Membrane Extraction of Aqueous Transition Metal Ions Using Commercial Nafion Gas Dryers

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Abstract

Membrane extraction is a widely employed technique for improving the sensitivity and/or selectivity of a chemical analysis. This paper reports a study on the membrane extraction of aqueous transition metal ions using commercially available Nafion gas dryer assemblies. Though designed and marketed for use with gaseous mixtures, results of this work indicate such assemblies can be effective for the selective extraction of aqueous mixtures after a simple pretreatment procedure not requiring physical modification of the unit. The analytical merit of this sampling approach was evaluated by examining various performance characteristics using aqueous Cu(II) as a model system.

Introduction

Membrane extraction is a widely employed means of separating and, in some cases, concentrating analytes prior to a chemical analysis (1). Examples of recent applications of membrane extraction include their use in sample preparation for gas chromatography of polychlorinated biphenyls (2) and liquid chromatography-mass spectrometry of explosives (3); monitoring plant fragrance emissions (4); and sampling groundwater for polycyclic aromatic hydrocarbons (5). Similar applications have been reported in the area of chemical sensor development, where extraction membranes are used to enhance the sensitivity and selectivity of probes designed for *in-situ* measurements. For example, a heavy metal sensor was described by Niessner et al. that used cation-exchange membranes to limit the permeation of species into the sensor's detection zones (6). More recently, Buffle et al. reported a similar sensor design that used a permeation liquid membrane containing an organic complexing agent selective for certain transition metal ions (7).

Work in the authors' laboratory has recently been directed towards the development of fiber optic sensors suitable for environmental and industrial process measurements that utilize spectroelectrochemical transduction schemes, with initial efforts focused on the determination of transition metal ions. In order to selectively sample these ions, the incorporation of a hollow fiber cation-exchange membrane into the sensor design is being explored. While searching unsuccessfully for a suitable, commercially available product for this application, a Nafion hollow fiber module designed to remove water vapor from gaseous streams was identified that showed promise for adaptation to aqueous samples (8). Described in this paper are the results of

studies aimed at assessing the suitability of these gas dryers for the selective extraction of transition metal ions from aqueous media.

Experimental

Reagents. The following chemical reagents were used as received from Fisher Scientific: cobalt(II) chloride, chromium(III) chloride, copper(II) sulfate, disodium ethylenediaminetetracetate (EDTA), nickel(II) choride, sodium bicarbonate, sodium carbonate, and sodium chloride. Solutions were typically prepared using deionized water and stored under refrigeration.

Apparatus. The experimental setup is illustrated in Figure 1 and consisted of a gas dryer (PermaPure, PD-50T-12-PP), a custom made bubble trap, a medium flow peristaltic pump (Fisher), a 1 cm flow cuvette (Uvonics), and a diode-array spectrophotometer (Agilent model 8453). The gas dryer was comprised of a bundle of fifty Nafion hollow fibers (ca. 30 cm length, 0.8 mm outer diameter, 0.3 mm inner diameter) housed in a polypropylene shell with ¼ in female NPT ports to accommodate fluid inlet and outlet connections. The sample solution was suspended above the dryer to permit its gravity-driven flow through the dryer shell (over the outer surfaces of the Nafion fibers), with the flow rate controlled by a pinch clamp at the end of the sample outlet tube. A peristaltic pump controlled the recirculating flow of extractant solution through the Nafion fibers, with the in-line bubble trap permitting visual measurement of the flow rate by timed drop counting.

Procedure. Prior to the first use of a dryer assembly in aqueous media, the Nafion fiber bundle was removed from the dryer shell, soaked overnight in distilled water to permit complete hydration and related swelling of the Nafion fibers, then carefully remounted within the shell. It

was found necessary to remove the fiber bundle from the dryer shell before hydration in order to prevent the kinking and, often, cracking of the Nafion fibers that resulted when swelling occurred in the confines of the dryer shell.

Experiments were begun by filling the dryer shell with deionized water, flushing the flow cuvette and Nafion fiber bundle with the desired extractant solution, and measuring a reference spectrum. A sample solution was then connected to the dryer shell and a gravity flow of ca. 8 mL/min established. Spectral data were acquired while the extractant solution was recirculated at ca. 5 mL/min. The dryer assembly was typically stored between experiments with both the dryer shell and Nafion fibers filled with 1 $\underline{M}$ aqueous NaCl.

Results and Discussion

Nafion is the Dupont trade name for a copolymer of tetrafluoroethylene and perfluoro-3,6-dioxa-4-methyl-7-octenesulfonyl fluoride. Ionizable sulfonic acid groups at side chain termini impart cation exchange properties to this polymer (9). For the experimental setup employed in this work, the transfer of a cation (e.g., Cu^{2+}) from the sample solution to the extractant within the lumen of a hollow Nafion fiber may be represented

$$Cu^{2+}_{(sample)} \rightleftharpoons Cu^{2+}_{(Nafion)} \rightleftharpoons Cu^{2+}_{(extractant)} \qquad (1)$$
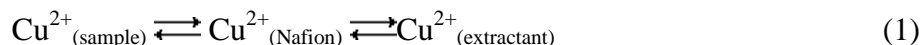
For such a system, both the distribution ratio ($C_{extractant} / C_{sample}$) and the rate of net transfer from sample to extractant will be greatest when the reverse transfer process (extractant to sample) is eliminated. This condition may be realized by including in the extractant solution a reagent that binds the cation to yield an anionic complex. Negatively charged species will not significantly permeate the Nafion membrane due to electrostatic repulsion by the side chain sulfonate groups, i.e., "Donnan exclusion" (10). EDTA is a commonly used chelating agent that satisfies this

criterion for a large number of metal ions, and it was chosen for use in the approach reported here.

Typical applications of EDTA require a basic medium to insure the predominant species is its completely deprotonated form, Y^{4-}, as this species is the most effective chelator. In this work, copper that permeates into the lumen of a Nafion fiber is thus essentially trapped there as the anionic complex CuY^{2-}:

$$Cu^{2+}_{(sample)} \rightleftharpoons Cu^{2+}_{(Nafion)} \rightleftharpoons Cu^{2+}_{(extractant)} \rightarrow CuY^{2-}_{(extractant)} \qquad (2)$$

The required basic medium is usually achieved via the complexing NH_3 / NH_4^+ buffer system in order to avoid precipitation of metal hydroxides. This system was found to be unsuitable for use in Nafion dryers, however, due to permeation and subsequent loss of both buffer components (11). A CO_3^{2-} / HCO_3^- buffer (pH ~ 10) was found to be a suitable alternative, as (a) both buffer components were effectively retained within the Nafion fibers and (b) precipitation of metal hydroxides was not observed at the employed concentration levels.

Figure 2 shows plots of absorbance versus time for extraction of 20 m$\underline{M}$ Cu^{2+} solutions using EDTA (upper) and NaCl (lower) extractants. The general forms of these curves are similar, exhibiting an initial lag time followed by a roughly linear increase in concentration. The greater slope observed for EDTA compared to the inert NaCl extractant is as expected per the discussion in the previous paragraph. Taking into account the molar absoprtivity maxima of CuY^{2-} and the copper(II) aqua complex (measured as approximately 90 and 40 $\underline{M}^{-1}cm^{-1}$ at ca. 740 and 800 nm, respectively), these plots indicate the use of EDTA increases the extraction rate by roughly 50%.

Complete removal of the target compound from the sample matrix is not practical in chemical sensing applications of membrane extraction, and the amount of analyte in the sample

is instead determined via measurement of the analyte extraction rate, $dC_{extractant} / dt$. Under conditions such as those employed in this work, the extraction rate is related to sample concentration, C_{sample}, via the equation

$$dC_{extractant} / dt = k \, C_{sample} \tag{3}$$

where k is the extraction rate constant, a constant dependent upon properties of the employed membrane, the analyte, and the extractant species (12). Figure 3 shows a calibration curve generated by plotting average extraction rate (measured as change in analyte concentration in the extractant per minute for two different dryers, $5 \leq N \leq 9$ for each concentration) versus sample copper(II) concentration. Quadratic regression yielded the best fit to the experimental data ($r^2 = 0.9989$), primarily a result of nonlinearity exhibited at low concentrations. This nonlinearity may be due to undersaturation of the Nafion phase at these concentrations, resulting in a less than maximal concentration gradient at the Nafion/extractant solution interface.

To demonstrate simultaneous extraction, an aqueous mixture of several transition metal ions was subjected to a recirculating extraction as described above. Figure 4 shows a plot of the relative change in metal ion concentration versus time. The relative change in concentration was plotted in order to account for differences in the employed metal ion sample concentrations. From these data, extraction rate constants of approximately 0.11, 0.20, 0.25, and 0.39 h^{-1} may be estimated for Cr^{3+}, Ni^{2+}, Co^{2+}, and Cu^{2+}, respectively.

In summary, commercially available Nafion gas dryers have been proven useful for the membrane extraction of metal ions from aqueous media. Use of an appropriate complexing extractant yields significantly greater extraction rates in these applications, and the simultaneous extraction of several metal ions has been demonstrated. Present efforts in the authors' lab are

directed towards coupling these hollow fiber assemblies with fiber optic spectroelectrochemical flow cells to yield sensors for environmental or industrial process monitoring applications.

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Figure Legends

Figure 1. Schematic diagram of the experimental setup showing flow paths for the sample (light arrows) and extractant (dark arrows) solutions.

Figure 2. Comparison of signal transients for extraction of 100 m$\underline{M}$ Cu(II) sample solutions using 1 $\underline{M}$ aqueous NaCl (lower) and 0.2 $\underline{M}$ EDTA (upper) extractants.

Figure 3. Dependence of average Cu(II) extraction rate on sample concentration using 0.2 $\underline{M}$ EDTA extractant. Error bars represent plus-or-minus the average standard deviation for the two dryers examined.

Figure 4. Comparison of rates for the simultaneous extraction of aqueous Co(II), Cr(III), Cu(II) and Ni(II) using 0.2 $\underline{M}$ EDTA extractant.

sample inlet

bubble trap

pump

gas
dryer

flow cuvette

sample
outlet