# Organic Analysis of Environmental Samples Using Liquid Chromatography with Diode Array and Fluorescence Detectors: An Overview

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#### TABLE OF CONTENTS LISTING

The table of contents for the journal will list your paper exactly as it appears below:

Organic Analysis of Environmental Samples Using Liquid Chromatography with Diode Array and Fluorescence Detectors: An Overview

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## Organic Analysis of Environmental Samples Using Liquid Chromatography with Diode Array and Fluorescence Detectors: An Overview

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This overview is focused to provide an useful guide of the families of organic pollutants that can be determined by liquid chromatography operating in reverse phase and ultraviolet/fluorescence detection. Eight families have been classified as the main groups to be considered: carbonyls, carboxyls, aromatics, phenols, phthalates, isocyanates, pesticides and emerging. The references have been selected based on analytical methods used in the environmental field, including both the well-established procedures and those more recently developed.

#### **KEYWORDS**

Fluorescence; liquid chromatography; organic pollutants; visible-ultraviolet

#### Introduction

As Samanidou points, [1] Liquid chromatography is the workhorse in routine analysis. In combination with ultraviolet (UV) and fluorescence (FLD) detectors, high performance liquid chromatography (HPLC) operating in reverse phase is considered as consolidated for the determination of numerous organic compounds. In spite of the limitation to confirm the analyte identity, UV and FLD detectors have significant advantages to continue being widely used.

Aspects such as marked reproducibility, robustness, low consuming costs, portable equipment, easy-to-use and widely available technique continues to be priority for laboratories. This is especially true when a large number of samples are handled, for instance, during monitoring programs in environmental studies.

Despite the requirement of fluorescent compounds is the main limitation to apply FLD detection, its sensitivity and selectivity remain remarkable. This type of detection is also advantageous because it is not very susceptible to matrix effects. A review of different types of luminescent spectrometric methods from 1990 to 2010 to determine pollutants in the environment was carried out by Vega Morales et al. [2] The determination of polycyclic aromatic hydrocarbons (PAHs), pesticides (carbamates, organophosphorus and benzimidazole), anti-inflammatory and antibiotics in different environmental matrices were documented.

Regarding UV detection, the interest to use this analytical tool lies in its universality and simplicity. In spite of its limited sensitivity and selectivity, HPLC/UV continues to be widely applied in environmental analysis.

Although, the development of direct analysis plays nowadays an important role in analytical studies, sample pretreatment is still mandatory in most analytical protocols. Hence, the continuous development in extraction step can lead to significant improvements. Moreover, life cycle con- 77 cept is gaining great interest too. In definite, green analytical 78 chemistry, low cost and minimized solvent consumption is 79 giving to interesting changes in extraction step.

It is, therefore, necessary to make a point in this article 81 about the main microextraction techniques that currently 82 participate in the analytical methodology. Regarding liquid 83 samples, these techniques are very briefly cited below.

Liquid phase microextraction (LPME). $^{[3,4]}$  Only several  $^{86}$ microliters of solvent are required to concentrate analytes from liquid samples.

Hollow fiber liquid phase microextraction (HF-LPME). A  $_{91}$ porous polypropylene hollow fiber is used for immobilization of organic solvent in its pores. Analytes are extracted  $\frac{1}{93}$ from the donor phase (i.e. water sample) into the acceptor  $\frac{1}{94}$ phase (i.e. organic solvent) that fills the inside of the fol- 95 low fiber.

Static mode: sample is stirred for extraction

Dinamic mode: small volumes of aqueous sample are repeatedly pulled in and out of the hollow fiber.

(DLLME). 101 liquid-liquid microextraction Extraction requires an extraction solvent, disperser solvent 102 and aqueous sample. A cloudy solution is formed, which can or not be centrifuged for separation. Modifications using 104 extraction solvents:

With higher or lower density of water

IL: Ionic liquids<sup>[5]</sup>

SMS: Supra molecular solvent, i.e. surfactants (variant: Cloud Point Extraction, changes on temperature and surfactant

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concentration produce to move aqueous analytes into a micelle phase for separation.

DES: Deep eutectic solvents, [6] with similar properties to IL.

Homogeneous liquid-liquid extraction. Initial condition for extraction is a homogeneous solution. Phase separation depends on temperature, salt effect, using a ternary solvent system and so forth.

• Miniaturized solid phase extraction (Miniaturized-SPE)<sup>[7]</sup>

Solvent-dispersive micro solid phase extraction (D-µSPE). Solid sorbent particles are dispersed into the sample solution. Phase separation can be achieved via centrifugation or filtration

Solvent free-solid phase microextraction (SPME). The method involves the use of a small microfiber to sorb analytes. The HPLC system requires an additional device as interface for solvent desorption of analytes.

Stir bar sorptive extraction (SBSE). Stir bars are coated with an apolar polymeric phase as sorbent to extract analytes while stirring.

Magnetic solid phase extraction (MSPE). Magnetic particles are coated with silica or alumina oxides to extract analytes by adsorption. Separation with an external magnetic field, without the need centrifugation or filtration

extraction in a packed syringe Approximately 1 mg of sorbent as conventional SPE columns is packed into a syringe or cartridge. Small particle size, i.e. 3 μm, are used, while 50-60 μm are used in traditional SPE.

For solid or semisolid samples, extraction methods based on more conventional techniques such as microwave assisted extraction (MAE), pressurized liquid extraction (PLE), ultrasonic extraction (US) remain being used by minimizing solvent consumption. In this sense, some modifications such as Matrix solid phase dispersion (MSPD) are reported. The sample is dispersed and blended in a solid support material, i.e. a derivatized silica. The mix is then transferred and packed into a syringe or cartridge for elution.

Among some of the most recent developments in sample treatment for HPLC analysis can be pointed:

Developments of LPME are leading to approaches such headspace to implement microscale mode. [8] Requirements of automation and design of special instrument are considered as future researches focused to eliminate the disadvantage to hold extraction solvent drop. Air burbles, vortex or ultrasound assisted DLLME are of the most used microextraction techniques. [9] Among their advantages, simplicity, low cost and short time are well known. However, for complex matrices, the technique presents limitations of selectivity and clean up efficiency. DLLME in combination with other techniques aims to eliminate associated drawbacks. Sajid and Alhooshani<sup>[10]</sup> recently reviewed most of the combined DLLME based methods. The article emphasizes the

improvement with respect to individual technique applications.

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Otherwise, DESs are emerging as novel green alternative with high potential to conventional extractants and ionic liquids.[11] Although, the application of these solvents for the determination of organics in environmental matrices is early reporting for now, its wide potential will lead to increase the number of published papers. [6]

The use of surfactants as disperser solvent for extraction<sup>[12,13]</sup> or component of mobile phase<sup>[14]</sup> are being also interesting alternatives for environment friendly and simple HPLC analysis. Micellar liquid chromatography using new types of sorbents such as monolithic columns can also improve the development of asequible analytical methods. [15] These columns provide a lower pressure drop which is advantageous to compensate the pressure increases caused by surfactants mobile phases. The use of ILs as new monomers to fabricate versatile monolithic columns are being widely reported based on its improved separation efficiency. [16] The increasing concern on automated procedures and online coupling will lead to make more attractive the use of HPLC/UV/FLD as analytical tool. Improvements such as low solvent volumes, handling reduction and reproducibility parameters will have to lead to its implementation in routine sample analysis, main analytical objective.

This review is focused to provide an useful guide on the families of organic pollutants which can be determined using reverse phase HPLC with UV or FLD detectors. We think this practical guide can help to the readers interested in knowing the potential of their analytical resources.

References where to find the information on the analytical methods have been compiled based on available literature from abstracts using Web of Science and the open literature. No online methods or interface, i.e. SPME-HPLC, which imply additional dispositive coupled to HPLC system have been included. For some family of compounds, analyses of other matrices have been considered when information of analytical methods was scarce.

#### **Carbonyls**

HPLC/UV coupled to chemical derivatization is one of the most widespread analytical techniques to determine this kind of volatile organic compounds. Carbonyls commonly measured include: formaldehyde, acetaldehyde, acetone, propionaldehyde, butyraldehyde, acetone, acroleine, valeraldehyde, hexaldehyde, tolualdehyde, crotonaldehyde, 2-butanone, benzaldehyde, glyoxal, methylglyoxal, being most of them aldehydes.

Analytical method have been highlighting by a previous derivatization with 2,4-dinitrophenylhydrazine (DNPH) and subsequent UV detection. [17,18] Determination of Carbonyls from C-1 to C-12 at trace levels in air and emission samples have been extensively studied by researchers, such as Possanzini et al. [19] Some studies were applied to water and wet deposition samples.<sup>[20]</sup> To date HPLC/UV analysis with DNPH derivatization is recognized as a standardized

method, especially for the most volatile carbonyls. [21] In fact, most of the found papers on the determination of carbonyls by DNPH are focused during intensive environmental studies (Table 1).

Blank contaminations are the main limitation of this reagent. As it happens with other methods of derivatization, there are associated issues in the measurement quality that analyst must consider. [31] Alternative hydrazine reagents have been rarely applied in environmental measurements.[32-34] The most recent papers continue to be focused for evaluating other hydrazine reagents to use with FLD<sup>[35]</sup> or UV detection.[36]

## Carboxylic acids

They are usually present together with aldehyde forms. Unlike carbonyl compounds, they are rarely analyzed by reverse phase HPLC. The major disadvantage for HPLC analysis under reversed-phase conditions is when organic acids are ionized and, thus, difficult to retain. This leads to the need to use buffered mobile phases at low pH. Derivatization of the carboxyl is then necessary. Moreover there are two additional reasons. First, this step is required

to measure at wavelength above 250 nm to avoid UV moni- 292 toring of many interference substances. Second, fatty acid 293 derivatives are decreased in polarity, therefore, increasing 294 both its retention and selectivity for HPLC analysis in 295 reverse phase.

2,4-Dibromoacetophenone and trimethylamine have been 297 used as derivatization reagents for UV detection.[37] In the 298 case of FLD detection, 9-Chloromethyl anthracene<sup>[38]</sup> and 2- 299 (11H-benzo[a]carbazol-11-yl) ethyl 4-methyl-benzene-sul- 300 fonate,  $^{[39]}$  monobromobimane  $^{[40]}$  are included as derivatiza- 301

Some polyphenolic compounds without a previous deri- 303 vatization have been also determined using HPLC/UV. [41,42] 304 In detail, eight phenolic compounds were studied, i.e. gallic, 305 caffeic, 4-hydroxy benzoic, vanillic, p-coumaric, syringic, 306 ferulic and sinapic acids. They are frequently analyzed by 307 HPLC, although, specific literature on the analysis of envir- 308 onmental samples to quantify fatty acids by UV or FLD is 309 very limited. Among them, 4-hydroxy benzoic, vanillic, 310 syringic are of environmental interest due to their role as 311 biomass burning tracers.

Analytical applications for the determination of carbox- 313 ylic acids by HPLC/UV/FLD are summarized in Table 2.

Table 1. HPLC/UV analysis of carbonyl compounds: environmental applications.

	Sample treatment		UV detection	
Aldehydes (number)	DNPH technique, solvent (mL)	Matrix (m³, mL)	LOD ( $\mu$ g m <sup>-3</sup> , ng mL <sup>-1</sup> )	Ref
(10)	SPE, acetonitrile(2)	Air: gas <sup>a</sup>	0.28-1.38	[22]b
(2)	US, DNPH/acetonitrile (5)	Air: PM (90) <sup>a</sup>	10–20	[23]
(10)+ acetone	SPE,acetonitrile(5)	Air (0.12) <sup>a</sup>	0.005	[24]b
+ acetone	IL-SDME, 1-octyl-3-methylimidazolium hexafluorophosphate (0.010)	Water (10)	0.25-2.03	[25]b
carbonyls(24), PAHs+ (16)	<b>US</b> , US: H <sub>2</sub> 0 (10), DNPH: (0.2)	Air: PM	2.4–10	[26]
(1)	SPE, acetonitrile	Indoor (0.08) <sup>a</sup>	0.5	[27]b
(2)+ acetone	Passive	Air <sup>a</sup>	7.6–8.8	[28]b
(14)+ acetone	SPE, acetonitrile (1)	Wet deposition $(13-44 \times 10^3)^a$	7–79	[29]b
(9)	Passive, Radiello®	Indoor/outdoor <sup>a</sup>	0.010-1.5	[30]b

<sup>&</sup>lt;sup>a</sup>Routinely analysis of real samples during environmental study.

Table 2. HPLC/UV/FLD analysis of carboxylic compounds.

Code on the Complete N	Sample treatment	Market (31)	Detection	100	D - C
Carboxylic (number)	Derivatization reagent	Matrix (m³, mL)	Technique	LOD	Ref
19) C8-C18	V/	Biological	UV	>0.005 ng	[43]a
	2,4-dibromoacetophenone				
	and trimethylamine. (2 chro-				
	matographic columns)	2			[42]a
11) C7-C18	Direct (MAE/SPE	<sup>a</sup> Plants	UV	0.17–2.2 ng	[42]d
	for extraction)	3		1	[44]a
2) C1-C2	Direct	<sup>a</sup> Indoor, museum	UV	650–8 μg mL <sup>-1</sup>	[45]a
1) C1	DNPH	Air	UV	0.8 μg m <sup>3</sup>	[37]a
C2 -C6	2.4.19	Biological	UV	$0.04  \mathrm{ng}  \mathrm{mL}^{-1}$	[57]4
	2,4-dibromoacetophenone				
-1.66	and trimethylamine	C 1	EL D	0.10, 2.5	[38]a
C1-C6	O Chlaman athal anthus and	Soil	FLD	0.18–2.5 pmol	(50)d
20) (10 (24	9-Chloromethyl anthracene	âDIt.	ELD.	0.56, 1.50	[39]a
20) C10-C24	2 (1111	<sup>a</sup> Plants	FLD	$0.56-1.59  \text{ng mL}^{-1}$	,-
	2-(11H-benzo[a]carbazol-11-				
	yl) ethyl 4-methyl-ben- zene-sulfonate				
1) C3	Monobromobimane	Sediment	FLD	$0.46  \mathrm{ng}  \mathrm{mL}^{-1}$	[40]
77-C11	Direct	Plants	UV	Not available	[41]a
_/-С11	Direct	rialits	UV	NOL AVAIIADIE	

<sup>&</sup>lt;sup>a</sup>Routinely analysis of real samples during an environmental study.

<sup>&</sup>lt;sup>b</sup>Article available online.

<sup>&</sup>lt;sup>b</sup>Article available online.

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Table 3. HPLC/UV/FLD analysis of PACs: environmental applications.

PAGS         Technique, sorbent         Matrix (g, mL)         LOD (pg mL <sup>-1</sup> , pg g <sup>-1</sup> )           PAHS (number)         (3)         MSPE, Fe <sub>3</sub> O <sub>4</sub> magnetic nanoparticles + IL nanoparticles + IL (appendix pictor)         Lake, river waters (300)         FLD         0.33-8.33           (4)+PAEs(4)         MSPE, Fe <sub>3</sub> O <sub>4</sub> magnetic nanoparticles (appendix pictor)         Waters (500)         FLD         UV         2-5 19-59           (4)+PAEs(4)         MSPE, Fe <sub>3</sub> O <sub>4</sub> magnetic nanoparticles (feel by pagendix pictor)         Natural water         FLD         UV         2-5 19-59           (6)         MSPE, Te <sub>1</sub> SO <sub>4</sub> magnetic nanoparticles (feel by pagendix pictor)         Water (200)         FLD         0.04-3.75	[47]a [48]a [49]
(3)	[48]a
Natural water	[48]a
Caged into hydrophilic barium alginate   ILD     SPE, Titanate Nanotube array modified by CetylTrinkethylAmmonium Bromide     (6)	[49]
Fled by	
(6)         MSPE, Fe <sub>3</sub> O <sub>4</sub> magnetic nanoparticles         Water (200)         FLD         0.04-3.75           (10)         μSPE, Sulfur μparticles         Sea,wastewaters (100)         UV         7-48           (6)         SBSE         Lake water         FLD         0.03-3.75           (5)         MSPE, Metal-Organic Framework, MSPE, Metal-Organic Framework, MSPE, Fe <sub>3</sub> O <sub>4</sub> /polydopamine         Lake water (20)         UV         2.8-27           (16)         LLME         Rain water         FLD         0.5-1.9           (6)         MSPE, Fe <sub>3</sub> O <sub>4</sub> /polydopamine         Tap,river water (500)         FLD         0.5-1.9           (6)         USE-SPE, Titania Nanotubes/Titanium plate modified         Soil         UV         2.9-52           (6)         MISPE, Graphene functionalized Silica gel         Water         UV         0.5-880           (6)         SBSE, Graphene-Stainless Steel Wir         Soil         0.2-50           (5)         MM-ILMSPE, Fe <sub>3</sub> O <sub>4</sub> magnetic nanoparticles + IL + Methyl Orange NanoParticles         Water (150)         FLD         0.05-2.94           (6)         SBSE-US, Polydimethylsiloxane and Metal-Organic Framework         River, lake water         FLD         0.05-2.94           (7)         ZIF-US         Water         FLD         0.04-4	
Variable   Variable	[50]a
(6) SBSE Lake water FLD 0.03-3,75 (5) MSPE, Metal-Organic Framework, Lake water (20) UV 2.8-27 (16) LLME Rain water FLD (16) MSPE, Fe3O <sub>4</sub> /polydopamine Tap,river water (500) FLD 0.5-1.9 (6) USE-SPE, Titania Nanotubes/Titanium plate modified (6) MISPE, Graphene functionalized Silica gel IL-DLLME Water UV 0.5-880 SBSE, Graphene-Stainless Steel Wir Soil 0.2-50 (5) MM-ILMSPE, Fe3O <sub>4</sub> magnetic Nanoparticles + IL + Methyl Orange NanoParticles (6) SBSE-US, Polydimethylsiloxane and Metal-Organic Framework (7) ZIF-US Water FLD 0.08-1.6 (4) HF-LPME, carbon Water FLD 0.04-4 (13) SPE, Styrene/DiVinylBenzene/Glycidyl Meth (500) FLD 0.004-0.23 MethAcrylate (12) SPE, N-Acetyl-L-Cysteine modified CdS Quantum Dots (5)+NAr(6) MSPE, Tetraazacalix[2]arene[2]triazine Natural waters FLD UV 0.09-0.15 6-11	[51]
(5) MSPE, Metal-Organic Framework, Lake water (20) UV 2.8–27 (16) LLME Rain water FLD (6) MSPE, Fe <sub>3</sub> O <sub>4</sub> /polydopamine Tap,river water (500) FLD 0.5–1.9 (6) USE-SPE, Titania Nanotubes/Titanium plate modified (6) MISPE, Graphene functionalized Silica gel IL-DLLME Water UV 2.9–52 Silica gel IL-DLLME Water UV 0.5–880 SBSE, Graphene-Stainless Steel Wir Soil 0.2–50 (5) MM-ILMSPE, Fe <sub>3</sub> O <sub>4</sub> magnetic Water (150) FLD 0.1–2 nanoparticles + IL + Methyl Orange NanoParticles (6) SBSE-US, Polydimethylsiloxane and Metal-Organic Framework (7) ZIF-US Water FLD 0.05–2.94 (4) HF-LPME, carbon Water FLD 0.08–1.6 (4) HF-LPME, carbon Water FLD 0.04–4 (13) SPE, Styrene/DiVinylBenzene/Glycidyl Water (500) FLD 0.004–0.23 (12) SPE, N-Acetyl-L-Cysteine modified CdS Quantum Dots (5)+NAr(6) MSPE, Tetraazacalix[2]arene[2]triazine Natural waters FLD UV 0.09–0.15 6–11	[52]
Comparison	[53]a
(6) MSPE, Fe <sub>3</sub> O <sub>4</sub> /polydopamine Tap,river water (500) FLD 0.5–1.9 (6) USE-SPE, Titania Nanotubes/Titanium plate modified (6) MISPE, Graphene functionalized Silica gel IL-DLLME Water UV 0.5–880 SBSE, Graphene-Stainless Steel Wir Soil 0.2–50 (5) MM-ILMSPE, Fe <sub>3</sub> O <sub>4</sub> magnetic Water (150) FLD 0.1–2 nanoparticles + IL + Methyl Orange NanoParticles NanoParticles (6) SBSE-US, Polydimethylsiloxane and Metal-Organic Framework (7) ZIF-US Water FLD 0.08–1.6 (4) HF-LPME, carbon Water FLD 0.08–1.6 (13) SPE, Styrene/DiVinylBenzene/Glycidyl Water (500) FLD 0.004–0.23 MethAcrylate (12) SPE, N-Acetyl-L-Cysteine modified CdS Quantum Dots (5)+NAr(6) MSPE, Tetraazacalix[2]arene[2]triazine Natural waters FLD UV 0.09–0.15 6–11	[54]
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nanoparticles + IL + Methyl Orange NanoParticles  (6) SBSE-US, Polydimethylsiloxane and Metal-Organic Framework  (7) ZIF-US Water FLD 0.08–1.6  (4) HF-LPME, carbon Water FLD 0.4–4  (13) SPE, Styrene/DiVinylBenzene/Glycidyl Water (500) FLD 0.004–0.23  MethAcrylate  (12) SPE, N-Acetyl-L-Cysteine modified CdS Tap water (500) FLD 1–100  Quantum Dots  (5)+NAr(6) MSPE, Tetraazacalix[2]arene[2]triazine Natural waters FLD UV 0.09–0.15 6–11	[59]
Metal-Organic Framework   (7)   ZIF-US   Water   FLD   0.08–1.6   (4)   HF-LPME, carbon   Water   FLD   0.4–4   (13)   SPE, Styrene/DiVinylBenzene/Glycidyl   Water (500)   FLD   0.004–0.23	[60]
(7)         ZIF-US         Water         FLD         0.08-1.6           (4)         HF-LPME, carbon         Water         FLD         0.4-4           (13)         SPE, Styrene/DiVinylBenzene/Glycidyl MethAcrylate         Water (500)         FLD         0.004-0.23           (12)         SPE, N-Acetyl-L-Cysteine modified CdS Quantum Dots         Tap water (500)         FLD         1-100           (5)+NAr(6)         MSPE, Tetraazacalix[2]arene[2]triazine         Natural waters         FLD UV         0.09-0.15 6-11	[61]
(4) HF-LPME, carbon Water FLD 0.4–4 (13) SPE, Styrene/DiVinylBenzene/Glycidyl Water (500) FLD 0.004–0.23  MethAcrylate (12) SPE, N-Acetyl-L-Cysteine modified CdS Quantum Dots (5)+NAr(6) MSPE, Tetraazacalix[2]arene[2]triazine Natural waters FLD UV 0.09–0.15 6–11	[62]a
(13) SPE, Styrene/DiVinylBenzene/Glycidyl Water (500) FLD 0.004–0.23 MethAcrylate (12) SPE, N-Acetyl-L-Cysteine modified CdS Tap water (500) FLD 1–100 Quantum Dots (5)+NAr(6) MSPE, Tetraazacalix[2]arene[2]triazine Natural waters FLD UV 0.09–0.15 6–11	[63]
(12)       SPE, N-Acetyl-L-Cysteine modified CdS Quantum Dots       Tap water (500)       FLD       1–100         (5)+NAr(6)       MSPE, Tetraazacalix[2]arene[2]triazine       Natural waters       FLD UV       0.09-0.15 6-11	[64]
	[65]a
	[66]
(3)+fluoroquinones + sulf- CPE, Triton X-100 Tap,surface,wastewater UV 40–380 anamides	[67]a
SFD-DESs, tetra-n-butyl ammonium Water FLD $0.7-6.6$ bromide $+$ carboxylic acids	[68]
OHPAHs (number)	
(1)+PAHs(2)+Acides (2) Agitation Soil (5–10) UV, FLD $3-4 \mu g mL^{-1}$	[69]a
(3) US PM FLD 6–190 fmol	[70]a
(2)+PAHs (10) US, methanol (10) bPM (135) FLD 1 ng mL <sup>-1</sup>	[71]a
NPAHs (number)	
	[72]a
.,	[73]
(3) Titanium (III) Water 68–629 pg	[74]
(4) US, sodium borohydride <sup>b</sup> Soil (0.5) FLD 14–1000	[75]a
(5)+ MAE, dichloromethane (20) bPM (225) FLD 4	[, 5]4
PAHs(12)+ OHPAHs(2) US,methanol(10) 1 BTEX (number)	re
(6) $N_2$ gas drag Water (100) UV $180-600$ ng mL <sup>-1</sup>	[76]a
(5)+PAHs (3) Direct Water UV	[77]

<sup>&</sup>lt;sup>a</sup>Article available online.

## **Aromatics**

Polycyclic aromatic compounds (PACs) can be divided into PAHs and derivatives of these such as nitro-derivatives (NPAHs), hydroxy-derivatives (OHPAHs) and quinonederivatives (PAHQ). The substitution, alkylation and hydrogenation of the molecules of PAHs result to their formation. Sixteen priority pollutant PAHs according to United States Environmental Protection Agency<sup>[46]</sup> can be analyzed using either UV or FLD, while derivatives are preferably quantified by FLD (Table 3). Other aromatics such as benzene, toluene, ethylbenzene, and o-m- and p-xylenes (BTEX), have been also included in this section for organization issue. They can be detected by UV (Table 3).

## Polycyclic aromatic hydrocarbons

The determination of the 16 PAHs considered as priority is well documented in literature, especially in atmosphere. [78,79] Naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benz[b]fluoranthene), benz[k]fluoranthene, benz[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, 1-methyl- naphthalene, 2-methyl-naphthalene are usually determined.

The analysis by means of HPLC in reverse phase by using both detectors is quite usual, applying very conventional chromatographic conditions. FLD detection is the most recommended for the analysis of PAHs by HPLC due to its high selectivity and sensitivity. However, higher extraction

<sup>&</sup>lt;sup>b</sup>Routinely analysis of real samples during an environmental study.

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efficiency should be searched when HPLC/DAD is used for the analysis of trace PAHs. Advances in this field include the enrichment of PAHs from environmental samples prior to HPLC analysis by using novel adsorbents to be applied as micro solid phase extraction (µSPE). Because this kind of HPLC analysis is really extensive, only papers from 2010 have been considered of interest in this review. The most recent reports are focused on the analysis of waters.

## Hydroxy polycyclic aromatic hidrocarbons

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While PAH determination have been broadly documented in environmental analysis, the quantification of hydroxy polycyclic aromatic hidrocarbons (OHPAHs) is actually rare, mainly in water and sediments. For extraction, these polar PAH metabolites need the addition of salts, i.e. Na<sub>2</sub>SiO<sub>3</sub>, <sup>[80]</sup> or polar solvents such as methanol<sup>[81]</sup> to effectively recover. Regarding HPLC/FLD determination, it is carried out with high sensitivity and without previous derivatization. [70,81] However, depending on the isomer to be analyzed, the selectivity of the technique may not be sufficient.

Hydroxyl derivates such as 1-hydroxy-pyrene and 2 phenanthrene been determined hydroxy have HPLC/FLD.

### Polycyclic aromatic hydrocarbons quinones

The presence of these compounds in atmosphere has been related to photo-oxidation of PAHs. A review of analytical procedures was carried out by Kishikawa and Kuroda in 2014. [82] The authors include analytical applications using UV to detect a few ng of naphtoquinone, 9,10-phenanthrenequinone and 9,10-anthraquinone in airborne particles. Regarding FLD analysis, bibliographic references based on the reduction of quinone to fluorescent hydroquinone using chemical reductants such as sodium borohydride, zinc, benzaldehyde and platinum are also included. In this case, reached detections were up to femtogram level.

## Nitro polycyclic aromatic hidrocarbons

HPLC analysis with FLD detection has been frequently used to determine nitro polycyclic aromatic hidrocarbons (NPAHs). [83,84] Some of them include nitro-naphthalene, nitro-phenanthrene, nitro-pyrene and nitro-fluoranthene. High selectivity of FLD quantification is advantageous on the presence of interferences produced, for example, by the original PAHs, which are much more abundant in samples. However, when not enough selectivity for proper separation of isomers is achieved, drawbacks are associated to limitations for identifying isomers.

The analysis requires a previous stage of derivatization for the reduction of the nitro group to the amino producing compounds with high fluorescence. Derivatization by sodium borohydride is economically affordable compared to others such as those using Pt columns.

There is a shortage of methodology to determine NPAHs by HPLC in waters.

## Benzene, toluene, ethyl benzene and xylene isomers

HPLC is very rarely applied to determine BTEX in environmental analysis. However, some applications using UV 531 detection have been reported in other fields, such as occupa-532 tional exposure and tars production from biomass gasifica-533 tion. [85,86] From an analytical point of view, HPLC could be 534 chosen for analysis because facilities a simultaneous separ- 535 ation of BTEX and other polar compounds, phenols 536 or aromatics.

#### **Phenols**

The term phenolics refer to an extremely large number of 541 compounds and many classifications can be established. 542 These compounds can be chlorinated, nitrated, methylated 543 or alkylated. They have been divided into at least ten groups 544 depending on their basic structure: phenols, phenolic acids, 545 hydroxyamic acids, naphthoquinones, xanthones, stilbenes, anthraquinones, flavonoids and lignin. Either they can be 547 also divided as industrial and natural phenolics by including more than 100 types of compounds. [87] It would encompass practically all the organics that may be of interest in this review. To address organization, we have considered 551 including in this chapter the works devoted to the analysis 553 of priority phenolics by the EPA and some relevant alkylphenols, such as nonylphenol and octylphenol. The list of 555 11 phenolic compounds includes: phenol, 4-nitro-phenol, 556 2,4-nitro-phenol, 2-chloro-phenol, 2-nitro-phenol, 2,4-557 dimethyl-phenol, 2-methyl-4, 6-dinitrophenol, 4-chloro-3-558 methyl-phenol, 2,4-dichloro-phenol, 2,4,6-trichloro-phenol 559 and penta-chloro-phenol.

Bisphenol A (4,4'-(propane-2,2-diil) diphenol) (BPA) has 561 been also included in this chapter. Analytical applications 562 for the referred phenols in different environmental matrices 563 are summarized in Table 4.

## Phenols and alkylphenols

The relatively low level of concentrations of phenols as 568 water pollutants leads to the need of a pre-concentration <sup>569</sup> stage to reach the trace levels. Thus, more recent studies are 570 focused to develop previous treatment step to HPLC quanti- 571 fication and improving extraction efficiency (Table 4). 572 Regarding detectors, UV detection has been commonly 573 employed as the preferred detector of HPLC when phenol concentrations are above 1 µg.mL<sup>-1</sup>. Literature on FLD 575 detection is mainly devoted to determine octylphenol and 576 nonylphenol. A detailed review on pre-concentration step 578 for the determination of chlorophenols in real environmental samples was carried out by de Morais et al. [116] The 580 authors stress the importance of sampling, storage and preconcentration stages for chromatographic analysis. In gen-  $_{582}$ eral, among the latest advances in the development of 583 microextraction techniques, the most recent papers on the 584 determination of phenols and alkylphenols, mainly water, 585 stand out.

Table 4. HPLC/UV/FD analysis of phenols and alkylphenols: environmental applications.

	Sample treatment			Detection	
Phenols (number)	Technique, sorbent/solvent (mL)	Matrix (mL,g)		LOD (ng $mL^{-1}$ , ng $g^{-1}$ )	
(11)	SPE, PSDB	Tap water	UV,	10–900	[88]a
(3)	MM-IL-MSPE, IL modified on Fe <sub>3</sub> O <sub>4</sub> nanoparticles	River, tap water (200)	UV	0.20-0.35	[89]a
(3)	LLE, dichloromethane (15)	Tap water	UV	5–15	[90]a
(2)	LLE, dichloromethane (1:20,water)	River, wastewater <sup>b</sup>	FLD	50-75	[91]a
(1)	SBSE, polydimethylsiloxane	Natural waters (30) <sup>b</sup>	FLD,	0.4-1.8	[92]a
(5)	DLLME-SDME, toluene	Environmental water	UV	0.016-0.084	[93]
(2)	SPE, Oasis <sup>®</sup> HLB	River, drinking Water (250)	UV,	25-30	[94]a
(2)	HF-LPME, dihexylether	Drinking, river, urban waste water	FLD	0.5	[95]a
(5)	Derivat.,coumarin-6-sulfonyl chloride	Tap,recycled water	FLD		[96]a
(2)	US-SPE, water/methanol-C18	Sediment (2) <sup>b</sup>	FLD	0.08	[97]a
	SBSE, polydimethylsiloxane $+$ covalent triazine framework	Environmental water	UV	0.080-0.30	[98]
Bisphenol					
A + phenols (number)					
(3)	IL-DLLME, 1-octyl-3-methylimidazolium hexafluorophosphate	Water	FLD	0.23-0.48	[99]
(1)	MAE-SPE	Wastewater(100) Sewage	UV	0.1 100	[100]
	HF-LLME	Sediment	UV	0.055-1.46	[101]
(7)	SBSE, metal organic framework	Water	UV	0.15-0.35	[102]
(2)	DLLME, chlorobenzene (0.2)	Water	FLD	0.002-0.0065	[103]
(6)	US-DLLME, chloroform (0.025)	Water (5)	UV	0.13-0.63	[104]a
(4)	DLLME, chlorobenzene (0.1)	Snow,tap Water (10)	UV	0.11-0.62	[105]a
(3)	μ <b>SPE</b> ,TiO <sub>2</sub> nanotubes	Water	FLD UV	0.012-0.036 0.022-0.093	[106]
	IL-HF-LPME, 1-octyl-3-methylimidazo- lium hexafluorophosphate	River water <sup>b</sup>	UV	0.03-0.1	[107]
(1)	MMSPD-DLLME, Fe <sub>3</sub> O <sub>4</sub> nanoparticles	Water	FLD	0.002	[108]
(1)	μ <b>SPE</b> , IL based surfactants on Fe <sub>3</sub> O <sub>4</sub> nanoparticles	Water (100)	UV	0.20–1.3	[109]a
(1)	SPE-DLLME, solidification of floating drop/undecanol (0.03)	Water (100)	FLD	0.002	[110]a
(1)	dispersive-SPE, dummy molecularly imprinted Fe <sub>3</sub> O <sub>4</sub> nanoparticle	Water	UV	0.3	[111]
(1)	US- μSPE, molecularly imprinted polymer	Drinking Water (20)	UV	0.07	[112]
(5)	HF-DLLE, membrane based µextraction	Water	UV	0.5-4.6	[113]
(1)	Surfactant coated TiO <sub>2</sub> , based nanoparticles	Water	UV	0.5	[114]
(1)	SBSE, carbon nanotubes in polyamide	Water (10)	UV	300	[115]
<u> </u>		. ,			

<sup>&</sup>lt;sup>a</sup>Article available online.

## Bisphenol A

The environmental interest to monitor Bisphenol A (4,4'-(propane-2,2-diil) diphenol) (BPA) is based on its estrogenic activities. Many papers are also focused to its determination and other estrogens such as 17 ß-estradiol, estriol, 17  $\alpha$ -ethynylestradiol, ethylhexyldiphenyl phosphate, estrone, diethylstilbestrol, 2-ethylhexyl-4-methoxy Cinnamate, benzophenone and brominated BPA derivatives (Table 4). In relation to environmental applications through both detectors, there is a rebound in the number of publications in recent years. The most found articles corresponded to environmental measures in aqueous matrices. BPA can be determined by HPLC using UV detection. [117,118] A poor resolution with the HPLC/FLD in high BPA levels has been noted. [119]

#### **Phthalates**

Literature on environmental monitoring of phthalic acid esters (PAEs) using HPLC with UV and FLD detectors is rarely

found.<sup>[120]</sup> This is especially so for phthalic acid di-esters, which are the most commonly monitored based on their widely environmental distribution.<sup>[121]</sup> However for determination of phthalic acid mono-esters (MPEs), primary metabolites of the di-esters, HPLC would be more suitable because the free fatty acid group makes the compound more polar.<sup>[122]</sup> Thus, HPLC analyses don't require previous derivatization, even direct analysis of aqueous samples could be carried out.

Among the scarce found literature, mono- and di-ethylhexyl phthalates have been determined using HPLC/UV for biological monitoring. [123-125] More recently, Fernández-Amado et al determined six EPA PAEs in low volume rainwater samples, using simple equipment based on monolithic columns and low reagent volumes. [126]

The main analytical problem comes for minimization of blanks. Errors are very common since their ubiquitous character. There is mostly a shortage of documentation regarding well-validated and suitable methods for the analysis of phthalate esters. Furthermore, there are no adequate reference materials for these compounds. [127]

<sup>&</sup>lt;sup>b</sup>Routinely analysis of real samples during an environmental study.

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Table 5. HPLC/UV/FD analysis of phthalates esters: environmental applications.

	Sample treatment	Sample treatment			
PAEs (number)	Techn, Sorbent/solvent	Matrix (g, mL)	Detection Technique	LOD (ng $mL^{-1}$ )	Ref
(6)	MAE, methanol	Sediment (2)	UV,FLD	Not found	[127]a
(3)	CPE, non ionic surfactant	Water (10)	UV	1.0-3.8	[128]a
(4)	SPE, titanate nanotubes	Water (1000)	FLD	0.019-0.039	[129]
(5)	IL-SPE, 1-dodecyl-3-methylimidazolium bromide	Water (300)	UV	0.12-0.17	[130]a
(4)	SPE, bamboo charcoal	Rain, tap water	UV	0.35-0.43	[131]
(5)	SPE, nylon nanofibers	Water	UV	0.002-0.033	[132]
(9)	PLE, subcritical water	Soil	UV		[133]
(4)	<b>LLE</b> , chloroform $+$ methanol $+$ salt	Water	ÜV	0.18-0.25	[134]
(4)	MSA-DLLME, dodecane & stirring	Water	ÜV	130–380	[135]
(4)	MSPE, Graphene-Fe₃O₄	Water (300)	ÜV	10–40	[136]a
(6)	DLLME, carbon tetrachloride	Water	ÜV	10-30	[137]
(6)	<b>LLE</b> , dichloromethane + petroleum ether	Mineral water	UV	0.12-0.50	[138]a

<sup>&</sup>lt;sup>a</sup>Article available online.

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Table 6. HPLC/UV/FD analysis of isocyanates: environmental applications

	Sample treatment	20	11	Detection	
Isocyanate (number)	Sample/derivatizing reagent, solvent (mL)	Matrix (L)	Techn	LOD ( $\mu g \ m^{-3}$ )	Ref
(4)	Impinger/tryptamine, dimethyl sulfoxide	Air	FLD	0.1–0.3 μg	[143]
(1)	Diffusive sampler, 4-nitro-7-piperazinobenzo-2-oxa-1,3-diazole, acetonitrile	Air	FLD	0.15–3	[144]
(5)	Adsorbent tube/a piperazine derivative reagent, acetonitrile (3)	Air (15)	UV FLD	>	[145]a
		-11		15–40 pmol 13–25 pmol	
(1)	XAD-7 tubes/pyridyl piperazine, acetonitrile	Air	FLD	3.3	[147]
(4)	PTFE filters/ pyridyl piperazine, acetonitrile + dimethyl sulfoxide (2)	Air (200) <sup>b</sup>	FLD	0.14-0.80	[139]a
(4)	Filter/ pyridyl piperazine, acetonitrile + dimethyl sulfoxide (2)	Air <sup>b</sup>	UV	1.1–2.9	[148]a

<sup>&</sup>lt;sup>a</sup>Article available online.

Table 5 includes a summary of the few works found for the determination of phthalates by HPLC/UV/FLD in environmental samples, mainly waters.

#### **Isocyanates**

The evaluation of occupational exposure of workers has been investigated frequently during environmental studies. Commonly studied compounds are phenylisocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, hexamethylene-diisocyanate and methylenebisphenyl-4,4-diisocyanate.

The analysis is carried out by a simultaneously derivatization and sampling. Derivatization is usually based on the group -N = C=O, which can react with water, alcohols or primary amines to give a urea or urethane derivative (carbamate). For sampling workplace air, filters against impingers are recommended. The main reason is to avoid the use of organic solvents for personal sampling. The formed derivatives allow generally both FLD and UV detection. Although, FLD detection is commonly preferred, both detectors operating in series increase selectivity of the analysis.

Therefore, filters are coated with fluorescent reagent prior to collection of air samples. After sampling, filters are extracted and analyzed. [139] A comparison between methods from National Institute for Occupational Safety Health (NIOSH) and Occupational Safety & Health Administration (OSHA) of USA to determine different isocyanate in workplace environment was reported in 1998. [140] Dahlin also reported in 2007 a detailed review on sampling and analysis of aerosol to determine isocyanates. [141] Piperazine derivatizing reagents are frequently used. [139,142-145]

The main limitations of sampling and analytical methods 791 to determine isocyanates using fluorescent reagents for workplace exposure were compiled by Streicher et al. [146] In 793 this sense, few advances have been reported since then to 794 795 improve determination of isocyanates by FLD detection.

Analytical determinations regarding isocyanate using FLD 796 and UV detection have been included in Table 6.

## Pesticides and degradation products

The literature related to the use of liquid chromatography for determination of pesticides is certainly extensive. This is mainly due to the polar characteristics, low volatility and 804 thermal instability of many pesticides. A complete monograph in the environmental analysis to determine pesticide 806 residues by HPLC was published by Tuzimski and Sherma 807 in 2015. [149] We have found the most recent review in 808 2018. [150] The article compiles available analytical methods 809 in a more briefly way. With the purpose of summarizing, we  $\frac{33}{810}$ refer to the major families of pesticides susceptible for analyzing by HPLC with UV and FLD detection, trying to bring  $\frac{1}{812}$ the studies published in the last decade.

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged 814 and Safe) sample preparation methods have been mainly 815 developed to monitor pesticides in different kind of samples 816 by its simplicity and efficiency. These methods do not use to 817 involve pre-concentration step of analytes. Thus an attractive 818 alternative is the combination of QuEChERS extraction and 819 pre-concentration methodology such as DLLME<sup>[151]</sup> to UV 820 and FLD detection. Once again, it is worth mentioning the 821 influence of the most recent techniques of sample treatment 822

<sup>&</sup>lt;sup>b</sup>Routinely analysis of real samples during an environmental study.

<sup>&</sup>lt;sup>b</sup>Routinely analysis of real samples during an environmental study.

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mination of pesticides.

Similarly to the study of phenols and alkylphenols, the literature found focuses on the development of analytical methods based on the most advanced micro extraction. For

in the improvement of the analytical methods for the deter-

**LPME**, DEs (0.05)+salt(0.5)

<sup>b</sup>Routinely analysis of real samples during an environmental study.

instance, a first application of LPME and the freezing of deep eutectic solvent (FLDES) has been developed to determine pesticide in environmental water samples. [152] Two or three green and affordable extractants are mixed to act as hydrogen bond donor or acceptor. The proprieties for extraction are similar to ionic liquids, but cheaper, easier to

produce and less toxic. The results were very promising to determine organic compounds in water samples.

0.05-0.5

UV

Table 7 lists representative analytical applications to determine pesticide using UV/FLD in environmental samples.

## Benzimidazole

Water (10)

Wastewater (200)

Some of the best known benzimidazole pesticides include: benomyl, carbendazim, tiabendazole, fuberidazole. HPLC has been widely used for the analysis of these compounds. However, HPLC-based methods often require a more

	Sample treatment	Detection			
Pesticide (number)	Technique, sorbent/solvent (mL, mg)	Matrix (mL)	Tech	LOD (ng mL $^{-1}$ , ng g $^{-1}$ )	Ref
Carbamates					[152]
(5)	DLLME	Water	UV	0.1-0.5	[153]
(1)+OP (1)	<b>DLLME</b> , acetonitrile(1)+tetrachloroethane (0.015)	Tap,river water (5)	FLD	0.012-0.016	[154]a
(2)	DLLME, tetrahydrofuran (0.75)+chloroform (0.080)	Water (5)	FLD	0.5-1.0	[155]a
	·	Soil (20)		1–1.6	
(6)	US + surfactant,chlorobenzene + chloroform	Water	UV	0.1-0.3	[156]
(3)	LLME + low temperature, acetonitrile	Water (2)	UV	5–10	[157]
(1)	LLE+derivatization, hexane(20)	Wastewater (500)	UV	13	[158]a
( )	μSPE + solid sorbent, Zeolite(40)	Water (7)	UV	4–4000	[159]
(3)	<b>SBSE</b> , zinc sulfide $+$ activated carbon $+$ IL	Tap,river mineral water	ÜV	0.3-0.5	[160]
Organophosphorus	Joseph Zine Samae   activated carbon   12	rap,river rimierar water	•	0.5 0.5	
(4)	IL-DLLME, alkyl-methylimidazolium hexafluorophos-	Water (5)	UV	0.1–5	[161]a
(4)	phate (0.035)	water (5)	OV	0.1-5	
(7)	US, surfactant	Water	UV	01.03	[162]
(7)				0.1-0.3 2-3	[163]a
(3)	DLLME, methanol (1.5)+chloroform (0.25)	Tap water (5)	UV		[164]a
(1)	IL-DLLME, tetrahydrafuran(0.26)+butyl methyl imi-	Water (8)	UV	0.2	[]
(=)	dazolium hexafluorophosphate (0.065)	- (122)		~ <i>~</i>	[165]a
(2)	SPE, Anionic resin	Tap water (100)	UV	90–200	[166]a
(4)	<b>DLLME</b> , acetonitrile + dodecanol	Water (10)	UV	0.25–1	[167]
(4)+PAHs(2)	<b>IL-MSPE</b> , acetonitrile (0.5)+dodecanol (0.1)	Water (8)	UV	0.25–1	
(2)	SPE	River water	UV	0.003	[168]
(3)	SPE, carbon nanofiber (15)	Water (1)	UV	0.090-0.22	[169]a
(3)	MSPE, nanoparticles (150)/tetrahydrofuran	Water (100)	-UV	0.01-0.25	[170]a
(2)	MSPE, silica coated Fe <sub>3</sub> O <sub>4</sub>	Water	UV	0.09-0.14	[171]
Phenylureas (3)	IL-DLLME, butyl methylimidazolium hexafluoro-	Snow,tap,lake waters (10)	UV	0.04-0.43	[172]a
	phosphate (0.065)		1 V		[173]a
	<b>DLLME</b> , acetone + toluene/carbon sulfhide(0.148)	Tap,river (5) waters	UV	0.01-0.5	[1/3]a
			50060	01	[174]-
(5)	SPE, C18/acetonitrile(1.5)	Tap water	UV	0.84-1.35	[174]a
(4)	Thin film µextraction, poly(vinyldene) fluoride	Natural water (20)	UV	0.1	[175]a
(4)	Agitation/methanol (10)	Soil (5)	UV	10–50	[176]a
Pyretroids	8	< / >			
(5)	IL-DLPME, hexyl-methyllmidazolium	Clean water	UV	0.28-0.60	[177]
	hexafluorophosphate				
Triazines					
(3)	MISPE, titanate nanoparticles	Water	UV	$3.00  \text{nmol L}^{-1}$	[178]a
	(1)	Soil		4.8 nmol kg <sup>1</sup>	
(7)	DLLME, 1-octanol (0.3)	Seawater (25)	UV	0.19-1.12	[179]
(9)	MSPD, graphitized carbon black/ethyl acetate (20)	Marine sediment	UV	22-37	[180]
(6)	HF-IL-MISPE, [hexyl-methyllmidazolium hexafluorophosphate	Water (10)	UV-	0.14-0.48	[181]
(6)	SBSE, polydimethylsiloxane	Lake water	UV	0.021-0.079	[182]
Multiclass pesticides					
(3)	SPE	Soil	UV	25-50	[183]
(4)	SPE, C18 (200)	Water (250)	ÜV	0.2	[184]a
(6)	IL-DLLME, hexyl- methylimidazolium hexafluoro-	Soil	FLD	<10	[185]
(0)	phosphate (118)	3011	ILD	<10	
(4)	MEPs, C18	Soil (2)	UV	0.050-0.58	[186]a
(1)	HEI J, CIO	Tap water	ΟV	0.050 0.50	
(4)	IL-DLLME,	Water	UV	0.1-1.8	[187]
	SDME, hexyl- methylimidazolium hexafluorophos-		UV	0.13-0.19	[188]a
(3)	phate ZnO nanoparticles	Water (10)	υv	0.13-0.19	-
(5)	Agitation, dichloromethane-ethyl acetate(40)	Soil (5)	UV	Not found	[189]a
(2)	Agitation, dictribionnethalie-ethyl acetate(40)	JUI (J)	υV	NOT TOUTIO	

thorough sample preparation step, particularly when the concentration levels are very low. Benomyl is quickly converted to carbendazim and is determined as such. Benzimidazole fungicides are strongly fluorescents.<sup>[2]</sup>

#### **Carbamates**

Among the most used, methidocarb, carbaryl, carbofuran or methomyl are included. FLD detection is commonly applied for the determination of carbamates. The methods are based on the postcolumn hydrolysis of *n*-methyl carbamates to methylamine and the subsequent derivatization with o-phthalaldehyde. Official organization, such as USEPA (United States Environmental Protection Agency), includes determination of n-methyl carbamates by FLD as standard protocol. [190]

## **Organophosphorous**

The determination of some organophosphous pesticides, i.e. dimethoate, ethion, malathion, phorate, phosalone and parathion, by HPLC was promptly reported. [191]

#### **Phenylureas**

HPLC is usually employed for quantitative analysis of phenylureas because they are polar and nonvolatile compounds. 1002 For example, USEPA Method 532 includes the determination of eight phenylurea herbicides in drinking water using 1005 UV detector. [192] In detail, the following compounds are 1006 included: diflubenzuron, diuron, fluometuron, linuron, prop- 1007 anil, siduron, tebuthiuron, thidiazuron. FLD detection has 1008 been also applied after derivatization. [193]

## **Pyrethroids**

Scarce literature presents application of UV or FLD for 1014 determination of pyretroids in environmental matrices. 1015 Among them, Feo et al. [194] reviewed a few published analyt- 1016 ical methods in 2010. The review includes application on 1017 biological samples using UV detection. Only a reference is cited for FLD detection after derivatizing by photochemically-induced fluorimetry.

CARBONYLS	Adehydes Cetones		PHENOLS AND ALKYLPHENO	DLS  Bisphenol A	CH <sub>2</sub>
	Celones	$R^1 \longrightarrow R^2$		ыѕрпены А	но-{
CARBOXYLIC ACIDS		R— OH	PHTHALATES		R <sup>1</sup>
PACs	PAHs		ISOCYANATES		R_N O
	OHPAHs	ОН	PESTICIDES	Benzimidazole	N N N N N N N N N N N N N N N N N N N
	PAHQ		χ.	Carbamates	$R^1 \longrightarrow R^2$
:4	NPAHs	NO2		Organophosphorus	O(S) R1—P—X P—X R2
	ВТЕХ			Phenylureas	$\begin{matrix} \begin{matrix} $
	~	CH <sub>3</sub>		Pyrethroids	$\mathbb{R}^{\frac{1}{2}} \longrightarrow \mathbb{Q}^{0}$ $\mathbb{R}^{\frac{1}{2}}$
		CH <sub>3</sub>		Triazines	R <sup>2</sup> N R
		CH <sub>3</sub>	EMERGINGS	Antibiotics	NH NH
					OH NICH3)2
					0     R  S  NH <sub>2</sub>    0

#### **Triazines**

Determination of triazines is easy by UV because of their strong absorbance at 220 nm. A relatively recent review on chromatographic methods for analysis of triazine herbicides was performed by Abbas et al. [195] The article reported analytical methods between 2011 and 2014 described by using DLLME, graphen, SPE, dynamic MAE, US assisted emulsification microextraction, resins XAD4 for the analysis in environmental matrices. Later papers are included in Table 7.

## **Emerging**

Currently, many works focus on the determination of chemicals in environmental analysis that are not commonly monitored but can be or are present due to their continued use. The term encompasses very different families of compounds such as surfactants, pharmaceuticals, personal care products, flame retardants, amine derivatives. [196]

Complex matrices of samples and extremely trace/subtrace concentrations are the main limiting factors to apply UV and FLD detectors in the analysis of emerging. Related literature is extremely limited compared to more sophisticated and expensive liquid chromatography. [197,198] However, they can be an alternative in samples with higher concentrations and the analysis of large set of samples during environmental monitoring studies. Once again novel developments involving microextraction stages should make up more research lines for using theses affordable detectors in routine laboratories. For instance, Shishov et al. [199] have developed a very interesting effervescence tablet-assisted approach for microextraction of water samples. This promising method involves dissolution of two effervescent tablets for on-site pretreatment reaching high enrichment factors. The authors used

	Camarda Arrastus ant		1	Detection	Ref
	Sample treatment Technique, sorbent (g) /solvent (mL)	Matrix (g, mL)	Tech	LOD (ng $g^{-1}$ , ng $mL^{-1}$ )	кет
PPCPs					
As,TC(1),FQ(1),penicillin G	SPE, Oasis <sup>®</sup> HLB	Wastewater (100)	UV	0.1–40	[200]
As	HF-LLME, nitro-xylene + diisobutyl ketone (0.007)	Lake water (12)	UV	0.11-0.77	[201]a
C	SPE, anion exchange	Wastewater	UV	100	[202]
Q(1),TC(1),TMP(1)	SPE,	Water	UV	100	[203]
5As(4)	MSPE, mixed hemimicelles on nanoparticles	Water (500)	UV	0.24-0.33	[204]
PPs(13)	SPE, C18	Wastewater (50) Soil (0.5)	UV	1.0–50	[205]a
Cephalosporin antibiotics	SPE, Oasis <sup>®</sup> HLB	Clean, wastewater (500)	UV	0.026-0.059	[206]
Qs(4), SAs(5)	Agitation	<sup>b</sup> Soil (2)	UV, FLD		[207]a
Endocrine disrupters (9)	SPE, Oasis <sup>®</sup> HLB	Polluted waters (2000)	UV	0.004-0.018	[208]
Indocrine disrupters(5)	MISPE,	Clean waters	UV		[209]
Indocrine disrupters (9)	SPE, Oasis <sup>®</sup> HLB	<sup>b</sup> Estuarine waters(2)	UV	0.003-0.012	[210]a
PPs(9), steroids(3)	SPE, Strata <sup>®</sup> X	Water (500–1000)	UV FLD	0.01–1.1	[211]a
PPs(3)	Specific sampler, Oasis HLB	<sup>b</sup> Waste water (150)	UV	0.2-4.1	[212]a
PPs(2)	DLLME + single drop, Undecanol (0.08)	Water (20)	UV	0.33-0.56	[213]
EQs(11)	SPE, cation exchange	bWastewater	FLD	20–100 pg	[214]
As(4)	DLLME + single drop, octanol/MeOH	Lake, wastewater (10)	UV	0.22-1.92	[215]
المعرب) اitroimidazole(3)	SPE, triazine framework	Water	UV	0.11-0.13	[216]
As(3),FQs(4),PAHs(4)	CPE, Triton X100 + hexafluoro isopropanol	Clean, wastewater (5)	UV	0.04–1.3	[67]a
Antidepressant (1)	DLLME	bWastewater	FLD	0.024	[217]
Parabens	DEEME	wastewater	TLU	0.024	
fullerenes (C <sub>60</sub> )	PLE	Soil, sediment	UV	20	[218]
8)	US-MISPE	Soil, sediment	UV	<1	[219]
1)+3 PAHs + BPA	IL-MAE, hexadecyl methyl imidazolium bromide	Sediments (0.1)	UV	40	[220]
-	HF-LPME	Water	UV	0.2	[221]
7)	D-μSPE, metal organic framework	Waters	UV	0.1	[222]
1)	MISPE	Wastewater	UV	2.4	[223]
ourfactants	MISTE	wastewater	OV	2.7	
NPEO, NP	MAE-SPE, hexane:acetone (1 mL H <sub>2</sub> O)	<sup>b</sup> Sludge (0.03–0.3)	FLD	1820-2860	[224]
NPEO, NP	US-SPE, methanol:water/C18	Soil (2)	FLD	60–520	[225]
.AS(4)+PAHs (16)	US-SPE, methanol	Sludge (1)	UV	6000-37000	[226]a
(10)	os si E, medianoi	Sidage (1)	FLD	2000-9000	
.AS(4)	MAE, methanol	Sludge (0.5 )	UV	250–2500	[227]a
3.13(1)	Wite, medianor	Sladge (0.5 )	FLD	330–1830	
.AS(4)	SPE, carbon nanotubes	River waters (500)	UV	0.02-0.03	[228]a
.AS(4)	Soxhlet-SPE/anion exchange	Waste water (10)	FLD	10	[229]a
	Š	Sludge (5)			[230]a
NPEO(8)	PLE-SPE, metanol/C18	<sup>b</sup> Soil (5)	FLD	6–60	[231]
AS(4)	MAE, methanol (25)	Sludge	FLD	3.3-5.4	[231]
Retardants	us sper	6 11 1	1137	20.42	[232]
Brominated (7)	US-SBSE	Soil,dust	UV	2.9–4.2	[233]
Perfluorinated carboxylic (11)	SPE, Derivatization	Water (100)	FLD	4.3–7.5	[234]
Brominated (3)+ phosphates (3)	<b>SPE,</b> bond elut ENV $+(\mu HPLC)$	<sup>b</sup> River (1000)	UV	0.008-0.518	[234]

<sup>&#</sup>x27;Article available online.

<sup>&</sup>lt;sup>b</sup>Routinely analysis of real samples during an environmental study.

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this strategy to determine testosterone, progesterone, estradiol and hydrocortisone by HPLC/UV in water samples.

The families of compounds susceptible to their analysis by UV/FLD considered in this review are indicated below. They have been added in decreasing order according to the number of works collected (Table 8).

## Pharmaceuticals and personal care products

#### **Antibiotics**

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The main families of antibiotics are chemically classified as Quinolones and fluoroquinolones (FQs), Tetracyclines (TCs), Sulfonamides (SAs), Trimezoprim (TMP). The chromatographic analysis can be performed with UV. FLD detector allows direct determination in FQs, while TCs and SAs require previous derivatization.

A review of analytical methods for the determination of fluoroquinolones and sulfonamides in water was carried out by Peixoto et al. [235] The authors include detailed information about analytical methods for determination 30 individantibiotics. One third of reported literature corresponded to bibliography using UV or FLD detectors and limits of detection in  $ng L^{-1}$  range by FLD are included. Other review of analytical techniques for determination of selected quinones includes both detectors as frequently used tools of analysis.<sup>[82]</sup> To a lesser extent they are also included in the review of Seifrtová et al. [236]

Sulfacetamide, sulfadiazine, sulfathiazole, sulfamerazine, sulfadimidine and sulfaquinoxaline are included among the most monitored sulfonamides. Analogously, the group of fluoroquinolones includes norfloxacin, enrofloxacin, ciprofloxacin, danofloxacin.

#### **Endocrin disruptors**

Estrogens belong to the family of the so-called steroid hormones, capable of replacing natural hormones and causing disorders in the process of reproduction and development. In 2010, Kozlowska-Tylingo et al. [237] carried out a review of the chromatographic methods applied to the determination of estrogen disruptors in environmental samples. The authors point to separations in reversed phase with conventional columns, using both UV and FLD detection.

Compounds frequently determined include estradion, estrone, daidzein, genistein, biochanin A, 17-alpha-ethynylestradiol, bisphenol A, 4-octyl phenol and 4-nonylphenol. Some of them have been included in the previous section of phenols.

## Pharmaceuticals active products

Other pharmaceutical contaminants, also referred to as pharmaceutical active products (PPs), comprise organics belonging to different therapeutic classes. Among the most frequently used have been determined

- carbamazepine (anti-epileptic),
- clofibric acid and fenofibrate (lipid regulators),

- ibuprofen, naproxen, ketoprofen, fenoprofen and diclofe- 1236 1237 nac (analgesic),
- ethinylestradiol, estradiol estrone (ster- 1238 1239 oid hormones),
- etoricoxib, salicylic acid, valdecoxib, nimesulide (anti- 1240 1241 inflammatory).

Patrolecco et al. [211] proposed determination of nine PPs 1243 in polluted waters using HPLC/UV/FLD. The method shows 1244 the feasibility of applying to real samples (LODs, 1245  $0.01-1.1 \text{ ng mL}^{-1}$ 1247

#### **UV** filters

1249 Reversed phase HPLC is widely used for determination of 1250 organic UV filters. [238] The most used UV filters are benzo- 1251 phenone-3, octyldimethyl-p-aminobenzoic acid, 4-methyl- 1252 benzylidene camphor, ethylhexyl methosycinnamate, 1253 octylmethoxycinnamate, octocrylene, butylmethoxydiben- 1254 zoylmethane, terephtalylidine dicamphorsulfonic ethylhexyltriazone. 1256

#### **Parabens**

1259 Some alkyl parabens, i.e. methyl, ethyl, isopropyl, propyl, isobutyl, butyl parabens, can be determined by HPLC/UV 1261 with detection limits below 0.1 ng mL<sup>-1</sup> in environemental 1262 waters. [222] The most recent literature is focused to develop 1263 new microextraction protocols for sample treatment. 1264

## **Surfactants**

1267 Environmental applications include determination of anionic and nonionic surfactants, such as linear alkylbenzene sulphonates (LAS) and nonylphenol polyethoxylates (NPEOS), 1270 respectively. The latter are usually analyzed together nonyl phenol (NP), its raw material. HPLC/UV/FLD have been 1272 widely used in the last decade, although it presents some-1273 time a lack of sensitivity and specificity at low 1274 concentrations.[230] 1275

## **Amine derivatives**

#### Aliphatic and aromatic amines

1279 A previous derivatization step is usually required to determine aromatic and mainly aliphatic amines by HPLC with 1281 both, UV and FLD detectors. A detailed review of HPLC  $_{1282}$ methods applied in the environment field was published by 1283 Fekete et al. [239] The article compiles more than twenty 1284 references of HPLC/UV/FLD analytical methods including 1285 different derivatization reagents. Primary and secondary 1286 amines generally require independent derivatization reagents 1287 For example, those such as o-phthaladehyde and 9-fluorenyl- 1288 methyl chloroformate are used for primary and secondary 1289 aliphatic amines, respectively. Simultaneous analysis of ali-1290 phatic and diamines has been also proposed. [240]

Short chain aliphatic amines such as methylamine, dime- 1292 thylamine, trimethylamine, ethylamine, diethylamine, pro- 1293 pylamine and butylamine are present in the atmosphere. 1294

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Among other, aromatic amines such as aniline, aniline derivates, toluidine can be determined in waters. [239,241]

#### **Nitramines**

Nitramines used in explosives or degradation products also are present in environment. EPA Method 8330 is intended for the trace analyses of hexahydro-1,3,5-tetranitro-1,3,5,7-tetrazocine, hexahydro-1,3,5-trinitro-1,3,5-triazine, 1,3,5-trinitrobenzene, 1,3-dinitrobenzene, methyl-2,4,6-trinitrophenylnitramine, nitrobenzene, 2,4,6-trinitrotoluene, dinitrotoluenes and nitrotoluenes by HPLC/UV. [242] Gaurav et al. carried out an exhaustive review in 2006 in the field of HPLC methods for the analysis of explosives. [243]

Other aliphatic (linear and cyclic) nitramines comes from postcombustion CO<sub>2</sub> capture technology. They can be also classified as emerging pollutants. Among the scarce literature on nitramines determination in environment, a review was performed by Lindahl et al. [244] The work highlighted as analytical shortcomings the need of more research on extraction step and suitable chromatographic liquid columns. Common names of nitramines are included, such as nitrodiethylamine, nitrodimethylamine, nitroethanolamine, nitromethylamine, nitropiperazine.

An evaluation of remedial technologies to removal nitrosamines, nitramines, amines and aldehydes within wash waters during amine-based carbon capture was developed by Shah et al. [245] In this work, the determination of 2 nitrosoamines, 5 nitramines and 3 amines were monitored by HPLC with UV detection. Miguel Mercader et al. [246] also monitored some nitrosamines during the study of its degradation in drinking water purification.

Nitrosodimethylamine is frequently determined a disinfection by-products in chlorinated waters. [247]

## Flame retardants

Scarce literature can be found on measurement of flame retardants by using UV or FLD detectors. Among the few works found, Wang et al. [104] conducted an optimization and evaluation to determine tetrabromobisphenol A and its five derivatives by using ultrasound-dispersive liquid-liquid microextraction. Only three references have been found (Table 8).

## **Conclusions**

The development and optimization of analytical procedures requiring no sophisticated and expensive instruments remains of great interest for many analytical laboratories. HPLC/UV/FLD is a robust and affordable analytical tool to use in routine monitoring. However, there is currently a shortage of literature when compared to a more sophisticated liquid chromatography. This work tries to make a claim about its application in environmental analytical measurements.

Current advances related to analyte extraction step must continue promoting the application of HPLC with UV and FLD detectors in environmental analysis. For instance, new liquid phase microextraction method with freezing deep eutectic solvent need increases of studies on the analysis of organic field. This emerging solvent involves very interesting advantages to contribute in the analysis of organic for its simplicity, low cost, low toxicity, and in general high potential to bring sensitivity. Likewise, methods based on effervescence tablet assisted to pretreatment of liquid samples on site seem especially interesting. Advantages such as in situ preparation, low cost, simplicity of operation and high enrichment factors make it necessary to study more applications in these promising new extracting agents.

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There is still a lack to assure the trueness and accuracy of the concentrations obtained with the most methods. The increasing research papers using microextraction techniques to improve sensitivity of HPLC/UV/FLD analysis need to expand well validated methods applied to real samples of unknown composition. Both the results of recoveries and precision obtained for spiked samples usually are better than those obtained from real samples, naturally contaminated samples. There is a lack of research papers on analytical method validation from analyses of real environmental samples. Comparability of data is essential and it's not always guaranteed. In other fields such as the pharmaceutical or food, the requirement of well validated analytical methods is essential.

## **Abbreviations**

		100-
μSPE	Micro Solid Phase Extraction	1383
Ald	Aldehydes	1384
BPA	Bisphenol A (4,4'-(propane-2,2-diil) diphenol)	1385
BTEX	Benzene, Toluene, Ethylbenzne and Xylene	1386
CPE	Cloud Point Extraction	1387
D-μSPE	Solvent-Dispersive Micro Solid Phase Extraction	
DÀD	Diode Array Detector	1388
DESs	Deep Eutectic Solvents	1389
DLLME	Dispersive Liquid-Liquid Micro Extraction	1390
DNPH	2,4-Dinitrophenylhydrazine	1391
FLD	Fluorescence Detector	1392
FQs	Quinolones and fluoroquinolones	1393
HF	Hollow Fiber	
HPLC	High Performance Liquid Chromatography	1394
IL	Ionic Liquids	1395
LAS	Linear Alkylbenzene Sulphonates	1396
LLME	Liquid Liquid Micro Extraction	1397
LPME	Liquid Phase Micro Extraction	1398
MAE	Microwave Assisted Extraction	1399
MEPs	Microextraction by Packed Sorbent	
MISPE	Moleculary Imprinted Solid Phase Extraction	1400
MM-ILMSPE	Magnetic Microsphere Ionic Liquid Micro Solid	1401
MCA	Phase Extraction	1402
MSA MSPD	Magnetic Stirring Assisted	1403
MSPE	Matrix Solid Phase Dispersion Magnetic Solid Phase Extraction	1404
NPAHs	Nitro Polycyclic Aromatic Hydrocarbons	1405
NPEOS	Nonylphenol polyethoxylates	1406
OHPAHs	Hydroxy Polycyclic Aromatic Hydrocarbons	
PACs	Polycyclic Aromatic Compounds	1407
PAEs	Phthalatic acid esters	1408
PAHQs	Polycyclic Aromatic Hydrocarbons Quinones	1409
PAHs	Polycyclic Aromatic Hydrocarbons	1410
PLE	Pressurized Liquid Extraction	1411
PM	Particulate Matter	1412
		1412

1413	PPs	Pharmaceutical active Products
1414	PPCPs	Pharmaceuticals and Personal Care Products
1415	PTFE	Poly tetrafluorethylen
1416	QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe
	SAs	Sulfonamides
1417	SBSE	Stir Bar Sorptive Extraction
1418	SDME	Single Drop Micro Extraction
1419	SFD	Solidification of Floating Drop
1420	SMS	SupraMolecular Solvent
	SPE	Solid Phase Extraction
1421	SPME	Solid Phase Microextraction
1422	TCs	Tetracyclines
1423	TMP	Trimezoprim
1424	US	Ultrasonic extraction
1425	USEPA	United States Environmental Protection Agency
1426	UV	Ultraviolet
	ZIF-US	Zeolitic Imidazolate Frameworks for
1427		Ultrasonic Extraction
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