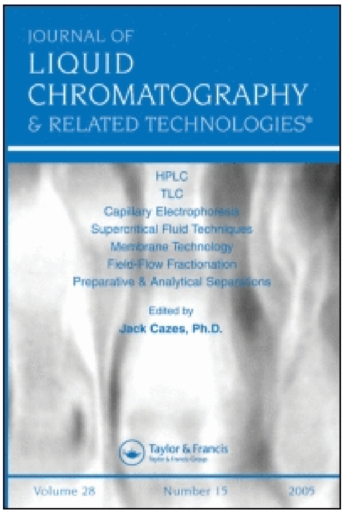

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UNTRADITIONAL APPLICATIONS OF COUNTERCURRENT CHROMATOGRAPHY

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UNTRADITIONAL APPLICATIONS OF COUNTERCURRENT CHROMATOGRAPHY

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ABSTRACT

Rotating coiled columns (RCC) have been traditionally applied to the separation and purification of organic solutes by countercurrent chromatography (CCC). The technique is based on the retention of one phase (stationary) of a two-phase solvent system in a rotating column without solid support under the action of centrifugal forces, while the other liquid phase (mobile) is being continuously pumped through. Solutes are subjected to a partition process between two phases and eluted in order of their partition coefficients. Within the last several years, some fundamentals and methods of inorganic separations by CCC in two-phase liquid systems, with different solvents and extracting reagents, have been developed. Procedures for the group pre-separation of rare earth and some rare (Zr, Hf, Nb, Ta) elements from multi-component matrices were proposed. The application of CCC to the purification and analysis of salt solutions has also been investigated.

Recently, it has been shown that rotating columns can be used for the separation of both solutes and particles, not only in liquid–liquid systems but in liquid–solid–liquid and liquid–solid

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systems as well. Procedures for the direct extraction of polynuclear aromatic hydrocarbons from a sewage sludge medium, and continuous fractionation of trace elements in soils were developed; suspensions and powdered solid samples being applied as the stationary phase in the column. It has been demonstrated, that RCC can be successfully used for the fractionation of micro particles. There is no stationary phase in this case. The centrifugal forces acting on RCC provide different migration speeds of the suspended sample components in one carrier fluid.

Key Words: Rotating coiled columns; Separation; Purification; Fractionation; Leaching; Rare and rare earth elements; Heavy metals; Polynuclear aromatic hydrocarbons; Sewage sludge; Soil

INTRODUCTION

Countercurrent chromatography (CCC), a support-free partition liquid chromatography,[1] is currently attracting great interest from investigators working on the separation and pre-concentration of organic and inorganic substances.[2] Two international conferences dedicated just to this method have been already organized (CCC-2000, Uxbridge, England, September 11–15, 2000 and CCC-2002, Beijing, China, April 15–20, 2002).

An important distinguishing feature of CCC as a chromatographic method is the absence of an adsorptive matrix for retaining the stationary phase. This feature determines the main advantages of the method,[1–3] such as the absence of solute loss due to interaction with the adsorptive matrix, a variety of two-phase liquid systems may be used, easy change from one partition system to another, the possibility to change a volume of the sample solution from 0.1 to 1000 mL or more, and a high preparation capacity is provided by a high ratio (up to 0.9) of the liquid stationary phase volume and the total column volume (this ratio is much higher than that for the stationary solid phase used in HPLC). It should be noted, that the problem of column packing is also eliminated in CCC.

A few devices providing retention of the stationary phase in the field of mass forces in the absence of a solid support have been suggested.[1,4] Among the various possible designs, the planetary centrifuge retains the liquid stationary phase effectively and enables the fastest and most efficient separation to be achieved.[1,4] A column (or a column unit) of a certain configuration rotates around its axis and simultaneously revolves around the central axis of the device with the aid of a planetary gear. Connecting tubes are free pending loops.

So far, the technique has been studied and used mainly for preparative and analytical separation of organic and bioorganic substances.[1,3,5] The studies of the past several years have shown that the technique can be applied to analytical and radiochemical separation, pre-concentration, and purification of inorganic substances in solutions, on a laboratory-scale by use of various two-phase liquid systems.[2,6–9] The chromatographic behavior of inorganic compounds, as well as organic compounds, is dependent on the properties of the system used: partition coefficients of substances to be separated and operating parameters of the planetary centrifuge, such as rotation and revolution speeds, direction and speed of the mobile phase pumping, internal diameter of RCC, and sample volume. However, the systems for inorganic separations are very different from those for organic separations, as in most cases they contain a complexing reagent (extracting ligand) in the organic stationary phase and mineral salts and/or acids in the aqueous mobile phase.[2,10,11] Using heterogeneous and homogeneous solid samples as the stationary phase, provides new possibilities for CCC.[12–14] Rotating columns can also be applied to the separation of micro particles in a field-flow fractionation method.[13,14] There is no stationary phase in this case. In the present review, the possibility of utilizing RCC in the analysis of various environmental samples (sewage sludge, soils, sediments, dissolved geological samples, natural waters) will be considered.

EXPERIMENTAL

The separations were performed on a planetary centrifuge with a one-layer[2,6,13–19] or three-layer[12] coiled PTFE column (tubing bore 1.5–1.8 mm), with an inner capacity of 20 mL. The rotation and revolution speeds were 400–700 rpm, whereas the mobile phase pumping rate was 1 mL/min (except for the fractionation of micro particles[15,16]).

A stationary phase (liquid,[2,6,8,9] solid,[13,14] or heterogeneous[12]) was retained in the rotating column, whereas a liquid mobile phase was continuously pumped through. The recovery of components to be separated was achieved by successive changing the eluents.

There was no stationary phase in the case of fractionation of micro particles.[15,16] The asymmetrical force field acting on the rotating coiled column provided different migration speeds of suspended sample components in one carrier fluid. Micro particles were separated by successively changing the mobile phase (carrier fluid) flow rate.

The collected fractions were analyzed using ICP-AES,[2,6,13,14,17–19] ICP-MS,[9] HPLC with a fluorescence detector,[12] and electronic microscopy.[16]

Separation of Trace Elements in Liquid–Liquid Systems

Due to the high loading capacity and the ability to use many well-known liquid–liquid extraction systems, CCC can be applied as a pre-concentration and/or pre-separation technique for various trace elements before their instrumental determination. The technique was utilized for pre-concentration and separation of rare, rare earth, and other elements from major constituents of various geological samples, after their decomposition for subsequent determination of elements by ICP-AES.[2,6,17–19] The extraction systems containing di-2-ethylhexylphosphoric acid, trioctylphosphine oxide, or diphenyl[dibutylcarbamoyl-methyl]phosphine oxide were shown to be applicable to the group separation of rare earth elements (REE) from dissolved samples of rocks, ores, and minerals (basalts, granites, dolomite, fluorite–barite–hydropatite ore, syenite, etc.).[2,6,18,19] It should be stressed, that all three systems provide the recovery of REE into a small eluate volume using one chromatographic run.

Group pre-separation of rare elements is desirable in the analysis of geological samples of different composition containing low concentrations of these elements. An extraction system based on a 0.1 mol/L solution of tetraoctylethylenediamine in chloroform, was used for the chromatographic pre-concentration of Zr, Hf, Nb, and Ta, and allows their elution into 7 mL of effluent (Fig. 1).[2,6,17] In the first stage, the four elements are concentrated in the stationary phase, whereas Cu, Al, alkali, alkaline-earth, rare earth, and other elements present in geological samples are not. Iron is partially eluted, but its complete elution is achieved using 0.1 mol/L HCl solution containing 5% ascorbic acid. Then, using 2.0 mol/L HCl solution, Zr, Hf, Nb, and Ta are recovered. At the column regeneration stage, Zn, Cd, and other elements are removed.

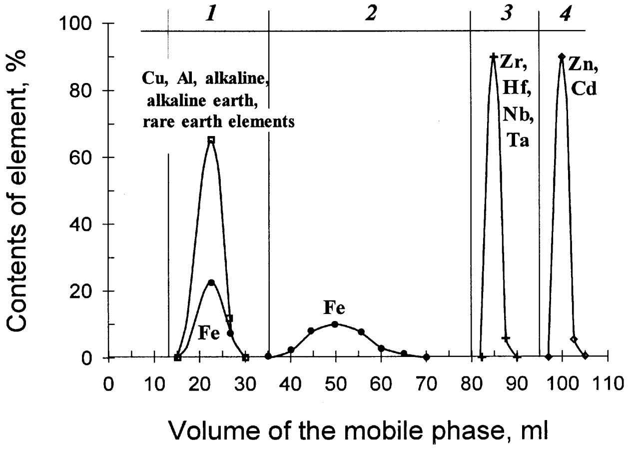

Figure 1. Pre-separation of Zr, Hf, Nb, and Ta from most of matrix components of geological samples.[2,6,17] Stationary phase (10 mL): 0.1 mol/L tetraoctylethylenediamine in chloroform. Mobile phase: 1—0.1 mol/L HCl + 0.01 mol/L $H_2C_2O_4$; 2—0.1 mol/L HCl + 0.5 mol/L $H_2C_4H_4O_6$; 3—2.0 mol/L HCl; 4-1.0 mol/L HNO_3.

The proposed methods of group separation of elements by CCC have the advantages of simplicity, versatility, and relatively short separation times.

The applicability of CCC to the purification of salt solutions (to obtain high-purity reagents, which, after evaporation, can be used for fusion decomposition procedures in trace analysis of high-tech ceramic and other materials) has been investigated.[8] In the case of a rotating column, the solutions are only in contact with Teflon, which is a quite inert material. Application of CCC to the purification of aqueous solutions of inorganic salts, such as $(NH_4)_2SO_4$, NH_4F, or NH_4Cl from a number of common metal impurities was shown by use of *N*,*N*-hexamethylenedithiocarbamic acid, diethyl-ammonium diethyldithiocarbamate, 8-hydroxyquinoline, dibenzo-18-crown-6 as extracting reagents.[8] Rotating coiled columns can also be used in the analysis of high-purity salt solutions.[9] Quantitative recoveries of rare earth, and some other elements from a high-purity solution of $CaCl_2$ (Merck) for their subsequent determination by ICP-MS, were achieved employing liquid systems on the basis of diphenyl[dibutylcarbamoylmethyl]phosphine oxide and other reagents.

Direct Separation of Polynuclear Aromatic Hydrocarbons (PAH) from a Sewage Sludge Medium

In recent years, a great number of studies dealt with different analytical techniques used for determining toxic organic compounds in various compartments of biosphere. Estimating the state of contamination of sewage sludge is an important problem, which is currently attracting the interest of investigators working in the field of ecology and environmental chemistry. Sewage sludge is a complex natural matrix containing solid suspended particles and, in most cases, the analytical procedures proposed are multistage, time-consuming, and require different methods of separation and determination.[20]

CCC can be used for the direct extraction and separation of some organic substances (e.g. xenobiotics) from a sewage sludge medium.[12] It has been shown, that heterogeneous samples can be retained in the rotating column. The sewage sludge (being, in fact a concentrated suspension) was the stationary phase in the column, whereas organic solvents (*n*-heptane, dichloromethane) or their mixtures were used as mobile phase. The volume of suspension retained in the column is dependent on the difference in densities between stationary and mobile phases, and operational parameters of the planetary centrifuge. In general, heterogeneous stationary phases behave like liquid ones.

The subsequent separation of some PAHs (naphthalene, pyrene, and benzo(g,h,i)perylene) from the sewage sludge medium using gradient elution mode, has been demonstrated (Fig. 2). At the first stage, highly *n*-heptane soluble

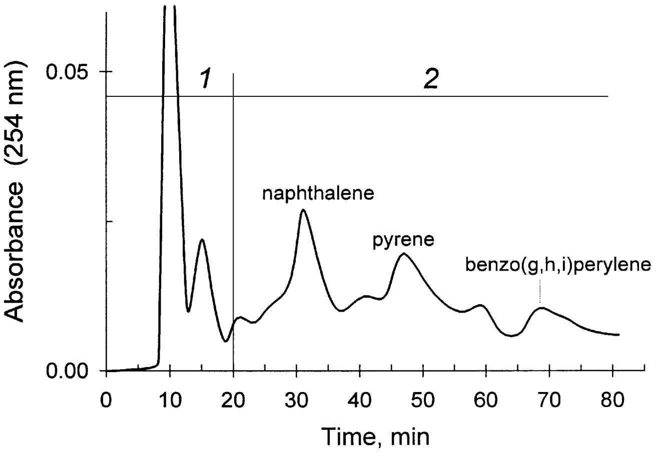

Figure 2. Separation of naphthalene, pyrene, and benzo(g,h,i)perylene from the sewage sludge medium.[12] Stationary phase (sample): saturated aqueous solution of enumerated PAHs, 2 mL + sewage sludge, 2 mL. Mobile phase: 1—*n*-heptane; 2—*n*-heptane/dichloro methane, gradient elution mode (concentration of dichloromethane increases from 0 to 20%). UV-detection at 254 nm.

constituents of the sewage sludge are eluted, whereas PAHs remain in the stationary phase. Then, with increasing the dichloromethane concentration in the mobile phase, the peaks of naphthalene, pyrene, and benzo(g,h,i)perylene appear. On the chromatogram one can see other peaks, which may correspond to other PAHs and contaminants present in the sewage sludge.

Although the subsequent separation of PAHs from the sewage sludge medium has been performed, a group CCC separation of PAHs followed by their quantitative determination by HPLC with a fluorescence detector can be more useful.[12] Procedures developed look promising as they give a possibility to analyze raw media (such as sewage sludge) without any sample pre-treatment.

Fractionation of Heavy Metals in Soils and Sediments

Estimating the contamination of soils is also a very important problem. Traditionally, in most studies dealing with the trace metal (TM) analysis, total contents of elements in the sample were considered. However, the mobility and bioavailability of TM depend strongly on their chemical form. Consequently, the data on total contents of elements are quite insufficient to estimate the possible risk of remobilization of TM under changing environmental conditions and potential uptake of liberated metals by biota. Thus, procedures for distinguishing different forms of TM are required.[21]

By using most of leaching schemes, TMs are operationally separated into several forms under the sequential action of different extractants.[21] This enables distinguishong TM species according to their possible risk for the environment. However, known procedures are rather laborious and time-consuming.

A new approach to performing the sequential extraction of trace elements from solid samples has been proposed.[13,14] It has been shown that rotating columns can be successfully applied to the dynamic leaching of heavy metals from soils and sediments. The recovery of trace elements may be achieved by successively changing the eluents. In this case, the crushed (powdered) solid sample is retained in the rotating column as the stationary phase, whereas aqueous solutions of complexing reagents, mineral acids, and salts are used as mobile phase. After the leaching procedure has been finished, the residue of the solid sample was removed from the column for subsequent analysis.[13,14]

The dynamics of fractionating some heavy metals according to Kersten–Foerstner's scheme[21] by use of RCC is shown in Fig. 3. As is seen from the elution

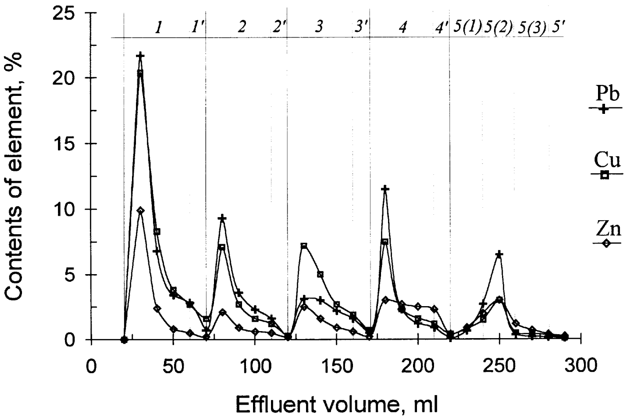

Figure 3. Continuous sequential extraction of trace metals (TM) from a soil sample on the basis of Kersten–Foerstner's scheme.[14] Stationary phase (sample): 0.5 g of Montana Soil N 1 (SRM 2710, NIST). Mobile phase (eluent):1—1 mol/L ammonium acetate, pH 7 (TM in exchangeable form); 2—1 mol/L acetic acid + NaOH to adjust pH 5 (TM in "carbonate" form); 3—0.01 mol/L $NH_2OH \cdot HCl$ + 0.01 mol/L HNO_3, pH 2 (TM bound to Mn oxides); 4—0.1 mol/L ammonium oxalate + HNO_3 to adjust pH 3 (TM bound to Fe and Al oxides); 5—(TM in sulfidic/organic form) (1)—30% H_2O_2, pH 2.4; (2)—30% H_2O_2 (1 mol/L ammonium acetate + 6% HNO_3), v/v = 1 + 3; (3)—1 mol/L ammonium acetate + 6% HNO_3; 1′, 2′, 3′, 4′, 5′—water.

curves, at stages 1–5 the greater contents of elements are recovered in 30–40 mL of the mobile phase. Separated fractions corresponding to different forms of TM are apparently not overlapped. Thus, despite the slow kinetics of TM recovery from solid samples, the use of multistage continuous extraction in RCC allowed us to reduce the contact time needed for the separation of each form (fraction) down to 30–40 min. (Traditional batch extraction experiment requires 5–16 hours for the separation of each fraction.[21]). In general, the elution curves obtained for the soil and sediment samples look similar, though the distribution of HM between leachable forms are different.[14] Hence, the types of the samples under study do not markedly affect the dynamics of the multistage extraction process in a rotating column.

The data on the fractionation of elements in the soil sample obtained by batch traditional sequential extraction (TSE) and continuous extraction in RCC are presented in Fig. 4. The contents of elements in the residual fractions are shown as well. As is seen from the diagrams, the extraction in RCC and TSE result in different patterns of element recoveries. The recoveries of Pb, Zn, and Cu in the first three fractions containing most bioavailable (and, consequently, dangerous) forms of HM are considerably higher if a dynamic multistage

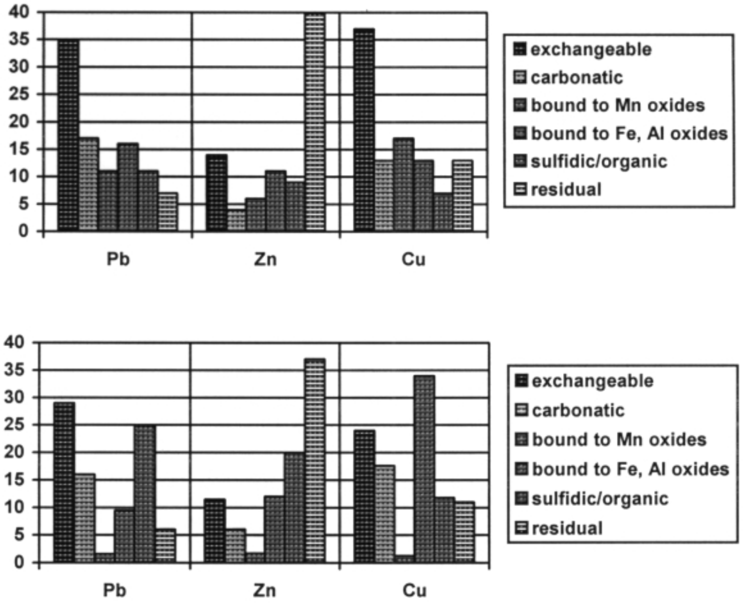

Figure 4. Fractionation of elements (recoveries, % of total content) in the soil sample on the basis of Kersten–Foerstner's scheme. Continuous extraction in RCC (above) and TSE (below).[14]

extraction in RCC is used. The recoveries of Pb, Zn, and Cu in the fourth and fifth fractions are higher in the case of TSE. However, the total contents of Pb, Zn, and Cu in the first five leachable fractions separated by the extraction in RCC and TSE are quite comparable, as well as the data on the residual fractions.[14]

Thus, five leaching steps of Kersten–Foerstner's scheme can be successfully performed in RCC. The procedure proposed is time saving and requires only 4–5 hours instead of several days needed for TSE. Besides, the complete automation is possible. Losses of a solid sample are minimal. If extraction in RCC is used, the total recoveries of elements in six fractions (five leachable and one residual) are 85–100% relative to certified values. For TSE the total recoveries are lower, 70–100%. The type of the sample matrix strongly affect the dynamic leaching process; however, in most cases the recoveries of easily mobilizable and bioavailable forms of TM are higher, if extraction in RCC is used. Natural environmental processes are always dynamic; consequently, continuous extraction in RCC may help to estimate the potential danger of TM more correctly than batch TSE.

The Kersten–Foerstner leaching scheme and the significantly different McLaren–Crawford scheme have been compared; the first one has been found to be preferable.[14]

Fractionation of Micro Particles

It should be noted that different pollutants may occur in aquatic systems as freely dissolved molecules or ions or associated with lager macromolecules, colloid or solid particles. The speciation analysis of contaminants is of great importance in determining their transport, toxicity, and other properties in natural waters. Field-flow fractionation (FFF) is a relatively new separation and sizing method, which is attractive to yield detailed information on complex environmental samples containing macromolecules and particulate species.[22]

It has been shown, that a rotating column can be used in a field-flow fractionation method.[15,16] A new coiled tube FFF technique employing a complex asymmetrical force field generated in planetary centrifuges is being developed. Among the other FFF techniques, CTFFF may be more similar to sedimentation FFF, utilizing a circular channel inserted inside a centrifugal basket.[22] In spite of the fact that both SdFFF and CTFFF employ the centrifugal force field, there are two important differences between these techniques to be mentioned. First, in the case of CTFFF the mixture to be separated is not introduced in a thin channel, but pumped with carrier fluid through a long rotating coiled tube. Second, in the planetary centrifuge used for performing CTFFF, particles and fluid in the coiled tube are under the action of the complex asymmetrical centrifugal force field. This field is dependent on the ratio of

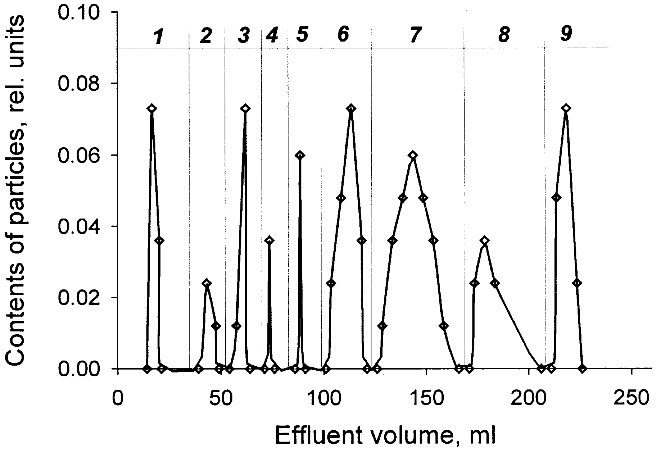

Figure 5. Fractionation of quartz particles with an irregular geometry.[16] Sample: quartz sand (RCR-70, mainly 1.2–20 μm) 20 mg. Mobile phase (carrier fluid): water. Column rotation speed: 90 rpm. Carrier fluid flow rate (F): 1—F = 0.15 mL/min (particles less than 1 μm); 2—F = 0.35 mL/min (particles about 1 μm); 3—F = 0.55 mL/min (particles about 1–2 μm); 4—F = 1.0 mL/min (particles about 2 μm); 5—F = 1.7 mL/min (particles about 2–3 μm); 6—F = 3.5 mL/min (particles about 5–7 μm); 7—F = 6.7 mL/min (particles about 7–8 μm); 8-F = 10 mL/min (particles about 10 μm); 9—F = 15 mL/min (particles larger 10 μm).

rotation and revolution radii. If necessary, this ratio can be changed in order to choose the optimal separation conditions.

First, CTFFF has been tested using a mixture of model particles in a single aqueous medium. Two colored latex beads (0.6 and 1.6 μm) were successfully separated to baseline resolution, the “step” elution mode being applied. Water was used as carrier fluid (mobile phase). Fractions were subsequently eluted from the coiled column by decreasing the column rotation speed and carrier fluid pumping rate.[15]

The separation of quartz particles with irregular geometry is shown in Fig. 5. The fractionation was performed by successively changing the mobile phase flow rate.[16] The recovered fractions were characterized by electronic microscopy. This separation may be important in the analysis of environmental samples because river and other natural waters contain quartz particles.

Further studies of different synthetic and environmental samples are needed to show the applicability of CTFFF to various analytical purposes.[15,16] A theoretical background of the method should also be developed.

Table 1. Untraditional CCC Separations: From Trace Elements to Micro Particles

Stationary Phase	Mobile Phase	Sample	Components to be Separated	References
Extracting reagent in an organic solvent	Aqueous solutions of mineral acids and salts	Dissolved geological samples	Rare, rare earth, and other elements	2, 6, 17–19
		Ultra pure salt solutions		8,9
Aqueous suspension (sample)	Organic solvents and their mixtures	Sewage sludge	Polynuclear aromatic hydrocarbons	12
Solid matter (sample)	Aqueous solutions of complexing reagents, mineral acids and salts	Soils, sediments	Different forms of trace metals	13, 14
NO stationary phase	Water	Aqueous suspension of micro particles (natural waters)	Micro particles and associated substances	15,16

CONCLUSIONS

The described untraditional applications of CCC are summarized in Table 1. Most of them look promising and can be useful in the analysis of complex environmental samples.

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