Baseline

Development of a solid-phase extraction system modified for preconcentration of emerging contaminants in large sample volumes from rivers of the lagoon system in the city of Rio de Janeiro, Brazil

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ABSTRACT

A single method modified for monitoring of emerging contaminants in river water was developed for large sample volumes. Water samples from rivers of the lagoon system in the city of Rio de Janeiro (Brazil) were analyzed by the SPE-HPLC-MS-TOF analytical method. Acetaminophen was detected in four rivers in the concentration range of 0.09 μg L^{-1} to 0.14 μg L^{-1}. Salicylic acid was also found in the four rivers in the concentration range of 1.65 μg L^{-1} to 4.81 μg L^{-1}. Bisphenol-A was detected in all rivers in the concentration range of 1.37 μg L^{-1} to 39.86 μg L^{-1}. Diclofenac was found in only one river, with concentration of 0.22 μg L^{-1}. The levels of emerging organic pollutants in the water samples of the Jacarepaguá hydrographical basin are significant. The compounds are not routinely monitored and present potential risks to environmental health.

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Emerging contaminants are chemical compounds found in medicines, packaged foods and cleaning products, among others. They are commonly found in environmental samples but are not routinely monitored despite the potential risk to environmental health they pose (Silva and Collins, 2011). Endocrine disruptors, substances that can cause changes in animal and human endocrine systems, are notable emerging contaminants, as well as non-steroidal anti-inflammatory drugs (NSAIDs), which are among the most consumed drugs (Rang et al., 2007). These pollutants are excreted by the body and several studies have reported them in waste and surface water (Patrolecco et al., 2013; Maldaner and Jardim, 2012; Campanha et al., 2014).

The extraction, purification and concentration of environmental samples are among the most important steps when measuring levels of emerging pollutants. Solid-phase extraction (SPE) allows faster analysis with a lower solvent consumption, lower risk of sample contamination and greater reproducibility, making it the most used method for preconcentration of emerging contaminants in water samples (Silva and Collins, 2011; Rang et al., 2007; Patrolecco et al., 2013; Campanha et al., 2014; Zhang and Zhou, 2007; Seifrtová et al., 2009; Bisceglia et al., 2010; Huerta-Fontela et al., 2010; Petrovic et al., 2010; Locatelli et

al., 2011; Wu et al., 2010; López-Serna et al., 2012; Biskarguenaga et al., 2012; Bono-Blay et al., 2012; Robles-Molina et al., 2014; Vulliet et al., 2014).

The conventional system known as SPE vacuum manifold is commercially available and effective for the preconcentration of environmental samples. However, it has some aspects that need improvement due to its cross-contamination risk, the need for continuous sample flow adjustment and process interruptions. The sample routing tubes must be carefully cleaned, and the residual water collected in the containers inside the manifold needs to be discarded from time to time during processing. Contact of the cartridge with the external environment also poses a risk of sample contamination. The analyst must adjust the vacuum and peristaltic pump flows synchronously and continuously. Additionally, this system is not designed to process large sample volumes and has a short lifetime when used in this application.

Some investigators have analyzed emerging contaminants present in large sample volumes using the conventional SPE vacuum manifolds (Biskarguenaga et al., 2012; Bono-Blay et al., 2012; Vulliet et al., 2014; López-Serna et al., 2012). Considering the limitations of the conventional system, Sodré et al. (2010) developed a system for solid-phase extraction of emerging contaminants in natural waters as an alternative to preconcentration of large sample volumes. This system proved to be better than the conventional SPE system used for comparison.

Nevertheless, other modifications can be implemented to facilitate operation, reduce risks of sample contamination, allow more refined adjustment of flow and increase the system's lifetime.

The aim of this study is to present a modified method for SPE extraction of emerging contaminants from large sample volumes. The system was applied for preconcentration of bisphenol-A, acetaminophen, salicylic acid and diclofenac, present in actual samples from four rivers in the state of Rio de Janeiro (Brazil) for further analysis by high-pressure liquid chromatography combined with time-of-flight mass spectrometry (HPLC-MS-TOF).

An automated SPE extraction system (Fig. 1) was designed for the simultaneous preconcentration of two water samples. The sample supply reservoirs are one-liter amber glass bottles, open to facilitate flow. All valves and fittings installed up to the SPE cartridge are made of stainless steel to prevent corrosion and contamination of the samples. The adapters for connecting the feed bottles and the SPE storage and waste cartridges are made of PTFE. The other connections are made of brass and do not contact the analytes. The residual water is collected in a four-liter amber glass bottle. The flexible hose does not make contact with the analytes and is used only to deliver the waste water to the residual bottle. The vacuum system is composed of a centrifugal pump (0.25 hp), which pumps the water to an injector to generate the vacuum. The vacuum system works with an operating pressure of about 13 psi. Since it is hermetically sealed, the system does not allow contact of the SPE cartridges with the outside environment. The operation is continuous even when the vacuum system fails, as the sample elutes through the cartridges by gravity, without the risk of the sorbents drying during processing. The system is designed so that the flow is adjusted only at the beginning of the extraction by means of needle valves, providing flexibility in the treatment of large sample volumes without the presence of an analyst during the entire process. The needle valves assure better sensitivity to adjust the volumetric flow of the sample.

An alternative vacuum system that consists of a vacuum diaphragm pump from Air Dimensions Inc. (PN: M161-BT-AB1), a pressure regulator valve from Swagelok (PN: SS-4CA-3) and a 0–15 psi gauge filled with glycerin from Ashcroft (PN: 50-1008S-02-L-0/15PSI-XGL) can also be used.

Table 1 lists the extraction system components numbered in Fig. 1, as well as their descriptions, quantities and technical specifications.

The glassware and system components were immersed in 5% neutral detergent for 24 h. All waste was mechanically removed using the following washing sequence: potable water (10 times), HPLC-grade acetone (1 time), distilled water (3 times), HPLC-grade ethanol (1 time) and ultrapure water (3 times). The non-volumetric glassware was dried for 1 h at 400 °C. The volumetric glassware and system components were dried at room temperature.

The analytical method used 6-mL Phenomenex Strata-X reverse phase cartridges, which contain 500 mg of sorbents. The cartridges were assembled in an SPE system using PTFE adapters, rods and nuts for fastening. Initially, all the extraction needle valves were kept closed, the pump was turned on and the cartridge was conditioned only after the vacuum pressure was stable. With the system power on, 6 mL of methanol (HPLC-grade), 6 mL of ultrapure water and 6 mL of ultrapure water acidified with HCl PA to pH values of 2 and 3 were added in sequence to the vials. The needle valves were adjusted for the slow conditioning of the cartridges.

After the cartridge conditioning, water samples were added to the system power flasks and the needle valve flow was adjusted to 6 mL/min and 1 s intervals between drops. The theoretical total percolation time for 1 L of sample was approximately 3 h. When the addition of the samples was completed, rinsing was carried out by introducing 10 mL of ultrapure water into each channel and vacuum was maintained for 10 min to ensure the proper drying of the SPE cartridges. The cartridges were then removed from the system and eluted with 8 mL of methanol. The analyte solutions were collected in 12-mL amber vials and dried with ultrapure nitrogen flow. The extract was reconstituted with 1 mL of methanol and stored in a 1.5-mL amber vial at −20 °C in the dark.

The average sample percolation time was 3.0 h and the relative standard deviation was 1.67% for nine extractions. Although some SPE
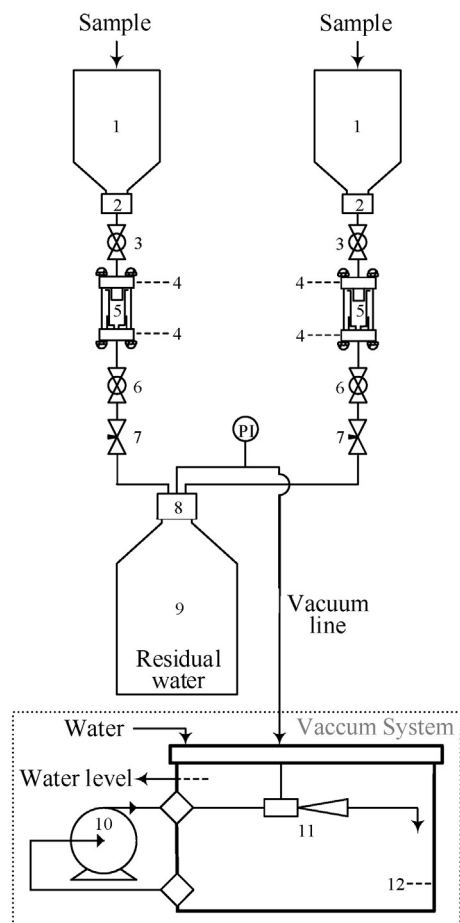

Fig. 1. Extraction system flowchart.

Table 1
Extraction system components.

No.	Description	Quantity	Specification
1	Bottle	2	Amber-1L[a]
2	Bottle adapter	2	PTFE[b]
3	Block valve	2	¼"[c]NPTF[d]–SS[e]
3	Connectors	4	"¼"NPTM[f]-SS
4	Cartridge adapters	4	PTFE
4	Connectors	2	¼"NPTM × ¼"OD[g]-SS
4	Rods and nuts	2	SS
5	Cartridge	2	PP[h]-6 mL[i]
6	Block valve	2	1/4"NPTF–B[j]
6	Connectors	4	¼"NPTM × ¼"OD-B
7	Needle valve	2	¼"OD-B
8	Bottle adapter	1	PTFE
8	Connectors	3	¼"NPTM × ¼"OD-B
9	Residue bottle	1	Amber-4 L
10	Pump	1	Centrifugal-0.5 hp[k]
11	Water ejector	1	PVC[l]
12	Water container	1	Plastic-20 L

[a] L: liter; [b]PTFE: polytetrafluoroesthyrene; [c]: inch; [d]NPTF: National Pipe Thread Female; [e]SS: stainless steel; [f]NPTM: National Pipe Thread Male; [g]OD: tube outside diameter; [h]PP: polypropylene; [i]mL: milliliters; [j]B: brass; [k]hp: horsepower; [l]PVC: polyvinyl chloride.