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Review

Flow analysis techniques as effective tools for the improved environmental analysis of organic compounds expressed as total indices

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ABSTRACT

The scope of this work is the accomplishment of an overview about the current state-of-the-art flow analysis techniques applied to the environmental determination of organic compounds expressed as total indices. Flow analysis techniques are proposed as effective tools for the quick obtention of preliminary chemical information about the occurrence of organic compounds on the environment prior to the use of more complex, time-consuming and expensive instrumental techniques. Recently improved flow-based methodologies for the determination of chemical oxygen demand, halogenated organic compounds and phenols are presented and discussed in detail. The aim of the present work is to demonstrate the highlight of flow-based techniques as vanguard tools on the determination of organic compounds in environmental water samples.

Contents

1. Introduction

In the present-day society a wide spectrum of analytical methodologies are extensively used providing us chemical information about the presence/quantity of target elements/compounds (from natural or anthropogenic sources). This chemical information becomes in a higher life-quality level.

There is different types or degrees of chemical information, from the obtention of qualitative (yes/no presence), to fully quantitative information for each individual specie contained in the sample. The obtention of more complete chemical information is related with an increase in effort, costs, time-consumed and difficulty [1].

In some situations, the analyst knows with security if the analyte is present in a sample (e.g. quality control analysis in pharmaceutical or food industry). In this case a quantitative analytical methodology with adequate features is required, in order to get the desired information.

In other situations, such as in the environmental analysis field (e.g. analysis of emerging pollutants), the most advanced analytical methodologies are usually based on the use of chromatographic techniques coupled to mass spectrometric detectors supplying precise quantitative chemical information about each analyte. In

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counterpoint of this, in some fields like the environmental analysis of pollutants, the target compounds are not often present in the analyzed samples, being the direct use of powerful separation techniques for these purposes an excessive loss of time and money, with the concomitant decrease of the chemical information obtained per time unit.

An intermediate point between qualitative (yes/no binary response) methods and fully quantitative methods are the total indices or sum parameters. Total indices are useful in order to get quantitative chemical information correlated with a concrete feature of the sample, but not for each concrete compound contained in it. Total indices provide useful chemical information about vast (up to millions of different compounds) and heterogeneous families of compounds, being the analysis of each one of them a hardly feasible task. The use of a total index determination allows the quick knowledge about the presence and the total amount of a concrete type of compounds contained in a sample, but the identification of each concrete analyte is not feasible.

Once an analytical methodology for the determination of a total index has been established, its automation simplifies the execution and increases the efficiency, approaching it to a real time measurement. Highly efficient tools for these purpose are the flow analysis techniques [2,3]. Furthermore, the required amounts of reagents/solvents are diminished and more environmentally friendly analytical methodologies can be developed. These automated methods are closer to the principles stated by the Green Chemistry movement [4], thus their relation with the Analytical Chemistry field [5]. And last but not least, the minimization of the exposure of the analyst in front of aggressive/hazardous chemicals or dangerous physical treatments.

2. Total indices or sum parameters

The role and principles of total indices in analytical chemistry were established by Baena and Valcárcel [6]. A total index or sum parameter is described as a group of compounds of similar nature, similar structure (e.g. PCBs, PAHs, etc.) or a concrete common characteristic (e.g. toxicity, hydrophobicity, acidity and oxidability). When a total index is defined, all the compounds involved in the measured property, contribute in a certain percentage to the single value obtained as a result.

As it was stated before, separation techniques coupled with mass spectrometric detectors are the most powerful techniques for environmental analysis, but when the time or costs per analysis are a predominant factor, the use of total indices becomes advantageous. It happens when the target compounds are not often found in the analyzed samples, allowing the total index measurement a fast way for the initial evidence of their potential presence. If the initial evidence is confirmed, more sophisticated techniques should be additionally used, obtaining more exhaustive chemical information. This was defined as Vanguard-Rearguard Strategies by Valcárcel and Cárdenas [7], where the total indices are defined as Vanguard Strategies, leaving the use of complex sample pretreatments followed to hyphenated techniques (e.g. gas chromatography–mass spectrometry) as Rearguard Strategies.

In Table 1, are listed various of the most commonly used total index parameters in the environmental analytical field.

3. Flow analysis techniques

Flow analysis techniques are well-established tools for the automation and miniaturization of analytical methodologies, providing advantages such as: (i) increased injections throughputs, (ii) high versatility, (iii) high robustness, (iv) new analytical improvements based on operating modes under non-stationary conditions, (v) decrease of the human exposure under hazardous chemical/physical sample pretreatments, (vi) more environmentally friendly procedures obtained due to process downscaling and (vii) use of alternative detection systems with the concomitant simplification of the operating conditions (viz. chemiluminescent detection).

The different types of flow analysis techniques are usually classified according to the device used for fluidic handling (Table 2). The use of flow analysis techniques allows the implementation of almost the totality of the sample pretreatments included on classic methodologies for the determination of environmental total indices, such as: (i) UV digestion, (ii) microwave digestion, (iii) sample distillation, (iv) liquid–liquid extraction, or (v) solid phase extraction, among others. By this reason, flow analysis techniques are useful tools for the fully automation of this type of analytical methodologies, achieving a highly efficient way for the unsupervised monitoring of total index parameters. It is also a noteworthy fact, the new applications in environmental analysis carried out by means of micro-total analysis systems (μTAS) [13], which in the next years could provide great achievements.

4. Recent developments on flow analysis techniques for the determination of environmental total indices of organic nature

The recent contributions of flow analysis techniques for the improvement of total indices for the assessment of organic com-

Table 1
Examples of total indices in environmental analysis.

Name	Abbreviation	Chemical information obtained	Result units
Chemical oxygen demand	COD	Amount of chemically oxidizable matter present in a liquid sample	Consumed mg O_2 L^{-1}
Total organic carbon	TOC	Amount of organic matter present in a sample	mg C L^{-1}
Dissolved organic carbon	DOC	Amount of organic matter remaining in a sample after filtration through a 0.45 μm pore size filter	mg C L^{-1}
Adsorbable organic halogens	AOX	Amount of Cl^-, Br^- and I^- organically bounded to organic compounds, which are adsorbable into activated charcoal	μg Cl^- L^{-1}
Extractable organic halogens	EOX	Amount of Cl^-, Br^- and I^- organically bounded to organic compounds, which are extractable in a determined organic solvent	μg Cl^- L^{-1}
Total organic chlorine	TOCl	Total Cl^- organically bounded to organic compounds, which are adsorbable on a XAD resin. Also exist TOF, TOBr and TOI	μg Cl^- L^{-1}
Biochemical oxygen demand	BOD	Amount of biologically oxidizable matter present in a sample	Consumed mg O_2 L^{-1}
Total suspended solids	TSS	Total solid matter per volume unit	mg solid matter L^{-1}
Total X (X = Hg, As, N, P, S, etc.)	TX	Total amount (from inorganic and organic nature) of a concrete element in a sample	mg X L^{-1}
Toxicity		It is the percentage of dead or property loss of an established microorganism culture, caused by contact with the sample. It can be acute or chronic	IC_{50} or LC_{50}
Phenolic index		Sum of the detectable phenols under defined conditions	μg phenol L^{-1}

Table 2
Summary of commonly used flow analysis techniques.

Technique	Abbreviation	Fluidic handling	Year	Reference
Flow injection analysis	FIA	Peristaltic pump	1975	[8]
Sequential injection analysis	SIA	Syringe pump with solenoid valve. Selection valve	1990	[9]
Multicommutated flow injection analysis	MCFIA	Peristaltic pump. Solenoid valves	1994	[10]
Multisyringe flow injection analysis	MSFIA	Up to four syringes with solenoid valves moved simultaneously by a single pump	1999	[11]
Multipumping flow systems	MPFS	Solenoid micropumps	2002	[12]

pounds in samples of environmental interest are exhibited and critically discussed. Concretely, the most notable improvements in the determination of some widely used environmental total indices like the chemical oxygen demand, the halogenated organic compounds or the phenolic index are described below.

4.1. *Chemical oxygen demand*

The chemical oxygen demand (COD) is a measure established for the quick assessment of the amount of both organic and inorganic matter contained in a water sample. The result is expressed as the required amount of oxygen (from a chemical oxidant) for the total oxidation of the compounds contained in the sample.

The classic procedure for the COD determination is based on sample mixing with strong sulphuric acid and a known excess of potassium dichromate. The mix is refluxed for 2 h. The remaining oxidant is titrated with ferrous ammonium sulphate, being the result of the titration expressed as the oxygen consumed by the sample.

This classic methodology presents important drawbacks, such as: (i) the use of hazardous chemicals including potassium dichromate, mercury sulphate (for the precipitation of the interfering chloride), silver sulphate (catalyst) and strong acids; (ii) these hazardous chemicals are used at very high temperatures; and (iii) very low analysis throughputs are obtained. In short, this is a popular analytical methodology, but implies a slow, tedious and dangerous procedure, involving the generation of big amounts of extremely hazardous wastes.

An alternative to the titrimetric quantification is the spectrophotometric (SPM) detection. SPM detection has been used since the earliest FIA systems for COD determination, involving on-line digestion by means of heating a mixture composed by the sample, a strong acid and permanganate [14] or dichromate [15] as oxidants. Increased analysis throughputs, waste reduction and less tedious operating conditions were obtained in comparison to manual methods.

Nowadays, these pioneer flow analysis methods have been improved following strategies based on advanced sample digestion procedures thus alternative detection systems, such as chemiluminescent or electrochemical detection. By this way, smart, quicker and more environmentally friendly strategies for the determination of the COD have been achieved. A summary of recently developed flow analysis systems for COD determination is presented in Table 3.

Classic FIA systems for COD determination with SPM detection have been improved recently [16]. Heating is replaced by UV-photocatalytic oxidation in the presence of acidic permanganate. COD is related with a decrease on the permanganate absorbance at 524 nm. This method provides fast, sensitive, accurate and cost-effective in situ COD determinations, thus avoiding the use of Ag_2SO_4 and $HgSO_4$. A schematic representation of a FIA manifold for this determination is shown in Fig. 1a.

Chemiluminescent (CL) detection is an efficient alternative to the classic SPM detection for COD measurements. Recent strategies based on FIA systems have been proposed for these purposes [17–20]. These systems are based on the reactivity between some products released or removed in the sample digestion procedures with appropriated chemiluminometric reagents. These are ozone [17], manganese(II) [18], chromium(III) [19] or free radicals [20].

Target compounds can be oxidized by the combined O_3–UV action, consuming O_3 with the concomitant CL signal decrease on the O_3–luminol–Co^{2+} reaction system. Studies using α-naphthol corroborate that UV-ozonation is a more efficient oxidation process than the classic $KMnO_4$ oxidation [17].

An alternative to the use of O_3, is the use of a strong cation exchange resin for the elimination of the traces of metals contained in the sample. By this way, after the digestion of the sample with $KMnO_4$, the only metal cation present is the gradually released

Table 3
Comparison of recent flow analysis systems for COD determination.

Flow technique	Digestion	Detection	Samples	LOD (mg L^{-1})	Linear range (mg L^{-1})	Injection throughput (h^{-1})	Reference
FIA	UV–$KMnO_4$	SPM at 524 nm	Freshwater	0.5	0.5–50	30	[16]
FIA	UV–O_3	O_3–luminol–Co^{2+} CL	Fresh and Sea water	–	0.5–20	–	[17]
FIA	$KMnO_4$	Mn^{2+}–luminol–H_2O_2 CL	Lake water	2	4–4000	40	[18]
μTAS	$K_2Cr_2O_7$	Cr^{3+}–luminol–H_2O_2 CL	Wastewater	100	270–10,000	–	[19]
FIA	UV	Luminol CL of the released free radicals	River and lake water	0.08	0.2–20	6–12	[20]
FIA	UV/TiO_2 packed bead reactor	O_2 electrode EC	Lake water	0.12	0.12–8	6	[21]
FIA	UV/TiO_2 packed bead reactor	EC using two O_2 electrodes (one placed before and one after digestion)	Water from dam reservoirs	0.5	0.5–9.5	3	[22]
FIA	Electrocatalytic oxidation at F-PbO_2 modified electrode	EC detection based in the current changes produced on the modified electrode	Wastewater	15	100–1200	–	[23]
FIA	Synergistic electrocatalytic–photocatalytic oxidation at a Ti/TiO_2/PbO_2 electrode	EC detection based in the current changes produced on the modified electrode	Wastewater	15	30–2500	–	[24]

CL, chemiluminescence detection; FIA, flow injection analysis; μTAS, micro-total analysis system; EC, electrochemical detection.

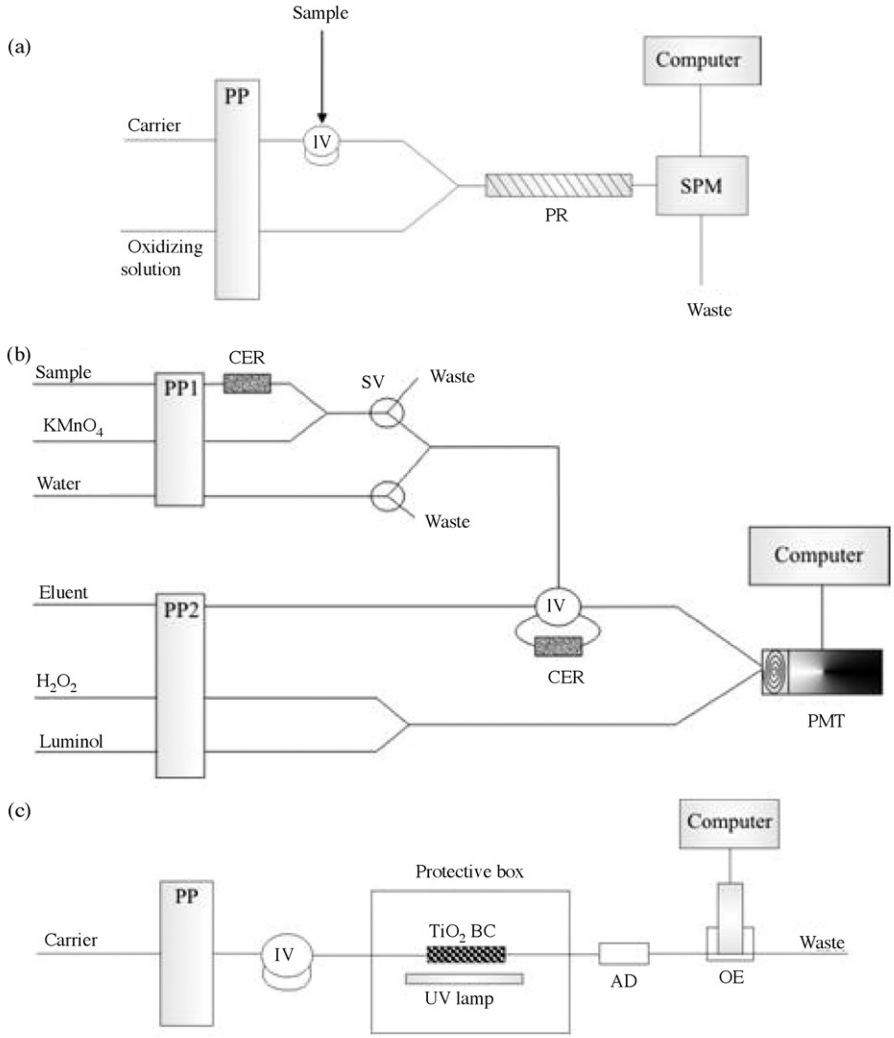

Fig. 1. Examples of FIA systems for the determination of COD using (a) spectrophotometric, (b) chemiluminescent and (c) electrochemical detection. PP, peristaltic pumps; IV, six-port rotating injection valve; PR, photo-reactor; SPM, spectrophotometer; CER, column filled with a strong cation exchange resin; SV, solenoid valves; PMT, photomultiplier equipped with a spiral shaped flow cell; TiO_2 BC, column filled with TiO_2 beads; AD, air damper; OE, oxygen electrode.

Mn^{2+} from the removed $KMnO_4$, which is preconcentrated into a second strong cation exchange resin. After elution with KCl, Mn^{2+} is quantified due to its catalytic action on the luminol–H_2O_2 reaction system, emitting a CL signal proportional to the COD value (Fig. 1b). This method provides a wide linear working range of three orders of magnitude and a high analysis throughput [18]. Other alternative to O_3 is based on the use of acidified $K_2Cr_2O_7$. The released Cr^{3+} is correlated with the COD amount. Cr^{3+} is also quantified by CL reaction with luminol–H_2O_2. The interferences caused by other metallic species are avoided by the addition of EDTA, due to the unfavorable competitive complexation of the Cr^{3+} in front of other metallic cations. This approach is not suitable for natural waters due to its low sensitivity, but it is suitable for COD measurements in wastewaters. Furthermore, it is an environmentally friendly alternative for COD measurements due to its implementation on a μTAS system using various independent syringe pumps as microfluidic handlers [19]. In natural waters, the COD determination is accomplished from the free radicals released by the single action of UV radiation and their subsequent reactivity with luminol [20]. This method allows the measurement of very low amounts of COD ($LOD < 100\ \mu g\ L^{-1}$).

Electrochemical detection is probably the most environmentally friendly alternative for COD measurements [21–24]. Recently improved methods are based on the implementation of UV/TiO_2 packed bead reactors for sample digestion followed by the measurement of the O_2 concentration changes using an amperometric sensor for O_2 detection [21,22] (see Fig. 1c). Other improvements in the COD determination using EC detection are based on the development of the entire analytical procedure (sample digestion + detection) at the same electrode surface. It is achieved by using an F-PbO_2 modified electrode [23], and improved later using a Ti/TiO_2/PbO_2 electrode [24].

4.2. Halogenated organic compounds

Halogenated organic compounds (HOCs) are a huge and heterogeneous group of carbon-based compounds presenting covalently bounded halogens in their structure, being an enormous effort, the quantification of each individual HOC potentially contained in a sample. On the one hand, HOCs are naturally produced in big amounts. On the other hand HOCs are massively produced from anthropogenic sources becoming in an environmental problem, even of global extension. By this reason, several total indices have been defined for that purpose, such as: adsorbable organic halogens (AOX), extractable organic halogens (EOX) or total organic chlorine (TOCl), among others.

The adsorbable organic halogens (AOX) parameter is the measurement of the sum of the adsorbable HOCs into activated charcoal

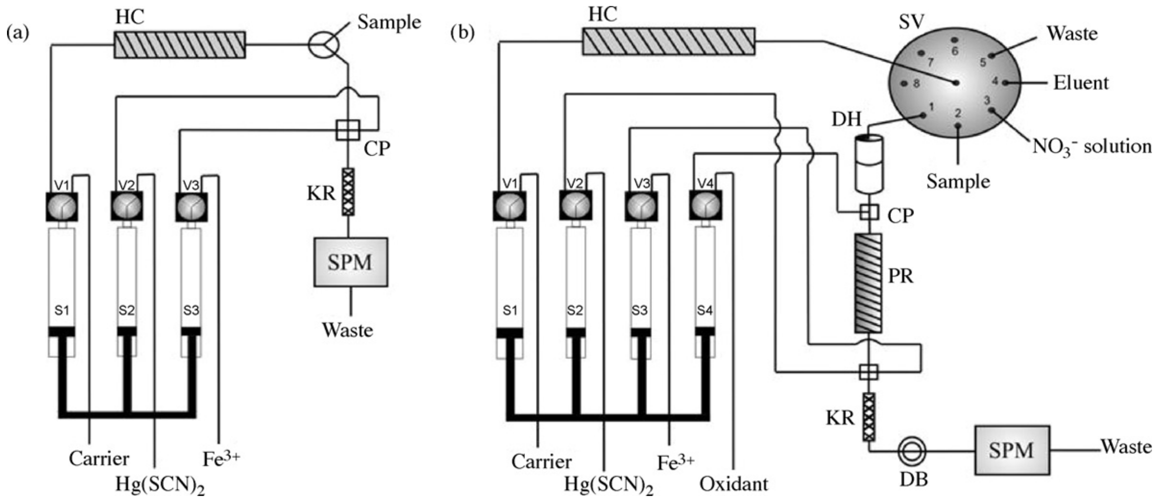

Fig. 2. Schematic representation of (a) MSFIA system for chloride determination and (b) MSFIA system for the determination of halogenated organic compounds as a total index. S1–S4, syringes; V1–V4, solenoid valves; HC, holding coil; SV, selection valve; DH, holder for the accommodation of the sorbent disk for SPE; CP, confluence point; PR, photo-reactor unit; KR, knotted reaction coil; DB, debubbler; SPM, spectrophotometer.

under specific conditions. Once the activated charcoal is free of inorganic halides, it is combusted at 950 °C in a pyrolytic oven, with the concomitant release of free hydrogen halides. These are quantified by means of coulometric titration [25]. Results are expressed as $\mu g\ Cl^- L^{-1}$ and represent the total Cl^-, Br^- and I^- (not F^-, due to a limitation of the technique) from organic origin. This official procedure presents a lack of automation with a concomitant low analysis throughput. By this reason, an automated quasi-continuous system for AOX monitoring was developed [26]. Exploiting a FIA system, AOX are preconcentrated and isolated in an activated charcoal cartridge. The cartridge is automatically discharged into a pyrolytic oven, being the released hydrogen halides in the HOCs digestion determined using plasma emission spectrometry. This method is also useful for TOF, TOCl and TOX determinations.

Exploiting the versatility of the MSFIA technique, a multicommutated method for the determination of Cl^- in waters using the $Hg(SCN)_2/Fe^{3+}$ SPM method (Fig. 2a) [27] was adapted for HOCs measurements (Fig. 2b) [28]. This was accomplished furnishing the MSFIA system with a miniaturized flow through device for the inline solid phase extraction (SPE) of HOCs, thus a UV-photocatalytic reactor for the digestion of the previously preconcentrated HOCs. The SPE procedure is carried out using 9 mm diameter poly(styrenedivinylbenzene) sorbent disks. Rinsing the sorbent with a $NaNO_3$ solution, the interfering inorganic halides are removed. HOCs are eluted using a 2-propanol/water solution. The eluate is mixed with a $Na_2S_2O_8$ solution and irradiated with UV light. The released hydrogen halides from the previous photolysis are quantified using the $Hg(SCN)_2/Fe^{3+}$ method. This system enables the inline completely automated determination of HOCs in a similar way to the AOX classic determination, in a matter of minutes instead of hours.

Simon et al. [29] developed a FIA system for the determination of the extractable TOCl, TOBr and TOI, being their sum the so-called EOX parameter. This system can be defined as a FIA system for the ion-selective determination of the EOX total index. This method is based on the use of a chromatomembrane cell [30] for the liquid–liquid extraction of EOX into hexane. Hexane is combusted in a pyrolytic oven, and the released hydrogen halides are absorbed into a hydrazine sulphate solution, which is injected into an ion chromatograph.

Fluorinated organic compounds are considered as emerging organic pollutants. Their fast screening as TOF is carried out satisfactorily using a FIA system [31]. Organic compounds are extracted off-line in a carbon-based solid phase (e.g. multi-walled carbon nanotubes, carbon nanofibers or activated carbon). Once the SPE has been carried out, sodium biphenyl is added directly onto the sorbent surface producing the release of free fluoride. The recovered fluoride is determined using a FIA system furnished with a fluoride ion-selective electrode. Alternatively, a FIA system with fluorimetric detection using quercetin and zirconium(IV) sulphate, was also used satisfactorily for the same purpose.

Mihalatos and Calokerinos [32] developed a FIA system for gas phase CL detection of halogenated hydrocarbons. This system is based on the injection of a current of O_2 into a photochemical reactor, where it is irradiated with UV light with the concomitant production of O_3. The released O_3 reacts with ethylene in a flow cell and the emitted CL is detected by a photomultiplier. When the sample is injected into the O_2 current, a part of the released ozone is consumed due to the oxidation of the halogenated hydrocarbons. The decrease on the CL signal is proportional to the amount of the target compounds.

4.3. *Phenolic index*

The presence of phenolic compounds in waters is used as an indicator of pollution from anthropogenic sources. Besides the natural presence of a plethora of natural phenolic and polyphenolic compounds, synthetic phenols are massively used by humans for diverse applications. Phenols are used directly as they are, as feed-stocks or generated as byproducts in petroleum, paper, dyes, tannery or pesticide industries, among others.

If the identification of the target compounds is not required, the use of total indices is the quickest way for the obtention of quantitative chemical information about phenol pollution. By this reason, several standard methods for the determination of phenolic compounds as total indices have been established. Some of these are based on the use of the FIA technique with SPM detection [33,34]. This classic methodology, known as the 4-aminoantipyrine (4-AAP) method is based on the oxidative coupling of some phenols with 4-AAP in alkaline medium aided with an oxidant ($K_3[Fe(CN)_6]$). The developed reaction product is SPM detected at 500 nm. But the 4-AAP method also presents some drawbacks. It is a very time-consuming methodology. The analytical procedure involves a tedious sample pretreatment. Poor recoveries for some para-substituted phenols are obtained. The method requires the use of hazardous chemicals at high concentrations with the concomi-

Table 4
Comparison of recent flow systems developed for phenolic index determination.

Flow technique	Pretreatment	Detection	Samples	LOD ($\mu g\,L^{-1}$)	Linear range ($\mu g\,L^{-1}$)	Injection throughput (h^{-1})	Reference
FIA	(1) Inline SPE (2) Reaction with 4-AAP/$K_3[(Fe(CN_6)]$	SPM 490 nm	Environmental and industrial waste waters	4	10–1000	12	[35]
FIA	(1) Reaction with 4-AAP/$K_3[(Fe(CN_6)]$ (2) SPE (optosensing)	SPM	–	1	5–500	–	[36]
SIA	Direct reaction with 4-AAP/$K_3[(Fe(CN_6)]$	SPM 510 nm	Waste waters	10	50–2500	24	[37]
MSFIA	(1) Inline SPE (2) Reaction with 4-AAP/$K_3[(Fe(CN_6)]$	SPM 510 nm	Certified reference material	2	10–280	4	[38]
MCFIA	Direct reaction with 4-AAP/$K_3[(Fe(CN_6)]$	SPM 500 nm	Natural and waste waters	1	10–100	90	[39]
MPFS	Direct reaction with nitroprusside/hydroxylamine	SPM 700 nm	Environmental and waste waters	13	50–3500	65	[40]
FIA	Direct reaction with rhodamine-6G/Ce^{4+}	CL	–	–	–	–	[41]
FIA	(1) Inline SPE (2) Reaction with acidic $KMnO_4$	CL	Ground and waste water	1	1–20	4	[42]
FIA	Direct reaction with acidic $KMnO_4$ sensitized with formaldehyde	CL	Waste water	3	5–1000	–	[43]
FIA	(1) Inline SPE (2) Reaction with luminol/$K_3[(Fe(CN_6)]$	CL	Natural waters	0.00066	0.0047–0.47	–	[44]
FIA	Sample acidification	EC	Waste water	37.6	94–9400	180	[45]
FIA	No pretreatment	EC	Waste water	8.3	18.8–18,800	–	[46]

tant generation of toxic wastes, thus the previous distillation of samples (for the elimination of potential interferences), among other drawbacks. By this reason, several improved applications for the determination of this total index have been recently proposed [35–46] (Table 4). These improvements are based on the exploitation of alternative detection systems to classic SPM detection, such as: long pathlength spectrophotometry [39], chemiluminescence [41–44] or electrochemical detection [45,46]. Thus, the use of more advanced flow analysis techniques, such as: SIA [37], MSFIA [38], MPFS [39] and MCFIA [40].

An improved sensitivity for the 4-AAP method automated in a FIA system is obtained with the use of inline SPE prior to SPM detection. This is achieved using a microcolumn packed with Amberlite XAD-4 resin for the preconcentration/isolation of phenols prior to their SPM detection [35]. Or by direct optosensing of the developed reaction product onto the same sorbent surface by using C18-modified silica resin, packed in a microcolumn [36].

Sequential flow analysis techniques have been also applied for the phenolic index determination through the 4-AAP method. As the volumes of reagents are perfectly controlled, the volume of waste products is drastically reduced, becoming in more environmentally friendly strategies. Some examples are, the direct determination of phenols using a SIA system [37], or the MSFIA system proposed by Oliveira et al. [38] combining in a single system (Fig. 3a) the advantageous characteristics of their predecessors; inline preconcentration [35] and low reagent consumption [37].

The previous methods are improved exploiting a MCFIA system furnished with a 1m long path length liquid waveguide capillary cell (LWCC) as flow cell for SPM measurements [39]. This MCFIA–LWCC system (Fig. 3b) allows a high analysis throughput of 90 h^{-1} and a 200-fold reduction of reagent consumption. As the sensitivity is enhanced with the use of the LWCC, some additional sample treatments such as SPE are not required. Another more environmentally friendly alternative for the SPM determination of the phenolic index is based on the use of solenoid micropumps as microfluidic handling devices, using nitroprusside/hydroxylamine as reagents, instead 4-AAP/ferricyanide [40].

Chemiluminescence is also an efficient detection system for the determination of phenolic compounds, achieving higher sensitivity than with classic SPM detection. Other advantageous features for the CL detection of phenolic compounds are: (i) the obtention of good recoveries for para-substituted phenols, thus (ii) the pre-distillation of the samples is not required.

Cui et al. [41] accomplished using a FIA system a study about the reactivity of the chemiluminescent reaction of phenolic compounds with rhodamine-6G/Ce^{4+} and its subsequent CL emission. The system was not applied to real samples. FIA was also combined with SPE using a microcolumn packed with Amberlite XAD-4 resin, thus detection based on the acidic permanganate CL [42]. Afterwards, the CL reaction between phenolic compounds and acidic permanganate was sensitized by the addition of formaldehyde, improving the sensitivity and achieving without preconcentration a LOD of only 3 $\mu g\,L^{-1}$ phenol [43]. The LOD of the previous CL methods was improved using a FIA system with inline SPE (microcolumn filled with C18-modified silica) prior to luminol/$K_3[Fe(CN)_6]$ CL detection. By this way an ultra-low limit of detection of only 0.66 ng L^{-1} phenol was achieved [44] (Fig. 3c).

Recent improvements on the determination of phenolic compounds as a total index have been achieved using electrochemical detection. As with CL detection, pre-distillation is not required and good recoveries for para-substituted phenols are achieved. Some examples of these are: (i) a biamperometric system for an irreversible redox couple, based on coupling the oxidation of phenolic compounds at a platinum-wire electrode and the concomitant reduction of permanganate in another analogous electrode obtaining a method with a high analysis throughput [45] or, (ii) the application of self-assembled monolayer-based tyrosinase biosensors for the amperometric determination of phenols [46], achieving a wide linear dynamic range of three orders of magnitude.

When the distillation of the sample is required, Quaresma et al. [47] developed a fast alternative for this pretreatment by using focused microwave-assisted sample distillation. A sample volume of 25 mL is distilled following the proposed procedure for 15 min. Obtained recoveries were of a 95% phenol in the distilled solution,

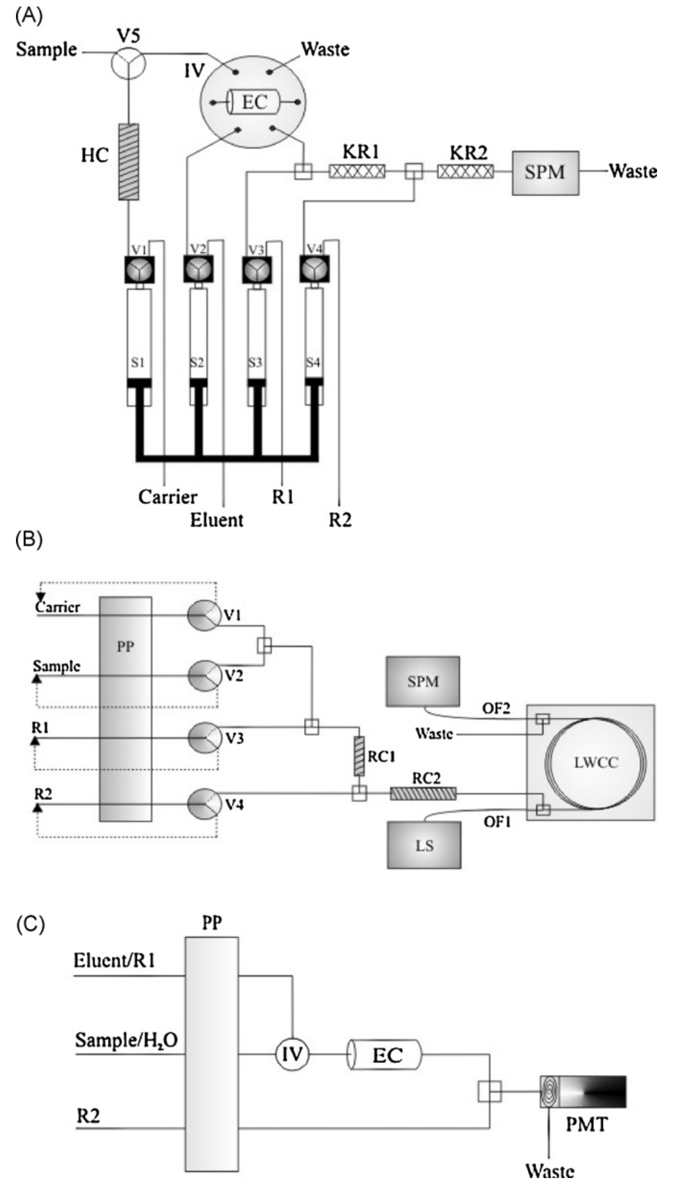

Fig. 3. Schematic representation of various alternatives based on flow analysis techniques for the determination of phenols as total indices. PP, peristaltic pump; V1–V5, solenoid valves; RC1–RC2, reaction coils; OF1–OF2, optical fibers; LS, UV–vis light source; SPM, spectrophotometer; LWCC, liquid waveguide capillary cell; HC, holding coil; IV, injection valve; S1–S4, syringes; KR1–KR2, knotted reaction coils; PMT, photomultiplier tube. (a) MSFIA system with inline SPE and spectrophotometric detection. R1, 4-aminoantipyrine; R2, $K_3[Fe(CN)_6]$. (b) MCFIA system with spectrophotometric detection based on the use of a 1 m LWCC as flow cell. EC, extraction column filled with Amberlite XAD-4 resin; R1, 4-aminoantipyrine; R2, $K_3[Fe(CN)_6]$. (c) FIA system with inline SPE and chemiluminescent detection. EC, extraction column filled with C_{18}-modified silica resin; eluent/R1, methanol–luminol (60%, v/v); R2, $K_3[Fe(CN)_6]$.

which is analyzed with the 4-AAP/$K_3[Fe(CN)_6]$ method implemented in a FIA system. Following this procedure, the obtained results are similar that those of the standard methods, but increasing the analysis throughput.

5. Concluding remarks and future outlook

From the above overview about the recent developments based on flow analysis techniques for COD, HOCs and phenolic compounds determination as total indices, we can set out the next conclusions:

- Total indices are indispensable tools for the quick obtention of preliminary chemical information about complex analytical systems.
- The classic methodologies for the determination of total indices are time-consuming, laborious, involves dangerous procedures, thus the generation of considerable amounts of toxic wastes. These disadvantageous features are diminished due to their implementation in flow analysis systems.
- In the recent years, classic FIA methods have been improved due to the development of more advanced flow analysis techniques and new types of detection systems. These advances in instrumentation induce a concomitant improvement of the analytical features of the developed methodologies, such as: higher analysis throughputs, lower detection limits, larger linear dynamic ranges, lower relative standard deviations, among others. Furthermore, they provide useful solutions to some limitations of classic techniques, thus new possibilities of chemical analysis.
- The process downscaling obtained using flow analysis-based systems enables the saving of reagents and solvents, being the new developed strategies for the determination of total indices more environmentally friendly [48,49] than the classic ones.

A possible future outlook about this topic could deal with the new possibilities offered by nanotechnology, providing new materials for improved SPE, sample digestion or developing new detectors. Other improvements could be achieved by the substitution of hazardous chemical reagents/solvents for other more benign ones (i.e. ionic liquids), besides the development of meso- and microfluidic devices, such as lab-on-valve (LOV) [50] or lab-on-chip (LOC)/μTAS systems [51].

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