Extraction-Spectrophotometric Determination of Low Amounts of Antimony in Metals and Alloys

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Modified extraction-spectrophotometric procedures have been used for determination of low amounts of antimony in various metallic materials. Use was made of the highly sensitive colour reaction of rhodamine B with the complex anion $[SbCl_6]^-$ in the medium of HCl, wherefrom the coloured product was extractible into organic phase and the maximum of its absorbance was at λ = 560 nm. Of the developed procedures the first one is based on direct extraction of the coloured product into toluene. In the second procedure first the $[SbCl_6]^-$ anion is extracted with n-amyl acetate from the medium of HCl in the presence of NH_4Cl. To the separated organic phase containing antimony, HCl, aqueous solution of rhodamine B, and toluene were added stepwise. By the procedures mentioned above it was possible to determine 3×10^{-5} to 1 mass % Sb in various metallic materials.

Determination of antimony with rhodamine B by extraction-spectrophotometric method is based on utilization of the coloured product (ionic associate), formed in the reaction of the complex anion $[SbCl_6]^-$ with the dye cation [1, 2]. The water-insoluble red-violet antimony associate with rhodamine B is well extractible into various organic solvents, which influence the position of the maximum (λ_{max} = 550—565 nm), shape, and intensity of the absorption band [3–7]. The presence of oxidation-reduction compounds in the analyzed solution often brings about a decomposition of the organic reagent or transformation of the complex anion $[SbCl_6]^-$ into other anion ($[SbCl_4]^-$) [8—11].

In spite of the fact that there are numerous reagents and procedures used for determination of antimony [12—14], the methods utilizing the above-mentioned reaction are still attractive, mainly in respect of their modification for the samples with complicated matrix.

Comparison of the results of determination of antimony by the already known procedures [14] with those obtained in determination of low amounts of Sb in steel, alloys based on iron, and in electrolytes of copper and its alloys using brilliant green showed that the latter were influenced by the complexity of the matrix [15, 16].

The aim of the present work was to elaborate a procedure for determination of low amounts of Sb with rhodamine B, which would provide reliable results in analysis of various materials with complicated matrix. Attention was paid mainly to new alloys based on Fe—Ni—Sb, used in electrotechnics and mechanical engineering as highly solid materials.

EXPERIMENTAL

Standard solutions of known amount of Sb, standards of various metallic materials (with appropriate content of Sb): low-alloy steel No. 162 (0.000 mass %) and No. 166 (0.035 %), grey cast iron No. 210 (0.14 %), and brass No. 310 (0.10 %) and No. 316 (0.005 %) (all from the Research Institute of ČKD, Prague) were used. Used were further Fe 6N (Mathey—Johnson, England) and electrolytic Cu 5N (Považské strojárne, Považská Bystrica). The samples of the Fe—Ni—Sb alloys were prepared by vacuum melting of the respective metals of high purity (4—6N) in an induction furnace IS I/2 (Leybold—Heraeus) at reduced pressure (10 Pa). Antimony was added into the melt right before casting. The 0.05 vol. % aqueous solution of rhodamine B was prepared 24 h prior to use. It was kept in a dark flask and was stable for 2 months. All other chemicals used were of anal. grade (Lachema, Brno).

Spectrophotometric measurements were performed with a UV—VIS 402 (Perkin—Elmer) spectrometer in the region of λ = 450—650 nm and a Spekol (Zeiss, Jena) photometer at λ = 560 nm in glass cells of 0.5, 1.0, 2.0, and 4.0 cm thickness.

Preparation of the Sample

The sample to be analyzed (filings, shavings; 0.2—5 g) was dissolved at moderate heating in the necessary amount of HNO_3 (φ_r = 1 : 1) with addition of concentrated H_2SO_4 (0.5—2 cm^3) and evaporated

until escape of white fumes of SO_3. When the sample contained graphite C (pig iron), Si (silicon steel), and Sn (bronze, brass) which precipitate in solid state as elemental carbon or in the form of hydrated oxides, to the cool sample water (40 cm^3) was added and such an amount of concentrated H_2SO_4 that its resulting concentration was 1.5 mol dm^{-3}. The solid admixtures were removed by filtration of the solution into a 50 cm^3 volumetric flask and washing with distilled water until the flask was made up to the mark. For the individual determinations by both processes aliquots containing up to 30 μg Sb were taken.

Determination of Sb

Procedure A. Into the analyzed sample containing up to 30 μg Sb, HNO_3 (φ_r = 1 : 1; 10 cm^3) and concentrated H_2SO_4 (3 cm^3) were added and the solution was evaporated until escape of white fumes of SO_3. To the cool residue HCl (φ_r = 1 : 1; 10 cm^3) was added, the solution was transferred into a separating funnel, 10 vol. % $SnCl_2$ (0.5 cm^3) was added and the solution was stirred. Then 10 vol. % $NaNO_2$ (1 cm^3) was added and the solution was stirred and allowed to oxidize precisely for 5 min (escape of nitrogen oxides). After 5 min 20 vol. % urea (1 cm^3) was added and the solution was stirred again. Then immediately water (25 cm^3) and 0.05 % aqueous solution of rhodamine B (5 cm^3) were added. After stirring toluene (10 cm^3) was added and the solution was stirred for 2 min. After separation of the layers the organic phase was analyzed photometrically in the wavelength region of 450—650 nm or absorbance was measured at 560 nm in cells of appropriate thickness. The comparative solution was pure toluene or the organic phase obtained in the same manner from the same chemicals without addition of the sample.

Procedure B. To the analyzed sample in a separating funnel, containing up to 30 μg Sb, the same volume of concentrated HCl, saturated solution of NH_4Cl (2—3 cm^3), and toluene (10 cm^3) were added. Toluene served for extraction of the HNO_3 residues, remaining in the solution after decomposition of the samples. After half a minute stirring the water phase was transferred into another separating funnel and 1 % solution of ascorbic acid was added dropwise until the first appearance of a black turbidity, which disappeared on stirring the solution. Then after exactly 5 min n-amyl acetate (5 cm^3) was added. After 1 min stirring the water phase was discarded and to the organic phase HCl (c = 6 mol dm^{-3}; 10 cm^3) and 40 vol. % KF (5 drops) were added and the solution was stirred. Then 0.05 vol. % aqueous solution of rhodamine B (10 cm^3) and toluene (5 cm^3) were added and the solution was stirred for half a minute. When the coloured organic phase was turbid, the solution was centrifuged to get a transparent solution for photometric analysis similar as in procedure *A*.

Evaluation. In mathematical-statistical treating of the results the classical evaluation relationships used for point estimate (s_M, $s_{\%\,M}$) and functional estimate (s_v, d_v, $d_{\%\,v}$) of statistical measurements [17, 18] were used. Used were further the relationships allowing to estimate the statistical characteristics of calibration curves as functions of the mass of the analyte in the analyzed system [19].

RESULTS AND DISCUSSION

The experimental results obtained in direct determinations (procedure *A*) showed that 2—4 M-HCl was the most suitable medium for extraction of the ionic associate of antimony with rhodamine B, because the intensity of the absorption band was maximum in this concentration range (Fig. 1, curve *1*). When c_{HCl} < 2 mol dm^{-3}, also part of the free reagent was extracted into the organic phase (Fig. 1, curve *2*).

In the procedure *B* with preliminary extraction the maximum absorbance of the ionic associate $[SbCl_6]^-$ with rhodamine B in the presence of saturated NH_4Cl solution (2—3 cm^3; increases the concentration of Cl^-) was achieved already at c_{HCl} > 4.5 mol dm^{-3} (Fig. 1, curve *4*), while in the absence of saturated

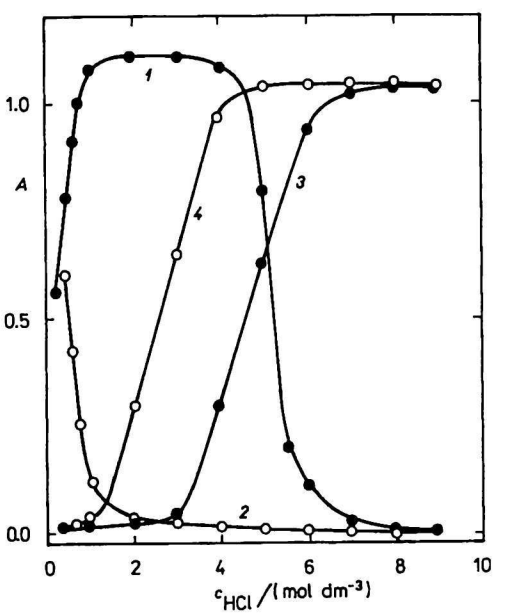

Fig. 1. Dependence of absorbance values of the ionic associate of Sb with rhodamine B on c_{HCl} at λ = 560 nm, 25 μg Sb in 10 cm^3 of organic phase, l = 0.50 cm. *1*. Direct determination; *2*. comparative experiment; *3*. extraction of Sb without addition of NH_4Cl; *4*. extraction of Sb with addition of NH_4Cl.

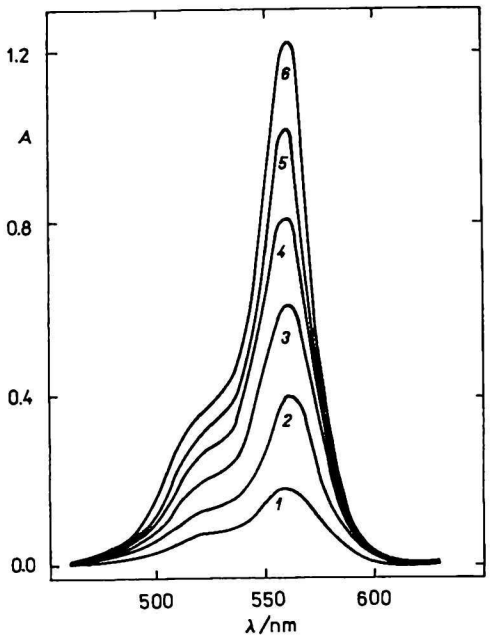

Fig. 2. Dependence of absorbance values of the ionic associate of Sb with rhodamine B on the amount of Sb (in μg) in 10 cm^3 of organic phase (l = 0.50 cm): *1*. 5; *2*. 10; *3*. 15; *4*. 20; *5*. 25; *6*. 30.

NH_4Cl solution the necessary concentration was $c_{HCl} \geqq 7.5$ mol dm^{-3} (Fig. 1, curve *3*).

The absorbance values of the ionic associate of antimony with rhodamine B measured at λ = 560 nm (Fig. 2) were calculated for the cell of the highest thickness (l = 4.00 cm). The obtained A values were then substituted into the equation of a straight line and the theoretical A values for the relationship $A = f(c)$ were calculated by the least-squares method. For the procedure A the following equation was used

$$A_{calc.}^{560} = (0.3588 \pm 0.0035)\rho_{Sb} + (0.067 \pm 0.037) \quad (1)$$

(The total number of determinations taken for calculation of statistical parameters of the calibration curve N = 35, the number of the individual concentrations ("knots") in the followed concentration range u = 7, the sum of squares of deviations of the measured values of the analyte from the values calculated by the least-squares method $\Sigma\Delta^2$ = 1.5922, the amount of Sb in the analyzed solution ρ = 1—30 μg in 10 cm^3, the thickness of the cell ℓ = 4 cm, and the correlation coefficient r = 0.9979.)

The dependence A on the mass of antimony in the analyte for procedure B is expressed by the relationship

$$A_{calc.}^{560} = (0.3344 \pm 0.0021)\rho_{Sb} - (0.080 \pm 0.014) \quad (2)$$

(N = 50, u = 10, $\Sigma\Delta^2$ = 0.4861, ρ_{Sb} = 0.5—30 μg/10 cm^3, ℓ = 4.00 cm, and r = 0.9996.)

Table 1. Parameters of Mathematical-Statistical Treatment of the Results Obtained in Determination of Low Amounts of Sb(V) by Procedure *A* (from Five Measurements at Seven Various Concentrations)

m_{Sb} (given) μg	m_{Sb} (found) μg	s_M	s_v	d_v	$d_{\%\,v}$
1.00	1.13	0.122	0.086	0.092	9.23
5.00	4.98	0.106	0.192	0.207	4.14
7.50	7.85	0.284	0.235	0.253	3.37
10.00	10.48	0.347	0.271	0.292	2.92
15.00	15.43	0.170	0.332	0.358	2.39
20.00	19.90	0.275	0.383	0.413	2.06
30.00	30.10	0.304	0.469	0.506	1.69

s_M – point estimate of absolute value of standard deviation of individual measurements, s_v – functional estimate of absolute value of standard deviation, d_v – functional estimate of absolute error, $d_{\%\,v}$ – functional estimate of relative error. Indices M and v at the symbols denote the measured and calculated values, respectively.

Table 2. Parameters of Mathematical-Statistical Treatment of the Results Obtained in Determination of Low Amounts of Sb(V) by Procedure *B* (from Five Measurements at Ten Various Concentrations)

m_{Sb} (given) μg	m_{Sb} (found) μg	s_M	s_v	d_v	$d_{\%\,v}$
0.50	0.89	0.020	0.031	0.034	6.72
1.00	1.20	0.079	0.044	0.048	4.75
2.50	2.49	0.079	0.070	0.075	3.00
5.00	4.91	0.114	0.099	0.106	2.12
7.50	7.24	0.220	0.121	0.130	1.73
10.00	10.06	0.357	0.140	0.150	1.50
15.00	14.80	0.325	0.172	0.184	1.23
20.00	19.92	0.506	0.198	0.212	1.06
25.00	25.22	0.476	0.221	0.238	0.95
30.00	30.38	0.184	0.243	0.267	0.87

The elaborated procedures were tested with solutions of standard samples (Tables 1 and 2), standard materials, and artificially prepared samples (Table 3). From the stock solutions various volumes, containing 5—5000 mg of the analyzed material, were pipetted and known amounts of antimony (0.5—30 μg) were added into each sample. The results of determinations and their statistical evaluations are summarized in Tables 1 and 2. Comparison of standard deviations showed that these estimates are nonmonotonous functions of the mass of the analyte in the analyzed material.

The knowledge obtained in determination of low amounts of antimony in standard samples was utilized in analysis of solid samples of metals and alloys (Table 3). It was found from comparison of procedures *A* and *B* in analysis of real samples that procedure *A* used with materials based on copper gave nonreproducible results, however, it was more suitable for analysis of steel than procedure *B*. This was manifested mainly by deformation of absorption bands brought about by time-dependent setting of equilibrium between the reacting components,

Table 3. Results of Determination of Low Amounts of Sb(V) with Rhodamine B

Material	Weight/mg	m_{Sb}(given)		m_{Sb}(found)			
				Procedure *A*		Procedure *B*	
		μg	%	μg	%	μg	%
Steel No. 162	100	0	0	1.2 ± 0.3	0.0012 ± 0.0003	*a*	
	200	0	0	3.2 ± 0.9	0.0016 ± 0.0004		
Steel No. 166	40	14	0.035	12.8 ± 0.7	0.032 ± 0.0017	*a*	
	80	28	0.035	28.0 ± 1.3	0.035 ± 0.0016		
Alloy No. 210	5	7	0.14	7.1 ± 0.4	0.142 ± 0.008	7.4 ± 0.5	0.148 ± 0.01
	10	14	0.14	14.3 ± 0.6	0.143 ± 0.006	14.9 ± 0.7	0.149 ± 0.007
Brass No. 310	10	10	0.10	9.9 ± 0.17	0.100 ± 0.002	10.0 ± 0.5	0.10 ± 0.0015
	20	20	0.10	20.2 ± 0.69	0.100 ± 0.003	20.0 ± 0.8	0.10 ± 0.0021
Brass No. 316	300	15	0.005	*b*		14.8 ± 0.6	0.0049 ± 0.0002
	500	25	0.005			25.9 ± 0.9	0.0052 ± 0.00018
Fe 6N	400	0	0	3.6 ± 0.4	0.0009 ± 0.0001	1.2 ± 0.3	0.0003 ± 0.00008
	700	0	0	6.3 ± 0.5	0.0010 ± 0.00008	1.8 ± 0.4	0.00026 ± 0.00005
Fe—Ni—Sb	10	15	0.15	14.8 ± 0.6	0.148 ± 0.006	15.2 ± 0.5	0.152 ± 0.005
	100	10	0.01	10.2 ± 0.9	0.010 ± 0.001	10.1 ± 0.3	0.010 ± 0.0008
	200	20	0.01	20.4 ± 0.7	0.010 ± 0.0004	19.8 ± 0.7	0.010 ± 0.0004
Cu 5N	2500	15	0.0006	*b*		14.8 ± 1.3	0.00059 ± 0.0004
	5000	30	0.0006			31.2 ± 1.4	0.00062 ± 0.0004
	3000	8.1	0.00027	*b*		8.5 ± 0.6	0.00027 ± 0.00002
	5000	13.5	0.00027			13.2 ± 0.5	0.00029 ± 0.00001

a) Little satisfactory results; the samples contained W; *b*) the results were not reproducible.

making the reproducibility of the individual measurements worse.

The less satisfactory results obtained by procedure *B* with materials based on iron were due to the fact that these contained tungsten. Its ionic associates in the medium of HCl also react with rhodamine B [20]. These are extractible into organic solvents, which explains the differences in determination of antimony by the procedures used in the present work.

In spite of the facts mentioned above it is evident from the results obtained in determination of low amounts of antimony in metals with complicated matrices that by the applied procedures it was possible to determine 3×10^{-5}—1 mass % Sb in non-iron metals and 10^{-3}—1 mass % Sb in alloys based on Fe. Under these limits the values of standard deviations increased inadequately.

For molar absorption coefficient ε Refs. [3, 14] give 1.28×10^4 m^2 mol^{-1} at 555 nm and Ref. [12] gives 0.97×10^4 m^2 mol^{-1} at 552 nm. The ε_{560} values (1.08×10^4 m^2 mol^{-1} and 1.02×10^4 m^2 mol^{-1}) calculated from the slopes of the calibration curves (eqns (*1*) and (*2*)) are in good agreement with the mean values of the literature data.

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