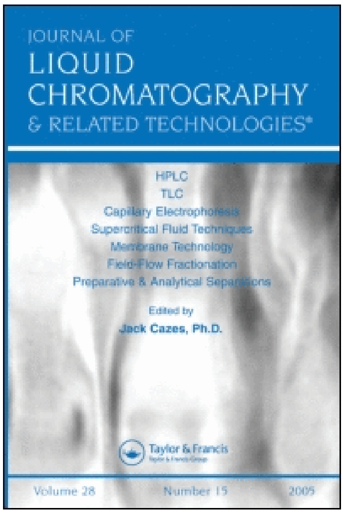

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Retention of Solids in Rotating Coiled Columns: The Effect of β Value and Tubing Material

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ABSTRACT

The retention behavior of suspended solids in rotating coiled columns (RCC) has been studied. It has been shown that the greater the β-value (ratio of rotation and revolution radii) the better the retention of solid matter. It has also been shown, that up to five grams of a polydisperse soil sample are completely retained in PTFE columns with a total inner capacity of 34 mL (3.2 mm tubing bore) for a wide range of experimental conditions (column rotation speed and mobile phase flow rate). The successful demonstration of the scale-up of solid suspension retention in RCC, will enhance the capabilities of the accelerated dynamic sequential extraction of trace elements (TE) and other organic and inorganic solutes from solid

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samples. This will not only be possible for the analysis of samples with elevated TE concentrations, but also for those with slightly elevated or "normal" TE concentrations. PTFE coiled columns have been found to be preferable to stainless steel ones.

Key Words: Countercurrent chromatography; Rotating coiled columns; Retention of solid particulate; Fractionation; Extraction from solids.

INTRODUCTION

Traditionally, rotating coiled columns (RCC) have been successfully applied in liquid countercurrent chromatography (CCC) using two immiscible solvent phases, where one is the retained "stationary" phase and the other the pumped "mobile" phase.[1] Solutes injected with the mobile phase are subjected to a partition process between these two immiscible phases and elute in order of their distribution ratios. Ito demonstrated, when he invented the process[2] and later, that it could also be used to separate cells based on their distribution ratio in aqueous two phase polymers systems[3] and on their size in single phase solutions.[4,5] All these experiments were conducted in "I" type non-synchronous coil planet centrifuges, where the "g" fields were relatively high and the coil rotational speeds were relatively low.

Recently, it has been shown that RCC can be used with synchronous "J" type coil planet centrifuges for the separation of both solutes and particles, not only in liquid–liquid systems but also in liquid–liquid–solid and liquid–solid systems.[6–8] A procedure has been developed for the direct recovery of some polyaromatic hydrocarbons from a sewage sludge medium without any sample pre-treatment.[6] It has been shown that heterogeneous samples can be successfully retained in the column and kept well mixed and agitated. The sewage sludge sample (in fact a concentrated suspension) was the stationary phase in the column, whereas organic solvents (heptane, dichloromethane) or their mixtures were used as mobile phase. Rotating coiled columns can also be used as a field-flow fractionation method for the separation of particles.[7] There is no stationary phase in this case. The asymmetrical force field acting on RCC results in different migration speeds for suspended sample components of different size in the mobile phase carrier fluid.

A new approach to performing an accelerated sequential extraction of trace elements (TE) from solid samples has also been proposed.[8] It has been shown that RCC can be successfully applied to the dynamic leaching of heavy metals from soils and sediments. A solid sample was retained in the rotating column as the stationary phase suspension under the action of centrifugal forces, while different eluents (aqueous solutions of complexing reagents, mineral salts, and acids) were sequentially pumped through. The procedure developed is time saving and requires only 4–5 hours instead of several days needed for traditional sequential extraction (TSE). Complete automation would be possible. In most cases, the recoveries of readily bioavailable and leachable forms of Pb, Zn, and Cd are higher, if a dynamic extraction in RCC is used. Losses of a solid sample are minimal. Since naturally occurring processes are always dynamic, continuous extraction in RCC may help to estimate the contents of leachable forms and their potential risk for the environment more correctly than batch TSE. The Kersten–Foerstner and McLaren–Crawford leaching schemes[9,10] have been compared, the first one has been found to be preferable.[8]

The accelerated sequential extraction procedure has been tested on soil and sediment samples characterized by highly elevated TE concentrations.[8] A solid sample (0.5 g) was retained in the rotating column with a total inner capacity of 20 mL. Ideally, larger volumes of the solid matter are required in order to analyse samples with slightly elevated or "normal" concentrations of TE. The objectives of this study is to scale-up the process by using tubing of larger bore and capacity and examine the retention of soil samples as the radius of the coil (or β value) changes for a range of different flow rates and rotational speeds. In this way, the retention behavior of solids in the RCC can be investigated before optimizing leaching procedures.

EXPERIMENTAL

Samples

A sample of soil from a Moscow region containing silt, clay, and sand fractions (colloids and solid particles started from about 0.1 μm) was preliminary dried and passed through a 250-μm screen.

Apparatus

The retention of solids was studied on a J-type coil planetary centrifuge (rotor radius $R = 110$ mm) with bobbins containing horizontal one-layer coiled PTFE tubing of constant volume, diameter, helix angle, and length. These bobbins were constructed by Brunel Institute for Bioengineering. The three bobbins used for the experiment had rotation radii $r = 42$, 68, and 95 mm. Hence, β-values (r/R) were 0.38, 0.62, and 0.86, respectively. The PTFE tubing coiled has an inner diameter of 3.2 mm, a total inner capacity of 34 mL, and a constant helix angle of 1.1°. The tubing length was 4.2 m for the three bobbins, producing 16 turns on the 4.2 cm spool, 10 turns on the 6.8 cm spool, and seven turns on the 9.5 cm spool. For all the three bobbins, the volumes of connecting tubes were 11 mL (7 and 4 mL before and after column, respectively).

A stainless steel column was also used, which had a β value of 0.82, capacity of 59.1 mL, bore of 3.73 mm, length of 5.65 m, and 10 loops. The helix angle (1.16) was approximately the same as for the PTFE coils.

Procedure

The soil sample (up to 5 g) was stirred in distilled water to obtain 25 mL of suspension. The suspension was introduced into the motionless column by using a peristaltic pump, at a flow rate of 15 mL/min. Subsequently, water (10 mL) was pumped at the same flow rate to remove any residual sample from connecting tubes and ensure that the sample was all completely in the column. Then, the column was rotated at a given speed and the flow rate was stopped for 5 min ("stop-flow" mode). After that, while the column was continuously rotated, water was pumped into the inlet at the set flow rate. Fractions (15 mL each) of the column effluent were collected. Fractions containing eluted particles were characterized by electron microscopy (electron microscope JEOL, JEM-2000 FX). For each series of experiments, the rotation speed (ω) was varied from 300 to 800 rpm in steps of 100 rpm, while the mobile phase pumping rate (F) was varied from 1 to 5 mL/min in steps of 1 mL/min.

For solids to be retained in the column, the flow should be in opposite direction to the column rotation. In other words, the mobile phase (water) should be pumped from the head to the tail end of the column. To remove particles from the column after each experiment, a flow rate (F) of 100 mL/min was used.

RESULTS AND DISCUSSION

Retention of Solid Matter in PTFE Columns with Different β-Values

Certain difficulties often arise when a solid sample is to be introduced into a column because connecting tubes and fitting connections can become blocked.[8] In the present study, it has been shown that up to 5 g of the soil sample suspended in water can be easily introduced into the PTFE column with a total inner capacity of 34 mL. Different mobile phase flow rates have been tested. The value of 15 mL/min was found to be preferable. Lower flow rates do not provide the needed migration of particles through connecting tubes, dense large particles being precipitated on the walls of the tubing. Higher flow rates lead to a significant broadening of the sample front in the column.

In studies on solids retention the mobile phase flow rate was varied from 1 to 5 mL/min. It should be noted, that in many cases, the kinetics of TE extraction from solid samples is slow. That is why, according to McLaren and Crawford's[9] scheme, the recovery of TE in exchangeable, "bound to specific sites" and organic forms by using calcium chloride, acetic acid, and potassium pyrophosphate, respectively, requires at least 24 hours of contact time for each step whereas, according to Kersten–Foerstner's[10] leaching scheme, 5–16 hours of contact time are needed for the separation of each fraction.[8] The use of multistage continuous extraction in RCC allowed one to reduce the contact time needed for the separation of each form (fraction) down to 30–40 min.[8] If the flow rate under the given experimental conditions (total column capacity of 34 mL, sample weight 5 g) is in the range 1–5 mL/min, the time of contact between the sample and the mobile phase is varied from about 30 to 6 min. Further decreasing the contact time seems to be unreasonable for extraction of any substances from solid samples.

The degree of soil sample retention for various mobile phase flows and rotational speeds in three PTFE columns of varying β value is shown in Fig. 1. As can be seen in Fig. 1(a), for the smallest β-value (0.38), relatively high rotation speed (700–800 rpm) and low mobile phase flow rate (1–2 mL/min) are required for the complete retention of the polydisperse soil sample. Hence, the "working zone" (zone I) is somewhat limited. Zone II corresponds to the elution of colloidal sub-micron particles, all other particles being retained in the column. By convention, zone II may also be considered as a working zone. As has been mentioned above, in leaching sequential extraction procedures, aqueous solutions of mineral acids and salts can be used as mobile phase.[8] In such solutions, amorphous and colloid particles can agglomerate with each other. Hence, their retention may be improved.[8] In other words, using diluted solutions of electrolytes as mobile phase may help to avoid the elution of colloids in zone II. Zone III is not a working zone and corresponds to the elution of colloids and fine (micron region) solid particles. A close up of the coil (stop of the mobile phase flow) following one of the runs (Fig. 2) shows the larger particles distributed toward the head end of the coil (right hand side). Note the flow is from right to left.

The degree of soil sample retention in the PTFE column with the medium β-value (0.62) is shown in Fig. 1(b) (the middle diagram) for a similar range of flow rates and rotational speeds. As can be seen, increasing the β-value increases the extent of the working zone (zone I). Complete retention of the soil sample is observed for a relatively wide range of column rotational speeds and mobile phase flow rates. If by convention, zone II is also considered as a working zone, then the whole range of rotation speeds from 400 to 800 rpm

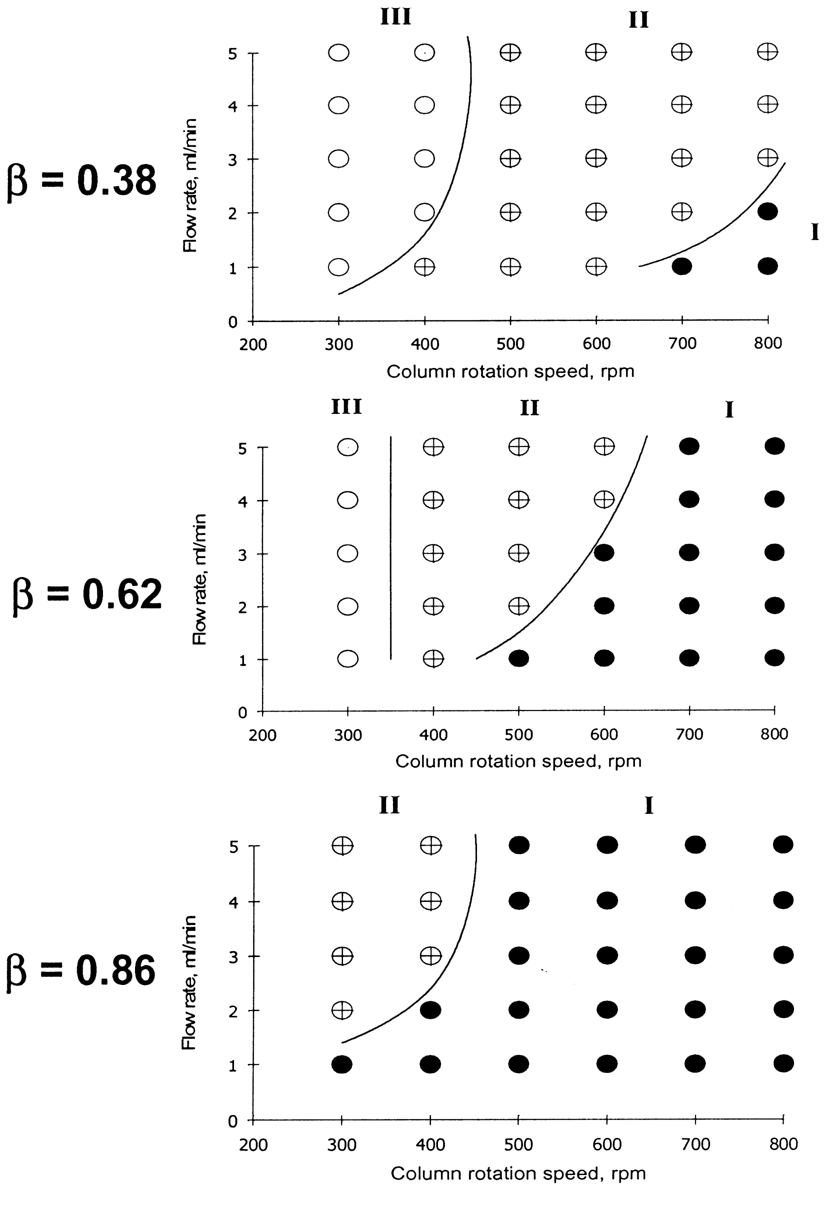

Figure 1. Retention of a soil sample (5 g) in PTFE columns with different β-values. Effects of column rotation speed and mobile phase flow rate. *Key:* ●, soil sample is completely retained in the column; ⊕, colloidal sub-micron particles can be eluted; O, colloids and fine solid particles (micron region) can be eluted.

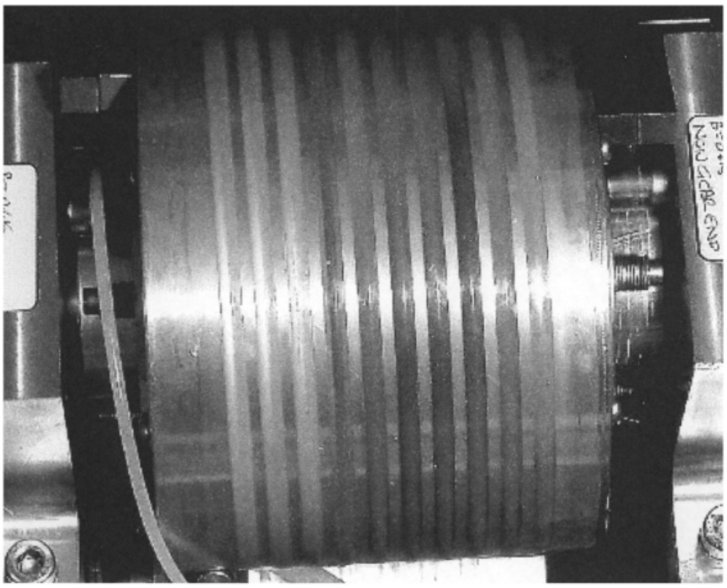

Figure 2. Close up photograph of the $\beta = 0.62$ coil showing the retention of solid particles concentrated toward the head end of the coil.

will be appropriate for sample retention. Zone III becomes narrow and restricted to a rotational speed of 300 rpm.

Further increasing the β-value (up to 0.86) results in a further increase in the extent of zone I [Fig. 1(c), the lower diagram], zone III completely disappearing. So, if the β-value is equal to 0.86, all the experimental conditions under study (rotation speed 300–800 rpm and flow rate 1–5 mL/min) may be principally used for the retention of soil samples and subsequent leaching of different solutes.

The higher the β-value is, the better the retention of solid matter. As β-value increases, the radial acceleration perpendicular to the tubing increases, while the tangential acceleration along the tubing remains constant. This phenomenon could be responsible for "pressing" the fine particles to the outer tube wall and, consequently, for their retention.

Retention of Solid Matter in Stainless Steel Columns

It was shown that stainless steel (SS) columns also retained solid suspended samples. When the rotation speed was 800 rpm, the soil sample

(5 g) was completely retained in the SS column with a tubing bore of 3.7 mm and β-value of 0.82 over the whole range of mobile phase flow rate from 1 to 5 mL/min. Decreasing the rotation speed to 700 rpm led to the elution of colloidal sub-micron particles.

However, it is very difficult to remove the soil sample from the motionless SS column after the experiment. Even a few liters of water pumped with the flow rate of 100 mL/min are insufficient to elute all particles. This might be due to certain interfacial phenomena occurring on the SS walls of the column. Besides, it is not very convenient to perform experiments related to the retention of solid matter in non-transparent SS columns, because a visual observation of the sample distribution inside the column becomes impossible. Hence, PTFE columns were considered preferable for retaining solid matter and subsequent leaching of different solutes.

CONCLUSIONS

It has been shown that the process of retaining solids in a RCC can be successfully "scaled up." Polydisperse soil samples of up to 5 g are completely retained in a PTFE column with the total inner capacity of 34 mL for a wide range of experimental conditions.

The results obtained are of importance for retaining environmental samples (soils, sediments) needed for subsequent dynamic leaching of different solutes. Furthermore, using suspended solids (e.g., sorbents modified by some reagents) as a free stationary phase in RCC may help to develop a new approach to performing different separation, purification, and even, fermentations processes.

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