THE USE OF CHELATES OF COPPER, NICKEL, COBALT, CADMIUM AND ZINC WITH HETEROCYCLIC AZODYES IN THE AAS DETERMINATION OF THESE ELEMENTS

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Received March 10th, 1978

Of the group of seven pyridyl, thiazolyl and quinolyl azodyes, 2-(2-pyridylazo)-1-naphthol was found to be the most useful for the extraction concentration of traces of copper, nickel, cobalt, cadmium and zinc in methyl isobutyl ketone and for their final determination by atomic absorption spectrophotometry with an acetylene–air flame or using a graphite atomizer. Atomic absorption spectrophotometry was also found to be useful in the study of extraction equilibria and for finding the optimum extraction conditions for these elements with heterocyclic azodyes.

Extraction of elements based on the use of chelates or ion associates with organic reagents into a suitable organic solvent before final determination of these elements by atomic absorption spectrophotometry (AAS) enables both concentration and selective separation of the elements from concentrated electrolyte solutions and also increases the sensitivity of the actual AAS determination and affects the detection limit of the elements. The organic solvent improves the effectiveness of the nebulization and increases the rate of vaporization of the aerosol droplets. The combustion of organic solvents and of the reagent and the formation of a metal chelate with the organic reagent generally favourably affect those chemical equilibria in the atomizer which increase the degree of atomization of the element determined[1–5]. The actual effect of the organic reagent and its chelate with the metal on the process of element atomization is, however, rather unclear[6–8].

The usefulness of the selected heterocyclic azodyes, 1-(2-pyridylazo)-2-naphthol, 2-(2-pyridylazo)-1-naphthol, 2-(2-benzothiazolylazo)-1-naphthol, 2-(2-quinolylazo)-1-naphthol, 1-(2-thiazolylazo)-2-naphthol, 2-(2-thiazolylazo)-4-methoxyphenol and 2-(2-thiazolylazo)-4-methylphenol and their chelates with Cu, Ni, Co, Cd and Zn after extraction into organic solvents for concentration of these elements and their determination by AAS using an acetylene–air flame and an electrothermal atomizer were studied in this work. AAS was also used for studying the extraction equilibria of these elements with the most suitable azodye, 2-(2-pyridylazo)-1-naphthol, and for optimization of the extraction conditions.

EXPERIMENTAL

Solutions and Chemicals

1-(2-Pyridylazo)-2-naphthol (2-PAN), 2-(2-pyridylazo)-1-naphthol (1-PAN), 2-(2-benzothiazolylazo)-1-naphthol (1-BAN), 2-(2-quinolylazo)-1-naphthol (1-QAN), 1-(2-thiazolylazo)-2-naphthol (2-TAN), 2-(2-thiazolylazo)-4-methoxyphenol (4-TAMP), 2-(2-thiazolylazo)-4-methylphenol (TAC) were in part commercial samples and in part were prepared by reaction of the corresponding hydrazine with 1,2-naphthoquinone in acid medium with repeated recrystallization from 50% (v/v) methanol. After separating on a frit the dyes were dried *in vacuo* in a dessicator over P_2O_5. The dye purity was verified by TLC on Silufol, impregnated with 0·05M-EDTA, using a benzene–methanol eluent (9 : 1). Solutions of the azodyes in ethanol or methyl isobutyl ketone (MIBK) were employed. Sodium perchlorate, potassium nitrate and sodium acetate were freed from traces of heavy metals by shaking in aqueous solution with a solution of 1-PAN in MIBK and recrystallization from the aqueous phase. The other metal salts and buffer components were purified by recrystallization. The initial standard solutions were copper nitrate ($1{\cdot}57 \,.\, 10^{-2}$M-Cu^{2+}), cobalt chloride ($1{\cdot}98 \,.\, 10^{-2}$M-Co^{2+}), nickel nitrate ($1{\cdot}70 \,.\, 10^{-2}$M-Ni^{2+}), cadmium chloride ($0{\cdot}89 \,.\, 10^{-2}$M-Cd^{2+}) and zinc chloride ($1{\cdot}53 \,.\, 10^{-2}$M-Zn^{2+}). The solutions were standardized by EDTA titration. A solution of $1{\cdot}32 \,.\, 10^{-3}$M-Co^{2+} labelled with ^{60}Co was employed for radiochemical measurements. The cobalt concentration was determined spectrophotometrically. The ionic strength of the solutions was $I = 0{\cdot}1$ when not designated otherwise. Organic solvents, MIBK, ethyl acetate, isopropyl acetate, n-butyl acetate, n-amyl acetate and xylene, were redistilled.

Instruments

A Perkin–Elmer 306 atomic absorption spectrophotometer with hollow cathode lamps from various manufacturers and characterized by the following parameter values was used (λ, slit width in nm, lamp current in mA): Cu (324·7; 0·7; 10), Co (240·7, 0·2, 15), Ni (232·0, 0·2, 15), Cd (228·8, 0·7, 4), Zn (213·9, 0·7, 8). A HGA-74 graphite cuvette, Varian CR-90 graphite rod, OP-205 pH meter (Radelkis, Budapest) with a GK 2302 B combination electrode (Radiometer, Copenhagen), standardized with Radiometer buffers of pH 4·01 and 7·00, Spekol (Zeiss, Jena) and Carry 118 spectrophotometers and γ-spectrophotometer Gamma counting system II 85 (Nuclear, Chicago) were employed.

Methods of Studies

The distribution ratio of the metal between the organic and aqueous phases, D,

$$D = \frac{c_{\mathrm{M,org}}}{c_{\mathrm{M,aq}}} \qquad (1)$$

was found by AAS and also radiochemically and spectrophotometrically for cobalt. The concentration of the metal in the organic phase was found by direct dispersion of this phase in the acetylene–air flame (air 15·0 l min^{-1}, acetylene 1·1 l min^{-1}) with a flame observation height of 0·8 cm for determining Cu and Zn and 1·0 cm for determining Co, Ni and Cd. Standard solutions in MIBK were prepared by extraction of increasing amounts of metal with 1-PAN into MIBK at the optimum pH for the extraction. Standard solutions of the 1-PAN chelate of the metals in MIBK were also prepared from 0—130 µl $1{\cdot}57 \,.\, 10^{-2}$M-Cu^{2+}, $1{\cdot}98 \,.\, 10^{-2}$M-Co^{2+}, $1{\cdot}70 \,.\, 10^{-2}$M-Ni^{2+}, $0{\cdot}89 \,.\, 10^{-2}$M-Cd^{2+} or $1{\cdot}53 \,.\, 10^{-2}$M-Zn^{2+}, 1 ml of $1{\cdot}10^{-2}$M 1-PAN in ethanol and 10 μl 1M tris(hydroxymethyl)aminomethane. After shaking the solution was diluted with 10^{-3}M-1-PAN in MIBK to 50 ml and formed a single phase. Both standardization methods yield the same results. After complete separation of the organic phase the aqueous phase was nebulized directly in the acetylene–air flame (22·5 l min^{-1} air and 3·9 l min^{-1} acetylene) and the evaluation was carried out using a calibration curve and the standard addition method. Aqueous solutions of the standard were prepared by shaking an aqueous solution of the metal with MIBK. For low concentrations of Ni and Co, 20 μl of the aqueous phase, adjusted to 0·1M-HNO_3 or $HClO_3$ or $HClO_4$, was placed in the HGA-74 graphite cuvette. The sample was first dried at 100°C (20 s) and then subjected to slow decomposition up to 500°C (45 s) for cobalt or up to 1 200°C (80 s) for nickel; atomization was then carried out at 2600°C (8 s) for cobalt and 2650°C (8 s) for nickel with an argon flow rate of 350 ml min^{-1}. Non-selective absorption does not occur in the presence of KNO_3; in the presence of $NaClO_4$, the use of the deuterium background corrector is necessary. Non-selective absorption in the determination of copper in the aqueous phase was completely eliminated by Zeeman modulation of the absorption resonance line in an alternating magnetic field using a CR-90 graphite rod on a home-made apparatus[9]. 10 μl of the aqueous phase were applied to the graphite rod, the sample was dried at 95°C (35 s), decomposed at 900°C and atomized at 2000°C (2 s) with a temperature increase of 500°C. s^{-1} with a nitrogen flow-rate of 2 l min^{-1}.

Spectrophotometric determination was carried out to find $\log D_M$ for the Co(III)–1-PAN system at 600 nm using the absorption of the organic phase according to relationship (*2*)

$$D_M = \frac{c_{M,org}}{c_{M,t} - c_{M,org}}\,, \qquad (2)$$

TABLE I

The Detection Limit and $\log D_M$ Values for Individual Metals in the Aqueous Phase After Extraction with 1-PAN into MIBK

Metal	Acetylene–air flame		Electrothermal atomization	
	detection limit, M	$\log D_M$	detection limit, M	$\log D_M$
Cu	0·4 . 10^{-6}	2·0	4·7 . 10^{-8a}	2·90^a
			3·15 . 10^{-8b}	3·10^b
Co	0·8 . 10^{-6}	1·7	0·02 . 10^{-6}	3·3
				2·0^c; 3·65^d
Ni	0·4 . 10^{-6}	2·0	0·12 . 10^{-6}	2·5
Cd	0·5 . 10^{-7}	2·9		
Zn	0·1 . 10^{-6}	2·6		

Detection limit = 3 s_{blank}; $\log D_M$ corresponds to the maximum attainable value at $c_M = 4 . 10^{-5}$M; ^{a} ClO_4^- medium, ^{b} NO_3^- medium, ac$^-$, $B_4O_7^{2-}$; ^{c} spectrophotometrically for (2·00 ± ± 0·04) . 10^{-6}M Co; ^{d} radiochemically at 45 000 pulses min^{-1} for solutions with 3·96 . 10^{-5}M-Co and detection limit 10 pulses min^{-1}.

where $c_{M,t} = c_{M,org} + c_{M,aq}$. Radiochemical determination of D_M in this system was carried out using 2 ml of each phase with the channel for the ^{60}Co photopeak energy 1·17 MeV and 1·33 MeV. The maximum attainable values of D_M using the individual methods are given in Table I.

The acid-base and extraction constants of the reagents were found graphically from the dependence $1/D_M = f([H])$ in acid media or $1/D_M = f(1/[H]^+)$ in alkaline media and using the two parameter method[10]. The extraction equilibria of the chelate, the number of dissociated protons, the stoichiometry and stability constants of the individual chelates were evaluated from the dependence of $\log D_M = f(pH)$ or $\log D_M = f(\log [HL]_0)$ at constant pH (see[11]), by the method of continuous variations in the spectrophotometric and atomic absorption versions at constant pH (ref.[12,13]) and by the two parameter method from the $\log D_M = f(-\log L)$ curves by comparison of the standard and experimental curves and considering the stepwise formation of the complexes.

The equilibrium constants of the reactions occurring in the given system

$$m\,M + l\,LH_x + n\,H^+ + s\,X \rightleftharpoons H_nM_m(LH_x)_lX_s\,, \qquad (A)$$

where $H_nM_m(LH_x)_lX_s$ is the complex in the aqueous or organic phase, were calculated using the general DISTR-LETAG minimization program[14–17]. This program is analogous to the LETAGROP-DISTR program[18], but it can be used on small and medium-sized computers. In this program the minimization criterion is defined by equation (3):

$$U = \sum_{i=1}^{N} (\log D_{M(exp)} - \log D_{M(calc)})^2\,. \qquad (3)$$

Values of the equilibrium extraction constants which yielded minimal values of the sum of the squares of the deviation of $\log D_M$ between the experimental and calculated values of the distribution coefficient were sought. The calculation of $D_{M(calc)}$ is carried out for each set of minimization parameters β'_i according to relationship (4)

$$D_M = \frac{\sum_{i=1}^{N} m\,.\,\beta'_i[H]^n\,[M]^m\,[LH_x]^l\,[X]^s\,r^{f_k}f_k}{[M] + \sum_{i=1}^{N} m\beta'_i[H]^n\,[M]^m\,[LH_x]^l\,[X]^s\,r^{f_k}(1 - f_k)}\,, \qquad (4)$$

where r is the ratio of the volume of the organic and aqueous phases and constant β'_i is defined by the relationship

$$\beta'_i = [M_mH_n(LH_x)_lX_s]\,[H]^{-n}\,[M]^{-m}\,[LH_x]^{-l}\,[X]^{-s}\,.$$

If general equilibrium (A) designates the equilibrium formation of the complex in the aqueous phase, then this is indicated by a coefficient value of $f_k = 0$. If it designates an extraction equilibrium, then the complex had a coefficient value of $f_k = 1$. In addition to the stoichiometric coefficients m, n, l, and s giving the complex composition, each complex also has a value of coefficient f_K, indicating whether the complex is in the organic or aqueous phase. This designation is the same as in the LETAGROP-DISTR program[18]. Dependence $\log D_M = f(pH)$ is known from the experimental data, which also yield the overall analytical concentration of components LH_x, M and X and, for the ternary and quaternary systems, also the values of the dissociation constants of the reagent LH_x.

RESULTS AND DISCUSSION

Extraction of Chelates of Zn, Cd, Cu, Co *and* Ni *with Selected* N-*Heterocyclic Azodyes into MIBK*

Maximum extraction of the whole group of elements ($\geqq 99\%$) occurs with TAC at $pH > 8{\cdot}9$, with TAMP at $pH > 7{\cdot}7$, with 2-TAN at $pH > 7{\cdot}7$, with 2-PAN at $pH > 8{\cdot}0$, with 1-PAN at $pH > 6,6$ with 1-BAN at $pH > 6{\cdot}5$ and with 1-QAN at $pH > 7{\cdot}6$ for reagent concentrations of $2 \,.\, 10^{-3}$M. Because of the easier phase separation at higher pH values, group extraction is most readily carried out with 1-PAN ($pK_{a2} = 10{\cdot}2$ (1-PAN) (ref.[17]), $pK_{a2} = 7{\cdot}4$ (1-BAN) (ref.[19]). The Co. Cu, Ni group is extracted practically quantitatively with 1-PAN into MIBK at $pH > 3{\cdot}5$. The AAS absorbance of the organic phase with 1-PAN is constant up to pH 11·5. With the chelates of the other azodyes, especially 2-PAN, TAMP and TAC, the absorbance decreases at $pH > 10$, probably as a result of formation of chelates of the $ML_n(OH)_x$ type.

Procedure: Aqueous solutions of Zn^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} with *I* 0·1 (NO_3^-) were shaken for 4 h on a horizontal shaker with solutions of 1-PAN, 1-BAN, 1-QAN, 2-PAN,

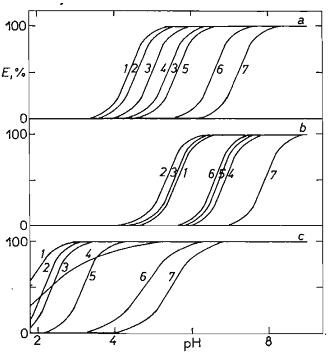

FIG. 1

Extraction Curves for Zn, Cd and Cu

$c_M = 4 \,.\, 10^{-5}$M, *a* $2 \,.\, 10^{-3}$ *b* reagent solution in MIBK is added, *I* 0·1 (NO_3^-), 4 h. extraction, *a* — Zn, *b* — Cd, *c* — Cu. Curve *1* 1-PAN, *2* 1-BAN, *3* 1-QAN, *4* 2-PAN, *5* 2-TAN, *6* TAMP, *7* TAC.

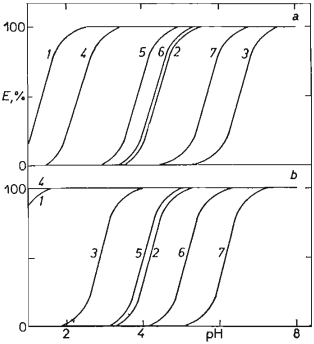

FIG. 2

Extraction Curves for Ni and Co

$c_M = 4{\cdot}10^{-5}$M, $c_L = 2 \,.\, 10^{-3}$M, the reagent solution in ethanol is added to the aqueous phase at pH 2, *I* 0·1 (NO_3^-), 1 h. extraction, *a* — Ni, *b* — Co. Curve *1* 1-PAN, *2* 1-BAN, *3* 1-QAN, *4* 2-PAN, *5* 2-TAN, *6* TAMP, *7* TAC.

2-TAN, TAMP or TAC in MIBK. After extraction, the volume of each phase was 5 ml. After phase separation, the metal concentration was found by AAS after dispersion of each phase in an acetylene-air flame. The dependences of %E on pH for extraction of Cu, Cd and Zn are depicted in Fig. 1. The extraction of cobalt and nickel into MIBK was still incomplete and irreproducible after 12 h, expecially in alkaline solutions. Complete extraction of the metals can be achieved only by formation of the chelate in the aqueous phase in acid solution. Consequently, a solution of the dye in ethanol (1 ml) was added to an aqueous solution of the metal of pH ≈ 2 and 5·2 ml of the aqueous phase was extracted for 1 h with 4·8 ml MIBK. After extraction, the volume of both phases was 5 ml. The ionic strength and 20% ethanol content are also related to a volume of 5 ml regardless of its distribution between the organic and aqueous phases. The concentration of metal in each phase was again found by AAS with an acetylene-air flame and the dependences of %*E* on pH are given in Fig. 2.

The Effect of Organic Solvents on the Determination of Cu, Co, Ni, Cd *and* Zn *as the* 1-PAN *Chelates in an Acetylene-Air Flame*

Optimum flame conditions for chelate dispersion in various solvents are given in Table II; Table III contains the detection limits and relative increase in the sensitivity of the determination in organic solvents compared to aqueous solutions. The greatest AAS sensitivity for the determination of copper, cobalt, nickel, cadmium and zinc is attained using ethyl acetate and isopropyl acetate. These solvents are, however,

TABLE II

Optimum Conditions for the Determination of Cu, Co, Ni, Cd and Zn as the 1-PAN Chelate in Various Solvents by AAS

Solvent	Cu		Co		Ni		Cd		Zn	
	C_2H_2	v_h[a]	C_2H_2	v_h	C_2H_2	v_h	C_2H_2	v_h	C_2H_2	v_h
	$l\,min^{-1}$	cm	$l\,min^{-1}$	cm	$l\,min^{-1}$	cm	$l\,min^{-1}$	cm	$l\,min^{-1}$	cm
Water	4·0	0·75	4·0	1·00	4·0	1·00	4·0	1·00	4·5	0·80
MIBK	1·1	0·80	1·1	1·00	1·1	1·00	1·1	1·00	1·1	0·80
Ethyl acetate	0·9	0·90	0·9	1·25	0·9	1·25	0·9	1·12	0·9	0·88
Isopropyl acetate	0·9	0·90	0·9	1·15	0·9	1·25	0·9	1·12	0·9	1·12
n-Butyl acetate	1·1	0·55	1·1	0·75	1·1	0·75	1·1	0·88	1·1	0·50
n-Amyl acetate	1·1	0·60	1·1	0·62	1·1	0·62	1·1	0·75	1·1	0·50
Xylene	0·9	0·70	0·9	0·75	0·9	0·75	0·9	0·88	0·9	0·50

[a] v_h is the observation height in the flame; air flow-rate of aqueous solutions 22·5 l min^{-1}, for organic solvents 15·0 l min^{-1}.

quite soluble in water and also increase the determination background. The optimum detection limit is generally attained using MIBK and butyl acetate.

Chelate preparation: 60—130 μl 1·57 . 10^{-2}M-Cu^{2+}, 1·98 . 10^{-2}M-Co^{2+}, 1·70 . 10^{-2}M-Ni^{2+}, 0·89 . 10^{-2}M-Cd^{2+} or 1·53 . 10^{-2}M-Zn^{2+} and 1 ml of 1 . 10^{-2}M-1-PAN in ethanol were thoroughly shaken with 10 μl of 1M tris(hydroxymethyl)aminomethane and diluted to 50 ml with 1 . 10^{-3}M-1-PAN in an organic solvent.

Extraction of 1-PAN *and Its Metal Chelates into* MIBK

Extraction of 1-PAN was carried out in a medium of 20% (v/v) ethanol of I 1·0 for pH < 2 and I 0·1 for pH > 2 for a period of 3 h (after extraction $V_{aq} = V_{org} = 10$ ml). The concentration of the reagent in both phases was determined spectrophotometrically, at 483 nm ($\varepsilon = 1{\cdot}65 \,.\, 10^4$) in the organic phase and at 464 nm ($\varepsilon = 1{\cdot}48 \,.\, 10^4$) in the aqueous phase for pH < 3 after adjusting to 1-M-$HClO_4$ with 2M-$HClO_4$ and for pH > 3 at 515 nm ($\varepsilon = 2{\cdot}3 \,.\, 10^4$) after adjustment with 0·5M-NaOH to a 0·1M-NaOH medium. The calculated values of the dissociation constants and distribution coefficients are given in Table IV.

Extraction of cadmium with 1-PAN. The red-purple chelate of cadmium with 1-PAN (λ_{max} 547 nm and 580 nm) was extracted from a medium of 20% ethanol for 2 h into MIBK (after extraction $V_{aq} = V_{org} = 5$ ml); log D_M is constant for $1-10$ h in the range 1 . $10^{-5}-4$. 10^{-5}M-Cd. The linear part of the dependence of log D_M on pH has a slope of 2 (Fig. 3), similar to the dependence of log D_M on log [HL] at pH 5·59. The Job plots for the nonaqueous phase at $c_0 = 2{\cdot}0 \,.\, 10^{-5}$M,

TABLE III

The Detection Limit and Relative Sensitivity Increase for the Determination of Cu, Co, Ni, Cd and Zn by AAS as the 1-PAN Chelate in Various Solvent Compared to the Determination in Water

Solvent	Detection limit, 10^5M					Rel. sensitivity increase				
	Cu	Co	Ni	Cd	Zn	Cu	Co	Ni	Cd	Zn
Water	0·018	0·051	0·114	0·0090	0·0276	1·0	1·0	1·0	1·0	1·0
MIBK	0·022	0·011	0·013	0·0026	0·0070	4·0	4·9	4·5	5·2	5·0
Ethyl acetate	0·014	0·023	0·025	0·0052	0·0080	5·1	5·3	4·5	5·5	5·0
Isopropyl acetate	0·014	0·028	0·031	0·0033	0·0087	5·1	5·3	5·0	5·5	5·7
n-Butyl acetate	0·018	0·013	0·029	0·0029	0·0067	3·6	4·7	3·9	4·6	4·4
n-Amyl acetate	0·025	0·018	0·035	0·0042	0·0114	3·3	4·2	3·7	4·2	4·2
Xylene	0·030	0·036	0·060	0·0052	0·0178	3·0	4·7	3·9	4·3	4·2

pH 9·52, $V_{org} : V_{aq} = 1 : 1$ have the theoretical shape and a sharp maximum for Cd : L = 1 : 2, both in the spectrophotometric measurement of the complex at 580 nm and in measurement of the cadmium absorbance by AAS. The calculation of the stability constants followed from the dependence of log D_M on pH using the two parameter method and a computer. The DISTR program was employed, using 43 experimental points and pK_{a1}, pK_{a2} and log K_D(HL) assuming the existence of equilibria

$$M^{2+} + HL \rightleftharpoons ML_{(aq)} + H^+ \tag{B}$$

$$M^{2+} + 2\,HL \rightleftharpoons ML_{2(aq)} + 2\,H^+ \tag{C}$$

$$M^{2+} + 2\,HL \rightleftharpoons ML_{2(org)} + 2\,H^+ , \tag{D}$$

(see Table V).

TABLE IV

Dissociation Constants K_a and Distribution Constants K_D(HL) for 1-PAN in MIBK

Constants	DISTR program	Two parameter method	Graphical method
pK_{a1}	2·092 ± 0·005	2·08	2·08
pK_{a2}	10·213 ± 0·009	10·18	10·18
log K_D(HL)	2·829 ± 0·009	2·82	2·82

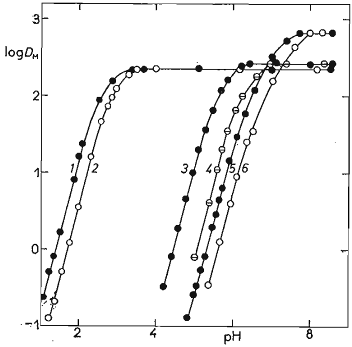

FIG. 3

The Dependence of log D_M on the pH of the Aqueous Phase in Extraction of Cd, Zn and Ni with 1-PAN into MIBK

$c_M = 4 \cdot 10^{-5}$M, $V_{org} : V_{aq} = 1$, I 0·1, c_L: ● 2 . 10^{-3}M, ○ 1 . 10^{-3}M, ⊖ 5 . 10^{-4}M. Curve 1, 2 Ni, ClO_4^-, 1·5 h extraction; 3, 4 Zn, NO_3^-, 2 h extraction, 5, 6 Cd, ClO_4^-, extraction for 2 h.

Extraction of zinc with 1-PAN. The red chelate of zinc with 1-PAN (λ_{max} 544 and 583 nm) was extracted from 20% ethanol for 2 h (the volume of the phase after extraction $V_{aq} = V_0 = 5$ ml). The slope of the linear part of the dependence of log D_M *vs* pH was 2 (Fig. 3), similar to the slope of the dependence of log D_M on log [HL] at pH 5·00. Log D_M does not change for extraction times of 1 – 4 h for concentrations of $10^{-5} - 4 . 10^{-5}$M-Zn^{2+}. The spectrophotometric and atomic absorption Job curves of the extract in MIBK for $c_0 = 2 . 10^{-5}$M at pH 9·52 and 583 nm or 228·8 nm have a maximum only for Zn : L = 1 : 2. The stability constants calculated from 30 experimental points by the two parameter method and using a computer are given in Table VI.

TABLE V

Stability Constant for the Cadmium Complex with 1-PAN and Distribution Constant $K_D(CdL_2)$ into MIBK

Constants	Two parameter method[a]	DISTR program	Ref. data
log β_1	9·00	8·70 ± 0·05	8·53[b]
log β_2	18·00	17·83 ± 0·024	17·59[b]
log $K_D(CdL_2)$	2·82	2·92 ± 0·02	—

[a] Parameters $a = 9·00$; $b = 0$; [b] ref.[15].

TABLE VI

Stability Constant of Zinc with 1-PAN and Distribution Constant $K_D(ZnL_2)$ into MIBK

Constants	Two parameter method[a]	DISTR program	Ref. data
log β_1	9·28	9·39 ± 0·10	10·30[b]
log β_2	19·96	20·07 ± 0·02	20·03[b]; 19·4[c] 19·6[d]
log $K_D(ZnL_2)$	2·42	2·42 ± 0·07	

[a] Parameters $a = 9·98$, $b = —0·7$; [b] ref.[15]; [c] ref.[16]; [d] ref.[17].

Extraction of nickel with 1-PAN. The red-purple chelate of nickel with 1-PAN (λ_{max} 552 and 593 nm) was extracted into MIBK for 1·5 h from a medium of 20% (v/v) ethanol (phase volume $V_{org} = V_{aq} = 5$ ml after extraction). The extraction equilibrium is established during 0·5–2 h. The dependence of log D_M on pH (Fig. 3) and log D_M on log [HL] at pH 2·01 have slopes of 2. The spectrophotometric and atomic absorption Job curves for 593 nm or 232·0 nm for pH 5·27 and $c_0 = 4 . 10^{-5}$M have a sharp maximum for a component ratio of Ni : L = 1 : 2. The two parameter method and calculation according to the DISTR program confirm, similar to the previous calculation, that complexes ML and ML_2 are formed stepwise and that the latter is extracted into MIBK. The stability constants of the complexes are given in Table VII. The large error in the calculation of log β_1 indicates that only a very small amount of complex ML is formed in the aqueous phase.

Extraction of copper with 1-PAN. Two different complexes are extracted into MIBK depending on the concentration of copper; at pH 6·50 and $c_L/c_M \geqq 2$, λ_{max} lies at 554 and 590 nm and for $c_L/c_M = 1$ at 569 nm. Spectrophotometric and absorption curves for Job plots at pH 2·57 indicate extraction of a complex with Cu : L = 1 : 1, at pH 6·80 a mixture of complexes with Cu : L = 1 : 1 and 1 : 2 and at pH 11·30 only the complex with Cu : L = 1 : 2. The extraction pH curve, log D_M *vs* pH, for 2 h extraction from a medium of 20% (v/v) ethanol and 0·1M-NO_3^- and for pH < 4 is linear with a slope of 1·0, which confirms the extraction of a chelate with a component ratio of Cu : L = 1 : 1. The effect of various anions at pH 1–2 confirms the formation and extraction of various ion associates with a ratio of M : L = = 1 : 1, whose stability increases in the order: $NO_3^- < Cl^- < ClO_4^- < Br^- < < SCN^-$. Only in the presence of sulphate does the slope of the dependence of log D_M on pH have a value of 2 and a complex with M : L = 1 : 2 is extracted, which is also confirmed by the slope of the dependence of log D_M on log [HL] at pH 2·36

TABLE VII

Stability Constant of the Nickel Complex with 1-PAN and Distribution Constant $K_D(NiL_2)$ into MIBK

Constants	Two parameter method[a]	DISTR program	Ref.
log β_1	12·10	7·81 ± 6·74	
log β_2	26·20	26·29 ± 0·01	23[b]
log $K_D(NiL_2)$	2·35	2·36 ± 0·01	

[a] Parameters $a = 13·10$, $b = -1$; [b] ref.[16].

in sulphate medium. In ClO_4^- and NO_3^- media at pH 1·11 and 1·26 the dependence of $\log D_M = f(\log [HL])$ again has a slope of 1. The slope of the dependence of $\log D_M$ on $\log [X]$ ($X = ClO_4^-, NO_3^-$) at pH 1·98 and a constant concentration of the ligand $c_L = 10^{-3}$M indicates that, in the presence of ClO_4^- and NO_3^-, the composition of the extractable ML^+X^- complex is unambiguous; however, in the region of the plateau on the extraction curve $\log D_M$ *vs* pH, the CuL_2 complex is also extracted. Log D_{Cu} does not change over 0·5–3 h extraction. The distribution coefficients of both complexes cannot be determined as, in the region of the plateau on the extraction curve, only a value of $\log D_{Cu} \geqq 2{\cdot}90$ was found for a ClO_4^- medium and $\log D_{Cu} \geqq 3{\cdot}10$ for a NO_3^- medium (Table I).

The dependence of $\log D_M$ on pH, $\log [HL]$ and $\log [X]$ (altogether 40 experimental points) was evaluated on a computer according to the DISTR program and the equilibrium constants for reaction (*E*) were calculated:

$$M^{2+} + HL + X^- \rightleftharpoons MLX_{(org)} + H^+ . \qquad (E)$$

For $X^- = NO_3^-$, $\log \beta' = 5{\cdot}09 \pm 0{\cdot}01$ and for $X^- = ClO_4^-$, $\log \beta' = 6{\cdot}38 \pm 0{\cdot}01$. The approximate values of constant β' can be found directly from the dependence

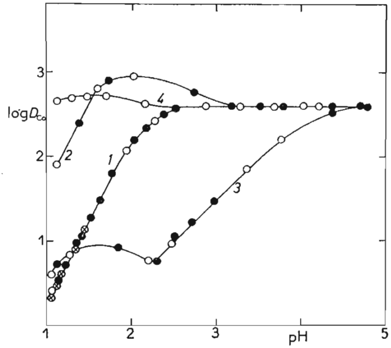

FIG. 4

The Dependence of $\log D_{Co}$ on the pH of the Aqueous Phase for Extraction of $4 \,.\, 10^{-5}$M-Co with $1 \,.\, 10^{-3}$M-1-PAN into MIBK in Various Media

4 h extraction on linear extractor, 12 h on a circular with ^{60}Co. AAS Data ●, with ^{60}Co ○, spectrophotometrically at 600 nm ⊗. Curve *1* 0·1M-NO_3^-, *2* 0·1M-ClO_4^-, *3* 0·1M-ClO_4 + 0·1M ascorbic acid, *4* 0·1M-NO_3^- + 0·01M-IO_4^-.

of log D_M on pH for 0·1M X^- and $c_L = 10^{-3}$M and log $D_M = 0$, according to the relationship log $\beta' = pH + \log(1 + K_{HL})$.

Extraction of cobalt with 1-PAN. In the extraction of an aqueous ethanolic solution of Co^{2+} (nitrate or chloride) with 1-PAN, a green complex is extracted in acid medium (640, 600 and 395 nm) and a blue complex from pH > 7 (578, 546 nm); in the presence of IO_4^- only the green and in the presence of ascorbic acid only the blue complex is extracted from pH > 2·8, ($c_M = 4 . 10^{-5}$M, $c_L = 10^{-3}$M, $I = 0·1$). The extraction curves for the complex of Co with 1-PAN in various media after extraction for 4 h into MIBK are depicted in Fig. 4. The value of log D_M did not change after 1 min extraction for 20 h. The slope of the linear part of the dependence of log D_M on pH for media of NO_3^- and ClO_4^- is 2; in the presence of ClO_4^- and IO_4^- the extraction curve is shifted to acid media and an anomalous maximum appears. The slope of the dependence of log D_M on log [HL] at pH 1·54 and for solutions with $c_M = 4 . 10^{-5}$M and $2 . 10^{-4}-2 . 10^{-3}$M-1-PAN is also 2 in the presence of 0·1M-HNO_3^-. The dependence of log D_M on log $[NO_3^-]$ at pH 1·64 and concentrations of $c_M = 4 . 10^{-5}$M, $c_L = 10^{-3}$M and 0·023 – 0·1M-NO_3^- has a slope of 1. Spectrophotometric and Job curves for media of NO_3^- and ClO_4^- at pH 2·30 – 11·50 and for $c_0 = 4 . 10^{-5}$M indicate the formation of a complex with Co : L = 1 : 2. With increasing concentration of Co^{2+} and a constant concentration of $c_L = 10^{-3}$M at pH 1·15, a decrease in the extraction of cobalt into MIBK was observed.

The results indicate the formation of the ternary complex $[Co(III)L_2]^+X^-$ ($X^- = ClO_4^-$ or NO_3^-), which is quantitatively extracted from pH > 2·6 in the presence of NO_3^- and from pH > 1·6 in the presence of ClO_4^-. In the presence of 1-PAN, spontaneous oxidation of Co(II) to Co(III) occurs; this process is instantaneous in the presence of IO_4^- or H_2O_2 (ref.[20]). In the presence of ascorbic acid the oxidation of Co(II) is suppressed and the blue Co(II)L_2 complex is formed and extracted quantitatively at pH > 4·75. This complex is also formed at pH > 7 in the absence of a reducing agent in ClO_4^- and NO_3^- media and in solutions with excess reagent, $c_L = 10^{-3}$M.

Group Extraction of Copper, Cadmium, Zinc, Cobalt and Nickel with 1-PAN *into* MIBK *for Determination of the Elements by* AAS

At $c_L = 2 . 10^{-3}$M and in media of 20% (v/v) ethanol the extraction of the individual metals at concentrations of $c_M \leqq 4 . 10^{-5}$M is quantitative after 5 minutes for Cu^{2+} at pH > 4·6, for Co^{2+} at pH > 4·4, for Ni^{2+} at pH > 3·0, for Cd^{2+} at pH > 7·7 and for Zn^{2+} at pH > 6·3 (the phase volumes after extraction, $V_{org} = V_{aq} = 5$ ml). The reaction components must be mixed at pH $\simeq$ 2. The whole group of elements is extracted at pH > 7·7 in the presence of 0·1M tris(hydroxymethylaminomethane) after 5 minutes.

Procedure: To 6 ml of a solution of the ion mixture of pH ≈ 2 is added 2 ml of 10^{-2}M 1-PAN solution in ethanol, 1 ml of 1M tris(hydroxymethyl)aminomethane and 1·4 ml of redistilled water. This mixture is extracted with 9·6 ml of MIBK in a test tube with a ground glass stopper for 5 minutes. After centrifugation, the organic phase is dispersed directly into an acetylene–air flame (15 l min^{-1} air and 1·1 l min^{-1} acetylene) and the absorbance is measured at an observation level of 1·0 cm for the determination of Co, Ni, and Cd and of 0·80 cm for the determination of Cu and Zn. The sensitivity of the determination of the elements is given in Table VIII. The microsampling technique was also found useful for 300 µl of extract and using a teflon crucible. The blank value must be considered in treating the recorded absorbance value.

In electrothermal atomization on a HGA-74 graphite cuvette, 20 µl of extract are employed, so that the extracted volume can be decreased to 1 ml of each phase. The extract is dried at 100°C (10 s), at 120°C (10 s) and with gradually increasing temperature at 300°C for 120 s. The sample decomposes at 900°C for Cu, 1200°C for Ni, 1100°C for Co, and 300°C for Cd and Zn after a period of 20 s; atomization occurs at 2550°C for Cu, at 2650°C for Ni, at 2600°C for Co and

TABLE VIII

Some Parameters for the Determination of Cu, Ni, Co, Zn and Cd in MIBK Extract with 1-PAN by Flame AAS

Element	Charact.[a] conc., ng ml^{-1}	Detection limit, ng ml^{-1}	Limit of linearity of the calibration curve, µg ml^{-1}
Cu	22·9	14·0	0·64
Ni	31·7	7·6	0·65
Co	26·5	6·5	1·18
Cd	7·7	2·9	0·28
Zn	5·2	4·6	0·13

Sensitivity of the Method[b]

Element		Molec. spectrophotometry[15]	
	AAS . 10^{-4}, M^{-1}	$\varepsilon \cdot 10^{-4}$	λ, nm
Cu	1·12	4·6	583
Ni	0·74	5·5	598
Co	0·90	3·2	548
Cd	5·8	—	—
Zn	5·0	5·2	587

[a] Characteristic concentration corresponds to $A = 0{\cdot}004$; [b] sensitivity (AAS) is the slope of the dependence of A *vs* c_M (mol l^{-1}) for $c_M \to 0$.

at 1900°C for Cd, and for Zn after a period of 8 s and with an argon flow-rate of 50 ml mim^{-1} for Cu, Ni, Cd, Co and 300 ml min^{-1} for Zn. Data on the sensitivity for the individual determinations are given in Table IX. Using a CR-90 graphite rod in a magnetic field with modulation of 100 Hz (see[9]), copper can be determined with MIBK extraction without prolonged drying with a detection limit of 10^{-8}M or 0·64 ng ml^{-1} Cu. The extraction can also be carried out at phase ratios of $V_{aq} : V_{org} = 10 : 1$, with extraction of 95·5% Ni, 97·5% Co, 98·7% Cu, 96·7% Zn and 98·5% Cd in a single extraction.

The Interfering Effect of Ions in Group Extraction into MIBK

In the extraction of solutions of 4 . 10^{-5}M Cu, Ni, Co, Zn and Cd at pH 8·5–9·5 (0·1M tris(hydroxymethyl)aminomethane buffer) in the presence of 10^{-3}M-1-PAN with a phase ratio of $V_{org} : V_{aq} = 1 : 1$, the following elements interfere: 5 . 10^{-4}M-Fe^{2+}, 10^{-3}M-Fe^{3+}, Pb^{2+}, Mn^{2+}, 10^{-4}M-Al^{3+}, Be^{2+}; 7 . 10^{-5}M-Sn^{2+}, 2 . 10^{-3}M-Hg^{2+}, 5 . 10^{-3}M-Ag^{+}, 0·7M Mg^{2+}, 1·2M-Ca^{2+}, Sr^{2+}, Ba^{2+}, Li^{+}, 1·5M-Na^{+}, K^{+}. Al^{3+} interferes primarily in the determination of Cd and Zn, which are not extracted at concentrations greater than 0·1M-Al^{3+}. Group extraction using 1-PAN in MIBK has been found to be useful in the analysis of K^{+}, Na^{+}, Li^{+}, Ca^{2+}, Sr^{2+} and Ba^{2+} salts.

Extraction and Determination of Microamounts of Cu, Co, Ni, Cd and Zn in KCl, KBr, KI, KNO_3, $NaClO_4$, KSCN, NaCl, K_2CrO_4, $Ca(NO_3)_2$, $BaCl_2$ and $SrCl_2$ Solutions

Over 95% of these microcomponents are extracted from 1M salt solutions. To 80 ml of the salt solution, acidified to pH 2 are added 2 ml of 10^{-2}M 1-PAN in ethanol, 5 ml of 1M tris) hydroxymethyl)aminomethane buffer and 12 ml of distilled water and the mixture is extracted with 11 ml of MIBK after 5 minutes. After separation and centrifugation of the phases, the organic phase is nebulized through the capillary into the flame.

TABLE IX

Parameters of the Method of Determining Cu, Co, Ni, Cd and Zn in MIBK Extracts after Electrothermal Atomization on HGA-74

	Sensitivity of determ. 10^{-4}, M^{-1}	Charact. conc.[a] ng . ml^{-1}	Detection limit, ng ml^{-1}	Limit of linearity of calc. curve ng ml^{-1}
Cu	7·5	3·37	2·54	318
Co	7·0	3·38	2·47	295
Ni	5·7	4·11	2·64	295
Cd	500	0·09	0·045	5·6
Zn	90	0·29	0·13	32·5

[a] The characteristic concentration corresponds to $A = 0{\cdot}004$.

The Determination of Cu, Cd and Zn in Potable Waters

50 ml of potable water is acidified with 1 ml of 0·5M-HNO_3, 1 ml of 10^{-2}M-1-PAN in ethanol is added along with 2·5 ml of 1M-tris(hydroxymethyl)aminomethane buffer. The mixture is extracted for 5 min with 5·5 ml of 2 . 10^{-3}M 1-PAN in MIBK. After the extraction, the organic phase is separated and centrifuged and 300 µl of the MIBK extract is nebulized in the flame from a teflon crucible for determination of Cu and Zn. Cd is determined after addition of 20 µl of extract to a graphite cuvette. The accuracy of the results was confirmed by emission spectral analysis and amalgam stripping polarography.

The Determination of Cu, Co and Ni in Metallic Aluminium

20 mg of metallic aluminium is dissolved in 2·5 ml of 6M-HCl, 0·5 ml of 10^{-2}M-1-PAN in ethanol are added, the solution is diluted to 25·5 ml with 0·1M potassium citrate and the pH is adjusted to pH > 6 if necessary. The extraction is carried out using 2·6 ml of 2 . 10^{-3}M-1-PAN in MIBK for 5 min. After centrifugation, 2·5 ml of the organic phase is added in 20 µl amounts to the graphite cuvette.

REFERENCES

1. Lemonda A. J., McClellan B. E.: Anal. Chem. *45*, 1455 (1973).
2. Culp J. M., Wingham R. L., Whealy R. D.: Anal. Chem. *43*, 1321 (1971).
3. Lerner L. A., Rusanov A. A., Nedler V. V.: Zh. Anal. Khim. *26*, 1697 (1971).
4. Routh M. W., Denton M. B.: Appl. Spectrosc. *30*, 344 (1976).
5. Grigoriev V. F., Lisienko D. G., Muzgin V. N.: Zh. Prikl. Spektrosk. *20*, 970 (1974).
6. Chakrabarti C. L., Singhal S. P.: Spectrochim. Acta *24B*, 663 (1969).
7. Sastri V. S., Chakrabarti C. L., Willis D. E.: Can. J. Chem. *47*, 583 (1969).
8. Fujiwara K., Haraguchi H., Fuwa K.: Anal. Chem. *44*, 1895 (1972).
9. Otruba V., Jambor J., Komárek J., Horák J., Sommer L.: Anal. Chim. Acta *101*, 367 (1978).
10. Dyrssen D., Sillén L. G.: Acta Chem. Scand. *7*, 663 (1953).
11. Starý J.: Chem. Listy *53*, 556 (1959).
12. Sommer L., Kubáň V., Havel J.: Folia Fac. Sci. Nat. Univ. J. E. Purkyně, Brno 11, *1*, 3 (1970).
13. Komárek J., Horák J., Sommer L.: This Journal *39*, 92 (1974).
14. Havel J., Vrchlabský M., Sekaninová J., Komárek J.: Scr. Fac. Sci. Nat. Univ. J. E. Purkyně, in press.
15. Kawase A.: Bunseki Kagaku *16*, 569 (1967).
16. Betteridge D., Todd P. K., Fernando Q., Freiser H.: Anal. Chem. *35*, 729 (1963).
17. Betteridge D., John D.: Analyst (London) *98*, 390 (1973).
18. Liem D. H.: Acta Chem. Scand. *25*, 1523 (1971).
19. Kawase A.: Bunseki Kagaku *17*, 56 (1968).
20. Komárek J.: Unpublished results.

Translated by M. Štulíková.