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Supplementary materials

Current developments in clinical sample preconcentration prior to elemental analysis by atomic spectrometry: A comprehensive literature review

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Unless specified as below, otherwise, the enrichment factor is calculated by the ratio of calibration curves with and without preconcentration

*The enrichment factor is calculated by ratio of extraction volume to the sample volume

**The enrichment factor is calculated by the ratio of concentration of the analyte with and without preconcentration

Table 1 Comparison of the use of ionic liquid, nanomaterials and surfactant in metal preconcentration of clinical matrix

	Ionic liquid (extraction solvent)	Nanomaterials (sorbent)	Surfactant (emulsifier, sorbent modifier)
Examples of materials used	$[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$, $[C_6MIM][BF_4]$	Modified MWCNT, modified Al_2O_3 or SiO_2, modified Fe_3O_4 NPs	Triton X-114, CTAB, PONPE 7.5
Detection	FAAS, ETAAS, HGAAS, ICPOES, ICPMS, LC-ICPMS		
Preconcentration technique	LPME, DLLME, DLME, HS-SDME, SSLME, MSPE, SPE, CPE, SPME		
Analyte reported in literature (speciation analysis has been found for the underlined elements)	Ag, <u>As</u>, Au, Cd, Co, <u>Cr</u>, Cu, <u>Hg</u>, Pb, Pd, Tl, V, Zn	Al, As, Au, Cd, Co, <u>Cr</u>, Cu, Fe, Hg, Ir, Mn, Ni, Pb, Pd, Pt, Rh, Ru, Se, V, Zn	Ag, Al, <u>As</u>, Bi, Cd, Co, <u>Cr</u>, Cu, <u>Hg</u>, Mn, Ni, Pb, Pd, <u>Sb</u>, <u>Se</u>, Tl, Zn, REEs
Matrix (in the order of descending frequency of application)	Hair, urine, blood, saliva, nail, serum, tissue	Hair, urine, tissue, plasma, serum	Urine, hair, blood, tissue, serum, bone ash, plasma, nail
Online analysis example	1. FI automated LPME: the solution mixture containing the dispersed IL phase is formed upon cooling in ice bath and then extracted into the Florisil-packed microcolumn for elution[1] 2. SI-DLLME: online mixing of dispersive solvent, extractant (IL) and sample solution, fine droplets of analyte containing IL are trapped in the polyurethane foam for further elution[2]	Simple setup can be constructed because the SPE procedure mainly consists of sample loading and elution steps which can be perform using peristaltic pump(s) with a packed column[4-9]	1. CME (SPME): surfactant is used in the preparation of the modified capillary in SPME[20] 2. FI online CPE: sample solution, surfactant, and chelating agent are loaded into a microcolumn packed with filtering materials, the adsorbed surfactant with extracted analyte are then eluted by suitable eluent in the subsequent step[6] 3. Surfactant coated SPE: sample solution is passed through the surfactant-modified microcolumn to allow the extraction to take place[20]
Comment	-Preferential extraction of different metal species by temperature control[3] -Only small amount (in terms of μL) of ionic liquid is needed in the extraction -Temperature control may be applied to assist the extraction	-More than ten publications introduced simultaneous extraction of different metals [4,5,7,10-19] -Some SPE column can be reused, this provides less variation between extractions, and more chemicals can be saved -Various modification can be made on the surface of nanomaterials sorbents to tune the extraction selectivity	-Reduction/oxidation prior to extraction may be required for speciation analysis[21-23] -A relatively mature technique, applications have been investigated on more than twenty metals -Temperature control is usually applied to assist the extraction

Table 2 Examples of ionic liquid based microextraction for metal analysis in clinical samples

Sample	Analyte	Technique	Extractant/dispersant/chelating agent/others)	Detection	LOD	EF	Ref
Hair, urine	Cu, Zn, Cd	IL-MSPE, nano	Fe_3O_4 @SiOH @[$MTOA^+$][Cl^-]	ICPOES	0.33-0.56 μg L^{-1}	10*	10
Hair	Pb	TC-IL-LPME	[C_4MIM][PF_6]/-/-/-	FAAS	5.8 μg L^{-1}	30*	24
Urine	Cr(III), Cr(VI)	TC-IL-LPME	[C_6MIM][PF_6]/-/APDC/Anti-sticking agent: Triton X-114	ETAAS	2.45-5.40 ng L^{-1}	42**	3
Urine	Tl	IL-DLLME, online	[C_6MIM][PF_6]/EtOH/-/-	FAAS	0.86 μg L^{-1}	290	2
Hair	Pb	IL-SSLME	[C_4MIM][PF_6]/Triton X-114/dithizone/-	FAAS	0.281 μg L^{-1}	82.6	25
Blood	Pb	TC-IL-DLME	[C_4MIM][PF_6]/-/APDC/-	FAAS	0.13 μg L^{-1}	93	26
Hair	Au, Ag	IL-DLLME	[C_6MIM][PF_6]/-/ N-(4-{4-[(anilinocarbothioyl)amino]benzyl}phenyl)-N-phenylthiourea/-	ETAAS	2.6-4.8 ng L^{-1}	48.3-48.7	27
Hair, nail	As(III), As(V)	IL-ISSFME	[C_6MIM][BF_4] with $NaPF_6$/-/APDC/-	ETAAS	6 ng L^{-1}	-	28
Blood, urine	As(III), As(V)	IL-DLLME	[C_4MIM]PF_6/acetone, CCl_4/APDC/back extractant: HCl	HGAAS	5 ng L^{-1}	-	29
Hair	iHg, oHg	CV-IL-HS-SDME	CYPHOS IL 101 with KMnO4/-/-/reductant: SnCl2	ETAAS	10 ng L^{-1}	75	30
Saliva	V	IL-FI-CIAME, online	[C_4MIM][PF_6]/-/5-Br-PADAP/anti-sticking agent: Triton X-100	ETAAS	4.8 ng L^{-1}	-	1
Saliva, urine	Co	IL-DLLME	[C_6MIM][PF_6]/MeOH/1N2N/anti-sticking agent: Triton X-114	ETAAS	3.8 ng L^{-1}	120	31
Serum, hair	Co, Hg, Pb	IL-CF-SDME	[C_4MIM][PF_6], PAN/-/-/ modifier: PAN	ETV-ICPMS	1.5-9.8 pg mL^{-1}	-	32

Table 3 Examples of nanomaterials based SPE for metal analysis in clinical samples

Sample	Analyte	Technique	Sorbent material, others	Detection	LOD	EF	Ref
Plasma, urine	Al(III), Cr(III)	nano-MSPE	MPA-TEOS-MNPs (Fe_3O_4)	ETAAS, FAAS	0.09-0.19 μg L^{-1}		11
Hair, urine	Cu, Zn, Cd	IL, nano-MSPE	Fe_3O_4 @SiOH @[$MTOA^+$][Cl^-]	ICPOES	0.33-0.56 μg L^{-1}	10*	10
Hair	Cr(III), Cu(II), Pb(II), Zn(II)	nano-MSPE	Dithizone modified silica coated Fe_3O_4	ICPOES	8-62 ng L^{-1}	-	13
Serum, urine	Cr(III), Cr	nano-MSPE	Fe_3O_4@ZrO_2	FAAS	0.69 μg L^{-1}	-	33
Urine	Pb(II)	nano-MSPE	Fe_3O_4	ETAAS	0.8 ng L^{-1}	200*	34
Hair	Pb(II), Cd(II), Cu(II)	nano-MSPE	Fe_3O_4/SiO_2/Schiff base	FAAS	0.12-0.19 μg L^{-1}	87.5*	14
Urine	V, Co, Ni, Cu, Zn, As, Se, Cd, Pb	nano-MSPE	$MnFe_2O_4$, chelating agent: APDC	ICPMS	0.01-0.7 μg L^{-1}	7.4-10	15
Urine	Cd	nano-SPE, FI, online	MWCNT (treated with H_2SO_4-$KMnO_4$)	ETA-AAS	0.01 μg L^{-1}	3.4	6
Hair	Zn(II)	nano-SPE	MWCNT-PAN	FAAS	0.07 ng L^{-1}	250*	35
Hair, urine	Cd(II)	nano-SPE	γ-Al_2O_3 modified with Schiff base	FAAS	0.14 μg L^{-1}	75*	36
Hair	Ru, Rh, Pd, Pt, Ir, Au	nano-MSPE, FI, online	Mercapto-functionalized silica coated Magnetite Fe_2O_3	ICPMS	1.7-2.5 ng L^{-1}		4
Urine	Pb(II), Cr(III)	nano-SPE	DNPH modified SDS coated alumina	FAAS	0.43-0.55 μg L^{-1}	266.6*	16
Hair	Pb(II), Cd(II)	nano-SPE	MWCNT-MnO_2	ETAAS	1.5-4.4 ng L^{-1}	100*	19
Hair, urine	Al(III)	nano-SPE	4-aminophenylarsonic acid modified nano-TiO_2/SiO_2	ICPOES	0.06 μg L^{-1}	150*	37
Hair	Cr(III), Cu(II), Ni(II), Cd(II)	nano	Salicylic acid modified, silica coated Fe_3O_4	FAAS	0.11-0.27 μg L^{-1}	200*	38
Bovine liver	Cd(II), Co(II), Ni(II), Pb(II), Fe(II), Cu(II), Zn(II)	nano-SPE disc	MWCNT, chelating agent: 8-Hydroxquinoline	FAAS	1-5.2 μg L^{-1}	60*	12
Cell	Cd, Hg, Pb	nano-MSPE	γ-MPTS modified silica coated MNPs (Fe)	ETV-ICPMS	0.72-1.12 ng L^{-1}	41.6-48.7	17
Hair	Cu(II), Ni(II)	nano-SPE, FI, online	MWCNT-6His tagged protein, chelating agent: iminodiacetic acid (IDA)	FAAS	0.31-0.63 μg L^{-1}	-	7
Urine	Mn(II), Co(II), Cu(II), Zn(II), Pb(II)	nano-MSPE, lab on valve	MNPs-PAA (Fe)	ICPMS	0.04-0.6 μg L^{-1}	-	5
Pig liver	Cd(II), Cu(II), Ni(II), Pb(II), Zn(II)	nano-SPE	Morin-SiO_2	ICPAES	0.091-0.2 μg L^{-1}	75*	18
Hair	Cd(II)	nano-SPE, FI, online	MWCNT-L-cysteine	FAAS	0.28 μg L^{-1}	-	8

Table 4 Examples of surfactant based microextraction for metal analysis in clinical samples

Sample	Analyte	Technique	Material (surfactant/chelating agent/others)	Detection	LOD	EF	Ref
Serum, urine	Zn(II), Cd(II)	CPE	Triton X-114/TTDM/-	FAAS	2-3 μg L^{-1}	23.89-25.60	39
Hair, blood	Pb	CPE	Triton X-114/dithizone/-	FAAS	0.08 μg L^{-1}	53	40
Serum	Cr(III), total Cr	CPE	Triton X-114/PAN (also acts as matrix modifier)/-	GFAAS	0.02 μg L^{-1}	83.5	21
Oyster tissue,-urine	As, Bi, Cd, Pb	CPE	Triton X-114/DDTP/-	ICPOES	0.047-0.28 μg L^{-1}	10-18	41
Hair	As	CPE	Triton X-114/pyronine B/-	ETAAS	0.022 μg L^{-1}	-	42
Blood	Pb(II)	CPE	Triton X-114/APDC, DDTC/-	FAAS	1.14 μg L^{-1}	42-56	43
Blood	Ag	CPE	Triton X-114/BHIS/-	FAAS	-	-	44
Hair, serum	Bi(III)	CPE, FI	Triton X-114/8-HQ/-	ICPOES	0.12 μg L^{-1}	81	45
Serum	Mn(II)	CME, FI, online	Template: CTAB, Mn(II), MPTS-silica coated capillary	ICPMS	10.3 ng L^{-1}	16.7	46
Blood	Zn	CPE	Triton X-114/quinaldine, PAN/-	FAAS	1.4-1.52 μg L^{-1}	26-30	47
Blood	Se(IV), total Se	CPE	Triton X-114/DAB/-	ETAAS	0.025 μg L^{-1}	-	23
Pig liver	REE	CPE, online	Triton X-114/with or without 8-HQ/-	ICPOES	41.4-448 pg mL^{-1}	-	48
Bone ash	Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn	CPE	Triton X-114/PAN, 5-Br-PADAP/-	ICPOES	0.3-40 μg L^{-1}	-	49
Human albumin	Al(III)	CPE	Triton X-114/PAN/-	GFAAS	0.06 ng mL^{-1}	34.8	50
Blood, urine	Cd(II), Pb(II), Pd(II), Ag(I)	CPE	Triton X-114/BIES/-	FAAS	1.4-2.8 ng mL^{-1}	39-48	51
Hair	Hg(II), mHg	CPE	Triton X-114/DDTC/-	LCICPMS	4-10 ng L^{-1}	21-42	52
Hair	mHg, phHg, iHg	CPE	Triton X-114/DDTC/-	LCICPMS	6-13 ng L^{-1}	18-57	53
Hair	Cu, Cd	Surfactant coated SPE, online	SDS coated activated alumina/1,10-phenantholine/-	FAAS	0.04-0.14 μg L^{-1}	116-175	20
Plasma, urine	Se(IV)	CPE	Triton X-114/o-phenylenediamine/-	ETAAS	0.09 ng mL^{-1}	63.5	54
Blood, liver	Cu(II)	CPE	Triton X-114/PDBDM/-	FAAS	0.6 ng mL^{-1}	41.1**	55
Blood, liver	Cu(II), Co(II), Ni(II)	CPE	Triton X-114/MPKO/-	FAAS	1.6-2.1 ng mL^{-1}	58-67	56
Urine	Cd	CPE	PONPE 7.5/5-Br-PADAP/-	ETAAS	0.008 μg L^{-1}	22	57
Hair, urine	Hg	CPE	PONPE 7.5/5-Br-PADAP/-	ETAAS	0.001-0.1 μg L^{-1}	22	58
Urine	Cd	CPE	Triton X-114/APDC/-	AAS	5 ng L^{-1}	15*	59
Hair	Al(III)	CPE	Triton X-114/PMBP/-	GFAAS	0.09 ng mL^{-1}	37	60
Blood, serum	Cd, Pb, Cu, Co, Ni	Two step CPE	Triton X-114/DDTC, PAR/-	ICPMS	0.04-0.1 μg L^{-1}	-	61
Urine	Tl(III)	Surfactant coated SPE	Silica C18 coated with cationic surfactant: Zephyramine	ICPMS, ETAAS	0.24 μg mL^{-1}		62
Hair, urine	Cd(II)	nano-SPE	γ-Al_2O_3 modified with Schiff base	FAAS	0.14 μg L^{-1}	75*	36
Urine	Pb(II), Cr(III)	nano-SPE	DNPH modified SLS coated alumina	FAAS	0.43-0.55 μg L^{-1}	266.7*	16

Table 5 Examples of automation in preconcentration for metal analysis in clinical samples

Sample	Analyte	Technique	Materials/reagent	Detection	LOD	EF	Ref
Serum, urine	REE	CME, FI	IDA modified poly(glycidyl methacrylatetrimethylolpropane trimethacrylate) monolithic capillary	ICPMS	0.08-0.97 ng L^{-1}	-	63
Urine	Tl	IL-DLLME, SI	PUF packed in microcolumn / [C_6MIM][PF_6], EtOH	FAAS	0.86 μg L^{-1}	290	2
Mussel tissue, urine	Cd(II), Pd(II), Cu(II)	SPE, FI	Bond Elut ® PlexaTM PCX polymer resin	FAAS	0.1-1.8 μg L^{-1}	90-95	64
Hair	As(III), As(V)	SI, SPE	$Y(OH)_3$ precipitate layer coated cellulose fibre particles /reductant: KI-ascorbic acid	HGAFS	17 ng L^{-1}	-	65
Hair	REE	SPE, FI	Walnut shell-packed microcolumn	ICPMS	2-34 pg g^{-1}	79-102	66
Serum	Mn(II)	IIP-CME, SPME, FI	Template: CTAB, Mn(II), MPTS-silica coated capillary	ICPMS	10.3 ng L^{-1}	-	46
Urine	Pb(II)	IIP-SPE, FI	Template: Pb(II), polyvinylimidazole-silica hybrid copolymer	TS-FF-AAS	0.75 μg L^{-1}	128	67
Urine	Cd	nano-SPE, FI	MWCNT (treated with H_2SO_4-$KMnO_4$)	ETA-AAS	0.01 μg L^{-1}	3.4	6
Hair	Ru, Rh, Pd, Pt, Ir, Au	nano-MSPE, FI (DSPE)	Mercapto-functionalized silica coated Magnetite Fe2O3	ICPMS	1.7-2.5 ng L-1	-	4
Pig liver	REE	CPE, FI	Silica gel packed microcolumn /Triton X-114, 8-HQ	ICPOES	41.4-448 pg mL^{-1}	-	53
Saliva	V	IL-FI-CIAME	[C_4MIM][PF_6], 5-Br-PADAP, Triton X-100	ETAAS	4.8 ng L^{-1}	-	1
Hair	Cu(II), Ni(II)	nano-SPE, FI	MWCNT-6His tagged protein, chelating agent: iminodiacetic acid (IDA)	FAAS	0.31-0.63 μg L^{-1}	-	7
Urine	Mn(II), Co(II), Cu(II), Zn(II), Pb(II)	nano-MSPE, lab on valve	MNPs-PAA (Fe)	ICPMS	0.04-0.6 μg L^{-1}	-	5
Hair	Cu, Cd	surfactant coated SPE, FI	SDS coated activated alumina /1,10-phenantholine	FAAS	0.04-0.14 μg L^{-1}	116-175	20
Urine	Cu, Fe, Mn, Ni	UAD-SPE, FI	Imminodiacetic functional group resin, Chelite Che	FAAS	0.5-1.1 μg L^{-1}	21.3-44.1	68
Urine	V(V), V(IV)	SPE, FI	L-methionine immobilised on controlled pore glass (CPG)	ICPOES	0.008 ng mL^{-1}	-	69
Hair	Cd(II)	nano-SPE, FI	MWCNT-L-cysteine	FAAS	0.28 μg L^{-1}	-	8
Hair, saliva, urine	Al	SPE, FI	L-methionine immobilized on controlled pore glass (CPG)	ICPOES	25 ng L^{-1}	-	70

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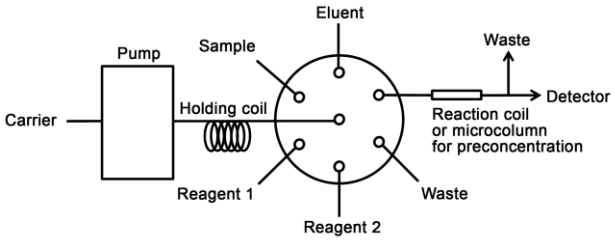

Figure 1 General configuration of flow injection manifold.

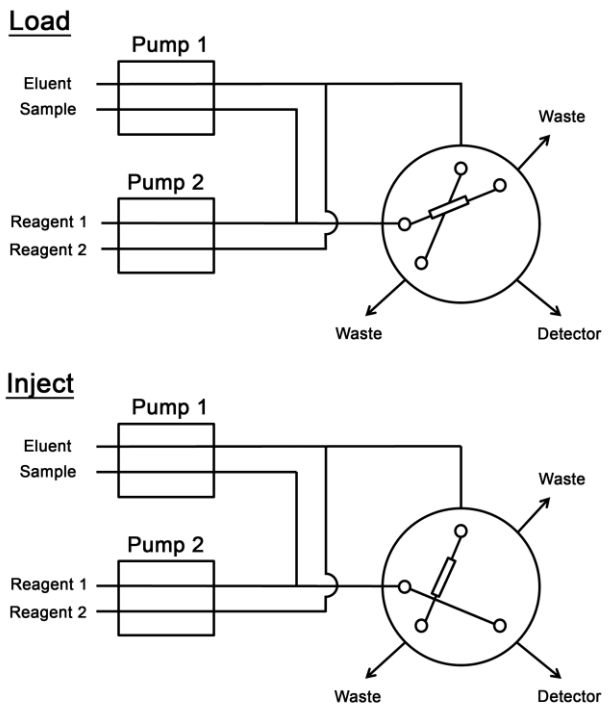

Figure 2 General configuration of sequential injection manifold.

Abbreviation

$[C_4MIM][PF_6]$	1-Butyl-3-methylimidazolium hexafluorophosphate
$[C_6MIM][PF_6]$	1-Hexyl-3-methylimidazolium hexafluorophosphate
$[C_4MIM][BF_4]$	1-Butyl-3-methylimidazolium tetrafluoroborate
$[MTOA^+][Cl^-]$	Methyltrioctylammonium chloride
1N2N	1-Nitroso-2-naphtol
5-Br-PADAP	2-(5-Bromo-2-pyridylazo)-5-diethyl-aminophenol
8-HQ	8-Hydroxyquinoline
γ -Al_2O_3	Sodium dodecyl sulfate (SDS) coated alumina nanoparticles
APDC	Ammonium pyrrolidinedithiocarbamate
BHIS	Bis((1H-benzo[d]imidazol-2yl)methyl) sulfane
BIES	Bis((1H-benzo[d]imidazol-2yl)ethyl) sulfane
CF	Cycle flow
CIAME	Cold-induced aggregation microextraction
CME	Capillary microextraction
CPE	Cloud point extraction
CPG	Controlled pore glass
CTAB	Cetyltrimethylammonium bromide
CV-ILAHS-SDME	Cold vapor ionic liquid-assisted headspace single drop microextraction
CYPHOS® IL 101	Tetradecyl(trihexyl)phosphonium chloride
DAB	Diaminobenzidine
DDTP	Diethyldithiophosphate
DLLME	Dispersive liquid-liquid microextraction
DLME	Dispersive liquid phase microextraction
DNPH	2,4-Dinitrophenlhydrazin
DSPE	Displacement solid phase extraction
EF	Enrichment factor
ETA-AAS	Electrothermal atomization atomic absorption spectroscopy
ETAAS	Electrothermal atomic absorption spectroscopy
ETV	Electrothermal vaporization
FAAS	Flame atomic absorption spectroscopy
FI	Flow injection
GFAAS	Graphite furnace atomic absorption spectroscopy
HF-LPME	Hollow fiber based-liquid phase microextraction
HGAAS	Hydride generation atomic absorption spectroscopy
HGAFS	Hydride generation atomic fluorescence spectroscopy
HS	Head space
ICPAES	Inductively coupled plasma atomic emission spectrometry
ICPOES	Inductively coupled plasma optical emission spectroscopy
ICPMS	Inductively coupled plasma mass spectrometry
IDA	Iminodiacetic acid
IIP	Ion-imprinted polymer
IL	Ionic liquid
ISSFME	In situ solvent formation microextraction
LC-ICPMS	Liquid chromatography-inductively coupled plasma mass spectrometry
LOD	Limit of detection
LPME	Liquid phase microextraction
MNPs	Magnetic nanoparticles
MPKO	Methyl-2-pyridylketone oxime
MPTS	3-Mercaptopropyl-trimethoxysilane
MSPE	Magnetic solid phase extraction
MWCNT	Multi-walled carbon nanotube
NPs	Nanoparticles
PAA	Polyacrylic acid
PAN	1-(2-Pyridylazo)-2-naphtol

PAR	4-(2-Pyridylazo)resorcinol
PDBDM	4-(Phenyl diazenyl) benzene-1,3-diamine
PMBP	1-Pphenyl-3-methyl-4-benzoyl-5-pyrazolone
PONPE 7.5	Polyethyleneglicolmono-*p*-nonyphenylether
PUF	Polyurethane foam
REEs	Rare earth elements
SDME	Solid phase microextraction
SI	Sequential injection
SPE	Solid phase extraction
SPME	Solid phase microextraction
SSLME	Single step in-syringe system for ionic liquid based liquid microextraction
TC	Temperature controlled
TEOS	Tetraethylorthosilicate
Triton X-100	4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol
Triton X-114	(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol
TS-FF-AAS	Flow-injection thermospray flame furnace atomic absorption spectrometry
TTDM	3,3’,3”,3’”-Tetraindolyl (terephthaloyl) dimethane
UAD	Ultrasound-assisted digestion