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## **Selective separation of elements from complex solution matrix with molecular recognition plus macrocycles attached to a solid-phase: A review**

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## **Abstract**

Solid-phase extraction (SPE) approach was introduced approximately five decades ago, and until then development of SPE materials is seamlessly continued. Lately, the SPE-based research is increasingly focused in developing more explicit materials to achieve meticulous separation of elements from complex solution matrices with high concentrations of interfering ions. One group of SPE materials includes those with macrocyclic ligands immobilized on a solid-phase, which are capable of selective separation and pre-concentration of elements, and such selectivity in metal retention is generally termed as molecular recognition. In the process, the designed ‘host’ material possesses a high degree of recognition to specific elements or groups of elements called ‘guest’, and the recognition capability remains effective at the very low concentrations of the ‘guest’ species or when those present in complex matrices. The routes to the development of element-selective SPEs, the operating principles, applications and limitations are discussed in this review.

## **Keywords**

Separation; element-selectivity; Macrocycles; Solid-phase extraction; Molecular recognition

## **1.0 Introduction**

Although metals and metalloids are ubiquitous in nature, the environmental concentrations of both toxic and essential elements have been largely increased mostly pursuant to anthropogenic activities related to the industrial development and improved living standards in modern societies. The growing extent of metal pollution also initiated a number of legislative measures, such as, the Restriction of Hazardous Substance (RoHS) directive [1], End of Life Vehicle (ELV) directive [2] or the European Union Council Directive [3]. The RoHS or ELV directive has been imposed to specify the limit of trace elements in the industrial products, while the EU directive defined the acceptable concentrations of different elements in cultivable soils.

Sensitive analytical techniques such as, flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectrometry, and so forth are available for precise analysis of trace elements in solution. An overall analytical process comprises a number of succeeding steps, including sampling, sample preparation, separation and quantification. Among the aforementioned steps, sample preparation is by far the most important error source in modern analytical method development due to the low species concentration or heterogeneous distribution of the analytes in the matrix as well as the complex nature of the sample matrices. Therefore, a clean-up/separation step is often recommended before the analytical determination of trace elements in effluent or industrial waste waters to avoid the interfering effect from the matrix ions or to facilitate preconcentration due to their low concentrations in samples. The techniques commonly used for separation of elements from the matrix components are co-precipitation [4, 5], solvent extraction or liquid-liquid extraction [6], cloud point extraction [7-10], membrane filtration

[11-14], and solid-phase extraction (SPE) [15]. Most of the conventional separation approaches undergo slow kinetics and, also, lose effectiveness when the concentration of the species to be separated is low, or when several other chemically-similar elements to the target species co-exist in the matrix. The SPE-approach coupled with macrocycles of molecular recognition capability was introduced as an effectual separation system, which possess sufficient specificity and superior affinity for the target element or group of elements over other closely related elements, even if these elements are present in high concentration. The review covers the background of the development of the SPE-systems with macrocycles, including the operating routes. The whys and wherefores of the selectivity behavior have been explained, and the application examples are compiled including the limitations in developments.

## **2.0 Development of SPE materials: activated carbon to macrocycles**

In SPE, analyte(s) is isolated from a solution by their transfer to and retention on a solid-phase sorbent packed in any of the following formats: micro-columns, cartridges, syringe barrels and disks. Regardless of the format used, SPE operation involves two major steps— sample loading and elution. Sample solution containing the analytes is allowed to percolate through the solid sorbent material for collection of the analytes in the sample loading step while the ‘captured’ analytes are back-extracted upon elution with a suitable solvent in the final step. A ‘conditioning’ step is always performed before the sample loading step to ensure the removal of any likely impurities contained in the sorbent or the packaging of the SPE system. It also allows the wetting of the packing material and the solvation of the SPE material. An optional washing step using a solvent having low elution strength is sometimes involved between the sample treatment and elution step to eliminate the unwanted matrix components without displacing the target analytes. The flow rates of the sample

loading and elution steps are required to be optimized to attain the quantitative separation performance [16-18]. The progress and developments in solid phase extraction (SPE) technique over the decades were discussed in a number of review articles [15, 18, 19], book sections [16, 17] and books [20-22]. Therefore, a detailed discussion on every single SPE-type is not included in this review. Instead, a timeline-based approach has been used to highlight the property-based development of SPE materials.

The first experimental application of SPE started approximately five decades ago with the application of granular activated carbon for the concentration of organic compounds from raw and filtered surface waters [15, 23]. An attempt to find the more suitable SPE material was started in the late 1960s to overcome the limiting factors of activated carbon due to its heterogeneous nature [15]. Riley and Taylor [24] introduced a cross-linked polystyrene resin, Amberlite XAD-1 for SPE separation of organic compounds from aqueous samples. The study stimulated the interest about Amberlite polymeric resins among other researchers in the 1970s. Consequently, other styrene-divinylbenzene Amberlites (XAD-2, XAD-4) and ethylene-dimethacrylate resins (XAD-7 and XAD-8) were introduced [25-32]. Other copolymers such as, Porapaks [33-35], Chromosorbs [36-41] and Tenax (2,6-diphenyl-p-phenylene oxide) [42-45] were also used for SPE procedures along with Amberlites. The search for the most appropriate SPE material includes the application of polyurethanes either as open-pore polyurethane [46, 47] or as polyurethane foam [48-57], polypropylene [58-60], polytetrafluoroethylene [61-64] or ion-exchange resins [65-68] etc.

There are too many aspects of the resin standardization that had to be considered prior to the analytical use of macroreticular resins, which initiated the evaluation of other types of SPE materials [15]. Applicability of bonded phases for SPE process was introduced in the middle of 1970s [15, 69]. Later, well standardized and relatively stable commercial SPE products with bonded silica became available, which resulted in the extensive use of these

materials in SPE procedures [15]. Although SPE procedures with different alkyl- or aryl-groups bonded with silica were reported, octadecyl-bonded silica is the most popular phase among the bonded phase employing silica's [15, 70-76].

During the search for the best SPE material, it became apparent that there was no universal material suitable for all purposes. It was observed that some of the SPE materials have the capability to interact with a variety of metal ions, while others are fairly specific for a particular ion [77-82]. Lately, there has been increasing interest in developing more explicit materials to use in the meticulous separation of ions from solutions containing complex matrices with high concentrations of interfering ions. Simultaneously, efforts to design more effective SPE systems besides the development of classical types of SPE materials were continued. Membrane extraction disks consisting of a fibrillated PTFE matrix enmeshed with bonded silica, polymers or ion exchangers were designed to achieve higher sample flow rate and selectivity in the separation process [83-85]. Selective affinity of SPE materials towards target substances can also be achieved with the use of molecularly imprinted polymers (MIPs). In MIPs, a chosen target molecule is used as a template through a casting procedure which is extracted afterwards, thus leaving complementary cavities behind. In the process, MIPs show a certain chemical affinity for the original molecule and were successfully used for selective extraction [86, 87]. Solid phase microextraction (SPME) is another new interesting SPE technique, which involves the use of a fiber coated with an extracting phase, that can be a liquid (polymer) or a solid (sorbent), which extracts different kinds of analytes from liquid or gas phase [88-91].

The efforts done in aiming for an optimum material for a particular application with the classical-type SPE application are also not stopped. Analyte-antibody interactions were used to design immunosorbent, which can be used as a classical SPE material. In this approach antibody produced against a target compound is immobilized on a solid phase to achieve

selective extraction [92-97]. One group of classical-type SPE system includes the use of macrocyclic chelants, such as crown ethers, immobilized on a silica or polymer support which was designed to attain selectivity in the separation process [98-107].

A timeline view of the development in SPE materials until the introduction of macrocycle-containing SPEs is illustrated in [Figure 1](#).

### **3.0 Operating route of macrocycles in metal separation**

Macrocyclic compounds have a considerable potential to be used as metal-selective reagents in the separation science due to their ability to form stable complexes with metal ions [108-110]. An enormous number of macrocyclic reagents with a variety of donor atoms, ring sizes, and ligand geometries have been prepared [111]. The foremost group of macrocyclic compounds is crown ethers, and the first crown ether was dibenzo-18-crown-6 [112]. In addition to the crown ethers, other kinds of macrocyclic ligands, e.g., macrocyclic polyamines, polysulphides, cyclic peptides, calixarenes, cyclophanes, and cyclodextrins are available as parent macro-rings [113-115]. A comparison of the parent macrocycles characteristics is summarized in [Table 1](#). Among the parent macrocycles, crown ethers possess excellent structural diversity followed by superior guest selectivity, and are particularly effective for binding hard metal ions [113].

Crown ethers contain oxygen, sulfur and nitrogen as donor atoms. The number of donor atoms in the crown ether unit determines the stability of the macrocycle-metal complex while the types of donor atoms decide the ion selectivity of the crown ethers [116]. The metal ion binding strength and selectivity can be strengthened by the introduction of one or more side arms into the crown ether unit, and the derivative is known as lariat ether [113, 117, 118]. Complexes containing species incorporated in the macrocyclic cavity are known as inclusion complexes, and different types of complexation between the macrocycle structure and the

target metal ions are likely [115]. Some possible types of complexation between  $K^+$  with diaza-18-crown-6, lariat ether and double armed crown ether as reported by Gandour et al. [119] and reproduced by Tsukube [113] are shown in Fig. 2a. Figure 2b shows the schematic illustration of the cation binding process with the armed macrocycles [113]. As shown in Fig. 2a, accommodation of  $K^+$  ion in a circular cavity of the parent macrocycle diaza-18-crown-6 **1** is observed. The  $K^+$  ion is coordinated to donor atoms of both crown ring and sidearm in the complex of lariat ether **2**, while it is completely accommodated in a three-dimensional cavity in the double armed crown ether **3** complex [113, 119]. Frequent use of the varying numbers of the sidearms by the armed macrocycles to bind the cations is observed as illustrated in Fig. 2b [113]. Hence, it can be briefly concluded that the selective separation of elements by macrocycles is managed either by the accommodation of ions within their circular cavity or in the three-dimensional cavity-like structures formed between the macro-ring and the sidearms. It also provides the advantage of designing a single macrocycle structure with a diverse selectivity option for target elements of distinctive ionic characters [120, 121] or a multiple-site receptor for different target species [122] as shown in Fig. 3.

Macrocycles have been employed for selective separation of metal ions from mixtures in bulk liquid membrane and/ or solvent extraction systems [116, 123, 124]. However, separation of metal ions using extraction or membrane systems is not considered as a cost-effective option due to the gradual loss of the expensive macrocyclic compounds from the organic membrane or layer [125]. The shortcoming was minimized by attaching the macrocyclic compounds to silica gel using a stable hydrocarbon-ether linkage [99, 100, 106, 125]. The efficiency of such systems lead to the development of new separation systems with the use of solid supported macrocycles, which are capable of high selectivity or recognition towards a particular species of metal or metalloid [104, 125].

#### 4.0 Selective solid-phase extraction of elements using macrocycle-aided molecular recognition

The process of recognition-based SPEs features steps of designing materials with pre-determined species-selectivity, attaching these to the supports, and their use to accomplish the required chemical separations. The designed ‘host’ materials, mostly containing macrocycles, possess a high degree of recognition to specific element or groups of elements called ‘guest’, and the recognition capability remains effective at the very low concentrations of the ‘guest’ species or when those present in complex matrices [104]. Synthesis of such materials includes a combined approach of organic synthesis and the study of cation complexation properties of the crown ethers to design and prepare macrocyclic ligands that will possess selective affinity to the target ions [102, 126, 127]. A compilation of schemes for synthesis of several crown ether varieties *e.g.* thiacrown ethers, diestercrown ethers, proton-ionizable crown ethers, chiral crown ethers, azacrown ethers and so forth is available [127]. As an example, ion-selective behavior of two 5-chloro-8-hydroxyquinoline (CHQ) substituted azacrown ethers (**1** and **2** in Fig. 4) is discussed as described by Zhang et al. [128] and Bordunov et al. [129]. In the azacrown ether structure **1**, two CHQ groups are attached to the macro ring through their positions 7 and exhibit selectivity to  $Mg^{2+}$  ion over other alkali and alkaline earth metal ions. The stronger affinity of **1** to  $Mg^{2+}$  ion maybe due to the incomplete interaction of the OH and quinoline nitrogen atoms in the CHQ groups with a cation bound within the macro ring. The quinoline nitrogens are sterically prevented from approaching the macro ring by the OH groups. Hence, the CHQ groups remain in the proper positions to selectively interact with  $Mg^{2+}$  and the macro ring. The CHQ groups, that are attached through their positions 2, in the macrocycle structure **2** exhibit better selectivity for  $K^+$  and  $Ba^{2+}$  ions. The selectivity behavior can be explained by the formation of a pseudo-cryptand structure pursuant to the overlapping of two CHQ groups. Hence, more stable  $K^+ \text{--} \mathbf{2}$  and  $Ba^{2+} \text{--} \mathbf{2}$  in

comparison to complexes of **2** with the alkali and alkaline earth cations are facilitating the selective collection of those ions [101].

The SPE materials with specific recognition capability are attached with any of the following support options, e.g., silica gel, titania, zirconia or other polymers. Silica gel is used mostly among the support materials due to its high hydrophilic character, large number of binding sites and substantial inert nature. Other options are adopted only when the silica gel cannot be used as the support such as, when the pH of solution is above 10 or when extreme purification of water is required, etc. [105, 130]. The silica gel-bound macrocycles having different element-selective properties and behaviors can be prepared as shown in the Fig. 5 as described in detail by Bradshaw et al. [125]. Macrocycle containing SPE-materials possesses a greater concentration of active sites compared to the conventional element-separation option in solid-phase as attributable to the enmeshed small microporous particles into the microfibrinous matrix. The approach also eliminates the channeling effect that recurrently appeared with packed-bed SPE processes [105, 131].

## **5.0 Applications and Limitations of SPEs with molecular recognition plus macrocycles in element-separation**

### **5.1 Applications**

#### *5.1.1 Selective separation of toxic elements*

The macrocycle-immobilized SPEs are used for the separation of a single or a group of toxic elements from the solution matrix. Advanced application of such SPE systems for inorganic analysis of the harmful elements was discussed elsewhere [132], and, hence, the section highlights the other related instances of molecular recognition dependent SPE-application.

The selective separation of lead from a high matrix electroless waste solution was achieved with the macrocycle-immobilized SPEs, namely, AnaLig Pb-01 and Pb-02 [133]. The AnaLig Pb-02 has also been used for the measurement of precise lead isotope ratio and its application to geochemical reference samples [134], or in the scheme of spectrophotometric lead determination in solution using 4-(2-pyridylazo)-resorcinol [135]. Furthermore, the macrocycle-immobilized Pb-selective SPEs have been successfully applied for the separation/preconcentration of lead from biological and environmental samples [132, 134, 136-140].

A combination of SPEs containing immobilized macrocyclic material, namely AnaLig TE-01, AnaLig AN-01 Si and AnaLig As-01 PA, was used for selective separation of water-soluble arsenic species: arsenite, arsenate, monomethylarsonic acid and dimethylarsinic acid [141]. A simple flow-based method was also developed for the discerning separation of tri- and pentavalent arsenic species from aqueous matrix using another macrocycle-immobilized SPE, specifically AnaLig An-02 [142]. The selectivity characteristics of AnaLig TE-01 towards arsenic [141] and iron-species [143] were further employed to formulate an approach for the treatment of spent iron-oxide coated sand from filters used in arsenic removal [144].

The application of silica gel-bound macrocycle systems for the selective separation of cadmium [145] from the metal-affluent matrix, or hexavalent chromium from the wastewaters [146] and conversion coatings [147] has been reported.

Selective separation of the ecotoxic transition metal ions (e.g., Co, Ni, Cu, Zn, Cd) from aqueous solutions was achieved using immobilized macrocyclic material containing a solid phase extraction system, namely AnaLig TE-05 [148, 149]. The AnaLig TE-01 SPE system was used for the nondestructive recovery of multiple elements, such as, As(V), Cd(II), Cr(III), Pb(II) and Se(IV), from the effluent containing excess aminopolycarboxylate chelant in solution [150, 151].

### 5.1.2 *Selective separation of rare and precious metals*

There are some non-ferrous metals, which are termed as *rare metals* due to the economic or technological difficulty in acquiring those metals in abundance, that are highly essential in a wide range of manufacturing areas, including machineries and electronics production. The SPE-systems with molecular recognition capabilities have been used for the recovery of *rare-termed* metals (e.g., indium) from the end-of-life e-waste [152] or from the waste effluent from the production process [153]. The macrocycle-immobilized AnaLig PM-series SPE systems have been used for the selective recovery of the precious metals, such as, Pt, Au, Pd [154, 155].

### 5.1.3 *Selective separation of radioactive elements*

The application of macrocycle-containing SPE-systems has been used for the separation of uranium from nuclear power plant waste [156]. The use of various SPE-systems with the selectivity to various radioactive elements, such as, Sr, Tc, Cs and Ra has also been reported [157-164] and evaluated for large-scale applications [164-167].

## 5.2 *Limitations*

The macrocycle-immobilized SPEs with molecular recognition competence are available typically from the commercial sources in recent days. Although the mass production approach creates the prospect of cost-minimization in the process of research, the patent-obligation decreases the option for detail appraisal of the product and opportunity of suggesting any enhancement or further development. Therefore, a particular SPE-system can be evaluated for a certain separation application while the working mechanism remained unexplained creating the inadequacies of the use of SPEs with selective recognition property in element-separation.

Moreover, the detail potential of the commercial SPE-product that claimed to have recognition selectivity towards a single element or group of elements is sometimes either not

included in detail in the brochures or seldom verified from the researchers having no competing interest. For example, Hasegawa et al. [153] proposed the application of the macrocycle-immobilized AnaLig TE 02 SPE for the quantitative separation of the indium or tin from the etching waste solution of the flat-panel display fabrication process after a comparative evaluation with other similar SPE-types (AnaLig TE 03, AnaLig TE 07, AnaLig TE 13 and AnaLig PM 02). The likely application prospect of AnaLig TE 02 SPE does not include the possibility of such separation in the product brochure though.

## **6.0 Conclusion**

The industrial endeavors are ever-increasing and a simultaneous adoption of stringent regulation rules to restrict the likely environmental consequences from the process effluent or discards will, therefore, create a huge market-demand for the element-specific separation approaches. The SPEs with the advantage of molecular recognition can be better utilized for the selective separation of environmentally hazardous or economically viable elements from the waste resources. Furthermore, the SPE-technique has the benefit of easy-automation, and the process can be coupled with suitable systems to achieve the benefit of recovery and recycling. The trends towards the SPE-material development having enhanced selectivity features will thus be expected to be continued, and anticipated to be considered as an indispensable part of the traditional research and development section of the companies in the forthcoming eras. We expect the development of innovative waste-treatment methodologies in conjunction with such SPE systems in the future.

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## References

- [1] RoHS Regulations – Government Guidance Notes, Department for Business, Innovation & Skills, Eco-design and Product Regulation Unit, Environmental & Technical Regulation Directorate, London, UK, 2010.
- [2] Council Directive 2000/53/EC on End of Life Vehicles, Environment Directorate, European Commission, Brussels, Belgium, 2003.
- [3] Council Directive 86/278/EEC on the Protection of the Environment, and in Particular of the Soil, When Sewage Sludge is used in Agriculture (In: EC Official Journal L181), European Community, Brussels, Belgium, 1986.
- [4] P. Patnaik, *Dean's Analytical Chemistry Handbook*, 2nd ed., McGraw-Hill, New York, 2004.
- [5] A. Townshend, E. Jackwerth, Precipitation of major constituents for trace preconcentration: Potential and problems, *Pure Appl. Chem.* 61 (1989) 1643–1656.
- [6] E. Müller, R. Berger, E. Blass, D. Sluyts, A. Pfennig, Liquid–Liquid Extraction, in: *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2000.
- [7] C.D. Stalikas, Micelle-mediated extraction as a tool for separation and preconcentration in metal analysis, *TRAC-Trend Anal. Chem.* 21 (2002) 343–355.
- [8] M.d.A. Bezerra, M.A.Z. Arruda, S.L.C. Ferreira, Cloud point extraction as a procedure of separation and pre-concentration for metal determination using spectroanalytical techniques: A review, *Appl. Spectrosc. Rev.* 40 (2005) 269–299.
- [9] H. Tani, T. Kamidate, H. Watanabe, Micelle-mediated extraction, *J. Chromatogr. A* 780 (1997) 229–241.
- [10] A. Sanz-Medel, M.d.R. Fernandez de la Campa, E.B. Gonzalez, M.L. Fernandez-Sanchez, Organised surfactant assemblies in analytical atomic spectrometry, *Spectrochim. Acta Part B* 54 (1999) 251–287.
- [11] I.-S. Chang, C.-H. Lee, Membrane filtration characteristics in membrane-coupled activated sludge system – The effect of physiological states of activated sludge on membrane fouling, *Desalination* 120 (1998) 221–233.
- [12] P. Eriksson, Nanofiltration extends the range of membrane filtration, *Environ. Prog.* 7 (1988) 58–62.
- [13] T. Ueda, K. Hata, Domestic wastewater treatment by a submerged membrane bioreactor with gravitational filtration, *Water Res.* 33 (1999) 2888–2892.
- [14] J. Wu, M.A. Eiteman, S.E. Law, Evaluation of membrane filtration and ozonation processes for treatment of reactive-dye wastewater, *J. Environ. Eng.-ASCE* 124 (1998) 272–277.
- [15] I. Liska, Fifty years of solid-phase extraction in water analysis – Historical development and overview, *J. Chromatogr. A* 885 (2000) 3–16.

- [16] C.F. Poole, Solid-phase extraction, in: D.W. Ian (Ed.) *Encyclopedia of Separation Science*, Academic Press, Oxford, 2000, pp. 1405–1416.
- [17] C.F. Poole, Solid-phase extraction with discs, in: D.W. Ian (Ed.) *Encyclopedia of Separation Science*, Academic Press, Oxford, 2000, pp. 4141–4148.
- [18] V. Camel, Solid phase extraction of trace elements, *Spectrochim. Acta B* 58 (2003) 1177–1233.
- [19] D.T. Rossi, N. Zhang, Automating solid-phase extraction: Current aspects and future prospects, *J. Chromatogr. A* 885 (2000) 97–113.
- [20] N.J.K. Simpson, *Solid-Phase Extraction: Principles, Techniques, and Applications*, in, Marcel Dekker, New York, 2000.
- [21] E.M. Thurman, M.S. Mills, *Solid-Phase Extraction: Principles and Practice*, John Wiley & Sons, New York, 1998.
- [22] J.S. Fritz, *Analytical Solid-Phase Extraction*, Wiley-VCH, New York, 1999.
- [23] H. Braus, F. Middleton, G. Walton, Organic chemical compounds in raw and filtered surface waters, *Anal. Chem.* 23 (1951) 1160–1164.
- [24] J.P. Riley, D. Taylor, The analytical concentration of traces of dissolved organic materials from sea water with Amberlite XAD-1 resin, *Anal. Chim. Acta* 46 (1969) 307–309.
- [25] A.K. Burnham, G.V. Calder, J.S. Fritz, G.A. Junk, H.J. Svec, R. Willis, Identification and estimation of neutral organic contaminants in potable water, *Anal. Chem.* 44 (1972) 139–142.
- [26] G.A. Junk, J.J. Richard, M.D. Grieser, D. Witiak, J.L. Witiak, M.D. Arguello, R. Vick, H.J. Svec, J.S. Fritz, G.V. Calder, Use of macroreticular resins in the analysis of water for trace organic contaminants, *J. Chromatogr. A* 99 (1974) 745–762.
- [27] P. Van Rossum, R.G. Webb, Isolation of organic water pollutants by XAD resins and carbon, *J. Chromatogr. A* 150 (1978) 381–392.
- [28] M.W. Tabor, J.C. Loper, Analytical Isolation, Separation and Identification of Mutagens from Nonvolatile Organics of Drinking Water, *Int. J. Environ. Anal. Chem.* 19 (1985) 281–318.
- [29] J.J. Richard, G.A. Junk, Determination of munitions present in water using macroreticular resins, *Anal. Chem.* 58 (1986) 723–725.
- [30] A. Przyjazny, Evaluation of the suitability of selected porous polymers for preconcentration of organosulphur compounds from water, *J. Chromatogr. A* 346 (1985) 61–67.
- [31] G.R. Aiken, E.M. Thurman, R.L. Malcolm, H.F. Walton, Comparison of XAD macroporous resins for the concentration of fulvic acid from aqueous solution, *Anal. Chem.* 51 (1979) 1799–1803.
- [32] P. Jones, G. Nickless, Characterization of non-ionic detergent of the polyethoxylated type from water systems : I. Evaluation of amberlite XAD-4 resin as an extractant for polyethoxylated material, *J. Chromatogr. A* 156 (1978) 87–97.

- [33] M. Krejčí, M. Roudná, Z. Vavrouch, Analysis of non-ionic surfactants of the alkylphenol type in the presence of mineral oil by means of liquid chromatography, *J. Chromatogr. A* 91 (1974) 549–556.
- [34] N.E. Moustafa, D.S. El-Desouki, Inverse gas chromatographic characterization of Porapak Q as an extractant of pollutants from aqueous media, *Chem. Pap.* 63 (2009) 371–376.
- [35] L. Ortega, R. Lopez, J. Cacho, V. Ferreira, Use of solid-liquid distribution coefficients to determine retention properties of Porapak-Q resins – Determination of optimal conditions to isolate alkyl-methoxypyrazines and beta-damascenone from wine, *J. Chromatogr. A* 931 (2001) 31–39.
- [36] B. Buke, U. Divrikli, M. Soylak, L. Elci, On-line preconcentration of copper as its pyrocatechol violet complex on Chromosorb 105 for flame atomic absorption spectrometric determinations, *J. Hazard. Mater.* 163 (2009) 1298–1302.
- [37] M. Tuzen, M. Soylak, Biosorption of aluminum on *Pseudomonas aeruginosa* loaded on Chromosorb 106 prior to its graphite furnace atomic absorption spectrometric determination, *J. Hazard. Mater.* 154 (2008) 519–525.
- [38] M. Tuzen, M. Soylak, Chromium speciation in environmental samples by solid phase extraction on Chromosorb 108, *J. Hazard. Mater.* 129 (2006) 266–273.
- [39] Y. Bakircioglu, D. Bakircioglu, N. Tokman, A novel preconcentration method for determination of iron and lead using Chromosorb-103 and flame atomic absorption spectrometry, *Anal. Chim. Acta* 547 (2005) 26–30.
- [40] N. Tokman, S. Akman, Determination of bismuth and cadmium after solid-phase extraction with Chromosorb-107 in a syringe, *Anal. Chim. Acta* 519 (2004) 87–91.
- [41] S. Saracoglu, M. Soylak, L. Elci, Preconcentration of Cu (II), Fe(III), Ni(II), Co(II) and Pb(II) ions in some manganese salts with solid phase extraction method using Chromosorb-102 resin, *Acta Chim. Slov.* 50 (2003) 807–814.
- [42] A. de la Cal, E. Eljarrat, T. Grotenhuis, D. Barcelo, Tenax<sup>®</sup> extraction as a tool to evaluate the availability of polybrominated diphenyl ethers, DDT, and DDT metabolites in sediments, *Environ. Toxicol. Chem.* 27 (2008) 1250–1256.
- [43] P. Oleszczuk, Tenax-TA extraction as predictor for free available content of polycyclic aromatic hydrocarbons (PAHs) in composted sewage sludges, *J. Environ. Monit.* 10 (2008) 883–888.
- [44] V. Leoni, G. Puccetti, A. Grella, Preliminary results on the use of Tenax<sup>®</sup> for the extraction of pesticides and polynuclear aromatic hydrocarbons from surface and drinking waters for analytical purposes, *J. Chromatogr. A* 106 (1975) 119–124.

- [45] V. Leoni, G. Puccetti, R.J. Colombo, A.M. D'Ovidio, The use of Tenax for the extraction of pesticides and polychlorinated biphenyls from water : II. Tests with artificially polluted and natural waters, *J. Chromatogr. A* 125 (1976) 399–407.
- [46] J.D. Navratil, R.E. Sievers, H.F. Walton, Open-pore polyurethane columns for collection and preconcentration of polynuclear aromatic hydrocarbons from water, *Anal. Chem.* 49 (1977) 2260–2263.
- [47] M.H. Mohamed, L.D. Wilson, J.V. Headley, K.M. Peru, Investigation of the sorption properties of beta-cyclodextrin-based polyurethanes with phenolic dyes and naphthenates, *J. Colloid Interface Sci.* 356 (2011) 217–226.
- [48] P.R. Musty, G. Nickless, The extraction and recovery of chlorinated insecticides and polychlorinated biphenyls from water using porous polyurethane foams, *J. Chromatogr. A* 100 (1974) 83–93.
- [49] D.K. Basu, J. Saxena, Monitoring of polynuclear aromatic hydrocarbons in water. II. Extraction and recovery of six representative compounds with polyurethane foams, *Environ. Sci. Technol.* 12 (1978) 791–795.
- [50] M.S. Elshahawi, M. Almehdi, Qualitative, semiquantitative and spectrophotometric determination of ruthenium(III) by solid-phase extraction with 3-hydroxy-2-methyl-1,4-naphthoquinone-4-oxime-loaded polyurethane foam columns, *J. Chromatogr. A* 697 (1995) 185–190.
- [51] V.A. Lemos, R.E. Santelli, M.S. de Carvalho, S.L.C. Ferreira, Application of polyurethane foam loaded with BTAC in an on-line preconcentration system: Cadmium determination by FAAS, *Spectrochim. Acta B* 55 (2000) 1497–1502.
- [52] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, On-line preconcentration and determination of copper, lead and chromium(VI) using unloaded polyurethane foam packed column by flame atomic absorption spectrometry in natural waters and biological samples, *Talanta* 58 (2002) 831–840.
- [53] M.F. El-shahat, E.A. Moawed, M.A.A. Zaid, Preconcentration and separation of iron, zinc, cadmium and mercury, from waste water using Nile blue a grafted polyurethane foam, *Talanta* 59 (2003) 851–866.
- [54] N. Burham, S.M. Abdel-Azeem, M.F. El-Shahat, Separation and determination of trace amounts of zinc, lead, cadmium and mercury in tap and Qaroun lake water using polyurethane foam functionalized with 4-hydroxytoluene and 4-hydroxyacetophenone, *Anal. Chim. Acta* 579 (2006) 193–201.
- [55] N. Burham, Separation and preconcentration system for lead and cadmium determination in natural samples using 2-aminoacetylthiophenol modified polyurethane foam, *Desalination* 249 (2009) 1199–1205.

- [56] H. Minamisawa, K. Mizushima, H. Asamoto, M. Minamisawa, K. Saitoh, T. Nakagama, Solid-phase extraction of chromium(VI) by polyurethane foam treated with hydrochloric acid, *Bunseki Kagaku* 59 (2010) 1163–1167.
- [57] N. Burham, S.M. Abdel-Azeem, M.F. El-Shahat, Determination of heavy metal ions in environmental samples employing preconcentration on novel resins of polyurethane foam linked with *o*-aminophenol or *o*-hydroxyphenylazonaphthol, *Int. J. Environ. Anal. Chem.* 91 (2011) 197–212.
- [58] M.R. Rice, H.S. Gold, Polypropylene as an adsorbent for trace organics in water, *Anal. Chem.* 56 (1984) 1436–1440.
- [59] R. Montes, I. Rodriguez, E. Rubi, M. Ramil, R. Cela, Suitability of polypropylene microporous membranes for liquid- and solid-phase extraction of halogenated anisoles from water samples, *J. Chromatogr. A* 1198 (2008) 21–26.
- [60] G.C. Bedendo, E. Carasek, Simultaneous liquid-liquid microextraction and polypropylene microporous membrane solid-phase extraction of organochlorine pesticides in water, tomato and strawberry samples, *J. Chromatogr. A* 1217 (2010) 7–13.
- [61] X.F. Li, W.R. Cullen, K.J. Reimer, In situ extraction/preconcentration of PCBs and PAHs from aqueous samples using polytetrafluoroethylene tubing, *Analyst* 127 (2002) 730–734.
- [62] Y.Q. Cai, G.B. Jiang, J.F. Liu, Solid-phase extraction of several phthalate esters from environmental water samples on a column packed with polytetrafluoroethylene turnings, *Anal. Sci.* 19 (2003) 1491–1494.
- [63] Z.H. Wang, X.P. Yan, Z.P. Wang, Z.P. Zhang, L.W. Liu, 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.* 17 (2006) 1258–1264.
- [64] L. Oliferova, M. Statkus, G. Tsysin, Y. Zolotov, On-line solid-phase extraction and high performance liquid chromatography determination of polycyclic aromatic hydrocarbons in water using polytetrafluoroethylene capillary, *Talanta* 72 (2007) 1386–1391.
- [65] C.D. Chriswell, R.C. Chang, J.S. Fritz, Chromatographic determination of phenols in water, *Anal. Chem.* 47 (1975) 1325–1329.
- [66] B. Maddah, A. Motahari, A. Moghimi, High capacity anion-exchange resin as a solid-phase extraction for determination of methylphosphonic acid, *Sep. Sci. Technol.* 45 (2010) 2363–2367.
- [67] M. Pesavento, E. Baldini, Study of sorption of copper(II) on complexing resin columns by solid phase extraction, *Anal. Chim. Acta* 389 (1999) 59–68.
- [68] D. Kara, N. Tekin, Solid-phase extraction and spectrophotometric determination of trace amounts of mercury in natural samples, *Microchim. Acta* 149 (2005) 193–198.

- [69] W.E. May, S.N. Chesler, S.P. Cram, Chromatographic analysis of hydrocarbons in marine sediments and seawater, *J. Chromatogr. Sci.* 13 (1975) 535–540.
- [70] M. Shamsipur, A.R. Ghiasvand, H. Sharghi, H. Naeimi, Solid phase extraction of ultra trace copper(II) using octadecyl silica membrane disks modified by a naphthol-derivative Schiff's base, *Anal. Chim. Acta* 408 (2000) 271–277.
- [71] Y. Yamini, N. Alizadeh, M. Shamsipur, Solid phase extraction and determination of ultra trace amounts of mercury(II) using octadecyl silica membrane disks modified by hexathia-18-crown-6-tetraone and cold vapour atomic absorption spectrometry, *Anal. Chim. Acta* 355 (1997) 69–74.
- [72] A.R. Ghiasvand, E. Mohagheghzadeh, Selective solid phase extraction and preconcentration of ultra trace molybdenum using modified C-18 membrane disks, *Asian J. Chem.* 17 (2005) 2143–2151.
- [73] M. Gerard, J.P. Barthelemy, A. Copin, Solid phase extraction (SPE) in two layers cartridge for simultaneous analysis of medium and highly polar pesticides in waters, *Int. J. Environ. Anal. Chem.* 80 (2001) 281–294.
- [74] G. Khayatian, S. Pouzesh, Solid phase extraction and flame atomic absorption spectroscopic determination of trace amounts of iron(III) using octadecyl silica membrane disks modified with 2-mercaptopyridine-1-oxide, *J. Iran Chem. Soc.* 4 (2007) 490–496.
- [75] M. Shamsipur, A. Avanes, M.K. Rofouei, H. Sharghi, G. Aghapour, Solid phase extraction and determination of ultra trace amounts of copper(II) using octadecyl silica membrane disks modified by 11-hydroxynaphthacene-5,12-quinone and flame atomic absorption spectrometry, *Talanta* 54 (2001) 863–869.
- [76] M. Shamsipur, F. Raoufi, H. Sharghi, Solid phase extraction and determination of lead in soil and water samples using octadecyl silica membrane disks modified by bis[1-hydroxy-9,10-anthraquinone-2-methyl]sulfide and flame atomic absorption spectrometry, *Talanta* 52 (2000) 637–643.
- [77] L. Ebdon, A.S. Fisher, S.J. Hill, P.J. Worsfold, On-line analyte preconcentration with atomic spectrometric detection, *J. Autom. Chem.* 13 (1991) 281–286.
- [78] V. Carbonell, A. Salvador, M. Guardia, Literature survey of the on-line preconcentration in flow-injection atomic spectrometric analysis, *Fresen. J. Anal. Chem.* 342 (1992) 529–537.
- [79] R.A. Nickson, S.J. Hill, P.J. Worsfold, Analytical perspective. Solid phase techniques for the preconcentration of trace metals from natural waters, *Anal. Proc.* 32 (1995) 387–395.
- [80] M. Ghaedi, F. Ahmadi, A. Shokrollahi, Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry, *J. Hazard. Mater.* 142 (2007) 272–278.

- [81] M. Ghaedi, E. Asadpour, A. Vafaie, Sensitized spectrophotometric determination of Cr(III) ion for speciation of chromium ion in surfactant media using  $\alpha$ -benzoin oxime, *Spectrochim. Acta Part A* 63 (2006) 182–188.
- [82] M. Ghaedi, A. Shokrollahi, A.H. Kianfar, A.S. Mirsadeghi, A. Pourfarokhi, M. Soylak, The determination of some heavy metals in food samples by flame atomic absorption spectrometry after their separation-preconcentration on bis salicyl aldehyde, 1,3 propan diimine (BSPDI) loaded on activated carbon, *J. Hazard. Mater.* 154 (2008) 128–134.
- [83] J. Triska, Extraction disks – New technology for solid-phase extraction, *Chem. Listy* 89 (1995) 223–232.
- [84] J. Triska, Testing of membrane extraction disks for analysis of 18 pesticides in marsh water samples by GC/MS, *Chromatographia* 40 (1995) 712–717.
- [85] C. Aguilar, F. Borrull, R.M. Marce, On-line and off-line solid-phase extraction with styrene-divinylbenzene-membrane extraction disks for determining pesticides in water by reversed-phase liquid chromatography diode-array detection, *J. Chromatogr. A* 754 (1996) 77–84.
- [86] J.P. Lai, X.W. He, H.S. Guo, H. Liang, A review on molecular imprinting technique, *Chinese J. Anal. Chem.* 29 (2001) 836–844.
- [87] L.I. Andersson, Molecular imprinting for drug bioanalysis – A review on the application of imprinted polymers to solid-phase extraction and binding assay, *J. Chromatogr. B* 739 (2000) 163–173.
- [88] S. Risticvic, V. Niri, D. Vuckovic, J. Pawliszyn, Recent developments in solid-phase microextraction, *Anal. Bioanal. Chem.* 393 (2009) 781–795.
- [89] J. Pawliszyn, *Handbook of Solid Phase Microextraction*, Chemical Industry Press, Beijing, 2009.
- [90] J. Pawliszyn, *Solid Phase Microextraction: Theory and Practice*, Wiley-VCH, New York, 1997.
- [91] J. Pawliszyn, *Applications of Solid Phase Microextraction*, Royal Society of Chemistry, Cambridge, 1999.
- [92] C. Pu, Y.F. Wu, H. Yang, A.P. Deng, Trace analysis of contraceptive drug levonorgestrel in wastewater samples by a newly developed indirect competitive enzyme-linked immunosorbent assay (ELISA) coupled with solid phase extraction, *Anal. Chim. Acta* 628 (2008) 73–79.
- [93] P. Wan, C.R. Santerre, D.C. Deardorff, Linking solid phase extraction and enzyme-linked immunosorbent assay to measure chlorpyrifos in fish tissue, *J. Food Sci.* 66 (2001) 274–277.
- [94] A. Farjam, G.J. De Jong, R.W. Frei, U.A. Th. Brinkman, W. Haasnoot, A.R.M. Hamers, R. Schilt, F.A. Huf, Immunoaffinity pre-column for selective on-line sample pre-treatment in

- high-performance liquid chromatography determination of 19-nortestosterone, *J. Chromatogr. A* 452 (1988) 419–433.
- [95] V. Pichon, L. Chen, M.C. Hennion, R. Daniel, A. Martel, F. Le Goffic, J. Abian, D. Barcelo, Preparation and evaluation of immunosorbents for selective trace enrichment of phenylurea and triazine herbicides in environmental waters, *Anal. Chem.* 67 (1995) 2451–2460.
- [96] I. Ferrer, V. Pichon, M.C. Hennion, D. Barceló, Automated sample preparation with extraction columns by means of anti-isoproturon immunosorbents for the determination of phenylurea herbicides in water followed by liquid chromatography-diode array detection and liquid chromatography-atmospheric pressure chemical ionization mass spectrometry, *J. Chromatogr. A* 777 (1997) 91–98.
- [97] M. Bouzige, V. Pichon, M.C. Hennion, On-line coupling of immunosorbent and liquid chromatographic analysis for the selective extraction and determination of polycyclic aromatic hydrocarbons in water samples at the ng l<sup>-1</sup> level, *J. Chromatogr. A* 823 (1998) 197–210.
- [98] E. Hosten, B. Welz, Evaluation of an immobilised macrocyclic material for on-line column preconcentration and separation of cadmium, copper and lead for electrothermal atomic absorption spectrometry, *Anal. Chim. Acta* 392 (1999) 55–65.
- [99] M.L. Bruening, D.M. Mitchell, J.S. Bradshaw, R.M. Izatt, R.L. Bruening, Effect of organic solvent and anion type on cation binding constants with silica gel bound macrocycles and their use in designing selective concentrator columns, *Anal. Chem.* 63 (1991) 21–24.
- [100] J.S. Bradshaw, R.L. Bruening, K.E. Krakowiak, B.J. Tarbet, M.L. Bruening, R.M. Izatt, J.J. Christensen, Preparation of silica gel-bound macrocycles and their cation-binding properties, *J. Chem. Soc., Chem. Commun.* (1988) 812–814.
- [101] J.S. Bradshaw, R.M. Izatt, P.B. Savage, R.L. Bruening, K.E. Krakowiak, The design of ion selective macrocycles and the solid-phase extraction of ions using molecular recognition technology: A synopsis, *Supramol. Chem.* 12 (2000) 23–26.
- [102] R.M. Izatt, Review of selective ion separations at BYU using liquid membrane and solid phase extraction procedures, *J. Inclusion Phenom. Macrocyclic Chem.* 29 (1997) 197–220.
- [103] R.M. Izatt, J.S. Bradshaw, R.L. Bruening, Accomplishment of difficult chemical separations using solid phase extraction, *Pure Appl. Chem.* 68 (1996) 1237–1241.
- [104] R.M. Izatt, J.S. Bradshaw, R.L. Bruening, M.L. Bruening, Solid phase extraction of ions of analytical interest using molecular recognition technology, *Am. Lab.* 26 (1994) 28C–28M.
- [105] R.M. Izatt, J.S. Bradshaw, R.L. Bruening, B.J. Tarbet, M.L. Bruening, Solid phase extraction of ions using molecular recognition technology, *Pure Appl. Chem.* 67 (1995) 1069–1074.

- [106] R.M. Izatt, R.L. Bruening, M.L. Bruening, B.J. Tarbet, K.E. Krakowiak, J.S. Bradshaw, J.J. Christensen, Removal and separation of metal ions from aqueous solutions using a silica-gel-bonded macrocycle system, *Anal. Chem.* 60 (1988) 1825–1826.
- [107] S.R. Izatt, R.L. Bruening, K.E. Krakowiak, R.M. Izatt, The selective separation of anions and cations in nuclear waste using commercially available molecular recognition technology (MRT) products, In: WM'03 Conference, Tucson, AZ, 2003.
- [108] M. Hiraoka, *Crown Compounds: Their Characteristics and Applications*, Elsevier, Amsterdam, 1982.
- [109] M. Hiraoka, *Crown Ethers and Analogous Compounds*, Elsevier, Amsterdam, 1992.
- [110] G.W. Gokel, *Crown Ethers and Cryptands*, Royal Society of Chemistry, Cambridge, 1991.
- [111] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, Thermodynamic and kinetic data for macrocycle interactions with cations and anions, *Chem. Rev.* 91 (1991) 1721–2085.
- [112] C.J. Pedersen, Cyclic polyethers and their complexes with metal salts, *J. Am. Chem. Soc.* 89 (1967) 7017–7036.
- [113] H. Tsukube, Double armed crown ethers and armed macrocycles as a new series of metal-selective reagents: A review, *Talanta* 40 (1993) 1313–1324.
- [114] R. Ludwig, Calixarenes in analytical and separation chemistry, *Fresen. J. Anal. Chem.* 367 (2000) 103–128.
- [115] L.F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, New York, 1990.
- [116] W. Walkowiak, C.A. Kozłowski, Macrocycle carriers for separation of metal ions in liquid membrane processes – A review, *Desalination* 240 (2009) 186–197.
- [117] R.A. Bartsch, I.-W. Yang, E.-G. Jeon, W. Walkowiak, W.A. Charewicz, Selective transport of alkali metal cations in solvent extraction by proton-ionizable dibenzocrown ethers, *J. Coord. Chem.* 27 (1992) 75–85.
- [118] G.W. Gokel, Lariat ethers: From simple sidearms to supramolecular systems, *Chem. Soc. Rev.* 21 (1992) 39–47.
- [119] R.D. Gandour, F.R. Fronczek, V.J. Gatto, C. Minganti, R.A. Schultz, B.D. White, K.A. Arnold, D. Mazzocchi, S.R. Miller, G.W. Gokel, Solid-state structural chemistry of lariat ether and BiBLE cation complexes: metal-ion identity and coordination number determine cavity size, *J. Am. Chem. Soc.* 108 (1986) 4078–4088.
- [120] J.M. Mahoney, A.M. Beatty, B.D. Smith, Selective recognition of an alkali halide contact ion-pair, *J. Am. Chem. Soc.* 123 (2001) 5847–5848.
- [121] J.M. Mahoney, A.M. Beatty, B.D. Smith, Selective solid-liquid extraction of lithium halide salts using a ditopic macrobicyclic receptor, *Inorg. Chem.* 43 (2004) 7617–7621.

- [122] T. Nabeshima, T. Saiki, J. Iwabuchi, S. Akine, Stepwise and dramatic enhancement of anion recognition with a triple-site receptor based on the calix[4]arene framework using two different cationic effectors, *J. Am. Chem. Soc.* 127 (2005) 5507–5511.
- [123] R.M. Izatt, G.A. Clark, J.S. Bradshaw, J.D. Lamb, J.J. Christensen, Macrocycle-facilitated transport of ions in liquid membrane systems, *Sep. Purif. Methods* 15 (1986) 21–72.
- [124] W. Walkowiak, M. Ulewicz, C. Kozłowski, Application of macrocycle compounds for metal ions separation and removal – A review, *Ars Separatoria Acta* 1 (2002) 87–98.
- [125] J.S. Bradshaw, R.M. Izatt, J.J. Christensen, K.E. Krakowiak, B.J. Tarbet, R.L. Bruening, S. Lifson, Stable silica gel-bound crown ethers. Selective separation of metal ions and a potential for separations of amine enantiomers, *J. Inclusion Phenom. Macrocyclic Chem.* 7 (1989) 127–136.
- [126] J.S. Bradshaw, R.M. Izatt, Crown ethers: The search for selective ion ligating agents, *Acc. Chem. Res.* 30 (1997) 338–345.
- [127] J.S. Bradshaw, Twenty-five years of "crowning" around: Synthesis of crown ethers at Brigham Young University, *J. Inclusion Phenom. Macrocyclic Chem.* 29 (1997) 221–246.
- [128] X.X. Zhang, A.V. Bordunov, J.S. Bradshaw, N.K. Dalley, X. Kou, R.M. Izatt, A new highly selective macrocycle for  $K^+$  and  $Ba^{2+}$ : Effect of formation of a pseudo second macroring through complexation, *J. Am. Chem. Soc.* 117 (1995) 11507–11511.
- [129] A.V. Bordunov, J.S. Bradshaw, X.X. Zhang, N.K. Dalley, X. Kou, R.M. Izatt, Synthesis and properties of 5-chloro-8-hydroxyquinoline-substituted azacrown ethers: A new family of highly metal ion-selective lariat ethers, *Inorg. Chem.* 35 (1996) 7229–7240.
- [130] J.F. Biernat, P. Konieczka, B.J. Tarbet, J.S. Bradshaw, R.M. Izatt, Complexing and chelating agents immobilized on silica gel and related materials and their application for sorption of inorganic species, *Sep. Purif. Methods* 23 (1994) 77–348.
- [131] G. Goken, R. Bruening, L. Bray, Solid phase extraction membranes for selective radionuclide separation, In: *AIChE Summer National Meeting*, Denver, CO, 1994.
- [132] Y. Furusho, M. Ono, M. Yamada, K. Ohashi, T. Kitade, K. Kuriyama, S. Ohta, Y. Inoue, S. Motomizu, Advanced solid phase extraction for inorganic analysis and its applications, *Bunseki Kagaku* 57 (2008) 969–989.
- [133] I.M.M. Rahman, Y. Furusho, Z.A. Begum, N. Izatt, R. Bruening, A. Sabarudin, H. Hasegawa, Separation of lead from high matrix electroless nickel plating waste solution using an ion-selective immobilized macrocycle system, *Microchem. J.* 98 (2011) 103–108.
- [134] M. Hattori, Y. Takaku, T. Shimamura, Novel rapid separation of lead using highly selective resin for measurement of precise lead isotope ratio and its application to geochemical reference samples, *Bunseki Kagaku* 57 (2008) 113–121.

- [135] I.M.M. Rahman, Y. Furusho, Z.A. Begum, R. Sato, H. Okumura, H. Honda, H. Hasegawa, Determination of lead in solution by solid phase extraction, elution, and spectrophotometric detection using 4-(2-pyridylazo)-resorcinol, *Cent. Eur. J. Chem.* 11 (2013) 672–678.
- [136] A. Sabarudin, N. Lenghor, Y. Liping, Y. Furusho, S. Motomizu, Automated online preconcentration system for the determination of trace amounts of lead using Pb-selective resin and inductively coupled plasma-atomic emission spectrometry, *Spectrosc. Lett.* 39 (2006) 669–682.
- [137] X.P. Yan, M. Sperling, B. Welz, Application of a macrocycle immobilized silica gel sorbent to flow injection on-line microcolumn preconcentration and separation coupled with flame atomic absorption spectrometry for interference-free determination of trace lead in biological and environmental samples, *Anal. Chem.* 71 (1999) 4216–4222.
- [138] M. Sperling, X.P. Yan, B. Welz, Electrothermal atomic absorption spectrometric determination of lead in high-purity reagents with flow-injection on-line microcolumn preconcentration and separation using a macrocycle immobilized silica gel sorbent, *Spectrochim. Acta Part B* 51 (1996) 1875–1889.
- [139] M. Kumai, K. Nakayama, Y. Furusho, T. Yamamoto, Y. Takamura, Quantitative determination of lead in soil by solid-phase extraction/liquid electrode plasma atomic emission spectrometry, *Bunseki Kagaku* 58 (2009) 561–567.
- [140] Y. Bakircioglu, S.R. Segade, E.R. Yourd, J.F. Tyson, Evaluation of Pb-Spec<sup>®</sup> for flow-injection solid-phase extraction preconcentration for the determination of trace lead in water and wine by flame atomic absorption spectrometry, *Anal. Chim. Acta* 485 (2003) 9–18.
- [141] I.M.M. Rahman, Z.A. Begum, M. Nakano, Y. Furusho, T. Maki, H. Hasegawa, Selective separation of arsenic species from aqueous solutions with immobilized macrocyclic material containing solid phase extraction columns, *Chemosphere* 82 (2011) 549–556.
- [142] I.M.M. Rahman, Z.A. Begum, Y. Furusho, S. Mizutani, T. Maki, H. Hasegawa, Selective separation of tri- and pentavalent arsenic in aqueous matrix with a macrocycle-immobilized solid-phase extraction system, *Water Air Soil Pollut.* 224 (2013) 1526.
- [143] H. Hasegawa, I.M.M. Rahman, S. Kinoshita, T. Maki, Y. Furusho, Separation of dissolved iron from the aqueous system with excess ligand, *Chemosphere* 82 (2011) 1161–1167.
- [144] I.M.M. Rahman, Z.A. Begum, H. Sawai, T. Maki, H. Hasegawa, Decontamination of spent iron-oxide coated sand from filters used in arsenic removal, *Chemosphere* 92 (2013) 196–200.
- [145] H. Hasegawa, I.M.M. Rahman, Z.A. Begum, Y. Umehara, T. Maki, Y. Furusho, S. Mizutani, A silica gel-bound macrocycle system for the selective separation of toxic cadmium from metal-affluent aqueous matrix, *Cent. Eur. J. Chem.* 11 (2013) 341–347.
- [146] Y. Furusho, M. Ono, M. Yamada, T. Kitade, S. Motomizu, Determination of Cr(VI) by solid-phase extraction with highly selective resin, *Bunseki Kagaku* 58 (2009) 147–152.

- [147] M. Kamaya, S. Yanagi, K. Nagashima, J. Wakui, Simple and sensitive determination of chromium (VI) in conversion coatings, *J. Surf. Finish. Soc. JPN* 59 (2008) 749–752.
- [148] O. Noguchi, M. Oshima, S. Motomizu, Enrichment with air-sandwiched method of on-line collection/concentration using chelating resin and simultaneous determination of trace elements by inductively coupled plasma atomic emission spectrometry, *Talanta* 78 (2009) 1235–1239.
- [149] I.M.M. Rahman, Y. Furusho, Z.A. Begum, A. Sabarudin, S. Motomizu, T. Maki, H. Hasegawa, Selective separation of some ecotoxic transition metal ions from aqueous solutions using immobilized macrocyclic material containing solid phase extraction system, *Cent. Eur. J. Chem.* 9 (2011) 1019–1026.
- [150] H. Hasegawa, I.M.M. Rahman, M. Nakano, Z.A. Begum, Y. Egawa, T. Maki, Y. Furusho, S. Mizutani, Recovery of toxic metal ions from washing effluent containing excess aminopolycarboxylate chelant in solution, *Water Res.* 45 (2011) 4844–4854.
- [151] H. Hasegawa, I.M.M. Rahman, S. Kinoshita, T. Maki, Y. Furusho, Non-destructive separation of metal ions from wastewater containing excess aminopolycarboxylate chelant in solution with an ion-selective immobilized macrocyclic material, *Chemosphere* 79 (2010) 193–198.
- [152] H. Hasegawa, I.M.M. Rahman, Y. Egawa, H. Sawai, Z.A. Begum, T. Maki, S. Mizutani, Chelant-induced reclamation of indium from the spent liquid crystal display panels with the aid of microwave irradiation, *J. Hazard. Mater.* 254–255 (2013) 10–17.
- [153] H. Hasegawa, I.M.M. Rahman, Y. Umehara, H. Sawai, T. Maki, Y. Furusho, S. Mizutani, Selective recovery of indium from the etching waste solution of the flat-panel display fabrication process, *Microchem. J.* 110 (2013) 133–139.
- [154] Y. Furusho, S.R. Izatt, R.L. Bruening, N.E. Izatt, S. Motomizu, Use of AnaLig<sup>®</sup> molecular recognition technology (MRT) products for analysis of gold and platinum group metals, In: International Precious Metals Institute, 32<sup>nd</sup> Annual Meeting, Phoenix, AZ, 2008.
- [155] N.E. Izatt, S.R. Izatt, L. Bruening, Metal separations of interest to the Chinese metallurgical industry, *J. Rare Earth* 28 (2010) 22–29.
- [156] S.R. Izatt, R.L. Bruening, N.E. Izatt, J.B. Dale, The application of molecular recognition technology (MRT) in the nuclear power cycle: From uranium mining and refining to power plant waste separation and recovery, as well as element analysis and isotope purification, In: WM'09 Conference, Phoenix, AZ, 2009.
- [157] N. Vajda, C.-K. Kim, Determination of radiostrontium isotopes: A review of analytical methodology, *Appl. Radiat. Isot.* 68 (2010) 2306–2326.
- [158] Y. Kameo, A. Katayama, A. Fujiwara, T. Haraga, M. Nakashima, Rapid determination of <sup>89</sup>Sr and <sup>90</sup>Sr in radioactive waste using Sr extraction disk and beta-ray spectrometer, *J. Radioanal. Nucl. Chem.* 274 (2007) 71–78.

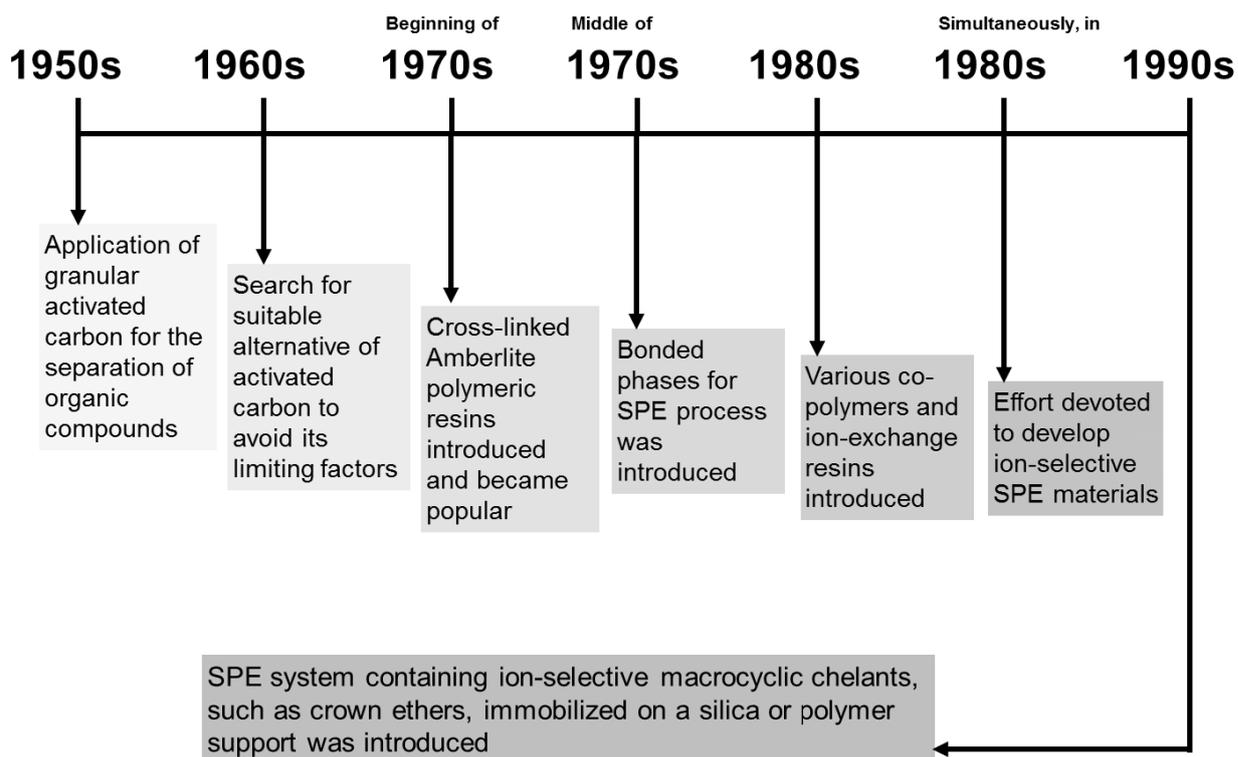
- [159] Y. Kameo, A. Katayama, A. Hoshi, T. Haraga, M. Nakashima, Simple determination of  $^{99}\text{Tc}$  in radioactive waste using Tc extraction disk and imaging plates, *Appl. Radiat. Isot.* 68 (2010) 139–143.
- [160] M. Condomines, S. Rihs, E. Lloret, J.L. Seidel, Determination of the four natural Ra isotopes in thermal waters by gamma-ray spectrometry, *Appl. Radiat. Isot.* 68 (2010) 384–391.
- [161] D.D. Lee, J.F. Walker, P.A. Taylor, D.W. Hendrickson, Cesium-removal flow studies using ion exchange, *Environ. Prog.* 16 (1997) 251–262.
- [162] W.D. King, W.A. Spencer, L.L. Hamm, S.E. Aleman, C.E. Duffey, M.A. Pettis, Column performance testing of SuperLig<sup>®</sup> 639 resin with simulated hanford waste supernates: Identification of the primary sorbing species and detailed characterization of their desorption profiles, *Sep. Sci. Technol.* 40 (2005) 383–394.
- [163] S.K. Fiskum, D.L. Blanchard, S.T. Arm, R.A. Peterson, Cesium removal from simulated and actual Hanford tank waste using ion exchange, *Sep. Sci. Technol.* 40 (2005) 51–67.
- [164] R.A. Peterson, S.K. Fiskum, S.T. Arm, D.L. Blanchard, Cesium removal demonstration using selected actual waste samples from the Hanford reservation tank farm, *Sep. Sci. Technol.* 41 (2006) 2361–2371.
- [165] T.A. Devol, J.P. Clements, A. Farawila, M.J. O'Hara, O.B. Egorov, J.W. Grate, Characterization and application of SuperLig<sup>®</sup> 620 solid phase extraction resin for automated process monitoring of  $^{90}\text{Sr}$ , *J. Radioanal. Nucl. Chem.* 282 (2009) 623–628.
- [166] S.K. Fiskum, D.L. Blanchard, M.J. Steele, J.J. Wagner, Analysis of spent SuperLig<sup>®</sup> 644 resin used for cesium removal from Hanford tank wastes, *Solvent Extr. Ion Exch.* 24 (2006) 65–79.
- [167] K. Adu-Wusu, N.M. Hassan, C.A. Nash, J.C. Marra, Sorption of cesium from aqueous waste solution on a SuperLig<sup>®</sup> 644 resin, *J. Radioanal. Nucl. Chem.* 267 (2006) 381–388.

**Table 1:** Comparative characteristics of the parent macrocycles

Macrocycle	Major guest	Structural diversity <sup>a</sup>	Guest selectivity <sup>a</sup>
Crown ether	Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> Ba <sup>2+</sup> , Ag <sup>+</sup> , Pb <sup>2+</sup> NH <sub>4</sub> <sup>+</sup> , RNH <sub>3</sub> <sup>+</sup>	A	A
Macrocyclic polyamine	Cu <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> polyanion	A	B
Macrocyclic polysulfide	Ag <sup>+</sup> , Pb <sup>2+</sup>	C	A
Cyclic peptide	Ca <sup>2+</sup> , Ba <sup>2+</sup> Cu <sup>2+</sup> , Zn <sup>2+</sup>	C	B
Calixarene	Na <sup>+</sup> , K <sup>+</sup> , Cs <sup>+</sup> Organic substrate	A	B
Cyclophane	Organic substrate	C	C
Cyclodextrin	Organic substrate	B	C

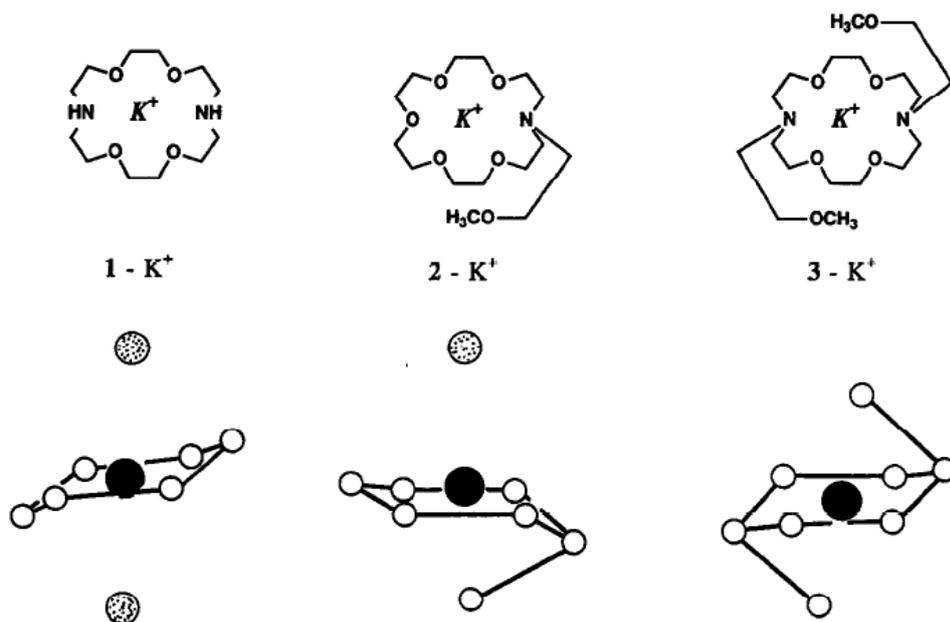
<sup>a</sup> A: excellent, B: fair, C: not good.

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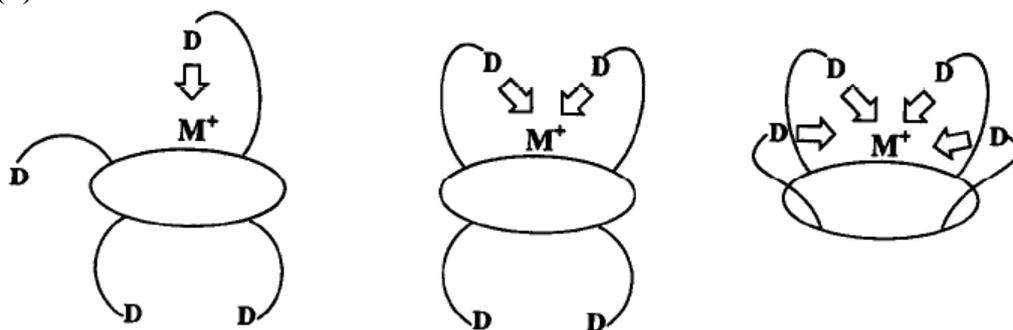


**Figure 1.** The development in SPEs until the introduction of macrocycle-containing SPEs: A timeline view.

(a)



(b)

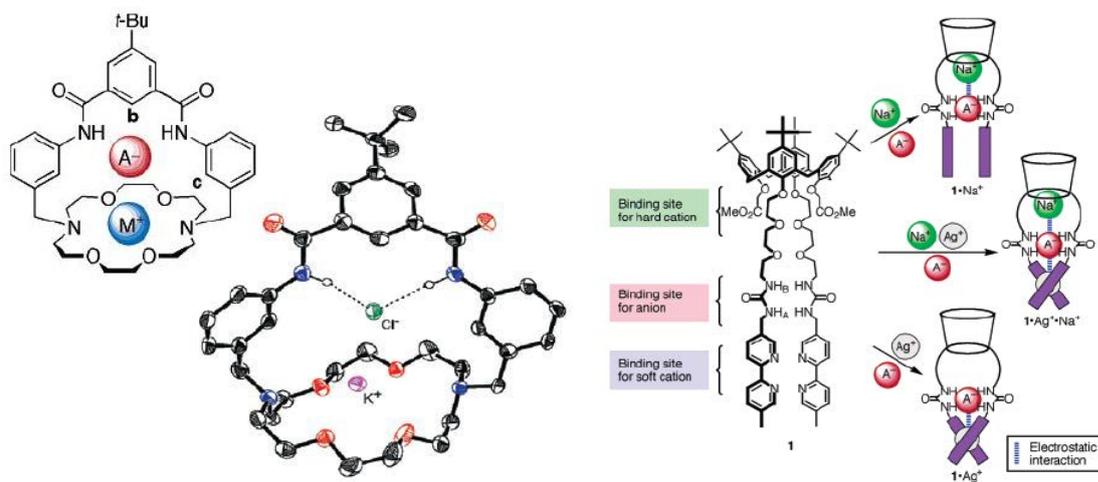


**Figure 2.** (a) Crystal structures of KI complexes with diaza-crown ether **1**, lariat ether **2**, and double armed crown ether **3**, (b) cation binding of armed macrocycles.

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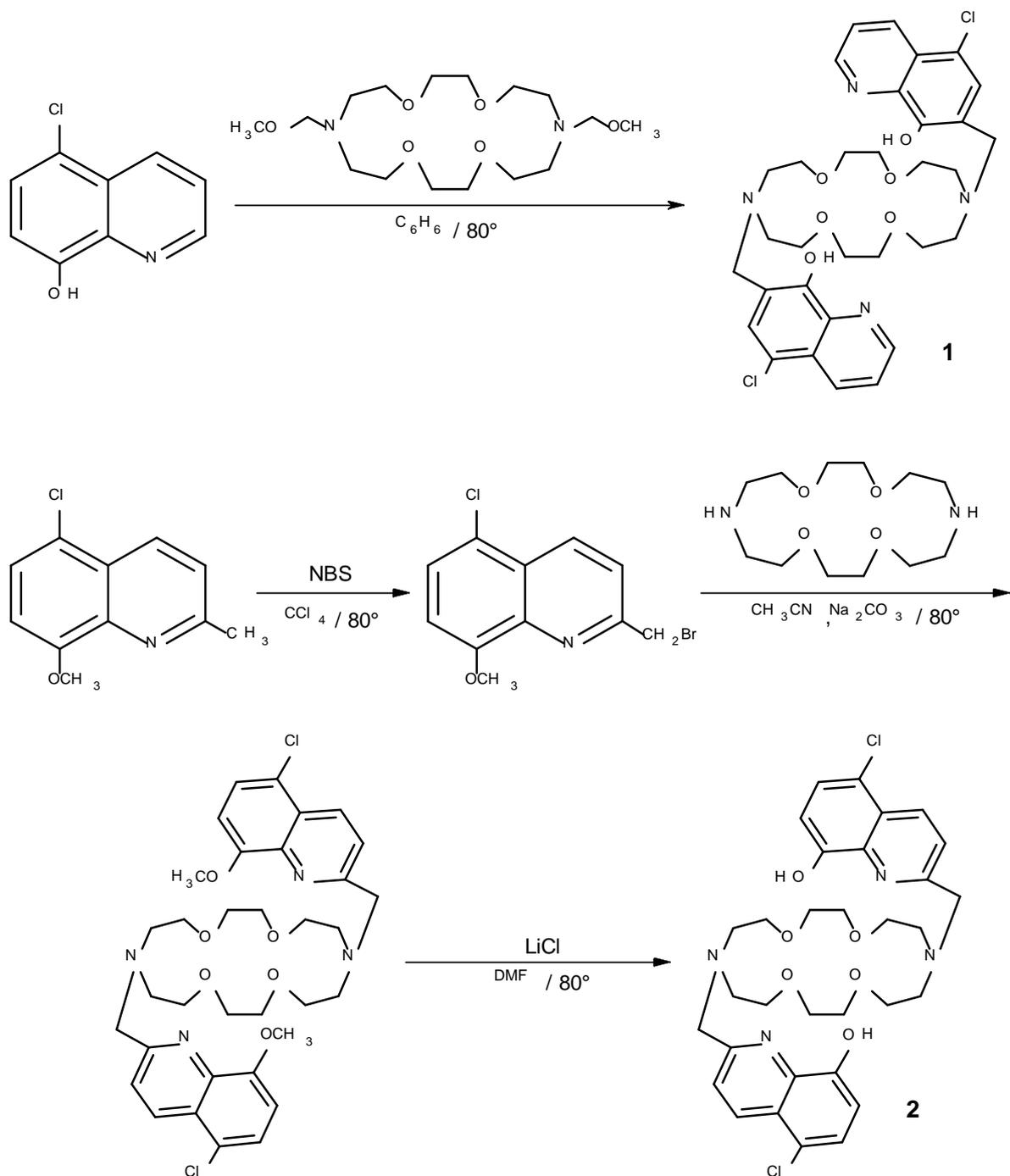
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**Figure 3.** Macrocyclic compounds with diverse selectivity options: (a) a macrobicyclic host structure that can accommodate both anion and cation species, (b) a multi-responsive host in which three different ion binding sites are arranged in a single structure.

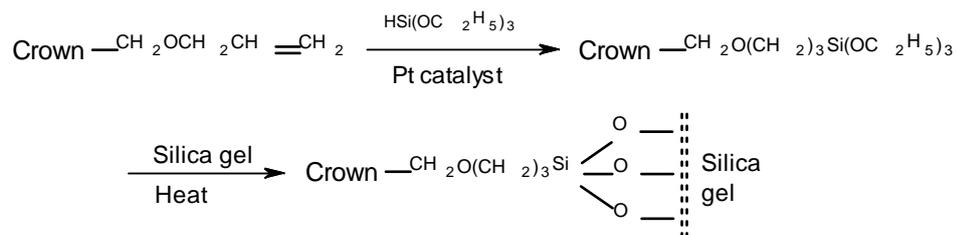
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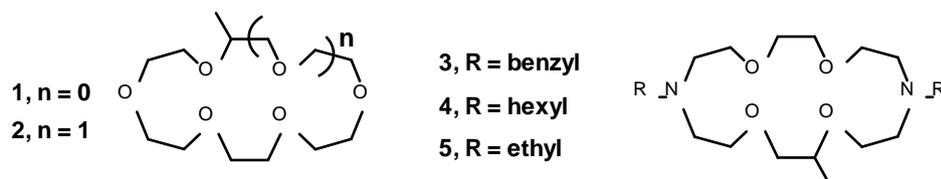
**Figure 4.** Scheme for the preparation of 5-chloro-8-hydroxyquinoline-substituted diaza-18-crown-6 macrocycles.

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**Crown Substituents**



**Figure 5.** Scheme for the preparation of silica gel-bound crown compounds

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