

Flow Injection Donnan Dialysis Preconcentration of Cations for Flame Atomic Absorption Spectrophotometry

John A. Koropchak* and Lori Allen

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901-4409

The sample loop of a conventional high-performance liquid chromatography injector is replaced by a coil of tubular cation-exchange tubing, enabling Donnan dialysis to be performed under static conditions while allowing enriched samples to be injected into a flame atomic absorption (FAA) spectrometer at optimum nebulizer flow rates. The receiver solution, containing a high percentage of dissolved solids, is only introduced into the flame for short times, which permits higher receiver concentrations to be used. Short tubing lengths provide higher enrichment, within the limits of sample dispersion, providing a compact dialysis cell. Decreasing the cation-exchange-membrane thickness reduces the dialysis time required for optimum enrichment. For the thin-wall tubing employed herein, 5-min dialyses provide 100-fold enrichment and limit-of-detection (LOD) improvement factors. The approach is demonstrated for the trace determination of lead in drinking water.

When an ion-exchange membrane separates a high ionic strength solution from a low ionic strength solution, ions of appropriate charge for the membrane are transported from the more concentrated solution to the more dilute solution. Since the membrane is impermeable to co-ions, ions from the dilute solution must diffuse to the more concentrated solution via a process termed Donnan dialysis in order to maintain electroneutrality (1). If the volume of the high ionic strength solution (receiver) is small compared to that of the low ionic strength solution (sample), enrichment of the dilute ions results (2). This process has been shown to provide essentially independent cation enrichment for samples of low to moderate ionic strength (2, 3) for both flat (4) and tubular (5) cation-exchange membranes.

Tubular membranes are particularly advantageous since they have high surface area to internal volume ratios and are readily interfaced to various detectors in on-line fashion. Modest success was initially reported for coupling tubular Donnan dialysis on-line with flame atomic absorption (FAA) demonstrated signal enhancement factors exceeding 20 with 5-min dialyses for a variety of cations (7). Enrichment factors were shown to increase with tubing length, lower receiver pHs, and temperature (7). Further, the analyte was concentrated into a normalized matrix, in which easily ionizable elements (EIE) could be included for ionization suppression (7). Finally, since co-ions are rejected with Donnan dialysis, interferences such as PO_4^{3-} on Ca^{2+} could be alleviated in an on-line fashion (7). In a later study, this approach was employed with indirectly coupled plasma atomic emission spectrometry (ICP-AES); high signal enhancement factors (>50) and alleviation of intra-alkali interferences were reported (8). A further characteristic of this approach was the minimal additional hardware requirements for conducting these experiments (i.e. the tubing, a peristaltic pump, and a stirrer) compared to that required for the normal FAA or ICP-AES experiments.

With either of these previous on-line experiments, receiver solution was continuously pumped through the tubing (bathed in sample solution) and into the nebulizer of the atomizer. Since typical receiver solutions contain 9-10% dissolved solids, this continuous introduction may periodically result in nebulizer, burner, or torch blockage (8). In addition, Donnan dialysis is optimized under static conditions while typical nebulizers are optimized at flow rates of 1-10 mL/min. Consequently, compromised flow rates were required for the on-line experiments (7, 8). In addition, enrichment factors increased with tubing length, which necessitated larger sample volumes and a bulky dialysis cell. Finally, typical turnaround analysis times were on the order of 20 min (7, 8).

Described herein is a flow injection approach to the Donnan dialysis FAA experiment, which is intended to overcome these less desirable characteristics. The coiled, tubular membrane is used as a direct replacement for the injection loop of a conventional sample injector. In this manner, the dialysis is conducted under static flow conditions, while the preconcentrated sample is injected at the optimum nebulizer flow rate and the receiver is introduced only during the injection. Characterization of relevant operating parameters and applications of the optimized experiment to drinking water analysis are described.

EXPERIMENTAL SECTION

The cation-exchange membrane employed for most of the Donnan dialysis experiments was 0.64 mm i.d. \times 0.89 mm o.d. tubing of various lengths made of Nafion 911 (Du Pont Polymer Products, Wilmington, DE). For some experiments, a thin-wall Nafion membrane (0.33 mm i.d. \times 0.48 mm o.d.) obtained from Perma-Pure Products (Farmingdale, NJ) was employed. The dimensions were for the dry tubing. In either case, the tubular membrane was affixed to a Rheodyne 7125 sample injector as depicted in Figure 1. The membranes were loosely coiled (to maximize solution contact) around a three-prong holder; the tubing ends were inserted into short lengths of 1.6 mm o.d. tetrafluoroethylene (TFE) tubing of appropriate inner diameter to fit snugly around the chosen membrane and were connected to the injector by using 1.6-mm Kel-F fingertight fittings from Upchurch Scientific (Oak Harbor, WA). When the compression type fittings are tightened, effective seals are made, preventing leakage at the operating pressures of the experiment, even with >5 mL/min of liquid flow.

Atomic absorption measurements were made by using a Varian AA-475 with the automatic gas control unit set at 13 L/min air and 1.7 L/min acetylene for Pb analyses and 13 L/min air and 1.4 L/min acetylene for Cu analyses. Analytical wavelengths were 217.0 nm for Pb and 324.7 nm for Cu.

To begin a dialysis experiment, the injector was placed in the LOAD mode and the tubular membrane was manually flushed and filled with the receiver solution (typically 0.5 M $\text{Sr}(\text{NO}_3)_2$ 1.20 mM $\text{Al}(\text{NO}_3)_3$ and 0.1 M HNO_3 in deionized, distilled water (DDW)) by using a syringe. The dialysis cell could then be lowered

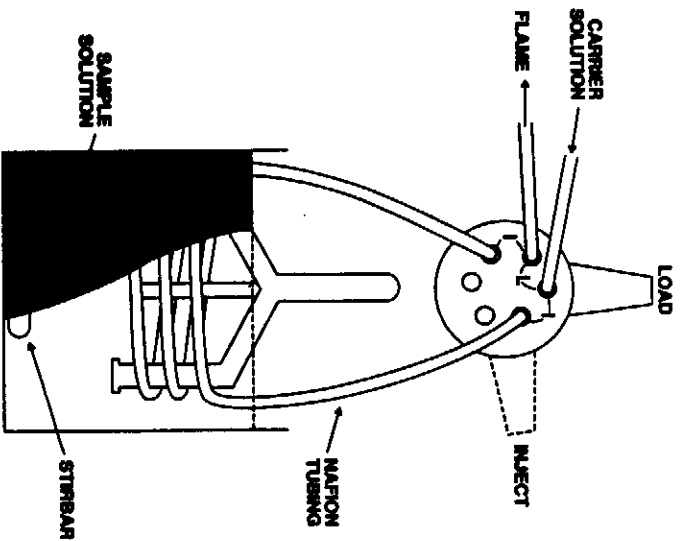


Figure 1. Diagram of the flow injection Dornan dialysis cell.

the appropriate time prior to injection. Carrier solutions were prepared with a pulse-damped Beckman 110B pump. During a dialysis, pure carrier solution was provided to the FAA nebulizer; 5.4 mL/min was typically employed since this was close to the optimum flow rate for direct aspiration. In the INJECT mode the carrier solution was directed through the tubular membrane, flushing the dialysate into the FAA and preparing the membrane for the next dialysis. In general, the carrier solution was pumped through the membrane until the signal returned to the base line. During this flushing, the outside of the membrane was rinsed with DDW.

All solutions were prepared from analytical reagent grade (or better) salts or acids dissolved in DDW or dilute HNO_3 . All glassware was scrupulously cleaned to include a final soak in dilute HNO_3 followed by a DDW rinse.

The criteria employed for the selection of cations comprising the receiver solution have been detailed earlier (7).

Limits of detection reported herein are based on $3 \times \sigma$ signal levels.

RESULTS AND DISCUSSION

The evaluation of the experiments described herein is typically reported in terms of enrichment factors (EFs), calculated as the ratio of the signal for the dialysis to the signal for the direct aspiration of the same sample. More precisely, an enrichment factor is defined as the ratio of the analyte concentration in the dialysate to that in the original sample (5). Since all of the EFs in this study were based on measurements of Cu^{2+} , for which signals were not affected by the receiver matrix, the more precise definition is maintained. For certain measurements where dispersion was shown to influence signals, the use of the EF term is less accurate. For consistency however, the EF term was employed throughout the study.

One of the early observations for the flow injection Dornan dialysis (FIDD) FAA experiment was that signals typically exhibited a bimodal peak shape with high time resolution, as shown in Figure 2. These different signals result from essentially two different analyte forms after dialysis: one corresponding to analyte in the receiver solution and a second corresponding to analyte that is affixed to the membrane. The solution-phase analyte is quickly flushed into the FAA upon injection, while ion-exchange reactions are required to remove the bound analyte fraction. If a low ionic strength receiver solution is employed (i.e. DDW), no Dornan dialysis can occur

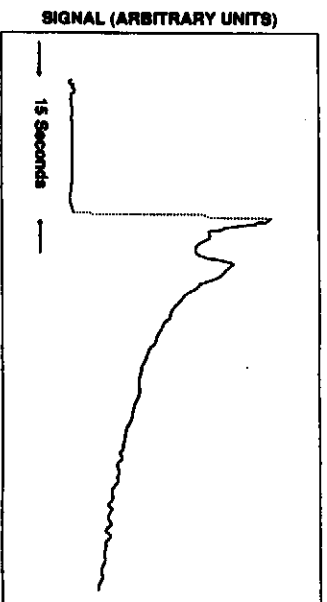


Figure 2. Raw data depicting bimodal signals for 5-min Dornan dialysis of 50 ng/mL Cu^{2+} using 3.25 m of thin-wall Nafion tubing; carrier, 5.4 mL/min 1.0 M HNO_3 ; receiver, 0.5 M $\text{Sr}(\text{NO}_3)_2$; 1.3 mM $\text{Al}(\text{NO}_3)_3$; 0.1 M HNO_3 ; 350-nL sample volume.

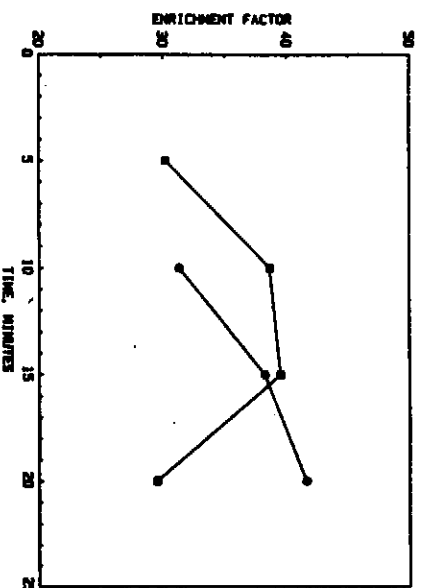


Figure 3. Enrichment factors versus dialysis time for first peak (\square) and second peak (\circ); dialyses of 250 ng/mL Cu^{2+} with 5 m of thick-wall Nafion tubing; other conditions as in Figure 2.

which is largely independent of the receiver solution, remains.

The magnitudes of both peak signals were dependent on the time for the dialysis, as shown in Figure 3. As indicated, maximum signals for the first peak were observed for relatively short dialysis times (515 min), while those for the second peak were initially lower and began to exceed signals for the first peak at times greater than 15 min. Since one goal of this work was to provide relatively short analysis times, signals for the first peak were employed in the remainder of these studies for the calculation of enrichment factors. For short dialysis times, the second peak typically appeared as a shoulder to the first peak.

The time for which the maximum signal is achieved for the first peak likely corresponds to the attainment of ion exchange or Dornan equilibrium for the system. The decline in signal for the first peak at later times corresponds to the movement of the system toward the different state of chemical equilibrium. These two states have previously been described for similar solution and cation-exchange membrane systems by Blaedel and Haupt (9). The times prior to the achievement of Dornan equilibrium involve primarily the Dornan dialysis process, which has been shown to provide enrichment that is largely matrix independent (2), an additional reason to emphasize the signals for the first peak. Signals for the latter process (second peak) would rely on competition between cations for available ion-exchange sites within the membrane.

Since the flow injection approach offered an alternative to the continuous introduction of receiver solution to the FAA, it was felt that more concentrated receiver solution could be tolerated, ideally providing higher mass transport rates and reduced analysis times. Table I indicates the effect of receiver composition on EF for 5-min dialyses of 250 ng/mL Cu^{2+}

Table I. Receiver Composition Effects on Enrichment Factors for Cu^{2+} .

receiver solution composition	enrichment factor
0.20 M $\text{Sr}(\text{NO}_3)_2$, 0.5 mM $\text{Al}(\text{NO}_3)_3$, 0.1 M HNO_3	18.7
0.36 M $\text{Sr}(\text{NO}_3)_2$, 0.9 mM $\text{Al}(\text{NO}_3)_3$, 0.1 M HNO_3	28.0
0.52 M $\text{Sr}(\text{NO}_3)_2$, 1.3 mM $\text{Al}(\text{NO}_3)_3$, 0.1 M HNO_3	31.8
0.68 M $\text{Sr}(\text{NO}_3)_2$, 1.7 mM $\text{Al}(\text{NO}_3)_3$, 0.1 M HNO_3	31.7
0.5 M $\text{Sr}(\text{NO}_3)_2$, 1.3 mM $\text{Al}(\text{NO}_3)_3$, 0.1 M HNO_3	28.1
0.5 M $\text{Sr}(\text{NO}_3)_2$, 1.3 mM $\text{Al}(\text{NO}_3)_3$, 0.2 M HNO_3	28.2
0.5 M $\text{Sr}(\text{NO}_3)_2$, 1.3 mM $\text{Al}(\text{NO}_3)_3$, 0.3 M HNO_3	29.2
0.5 M $\text{Sr}(\text{NO}_3)_2$, 1.3 mM $\text{Al}(\text{NO}_3)_3$, 0.4 M HNO_3	25.5

*Five-minute dialyses of 250 ng/mL Cu^{2+} from 400-mL samples using a 5-m coil of thick-wall tubing; carrier flow was 5.4 mL/min 0.1 M HNO_3 .

Table II. Carrier Stream and Receiver Effects on Enrichment Factors and Analysis Times*

carrier compn	receiver compn	enrichment factor	anal. time, min
0.2 M Sr^{2+} , 0.5 mM Al^{3+} , 0.1 M HNO_3	0.2 M Sr^{2+} , 0.5 mM Al^{3+} , 0.1 M HNO_3	38.7	>8
0.1 M HNO_3	0.2 M Sr^{2+} , 0.5 mM Al^{3+} , 0.1 M HNO_3	25.9	>8
1.0 M HNO_3	0.2 M Sr^{2+} , 0.5 mM Al^{3+} , 0.1 M HNO_3	22.5	8
1.0 M HNO_3	0.52 M Sr^{2+} , 1.3 mM Al^{3+} , 0.1 M HNO_3	46.7	<5

*Ten-minute dialysis of 250 ng/mL Cu^{2+} from 400-mL samples using a 5-m coil of thick-wall tubing; carrier flow rate was 5.4 mL/min.

the same as the aspiration rate for direct analyses. Varied in these experiments were the concentrations of $\text{Sr}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ (as multiples of our previous receiver—0.2 M $\text{Sr}(\text{NO}_3)_2$, 0.5 mM $\text{Al}(\text{NO}_3)_3$) and pH (as HNO_3 concentration). As shown in the table, increasing the receiver concentration about 2.6 times provided a 70% increase in signal while increases in receiver pH had little effect on the results for 5-min dialyses. Consequently, the receiver composition employed for the remainder of these studies was a 0.5 M $\text{Sr}(\text{NO}_3)_2$, 1.2 mM $\text{Al}(\text{NO}_3)_3$, 0.1 M HNO_3 solution. No problems of nebular or flame blockage were encountered with this concentrator receiver (~11% dissolved solids) during any subsequent studies.

Although the signals resulting from the second peaks described earlier were considered of lesser analytical utility than those corresponding to Donnan dialysis, these signals represented a limitation to the turnaround time for the use of a particular membrane cell. In order to prepare the membrane for the next analysis, prevent contamination of the next sample, and reestablish a base-line signal, this residual analyte must be efficiently removed from the membrane. Since this removal is primarily dependent on exchange reactions with cations in the carrier stream, a variety of carrier stream compositions were evaluated as indicated in Table II. The analysis times indicated correspond to the times from injection to the reestablishment of the original base-line signal. For the combination of the 1.0 M HNO_3 carrier and the 0.5 M $\text{Sr}(\text{NO}_3)_2$, 1.2 mM $\text{Al}(\text{NO}_3)_3$, 0.1 M HNO_3 receiver, the turnaround times were on the order of 2–3 min. Further, no analyte carryover was indicated by the absence of any signal for the dialysis of blank solutions following the dialysis of standards. This combination was therefore employed for the

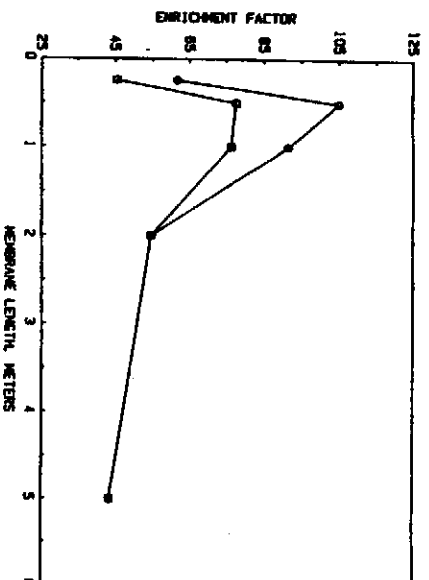


Figure 4. Enrichment factor versus Nafion tubing length for high-dead-volume (\circ) and low-dead-volume (\square) sample transfer, 10-min dialyses of 50 ng/mL Cu^{2+} using thick-wall Nafion tubing; other conditions as in Figure 2.

Enrichment factors obtained for Cu^{2+} as a function of tubing length for 10-min dialyses of 50 ng/mL Cu^{2+} are indicated in Figure 4. The lower curve is data obtained for our initial experiment for which the dead volume between the injector and FAA was 0.35 mL. As indicated, enrichment factors improved as the tubing length decreased down to 1 m. The reason for this increase lies with the fact that the sample to receiver volume ratio increases as the tubing length decreases. This contrasts with data for continuous, on-line dialysis (7, 8) for which long tubing lengths provided the highest signal enhancement. In those cases, the effective residence time of a particular segment of receiver solution was increased as the length increased. For tubing lengths 52 m, the dialysis cell is quite compact.

The trend of enhanced enrichment for shorter tubing lengths was not continued below 1 m for the data in the lower curve of Figure 4. Since the internal volume of this tubing is approximately 320 $\mu\text{L}/\text{m}$, it was felt that dispersion effects might be substantial with tubing lengths less than 1 m. The data for the upper curve were obtained after the dead volume between the injector and FAA had been reduced to 0.013 mL. With this reduced dispersion, the trend for increased enrichment continued to 0.5 m of tubing, indicating the importance of dead volume to these experiments. Also indicated are enrichment factors exceeding 100, obtained with a 10-min dialysis with 0.5-m tubing lengths.

Another factor that can affect Donnan dialysis is the actual sample volume employed, since this affects the sample to receiver volume ratio and the total amount of analyte available. Figure 5 shows the effect of sample volume on EF for two lengths of tubing. In either case, a slight decline in EF for sample volumes less than 500 mL was observed. For highest EFs, sample volumes exceeding this value should be employed. Of further importance, errors in sample volume measurement may affect signal measurement precision and accuracy. Such effects would be small on the basis of Figure 5, especially for sample volumes greater than or equal to 500 mL. To reduce sample handling and preparation requirements, 360-mL sample volumes were used for the remainder of this study.

A limiting factor to the achievement of equilibrium with a membrane system is typically the rate of mass transfer across the membrane. For any membrane type, this rate will be determined by the ionic strength gradient across the membrane, as well as the membrane thickness and other factors (9). As indicated in Figure 3, dialysis times between 10 and 15 min provide optimum enrichment for tubing with a 0.25-mm wall thickness (dry). When a thinner wall tubing (0.15

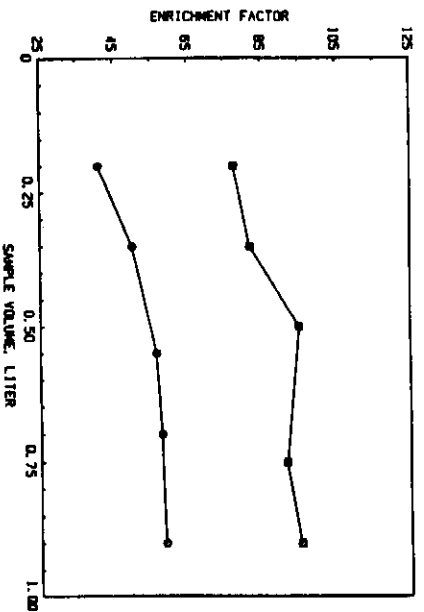


Figure 5. Enrichment factor versus sample volume for 1.0- (□) and 2.0-m (○) thick-wall Nalston tubing lengths; other conditions as in Figure 2.

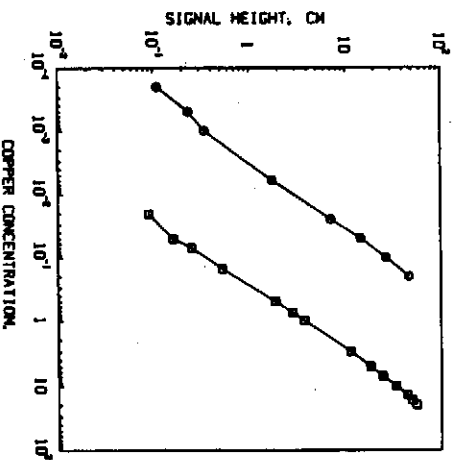


Figure 6. Calibration data for 10-min Donnan dialyses (○) and for direct aspiration (□); 1 m of thick-wall tubing; other conditions as in Figure 2.

to 5 min. All other characteristics of the experiment were essentially identical with those for the thicker membrane, except that 0.8 m of the thin-wall tubing provided the highest enrichment compared to 0.5 m for the thicker tubing. The fact that optimum enrichment was provided with a slightly longer tubing length can be attributed to the smaller internal volume of the thinner tubing ($\sim 100 \mu\text{l}/\text{m}$) and the dispersion effects described earlier.

From the conditions established thus far, calibration data for the Donnan dialysis experiment were determined. Figure 6 compares results for direct aspiration (□) with those for 10-min Donnan dialyses (○) of copper standards. As indicated, the dialysis results were linear, and the primary effect was to shift the calibration curve to a lower concentration range. In this case, a decrease by a factor of about 100 in LOD for Cu^{2+} was demonstrated (down to 0.2 $\mu\text{g}/\text{mL}$). Similar data were typically obtained for other cations. Also indicated in Figure 6 is the independence of FIDD enrichment on sample concentration, as evidenced by the parallel nature of the two calibration curves. This allows calibration data for direct aspiration measurements to be used to calibrate FIDD measurements, with periodic determination of the enrichment factor. Precision for FIDD-FAA was typically 3–5% RSD compared to 1% RSD provided by direct aspiration.

Using a 1-m length of the thick-wall membrane and a dialysis time of 10 min, we studied the effect of sample ionic strength, using NaNO_3 or $\text{Pb}(\text{NO}_3)_2$, as ionic strength adjusters. As reported previously by Cox et al. (2) for flat membranes, enrichment factors for FIDD were found to be constant up

composition for mixtures of cations. For higher ionic strength solutions, standard addition procedures are recommended (2).

The calculated LOD for Pb^{2+} with the use of FIDD-FAA was about 1 ng/mL . This LOD was of particular interest since the EPA limit on Pb in drinking water was recently lowered to 5 ng/mL . The LOD for direct aspiration FAA was typically 90 ng/mL . To test the applicability of the FIDD-FAA experiment to drinking water analysis, tap water samples were spiked at the 5 ng/mL level and acidified to pH ~ 3.5 . The average recovery of Pb^{2+} was $103 \pm 16\%$, indicating the usefulness of this approach to drinking water analysis.

CONCLUSIONS

Flow injection Donnan dialysis has been shown to be a simple, rapid means for obtaining large (>100) improvements in LOD for flame atomic absorption analysis. The degree of LOD enhancement can be controlled for a particular application through adjustment of the membrane tubing length, dialysis time, sample volume, carrier flow rate, and membrane thickness. Only about 8 min is required (dialysis time plus flush) to obtain near-optimum enrichment factors (~ 100) with the thin-wall membrane. By the use of multiple dialysis cells, the effective analysis time could be reduced to the time required for signal generation and cell flushing, thus providing high sample throughput (20–30 per hour). Based on the simple hardware requirements, the FIDD approach readily lends itself to automation, unlike more traditional enrichment techniques, such as precipitation or solvent extraction (10).

The Donnan dialysis technique also has advantages over ion-exchange preconcentration since enrichment factors have been shown to be comparable for a wide range of cations (2, 4, 7), while those for flow injection ion-exchange procedures have been shown to vary substantially due to differences in cation selectivity coefficients (11). Like Donnan dialysis, ion-exchange preconcentration methods are effectively subject to sample ionic strength limitations (11).

Registry No. Cu, 7440-50-8; Pb, 7439-92-1; water, 7732-18-5.

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