Available online at www.sciencedirect.com

SCIENCE DIRECT®

Talanta 64 (2004) 190–195

Talanta

www.elsevier.com/locate/talanta

Cd(II) determination in the presence of aqueous micellar solutions

H.D. Fiedler*, J.L. Westrup, A.J. Souza, A.D. Pavei, C.U. Chagas, F. Nome

Departamento de Química, Universidade Federal de Santa Catarina, CEP 88040-900, Florianópolis, SC, Brazil

Received 26 November 2003; received in revised form 6 February 2004; accepted 6 February 2004

Abstract

The equilibrium constants and molar absorptivities for the fast formation of a 1:3 complex between cadmium(II) (Cd(II)) and dithizonate anion, in the presence of cationic and non-ionic surfactants, allowed a simple and fast spectrophotometric determination of total cadmium. Indeed, the molar absorptivities of the Cd(II)–dithizone (Dz) complex formed in the presence of the neutral Triton X-100 and cationic cetyltrimethylammonium bromide (CTAB) surfactants are almost twice the value observed in the standard method and the maxima of absorption are shifted by about 40 nm when compared with the standard method. Clearly, the use of neutral and cationic surfactants promotes a higher value of the molar absorptivities of the complex, resulting in an increase in the sensitivity of the method. Application of the method to the desorption of Cd(II) ions from clays is illustrated.

Keywords: Molar absorptivities; Cd(II); Dithizone complex; Surfactants; Aqueous micelles

1. Introduction

Micellar solutions help to incorporate selectively and, therefore, increase the solubility of organic dyes [1,2]. This compartmentalisation effect allowed the development of micellar chromatography [3], cloud point extraction [4] and substantial rate increases in a variety of reactions [5]. Besides, the increase of solubility permits the development of analytical methods in which the use of organic solvents and/or extraction steps are avoided. This last observation prompted us to use micellar solutions in the spectrophotometric method based on the reaction of cadmium and dithizone (Dz), which under controlled conditions, forms a rose colour that can be extracted with chloroform [6].

Cadmium, one of the most toxic non-radioactive element, is insidious and exhibits latent toxicity, and appears in the environment as a result of a variety of industrial processes. Availability of Cd(II) in the environment depends on a variety of factors which include pH, nature and concentration of ligands and complexing ions, type of sorbents present, ageing of the substrate and residence time of the metal ion at the surface and temperature [7].

Although inorganic complexation reactions reach equilibrium quickly in natural waters, some sorption and desorption processes at surfaces are slower and sometimes diffusion limited, reflecting differences in concentration and chemistry of natural waters processes [7–9]. In this sense, hydrated oxides of Al, Fe, Mn and aluminosilicates such as clays are ubiquitous in the aqueous environment, and their surface physicochemical properties affect and control a variety of phenomena, including dissolution, precipitation and sorption processes. Thus, kinetics and thermodynamic parameters of the interaction of aqueous solutions with mineral surfaces affect the composition, pH buffering and quality of natural waters, the formation of soil and the mobility of heavy metal contaminants [10–13]. It is important to remark that, due to the importance of the interactions described above, typical operational procedures for metal ion speciation in soils and sediments depend heavily on the kinetics of the extraction procedure [7–9, 14–17].

Thus, the present work describes the complexation reaction between cadmium(II) and dithizone in the presence of neutral and cationic surfactants, such as Triton X-100 and

---

* Corresponding author. Tel.: +55-48-331-9230;
fax: +55-48-331-9711.
E-mail address: fiedler@qmc.ufsc.br (H.D. Fiedler).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.02.008

cetyltrimethylammonium bromide (CTAB), respectively, and illustrates how the method can be used to examine the kinetics of desorption of Cd(II) from a montmorillonite clay.

2. Experimental section

2.1. Materials

A standard solution of cadmium (1 mg ml^{-1}) was prepared by dissolving ≈1.0 g pure cadmium p.a. (Vetec) in 1000 ml water, containing 2% of concentrated HNO_3 (nitric acid 70% Carlo Erba). Calibration solutions were prepared daily by appropriate dilution of metal stock solutions and all the analytical procedures were done in a laminar flow hood (TROX®-100 class).

Surfactants Triton X-100 (Sigma), sodium dodecylsulfate (SDS) (Sigma) and cetyltrimethylammonium bromide (Aldrich) were the best available reagent grades and were purified as described elsewhere [5]. Surface tension versus concentration measurements showed no minima in all cases [5].

Doubly deionised water with conductivity less than 17.3 μS cm, obtained from a Nanopure™ Analytical Deionization System (type D-4700) was used to prepare the standard solutions and reagents. All vessels in contact with samples or reagents were cleaned by soaking in 5.8 mol l^{-1} HNO_3 (overnight) and rinsed repeatedly with deionised water before use.

2.2. Instrumentation and methods

Spectrophotometric measurements were carried out at 25 ± 0.1 °C, in the water-jacketed cell compartments of both HP-8453 diode array and Shimadzu UV-210A spectrophotometers, which were calibrated with NIST traceable UV-Vis reference materials. Surface tension measurements were carried out by use of a surface tensiometer based on the drop weight method.

The pH was measured with a Beckman model Φ71 pH meter. The glass electrode was calibrated against standard buffers in a thermostatic stirred vessel at a temperature of 25.0 ± 0.1 °C. The pH of the buffers was adjusted to the desired value with NaOH.

In all the desorption experiments, the Cd(II) concentration was determined by mixing 1 ml of the filtered sample with 2 ml of 3 M NaOH and 2 ml of an aqueous solution of Triton X-100 5% containing 3.0 × 10^{-4} M dithizone. The final volume was completed to 10 ml and the absorbance of the samples were determined at 549 nm.

2.3. Desorption experiments

The desorption experiments were carried out after an initial incubation time of 24 h in conditions similar to those described above. The desorption was started by adding 25 ml of a background electrolyte consisting of 0.10 M citrate buffer and the suspensions were kept at 25 °C in the same thermostatic bath and conditions of the sorption experiments. The citrate buffer effectively complexes all the desorbed Cd(II) ion, preventing back adsorption of the metal in the clay surface (see below). Samples collected at different times were filtered through 0.45 μm membranes and the desorbed Cd(II) ions were determined as described above.

3. Results and discussion

3.1. Complexation of Cd(II) and dithizone

It is well known that cadmium ions react with dithizone to form a pink to red complex, which is insoluble in water and soluble in chloroform. The stoichiometry of such a complex corresponds to 1 mol of Cd(II) reacting with 2 mol of dithizone [6]. The results obtained for the complex formation reaction between Cd(II) and dithizone, followed spectrophotometrically at constant concentration of total Cd(II) and in the presence of cationic and non-ionic surfactants, in the aqueous pseudophase, are given as a function of pH in Fig. 1. Under the experimental conditions, dithizone and its conjugate base should bind quantitatively to the micelle so its deprotonation depends only on the acid dissociation constant and deprotonating power in the micellar pseudophase. Upon reaction, the hydrophobic Cd(II) dithizone complex should be readily incorporated in the micellar phase. As can be seen, the results show that the absorbance at 540 nm increases as a function of pH, reaching a maximum at about pH 13 for both Triton X-100 and CTAB. It is important to remark that, for the quantitative complexation of Cd(II), the pH in solution should be greater than 13, most probably dithizonate anion is the reactive species in the complex formation reaction.

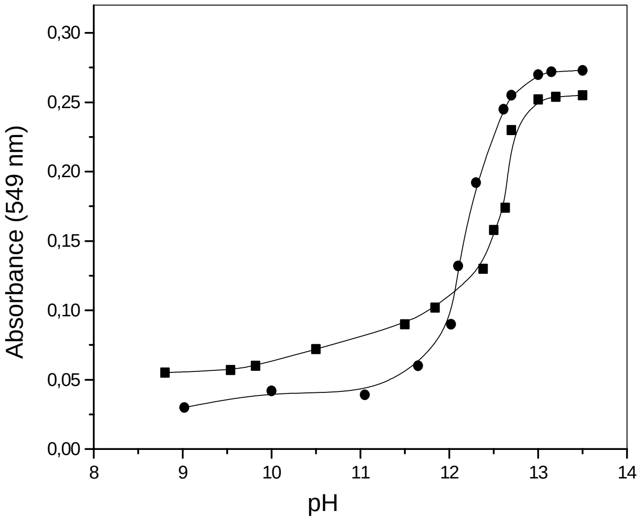


Fig. 1. Absorbance of the cadmium dithizonate complex as a function of pH in the presence of (●) 0.02 mol l^{-1} CTAB and (■) 1% Triton X-100.

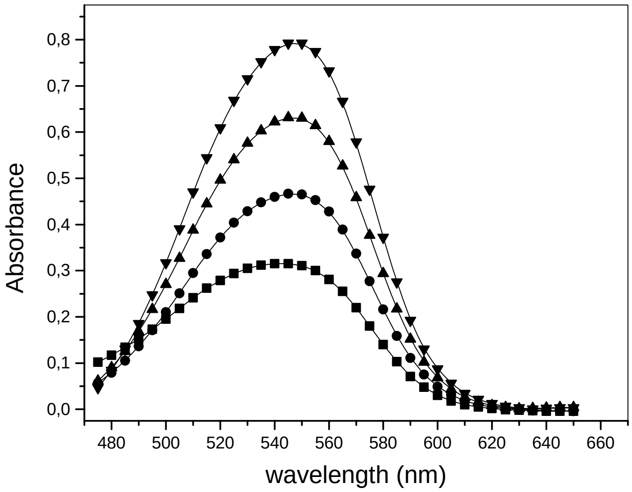


Fig. 2. Visible spectra obtained for samples containing (▼) 1.04×10^{-5}, (▲) 0.83×10^{-5}, (●) 0.63×10^{-5} and (■) 0.41×10^{-5} mol l^{-1} Cd (II), after attainment of equilibrium, in the presence of 6.0×10^{-5} mol l^{-1} dithizone at pH 13 and temperature 25 °C, CTAB.

When SDS was used as surfactant, the absorbance for the reaction did not reach a similar plateau and the reaction was not studied in detail due to the instability of the complex formed. Experiments in the plateau region, for both CTAB and Triton X-100 show that in the presence of an excess of dithizone, the absorbance increases as a function of Cd(II) concentration (Fig. 2) and, at fixed Cd(II), the absorbance increases as a function of concentration of dithizone (Fig. 3a). Indeed, as shown in Table 1, the molar absorptivities of the Cd(II) dithizone complex formed in the presence of the neutral and cationic surfactant are almost twice the value observed in sodium dodecyl sulfate and, the maxima of absorption in Triton X-100 and CTAB are also shifted by about 40 nm when compared with the standard method, which gives a molar absorptivity of 58,600 l mol^{-1} cm^{-1} at 518 nm.

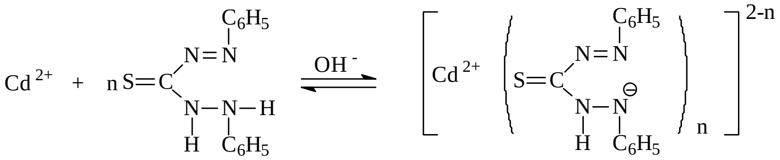
Clearly, the use of cationic or neutral surfactants promotes a higher value of the molar absorptivities of the complex, resulting in an increase in the sensitivity (lower limit of detection) of the method.

Table 1
Molar absorptivities, wavelengths of maximum absorption and limits of detection for the Cd(II) determination with dithizone in the presence and absence of surfactants

	Wavelength (nm)	Molar absorptivity	Limit of detection (mol l^{-1})
Triton X-100	549	78,350	2.6E−7
CTAB	549	82,500	4.0E−7
SDS	510	44,670	–
Standard method	518	58,600	6.0E−7

Interactions of hydrophilic ions, e.g. OH$^-$, with ionic micelles are probably governed largely by Coulombic forces and should, to a crude approximation, follow the exponential of the charge density at the micellar surface. As a result, counterion concentrations at micellar surfaces are high and fall sharply with distance [5]. Thus, if we make the simplifying assumption that the indicator pK_a is the same in water and in the micelles, we can predict that addition of the cationic surfactant should increase the concentration of hydrophilic anions, e.g. OH$^-$, at surfaces of cationic micelles, while addition of SDS obviously results in a negative charge density at the micellar surface, and should decrease the concentration of OH$^-$ and pH$_{app}$ [5]. Thus, SDS prevents the formation of the dithizonate anion, while the formation of the conjugated base of dithizone is favoured in cationic surfactants.

As expected, the increase of absorbance as a function of the concentration of dithizone observed in Fig. 3a is consistent with the formation of the cadmium dithizonate complex as shown in Eq. (1), where n indicates the stoichiometry of the reaction.



(1)

Using the data shown in Fig. 3a, for the variation of the absorbance with the increase of the concentration of dithizone, it was possible to study the equilibrium represented in Eq. (2), where the parameters n and K_{eq} are related to the equilibrium concentrations of the different chemical species involved in the reaction. From Eq. (1) it is possible to derive Eq. (2),

$$\log\left(\frac{A_{int}}{A_{com} - A_{int}}\right) = \log K_{eq} + n \log[\mathrm{Dz}]_{free} \qquad (2)$$

where the slope and intercept allow the calculation of the stoichiometry in relation to dithizone (n) and the equilibrium constant (K_{eq}). The terms A_{int} and A_{com} refer to the absorbances of solutions where Cd(II) has been either partially or totally complexed by the Dz ligand, respectively. Linear plots derived from the curves of Fig. 3a are presented in Fig. 3b for the surfactants Triton X-100 and CTAB. It is important to remark that while the determination of n is not affected by the presence of micelles in solution, the equilibrium constant in Eq. (2) corresponds to an apparent equilibrium constant, including all the compartmentalisation effects normally observed in micellar systems [5].

The data calculated from the plots shown in Fig. 3b are contained in Table 2, showing that the stoichiometry of the reaction is consistent with the reaction of 1 mol of cadmium(II) ion with 3 mol of the dithizonate anion. The observed complex formation in the presence of micelles shows

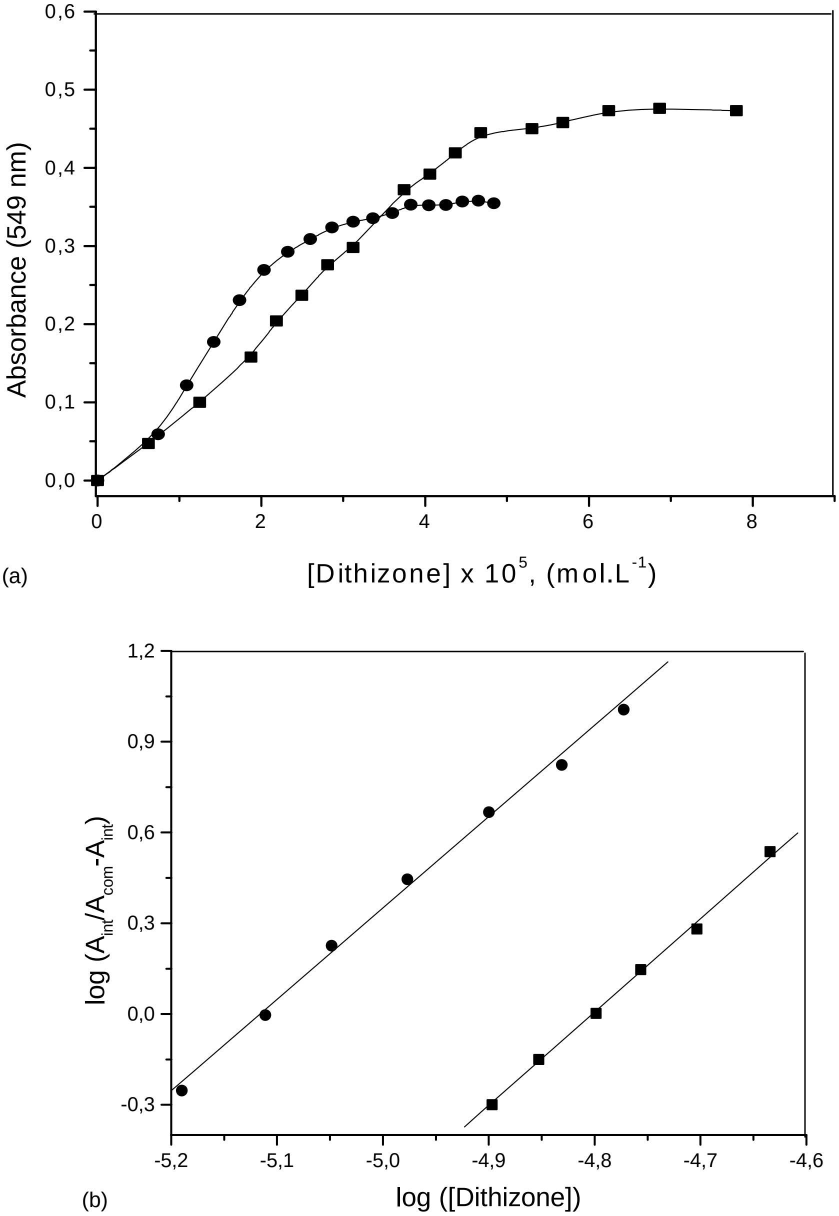


Fig. 3. (a) Absorbance of the cadmium dithizonate complex as a function of the concentration of dithizone in solutions containing (●) 4.29×10^{-6} mol l^{-1} Cd(II), in the presence of 0.02 mol l^{-1} CTAB and (■) 6.04×10^{-6} mol l^{-1} Cd (II) and 1% Triton X-100 and (b) logarithmic plot of the concentration ratio of complexed and free Cd(II) ion as a function of the concentration of dithizone, in the presence of (●) 0.02 mol l^{-1} CTAB and (■) 1% Triton X-100.

a different complex formation than that observed in the traditional procedure, which is 1:2. Thus, the characteristic physicochemical properties of the micellar interface promote changes in both the sensitivity and the wavelength of maximum absorption, through the formation of a formally different cadmium dithizonate complex. Clearly, the increase in equilibrium constant and the higher value of the molar absorptivities are the result of the change in the structure of the complex. Thus, the micellar promoted increase in sensitivity of the method is not the result of a typical micellar effect on molar absorptivities, but the result of the micelle favouring the formation of a different complex between Cd(II) and dithizone.

Table 2
Equilibrium parameters observed for the complexation of Cd(II) and dithizone

Parameter	$\log K_{eq}$	n
Triton X-100	14.82	3.08
CTAB	15.45	3.02

3.2. Desorption of Cd(II) from montmorillonite

As should be expected, the adsorption and desorption of the metals depends strongly on the nature of the clay mineral

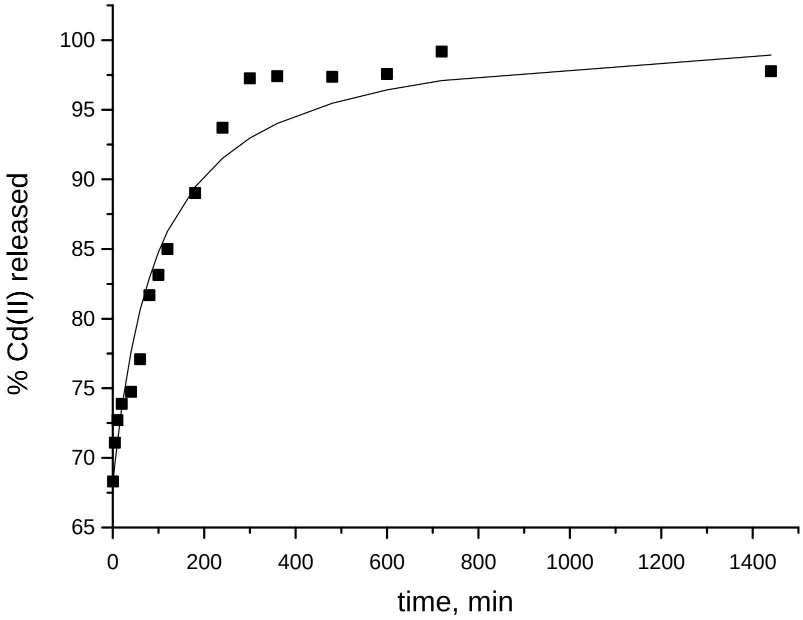


Fig. 4. Desorption of Cd(II) at 25 °C and pH 7.0, in the presence of 0.1 mol l^{-1} citrate buffer from montmorillonite (●) samples.

and on the concentration of the chemical species present in solution, which acting as complexants can promote desorption of the metal ion or enhancement in the adsorption [7–9]. Since citric acid complexes Cd(II) with a reasonably high stability constant ($\log K = 3.66$ at 25 °C, $\mu = 0.1$) the decrease in free metal ion in solution and the capability of the complexant to retain Cd(II) in solution allowed the study of the desorption of Cd(II) from the clay's surfaces [14–17].

Fig. 4 shows the desorption process of Cd(II) for montmorillonite. It can be seen that montmorillonite shows a fast release of 70% of the sorbed Cd(II), followed by a slow process that reaches equilibrium in around 400 min. Clearly, the fast step of the observed kinetic behaviour must be the desorption from the readily available sites on the surface of montmorillonite, while the slow process must correspond to the release of Cd(II) from sites on the interior of the solid clay, via either a pore diffusion model or a homogeneous solid phase diffusion model. The desorption kinetics are consistent with the physical data, since montmorillonite has a highly microporous structure and has a large number of Si sites exposed to the solution due to its interlayer expansion, which account for 97% of the available sites in the montmorillonite clay [18].

4. Conclusions

The proposed method shows a good repeatibility and recovers the added Cd(II) quantitatively. The favourable equilibrium constants and increased molar absorptivities of the fast formation of the Cd(II) dithizonate complex, in the presence of cationic and non-ionic surfactants, result in a simple and fast spectrophotometric method for the determination of total cadmium that can be conveniently adapted to flow or other in-line processes, besides being of general utility to study desorption of Cd(II) ions from clays.

Acknowledgements

The authors are grateful to PRONEX, CNPq and Capes for financial support.

References

[1] F. Nome, S.A. Chang, J.H. Fendler, J. Chem. Soc., Faraday Trans. 72 (1976) 296.
[2] J.R. Escabi-Perez, F. Nome, J.H. Fendler, J. Am. Chem. Soc. 99 (1977) 7749.
[3] D.W. Armstrong, F. Nome, Anal. Chem. 53 (1981) 1662.
[4] M. Mesquita, V. Frescura, A.J. Curtius, F. Nome, Anal. At. Spectrom. 13 (1998) 1369.
[5] C.A. Bunton, F. Nome, F.H. Quina, L.S. Romsted, Acc. Chem. Res. 24 (1991) 357.
[6] M.A.H. Franson, L.S. Clesceri, A.E. Greenberg, A.D. Eaton (Eds.), Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, USA, 1998.
[7] A. Tessier, D.R. Turner (Eds.), Metal Speciation and Bioavailability in Aquatic Systems, IUPAC, Wiley, Oxford, UK, 1995.
[8] W. Stumm, J.J. Morgan, Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters, third ed., Wiley, New York, 1996.
[9] R.A. Nome, C.M. Martinez, F. Nome, H.D. Fiedler, Environ. Toxicol. Chem. 20 (2001) 693.
[10] G.E. Brown Jr., V.E. Henrich, W.H. Casey, D.L. Clark, C. Eggleston, A. Felmy, D.W. Goodman, M. Grätzel, G. Maciel, M.I. McCarthy, K.H. Nealson, D.A. Sverjensky, M.F. Toney, J.M. Zachara, Chem. Rev. 99 (1999) 77.
[11] G. Attard, C. Barnes, Surfaces, Oxford University Press, UK, 2001 (Chapter 1).

[12] G.E. Brown Jr., Science 294 (2001) 67.

[13] A.G. Howard, Aquatic Environmental Chemistry, Oxford University Press, UK, 1998.

[14] W.F. Pickering, Ore Geol. Rev. 1 (1986) 83.

[15] Ph. Quevauviller, G. Rauret, H. Muntau, A.M. Ure, R. Rubio, J.F. Lopez-Sanchez, H.D. Fiedler, B. Griepink, Fresenius J. Anal. Chem. 349 (1994) 808.

[16] H.D. Fiedler, J.F. López-Sánchez, R. Rubio, G. Rauret, Ph. Quevauviller, A.M. Ure, H. Muntau, Analyst 119 (1994) 1109.

[17] J.F. López-Sánchez, A. Sahuquillo, H.D. Fiedler, R. Rubio, G. Rauret, H. Muntau, Ph. Quevauviller, Analyst 123 (1998) 1275.

[18] P.C. Schulthess, P.C. Huang, Soil Sci. Soc. Am. J. 54 (1990) 679.