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In tube-solid phase microextraction-nano liquid chromatography: Application to the determination of intact and degraded polar triazines in waters and recovered struvite

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ABSTRACT

In-tube solid-phase microextraction (IT-SPME) coupled to miniaturized liquid chromatography (LC) techniques are attractive mainly due to the column efficiency improvement, sensitivity enhancement and reduction of solvent consumption. In addition, the nanomaterials based sorbents can play a key role in the improvement of the extraction efficiency taking into account their interesting physical and chemical properties. Thus, in this work the performance of IT-SPME coupled to nano LC (NanoLC) has been compared with the performance of IT-SPME coupled to capillary LC (CapLC) with similar configurations for the determination of polar triazines including their degradation products. In both cases, a DAD detector was used. Different extractive phases such as TRB-5, TRB-5/c-SWNTs, TRB-5/c-MWNTs capillary columns have been tested. The dimensions of the capillary columns were 0.32 mm id × 40 cm length and 0.1 or 0.075 mm i.d. × 15 cm length for the couplings with CapLC and NanoLC, respectively. The processed volume was 4 mL for CapLC and 0.5 mL for NanoLC. The elution was carried out with ACN:H_2O (30:70, v/v). IT-SPME-NanoLC has shown a higher performance than IT-SPME-CapLC for the target analytes demonstrating the enhancement of the extraction efficiency with the former configuration. A new phase TEOS-MTEOS-SiO_2NPs has been also proposed for IT-SPME-NanoLC, which improves the retention of polar compounds. Compared with previously published works, improved LODs were achieved (0.025–0.5 μg L^{-1}). The practical application of the proposed procedure has been demonstrated for the analysis of water samples and recovered struvite samples from wastewater treatment plants. Therefore, the proposed procedure can be an alternative method for regulatory purposes.

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1. Introduction

One of the main goals in current analytical chemistry is the miniaturization of analytical systems in order to achieve exhaustive and real information from samples, in as short a time as possible and taking into account environmental issues and cost-effectiveness. An example is the reduction of the inner diameter (i.d) of analytical columns to develop miniaturized LC techniques such as Capillary LC (CapLC) and Nano LC (NanoLC). The i.d.s are typically between 100 and 500 μm and up to 100 μm for CapLC and NanoLC, respectively [1,2].

The flow rates for CapLC are between 1 and 20 μL min^{-1} and less than 1 μL min^{-1} for NanoLC. As a result, consumption of mobile phases are reduced, which is a very positive factor from the perspective of Green Chemistry [3–5]. Moreover, the low flow rate enables a new mechanism of interactions giving rise to an enhancement of the selectivity [5]. In addition, the decrease of the chromatographic dilution results in a signal to noise improvement and a higher sensitivity than that provided by conventional LC (ConvenLC) systems [6].

Sample injection for miniaturized LC techniques can be carried out by using several configurations: direct and column switching for CapLC and NanoLC coupling. In addition, vented column mode can also be used for the coupling with NanoLC. Fig. 1 shows a schematic diagram of the three approaches used for NanoLC (see Table 1). In the first approach, the sample is directly injected onto the precolumn or column via a valve by using low volumes (Fig. 1A). A two-dimensions set-up is used in the vented column mode. Firstly, the sample is loaded in a system with conventional or capillary dimensions by using a pump. After loading, the valve is switched, then the wasted position is closed and the solvent is forced to pass to the analytical column (Fig. 1B). The switching

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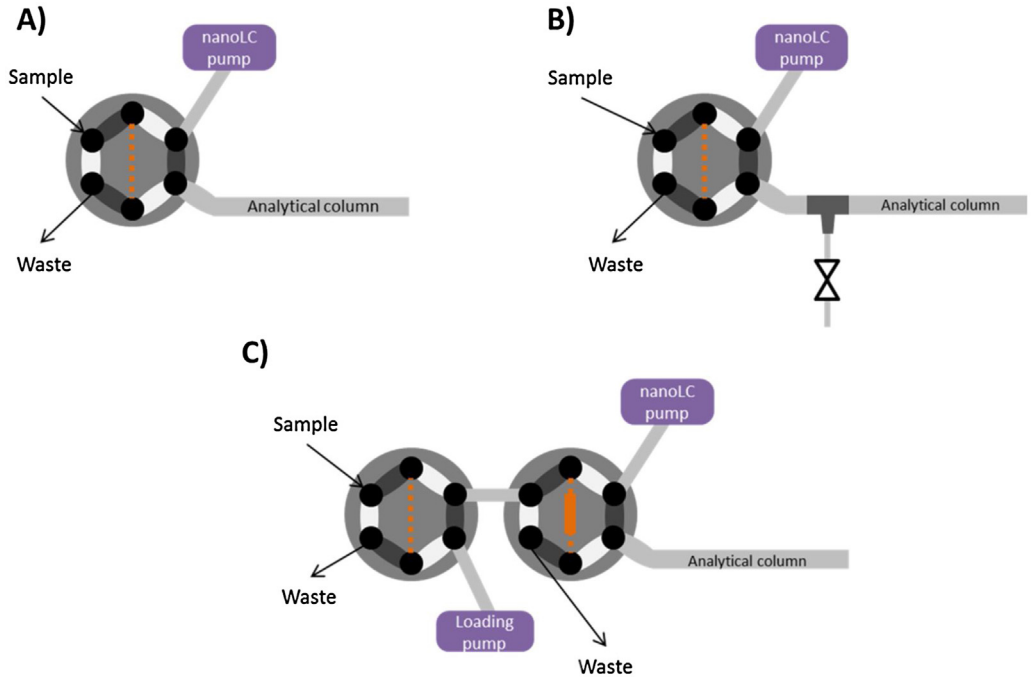

Fig. 1. NanoLC sample injection approaches. A) Direct injection, B) Column switching and C) Vented column mode.

Table 1
Examples of application and characteristics of different proposed NanoLC based procedures. See Fig. 1 for the approaches used for sample injection.

Analyte	Matrix	Analytical column	Sample injection (Volume)	Device	LOD	ref
Emerging pollutants	Benthic invertebrates	C18 75 μm × 15 cm (3 μm)	Switching Autosampler 2 valves; (60 μL)	NanoLC–MS/MS	120–0.1 ng g^{-1}	[8]
Organophosphorus pesticides	Water	C18 100 μm x 43 cm (5 μm)	Switching 1 valve; (50 μL)	NanoLC–MS	9000–20 ng mL^{-1}	[9]
Diclofenac	Water	C18 75 μm x 5 cm (3.5 μm)	Switching 2 valves; (8 μL)	NanoLC-DAD	1 ng mL^{-1}	[10]
Free fatty acids	Mussel	C18 75 μm x 250 cm (3 μm)	Switching 1 valve; (30 nL)	NanoLC-EI-MS	2.25–0.2 ng mL^{-1}	[11]
Pesticides	Food	C18 75 μm x 1 5 cm (3 μm)	Autosampler (5 μL)	NanoLC-DBDI	10 ng mL^{-1}	[12]
Drugs	Urine	C18 50 μm x 150 cm (2 μm)	Autosampler (5 μL)	NanoLC-HRMS/MS	10–100 ng mL^{-1}	[13]
Organophosphorus pesticides	Baby foods	C18 100 μm x 25 cm	Manual sampler (1 μL)	NanoLC-UV/vis	4.4–37.5 ng mL^{-1}	[14]
Peptides	Biological	C18 75 μm x 14 cm (5 μm)	column vent (10 μL)	NanoLC–MS/MS	–	[15]
Peptides	Biological	C18 75 μm x 10 cm (5 μm)	column vent (14 μL)	NanoLC–MS	–	[16]
Triazines and degradation products	Water and struvite	C18 75 μm x 5 cm (3.5 μm)	Direct injection (500 μL)	NanoLC-DAD	500–25 ng L^{-1}	This work

setup consists of a system with two pumps and two valves of six ports or one valve of 10 ports (Fig. 1C). In this system, the sample is injected and concentrated on the trap column using one of the pumps, generally a capillary pump and after turning on the valve, the nanopump elutes the analytes off the trap column and separates them in the analytical column [7]. Examples of these approaches can be seen in Table 1, which also shows the application fields and the limits of detection achieved for different compounds [8–16].

Although the sample dilution ratio for CapLC or NanoLC is lower than that achieved in ConvenLC, sensitivity for some applications is not satisfactory mainly due to the low sample volume used. Moreover, some samples cannot be directly analyzed, requiring a clean-up step [17,18]. To solve these drawbacks, IT-SPME is an attractive technique since this procedure integrates the on-line extraction and pre-concentration [19]. Good sensitivities are achieved although the extraction of the analytes is not exhaustive because the volume or amount of sample processed by IT-SPME is high relative to extracting phase. IT-SPME has shown to be a versatile tool in different application fields [12–15].

The most widely used capillaries for IT-SPME are segments of open capillary columns, generally commercial GC columns. However, the main limitation is the low extraction efficiency achieved with these capillaries. Therefore, most research is focused on the development of new extractive materials improving both, selectivity and extractive capacity. A variety of alternative capillary coatings is needed to improve sensitivity, selectivity, stability and extraction time [18]. The choice of extractive phases mainly depends on the properties of analyte (e.g. polarity, structure, functional groups and charge, between others) [20]. Recently, new extractive phases as sorbent materials for IT-SPME have been prepared in the laboratory by modifying the commercial GC capillary columns with CNTs [21], graphene [22] or Fe_2O_3-NPs [23]. In addition, new phases using different methods as sol-gel [24], liquid phase deposition [25] or electrodeposition [26] have also been proposed.

In this work, a new polar-coated capillary based on tetramethyl orthosilicate (TEOS) and trimethoxymethylsilane (MTEOS) containing SiO_2 nanoparticles (NPs) is obtained. The main advantages of using TEOS-MTEOS in SPME were described: I) homogeneity and porosity of coating, II) a single-steep coating process and III) higher mechanical, thermal and solvent stability due the chemical bonding between the sorbent and support (Si—O—Si) [27]. Its use for

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