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Evaluation of strong cation-exchange polymers for the determination of drugs by solid-phase extraction–liquid chromatography–tandem mass spectrometry☆

Núria Fontanals[a,*], Núria Miralles[a], Norhayati Abdullah[b], Arlene Davies[b], Núria Gilart[a], P.A.G. Cormack[b]

[a] Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Campus Sescelades Marcel lí Domingo, s/n, 43007 Tarragona, Spain
[b] WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, Scotland, UK

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ABSTRACT

This paper presents eight distinct strong cation-exchange resins, all of which were derived from precursor resins that had been synthesised using either precipitation polymerisation or non-aqueous dispersion polymerisation. The precursor resins were transformed into the corresponding strong cation-exchange resins by hypercrosslinking followed by polymer analogous reactions, to yield materials with high specific surface areas and strong cation-exchange character. These novel resins were then evaluated as strong cation-exchange (SCX) sorbents in the solid-phase extraction (SPE) of a group of drugs from aqueous samples. Following preliminary experiments, the two best-performing resins were then evaluated in solid-phase extraction–liquid chromatography–tandem mass spectrometry (SPE/LC–MS/MS) to determine a group of drugs from sewage samples. In general, use of these sorbents led to excellent recovery values (75–100%) for most of the target drugs and negligible matrix effects (ME) (<20% ion suppression/enhancement of the analyte signal), when 50 mL and 25 mL of effluent and influent sewage water samples, respectively, were percolated through the resins. Finally, a validated method based on SPE/LC–MS/MS was used to quantify the target drugs present in different sewage samples.

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1. Introduction

In modern society, the numbers of drugs in widespread use is increasing. These drugs can be released into the environment *via* sewage systems or incorrect disposal methods. Although these waters pass through sewage treatment plants (STP), these drugs are often not removed completely by the treatments processes. As a result, they are often found in surface and wastewaters at ng/L levels [1,2]. In view of this, new analytical techniques should be developed. These analytical techniques include sample preparation followed by liquid chromatography coupled with mass spectrometry (LC–MS) or tandem mass spectrometry (LC–MS/MS), to enable the determination of these drugs at the required low concentration levels [3–5].

Sample preparation must enrich the analytes, and should reduce the matrix effect (ME) on subsequent LC–MS analysis to obtain reliable and repeatable results. For liquid samples, some green solvent-extraction techniques have been developed [6]; regarding to sorptive-extraction techniques, solid-phase extraction (SPE) is usually the technique of choice [7] because of its versatility arising from the ready availability of different sorbent types. In recent years, research into SPE sorbents has focused on improving capacity (enhancing the preconcentration factor) and selectivity (improving the clean-up effectiveness) within a single material, leading to the emergence of what are known as mixed-mode polymeric sorbents. These sorbents combine a polymeric skeleton with ionic groups, with two types of interactions available: reversed-phase (RP) (from the skeleton) and ion-exchange (from the ionic groups). Mixed-mode sorbents are classified depending on whether the ionic group attached to the resin is cationic or anionic, but also whether the ionic group is strong or weak. The most common of these ionic groups are sulfonic acids and carboxylic acids for strong

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* Corresponding author. Tel.: +34 977 55 86 29; fax: +34 977 55 84 46.
E-mail address: nuria.fontanals@urv.cat (N. Fontanals).

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and weak-cation exchange sorbents, respectively; and quaternary amines for strong anion-exchange, and tertiary, secondary and primary amines for weak anion-exchange. A benefit of mixed-mode sorbents is that the ion-exchange interaction between the sorbent and the analytes and/or interferences is turned on and off by the careful control of the pH of the washing and elution solvents, resulting in the selective protonation or deprotonation of the analytes or interferences, and even the sorbent (in the case of weak ion-exchange sorbents). Thus, the interferences and analytes can be eluted separately during the washing and elution steps, respectively, as a consequence of the careful, rational selection of pH and the solvent in each SPE step [8].

At present, mixed-mode sorbents are one of the main focuses of research for manufacturers and companies. One of the reasons for this is, generally, the need for cleaner extracts from SPE and, in particular, avoidance of ion-suppression/enhancement when these extracts are injected into LC–MS or LC–MS/MS systems [4,9–11]. Therefore, despite being relatively new, they have been applied in various fields to extract different types of analytes in a selective manner from the matrix interference usually present in complex samples, such as those of biological, foodstuff and environmental origin [8,9]; thus, it is a constant evolving field.

In recent years, several SPE sorbent companies have launched strong or weak cation-exchange (SCX or WCX, respectively), and strong or weak anion-exchange (SAX or WAX, respectively) variants of such well-known sorbent precursors, including Oasis (Waters), Strata (Phenomenex), Bond Elut Plexa (Agilent Technologies), and Evolute (Biotage), among others. These commercially available mixed-mode sorbents are characterised by their macroreticular structures, specific surface areas from 600 to 800 m^2/g, mean particle diameters from 50 to 100 μm and, in some cases, a degree of hydrophilicity [8].

To improve the features of the mixed-mode sorbents available in the market, our research group has been working on improving the morphological properties (by exploiting hypercrosslinked polymer microspheres pioneered by Davankov in the 1970s [12,13]) and the introduction of ionic moieties, so that they can exhibit higher levels of RP and ionic interactions with the analytes. So far, we have prepared and evaluated, *via* SPE, hypercrosslinked polymer microspheres modified with 1,2-diethylamine and piperazine moieties, dimethylbutylamine and carboxylic acid moieties to impart WAX, SAX and WCX character onto the sorbents. The results obtained with these resins were promising and better than those from commercial available sorbents [8]. These suitable results were attributed to the enhanced structural properties of these mixed-mode sorbents.

In view of this, we present eight different in-house prepared SCX materials. These materials differ in terms of their morphological properties and ion-exchange capacity, which are attributed to the different synthetic approaches used during their preparation. We have evaluated these different SCX materials in the following terms: capacity to enrich target analytes and effectiveness in cleaning-up the interferences in the matrix samples; ability to reduce the ME encountered when analytes are determined by LC–MS/MS from complex environmental samples.

2. Experimental part

2.1. Materials

The reagents used for the polymer synthesis were *para*-vinylbenzyl chloride (VBC) (95% grade), divinylbenzene (DVB) (80% grade), styrene (St) (99% grade), ethylene glycol dimethacrylate (EGDMA) (98% grade), poly(*N*-vinylpyrrolidone) (PVP) 55 ($M_W \sim 55{,}000$) and Triton X-305, all supplied by Sigma-Aldrich (Steinheim, Germany). The monomers were purified by passing them through a short column of neutral alumina. 2,2′-Azo*bis*(isobutyronitrile) (AIBN), supplied by BDH (Poole, U.K.) was recrystallised from acetone at low temperature. Anhydrous 1,2-dichloroethane (DCE), iron(III) chloride, chlorosulfonic acid, lauric acid and tetraethyl ammonium bromide (TEABr) (or sodium chloride—NaCl) were supplied by Sigma-Aldrich; all were of high purity as supplied and not purified further prior to use.

The additional reagents used in the preparation of the HXLNAD-SCX sorbents were 1,2-dichloroethane (DCE) (99.8% grade) and concentrated sulfuric acid (95–97%), both supplied by Sigma-Aldrich, and distilled water. All reagents were used as received.

We selected some therapeutic drugs with basic and acidic groups to evaluate the performance of the different sorbents. They included: trimethoprim, caffeine, antipyrine, atenolol, ranitidine, metoprolol, propranolol, carbamazepine, clofibric acid, salicylic acid, ibuprofen and diclofenac. They were obtained from Sigma-Aldrich. Standard stock solutions of each analyte were prepared at 1000 mg/L in methanol (MeOH). We also selected the following illicit drugs: morphine, cocaine, methadone and codeine, and their metabolites, 6-acetylmorphine, benzoylecgonine, 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP) and dihydrocodeine, respectively. They were purchased from Cerilliant (Round Rock, TX, USA) as solutions in MeOH at a concentration of 1000 mg/L. A mixed solution of all analytes in MeOH at 50 mg/L was prepared weekly. All standard solutions were stored at −20 °C. Working solutions were prepared daily by an appropriate dilution of the mixed solution with ultrapure water, which was obtained from a water purification system (Veolia, Sant Cugat del Vallès, Spain). Table 1 presents the pK_a values of these analytes.

Acetonitrile (ACN) and MeOH were of HPLC grade and from Prolabo (Llinars del Vallès, Spain). Nitrogen (N_2) was supplied by Carburos Metálicos (Tarragona, Spain). Hydrochloric acid (HCl) (37%), formic acid (HCOOH) (≥95%), ammonium hydroxide solution (NH_4OH) (28%) and sodium hydroxide (NaOH) (≥98%) were purchased from Sigma-Aldrich.

2.2. Resin synthesis

Two type of polymerisations, namely non-aqueous dispersion polymerisation (NAD) and precipitation polymerisation (PP) were adopted to prepare the precursor particles [14].

For NAD polymerisations, PVP-55 (6% w/w), Triton X-305 (2% w/w), AIBN (2–6% w/w), styrene (50–90% w/w) (all the percentages are relative to the total mass of monomer in the monomer feed), half of the VBC and 47.5 mL of ethanol were added into a 500 mL five-necked, round-bottomed flask fitted with an overhead stirrer, condenser and nitrogen inlet. Once a homogenous solution had formed at room temperature, the solution was bubbled with nitrogen gas at room temperature for 30 min. The flask was then placed into an oil bath set at 70 °C, and stirred mechanically using a four-bladed PTFE stirrer at 160 rpm. EGDMA (1% w/w relative to total mass of monomer in the feed) and the second half of the VBC was dissolved in a second portion of ethanol (47.5 mL) at 70 °C under nitrogen. One hour after the start of the polymerisation, the hot solution containing EGDMA and VBC was added dropwise into the reaction vessel. The reaction was continued for a further 24 h under constant agitation. The particles that were obtained were centrifuged for 10 min at 3000 rpm and then washed 2 times in ethanol and 2 times in methanol (the particles were suspended in the appropriate wash solvent and centrifuged between each washing step). The particles were filtered using vacuum filtration on a 0.2 μm nylon membrane filter and dried overnight *in vacuo* at 40 °C.

For the PP polymerisations, the comonomers (75% (w/w) VBC and 25% (w/w) DVB) (2% w/v total monomer in feed relative to solvent) and AIBN (2 mol% relative to polymerisable double

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