SILICA GEL WITH ADSORBED ADOGEN 464 AS AN ANALYTICAL SAMPLING TOOL FOR ANIONS

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Summary—A solid extractant made with the liquid anion-exchanger Adogen 464 supported on silica gel has been prepared and its potential as a resin-like exchange material has been evaluated. In acid media it furnishes a ready available, inexpensive tool for recovery of anionic metal complexes as well as simple anions and for elimination of complex matrices. Copper and cobalt have been recovered (with a concentration factor of 20) from sea-water, natural water, metal alloys and industrial electroplating baths and measured by atomic-absorption spectrophotometry. The detection limits for copper and cobalt are 0.2 and 0.4 ng/ml respectively and interferences are minimal. Chromium(VI) has been separated from chromium(III), and a concentration factor of 40 and a detection limit of 0.2 ng/ml have been achieved.

Liquid ion-exchangers have found wide use in the determination of metal ions.[1] In particular, anionic halide complexes have been used in extraction systems[2,3] and in multielement separative techniques for elimination of matrix effects.[4] Metal thiocyanate complexes have similarly been used.[5-7] However, a number of variables such as the organic solvents used, the ionic strength, and charge on the ions involved, can make this method time-consuming. A different approach is based on use of chelating resins (*e.g.*, Chelex 100) as a preconcentration tool for natural waters and sea-water.[8] Comparative studies[9] have shown almost quantitative recovery of zinc from sea-water but poor collection of cobalt and manganese, even with selectively silylated substrates.[10] Recently, anion-exchange resins loaded with ionic or non-ionic metal-chelating groups have been utilized as preconcentration substrates,[11,12] but show lack of stability in high ionic strength media. Water-insoluble chelating substrates supported on silica gel provide a rapid and selective method.[13,14]

In the present work we examine the use of liquid anion-exchangers supported on silica gel as a sorption system for anionic complexes, and establish its usefulness in the quantitative determination of copper, cobalt and chromium(VI) in systems such as natural waters or solutions of high ionic strength.

EXPERIMENTAL

Reagents

Stock copper and cobalt solutions (100 μg/ml) were used, and working solutions were made by diluting the stock solutions with $10^{-3}M$ potassium thiocyanate acidified with sulphuric acid. The stock dichromate solution was $10^{-3}M$, and was diluted with demineralized water to give working solutions. The standard chromium(III) solutions were obtained by dilution of Merck "Titrisol" chromium(III) solution. The silica gel (Merck Kieselgel 60) was sieved and the 60–80 mesh fraction was twice digested in nitric acid,

washed with demineralized water and dried at 110° for a day. Adogen 464 was used as received from Aldrich Chemical Co. Analytical-grade chemicals were used throughout.

Apparatus

A Perkin–Elmer model 300 atomic-absorption spectrophotometer and HGA 2200 graphite-furnace atomizer were used for metal determination. The conditions are listed in Table 1. A Netzsch simultaneous thermal analysis model 429 and a Perkin–Elmer 298 infrared spectrophotometer were used to determine the amount of Adogen 464 on the silica gel.

In the chromium work, all glassware was soaked for at least an hour in $6M$ hydrochloric acid before use, and was never exposed to other chromium solutions.

Preparation of the loaded silica gel

Cleaned silica gel (100 g) was soaked in 250 ml of dichloromethane containing a weighed amount of Adogen 464. The mixture was stirred mechanically for 3 hr and then the solvent was evaporated under reduced pressure at room temperature and the air-dried product was stored in a bottle.

Elution of liquid anion-exchanger, as a function of pH

A 20-g sample of 10% Adogen 464/silica gel, loaded in a glass tube (bore 22 mm, bed height 90 mm), was eluted with demineralized water adjusted to the desired pH with hydrochloric acid, at a flow-rate of 4 ml/min. The silica gel was then extruded, dried at 120° for 3 hr and analysed for residual Adogen by differential thermal analysis and infrared spectroscopy.

Procedures for batch experiments

Extraction as a function of pH. A 0.5-g portion of 3% Adogen 464 silica gel was stirred mechanically with 50 ml of $10^{-3}M$ potassium thiocyanate at the desired pH and containing copper or cobalt (100 ng/ml), for 20 min. The solution was then filtered and analysed for metal by atomic-absorption spectrometry (AAS). For chromium, a 1-g portion of Adogen 464/silica gel was stirred mechanically for 20 min with 40 ml of 70-ng/ml chromium(VI) or chromium(III) solution acidified to the desired pH with sulphuric acid, and the solution was then analysed for chromium by electrothermal AAS.

Capacity study. The procedure just described was used to

Table 1. Conditions for AAS determinations

	Cu	Co	Cr
Resonance line, *nm*	324.7	240.7	357.9
Band-pass, *nm*	0.7	0.2	0.7
Ashing temperature, °C	700	700	900
Ashing time, *sec*	40	40	20
Atomization temperature, °C	2500	2500	2700
Atomization time, *sec*	5	5	5

determine the capacity of the 5% Adogen 464/silica system with respect to $10^{-2}M$ potassium thiocyanate containing 20 μg of copper and cobalt per ml, at the desired pH, or with respect to 500-μg/ml dichromate solution.

Rate of extraction. A 1-g portion of loaded silica gel was stirred with 40 ml of chromium solution buffered at pH 0.7 or 4.3, and portions of solution were abstracted at various intervals of time and analysed by electrothermal AAS.

General column procedure

For copper and cobalt a 6-mm bore glass column was loaded with 1.2–1.8 g of 3% Adogen 464/silica gel, which gave bed heights ranging from 6 to 8 cm. A known volume of $10^{-3}M$ potassium thiocyanate acidified to pH 1.7–1.8 with sulphuric acid and containing copper or cobalt was passed through the column at a rate of 2 ml/min under mild suction. After washing with 5 ml of demineralized water the column was stripped with 0.5 ml of concentrated nitric acid plus 0.5 ml of 30% hydrogen peroxide solution and the metal removed was determined by AAS.

For chromium the column had a bore of 0.8 cm and was loaded with 1.2 g of Adogen 464/silica gel (bed height 6 cm). Standard solutions [200 ml, containing 0.100–3.40 μg of Cr(VI) or Cr(III)] were prepared by dilution of 10-μg/ml stock solution and analysed within minutes of preparation. The solutions were adjusted to pH 2.0 with sulphuric acid and passed through the column at 2 ml/min. The column was washed with 10 ml of demineralized water and stripped with 2 ml of concentrated nitric acid. The strippings were diluted to the appropriate volume (5 or 10 ml) with water, and the chromium determined by electrothermal AAS.
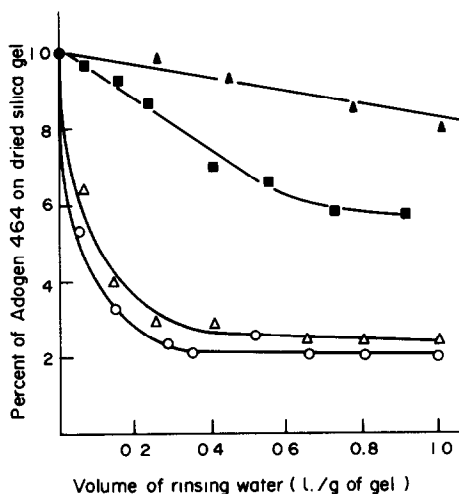
Extraction of copper or cobalt from nickel electroplating baths. A sample of the bath solution was filtered through a 0.8-μm Millipore disc, and 100 ml were analysed as already described.

RESULTS AND DISCUSSION

The stability of the Adogen 464/silica gel was evaluated by leaching of the exchanger at different pH values from a column initially loaded at the 10% level (Fig. 1). Since the Blakeley and Zatka[15] method for determining the quaternary ammonium salt proved useless, differential thermal analysis and infrared spectroscopy (measurement of the 2930-cm^{-1} C–H stretching band) were used. The high retention of Adogen 464 at low pH makes the system similar to the modified anionic resins[11] or to the supported chelating substrates.[12]

The effect of pH on the extraction of the copper and cobalt thiocyanate complexes was examined by the batch method (Fig. 2). Copper is completely extracted over a wide range of pH, and the optimum pH range for cobalt is 1.4–2.5. The recovery, however, must be regarded as including the effect of the silica gel itself, since the hydroxyl groups of the gel are capable of complexing many metal ions. In particular, complete adsorption of copper, manganese, zinc and
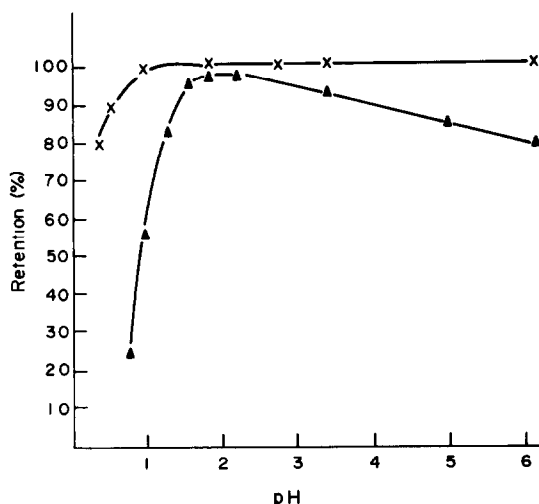

Fig. 1. Per cent of liquid anion-exchanger retained as a function of washing volumes: ▲ pH = 0, ■ pH = 2, △ pH = 4, ○ pH = 6.5.

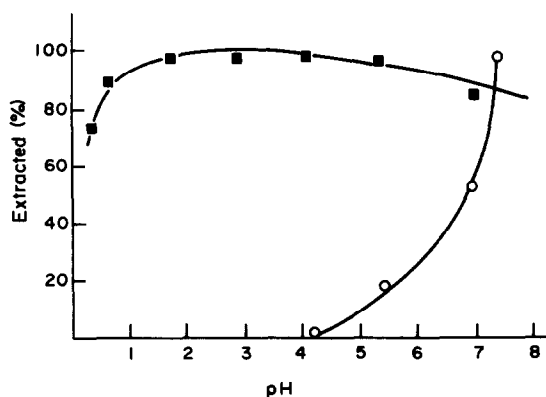Fig. 2. Per cent retention as a function of pH: copper (×) and cobalt (▲).

Fig. 3. Extraction of chromium on silica gel treated with Adogen 464, as a function of pH: ■ Cr (VI), ○ Cr (III).

silver at pH > 5 on untreated silica gel has been reported,[16] whereas cobalt ions are bonded only up to 5% from natural and sea-waters.

To maintain the selectivity and overall capacity, the thiocyanate metal complexes were adsorbed at pH 1.7–1.8. The capacity of the 5% Adogen 464/silica gel for the cobalt and copper thiocyanate complexes at pH 1.7 (20 min contact time) was found to be 0.028 and 0.025 mmole respectively, per gram of loaded silica. These values are consistent with sorption of hexathiocyanato metal complexes,[17] in contrast to the corresponding solvent extraction system. These capacities are in good agreement with those observed for silica-gel systems,[13,14] though less than a tenth of those for silylated immobilized reagents.[16]

Similar experiments were performed to obtain distribution curves for chromium(III) and chromium(VI), the results being shown in Fig. 3. The optimum pH is 2 for avoidance of sorption of chromium(III) and to keep the Adogen 464 loading as high as possible. The capacity for chromium(VI) at pH 2 (20 min contact time) is 0.020 mmole per gram of loaded silica. The rate of extraction of chromium(VI) is shown in Fig. 4.
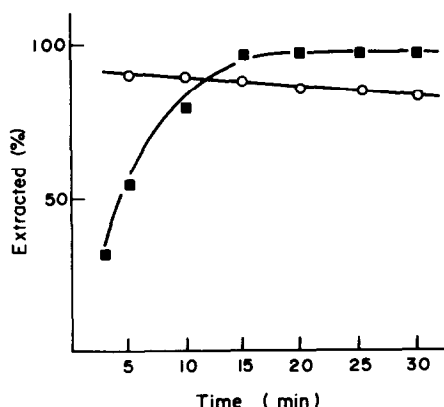
Table 2. Recovery of copper and cobalt ions from 100 ml of solution, on a column of silica gel treated with Adogen 464.

	Initial concentration, ng/ml	Adogen–SiO$_2$, g	Recovery, %
Co	100	1.5	100
	100	1.2	98.2
	10	1.8	99.2
	10	1.5	99.3
Cu	10	1.5	98.8
	10	1.8	97.9
	100	1.8	98.2
	100	1.5	98.9

The recovery of copper and cobalt in the concentration range from 10 to 100 ng/ml, from $10^{-3}M$ thiocyanate solution, is quantitative at flow-rates of 1–2 ml/min (Table 2). The most efficient stripping (i.e., giving the lowest standard deviation) is obtained with concentrated nitric acid and hydrogen peroxide, whereas other systems such as ammonia solution or acetic acid fail to give satisfactory results. However, the method will give an enrichment factor of only about 10 or 20 (for final volumes of 10 or 5 ml respectively) since the recovery ratio is considerably lowered if water samples of more than 200–300 ml are used.

Other metals giving thiocyanate complexes, such as manganese and iron, have been examined for potential interference (Table 3). In the column system there is no interference in the recovery of traces of copper and cobalt. Since nickel does not inhibit the copper or cobalt recovery at any concentration, this method can safely be used for matrices such as nickel alloys, nickel electroplating baths, nickel ores, etc., besides

Table 3. Recovery of copper and cobalt from 100 ml of solution, on a column of silica gel treated with Adogen 464, in the presence of added Zn, Fe, Mn and Ni

Initial concn., ng/ml			Ratio, $\dfrac{[\text{Test ion}]}{[\text{Foreign ion}]}$	Recovery, %	
[Test ion], ng/ml		Foreign ion		Co	Cu
Cu	10	Co	1:1	98.9	98.4
	10	Co	1:10	98.3	98.8
	100	Co	10:1		100.8
	100	Co	10:1	99.2	99.0
	10	Co	1:500		97.8
	10	Co	1:1000		101.2
	10	Zn	1:500		99.8
	10	Mn	1:500		97.8
	10	Fe	1:500		98.5
Co	10	Ni	1:10	99.1	
	10	Ni	1:50	98.7	
	10	Ni	1:500	99.4	
	10	Ni	1:1000	99.2	
Cu	10	Ni	1:50		99.3
	10	Ni	1:500		98.5

Fig. 4. Extraction of chromium (VI) on silica gel treated with Adogen 464, as a function of time: ○ pH = 0.7, ■ pH = 4.3

Table 4. Recovery of chromium (VI) in the presence of chromium (III)*

Cr(VI) taken, μg	Cr(III) taken, μg	Recovery, %
0.05	10	101
0.5	10	100
1	10	99
5	10	99
10	10	99
10	100	99
10	1000	105
17	100	102

*For 100 ml, pH 2.

solutions where the low metal content is not directly detectable because of matrix effects. These advantages are well illustrated by the examples below.

For chromium(VI) the recovery was quantitative for 100 ml of solution containing 0.05–17 μg of chromium (Table 4). Stripping was done most efficiently with a small volume of concentrated nitric acid. The method does not allow a concentration factor of more than 40, because the recovery is considerably lower if a large sample volume (>400 ml) is used. The detection limit for chromium(VI), defined as twice the standard deviation of the blank signal, is 0.2 ng/ml. The method is particularly useful for total chromium determination, since any chromium(III) can be oxidized with permanganate in acid medium, and the excess of oxidant need not be destroyed, since it is held at the top of the column, and the manganese(IV) produced does not interfere because it is not desorbed in the stripping process for chromium(VI). As use of sodium azide for reducing the excess of permanganate is thus avoided, there is no risk of loss of chromium(VI) by azide reduction (Table 5).

Copper determination in natural and sea-water

The direct AAS determination of metal traces in sea-water is well developed but satisfactory results have been achieved only for iron and zinc, whereas for lead, copper, nickel and cobalt, only higher con-

Table 5. Recovery of total chromium

Cr(VI)	Cr(III)	Recovery, %
10.0	1.0	99
10.0	5.0	99
10.0	10.0	97
0.5	—	98
1.0	—	102
10.0	10.0	89†
100	10.0	92†

Taken*, ng

*In 100 ml, pH 2.
†Sodium azide was used to destroy the excess of permanganate.

Table 6. Determination of copper in sea-water (Porto Novo harbour)

Cu added, ng/ml	Found, ng/ml	Std. devn., ng/ml
—	0.8	0.05
2	2.3	0.05
4	4.8	0.03

Table 7. Copper determination in natural water containing: Na^+ 3.4 $\mu g/ml$, K^+ 1.15 $\mu g/ml$, Ca^{2+} 65 $\mu g/ml$, Mg^{2+} 8.8 $\mu g/ml$, SO_4^{2-} 24.9 $\mu g/ml$

Cu added, ng/ml	Cu found, ng/ml	Std. devn., ng/ml
—	2.1	0.05
—	2.3	0.06
3	5.3	0.08
3	5.2	0.09
6	8.2	0.15
6	8.1	0.12

centrations are reliably determined.[18,19] The Adogen 464/silica gel system can conveniently be used to detect copper ions in either natural or sea-water at values as low as 0.2 ng/ml (Tables 6 and 7), but because of its low concentration (0.01–0.046 ng/ml in sea-water and 0.037–0.35 ng/ml in river water),[20] a 20-fold enrichment factor does not necessarily allow cobalt to reach its detection limit of 0.4 ng/ml and be safely detected.

Copper and cobalt determination in other matrices

The reliability of the method has been verified by analysis of nickel electroplating baths, where contamination with cobalt and copper can cause loss of quality; satisfactory results can be achieved for Ni/Cu ratios of 5×10^5 and Ni/Co of 4×10^4 (Table 8). The amounts of organic substances such as surfactants and brightening agents usually present in the baths do not interfere. The analysis of standard alloys for copper (Table 9) provided standard deviations of 0.00095 and 0.0041% for copper contents of 0.045 and 0.170% respectively.

Table 8. Copper and cobalt determination in nickel electroplating bath

Cu added, ng/ml	Cu found*, ng/ml	Co added, $\mu g/ml$	Co found*, $\mu g/ml$
—	199 (6)	—	2.44 (0.03)
—	209 (8)	—	2.50 (0.02)
100	318 (6)	2.5	5.05 (0.05)
200	411 (12)	5.0	7.50 (0.08)

*Standard deviation (10 replicates) shown in brackets.

Table 9. Determination of copper in BCS standard 182/2 (Al alloy with 11% Si; Cu content 0.045%) and BCS standard 403 (low-alloy steel; Cu content 0.170%).

Sample	Cu found, %	Std. devn., % (10 replicates)
BCS 182/2	0.0454	0.0011
	0.0450	0.0008
	0.0448	0.0010
BCS 403	0.168	0.004
	0.171	0.004
	0.173	0.004

REFERENCES

1. H. Green, *Talanta*, 1973, **20**, 139.
2. F. G. Seeley and D. J. Crouse, *J. Chem. Eng.*, 1966, **11**, 424.
3. C. W. McDonald and F. L. Moore, *Anal. Chem.*, 1973, **45**, 983.
4. J. R. Clark and J. G. Vlets, *ibid.*, 1981, **53**, 61, 65.
5. R. Přibil and J. Adam, *Talanta*, 1973, **20**, 49.
6. H. M. N. H. Irving and A. D. Damodaran, *Anal. Chim. Acta*, 1970, **50**, 277.
7. A. R. Burkin, N. M. Rice and M. J. Rogers, *J. C. S. Dalton*, 1974, 213.
8. J. Lamathe, *Anal. Chim. Acta*, 1979, **104**, 307.
9. J. Smits, J. Nelissen and R. Van Grieken, *ibid.*, 1979, **111**, 215.
10. D. E. Leyden, G. H. Luttrell, A. E. Sloan and N. G. DeAngelis, *ibid.*, 1976, **84**, 97; D. E. Leyden, G. H. Luttrell, W. K. Nonidez and D. B. Werho, *Anal. Chem.*, 1976, **48**, 67.
11. M. Chikuma, M. Nakayama, T. Itoh, H. Tanaka and K. Itoh, *Talanta*, 1980, **27**, 807.
12. H. Akaiwa, H. Kawamoto and K. Ogura, *ibid.*, 1981, **28**, 337.
13. K. Terada and K. Nakamura, *ibid.*, 1981, **28**, 123.
14. K. Terada, K. Morimoto and T. Kiba, *Anal. Chim. Acta*, 1980, **116**, 127.
15. St. J. H. Blakeley and V. J. Zatka, *ibid.*, 1975, **74**, 139.
16. D. E. Leyden and G. H. Luttrell, *Anal. Chem.*, 1975, **47**, 1612.
17. P. W. West and C. G. de Vries, *ibid.*, 1951, **23**, 334.
18. R. J. T. Graham and A. Carr, *J. Chromatog.*, 1970, **46**, 293.
19. T. H. Donnelly and J. Ferguson, *Appl. Spectrosc.*, 1975, **29**, 158.
20. K. H. Wedepohl, C. W. Correns, D. M. Shaw, K. K. Turekian and J. Zemann, 1978. *Handbook of Geochemistry*, Vol. II/3, Springer-Verlag, New York.