EXTRACTION-PHOTOMETRIC DETERMINATION OF INDIUM WITH 8-QUINOLINOL IN LAYERED CRYSTALS OF THE TYPE $A_2^{V}B_3^{VI}$

Jitka ŠRÁMKOVÁ, Stanislav KOTRLÝ and Yvona KALISCHOVÁ

Department of Analytical Chemistry,
Institute of Chemical Technology, 532 10 Pardubice

A method for determining indium in milligram samples of indium-doped crystals of bismuth telluride is described. The pH effect of the aqueous phase ($V_{aq} = 40$ ml) on the extraction yield is examined, also by considering the results computed with the data so far published. In a single extraction at pH 3·6—4·2 (acetate buffer) the tris(8-quinolinolato)indium(III) chelate is quantitatively transferred to the chloroform phase ($V_{org} = 10$ ml). Bismuth present in excess is masked with thiosulfate. The absorbance of the chloroform extract is measured at 400 nm in a glass cell of 10-mm path-length (or in a 50-mm cell when $m(\text{In}) < 20$ µg). A blank extraction is carried out simultaneously with the use of a solution of pure Bi_2Te_3 and taken as reference. The calibration within the range of 10—130 µg of In(III) is performed by adding a standard indium(III) solution to the matrix solution obtained by dissolving pure Bi_2Te_3. The accuracy of the method has been checked by analysis of polycrystalline reference materials of known composition. The method is applicable for the analysis of milligram samples containing 0·6—5% of indium, with a relative standard deviation of 1—4%.

One of the challenging problems of microchemical analysis at present is the assessment of nonstoichiometry of individual components in a small piece of semiconducting crystal which is under investigation. Every single crystal sample, which has a weight of several milligrams, is an individual and valuable specimen; therefore, highly reliable methods for the microgram range are needed for analysis. The determination of indium, which is a minor component with concentration gradient in mixed crystals of the type $\left(Bi_{1-x}In_x\right)_2 Te_3$, was necessary for the investigation of thermoelectric properties of these layered monocrystals[1,2].

At present, there is little information available in the literature on the methods suitable for the determination of indium in milligram samples of similar materials. In determinations of nonstoichiometric components in semiconducting materials decigram samples are usually required. Preferably titrimetric, gravimetric, and coulometric methods have been employed. For example, Danzaki et al.[3] have worked out a determination of bismuth and indium in the thermoelectric telluride. A 0·1-g sample was dissolved, the two metals separated by hydrolysis and, after dissolving the precipitate in nitric acid and adding an excess of EDTA, bismuth and indium

were determined successively by a visual back-titration with Methylthymol Blue as indicator. Our preliminary experiments indicated that a more sensitive and selective method should be chosen to determine indium in bismuth telluride crystals. 8-Quinolinol was found to be a suitable reagent for this purpose and the amount of information available on its analytical properties suggested that a reliable procedure might be developed.

The applicability of 8-quinolinol in extraction-photometric determinations of indium(III) has been treated concisely in monographic literature[4−6]. Some older papers provide essential information on the choice of wavelength[7] (395 − 400 nm), on the absorption spectra of 8-quinolinol and the indium(III) chelate in chloroform[8], and on the approximate pH value for attaining a complete extraction[7,9]. The equilibrium constants of species taking part in the 8-quinolinol–indium(III) extraction system are also listed in critical compilations[10]. The equilibrium involved can be treated theoretically with the use of the protonation constants (e.g. see refs[11,12]), the consecutive stability constants of indium(III) complexes, and the relevant partition constants[9,13−15]. Further investigations of these equilibria have been reported in recent years[16,17]. However, a survey of literature has revealed that the extraction of indium(III) with 8-quinolinol has found so far only few practical applications. This fact is evidently due to a low selectivity of the reaction. For example, 8-quinolinol was used for a photometric finish after the separation of traces of indium with the use of a dithizone extraction from a matrix of germanium[18]. Similar determination was used in combination with a rather complicated procedure of separation from a solution obtained by decomposition of an ore[19]. A substoichiometric extraction with 8-quinolinol was used in neutron activation analysis to determine nanogram amounts of indium in semiconductor-grade silicon[20]. Masking agents for bismuth, which interferes in the extraction of indium, have not been studied in some detail so far.

EXPERIMENTAL

Reagents and Apparatus

Standard indium(III) solution, $0.01 \ mol \ l^{-1}$, was prepared by dissolving an exactly weighed amount of pure indium metal (99·999%) in 10 ml of dilute nitric acid (1 : 1). Oxides of nitrogen were removed by warming on a steam bath. Then the solution was evaporated to dryness, the residue moistened with 5 ml of 1M nitric acid and dissolved in about 100 ml of redistilled water. After transferring into a 1 000-ml graduated flask the solution was diluted to the mark. Dilute standard solution containing $5 . 10^{-4} \ mol \ l^{-1}$ of In(III) was prepared by exact dilution of the standard 0·01M stock solution. Redistilled water acidified with nitric acid was used to obtain a resulting acid concentration of about $0.001 \ mol \ l^{-1}$. The concentration of indium in the two standard solutions was determined chelometrically using Xylenol Orange which proved to be an optimum indicator[21] not only for direct visual titrations but also for photometric microtitrations

with 0·01M EDTA (pH $\approx$ 2·9, 540 nm). For standardization of EDTA pure bismuth metal and dried lead chloride were used as standard substances.

Sodium acetate solution (0·22 mol l^{-1}) for pH adjustment was prepared by dissolving CH$_3$COONa.3H$_2$O of analytical grade (Lachema, Brno) in redistilled water. Sodium thiosulfate solution (approx. 2 wt.%) was stabilized with a small amount of sodium carbonate ($\approx$ 0·1 g per 1 000 ml).

8-Quinolinol solution (approx. 0·25 wt.%). 8-Quinolinol of analytical grade (Lachema, Brno) was twice crystallized from hot ethanol and dried. The 8-quinolinol reagent was prepared by dissolving 0·5 g of quinolinol in 50 ml of redistilled water acidified with 1 ml of conc. acetic acid. Dissolution was made easier by stirring and warming to 50—60°C. Then the solution was diluted to 200 ml. This reagent solution should not be kept for more than 1 week. Chloroform for extractions and other solvents used were twice distilled.

A spectrophotometer VSU 2-G (C. Zeiss, Jena, G.D.R.) was used. The absorbance of extracts was measured at a wavelength of 400 nm (slit-width of 0·2 mm), both against a blank extract and pure chloroform as reference, using 10-mm and 50-mm glass cells (type "8", Zeiss). It is essential to prevent evaporation of the solvent, which is a source of error. PTFE caps, made to fit closely, may be used with advantage.

A pH-meter, model OP-211/1 (Radelkis, Budapest), equipped with a Radelkis combined glass electrode OP-0808P, was standardized with buffers of the practical pH scale (e.g. by using a saturated solution of potassium hydrogentartarate, pH = 3·56 at 25°C).

The effect of pH on the extraction yield was studied with the use of a mixed buffer containing sodium acetate (0·25 mol l^{-1}), hydroxyacetic acid (0·05 mol l^{-1}), and monochloroacetic acid (0·15 mol l^{-1}). To investigate the buffer region a 10-ml aliquot of the buffer stock solution was mixed with the other components as for an actual extraction (see the procedure), only instead of the sample solution a 5-ml aliquot of the matrix solution of pure bismuth telluride was added. The dependence of pH on the additions of 0·1M sodium hydroxide was obtained in form of a slightly bent curve which made possible preparation of mixed buffers within the range of pH 2·7—4·4.

The pipettes were calibrated. In washing-up glass cells and other glassware were also rinsed with dilute nitric acid (1 : 10).

Recommended Procedures

Decomposition of samples. The concentration of indium(III) in a solution obtained by dissolving a milligram sample of bismuth-indium telluride should be within the range of 20 to 225 μmol l^{-1}, which corresponds to 2—26 μg ml^{-1} of In(III). To facilitate alternative modifications the following procedure is given here for a sample weight of 10—60 mg and a final volume of 100 ml.

A sample, the surface of which is degreased and purified if necessary, is dissolved in 10 ml of dilute nitric acid (1 : 4) by warming on a steam bath just to expel oxides of nitrogen (about 10 min). After cooling the solution is diluted with 20 ml of 0·2M-HNO$_3$ and transferred into a 100-ml graduated flask. For washings and the dilution to volume 5 . 10^{-3}M nitric acid is used; so the resulting acid concentration is approx. 0·3 mol l^{-1}. An alkalimetric check is advisable if the procedure is to be modified.

Extraction-photometric determination. Extraction is carried out in a 100-ml separating funnel in which the following reagents are mixed first: 10 ml of 0·22M sodium acetate, 5 ml of 0·25% 8-quinolinol, and 5 ml of 2% sodium thiosulfate; then a 5-ml aliquot of the sample solution is added. The aqueous phase is diluted to a volume of 40 ml with water and extracted with 10 ml

of chloroform for 4 min. The extract is transferred into a dry 50-mm cell with the aid of a filtering tube into which the stem of the funnel is inserted. A small filter paper, dried at 105°C, is used to remove droplets of water. Contamination with dust particles and especially evaporation of chloroform should be prevented with the use of well-fitting PTFE caps. The same procedure is used for a blank extraction, only the sample solution is replaced with a matrix solution obtained by dissolving pure bismuth telluride. The absorbance of the sample extract is measured against the matrix blank as reference.

RESULTS AND DISCUSSION

As in other similar applications of 8-quinolinol (Hox), the determination of indium is based on a different light absorption of the yellow tris(8-quinolinolato)indium(III) chelate and of the remaining excess of uncomplexed reagent in the chloroform extract. In agreement with the previous studies[7,18], and as indicated by the curves in Fig. 1, it was possible to use a wavelength of 400 nm for further experiments. In this region of the visible the absorbance of Hox and of the impurities present in the extract decreases slowly (curve 2), forming an absorption background which has to be compensated.

Effect of pH of the Aqueous Solution

The consecutive formation of 8-quinolinolato-indium(III) complexes in an aqueous solution containing an excess of free 8-quinolinol is characterized by the following overall concentration stability constants[14]: $\log \beta_1 = 12 \cdot 00$; $\log \beta_2 = 23 \cdot 99$; $\log \beta_3 = 35 \cdot 47$; $I = 0 \cdot 1 \text{ mol l}^{-1}$ (NaClO$_4$), $25 \pm 0 \cdot 2°C$. The uncharged chelate In(ox)$_3$ is transferred into the organic nonpolar phase; for its distribution between chloroform and water the partition constant[14] is $K_D = 1\ 235 \pm 20$. The extraction system of indium(III) is considerably influenced by pH of the aqueous phase, as indicated[11] by the concentration protonation constants of 8-quinolinol: $\log K_{H1}(ox^- + H^+ = Hox) = 9 \cdot 66$; $\log K_{H2}(Hox + H^+ = H_2ox^+) = 5 \cdot 00$ $(I = 0 \cdot 1 \text{ mol l}^{-1}; 25°C)$. The partition constant (chloroform/water) is $K_D(Hox) = 457$ (see also ref.[12]). The other side-reactions in a mildly acidic medium are less significant. The hydrolysis of indium(III) in the presence of acetate begins to influence the equilibrium at pH $3 \cdot 5 - 4 \cdot 0$ (ref.[22]). In presence of an excess of 8-quinolinol the effect of hydrolysis is evidently negligible.

As the above-given constants are valid for a medium of pure perchlorate, the effect of pH of the aqueous phase (40 ml) on the extraction of indium(III) into chloroform (10 ml) was investigated under experimental conditions approaching those of the extractions of samples. Indium(III) was added as an aliquot of a stock solution obtained by dissolving a standard reference material SRM3 (see Tables I and II). Mixed buffers, containing monochloroacetic and hydroxyacetic acid and sodium acetate, were used for the adjustment of pH. The absorbance of the chloroform phase

was measured for a 10-mm path-length against a blank extract as reference, which was carried out simultaneously for each pH value of the aqueous phase. The pH-dependence shown in Fig. 2 indicates that a practically constant absorbance is attained above pH 3·5, with a mean value of $\langle A_{max} \rangle = 0·436$ $(n = 12, \ s = 7·6 \cdot 10^{-3})$. In the extraction system under consideration the total amounts of the reactants are $n(In^{3+}) = 0·602$ µmol and $n(Hox)_{total} = 81·8$ µmol (more than a 100-fold excess of the extracting agent is used; $V_{org}/V_{aq} = 0·25$). For $D_c(In^{3+}) = 1$ an estimate of $pH_{1/2}$ is 2·65 (Fig. 2).

The relative proportions of individual species taking part in the equilibrium can be estimated with the use of the equilibrium constants given above. An effective mathematical treatment of the system being considered will be discussed in detail elsewhere; here, only some results are given. For example, the relative amounts of the equilibrium species at pH 2·86 (Fig. 2) and at pH 4 (a complete extraction of In^{3+}) can be represented by the relative amount of 8-quinolinol in individual species, with
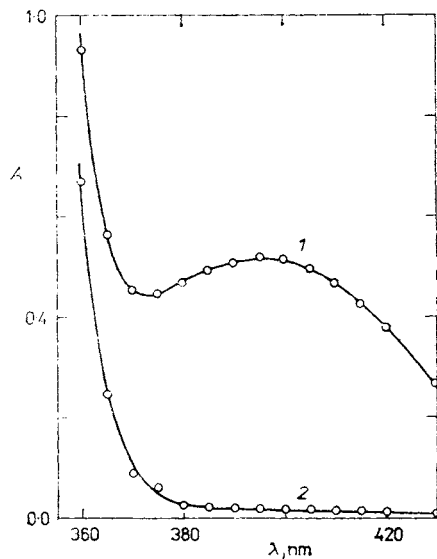

FIG. 1

Absorbance curves of chloroform extracts, $V_{aq} = 40$ ml, pH = 4·0; $V_{org} = 10$ ml. 1 tris(8-quinolinolato)indium(III) chelate in $CHCl_3$, $m(In) = 79·9$ µg, i.e. $c(In(ox)_3) \approx$ ≈ 70 µmol l^{-1}; 2 chloroform extract from a solution of pure matrix of Bi_2Te_3, containing $n(Bi^{3+}) \approx 8$ µmol
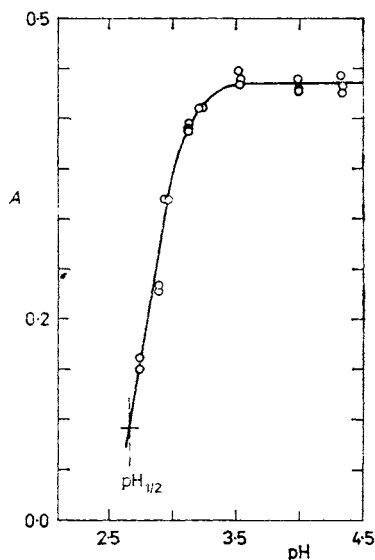
FIG. 2

pH-Dependence of absorbance in extraction-photometric determination of indium. Measured against a blank extract as reference, 400 nm, $d = 10$ mm; $V_{aq} = 40$ ml, $m(In) =$ $= 70·9$ µg; $V_{org} = 10$ ml

respect to the total amount of substance, $n(\mathrm{Hox})_{\mathrm{total}}$, present in the extraction system:

pH	$\mathrm{In(ox)_{3,org}}$	$\mathrm{Hox_{org}}$	$\mathrm{H_2ox^+_{aq}}$	$\mathrm{Hox_{aq}}$	$-\log[\mathrm{ox^-}]_{\mathrm{aq}}$
2·86	1·15%	44·1%	54·4%	0·4%	11·91
4·00	2·2%	89·1%	7·9%	0·8%	10·46

The pH-dependence of log $D_c(\mathrm{In^{3+}})$, evaluated for experiments shown in Fig. 2, has a slope value close to 3, which indicates a predominance of the complex $\mathrm{In(ox)_3}$.

The relationship A–pH, in a region where $D_c \approx 1$, can be used also for the estimation of a conditional extraction konstant, $K'_{ex} = [\mathrm{In(ox)_3}]_{\mathrm{org}}/\{[\mathrm{In'}]_{\mathrm{aq}}[\mathrm{ox^-}]^3_{\mathrm{aq}}\}$, where $[\mathrm{In'}]_{\mathrm{aq}}$ denotes a conditional concentration of indium(III) defined for the side-reactions occurring in the aqueous solution. A value of log $K'_{ex} = 37·0$ (for pH range $2·6 - 2·8$, $I = 0·10 \, \mathrm{mol \, l^{-1}}$, $c(\mathrm{AcOH}) = 0·055 \, \mathrm{mol \, l^{-1}}$, $23 \pm 2°\mathrm{C}$) was obtained by introducing a correction for the presence of consecutive 8-quinolinolato--complexes in the aqueous phase. Zolotov and Lambrev[14] have reported a value of log $K_{ex} = 38·56$ for perchlorate medium. Acetate is not, therefore, found to be an interfering species; the effect of thiosulfate remains unclear. With the value of K'_{ex} the extraction yield at pH 4·0 is $D_c(\mathrm{In^{3+}}) \approx 270$, $E \approx 99\%$. This result confirms the interpretation of the pH-dependence shown in Fig. 2.

TABLE I

Accuracy check of the method with the use of reference polycrystalline materials. Wavelength 400 nm, $d = 10$ mm; aqueous phase, pH $3·82 - 3·91$

Sample	Indium content, wt.%		Difference wt.%	Student's test[a]	
	calculated	found		ν	t
SRM1	0·722	0·650 ± 0·031	−0·072	5	2·483
SRM2	1·158	1·146 ± 0·037	−0·012	6	0·300
SRM3-1[b]	2·936	2·902 ± 0·019	−0·034	5	1·189
SRM3-2	2·936	2·968 ± 0·052	+0·032	5	0·640
SRM4	4·458	4·407 ± 0·070	−0·051	7	0·607
SRM5	6·018	5·991 ± 0·068	−0·027	5	0·415

[a] Critical values ($\nu = n - 1$) $t_{0.025}(\nu)$: (5) 2·571; (6) 2·447; (7) 2·365; [b] standard reference material SRM3 was analysed by weighing out two different portions (see Table II).

Calibration of the Method

The calibration was carried out in two stages under conditions found as optimum: $\lambda = 400$ nm; aqueous phase, $V_{aq} = 40$ ml, acetate buffer, pH $3.8 - 4.1$; $CHCl_3$, $V_{org} = 10$ ml. As found in preliminary experiments, the excess of thiosulfate $(50 - 100$--fold with respect to $n(Bi^{3+}))$ was adequate for masking of bismuth.

First, the calibration was executed with the use of a dilute standard indium(III) solution, $c(In^{3+}) = 4.98 \cdot 10^{-4}$ mol l^{-1}. Necessary concentration range was estimated taking into account the indium content in materials to be analysed and the probable weight of samples of the telluride crystals.

TABLE II
Determination of indium(III) in reference polycrystalline materials and in samples of layered monocrystals

Sample	Taken mg	Number of detn.	$\langle A \rangle$	In found wt.%	s_r %
SRM1	56·8[a]	6	0·121 ± 0·005	0·650 ± 0·031	4·5
SRM2	55·3	7	0·203 ± 0·006	1·146 ± 0·037	3·5
SRM3-1	40·4	6	0·369 ± 0·002	2·902 ± 0·019	0·6
SRM3-2	54·8	6	0·510 ± 0·009	2·968 ± 0·052	1·7
SRM4	56·2	8	0·773 ± 0·012	4·407 ± 0·070	1·9
SRM5	40·4	6	0·756 ± 0·009	5·991 ± 0·068	1·1
TS1	55·8	4[b]	0·116 ± 0·008	0·637 ± 0·046	4·9
TS2	55·9	6	0·325 ± 0·009	1·838 ± 0·055	2·8
TS3	58·4	6	0·610 ± 0·012	3·338 ± 0·068	2·0
TS4	54·3	8	0·693 ± 0·007	4·081 ± 0·042	1·2
S1	4·041[c]	4[d]	0·155 ± 0·008	0·599 ± 0·031	3·5
S2	12·683	4	0·131 ± 0·004	0·796 ± 0·027	2·3
S3	10·061	4	0·117 ± 0·001	0·889 ± 0·012	0·9
S4-1	9·058	4	0·144 ± 0·002	1·225 ± 0·019	1·1
S4-2	3·099	4[d]	0·238 ± 0·014	1·209 ± 0·074	4·1
S5	5·461	4	0·100 ± 0·009	1·382 ± 0·128	6·2
S6	7·052	4	0·169 ± 0·009	1·860 ± 0·107	3·9
S7	10·596	4	0·260 ± 0·004	1·935 ± 0·033	1·2
S8	5·092	4	0·157 ± 0·010	2·382 ± 0·160	4·5
S9	7·601	4	0·237 ± 0·009	2·451 ± 0·092	2·5
S10	7·936	4	0·353 ± 0·006	3·530 ± 0·059	1·1
S11	5·107	4	0·308 ± 0·001	4·770 ± 0·023	0·3

[a] Solutions of samples SRM1—TS4 were diluted in 100-ml graduated flasks to volume; [b] for a number of determinations $n \leq 5$ the estimates were calculated from the range by the Dean and Dixon method; [c] the final volume for samples S1—S11 was 25 ml; [d] measured in 50-mm cells.

To a solution obtained by dissolving pure Bi_2Te_3 $(53-54$ mg/100 ml) a certain volume of the standard indium(III) solution was added from a burette into a 100-ml graduated flask; then the solution was diluted to the mark. In this way five calibration solutions, corresponding to 10, 20, 48·5, 80 and 128·5 μg of In(III) per a 5-ml aliquot, were prepared. In all five series of 4 or 6 extractions a constant arrangement of the recommended procedure was strictly observed. For higher amounts of indium(III) $(m(\text{In}) > 20$ μg) an optimum range of the absorbance was obtained for a 10-mm path-length. In the case of lower amounts of In(III) the absorbance was also measured in a 50-mm cell. For two extractions of samples always one matrix blank was extracted simultaneously, taking a 5-ml aliquot of a solution obtained by dissolving corresponding mass of pure Bi_2Te_3.

For the calibration with 10-mm cells the following regression line (significance level $\alpha = 0·05$, total number of experiments $n = 26$, and $s_{yx} = 0·0077$) was calculated

$$A = (0·0062 \pm 0·0056) + (6·208 \pm 0·073) \cdot 10^{-3} \, m(\text{In}) \qquad (1)$$

where $m(\text{In})$ is an amount of indium(III) in μg/5 ml of the sample solution. For all calibration experiments a pooled estimate of the standard deviation of absorbance was $6·4 \cdot 10^{-3}$.

With auxiliary measurements in 50-mm cells the photometric error was somewhat greater. Consequently, Student's test indicated that this calibration was adequately represented by a regression line (2 calibration sets, $n = 8$, $s_{yx} = 0·0123$) passing through the origin

$$A = (3·156 \pm 0·068) \cdot 10^{-2} \, m(\text{In}) . \qquad (2)$$

Secondly, the calibration of the method and also its applicability for analysis of layered crystals were tested with the use of a polycrystalline modification of bismuth--indium telluride. The procedure of synthesis for this material was modified to yield a homogeneous composition; therefore, it was possible to calculate the content of individual components in a sample from the weights of elements taken for the synthesis. So standard reference materials (denoted as SRM1−SRM5) of known composition were prepared to correspond to typical samples of layered crystals.

In dissolution of the reference materials, in all extractions and photometric measurements the recommended procedure was strictly applied. Statistical evaluation of particular series of extractions is shown in detail in Table II. By comparison with the results listed in Table I the reliability of the method can be seen. The error of the method becomes more evident, of course, for a lower amount of indium $(<1$ wt.%). The majority of deviations, expressed as absolute values of the differences between a known indium content and the amount found, are close to a mean value of 0·038%. As shown by Student's tests $(\alpha = 0·05)$ there are no significant differences between the analytical results and known amounts of indium in the standard materials.

Moreover, the results of analysis of the reference materials confirm the accuracy of the calibration procedure with the use of a precisely standardized solution of indium(III). The addition of thiosulfate to the aqueous phase provides effective masking of bismuth and causes no significant decrease of precision and accuracy of the method.

Effect of Blank Tests

A considerable number of absorbance values for the blank extractions, measured against pure chloroform as reference, was obtained during the development of the method, in repeated calibrations, and in numerous assays of indium under practically identical conditions $(n = 65)$. Glass cells of 10-mm path-length were carefully paired; thus it was possible to analyse statistically the blank sets. The whole set was evaluated with the use of a complex statistical program. Among the computed estimates only the skewness was lower than the calculated critical value. The chi-square test, with the data partitioned into 9 classes, also indicated that the hypothesis of normal distribution of the blanks should be rejected.

Critical analysis of the blanks lead to a conclusion that systematic attention should be given to fluctuations and trends of the blanks. The spectrophotometry of the blank extractions (cf. Fig. 1) revealed that the absorbance of a blank at 400 nm was predominantly influenced by the presence of the free form Hox of 8-quinolinol; this was also confirmed by the calculation of the relative amounts of individual equilibrium species in the extraction system. So a blank value is also affected by the purity of the reagent. However, the reproducibility of a blank extraction may also be influenced by a number of factors affecting the partition of 8-quinolinol between chloroform and water (cf. ref.[12]). Our experiments also confirmed a significant matrix effect on the blank values. The matrix solution for blanks should be prepared by dissolving an amount of pure Bi_2Te_3 which corresponds to a certain mass of the sample. It was also interesting to realize that the absorbance values were more scattered for typical reagent blanks, i.e. for extractions from solutions having the same pH and concentrations of pure salts $(NO_3^-, CH_3COO^-, CH_3COOH, S_2O_3^{2-},$ $Na^+)$ but containing no products of the dissolution of bismuth telluride.

Under carefully controlled experimental conditions it was possible to stabilize the blank values satisfactorily within several days. For example, a set of extractions $(n = 29)$, corresponding to serial determinations of indium in samples S1−S11, had a mean absorbance value 0.0183 $(d = 10$ mm, vs $CHCl_3)$ and a standard deviation, $s = 2.7 . 10^{-3}$, which was practically on the level of a photometric error.

A blank extraction should be performed simultaneously: one blank was always included with two extractions of samples. In this way it was possible to achieve more reliable results. However, further attention should be given to the theoretical analysis of blanks in similar cases.

Analysis of Layered Crystals

Monocrystals of bismuth-indium telluride are relatively soft and liable to split in thin layers. Samples taken for physical measurements were cut out in form of a small rectangle (with a mass of several mg) from a triangular crystal plate which was 6 − 8 cm long and 0·02 − 0·1 mm thick. As there is a considerable concentration gradient of indium along the monocrystal, every sample taken from the monocrystal is an individual specimen which cannot be replaced easily by another piece of the crystal.

The concentration range necessary for the determination of indium was checked with the use of solutions of test samples (TS1 − TS4), which were prepared by dissolving greater pieces of the crystals (see Table II) in dilute nitric acid. The same procedure was then used to dissolve the samples of monocrystals. The sample weights (cf. Table II) corresponded to 10 − 60 mg (taken for a final volume of 100 ml). However, the procedure of dissolution should be modified according to the actual weight of the crystal sample and the volume (e.g. 25 ml) chosen for a final dilution. In any case, the resulting acid concentration should be close to a value of $c(HNO_3) \approx$ $\approx 0·3$ mol l^{-1}.

The number of repeated extractions of a certain sample solution was necessarily restricted by its volume. The absorbance of chlorofom extracts was measured in 10-mm cells against a matrix blank as reference; only in the case of a low indium amount the extract was also measured in a 50-mm cell.

The results of analysis of crystal samples S1 − S11 are listed in Table II together with the statistical evaluation of particular extraction series. It is evident that an adequate level of precision can be achieved within the whole concentration range required for the analysis of the crystal samples. Except for one series of extractions the relative standard deviation was within the range of 1 − 4%. The results of determinations of indium in layered crystals, some of which are reported here, made feasible the interpretation of their physical properties[23].

REFERENCES

1. Lošťák P., Horák J., Koudelka L.: *European Meeting Crystal Growth 82, Materials for Electronics, Prague 1982*, p. 354.
2. Lošťák P., Horák J., Koudelka L.: Phys. Status Solidi A *76*, K71 (1983).
3. Danzaki Y., Shoji T., Sase M., Takeyama S.: Bunseki Kagaku *32*, 89 (1983).
4. Sendel E.: *Kolorimetricheskie metody opredeleniya sledov metallov*, p. 421−32. Mir, Moscow 1964.
5. Starý J.: *The Solvent Extraction of Metal Chelates*, p. 80. Pergamon Press, Oxford 1964.
6. Koch O. G., Koch-Dedic G. A.: *Handbuch der Spurenanalyse*, Teil 2, p. 785. Springer, Berlin 1974.

7. Moeller T.: Ind. Eng. Chem., Anal. Ed. *15*, 270 (1943).
8. Moeller T., Cohen A. J.: J. Am. Chem. Soc. *72*, 3546 (1950).
9. Starý J.: Anal. Chim. Acta *28*, 132 (1963).
10. Starý J., Zolotov J. A., Petrukhin O. M.: *IUPAC Chem. Data Ser.*, Vol. 24. Pergamon Press, Oxford 1979.
11. Dyrssen D.: Svensk Kem. Tid. *64*, 213 (1952).
12. Morin S. J., Iofa B. Z.: Zh. Anal. Khim. *38*, 348 (1983).
13. Schweitzer G. K., Coe G. R.: Anal. Chim. Acta *24*, 311 (1961).
14. Zolotov J. A., Lambrev V. G.: Zh. Anal. Khim. *20*, 1153 (1965).
15. Schweitzer G. K., Andersen M. M.: J. Inorg. Nucl. Chem. *30*, 1051 (1968).
16. Morin S. J., Iofa B. Z.: Zh. Anal. Khim. *38*, 164 (1983).
17. Rane A. T., Nepali D. R.: Indian J. Chem., A *25*, 846 (1986).
18. Luke C. L., Campbell M. E.: Anal. Chem. *28*, 1340 (1956).
19. Akimov V. K., Zhgenti K. A., Busev A. I.: Zavod. Lab. *39*, 948 (1973).
20. Zmijewska W.: J. Radioanal. Chem. *20*, 521 (1974).
21. Kalischová Y.: *Thesis.* Institute of Chemical Technology, Pardubice 1987.
22. Kragten J.: *Atlas of Metal–Ligand Equilibria in Aqueous Solution,* p. 402. Ellis Horwood, Chichester 1978.
23. Jansa L.: *Thesis.* Institute of Chemical Technology, Pardubice 1988.

Translated by the author (S.K.).