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Suspension column for recovery and separation of substances using ultrasound-assisted retention of bead sorbents

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ABSTRACT

A novel approach to sorption recovery and separation of different substances is proposed which is based on the use of suspended bead sorbents instead of conventional packed beds of such sorbents. This makes it possible to employ small-sized beads which are trapped in a low-pressure column due to ultrasound-assisted retention, without any frits to hold the sorption material. A flow system including a separation mini-column, named herein a suspension column, has been developed and tested by the studies of solid phase extraction (SPE) of trace metals from bi-distilled water and sea water using a 150-μL column with a silica-based sorbent containing iminodiacetic groups (DIAPAK IDA) and having a grain size of 6 μm. The adsorption properties of DIAPAK IDA suspension (9.5 mg) were evaluated through adsorption/desorption experiments, where the effect of solution pH and eluent on the SPE of trace metals were examined by ICP-MS or ICP-AES measurements. When sample solution was adjusted to pH 8.0 and 1 mol L^{-1} nitric acid was used as eluent, very good recoveries of more than 90% were obtained for a number of elements in a single-step extraction. To demonstrate the versatility of the approach proposed and to show another advantage of ultrasonic field (acceleration of sorbate/sorbent interaction), a similar system was used for heterogeneous immunoassays of some antigens in ultrasonic field using agarose sorbents modified by corresponding antibodies. It has been shown that immunoglobulins, chlamidia, and brucellos bacteria can be quantitatively adsorbed on 15-μm sorbent (15 particles in 50 μL) and directly determined in a 50-μL mini-chamber using fluorescence detection.

1. Introduction

Sorption methods are very widely used in science and technology for the separation and enrichment of solutes from a liquid phase. The sorbents available are mostly granular solid particles of a diverse chemical nature. In analytical chemistry, sorption, which is currently often named solid-phase extraction (SPE), is a method of sample preparation that concentrates and purifies analytes of any nature from solution by recovery onto a column, cartridge, or other sorption unit, followed by elution of the analyte with a solvent appropriate for instrumental analysis. Beaded sorbents are usually used as packed beds retained in a column or cartridge by polypropylene or other frits at either ends of the sorption unit to hold the packing sorption material in place when a solution is passed through [1–3]. Spherical beads of 40–100 μm in diameter are most commonly used. The units filled with such relatively large beads enable the separation process to be operated at a low pressure that makes it possible to use a peristaltic or another simple pump and other simple components of the whole flow separation system.

The separation column efficiency can be improved by decreasing the sorbent beads size as surface area of smaller particles is larger, the rate of contact is higher, and the rate of mass transfer between the sorbent and liquid phase is greater [2,3]. This is why HPLC columns as well as preconcentration units, on-line connected to HPLC columns [4], typically have particles that range in diameter from 5 to 3 or even to 2 μm. The pressure generated by the resistance of the column to liquid flow is inversely proportional to the square of particle diameter [5,6]. Therefore, the separation with a column packed with particles of less than 10 μm in diameter requires pressures from several hundred to more than one thousand bar. To employ sorption columns with smaller beads, on one hand, and to avoid utilization of high-pressure pumps, valves, and lines, on the other hand, columns filled with a sorbent suspension instead of packed columns seem to be perspective.

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The pressure drop across a suspension column will be low compared with that of a packed column. However, the sorbent in the form of suspension can be applicable only if the suspension is held in a liquid flow without any frits; otherwise the slurry will be removed from the column together with analytes during the separation process. This could be possible if suspension particles are retained in a flow unit due to the application of an external force field (hydrodynamic, thermal, electrical, acoustic, etc.). Such fields are used for the separation of particles in field-flow fractionation (FFF) and related techniques which are based on different retentions of particles according to their size and density [7]. We suggested that under the conditions for complete force field-assisted retention of sorbent particles, distributed in the bulk of intercolumn liquid, one could obtain a low-pressure flow through a column containing a suspension of small particles (10 μm and less) most efficient for separating solutes and not generating any significant back pressure.

Suspension (fluidized bed) columns can have one more advantage. Contrary to classical packed beds, fluidization of solid adsorbents provides a practical option to process crude samples containing high-molecular solutes and particulate matter of inorganic, organic, or bioorganic origin. A technological bioseparation mode [8] was proposed where microbeads were inside a column by an upward liquid stream generated by sample solutions. As a result of the increased interbead porosity, fluidized beds allowed the separation of proteins contained in clude feed stocks. However, the beaded sorbents of modified porous oxides had particles as large as 70 μm in diameter. Fluidized beds were also used in flow analysis of plant digests [9].

Ultrasound is successfully used at different steps of the analytical process, including sample preparation for subsequent detection of various solutes [10]. During the last decade, acoustic radiation forces have been also applied to the manipulation of micrometer sized suspended particles [11]. A combination of such a force field with an appropriate flow system allowed the development of novel schemes for inorganic and polymer particles retention, separation, and characterization. It follows from the results reported that there should be conditions under which sorbent beads can be fully retained in a column in the form of suspention. Unlike other FFF techniques, where the force field is applied across the sample flow in a long rectangular channel, in acoustic FFF the field can be applied along the solution flow in a mini-chamber or column [12–14]. This is reasonable when the particles, having a density different from that of a surrounding medium, are subjected to sedimentation. Such an instrumental approach was used in our paper, although not for fractionation of particles but for the complete retention of sorbent particles in the standing acoustic wave field formed in the separating suspension unit.

Effective sorption, aggregation, and separation of biopolymers and cells in ultrasonic standing wave field may be due to intensification of mass transfer in such a field [15,16]. It is known that ultrasound can have a great effect on the kinetics of metal ion sorption by complexing and ion-exchange sorbents due to acoustic microflows which increase the mass transfer in the liquid phase. Therefore, ultrasound field may play two roles in sorption processes: retention of sorbent beads in a low-pressure suspention column and simultaneous acceleration of the processes owing to faster solute/sorbent interactions. This may be important because the transfer from a packed column to a suspension one will result in higher porosity, i.e., in longer interparticle distances that can cause kinetic problems.

The aim of the present study was to show the possibility of recovery, separation, and preconcentration of different analytes on a suspention column in an acoustic field.

2. Experimental

2.1. Instrumentation

A 56-Channel polychromator ICAP-61 (Thermo Jarrell Ash, USA) was used for determination of Na, K, Mg, and Fe. The operating conditions for this instrument are given in Table 1. A quadrupole mass spectrometer X-7 (Thermo Electron, USA) was used for the measurement of other elements studied. The operating conditions of the spectrometer are summarized in Table 2.

The antigens studied were measured directly in the mini-column using a fluorescence detector (Institute of Analytical Instrumentation, St.-Peterburg) operated at a wave-length of 490 (excitation) and 520 nm (detection). The pH values were measured with a pH-meter Ecotest 2000 (Ekonix, Russia). A laser analyzer for microparticles Laska 1K (Lumex, Russia) and a spectrophotometer Ecotest 2020 (Ekonix, Russia), operated at a wave-length of 525 nm were used to check the size of sorbent beads and control their retention in the suspension columns. The sample, washing solution, and eluent were fed by a peristaltic pump P-1 (Pharmacia Fine Chemicals, Sweden). Another pump (Sicce, Italy) was used for water cooling the ultrasonic suspension column.

2.2. Standard solutions, reagents, and sorbents

Stock standard solutions of metals were prepared by diluting a calibration standard solution ICP-MS-68A (High Purity Standards, USA). The concentration in stock solution was about 0.2 $\mu g\ L^{-1}$ for each element except for Na (4.5 $\mu g\ L^{-1}$) and K (27.1 $\mu g\ L^{-1}$). Analytical-reagent grades HNO_3 and NH_4OH were used to adjust the pH of metal solution in bi-distilled water. Seawater samples collected from a Kara Sea coastal area were spiked with aliquots of the same calibration standard solution.

Diasorb IDA metal complexing sorbent was purchased from Biochimmak (Russia). According to the manufacturer, the sorbent

Table 1
Operating conditions for the ICAP-61 instrument.

R.f. power	1200 W
Reflected power	< 5 W
Plasma gas flow rate	18 L min^{-1}
Auxiliary gas flow rate	0.9 L min^{-1}
Aerosol carrier gas flow rate	0.6 L min^{-1}
Solution uptake rate	1.0 mL min^{-1}
Nebulizer	Cross-flow type
Observation height	14 mm above load coil

Table 2
Operating conditions for the X-7 instrument.

Spectrometer parameters			
RF generator power		1250 W	
Nebulizer		Polycon	
Spray chamber		cooled at 3 °C	
Plasma gas flow rate		12 L min^{-1}	
Auxiliary flow rate		0.9 L min^{-1}	
Nebulizer flow rate		0.9 L min^{-1}	
Sample update		0.8 mL min^{-1}	
Resolution		0.8 atomic mass unit	
Parameters of mass-spectrum measurements			
Detector mode		Double (pulse counting and analogous)	
Scanning mode		Survey scan and peak jumping	
Setting for survey scan		*Setting for peak jumping*	
Number of runs	10	Sweeps	25
Dwell time	0.6 ms	Dwell time	10 ms
Channels per mass	10	Channels per mass	1
Acquisition duration	13.2 s	Acquisition duration	34 s

grain size was 6 μm, pore diameter 100 Å, complexing group capacity 0.2 mmol g^{-1} with respect to Cu^{2+}.

Phosphate buffer solutions with pH 7.4 for immunoassays were prepared in Institute of Analytical Instrumentation (St.-Peterburg). Agarose immunosorbents for antigens (chlamydia, brucellos bacteria, and FITC-labeled mouse immunoglobulins) were obtained in the Institute of Virusology (Moscow). The immunosorbents bead size was 15 μm, and their content in the working aqueous suspension was 15 particles per 50 μL. The antigen body sizes are given in Table 5. Aqueous solutions of antibodies to chlamydia and brucellos, marked by a luminescence label (FITC), were used as conjugates.

2.3. Separation systems and procedures

The flow system developed for on-line SPE of metal ions and their subsequent elution is depicted in Fig. 1. The adsorption, elution, and washing steps of the recovery procedure were carried out in a glass mini-column (6) with a height of 12 mm and an inner diameter of 4 mm (volume 150 μL). Ultrasonic radiation was applied by means of a ceramic piezoelectric transducer (8) with 2.65 MHz frequency. The transducer, providing the ultrasound intensity in the column 10 W cm^{-2}, was operated by a PC (10) using a Bluetooth USB adapter (9) (Brama, Canada). Because ultrasonic irradiation causes unwelcome heat dissipation, the column was cooled by means of a glass bath (5) through which cooling water was circulating by the help of a pump (3) from a water reservoir (1).

The analytical cycle was started by actuating the pump (4) to introduce 10 mL of aqueous sorbent suspension. The first 3 mL passed through the column (equal to the volume of the whole system) was discarded and then the column was washed with 20 mL of bi-distilled water with pH 6. If the ultrasound source was then switched off, the sorbent particles deposited on the bottom of the column, but after switching on the source the sorbent beads occupied again the whole column volume and held as static suspension against the solution flow. The metals were extracted from 10 mL, if otherwise states, of sample solution having different pH values. The elution was carried out by 5 mL of 1 mol L^{-1} HNO_3 and the eluates were collected for subsequent ICP measurements. After the elution step, the column was rinsed by 5 mL of 0.1 mol L^{-1} HNO_3 and later by 10 mL of bi-distilled water, and then the column was ready for the next adsorption/desorption run.

A flow system used for the recovery of some antigens in ultrasound field was similar to that applied to SPE of metal ions, although the mini-column and procedures were different. The column was made of quartz glass and had an inner volume of 50 μL. An immunosorbent suspension was introduced into the column and then the following liquids were passed: a sample of one of the antigens (5 μL), phosphate buffer solution, and a conjugate. Afterwards, the flow was stopped for a time from 10 to 100 s, and then the same buffer solution was passed again to remove non-bound conjugate. The volume of each solution, except for the sample, was 1 mL, the pumping rate was 1 mL min^{-1} in all the cases. The luminescence intensity due to the sorbent in the column was measured and compared with the intensity due to the immunosorbent completely saturated with the corresponding antibodies and conjugate. This made it possible to calculate the stopped-flow step time needed for quantitative adsorption of antigens.

3. Results and discussion

3.1. Retention of sorbents

According to papers [12–14] devoted to separation of particles in an ultrasonic field, three main upward and downward forces affect particle retention in a coupled acoustic-gravity field at parallel application of ultrasonic and fluid flow forces. The upward forces are Stokes ones (F_S) and an ultrasonic radiation one (F_R). The downward force is a gravity (sedimentation) one (F_G) if an individual particle density is higher than that of water and aqueous solution used. The latter is our case because a DIASORB IDA particle density is about 2.2 g cm^{-3}. The conditions for complete retention of suspension held in a flow system ($F_S+F_R=F_G$) have been studied at fixed ultrasound frequency and intensity at different water flow rates and volumes.

Relationships between DIASORB IDA retention in ultrasonic field and water volumes passed through the mini-column were

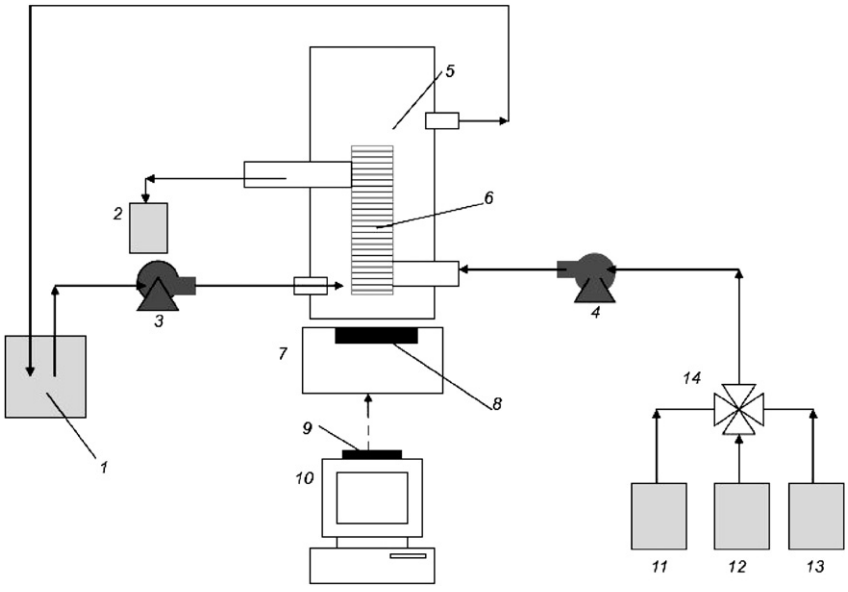

Fig. 1. Schematic representation of the flow system with a sorbent suspension column: 1—cooling water, 2—collector for eluate and washing solution, 3, 4—pumps, 5—water bath, 6—column, 7—ultrasonic unit body, 8—transducer, 9—bluetooth USB adapter, 10—computer, 11—sample, 12—washing solution, 13—eluent, and 14—valve.

obtained at different water flow rates (Figs. 2). The aim of this preliminary study was to know the conditions for holding the sorbent suspention in a flow system to be used for subsequent studies of metal recovery from aqueous solutions. The initial sorbent mass was 10 mg, the flow rates varied from 8 (corresponds to the pumping rate 1 mL min^{-1}) to 40 mL min^{-1} cm^{-2} for a column with an inner diameter of 4 mm. It is seen from this figure that, at a pumping rate of 1 mL min^{-1}, 9.5 mg of the sorbent is completely retained in the suspension ultrasonic column after the removal of excess 5% of the sorbent. Further metal adsorption/desorption experiments were carried out with 9.5 mg of DIAPAK IDA at a pumping rate of 1 mL min^{-1}, although higher rates can be applied (Fig. 2) if the sorbent mass is smaller.

It has been also shown that 20 and 30 mg of the sorbent can be retained in our column as well under the conditions chosen. The permeability of water through the column containing from 10 to 30 mg of the sorbent was similar. However, our further experiments on metal extraction have shown that a smaller amount of DIAPAK IDA (about 10 mg) is sufficient for the recovery of more than 20 elements studied.

Retention of agarose-based immunosorbents in the ultrasonic suspension mini-column used was also estimated. No sorbent was found in 50 mL of water passed through the column to which the sorbent suspension was preliminary introduced, if the pumping rate did not exceed 2 mL min^{-1}. The further adsorption experiments were carried out at a pumping rate of 1 mL min^{-1}.

3.2. Metal extraction and elution

DIAPAK IDA was shown to be useful for solid phase extraction (SPE) of some metal ions [17,18]. SPE cartridges packed with 500 mg of 100-μm beads were applied to recover Fe^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solutions, whereas a mini-column bearing 30 mg of the same material was successfully used for the preseparation of Cd, Pb, and Cu for their subsequent atomic-absorption determination in some dairy products. In the second case, a complete recovery of the three elements was achieved after the addition of a CH_3COONH_4 solution to the samples.

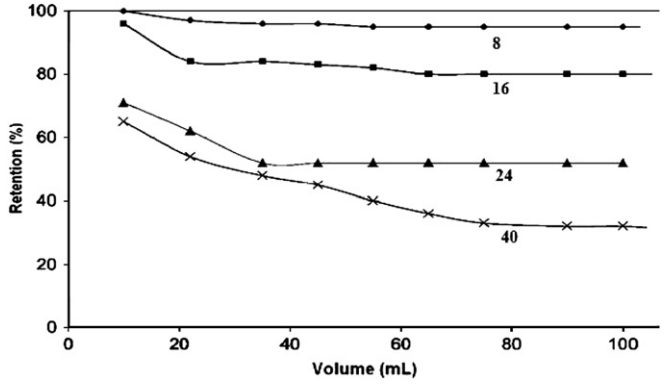

Fig. 2. Relationship between DIASORB IDA (6 μm) retention in ultrasonic field and water volume passed through a suspension mini-column of 150 μL at different flow rates (from 8 to 40 mL min^{-1} cm^{-2}).

In our studies we used a suspension column (instead of a packed-bed cartridge or column) containing only 9.5 mg of the same sorbent but having much smaller beads (6 μm in diameter). The effects of sample solution pH on the recoveries of 18 trace metals are seen in Fig. 3. Very good recoveries exceeding 95% were obtained for all these metals extracted from 10 mL of sample solution at pH 8. Under the same conditions, the recovery efficiencies for Al, As, Tl, and V were over 70%, whereas Na, K, and Mg were extracted by less than 2%. Table 3 summarizes the results of the SPE of REEs, Y, Th, and U from 10 and 80 mL of sample solution. It is seen from these results that metal ions can be extracted from larger volumes of sample solutions although the recoveries are a bit lower in the extraction from 80-mL samples.

Because Na, K, and Mg were not adsorbed on the sorbent used, an attempt was made to recover some metals from seawater samples spiked with some trace elements. The results obtained show that the ultrasonic suspension column can be applied to recover trace metals from more complicated samples Table 4. Diluted nitric acid was recommended for elution of trace metals adsorbed on DIAPAK IDA [17,18]. It was found from our experiments that over 95% of the adsorbed metals were eluted with 2–5 mL of 1 mol L^{-1} HNO_3 after SPE from distilled or sea water samples.

3.3. Recovery of antigens

The results obtained in this work clearly demonstrate that acoustic radiation forces are capable not only of trapping microbeads against a flow but also of accelerating immunoassays

Table 3
Recoveries (E, %) of U^{6+}, Th^{4+}, Y^{3+} and lanthanides (Ln^{3+}) from different volumes (V) of aqueous solution at pH 8. Three replicate extractions, average extraction reproducibility $E \pm 3\%$.

Metal	V (mL)		Metal	V (mL)	
	10	80		10	80
U	97	93	Gd	95	92
Th	97	94	Tb	95	91
Y	96	92	Dy	96	93
La	100	93	Ho	96	92
Ce	96	93	Er	96	92
Pr	95	93	Tm	96	93
Sm	96	93	Yb	97	93
Eu	96	93	Lu	96	93

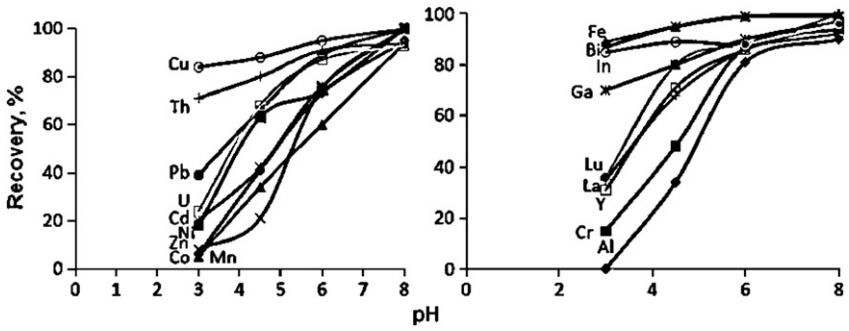

Fig. 3. pH-dependent SPE recoveries for different metals from aqueous solutions on a suspension mini-column with sorbent DIAPAK IDA.

Table 4
Recoveries (E, %) for metals from spiked distilled (pH 8) and sea[a] water samples (80 mL). Three replicate recoveries with average reproducibility $E \pm 3\%$.

Metal	Water		Metal	Water	
	Distilled	Sea		Distilled	Sea
Al	90	98	Ni	92	99
Fe	99	99	Co	94	97
Cr	92	90	Cu	95	99
Ln[b]	93	91	Zn	90	98
U	93	91	Pb	90	99

[a] From Kara Sea.
[b] Average for all lanthanides.

Table 5
Stopped-flow step (incubation) time required for quantitative (> 95%) adsorption of antigens on agarose-based sorbents in ultrasound-assisted (US) system and under batch conditions without ultrasound.

Sorbate	Size (μm)	Time	
		With US (s)	Without US (h)
Immunoglobulins	0.04	14	1
Chlamydia	0.3	50	1
Brucellos	1.2 × 0.4	80	2

compared with those performed by plate arrays without ultrasound [19]. As was mentioned above, this could be expected because of the high surface area of microbeads which promote higher rates of reactions between bio-molecules or cells and microsorbents. Tables 5 shows the time of the stopped-flow step of the recovery procedure required for quantitative adsorption of antigens on agarose-based sorbents in our ultrasounic-assisted flow system and under batch conditions (plate arrays) for corresponding antigen/antibody interactions without ultrasound.

As can be seen from the data in Table 5, a practically complete adsorption of immunoglobulins, *chlamydia*, and *brucellos* bacteria on the immunosorbents modified by corresponding antibodies is achieved within 14–80 s, while a quantitative antigen/antibody interaction under batch conditions takes 1–2 h that is dramatically different from the periods of time estimated under the influence of acoustic forces. If the stopped-flow time is 120 s, the recovery efficiencies for immunoglobulins, chlamydia, and brucellos bodies are 98%, 97%, and 96 ± 5%, respectively ($n=3$).

4. Conclusion

It has been shown that under the influence of ultrasonic field sorbent beads as small as a few microns can be completely retained in a flow mini-column in the form of suspension and applied as fluidized beds instead of conventional packed beds. Such small beads are known to be more efficient sorbents than the grains of 40–100 μm traditionally used in solid phase extraction to avoid applying high pressures to overcome a pressure drop across the SPE column or cartridge. Using a flow system developed, numerous metal ions were recovered from aqueous solution of different compositions. The efficiency of extraction was confirmed by comparison of the molar capacity of 6-μm complexing sorbent DIAPAK IDA (0.2 mmol g^{-1}) and the total molar amount of all the recovered metals (0.17 mmols with respect to one gram of the sorbent). This means that almost stoichiometric amounts of metals can be recovered, although iminodiacetic groups of DIAPAK IDA are known to be not very strong complexing groups.

The experiments carried out with sorbents of biological origin distinctly show another advantage of the system proposed: acoustic field may simultaneously play another role—acceleration of sorbent/sorbate interactions. In addition, suspended beds make it possible to work with bulky sorbates which are difficult to separate on packed beds through which such sorbates do not penetrate properly. It should be also noted that the viability of cells and other entities of biological origin is maintained at the ultrasound intensity level used in our studies [10,11,19].

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