Liquid-Liquid Micro Batch Extraction System for Rapid Separation

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The liquid-liquid micro batch extraction system, LMES, was developed for rapid separation of a trace amount of metal ions. The equipment is composed of three simple extraction cells for phase mixing, phase separation, and solvent collection. Separation could be completed in a single operation lasting only a minute, from solvent extraction to preparation for alpha-ray spectrometry.

Traditional batchwise solvent extraction has been a basic and powerful method of concentrating and purifying a desired ion and of evaluating chemical reactions such as complex formations and ion transfer mechanisms through a liquid-liquid interface. A factor of particular importance in the investigation of chemical properties of short-lived and microtrace elements by means of liquid-liquid extraction is the necessity for a rapid and advanced separation system including features such as prevention of contamination from chemical reagents and mechanical instruments. In order to shorten the time needed for the extraction operation, some operations should be simplified. Such operations include, for instance, the preparation of aqueous and organic solutions, phase mixing with the aid of a mechanical shaker, phase separation by a centrifuge or a standing, and so on. To facilitate rapid operation, many researchers have designed instruments for flow-type rather than batch-type extraction separation. However, even in the novel flow reaction field on a microchip, it is still difficult to understand the complexation-reaction at the interface.[1,2] In early studies, a flow cell (500 µL in volume) was designed for the study of ion-pair extraction by flow injection analysis.[3] This cell, with a small magnetic stirring bar to mix water-chloroform phases, carried out continuous phase separation by using a polytetrafluoroethylene (PTFE) membrane that passes only the organic phase.

The concept of the phase separation technique used in the flow system is also applicable to the batchwise system. In the present work, the authors developed a traditional but novel technique in a batchwise, rapid, and micro solvent extraction system. The extraction of uranium as an alpha emitter was demonstrated to show the applicability of the developed method. The equipment downsized for this system can control quite a low solvent volume of just several dozen microliters. Also, a desktop-type microtube mixer and a portable minicentrifuge were applied to this system for phase mixing and phase separation, respectively. As a result, the shaking time to batch-equilibrium between the two phases is expected to shorten. The time required to finish one operation is less than one minute. Furthermore, the volume reduction of reagent to a level less than a hundredth of the conventional extraction method (5 to 100 mL in all) diminishes the risk of contamination from impurity of chemicals and from chemical and radioactive hazards. The low volume system also contributes to environmental protection.

The developed liquid-liquid micro batch extraction system, LMES, is composed of three simple extraction cells for (a) phase mixing, (b) phase separation, and (c) collection of a solvent. These cells are made of polypropylene, which is not corroded quickly by general solvents except for some concentrated acids and organic solvents.[5] In addition to this, it can easily be controlled by heat, and is economical and disposable, with no risk of cross contamination. The apparatus used in the LMES is composed of three cells. The mixing cell for mixing the two phases is conical in shape (ca. 30 mm in height and 3 mm in the base diameter) as shown in Figure 1a. The design of the phase separator with centrifugation in Figure 1b includes a hydrophobic PTFE membrane filter (pore size 3.0 µm, porosity 83%, 75 µm in thickness, and 8 mm in diameter) in the bottom of the cell. In the centrifugal phase separation process, the organic phase is recovered in the collection cell (Figure 1c).

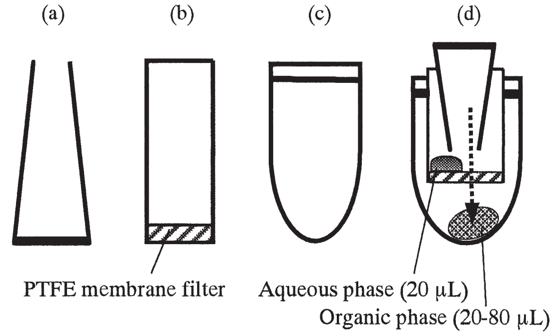

Figure 1. Apparatus used in the LMES, (a) mixing cell, (b) phase separator, (c) collection cell, and (d) assembly of three cells for centrifuge.

In order to evaluate the applicability of the LMES, the extraction of uranium by tributylphosphate (TBP) as an extractant was investigated. An aqueous phase of 20 µL containing 10^{-3} mol dm^{-3} (M) UO_2^{2+} in 4 M HNO_3 was shaken vigorously for 10 s at 298 ± 1 K with 20 to 80 µL of dodecane–30%(v/v) TBP presaturated with 4 M HNO_3 in the mixing cell. A shaking time of 10 s by a microtube mixer was found to be long enough to attain the extraction equilibrium. After centrifugation of the assembly cell unit as shown in Figure 1d by a portable minicentrifuge for 15 s, the organic phase was recovered in the collection cell thorough the PTFE membrane, while the aqueous phase remained on the membrane of phase separator. The inside of each cell was washed with 10 µL of 0.1 M HNO_3 solution. The extracted solution together with the washing solution was put on a hot stainless disk by micropipette. The concentration was determined by alpha-ray spectrometry using a 1 cm^2 silicon detector (EG&G ORTEC) with counting efficiency of 15% and a background less than 0.02 counts ks^{-1} over the energy range of interest.

The extraction equilibrium can be written as

$$UO_2^{2+} + 2NO_3^- + 2TBP \leftrightarrows UO_2(NO_3)_2(TBP)_2 \quad (1)$$

In Table 1, the apparent extractability of uranium, E_{app}, and the total recovery, R, were summarized. The E_{app} achieved over 97% independent of the volume of organic phase. This result supposes that uranium could be extracted quantitatively into the micro volume of organic phase in a short time. However, the recovery decreased when the volume of organic phase decreased. The value of net (apparent) peak area of alpha spectrometry, S_{app}, was plotted against the volume of organic phase V_{org} in Figure 2. It is found that S_{app} exponentially decreases along with a decrease in the initial volume of organic phase. Two factors might be contributed predominantly to the decrease of S_{app}; (a) permeation loss of organic phase into the PTFE membrane which was fitted in the phase separator, and (b) recovery loss caused by handling in the whole process. These contributions were evaluated from the following equations.

$$S_{app} = S_{std}D(V_{org} - V_a)/(V_{aq} + V_{org}D) - S_b \quad (2)$$

$$V_b = V_{org}S_b/(S_b + S_{app}) \quad (3)$$

where subscript a is the loss of organic phase immersed by the membrane, subscript b is the handling loss as mentioned above, and D denotes the distribution ratio defined as $[U]_{org}/[U]_{aq}$. Here, D in the 30% TBP–4M HNO_3 extraction system was referred as 42.7,[6] V_{aq} was 20 μL, and the peak area, S_{std}, equivalent for 20 μL of 10^{-3} M uranium standard solution was 9.2 counts ks^{-1}. The constants of V_a and V_b in eqs 2 and 3 were determined to be 6.3 ± 0.9 and 0.8 ± 1.4 μL, respectively, by a curve fitting of these plots in Figure 2. Especially, the value of V_b may be reproducible if the solvent recovery method in the order of microliter is improved further. Since V_a and V_b may change depending on the volatility and viscosity of the selected solvent, these values should be estimated preliminarily for the other solvent system in the future study.

Table 1. V_{org}[a] dependence of apparent extractability and total recovery of uranium in both phases

V_{org}/μL	20	30	40	50	60	80
E_{app}[b]/%	97 ± 2	97 ± 2	99 ± 1	97 ± 1	99 ± 1	98 ± 1
R[c]%	69 ± 3	75 ± 6	84 ± 6	91 ± 4	86 ± 8	92 ± 7

[a] V_{aq} was constant as 20 μL of 10^{-3} M UO_2^{2+}, where subscripts org and aq denote the organic phase and the aqueous phase, respectively. [b] The apparent extractability defined as $[U]_{org}/([U]_{aq}+[U]_{org})*100$. [c] R defined as the ratio of the sum of net counts in both phases after equilibrium to the net count for the initial solution.

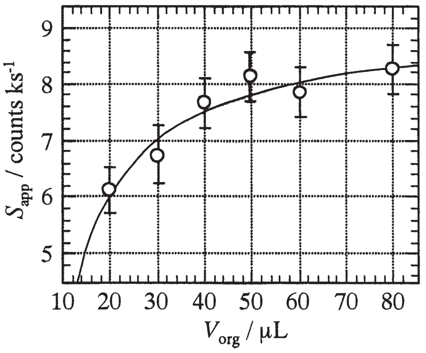

Figure 2. Alpha counting of uranium in the organic phase after extraction by the LMES as a function of the initial volume of organic solution.

For the determination by alpha-ray spectroscopy, the extracted solution containing uranium is needed to dry up on a hot stainless disk. The time for dryness was within 5 s, because the sample volume of aqueous phase was just 20 μL which was treated by the LMES. Also, the extracted species even in the nonvolatile mixture of TBP and dodecane could be fixed on the disk directly within only 10 s without back-extraction into an aqueous phase.

The developed LMES as a batch system instead of a flow system could be completed in under a minute considering the time required for one separation process, from solvent extraction to preparation for alpha counting. On the other hand, the traditional method needs 5 to 100 mL in each phase, and takes several minutes at least. The LMES as a batch system not a flow one will be established as a novel methodology to investigate chemical properties of a trace amount of new element and its compound. For the rapid extraction with a higher precision, the mechanical apparatus in the LMES must be designed. This method has also some flexibility to the fundamental study of the extraction mechanism for pH and ion strength dependences, and kinetics.

References

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