

ANALYTICAL APPLICATION OF SUPPORTED LIQUID MEMBRANES IN TRACE METAL EXTRACTION AND SPECIATION

Kuria Ndungu

Environmental Toxicology Department/WIGS, University of California, Santa Cruz, CA 95064, USA,
Email: kndungu@es.ucsc.edu

Nii-Kotey Djane, Lennart Mathiasson and Jan Åke Jönsson

Department of Analytical Chemistry, Lund University, S-221 00 Lund, Sweden

Abstract

The supported liquid membrane (SLM) procedure is an emerging trace metal preconcentration technique, that precludes many of the problems (e.g., labor intensity, time, and use of large amounts of reagents) that are characteristic of the liquid-liquid extraction (LLE) which has been a standard extraction and preconcentration method for trace metal analysis for several decades. SLM takes advantage of LLE's ability to tune the extraction selectivity by chemical means but unlike LLE, it is easily automated and can be readily coupled to sensitive detectors such as electrochemical or spectroscopic.

Since SLM is selective to the free and/or lipophilic species of the analyte, it often provides a more accurate measure on bioavailability and toxicity of metals in solution than the total dissolved (e.g., $< 0.45 \mu\text{m}$) metal concentration measurements. Additionally, more rigorous speciation measurements can also be performed by combining different SLM units in series (e.g., cationic trivalent chromium and anionic hexavalent chromium can be selectively enriched without an independent chromatographic procedure). These advantages are illustrated in preliminary applications of SLM to measure trace metal concentrations and speciation in natural waters and urine

Introduction

The two most widely used methods for separating trace metal ions in liquid samples from the interfering matrix are liquid-liquid extraction (LLE) and solid phase extraction (SPE). Although LLE offers high enrichment factors and has a higher potential compared to SPE, to chemically tune the separation by incorporating selective reagents, it is an expensive and difficult method to automate. SPE is easier to automate and requires minimal reagent use but suffers from the risk of clogging and/or low breakthrough volumes.

Supported liquid membrane (SLM) is a relatively new technique in comparison, which precludes most of the above problems. The permeation of metal species through SLM involves a simultaneous combination of an extraction and a stripping occurring in non-equilibrium conditions. The SLM system employs two aqueous phases: (1) a source (donor) solution containing the analyte(s) to be extracted and (2) a strip (acceptor) solution into which the analyte(s) is trapped. Those two phases are separated by an immiscible organic solvent immobilized on a thin microporous membrane. By using strip solutions volumes much smaller than source solution volumes, the analyte can be preconcentrated. SLM offers a number of advantages compared to other sample pre-treatment methods traditionally used in trace metal analysis: (1) high selectivity and clean extracts from complex matrices (2) high degree of concentration enrichment (3) easy on-line connection to analytical instruments (electrochemical and spectroscopic) and (4) near-total avoidance of organic solvents (Jönsson and Mathiasson, 1999 a).

Only a few analytical applications of SLM in trace metal analysis have been reported (Djane et al., 1997, Keller and Buffle, 2000) and very few on speciation (Ndungu et al., 1999). This paper summarizes some of the applications of SLM in trace metal analysis and speciation

Theory

SLM methodology is based on diffusive transport of metal ions across a hydrophobic liquid membrane from a flowing aqueous solution (donor) to a stagnant aqueous solution (acceptor). The theory for mass transfer of analyte species and trapping have been detailed elsewhere (Jönsson and Mathiasson, 1999 b) For an efficient enrichment, the following conditions must be fulfilled:

(i) metal ions in the sample solution must form uncharged species before or in connection with the diffusive transport across the SLM

Determination of metal ions in River water

Trace metal ions Cd, Cu and Pb were preconcentrated from river water samples using the automated SLM set-up illustrated in figure 2 above. The SLM contained di-2-ethylhexyl phosphoric acid (DEHPA) (40% m/m) dissolved in kerosene. A proton gradient (figure 1 a) provided the driving force for the mass transport of the metal ions across the membrane. Results obtained for the determination of the trace metal ions Cd, Cu and Pb in SLRS-2 riverine water reference material (table 1) were within the certified range

Table 1. Results for the determination of the metal ions Cd, Cu, and Pb in SLRS-2 riverine water reference material

Metal	Mean value ^a (µg/l)	Certified value (µg/l)
Cd	0.032 (0.005)	0.028 (0.004)
Cu	2.48 (0.13)	2.76 (0.17)
Pb	0.148 (0.026)	0.129 (0.011)

^aStandard deviation of 6 determinations, 2 hr preconcentration period

Determination of lead in Urine: SLM-AAS

The determination of trace metals in urine is complicated by the complexity of the sample matrix. SLM was used to preconcentrate Pb in urine prior to GFAAS or FAAS determination. The only sample preparation needed prior to extraction was a pH adjustment (to pH 3.0 with HNO₃). Figure 4 illustrates a comparison of lead concentration values obtained by ICP-MS and AAS after SLM enrichment (Djane and Bergdahl., 1997).

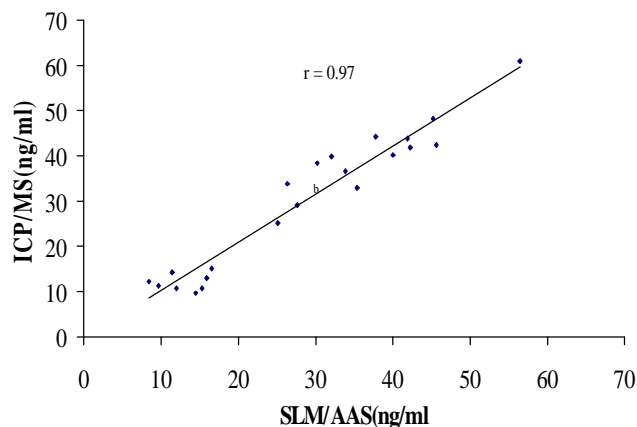


Figure 4. Validation of the SLM/AAS methodology for lead determination in urine by comparison with results obtained with ICP-MS. Sample: urine adjusted to pH 3.0, SLM: 40 % DEHPA in kerosene. Acceptor solution: 1.0 M HNO₃

Lead in Urine: Online SLM- PSA

Lead in urine samples was also determined by coupling of SLM (40% m/m DEHPA in kerosene) sample clean-up and enrichment to potentiometric stripping analysis (PSA) in a flow system using mercury-coated reticulated vitreous carbon (RVC) as the electrode material. The only sample pretreatment required was a simple pH adjustment. For a 10 min SLM enrichment, (including a 5 min electrodeposition on the RVC electrode at -1.0 V (versus Ag/AgCl) the detection limit for lead was 0.3 µg/l. The relative standard deviation for lead concentrations in the range 4-20 µg/l was 0.05%. (Djane et al, 1998)

Chromium speciation

Analysis of Cr (III) and Cr (VI) normally requires a chromatographic separation prior to determination. The ability to tune the selectivity in SLM extraction by incorporating different extractants was used to selectively enrich Cr (III) and Cr (VI) prior to their detection using GFAAS without the need of an independent chromatographic step by combining two SLM units in series. The first SLM, containing the acidic extractant di-2-ethylhexyl phosphoric acid, extracts trivalent chromium while the second containing the basic extractant, Methyltrioctyl ammoniumchloride (Aliquat-336) extracts anionic hexavalent chromium species.

By combining a Cr(VI)-selective SLM extraction step with a Cr(VI)-specific spectrophotometric detection (after complexation with 1,5-Diphenylcarbazine (DPC), Cr(VI) could be determined on-line in presence of a hundred fold excess of Cr(III) (table 2). The results obtained (mean \pm standard deviation) for the on-line determination of Cr(VI) (40.13 ± 0.82 , $n = 3$) in a certified reference material (welding dust loaded on a glass fiber filter (CRM 545) after off-line ultrasonic extraction using an ammonium buffer was in good agreement with certified value of 39.47 ± 1.30 g/kg (Ndung'u et al., 1999)

Table 2. Determination of Cr(VI) in presence of excess Cr(III) in spiked filter paper (40 mg) and acid washed sand (0.2 g) after ultrasonic extraction using ammonium (pH = 8.0). Each concentration is a mean of three determinations (SD in brackets). The samples were ultrasonicated for 30 min at 40°C in 20 ml of buffer solution prior to on-line SLM extraction and spectrophotometric determination after complexation with DPC.

	Added Cr(VI) + 250 ($\mu\text{g/g}$) Cr(III)	Recovered Cr(VI) ($\mu\text{g/g}$)	Cr(VI) Recovery (%)
Acid-washed sand	2.50	2.46 (0.13)	98
Filter paper	25.0	25.9 (3.6)	104

Conclusion

The supported liquid membrane procedure is an emerging trace metal preconcentration technique, that precludes many of the problems (e.g., labor intensity, time, and use of large amounts of reagents) that are characteristic of liquid-liquid extraction. Its ability to process complex sample matrices containing dissolved solids such as natural waters and urine with minimal sample handling and ease of on-line coupling to sensitive detectors, makes it attractive for trace metal analysis and speciation.

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