

# Flow Injection Donnan Dialysis Preconcentration of Trace Metal Cations for Inductively Coupled Plasma Atomic Emission Spectrometry

Narasimhan Kasthurikrishnan and John A. Koropchak\*

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

The on-line combination of flow injection Donnan dialysis (FIDD) with inductively coupled plasma atomic emission spectrometry (ICP-AES) is shown to provide enrichment factors of over 200 for cations with an 8-min dialysis time, allowing nanogram per liter level detection limits. These results are obtained for receiver solutions consisting either of  $\text{Sr}^{2+}$  or  $\text{Mg}^{2+}$ , providing complementary free spectral ranges and the applicability of FIDD-ICP-AES to trace metal cation analysis for both transition and rare earth elements. The enrichment factors obtained are linear over a wide range of concentrations and limits of detection (LODs) approximately 100 times lower than for direct aspiration are obtained using modest experimental conditions. Additional improvements in enrichment factors are obtained with increases in dialysis time and/or final sample solution temperature. A signal enhancement factor of 650 with an LOD of 11 ng/L for monovalent silver cation is demonstrated using a 30-min dialysis, a 42 °C final solution temperature, and longer lengths of cation-exchange tubing.

Donnan dialysis is a process which can preconcentrate a given ionic species, either cation or anion, into a concentrated electrolyte solution by establishing an ionic strength gradient across an ion-exchange membrane.<sup>1</sup> The electrolyte solution of higher ionic strength, known as the receiver solution, is maintained at a lower volume than the sample solution containing the ion of interest.<sup>2</sup> For cation Donnan dialysis, cation-exchange membranes are used. These membranes are highly permselective to cations; that is, in principle anions cannot diffuse through the membrane. Under the influence of the ionic strength gradient, cations from the receiver diffuse into the sample solution. Since anions are impermeable to the membrane, cations from the sample solution must diffuse through the membrane into the receiver in order to maintain electroneutrality. The latter process is the phenomenon termed Donnan dialysis. As the volume difference between the receiver and sample solution is large and the sample ions are efficiently transported to the receiver, preconcentration within the receiver results. Of the two types of cation-exchange membranes that are commonly used, tubular cation-exchange membranes have shown to provide higher enrichment than flat cation exchange membranes due to their decreased receiver volume to surface area ratio.<sup>3</sup> On-line studies of tubular cation-exchange membranes of various thickness have determined better preconcentration factors per unit time for the thin-wall membranes.<sup>4</sup> This is due to the increased transport rate across the membrane, as Donnan dialysis is constrained by the processes that occur in the bulk of the membrane.

With Donnan dialysis, one can reject counterion interferences,<sup>5</sup> normalize matrices,<sup>3,5</sup> and achieve sample matrix independent enrichment over a wide range of conditions.<sup>6</sup>

The compatibility of Donnan dialysis with voltammetry,<sup>3</sup> high-pressure ion-exchange chromatography,<sup>7</sup> pulse polarography,<sup>2</sup> and flame atomic absorption spectrometry (FAAS) has been described.<sup>4</sup> With FAAS on-line tubular experiments, a compromise between optimum Donnan dialysis flow rate (static) and the high flow rate (3–6 mL/min) of FAAS had to be achieved. ICP-AES measurements provide considerably lower LODs and require much lower flow rates as compared to FAAS. Replacing FAAS with ICP-AES should result in better limits of detection (LODs) with a Donnan dialysis process. The approach to combine Donnan dialysis in a continuous-flow mode with ICP-AES has been demonstrated using conventional- and low-flow nebulizer systems.<sup>8</sup> Previously, FAAS or ICP-AES experiments performed with continuous aspiration of the receiver solution containing 3–10% dissolved solids resulted in nebulizer, burner, or torch blockage.<sup>9</sup> On-line preconcentration studies with the use of a tubular ion-exchange membrane and flow injection technique (flow injection Donnan dialysis or FIDD) have provided high enrichment factors and about 100 times lower LODs than for direct aspiration with FAAS within approximately 5 min.<sup>4</sup> With flow injection techniques, the sample that is preconcentrated in the receiver solution is fed to the nebulizer or torch for only short periods of time, alleviating blockage problems. Thus, the extension of FIDD to ICP emission techniques appears promising.

In this work we are demonstrating the applicability of flow injection Donnan dialysis (FIDD) with ICP-AES as the detector for a wide variety of cations. Since the selection of receiver solution plays an important role in FIDD, the ideal receiver solution for ICP-AES is discussed. Particular attention is paid to the various interferences involved in a typical ICP-AES experiment, such as spectral and matrix interferences that affect the signal enhancement. The difference between signal enhancement factor (SEF) and enrichment factor (EF) is elucidated, and the importance of variables such as dialysis time and temperature on signal enhancement is characterized. Discussion of results describing the concentration independence of SEF and dispersion effects on signal enhancements are included.

## EXPERIMENTAL SECTION

Donnan dialysis studies were performed using 0.33-mm-i.d. x 0.51-mm-o.d thin wall Nafion 311 cation-exchange tubing (Perma Pure Products, Toms River, NJ). These dimensions are for the dry tubing. In order to maximize contact with the sample solution,

(1) Wallace, R. M. *Ind. Eng. Chem., Process Design Dev.* 1967, 6, 423.  
(2) Cox, J. A.; Gray, T.; Yoon, K. S.; Twardowski, Z. *Analyst (London)* 1984, 109, 1603.  
(3) Cox, J. A.; Twardowski, Z. *Anal. Chem.* 1980, 52, 1503.  
(4) Koropchak, J. A.; Allen, L. *Anal. Chem.* 1989, 61, 1410.

(5) Koropchak, J. A.; Dabek-Zlotorzynska, E. *Appl. Spectrosc.* 1987, 41, 1261.  
(6) Cox, J. A.; Twardowski, Z. *Anal. Chem. Acta* 1980, 119, 39.  
(7) DiNunzio, J. E.; Jubara, M. *Anal. Chem.* 1983, 55, 1013.  
(8) Koropchak, J. A.; Dabek-Zlotorzynska, E. *Anal. Chem.* 1988, 60, 328.

the tubing was loosely coiled around a three-prong holder. The dialysis experimental set up used was very similar to the one described previously.<sup>4</sup> The cation-exchange membranes were stored in deionized distilled water (DDW) at all times, except when dialyzing. Unless stated otherwise, all dialysis experiments were carried out for 8 min at room temperature (23 °C). No extensive pretreatment of the membrane was necessary before the start of a dialysis experiment other than flushing the membrane with carrier to achieve base line signal followed by injection of 5-mL receiver solution. Once the base-line signal was obtained, the injection loop (i.e. the tubular ion-exchange membrane) was washed externally with DDW, filled with receiver solution, removed from DDW, and inserted into the sample solution. Stirring of the sample solution and timing of the dialysis began. Stirring here was achieved magnetically using a hot plate stirrer. At the end of the predetermined time of dialysis, the sample was injected, the signal measured, the flow to the ICP disconnected, and the membrane flushed with higher flow rates of the carrier after replacing the membrane in DDW to ensure a quick return of the signal to the base line. Though the optimum operating sample volume is 500 mL, or more, for Donnan dialysis,<sup>4</sup> the sample volume was fixed at 350 mL for these studies for convenient sample handling purposes. The length of the cation-exchange membrane tubing used in these studies was 0.95 m for most studies, and the nitric acid carrier solution concentration was 1 M. To demonstrate higher enrichment factors for some studies, a 500-mL sample solution volume and a 2-m-length tubing was used. The flow rate of the carrier stream for the flow injected dialysates was 1.5 mL/min for all the elements except for Pb and Tl where the flow rate was 1.3 mL/min. All solutions were prepared from analytical reagent-grade (or better) salts or acids dissolved in DDW or dilute nitric acid. All glassware was scrupulously cleaned by soaking in nitric acid followed by storage with DDW until usage. Limits of detection reported here are based on 3 × standard deviation of the blank.

The spectrometric measurement system consisted of a Perkin-Elmer (Norwalk, CT) 5500 ICP modified with a dynamic background correction facility. The spectrometer was purged with nitrogen gas for studies with short wavelengths (below 200 nm). The monochromator for this system is a Czerny-Turner design with a 408-mm focal length and a grating having 2880 lines/mm and blazed at 210 nm. A Wavetek (San Diego, CA) Sweep/Trigger VCG Model 1114 provided the modulation of frequency and amplitude for a quartz refraction plate located prior to the exit slit of the spectrometer. A Keithley (Cleveland, OH) Model 485 picoammeter provided the signal amplification, and a Stanford Research Systems (Palo Alto, CA) SR 510 lock-in-amplifier provided the final background corrected signals. The output from the lock-in-amplifier was connected to a Fisher Recordall Series 5000 linear chart recorder for almost all the studies, except for cases where the output from the picoammeter was input to a Multitech 700 PC via a Metrabyte (Taunton, MA) DAS-6 interface. The computer used for signal readout in this case was equipped with Asystant Plus Software (MacMillan, New York). The computer data acquisition was used primarily for the collection and storage of wide wavelength range spectral scans.

A cross-flow nebulizer was used for all studies. Direct aspiration linear calibration curves for various elements were obtained by feeding the sample solution into the cross flow ICP nebulizer with a Gilson (Middleton, WI) Minipuls 2 peristaltic pump. In most cases, plasma operating conditions were 14 L/min coolant, 1 L/min auxiliary, and 1.1 KW of power. Measurements were made in the normal analytical zone (NAZ) at 15-mm observation height above the load coil, except in the case of Tl<sup>+</sup> where the height was 18 mm. Dispersion values are reported as the ratio of the true analyte concentration to the observed concentration of the analyte at the detector. The observed concentration at the detector was determined by injecting the same analyte concentration through the membrane. Matrix effects are expressed as the percent reduction in signal intensity of the analyte to the true signal intensity of the analyte in the absence of a matrix.

## RESULTS AND DISCUSSION

Throughout this report we will be describing Donnan dialysis in terms of signal-enhancement factors (SEFs) as

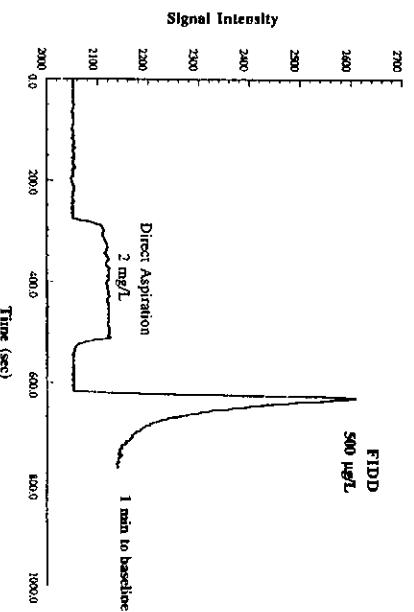


Figure 1. Typical raw data for Donnan dialysis (500 µg/L) and direct aspiration (2 mg/L) of Pb<sup>2+</sup> with a 3-min dialysis and room temperature sample solution using a Mg<sup>2+</sup> receiver.

opposed to enrichment factor (EFs). The EF is the ratio of the concentration of the ionic species of interest after dialysis in the receiver to that of its initial concentration in the sample and thus describes the exact level of preconcentration. The SEF is the ratio of the peak signal for on-line Donnan dialysis to the steady-state signal resulting from direct aspiration at the optimized flow rate of that particular instrument (an ICP-AES in this case). In an ideal case, the SEF observed should be the same as the EF. With an ICP-AES and FIDD combination, matrix effects, dispersion, and spectral interferences may cause the SEF to differ from the EF. Matrix effects occur when the analyte of interest is present in a highly concentrated matrix. More often than not, the analyte signal intensity is reduced due to the matrix, and thus the SEF obtained is lower than the EF. But, it is possible that the analyte signal intensity may be enhanced for certain elements under different conditions of operation. In such cases, the SEF obtained would be higher than the EF. Dispersion effects are associated with flow injection techniques and generally reduce the analyte signal intensity, resulting in a lower SEF. Spectral interferences are of various types, and like matrix effects can either reduce or enhance analyte signal intensity, resulting in lower or higher SEFs. Thus the deviation of SEF from EF may be positive or negative due to the above mentioned factors.

Figure 1 shows typical raw data for the Donnan dialysis process signal where a 0.5 mg/L Pb<sup>2+</sup> sample solution was dialyzed for 3 min. At the end of the 3 min of preconcentration, the sample was injected and the signal measured. Figure 1 shows the peak sharpness and shape of the Donnan dialysis signal. Data acquisition was terminated with 1 min remaining for the signal to reach base line. Since direct aspiration of a 2 mg/L Pb<sup>2+</sup> solution provided a signal height (background subtracted) of about 70 units on the Y axis, direct aspiration of a 500 µg/L solution would give a signal height of 17.5 units, assuming a linear calibration curve. The standard deviations obtained for blank solutions by both direct aspiration and Donnan dialysis were observed to be the same. Thus, if one were to calculate an SEF for Pb<sup>2+</sup> in this case, it would be the ratio of the respective signal heights by Donnan dialysis and direct aspiration. In this case, the calculated SEF would be 570/17.5 or 32.

An important step in performing a FIDD-ICP technique is to select the receiver which would yield the best SEF and be compatible with the ICP. Unlike studies of FIDD-FAAS, for measurements using an ICP various types of spectral interferences, which might limit the selection of receiver electrolyte, need to be considered. The problem created by line overlap interference may lead to positive errors in SEF determinations and degraded signal-to-noise ratios, especially

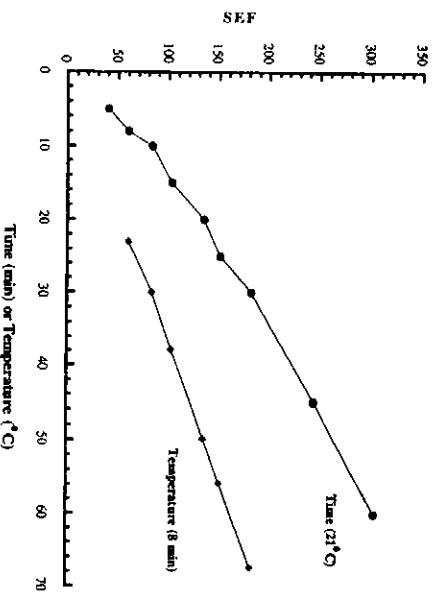


Figure 4. Signal enhancement factors as a function of dialysis time for sample solutions fixed at 21 °C (●) and as a function of sample solution temperature with an 8-min dialysis time (◆). The magnesium receiver was used for all experiments.

Of the parameters that affect the Donnan dialysis preconcentration process, the dialysis time, and temperature of the sample solution are particularly important. We investigated the effect of these variables using a fixed membrane tubing length, stirring rate, and sample volume. The effects of sample solution temperature and dialysis time for divalent cadmium with a magnesium receiver are shown in Figure 4. For the solution temperature studies, the dialysis time was fixed at 8 min, and for the dialysis time study, the sample solution was maintained at room temperature (23 °C). For higher temperature studies, a temperature gradient of the sample solution from room temperature to the final desired temperature was achieved within the fixed 8-min dialysis by varying the rate of increase. SEFs were found to increase from 60 to 180 as the final temperature of the sample solution was varied from room temperature to 65 °C. The increase in SEF with increased temperature results from the increased transfer rate across the membrane. An earlier study reported an increase of 4% in the transfer rate across the membrane per degree for  $\text{Li}^+$  using a KCl receiver and a temperature-controlled bath.<sup>12</sup> Our studies were performed by providing a temperature gradient rather than constant maintenance of temperature. In addition to  $\text{Cd}^{2+}$ , our studies performed with other elements ( $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ) confirmed the trend of increased SEFs with increased temperatures. Figure 4 also shows SEFs increasing from 40 to over 300 as the dialysis time increased from 5 to 60 min. Using the combination of high sample temperatures and longer dialysis times, exceedingly high SEFs can be obtained. Increases in temperature and time provide increases in SEF that are additive of the two effects. For example an 8-min dialysis of  $\text{Cd}^{2+}$  with the sample solution at 21 °C provided an SEF of 64 (reference SEF), and increasing the dialysis time to 15 min at 21 °C gave an SEF of 100 (an increase of 36 in SEF). An increase in temperature from 21 to 36 °C with 8-min dialysis provided a SEF of 98 with an increase of 2.67 °C in SEF (35 increase in SEF). When an experiment was performed with a dialysis time to 15 min and a sample solution temperature of 34 °C, an SEF of 134 was obtained (an increase of 70 in SEF). The net increase in SEF (70) is thus found to be approximately the sum of the cumulative increases in SEF (36 + 35) that would be obtained if the experiments for increasing dialysis time and temperature are performed separately. This additive effect helps one to predict the SEF that would be obtained when both time and temperature are varied. Of the other variables, previous workers have reported that increasing the rate of stirring

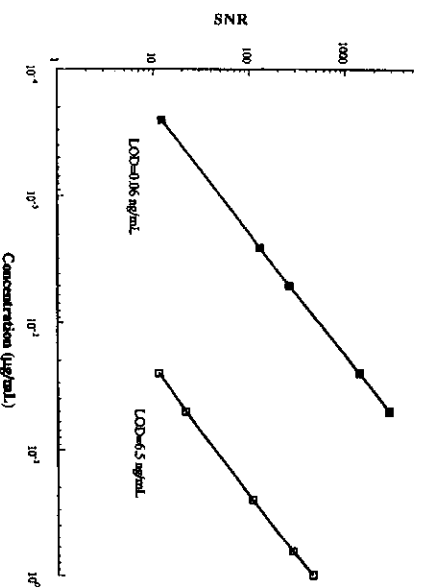


Figure 5. A log-log plot of signal to noise ratio against concentration for  $\text{Ag}^+$  with FIDD-ICP-AES (■) and with direct aspiration (□). The magnesium receiver, an 8-min dialysis, and room temperature solutions were employed for FIDD-ICP-AES.

Table II. Comparison of Detection Limits<sup>a</sup>

element	wavelength (nm)	limit of detection (µg/L)		SEF
		direct aspiration	Donnan dialysis	
Ag(I)	328.06	6.5	0.06	120
Cd(II)	214.43	6.42	0.10	64
Cr(III)	205.55	19.00	0.5	38
Ca(II)	324.75	4.45	0.04	113
Fe(II)	238.20	8.2	0.13	70
Pb(II)	221.60	22.9	0.3	70
Ph(II)	220.35	62	0.8	85
Tl(I)	190.86	162	1.82	108
Zn(II)	213.80	4.5	0.06	96
La(III)	333.75	13	0.28	45
Nd(III)	401.23	42	0.84	50

<sup>a</sup> The SEFs obtained here are with 8-min dialysis at room temperature (21–23 °C) using strontium receiver for copper and magnesium receiver for all other elements. SEF, signal enhancement factor. Plasma operating conditions are mentioned in the Experimental Section. The valences of the cations are given in parentheses.

from 4 to 7 Hz has doubled the transport rate, resulting in increased SEFs.<sup>12</sup>

Typical log-log plots of SNR versus concentration obtained using either Donnan dialysis or direct aspiration for  $\text{Ag}^+$  are shown in Figure 5 with their respective detection limits. The plot shows the high linearity of response obtained after Donnan dialysis of a wide range of analyte concentrations, confirming the concentration independence of SEF. The significant difference in the LODs for direct aspiration (6.5 µg/L) and Donnan dialysis (60 ng/L) for silver is a representation of the preconcentrating efficiency of Donnan dialysis process for that element. These results were obtained for a moderately short dialysis time (8 min) and low sample solution temperature (23 °C).

The applicability of Donnan dialysis to a wide variety of cations is evident from Table II, which lists the various elements studied, the wavelength chosen, both Donnan dialysis and direct aspiration LODs, and their respective signal enhancement factors. For the determination of this data, a relatively short dialysis time, low sample temperature (23 °C), and 350-mL sample volume were chosen as compromise conditions of convenience. By using higher sample temperatures or longer dialysis times, lower LODs and higher SEFs can be obtained. It is clear that one can detect concentrations as low as 40 ng/L with Donnan dialysis for  $\text{Cu}^{2+}$  and nanogram per liter levels of the other elements for these compromise conditions. Hence, the combination of FIDD and ICP-AES provides nanogram per liter detection limits with very short

Table I. Receiver Effect\*

Receiver	SEF		
	Cu	Pb	Tl
0.2 M magnesium sulfate,		85	84
0.5 mM aluminum nitrate,			
0.1 M nitric acid			
0.5 M strontium nitrate,	75	80	72
1.2 mM aluminum nitrate,			
0.1 M nitric acid			
0.25 M cesium nitrate,	65	80	71
0.25 M cesium nitrate,			
1.2 mM aluminum nitrate,			
0.1 M nitric acid			
0.25 M strontium nitrate,	65	81	76
0.25 M rubidium nitrate,			
1.2 mM aluminum nitrate,			
0.1 M nitric acid			

\* The wavelengths for the elements are the same as given in Table II. SEF signal enhancement factor. Flow rates: 1.3 ml/min for Pb and Tl, 1.5 ml/min for Cu. The room temperature was 20 °C.

if the receiver is the contributing source. This spectral problem caused by concomitant line overlap may be eliminated simply by choosing an alternate wavelength where there is no overlap from the interferent. But the detection limits for the alternate analyte line wavelength may be worse and some compromise may be required. The important criteria involved in selecting a receiver electrolyte are the valencies of the receiver cations and their affinities for exchange sites on the membrane. Previous studies have shown that a 0.2 M  $Mg^{2+}$ -0.5 mM  $Al^{3+}$  combination at pH 1 yields similar EFs for monovalent as well as divalent sample cations.<sup>2</sup> The  $Al^{3+}$  cation present in the receiver solution has strong affinity for negative exchange sulfonate sites on the membrane, thereby allowing lower selectivity analyte ions to diffuse efficiently.<sup>9</sup> This is because volume diffusion (movement of analyte ions across solvent filled channels of the membrane) instead of chemical kinetics will limit the rate of transport in such a case.<sup>10</sup> For the selection of counterions to the receiver cations, sulfate anions are preferred as they are less Donnan permeable than chlorides and nitrate.<sup>11</sup> Our studies with various receivers resulted in similar SEFs as shown in Table I. Studies were performed with three different elements using four different receiver combinations. All the elements behaved similarly, except for slightly higher SEFs with the magnesium receiver. The results obtained in Table I allow the flexibility of choosing an alternate receiver electrolyte for the pre-concentration step in the case of a line overlap spectral problem. Thus, in case of a spectral line overlap interference from the receiver electrolyte, one can switch to an alternate receiver electrolyte without sacrificing SEFs. This is important, as SEFs are a direct reflection of the preconcentrating efficiency of the Donnan dialysis process. Secondly, no compromise in LODs is required, as there is no need to choose an alternate wavelength of the analyte.

Figures 2 and 3 depict the spectral scans obtained during the continuous input of primarily magnesium and strontium receiver, respectively. Clearly, the strontium receiver is preferable for wavelengths ranging from 248 to 330 nm, whereas the magnesium receiver is more suitable for the wavelength range of 218–275 nm. Other than the prominent clean spectral regions of the receivers, a closer look at the two spectra reveals their complementary nature. The high amount of dissolved solids in the receiver is shown by the intense

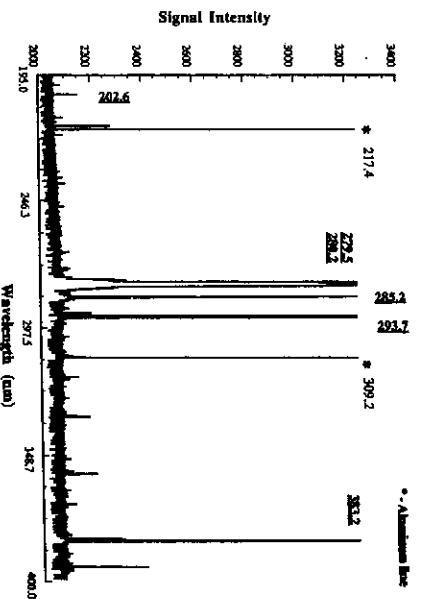


Figure 2. Spectrum obtained during continuous aspiration of the  $Mg^{2+}$  receiver (0.2 M magnesium sulfate, 0.5 mM aluminum nitrate, 0.5 M aluminum sulfate, and 0.1 M nitric acid). Asterisk-marked numbers show prominent aluminum lines, and the underlined numbers in bold print stand for magnesium lines.

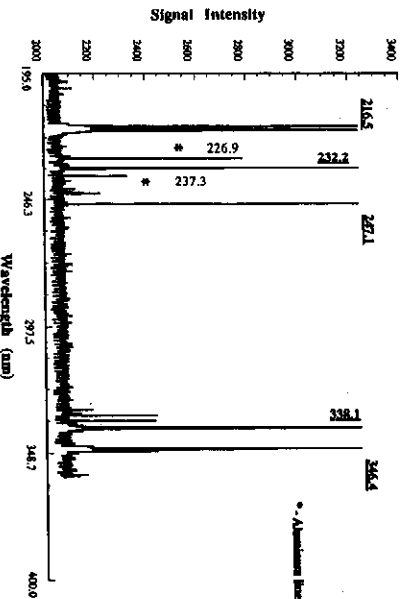


Figure 3. Strontium receiver spectrum obtained with continuous aspiration of the  $Sr^{2+}$  receiver (0.5 M strontium nitrate, 1.2 mM aluminum nitrate, and 0.1 M nitric acid). Asterisk-marked numbers show prominent aluminum lines, and the underlined numbers in bold print stand for strontium lines.

peaks for both magnesium and strontium. Thus, a possibility of wing overlap spectral interference exists, and for the same reason it would be unwise to choose the magnesium receiver for an element of wavelength 278 nm or strontium receiver for an element of wavelength 215 nm. An example of such a case would be divalent cadmium at 214.45 nm where one is restricted to the use of the magnesium receiver. Since aluminum is present in very low concentrations within the receiver, there are only a few intense aluminum lines in the spectra. Though the wavelength scans shown here provide the necessary information about the choice of receiver, a confirmatory study of the selected receiver should be done at the wavelength desired by actual injection through the membrane at the highest sensitivity level possible. This eliminates interference from any weak lines that are not visible in the spectra obtained. For example,  $Cu^{2+}$  at 324.7-nm wavelength suffered from spectral line overlap interference from the magnesium receiver, whereas there was no interference in the case of strontium receiver. Once the extent of interference, if any, is known, the analyst has the choice of either avoiding the interfering spectral region or operating at such high concentration levels of the analyte so as to render the contribution from the interferent insignificant. In our studies with a wide range of elements, we used the magnesium receiver for all elements except  $Cu^{2+}$ , where a strontium-based receiver was used due to line overlap spectral interference from magnesium.

(9) DiNunzio, J. E.; Wilson, R. L.; Gatchell, F. P. *Talanta* 1983, 30, 57.

(10) Cox, J. A.; Twardowski, Z. *Anal. Lett.* 1980, 13 (A 14), 1283.

(11) Cox, J. A.; Galek, R.; Litwinski, G. R.; Carnahan, J. W.; Trochimczuk, W. *Anal. Chem.* 1982, 54, 1153.

Table III. Comparison of SEF and EF<sup>a</sup>

element	SEF	dispersion	matrix effects (%)	EF
Cd(II)	64	2.0	24	159
Cr(III)	38	2.0	20	93
Cu(II)	113	2.0	9	230
Ni(II)	70	2.0	18	167
Tl(II)	108	1.8	18	234
Zn(II)	96	2.0	8	209

<sup>a</sup> The wavelengths and plasma operating conditions for the elements were the same as given in Table II. The comparison between SEF and EF is made for an 8-min dialysis time.

dialysis times at room temperature. Of the transition elements, Cr<sup>3+</sup> is known to form kinetically inert complexes, and the replacement of water molecules that are coordinated to Cr<sup>3+</sup> by other ligands is a slow process at room temperature. The Cr<sup>3+</sup> complexes persist in solution even under thermodynamically unstable conditions, making chromium substitution inert. One hypothesis is that the slow kinetics of ligand exchange is the cause for the lower SEF of trivalent chromium ion. In addition to the trivalent chromium from transition elements, the table also includes SEF data for a few trivalent ions from the lanthanide series. In these cases, the SEFs are also lower than those for mono- and divalent transition elements, but are slightly higher than for Cr<sup>3+</sup>. Although the slow kinetics of ligand exchange may limit the SEF in case of Cr<sup>3+</sup>, the additional SEF data for trivalent lanthanides indicates a possibility of SEFs being lower with trivalent cation Donnan dialysis in general. In such a case, the difference in SEFs for the mono- and divalent transition elements compared with trivalent cations could be explained. The difference in SEFs between Cr<sup>3+</sup> and lanthanide trivalent cations could be due to the added effect of slow kinetics of ligand exchange with Cr<sup>3+</sup>. Preconcentration of trivalent rare earth elements by Donnan dialysis has been described, and lower enrichment factors were reported, compared to divalent cations.<sup>9</sup> Cox and DiNunzio observed that trivalently charged cations would be more susceptible to interference effects from multicharged cations in the sample compared to divalent cation.<sup>12</sup> We performed preliminary studies with a divalent (Pb<sup>2+</sup>) and a trivalent (Cr<sup>3+</sup>) sample cation by adding increasing concentrations of a trivalent cation (Nd<sup>3+</sup>) to serve the purpose of an interferent. The results obtained by us indicate no difference in behavior among the di- and trivalent cations in the presence of an interferent. An interference was observed in both cases only when the typical ionic strength limit of Donnan dialysis (0.01 M) was reached. Further investigation into the behavior of trivalent cations is presently underway.

Based on our definition of SEF, the EF should be higher with FIDD-ICP-AES as measurements with ICP-AES suffer from matrix effects considering that the concentration of Mg<sup>2+</sup> in the receiver is 24 g/L. Moreover, with any flow injection technique, band broadening (dispersion) is a common occurrence. Dispersion can occur both by convection and diffusion. With narrow tubing sizes, diffusion perpendicular to the flow direction (radial diffusion) might occur. In such a case, the signals obtained would be Gaussian-shaped due to the combined effect of convection and radial diffusion. The signal shapes that we obtain indicate that convection was the main dispersion phenomenon with FIDD under the operating conditions described. Dispersion is governed by the tubing length, flow rate, and sample volume. Increased dialyzed sample volumes will decrease dispersion, whereas larger transport tube lengths will result in an increase. Previously with on-line continuous analysis, SEFs were reported to be higher with longer lengths of tubing.<sup>5,8</sup> With FIDD-FAAS, however, EFs were reported to show an optimum between 0.5 and 1 m for the thick-wall membranes and then reduce further with increasing lengths.<sup>4</sup> This is because sample to receiver volume ratio decreases with increasing lengths of the tubing. The above trend was not continued below 0.5 m due to substantial dispersion effects that occurred with reduced receiver sample volumes. Thus in FIDD, a compromise between membrane length and receiver sample volume is desired. As our studies involved thinner membranes, the optimum tubing length should shift from that of thicker membranes to longer membrane lengths. This is explained by the fact that it would take longer lengths of thinner membranes compared to thicker for a fixed receiver

sample volume which is crucial due to its dispersion effects. Our studies found the optimum length to be around 2 m for the type of membrane that we used. Another factor of significance with FIDD that affects the SEF is the extra-injector flow volume. The effect of low and high volumes on SEFs have been studied.<sup>4</sup> By minimizing this volume, dispersion effects are lower and higher SEFs can be attained.

Table III lists the matrix effects and dispersion levels determined for various elements, showing that the actual EFs are higher than the SEFs that we are reporting throughout. Most ICP-AES instruments operated under recommended conditions in the presence of a high dissolved solids matrix cause a depression in signal. Matrix effect studies previously done show that neither the nebulizer nor the changes in test solution uptake rate are responsible for this depression.<sup>13</sup> Most studies that we performed were under conditions typically optimum for multielement analysis, although measurements were made in a single element mode. Signal depressions of about 18–25% for Ni<sup>2+</sup>, Cd<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>2+</sup>, Pb<sup>2+</sup>, and Tl<sup>+</sup> were observed with the magnesium receiver compared to measurements using a dilute HNO<sub>3</sub> sample matrix. For Cu<sup>2+</sup>, there was less than 10% depression with the strontium receiver. Zn<sup>2+</sup> at the chosen wavelength showed an 8% depression with the magnesium receiver. The studies shown here tend to agree with those reported by Thompson.<sup>13</sup> It is important to emphasize, however, that the matrix of the receiver solution is not significantly altered by the dialysis process such that the matrix of the analyte after dialysis is essentially constant from sample to sample, independent of the original sample composition. Thus, these results only illustrate the difference between SEFs and EFs for FIDD-ICP-AES, and not a matrix interference.

We investigated the combined effect of various optimum parameters on the SEF for Ag<sup>+</sup>. Figure 6 shows the signal resulting from the Donnan dialysis of 60 ng/L silver with a 30-min dialysis time, a 0.7 °C/min temperature gradient (initial and final values being 21 and 42 °C, respectively), 500-mL sample volume, and 2-m tubing length. A signal to noise ratio (SNR) of 16.2 was obtained for this concentration, corresponding to an SEF of 650. This improvement in SEF is due to the additive nature of the various effects of higher temperature, longer tubing length, larger sample volume, and longer dialysis time. The figure shows that the signal obtained for the dialysis is entirely due to the analyte, as the blank dialysis performed under identical conditions with the magnesium receiver did not result in a change in the background level. The detection limit for FIDD-ICP-AES was lowered from 60 ng/L to 11 ng/L by using the higher temperature, longer dialysis time, larger sample volume, and longer tubing length. The combined effect of the various parameters is a way to attain low LODs for ultratrace analyses.

(13) Thompson, M.; Ramsey, M. H. *Analyst* 1985, 110, 1413.

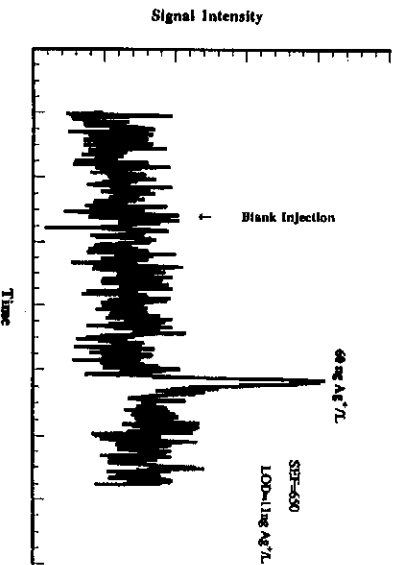


Figure 8. A plot of signal intensity vs time for silver with magnesium-urn receiver is obtained with a 30-min dialysis, temperature gradient of 0.7 deg/min (initial, 21 °C; final, 42 °C), and 2 m of tubing. The analyte concentration was 60 ng/L. The arrow indicates the instant when the dialysate of a blank solution (DDW) was injected after performing a dialysis under conditions similar to that for the analyte.

### CONCLUSION

An attractive feature of FIDD for preconcentration is that hardware requirements are minimally different than those for direct aspiration analysis. Only the tubing and a stirrer are required beyond the typical instrumental setup for ICP-AES, making it a simple, low-cost addition to the experiment. SEFs of approximately 100 can be obtained for an 8-min dialysis of a room temperature solution. One can achieve increased SEFs and much lower LODs by increasing the temperature of the sample and by increasing the dialysis time. If in addition to the above we increase the sample

volume, optimize the tubing length for a particular type of membrane, and minimize dead volumes, LODs down to picograms per liter can be realized. Thus, if one deems it necessary to achieve a certain fixed SEF, a variety of factors can be adjusted to achieve that level. Another feature of the technique is that all cations from the sample are simultaneously preconcentrated with cation Donnan dialysis. Thus, the technique is amenable to simultaneous multielement analysis with ICP-AES, using a direct reading spectrometer. As is true of cation preconcentration with a cation-exchange membrane, anion preconcentration can be performed with an anion-exchange membrane. However, the SEFs obtained in the latter case would be significantly lower as good-quality tubular anion-exchange membranes are still unavailable. Neutral, or counterionic metal forms are not extracted during the Donnan dialysis process, and hence, the process can be used for metal speciation studies.<sup>14</sup> If Donnan dialysis is combined with ICP-MS, in addition to the possibility of extremely low LODs, some counterion isobaric interferences might be reduced. The main limitations to the Donnan dialysis technique are its ability to function only in a specified range of ionic strengths and the requirement for relatively large sample volumes for highest enrichment.

### ACKNOWLEDGMENT

We are grateful to Perma Pure Corp. for providing us with the cation-exchange membranes. We also thank the Office of Research Development and Administration, SIU-C, for financial support of this project.

(14) Cox, J. A.; Slonawska, K.; Gatchell, D. K. *Anal. Chem.* 1984, 56, 650.

RECEIVED for review October 26, 1992. Accepted January 2, 1993.