Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Noble Metals by Donnan Dialysis

Krystyna Brajter[a]; Krystyna Slonawska[a]
[a] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WARSAW, WARSAW, POLAND

To cite this Article Brajter, Krystyna and Slonawska, Krystyna(1988) 'Separation of Noble Metals by Donnan Dialysis', Separation Science and Technology, 23: 4, 321 — 331
To link to this Article: DOI: 10.1080/01496398808060707
URL: http://dx.doi.org/10.1080/01496398808060707

SEPARATION SCIENCE AND TECHNOLOGY, **23**(4 & 5), pp. 321-331, 1988

Separation of Noble Metals by Donnan Dialysis

KRYSTYNA BRAJTER and KRYSTYNA SLONAWSKA
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WARSAW
PASTEURA 1, 02-093 WARSAW, POLAND

Abstract

Donnan dialysis has been demonstrated to be a useful technique not only for the enrichment of metal ions but also for their separation. Our studies indicate that Donnan dialysis may be applied to the separation of gold from some platinum group metal ions. It was found that after Donnan dialysis, some tested metal ions—as chloride complexes—were distributed among three phases: sample, receiver electrolyte, and membrane. Different receiver solutions as well as different ligands were investigated to differentiate the transport rate.

The possibilities of the application of the Donnan dialysis of metal ions for their preconcentration, speciation, and separation is the reason for the great attention paid lately to this method (*1–7*). In a previous paper we demonstrated that the separation of platinum metal ions on the basis of Donnan dialysis across anion-exchange membranes is possible (*7*). The most interesting results obtained by Donnan dialysis of platinum metals is their distribution among three phases: sample, anion-exchange membrane, and receiver electrolyte. The separation of platinum metal ions by that technique is influenced greatly by the receiver electrolyte composition (*7*). We confirmed that there is some similarity between the affinities of chloride complexes of platinum metal ions toward anion-exchange membrane and toward anion-exchange resin (*7*).

The aim of the presented paper was to test the possibilities of the separation and preconcentration of gold from some platinum group metal ions by Donnan dialysis. We investigated the influence of the receiver electrolyte and sample composition on Donnan dialysis of gold. We used sodium sulfite and ethylenediamine as the complexing agents added to the sample. Both ligands strongly influence the results of Donnan dialysis.

EXPERIMENTAL

The work was performed with P-1010 cation-exchange membranes and P-1035 anion-exchange membranes (RAI Research Corp., New York). They were pretreated in 1 *M* HCl prior to initial use. Before each dialysis they were soaked in a saolution of the same composition as the receiver electrolyte for 1 h.

The dialysis cell was constructed from a Teflon tube. The membrane (2.5 cm diameter) was used to close one end and was held by a threaded Teflon sleeve. The dialysis cell, containing 5 mL of receiver solution, was placed in 50 mL of sample (magnetically stirred) to initiate the experiment. The dialysis time was 1 h. After dialysis the receiver chamber content was transferred to a 10-mL volumetric flask, and the residual sample to a 100-mL volumetric flask. Both were diluted to volume with water. The concentrations of the metals were determined by atomic absorption spectrometry (Beckman Model 1272 with a graphite furnace atomizer Perkin-Elmer HGA-74).

All chemicals used were Reagent Grade. Doubly distilled water was used for preparing all solutions. The solutions of Rh, Pd, Pt, and Au were prepared from the chlorides of these metals (Koch Light Laboratories). The metals were in the form of anionic chloro complexes. The pH was adjusted with dilute HCl or NaOH prior to dialysis.

The metal ions were recovered from the cation-exchange membranes after dialysis by soaking them in 1 *M* HNO_3 for 1 h. From the anion-exchange membranes the metal ions were recovered by soaking the membranes as follows: for Pd(II) in 1 *M* HCl for 1 h, for Pt(IV) in 0.5 *M* NaCl for 3 h, and for Au(III) in 0.5 *M* HNO_3 and 90% v/v acetone for 30 min and then in 1 *M* HNO_3 for 1 h.

The data are reported in terms of the enrichment factor EF (defined as the ratio of metal concentration in the receiver electrolyte after dialysis to the initial sample concentration) and percent of the metal retained in the sample or on the membrane phase after dialysis. The last one was determined by difference between the initial concentration and the final solution phase concentration.

RESULTS AND DISCUSSION

The preliminary experiments were performed to establish the influence of the receiver electrolyte composition on the Donnan dialysis of chloroauric complexes. The following electrolytes were used: chloride (NH_4Cl), nitrate (NH_4NO_3) and sulfates (Na_2SO_4, $(NH_4)_2SO_4$). The data in Table 1 show that the anion-exchange membrane is practically impermeable to the chloroauric complex. The complex is admitted to the membrane and thus has great difficulty in passing from the sample into the receiver. The anion-exchange membrane prevents diffusion of chloroauric complex almost completely due to the anion-exchange process occurring in the membrane phase. The chloroauric complex is characterized by an extremely high affinity for the quaternary ammonium groups of the membrane, and as a result, the gold is significantly retained on the membrane.

The anionic species of the receiver electrolyte influences the degree of retention of the chloroauric complex on the membrane phase. There is some agreement between the affinity of the anionic species of the receiver electrolyte toward the fixed sites of the membrane and retention of the chloroauric complex. Anions characterized by low affinity (sulfates) have higher retention. Those characterized by high affinity (nitrates) cause a decrease in retention. This result supports the hypothesis of the influence of receiver electrolyte composition on the chemistry at the sample-

TABLE 1
Effect of the Receiver Electrolyte on Donnan Dialysis of Au(III)[a]

		% of Au retained	
Receiver[b]	EF[c]	In sample	On membrane[d]
NH_4Cl	0.01	62	37
NaCl	0	51	49
NH_4NO_3	0.01	53	46
Na_2SO_4	0	37	63
$(NH_4)_2SO_4$	0	49	51

[a] Anion-exchange membrane; dialysis time, 1 h; concentration of $AuCl_4^-$ in sample, 5.9×10^{-5} *M*.

[b] All receivers 0.5 *M*.

[c] Enrichment factor EF is defined as the concentration of Au in the receiver after dialysis divided by the initial sample concentration.

[d] Determined by difference between the initial concentration and the final solution-phase concentration.

membrane interface (*1*). The very important result of our experiments is the distribution of the chloroauric complex between two phases: membrane and sample rather than between three phases (membrane, sample, and receiver solution) (*7*).

Dialysis of Chloroauric Complex with Ethylenediamine as a Sample Matrix

A set of similar experiments in which anion- or cation-exchange membranes were used was performed. Gold was taken as a chloroauric complex in all experiments. In the samples the concentration of ethylenediamine was 2.9×10^{-2} *M*. The composition of the receiver solution was constant (0.5 *M* NH_4NO_3). In Donnan dialysis experiments performed with anion-exchange membranes by increasing the ethylenediamine concentration, drastic decreases of the amount of gold on the membrane were obtained (Fig. 1a). Dialysis of the chloroauric complex without ethylenediamine as a sample matrix resulted in the distribution

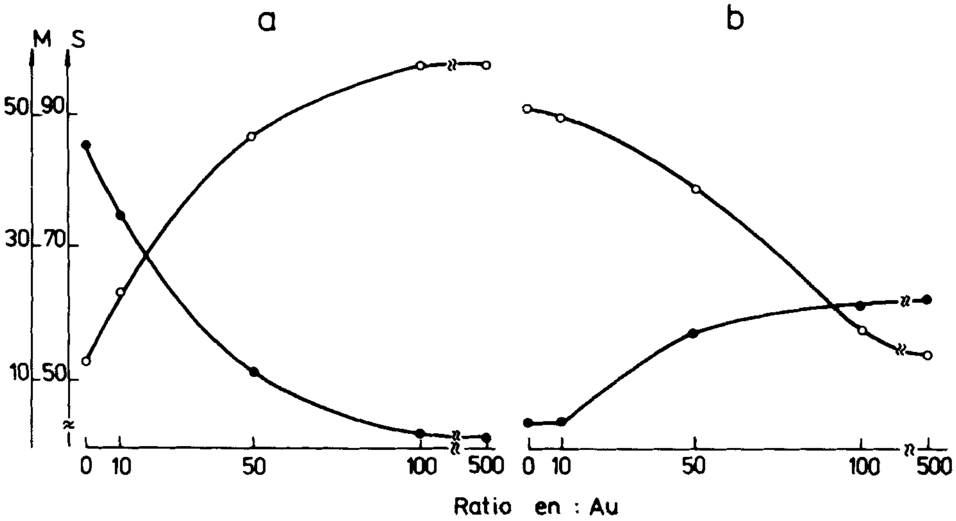

FIG. 1. Effect of ethylenediamine as a sample matrix on the Donnan dialysis of Au complexes: (a) anion-exchange membrane, (b) cation-exchange membrane. (○) Percent of Au retained in the sample (Scale S). (●) Percent of Au retained on the membrane (Scale M). Receiver, 0.5 *M* NH_4NO_3; dialysis time, 1 h, concentration of $AuCl_4^-$ in the sample, 5.9×10^{-5} *M*.

of gold into only two phases: membrane and sample. This was also the case in the presence of amine. It was observed that at some ethylenediamine concentration level the transport of gold into the membrane did not occur. The amount of gold on the membrane and in the receiver solution was zero.

When a cation-exchange membrane was used at the same experimental conditions with an increase of ethylenediamine concentration, an increase of the enrichment factor as well was an increase in the retention of gold on the membrane was obtained (Fig. 1b). The results of above experiments can be explained by assuming that ethylenediamine acts as a ligand, transforming the chloroauric complex of gold into another, probably $(AuenCl_2)^+$, four-coordinated positively charged mixed complex. The increase of ethylenediamine concentration favors the formation of the new complex which is excluded from the anion-exchange membrane by Donnan potential (Donnan exclusion) due to its positive charge. There is a very low probability that amine (weak electrolyte) influences the rate of transport of the chloroauric complex (assuming that the formation of $(AuenCl_2)^+$ does not occur). The composition of the auricethylenediaminechloro complex is assumed, not proved.

Dialysis of Chloroauric Complex with Sulfite as a Sample Matrix

The experiments were performed using anion-exchange membranes only. Gold as the chloroauric complex was used. The results presented in Table 2 show that the chloroauric complex is not dialyzed at zero to low Na_2SO_3 concentrations. When the concentration of sodium sulfite as the sample matrix is increased, the enrichment factor of gold is first increased and then, at higher Na_2SO_3 concentrations, decreases. At the same time, the retention of gold on the membrane dramatically decreases. Quantitative retention of gold in the sample is obtained if the concentration of Na_2SO_3 is equal to 6×10^{-2} *M*. In the concentration range 6×10^{-5} to 6×10^{-2} *M*, different complexes are probably formed, and they are Donnan dialyzed to chloroauric complexes. When the sulfite concentration is less than about 6×10^{-3} *M*, the difference in ionic strength between the sample and the receiver solution is large enough to permit the transfer of the formed complexes of gold across the anion-exchange membrane. At higher concentrations of Na_2SO_3 the concentration gradient may be too small to permit effective transport. The enrichment factor decreased (Fig. 2).

It is extremely difficult to postulate the mechanism of the reaction in the sample between the chloroauric complex and sodium sulfite. It is

TABLE 2
Effect of the Presence of Na_2SO_3 in the Sample on Donnan Dialysis of Au Complexes[a]

Concentration of Na_2SO_3 (*M*)	% of Au retained In sample	In receiver	On membrane
0	53	0.8	46
6×10^{-5}	54	1.4	45
6×10^{-4}	55	35	10
3×10^{-4}	74	30	0
6×10^{-3}	87	22	0
3×10^{-2}	83	10	7
6×10^{-2}	96	7	0

[a] Anion-exchange membrane; receiver, 0.5 *M* NH_4NO_3; dialysis time, 1 h; sample concentration of Au(III), 6×10^{-5} *M*.

possible that auric sulfates are formed (according to the literature, they are not very stable), but it is more likely that polymerized aurous sulfite complexes are formed. [Au(I) complexes are usually monomeric although not invariably.] There is no information about these complexes in the literature.

In all experiments no precipitation of gold (Kassius purple) was observed after addition of sulfite or of amine.

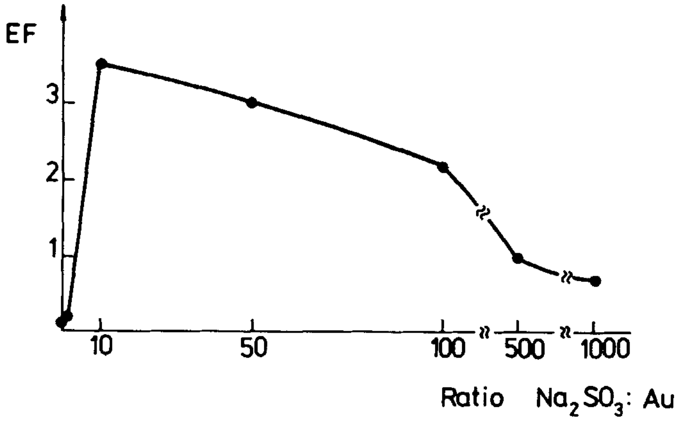

FIG. 2. Effect of sodium sulfite as a sample matrix on the Donnan dialysis of Au complexes. Anion-exchange membrane; receiver, 0.5 *M* NH_4NO_3; dialysis time, 1 h; concentration of $AuCl_4^-$ in the sample, 5.9×10^{-5} *M*.

Separation of Mixtures by Donnan Dialysis in the Presence of Ethylenediamine

The experiments were performed using cation-exchange membranes. In Table 3 the results obtained when mixtures of gold and platinum metals were dialyzed in the presence of ethylenediamine are summarized. As far as enrichment factors are concerned, the results are not the best for Donnan enrichment of gold. If the amounts of gold retained on the membrane phase are considered, the results presented in Table 3 are very promising. All metals are retained to some degree on the membrane, but gold is especially strongly bound. An almost selective preconcentration of gold on the membrane was achieved at suitable experimental conditions. This supports the development of a new, nonconventional method of separation based on distribution among three phases: membrane, receiver solution, and sample.

TABLE 3

Separation of Mixtures by Donnan Dialysis in the Presence of Ethylenediamine[a]

	Sample component	pH	EF	% Retained on membrane
1.	Au	4.9	0.6	51
	Rh		0.3	1.5
	Au	6.4	0.4	42
	Rh		1.4	0
	Au	7.3	1.3	38
	Rh		0.5	5
2.	Au	7.3	0.4	36
	Rh		0.5	5
3.	Au	6.4	0.4	16
	Pt		0.5	0
	Au	7.3	0.7	33
	Pt		0.8	5
	Au	8.3	0.6	25
	Pt		1.0	0.4
	Au	9.1	0.6	23
	Pt		0.8	0
4.	Au	9.1	0.5	60
	Pt		0	4

[a] Cation-exchange membrane; receiver, 0.5 *M* NH_4NO_3; dialysis time, 1 h; in all cases a 100-fold excess of ethylenediamine to Au was used. Concentrations in the samples: (1) Au(III) 5.9×10^{-6} *M* and Rh(III) 9.5×10^{-5} *M*; (2) Au(III) 5.9×10^{-5} *M* and Rh(III) 9.5×10^{-5} *M*; (3) Au(III) 5.9×10^{-5} *M* and Pt(IV) 5.9×10^{-5} *M*; (4) Au(III) 5.9×10^{-6} *M* and Pt(IV) 5.9×10^{-5} *M*.

Separation of Au-Rh

When the mixture of Au-Rh was dialyzed, selective isolation of gold on the membrane was obtained. Rhodium is not dialyzed nor retained on the membrane in the pH range investigated, but compared to gold its enrichment in the sample is excellent. Gold is enriched on the membrane due to ion-exchange processes occurring in the membrane phase, which prevent the transport of gold complexes though the membrane.

Separation of Au-Pt

After dialysis of the Au-Pt mixture (at pH 9.1), platinum is left in the sample when gold is preconcentrated on the membrane. Platinum is not dialyzed in the presence of ethylenediamine. Gold complexes react with ion-exchange sites of the membrane, and as a result they are very strongly bound to the membrane phase.

Separation of Mixtures by Donnan Dialysis in the Presence of Sodium Sulfite

The experiments were performed using anion-exchange membranes. Sulfite does not influence the dialysis of platnium group metals (Table 4). Support for that conclusion is given by a comparison of the enrichment factors obtained for the platinum group metals under study when they were dialyzed in the absence of sulfite (*7*) compared with those obtained when Donnan dialysis was performed in the presence of Na_2SO_3 (Table 4). A difference between the results obtained when the mixtures were

TABLE 4
Effect of the Presence of Na_2SO_3 in the Sample on Donnan Dialysis of Rh, Pt, and Pd[a]

Sample component	pH	EF	% Retained on membrane
Rh	4.1	0.7	0.1
Pt	5.1	0.4	24
Pd	4.9	0.4	4

[a] Anion-exchange membrane; receiver, 0.5 *M* NH_4NO_3; dialysis time, 1 h; concentration of Na_2SO_3, 2.9×10^{-4} *M*. Each sample contained only a single metal at a concentration of Rh(III) 9.5×10^{-5} *M*, Pt(IV) 5.9×10^{-5} *M*, and Pd(II) 1.1×10^{-4} *M*.

dialyzed and those when gold was dialyzed as a single metal in the presence of sulfite was observed.

Separation of Au-Rh

In the system Au-Rh with sodium sulfite as a sample component, separation may be obtained due to the retention of gold on the anion-exchange membrane. Rhodium is not dialyzed nor is it retained on the membrane, but it is enriched in the sample. Gold is enriched on the membrane phase due to processes occurring in the membrane. If gold was used as a single component sample at similar sulfite concentrations, its retention on the membrane was near zero.

Separation of Au-Pd

Separation of Au-Pd mixtures was also obtained due to the distribution of metals into three phases. Palladium is enriched on the membrane, and gold is enriched in the receiver solution on the basis of Donnan dialysis. The best results were obtained at pH 8.3. Palladium is retained on the membrane to almost to the same degree in the presence or absence of sulfite.

Separation of Au-Pt

Both gold and platinum are dialyzed at pH 8.3, and a rather high enrichment factor for gold was obtained (Table 5). The decrease of the retention of gold on the membrane was drastic. Separation of Au and Pt on the basis of Donnan dialysis is obtained—the enrichment factor for gold was 6.4 and for platinum was 3.0. If distribution among three phases is consider, excellent enrichment of platinum on the membrane is obtained. Gold is practically all in the receiver solution and sample, and platinum is on the membrane to 43% of its initial amount.

The mechanism of Donnan dialysis in the systems investigated may be compared to the systems with weak acid or with weak bases and acids. In both cases one of the counterions is selectively bound to ion-exchange sites and the membrane phase is enriched in that ionic species. The main difference is that in the systems investigated the affinity of the chloroauric complex to the anion-exchange sites are more strongly pronounced.

Metals bound to the ion-exchange sites of the membranes can be

TABLE 5
Separation of Mixtures by Donnan Dialysis in the Presence of Sodium Sulfite[a]

	Sample component[b]	pH	EF	% Retained on membrane
1.	Au	5.0	2.1	26
	Rh		0.7	5
	Au	6.1	0.2	23
	Rh		0.5	4
	Au	7.2	1.6	24
	Rh		0.7	0.2
	Au	8.2	1.4	24
	Rh		0.01	1
2.	Au	5.2	1.9	16
	Pd		0.8	10
	Au	8.3	1.0	2.5
	Pd		0	16
3.	Au	5.2	2.7	24
	Pt		0.3	18
	Au	8.3	6.4	4
	Pt		3.0	43

[a] Anion-exchange membrane; receiver, 0.5 *M* NH_4NO_3; dialysis time, 1 h; concentration of Na_2SO_3, 3×10^{-4} *M*.

[b] The sample concentrations were as following: (1) Au(III) 5.9×10^{-6} *M* and Rh(III) 9.5×10^{-5} *M*; (2) Au(III) 5.9×10^{-6} *M* and Pd(II) 1.1×10^{-4} *M*; (3) Au(III) 5.9×10^{-6} *M* and Pt(IV) 5.9×10^{-5} *M*.

recovered from the membrane phase after dialysis by soaking the membranes in suitable solutions (see Experimental).

The data obtained demonstrate the possibility of the separating mixtures of gold and some platinum metal ions by Donnan dialysis in the presence of nontypical complexing agents due to the partitioning of metal ions among three or two phases.

REFERENCES

1. J. A. Cox and J. E. DiNunzio, "Donnan Dialysis Enrichment of Cations," *Anal. Chem.*, *49*, 1272 (1977).
2. J. A. Cox and Z. Twardowski, "Tubular Flow Donnan Dialysis," *Ibid.*, *52*, 1503 (1980).
3. J. A. Cox, E. Olbrych, and K. Brajter, "Separation of Mixtures of Cations by Donnan Dialysis," *Ibid.*, *53*, 1308 (1981).
4. R. L. Wilson and J. E. DiNunzio, "Enrichment of Nickel and Cobalt in Natural Hard Water by Donnan Dialysis," *Ibid.*, *53*, 692 (1981).
5. J. E. DiNunzio, R. L. Wilson, and F. P. Gatchell, "Preconcentration of Some Transition and Rare-Earth Elements by Donnan Dialysis," *Talanta*, *30*, 57 (1983).

6. J. A. Cox, K. Slonawska, F. P. Gatchell, and A. G. Hiebert, "Metal Speciation by Donnan Dialysis," *Anal. Chem.*, *56*, 650 (1984).
7. K. Brajter, K. Slonawska, and J. A. Cox, "Separation of Platinum Group Metal Ions by Donnan Dialysis," *Ibid.*, *57*, 2403 (1985).

Received by editor March 20, 1987