

OPTIMIZATION OF THE SPECTROPHOTOMETRIC DETERMINATION OF MERCURY USING COPPER(II) DIETHANOLDITHIOCARBAMATE

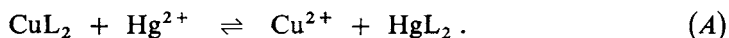
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The work deals with the optimization of the conditions for the spectrophotometric determination of mercury using copper(II) diethanoldithiocarbamate $[\text{Cu}((\text{HOCH}_2\text{CH}_2)_2\text{NCS}_2)_2]$ (*I*). The determination is based on replacement of Cu^{2+} ions by Hg^{2+} ions in complex *I* in acidic aqueous acetone medium and measuring the decrease in the absorbance at the absorption maximum of complex *I* ($\lambda = 440$ nm). The statistical importance of the factors affecting the analytical signal (absorbance) was found by the analysis of variance. The analytical signal is affected most by the pH value, the concentration of Cu^{2+} ions, and the acetone content. The best results were obtained at $\text{pH} \sim 2$ and an acetone content of 15% (v/v). The analytical calibration curve is non-linear. The determination limit is $50 \mu\text{g Hg}$ in 1 dm^3 . The method is useful for the rapid determination of mercury with a precision of $\pm 5\%$ in colourless solutions not containing Cu^{2+} or Ag^+ ions or strong oxidants.

The analysis of waste waters with low mercury contents often requires a fast and simple method of determination, not requiring complex experimental apparatus. This paper deals with optimization of a rapid method for the determination of mercury^{1,2} based on the bleaching of a solution of copper(II) diethanoldithiocarbamate $[\text{Cu}((\text{HOCH}_2\text{CH}_2)_2\text{NCS}_2)_2] - \text{CuL}_2$, where L is the diethanoldithiocarbamate ligand — by Hg^{2+} ions:



No extraction is required as replacement reaction (A) occurs in homogeneous medium. Optimization of the method was based on the main principles in optimization of analytical procedures, which have been discussed in a number of works^{3,4}.

EXPERIMENTAL

The chemicals and solvents used were of *p.a.* purity. Methanol and acetone were purified by the procedure in ref.⁵. Dithizone (Lachema, Brno) was purified by the procedure in ref.⁶.

Reagent Preparation

Potassium diethanoldithiocarbamate, $(\text{HOCH}_2\text{CH}_2)_2\text{NCS}_2\text{K} \cdot 0.5 \text{ H}_2\text{O}$: to 0.1 mol of diethanol-

amine was added 0.1 mol KOH and enough water to form a clear solution. The solution was cooled to below 10°C and hydrogen sulphide was added dropwise in an amount of 0.1 mol. After reaction of all the hydrogen sulphide, the solution was evaporated on a rotating evaporator at room temperature; a yellow to yellow brown product was precipitated. The product was washed with acetone and dissolved in a small amount of water. Addition of a large excess of acetone led to precipitation of a white crystalline substance. For $C_5H_{11}O_{2.5}NS_2K$ ($M_r = 228.3$) was calculated: 26.28% C, 4.86% H, 6.13% N, and found: 26.53% C, 4.49% H, 6.09% N.

Copper(II) and mercury(II) bis(diethanoldithiocarbamate) [$Cu((HOCH_2CH_2)_2NCS_2)_2$] and [$Hg((HOCH_2CH_2)_2NCS_2)_2$]: 1.5 g of potassium diethanoldithiocarbamate was dissolved in 250 cm^3 water cooled to below 10°C. A small excess of a solution of $CuSO_4 \cdot 5 H_2O$ or $Hg(NO_3)_2 \cdot 0.5 H_2O$ was added with stirring and the solution was diluted with water to a volume of 800 cm^3 . After one hour the precipitated substance was filtered off and washed several times with water and then methanol. After drying the precipitate was recrystallized from dimethylformamide. For $C_{10}H_{20}O_4N_2S_4Cu$ ($M_r = 424.1$) calculated: 28.32% C, 4.75% H, 6.61% N; found: 27.42% C, 4.79% H, 6.64% N. For $C_{10}H_{20}O_4N_2S_4Hg$ ($M_r = 561.1$) calculated: 21.41% C, 3.59% H, 4.49% N; found: 20.95% C, 3.66% H, 4.93% N.

The pH values of the solutions were adjusted using universal Britton-Robinson buffer solution. In the factor experiments the absorbance of solutions with the following compositions were measured: 1 cm^3 Hg solution ($5 \cdot 10^{-5}$ mol dm^{-3}) + 5 cm^3 buffer solution + 1 cm^3 CuL_2 solution ($1 \cdot 10^{-4}$ mol dm^{-3}) in a suitable solvent + 3 cm^3 solvent. The absorbance was measured in 5 cm cuvettes at a wave-length of $\lambda = 440$ nm against distilled water.

The spectrophotometric measurements were carried out using Specord UV VIS and Spekol 10 spectrophotometers (Carl Zeiss, Jena, GDR).

The pH was measured using an OP-201/2 pH meter (Radelkis, Budapest, Hungary).

The C, H, and N contents of the prepared compounds were found using a Carlo Erba (model 1102) analyzer.

Calculations were carried out using a Comcucorp 610 table-top computer with a 36 kbyte operational memory. The parameters of the linear and quadratic dependences were calculated by the usual least squares method. The equilibrium constants of reaction (B) were calculated using the simplex method of nonlinear regression. The algorithm of the program used in BASIC language was similar to that given by Morgan and Deming⁷.

RESULTS AND DISCUSSION

As the Hg(II) complexes of dithiocarbamates have much higher stability constants than the similar Cu(II) complexes⁸, reaction (A) is strongly shifted to the right. The diethanoldithiocarbamate ligand was selected for the indirect determination of mercury in aqueous media because of the sufficient solubility of the Hg(II) and Cu(II) complexes in water and in polar solvents. The solubilities of HgL_2 and CuL_2 in water are about $1 \cdot 10^{-4}$ mol dm^{-3} , and are even larger in methanol and acetone⁹.

Addition of an $Hg(NO_3)_2$ solution to an aqueous solution of CuL_2 leads to bleaching of the original yellow-brown colour. The absorption maximum of the HgL_2 complex appears on the absorption spectra (Fig. 1), in agreement with reaction (A). This complex does not absorb in the VIS region, as $d-d$ transitions and transitions connected with charge transfer from the ligand to the metal are not possible in this complex. The intense absorption bands in the UV region correspond to transitions

within the ligand and to charge transfer from the metal to the ligand¹⁰. In the copper complex, the absorption bands in the VIS region are a result of $d-d$ transitions and charge transfer from the ligand to the metal¹¹.

Reaction (A) is very fast; equilibrium is established almost instantly after mixing the reactants. The decrease in the absorbance at $\lambda = 440$ nm depends on the concentration of Hg^{2+} ions, on the presence of Cu^{2+} ions, on the amount of organic solvent (methanol, acetone) added and on the time of standing.

In optimization of the method, the analytical signal was selected as the absorbance at the absorption maximum of the CuL_2 complex ($\lambda_{\text{max}} = 440$ nm). A complete factor test of the 2^N type, where N is the number of factors¹², was used in selection of the statistically important factors affecting the analytical signal. Factor experiments were carried out in three media, water, water-methanol, and water-acetone. The factors studied were selected on the basis of preliminary experiments; the high (H) and low (L) values are listed in Table I. The measuring procedure for $r \cdot 2^N$ experiments (r is the number of parallel measurements, $r = 3$) is given in the experimental. The measured absorbance values were treated according to the procedure in ref.³. The results are listed in Table II.

Comparison of the F -test results for the individual parameters and their interactions with the critical value of the Fisher distribution indicated that the time of standing of the reaction mixture has no significant effect on the absorbance at $\lambda = 440$ nm. On the other hand, the pH of the solution strongly affects the absorbance value in all media and especially in water-acetone medium. A similar significant effect was observed for Cu^{2+} ions. The concentration of methanol or acetone has a smaller

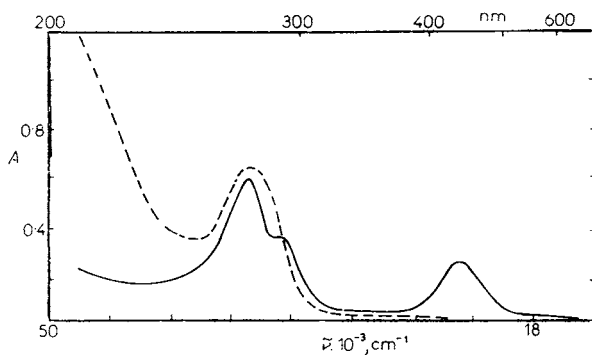


FIG. 1

The absorption spectra of methanol solutions of CuL_2 ($c = 2.5 \cdot 10^{-5} \text{ mol dm}^{-3}$) — full line — and $[\text{Hg}((\text{HOCH}_2\text{CH}_2)_2\text{NCS}_2)_2]$ ($c = 2 \cdot 10^{-5} \text{ mol dm}^{-3}$) — dashed line. Cuvette thickness 1 cm

but significant effect on the analytical signal. It thus follows that the time of standing of the reagent solution (CuL_2) in methanol also affects the absorbance value. This effect was not found for acetone.

The reproducibility of the measurement characterized by the sum of squares s^2 was best in water–acetone medium and worse in water–methanol medium. The results in aqueous medium were by far the worst. Consequently, subsequent measurements were carried out in water–acetone medium.

The Effect of pH

In all media, the analytical signal was affected by the pH value. The CuL_2 complex is poorly stable in strongly acidic and basic media. In acidic media it decomposes to form diethanolamine, Cu^{2+} , and hydrogen sulphide. In basic media a nucleophilic substitution of the ligand by OH^- ions probably occurs with simultaneous decomposition of the dithiocarbamate ligand to form isothiocyanate¹³. In the pH range from 1.5 to 7 the complex is relatively stable. The intensity of the absorption band at $\lambda = 440$ nm is markedly affected by the pH value (Fig. 2); the more acid the solution is, the more intense is the absorption band. The shift of the absorption band into the blue region with decreasing pH value can also be observed.

TABLE I
Studied factors in the various media and their low (L) and high (H) values

Medium	Factor studied	Factor units	Factor designation	L	H
Water	pH	—	A	2	6
	conc. of Cu^{2+} ions	mol dm^{-3}	B	0	10^{-4}
	time of standing of reaction mixture	min	C	2	15
	time of standing of the reagents ^a	d	D	1	14
Water–methanol	pH	—	A	2	6
	concentration of Cu^{2+} ions	mol dm^{-3}	B	0	10^{-4}
Water–acetone	time of standing of the reagents ^b	d	C	1	14
	solvent content ^c	% (v/v)	D	10	30

^a 10^{-4} mol CuL_2 in 1 dm^3 water; ^b 10^{-4} mol CuL_2 in 1 dm^3 methanol or acetone; ^c methanol or acetone.

The Effect of the Concentration of Methanol and Acetone and the Time of Standing of the CuL_2 Solution on the Analytical Signal

An increase in the concentration of methanol or acetone in the CuL_2 complex solution leads to an increase in the intensity of the absorption band at $\lambda = 440$ nm. The position and shape of the absorption band remains practically unchanged.

The stock solutions of CuL_2 in water and methanol were not stable: after several days a marked decrease in the intensity of the absorption band at $\lambda = 440$ nm was observed, with formation of a new band below 210 nm, indicating decomposition of the complex and release of hydrogen sulphide. The acetone solution of CuL_2 was stable for at least several months.

The Effect of Cu^{2+} Ions

A change in the absorption spectrum of the complex was observed after addition of a solution of a cupric salt to a CuL_2 solution. This change is most marked in the VIS region (Fig. 3). An increase in the concentration of Cu^{2+} ions gradually decreases the absorption band at $\lambda = 440$ nm with formation of a new absorption band below $\lambda = 400$ nm, with simultaneous appearance of an isobestic point at $\lambda = 405$ nm. The greatest changes were observed in solutions with pH = 2 to 5. At higher pH values, the changes in the absorption spectra below $\lambda = 400$ nm are negligible.

These observations indicate that a reaction occurs between Cu^{2+} ions and the CuL_2 complex with formation of the CuL^+ complex. Similar dithiocarbamate

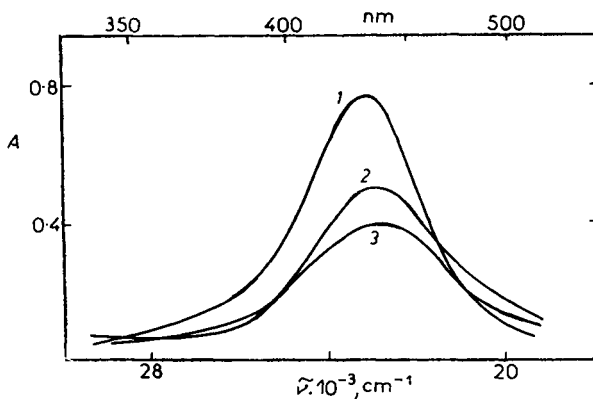


FIG. 2

Absorption spectra of aqueous solutions of CuL_2 ($c = 5 \cdot 10^{-5}$ mol dm^{-3}); HCl medium ($c = 0.1$ mol dm^{-3}) 1, pH = 3.3 2 and 9.0 3, 1 cm cuvettes

TABLE II
Results of factor experiments^a

Factors and their interactions	Water		Water-methanol		Water-acetone	
	s_p	F	s_p	F	s_p	F
A	$1.3 \cdot 10^{-1}$	188	$5.1 \cdot 10^{-1}$	990	$5.9 \cdot 10^{-1}$	45 000
B	$7.5 \cdot 10^{-2}$	103	$2.0 \cdot 10^{-1}$	410	$3.9 \cdot 10^{-2}$	3 000
AB	$4.3 \cdot 10^{-3}$	5.9	$3.2 \cdot 10^{-3}$	62	$9.2 \cdot 10^{-3}$	700
C	$6.1 \cdot 10^{-5}$	0.1	$6.1 \cdot 10^{-2}$	1 200	$5.2 \cdot 10^{-7}$	0.0
AC	$6.1 \cdot 10^{-3}$	8.4	$6.4 \cdot 10^{-4}$	12	$4.2 \cdot 10^{-5}$	3.2
BC	$8.7 \cdot 10^{-3}$	12	$1.8 \cdot 10^{-4}$	3.4	$4.7 \cdot 10^{-6}$	0.4
ABC	$2.1 \cdot 10^{-5}$	0.0	$3.0 \cdot 10^{-3}$	58	$1.1 \cdot 10^{-5}$	0.8
D	$4.0 \cdot 10^{-2}$	55	$8.1 \cdot 10^{-3}$	160	$8.8 \cdot 10^{-2}$	6 700
AD	$2.8 \cdot 10^{-2}$	39	$1.2 \cdot 10^{-4}$	2.4	$2.8 \cdot 10^{-2}$	2 100
BD	$6.5 \cdot 10^{-2}$	90	$1.4 \cdot 10^{-4}$	2.8	$3.3 \cdot 10^{-3}$	250
ABD	$1.5 \cdot 10^{-3}$	2.1	$7.0 \cdot 10^{-4}$	14	$1.1 \cdot 10^{-1}$	8 100
CD	$1.4 \cdot 10^{-2}$	20	$3.4 \cdot 10^{-4}$	6.6	$2.3 \cdot 10^{-5}$	1.7
ACD	$1.6 \cdot 10^{-3}$	2.2	$2.8 \cdot 10^{-3}$	55	$3.9 \cdot 10^{-5}$	2.9
BCD	$6.8 \cdot 10^{-4}$	0.9	$1.5 \cdot 10^{-5}$	0.3	$1.0 \cdot 10^{-6}$	0.1
ABCD	$6.9 \cdot 10^{-3}$	9.5	$4.5 \cdot 10^{-4}$	8.8	$5.2 \cdot 10^{-7}$	0.0
Sum of squares s^2	$7.2 \cdot 10^{-4}$		$5.2 \cdot 10^{-5}$		$1.3 \cdot 10^{-5}$	

^a Critical value of the Fisher distribution for significance level $\alpha = 0.05$ and for degree of freedom $\nu = (1, 32)$, $F_{crit} = 4.49$; variability $s_p = [P]^2 / (r \cdot 2^N)$, where $[P]$ is the algebraic sum of the absorbance values for all the procedures⁴; $F = s_p / s^2$.

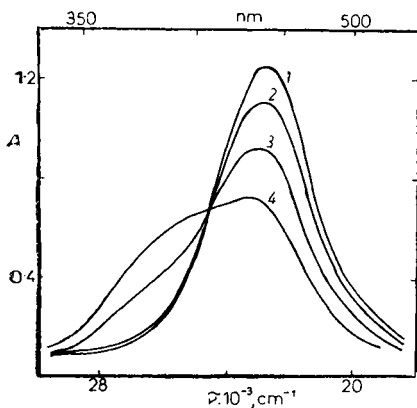
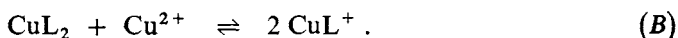


FIG. 3

Absorption spectra of the $\text{CuL}_2\text{-Cu}^{2+}$ system. $c(\text{CuL}_2) = 2 \cdot 10^{-5} \text{ mol dm}^{-3}$, $c(\text{Cu}^{2+})$ 8. $10^{-7} \text{ mol dm}^{-3}$ 2, $1.2 \cdot 10^{-5} \text{ mol dm}^{-3}$ 3, $4 \cdot 10^{-5} \text{ mol dm}^{-3}$ 4, without addition of Cu^{2+} ions 1. Water-acetone medium (4 : 1), buffer solution with $\text{pH} = 5$. .5 cm cuvettes

complexes were observed for the Ni(II) ion^{14,15}. The reaction between Cu²⁺ ions and the CuL₂ complex can be written as



It follows for the formal equilibrium constant of reaction (B) that:

$$K' = \frac{[\text{CuL}^+]^2}{[\text{CuL}_2][\text{Cu}^{2+}]}, \quad (1)$$

where the square brackets indicate equilibrium concentrations.

It follows from mass balance and the presence of two substances absorbing in the VIS region, using Eq. (2):

$$A = \varepsilon_1 \cdot [\text{CuL}^+] \cdot d + \varepsilon_2 \cdot [\text{CuL}_2] \cdot d, \quad (2)$$

where ε_1 and ε_2 are the molar absorption coefficients of the CuL⁺ and CuL₂ complexes, respectively, d is the cuvette thickness in cm, that the formal equilibrium constant can be expressed as

$$K' = \frac{4(\varepsilon_2 \cdot [\text{CuL}_2]_0 \cdot d - A)^2}{(A - 2\varepsilon_1 \cdot [\text{CuL}_2]_0 \cdot d)((\varepsilon_2 - 2\varepsilon_1) \cdot [\text{Cu}^{2+}]_0 \cdot d - \varepsilon_2[\text{CuL}_2]_0 \cdot d + A)}, \quad (3)$$

where $[\text{CuL}_2]_0$ and $[\text{Cu}^{2+}]_0$ are the initial concentrations of the CuL₂ complex and Cu²⁺ ions.

K' cannot be calculated from Eq. (3) because the value of the molar absorption coefficient ε_1 is not known. Thus the simplex method of finding parameters was selected for calculation of the K' and ε_1 values. After rearrangement of Eq. (3), these parameters were sought by minimization of the following objective function:

$$U = \sum_{i=1}^w \sum_{j=1}^s (y_{ij} - f([\text{CuL}_2]_{0j}, [\text{Cu}^{2+}]_{0j}, K', \varepsilon_{1i}, A_{ij}))^2, \quad (4)$$

where $y_{ij} = 4(\varepsilon_{2i} \cdot [\text{CuL}_2]_{0j} \cdot d - A_{ij})^2$ and

$$f([\text{CuL}_2]_{0j}, [\text{Cu}^{2+}]_{0j}, K', \varepsilon_{1i}, A_{ij}) = K' \cdot (A_{ij} - 2\varepsilon_{1i} \cdot [\text{CuL}_2]_{0j} \cdot d) \cdot ((\varepsilon_{2i} - 2\varepsilon_{1i}) \cdot [\text{Cu}^{2+}]_{0j} \cdot d - \varepsilon_{2i} \cdot [\text{CuL}_2]_{0j} \cdot d + A_{ij})$$

for the i -th wavelength and j -th solution.

Table III lists the calculated estimates of the formal equilibrium constant for various pH values in water and water–acetone media. Fig. 4 depicts the agreement of the calculated dependence of the absorbance on the concentration of Cu^{2+} ions with the experimental values. It follows from the results obtained that equilibrium (B) is shifted more to the right in aqueous medium than in water–acetone medium. This is probably connected with the stabilizing effect of the more polar medium with formation of an ionic compound, CuL^+ . The highest K' value was observed in solutions with pH 4 to 5.

The absorption spectrum of the CuL^+ complex could be calculated from the results obtained (Fig. 5). Compared with the spectrum of the CuL_2 complex, the absorption

TABLE III
Estimated formal equilibrium constants K' of reaction (B) calculated by the simplex method

pH	Water ^a	Water–acetone
2	—	0.36 ± 0.05
3	—	0.90 ± 0.05
4	4.3 ± 0.2	1.41 ± 0.10
5	3.3 ± 0.2	1.40 ± 0.10
6	0.78 ± 0.10	0.13 ± 0.03
7	0.48 ± 0.05	0.11 ± 0.03
8	0.43 ± 0.05	0.20 ± 0.05
9	0.73 ± 0.10	0.17 ± 0.03

^a Measurements at lower pH values were poorly reproducible because of rapid decomposition of the CuL_2 complex.

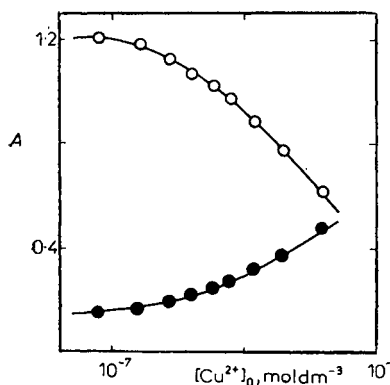


FIG. 4
Dependence of the absorbance on the initial concentration of Cu^{2+} ions in solution at a wavelength of 444 nm (O) and 370 nm (●). Water–acetone medium, pH 5, initial concentration of $\text{CuL}_2 = 2 \cdot 10^{-5} \text{ mol dm}^{-3}$, 1 cm cuvettes

band of CuL_2 is shifted to shorter wavelengths, and is far less intense than that of the original compound. Both the shift and the decrease in the intensity of the absorption band are connected with the presence of a single dithiocarbamate ligand in the coordination sphere of the copper atom. The absorption spectrum of the CuL^+ complex is strongly affected by the pH value. On an increase in the pH, the absorption maximum is shifted to shorter wavelengths. This blue shift may be connected with the formation of species of the $\text{CuL}(\text{OH})$ type.

It follows from these observations that the Cu^{2+} ion interferes in the determination as a result of a decrease in the concentration of the CuL_2 complex through reaction (B). In addition, ions released as a result of reaction (A) react with the remaining CuL_2 molecules (reaction (B)), so that the decrease in the concentration of complex CuL_2 will not exhibit an equimolar dependence on the mercury content.

Optimization of the pH and Acetone Content

The pH and acetone content were optimized by the simple simplex optimization¹⁶. The determination limit for mercury was selected as the optimization criterion.

The optimum combination of these factors was found to be $\text{pH} = 2$ for the buffer used and an acetone content of 15% (v/v). The values obtained are in agreement with the observations in the previous sections. At lower pH values, the CuL_2 complex has the highest molar absorption coefficient value, with a marked effect on the determination limit. An increase in the acetone concentration also leads to an increase in the $\varepsilon(\text{CuL}_2)$ value but it follows from the results of factor experiments (Table II) that the pH value and the acetone content are strongly interacting factors. Thus $\varepsilon(\text{CuL}_2)$ is affected by the combination of these factors.

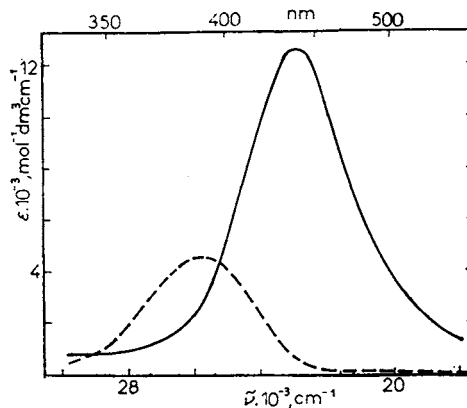


FIG. 5
Calculated absorption spectrum of the CuL^+ complex (dashed line) and absorption spectrum of the CuL_2 complex (full line)

The optimum procedure for the determination of mercury with copper(II) diethanoldithiocarbamate is the following: A neutral sample with a volume of less than 17.5 cm³ and mercury content of less than 12 µg is placed in a 50 cm³ volumetric flask and mixed with 25 cm³ Britton–Robinson buffer with pH = 2 and 7.5 cm³ CuL₂ solution in acetone ($c(\text{CuL}_2) = 5 \cdot 10^{-5} \text{ mol dm}^{-3}$). The solution is diluted to the mark with distilled water and the absorbance is measured at $\lambda = 440 \text{ nm}$ in a 5 cm cuvette against distilled water.

Statistical Evaluation of the Method

The procedure developed above was used to draw up a calibration curve for the determination of mercury which was, as expected, nonlinear over the whole range (Fig. 6) and could be fitted by a second degree polynomial:

$$A = a_0 + a_1c + a_2c^2, \quad (5)$$

where c is the mercury concentration in the measured solution. A further increase in the degree of the polynomial was not reflected in a statistically significant decrease in the standard deviation of the residuals.

The following values of parameters a_0 , a_1 , and a_2 were found: $a_0 = 0.421 \pm 0.001$, $a_1 = -(5.22 \pm 0.05) \cdot 10^5$, $a_2 = (1.67 \pm 0.02) \cdot 10^{11}$.

Because of the nonlinearity of the analytical calibration dependence, calculation of the region of reliability of the results is far more difficult than for the linear dependence^{17,18}. The following relationship can be derived for a nonlinear calibration curve expressed by equation (5) for the reliability interval of the results:

$$\begin{aligned} (-\hat{a}_1 - \sqrt{[\hat{a}_1^2 + 4\hat{a}_2(\hat{a}_1 \cdot \hat{c}^* + \hat{a}_2 \cdot \hat{c}^{*2} + t_{\alpha, \nu} \cdot s)]) / (2\hat{a}_2)} \leq c^* \leq \\ \leq (\hat{a}_1 - \sqrt{[\hat{a}_1^2 + 4\hat{a}_2(\hat{a}_1 \cdot \hat{c}^* + \hat{a}_2 \cdot \hat{c}^{*2} - t_{\alpha, \nu} \cdot a)]) / (2\hat{a}_2)}, \end{aligned} \quad (6)$$

where $s = \sqrt{(s_r^2/M + s_0^2 + s_1^2 \cdot c^* + s_2^2 \cdot c^{*2})}$; c^* is the actual result value, \hat{c}^* is the value found experimentally from Eq. (5), M is the number of parallel determinations, s_r^2 is the residual variance in the determination of parameters a_0 , a_1 and a_2 , s_0 , s_1 and s_2 are their standard deviations and $t_{\alpha, \nu}$ is the critical value of the Student distribution for significance level α and for degree of freedom $\nu = N - 3$, where N is the number of points used in constructing the analytical calibration curve.

The range of reliability of the results was calculated using Eq. (6) for 3 parallel determinations. The relative width of the reliability band is smallest in the mercury concentration range from $3 \cdot 10^{-7}$ to $1.1 \cdot 10^{-6} \text{ mol dm}^{-3}$, where it varies around 10%. The determination limit for mercury (calculated from ten times the standard deviation of the blank results) was found to be 50 µg dm^{-3} .

The accuracy of the method was verified using model samples with a mercury concentration of 0.1 to 10 $\mu\text{g cm}^{-3}$. Accurate results (verified by the *t*-test) were obtained in the absence of Ag^+ and Cu^{2+} ions and strong oxidants.

This method was compared to the dithizone method for determining mercury according to the procedure⁶. Both methods yield identical results, but the optimized method is shorter (one analysis takes 2 to 4 min), and requires half as many operations and solutions as the dithizone method. The higher determination limit (equal to about

TABLE IV

Comparison of the results of the determination of mercury in actual samples by the copper(II) diethanoldithiocarbamate (*A*) and dithizone (*B*) methods

Mercury content in the sample, $\mu\text{g cm}^{-3}$	
<i>A</i>	<i>B</i>
1.57 ± 0.08	1.57 ± 0.03
1.95 ± 0.10	1.92 ± 0.04
1.80 ± 0.09	1.83 ± 0.04
1.48 ± 0.07	1.48 ± 0.03
1.55 ± 0.08	1.53 ± 0.03

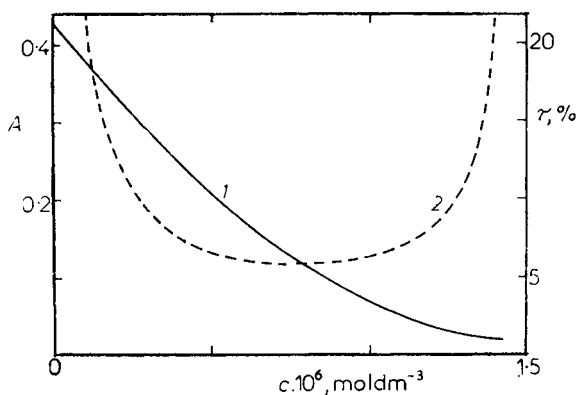


FIG. 6

Analytical calibration curve for the determination of mercury 1; dependence of the relative width of the reliability interval (τ) on the mercury concentration in the measured solution for 3 parallel determinations 2

$10 \mu\text{g dm}^{-3}$ in the dithizone method) and interference from Cu^{2+} ions and coloured species in the solution are disadvantages.

Table IV lists the results of the determination of mercury in actual waste water samples from the manufacture of PVC, using these two methods.

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