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Review

Ion-pair solid-phase extraction

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Abstract

Solid-phase extraction (SPE) is a technique widely employed by analytical chemists. SPE cartridges are available in a wide variety of formats containing media with diverse chemistries. This paper will review ion-pair SPE, one of the less frequently applied, and presumably less well-known techniques. Advantages of this technique over more conventional reversed-phase or ion-exchange SPE include selectivity, compatibility with rapid evaporative concentration, and potential application to multiclass multiresidue analysis. © 2000 Published by Elsevier Science B.V.

Keywords: Reviews; Ion-pair solid-phase extraction; solid-phase extraction

Contents

1. Introduction

Solid-phase extraction (SPE) has been available to analytical chemists for more than two decades [1]. Improvements in SPE manufacturing reproducibility, as well as inherent ease of use and hazardous waste reduction, have led to the widespread adoption of SPE sample preparation in many official methods. Several SPE formats are commercially available, ranging from the original cartridges, to disks, to microextraction fibers. Automated approaches include column-switching and robotics using either single cartridges or 96-well plates. The American Chemical Society recently sponsored a symposium on sample preparation, with emphasis on SPE [2]. The symposium was reviewed in detail by Majors and Raynie [3]. There are many other excellent reviews of SPE; their coverage will not be repeated in this article. The focus of this review is a rarely encountered, and possibly underutilized, variation of reversed-phase SPE using ion-pairing reagents.

2. Background

Ion-pair (IP) reagents have long been known and used for their ability to change selectivity and increase retention of highly polar compounds on

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reversed-phase (RP) analytical columns [4–6]. Highly polar analytes that exhibit poor retention on RP media are often ionic. Typical IP reagents contain a nonpolar portion, such as a long chain aliphatic hydrocarbon, and a polar portion, such as an acid or base. The polar portion of the IP reagent interacts with the charged group on the analyte, forming an ''ion-pair.'' The nonpolar portion interacts with the RP media. Retention of an analyte may be enhanced by increasing the concentration of the IP reagent and also by increasing the carbon chain length on the IP reagent [4].

Table 1 lists commonly used IP reagents. Reagents are available for both acidic and basic analytes. Most are nonvolatile and, hence, more difficult to use with liquid chromatography–mass spectrometry (LC–MS). However, the perfluorocarboxylic acids, originally used for preparative LC and subsequent lyophylization of aminoglycosides [7], are volatile and have been used in IP RP LC–MS [8–11].

3. Ion-pair extraction

Table 2 lists several compounds which have been analyzed using IP–SPE. It includes analytes of pharmaceutical, environmental and food quality control interest. This is a technique which appeared [12] shortly after the advent of SPE, but which has been utilized by relatively few laboratories. Few, if any, SPE manufacturers include IP as an option for reversed-phase SPE in the directions shipped with their products. Typical SPE method development guides [36–38] direct the analyst to normal-phase SPE or, if the analyte is in aqueous solution, ion-exchange SPE for polar analytes.

IP SPE typically is performed much the same as reversed-phase SPE, with one or two additional steps. The analytes of interest are usually highly polar. The samples are predominantly aqueous solutions. Cartridges containing C_{18} [9,12,13,15,17–31,33,34], phenyl [16], cyclohexyl [19], and polymeric [19–24] media have been used in IP SPE. When used ''off-line'', cartridges are typically activated according the manufacturer's directions using methanol and water, followed by a solution of the IP reagent. IP reagent concentrations used range from 0.005 *M* to 0.2 *M*. The same IP reagent is added to the samples before applying them to the conditioned cartridges. The cartridges may be washed with aqueous IP reagent before elution with a stronger solvent, which may or may not contain the same IP

Table 1
Common ion-pair reagents

For basic analytes	For acidic analytes
(Most as sodium salt)	Triethylamine
Propanesulfonic acid	Tetramethylammonium bromide (or hydrogen sulfate)
Butanesulfonic acid	Tetraethylammonium bromide (or hydrogen sulfate)
1-Pentanesulfonic acid	Tetrapropylammonium bromide (or hydrogen sulfate)
1-Hexanesulfonic acid	Tetrabutylammonium bromide (or phosphate, iodide)
1-Heptanesulfonic acid	Tetrapentylammonium bromide
1-Octanesulfonic acid	Tetrahexylammonium bromide (or hydrogen sulfate)
1-Nonanesulfonic acid	Tetraheptyl ammonium bromide
1-Decanesulfonic acid	Tetraoctyl ammonium bromide
1-Dodecanesulfonic acid	
Dodecylsulfate, sodium salt	Hexadecyltrimethyl ammonium hydroxide (or bromide, hydrogen sulfate)
Dioctylsulphosuccinate, sodium salt	Decamethylenebis(trimethylammonium bromide)
Trifluoroacetic acid	
Pentafluoroproprionic acid	
Heptafluorobutyric acid	
Bis-2-ethylhexylphosphate	

reagent. If necessary, sample volume can be reduced by evaporation prior to analysis.

Both normal-phase and ion-exchange SPE have been successfully used for one or more of the analytes listed in Table 2. IP SPE offers some advantages over normal-phase or ion-exchange SPE. First, it is compatible with aqueous solutions and does not require previous dissolution or extraction into a nonpolar solvent, as does normal-phase SPE. Limited analyte solubility can preclude use of normal-phase SPE [27]. Haagsma et al. [28], early users of IP SPE, found that elution buffers used in ion-exchange SPE interfered with the subsequent derivatization of spectinomycin. RP SPEs, including those used with IP reagents, are typically eluted with an organic solvent such as methanol, which is easily evaporated. For this reason, RP SPE is often more compatible with subsequent techniques such as derivatization or MS. Finally, for some combinations of analyte and matrix, ion-exchange SPE simply doesn't work very well [9,39].

SPE often results in lower detection limits compared to other methods of sample preparation. This is also true for IP SPE. Carson et al. [9] found the limit of confirmation for spectinomycin in milk by LC–MS (ion trap) analysis decreased from 200 ng/ml (using deproteination and a methylene chloride wash) to 50 ng/ml using deproteination and IP (heptafluorobutyric acid) extraction on a C_{18} cartridge. IP SPE also decreased the amount of matrix components entering the ion trap mass spectrometer, reducing the ''matrix effect''and improving quantitative performance of the instrument.

Addition of an IP reagent improves the retention of some polar compounds on RP SPE media. For environmental analyses for water contaminants, this means a larger volume of the sample can be applied to the cartridge, with a corresponding increase in the concentration factor and reduction of the method limit of detection. Table 3, from Pocurrull et al. [21], compares recovery of 13 phenolic compounds from a polymeric cartridge without and with 5 m*M* tetrabutylammonium bromide. Addition of the IP reagent allowed good recovery of the most polar analyte, phenol, even from 500 ml water.

Combining IP SPE with other SPE can yield substantial cleanup. Busto et al. [17] used a ''two-dimensional'' extraction of biogenic amines from wine. In the first step, interfering polyphenolic compounds, which tended to saturate the C_{18} SPEs, were removed by passage through either a conventionally conditioned C_{18} or a strong anion-exchange SPE. The unretained material, containing the amines, was then treated with an IP reagent and concentrated by IP SPE on a C_{18} cartridge. Octane-, decane-, and dodecanesulfonic acid were evaluated as IP reagents. Use of the IP reagents also improved recovery of the amines from the evaporation step. Decanesulfonic acid at 200 m*M*, pH 4.5, gave the best overall recoveries for the 15 amines in the study. Applying the SPE steps resulted in limits of detection below 90 μg/l, increasing method sensitivity approximately 4-fold compared to direct injection.

Edder et al. [33] isolated the aminoglycoside streptomycin from a variety of food substances (honey, milk, meat, liver, kidney) by extraction on a cation-exchange cartridge followed by IP (hexanesulfonate, 10 m*M* to activate, approximately 50 m*M* in sample) extraction on a C_{18} cartridge. Addition of IP reagent to the methanolic SPE eluates before evaporation prevented loss of the analyte during the drying step in this case, also.

One disadvantage of IP SPE is that occasionally there are problems with lot-to-lot differences of IP reagents that lead to variable recovery. Use of IP SPE may also add complexity to the method development process. As with IP RP chromatography [4–6], some optimization of IP reagent choice, concentration, pH, organic solvent strength, and solid-phase media choice may be required for best recoveries from IP SPE. For example, Jørgensen [27] found that addition of methanol prior to extraction, as well as addition of tetrabutylammonium acetate and pH control, was necessary for good recovery of pamoic acid from serum. The methanol was presumed to release protein-bound pamoic acid.

Most of the work described above used ''off-line'' SPE cartridges. Two laboratories have also pioneered work using automated on-line IP SPE coupled to LC for multianalyte analysis [25], coupled to either to LC [21] or supercritical fluid chromatography (SFC) [22] for the analysis of phenol and nitrophenols in water, and coupled to LC [23] or LC–MS [24] for the analysis of naphthalenesulfonates in water. SFC coupling was more complicated to set up, since drying of the SPE cartridge was required. However,

Table 2
Applications using ion-pair solid-phase extraction

Analyte	Class	Matrix	SPE phase	IP reagent	Analysis	Range	Ref.
paraquat diquat	herbicide	urine	C_{18}	heptanesulfonate	IP RP LC–UV	1–250 μg/ml	[12]
paraquat	herbicide	rat brain	C_{18}	heptanesulfonate	IP RP LC–UV	<15–360 ng/g	[13]
mezlocillin	antibiotic	serum	not specified	tetrabutylammonium phosphate	IP RP LC–UV	10–300 mg/l	[14]
amoxicillin	antibiotic	urine	C_{18}	tetrabutylammonium bromide	RP LC–UV	5–500 mg/l	[15]
cimetidine	H_2 receptor antagonist	plasma	phenyl	octanesulfonate	IP RP LC–UV	5–2500 ng/ml	[16]
15 amines	biogenic amines	wine	C_{18}	octane-, decane- and dodecane-sulfonate	*o*-phthalaldehyde derviatization and RP LC–fluor	varies <0.1–8 mg/l	[17]
amines	biogenic amines	soy sauce		dodecylbenzenesulfonic acid	fluorescein derivatization and MEKC–LIF[a]	>0.1 μg/ml	[18]
13 phenols	polar phenols	water	C_{18} cyclohexyl carbon 2 polymeric	tetrabutylammonium bromide	RP LC–UV	varies 0.1–200 μg/l	[19–21]
phenol, 4 nitrophenols	polar phenols	water	(on-line) C_{18} 2 polymeric	tetrabutylammonium bromide	SFC–UV	varies 1–40 μg/l	[22]
naphthalene- sulfonates	dye precursors, plasticizers	water	(on-line) C_{18} polymeric	tetrabutylammonium bromide	IP RP LC–UV	<0.25–? μg/l	[23]
naphthalene- sulfonates	dye precursors, plasticizers	water	(on-line) C_{18} polymeric	triethylamine	IP RP LC–MS (single quad)	0.05–1 μg/l	[24]
carboxylic acids, phenols, aromatic sulfonic acids, chlorinated phenoxy acids	highly polar herbicides	water	(on-line) C_{18}	tetrabutylammonium	IP RP LC–UV		[25]

fenoxaprop-ethyl fenoxaprop	pesticide	water	C_{18}	triethylamine	IP RP LC–UV		[26]
pamoic acid	pharmaceutical counter ion	serum	C_{18}	tetrabutylammonium bromide	IP RP LC-fluorescence	2–200 ng/ml	[27]
spectinomycin	aminocylitol antibiotic	plasma	C_{18}	sodium dioctylsulphosuccinate, citrate	naphthalene sulphonyl chloride derivatisation, RP LC–UV, column-switching	40–? ng/ml	[28]
spectinomycin	aminocylitol antibiotic	plasma	C_{18}	sodium dioctylsulphosuccinate, citrate	cation-exchange LC with post-column *o*-phthalaldehyde derviatisation, fluorescence	0.1–100 μg/ml	[29]
dihydrostreptomycin streptomycin	aminoglycoside antibiotics	milk	C_{18}	heptanesulfonic acid	IP RP LC post-column derivitisation ninhydrin, fluorescence	25–400 ng/ml	[30]
streptomycin, dihydrostreptomycin	aminoglycoside antibiotics	milk	C_{18}	hexanesulfonic acid	IP RP LC post-column derivitisation With fluorescence	10–200 μg/kg	[31]
5 aminoglycosides, spectinomycin	antibiotics	tissue, milk	RP	heptafluorobutyric acid	IP RP LC–MS–MS (ESI triple quad)	0.05–2 mg/kg	[32]
spectinomycin	aminocylitol antibiotic	milk	C_{18}	heptafluorobutyric acid	IP RP LC–MS–MS (ESI ion trap)	0.1–5 μg/ml	[9]
streptomycin	aminoglycoside antibiotic	food: tissues milk honey	(SCX and) C_{18}	heptanesulphonate	IP RP LC post-column derivitisation fluorescence	varies 10–400 μg/kg (honey)	[33]
cocaine, nicotine, eserine, cinchonine strychnine	alkaloids	milk juice	C_{18}	sodium octyl sulfonate	IP RP LC–UV	40–200 μg/ml	[34]
levamisole	anthelmintic	sheep plasma		octane sulfonic acid	IP RP (phenyl) LC–UV	50–3750 ng/ml	[35]

[a] Micellar electrokinetic chromatography with laser-induced fluorescence detection.

Table 3
Mean recoveries, R(n=3). of the solid-phase extraction with the highly cross-linked styrene–divinylbenzene copolymer for different volumes of a solution of 10 μg l^{-1} of phenolic compounds in Milli-Q-purified water [21]

Compound[a]	Volume (ml)											
	250				500				1000			
	Without TBA[a]		With TBA		Without TBA		With TBA		Without TBA		With TBA	
	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)
Ph	76	8.4	97	4.1	44	8.3	90	4.3	17	8.7	54	8.2
4-NP	100	3.8	101	3.8	100	3.9	100	3.8	83	6.5	98	4.3
2,4-DNP	98	3.3	100	3.2	97	3.5	98	3.4	100	3.5	98	3.6
2-CP	99	4.9	102	4.7	96	5.1	98	5.5	97	5.1	96	5.2
2-NP	97	3.9	99	3.6	98	3.8	97	4.5	100	3.8	101	3.7
2,6-DMP	102	4.3	102	4.2	98	4.7	98	4.6	98	4.7	98	4.9
2,4-DMP	98	4.6	100	4.6	101	4.5	98	4.6	99	4.5	96	4.6
2-M-4,6-DNP	97	5.6	98	6.6	97	6.2	97	6.1	99	6.2	99	6.3
4-C-3-MP	102	7.6	103	6.9	99	7.3	96	7.5	100	7.3	99	7.5
2,4-DCP	100	5.8	102	5.7	93	6.4	96	6.1	92	6.4	100	5.7
2,4,6-TMP	96	3.5	99	3.9	100	3.8	101	3.7	100	3.8	102	3.9
2,4,6-TCP	95	6.5	100	6.2	90	6.7	93	6.4	90	6.7	91	6.7
PCP	76	7.6	76	7.9	76	8.4	77	7.9	75	8.4	76	7.6

[a] TBA, tetrabutylammonium bromide; Ph, phenol; NP, nitrophenol; DNP, dinitrophenol; CP, chlorophenol; DMP, dimethylphenol; MP, methylphenol; DCP, dichlorophenol; TMP, trimethylphenol; TCP, trichlorophenol; PCP, pentachlorophenol. Reprinted with permission from [21].

in the analysis of phenolic compounds, the investigators found that SFC was advantageous over LC due to shorter analysis times and better separation of the analyte phenol from matrix interference [21].

While not strictly an IP SPE application, Okuda and coworkers effectively used on-line conventional RP SPE coupled to IP RP LC for the analysis of methotrexate [40] and furosemide [41] in serum. Both of these compounds may be analyzed by LC without addition of IP reagents in the mobile phase. However, peak deterioration of the on-line SPE cartridge due to serum protein buildup eventually resulted in peak broadening in the subsequent analytical chromatography, limiting the number of analyses which could be performed. The authors were able to enrich the analyte on top of the analytical column by adding IP reagent (15 m*M* tetrabutylammonium bromide) to the analytical column mobile phase. This compensated for any peak deterioration in the on-line SPE, enabling 50 repeated direct serum injections on a single pretreatment SPE column.

Even though this is primarily an SPE methodology review, it is worth mentioning that ion-pairing can be used to facilitate other modes of extraction. Thomsen and Willumsen [42], employing LC–UV analysis, used the IP reagent bis-2-ethylhexylphosphate for the liquid–liquid extraction (LLE) of methylimidazole from the food additives ammonia caramel colors. Their detection limit was fairly high at 5 mg/kg. Fernandes and Ferreira [43] used the same IP LLE, but with derivatization and gas chromatography–MS to achieve greater specificity and a much lower detection limit, 0.25 mg/kg. IP LLE has also been used for the GC–MS analysis of mercaptic acid conjugates in urine [44], and for the LC analysis of apramycin in swine kidney [45], pamidronate in urine [46], and linear alkylbenzenesufonate surfactant in fish [47].

Finally, IP has been used in supercritical fluid extraction (SFE). Field et al. [48] analyzed secondary alkanesulfonates and linear alkylbenzene surfactants in sewage sludge samples by adding tetrabutylammonium hydrogen sulfate to the samples prior to their extraction with CO_2. Eckard and Taylor [49] used IP SFE to extract pseudoephedrine hydrochloride from a spiked sand sample. In this case, the IP reagent added was 1-heptanesulfonic acid, sodium salt, dissolved in methanol and added to the sample.

Trapped analyte was analyzed by LC. Using 20% methanol modified CO_2, recovery of pseudoephedrine increased from 89% without IP to 99% with IP. Suto et al. [50] determined berberine and palmitine (alkaloids) in Phellodendri Cortex (a traditional herbal medicine) using IP SFE coupled on-line to IP SFC. Dioctyl sulfosuccinate, 100 m*M*, was added to the methanol used at 10% to modify the CO_2 in the extraction, extracts were trapped on a silica SFC column, and then eluted with a mobile phase containing 15% 100 m*M* dioctyl sulfosuccinate in methanol. Dioctyl sulfosuccinate was chosen as the IP reagent because the investigators found that it had greater solubility in SF CO_2 than either sodium dodecylsulfate or sodium 1-heptanesulfonate. Use of the methanolic IP reagent in the extraction increased alkaloid yield 4-fold over use of methanol alone as a CO_2 modifier.

4. Conclusion

IP SPE is a useful addition to the arsenal of techniques available to the analytical chemist. Compared to other SPE techniques, it offers advantages of unique selectivity, compatibility with aqueous samples, and ease of extract treatment with subsequent analytical steps such as evaporation and derivatization. A wide variety of IP reagents is available and suitable for the extraction of either acidic or basic polar compounds. To date, IP SPE has been used by only a few laboratories. It is hoped this review will encourage more analysts to try this technique.

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