



ANALYTICAL APPLICATION OF SILICA GEL MODIFIED WITH DIDECYLAMINOETHYL- β -TRIDECYLAMMONIUM IODIDE

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Summary—Sorption of a high molecular weight quaternary ammonium salt, didecylaminoethyl- β -tridecylammonium iodide (DDATD) on different types of sorbents was investigated. The nature of reagent adsorption on silica gel was examined by spectroscopic and computer methods. The sorption of anionic metal complexes of cobalt, copper, zinc and manganese on silica gel modified with DDATD was studied. The possibility of recovery of cobalt and copper thiocyanate complexes and their further atomic absorption determination is shown. Modified sorbent was applied to cobalt chemiluminescence and determined in natural water and a nickel preparation (detection limit, 2 $\mu\text{g/l}$).

High molecular weight amines and quaternary ammonium salts have found wide application for the extraction recovery of anionic metal complexes.^{1,2} The extraction-spectro photometric determination of cobalt thiocyanate complexes from different sources is known.³⁻⁵

Long chain quaternary ammonium salts can also be adsorbed on porous sorbents, silica gel in particular.^{6,7} Silica gels modified in this way acquire anion-exchange properties and can be used repeatedly for anion determination. They possess the properties of chemically modified silica gels.⁸

Anion exchange resins and silica gel loaded with high molecular weight amines and quaternary ammonium salts have been used for metal ion preconcentration.⁹⁻¹¹ Modified sorbents studied showed a lack of stability in high ionic strength media and lower recovery if more than 300 ml of solution were used.

Some tests of cobalt thiocyanate complexes detection using Amberlite LA-1 (N-dodecyl-(trialkylmethyl)amine) impregnated paper¹² and foam cubes¹³ have been carried out. The detection limits are 5 and 0.3 mg/l ., respectively.

In the present work we investigate the nature of sorption of didecylaminoethyl- β -tridecylammonium iodide (DDATD) on different types of sorbents and the possibility of analytical appli-

cation of modified silica gel to some heavy metal ion determination.

EXPERIMENTAL

Reagents

Water was purified according to Ref. 14. Standard metal solutions ($10^{-2}M$) and sodium thiocyanate solution ($4M$) were prepared by dissolving appropriate salts. These solutions were acidified with HNO_3 and further diluted as required. All reagents were of analytical grade. 4-(2-pyridylazo)Resorcinol, monosodium salt hydrate (PAR) (Reanal) was purified by following Ref. 15, $10^{-3}M$ solution was used. Solution of DDATD in hexane ($2 \times 10^{-2}M$) was obtained from reagent containing 95% of the main substance.¹⁶ Silica gel (Chemapol L 40/100) was digested in nitric acid, washed with water and dried at 80°C for a day.

Apparatus

A spectrophotometer UV/Vis Specord M-40 was used for spectrophotometric measurements, a Bruker spectrometer of SXR type (working frequency 200 MHz) with hexamethylsilicon as a standard was used for PMR measurements. An IBM PC/AT personal computer was used for calculations. Atomic absorption measurements were recorded on a model Saturn atomic-absorption spectrometer (Severodonetsk) equipped with a standard burner for use with an

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air-propane-butane flame. Standard hollow-cathode lamps were applied as a line source for all elements.

A potentiometer model EV-74 with glass electrode was used for pH measurements. A chemiluminescence photometer¹⁷ with glass cell was used for the chemiluminescence intensity measurements.

A peristaltic pump equipped with a variable-speed control was applied to ensure a constant flow of solution through the reagent phase.

Procedures

Investigation of DDATD sorption on silica gel.

Silica gel (0.1 g) was stirred with 10 ml of 0.5–8.0 mM DDATD solution in hexane for 30 min. The DDATD residue in hexane was controlled spectrophotometrically using the absorbance of ion-pair $(Am)_2Co(NCS)_4$.¹⁸ The loaded silica gel was prepared as follows: silica gel (5 g) was stirred mechanically with 60 ml of $2 \times 10^{-2} M$ DDATD solution in hexane for 1 hr, centrifuged and dried at 60°C for 2 hr. The loaded silica gel contained 0.24 mmol/g DDATD.

Standard procedure for preconcentration.

Batch experiments. The sample solution (10–100 ml) containing known amount of metal ions (2–100 μg) was adjusted to the appropriate pH, placed into a 100–250 ml standard flask, 0.4–4.0 ml of 4M NaSCN were carefully added and stirred mechanically with 0.2 g of the loaded silica gel for 10–30 min. Then sorbent was filtered through a dry filter paper and dried at room temperature. The sorption of thiocyanate metal complexes was controlled spectrophotometrically with PAR¹⁵ (residue in water solution) and on silica gel by solid phase spectrophotometry,¹⁹ diffusion reflection spectra (cobalt) or AAS after desorption. The desorption of metal ions was carried out with 5 ml of 0.05M EDTA, or 5 ml of hexane:acetone (1:1) mixture by stirring with 0.2 g of sorbent for 30 min. The eluate was filtered and diluted to 10 ml with water or butanol, respectively.

Dynamic experiments. The loaded silica gel (0.2 g) was placed into special teflon cartridge (length 5 mm. i.d. 8 mm). A given volume of aqueous sample (up to 1 l.) containing a known amount of metal ions (2–100 μg) was adjusted to a suitable pH then a suitable amount of 4M NaSCN was added and percolated through the cartridge at a flow-rate 10 ml/min by means of a peristaltic pump. The concentrate was dried at

60°. The recovery of cobalt was analysed by diffusion reflection spectra, visually or chemiluminescence after desorption with 0.05M EDTA.

RESULTS AND DISCUSSION

Nature of DDATD sorption

The sorption of DDATD was studied on more than 20 different types of sorbents (sillipore, Sephadex, silica gel, porapak, polysorb, *etc.*). It was found that the best were sorbents containing Si-OH or polyethylenylene groups—silica gel and porapak T.

The dependence of the DDATD sorption value (C^s) on DDATD concentration in hexane is represented in Fig. 1. The silica capacity for DDATD was 0.5 mmol/g. In the work silica gel containing 0.24 mmol/g of DDATD was used.

PMR spectroscopic investigation of DDATD on the sorbents surface and in CCl_4 was carried out to ascertain the nature of DDATD sorption. Results showed the possibility of hydrogen bond formation between ternary DDATD nitrogen and OH-groups of the sorbents.

A computer modeling of the interaction between DDATD and the surface of silica gel was made. Geometrical optimization of all objects was performed with the Molecular Modeling Package version ATOM87 (Oxford Electronic Publishing). The geometrical data obtained from the modeling were used for quantum chemical calculation by the CNDOIR method of the electron density in the amine molecule and on the surface of silica gel. The results showed that the electronic charge of ternary nitrogen equalled $-0.16 e^-$ and tertiary nitrogen equalled zero. Charges of silicon atoms on the surface were in the range of 0.95–0.98 e^- and those of oxygen and hydrogen atoms were

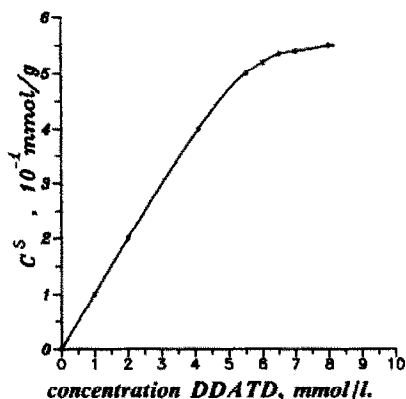


Fig. 1. The isotherm of DDATD adsorption on silica gel. $m_{SiO_2} = 0.1$ g, $V_{hexane} = 10$ ml.

in the range of -0.38 to $0.45 e^-$ and 0.12 to $0.13 e^-$, respectively. These data support the possibility of interaction between amine and the surface not only by physical adsorption but also from the appearance of a hydrogen bond between the hydrogen atom of Si-OH group and ternary amine nitrogen. It was confirmed by sorption of DDATD on silica gel and porapak T and its desorption in acid medium. As a result

of hydrogen bond creation, the ternary nitrogen atom became tertiary with a formal positive charge. It led to the formation of two centers of coordination in amine for the $[M(NCS)_4]^{2-}$ anion. However, these centers were affected by steric shielding of hydrophobic alkyl radicals. One of the nitrogen atoms was affected by the steric shielding of the silica gel surface.²⁰ So the interaction between complexes $[M(NCS)_4]^{2-}$ and DDATD on the surface of silica gel was the result of ion associate formation, not complexation.

Study of metals sorption

Sorption of thiocyanate complexes of Co^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} on loaded silica gel was studied. The dependence of metal ion recovery on pH of solution was examined by the batch method (Fig. 2). All metals studied had maximum recovery on loaded silica gel in the range of pH 5-7 and very low recovery on untreated silica gel. The effect of thiocyanate concentration on the sorption of metal complexes is shown in Fig. 3. Optimum thiocyanate concentration was $4 \cdot 10^{-2} M$ and metal ions concentration $10^{-4} M$.

The chelating capacity for metal ions was measured by the batch method. A value of 0.12 mmol/g was obtained for Cu^{2+} , Co^{2+} and Zn^{2+} (Fig. 4). The recovery of these metals was 98.8%. Manganese recovery was only 30% and nickel was not recovered. It was shown earlier²¹ that the complex $(DDATD)_2M(NCS)_4$ for Co^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} prevailed on the surface under the mentioned conditions.

The quantitative recovery of Co^{2+} , Cu^{2+} , Zn^{2+} was reached at 1 min from a 10 ml water

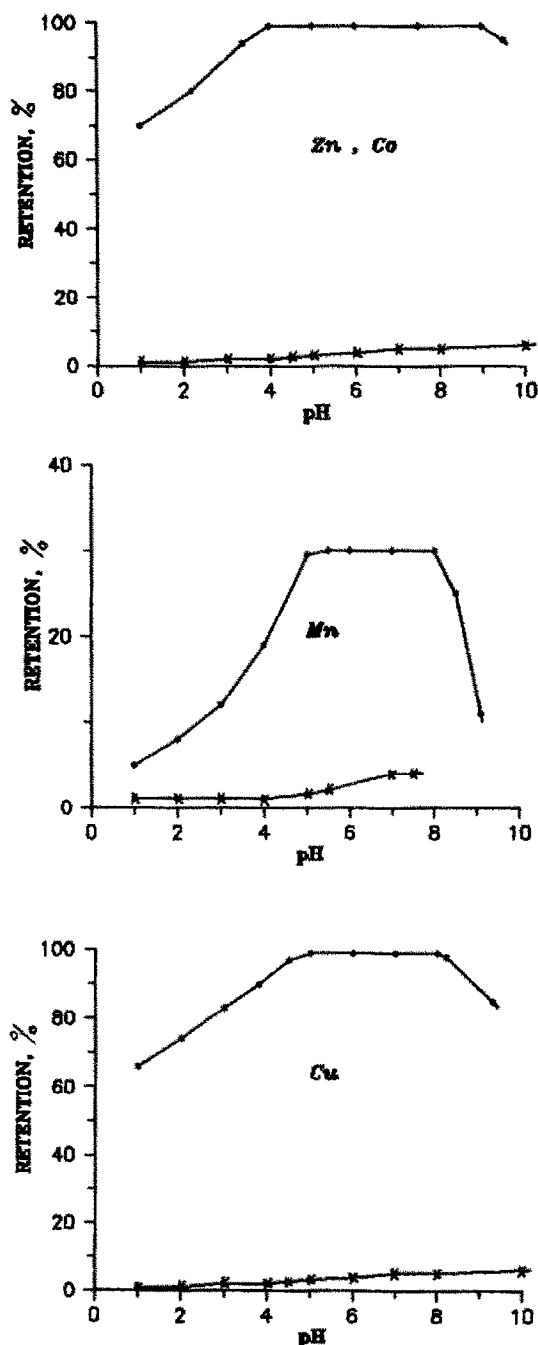


Fig. 2. Effects of pH on recovery of metal complexes. DDATD-SG (—), untreated silica gel (—x—).

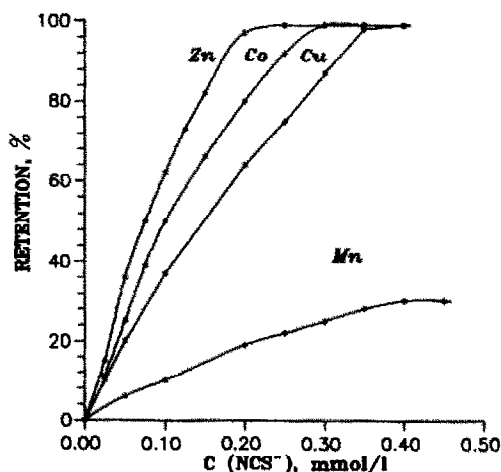


Fig. 3. Effects of thiocyanate concentration on sorption of metal complexes on DDATD-SG. $C_M = 10^{-4} M$, pH 6.

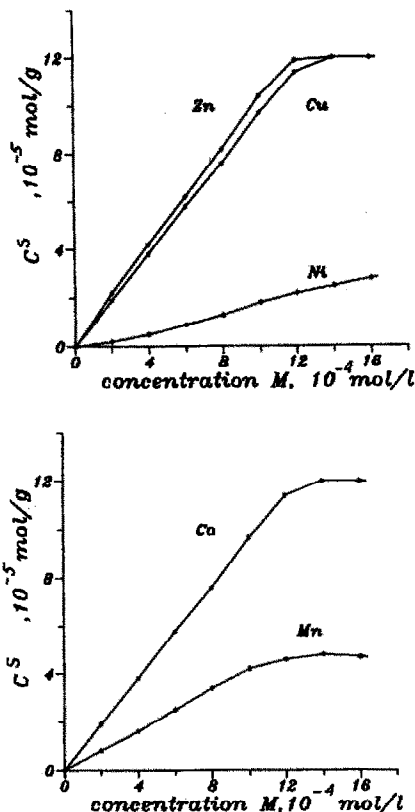


Fig. 4. The isotherms of metal thiocyanate complexes sorption on DDATD-SG. $C_{\text{DDATD}}^i = 0.24$ mmol/g, $C_{\text{NCS}^-} = 0.1M$, $m_{\text{SiO}_2} = 0.1$ g, $V_{\text{aq}} = 10$ ml, pH 6.

sample and 20 min from a 100 ml water sample for the batch method. For the dynamic method a flow rate of 10 ml/min was sufficient to obtain the same results. One litre of water sample can be passed through the cartridge with 0.1–0.2 g of the sorbent.

The results of cobalt, copper and zinc desorption with EDTA and organic solvents are represented in Table 1. The elution degree of cobalt and copper was 98% and zinc only 60%. Thus copper and cobalt can be determined in the eluate by AAS and chemiluminescence or visually on the surface $[\text{Co}(\text{NCS})_4]^{2-}$. Zinc may be analysed by AAS with electrothermal atomization on the sorbent surface.

Table 1. Desorption of 100 μg of metal ions from DDATD-SG

Ion	Found (μg) $\bar{x} \pm \Delta x$	
	EDTA (0.05M)	Hexane:acetone (1:1)
Cu^{2+}	96 ± 4	101 ± 3
Co^{2+}	99 ± 3	100 ± 5
Zn^{2+}	25 ± 4	30 ± 6

$m_{\text{SiO}_2} = 0.2$ g, $V = 10$ ml ($n = 4$, $P = 0.95$, AAS measurements).

The influence of other ions forming thiocyanate complexes on cobalt and copper determination was examined. The results obtained by the batch method are shown in Table 2. At the given concentration levels, none of the ions interfered with the retention of cobalt and copper at trace levels. Iron(III) and nickel(II) did not interfere up to 0.5 mg/l. and 1 g/l., respectively, so the method can be used for cobalt and copper determination in natural water and nickel preparations.

Cobalt and copper determination in model solutions

The solution (100 ml) containing 10–50 μg of copper and cobalt and 50 μg of Fe(III); 10 μg of Mn(II), 100 μg of Zn(II) were treated by 4 ml of 4M NaSCN and analysed by the batch method. The metal ions were eluted with 5 ml of hexane:acetone (1:1) mixture. The eluate was diluted to 10 ml with butanol and analysed by AAS. The results are shown in Table 3. The calibration graph is linear in the range of 0.1–2 $\mu\text{g}/\text{ml}$. Calibration equations are: y (h, mm) = $9 + 28 x$ (Cu, μg), $r = 0.995$ and y (h, mm) = $1.4 + 22.1 x$ (Co, μg), $r = 0.998$.

Method of cobalt determination in water

The sample of natural water (1 l.) treated by 7 ml of concentrated nitric acid according to Ref. 15 was adjusted to pH 5 by NaOH. Then 40 ml of 4M NaSCN was added and

Table 2. Effect of foreign ions on recovery of 10 μg of copper(II) and cobalt(II) from 100 ml of solution

Foreign ion	Added (μg , mg*)	Recovery (%)		Foreign ion	Added (μg , mg*)	Recovery (%)	
		Co^{2+}	Cu^{2+}			Co^{2+}	Cu^{2+}
Fe^{3+}	25	98.7	98.7	Cu^{2+}	100	98.8	—
	50	98.5	98.9	Co^{2+}	10	—	98.8
	100	98.2	98.4		50	—	98.7
Zn^{2+}	100	98.8	98.9	*Na ⁺	0.23	98.7	98.6
Mn^{2+}	100	98.9	98.8	*Ca ²⁺	0.40	98.8	98.8
Ni^{2+}	100*	98.7	98.7	*Mg ²⁺	0.24	98.9	98.7

Table 3. The results of AAS determination of cobalt and copper in model solutions containing ($\mu\text{g/ml}$): Fe, 0.5; Zn, 1.0; Mn, 0.1

Ion	Added ($\mu\text{g/ml}$)	Found ($\mu\text{g/ml}$)	S_r
Cu^{2+}	0.25	0.24	0.04
	0.50	0.51	0.03
Co^{2+}	0.25	0.23	0.05
	0.50	0.52	0.03

$N = 4$, $P = 0.95$.

the dynamic method applied using 0.2 g of loaded silica gel. The colour of concentrate was compared with standards prepared by the same way from distilled water containing 2, 5, 10, 25, 50, 75 and 100 μg cobalt. The scale was stable for 1 year. The detection limit was 2 $\mu\text{g/l}$. The correctness of data was examined spectrophotometrically with nitrozo-R-salt.¹⁵

Cobalt determination in nickel sulfate

Analytical grade preparation $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (1 g) was dissolved in dilute sulfuric acid (pH 3) and diluted to 1 l. by purified water. Then, 25 ml of 4M NaSCN was added and the dynamic method applied using 0.1 g of loaded silica gel. Cobalt was eluted with 5 ml of 0.05M EDTA by batch method. The eluate was mineralized¹⁵ and analysed by the chemiluminescence method.²² The equation of calibration graph is $y(\text{relative units}, 10^2) = 7 + 5x(10^{-5} \text{ mM})$, $r = 0.985$. The blank solution was NiSO_4 without cobalt. The results of determination are: Co added, $5.9 \times 10^{-5}\%$, found $(5.9 \pm 0.7) \times 10^{-5}\%$. The detection limit was $2 \times 10^{-6}\%$, $S_r < 0.2$.

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