

Retention of Some Metal Ions and Their Separation on Silica Gel Modified with Acid Red 88

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Abstract. Acid Red 88 is strongly extracted by chloroform solutions of Aliquat 336 by an ion exchange mechanism and for its reextraction from the ion pair formed, relatively high concentrations of mineral acids are required. By impregnation of silica with the ion pairs between the cation of Aliquat 336 and the anion of the dye a chelating sorbent for metal ions can be obtained. The sorbent prepared may be successfully used for separation of mixtures of various metal ions by the column extraction chromatography technique, additional purification of sodium and potassium salts from ions of heavy metals and for concentration of trace amounts of ions of various metals from aqueous solutions followed by their quantitative determination. The sorbent can be used repeatedly in the process of sorption and desorption of metal ions (especially those forming less stable complexes with the reagent) after regeneration with solutions of perchloric acid.

Key words: Acid Red 88; chelating sorbent; extraction chromatography; purification of alkali metal salts.

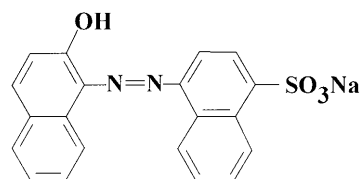
Recent progress in the chemical analysis of trace metals is mainly connected with the evaluation and improvement of various separation and trace concentration methods among which the extraction and chromatographic techniques are frequently applied. These techniques are simple to use and allow the simultaneous preconcentration and separation of the studied traces.

In the trace analysis of metal ions an important role is played by solid and liquid ion exchangers and the so-called chelating sorbents prepared on their basis [1]. Many methods for the preparation of chelating sorbents have been presented in the monographs of

Myasoedova and Savvin [2], Mizuike [3] and Braun and Ghersini [4]. Chemically modified silica has also found wide applications [5]. Chelating sorbents can also be prepared in a simple way by impregnation of silica with ion pairs formed by an alkylammonium salt (cation) and the anion of the sulfonated chelating reagent [6]. In this way, a number of new chelating sorbents has been prepared and investigated for numerous metal cations. Sorbents containing some sulfonated dihydroxyazo dyes such as Eriochrome Black T [7], Calconcarboxylic acid [8] and Calcon [9] have been proposed as sorbents in the trace analysis of metal ions. They can be used for preconcentration of trace amounts of these ions, for their separation from macroamounts of other metal ions and for the separation of their mixtures by column extraction chromatography.

Sulfonated monohydroxyazo chelating reagents have not been used so far to prepare this type of sorbent. Because these reagents also form complexes with metal ions, we decided to use them to prepare analogous sorbents.

This paper presents the results of investigations of liquid-liquid extraction of Acid Red 88 by solutions of Aliquat 336 in chloroform and the possibility of application in trace analysis of metals ions of a new sorbent formed by impregnation of silica with ion pairs obtained in the extraction process.



Acid Red 88

Experimental

All experiments were performed at room temperature (20 ± 1 °C).

Reagents and Solutions

Aliquat 336 (General Mills Chemicals, Inc., USA) containing 93% (m/m) quaternary alkylammonium chloride was purified from iron by shaking a 0.1 mol L^{-1} solution in chloroform with an equal volume of 0.1 mol L^{-1} hydrochloric acid and subsequently five times with distilled water and then by filtering the organic phase through a cellulose filter.

Acid Red 88 (Aldrich, Germany), was recrystallised from ethanol before use. Silica gel 100 (0.063–0.2 mm) (Merck, Darmstadt, Germany), previously fractionated (the fraction of particle size 0.1–0.2 mm being collected) and purified from iron in the manner described previously [10], was used as support for the stationary phase.

Aqueous metal solutions were prepared by dilution of Titrisol standard metal salt solutions (Merck). Working solutions were freshly prepared from standard metal salt solutions by dilution with doubly distilled water previously adjusted to an appropriate pH value with 1 mol L^{-1} hydrochloric acid (pH 1), acetate buffer (pH 3 and 6), tetraborate buffer (pH 9) or sodium hydroxide (pH 12).

Freshly distilled chloroform of analytical grade was used as diluent of Aliquat 336.

Solutions of HClO_4 and HCl (Suprapur, Merck) were used as eluents.

Apparatus

A double-beam UV-VIS recording spectrophotometer Specord M 40 (Zeiss, Jena, Germany) with 1-cm quartz cells was used for spectrophotometric measurements.

A Pye Unicam (Cambridge, UK) single-beam atomic absorption spectrometer was used for the determination of the metals, except Al, which was determined by spectrophotometry with Alizarin Red S at 500 nm, using a Spekol 11 visible spectrophotometer (Zeiss, Jena, Germany). All pH measurements were performed with a Mera-Elwro N517 (Wrocław, Poland) direct-reading pH meter, a glass-silver/silver chloride combination electrode. A voltammetric analyser UPE-2a (Radius, Gdańsk, Poland) was used in the determination of trace amounts of Pb, Cd, Cu and Zn in NaCl solution by anodic stripping voltammetry. A graphite electrode, impregnated with epoxy resin and coated with a mercury film *in situ*, was used as a working electrode having a working area of 12.5 mm^2 . The details of the preparation of this electrode have been described by Sykut et al. [11].

Procedure

Extraction of Acid Red 88 was performed by shaking for 15 min equal volumes of the acidic or alkaline aqueous reagent solution (previously adjusted to an appropriate pH value) and the chloroform solutions of Aliquat 336 in cylindrical separating funnels. After separating the phases, the lower (organic) phase was filtered through a cellulose filter to remove the remaining aqueous solution and the aqueous phase was centrifuged. Acid Red 88 was determined in the aqueous phase spectrophotometrically ($\lambda_{\text{max}} = 505 \text{ nm}$) on the basis of appropriate calibration graphs. Concentration of the dye in the organic phase was calculated from the difference between the dye concentration in the initial aqueous solution and its concentration in

the aqueous phase after the extraction. Stripping (reextraction) of the dye from the organic phases with aqueous solutions of mineral acids was performed in the following manner: 5 mL of the organic solution was shaken for 10 min with equal volumes of appropriate aqueous acid solutions. The aqueous phase was subsequently centrifuged and the dye was then determined spectrophotometrically at 505 nm.

The impregnating solution was prepared by shaking an appropriate volume of a 0.01 mol L^{-1} solution of Aliquat 336 in freshly distilled chloroform with 5 volumes of a 0.001 mol L^{-1} aqueous solution of Acid Red 88. After separating the phases, the organic phase was passed through a cellulose filter to remove the residual aqueous phase. Silica gel was impregnated with a chloroform solution of a mixture of Aliquat 336 and Acid Red 88 in the following manner: A 200 mL portion of the organic solution (containing 1 mmol of dye and 2 mmol of Aliquat 336) was mixed with 8.82 g of silica gel. The diluent was then removed with use of a vacuum evaporator on a water-bath. A 1 g amount of the chelating sorbent obtained contained 0.1 mmol of Acid Red 88 and 0.2 mmol of Aliquat 336.

Small polypropylene columns (55 mm × 5 mm) (J. T. Baker, Phillipsburg, NJ, USA) were packed with 0.4 g of dry sorbent and used to measure the relative capacity of the sorbent towards different metal ions. A 5 mL portion of each solution (previously adjusted to an appropriate pH), containing 0.5 mg of the metal to be determined, were passed through each column for 5 min. Each percolate was analysed to determine the residual metal ion concentration.

Columns (65 mm × 13 mm) packed with 5 g of dried sorbent were used to study the separation of metal ion mixtures. After conditioning the column with 1 mL of Michaelis buffer solution of pH 7, 10 mL of the synthetic solution at pH 7, containing 100 µg of each separate metal ion, were passed through the column. The metals were then eluted with HClO_4 solutions, and the eluate was collected in 5 mL fractions.

Voltammetric determinations of the metals were performed by passing 10 mL of 0.5 mol L^{-1} NaCl through columns packed with 1 g of the sorbent. Standard solutions of Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} were also introduced (the concentration of each metal ion added in the solution was then 20 µg/mL). The solutions were electrolysed for 3 min. at -1.3 V . Anodic oxidation of the metals was performed with a change in potential of $10 \text{ mV} \cdot \text{s}^{-1}$. Oxygen was removed by bubbling the solutions with high-purity argon.

Elution of Acid Red 88 from the sorbent with aqueous solutions of mineral acids was performed in the following manner: A 0.1 g amount of the obtained sorbent was shaken for 10 min with 5 mL of an appropriate acid solution in small tubes. The solution was subsequently centrifuged and the dye was determined by spectrophotometry at 505 nm with reference to a calibration graph.

Results and Discussion

Liquid-Liquid Extraction of Acid Red 88

The main purpose of the experiments were the preparation of a chelating sorbent containing Acid Red 88 and the investigation of its properties. However, it seemed interesting to carry out liquid-liquid extraction experiments in the system chloroform – water – liquid anion exchanger Aliquat 336 (tricaprylmethylammonium chloride) to investigate the molecular

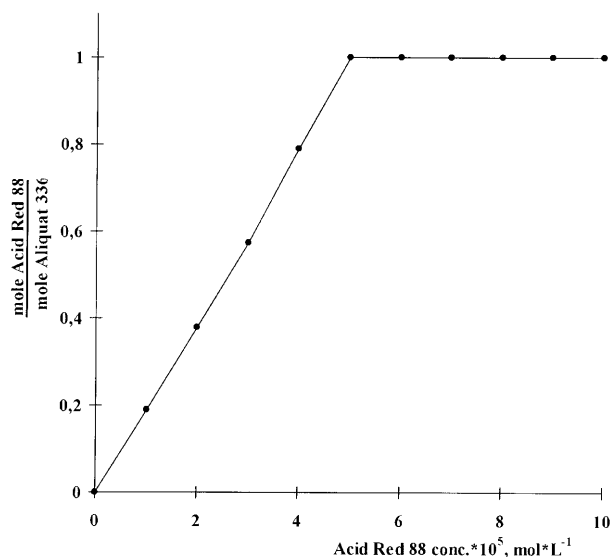
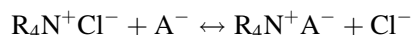


Fig. 1. Mole ratio of Acid Red 88 Aliquat 336 vs. dye concentration in the initial aqueous solution. Extractant $-5 \cdot 10^{-5}$ mol L $^{-1}$ Aliquat 336 in chloroform

mechanism of extraction to determine the stoichiometry of the ion pairs formed and their stability.

The absorption spectra of aqueous solutions of Acid Red 88 are almost identical (shapes and absorption maxima) in the whole pH range (1–12). Similar spectra are also obtained for the organic phases after extraction. It means that irrespective of pH only the sulfonic group of the colour reagent is dissociated. Since chloroform does not extract the reagent, the process of extraction by Aliquat 336 can be described by ion exchange:



where $R_4N^+Cl^-$ denotes Aliquat 336 and A^- the Acid Red 88 anion.

The ion exchange process of the extraction of the reagent is also confirmed by Fig. 1: the maximal amount of moles of the dye corresponding to 1 mol of Aliquat 336 is equal to 1, irrespective of pH of the initial aqueous solution.

The investigations of reextraction of Acid Red 88 from the ion pairs formed in the organic phase by solutions indicate that while the reextraction by solutions of perchloric acid occurs already at relatively low concentrations of acid (which is in agreement with the high affinity of ClO_4^- ions to the tetraalkylammonium cation), the reextraction with other mineral acids requires high concentrations of the acids (Fig. 2).

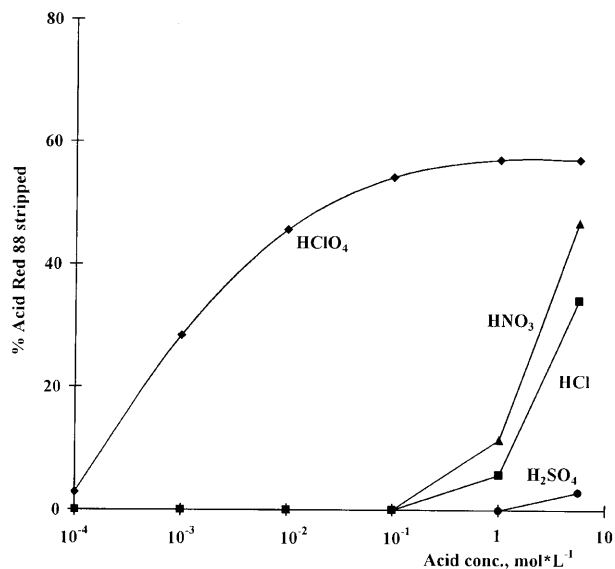


Fig. 2. Percent of Acid Red 88 stripped from the organic phase after extraction with aqueous solutions of mineral acids. The concentration of dye in the initial aqueous solution was 10^{-4} mol L $^{-1}$. Extractant -10^{-4} mol L $^{-1}$ Aliquat 336 in chloroform

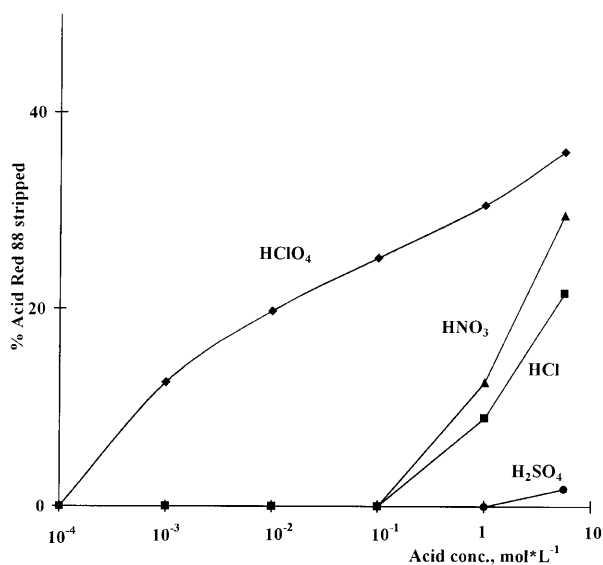


Fig. 3. Percent of Acid Red 88 stripped from the organic phase after extraction with aqueous solutions of mineral acids. The concentration of dye in initial aqueous solution was 10^{-4} mol L $^{-1}$. Extractant $-2 \cdot 10^{-4}$ mol L $^{-1}$ Aliquat 336 in chloroform

It follows from Fig. 3 that double increase of amount of Aliquat 336 in the extraction process markedly increases the concentrations of acids required for reextraction of Acid Red 88.

Extensive extraction of the dye by Aliquat 336 is indicated by high values of extraction coefficient and their high values of percent extraction in Table 1.

Table 1. Distribution coefficient (D) and extraction percentage (%E) of Acid Red 88 with Aliquat 336 in chloroform

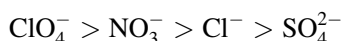
Initial solutions		D pH 1–12	%E
Concentration of Acid Red 88 in aqueous solution mole L ⁻¹	Concentration of Aliquat 336 in chloroform mole L ⁻¹		
10 ⁻⁴	10 ⁻⁴	660	99.8
10 ⁻⁴	2*10 ⁻⁴	870	99.9

Since in the formation of ion pairs with alkylammonium cations only the sulfonic group of the reagent is engaged, the ion pairs formed retain the ability to form complexes with metal ions and can be used to impregnate silica in order to prepare the chelating solvent.

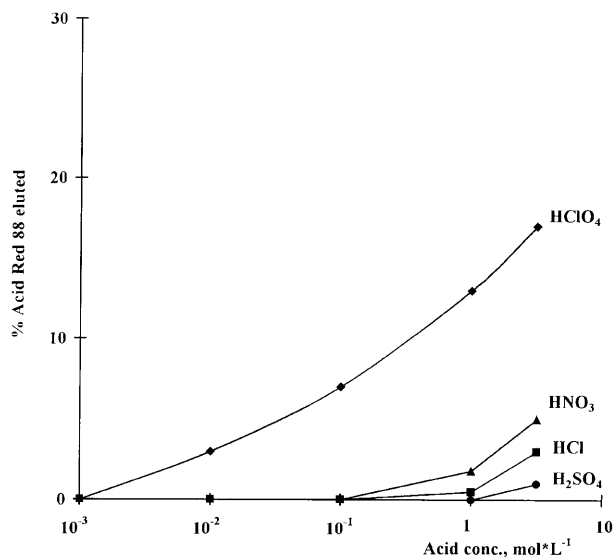
Investigation of Sorption and Elution of Chosen Metals on the Acid Red 88 Sorbent

The chemical formula of the reagent (a single sulfonic group in the molecule) suggested, which was confirmed in the study of liquid-liquid extraction, that the ion pairs are formed in the stoichiometric ratio of the reagent and alkylammonium cation equal to 1:1. However, the organic phase used to prepare the chelating sorbent contained a double amount of Aliquat 336 in comparison to the stoichiometric amount since the surplus of Aliquat 336 plays an essential role in the process of binding the ion pairs to the silica surface.

In the investigations of elution of Acid Red 88 from the sorbent it was found that the concentrations of the mineral acids at which elution of the dye starts are different (Fig. 4). The result is analogous to other sulfonated chelating reagents, where the elution of reagents required considerably higher concentrations of acids than for reextraction of these reagents from the ion pairs formed in the extraction process (Fig. 3). The sequence of the affinity of the alkylammonium cation to inorganic anions has also been confirmed; it is equivalent to the sequence of abilities of these anions to displace the chelating reagents from the ion pairs formed with Aliquat 336:



The investigations of the sorption of ions of 14 metals chosen on the sorbent show that the relative

**Fig. 4.** Percent of Acid Red 88 eluted from silica gel impregnated with a mixture of Aliquat 336 and Acid Red 88 as a function of concentration of mineral acids used as eluents. 0.1 g of the sorbent contained 10 micromoles of Acid Red 88 and 20 micromoles of Aliquat 336**Table 2.** Relative capacities of the sorbent toward metal ions ($\mu\text{mol}\cdot\text{g}^{-1}$) determined by dynamic method at flow rate of $1\text{ mL}\cdot\text{min}^{-1}$ and the minimal concentrations of acid (mol L^{-1}) required for elution. One gram of the chelating sorbent contained 0.1 mmol Acid Red 88 and 0.2 mmol Aliquat 336

Metal	Sorption at pH				Elution	
	1	3	6	9	HClO ₄	HCl
Na	0.0	0.0	0.0	0.0	–	–
K	0.0	0.0	0.0	0.0	–	–
Ca	0.0	0.0	3.3	24.5	0.0001	0.0001
Mg	0.0	0.0	3.6	26.2	0.0001	0.0001
Al	0.0	0.0	1.2	12.4	0.0001	0.005
Cu	0.3	3.2	7.4	12.1	0.01	0.05
Fe(III)	3.9	*	*	*	0.1	0.5
Ni	0.0	3.4	6.6	11.3	0.001	0.005
Co	1.4	6.3	9.8	15.1	0.01	0.1
Cd	0.0	0.0	6.6	11.7	0.0005	0.001
Zn	0.0	0.0	5.6	16.2	0.0005	0.001
Cr(III)	0.0	1.7	8.5	17.5	0.005	0.01
Mn	0.0	0.0	1.8	7.6	0.0005	0.001
Pb	0.0	2.0	6.4	12.1	0.005	–

*-Hydrolysis.

sorption capacity increases with the pH of the aqueous solutions of these ions. At the same time, the pH values at which the sorption of ions of the metals begins are quite different. The concentrations of acids (HClO₄ and HCl) at which the elution of the retained ions starts are also different (Table 2). The metal ions which form with Acid Red 88 complexes of lower

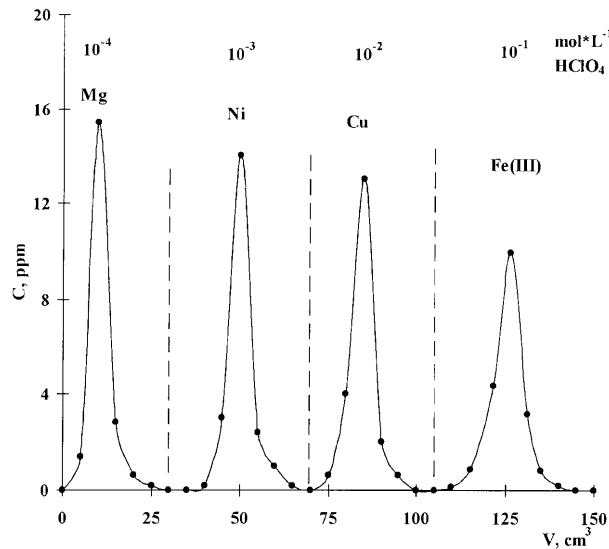


Fig. 5. Separation of metal ion mixtures containing 100 μg of each metal ion, on silica gel treated with a mixture of Aliquat 336 and Acid Red 88. Columns packed with 5 g of sorbent. Mean flow rate: $1 \text{ mL} \cdot \text{min}^{-1}$

stability (e.g. Ca, Mg, Cd, Zn) are eluted by very dilute solutions of acids; on the other hand, for the elution of metal ions which form more stable complexes (Cu, Co and especially Fe(III)) more concentrated solutions of acids should be applied. Different concentrations of perchloric acid required for the elution of metal ions may be utilized for the separation of some mixtures of the metals.

An example of such extraction-chromatographic separations of (synthetic) mixtures on a column with the sorbent investigated by stepwise elution with solutions of perchloric acid is illustrated in Fig. 5. The peaks are quite sharp and the recovery of the metals is 98.0–98.5%. Hydrochloric acid is less suitable for this purpose, since it forms anionic chloride complexes with many metals sometimes of high stability which considerably complicates the separation process.

One experiment was performed for the separation and preconcentration of traces of some heavy metals from macroamounts of alkali or alkaline earth metal ions. A 200 mL volume of the synthetic solution of composition similar to sea water (the solution contained 1% Na, 0.14% Mg, 0.05% Ca and K, and $5 \cdot 10^{-5}\%$ Zn, Fe(III) and Cu) was adjusted to pH 4.0. The passage of this solution through the column packed with 5 g of the sorbent caused full retention of the heavy metal ions, contrary to the alkali and alkaline earth metal ions which were found in the

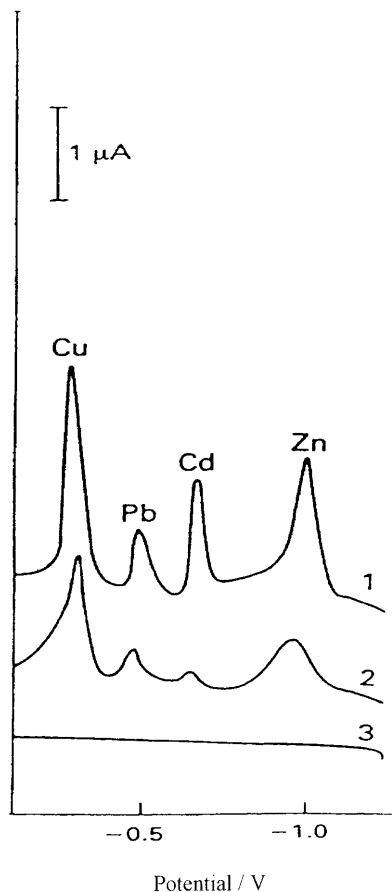


Fig. 6. Voltammograms for 10 mL volumes of aqueous chloride solutions after 3 min. electrolysis at -1.3 V . Curves: 1 0.5 mol L^{-1} NaCl (analytical grade) to which Zn, Cd, Pb, and Cu were added (the concentration of each metal ion was $20 \mu\text{g/mL}$); 2 0.5 mol L^{-1} NaCl (analytical grade); 3 sample 2 after treatment

collected eluate. The retained metal ions (Cu, Fe(III) and Zn) were then eluted with 5 mL of 0.5 mol L^{-1} perchloric acid and determined in the eluate by AAS. Recoveries higher than 98% were found for all retained metal ions.

Since the sorbent prepared does not bind Na^+ and K^+ ions, it may be applied for the elimination of the ions of heavy metals from the solutions of sodium and potassium salts. The results of determinations of heavy metals in the solutions of salts of alkali metals passed through the columns of the sorbent indicate that its use is possible and effective (Fig. 6). The concentrations of acids which elute the reagent are generally higher than the concentrations of acids eluting the majority of the metals previously retained on the sorbent so that columns may be regenerated by solutions of acids and after washing with water used

repeatedly many times. This supposition was again verified in repetitive sorption-elution tests using Zn, Cd, Pb and Cu. Tests performed five times with the same column showed reproducible results. It should also be mentioned that ion pairs sorbed on the silica carrier can be easily removed (together with the sorbed metal ions) with small volumes of a polar solvent – methanol or acetone, as in the case of other sorbents of this type [12].

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