Green sample preparation methods in the environmental monitoring of aquatic organic pollutants

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Abstract

Sample preparation in analytical chemistry can have considerable environmental impacts. This paper highlights sampling and sample preparation methods relating to organic pollutants in water, which have been published over the last two years (2019-current) and aim to address green chemistry concerns such as solvent and reagent use and energy consumption. Samplers which combine analyte pre-concentration with sampling are advantageous, whilst microextraction techniques continue to receive extensive research interest. These include solid phase microextraction, micro-solid phase extraction, dispersive liquid-liquid microextraction, single drop extraction, stir bar sorptive extraction and QuEChERS. Developments have focussed on the synthesis of novel sorptive materials for extraction applications and on alternative extraction setups. The provision of analytical methods which are facile, effective and green continue to pose challenges and will require future innovations to be fully realised.

Keywords: organic pollutant; water pollutant; solid phase microextraction; micro-solid phase extraction; sample preparation; green analytical chemistry

1. Introduction

The monitoring of environmental pollutants is critical in determining sources thereof, as well as in managing and mitigating potential environment and human health impacts. In performing such monitoring, it is important that green analytical chemistry considerations be carefully employed, in order to ensure that monitoring itself does not incur unnecessary environmental impacts. Green chemistry principles should thus be employed in all aspects of analysis of environmental pollutants, from sampling, through sample preparation to the analysis itself. These principles, as they relate to sampling and sample preparation of aqueous organic pollutants, are summarised in Fig. 1 and include chemical usage (particularly that of solvents) and energy use arising from both transportation of samples and extraction processes.

Advances since 2019 in the sampling and sample preparation of organic environmental pollutants in water matrices are reviewed here, with respect to approaches which have the potential to improve the environmental friendliness of the resulting methods as compared to current alternatives. It should be noted that trade-offs may be incurred in the development of novel approaches to

environmental monitoring, in that not all green chemistry aspects and analytical figures of merit, such as selectivity and sensitivity, may be simultaneously optimised. The relevant advantages and disadvantages of the proposed methods are therefore highlighted to guide potential future research directions.
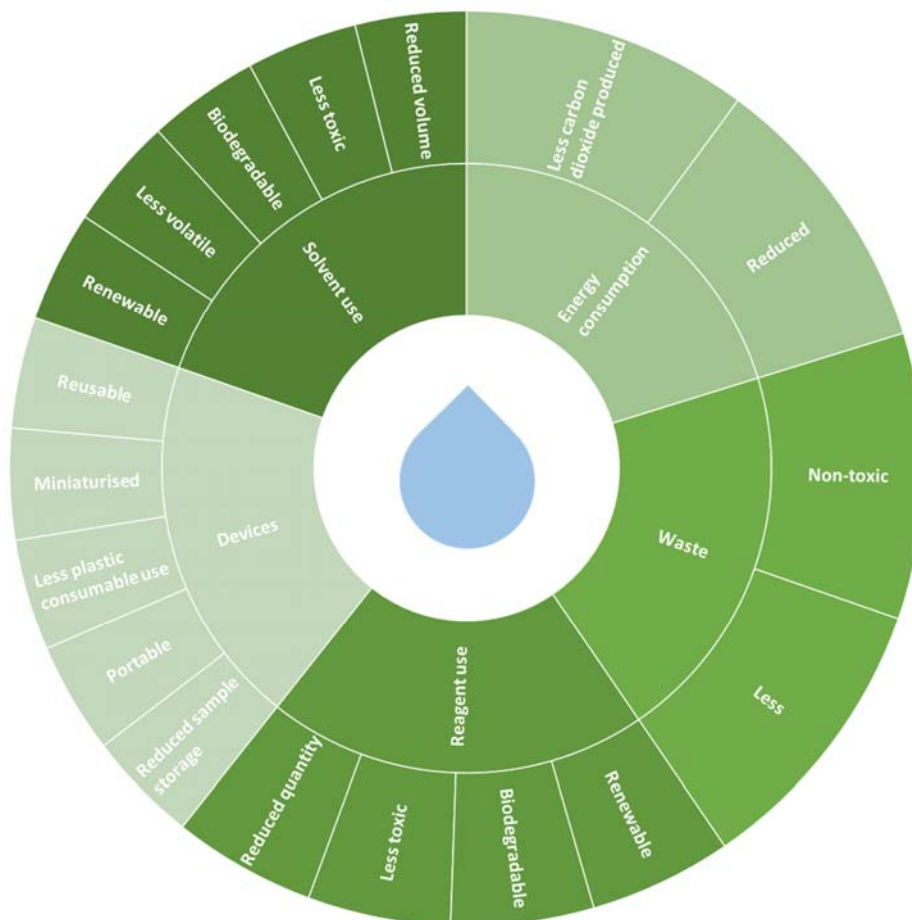

Figure 1: Primary green analytical chemistry considerations in the sampling and extraction of aqueous organic pollutants.

2. Sampling

Green sampling strategies avoid the use of energy in sampling itself, as well as in the transport of samples to the laboratory for analysis. A number of sampling devices have been recently devised which combine sampling and extraction and these are discussed in this section.

Passive samplers for aquatic organic pollutants have numerous green chemistry benefits, including the avoidance of transportation of large sample volumes and energy usage in sampling. Detailed reviews on the use of passive sampling in this context are available [1]. The development of alternative passive sampling configurations continues to receive research interest, such as the coating of stainless steel bolts with hydrophilic-lipophilic balanced (HLB) particles and polyacrylonitrile (PAN) in a type of solid phase microextraction [2]. The bolts formed a component of a robust polytetrafluoroethylene (PTFE) passive sampler (Fig. 2) for organic pollutants in water, and

eliminated the need to transport large sample volumes. A 75 min vortex extraction with 800 µL of acetonitrile/water desorption solvent was, however, required for each bolt.
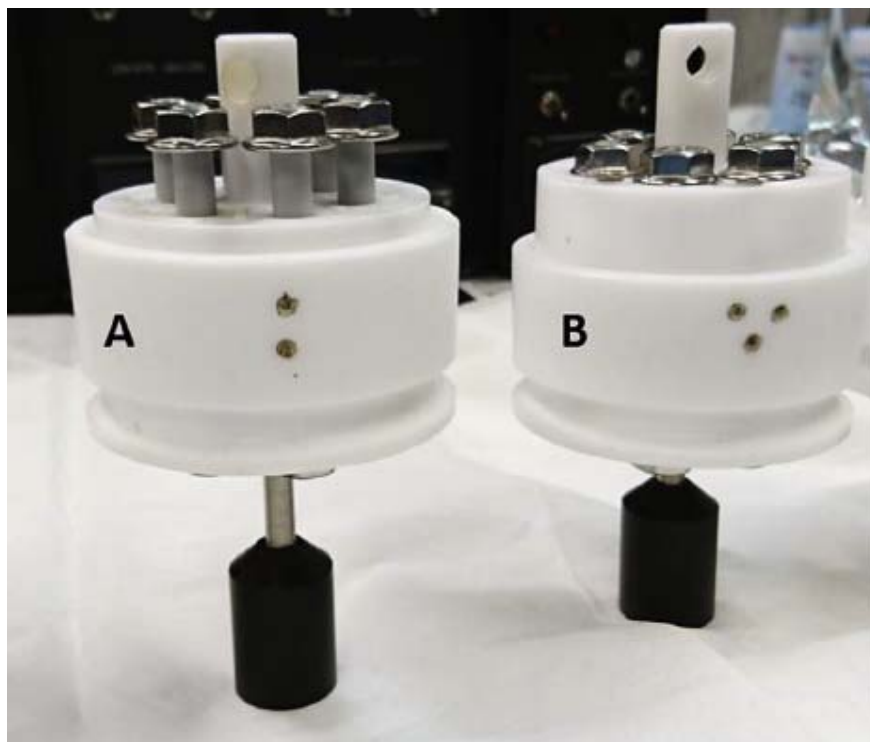

Figure 2: A coated bolt passive sampler in A) sampling and B) sealed position [Reprinted from *Environ. Pollut*, 252, J.J. Grandy, M. Lashgari, H. Vander Heide, J. Poole, J. Pawliszyn, Introducing a mechanically robust SPME sampler for the on-site sampling and extraction of a wide range of untargeted pollutants in environmental waters, pp. 825-834 (ref 2), Copyright 2019, with permission from Elsevier].

A passive sampler, based on hollow fibre liquid phase microextraction (HF-LPME) using ethyl decanoate acceptor solvent, has been developed for pesticides in water [3]. Simple, recyclable and cost effective materials were employed in the device, where the liquid phase microextraction system was housed in a perforated polyethylene terephthalate (PET) bottle. The acceptor solvent was injected directly into a GC-MS for analysis, avoiding additional solvent extraction, pre-concentration and cleanup steps, with their associated environmental impacts.

A membrane passive sampler using hydrophilic-lipophilic balance sorbent embedded in a cellulose acetate membrane was tested to provide for the simultaneous sampling of both hydrophilic and hydrophobic organic aqueous pollutants [4]. This can reduce the sample volume required and sample preparation steps for more comprehensive analyses. Another passive sampler for organic aquatic pollutants (namely triclocarban, triclosan and methyl triclosan in river water) has been developed which utilises a cyclodextrin polymer membrane as the binding phase in a diffusive gradient in thin film (DGT) sampler [5]. Although cyclodextrin may be considered green and eco-friendly, the synthesis of the cyclodextrin polymer, which was necessary as cyclodextrin is water soluble, requires the use of hazardous chemicals as solvents, grafting agents and catalysts (including dimethylformamide and hexamethylene diisocynate). A mesoporous imprinted polymer based DGT

passive sampler was manufactured for the sampling and pre-concentration of the flame retardant tetrabromobisphenol A in water [6]. Although this approach has the green chemistry advantages associated with passive sampling, the use of the target analyte in the imprinting process requires careful waste management, and solvent extraction of the device was required prior to HPLC analysis.

A method for the analysis of volatile organic compounds (VOCs) in water, specifically benzene, toluene, ethylbenzene and xylenes (BTEX), has been described which is based on the adsorption of analytes into a polydimethylsiloxane/divinylbenzene (PDMS/DVB) coating on the inner walls of a sample bottle [7]. The approach holds promising green chemistry advantages as the analytes are thermally desorbed from the bottle for analysis by a portable GC-MS, negating the need for solvent extraction and sample transportation.

The provision of power for active water sampling is a challenge both in terms of green chemistry approaches as well as logistics. Lin et al. [8] overcame this by employing an osmotic pump to actively sample herbicides in surface water onto commercial solid phase extraction sorbents. The authors employed ion exchange resins in the inlet chamber of the osmotic pump to remove sodium and chloride ions and thereby allow for smooth and constant sampling flow.

3. Sample preparation

In terms of green analytical methods for the preparation of environmental samples for analysis, much emphasis continues to be placed on reducing the use of solvents as well as reducing the sample volume required, which in turn has a positive impact on reduced energy requirements for sample transportation. Therefore research has proceeded towards the development of alternative microextraction sorbents and configurations, which enhance organic analyte extraction and reduce matrix interferences, but uphold green chemistry principles. In addition, there has been an ongoing focus on the development of alternative solvents which are biodegradable and less toxic than conventional solvents which are also highly volatile and flammable [9]. A comprehensive review of the history and development of green extraction techniques in green analytical chemistry was published in 2019 [10] as well as a review on green sample preparation strategies for environmental samples [11], which covered both inorganic and organic analytes. In this section recent progress in this field focusing on organic pollutants in water is reviewed.

3.1 Solid phase microextraction

Solid phase microextraction (SPME) can be considered a green approach to sample preparation, as solvent back extraction of analytes may not be required and sample volumes are typically small, therefore promising novel SPME sorbents and configurations are relevant from a green chemistry perspective.

An approach to using bare (uncoated) polypropylene hollow fibres for SPME of estrogens from water samples has been tested with high performance liquid chromatographic analysis (HPLC) [12]. Although this method removes the need for additional sorbent coatings and thus has green chemistry benefits, the reduced capacity and retention of the fibres resulted in the need for the use of three long (30 cm) fibre portions per 60 mL sample.

Novel SPME fibres have been developed based on alternative polymers which extract target organic pollutants from samples more efficiently. A recent example is co-polymerised styrene and poly(ethylene glycol) diacrylate on quartz fibres for the detection of pharmaceuticals in water, which provided extraction efficiencies up to 278 times that of PDMS fibres [13]. Unfortunately, the method required solvent extraction of the disposable fibres, although the volume was small (150 μL of methanol with shaking for 1 hour).

Indeed, the development of alternative sorbents for the SPME of organic pollutants from environmental samples continues to receive research attention. Many of these studies aim to reduce the costs or complexities of methods and to improve extraction efficiencies, selectivity and reusability. Recent reviews on research in this regard have been published which focus on nanomaterials as SPME sorbents, primarily for organic pollutants in water samples [14, 15]. Nanomaterials (NMs) have been primarily employed as a high surface area SPME fibre coating (after suitable immobilization) or in dispersive SPME approaches. Thermal, mechanical and chemical stability, and catalytic activity of these materials may be of concern in use, which may lead to adduct formation and loss of analytes. From a green chemistry perspective, concerns regarding the use of NMs are primarily the use of toxic chemicals in the synthesis thereof and/or in the final product, as well as reuse potential. The development of more environmentally friendly synthetic routes and final products which can be reused should thus be focused on going forward.

Deep eutectic solvents (DESs) are generally biodegradable and of low toxicity, therefore a green approach based on a hydrophobic ethylparaben and methyl trioctyl ammonium chloride DES sol-gel coated PDMS SPME fibre was developed for headspace sampling of toluene, ethylbenzene and o-xylene in water in order to enhance extraction efficiency [16].

The synthesis of metal-organic framework (MOF) based SPME fibres for environmental monitoring applications has been attempted to enhance selectivity due to their tunable uniform nanoscale cavities, mechanical stability and high adsorption affinities. Suwannakot et al. [17] tested four water-resistant MOFs which were grown *in situ* on stainless steel needles pre-coated with poly(dopamine) adhesive as a means to pre-concentrate perfluorooctanoic acid (PFOA) from water samples (Fig. 3). In this case, sand paper was used to scratch the surface of the needles before coating, which is a greener approach to using HF. In addition, small sample volumes (5 mL) were required and mild agitation was employed over the 3 min extraction period. The probe was desorbed in <10 μL of methanol which was then nanoelectrosprayed directly into a mass spectrometer for PFOA detection at low ng L^{-1} levels. Disadvantages are that the prepared probes are for single use and have to be stored under vacuum to maintain their adsorption capacity.
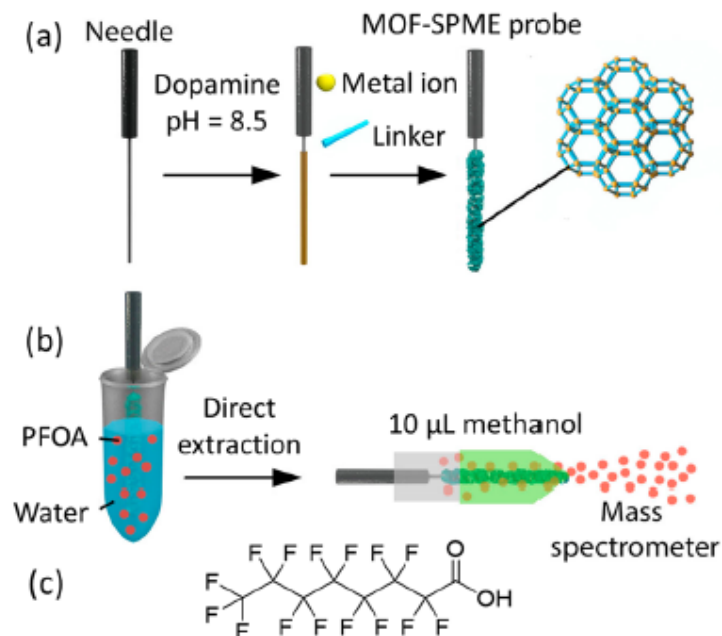
Figure 3: MOF-coated probes for SPME of PFOA in water. (a) Preparation of the probe via *in situ* MOF growth onto a dopamine coated needle. (b) Analyte pre-concentration by MOF-SPME followed by desorption in methanol in a nanoelectrospray emitter before analysis by mass spectrometry. (c) A linear PFOA molecule [Reprinted with permission from P. Suwannakot, et al., Metal-Organic Framework-Enhanced Solid-Phase Microextraction Mass Spectrometry for the Direct and Rapid Detection of Perfluorooctanoic Acid in Environmental Water Samples, *Anal. Chem*. 92 (2020) 6900-6908 (ref 17). Copyright 2020 American Chemical Society].

A MOF coated copper wire has been used for the SPME of PAHs from water, whereby the copper wire served as a substrate as well as a source of copper for the MOF membrane growth in aqueous solution [18], which is seen as an environmentally-friendly synthesis strategy. The extraction device was found to be durable, allowing for more than 150 repeat extractions and was efficient due to π-π interactions between the PAHs and the MOF. A zinc mixed-ligand microporous MOF was subsequently reported for SPME of PAHs in water [19], which had good thermal stability and was used more than 200 times with no appreciable loss in extraction efficiency. Kong et al. [20] found that a solvothermal method performed best (in terms of thermal stability, extraction capacity and lifetime) for the synthesis of a MOF zeolite imidazolate framework. The product was coated onto a stainless steel wire for SPME use in PAH and nitro-PAH determinations in environmental water samples. Green chemistry drawbacks of the technique include the use of DMF in MOF synthesis and HF in etching of the stainless steel wire prior to coating.

Covalent organic frameworks (COFs), which are porous crystalline materials, are also receiving research attention for use as a SPME sorbent phase. Wen et al. [21], for example, used a β-ketoenamine-linked COF coating to extract synthetic musks from water samples, which was efficient due to strong π-π interactions between the target analytes and the hydrophobic sorbent. The same COF has been applied to SPME of polybrominated diphenyl ethers [22], whilst a porous monolith-based adsorbent for the SPME of sulphonamides from water was prepared from 4-vinylbenzoic acid and 4-vinylphenylboronic acid monomers copolymerised with divinylbenzene [23]. Although SPME is

considered a green extraction technique, the use of silicone glue, strong acids (HCl and HF) and solvents in the synthetic procedures of coated fibres are potential drawbacks in this regard.

A number of studies have employed carbonisation of biomass to produce carbon SPME adsorbent fibre coatings for organic aquatic pollutants such as silk fibres and peanut shells for aqueous PAH extraction [24, 25]. Although carbon may be considered more environmentally friendly than some other sorbent materials, particularly when the biomass source employs waste material, it has to be remembered that energy is used in carbonising the materials and often solvent washing steps (and in some cases also HF) are employed in cleaning the material produced prior to use.

A recent study combined fluorescence sensing with SPME as a means for novel sample pre-treatment [26]. The target analyte, 2-nitroaniline in environmental water samples, caused fluorescence quenching of N-doped carbon dots (CDs) immobilised on a SPME fibre using PDMS. This qualitative visual screening procedure reduced the number of samples requiring GC-MS analyses, thereby reducing environmental impact. The environmental safety of the reusable device was verified by *in vivo* tests with *Daphnia magna*.

The SPME Arrow is an adapted SPME method, which may provide lower detection limits due to the larger volume of sorbent phase employed, as well as enhanced reusability and lifetime due to the more robust design of the extraction device. Direct immersion of a SPME Arrow (DVB/CWR/PDMS) in water followed by GC-MS analysis, for example, was found to be between 6 and 65 times more sensitive than classical SPME in the determination of selected pesticides [27].

In-tube SPME (IT-SPME) is considered a green sample preparation technique which combines miniaturisation, low solvent use and on-line analysis. IT-SPME utilising polymeric coated capillaries reinforced with metal oxide nanoparticles (TiO_2 and CuO) coupled to nano-liquid chromatography (nanoLC) with UV diode array detection (DAD), has been used for the monitoring of tribenuron methyl in environmental waters [28]. The extractive capillaries were inserted into the nanoLC system, allowing for transfer of extracted analytes into the chromatographic column for separation and detection. It was shown to have the added benefit of preventing hydrolysis and degradation of this analyte, which typically occurred during sample preparation, as the IT-SPME method allowed for direct analysis of the samples after filtration with no organic solvent and buffers required.

3.2 Solid phase extraction

Similar novel sorbents to those discussed with respect to SPME have been developed for solid phase extraction (SPE) applications. A review of novel materials which have been synthesised specifically for dSPE, d-μ-SPE and magnetic SPE (MSPE) of PAHs from environmental water samples has been recently published [29]. A recent study reported the development of a pipette tip based μ-SPE method employing graphene nanosheets (10 mg) for triclosan in water [30]. The method was semi-automated by using an auto-syringe infusion pump. The adsorbent material could be reused 20 times and 1 mL of acetone was used to desorb the analytes.

A dispersive micro-solid phase extraction (d-μ-SPE) approach has been tested for polycyclic aromatic compounds (PAHs, quinones and nitro-PAHs) in fresh and marine water [31]. A customised glass device was used for extractions with C_{18} sorbent where dispersion thereof in the sample was

achieved by vortexing. The filtration of the sorbent and desorption with *n*-hexane was performed in a microextraction unit with direct injection into a GC-MS for analysis. No cleanup or fractionation steps were required and a relatively small amount (100 mg) of sorbent was used, which are positive green chemistry considerations of the proposed method.

Magnetic SPE (MSPE) sorbents eliminate the need for packing into a column configuration, as the sorbent can be separated from the sample by means of a magnet avoiding the use of an energy source; and the sorbent may be recycled. Li et al. [32] employed this approach in the synthesis of a magnetic polyethyleneimine functionalised reduced graphene oxide sorbent to extract polar non-steroidal anti-inflammatory drugs from tap water, river water and groundwater. After magnetic separation, the analytes were desorbed from the particles by means of vortexing with methanol for analysis by HPLC-DAD. The sorbent could be reused for up to ten cycles.

Fluorine and nitrogen functionalised magnetic graphene has similarly been employed for the MSPE of perfluoroalkyl and polyfluoroalkyl substances in environmental water samples. HPLC-Orbitrap HRMS analysis was performed after back extraction of the sorbent (which could be reused up to five times) with methanol/water followed by reconstitution with acetonitrile [33].

3.3 Liquid-liquid extraction

Recent developments in microextraction techniques of organic analytes from water samples which are based on liquid-liquid extractions, such as dispersive liquid-liquid microextraction (DLLME), have included the synthesis of novel deep eutectic solvents (DESs) for this application (DES-DLLME), as reviewed by Lu, Liu and Wu [34]. Avoidance of the need for additional chemical additives, such as disperser solvents, and the use of eco-friendly solvents (specifically DESs which are biodegradable and of low toxicity), are beneficial from an environmental perspective regarding these methods which employ low solvent volumes. A vortex-assisted DES-DLLME approach has been applied to the extraction of growth regulating auxin compounds in water, for example [35], where the hydrophobic DES was comprised of isoamyl alcohol and trioctylmethylammonium chloride. Extraction in 200 μL of DES and 200 μL of methanol took place in 1 min, and after 3 min phase separation by centrifugation, the DES phase was diluted with isopropanol prior to analysis by HPLC with UV detection.

A novel low density DES was prepared by mixing trihexyl(tetradecyl)phosphonium chloride and decanol (molar ratio of 1:2) which was dispersed in aqueous samples by means of ultrasound. After centrifugation to separate the phases, the aqueous phase was solidified by freezing, whilst the DES extractant was diluted with methanol prior to analysis for target aromatic amines by HPLC-UV [36]. A slightly different approach to using DES-DLLME was reported, where the floating DES organic droplet was frozen after extraction of endocrine disrupting compounds from water [37]. A ternary DES was synthesised by combining fatty acids, which served as the hydrogen bond acceptors and donors. The sample and DES mixture was repeatedly aspirated and injected using a syringe to enhance mixing and extraction, and after separation the extract was diluted with acetonitrile prior to HPLC-PDA analysis. The authors compared their proposed method to a number of others and reported that it was environmentally friendly.

Sample enrichment with respect to steroids in water was tested by the same authors using 2-dodecanol as extractant and a DES (tetrabutylammonium bromide: acetic acid) as the dispersive

solvent, which included solidification of the floating organic droplet upon cooling (DES-DLLME-SFOD) which was subsequently analysed by HPLC-DAD [38]. The method was evaluated to be an eco-friendly alternative to conventional organic dispersers by means of the Analytical Eco-Scale and the Green Analytical Procedure Index.

3.4 Single drop microextraction

Single drop microextraction (SDME) provides a means of enriching sample analytes using a very small volume of extraction solvent. Recent research in this regard has included the development of methods which utilise a DES as a more environmentally friendly extraction solvent, such as head space-SDME of PAHs from water samples, prior to GC-MS analysis [39]. Back-extraction of the analytes (extracted into a 15 µL microdroplet) into 10 µL of *n*-hexane was, however, required prior to analysis as the low volatility and high viscosity of DESs (in this case prepared from choline chloride and oxalic acid) make them poorly compatible with GC.

3.5 Stir bar sorptive extraction

Ice concentration linked with extractive stirrer bars (ICECLES, Fig. 4) was compared to stir bar sorptive extraction (SBSE) and SPME for pesticides in drinking water, and was found to provide improved extraction efficiency, as noted by enhanced thermal desorption-GC-MS (TD-GC-MS) or LC-MS/MS peak areas after back extraction [40]. This approach is green in the sense that no organic solvent is required if TD-GC-MS is employed or small amounts (500 µL of methanol) if back extraction is required, and thus minimal organic solvent waste is generated, although energy is required to pump the coolant through the system and for TD (which may also require liquid nitrogen to focus desorbed analytes).
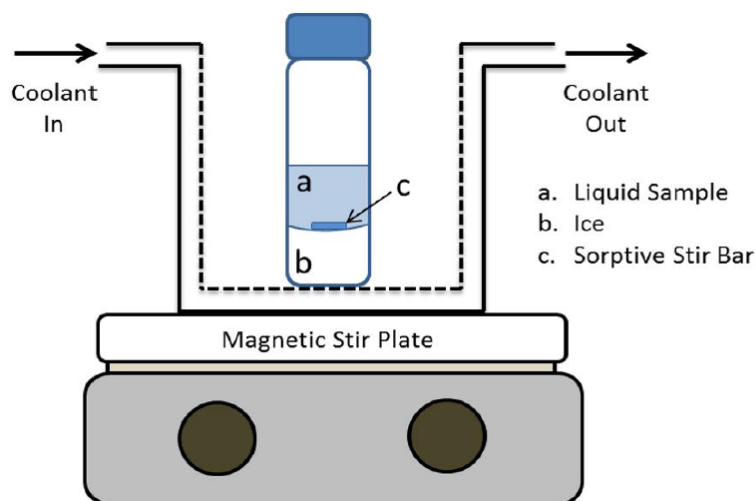

Figure 4: The ICECLES experimental setup, showing the flow of coolant through a double-glass beaker allowing for freezing of the aqueous sample from the bottom to the top whilst analytes are extracted into the spinning stir bar [Reprinted from *J. Chromatogr. A*., 1622, C.S. Skaggs, A.H. Alluhayb, B.A. Logue, Comparison of the extraction efficiency of ice concentration linked with extractive stirrer, stir bar sorptive extraction, and solid-phase microextraction for pesticides from drinking water, 461102 (ref 40). Copyright 2020, with permission from Elsevier].

Carboxyl functionalised microporous organic networks have been investigated as coating material of stir bars for extraction of phenylurea herbicides from water samples [41]. Although the coating was shown to be an effective and reusable adsorbent for these analytes, reagent use in synthesis and back extraction into acetonitrile prior to analysis need to be borne in mind when considering the potential environmental impacts of the method. Electrospun polyacrylonitrile (PAN) has been tested as a stir bar coating in SBME for the extraction of low molecular weight PAHs from water, where the coating could be reused 200 times [42]. Here DMF and acetone were, however, used in coating synthesis and analyte back extraction, respectively.

3.6 Quick Easy Cheap Efficient Rugged and Safe (QuEChERS)

The Quick Easy Cheap Efficient Rugged and Safe (QuEChERS) approach to sample preparation reduces solvent use, although it does typically employ a considerable amount of disposable plastic laboratory ware. QuEChERS has been employed with switchable solvent liquid phase extraction (SS-LPME) to pre-concentrate the pesticide fenazaquin from water samples prior to GC-MS analysis [43]. Carbon dioxide was added to protonate the N,N-dimethylbenzylamine solvent to make it water soluble and then later removed to switch it back to a low polarity, water immiscible solvent. The sample volume was 8 mL and 0.50 mL of the switchable solvent was used in this approach.

QuEChERS has also been used to determine estrogens in aquaculture influent water, whereby a 500-fold concentration factor (initial sample volume of 20 mL and final extract volume of 40 µL) was required to allow for quantitation at ng L^{-1} levels by HPLC-MS [44]. Steps involving evaporation to dryness have energy consumption disadvantages, however the method avoided filtration with associated analyte losses which is needed for SPE of this matrix.

4   Conclusions

It should be borne in mind that developments in sampling and analyte pre-concentration which employ green chemistry principles may be complemented by analytical techniques which are environmentally friendly, such nano liquid chromatographic (nanoLC) and ultra high performance liquid chromatographic (UHPLC) systems which require both lower mobile phase and sample volumes. Advances in instrumental systems, such as accurate mass detectors, advanced chromatographic systems and deconvolution software, provide selectivity and sensitivity, decreasing the need for extensive sample preparation steps and thereby reducing environmental impact. Indeed, the use of multivariate calibration and mathematical treatment of fluorescence spectra of pesticide contaminated water samples has shown promise as an environmentally friendly alternative to chromatography-mass spectrometry based methods [45]. Microfluidic paper-based analytical devices (refer to reviews [46] and [47]), lab on a chip [48] and smart phone [49] analytical platforms also hold promise for determining levels of organic environmental pollutants in water in a greener manner, although selectivity and sensitivity remain challenges.

It is clear that there have been a number of recent developments in the sampling, extraction and pre-concentration methods for organic pollutants in water, which have the potential to reduce the environmental impacts of such analyses. However, the impacts of synthesising extraction media and the reuse potential thereof continue to pose challenges in the realisation of green analytical chemistry methods.

Declaration of interest: None

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