DE GRUYTER Physical Sciences Reviews. 2016; 20160056

Bin Hu / Man He / Beibei Chen / Zucheng Jiang

Separation/Preconcentration Techniques for Rare Earth Elements Analysis

Abstract:
The main aim of this chapter exactly characterizes the contribution. The analytical chemistry of the rare earth elements (REEs) very often is highly complicated and the determination of a specific element is impossible without a sample pre-concentration. Sample preparation can be carried out either by separation of the REEs from the matrix or by concentrating the REEs. The separation of REEs from each other is mainly made by chromatography.
At the beginning of REE analysis, the method of precipitation/coprecipitation was applied for the treatment of REE mixtures. The method is not applicable for the separation of trace amounts of REEs. The majority of the methods used are based on the distribution of REEs in a two-phase system, a liquid–liquid or a liquid–solid system. Various techniques have been developed for the liquid–liquid extraction (LLE), in particular the liquid phase micro-extraction. The extraction is always combined with a pre-concentration of the REEs in a single drop of extractant or in a hollow fiber filled with the extractant. Further modified techniques for special applications and for difficult REE separation have been developed. Compared to the LLE, the solid phase micro-extraction is preferred. The method is robust and easy to handle, in which the solid phase loaded with the REEs can be used directly for subsequent determination methods. At present, very new solid materials, like nanotubes, are developed and tested for solid phase extraction.

Keywords: rare earth elements, pre-concentration techniques, liquid-liquid extraction, liquid phase microextraction, solid phase extraction, solid phase microextraction

DOI: 10.1515/psr-2016-0056

1 Introduction

Rare earth elements (REEs) have been widely used in functional materials, catalysts, and other products in industry, diagnosis reagents of magnetic resonance imaging (MRI) in medicine and some fertilizers in agriculture (especially in China). As a result of their usage, more and more REEs are getting into the environment, food chain and organisms. The concentration of REEs in biological samples and environmental samples such as atmosphere, soil and natural water is around ppm–ppb level; the concentration of REEs in sea water is around ppt level; the requirements for ultra-high purity rare earth materials demand for a detection limit of ppb–ppt level for the ultra-trace REE impurities. Accordingly, much higher sensitivity is demanded for the quantification of trace/ultra-trace REEs in real-world samples. On the other hand, the separation among REEs has always been a challenging hot topic due to their similar chemical properties.

2 Chemical separation techniques for REEs

For the determination of trace REEs in biological and environmental samples, appropriate separation/preconcentration techniques are usually required to separate the complex matrix, preconcentrate interesting REEs and bring REEs in a suitable form for subsequent instrumental analysis. The most widely used techniques for the separation and/or preconcentration of trace REEs include precipitation/coprecipitation, liquid–liquid extraction (LLE), liquid phase microextraction (LPME), solid phase extraction (SPE) and solid phase microextraction.

Bin Hu is the corresponding author.

2.1 Precipitation/coprecipitation

2.1.1 Oxalate precipitation

Precipitants for REEs include oxalic acid, diphenyl glycolic acid, cinnamic acid, mandelic acid (for the precipitation of Sc), methylene phosphoric acid (for the precipitation of La) and 8-hydroxy quinoline (for the precipitation of Eu, Gd and Sm). Among them, oxalic acid is the mostly employed precipitant for REEs. Oxalate gravimetric method based on the precipitation of RE oxalate had been used as a routine analytical method for the determination of total REEs and is suitable for the samples with content of REEs of above 5 %.

Oxalate gravimetric method is performed by weighing the burned precipitate obtained by oxalate precipitation and separation. Oxalic acid is spiked into the weak acidic solution containing REEs, resulting in colored RE oxalate precipitation as $RE_2(C_2O_4)_3 \cdot nH_2O$, $n = 5, 6, 9$ or 10. Dimethyl oxalate or oxalic acid acetone is usually used as the precipitant in homogeneous precipitation; ammonium oxalate is preferred for a good separation when the content of iron is 40 times higher than that of REEs. Alkali metal oxalates are unsuitable as the precipitant for REEs for that alkali metal would form insoluble complex salt with REEs which would be introduced into the precipitate, or form soluble oxalic acid complexes with yttrium group REEs which lead to incomplete precipitation of REEs.

There are series of factors influencing oxalate gravimetric method, including solubility of RE oxalate, oxalate activity, temperature, stirring and aging time, ammonium salt and other coexisting ions, and the medium. The details could be found in the book on REEs [1].

2.1.2 Coprecipitation

Coprecipitation is a conventional separation/preconcentration technique, which is suitable for the separation of trace REEs from the large number of common elements in complicated samples.

The carrier (also called trapping agent) is very important in coprecipitation. Generally, the carrier should meet the following requirements: (1) featuring with similar chemical composition and structure to RE precipitate; (2) the usage should be as low as possible; (3) no interference for subsequent analysis and no need for secondary separation. The fluorides, hydroxides, oxalates or metal organic chelates of REEs are generally used as the carrier for their coprecipitation. It should be noted that if inductively coupled plasma-optical emission spectrometry/mass spectrometry (ICP-OES/MS) is employed for the subsequent detection, small amounts of interfering substances that remained in the precipitation will not interfere with the determination of REEs due to the good elemental selectivity of ICP-OES/MS. In other words, the requirement for separation efficiency in coprecipitation is not very stringent when ICP-OES/MS detection is used after coprecipitation.

Flotation technique for separation of REEs is another form of coprecipitation. Zhang et al. [2] employed $Fe(OH)_3$ as the precipitant, oleic acid as the surfactant and processed the precipitation and flotation of trace REEs effectively under pH 8–9. Some representatives for the trace REEs analysis by using coprecipitation and ICP-OES/MS determination are listed in Table 1.

Table 1: Application of coprecipitation-ICP-OES/MS for trace REEs analysis.

Sample	Analytes	Carrier	Operation process	Ref.
Soil, plant and environmental water	Ce, La, Y and Yb	Mixture of PAN and 5-Br-PADAP 2-(5-bromo-2-pyridylazo)5-(diethylamino)phenol	Samples are adjusted to pH 8, spiked with co-precipitating agent (carrier), maintained at 60–80°C for 30 min, filtered after 2 h settling; the precipitate is dissolved by HNO_3 and $HClO_4$ prior to ICP-OES detection	[2]
Silicate rocks	REEs and Y	Calcium oxalates	The rock sample was decomposed by HF and $HClO_4$, followed by precipitation of REE and Y as oxalates, with calcium as carrier. The oxalate precipitate is ignited to the oxide and then dissolved in diluted HNO_3 for ICP-OES detection	[3]
Geological samples	REEs	Calcium oxalates	The sample was decomposed by HF, HNO_3 and $HClO_4$, and the residue was dissolved in HCl. The solution was adjusted to pH 3.5–4, followed by precipitation of REE as oxalates and cation-exchange column separation in 6 mol/L HNO_3	[4]

Soils and sediments	REE, Cd, In, Tl, Th, Nb, Ta, Zr and Hf	$Ti(OH)_4$–$Fe(OH)_3$	The sample was alkaline fused by $NaOH$–Na_2O_2 and co-precipitated by $Ti(OH)_4$–$Fe(OH)_3$. The precipitate was dissolved with inverse aqua regia and determined by ICP-MS	[5]
Sea water	REEs and Y, Mn, Co and Cr	$Mg(OH)_2$	The sample was adjusted to pH 9.5 by aqueous NH_3, which led to precipitation of magnesium hydroxides. The $Mg(OH)_2$ precipitate was dissolved in diluted HNO_3 solution for subsequent ICP-MS detection	[6]

3 Liquid–liquid extraction

LLE is generally a two-phase solvent extraction, aiming to separate interesting analyte based on its different distribution coefficients in two immiscible solvents. The greater the difference in the solubility of interesting analyte between the extraction solvent and original aqueous solution is, along with greater distribution coefficient, the better is the extraction performance for separation. The distribution coefficient depends on the extraction temperature, solvent and the characteristics of target analyte. And the factors affecting the extraction performance mainly include the extraction solvent (extractant), the solubility difference between the extractant and original aqueous solution and the contacting of two phases during extraction. Under a certain condition for a specific analyte, the selection of extractant significantly determines the extraction performance.

Since acetone, ether or alcohols were employed for the extraction of REEs in 1937, new extractants and strategies for the extraction of REEs are emerging prominently. Tributyl phosphate was used to extract Ce^{4+} and RE^{3+} first in 1949 and then to separate RE^{3+} from each other successfully. Di(2-ethylhexyl)phosphate (P204), naphthenic acid and methyl trialkylammonium chloride were employed for the separation and purification of REEs in the production process from the 1970s.

3.1 Affecting factors for LLE of REEs

LLE is commonly used for the separation of REEs from non-REEs, group separation of REEs and separation of single REE to improve the sensitivity and selectivity for REEs analysis. And the affecting factors for LLE of REEs are mainly the selection of extractants, extractant concentration, medium pH and salting-out agents.

3.2 Extractants for REEs

In practical analysis, an appropriate extractant is required to feature with good selectivity, low water solubility, high extraction capacity, good stability and safety; in terms of chemical property, low density, high surface tension, low viscosity and high boiling point and flash point are required. According to the structure and property, along with the extraction mechanism, the extractants for REEs can be divided into neutral phosphorus compounds, acidic phosphorus compounds, organic amines, neutral oxygen-containing compounds, chelates and others (including supramolecule, e.g., crown ethers and calixarene).

3.2.1 Neutral phosphorus compounds

The basic structure is $(RO)_3PO$ or R_3PO, without dissociable H, alkyl or alkoxy connected with P. Their structure, property and other constants are listed in Table 2.

Table 2: Neutral phosphorus extractants for REEs extraction.

Name	**Structural formula**	**Trade names and abbreviation**	**Solubility (H_2O, g/L)**
Dibutyl phosphate	$(nC_4H_9O)_3PO$	TBP	0.38
Diisoamyl methyl phosphonate	$CH_3P(O)(C_5H_{11}-i)$	P218, DAMP	3.39

Dimethyl methyl phosphate heptyl ester	$CH_3PO(OCHCH_3(CH_2)_5CH_3)$	P350	0.14
Isopropyl bis-(2-ethylhexyl)phosphate	$i\text{-}C_3H_7(O)(OC_8H_{17}-i)_2$	P277	0.01
Dibutyl butanephosphonate	$C_4H_9P(O)(OC_4H_9)_2$	P205, DBBP	
Dibutyl butyl phosphate	$(C_4H_9)_2PO(OC_4H_9)$	P203, BDBP	
Trioctylphosphine oxide	$(nC_8H_{17})_3PO$	P201, TOPO	0.09
Dibutyltin oxide	$(nC_4H_9)_3PO$	TBPO	
Oxide di-(2-ethylhexyl) phosphine	$(CH_3(CH_2)_3)CH(C_2H_5)CH_2)_3PO$	TEHPO	

These extractants have phosphoryl (P=O), and the high electron density on O atom favors the coordination with RE ions. The electronegativity of RO-group is higher than that of R-group (R is electron-donating group), and the electron density on O atom in P=O is decreased, decreasing the complexation ability with REE ions (Table 3).

Table 3: The effect of substituents on REEs extraction by neutral phosphorus agents [7].

	The structure of extractants			
D_{RE}	**Bu_3PO(TBP)**	**$Bu_2(BuO)PO$**	**$Bu(BuO)_2PO$**	**$(BuO)_3PO$**
Ce	4.25	1.96	0.291	0.026
Pm	6.00	2.95	0.613	0.050
Y	12.3	3.61	0.419	0.044

Note: Extractant: 0.1 mol/L (benzene as solvent); [HNO_3] 3 mol/L, Ce^{144}, Pm^{147}, Y^{90}.

TBP and P350 are specific representatives of neutral phosphorus. REE ions could be well extracted by TBP in nitric acid above 10 mol/L and the partition coefficient is listed in Table 4. The extracted complex is $RE(NO_3)_3{\cdot}3TBP$. As can be seen from Table 4, the extraction ability of TBP for heavy RE ions is better than that for light RE ions, and the separation factor for neighboring RE ions is relative low, making it very difficult for the separation of neighboring single RE ions. P350 can extract RE ions well under low-acidity condition; compared with TBP, P350 presents higher extraction efficiency, higher separation factor and lower water solubility. The extracted complex is in the form of $RE(NO_3)_3{\cdot}3P350$, and the distribution ratio is increasing with the increase of the atomic number.

Table 4: Distribution coefficient (*D*) for REEs extraction by TBP [8].

RE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
HNO_3 (mol/L)	14	14	14	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.0
D	0.09	0.3	1.1					1.0	1.6	2.1	2.9	4.4	5.9	7.2	14

3.2.2 Acidic phosphorus compounds

The basic structure is $(RO)_2PO(OH)$ or $(RO)PO(OH)_2$, and $R(RO)PO(OH)$ or $R_2PO(OH)$. Neutral phosphorus is alkyl phosphates and acidic phosphorus is alkyl phosphoric acid, by substitution or esterification of one or two –OH in orthophosphate molecule. H^+ would easily dissociate from the left hydroxyl and make the molecule acidic. These compounds are called acidic phosphorus (Table 5).

Table 5: Acidic phosphorus extractants.

Name	Structural formula and pK_a	Trade names and abbreviation	Solubility (H_2O, g/L)
Di(isooctyl)phosphate	$(C_4H_9CH(C_2H_5CH_2O)_2PO(OH)3.32$	P204, D2EHPA, HDEHP	0.02
Phosphoricacidethylhexylester	$(C_4H_9CH(C_2H_5CH_2O)PO$ $(C_4H_9CH(C_2H_5)CH_2)(OH)4.10$	P507, HEHEHP,PC88A	0.08

Bis(1-methylheptyl)phosphate	$(C_6H_{13}CH(CH_4)O)_2$ PO(OH)3.22	P215	0.02
Di-iso-octyl Phosphonate	$(C_4H_9CH(C_2H_5)CH_2)_2$ PO(OH)4.98	P227	
Lauryl alcohol phosphate acid ester	$n\text{-}C_{12}H_{25}OPO(OH)_2$	P501, DDPA	0.20
Phosphoric aciddiphenyl ethylhexyl ester	$(C_4H_9CH(C_2H_5CH_2O)C_6H_5PO(OH)3.12$	P406, HEHPHP	
Dibutyl phosphate	$(C_4H_9O)_2PO(OH)$	DBP	
Monoalkyl phosphate	$RCHR{\cdot}CH_2OPO(OH)_2$	P538	0.05

There are hydroxyl groups in these extractants, and H is easily substituted by RE^{3+}; P=O would easily coordinate with RE^{3+}; thus, these acidic phosphorus extractants exhibit good extraction ability for RE ions either under low-acidity or high-acidity condition. In $(RO)_2PO(OH)$, R-substitutes RO-group, increasing the electron density on O atom in –OH, making H difficult to dissociate and decreasing the replacement extent for RE^{3+} (Table 6).

Table 6: The structure of acidic phosphate extractants and their properties for REE extraction [9].

Number	Structural formula	p*K*a	Extraction equilibrium constants(*K*)				Separation factor(α)	
			Nd	Sm	Y	Yb	Sm/Nd	Yb/Y
1	$(\text{iso-}C_8H_{17}O)_2P(O)OH$	2.74	6.8×10^{-3}	4.9×10^{-2}	1.0×10^{-1}	3.7×10^{-1}	7.2	3.7
2	$(\text{sec-}C_8H_{17}O)_2P(O)OH$	3.19	5.6×10^{-4}	6.4×10^{-3}	4.1×10^{-1}	3.3	11.4	8.0
3	$i\text{-}C_8H_{17}PO\ (OC_8H_17-i)_2$	4.09	8.4×10^{-5}	8.8×10^{-4}	1.4×10^{-1}	8.9×10^{-1}	10.5	6.4
4	$C_6H_5PO\ (OC_8H_17-i)$	2.99	2.2	4.2×10	1.7×10^3	2.2×10^{-4}	19.1	12.9
5	$\text{Cyc-}C_6H_{11}PO\ (OC_8H_17-i)$	3.87	1.6×10^{-3}	2.8×10^{-2}	3.4	3.5×10	17.5	10.3
6	$(\text{iso-}C_8H_17)_2\ PO(OH)$	5.45	4.0×10^{-8}	3.2×10^{-9}	4.1×10^{-5}	6.1×10^{-4}	8.0	14.8
7	$(n\text{-}C_8H_17)_2\ PO(OH)$	5.71	1.2×10^{-4}	1.8×10^{-3}	4.1×10	1.8	15	4.4
8	$(\text{iso-}C_8H_{17}O)PO(OH)_2$	3.60	6.7×10^{-4}	2.2×10^5	6.4×10^{-4}	2.0×10^5	3.3	3.1
9	$(\text{iso-}C_{18}H_{37}O)PO(OH)_2$	9.10	3.8×10^5	4.1×10^5	2.9×10^5	9.8×10^5	1.1	3.4
10	$\text{iso-}C_8H_{17}PO(OH)_2$	4.7210.40	3.7×10^{-3}	1.2×10^{-4}	6.3×10^3	8.1×10^{-3}		
11	$\text{iso-}C_{18}H_{37}PO(OH)_2$	3.889.37	7.6×10^2	1.3×10^3	9.4×10^2	4.3×10^3	1.6	4.6

3.2.3 Oxygen-containing organic extractants

Some alcohols, ketones and carboxylic acids can also be used as the extractants for REEs (Table 7). RE^{3+} is a hard acid; oxygen-containing organic extractants are hard bases, and they can form complexes according to HSAB theory, while the extraction mechanisms are different. For alcohols, ketones, ether and ester, RE ions are extracted by oxygen-based coordination or hydrogen bonding. For carboxylic acids, RE ions are extracted by ion exchanging between H^+ and RE ions; the acidity affects the extraction significantly; to decrease the water solubility of the carboxylic acids, carbochain of C_7–C_9 are usually employed, and carbochain longer than C_{10} is unsuitable for the extraction due to the decreasing *K*a. Fatty acid with branched-chain exhibits good extraction selectivity, along with steric effect.

Table 7: Some oxygen-containing extractants for REEs.

Name	Structural formula	Trade names and abbreviation	Solubility (H_2O, g/L)
Naphthenic acid	$R_1R_2R_3R_4C_5H_{10}(CH_2)nCOOH$	Naphthenic acid, nphthanic	0.09

Versatic acid	$R_1R_2C(CH_3)COOH$	C547, Versatic911	2.50
Methyl isobutyl ketone	$CH_3CH(CH_3)CH_2COCH_3$	4-Methyl-2-pentanone, MIBK, hexone	19.1
sec-Caprylic alcohol	$C_6H_{13}CH(CH_3)OH$	2-Octanol, octanol 2	1.0
$\beta-$Primary alcohol	$RCHRCH_2OH$	A1416	

3.2.4 Nitrogen-containing compounds

Amine-based extractants are one of the most useful nitrogen-containing extractants for RE ions, including primary amines, secondary amines, tertiary and quaternary ammonium salts. Organic amines with molecular weight of around 250–600 are suitable for the extraction of RE ions because they are insoluble in water; they can form stable salts in strong acid and the anion exchange ability in salts follow the order of $ClO_4^- > NO_3^- > HSO_4^- > F^-$; they form associated complex with RE anionic complex and can be extracted by organic solvents, thus amine-based extractants are also called as liquid ionic extractants.

$$RE^{3+} + 6NO_3^- + 3R_3NH^+NO_3^- \quad \text{or}$$
$$R_4^+NNO_{3(O)} = [(R_3NH^+ \text{ or } R_4^+N)_3(RE(NO_3)_6^{3-})]_{(O)} + 3NO_3^-$$

Quaternary ammonium salts can extract RE anionic complex in acidic or neutral solution. Table 8 lists some nitrogen-containing extractants for RE ions.

Table 8: Some nitrogen-containing extractants for REEs.

Name	Structural formula	Trade names and abbreviation	Solubility (H_2O, g/L)
Se-carbon primary amine	$(C_nH_{2n+1})_2CHNH_2$ ($n = 9$–11)	N1923, AH:9	0.04
Multi-branched hexadecyl tertiary carbon primary amine	$CH_3C(CH_3)_2[CH_2C(CH_3)_2]_3NH_2$	N116, Prirnene JM.T	0.05 g (0.5 mol/L H_2SO_4)
N-Dodecenyl (trialkyl methyl) amine	$CH_3[C(CH_2)_2CH_2]_2C(CH_3)_2$ $NHCH_2CHCH(CH_2C(CH_2)_2)\text{-}CH_3$	AmberliteL A-1	0.015–20 g (0.5 mol/L H_2SO_4)
N-Lauryl (meth alkyl) amine	$C(R_1)(R_2)R_3NHCH_2(CH_2)_{10}CH_3$	AmberliteL A-2	
Dioctylamine	$(CH_3(CH_2)_7)_3N$	N204, TOA, and TNOA	
Triisooctylamine	$(CH_3C(CH_3)_2CH_2CH(CH_3)CH_2)_3N$	TIOA	
Triheptylamine	$(C_7H_15)_3N$	N208	
Tribromoaniline	$(C_6H_5CH_2)_3N$	TBA	
Trialkylamine	$(C_nH_{2n-1})_3N$, $n = 8$–10	N235, Alamine336	0.01
Chloride methyl trialkyl amine	$[(C_nH_{2n-1})_3NCH_3]Cl$, $n = 6$–10	N263, Aliquat336	0.04

The separation performance of primary amine is unsatisfying to single RE, and the extraction of La to Sm by primary amine can be easily obtained while the extraction efficiency is decreased after Sm. Li et al. [10] used N1923 to extract REEs from sulfuric acid matrix, and found that the extraction efficiency of REEs decreases as atomic number increases, exhibiting “tetrad effect”; while in perchloric acid medium, the extraction efficiency of REEs increases as atomic number increases, also exhibiting “tetrad effect” [11]. Secondary amine, e.g., N235, is mainly octyl, similar to trioctylamine, and can extract REEs in the presence of salting-out agents. Trioctylamine as a colorless viscous liquid is soluble in organic solvents, and its applications in metal ions extraction is reviewed [12].

N263, trialkyl methyl ammonium chloride, consisting of 8–10 carbon atoms in its alkyl carbon chain, is a quaternary ammonium salt that frequently used in REEs extraction. Its performance and composition are similar to Aliquat336. It is a viscous liquid, with high extraction capacity and excellent selectivity, and is suitable for a variety of inorganic acid system. The distribution ratio of REEs in the N263-$LiNO_3$ system is decreased with increasing the atomic number of REEs, showing an “inverted order” (Table 9); while a “positive sequence” is obtained in the N263-NH_4SCN system (Table 10). For amine extractants, the effect of their structure and spatial effects on the extraction efficiency is also very significant.

Table 9: Distribution ratio of REEs in N263–nitrate system.

RE^{3+}	La	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Distribution ratio (D)	4.4	4.0	1.59	0.41	0.15	0.13	0.13	0.086	0.058	0.022	0.021	0.013	0.031
Separation factor (α_{RE}/γ)	140	128	50.7	13.2	4.8	4.3	4.2	2.7	1.86	0.70	0.67	0.43	

Note: HNO_3, 0.1 mol/L; N263, 400 g/L; V(o)/V(aq) = 4:1.

Table 10: Distribution ratio of REEs in N263–thiocyanic acid system.

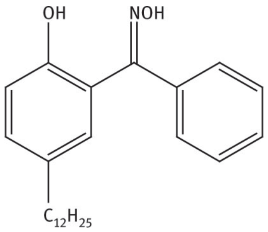
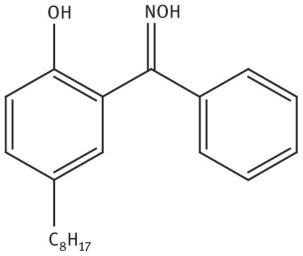
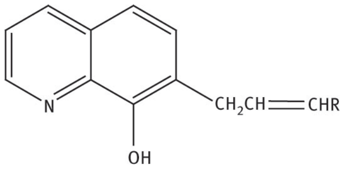
RE^{3+}	La	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Distribution ratio (D)	0.52	1.09	1.29	2.06	7.19	3.05	3.30	4.76	7.26	17.87	30.94	59.30	2.14
Separation factor (α_{RE}/γ)	0.25	0.51	0.60	0.96	3.36	1.43	1.55	2.23	3.40	8.32	14.5	27.8	

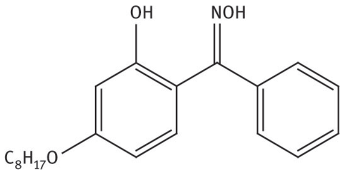
Note: NH_4NCS, pH = 1; N263, 0.7 mol/L; $V(o)/V(aq)$ = 4:1.

3.2.5 Chelate extractant for REEs

Chelate extractants can form stable electrically neutral complex with RE ions which can be extracted by organic solvents. Besides β-diketones (e.g., acetylacetone, thenoyltrifluoroacetone [TTA], 1-phenyl-3-methyl-4-benzoylpyrazolone [PMBP]), homologs of 8-hydroxyquinoline and ketoxime derivatives (Table 11) are also commonly used chelating extractants for REEs.

Table 11: Some chelating agent for REEs extraction.

Name	Structural formula	Trade names and abbreviation	Solubility (H_2O, g/L)
Lauryl hydroximic acid	$i\text{-}C_{11}H_{23}CONHOH$	H106	0.02
5,8-Diethyl-7-hydroxy-6-dodecanone oxime	$CH_8(CH_2)_3CH(C_2H_5CH(OH)C(NOH)$ $CH(C_2H_5)(CH_2)_3CH_3$	N509, LIX-63	
2-Hydroxy-5-dodecyl benzophenone oxime		3045, LIX64	
2-Hydroxy-5-octyl benzophenone oxime		N510	0.005
2-Hydroxy-5-sec-octyl oxy benzophenoneoxime		N530	0.001

7-Dodecenyl-8-hydroxyl-quinoline		N601, Kelex100	0.003

TTA, colorless acicular crystal, is soluble in benzene, methylbenzene and other organic solvents. And RE^{3+} can be extracted by TAA at pH 3–4 (Table 12). TTA is usually employed to synergistically extract REEs with other solvents such as ethylenediamine, 2,2,2-terpyridine and neutral phosphorus reagents.

Table 12: Extraction constants for REEs extraction by PMBP and TTA [13].

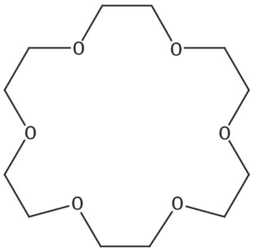
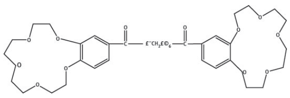
RE^{3+}	La	Ce	Pr	Nd	Pm	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
pK_α (TTA)	10.51	9.45	8.85	8.58	8.06	7.68	7.57	7.51	7.03	7.25	7.2	6.96	6.72	6.77	
pK_α (PMBP)	7.194.40	6.56	5.81	5.67		5.00	4.77		4.42				3.89		

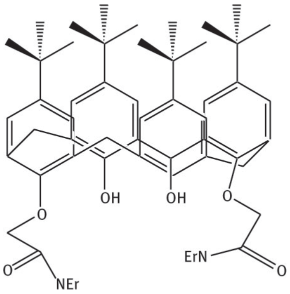
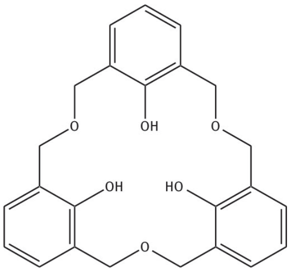
PMBP [5] is also a good β-diketone reagent for REEs extraction, with higher extraction capacity, acidity and faster reaction dynamic compared with TTA, and it has become one of the main extraction agent for the separation and preconcentration of REEs. 1-pheny-3-methyl-4-acetyl-pyrazolone is a homolog of PMBP, and the extraction efficiency of heavy REEs could reach more than 90 % under pH3. Oxime and hydroxylamine compounds have been investigated for heavy REEs extraction. Haraguchi et al. [14] synthesized several *N*-phenyl hydroxamic acid, among them, 2-hexyl-*N*-phenyl-decyl hydroxyl oxime acid is considered as the most suitable agent for the extraction of heavy REEs; the extraction capacity of *N*-*p*-methoxybenzoyl, -*p*(*n*, *iso*, *t*)-butylbenzoyl, -propoxybenzoyl, -*m*-nitrobenzoyl, -*m*-cyanobenzoyl-*N*-phenylhydroxylamine for REEs was discussed, along with, the effects of substituent in extractant molecules and the acidity of the reagents on the separation factor between REEs; it was found that the smaller the pK value of the extractant is, the greater the extraction constant is [15–18].

3.2.6 Supramolecular extractants and others

Crown ethers and calixarenes are supramolecular compounds which can be used for the complexing and extraction of REEs [19, 20]. In the presence of counter anions, 18-crown-6 and benzo15-crown-5 exhibit very high extraction efficiency for REEs; Inoue et al. [21] used dicrown ether to extract REEs-picric acid complexes, and the extraction efficiency was increased. Calixarene has also been studied for the extraction of REEs [22], and some supramolecular compounds as REEs extractants are listed in Table 13. Calixarene 1,3-bis(diethylamide)generation of calixarenes [4] exhibits a high extraction efficiency for REEs, which is 20–22 % higher than that obtained by crown ether and dicrown ether.

Table 13: Some supramolecular as REEs extractants.

Name	Structural formula	RE^{3+}	Counter anion	Solvent	Ref.
18-Crown-6		La–LuLa–Ga	ClO_4^- Picric acid	$CH_2Cl_2CH_2Cl_2$	[20][23]
Octanedione 1,8-bis(4-benzo-15-crown-5)		La–Gd	Picric acid	CH_2Cl_2	[21]

1,3-bis(ethylenedioxy amide) is substituted calixarene		La–Lu	Picric acid	CH_2Cl_2	[24]
Hexahomotrioxacalix [3]arene		Sc, La, Y and Lu	DMSO		[25]

Sulfoxide with S–O bond is also a good extractant for REEs. Among them, dimethylsulfoxide was one of the most commonly used, which can form ionic associates soluble in benzene in the presence of anions, such as ClO_4^- or SCN^-. Besides, pentylsulfoxide, di-*n*-octylsulfoxide and tetramethylenesulfoxide were also effective in REE's extraction. Bis (2-ethylhexyl) sulfoxide can extract REE-SCN^- complex into benzene.

Light REEs can be extracted by employing crown ether 18-crown-6 [26] and benzo-15-crown-5 [27]; with the existence of pentadecafluorinecaprilate, light REEs could be extracted by 18-crown-6 in ionic association form [28].

3.3 Extractant concentration and extraction equilibrium constant

Distribution coefficient (D) is proportional to nth power of free extractant concentration; if free extractant concentration is increased by two times, D is increased by 2^n times. When P204 is used for the extraction of RE ions, D is proportional to 3 power of the concentration of P204 dimer; the increase of the concentration of the extractant is beneficial to the extraction of interesting ions.

The higher the stability constant for the complex is formed by REE ions and the extractant, the complex is more stable and more easily to be extracted. Given a specific extractant for the extraction of RE ions, the stability of the complex is related to the charge and radius of RE ions. For RE ions with the same valence, the radius decreases with the increase of the atomic number, and the formed complex stability and extraction equilibrium constant increase with the increase of atomic number (Table 14), while the separation factors for the neighboring RE ions are not increasing with the increase of atomic number (Table 15). Thus, the extraction efficiency of REE ions and the separation factors for neighboring RE ions should be considered simultaneously, and the latter is sometimes more important.

Table 14: Extraction equilibrium constants (K) for REE extraction by P204.

RE^{3+}	**Pm**	**Sm**	**Eu**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**	**Lu**	**Y**
log K	–1.73	–0.95	–0.83	0.4	0.88	1.25	1.75	2.27	2.94	1.63

Table 15: Separation factor for REE extraction by P204.

REE pair	**Ce/La**	**Pr/Ce**	**Nd/Pr**	**Pm/Nd**	**Sm/Pm**	**Eu/Sm**	**Gd/Eu**
Separation factor	2.8	1.5	1.3	2.7	3.2	2.2	1.5
REE pair	**Tb/Gd**	**Dy/Tb**	**Ho/Dy**	**Er/Ho**	**Tm/Er**	**Yb/Tm**	**Lu/Yb**
Separation factor	5.3	2.8	2.2	3.0	3.5	3.0	2.0

3.4 Medium pH

In acidic complex extraction system for REEs, the effect of pH on D of REE ions in two phases is very obvious. Within a specific acidic complex extraction system, D will increase by $10n$ times (n is the valence of RE ions) when pH is increased by 1 unit. If the volume of two phases are the same, when $D = 1$, half of RE ions are extracted, and the pH is called half extraction pH value, denoted by $\mathrm{pH}_{1/2}$.

$$\mathrm{pH}_{1/2} = -1/n \log K - \log(\mathrm{HL})_\mathrm{o}$$

where K is the extraction equilibrium constant and $(\mathrm{HL})_\mathrm{o}$ is the concentration of extractant (HL) in organic phase. As can be seen, the higher K or $[\mathrm{HL}]_\mathrm{o}$ is, the lower the $\mathrm{pH}_{1/2}$ is, indicating RE ions can be extracted more easily. So $\mathrm{pH}_{1/2}$ is used to show the extraction ability for metal ions with the same valence. The $\mathrm{pH}_{1/2}$ for Y extraction by naphthenic acid is the highest among other ions (Table 16), indicating D of Y is the lowest.

Table 16: $\mathrm{pH}_{1/2}$ for RE ions extraction by naphthenic acid.

RE^{3+}	**La**	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Y**
$\mathrm{pH}_{1/2}$	3.95	3.89	3.78	3.74	4.1	3.73	3.62	3.76	–	3.73	3.97	3.84	3.92	4.02	–	4.30

P204 and P507 are specific representatives of acidic phosphorus extractants. The extraction ability of P204 is increasing with the increasing of the atomic number of REE (Table 17), and the difference between light and heavy REEs is obvious. P204 form dimeric polymer through hydrogen bonding in nonpolar solvents (e.g., benzene, CCl_4), REE ions coordinates with three dimers by replacing three H in it and form neutral six coordinate complex, which is easily dissolved in organic solvents, with the extraction mechanism of cation exchange. In the nitric acid or hydrochloric acid matrix, the extraction efficiency of P204 for REEs will decrease with the increase of the matrix acidity. The basic structure of P507 is similar to that of P204, the reaction for the extraction of REEs is similar along with the performance variation. Due to the C–P bond in P507, the extraction ability of P507 is lower than that of P204, while P507 is featured with easy back-extraction and uneasy emulsification.

Table 17: Distribution ratio and separation factors (α) of REEs (III) by P204[1].

RE(III)	**La**	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**
D	1.3×10^{-4}	3.6×10^{-4}	5.4×10^{-4}	7.0×10^{-4}	1.9×10^{-4}	5.9×10^{-4}	0.013	0.019
$a_{Z_{n+1/n}}$	2.8	1.5	1.3	2.7	3.2	2.2	1.6	5.3
RE	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Y**
D	0.100	0.28	0.62	1.4	4.9	14.7	39.4	1.00
$a_{Z_{n+1/n}}$	2.8	2.2	3.0	3.5	3.0	2.0		

3.5 Salting-out agent

In a neutral complex extraction system (e.g., REEs extraction by TBP), the extraction efficiency would be improved by adding salting-out agents (e.g., $LiNO_3$, NH_4NO_3), because the concentration of NO_3^- would be increased with the addition of salting-out agents, benefiting the increasing of D. Additionally, the hydration of salting-out agents would decrease the concentration of free water molecules in the extraction system, reducing the concentration of hydrated RE ions and increasing the activity of RE ions.

Dimethyl methyl phosphate heptyl ester (P350) presents much better performance for REEs extraction than TBP, the effect of concentration of salting-out agents $LiNO_3$ on D and separation factor (α) in the separation of La and Pr is very significant (Table 18).

Table 18: Effect of $LiNO_3$ on the extraction of La^{3+} and Pr^{3+} by P350.

	Distribution ratio		
$LiNO_3$(mol/L)	**$D(Pr^{3+})$**	**$D(La^{3+})$**	**Separation factor (α) Pr^{3+}/La^{3+}**
1	0.201	0.151	1.33
2	0.426	0.155	2.72
3	0.594	0.186	3.19

4	0.697	0.183	3.81
5	1.28	0.240	5.34
6	1.47	0.254	5.78

In the ion association complex extraction system, the addition of salting-out agents would also help the extraction of REE ions (Table 19). In the extraction of REE ions by N263, salting-out agents can participate the ion association complex formation as reactants, and increase the average activity coefficient of $RE(NO_3)_n$. On the other hand, salting-out agents as complexing agents can improve the complexing of REE, and decrease the distribution ratio.

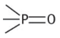
Table 19: Effect of salting-out agents on the extraction efficiency of Eu^{3+}

$Al(NO_3)_3$		**$LiNO_3$**		**NH_4NO_3**	
***C* (mol/L)**	**EE (%)**	***C* (mol/L)**	**EE (%)**	***C* (mol/L)**	**EE (%)**
0.2	2.2	0.6	3.6	2.0	16.6
0.4	12.2	1.2	18.9	4.1	51.1
0.8	62.1	2.4	74.5	5.1	67.1
1.2	92.7	3.7	95.9	7.1	88.8
1.6	98.8	4.9	99.5	8.2	94.0

C, Concentration; EE, extraction efficiency.

3.6 Extraction systems for REEs and their application

3.6.1 Neutral complex extraction system

In this extraction system, the extracted RE complexes are neutral salts such as $RE(SCN)_3$ and $RE(NO_3)_3$, and the employed extractants are neutral organics such as TBP and trioctylphosphine oxide (TOPO).  in neutral extractants would complex with RE ions and form insoluble neutral complexes such as $La(NO_3)_3{\cdot}3TBP$ and $Ce(SCN)_3{\cdot}4TOPO$ which can be extracted by organic solvents. The neutral extraction system is discussed as follows by using extraction REEs with TBP as the representative:

$$\begin{gathered} RE^{3+} + 3NO_3^- + 3TBP \rightarrow RE(NO_3)_3 \cdot 3TBP \\ \text{The equilibrium constant}(K)\,K = \frac{[RE(NO_3)_3{\cdot}3TBP]}{[RE^{3+}][NO_3^-]^3[TBP]^3} \end{gathered} \tag{1}$$

The distribution coefficient (D) of REE ions between two phases:

$$D = \frac{[RE(NO_3)_3 \cdot 3TBP]}{[RE^{3+}]} \tag{2}$$

Combining eqs (1) and (2),

$$D = K[NO_3^-]^3[TBP]^3 \tag{3}$$

As can be seen, D of REE ions between two phases is proportional to the equilibrium constant, the concentration of NO_3^- in aqueous phase and concentration of TBP in organic phase under equilibrium condition. The size and charge of RE ions also affect the extraction process, and D for RE^{4+} is higher than the corresponding RE^{3+}; for RE^{3+}, the smaller the radius, much more stable for the formed RE complexes. The order of the D for REEs extraction by TBP is as follows: Lu > Yb > Tm > Er > Ho > Dy > Y > Tb > Gd > Eu > Sm > Pm > Nd > Pr > Ce > La. In other words, D increases with the increase of atomic number, or with the decrease of atomic radius. The effect of NO_3^- concentration in aqueous phase on the extraction of light and heavy REEs is different [29].

3.6.2 Acidic complex extraction system

In acidic complex extraction system, organic weak acid (HL or H_2L) acts as the extractants, which can be chelate extractants (e.g., β-diketones), acidic phosphorus extraction agent (e.g., P204) or carboxylic acid (e.g., naphthenic acid). The extraction mechanism is based on the cation ions exchange between RE ions and H^+ in the employed extractants, and the hydrophobic complex formed by RE ions and the extractant is extracted into the organic solvents. P204 is a commonly used extractant for REEs extraction and separation, the reaction is as follows.

$$RE^{3+} + 3H_2L_{2(O)} = RE(HL_2)_{3(O)} + 3H^+$$

The extraction equilibrium constant (K):

$$K = \frac{[RE(HL_2)_3]_{(o)}[H^+]^3}{[RE^{3+}][H_2L_2]^3_{(o)}} \tag{4}$$

The distribution ratio (D) of REE ions between two phases:

$$D = \frac{[RE(HL_2)^3]_{(o)}}{[RE^{3+}]} \tag{5}$$

Substituting eq. (4) into eq. (5),

$$D = \frac{K[H_2L_2)]^3_{(o)}}{[H^+]^3} \tag{6}$$

For REE ions with any valence, eq. (6) is changed into

$$D = \frac{K[HL]^n_{(o)}}{[H^+]^n} \tag{7}$$

Taking the logarithm on both sides of the formula

$$\log D = \log K + n\log[HL]_{(o)} + n\text{pH} \tag{8}$$

Equation (8) is the basic formula for acidic extraction system for REEs.

Butyric acid, α-ethylbutyric acid, α-chloro fatty acid can be used to extract and separate REEs from non-REEs. The distribution ratio of REEs during the extraction by α-ethylbutyric acid shows “tetrad effect” with the increasing of their atomic numbers.

PMBP–benzene could extract REEs and Th into organic phase under pH 5.5, and the extracted REEs can be back-extracted by 2–3 mol/L formic acid, while Th left in the organic phase which can be back-extracted by 2.4–6 mol/L HCL. By using Arsenazo III, the determination of Th and REEs could be achieved simultaneously in one sample. In the solution of 15 % ammonium thiocyanate and 60 % sulfosalicylic acid, PMBP–benzene solution also can be used to separate REEs from a large amount of common elements under pH 5–5.7. After back-extracted by 0.01 mol/L HCl, the trace REEs in the steel and alloy could be determined by the arsenazo III spectrophotometry [30].

With P204 as the extractant, crude separation of yttrium and heavy REEs from light REEs groups in sulfuric acid system could be achieved by changing pH, extractant concentration and extraction series. Heavy REEs could be separated from light REEs in 0.7–0.9 mol/L HNO_3 by using P204-benzene extractant. In the extraction of REEs from 0.1 mol/L HCl into toluene by using 2-ethylhexyl-(3-pentadecylphenyl)phosphate acid, it could be found that the extraction of heavy REEs was better than medium and light REEs and the obtained extraction efficiency was higher than that obtained by other organophosphorus extractants [31]. Bis(4-dicyclohexyl)phosphate acid (D4DCHPA)–xylene can also be used for REEs group separation [32].

3.6.3 Ion association complex extraction system

The extractants used in this system are organic amines and quaternary ammonium salt or oxygen-containing ketones, alcohols and ether, the extracted compounds are RE complex cations or anions. Organic amines associate with RE complex anions by ammonium, and oxygen-containing organic solvents associate with RE complex anions, forming associated complex which can be extracted into organic solvents. During the extraction process, the exchange between anions and anions occurs, and the extraction system and affecting factors are discussed as follows by using extraction of Nd^{3+} by N263 as the representative.

Before use, N263 is transformed into methyl trialkyl ammonium nitrate by nitric acid or nitrate, and the reaction is

$$Nd^{3+} + 3NO_3^- + 3/2(R_3CH_3N^+NO_3^-)_2 = Nd(NO_3)_3 \cdot 3(R_3CH_3N^+NO_3^-)$$

The effect of acidity on the reaction is complicated because there are a variety of existing species of the complex anions and the extractant which affected by the acidity. Increasing the concentration of nitric acid help the formation of Nd $(NO_3^-)_{3-6}$ and the extraction; while $R_3CH_3N^+ \cdot NO_3^- \cdot H_3O^+ \cdot NO_3^-$ forms with the increase of nitric acid concentration, decreasing the concentration of $R_3CH_3N^+ \cdot NO_3^-$ and deteriorating the extraction. Thus, the effect of acidity in a certain range on the extraction of RE ions is negligible. High concentration of the extractant is beneficial to REE extraction, while polymerization would occur among the extractants, worsening the separation factors between RE ions.

Above all, in the ion association complex extraction system, the extraction by using quaternary ammonium salts can be performed in diluted acidic matrix; the oxygen-containing organic extractants exhibit good extraction performance for REEs under high acidity and the extraction efficiency is affected by the acidity significantly.

N263–xylene was used to separate REEs in the steel from other coexisting elements, while the interference of Zr was masked by adding EDTA before extraction. Benzyl chloride dimethyl myristyl ammonium and 2,3-naphthalenediol–chloroform solution were used to extract REEs from sodium acetate buffer based on ionic association reaction, followed by ICP-OES detection [33].

3.6.4 Synergistic extraction system

As early as in 1954, it was found that the distribution ratio for RE ions obtained by using TTA and TBP simultaneously is higher than the sum of the distribution obtained by either of them. With the development of extraction chemistry, the synergistic extraction of REEs has been getting more and more attention. The synergistic extraction system consisting of TTA and neutral phosphorus extractants is the most concerned one, three extraction systems as mentioned above can all be involved in the synergistic extraction system (Table 20). The system combining acidic chelating with neutral complexing also exhibits significant synergistic effect.

Table 20: Classification of the synergistic extraction system.

Classification		Example
Dual heterogeneous synergistic extraction system	Chelating and neutral complexing	$Eu^{3+}/H_2O–HNO_3/TTA + TBP$ (cyclohexane)
	Chelating and ion association	$Th^{4+}/HCl + LiCl/TTA + TOA$ (benzene)
	Neutral complexing and ion association	$PuO_2^{2+}/H_2O-HNO_3/TBP+TBAN$ (kerosene)
Dual homogeneous synergistic extraction system	Chelating synergistic extraction	$RE^{3+}/H_2O–HNO_3//HA + TTA$ (benzene)
	Neutral complexing synergistic extraction	$RE^{3+}/H_2O–HNO_3//TBPO + TOPO$ (kerosene)
	Ion association synergistic extraction	$Pa^{3+}/H_2O–HCl/RCOR + ROH$
Other synergistic extraction system	Ternary system involving chelating, neutral complexing and ion association	$UO_2^{2+}/H_2O - H_2SO_4/D2EHPA + TBP +$ R3A(kerosene)

The mechanism for synergistic extraction is complicated. For the synergistic extraction system involving acidic and neutral extractants, it is based on adducting and substitution mechanism, also affected by the size, charge and coordination geometry of the ion (Table 21).

Table 21: Synergistic extraction of REEs by β-diketones and TBP.

RE^{3+}	Extractants (cyclohexane as the solvent)					
	HFA–TBP		TAA–TBP		FHD–TBP	
	log	log *K*	log	log *K*	log	log *K*
Eu	10.84	5.05	–	–2.22	10.00	10.06
Nd	10.50	4.35	–	–2.77	9.96	9.95
Tm	10.76	4.63	–	–2.62	10.20	10.47

The system of TTA–TBP was applied for the separation of Eu^{3+} from Am [34]. PMBP–TOPO–benzene system can be effectively used to separate REEs, U and Th from niobite [35]. The extraction performance of the 5, 7-

dichloro-8-hydroxyquinoline–chloroform solution for REEs (La, Eu and Lu) could be improved in the presence of tetrabutyl ammonium or TOPO [36].

4 Liquid phase microextraction

LPME is developed based on LLE [37, 38]. Compared with traditional LLE, LPME is environmentally friendly with the consumption of very small amount of organic solvent (only a few microliters or tens of microliters); the operation of LPME is much simpler, avoiding time-consuming step in LLE; and LPME can provide a comparable or even better enrichment factor (EF). LPME integrates the sampling, extraction and concentration in one step, and can be easily combined with various modern analytical instruments (e.g., HPLC, CE, GC, GFAAS). It has been employed in the fields of environmental monitoring, food safety and pharmaceutical analysis.

In 1996, Liu and Dasgupta [38] reported a drop-in-drop system (Figure 1) to extract sodium dodecyl sulfate, in which a 1.3-μL microdrop of a water-immiscible organic solvent was immersed into a large flowing aqueous drop to accomplish the extraction process. At almost the same time, Jeannot and Cantwell [37] introduced a procedure that they termed solvent microextraction. In this configuration (Figure 2), a droplet of 1-octanol was held at the end of a Teflon rod and suspended in a stirred aqueous sample solution. After extraction, the Teflon rod was withdrawn from the aqueous solution; the organic phase was sampled with a microsyringe and injected into a GC system for analysis. One disadvantage of the aforementioned methods is that extraction and injection have to be performed separately with different apparatus. In order to overcome this shortcoming, Jeannot and Cantwell [39] developed a microextraction method in 1997, which was performed simply by suspending a 1-μL drop directly from the tip of a microsyringe needle immersed in a stirred aqueous solution containing target analytes, the post-extraction microdrop was retracted back into the microsyringe and transferred into GC for further analysis. In this configuration, the microsyringe served as both the solvent holder and the GC sampling injector, which make the extraction and injection integrated in a single device (Figure 3). This represents a desirable convenience of the microextraction operation, and led to the appearance of some new LPME configurations, such as single-drop microextraction (SDME) and hollow fiber (HF)-LPME.

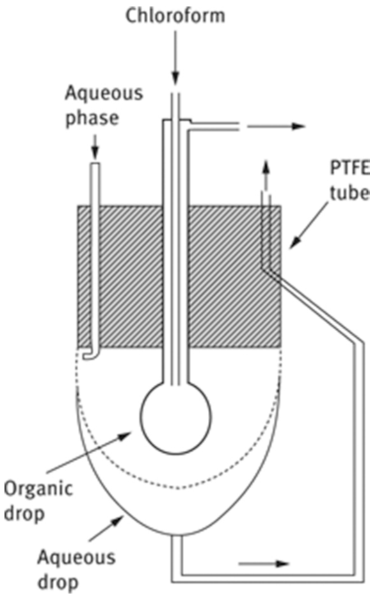


Figure 1: Schematic diagram of “drop in drop” system [38].

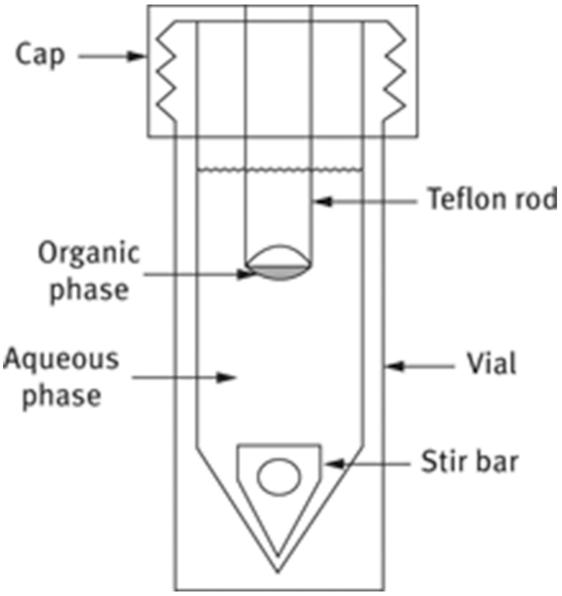


Figure 2: Schematic diagram of solvent microextraction based on Teflon rod [37].

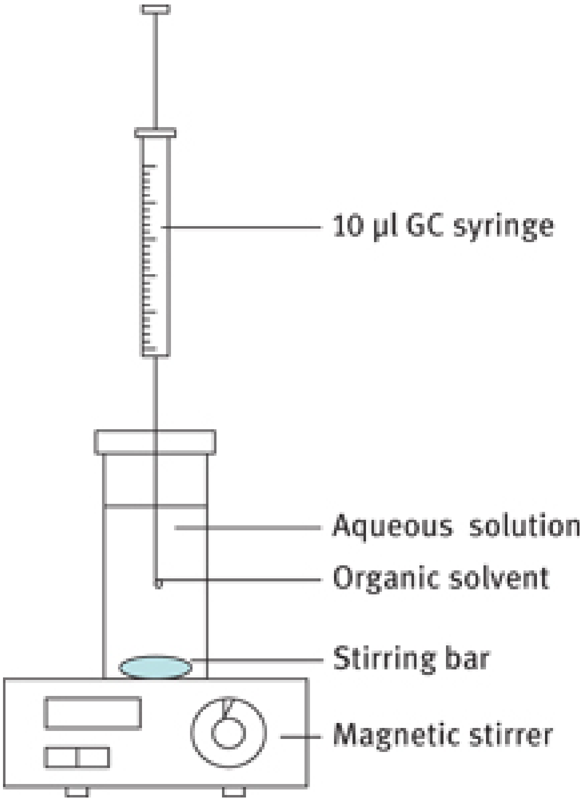


Figure 3: Schematic diagram of solvent microextraction based on microsyringe [39].

4.1 Operation modes and mechanism

To extremely decrease the volume of the extractant phase and simplify the experimental apparatus and operation procedure, analysts have spent a lot of energy on the configuration of experimental apparatus and exploration of microextraction mechanisms. So far, the most representative techniques in LPME include SDME, HF-LPME, dispersive liquid–liquid microextraction (DLLME) and solidified floating organic drop microextraction (SFODME).

4.2 Single-drop microextraction

In this extraction mode (Figure 6), the extractant is suspended on the needle tip of the microsyringe, and immersed in the sample solution, contacting directly with target analytes and sample matrix. Since the extraction medium is in the form of a single drop, this type of microextraction is called SDME. Direct-SDME or direct immersion (DI)-SDME, in which the extraction medium without any special supporter, is simple and inexpensive.

In direct-SDME, the analyte (A) is distributed between aqueous sample solution and organic solvent [40]:

$$\text{A(donor phase)} \longleftrightarrow \text{A(acceptor phase)} \tag{9}$$

The distribution coefficient of A between two phases ($K_{\text{org/d}}$) can be defined as

$$K_{\text{org/d}} = \frac{C_{\text{eq,ord}}}{C_{\text{eq,d}}} \tag{10}$$

where $C_{\text{eq,org}}$ and $C_{\text{eq,d}}$ are the concentration of A in organic phase (acceptor phase) and sample solution (donor phase), respectively, under equilibrium.

Then $C_{\text{eq,ord}}$ can be calculated by eq. (20):

$$C_{\text{eq,ord}} = \frac{K_{\text{org/d}} C_{\text{i}} V_{\text{d}}}{K_{\text{org/d}} V_{\text{org}} + V_{\text{d}}} \tag{11}$$

where C_{i} is the initial concentration of A in sample solution, V_{d} and V_{org} are the volume of sample solution and organic solvent, respectively.

As can be seen from eq. (20), a high $K_{\text{org/d}}$ is beneficial to the extraction.

The two-phase micro-extraction mode is only applicable to a strong or moderate lipophilic analyte ($K_{\text{org/d}} > 500$) instead of strongly hydrophilic analyte [40]; for acidic or alkaline analyte, the analyte should be existing in deprotonated form for extraction by adjusting sample pH to increase the partition coefficient.

To achieve the LPME of REE ions, PMBP–benzene was used as the extraction solvent (10 µL), and a 500-fold EF for La was obtained [41]. In this microextraction procedure as shown in Figure 4, perfluoroalkoxy (PFA) tubing was used to connect the extraction chamber, and a constant-flow pump and a 10-L microsyringe were employed to introduce the aqueous solution and extraction solvent, respectively. The sample solution was continuously pumped "around" the drop, allowing the analytes to be extracted efficiently. It is called continuous-flow microextraction. With some modification to the continuous-flow SDME setup that the waste outlet of tubing was placed into the sample reservoir, cycle-flow SDME was developed and successfully applied in the determination of trace metals in biological samples [42]. It allows further reduction in the sample size and non-attended operation since there is no danger of the sample vial running out.

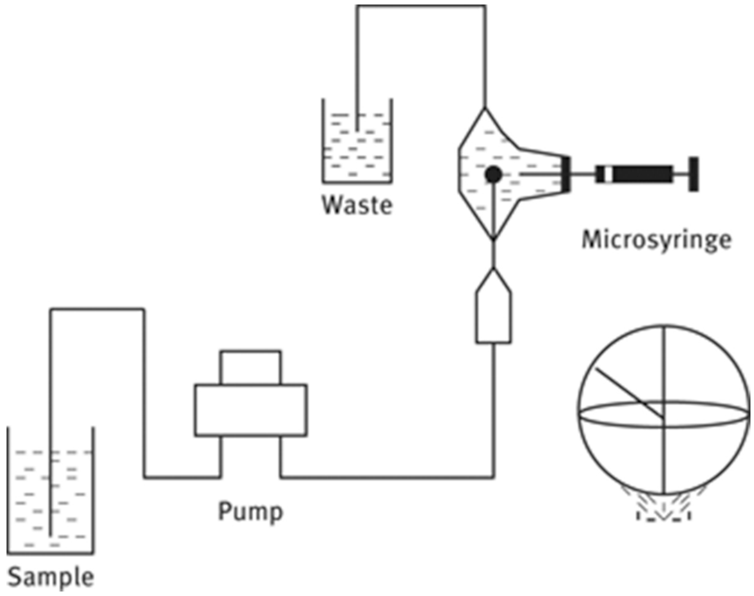


Figure 4: The experimental setup for continuous-flow SDME [41, 42].

Besides the two-phase microextraction mode mentioned above, Ma and Cantwell [43] combined solvent microextraction with simultaneous back extraction into a single microdrop, which was called three-phase (liquid–liquid–liquid) microextraction. As shown in Figure 5, *n*-octane was employed as an organic liquid membrane, confined inside a Teflon ring over a buffered aqueous sample solution. With the help of a microsyringe, a microdrop was left suspended inside the organic liquid membrane. The target analytes were initially extracted into the organic liquid membrane (neutral at high pH) and back extracted simultaneously into the acidic microdrop (protonated at low pH).

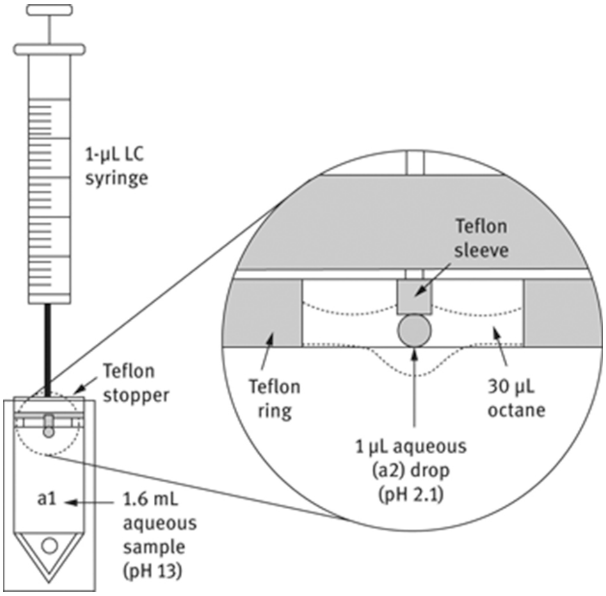


Figure 5: Schematic diagram of “Ma and Cantwell” type three-phase SDME [43].

In three-phase SDME, the analytes are extracted from an aqueous donor phase to an aqueous acceptor drop covered with an organic layer. Due to the large volume ratio between the sample donor phase and the acceptor drop as well as the thin organic layer, high EFs can be obtained with three-phase SDME in a short time. The convenience and efficiency of in-line coupling with some analytical instrument, e.g., CE, are additional advantages of three-phase SDME. Most acidic or basic analytes can be enriched by adjusting the pH to promote neutral forms of the analytes in the donor phase and their charged forms in the acceptor phase in three-phase SDME.

Besides the acidic or basic analytes, three-phase microextraction coupled with CE-UV was employed for the analysis of trace REEs by using 40 mmol/L PMBP as the extractant and 4 % (v/v) formic acid as back-extraction solution [44]. Under the optimized conditions, the LODs of REEs were in the range of 0.19–0.70 ng/mL. The developed method was successfully applied to the determination of trace amounts of REEs in water samples.

4.3 Hollow fiber liquid phase microextraction

SDME is simple, inexpensive, rapid and available for headspace extraction, whereas requires careful and elaborate manual operations to overcome the problem of drop dislodgment, which would deteriorate the reproducibility. Prolonged extraction times and faster stirring rates are unfavorable in SDME, since they typically result in drop dissolution and/or dislodgment. In order to solve this problem, in 1999, Pedersen-Bjergaard and coworkers [45] introduced a method named HF-LPME, in which the micro-extract is contained within the lumen of a porous hollow fiber. With the hollow fiber supporting/protecting the micro-extract, HF-LPME is much more robust than SDME with extra sample clean-up ability. Similar to SDME, HF-LPME can also be performed in both two-phase and three-phase microextraction modes. In the two-phase HF-LPME, the analyte is extracted from the aqueous sample into the organic phase immobilized in the pores and lumen of the hollow fiber. In the three-phase mode (hollow fiber liquid–liquid–liquid microextraction [HF-LLLME]), the analyte is extracted from the aqueous sample through the organic solvent immobilized in the pores of the hollow fiber into another aqueous phase (acceptor phase) presented inside the lumen of the hollow fiber.

4.4 Two-phase HF-LPME

Figure 6 presents the schematic diagram of two-phase HF-LPME. In this operation mode, the extractants immobilized in the pores and the lumen of the hollow fiber are the same organic solvent, and the analytes are extracted from the aqueous sample (donor phase) directly into the organic acceptor solution. The extraction mechanism is similar to that specified in the section of Direct-SDME. HF-LPME is the most used LPME mode and it can be applied for the analytes with solubility in an organic solvent immiscible with water substantially higher than that in an aqueous medium.

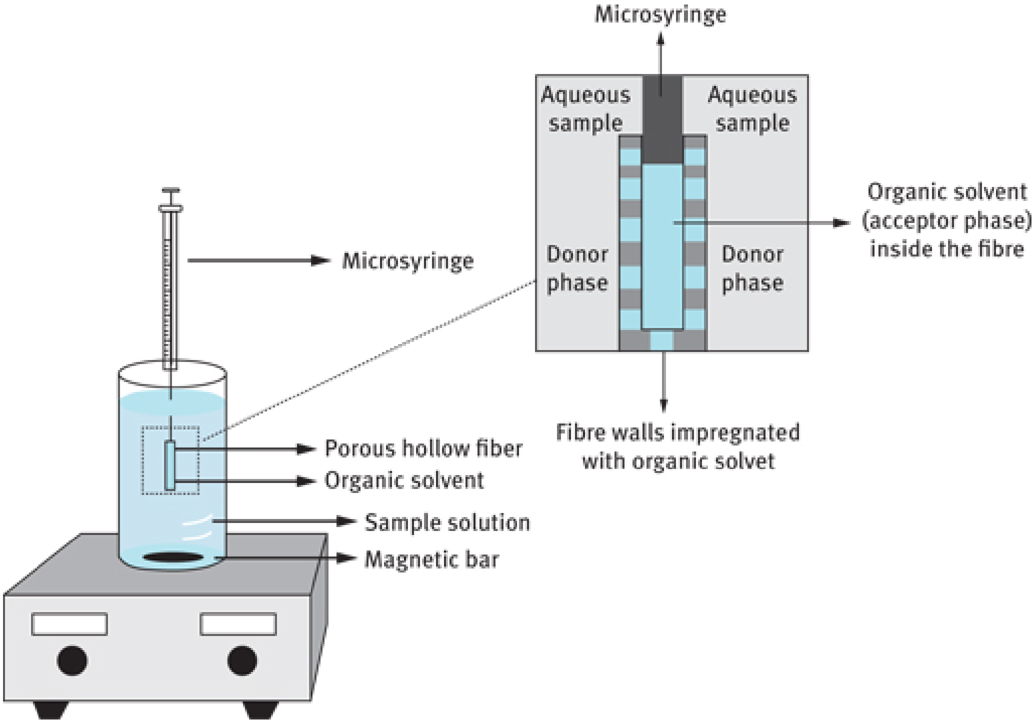


Figure 6: Schematic diagram of two-phase HF-LPME.

Compared with direct-SDME, two-phase HF-LPME is much stable and simple in terms of operation due to the accommodation and protection of the organic solvents in the hollow fiber.

4.5 Three-phase HF-LPME

Figure 7 presents the schematic diagram of three-phase HF-LPME, also called HF-LLLME. The analyte is extracted from aqueous sample solution through a thin phase of organic solvent inside the lumen of the pores of a polypropylene hollow fiber and finally into an acidic/alkaline acceptor solution inside the hollow fiber. Up to now, this extraction mode is limited to basic or acidic analytes whose solubility can be adjusted in the donor and acceptor solution, without application on the analysis of REEs. For example, in order to extract basic compounds, pH of the sample has to be adjusted into the alkaline region to suppress the solubility of the analyte in aqueous sample solution (donor phase), whereas pH in the acceptor solution should be low to promote the solubility of analyte in the acceptor phase. In this manner, the basic compounds may easily be extracted into the organic phase and further into the acceptor phase. And for acidic analytes, the pH adjustment is just reversed. Following extraction, the aqueous acceptor solution is directly injected into CE, HPLC/LC–MS or other detection techniques for subsequent analysis. In this three-phase system, the acceptor phase is aqueous, which is compatible with HPLC or CE analysis. The acceptor phase in three-phase HF-LPME can also be organic, involving two immiscible organic solvents immobilized in the pores of the HF and filled in its lumen, respectively.

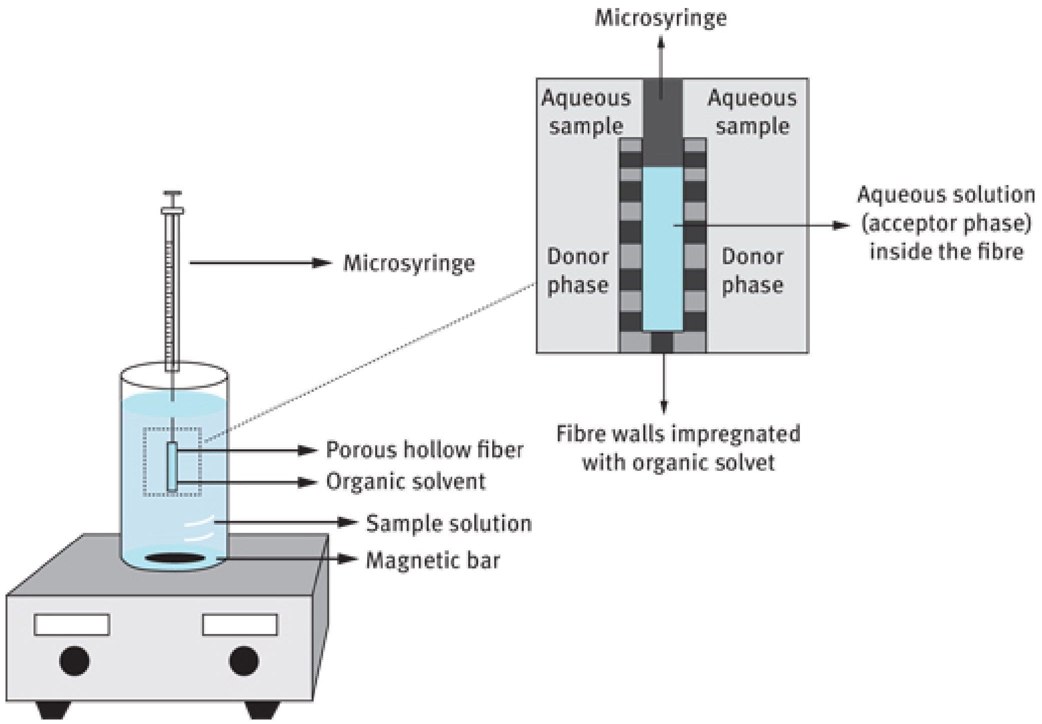


Figure 7: Schematic diagram of three-phase HF-LPME.

In three-phase HF-LPME, the extraction process of analyte (A) can be specified as follows [40]:

$$\text{A(donor phase)} \longleftrightarrow \text{A(organic phase)} \longleftrightarrow \text{A(acceptor phase)}$$

The distribution coefficient of A between organic phase and donor phase ($K_{\text{org/d}}$) and that between acceptor phase and organic phase ($K_{\text{a/org}}$) can be expressed as:

$$K_{\text{org/d}} = \frac{C_{\text{eq,ord}}}{C_{\text{eq,d}}} \tag{12}$$

$$K_{\text{a/org}} = \frac{C_{\text{eq,a}}}{C_{\text{eq,ord}}} \tag{13}$$

where $C_{\text{eq,a}}$ is the concentration of A in acceptor phase under equilibrium, and the total distribution coefficient of A between acceptor phase and donor phase ($K_{\text{a/d}}$) can be expressed as

$$K_{\text{a/d}} = \frac{C_{\text{eq,a}}}{C_{\text{eq,d}}} = K_{\text{org/d}} K_{\text{a/org}} \tag{14}$$

In the three-phase HF-LPME system, the extraction efficiency is not only affected by $K_{\text{org/d}}$, but also $K_{\text{a/org}}$, both of which determine the whole extraction process.

Under equilibrium, the concentration of A in acceptor phase ($C_{\text{eq,a}}$) can be calculated by

$$C_{\text{eq,a}} = \frac{K_{\text{a/d}} C_{\text{i}} V_{\text{d}}}{K_{\text{a/d}} V_{\text{a}} + K_{\text{org/d}} V_{\text{org}} + V_{\text{d}}} \tag{15}$$

where C_{i} is the initial concentration of A in sample solution (donor phase), and V_{d}, V_{a} and V_{org} are the volume of sample solution, acceptor phase and organic solvent, respectively.

4.6 Dispersive liquid–liquid microextraction

Based on ternary component solvent system, DLLME was introduced by Assadi and co-workers in 2006 [46]. The operation mode and required apparatus of DLLME are quite different from SDME and HF-LPME. Briefly, a mixture of a water-immiscible extraction solvent and a so-called dispersing solvent, miscible in both phases, is rapidly injected into the aqueous sample solution by a microsyringe, resulting in a cloudy solution which consists of fine particles of the extraction solvent dispersed in the aqueous phase. In this step, the disperser solvent could help the extraction solvent distributed homogeneously in the whole aqueous solution in a short time, resulting in a large contact area between extraction solvent and aqueous sample, and a consequent rapid attainment of extraction equilibrium. By centrifugation, a small volume of extraction solvent (containing the extracted target analytes) sedimented in the bottom of the conical test tube was obtained and then transferred for subsequent analysis (Figure 8).

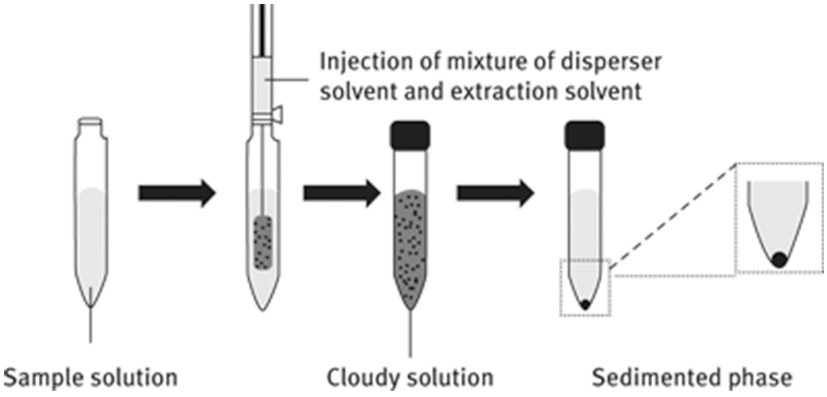


Figure 8: Schematic diagram of DLLME.

For DLLME, the extraction time is defined as the time from the injection of dispersant solution into the sample to centrifugation. Since the contact area between the extractants and the sample solution is quite large, the phase transition from water to the extraction phase is very fast. In DLLME, the EF is defined as the ratio of analyte concentration in the aqueous phase and extraction phase, and extraction recovery (R) (or extraction efficiency) is defined as the ratio of the total amount of analyte in the extraction phase and the aqueous solution. It can be expressed as

$$\mathrm{EF} = \frac{C_{\mathrm{sed}}}{C_{\mathrm{o}}} \tag{16}$$

$$R = \frac{C_{\mathrm{sed}} \times V_{\mathrm{sed}}}{C_{\mathrm{o}} \times V_{\mathrm{aq}}} \tag{17}$$

$$R = \frac{V_{\mathrm{sed}}}{V_{\mathrm{aq}}} \times \mathrm{EF} \tag{18}$$

where C_{sed} is the concentration of analyte in the extraction phase, V_{sed} is the volume of extraction phase, C_0 is the initial concentration of analyte in sample solution, V_{aq} is the volume of sample solution and R is extraction recovery (efficiency).

DLLME is a modified solvent extraction method, in which the extraction time is greatly reduced comparing with the other two methods mentioned above. The apparatus involved in the DLLME operation procedure just includes a microsyringe, a centrifuge and some conical test tubes. There is no need for magnetic stirrer, magneton for agitation, hollow fiber and no trouble in the possibility of extraction drop dislodgment. DLLME has some advantages such as simplicity of the operation, rapidity, low sample consumption, low cost, high recovery and high EF. Nevertheless, the reproducibility and anti-interference ability of DLLME are not very satisfactory.

The disperser solvent is required to be miscible with water and extractants, and acetone, methanol and acetonitrile are the mostly used disperser solvents. The extractants are usually required to be immiscible with water with higher density than water and good extraction capacity for target analytes.

Mallah et al. [47] used ionic liquids, 1-hydroxy-2,5-pyrrolidinedione (HYD), in a DLLME for determination of trace REEs in uranium dioxide powder. In this process, an appropriate mixture of extraction solvent and disperser solvent is rapidly injected into an aqueous sample containing Sm Eu, Gd and Dy complexes with HYD, and consequently a cloudy solution is formed. After centrifugation of this solution, the whole enriched phase was determined by ICP-OES. The experimental results indicate that the hexafluorophosphate anions with a partial ion exchange mechanism in ionic liquid solvents play a key role in the electrical neutralization of the lanthanoid complex in DLLME.

Chandrasekaran [48] developed a method based on DLLME and ICP-QMS for the simultaneous extraction and preconcentration of 14 REEs in groundwater. In this method, the REEs are complexed with 2,6-pyridinedicarboxylic acid (2,6-PDCA) in the presence of Aliquat-336 (tricaprylmethylammonium chloride), which enhanced the hydrophobicity of the ion-association complex, resulting in its improved extraction into chloroform. The extraction was carried out after adjusting the pH of the water sample to 4. The REE ions were back extracted from the chloroform layer with nitric acid for determination by ICP-QMS. Under optimum conditions, an average EF of 97 was obtained for 50 mL of water sample for ICP-QMS determination.

DLLME would provide relatively high EFs (e.g., 100-fold), while is generally suitable for water sample analysis due to limited anti-interference capability. Since SPE has excellent sample cleanup ability, DLLME has high EFs, and the desorption solvent of SPE matches the DLLME well, the coupling of SPE and DLLME will endow the dual extraction technique both excellent anti-interference ability and high EFs. Guo et al. [49] proposed a simple and efficient two-step method based on dispersive (D)-SPE and DLLME for the separation and preconcentration of 15 REEs from environmental water and sediment samples, followed by electrothermal vaporization (ETV)-ICP-MS detection. With Chelex 100 as the adsorbent of D-SPE, target REEs were first extracted and the retained REEs were then desorbed by 0.1 mol/L HNO_3. After 125 mmol/L Tris and 40 mmol/L PMBP were added into the above elution solution, target REEs were further preconcentrated into CCl_4 by DLLME. The developed dual extraction technique exhibited high EFs (234–566-fold) and good anti-interference ability.

4.7 Solidified floating organic drop microextraction

SFODME is another new LPME technique introduced by Khalili Zanjani et al. [50], in which small volume of an organic solvent with a melting point near the room temperature (in the range of 10–30°C) is floated on the surface of aqueous solution. The aqueous phase is then stirred for a prescribed period of time, and the sample is transferred into an ice bath. When the organic solvent is solidified, it is transferred into a small conical vial and the melted organic solvent is used for subsequent determination (Figure 9). Compared with conventional solvent extraction, it also has the advantage of great reduction in the amount of organic solvent and thus great enhancement of the EF. It is featured with simple operation, easy batch operation; high stirring rate sustainable, avoiding the problem of unstable drop in SDME and easy separation of organic phase and water phase after solidification.

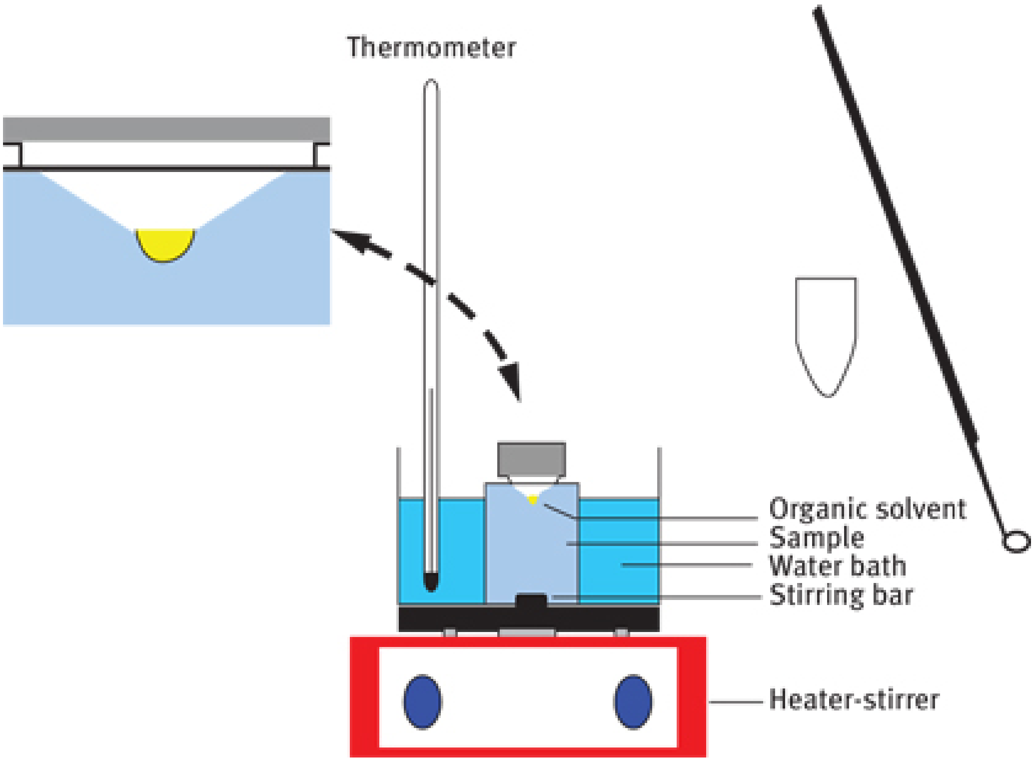


Figure 9: Schematic diagram of SFODME apparatus [50].

SFODME is based on equilibrium extraction. The affecting factors found in eqs (19, [20], 21) present the calculation of EF [51].

$$C_{\mathrm{o,f}} = KC_{\mathrm{aq,f}} = \frac{KC_{\mathrm{aq,i}}}{1 + K(V_{\mathrm{o}}/V_{\mathrm{aq}})} \tag{19}$$

$$\frac{\mathrm{d}C_{\mathrm{o}}}{\mathrm{d}t} = \frac{A_{\mathrm{i}}\beta \times (KC_{\mathrm{aq}} - C_{\mathrm{o}})}{V_{\mathrm{o}}} \tag{20}$$

$$\mathrm{EF} = \frac{C_{\mathrm{o,f}}}{C_{\mathrm{aq,i}}} \tag{21}$$

where $C_{\mathrm{o,f}}$ is the final concentration of analyte in organic phase, $C_{\mathrm{aq,f}}$ and $C_{\mathrm{aq,i}}$ are the final and initial concentration of analyte in sample solution (water phase), V_{o} and V_{aq} are the volume of organic phase and sample solution (water phase) at a certain time (t), A_{i} is the contact area between organic phase and water phase, β is the mass transfer coefficient, $C_{\mathrm{o,f}}$ is the final concentration of analyte in organic phase obtained by the calibration.

In SFODME, the main affecting factor is the selection of organic extraction solvent. It should meet the following requirements: (1) immiscible with water; (2) melting point is around room temperature (10–30°C); (3) good extraction ability for target analytes; (4) the density is less than water; (5) compatible to the employed instruments (e.g., GC, HPLC, AAS and ICP-OES). The suitable organic solvents include *n*-undecyl alcohol, *n*-dodecanol, 2-dodecanol, 1-bromo-hexadecane, 1,10-dichloro-decane and 1-chloro-octadecyl, and *n*-undecyl and *n*-dodecanol are the most commonly used organic solvents in SFODME.

Chen et al. [52] employed a SFODME-based method for the determination of trace Dy and Y in biological and environmental water samples followed by ETV-ICP-MS detection. 1-(2-Pyridylazo)-2-naphthol (PAN) was used as both chelating reagent in SFODME and chemical modifier in ETV for separation, preconcentration and volatilization of the REEs prior to their determination.

4.8 Affecting factors in LPME

The affecting factors are different in different LPME extraction modes. While the main affecting factors include extraction solvent, sample pH, stirring rate, extraction time, extraction temperature and ionic strength. For the extraction of REEs, the selection of chelating agent is very important, which refers to the section of “LLE of REEs”.

In general, the selection of extractants is mainly based on “like dissolves like” principle. And the following properties are preferred practically: (1) insoluble in water or very low solubility in water; (2) high boiling point and low saturated vapor pressure, to reduce the evaporation loss during extraction; (3) the distribution coefficient of analytes between the organic and aqueous phases is high. Table 22 lists the common organic solvents with corresponding properties.

Table 22: Physical properties of the extractants used in LPME.

Extractant	**Boiling point (°C)**	**Vapor pressure (T)**	**Water solubility (mg/L)**	**Density (g/cm^3)**	**Viscosity (cP)**	**Surface tension (dyn/cm)**	**Dipole moment (D)**	**Dielectric constant**
Cyclohexane	80.7	97.8	55	0.78	0.9	24.65	0.00	2.02 (20°C)
n-Hexane	68.7	151.3	12	0.65	0.29	17.94	0.08	1.88
Octane	125.7	14.0	6.6×10^{-3}	0.70	0.51	21.18	0.00	1.95 (20°C)
Iso-octane	99.2	49	2.4	0.69	0.50 (20°C)	18.8	0.00	1.94 (20°C)
Decane	174.2	1.3	0.05	0.73	0.86	23.37	0.00	1.99 (20°C)
Benzene	80.1	95.2	1,791	0.87	0.60	28.2	0.00	2.27
Toluene	110.6	28.5	515	0.86	0.55	27.92	0.31	2.38
o-Xylene	144.4	6.6	175	0.88	0.76	29.49	0.45	2.57 (20°C)
m-Xylene	139.1	8.3	146	0.86	0.58	28.10	0.30	2.37 (20°C)
p-Xylene	138.4	8.7	156	0.86	0.60	27.76	0.02	2.27 (20°C)
Ethylbenzene	136.2	9.6	152	0.86	0.64	28.48	0.37	2.40 (20°C)
1-Octanol	195.2	0.08	5.38	0.82	7.36	26.92	1.76	10.34 (20°C)
Benzyl alcohol	205.4	0.11	800	1.04	4.65 (30°C)	39.44	1.66	13.1 (20°C)
MIBK	117.4	18.8	1,700	0.80	0.55	23.64 (20°C)	–	13.11 (20° C)
Chlorobenzene	131.7	11.7	327	1.10 (20°C)	0.72 (20°C)	31.98 (30°C)	1.62	5.62
Phenetole	172	1.28	–	0.97 (20°C)	1.16 (25° C)	32.85 (22°C)	3.33	4.22
Dichlorometane	39.6	435.8	1,990	1.32	0.39 (30°C)	26.54 (30° C)	1.14	8.93
Chloroform	61.2	194.8	8,500	1.48	0.54	26.53	1.15	4.81 (20°C)
Tetrach loroemethene	76.6	115.2	770	1.58	0.90	26.13	0.00	2.23
1,2-Dichloroethane	83.5	83.3 (20°C)	8,100 (20°C)	1.25	0.73 (30°C)	30.84 (30°C)	1.83	10.37
1,2-Dichlorobenzene	180.5	1.3	156	1.30	1.32	26.48 (20°C)	2.14	9.93
Tetrach loroethylene	121.1	18.5	150	1.61	0.80 (30°C)	31.30	0.00	2.28
Bromobenzene	155.9	4.2	424	1.48	1.01 (30°C)	35.09 (30°C)	1.55	5.40
Nitrobenzene	210.8	0.28	1,900 (20°C)	1.20	1.62 (30°C)	42.17 (30°C)	4.00	34.78
Carbon disulfide	46.2	361.6	2,100 (20° C)}	1.29	0.36 (20°C)	32.25 (20°C)	0.06	2.64
[C_4MIM][PF_6]	–	–	18,800	1.36–1.37	148–450	48.8–49.8	–	–
[C_6MIM][PF_6]	–	–	7,500	1.29–1.31	560–586	–	–	–
[C_8MIM][PF_6]	–	–	2,000	1.20–1.23	682–710	34.2–36.5	–	–
[C_6MIM][Tf_2N]	–	–	3,400	1.33	–	–	–	–
Water	100.0	23.8	∞	1.00	0.89	71.81	1.82	78.36

Sample pH is usually adjusted to make target analytes existing in non-ionic form reducing their solubility in water and promoting the extraction. For the REEs extraction system which is mainly based on chelation or complexation reactions, pH mainly affect the stability of chelates or complexes, thus affecting the extraction.

Stirring rate is a dynamic factor affecting the extraction. In LPME process, the mass transfer of analytes is determined by the diffusion rate and the thickness of diffusion layer between sample solution and the organic solvent. Based on the theory of convection–diffusion, efficient stirring can accelerate the diffusion rate of the analyte and reduces the thickness of the diffusion layer. Thus, increasing the stirring rate would generally accelerate the extraction, and reduce the extraction time. While, when the stirring rate is too high, some negative impact would occur, e.g., extraction single drops is unstable, bubbles adhered on the surface of the hollow fiber membrane appear and impede extraction, or the dissolving loss of the organic extraction solvent is accelerated.

MIBK: 4-methyl-2-pentanone [C_6MIM][PF_6] 1-hexyl-3-methylimidazolium hexafluorophosphate. LPME of target analytes is a process based on their distribution between the sample solution and the extraction phase, and the maximum extraction efficiency would be obtained when the extraction equilibrium is reached. For the analytes with high distribution coefficient and fast mass transfer speed, the extraction equilibrium can be achieved in a short time, which is an incomplete extraction under equilibrium. However, for analytes with relatively low distribution coefficient or low mass transfer speed, long time are needed to reach the extraction equilibrium, and in this case, the extraction is usually processed under non-equilibrium state, during which the extraction time is strictly controlled to ensure the reproducibility.

Extraction temperature has a double impact on the extraction process in terms of thermodynamics and kinetics. In general, increasing the sample temperature would increase molecular motion, the diffusion coefficient of the analyte, and the mass transfer rate of the analyte, thus speeding up the extraction. However, increasing the extraction temperature would reduce the partition coefficient of the analyte, increase the water solubility of the organic solvent, resulting in lower extraction efficiency. Moreover, when the temperature is too high, small bubbles would occur in the aqueous phase, which is attached to the surface of the extraction solvent, hindering the extraction.

The addition of some inorganic salt, e.g., NaCl, Na_2SO_4, would increase the ionic strength of the sample solution, decrease the solubility of analytes in sample solution due to salt-out effect, increasing the distribution of analytes in the extraction phase and thus the extraction efficiency. While sometimes the salt addition would inhibit the extraction which is explained by that the salt would change the physical property of the extraction film and thus the diffusion rate of target analyte in the extraction phase.

4.9 Cloud point extraction

Cloud point extraction (CPE) is a new LLE mode which is based on the fact that most nonionic surfactants can form micelles in aqueous solutions and become turbid when they are heated beyond a temperature called the cloud point temperature (CPT). Above the CPT the micellar solution separates into a small volume of surfactant-rich phase and a diluted aqueous phase, in which the surfactant concentration is close to the critical micellar concentration (CMC). Any analyte solubilized in the hydrophobic core of the micelles, will be separated and concentrated in the small volume (usually in the range of 50–250 μL) of the surfactant-rich phase. This process is reversible, and two phases would combine into one phase when the temperature is lower than CMC. When the temperature is increasing, the micelle size of the surfactant is increasing, causing the hydrogen bonding not strong enough to keep the water molecule connected to the O atom of ether.

4.9.1 Application of CPE for trace REEs analysis

REEs react with complexants and produce hydrophobic complexes that are entrapped into the micelles and then into the surfactant-rich phase. Due to the viscosity and organic content of the surfactant-rich phase, appropriate sample introduction systems or nebulizers are required, such as employment of a free-clogging nebulizer, chemical vapor generation and micronebulization/aerosol desolvation. Table 23 lists the REEs extraction systems by CPE, along with subsequent detection technique.

Table 23: Applications of CPE for trace REEs analysis.

Analytes	Surfactant	Complexant	Enrichment factor	Detection	LOD	Sample	Ref.

REEs	Triton X-114	8-HQ	7.9–9.2	ICP-OES	41.4(Yb)–448 ng/L(Gd)	Tea leaves and mushroom	[53]
		Nocomplexant	5.4–8.1		69.0(Sc)–509.5 ng/L(Sm)		
REEs	Triton X-114	TTA	9–14	ICP-OES	2 (Pr)–103(Lu) ng/L	River water	[54]
Dy, Er, Eu, Gd, Ho, La, Lu, Pr, Sm, Tb, Tm and Yb	PONPE-7.5	PAN	70	NAA	0.27 (Yb)–3.07(Eu) ng/g	[55]	
Eu(III)	Triton X-114	Alizarinred S	22	FAAS	6 ng/mL	Water	[56]
REEs	Triton X-114	(*i*-pr)DGA	140	ICP-MS	0.2–30 ng/L	Soil	[57]

8-HQ: 8-hydroquinolein; TTA: 1-(2-thenoyl)-3,3,3-trifluoraceton; (*i*-pr)DGA: *N*,*N*,*N*′,*N*′-tetraisopropyl diglycolamide.

4.9.2 Affecting factors

4.9.2.1 Surfactants

Surfactants generally consist of a hydrophobic and a hydrophilic moiety, and the CPT is related to the chain length of hydrophilic and hydrophobic moiety in the surfactants. With the same hydrophobic moiety, CPT would increase with the increase of hydrophilic chain length; on the contrary, CPT declines with the increase of the hydrophobic chain length. Besides nonionic surfactants, amphoteric ionic surfactant exhibits cloud point phenomenon. Some anionic surfactants (e.g., sodium dodecyl sulfate [SDS], sodium dodecyl benzene sulfonate [SDBS] and sodium dodecyl sulfonate [SDSA]) in aqueous high concentration HCl medium would also appear phase separation. Table 24 lists the frequently used surfactants in CPE, along with the structure, CMC and CPT.

Table 24: Surfactants commonly used in CPE.

Surfactants			
Chemical name	**Commercial name in series**	**CMC (mmol/L)**	**CPT (°C)**
Polyoxyethylene fatty alcohol	Brij 30	0.02–0.06	2–7
	Brij 35	0.06	>100
	Brij 56	0.0006	64–69
P-*tert*-octyl phenyl polyethylene glycol ether	Triton X-100	0.17–0.30	64–65
	Triton X-114	0.20–0.35	22–25
N-alkyl phenyl polyethylene glycol ether	PONPE-7.5	0.085	5–20
	PONPE-10	0.07–0.085	62–65
Amphoteric ionic surfactants	C_9APSO_4	4.5	65
	C_8-lecithin		45

Increasing the surfactant concentration would improve the extraction efficiency, increase the ratio of two-phase volume, and simultaneously reduce the EF and distribution coefficient. In order to increase EF, a low surfactant concentration is preferred, while too low surfactant concentration would lead to difficult separation of the sedimented phase from sample solution, deteriorating the accuracy and reproducibility.

4.9.2.2 Sample pH and chelating agent

For the extraction of REE ions, a chelating agent is necessary to transform REEs into a hydrophobic form, which is then extracted into the surfactants. pH should be appropriate for the formation of REEs complex. However, most of the complexation system for REEs occurs in slightly acidic pH (Figure 10), which is incompatible with digested solid samples which is generally strong acidic. Ohashi et al. [58] show good extraction in a more acidic media (pH = 3) for La, Eu and Lu(III), while higher concentrations of surfactant were needed to counter the effect of the acidic media on the extraction. And the EF would be reduced and LOD would be deteriorated due to the low extraction efficiency.

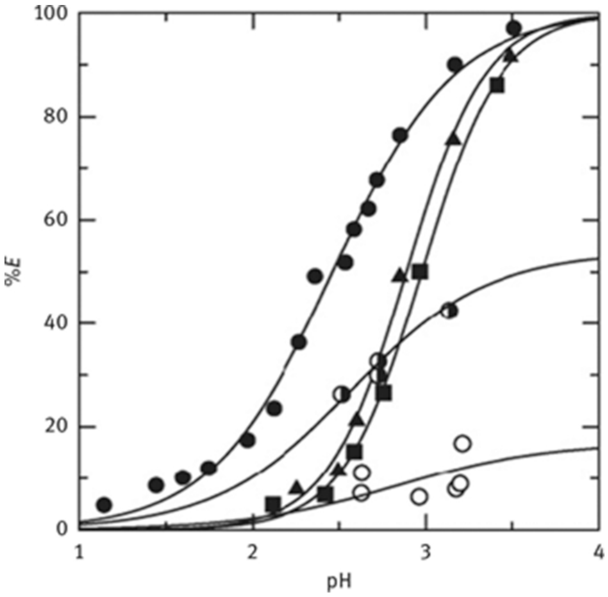


Figure 10: Extraction percentage of La(III), Eu(III) and Lu(III) vs.pH without chelating agents. Circle, La(III); triangle, Eu(III); square,Lu(III); closed, Aldrich (lot no. 13112LB); half closed, Aldrich (lot no.03615HC); open, Nacalai Tesque; Ln(III), 3.6×10^{-5} mol/L; Triton X-100,2.0 % (v/v); $I = 0.01$ mol/L (pH > 2.0) and 0.1 mol/L (pH < 2.0)with (H, Na)ClO_4 [58].

The behaviors of La(III), Eu(III) and Lu(III) in CPE with and without di(2-ethylhexyl) phosphoric acid (HDEHP) as the complexant, Triton X-100 as the surfactant, were investigated [58]. It was suggested that the extraction of Ln(III) into the surfactant-rich phase without added chelating agent was caused by the impurities contained in Triton X-100. The extraction percentage more than 91 % for all test REEs was obtained using 3.0×10^{-5} mol/L HDEHP and 2.0 % (v/v) Triton X-100. From the equilibrium analysis, it was clarified that Ln(III) was extracted as $Ln(DEHP)_3$ into the surfactant-rich phase. Besides, Li et al. [53] proposed an on-line CPE system with ICP-OES detection with/without 8-HQ as complexant for trace analysis of REEs in biological samples. The experimental results indicated that: (1) the use of on-line CPE greatly simplifies the extraction procedure; (2) LODs for REEs obtained by on-line CPE-ICP-OES with 8-Ox as chelating agent were slightly better than that obtained by on-line CPE-ICP-OES without 8-Ox as chelating agent, and the RSDs of the two methods were comparable; (3) both on-line CPE-ICP-OES systems had good selectivity and could be used for the biological sample analysis.

4.9.2.3 Extraction temperature and time and centrifugation time

The extraction temperature and time are determined by the properties of surfactants and the extracted compounds. Generally, the extraction temperature is 15–20°C higher than the CPT of the employed surfactant. Increasing extraction time would increase the extraction efficiency, while too long extraction time hardly affect the extraction efficiency, and 30 min extraction is commonly used for a good extraction efficiency.

Increasing the centrifugation time would initially increase the extraction efficiency and distribution coefficient, which will be constant after a long extraction time. For a CPE system with relative high CPT, too long centrifugation would lead to the reversion of phase separation, decreasing the extraction efficiency.

4.9.2.4 Ionic strength

The ionic strength hardly affects the extraction efficiency and distribution coefficient. The addition of some inert salt would change the cloud point of the surfactant, favoring the separation of two phases.

5 Solid phase extraction

SPE is currently the most frequently used sample pretreatment technique in real sample analysis [59], featuring with high EFs, rapid phase separation, low organic solvent consumption, simple operation, as well as easy-to-automate. The principal goals of SPE are trace enrichment (concentration), matrix simplification (sample clean-up) and medium exchange (transfer from the sample matrix to a different solvent or to the gas phase)

[60]. Usually, the analytes are transferred from a mobile phase (gas, fluid or liquid) [61] to the solid phase where they are retained for the duration of the sampling process. The solid phase is then isolated from the sample and the analytes are recovered by elution using a liquid or fluid, or by thermal desorption into the gas phase. The adsorption process of target analytes on the adsorbents depends on the physical/chemical form of analytes, specific surface properties of the adsorbent and the experimental conditions, such as pH, temperature and analytes concentration. The adsorption involves interactions between the analytes and sorbents with various functional groups and ion exchange processes.

The adsorbent plays a key role in SPE-based methodology because it determines the selectivity, affinity and capacity. The ideal SPE adsorbents are expected to feature with the following characteristics: (1) porosity, having a large specific surface area; (2) low blank; (3) high chemical and mechanical stability; (4) fast kinetics of adsorption and desorption; (5) reversible adsorption; (6) high selectivity; (7) high recovery rate. Besides the conventional materials such as organic chelate resin [62], activated carbon [63], activated alumina [64] and microcrystalline material [65], a variety of novel materials including carbonaceous materials [66–68], molecular/ion imprinted polymers [69, 70], nanostructured materials [71–74], mesoporous materials [75–77], restricted access materials (RAM) [78, 79], monolithic materials [80, 81], magnetic materials and metal-organic frameworks (MOFs) [82–84], have been employed in SPE. The application of various SPE adsorbents in trace REEs analysis is listed in Table 25.

Table 25: Application of various SPE adsorbents in trace REEs analysis.

Materials	Elements	Detection	LOD (ng/L)	Adsorption capacity (mg/g)	Samples	Ref.
C_{18} silica cartridge modified with PAN	Ce, Dy, La, Sm and Y	ICP-OES	11–37		Spring, well, tap water and seawater	[85]
Silica gel column	La, Eu and Yb (PMBP complex)	ICP-OES	34–82		GBW07603, lake water and synthetic seawater	[86]
Microcolumn packed with MWNTs	La, Sm, Eu, Gd, Tb, Ho and Yb	ICP-OES	3–57	7.23–9.93	GBW07605, lake water and synthetic seawater	[87]
Ion-imprinted polystyrene resins	Y, La, Nd, Eu, Gd, Tb and Yb	FAAS, ICP-OES		8.9 ± 0.2 (Y)		[88]
Maleic acid grafted PTFE fibers	All lanthanides except Pm	ICP-MS	0.001–0.02	0.31 mmol/g (La)	GBW07312, GBW07313, GBW07405, seawater and river water	[89]
Fullerene derivatives poly(*b*-styryl)-(12-methanofullerene-C60)-61-formo hydroxamic acid	Ce, La, Pr, Nd, Smand Gd	ICP-MS	0.9–3.5	1.25–2.15 mmol/g	Standard reference material (BCR-1, SO-Z, NBS 163), seawater	[66]
Carbon nanofibers	La, Eu, Gd and Yb	ICP-MS	0.36–0.6	14.2–19.1GBW07605GBW08571	Tea leaves	[90]
Mesoporous TiO_2	V, Ce, Dy, Eu, Laand Yb	ICP-OES	30–350	13.1–26.5	coal fly ash, water samples (river, pond, well and lake)	[91]
Tulsion CH-90 resin	$^{152,154}Eu$	NaI (Tl) gamma scintillation detector		GBW074010.31 mmol/g		[92]
Chitosan-based chelating resin functionalized with EDTA	All REEs except Pm	ICP-MS	0.12–5.6		Seawater	[93]
Nano-pore samarium (III)-imprinted polymer	Sm	ICP-OES				[94]
Silica gel modified with MTPB	Sc	ICP-OES	85 ng/g	0.6 mmol/g	Shrubbery leaves, Tibet soil, balsam pear leaves and lotus leaves	[95]
Octadecyl silica minicolumn	Ce, Dy, La, Sm, Y and Yb	ICP-OES	90–400		Seawater, tap water and well	[96]
Microcartridge containing C18-derivatized silica particles	La and Gd	CZE with diode array detector	0.02 (La)0.08 (Gd)		Tap water	[97]
Syringe-driven chelating columns	All lanthanides except Pm	ICP-MS	0.005–0.09		Seawater	[98]

Amberlite XAD-4 resin with monoaza dibenzo 18-crown-6	La, Nd and Sm	ICP-OES	3,900–7,400	0.055–0.066 mmol/g		[99]
Bis-(2-ethylhexyl)-phosphate (HDEHP) coated reverse phase C18	Gd and Gd-based MRI contrast agents	ICP-MS	22–38		Surface water and waste water	[100]
Bentonite modified with *N*-(2-hydroxyethyl) ethylenediamine	Sm	ICP-OES	600	17.7	GBW07602, waste water	[101]
MWNTs with tannic acid	La, Tb and Lu	MPT-AES		3.97–8.55		[102]
Activated carbon modified with benzoyl hydrazine	Eu	ICP-OES	73 ng/g	59.8	GBW07402 GBW07308 Yellow River sediments,orange leaves, balsampear leaves	[103]
TiO_2–graphene composite	La, Tb and Ho	MPT-AES	1,600–2,800		GBW07313REE oxide samples	[104]
Nanoporous silica functionalized with *N′*-[(2-hydroxy phenyl)methylene] benzohydrazide	Dy	ICP-OES	50	47	Tap water, seawater and river water	[105]
High-dispersion-type MW-CNTs attached to polymerbeads (TSK^{TM})	All REEs except Sc and Pm	ICP-MS	0.016–0.159	70.0 ± 5.1 (La)	Seawater	[106]
Walnut shell packed microcolumn	All REEs except Sc and Pm	ICP-MS	0.01–0.17		Sediment, copper ore, tea leaf, human hair and food and agricultural products	[107]
Eu-imprinted polymer nanoparticles	Eu	Electro-chemistry	23,000		Synthetic water, river water, tap water	[108]
TiO_2 nanotube packed microcolumn	La, Ce, Eu, Gd, Lu and Yb	ICP-MS	10.1–14.7	0.19–1.2	GBW07605 (tea leaves) natural water	[109]
Carbon-ferrite magnetic nanocomposite	La, Sm, Nd and Pr	ICP-OES	500–10,000		IAEA-soil-7	[110]
4-(2-Thiazolylazo) resorcinol immobilized Chromosorb 106	All lanthanides except La and Pm	ICP-MS	0.06–0.31	0.081–0.108 mmol/g	Estuarine water, Coastal seawater	[111]
Pr^{3+} ion surface-imprinted HQ-PHEMA/SiO_2	Pr^{3+}	UV–vis (with EDTAtitration)		0.013 mmol/g		[112]
Oxidized multiwalled carbon nanotubes packed minicolumn	Sc	ICP-OES	4		Acid mine drainage	[113]
2,6-Pyridinedicarboxaldehyde-functionalized Amberlite XAD-4 resin	Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu and Ce	ICP-OES	7–150	0.0490–0.0667 mmol/g	SPS-SW2 Batch 127 seawater, tap water	[114]
8-Hydroxy-2-quinolinecarboxaldehyde functionalized	Pr, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Yb and Lu	ICP-OES	10–420	0.0496–0.112	SPS-SW2 Batch 127 seawater, tap water	[115]

Amberlite XAD-4 resin paced minicolumnCoriolus versicolor immobilized Amberlite XAD-4	La	ICP-OES	270	16.6 mg for 0.25 g C versicolor immobilized on 1.0 g of Amberlite XAD-4	Tap water, river water	[116]
Y(III) imprinted polymer	Y	ICP-OES	900	18.5	Standard rock reference material, radioyttrium	[117]
Fe_3O_4@SiO_2@polyaniline–graphene oxide composite	All REEs except Sc and Pm	ICP-MS	0.04–1.49	7.7–16.3	GBW07605, tea leaves, lake water, river water	[118]
Fe_3O_4@SiO_2–$(CH_2)_3$–*S*-cinchonidine	Eu	ICP-OES	40	26.5	Mineral water, agricultural water, tap water and spring water	[119]
Double-ion imprinted polymer @magnetic nanoparticles	Ce and Gd	Electro-chemistry	70 (Ce)190 (Gd)			[120]
Transcarpathian clinoptilolite (thermally activated at 350°C)	Tb	UV–vis	750	≈6.0	Synthetic water	[121]
Graphene oxide–TiO_2 composite	La, Ce, Eu, Dy and Yb	ICP-OES	130–410	16.6–28.7	River water, lake water, seawater and sediment	[122]

5.1 Carbon nanotubes and graphene oxide

Carbon nanotubes (CNTs), which were first discovered by Iijima [123], have led research to new area in many interdisciplinary investigations as the advantages of CNTs are unique structural, electronic, optoelectronic, semiconductor, mechanical, chemical and physical properties. CNTs can be described as a graphite sheet rolled up into a nanoscale-tube (which are single-wall carbon nanotubes [SWCNTs]), or with additional graphene tubes around the core of an SWCNT (which are multi-wall CNTs (MWCNTs)). These CNTs have diameters in the range between fractions of nanometers and tens of nanometers and lengths up to several centimeters with both their ends normally capped by fullerene-like structures.

Although raw CNTs walls are not reactive, oxidation of CNTs (by using such as HNO_3, NaOCl and $KMnO_4$ solutions) can lead to surface functionalization with oxygen-containing groups (e.g., carboxylic, carbonyl and hydroxyl group), allowing retention of cations [124]. These functional groups cause a rise in negative charge on carbon surface and the oxygen atoms in functional groups donate single pair of electrons to metal ions, consequently increasing their cation exchange capacity [125]. It is commonly believed that the chemical interaction between the metal ions and the surface functional groups of CNTs is the major sorption mechanism.

The oxidation of MWCNTs with concentrated nitric acid lead to the surface functionalization with oxygen-containing groups, and the isoelectric point (IEP) of MWCNTs shifts to the lower pH values. When the pH of the solution is higher than the IEP of the oxidized MWCNTs, the negative charge on the surface provides electrostatic attractions that are favorable for adsorbing cations. The decrease of pH leads to the neutralization of surface charge, so the adsorption of cations onto MWCNTs decreases quickly. Liang et al. [126] investigated the adsorption behavior of REEs on MWCNTs and found that quantitative adsorption (>95 %) for the target REEs ions was obtained when the pH exceed 3.0, and pH 4.0 was selected as the optimum condition for the SPE of REE ions, followed by elution with 1.0 mol/L HNO_3 and ICP-OES detection. The detection limits of this method for REEs was between 3 and 57 ng/L, and the relative standard deviations for the determination of REEs at 10 µg/L level were found to be less than 6 % when processing 100-mL sample solution.

Su et al. [118] prepared a Fe_3O_4@SiO_2@polyaniline–graphene oxide composite (MPANI-GO) through a simple non-covalent method and applied it to magnetic solid phase extraction (MSPE) of trace REEs in tea leaves and environmental water samples followed by ICP-MS determination. The GO plays a key role in the adsorption of REEs on MPANI-GO and the function of MPANI was mainly to anchor and magnetically functionalize GO. The adsorption mechanism of the REEs on the MPANI-GO could be attributed to the chelation of the functional groups of GO containing hydroxyl, epoxide, carboxyl, and carbonyl groups with REEs. When 0.5 mol/L HNO_3 was used as the eluting agent, the MPANI-GO can be reused for more than 30 times without obvious decrease of the recoveries of REEs. It should be also noted that the prepared magnetic nanoparticles are superparamagnetic, which could be attracted to a magnetic field but retain no residual magnetism after the field is removed. During the extraction, the suspended superparamagnetic nanoparticles adhered to the target REEs can be removed very fast from a matrix using a magnetic field, and they do not agglomerate after removal of the field.

5.2 Silica-based materials

Modified silica gel merits good selectivity, high mass-exchange characteristics and good mechanical stability. Immobilization of organic functional groups on a siliceous surface has been successfully employed to produce varieties of modified silica gel. In this process, an organic reagent or a synthesized organic molecule containing the desired functional group is directly attached to the support, or to the original chain bonded to the support *via* a sequence of reactions to increase the main chain, where other basic centers can be added to ensure the enhancement of a specific adsorption.

Based on the hard–soft acid–base theory, chemically stable metal chelates can be formed between REEs and β-diketone reagents (e.g., acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone) under suitable experimental conditions. These reagents, as derivatization reagents, have been successfully applied in GC analytical systems. Zhang et al. [127] prepared an acetylacetone-modified silica gel (ACACSG) for the preconcentration of trace REEs in environmental and biological samples. The maximum adsorption percentages for target REEs were obtained at pH 6.0–8.0. Two possible mechanisms could be used for the explanation of the adsorption of the REEs on ACACSG. First, REEs were adsorbed through the affinity of =O of acetylacetone. Second, the REEs were adsorbed on ACACSG by electrostatic action between REEs and the charge on silica gel surface. In the acidic medium, the first mechanism plays a dominating role. When the pH increases, the –OH on the surface of silica gel provides the ability of binding cation. Both mechanisms work, so the adsorption of REEs onto ACACSG increases quickly.

5.3 Chelating resin and ionic-exchange resin

Various chelating agents have been immobilized on polymeric supports to produce chelating sorbents for determination of REEs by SPE in natural water samples. These functional groups include 8-HQ [128], iminodiacetate (IDA) [129, 130], hydroxamic acid [131], 2-amino-5-hydroxy benzoic acid [132], 2,6-diacetylpyridine [133] and fluorinated β-diketone [134]. Chemical immobilization offers the ability to customize the sorption medium with different functional groups to improve selectivity, sorption capacity and reusability.

Fu et al. [135] synthesized alkyl phosphinic acid resin (APAR) for on-line preconcentration of trace REEs, followed by ICP-MS determination. REEs in seawater could be on-line concentrated on the APAR packed column, and eluted from the column with 0.5 mL 0.1 mol/L HNO_3 within 30 s. An EF of nearly 400 can be achieved for all REEs when the seawater sample volume was 200 mL, while the matrix and coexisting spectrally interfering ions such as Ba, Sn and Sb could be simultaneously separated. Zeereen et al. [111] prepared a new chelating resin by immobilizing 4-(2-thiazolylazo) resorcinol (TAR) on Chromosorb 106 and investigated the adsorption behavior of REEs on it. It was found that the REEs were quantitatively retained from saline solutions on the Chromosorb 106-TAR resin at pH 5.0 and can be eluted with 1 % (v/v) HNO_3. The resin possesses large sorption capacity for REEs ranging from 81.1 µmol/g for Lu and 108 µmol/g for Nd. Gupte et al. [136] employed resorcin [4]calixpyrrole and its azo derivative impregnated Amberlite XAD-2 resin for the preconcentration of La^{3+} and Ce^{3+}. The resin was found to be highly selective for these two REE ions in the presence of various electrolytes at a particular pH. Table 26 presents some adsorption capacity for La^{3+} and Ce^{3+}.

Table 26: Adsorption capacity (mg/g) of La^{3+} and Ce^{3+} on some chelating resin [136].

Adsorbents	La^{3+}	Ce^{3+}
Aliquat-336–Amberlite XAD-4	4.73	
Amberlite XAD-4 resin–bicine ligands	48.6	
Calix [4]arene-*o*-vanillinsemicarbazone–merrifield resin	25.2	28.1
Amberlite XAD-16 (AXAD-16)-*N*,*N*-dihexylcarbamoylmethyl	188	–
Phosphonic acid, Amberlite XAD-4-(*o*-vanillinsemicarbazone)	2.30	2.48
Calix [4]arene-semicarbazone–merrifield's peptide resin	1.88	1.44
Merrifield chloromethylated resin–(dimethyl amino-phosphonomethyl)-phosphonic acid (MCM–DAPPA)	169	
Azocalix [4]pyrrole Amberlite XAD-2 polymeric chelating resin	107, 111	88.2, 89.9

Separation of REEs by ion chromatography on a Dionex Ion Pac CS3 column (sulfonic acid type) has been achieved by both isocratic and gradient elution with HIBA as the mobile phase [137]. It was shown that the plate height for Y was distinctly smaller than those for REEs with similar ionic radii. An improved combined isocratic-gradient elution procedure was devised for separation of Sc, Y, La and the lanthanides in one run. By using strongly basic anion-exchanger (QAE-SephadexA-25), Gd complexed with negatively charged humic substances (humic and fulvic acids) was collected from sample solution [138]. A Gd-based MRI contrast agent (diethylenetriamine-*N*,*N*,N', N'', N'''-pentaacetato aquo gadolinium(III), Gd–$DTPA^{2-}$) was simultaneously collected on the same column. The Gd–DTPA complex was desorbed by anion-exchange with 50-mM tetramethyl ammonium sulfate, leaving the Gd–humic complexes on the column. The Gd–humic complexes were subsequently dissociated with 1 M nitric acid to desorb the humic fraction of Gd. The 2-step desorption with small volumes of the eluting agents allowed 100-fold preconcentration for the fractionation analysis of Gd at low ng/L levels by ICP-MS. On the other hand, Gd(III) neither complexed with humic substances nor DTPA, i.e., free species, was not adsorbed on the column.

The details on relevant chromatographic separation of REEs can be referred from the section of "Liquid chromatographic separations of REEs".

5.4 Metal oxide nanostructured materials

Nanoparticles are often defined as particles of less than 100 nm in diameter. The nanoparticles exhibit new or enhanced size-dependent properties compared with larger particles of the same material. Depending on the chemistry of the constituent atoms, nanoparticles are known to exhibit remarkable adsorption properties due to their enhanced surface area and large interface volume. Nano-sized inorganic oxides are widely used in SPE for the preconcentration/separation of metal ions because it can adsorb metal ions with high adsorption capacity. Different types of nanoparticles, such as nanometer-sized powder materials, mesoporous nanoparticles and magnetic nanoparticles, have been applied in SPE of REE ions.

The effect of pH on the adsorption characteristics of La^{3+} and La complexes of citric acid, 2-hydroxyisobutyric acid (HIBA), and humic acid on nanometer-sized TiO_2 was investigated [139]. It was found that there is an obvious difference between the adsorption of free La^{3+} and La complexes on nanometer-sized TiO_2 with pH changing from 4.0 to 6.5. Quantitative adsorption of lanthanum citrate, lanthanum HIBA and lanthanum humic complexes were achieved in a pH ranging from 4.0 to 8.0, whereas free La^{3+} cannot be quantitatively adsorbed until the pH value is up to 6.5. However, if the pH value was lower than 4.0 (pH 3.5 for lanthanum citrate), the adsorption of lanthanum citrate and lanthanum humate complexes declined remarkably due to incomplete complexing between La^{3+} and the organic ligands (the first acid dissociation constants [p*K*a] of the citric acid and the 2-hydroxyisobutyric acid are 3.13 and 3.72, respectively).

These nanometer-sized metal oxides are not selective and not suitable for samples with complicated matrices. In order to improve selectivity of the nanoparticles, the modification of the adsorption material is usually required. The most often used method is to load a kind of specific chelate reagent by physical or chemical procedure on the surface of this material. The former method is simple but the loaded reagent is prone to leakage. PAN, PMBP, 8-HQ and dithizone were commonly used as modifiers on metal oxides nanoparticles. Due to the chelating ability of the loaded reagent with the target analytes, selectivity of the nanoparticles could be improved. Jon et al. [140] employed PMBP physically immobilized nanometer Al_2O_3 as the adsorbents for the extraction of REE ions Sc^{3+}, Y^{3+} and La^{3+}. The interesting ions can be adsorbed quantitatively on the above material at pH = 4.5 and the analytes adsorbed on the column can be eluted with 0.5 mol/L HCl. The dynamic adsorption capacity of target REEs on the modified nanometer Al_2O_3 are 5.7 (Sc), 13.1 (Y) and 15.5 (La) mg/g, respectively. However, these materials prepared by the physical method are not stable, and the chemically bonded materials are more stable and could be used repeatedly.

Mesoporous nanoparticles are special kind of mesoporous materials. The particle size of the material was less than 100 nm, while it has mesoporous on the particles. The application of the material as adsorbent has been viewed in three perspectives: (1) As a new nanometer material with unsaturated surface atoms that can bind with other atoms, it possess highly chemical activity, very high adsorption capacity and selective adsorption of metal ions. (2) Due to its large surface area, mesoporous material provides more active sites, this results in achieving equilibrium adsorption in short time. (3) By virtue of mesoporous structure, fast adsorption and desorption has been obtained. Huang et al. [77] employed mesoporous TiO_2 nanoparticles as column packing sorbent for flow injection micro-column preconcentration on-line coupled with ICP-OES determination of trace metals (including REEs) in environmental samples. The results showed mesoporous TiO_2 possesses a high adsorption capacity toward the metal ions and the adsorbent was suitable for the preconcentration of trace metal ions in samples with complicated matrix, and is highly stable with long column life time, enabling more than one hundred of load and elution cycles to be performed without loss of analytical performance.

5.5 Ion-imprinted materials

Ion-imprinted polymers (IIPs) are similar to molecular-imprinted polymers (MIPs), but they can recognize metal ions after imprinting and retain all the virtues of MIPs. IIPs have outstanding advantages such as predetermined selectivity in addition to being simple and convenient to prepare. Traditional IIP exhibits poor site accessibility to the target ions because the functionality is totally embedded by high cross-linking density in the polymer matrices. In order to obtain IIP with high selectivity and easy site accessibility for target ions, efforts have been made to deal with the issue of accessibility by imprinting on the matrix surfaces. Recently, surface imprinting technique attracted extensive research interest due to good accessibility to the target species, low mass-transfer resistance, and completed removal of templates, fast adsorption kinetics and ease of preparation.

Meng et al. [141] prepared a novel Ce^{3+} ion imprinted silica based on the supported material of ordered mesoporous silica SBA-15 by surface imprinting technique via reversible addition-fragmentation chain transfer polymerization. The results showed that the synthesized material possessed high-ordered mesoporous structure and showed high selectivity and satisfied adsorption capacity for adsorption of Ce^{3+}. Zhang et al. [142] synthesized Dy^{3+}-imprinted TTA modified silica gel sorbent by surface imprinting technique and employed it as a selective SPE sorbent for on-line extraction and subsequent ICP-OES determination of Dy^{3+}. The largest selectivity coefficient for Dy^{3+} in the presence of competitive ions such as La^{3+}, Nd^{3+} and Gd^{3+} was above 350. The static adsorption capacity and selectivity coefficient of the imprinted sorbent are higher than those of the non-imprinted sorbent and the imprinted TTA modified silica gel sorbent offered a fast kinetics for the adsorption and desorption of Dy^{3+}. With a sample loading flow rate of 2.5 mL/min for 48 s preconcentration and elution flow rate of 1.5 mL/min for 8 s elution, an EF of 10 and the sample frequency of 40 samples/h were obtained.

5.6 Metal-organic frameworks (MOFs)

MOFs are a new class of hybrid inorganic–organic microporous crystalline materials self-assembled straightforwardly from metal ions with organic linkers via coordination bonds. Due to their unique physical and chemical properties, (e.g., permanent nanoscale pore structure, uniform pore size, large specific surface area and good thermal stability), MOFs demonstrated great application prospect in hydrogen storage, gas separation, the catalytic, sensors and biological imaging. The inherent high-specific surface area (appr. 5,000 m^2/g) indicates a large adsorption capacity; the uniform pore structure with certain pore size allows a selective adsorption of molecular with less pore size; the functionalization in their pores or outer surface can be achieved easily. While the application of MOFs-based sorbents is mainly limited in simple water samples or simulated samples (in organic solvents) presently.

Ln^{3+}@bio-MOF-1 were synthesized via postsynthetic cation exchange of bio-MOF-1 with Tb^{3+}, Sm^{3+}, Eu^{3+} or Yb^{3+}, and their photophysical properties were studied [143]. It is demonstrated that bio-MOF-1 encapsulates and sensitizes visible and near-infrared emitting lanthanide cations in aqueous solution. The development and application of MOFs in trace REEs is greatly expected although it is relatively scarce presently.

5.7 Restricted access materials

RAMs are a class of biocompatible adsorbent particles enabling the direct extraction of analytes from biological fluid (e.g., plasma and urine). The separation mechanism is based on the hydrophilic effect and size exclusion. To be brief, a hydrophilic barrier enables the small molecules to permeate through the inner part of the material; meanwhile, it excludes the macromolecules by physical or chemical means on the surface of the material. They have been successfully used as separation media for the analysis of environmental and biological samples in recent years. In LC pre-column, the commercialized alkyl-diol silica (ADS) was frequently applied as RAM for the clean-up of complex biological samples, such as blood, serum, urine and milk. And the mechanism was explained by that the outer surface (hydrophilic diol group) repelled macromolecules (such as proteins, nucleic acids), while the internal surface, comprising hydrophobic reversed-phase (C_4, C_8 or C_18), retained analytes that penetrate through the porous layer.

Yan et al. [144] prepared restricted accessed magnetic nanoparticles by self-assembly of a nonionic surfactant (Tween-20) onto the PAR functionalized magnetic nanoparticles (MNPs). It was found that the as-prepared restricted accessed Fe_3O_4@SiO_2@PAR nanoparticles have a porous structure with BET surface area of around 99.4 m^2/g, average pore size of about 6.14 nm and pore volume of 0.47 cm^3/g, respectively. Besides, the prepared restricted accessed Fe_3O_4@SiO_2@PAR showed a good size exclusion property toward protein, providing an application potential for the direct analysis of biological samples. Based on it, a novel method of restricted accessed MSPE combined with ICP-MS was developed for the direct determination of trace metal ions in human fluids. Under the optimum conditions, the adsorption capacity of La(III) and Nd(III) on the as-prepared restricted accessed Fe_3O_4@SiO_2@PAR were 33.7 and 36.9 mg/g, respectively.

5.8 Capillary microextraction

In 1990, Pawliszyn et al. proposed solid phase microextraction (SPME) [145] as a new pretreatment technique. It integrates extraction, preconcentration and sampling into one step, featuring with simple operation, low consumption of solvents/sample, good reproducibility, high efficiency and can be hyphenated with various detection techniques. It was commercialized by Supelco Corporation in 1993 and has been applied extensively in a variety of fields [146–148]. While the application of SPME in the analysis of trace elements and their species is relatively scarce [149].

Eisert and Pawliszyn [150] proposed another operation mode for fiber-SPME in 1997 – capillary microectraction (CME) – also called in-tube SPME. Figure 11 presents a schematic diagram of in-tube SPME combined with LC–MS system [151].

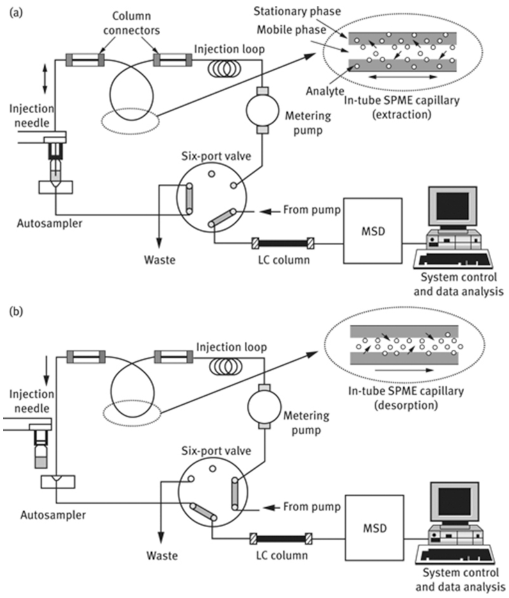


Figure 11: Schematic diagram of the in-tube SPME/LC/MS system [151]. (A) load position (extraction phase) and (B) injection position (desorption phase).

The main difference between fiber-SPME and CME is the coating which is coated on the surface of the fiber for the former one while on the inside surface in the capillary for the latter. Compared with fiber-SPME, CME can be easily online combined with HPLC or CE, improving the producibility; the problem of coating easily swelling or falling off in some organic solvents is overcome, lowering the analytical cost; it can be used for strong polar analytes analysis, widening the application field; the thickness of the extraction coating in CME (0.1–1.5 µm) is far less than that in fiber-SPME (10–100 µm), and the contacting surface between the coating and analytes is larger than that in fiber-SPME, shortening the required time to attain the equilibrium. CME needs that the sample solution should be clean, otherwise the particles would block the capillary column or the flow channel.

CME can be divided into three operation modes [152], which include open-tubular CME, packed CME and monolithic CME. The application of CME in trace REEs analysis is scarce presently.

Wu et al. [153] prepared a Congo red (CR) modified SWCNTs coated fused-silica capillary for CME of trace La, Eu, Dy and Y in human hair followed by fluorinating assisted (F)ETV-ICP-OES determination. The maximum adsorption capacities of the CR-SWCNTs coated capillary evaluated from the breakthrough curve were 0.8, 0.7, 0.7 and 0.7 µg/m for La, Eu, Dy and Y, respectively. The proposed method was applied to the analysis of real-world human hair sample, featuring with simplicity, high sensitivity and less sample/reagents consumption. Zhang et al. [154] synthesized an IDA modified poly(glycidyl methacrylate-trimethylolpropane trimethacrylate) [poly(IDAGMA-TRIM)] monolithic capillary and used it for the selective extraction and preconcentration of REEs. Based on it, a novel method of poly(IDA-GMA-TRIM)-based CME on-line coupled to microconcentric nebulization (MCN)-ICP-MS was developed for the determination of ultra-trace REEs in biological samples (urine and serum). Under the optimal conditions, the LODs for REEs were in the range of 0.08 (Er)–0.97 ng/L (Nd) with a sampling frequency of 8.5/h. The method is featured with high sensitivity and sample throughput, low sample consumption and contamination risks, easy operation, wide pH application range and good tolerance to the matrix interferences.

A novel method of TiO_2 nanoparticles (NPs) functionalized monolithic CME on-line coupling with ICP-MS was developed for the sequential determination of Gd^{3+} and Gd-based contrast agents in human urine samples [155]. The monolithic capillary was prepared by embedding anatase TiO_2 NP_S in the poly(methacrylic acid–ethylene glycol dimethacrylate) (MAA–EDMA) framework. The Gd^{3+} and Gd-based contrast agents (such as gadolinium–diethylene triamine pentaacetic acid (Gd–DTPA) and Gd–DTPA–bismethylamide (Gd–DTPA–BMA)) display different adsorption behaviors on the prepared monolithic capillary which possesses the adsorption properties of both anatase TiO_2 NP_S and poly(MAA–EDMA) monolith. As shown in Figure 12, in the presence of PBS, Gd^{3+} was adsorbed completely on the poly(MAA–EDMA–TiO_2 NPs) monolithic capillary in a relatively wide pH range (2–9), whereas Gd–DTPA could be retained quantitatively on the monolith in the pH range of 2–3 and a sharp decrease of adsorption percentage of Gd–DTPA was observed when pH was higher than 4. It was speculated that in the presence of PBS, Gd–DTPA first reacted with PO_4^{3-} to form a ternary complex (structure shown in Figure 12) because the interaction between Gd–DTPA and phosphate is stronger than that between Gd–DTPA and TiO_2 NPs. This ternary complex could be easily adsorbed by the prepared poly(MAA–EDMA TiO_2 NPs) monolithic capillary due to the good affinity of TiO_2 NPs to phosphate group at pH 2–3.

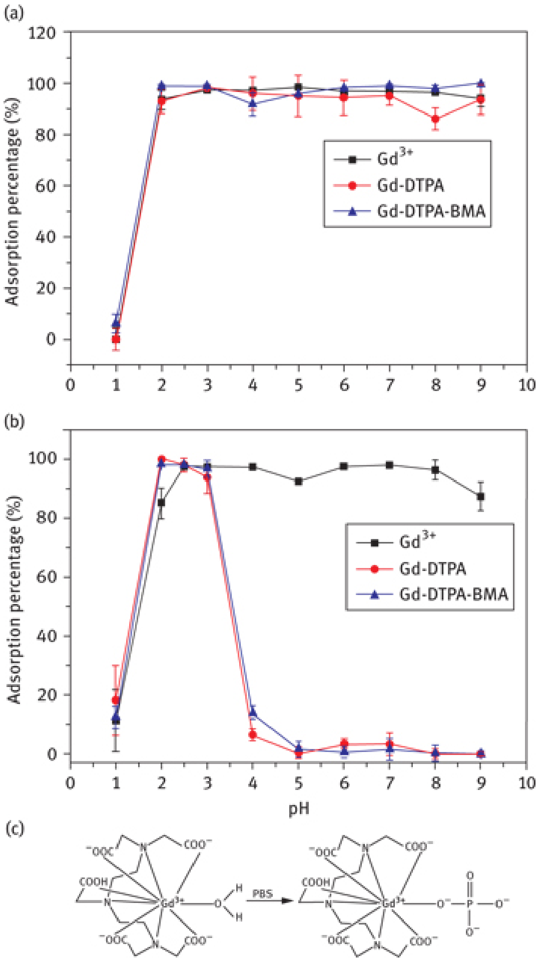


Figure 12: Effect of pH on the adsorption behavior of Gd^{3+}, Gd–DTPAand Gd–DTPA–BMA in the absence (a) or presence (b) of PBS, andthe formation of the deduced ternary complex (c) [155].

Acknowledgment

This article is also available in: Golloch, Handbook of Rare Earth Elements. De Gruyter (2016), isbn 978–3–11–036523–8.

Notes

1 Extraction medium: $HClO_4$.

References

[1] Jiang, ZC, Cai RX, Zhang HS. Rare Earth Elements Analytical Chemistry. Beijing, PRC, Science Press, 2000.
[2] Zhang DL. Rapid determination of rare earth elements in water-soil-plant samples by ICP-AES. Chin J Anal Lab 1988, 3, 7, 61–62.
[3] Roychowdhury P, Roy NK, Das DK, Das AK. Determination of rare-earth elements and Yttrium in silicate rocks by sequential inductively-coupled plasma emission spectrometry. Talanta 1989, 36, 12, 1183–6.
[4] Iwasaki K, Haraguchi H. Determination of rare earth elements in geological samples by inductively-coupled plasma atomic emission spectrometry after oxalate coprecipitation and cation-exchange column separation. Anal Chim Acta 1988, 208, 163–72.
[5] Duan TC, Chen HT, Zeng XJ. Determination of rare and rare earth elements in soils and sediments by ICP-MS using Ti(OH)4-Fe(OH)3 co-precipitation preconcentration. J Anal At Spectrom 2002, 17, 4, 410–3.
[6] Freslon N, Bayon G, Birot D, Bollinger C, Barrat JA. Determination of rare earth elements and other trace elements (Y, Mn, Co, Cr) in seawater using Tm addition and Mg(OH)2 co-precipitation. Talanta 2011, 85, 1, 582–7.
[7] Xu GX, Yuan CY. Solvent Extraction of Rare Earth. Beijing, PRC, Science Press, 1987.
[8] Hunan Metallurgical Research Institut. Rare Earth Metallurgical Analysis, 1973.

[9] Yuan CY, Ye WZ, Ma HL et al. The synthesis and chemical structures of acidic phosphorus (Phosphine) and the extraction performance for Neodymium, Samarium, Ytterbium and Yttrium. Sci Chin, Ser B, 1982, 27, 3, 193–203.
[10] Li DQ, Ji ER, Xu W, Yu DY, Zeng GF, Ni JZ. Extraction mechanism of rare earth elements (III), iron (III) and thorium (IV) from sulfuric acid solutions by primary amine N1923. Chin J Appl Chem 1987, 4, 2, 36–41.
[11] Ni ZA, Li YX. Extraction mechanism for the extraction of perchloric acid rare earth by N1923. Rare Earth Elem 1991, 12, 1, 49–52.
[12] Green H. Uses of liquid ion-exchangers in inorganic analysis. Talanta 1973, 20, 2, 139–61.
[13] Stary J. The Solvent Extraction of Metal Chelates. New York, Pergamon Press New York, 1964.
[14] Haraguchi K, Yamazaki Y, Saitoh T, Kamidate T, Watanabe H. Solvent-extraction of lanthanoids(III) with N-alkylcarbonyl-substituted N-phenylhydroxylamines. Anal Sci 1990, 6, 6, 877–82.
[15] Inoue S. Solvent-extraction of lanthanoids with N-p-methoxybenzoyl- and N-p-octyloxybenzoyl-N-phenylhydroxylamine. Anal Sci 1991, 7, 1, 125–8.
[16] Inoue S. Solvent-extraction of lanthanides with N-m-nitrobenzoyl- and N-m-cyanobenzoyl-N-phenylhydroxylamine. Solvent Extr Ion Exch 1995, 13, 2, 313–22.
[17] Inoue S. Solvent-extraction of lanthanoids(III) with dinitrobenzoyl-N-phenylhydroxylamine. Anal Sci 1994, 10, 2, 315–30.
[18] Inoue S, Zhang QB, Uto M. Steric Effect of substituents on the extraction of lanthanoids(III) with N-p-(n-, iso- and tert-)butylbenzoyl-N-phenylhydroxylamine. Talanta 1997, 44, 8, 1455–62.
[19] Nakagawa K, Okada S, Inoue Y, Tai A, Hakushi T. Solvent-extraction of lanthanoid picrates with crown ethers – preferential sandwich complexation and unique cation selectivities. Anal Chem 1988, 60, 22, 2527–31.
[20] Kitatsuji K, Meguro Y, Yoshida Z, Yamamoto T, Nishizawa K. Synergistic Ion-Pair Extraction of lanthanide(III) with thenoyltrifluoroacetone and crown-ether into 1,2-dichloroethane, Solv Extr Ion Exch 1995, 13, 2, 289–300.
[21] Inoue Y, Nakagawa K, Hakushi T. Solvent-extraction of lanthanoid(III) picrates with a Bis(crown ether)-enhanced extractability through double-sandwich complexation. J Chem SocDalton Trans 1993, 15, 2279–81.
[22] Beer PD, Drew MGB, Grieve A, Ogden MI. Lanthanide picrate complexes and picric acid adduct of a Calix[4]arene diamide. syntheses and structures of Tm[(LH−2)A], [Ce(LH−2)(MeOH)2A]·HA, [PrLa3] and L·2HA{L = 5,11,17,23-tetra-tert-butyl-25,27-bis(diethylcarbamoylmethoxy)- 26,28-dihydroxycalix[4]arene, HA=picric acid}. J Chem Soc Dalton Trans 1995, 21, 3455–66
[23] Inoue Y, Nakagawa K, Hakushi T. Solvent isotope effect in ion-pair extraction of aqueous lanthanoid(III) picrates with a crown-ether. J Chem Soc Dalton Trans 1993, 8, 1333–6.
[24] Beer PD, Drew MG, Kann M, Leeson PB, Ogden MI, Williams G. Lanthanide structures, coordination, and extraction investigations of a 1,3-bis(diethyl amide)-substituted Calix[4]arene ligand. Inorg Chem 1996, 35, 8, 2202–11.
[25] Daitch CE, Hampton PD, Duesler EN. Selective binding of group IIIA and lanthanide metals by hexahomotrioxacalix[3]arene macrocycles. J Am Chem Soc 1996, 118, 33, 7769–73.
[26] Frazier R, Wai CM. The effect of solvents on the extraction of lanthanoids with 18-crown-6 and trichloroacetate. J Radio Nucl Chem 1992, 159, 1, 63–9.
[27] Mathur JN, Choppin GR. The interaction of crown ethers with beta-diketonate complexes of f-elements. Solvent Extr Ion Exch 1993, 11, 1, 1–18.
[28] Imura H, Mito H. Selective extraction of light lanthanides(III) with 18-crown-6 and perfluorooctanoate. J Radioanal Nucl Chem Art 1995, 189, 2, 229–35.
[29] Fidelis I. Temperature Effect on the extraction of lanthanides in the TBP-HNO3 system. J Inorg Nucl Chem 1970, 32, 3, 997–1003.
[30] Peng CL. Separation and determination of trace rare earth elements in nickel-based high-temperature alloy and aluminium alloy. Chin Sci Bullet1973, 4, 170–3.
[31] Sreelatha S, Prasada Rao T, Narayanan CS, Damodaran AD. Extraction equilibria of rare earths by a new reagent (2-ethylhexyl-3-pentadecylphenyl) phosphoric acid. Talanta 1994, 41, 3, 433–8.
[32] Yoshizuka K, Kosaka H, Shinohara T, Ohto K, Inoue K. Structural Effect of phosphoric esters having bulky substituents on the extraction of rare earth elements. Bull Chem Soc Japan 1996, 69, 3, 589–96.
[33] Takayanagi T, Yotsuyanagi T. Ion-associate solvent-extraction and separation of lanthanides(III) with 2,3-naphthalenediol and benzyldimethyltetradecylammonium chloride. Bull Chem Soc Japan 1994, 67, 7, 1835–9.
[34] Korotkin YS. Use of synergistic effects in extraction chromatography. I. Behavior of Americium and Europium in the system TTA-TBP. Sov Radiochem 1981, 23, 2, 140–5.
[35] Qin GR, Li SX. Synergistic extraction of uranium and rare earth elements with different synergistic extraction system involving PMBP. Chinese Journal of Analysis Laboratory 1983, (5), 19–22
[36] Noro J, Sekine T. Solvent-extraction of lanthanum(III), europium(III), and lutetium(III) with 5,7-dichloro-8-quinolinol into chloroform in the absence and presence of tetrabutylammonium ions or triocytlphosphine oxide. Bull Chem Soc Japan 1993, 66, 9, 2564–9.
[37] Jeannot MA, Cantwell FF. Solvent microextraction into a single drop. Anal Chem 1996, 68, 13, 2236–40.
[38] Liu H, Dasgupta PK. Analytical chemistry in a drop. Solvent extraction in a microdrop. Anal Chem 1996, 68, 11, 1817–21.
[39] Jeannot MA, Cantwell FF. Mass transfer characteristics of solvent extraction into a single drop at the tip of a syringe needle. Anal Chem 1997, 69, 235–9.
[40] Ho TS, Pedersen-Bjergaard S, Rasmussen KE. Recovery, enrichment and Selectivity in liquid-phase microextraction-comparison with conventional liquid-liquid extraction. J Chrom A 2002, 963, 1–2, 3–17.
[41] Wu YL, Jiang ZC, Hu B. A Novel micro drop solvent extraction technique combined with low temperature electrothermal vaporization ICP-AES for ultra trace element analysis. Chem J Chin Univ Chin 2003, 24, 10, 1793–4.
[42] Xia LB, Hu B, Jiang ZC, Wu YL, Liang Y. Single-drop microextraction combined with low-temperature electrothermal vaporization ICPMS for the determination of trace Be, Co, Pd, and Cd in biological samples. Anal Chem 2004, 76, 10, 2910–5.
[43] Ma MH, Cantwell FF. Solvent microextraction with simultaneous back-extraction for sample cleanup and preconcentration: Preconcentration into a single microdrop. Anal Chem 1999, 71, 2, 388–93.

[44] Liu XJ, Fan ZF. Liquid-liquid-liquid micro extraction combined with CE for the determination of rare earth elements in water samples. Chromatographia 2009, 70, 3–4, 481–7.
[45] Pedersen-Bjergaard S, Rasmussen KE. Liquid-liquid-liquid microextraction for sample preparation of biological fluids prior to capillary electrophoresis. Anal Chem 1999, 71, 14, 2650–6.
[46] Rezaee M, Assadi Y, Hosseinia MRM, Aghaee E, Ahmadi F, Berijani S. Determination of organic compounds in water using dispersive liquid-liquid microextraction. J Chromatogr A2006, 1116(1–2), 1–9.
[47] Mallah MH, Shemirani F, Maragheh MG. Ionic liquids for simultaneous preconcentration of some lanthanoids using dispersive liquid-liquid microextraction technique in uranium dioxide powder. Environ Sci Technol 2009, 43, 6, 1947–51.
[48] Chandrasekaran K, Karunasagar D, Arunachalam J. Dispersive liquid-liquid micro-extraction for simultaneous preconcentration of 14 lanthanides at parts per trillion levels from groundwater and determination using a micro-flow nebulizer in inductively coupled plasma-quadrupole mass spectrometry. J Anal At Spectrom 2012, 27, 6, 1024–31.
[49] Guo XQ, Tang XT, He M, et al. Dual dispersive extraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry for determination of trace REEs in water and sediment samples. RSC Adv 2014, 4, 38, 19960–9.
[50] Zanjani MRK, Yamini Y, Shariati S, Jonsson JA. A New liquid-phase microextraction method based on solidification of floating organic drop. Anal Chim Acta 2007, 585, 2, 286–93.
[51] Ganjali MR, Sobhi HR, Farahani H, Norouzi P, Dinarvand R, Kashtiaray A. Solid drop based liquid-phase microextraction. J Chromatogr A 2010, 1217, 16, 2337–41.
[52] Chen SZ, Zhu SP, Lu DB. Solidified floating organic drop microextraction for the determination of trace Dy and Y by electrothermal vaporization inductively coupled plasma mass spectrometry. At Spectrosc 2014, 35, 1, 1–6.
[53] Li YJ, Hu B. Cloud Point Extraction with/without chelating agent on-line coupled with inductively coupled plasma optical emission spectrometry for the determination of trace rare earth elements in biological samples. J Hazard Mater 2010, 174, 1–3, 534–40.
[54] Depoi FD, Bentlin FR, Ferrao MF, Pozebon D. Multivariate optimization for cloud point extraction and determination of lanthanides. Anal Methods 2012, 4, 9, 2809–14.
[55] Perez-Gramatges A, Chatt A. Preconcentration neutron activation analysis of lanthanides by cloud point extraction using PAN. J Radioanal Nucl Chem 2006, 269, 2, 491–7.
[56] Nouh EA. Micelle mediated extraction for preconcentration of Eu(III) prior to determination by flame atomic absorption spectrometry. J Ind Eng Chem 2015, 24, 87–91.
[57] Labrecque C, Lariviere D. Quantification of rare earth elements using cloud point extraction with diglycolamide and ICP-MS for environmental analysis. Anal Methods 2014, 6, 23, 9291–8.
[58] Ohashi A, Hashimoto T, Imura H, Ohashi K. Cloud point extraction equilibrium of lanthanum(III), europium(III) and lutetium(III) using Di(2-ethylhexyl)phosphoric acid and triton X-100. Talanta 2007, 73, 5, 893–8.
[59] Camel V. Solid phase extraction of trace elements. Spectrochim Acta Part B: At Spectrosc 2003, 58 7, 1177–233.
[60] Poole CF. New trends in solid-phase extraction. TRAC Trends Anal Chem 2003, 22, 6, 362–73.
[61] Melo LFC, Collins CH, Jardim ICSF. New materials for solid-phase extraction and multiclass high-performance liquid chromatographic analysis of pesticides in grapes. J Chromatogr A 2004, 1032, 1–2, 51–8
[62] Kumar M, Rathore DPS, Singh AK. Pyrogallol immobilized amberlite XAD-2: A newly designed collector for enrichment of metal ions prior to their determination by flame atomic absorption spectrometry. Mikrochim Acta 2001, 137, 3–4, 127–34.
[63] Strelko V, Malik DJ, Streat M. Interpretation of transition metal sorption behavior by oxidized active carbons and other adsorbents. Sep Sci Technol 2004, 39, 8, 1885–905.
[64] Marques MJ, Morales-Rubio A, Salvador A, de la Guardia M. Chromium speciation using activated alumina microcolumns and sequential injection analysis-flame atomic absorption spectrometry. Talanta 2001, 53, 6, 1229–39.
[65] Wie ZG, Hong FS, Yin M, et al. Off-line separation and determination of rare earth elements associated with chloroplast pigments of hyperaccumulator dicranopteris dichotoma by normal-phase liquid chromatography and ICP-MS. Anal Bioanal Chem 2004, 380, 4, 677–82.
[66] Agrawal YK. Poly(Beta-Styryl)-(1,2-methanofullerene-C60)-61-formo, hydroxamic acid for the solid phase extraction. Sep Preconcentration Rare Earth Elem Fullerenes Nanotubes Carbon Nanostruct 2007, 15, 5, 353–65.
[67] Li YH, Wang SG, Wie JQ, et al. Lead adsorption on carbon nanotubes. Chem Phys Lett 2002, 357, 3–4, 263–6.
[68] Di ZC, Ding J, Peng XJ, Li YH, Luan ZK, Liang J. Chromium Adsorption by aligned carbon nanotubes supported ceria nanoparticles. Chemosphere 2006, 62, 5, 861–5.
[69] Lv YK, Wang LM, Yang L, Zhao CX, Sun HW. Synthesis and application of molecularly imprinted poly(methacrylic acid)-silica hybrid composite material for selective solid-phase extraction and high-performance liquid chromatography determination of oxytetracycline residues in milk. J Chromatogr A 2012, 1227, 48–53.
[70] Zambrzycka E, Roszko D, Leśniewska B, Wilczewska AZ, Godlewska–Żyłkiewicz B. Studies of ion-imprinted polymers for solid-phase extraction of ruthenium from environmental samples before its determination by electrothermal atomic absorption spectrometry. Spectrochim Acta Part B: At Spectrosc 2011, 66, 7, 508–16.
[71] Pu XL, Hu B, Jiang ZC, Huang CZ. Speciation of dissolved iron(ii) and iron(iii) in environmental water samples by gallic acid-modified nanometer-sized alumina micro-column separation and ICP-MS Determination. Anal 2005, 130, 8, 1175–81.
[72] Liang P, Qin YC, Hu B, Li CX, Peng TY, Jiang ZC. Study of the adsorption behavior of heavy metal ions on nanometer-size titanium dioxide with ICP-AES. Fresenius J Anal Chem 2000, 368, 6, 638–40.
[73] Liang P, Shi TQ, Lu HB, Jiang ZC, Hu B. Speciation of Cr(III) and Cr(VI) by nanometer titanium dioxide micro-column and inductively coupled plasma atomic emission spectrometry. Spectrochim Acta Part B At Spectrosc 2003, 58, 9, 1709–14.
[74] Yin J, Jiang ZC, Chang G, Hu B. Simultaneous on-line preconcentration and determination of trace metals in environmental samples by flow injection combined with inductively coupled plasma mass spectrometry using a nanometer-sized alumina packed micro-column. Anal Chim Acta 2005, 540, 2, 333–9.

[75] Sawicki R, Mercier L. Evaluation of mesoporous cyclodextrin-silica nanocomposites for the removal of pesticides from aqueous media. Environ Sci Technol 2006, 40, 6, 1978–83.

[76] Tian RJ, Ye ML, Hu LH, Li X, Zou HF. Selective extraction of peptides in acidic human plasma by porous silica nanoparticles for peptidome analysis with 2-D LC-MS/MS. J Sep Sci 2007, 30, 14, 2204–9.

[77] Huang CZ, Jiang ZC, Hu B. Mesoporous Titanium Dioxide as a novel solid-phase extraction material for flow injection micro-column preconcentration on-line coupled with ICP-OES determination of trace metals in environmental samples. Talanta 2007, 73, 2, 274–81.

[78] Jiang HM, Hu B, Chen BB, Xia LB. Hollow fiber liquid phase microextraction combined with electrothermal atomic absorption spectrometry for the speciation of arsenic (III) and arsenic (V) in fresh waters and human hair extracts. Anal Chim Acta 2009, 634, 1, 15–21.

[79] Wang F, Guan YF, Zhang S, Xia Y. Hydrophilic Modification of silica–titania mesoporous materials as restricted-access matrix adsorbents for enrichment of phosphopeptides. J Chromatogr A 2012, 1246, 76–83.

[80] Zhang Y, Liu HY, Zhang XY, Lei H, Bai LG, Yang GL. On-line solid phase extraction using organic-inorganic hybrid monolithic columns for the determination of trace B-lactam antibiotics in milk and water samples. Talanta 2013, 104, 17–21.

[81] Choi K, Ng AHC, Fobel R, et al. Automated digital microfluidic platform for magnetic-particle-based immunoassays with optimization by design of experiments. Anal Chem 2013, 85, 20, 9638–46.

[82] Gu ZY, Chen YJ, Jiang JQ, Yan XP. Metal-organic frameworks for efficient enrichment of peptides with simultaneous exclusion of proteins from complex biological samples. Chem Commun 2011, 47, 16, 4787–9.

[83] Ni Z, Jerrell JP, Cadwallader KR, Masel RI. Metal-organic frameworks as adsorbents for trapping and preconcentration of organic phosphonates. Anal Chem 2007, 79, 4, 1290–3.

[84] Zhou YY, Yan XP, Kim KN, Wang SW, Liu MG. Exploration of coordination polymer as sorbent for flow injection solid-phase extraction on-line coupled with high-performance liquid chromatography for determination of polycyclic aromatic hydrocarbons in environmental materials. J Chromatogr A 2006, 1116, 1–2, 172–8.

[85] Bahramifar N, Yamini Y. On-line preconcentration of some rare earth elements in water samples using C-18-cartridge modified with 1-(2-pyridylazo) 2-naphtol (PAN) prior to simultaneous determination by inductively coupled plasma optical emission spectrometry (ICP-OES). Anal Chim Acta 2005, 540, 2, 325–32.

[86] Liang P, Fa WJ. Determination of La, Eu and Yb in water samples by inductively coupled plasma atomic emission spectrometry after solid phase extraction of their 1-phenyl-3-methyl-4-benzoylpyrazol-5-One complexes on silica gel column. Microchim Acta 2005,150, 1, 15–9.

[87] Liang P, Liu Y, Guo L. Determination of trace rare earth elements by inductively coupled plasma atomic emission spectrometry after preconcentration with multiwalled carbon nanotubes. Spectrochim Acta Part B At Spectrosc 2005, 60, 1, 125–9.

[88] Chauvin AS, Bunzli JCG, Bochud F, Scopelliti R, Froidevaux P. Use of dipicolinate-based complexes for producing ion-imprinted polystyrene resins for the extraction of Yttrium-90 and heavy lanthanide cations. Chem Eur J 2006, 12, 26, 6852–64.

[89] Wang ZH, Yan XP, Wang ZP, Zhang ZP, Liu LW. Flow injection on-line solid phase extraction coupled with inductively coupled plasma mass spectrometry for determination of (ultra)trace rare earth elements in environmental materials using maleic acid grafted polytetrafluoroethylene fibers as sorbent. J Am Soc Mass Spectrom 2006, 17, 9, 1258–64.

[90] Chen SZ, Xiao MF, Lu DB, Zhan XL. Carbon nanofibers as solid-phase extraction adsorbent for the preconcentration of trace rare earth elements and their determination by inductively coupled plasma mass spectrometry. Anal Lett 2007, 40, 11, 2105–15.

[91] Huang CZ, Jiang ZC, Hu B. Mesoporous titanium dioxide as a novel solid-phase extraction material for flow injection micro-column preconcentration on-line coupled with ICP-OES determination of trace metals in environmental samples. Talanta 2007, 73, 2, 274–81.

[92] Dutta S, Mohapatra PK, Dhekane GD, Das AK, Manchanda VK. Solid phase extraction of europium and uranium using tulsion CH-90 Resin. Desalination 2008, 232, 1–3, 216–24.

[93] Katarina RK, Takayanagi T, Oshita K, Oshima M, Motomizu S. Sample pretreatment Using chitosan-based chelating resin for the determination of trace metals in seawater samples by inductively coupled plasma-mass spectrometry. Anal Sci 2008, 24, 12, 1537–44.

[94] Shirvani-Arani S, Ahmadi SJ, Bahrami-Samani A, Ghannadi-Maragheh M. Synthesis of nano-pore samarium (III)-imprinted polymer for preconcentrative separation of samarium ions from other lanthanide ions via solid phase extraction. Anal Chim Acta 2008, 623, 1, 82–8.

[95] Zhang LL, Chang XJ, Zhai YH, et al. Selective solid phase extraction of trace Sc(III) from environmental samples using silica gel modified with 4-(2-morinyldiazenyl)-N-(3-(trimethylsilyl)propyl)benzamide. Anal Chim Acta 2008, 629, 1–2, 84–91.

[96] Shariati S, Yamini Y, Faraji M, Saleh A. On-line solid phase extraction coupled to ICP-OES for simultaneous preconcentration and determination of some transition elements. Microchim Acta 2009, 165, 1–2, 65–72.

[97] Vizioli N, Gil R, Martinez LD, Silva MF. On-line solid phase extraction CZE for the simultaneous determination of lanthanum and gadolinium at picogram per liter levels. Electrophoresis 2009, 30, 15, 2681–7.

[98] Zhu YB, Umemura T, Haraguchi H, Inagaki K, Chiba K. Determination of REEs in seawater by ICP-MS after on-line preconcentration using a syringe-driven chelating column. Talanta 2009, 78, 3, 891–5.

[99] Dave SR, Kaur H, Menon SK. Selective solid-phase extraction of rare earth elements by the chemically modified amberlite XAD-4 resin with azacrown ether. React Funct Polym 2010, 70, 9, 692–8.

[100] Raju CSK, Lueck D, Scharf H, Jakubowski N, Panne U. A Novel solid phase extraction method for pre-concentration of gadolinium and gadolinium based MRI contrast agents from the environment. J Anal At Spectrom 2010, 25, 10, 1573–80.

[101] Li DD, Chang XJ, Hu Z, Wang QH, Li RJ, Chai XL. Samarium (III) adsorption on bentonite modified with N-(2-hydroxyethyl) ethylenediamine. Talanta 2011, 83, 5, 1742–7.

[102] Tong SS, Zhao SJ, Zhou WH, Li RG, Jia Q. Modification of multi-walled carbon nanotubes with tannic acid for the adsorption of La, Tb and Lu ions. Microchim Acta 2011, 174, 3–4, 257–64.

[103] Wang QH, Chang XJ, Hu Z, Li DD, Li RJ, Chai XL. Preconcentration of Erbium(III) ions from environmental samples using activated carbon modified with benzoyl hydrazine. Microchim Acta 2011, 172, 3–4, 395–402.

[104] Zhang JL, Cheng RM, Tong SS, et al. Microwave plasma torch-atomic emission spectrometry for the on-line determination of rare earth elements based on flow injection preconcentration by TiO2-graphene composite. Talanta 2011, 86, 114–20.

[105] Berijani S, Ganjali MR, Sereshti H, Norouzi P. A selective modified nanoporous silica as sorbent for separation and preconcentration of dysprosium in water samples prior to ICP-OES determination. Int J Environ Anal Chem 2012, 92, 3, 355–65.

[106] Cho J, Chung K, Choi MS, Kim H. Analysis of rare earth elements in seawater by inductively coupled plasma mass spectrometry after pre-concentration using TSKTM-HD-MW-CNTs (highly dispersive multi-walled carbon nanotubes. Talanta 2012, 99, 369–74.

[107] Li Y, Yang JL, Jiang Y. Trace Rare Earth element detection in food and agricultural products based on flow injection walnut shell packed microcolumn preconcentration coupled with inductively coupled plasma mass spectrometry. J Agric Food Chem 2012, 60, 12, 3033–41.

[108] Alizadeh T, Amjadi S. Synthesis of nano-sized Eu3+-imprinted polymer and its application for indirect voltammetric determination of europium. Talanta 2013, 106, 431–9.

[109] Chen SZ, Zhu SP, Lu DB. Titanium dioxide nanotubes as solid-phase extraction adsorbent for on-line preconcentration and determination of trace rare earth elements by inductively coupled plasma mass spectrometry. Microchem J 2013, 110, 89–93.

[110] Tajabadi F, Yamini Y, Sovizi MR. Carbon-based magnetic nanocomposites in solid phase dispersion for the preconcentration some of lanthanides, followed by their quantitation via ICP-OES. Microchim Acta 2013, 180, 1–2, 65–73.

[111] Zereen F, Yilmaz V, Arslan Z. Solid phase extraction of rare earth elements in seawater and estuarine water with 4-(2-Thiazolylazo) resorcinol immobilized chromosorb 106 for determination by inductively coupled plasma mass spectrometry. Microchem J 2013, 110, 178–84.

[112] Gao BJ, Zhang QJ, Xu Y. Study on recognition and separation of rare earth ions at picometre scale by using efficient ion-surface imprinted polymer materials. Hydrometall 2014, 150, 83–91.

[113] Jerez J, Isaguirre AC, Bazán C, Martinez LD, Cerutti S. Determination of scandium in acid mine drainage by ICP-OES with flow injection on-line preconcentration using oxidized multiwalled carbon nanotubes. Talanta 2014, 124, 89–94.

[114] Karadas C, Kara D. Preconcentration of rare earth elements using amberlite XAD-4 modified with 2,6-pyridinedicarboxaldehyde and their determination by inductively coupled plasma optical emission spectrometry. Water Air Soil Poll 2014, 225, 5, 1972–81.

[115] Karadas C, Kara D. Determination of rare earth elements by solid phase extraction using chemically modified amberlite XAD-4 resin and inductively coupled plasma-optical emission spectrometry. Water Air Soil Poll 2014, 225, 11, 2192–201.

[116] Ozdemir S, Okumus V, Dundar A, Celik KS, Yuksel U, Kilinc E. Selective preconcentration of lanthanum(III) by coriolus versicolor immobilised on amberlite XAD-4 and its determination by ICP-OES. Int J Environ Anal Chem 2014, 94, 6, 533–45.

[117] Sarabadani P, Sadeghi M, Payehghadr M, Es′haghi Z. Synthesis and characterization of a novel nanostructured ion-imprinted polymer for pre-concentration of Y(III) ions. Anal Methods 2014, 6, 3, 741–9.

[118] Su SW, Chen BB, He M, Hu B, Xiao ZW. Determination of trace/ultratrace rare earth elements in environmental samples by ICP-MS after magnetic solid phase extraction with Fe3O4@SiO2@polyaniline-graphene oxide composite. Talanta 2014, 119, 458–66.

[119] Berijani S, Ganjali MR, Sereshti H, Tabatabaei SH, Norouzi P. Application of a new modified magnetic nanoparticle as a selective sorbent for preconcentration and extraction of Europium in environmental water samples prior to ICP-OES determination. J Iran Chem Soc 2015, 12, 4, 737–42.

[120] Prasad BB, Jauhari D. Double-Ion Imprinted Polymer @magnetic nanoparticles modified screen printed carbon electrode for simultaneous analysis of cerium and gadolinium ions. Anal Chim Acta 2015, 875, 83–91.

[121] Vasylechko VO, Gryshchouk GV, Zakordonskiy VP, Vyviurska O, Pashuk AV. A Solid-phase extraction method using transcarpathian clinoptilolite for preconcentration of trace amounts of terbium in water samples. Chem Cent J 2015, 9, 1, 1–7.

[122] Zhang YN, Zhong C, Zhang QY, Chen BB, He M, Hu B. Graphene oxide-TiO2 composite as a novel adsorbent for the preconcentration of heavy metals and rare earth elements in environmental samples followed by on-line inductively coupled plasma optical emission spectrometry detection. RSC Adv 2015, 5, 8, 5996–6005.

[123] Iijima S. Helical microtubules of graphitic carbon. Nature 1991, 354, 56–58.

[124] Trojanowicz M. Analytical applications of carbon nanotubes: A review. TRAC Trends Anal Chem 2006, 25, 5, 480–9.

[125] Lu CY, Liu CT. Removal of nickel(II) from aqueous solution by carbon nanotubes. J Chem Technol Biotechnol 2006, 81, 12, 1932–40.

[126] Liang P, Liu Y, Guo L. Determination of trace rare earth elements by inductively coupled plasma atomic emission spectrometry after preconcentration with multiwalled carbon nanotubes. Spectrochim Acta Part B: At Spectrosc 2005, 60, 1, 125–9.

[127] Zhang N, Huang C, Hu B. ICP-AES Determination of trace rare earth elements in environmental and food samples by on-line separation and preconcentration with acetylacetone-modified silica gel using microcolumn. Anal Sci 2007, 23, 8, 997–1002.

[128] Kajiya T, Aihara M, Hirata S. Determination of rare earth elements in seawater by inductively coupled plasma mass spectrometry with on-line column pre-concentration using 8-quinolinole-immobilized fluorinated metal alkoxide glass. Spectrochim Acta Part B At Spectrosc 2004, 59, 4, 543–50.

[129] Willie SN, Sturgeon RE. Determination of transition and rare earth elements in seawater by flow injection inductively coupled plasma time-of-flight mass spectrometry. Spectrochim Acta Part B At Spectrosc 2001, 56, 9, 1707–16.

[130] Hirata S, Kajiya T, Aihara M, Honda K, Shikino O. Determination of rare earth elements in seawater by on-line column preconcentration inductively coupled plasma mass spectrometry. Talanta 2002, 58, 6, 1185–94.

[131] Kumar SA, Pandey SP, Shenoy NS, Kumar SD. Matrix separation and preconcentration of rare earth elements from seawater by poly hydroxamic acid cartridge followed by determination using ICP-MS. Desalination 2011, 281, 49–54.

[132] Sabarudin A, Lenghor N, Oshima M, et al. Sequential-injection on-line preconcentration using chitosan resin functionalized with 2-amino-5-hydroxy benzoic acid for the determination of trace elements in environmental water samples by inductively coupled plasma-atomic emission spectrometry. Talanta 2007, 72, 5, 1609–17.

[133] Karadas C, Kara D, Fisher A. Determination of rare earth elements in seawater by inductively coupled plasma mass spectrometry with off-line column preconcentration using 2,6-diacetylpyridine functionalized amber lite XAD-4. Anal Chim Acta 2011, 689, 2, 184–9.

[134] Waqar F, Jan S, Mohammad B, Hakim M, Alam S, Yawar W. Preconcentration of rare earth elements in seawater with chelating resin having fluorinated beta-diketone immobilized on styrene divinyl benzene for their determination by ICP-OES. J Chin Chem Soc 2009, 56(2), 335–40.

[135] Fu Q, Yang LM, Wang QQ. On-line preconcentration with a novel alkyl phosphinic acid extraction resin coupled with inductively coupled plasma mass spectrometry for determination of trace rare earth elements in seawater. Talanta 2007, 72, 4, 1248–54.

[136] Gupte HS, Bhatt KD, Jain VK, Vyas DJ, Makwana BA. Azo resorcin[4] calixpyrrole grafted amberlite XAD-2 polymer: An efficient solid phase extractant for separation and preconcentration of La(III) and Ce(III) from natural geological samples. J Inclusion Phenom Macrocyclic Chem 2015, 81, 3–4, 409–22.

[137] Dybczynski R, Kulisa K. Effect of temperature and the mechanism of zone spreading during cation-exchange separation of rare earth elements by ion chromatography. Chromatographia 2005,61, 11–12, 573–80.

[138] Matsumiya H, Inoue H, Hiraide M. Separation of Gd-humic complexes and Gd-based magnetic resonance imaging contrast agent in river water with QAE-sephadex A-25 for the fractionation analysis. Talanta 2014, 128, 500–4.

[139] Li SQ, Hu B, Jiang ZC, Liang P, Li X, Xia LB. Selective separation of La3+ and lanthanum organic complexes with nanometer-sized titanium dioxide and their detection by using fluorination-assisted electrothermal vaporization ICP-AES with in-situ matrix removal. Environ Sci Technol 2004, 38, 7, 2248–51.

[140] Jon GG, Pu XL, Jiang ZC, Hu B. Separation/preconcentration of trace rare earth elements by micro-column packed with immobilized 1-phenyl-3-methyl-4-bonzoil-5-pyrazone on nanometer Al2O3 and their determination by inductively coupled plasma-atomic emission spectrometry. Chin J Anal Chem 2005, 33, 2, 207–10.

[141] Meng MJ, Meng XG, Liu Y, et al. An ion-imprinted functionalized SBA-15 adsorbent synthesized by surface imprinting technique via reversible addition-fragmentation chain transfer polymerization for selective removal of Ce(III) from aqueous solution. J Hazard Mater 2014, 278, 134–43.

[142] Zhang N, Hu B, Huang CZ. A New ion-imprinted silica gel sorbent for on-line selective solid-phase extraction of Dysprosium(III) with detection by inductively coupled plasma-atomic emission spectrometry. Anal Chim Acta 2007, 597, 1, 12–8.

[143] An J, Shade CM, Chengelis-Czegan DA, Petoud S, Rosi NL. Zinc-adeninate metal-organic framework for aqueous encapsulation and sensitization of near-infrared and visible emitting lanthanide cations. J Am Chem Soc 2011, 133, 5, 1220–3.

[144] Yan P, He M, Chen BB, Hu B. Restricted accessed nanoparticles for direct magnetic solid phase extraction of trace metal ions from human fluids followed by inductively coupled plasma mass spectrometry detection. Analyst 2015, 140, 12, 4298–306.

[145] Arthur CL, Pawliszyn J. Solid Phase Microextraction with thermal desorption using fused silica optical fibers. Anal Chem 1990, 62, 2145–8.

[146] Kumar A, Gaurav Malik AK, Tewary DK, Singh B A Review on development of solid phase microextraction fibers by sol-gel methods and their applications. Anal Chim Acta 2008, 610, 1, 1–14.

[147] Ouyang G, Pawliszyn J. A Critical review in calibration methods for solid-phase microextraction. Anal Chim Acta 2008, 627, 2, 184–97.

[148] Kumar A, Malik AK. A review on the hyphenation of solid phase microextraction with capillary electrophoresis and mass spectrometry, Crit Rev Anal Chem 2009, 39, 2, 81–8.

[149] Musteata FM, Pawliszyn J. Bioanalytical Applications of solid-phase microextraction. TRAC Trends Anal Chem 2007, 26, 1, 36–45.

[150] Eisert R, Pawliszyn J. Automated In-tube Solid-phase microextraction coupled to high-performance liquid chromatography. Anal Chem 1997, 69, 3140–7.

[151] Kataoka′ H, Narimatsu S, Lord HL, Pawliszyn J. Automated in tube solid-phase microextraction coupled with liquid chromatography/-electrospray ionization mass spectrometry for the determination of beta-blockers and metabolites in urine and serum samples. Anal Chem 1999,71, 19, 4237–44.

[152] Li W, Fries DP, Malik A. Sol-gel stationary phases for capillary electrochromatography. J Chromatogr A 2004, 1044, 1–2, 23–52.

[153] Wu SW, Hu CG, He M, Chen BB, Hu B. Capillary microextraction combined with fluorinating assisted electrothermal vaporization inductively coupled plasma optical emission spectrometry for the determination of trace lanthanum, europium, dysprosium and yttrium in human hair. Talanta 2013, 115, 342–8.

[154] Zhang L, Chen BB, He M, Hu B. Polymer Monolithic Capillary microextraction combined on-line with inductively coupled plasma mass spectrometry for the determination of trace rare earth elements in biological samples. J Sep Sci 2013, 36, 13, 2158–67.

[155] Liu XL, Chen BB, Zhang L, et al. TiO2 nanoparticles functionalized monolithic capillary microextraction online coupled with inductively coupled plasma mass spectrometry for the analysis of Gd ion and Gd-based contrast agents in human urine. Anal Chem 2015, 87, 17, 8949–56.