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ATOMIC ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF GOLD WITH PRECONCENTRATION BY DONNAN DIALYSIS

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Summary—Donnan dialysis enrichment with tubular cation-exchange membrane was used as a preconcentration method prior to determination of gold by flame atomic absorption spectrometry (FAAS). The value of enrichment factor can be controlled for a particular application through adjustment of the membrane tuning length, dialysis time, carrier flow rate, composition of the receiver solution and by addition of complexing ligand to the receiver or the sample solution. For 10 min dialysis enrichment factor above 3 can be achieved. The detection limit (signal-to-noise ratio = 3) of 35 ng/ml was obtained. RSD at 0.2 μg/ml level was 4.7% ($n = 6$). The results of dialysis of noble metals mixtures are demonstrated.

The determination of trace amounts of ions in real samples often requires pretreatment steps. The matrix components may cause chemical and spectral interferences during measurements or the sensitivity of the analytical methods may be insufficient to perform the determinations without preconcentration.

Donnan dialysis has been demonstrated to be a useful technique for matrix normalization[1–4] and preconcentration of ions.[5–18] In this procedure, the sample is separated from a receiver electrolyte of a relatively high ionic strength by an ion-exchange membrane. As long as the receiver volume is much less than that of the sample, high enrichment factors can be attained. Quantification is based on linear calibration curves that are generated with a fixed-time kinetic model. Donnan dialysis has been used successfully for the preconcentration of nitrate,[1] copper,[5,7,10,16] nickel,[9,13] cobalt,[9] lead[15] and uranium,[18] among many other ionic species. By using the ion-exchange membranes the enrichment and separation of platinum group metals[10,14,19] and gold[12,17] was achieved. Dialysis was also utilized for the investigation of heavy metal speciation in natural waters.[20]

The preconcentration capability of Donnan dialysis depends upon the rate of ion transport through the membrane. Several limiting steps for the overall flux in this method have been postulated including concentration polarization at the solution–membrane interfaces and mass transport resistance within the membrane.[21–23] The influence of the membrane structure and the receiver composition on the dialysis rate have also been examined.[7,19,24–26]

Donnan dialysis with a static receiver solution yields only modest enrichment factors; values less than 10 were achieved with 1 hr dialysis.[7,9,12,17,19] The small diameter of the tubular membranes are particularly advantageous since they have high ratio of the surface area to internal volume. Flow dialyzing systems with tubular ion-exchange membranes were used for the preconcentration of the species with the elimination of matrix interferences in analytical voltammetry,[5] potentiometry,[27] ion chromatography[3,4,6] and atomic spectrometry.[15,28–30] The tubular membranes bathed in an appropriate solution can be utilized for replacement ion chromatography. Eluted, resolved species are replaced by the same indicator component, which can be then monitored with flow-through AAS,[31] spectrophotometric[32] and potentiometric[33,34] detectors. Those references demonstrate that tubular Donnan dialysis systems can be applied in on-line procedures.

In the present paper a procedure based upon dialytic preconcentration of gold for flame atomic absorption determination was developed. Factors influencing the efficiency of dialytic enrichment were established. The application of Donnan dialysis for the enrichment and recovery of gold seems to be an attractive alternative to ion exchange chromatography and solvent extraction, which are the most often processes used for this purpose.

EXPERIMENTAL

The cation exchange membrane employed for dialysis experiments was 0.31 mm i.d. × 0.76 mm o.d. tubing of various lengths made of Nafion 811X (Perma Pure Products, Farmingdale, U.S.A.). The Nafion tubing was wrapped around the square cross-section glass frame which for dialysis was inserted into a beaker containing magnetically stirred sample. The tubular dialyzer was coupled to a multichannel peristaltic pump (Ismatec, Zurich, Switzerland) with 0.45 mm i.d. Teflon tubing. 5 ml of the receiver electrolyte was circulated through the tubing for a prescribed time and then diverted into a 10 ml volumetric flask, and diluted to a given volume with distilled water After each set of experiments, the tubular membrane surface was bathed in deionized water, while a mixture containing $0.3M$ NH_4Br and $1M$ HNO_3 was pumped through the tubing for 10 min at flow rate 2 ml/min.

Atomic absorption measurements were made with a Zeiss Jena model AAS-30 spectrometer and an air–acetylene flame. All solutions were prepared from analytical grade reagents dissolved in a deionized water from the Waters Milli-Q system.

The data are reported in terms of enrichment factor (EF) calculated as the ratio of the analyte concentration in the dialysate to that in the initial sample

RESULTS AND DISCUSSION

Effect of hydrodynamic conditions and time of dialysis

It was shown earlier that the transport of chloro complexes of Au(III) across an anion exchange membrane does not occur because of their high affinity for the fixed sites of the membrane.[12,35] Therefore, gold is mostly distributed between the sample and the membrane phase. The anionic species of the receiver electrolyte influenced to some degree the retention of chloro complexes of gold in the membrane phase. More effective is the addition of ethylene–diamine to the sample, because it forms positively charged, mixed complexes of Au(III) in the presence of chloride or bromide.[17] These complexes are transported through the cation-exchange membrane. Donnan dialysis performed for this sample solutions with flat membrane yields however very low preconcentration; an enrichment factor of only 2.4 was obtained for 4 hr dialysis. In the present study the tubular cation-exchange membrane was applied to obtain more effective enrichment and hence an improvement in detection limit for flame atomic absorption analysis of gold.

In the initial experiment, in order to verify the expected advantage of the tubular membranes, the effect of flow rate on the enrichment factor (EF) was examined The non-circulating mode was used for these measurements; here, the receiver electrolyte was continuously pumped through the cation-exchange tubing into a volumetric flask. In the samples containing $[AuBr_4]^-$ at a concentration of $6 \times 10^{-5}M$, a 50-fold excess of ethylenediamine over the total concentration of gold was used. As shown in Fig. 1, low flow rate the highest EF values are observed because of longer residence time of the receiver solution in the cation-exchange tubing. When the results are interpreted as EF per unit time, so called concentration efficiency,[36] greater preconcentration is found at the higher flow rates. At the same time, the amount of gold retained in the membrane phase decreases. The higher flow rate causes a decrease of the diffusion layer thickness at the membrane–receiver interface thereby diminishing the concentration polarization.

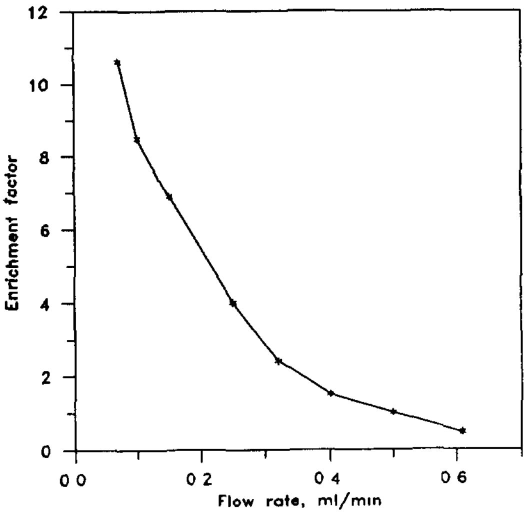

Fig 1 Effect of the flow rate on the enrichment factor in non-circulated mode of dialysis using $0.3M$ NH_4Br receiver solution Dialysis of $6 \times 10^{-5}M$ $AuBr_4^-$ + 3 mM ethylenediamine solution with 2 m of Nafion tubing and 500 ml of sample volume

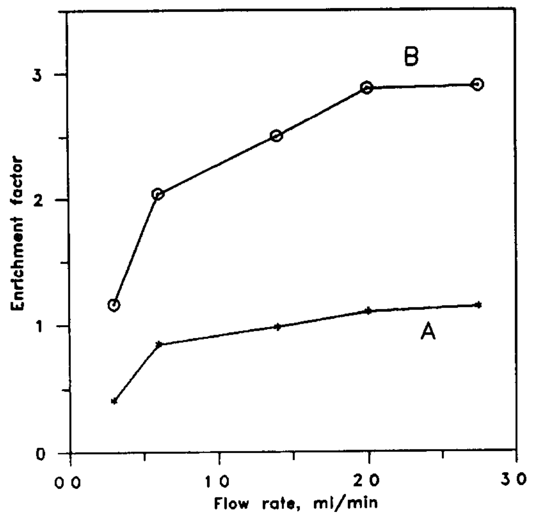

Fig 2 Effect of the flow rate on the enrichment factor in dialysis with circulation of the receiver solution for 5 (A) and 10 min (B) dialysis time Other conditions as in Fig 1

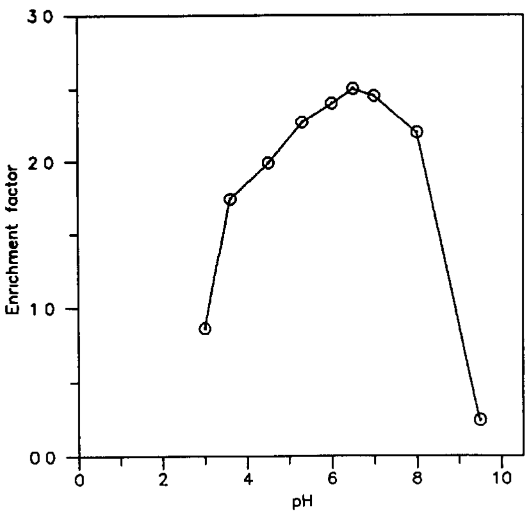

Fig. 4. Effect of pH on 10 min dialysis of $AuBr_4^-$ in the presence of ethylenediamine, 0.3M NH_4Br receiver solution was circulated with flow rate 1.2 ml/min

A greater enrichment efficiency can be achieved by circulation of the receiver solution through the tubing for a given period of time (Fig. 2). However, at flow rates greater than 2 ml/min the constant enrichment factor value was found. It was already reported that for Donnan dialysis using the Nafion tubing the enrichment efficiency reached its maximum at a receiver solution flow rate 3 ml/min.[5]

As it is shown in Fig. 3, for a dialysis time up to 15 min the amount of gold in the receiver solution increases linearity with the dialysis time. The five-fold enrichment, which is achieved for 20 min dialysis time, provides a significant improvement in comparison to Donnan dialysis with the static receiver.[17]

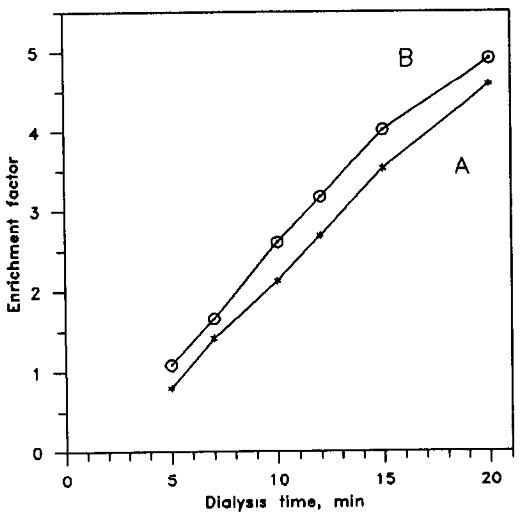

Fig 3. Effect of dialysis time on enrichment factor at flow rate of the receiver solution 0.6 (A) and 1.2 (B) ml/min Other conditions as in Fig 1

Another factor that can affect Donnan dialysis is the sample volume, since this influence on the sample to receiver volume ratio 15% decline in enrichment factor for gold was observed when the sample volume decreased from 800 to 250 ml. To reduce sample handling and preparation requirements, 500 ml sample volumes were used for further study.

Effect of chemical conditions

As already discussed in the literature, the efficiency of metal ion dialysis depends on such factors as the composition and concentration of the receiver solution,[7,19,24–26] the pH of the solutions on both sides of the membrane,[10,14,17] and the presence of other cations in the sample [7,10,14] The importance of some of those factors for dialysis of bromocomplexes of Au(III) in the presence of ethylenediamine (en) was investigated in this study for tubular cation-exchange membrane.

The influence of pH of the sample solution on the dialysis results for gold is shown in Fig. 4. When the receiver solution was circulated for 10 min at flow rate 1.2 ml/min the maximum enrichment was obtained in pH range 6–7.

The enrichment factor for gold is independent of en concentration when this ligand is present in the sample at a 50–200-fold excess over the molar concentration of metal (Fig. 5). At higher concentrations the difference in ionic strength between the sample and the receiver electrolyte is too small to permit effective transport and the enrichment factor value decreases. Dialysis performed in the presence of ethylenediamine in the receiver solution resulted in a decrease of the transport of gold complexes through the membrane. At the same time an increase of the metal ions uptake in the membrane phase was observed. The distribution of metal ions among three phases is disadvantageous for analytical application where complete transport to the receiver solution or retention in the membrane phase is preferred.

Because we found earlier[12,14,17,19,35] that the nature of the counterion of the receiver electrolyte influences the transport across ion-exchange membranes, in this study the receiver electrolyte composition was optimized to obtain a maximum enrichment of gold and maximum sensitivity for its determination by FAAS. From the results shown in Table 1 it can be seen that bromide ions in the receiver solution allows us to achieve high enrichment, probably due to favoring the formation of the mixed complex $[AuBr_2en]^+$. This complex is more readily transported through the cation-exchange membrane than $[Auen_2]^{3+}$, which is formed in the presence of chloride ions[37] Sulphate is preferred over nitrate as the anion in the receiver because it penetrates the cation exchange membrane to a lesser extent.[25]

The counter-ions present in the receiver may be put into following sequence regarding their effect on increase of efficiency of gold preconcentration:

$$Mg^{2+} < Na^+ < K^+ < NH_4^+$$

This sequence is almost opposite to the affinity of these cations for the sulphonate sites in the cation-exchange membrane and results on the Donnan dialysis of other ions.[7] Usually Mg^{2+} ions are effective because they decrease the residence time of test ion on the sulphonate sites of the membrane.[7] The results suggest that the major factor, which facilitates the transport across the membrane, is the interaction of the NH_4^+ ions with the gold complex.

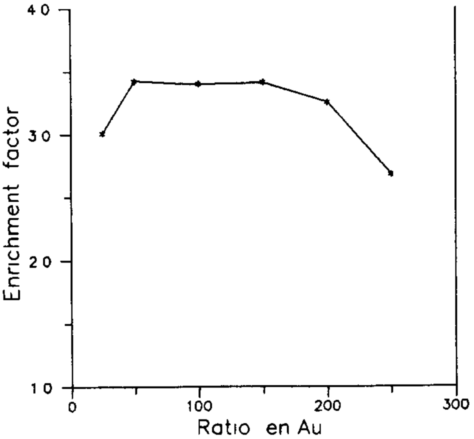

Fig 5 Effect of the excess of ethylenediamine in a sample Dialysis time 10 min

Table 1 Effect of the composition of receiver solution on the effectiveness of Donnan dialysis of gold complexes Dialysis of $6 \times 10^{-5}M$ $AuBr_4^-$ + 3m*M* ethylenediamine using 500 ml sample volume and 2m of Nafion tubing Receiver solution was circulated with flow rate 1.2 ml/min

Receiver*	Enrichment factor
NH_4Br	3.4
KBr	2.4
NaBr	1.5
$(NH_4)_2SO_4$	2.0
K_2SO_4	1.3
Na_2SO_4	0.7
$MgSO_4$	0.2
NH_4Cl	1.7
KCl	0.7
NaCl	0.3
$MgCl_2$	0.3
NH_4NO_3	1.2
KNO_3	1.1
$NaNO_3$	0.6
$Mg(NO_3)_2$	0.4

*All solutions 0.5*M*

Ammonium salts as the receiver electrolytes allow not only to obtain the greatest enrichment factor value for gold but also they have been used as a chemical modifier to help volatilize interfering halide salts in AAS determinations.[38]

The ionic strength of the receiver electrolyte was found to control the enrichment rate of Au(III). The enrichment factor increases rapidly with increasing concentration of NH_4Br up to 0.5*M*; above this concentration the transport rate of gold complexes decreases.

The value of enrichment factor as a function of tubing length obtained for 10 min dialysis is shown in Fig. 6. The longest tubing provided the highest signal enhancement due to increase the effective residence time of a particular segment of receiver solution.

Performance of dialysis in optimized conditions

From the conditions established thus far, calibration data for the Donnan dialysis experiments were determined. Typical log–log plots

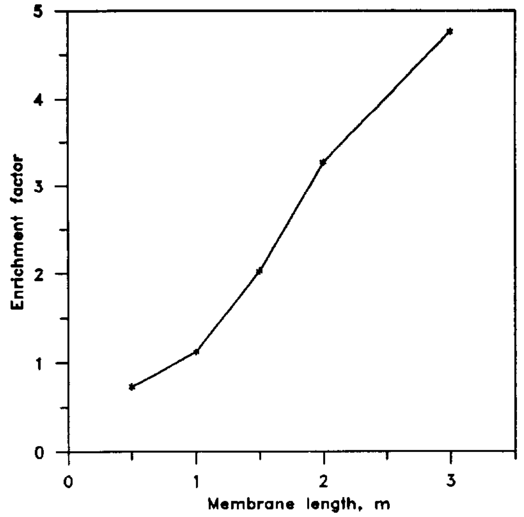

Fig 6 Effect of length of Nafion tubing on the enrichment factor values for 10 min dialysis of 6 × $10^{-5}M$ $AuBr_4^-$ + 3 mM ethylediamine solution at pH 6 5 using 500 ml sample volume and 0 5M NH_4Br as the receiver solution circulated at flow rate 1 2 ml/min

of absorbance versus concentration using either Donnan dialysis or direct aspiration of gold standards are shown in Fig. 7. The plot shows the good linearity of response obtained after Donnan dialysis of a wide range of analyte concentrations. The difference in detection limit (based on triple value of standard deviation of the blank) for direct aspiration (0.12 μg/ml) and Donnan dialysis (35 ng/ml) for gold is a representation of the preconcentration efficiency of Donnan dialysis process for that element. These results were obtained for a moderate tubing length (2 m) and short dialysis time (10 min). Precision for Donnan dialysis–FAAS method was 4.3% RSDat 0.2 μg/ml level, compared to 1.4% RSD provided by direct aspiration of 1.0 μg/ml gold solution.

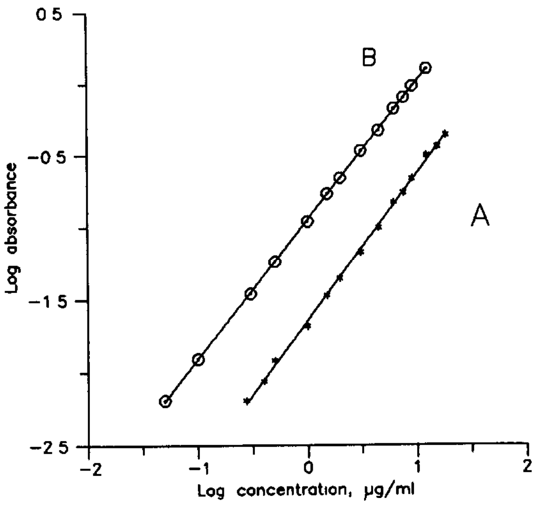

Fig. 7 Calibration plots obtained for direct FAAS measurement with conventional aspiration (A) and for the receiver solution after 10 min dialysis of gold solutions (B) Conditions as in Fig. 6.

Table 2. Results of dialysis of mixtures of noble metals using 2 m Nafion tubing. Other conditions as in Fig. 5

Sample component	EF	Metal retained in the membrane (%)
3 1 × $10^{-5}M$ Au(III)	2 5	~0 4
2.3 × $10^{-5}M$ Pd(II)	1 4	21
1.2 × $10^{-5}M$ Pt(IV)	0	0
3 × $10^{-6}M$ Ir(IV)	0	0
5 × $10^{-6}M$ Rh(III)	0	0
3.1 × $10^{-5}M$ Au(III)	2 0	0
11 4 × $10^{-5}M$ Pd(II)	0 7	19
1 2 × $10^{-5}M$ Pt(IV)	0	~0 3
3 × $10^{-6}M$ Ir(IV)	0	0
5 × $10^{-6}M$ Rh(III)	0	0

It was reported earlier[14] that Pd(II) in the presence of ethylenediamine forms mixed complexes, probably $[PdBr_2en]$ or $[Pd(H_2O)_2en]^{2+}$, which are transported through a cation-exchange membrane. The optimum pH of a sample solution for the transport rate of palladium was 10. The dialysis carried out for the mixture of Au(III) and Pd(II) in the presence of ethylenediamine at pH 6.5 indicated enhancement of gold preconcentration in the presence of palladium. When a 5 ml aliquot of a receiver of 0.5M NH_4Br was circulated for 10 min at 1.2 ml/min values of EF of 3.2 and 3.6 for gold were obtained from a sample containing 3.1 × $10^{-5}M$ Au(III) and 3.1 × $10^{-5}M$ Au(III) and 2.3 × $10^{-5}M$ Pd(II), respectively. Palladium is also preconcentrated in the receiver solution, however EF for that metal is much lower than for gold. In optimized enrichment conditions for gold, palladium is distributed among three phases. sample (77–80%), receiver solution (1–5%) and membrane phase (20–22%). In a 10-min dialysis the preconcentration of gold into the receiver is 9-times greater than that of palladium. From the amounts retained in the membrane, Pd(II) can be enriched by factors of 40 from Au(III).

Table 2 summarizes results of a dialysis of noble metals mixtures. In the presence of other platinum group metal ions preconcentration of gold in the receiver solution slightly decreases. However, Au(III) can be selectively separated from Pt(IV), Ir(IV) and Rh(III), which under those conditions, form negatively charged complexes with halides and remain in the sample solution. So in addition to preconcentration Donnan dialysis is a useful technique for separation.

CONCLUSIONS

The combination of tubular flow Donnan dialysis with FAAS method provides a simple means of enhancing analytical signals and improvement of detection limit for determination of gold. Separation from some other platinum group metals is also provided since the membrane is impermeable to co-ions. When no intermediate steps are required prior to the analysis, Donnan dialysis is an attractive alternative to other preconcentration techniques such as solvent extraction or ion exchange. The proposed method can be easily automated and adapted to continuous monitoring. The developed preconcentration system can be coupled to various detection instrumentation.

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