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Multisyringe Flow Injection Analysis for Environmental Monitoring: Applications and Recent Trends

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1. Introduction

Multisyringe flow injection analysis (MSFIA) was introduced by Víctor Cerdà and co-workers in 1999 (Cerdà et al., 1999) as a robust alternative to its predecessor flow injection techniques, combining the multi-channel operation of flow injection analysis (Ruzicka & Hansen, 1975) with the possibility of flow reversal and selection of the exact volume of sample and reagent required for analysis as presented in sequential injection analysis (Ruzicka & Marshall, 1990). Generally, flow injection systems are automation tools where, in opposition to batch conventional assays, physico-chemical equilibrium is not attained prior to determination. Hence, flow injection analysis is based in three principles: (1) reproducible sample injection or insertion in a flowing carrier stream; (2) controlled dispersion of the sample zone; and (3) reproducible timing of its movement from the injector point to the detection system.

Since its inception, MSFIA has been the basis for automation of more than 120 different assays, reviewed in several publications (Almeida et al., 2011; Magalhães et al., 2009; Maya et al., 2009; Segundo & Magalhães, 2006). This type of automatic flow injection systems is based on the utilization of a multisyringe burette, depicted schematically in Fig. 1A and 1B. It is a multiple channel piston pump, containing up to four syringes, driven by a single motor of a usual automatic burette and controlled by computer software through a serial port. A two-way commutation valve is connected to the head of each syringe, allowing optional coupling to the manifold lines or to the solution reservoir.

Because the four syringes are driven by the same motor, all pistons move at once in the same direction either delivering (dispense operation) or loading the syringes (pickup operation) with liquids. Considering that the commutation valves can be placed in two positions, there are four possibilities for flow management as depicted in Fig. 1C. Hence, when the pistons are moving upwards, it is possible to dispense liquid into the flow system or send it back to its reservoir. This feature enables that only the necessary amount of reagent solution is introduced into the flow system. Furthermore, when the pistons are moving downwards, it is possible to refill the syringes with solutions present in the respective vessel or to aspirate solutions from the system in order to perform the sampling operation.
Fig. 1. Schematic representation of multisyringe apparatus, with indication of the different components (A) or simplified (B). Flow management possibilities for one syringe during operation of multisyringe apparatus are also given (C). MS = multisyringe; S = syringe, V = commutation valve.
Syringes with different volumes, ranging from 0.5 to 25 ml are available, enabling the application of a wide range of flow rates. For example, for a 5 ml syringe, flow rates ranging from 0.28 to 15 ml min\(^{-1}\) may be attained (Miró et al., 2002). Nevertheless, once the flow rate (and volume) is fixed for one syringe, it is also defined for the other channels, and it will depend on the ratio between syringe capacities as different syringes can be placed in any of the four positions.

Finally, MSFIA manifolds are not restricted to the syringes and the respective commutation valves. The presence of four digital outputs, each capable of providing 12 V/0.5 A, allows the utilization of up to 12 additional commutation valves, also controlled through the multisyringe apparatus. These extra commutation valves are often necessary to assemble a flow network, where analyte determination and sample treatment can be implemented by including confluences for reagent addition, suitable detectors (spectrophotometers, fluorimeters, flame or atomic emission spectrometers) and devices for mass transfer (gas diffusion or dialysis units), for instance.

### 2. Applications of MSFIA to environmental monitoring

MSFIA systems have been successfully applied to the determination of more than 20 species in environmental samples as illustrated in Tables 1 and 2. Several applications were targeted to plant macronutrients, such as potassium and phosphorus, and also to micronutrients, including boron, iron and selenium (Table 1). These species were quantified in different types of water (natural and seawater) and also in soil extracts or even soil slurries when applying flame emission spectrometry for determination of potassium (Almeida et al., 2008). The introduction of aqueous samples in flow systems is rather trivial, while manipulation of samples containing suspended solids is not common, requiring a special manifold design employing larger commutation valves and large bore tubing (Almeida et al., 2008).

In fact, solid environmental samples were successfully handled within MSFIA systems. Extraction of potassium contained in 1.8 g of soil was performed in-line, prior to potentiometric determination. The soil was placed in a container where 9 ml of Morgan extractant solution was delivered automatically by one of the syringes. After 6 min, in-line filtration took place, and a small portion of filtrate (100 µl) was sent to the potentiometric detector after in-line addition of an ionic strength adjusting buffer. Different soils were analyzed consecutively without carry-over effects and the filtration unit was reutilized up to 10 times (Almeida et al., 2006).

Besides the determination of total extractable content, MSFIA systems have been employed to dynamic fractionation testing schemes, profiting from its inherent capabilities of controllable flow programming. In fact, Miró and co-workers developed a multiple stirred-flow chamber assembly, containing up to three parallel extractors, to perform sequential extraction of readily mobilizable fractions of trace elements (Cu, Cd, Ni, Pb, Zn) in fly ashes (Boonjob et al., 2008). Though the detection step was performed off-line (not automated) on each 10 ml fraction collected, the MSFIA system still provided information about overall extractable pools in less than 2 hours, a drastic reduction of time when compared to 18 to 24 hours required per fraction in equilibrium leaching tests. Moreover, the implementation of a sequential leaching scheme was easily accommodated in MSFIA, due to its inherent flow features and also by housing different extracting solutions (water, 0.11 M acetic acid, 0.11 M acetic acid/acetate buffer) simultaneously in each syringe of the multisyringe burette.
Table 1. MSFIA methods for nutrient assessment and monitoring

<table>
<thead>
<tr>
<th>Analyzed species</th>
<th>Sample type</th>
<th>In-line sample treatment</th>
<th>Determination throughput (h⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron (available)</td>
<td>Soil extract</td>
<td>---</td>
<td>15</td>
<td>(Gomes et al., 2005)</td>
</tr>
<tr>
<td>Iron (available)</td>
<td>Soil extract</td>
<td>---</td>
<td>34</td>
<td>(Gomes et al., 2005)</td>
</tr>
<tr>
<td>Iron (total)</td>
<td>Water</td>
<td>Solid phase extraction</td>
<td>12</td>
<td>(Pascoa et al., 2009)</td>
</tr>
<tr>
<td>Iron (total) and Fe(III)</td>
<td>Water</td>
<td>---</td>
<td>60</td>
<td>(Pons et al., 2004)</td>
</tr>
<tr>
<td>Iron (total) and Fe(III)</td>
<td>Water (natural and seawater)</td>
<td>Solid phase extraction</td>
<td>5 - 10</td>
<td>(Pons et al., 2004, 2005a, 2005b)</td>
</tr>
<tr>
<td>Phosphate</td>
<td>Water</td>
<td>Solid phase extraction</td>
<td>11</td>
<td>(Morais et al., 2004)</td>
</tr>
<tr>
<td>Phosphate</td>
<td>Soil extract</td>
<td>In-line sequential extraction</td>
<td>Not given</td>
<td>(Buanuam et al., 2007)</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>Soil extract</td>
<td>---</td>
<td>15</td>
<td>(Almeida et al., 2005)</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>Water</td>
<td>Microwave digestion</td>
<td>12</td>
<td>(Almeida et al., 2004)</td>
</tr>
<tr>
<td>Potassium</td>
<td>Soil extracts</td>
<td>Extraction and in-line filtration</td>
<td>13</td>
<td>(Almeida et al., 2006)</td>
</tr>
<tr>
<td>Potassium</td>
<td>Soil slurries</td>
<td>---</td>
<td>28</td>
<td>(Almeida et al., 2008)</td>
</tr>
<tr>
<td>Selenium</td>
<td>Sea lettuce</td>
<td>---</td>
<td>84</td>
<td>(Semenova et al., 2003)</td>
</tr>
<tr>
<td>Selenium</td>
<td>Water (natural and seawater)</td>
<td>Solid phase extraction</td>
<td>8</td>
<td>(Serra et al., 2010)</td>
</tr>
</tbody>
</table>

The same group proposed a fully automated strategy for fractionation of orthophosphate in soil samples and in-line spectrophotometric determination resorting to molybdenum blue reaction (Buanuam et al., 2007). The system integrated dynamic sequential extraction using 1 M ammonium chloride solution, 0.1 M sodium hydroxide solution and 0.5 M hydrochloric acid solution as extractants according to the Hieltjes–Lijklema scheme. Solid soil samples were placed in a flow-through customized dual conical chamber (Chomchoei et al., 2004), which could be filled with up to 300 mg of soil. Compared to conventional batch equilibrium procedures, the automatic dynamic fractionation system offered further knowledge on: (i) the extraction kinetics, (ii) the content of phosphorus in available pools, (iii) the efficiency of the leachants and (iv) the actual extractant volume required for quantitative release of orthophosphate. The automatic MSFIA extraction scheme was also validated through application to certified reference material SRM 2704 river sediment and SRM 2711 Montana soil.

Recently, a similar strategy was applied for automated dynamic extraction and determination of readily bioaccessible chromium(VI) in soils. Besides the extraction capabilities, the automatic MSFIA system also fostered in-line quantification of Cr(VI)
after derivatization using 1,5-diphenylcarbazide and in-line adjustment of Cr(VI) concentration prior to determination. This last feature was attained by incorporating a dilution chamber (for extracts from highly contaminated samples) and another flow-through column filled with multi-walled carbon nanotubes for preconcentration of Cr-1,5-diphenylcarbazide (for extracts or fractions with low Cr(VI) concentration). The MSFIA system was successfully applied to SRM 2701 soil, providing the extraction kinetics for sequential extraction using water and an acid rain surrogate. The automatic integration of extraction and Cr(VI) determination also allowed the minimization of interconversion between Cr oxidation states often observed when determination is not carried out immediately after extraction.

In fact, several MSFIA systems were developed for monitoring of environmental pollutants as indicated in Table 2. Both organic and inorganic species were targeted, with a focus on water analysis. In this context, in-line sample treatment is undeniably a requisite when devising monitoring schemes with real environmental samples. There are two main reasons for this. First, analytes, particularly pollutants, are generally present at low concentrations (ppt or ppb range) in these samples, requiring a preconcentration step in order to meet the linear working range offered by the available detection systems. Secondly, the target analyte may be strongly bound or entrapped in the sample matrix or it can present different forms concerning its oxidation state. Hence, solid phase extraction has been frequently implemented in-line, aiming the enrichment and selective uptake of analytes. It has been applied for the determination of trace levels of phosphate (5 – 50 µg l$^{-1}$ of P) in natural waters combined to chemiluminescence detection (Morais et al., 2004), for determination of selenium (5.7 - 1290 µg l$^{-1}$) in natural and seawater (Serra et al., 2010) and for determination of trace iron (0.05 – 8 µg l$^{-1}$; 0.2 – 42 µg l$^{-1}$) in waters (Pascoa et al., 2009; Pons et al., 2004, 2005a, 2005b) as far as nutrient analysis is concerned.

Solid phase extraction has also been employed in more than half of the applications focusing on pollutants monitoring and it was implemented in several ways. In flow injection systems, sorbents are generally packed in flow-through columns, which are sequentially percolated by conditioning solution, sample, washing solution and eluent, fostering selective retention of target analyte(s), followed by its/their elution after sample matrix removal. This strategy has also been implemented in MSFIA for determination of total phenolics in waters, using Amberlite XAD-4 as sorbent and in-line derivatization with 4-aminoantipyrine (Oliveira et al., 2005). This MSFIA system was further improved and coupled to liquid chromatography, allowing on-line preconcentration and determination of eleven priority phenolic pollutants in water and soil samples (Oliveira et al., 2009).

Extraction membranes, containing different functional groups, have also been employed in MSFIA systems as they are an advantageous alternative to particulate sorbents because they allow higher flow rates (providing high determination throughputs) and low backpressure, avoiding leakages and clogging. Several applications have been reported, namely for preconcentration of nitrophenols and their determination after elution (Manera et al., 2007a) or using optosensing (Manera et al., 2007b) by probing the extraction membrane with a bifurcated optical fiber connected to a CCD spectrometer. In fact, the utilization of optosensors in MSFIA systems is simplified because all solutions required (sample, conditioning and regenerating solutions) can be automatically delivered by the multisyringe burette in a precise and timely way. Hence, optosensing has also been applied in MSFIA systems for trace level determination of 1-naphthylamine in water samples (Guzmán-Mar et al., 2006b) and determination of sulphide (Ferrer et al., 2005b).
<table>
<thead>
<tr>
<th>Analyzed species</th>
<th>Sample type</th>
<th>In-line sample treatment</th>
<th>Determination throughput (h⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>Water, fish muscle and liver</td>
<td>---</td>
<td>108</td>
<td>(Semenova et al., 2002)</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Water</td>
<td>Solid phase extraction</td>
<td>9</td>
<td>(Long et al., 2006)</td>
</tr>
<tr>
<td>Arsenic (total inorganic and As(III))</td>
<td>Water, sea lettuce</td>
<td>---</td>
<td>10</td>
<td>(Leal et al., 2006a)</td>
</tr>
<tr>
<td>Azinphos methyl</td>
<td>Water</td>
<td>Hydrolysis</td>
<td>7</td>
<td>(Ornelas-Soto et al., 2009)</td>
</tr>
<tr>
<td>Chlorotriazine herbicides</td>
<td>Water and soil extracts</td>
<td>Solid phase extraction</td>
<td>Not given</td>
<td>(Boonjob et al., 2011; Boonjob et al., 2010)</td>
</tr>
<tr>
<td>Chromium(VI)</td>
<td>Soil leachates</td>
<td>In-line extraction</td>
<td>Not given</td>
<td>(Rosende et al., 2011)</td>
</tr>
<tr>
<td>Halogenated organic carbons</td>
<td>Water and leachates</td>
<td>Solid phase extraction</td>
<td>9</td>
<td>(Maya et al., 2008)</td>
</tr>
<tr>
<td>Mercury</td>
<td>Water, fish muscle</td>
<td>---</td>
<td>44</td>
<td>(Leal et al., 2006a)</td>
</tr>
<tr>
<td>Mercury</td>
<td>Water and leachates</td>
<td>Solid phase extraction</td>
<td>30</td>
<td>(Serra et al., 2008)</td>
</tr>
<tr>
<td>Mercury (inorganic and organic)</td>
<td>Water, fish muscle</td>
<td>Solid phase extraction</td>
<td>14</td>
<td>(Serra et al., 2009)</td>
</tr>
<tr>
<td>1-Naphthylamine</td>
<td>Water</td>
<td>---</td>
<td>90</td>
<td>(Guzmán-Mar et al., 2006a)</td>
</tr>
<tr>
<td>1-Naphthylamine</td>
<td>Water</td>
<td>Solid phase extraction</td>
<td>14</td>
<td>(Guzmán-Mar et al., 2006a)</td>
</tr>
<tr>
<td>Nitrophenols</td>
<td>Water, seawater and waste leachates</td>
<td>Solid phase extraction</td>
<td>3 - 11</td>
<td>(Horstkotte et al., 2008; Manera et al., 2007a; Manera et al., 2007b)</td>
</tr>
<tr>
<td>Nitrophenols</td>
<td>Water</td>
<td>Liquid-liquid extraction</td>
<td>11</td>
<td>(Miró et al., 2001)</td>
</tr>
<tr>
<td>Pharmaceutical residues (NSAIDs)</td>
<td>Water</td>
<td>Solid phase extraction</td>
<td>Not given</td>
<td>(Quintana et al., 2006)</td>
</tr>
<tr>
<td>Pharmaceutical residues (thiazide diuretics) (total)</td>
<td>Water and solid waste leachates</td>
<td>Solid phase extraction</td>
<td>12</td>
<td>(Maya et al., 2010)</td>
</tr>
<tr>
<td>Phenolic compounds</td>
<td>Water</td>
<td>Solid phase extraction</td>
<td>4 - 16</td>
<td>(Oliveira et al., 2005)</td>
</tr>
<tr>
<td>Phenolic compounds (total)</td>
<td>Water and solid waste leachates</td>
<td>Solid phase extraction</td>
<td>4 - 10</td>
<td>(Oliveira et al., 2009)</td>
</tr>
<tr>
<td>Polychlorinated biphenyls</td>
<td>Solid waste leachates</td>
<td>Solid phase extraction</td>
<td>Not given</td>
<td>(Quintana et al., 2009)</td>
</tr>
<tr>
<td>Sulphide</td>
<td>Water</td>
<td>Solid phase extraction</td>
<td>45</td>
<td>(Ferrer et al., 2004)</td>
</tr>
<tr>
<td>Sulphide</td>
<td>Wastewater</td>
<td>Analyte separation by gas diffusion</td>
<td>13 - 20</td>
<td>(de Armas et al., 2004; Maya et al., 2007)</td>
</tr>
<tr>
<td>Sulphide</td>
<td>Waters (fresh, seawater and wastewater)</td>
<td>Solid phase extraction</td>
<td>5 - 8</td>
<td>(Ferrer et al., 2005a, 2005b; Ferrer et al., 2006)</td>
</tr>
<tr>
<td>Warfarin</td>
<td>Water</td>
<td>Solid phase extraction</td>
<td>12</td>
<td>(de Armas et al., 2002)</td>
</tr>
<tr>
<td>Sulphonated azo dyes</td>
<td>Water</td>
<td>Solid phase extraction</td>
<td>7.5</td>
<td>(Fernandez et al., 2010)</td>
</tr>
<tr>
<td>UV filters</td>
<td>Water</td>
<td>Solid phase extraction</td>
<td>7</td>
<td>(Oliveira et al., 2010)</td>
</tr>
</tbody>
</table>

Table 2. MSFIA methods for assessment and monitoring of pollutants
MSFIA systems were also devised for speciation of arsenic (Leal et al., 2006b) and mercury (Serra et al., 2009) in environmental samples. For arsenic, As(III) was quantified by atomic fluorescence spectrometry while As(V) was assessed by difference from total As content, determined for the same sample after in-line reduction of As(V) to As(III) by automatic addition of potassium iodide and ascorbic acid. For mercury, atomic fluorescence spectrometry was also employed and speciation between inorganic and organic (methylmercury) forms was performed by selectively retaining mercury tetrachloro complex in an anion exchange membrane, while organic mercury was directed towards a flow-through UV digestor before detection. Inorganic mercury was later eluted from the membrane by in-line reduction with tin chloride, allowing a limit of detection of 16 ng l\(^{-1}\).

Besides the reduction of intervention from laboratory technicians in the analytical operations, automation of environmental assays by MSFIA provided also an acceptable determination throughput, ranging from 7.5 to 108 determinations per hour in automatic systems where no sample treatment was required or where it was performed off-line. For MSFIA systems comprising in-line sample treatment, determination throughputs ranged from 3 to 30 determinations per hour, which are excellent figures. For instance, the determination of total phosphorus in waste water samples was carried out with a determination throughput of 12 determinations per hour by implementing in-line microwave digestion of samples (Almeida et al., 2004). This is a significant reduction of the assay time when compared to the conventional batch digestion that took about 2 hours for quantitative measurements.

3. Recent trends for sample treatment

As mentioned before, environmental samples comprise complex matrices where target analytes are not generally amenable to direct determination by instrumental analysis, requiring sample treatments. Regarding this aspect, solid phase extraction is undoubtedly the most common treatment applied in MSFIA systems as shown in Tables 1 and 2. Besides the examples presented before in the text, MSFIA capabilities have been recently exploited to perform solid phase extraction using bead injection (BI) prior to chromatographic analysis.

The bead injection concept consists of handling solid suspensions in a fully automatic fashion, where the solid-phase sorbent, presented as micrometric beads, is renewed in each individual analytical cycle, rendering a fresh portion of sorbent for each analysis. Moreover, bead injection allows the simultaneous monitoring of both effluent and solid phase itself (optosensing) in real time, which brings complementary and enhanced insight into the solid phase extraction procedure in a single assay (Gutzman et al., 2006).

The bead injection concept is often associated to the lab-on-valve (LOV) platform. The LOV module comprises a monolithic structure with microconduits machined in a polymethylmethacrylate or polyetherimide unit, which is mounted atop a multiposition valve (Fig. 2), representing a step forward towards automation and miniaturization of flow injection systems. The LOV-BI approach offers two main advantages, not matched by any other automatic, flow-based solid phase extraction scheme: (i) the automatic renewal of sorbent, without any intervention of operator or replacement of devices or physical parts of the system, so as to circumvent the progressive deactivation and tighter packing of permanent in-line solid phase extraction cartridges; and (ii) the accurate metering of sorbent and eluate quantities by resorting to bi-directional programmable flow, as precisely controlled by the multisyringe burette (Miró et al., 2011).
However, reliable manipulation of bead suspensions within the flow manifold is the major challenge in mechanized BI protocols for repeatable trapping of beads in microcolumns with subsequent minimization of the uncertainty measurement of the overall analytical method. Initially, spherical shape, uniform size distribution and water-wettability (for reversed-phase materials) were identified as imperative requisites for sorbent selection. Recently, novel strategies for microfluidic handling the sorbent suspensions have been proposed (Oliveira et al., 2011), extending the application of LOV-BI to a larger scope of sorbents, not fitting the previous requirements and opening up new opportunities for preconcentration using molecular imprinted polymers for pharmaceutical residue analysis, for instance.

The hyphenation of LOV-BI-MSFIA to chromatography provided a step further on automation for environmental analysis as sample preparation and analyte separation by chromatography were integrated. Previous automation of sample treatment prior to chromatographic analysis involved robotic analyzers, meaning high equipment costs and expensive operation. By using LOV-BI-MSFIA, while one sample is injected in the chromatographic equipment, the following sample is processed in the MSFIA equipment for matrix removal and analyte enrichment. This is an important, advantageous aspect when dealing with labile analytes that cannot sit on automatic injectors for a long time.

As depicted in Fig. 2, connecting the liquid chromatograph equipment to LOV-BI-MSFIA is rather simple requiring that one of the lateral ports of the LOV platform is directly connected to the injection valve present in the chromatograph, allowing the introduction into the injection loop of all eluate or merely a fraction of it via heart-cut injection protocols. The transfer of the entire volume of eluate into the separation system is essential to reach low limits of detection required by analysis of pollutants in environmental samples, especially when using low-sensitivity detectors, for instance UV spectrophotometers. This approach, along with the handling of a well-defined volume of sample (about 10 ml), fostered the determination of non-steroidal anti-inflammatory drugs (NSAIDs) (Quintana et al., 2006) and chlorotriazine herbicides and some of its metabolites (Boonjob et al., 2010) in environmental samples at the low-µg l\(^{-1}\) level (Table 3). The screening of UV filters in swimming pool and seawaters also profited from the combination LOV-BI-MSFIA (Oliveira et al., 2010). In-line dilution was necessary after analyte elution in order to match the eluate composition to the aqueous content of the mobile phase, avoiding band broadening problems.

<table>
<thead>
<tr>
<th>Analyzed species</th>
<th>Working range</th>
<th>Limit of detection</th>
<th>Precision (RSD%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorotriazine herbicides</td>
<td>0.1 - 10 µg l(^{-1})</td>
<td>0.02 – 0.04 µg l(^{-1})</td>
<td>&lt;5.5</td>
<td>(Boonjob et al., 2010)</td>
</tr>
<tr>
<td>Pharmaceutical residues (NSAIDs)</td>
<td>0.4 - 40 µg l(^{-1})</td>
<td>0.02 – 0.67 µg l(^{-1})</td>
<td>&lt;11</td>
<td>(Quintana et al., 2006)</td>
</tr>
<tr>
<td>Polychlorinated biphenyls</td>
<td>2 - 100 ng l(^{-1})</td>
<td>0.5 – 6.1 ng l(^{-1})</td>
<td>&lt;9</td>
<td>(Quintana et al., 2009)</td>
</tr>
<tr>
<td>UV filters</td>
<td>5 - 160 µg l(^{-1})</td>
<td>0.45 – 3.2 µg l(^{-1})</td>
<td>&lt;13</td>
<td>(Oliveira et al., 2010)</td>
</tr>
</tbody>
</table>

Table 3. Analytical figures of LOV-BI-MSFIA system coupled to chromatographic separation
The hyphenation of LOV-BI-MSFIA to gas chromatography is not as simple as it is for liquid chromatography. First, lower injection volumes are required and the analytes should be eluted in a solvent prone to fast vaporization. In fact, only one application has been described so far, where low values for limit of detection were attained through the automatic, on-line transfer of all eluate to a gas chromatograph equipped with an electron capture detector and a programmable temperature vaporization injector for determination of polychlorinated biphenyls in solid-waste leachates at the 2–100 ng L\(^{-1}\) range (Quintana et al, 2009).

4. Conclusions

MSFIA is undoubtedly a suitable automation tool for implementation of environmental analysis. Considering the examples presented here, the proof of concept has been given, shown by application to a large suite of species, comprehending nutrients and pollutants in several environmental matrices. The determination throughputs attained are suitable for most applications sought in environmental monitoring schemes and field deployment is possible for many of the MSFIA systems developed, as long as periodic reagent refilling is guaranteed.

Automation and integration of sample treatment to instrumental quantification of analytes was successfully demonstrated, profiting from the multichannel operation of MSFIA equipment. However, some unique features provided by MSFIA are underexploited for environmental analysis. Recent work regarding LOV-BI-MSFIA coupled to chromatography are still in its infancy and will certainly grow into more reliable, comprehensive analyzers for monitoring of emerging pollutants.

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