

ATOMIC ABSORPTION OF ZINC AFTER EXTRACTION OF ITS CHELATE WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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Extraction of Zn^{2+} with 1-(2-pyridylazo)-2-naphthol (PAN) in benzene and methyl isobutyl ketone, resp., was studied by means of atomic absorption, and the methods of determination of zinc by atomic absorption in the two systems were compared. The latter medium is suitable for the determination of zinc traces in concentrated solutions of alkali and alkali earth salts.

Atomic-absorption determination of an element after preceding extraction of its chelates with organic reagents into organic solvents is widely used, owing to the enrichment of the traces of the element; the sensitivity of atomic absorption also increases, when selected organic solvents are nebulized¹. Atomic absorption enables also the extraction equilibria of metal chelates and ionic associates to be evaluated rapidly, even if no suitable radioactive isotope of the element determined is available. Zinc has been determined by atomic absorption after the extraction of its chelate with dithizone into ethyl propionate^{2,4}, into methyl isobutyl ketone³, chelate with 8-hydroxyquinoline into methyl isobutyl ketone³, chelate with cupferrone and with ammonium pyrrolidine dithiocarbamate into methyl isobutyl ketone^{5,6}.

In this work, a method for the determination of zinc by atomic absorption spectroscopy after a preceding extraction in the system Zn^{2+} -PAN-benzene and Zn^{2+} -PAN-methyl isobutyl ketone (PAN = 1-(2-pyridylazo)-2-naphthol) was developed. The interpretation of the data obtained by atomic absorption confirmed a simple extraction equilibrium for benzene and methyl isobutyl ketone, identical with the results obtained previously⁷ by means of other techniques. At the same time, the technique of atomic absorption proved to be as reliable for the evaluation of extraction data as the radiochemical and spectroscopic methods.

EXPERIMENTAL AND RESULTS

Reagents and Apparatus

Standard solution of zinc nitrate in 0.05M-HNO₃ containing 10.00 mg Zn in 1 ml was standardized with EDTA on xylene orange. 1-(2-Pyridylazo)-2-naphthol (PAN), Lachema, was recrystallized from methanol. The stock solutions in benzene and methyl isobutyl ketone, resp., were $2 \cdot 10^{-3}$ M.

All the chemicals used were analytically pure or were purified by crystallization or rectification.

In some cases, traces of heavy metals were extracted from solutions of reagents with 10^{-3} M-PAN in benzene.

Atomic absorption was measured by using a UNICAM SP 90 instrument with a modulated source, spray chamber, laminar burner, and premixed gas mixture acetylene-air, and a zinc hollow cathode (NHKG Ostrava-Kuncice, VVUÚ Ostrava-Radvanice) with $I = 8$ mA. The line 213.9 nm was evaluated; the slot burner width was 10 cm, height 10 mm, slit 0.4 mm. The flow rates of air and acetylene were 5.0 and 1.0 l/min, resp., for aqueous solutions or mixed solutions with dimethylformamide, for 1-butanol, isoamyl alcohol, diisobutyl ketone, n-butyl acetate, or isoamyl acetate, and 5.0 and 0.7 l/min, resp., when methyl isobutyl ketone or ethyl acetate were nebulized.

A precise pH-meter OP-205 (Hungary) with a combined electrode GK 230 2B, and a spectrophotometer Spekol Zeiss (GDR) with an attached amplifier were also used.

Measurement Technique

The distribution ratio $D = (c_{Zn})_{org}/(c_{Zn})_{aq}$ was evaluated from two independent calibration curves for the two phases, $A = f(c_{Zn})$. The possible shift of the calibration curves between several measurements was corrected by measuring periodically a standard solution of zinc under defined conditions. The distribution ratio D was also determined by measuring the absorbances of the extracts after the first and the successive extractions. For the extraction with benzene, successive extractions with methyl isobutyl ketone were also carried out.

5 ml of the aqueous phase, containing 0.1M potassium nitrate, a buffer, and Zn^{2+} , were extracted with 5 ml of solution of PAN in the organic phase for a time up to 3 h at 20°C. The aqueous phase was saturated with the organic solvent prior to extraction.

The following simplified relations were used for the interpretation of the extraction equilibria of the chelate ML_N :

$$K_{a1} = [HL][H]/[H_2L] = 10^{-1.9}, \quad (1)$$

$$K_{a2} = [H][L]/[HL] = 10^{-12.2} \quad (\text{aqueous dioxan, 20\% v/v}), \quad (2)$$

$$K_{D(HL)} = [HL]_{org}/[HL]_{aq}, \quad (3)$$

$$K_{D(ML_N)} = [ML_N]_{org}/[ML_N]_{aq}, \quad (4)$$

$$K_{ex} = [ML_N]_{org} [H]_{aq}^N / [M]_{aq} [HL]_{org}^N, \quad (5)$$

$$\beta_N = [ML_N]/[M][L]^N, \quad (6)$$

$$\beta_N = K_{ex} \cdot K_{D(HL)}^2 / K_{a2}^2 \cdot K_{D(ML_N)}, \quad (7)$$

$$\log D = \log K_{ex} + N \text{pH} + N \log [HL]_{org}, \quad (8)$$

$$\text{pL} = -\log [L] = \text{p}K_{a2} - \text{pH} - \log [HL]_{org} + \log (K_{D(HL)} + K_{a2}/[H] + 1), \quad (9)$$

for $c_{HL} \gg c_M$.

The data required were obtained from the plots $\log D = f(\text{pL})$, $\log D = f(\text{pH})$ and from the curves, of continuous variations for the nonaqueous phase. From those dependences and from the equations (1)–(9), the values $\log D$, K_{ex} , and β_N were calculated (Table I).

The β_n values were obtained by means of the two-parameter method^{8,9}; β_n expressed through the parameters a and b is then

$$\beta_n = n \cdot a + b \cdot n \cdot (N - n), \quad \text{where } \beta_n = [\text{ML}_n]/[\text{M}][\text{L}]^n.$$

The coefficient of variation, $v(\%) = R_A \cdot k_n \cdot 100/\bar{A}$, and the relative width of the confidence interval, $r(\%) = 2K_n \cdot R_c \cdot 100/c$ (ref.^{10,11}), were used to express the accuracy of the method with the 95% confidence. For each concentration of zinc, six absorbance values were measured, from which the coefficient of variation was then calculated. The relative width of the confidence interval was then evaluated for the concentration values. The value of variation range (R_c) for a given concentration was obtained from the measured absorbances and from the calibration curve, constructed by using the mean absorbance values \bar{A} . The sensitivity is represented by the slope of the linear part of the calibration curve, and therefore it is limited by the absorbance interval. Concentration of zinc corresponding to the absorbance $A = \bar{A}_{\text{blank}} + 3s$, where s is the standard deviation from 20 blank analyses, is given as the detection limit.

Distribution Coefficient of PAN

5 ml of the aqueous phase, containing 0.1M-KNO₃ and 0.1M acetate or Tris (resulting pH 6.25–9.10) were shaken with 5 ml of $4 \cdot 10^{-2}$ M-PAN in methyl isobutyl ketone in 20 ml extraction tubes for 3 h at 20°C. After centrifugation, the absorbance of the aqueous phase was measured at 465 nm in 1 cm cell, and the concentration was evaluated from the calibration curve. The concentration of the ligand in the nonaqueous phase was calculated from the difference.

For methyl isobutyl ketone, $\log K_{D(\text{HL})} = 3.70$ (mean of 15 values for pH 6.25–9.10). For benzene, the value $\log K_{D(\text{HL})} = 3.64$ was taken⁷.

EXTRACTION OF ZINC IN THE SYSTEM PAN–BENZENE

After a 3 h extraction ($V_{\text{org}} : V_{\text{aq}} = 5 \text{ ml} : 5 \text{ ml}$) and a perfect phase separation, 0.5 ml of 1.4M-HNO₃ is added to 2 ml of the aqueous phase containing ≤ 10 p.p.m. Zn, 0.1M-KNO₃, and 0.05–0.20M concentration of the buffer base, and the mixture is nebulized under the above mentioned conditions. At the same time, 3 ml of the benzene phase, containing ≤ 10 p.p.m. Zn and $2 \cdot 10^{-3}$ M-PAN, are evaporated

TABLE I
Some Data on Chelate ZnL₂ with PAN

Medium	$\log K_{D(\text{MLN})}$	$\log K_{\text{ex}}$	$\log \beta_1^a$	$\log \beta_2^a$	$\log \beta_2^b$
Benzene	1.95	–5.26	12.26	24.52	24.48
Methyl isobutyl ketone	2.60	–4.66	12.30	24.60	24.54

^a Parameters: benzene $a = 12.26$, $b = 0$; methyl isobutyl ketone $a = 12.30$, $b = 0$; ^b calculated from (7).

cautiously to dryness in a microbeaker placed in a heated dessicator at the temperature of 60°C (approximately for 3 h); the evaporation residue is dissolved in 0.9 ml of dimethylformamide, 2.1 ml of 0.1M-HCl are then added and the homogenized mixture is nebulized in the flame. PAN does not interfere in concentrations up to $8 \cdot 10^{-3}$ mol/l in 30% (v/v) dimethylformamide; at higher concentrations a precipitate is formed. Dimethylformamide, 20–30% (v/v), does not affect the absorbance of zinc. In solutions with $c_L = (1-2) \cdot 10^{-3}$ mol/l and with 10 p.p.m. Zn, the maximum yield of extraction of the Zn-chelate with PAN is attained at $\text{pH} \geq 8$. A 20 min extraction is sufficient for systems with an excess of the ligand, $2 \cdot 10^{-3}$ mol/l, and with $\text{pH} \geq 8$. The limit value of $\log D = \log K_{D(\text{ML})} = \log \frac{[\text{ML}_{N(\text{org})}]}{[\text{ML}_{N(\text{aq})}]} = 1.95$ is in a good agreement with that reported by Navrátil⁷. The dependences $\log D = f(\text{pH})$ and $\log D = f(\text{pL})$ are given in Fig. 1 and Fig. 2, resp.

Curves of Continuous Variations

The curves $A_{\text{org}} = f(c_M/(c_M + c_L))$ display a maximum for the molar ratio $M : L = 1 : 2$ at $\text{pH} 5.58$ (0.2M acetate), $\text{pH} 8.27$ (0.05M triethanolamine), and $\text{pH} 9.07$ (0.05M ammoniacal buffer) after a 3 h equilibration (Fig. 3). The absorbance of the nonaqueous phase was corrected to the blank of solutions of the components, containing also the buffer and 0.1M-KNO₃.

For all the procedures, the formation of the ZnL^+ and ZnL_2 particles in the system Zn^{2+} -PAN-benzene was proved unambiguously. Only the chelate ZnL_2 is extracted, no other reagent being added on the chelate. This is in accordance with the findings reported recently⁷. The values β_1 and β_2 are given in Table I.

Analytical Utilization

A quantitative extraction of zinc in contents up to 40 µg is attained at $\text{pH} 8-9$ in the presence of $c_L = 2 \cdot 10^{-3}$ mol/l after a 20 min equilibration, in the medium of 0.05M triethanolamine and 0.1M-KNO₃ and with the phase ratio $V_{\text{org}} : V_{\text{aq}} = 1 : 1 - 1 : 10$. 5 ml of the benzene phase were always used for extraction and the aqueous phase was saturated with benzene. The extraction of zinc is not interfered by the medium of 0.5M sodium perchlorate, 0.5M sodium sulfate, 1M sodium chloride, 1M potassium nitrate at $\text{pH} \geq 8.6$ (0.05M triethanolamine, $c_L = 2 \cdot 10^{-3}$ mol/l); the buffers of borate or triethanolamine do not interfere up to the 0.1M base concentration at $\text{pH} 8.6-9.4$ and with the phase ratio 1 : 1.

Effect of Some Ions

Ions yielding extractable chelates with PAN interfere even at low concentrations. If Al^{3+} is present, the value of $\text{pH} \geq 9.5$ is more suitable for the extraction. Cd^{2+}

and Cu^{2+} are masked with an excess of iodide at pH 8.6, the resulting iodine is reduced by thiosulfate. Fe^{3+} , Al^{3+} are masked with an excess of fluoride ions only partly, they interfere in the extraction of zinc. 5-Sulfosalicylic, tartaric, and citric acids are not suitable for the masking of Fe^{3+} or Al^{3+} in the conditions of zinc extraction¹² (Table II).

TABLE II

Effect of Ions on the Extraction — AAS Determination of Zinc

Extraction into benzene, 23.04 μg Zn, 0.1M triethanolamine, $5 \cdot 10^{-3}\text{M}$ -PAN, phase ratio 1 : 1.5 ml organic phase, extraction 60 min.

Ion	Counter-Ion	Amount ^a
Pb^{2+}	NO_3^-	140 mg
Cd^{2+}	SO_4^{2-}	600 μg , 46 mg ^b
Cu^{2+}	NO_3^-	900 μg , 25.8 mg ^b
Fe^{3+}	Cl^-	400 μg , 10 mg ^c
Al^{3+}	Cl^-	360 μg , 10 mg ^d
Mg^{2+}	Cl^-	100 mg
Sn^{2+}	Cl^-	400 μg
$\text{Sn}^{1\text{V}}$	Cl^-	100 mg

^a Amount leading to $\pm 2\%$ deviation as compared with the absorbance of pure Zn solutions;

^b 10 g KI and 0.6 g $\text{Na}_2\text{S}_2\text{O}_5 \cdot 5 \text{H}_2\text{O}$ added; ^c 0.3 g $\text{KF} \cdot 2 \text{H}_2\text{O}$ added, pH 8.6; ^d 0.6 g $\text{KF} \cdot 2 \text{H}_2\text{O}$ added, pH 8.6.

TABLE III

Extraction of Zn from 1M Solutions of Salts into Methyl Isobutyl Ketone

10 μg Zn, 5 ml organic phase, phase ratio 1 : 10, $2 \cdot 10^{-3}\text{M}$ -PAN, extraction for 20min, pH 9.7–10.5, 0.25M-Tris.

Salt	Extraction portion after first extraction %	Salt	Extraction portion after first extraction %
NaCl	95	$\text{Ca}(\text{NO}_3)_2$	97
KCl	97	SrCl_2	94
LiCl	97	BaCl_2	91
Na_2SO_4	96	NH_4Cl	22

For the extraction of zinc with PAN as ZnL_2 into benzene, evaporation, and dissolving the residue in a mixture of 0.1M-HCl and dimethylformamide, the coefficient of variation is 2.1–3.6%, the relative width of the confidence interval 4.2–4.6% in the range of the calibration curve, 0.1–8 p.p.m. Zn. The 1% absorption ($A = 0.004$) is caused by 0.042 p.p.m. Zn, the detection limit is 0.021 p.p.m. Zn, sensitivity 0.095 absorbance/p.p.m. for limiting $A = 0-0.07$.

EXTRACTION OF ZINC SYSTEM PAN-METHYL ISOBUTYL KETONE

Effect of pH

Absorbance as well as the distribution ratio attain their maximum values at $pH \geq 8$, as follows from Fig. 1. The dependence $\log D = f(pH)$ indicates unambiguously the abstraction of two protons during the formation and extraction of the chelate of zinc with PAN. In addition, the plot $\log D$ vs pL (Fig. 2) exhibits mostly the slope of 2, the data of $\log D$ are equal for different ligand concentrations, no free ligand adds, and no protonized chelates are formed. The values of β_1 and β_2 are listed

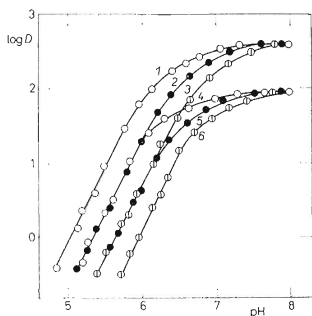


FIG. 1

Dependence $\log D = f(pH)$ for Extraction in the System Zn^{2+} -PAN

0.1M- KNO_3 , 0.1M sodium acetate or Tris, phase ratio 1:1, 5 ml organic phase, extraction for 3 h. 1, 2, 3 extraction of 2 p.p.m. Zn into methyl isobutyl ketone; 4, 5, 6 extraction of 8 p.p.m. Zn into benzene. \odot $0.5 \cdot 10^{-3}$ M-PAN, \bullet $1 \cdot 10^{-3}$ M-PAN, \circ $2 \cdot 10^{-3}$ M-PAN.

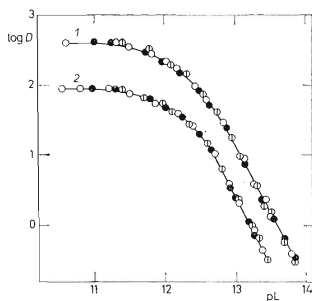


FIG. 2

Dependence $\log D = f(pL)$ for Extraction in the System Zn^{2+} -PAN

0.1M- KNO_3 , 0.1M acetate or Tris, phase ratio 1:1.5 ml organic phase, extraction for 3 h. 1 extraction of 2 p.p.m. Zn into methyl isobutyl ketone, 2 extraction of 8 p.p.m. Zn into benzene. \odot $0.5 \cdot 10^{-3}$ M-PAN, \bullet $1 \cdot 10^{-3}$ M-PAN, \circ $2 \cdot 10^{-3}$ M-PAN.

in Table I. The curves of continuous variations, $A_{\text{org}} = f(c_M/(c_M + c_L))$, display — after a phase equilibration for 180 min — a marked maximum for M : L = 1 : 2 at pH 5·80, 9·20, 10·40 in the presence of a buffer and 0·1M-KNO₃ (Fig. 4).

Analytical Utilization and Procedure

Tris does not interfere in the extraction of ZnL₂ into methyl isobutyl ketone up to the concentration of 1 mol/l, and suits for pH 8·0–11·0. Sodium tetraborate (pH 9) and triethanolamine (pH 10) do not interfere either, up to the concentrations 0·7 and 0·1 mol/l, resp., during the extraction with $2 \cdot 10^{-3}$ M-PAN in methyl isobutyl ketone with the phase ratios $V_{\text{org}} : V_{\text{aq}} = 1 : 1 - 1 : 10$. For those ratios, the extraction of $\leq 10 \mu\text{g}$ Zn is quantitative in 20 min. The effect of some salts on the extraction of zinc is illustrated by Table III. The extraction of $\geq 10 \mu\text{g}$ Zn is practically

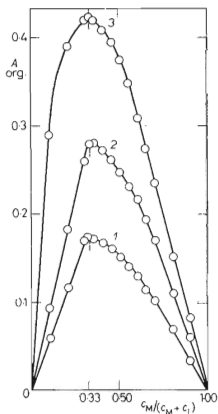


FIG. 3

Job's Extraction Curves in the System Zn–Benzene–PAN

0·1M-KNO₃, extraction for 3 h. 1 pH 9·07 (0·05M ammoniacal buffer), $c_M = c_L = 1 \cdot 23 \cdot 10^{-4}$ mol/l; 2 pH 8·27 (0·05M triethanolamine), $c_M = c_L = 2 \cdot 46 \cdot 10^{-4}$ mol/l; 3 pH 5·58 (0·20M sodium acetate), $c_M = c_L = 1 \cdot 23 \cdot 10^{-3}$ mol/l.

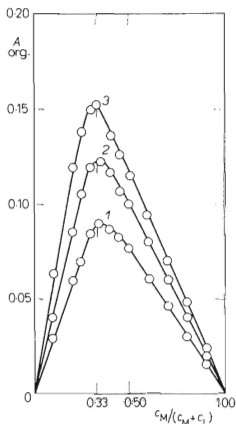


FIG. 4

Job's Extraction Curves in the System Zn–Methyl Isobutyl Ketone–PAN

0·1M-KNO₃, extraction for 3 h. 1 pH 10·47 (0·2M-Tris), $c_M = c_L = 1 \cdot 23 \cdot 10^{-5}$ mol/l; 2 pH 9·20 (0·01M-Tris), $c_M = c_L = 2 \cdot 46 \cdot 10^{-5}$ mol/l; 3 pH 5·80 (0·20M sodium acetate), $c_M = c_L = 1 \cdot 23 \cdot 10^{-4}$ mol/l.

unaffected by the 1M concentration of sodium, potassium, calcium, strontium, barium, and lithium salts at pH 8–11. Ammonium salts, however, interfere considerably at concentrations >0.1 mol/l; *e.g.*, in solutions of 2M-NH₄Cl the extraction is completely suppressed.

The pH value of 25 ml of the sample solution, containing ≤ 1 M concentration of the salt and ≤ 10 μ g Zn, is set to 8–11 by 1M solution of Tris. The solution is brought to the volume of 50 ml with water saturated with methyl isobutyl ketone and extracted after 20 min with three 5 ml portions of $2 \cdot 10^{-3}$ M-PAN in methyl isobutyl ketone saturated with water. The extracts are nebulized gradually and the concentrations read from the calibration curve are summed up. The solvent saturated with water serves as the blank.

In this case, the coefficient of variation is 1.4–2.3% and the relative width of the confidence interval is 2.8–3.4% in the range of the calibration curve, 0.02–2 p.p.m. Zn. 1% absorption ($A = 0.004$) corresponds to 0.011 p.p.m. Zn, the detection limit is 0.005 p.p.m. Zn, sensitivity 0.370 absorbance/p.p.m. Zn for limiting $A = 0-0.1$. The direct nebulizing of the extract is more convenient, regarding the higher sensitivity and lower detection limit, higher reproducibility, and shorter time required for analysis.

Atomic Absorption of Zinc in Various Solvents After Extraction of ZnL₂ with PAN

5 ml of the aqueous solution was extracted with 5 ml of $2 \cdot 10^{-3}$ M solution of PAN in the organic solvent. The aqueous solution contained 10 μ g Zn, 0.1M-KNO₃, 0.1M-Tris (pH 9.1). After 1 h extraction and phase separation, the extracts were nebulized in the flame. The blank solution was always represented by the corresponding solvent saturated with water. The quantitateness of extraction was checked by measuring the absorbance of the aqueous phase. Absorbances of the extracts for a given concentration of zinc were related to those of the aqueous solutions. Thus, for 1-butanol, isoamyl alcohol, diisobutyl ketone, methyl isobutyl ketone, ethyl acetate, n-butyl acetate, and isoamyl acetate the absorbances are 1.7, 1.4, 2.7, 3.9, 4.6, 3.6, and 3.1 times, resp., higher than those obtained in water for equal concentrations of zinc.

From this point of view, the most sensitive are the measurements in ethyl acetate and methyl isobutyl ketone. This fact can be obviously extended also to other metals¹³. This behaviour of solvents can be related to their viscosity (cP), descending in the series isoamyl alcohol (4.3) > 1-butanol (2.98) > diisobutyl ketone (0.903) > isoamyl acetate (0.87) > n-butyl acetate (0.734) > methyl isobutyl ketone (0.590) > ethyl acetate (0.452).

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