiotic** Compound that is foreign to a living organism. Main xenobiotics include drugs, carcinogens, and various compounds that were introduced artificially into the environment.

[1] Modified from definition of the International Union of Pure and Applied Chemistry.