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

Preconcentration of Iron by Complexation and Ultrafiltration

C. Sarzanini[a]; P. Masse[b]; E. Mentasti[a]; A. Verdier[b]
[a] DIPARTIMENTO DI CHIMICA, ANALITICA UNTVERSITA DI TORINO, TORINO, ITALY [b] LABORATOIRE DE CHIMIE ORGANIQUE APPLIQUEE INSTITUT NATIONAL DES SCIENCES, TOULOUSE CEDEX, FRANCE

To cite this Article Sarzanini, C. , Masse, P. , Mentasti, E. and Verdier, A.(1990) 'Preconcentration of Iron by Complexation and Ultrafiltration', Separation Science and Technology, 25: 6, 729 — 737
To link to this Article: DOI: 10.1080/01496399008050362
URL: http://dx.doi.org/10.1080/01496399008050362

SEPARATION SCIENCE AND TECHNOLOGY, 25(6), pp. 729-737, 1990

Preconcentration of Iron by Complexation and Ultrafiltration

C. SARZANINI*

DIPARTIMENTO DI CHIMICA ANALITICA
UNIVERSITA DI TORINO
V. P. GIURIA 5, 10125 TORINO, ITALY

P. MASSE

LABORATOIRE DE CHIMIE ORGANIQUE APPLIQUEE
INSTITUT NATIONAL DES SCIENCES APPLIQUEE
AVENUE DE RANGUEIL, 31077 TOULOUSE CEDEX, FRANCE

E. MENTASTI

DIPARTIMENTO DI CHIMICA ANALITICA
UNIVERSITA DI TORINO
V. P. GIURIA 5, 10125 TORINO, ITALY

A. VERDIER

LABORATOIRE DE CHIMIE ORGANIQUE APPLIQUEE
INSTITUT NATIONAL DES SCIENCES APPLIQUEE
AVENUE DE RANGUEIL, 31077 TOULOUSE CEDEX, FRANCE

Abstract

We previously investigated the reactions of 1,2-dihydroxybenzene-3,5-disulfonic acid (Tiron) with metal ions for developing preconcentration techniques based on liquid-solid ion-exchange. The goals of these methods are the reduction of the detection limits and of matrix interferences in instrumental determinations, and their use in toxic metal removal from polluted waters. In this paper the effect

---

*To whom correspondence should be addressed.

of a cationic polyelectrolyte (Multifloc C 563, PROTEX) on the formation of iron-Tiron complexes and the effect on the behavior of such complexes in ultrafiltration experiments are investigated. Discontinuous ultrafiltration experiments were performed with neutral membranes, and metal-ligan, ligand-C 563, and metal-ligand-C 563 systems were investigated. The operational conditions and the resutls of metal ion retention and preconcentration are presented.

INTRODUCTION

The use of ultrafiltration for measurements of stability constants of metal complexes with ligands (*1-3*), such as its application in separation (*4, 5*) or removal of heavy metal ions (*6-8*) or organic compounds (*9-11*) from natural waters and other liquid medium, is well known. In previous studies on metal ion preconcentration (*12-14*) we found that complexes of metals with sulfonato ligands are more strongly retained than free ligands on anion-exchange resins, and the apparent stability constants of metal complexes with ligands bound on the resin are greater than those of the same unbound ligands, so the coordinating ability of Tiron in the resin may be increased. This fact was elucidated, and it was shown that ion-exchange resins (*15*) and cationic surfactants (*16*) modify the species distribution of metal-ligand complexes and the stability constants of ligands.

The chemistry of Tiron and its reaction with iron(III) have been extensively studied (*17*). This paper studies the efficiency of discontinuous ultrafiltration on the retention of iron-Tiron complexes as a function of pH and the influence of cationic polyelectrolyte on these equilibria.

EXPERIMENTAL

Instrumentation

Metal concentrations were evaluated by inductively coupled plasma atomic-emission spectrometry, ICP-AES (Plasma 300, Allied Analytical System). All measurements were made with background correction, and blanks were run between every sample.

Acidic oxidative digestions of the samples were performed with a microwave oven (WI 40, White-Westinghouse, maximum power 1350 W) equipped with pressure relief type Teflon-PFA vessels.

Polyelectrolyte (Protex C 563) concentrations were evaluated by TOC measurements (Ionix, Mod. 1254).

A batch ultrafiltration apparatus equipped with a stirred cell (Amicon M. 52) and Amicon YM 5 membranes (cut-off > 5000 MW) were used. The cell was thermostated at 25 ± 0.2°C.

Reagents

1,2-Dihydroxy-3, 5-benzenedisulfonic disodium salt (Tiron, T, C. Erba) was dissolved, 3.581×10^{-3} *M*, in ultrapure water (UW).

Polyammonium quaternary chloride (Protex C 563, P) solutions were prepared (8% v/v) in UW starting from an industrial rough product, mainly used as a flocculant in water treatment, without additional purification.

Standard solutions of Fe(III) (1.000 g/mL, metal concentration, C. Erba) were diluted to the desired concentrations with UW.

All other regents were analytical grade.

Procedure

All the samples were prepared and analyzed according to the following procedure.

1.675 mL Fe(III) (1.000 mg/L) was added to 50.0 mL Tiron (3.581×10^{-3} *M*) to create a 1:6 metal-to-ligand molar ratio. The samples were brought to the required pH at a final volume of 100.0 mL. Samples containing the polyelectrolyte were prepared by adding 25.0 mL P (8% v/v), previously brought to the desired pH. These samples were brought to 100.0 mL at constant pH and were stirred overnight to complete the P-T or Fe-P-T interactions.

Ultrafiltration was carried out in a batch-stirred cell equipped with nonionic membranes (Amicon YM 5). The effective membrane area was 12.5 cm^2, the feed volume was 50.0 mL, and the applied pressure was 2.0 bar, controlled by nitrogen gas. The membranes were washed by filtering about 50 mL UW; this procedure was found to eliminate organic and iron contaminations (*18*). The permeation rate of UW was measured both before and after the ultrafiltration of samples to verify the absence of fouling phenomena.

Samples (50.0 mL) were introduced in the ultrafiltration cell. Fractions, the first one of 5.0 mL and the following portions of 10.0 mL, were collected until the permeate volume reached 45.0 mL. The methods used to evaluate the concentrations of Fe, T, and P in the permeate and retentate (5.0 mL) were described above.

Fe(III): 0.5–2.5 mL samples were used in Fe(III) determinations. Some difficulties were associated with the matrix of the sample: the high viscosity, which allows incorrect values in ICP-AES determinations by modifying the sample flow rate, and the high content of organic matter, which interferes in atomization and spectrometric determinations, were overcome by a pretreatment. All samples were digested in a microwave oven after the addition of 2.0 mL of 30% H_2O_2 and 2.0 mL of 65% HNO_3 for half an hour at 40% power (540 W). The treatment was repeated twice, and the sample was diluted to the proper volume. Blanks were run in the same way and tested for a correct evaluation of sample concentrations.

P: 1.0 mL portions diluted to 100.0 mL were employed in TOC determinations. The evaluation of polyelectrolyte concentration was unaffected by the presence of Tiron.

T: 0.025 to 0.5 mL portions were added of 1.0 mL H_2SO_4 (1.0 *M*) and brought to 5.0 mL with UW. This treatment was required to avoid spectrophotometric interferences in the determination of Tiron concentration due to polyelectrolyte or metal ion interaction with the ligand.

RESULTS AND DISCUSSION

To avoid incorrect evaluations of the following results, preliminary experiments were performed to detect the retention of free species of metal ions and ligand. The retention of iron occurs only when high pH's are reached and can be attributed to the precipitation of hydroxylated species. This phenomenon does not interfere because, if one considers the complexes, the presence of Tiron avoids the formation of these species. In addition, it was also found that retention does not act on the free ligand, so the subsequent results can be attributed only to the interactions of the metal–ligand complexes with the membrane. The presence of surface tension activity and of surfactant micelle were also investigated for the concentrations of ligand and polyelectrolyte considered, and the results showed the absence of these phenomena.

The first set of experiments was performed to evaluate the efficiency of ultrafiltration with respect to the stoichiometry of the iron–Tiron complexes (Fe-T, Fe-T_2, and Fe-T_3). Samples (50.0 mL) at the same concentrations [$T = 1.79 \times 10^{-3}$ *M* and $Fe(III) = 2.98 \times 10^{-4}$ *M*] were ultrafiltered (see Procedure section) at different pH's. The selected pH values were 2, 5, and 9, which enabled us to operate in the presence of 1:1, 1:2, and 1:3 (metal-to-ligand ratio) complexes, respectively. Table 1 shows the behavior of T and Fe(III) concentrations in the ultrafiltrate and retentate fractions. For pH 2, in the presence of th Fe-T complex, a steady-state is reached between the permeate and the retentate, as evidenced by the homogeneous number of micromoles in each fraction. The release of the complex results in a poor recovery of iron.

From experiments at an increased pH, the effect of the modified stoichiometry of the complex on the percent of retention is evident. The higher values of recovery, 46 and 77% at pH 5 and 9, respectively, can be attributed to the steric configuration of th Fe-T_2 and Fe-T_3 complexes, with tetrahedral and octahedral as the most probable configurations. This geometry with a larger steric hindrance justifies a greater interaction with

TABLE 1
Tiron and Fe(III) Distribution (μmoles and relative %) in Ultrafiltrate (U) and Retentate (R) Fractions at Various pH Values

		Tiron		Fe(III)	
pH	Fraction[a]	μmoles	%	μmoles	%
2	U1	8.2	8.7	1.3	8.5
	U2	19.1	20.2	2.8	18.2
	U3	14.9	15.8	2.8	18.7
	U4	18.6	19.7	3.2	21.0
	U5	19.1	20.2	3.2	21.3
	R6	14.5	15.4	1.9	12.3
5	U1	6.1	6.6	0.5	3.1
	U2	13.7	14.7	1.3	8.0
	U3	15.0	16.1	1.6	9.8
	U4	16.0	17.2	2.0	12.3
	U5	20.2	21.7	3.4	20.9
	R6	22.1	23.7	7.5	46.0
9	U1	4.4	4.6	0.2	1.1
	U2	9.9	10.2	0.4	2.3
	U3	11.0	11.4	0.5	2.9
	U4	12.3	12.7	0.7	4.0
	U5	19.1	19.8	2.3	13.2
	R6	40.0	41.4	13.3	76.4

[a] U1 and R6, 5.0 mL; U2–U5, 10.0 mL.

the membrane and a higher recovery of iron. It must be pointed out that by increasing the pH, iron recovery is increased and the quantity of retained Tiron shifts from the equilibrium value to the stoichiometric value of the complex (Fe-T_3 for pH 9.0) in the retentate.

The second set of experiments was performed at the same pH's previously considered by adding a constant quantity of polyelectrolyte (see Procedure section), and the samples were prepared in order to show Fe-T-P interactions and to avoid T-P interactions. In fact, the polyelectrolyte (quaternary ammonium salt) is able to ion-pair with the sulfonato groups of the complexes or of the ligand, and in the last case the number of molecules of free Tiron available for iron complexation is reduced. On the other hand, it has been experimentally shown that when Fe-T and Fe-T_2 solutions, as characterized by different UV-visible absorption patterns, are mixed with polyelectrolyte solutions (pH 2 and pH 5, respectively),

TABLE 2
Tiron, Fe(III), and Polyelectrolyte Distribution (μmoles and relative %) in Ultrafiltrate (U) and Retentate (R) Fractions at Various pH Values

		Tiron		Fe(III)		P
pH	Fraction[a]	μmoles	%	μmoles	%	(%)
2	U1	0.6	0.6	0.7	4.7	2.9
	U2	1.3	1.4	1.8	12.2	3.4
	U3	1.7	1.8	1.7	11.5	4.1
	U4	3.1	3.2	1.7	11.5	5.7
	U5	9.8	10.2	1.5	10.1	15.2
	R6	79.6	82.8	7.4	50.0	68.7
5	U1	0.4	0.4	0.1	0.7	2.2
	U2	0.9	1.0	0.2	1.4	3.8
	U3	1.2	1.3	0.1	0.7	4.6
	U4	2.4	2.6	0.2	1.4	6.2
	U5	7.8	8.6	0.8	5.8	14.9
	R6	77.9	86.0	12.5	89.9	68.4
9	U1	0.2	0.2	0.0	0.0	1.2
	U2	0.3	0.3	0.1	0.6	2.2
	U3	0.4	0.4	0.1	0.6	2.9
	U4	0.8	0.8	0.1	0.6	3.7
	U5	4.8	5.0	0.5	3.0	8.6
	R6	89.5	93.2	15.9	95.2	81.4

[a] U1 and R6, 5.0 mL; U2–U5, 10.0 mL.

they show a color change corresponding to the formation of Fe-T_2 and Fe-T_3, respectively. This fact can only be attributed to a rearrangement of molecular distribution on the surface of the polyelectrolyte. Experimental results are shown in Table 2 for the ultrafiltration of Fe T-P systems at pH 2, 5, and 9. It is clear that the presence of polyelectrolyte improves iron retention, so that 50 and 95% of Fe(III) is recovered at pH 2 and 9, respectively. After taking into account these results and the preliminary considerations, T-P ultrafiltrations were also performed at the same concentrations and pH's used for the Fe-T-P systems. Comparison of the retention (%) of Tiron for T-P ultrafiltration (Table 3) with the results of Table 2 shows a quite similar retention of the ligand in T-P or Fe-T-P ultrafiltration. The T retention (%) fits with the values obtained for Fe-T-P systems. This fact suggests that the mechanism acting in the iron retention is the one previously considered. The quantity of Tiron retained at pH 2

TABLE 3

Tiron and Polyelectrolyte Distribution (μmoles and relative %) in Ultrafiltrate (U) and Retentate (R) Fractions at Various pH Values

pH	Fractions[a]	Tiron		P
		μmoles	%	(%)
2	U1	0.4	0.5	1.3
	U2	1.3	1.5	3.6
	U3	1.7	2.0	4.3
	U4	2.7	3.2	6.9
	U5	10.6	12.4	18.1
	R6	69.1	80.5	65.7
5	U1	0.3	0.3	2.0
	U2	0.9	1.0	4.7
	U3	1.5	1.6	4.7
	U4	2.9	3.1	7.3
	U5	11.4	12.2	9.3
	R6	76.4	81.8	72.0
9	U1	0.7	0.8	2.2
	U2	1.0	1.1	3.8
	U3	1.1	1.2	4.6
	U4	1.4	1.6	5.6
	U5	6.9	7.6	12.1
	R6	79.3	87.7	71.7

[a] U1 and R6, 5.0 mL; U2–U5, 10.0 mL.

TABLE 4

Polyelectrolyte Distribution (%) in Ultrafiltrate (U) and Retentate (R) Fractions at Various pH Values

	P (%)		
Fraction[a]	pH 2	pH 5	pH 9
U1	1.7	2.2	1.7
U2	4.1	4.6	3.8
U3	4.9	5.5	5.1
U4	7.2	7.8	5.4
U5	14.7	20.1	14.1
R6	67.5	59.8	69.9

[a] U1 and R6, 5.0 mL; U2-U5, 10.0 mL.

(Table 3) is larger than that required to originate the Fe-T complex, so if the retention is considered a function of the ion-pairing mechanism, a total recovery of iron is expected at this pH. The reduced recovery of Fe may be attributed to the fact that not all Fe-T is converted to Fe-T_2, and a stronger interaction with P occurs for the latter.

Because the concentration of P in the permeate and in the retentate may become a limiting parameter, ultrafiltrations were performed to evaluate its behavior. The results (Table 4) show that the permeate and retentate concentrations of P are the same in the corresponding fractions for all the conditions considered. The small quantities of P that flowed through may be attributed to the rough nature of the commercial product which contains low molecular weight units; however, these do not significantly affect the ultrafiltration performance.

CONCLUSIONS

The method is a powerful concentration technique for the recovery of heavy metals, and additional experiments on this promising approach are in progress.

In order to clarify the mechanism, we are synthesizing and testing new products with high and well-defined molecular weights which will furnish total retention in this ultrafiltration procedure.

Acknowledgment

Support from Consiglio Nazionale delle Ricerche, Italia, is acknowledged.

REFERENCES

1. W. F. Blatt, *Membrane Separation Processes* (P. Meares, ed.), Elsevier, Amsterdam, 1976, pp. 81-120.
2. J. Tuschall and P. L. Brezonik, *Anal. Chim Acta, 149,* 47 (1983).
3. J. Buffle and C. Staub, *Anal. Chem., 56,* 2837 (1984).
4. Q. T. Nguyen, P. Aptel, and J. Neel, *J. Membr. Sep. Sci., 6,* 71 (1980).
5. P. Masse, T. B. Choe, and A. Verdier, *Ann. Chim. (Rome), 77,* 925 (1987).
6. H. Strathmann, *Sep. Sci. Technol., 20,* 519 (1980).
7. F. Aulas, M. Rumeau, R. Renaud, and B. Tyburce, *Inf. Chim., 145,* 204 (1980).
8. T. B. Choe, P. Masse, J. Bonnet, C. H. Lee, and A. Verdier, *Tech. Eau, 15*(21), 438 (1983).
9. D. Bhattacharyya, J. L. Bewley, and R. B. Grieves, *J. Water Pollut. Control Fed., 46,* 2372 (1974).
10. E. Martins, M. Bengtsson, and G. Johansson, *Anal. Chim. Acta, 169,* 31 (1985).
11. M. Igawa, T. Tachibana, K. Yoshide, M. Tanaka, and M. Seno, *Chem. Lett. (Chem. Soc.. Jpn.),* p. 1527 (1984).
12. C. Sarzanini, E. Mentasti, M. C. Gennaro, and C. Baiocchi, *Ann. Chim. (Rome), 73,* 385 (1983).
13. C. Sarzanini, E. Mentasti, M. C. Gennaro, and E. Marengo, *Anal. Chem., 57,* 1960 (1985).
14. M. C. Gennaro, C. Sarzanini, E. Mentasti, and C. Baiocchi, *Anal. Chim. Acta, 174,* 259 (1985).
15. M. A. Shriadah and K. Ohzeki, *Analyst, 111,* 197 (1986).
16. K. Goto, S. Taguchi, K. Miyabe, and K. Haruyama, *Talanta, 29,* 575 (1982).
17. E. Mentasti, E. Pelizzetti, and G. Saini, *J. Inorg. Nucl. Chem., 38,* 785 (1976).
18. J. Buffle, P. Deladoey, J. Zumstein, and W. Haerdi, *Schweiz. Z. Hydrol., 44,* 325 (1982).

Received by editor June 26, 1989