

## PHOTOMETRIC DETERMINATION OF ALUMINIUM AND ZINC WITH SALICYLALDEHYDE SEMICARBAZONE

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The effect of some tensides on the absorption, excitation, and fluorescence spectra of Al and Zn complexes of salicylaldehyde semicarbazone in aqueous-alcoholic solutions and on their extractability into ethyl acetate has been studied. The shape of the absorption spectra is unaffected by the presence of the tensides while the time of the complex formation is shorter. The complexes are extractable into ethyl acetate in the presence of the anionactive tenside tested, sodium lauryl sulphate. The optimum conditions for the spectrophotometric and fluorometric determination of Al and Zn have been established. The limit of determination is  $2 \text{ ng ml}^{-1}$  (pH 3.8–4.8) for Al and  $50 \text{ ng ml}^{-1}$  (pH 8.4–8.6) for Zn. Using thiosulphate or fluoride as masking agents, Zn can be determined in a concentration of  $2 \text{ } \mu\text{g ml}^{-1}$  in the presence of the same quantity of Al or Cu, or in the presence of a tenfold excess of Fe, with a relative standard deviation of 1.5%.

Tensides are known to affect favourably the sensitivity of a number of spectrophotometric determinations of metal ions with organic reagents, or their extractability into organic solvents. This is explained in terms of the formation of ternary complexes or ionic associates, or concentration of reagent on the tenside micelles (*e.g.*, refs<sup>1–3</sup>) associated with bathochromic and hyperchromic effects in the absorption spectra. Tensides are also capable of increasing the intensity of fluorescence of some complexes, use of which has been made, *e.g.*, in the fluorometric methods of determination of Al, Ga, and In with lumogallion<sup>4</sup>.

The aim of the present work was to examine the effect of four tensides, *viz.* the cationactive 1-ethoxycarbonylpentadecyltrimethylammonium bromide (Septonex), cetyltrimethylammonium bromide, the anionactive sodium lauryl sulphate, and the nonionic polyvinylpyrrolidone, on the absorption, excitation, and fluorescence spectra of aluminium and zinc complexes of salicylaldehyde semicarbazone (SSC), a reagent suggested previously for the fluorometric determination of zinc<sup>5</sup>. The optimum conditions of the determination of Al and Zn in trace amounts were also sought.

### EXPERIMENTAL

#### Chemicals and Apparatus

Solution of salicylaldehyde semicarbazone<sup>5</sup> in ethanol freed from fluorescent impurities by distilla-

tion was prepared freshly every other day and stored in darkness to avoid its slow decomposition<sup>6</sup>. Solution of the reagent in redistilled ethyl acetate remains steady for a minimum of a week.

Aqueous solutions of Septonex (Slovakofarma, Hlohovec),  $0.01 \text{ mol l}^{-1}$ ; polyvinylpyrrolidone 360 000 (Fluka, Buchs), 0.23% and sodium lauryl sulphate (Lachema, Brno), 2%. Ethanol solution of cetyltrimethylammonium bromide (Lachema, Brno), 0.7%.

Acetate, glycine, and citrate buffers<sup>7</sup> and buffer containing tris(hydroxymethyl)aminomethane and maleic acid<sup>8</sup>, whose ionic strength was adjusted with KCl,  $\text{NaNO}_3$ , or  $\text{NaClO}_4$  to  $I = 0.25$ . The metal salt solutions were prepared by dissolving reagent grade chemicals in deionized water. The titre of the 0.1M stock solutions of aluminium nitrate and zinc nitrate was determined chelometrically and the solutions were diluted to the requisite concentrations prior to use.

The absorption spectra were scanned on a Specord UV-VIS instrument using 1 cm cells, the absorbances were measured on a Spekol instrument (both Carl Zeiss, Jena) using 2 cm cells. The excitation and fluorescence spectra were recorded on an Aminco-Bowman spectrofluorometer equipped with an excitation and emission diaphragm 1 mm and an X-Y plotter; 1 cm cells were used. The fluorescence intensities obtained at various gain values were related to gain 100.

### Procedure

For the spectrophotometric and fluorometric measurements of the aqueous-alcoholic solutions (40% (V/V) ethanol), 0–5 ml of metal salt solution, 2 ml of buffer solution, 0–1 ml of masking agent solution, 0–10 ml of SSC solution, and 0–3 ml of tenside solution were placed successively in a 25 ml volumetric flask, the mixture was diluted with ethanol to 10 ml, cooled down, diluted to the mark with water, and thermostatted at  $20^\circ\text{C}$  (unless stated otherwise). The absorbances and fluorescence intensities were measured against blank solutions.

For the extraction experiments, 0–2 ml of metal salt solution, 2 ml of buffer solution, and 0–1 ml of tenside solution were placed in a 10 ml test tube with ground-in stopper, the mixture was diluted to 5 ml with water, and 2 ml of SSC solution in ethyl acetate was added. The system

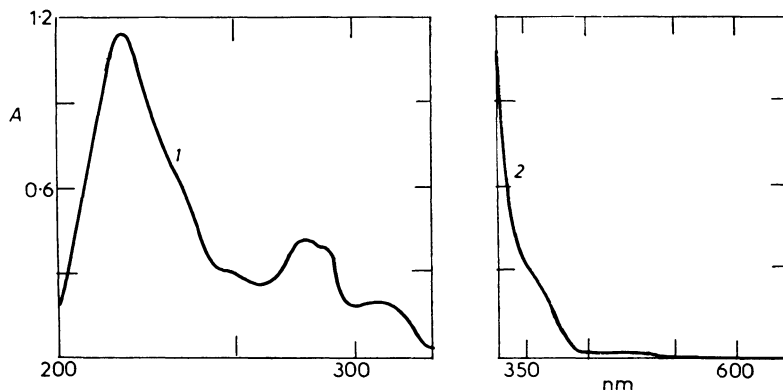


FIG. 1

Absorption spectra of aluminium complex of salicylaldehyde semicarbazone. pH 4.6 (acetate buffer), cell 1 cm.  $c_{\text{Al}}$  and  $c_{\text{SSC}}$  ( $\mu\text{mol l}^{-1}$ ): 1 6.36, 21.3; 2 63.6, 213

was agitated on a shaking machine, the organic phase was drawn off with a pipet, filtered over dry filter paper with several crystals of anhydrous sodium sulphate, and its fluorescence was measured in 3 mm cells.

#### Data Handling

The absorbances or fluorescence intensities ( $Y$ ) were measured in triplicate for samples containing the metal salt in a concentration  $c$  (in  $\text{mol l}^{-1}$ ), and subjected to polynomial regression analysis using the POLGR program to give the coefficients of the equation<sup>9-11</sup>

$$Y = Y_0 + \beta_1 c + \beta_2 c^2 + \dots + \beta_n c^n. \quad (1)$$

The limit of determination was calculated as

$$Y_{\min} = Y_0 + 10s_{Y_0}, \quad (2)$$

where  $s_{Y_0}$  is the standard deviation estimate for the absorbance or the fluorescence intensity of the blank.

## RESULTS

### *Spectrophotometric Measurements*

The absorption spectra of the Al and Zn complexes of SSC are shown in Figs 1 and 2, respectively. The absorption peaks of the complexes lie at 354 and 358 nm, respectively. The absorbances attain their maxima approximately 20 min after the mixture preparation. The tensides, in concentrations of  $10^{-3}$ – $10^{-2}$   $\text{mol l}^{-1}$  ( $10^{-6}$  to

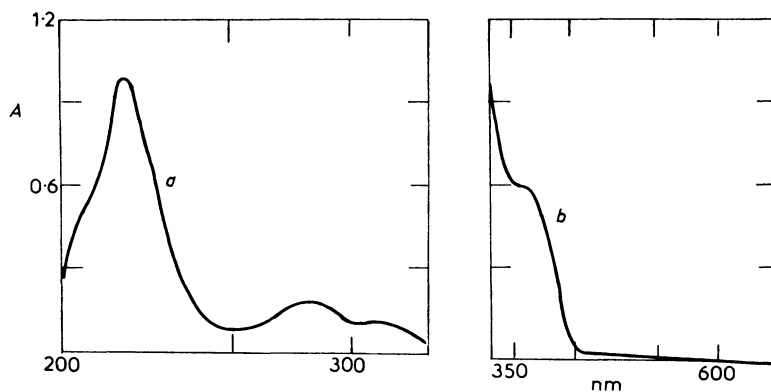


FIG. 2

Absorption spectra of zinc complex of salicylaldehyde semicarbazone. pH 5.83 (acetate buffer), cell 1 cm.  $c_{\text{Zn}}$  and  $c_{\text{SSC}}$  ( $\mu\text{mol l}^{-1}$ ): a 46.5, 58.5; b 465, 235

$10^{-7} \text{ mol l}^{-1}$  for polyvinylpyrrolidone), do not affect the absorption peak positions to within 2–4 nm, nor do they affect the absorptivity values, while the absorbances attain their maximum values in a time as short as 5 min.

Studying the conditions for the determination of Al and Zn, the absorbances or the fluorescence intensities were measured for solutions containing the metal ions and the reagent in various proportions and at different pH values<sup>6</sup>. The optimum conditions found are given in Table I. The absorbances remain virtually unaffected by changes in the ionic strength over the region of 0–0.5 mol l<sup>-1</sup>, and decrease about 0.05 units if the temperature, in the region of 10–25°C, is increased by 1°C. The calibration plot for Al is linear up to the concentration of  $3.4 \cdot 10^{-5} \text{ mol l}^{-1}$  ( $Y_0 = 0.028$ ,  $\beta_1 = 1.51 \cdot 10^4$ ;  $s_{Y_0} = 3.2 \cdot 10^{-3}$ , for the cell thickness of 2 cm), zinc obeys the regression curve equation with the coefficients  $Y_0 = 0.029$ ,  $\beta_1 = 3.88 \cdot 10^4$ ,  $\beta_2 = -2.01 \cdot 10^8$ ;  $s_{Y_0} = 3.2 \cdot 10^{-3}$ .

### Fluorescence Measurements

The excitation and fluorescence spectra of the complexes are shown in Figs 3 and 4. The tensides, in concentrations as above, have virtually no effect on the fluorescence

TABLE I

Optimum conditions for the photometric determination of aluminium and zinc with salicylaldehyde semicarbazone

Parameter	Optimum conditions for the determination by					
	absorption photometry <sup>a</sup>		fluorometry		extraction fluorometry	
	Al	Zn	Al	Zn	Al	Zn
$\lambda_{\text{abs (exc)}}$ , nm	354	358	358	350	358	350
$\lambda_{\text{em}}$ , nm	—	—	435	460	434	460
buffer	acetate	Tris	acetate	Tris	acetate	Tris
pH region	5.0–5.3	8.4–8.6	3.8–4.8	5.9–6.6	4.83	6.65
$c_{\text{SSC}}$ , mmol l <sup>-1</sup>	1	1	1	0.5	2.5	2.5
$w_{\text{SLS}}$ , %					0.05–0.2	0.05–0.2
usable region, $\mu\text{mol l}^{-1}$	up to 34	up to 40	up to 40	up to 40	up to 100	up to 100
limit of determination, ng ml <sup>-1</sup>	60	54	1.8	98	400	600

<sup>a</sup> Cell 2 cm.

peak positions and intensities. The optimum conditions for the fluorometric determination of Al and Zn are given in Table I. The emission intensity is practically unaffected by ionic strength varied over the range of 0–0.5 mol l<sup>-1</sup>, and decreases about 10% on increasing the temperature by 1°C within the region of 15–25°C. The regression coefficients in the calibration plot equations are  $Y_0 = 0.291$ ,  $\beta_1 = 5.37 \cdot 10^5$ ,  $\beta_2 = -5.096 \cdot 10^9$ ;  $s_{Y_0} = 0.0352$  for Al, and  $Y_0 = 1.24$ ,  $\beta_1 = 9.55 \cdot 10^4$ ,  $\beta_2 = -2 \cdot 10^8$ ;  $s_{Y_0} = 0.0192$  for Zn.

### *Fluorometric Determination of Aluminium and Zinc in the Presence of Copper(II) and Iron(III)*

The fluorescence of the aluminium and zinc complexes of SSC is suppressed by copper(II) and iron(III) ions. Attempts were therefore made to eliminate this effect by masking the interfering ions with fluoride or thiosulphate. When using the latter, the temperature must be held below 20°C, otherwise the masking agent decomposes at the pH applied and sulphur is observed to separate.

The fluorescence intensity of the complexes, however, decreases with increasing concentration of thiosulphate in the mixture, and neither copper nor iron can be masked in the determination of aluminium (Fe(II) gives a violet complex with SSC). Zinc can be determined in the presence of copper up to a concentration of the latter

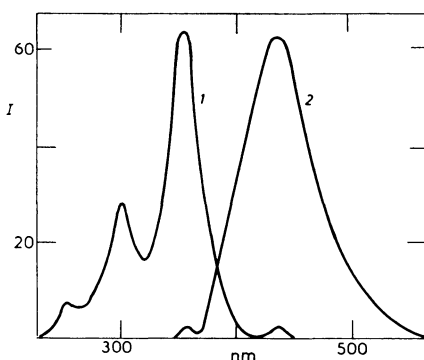


FIG. 3

Excitation and fluorescence spectra of aluminium complex of salicylaldehyde semicarbazone. 1 Excitation,  $\lambda_{em} = 435$  nm; 2 emission,  $\lambda_{exc} = 360$  nm.  $c_{Al} = 339 \mu\text{mol} \cdot \text{l}^{-1}$ ,  $c_{SSC} = 896 \mu\text{mol} \cdot \text{l}^{-1}$ , pH 4.6 (acetate buffer), cell 1 cm

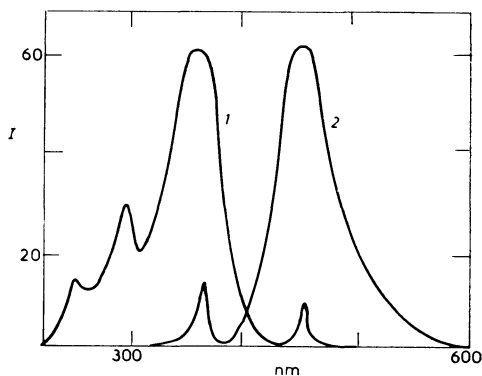


FIG. 4

Excitation and fluorescence spectra of zinc complex of salicylaldehyde semicarbazone. 1 Excitation,  $\lambda_{em} = 450$  nm. 2 emission,  $\lambda_{exc} = 356$  nm.  $c_{Zn} = 313 \mu\text{mol} \cdot \text{l}^{-1}$ ,  $c_{SSC} = 896 \mu\text{mol} \cdot \text{l}^{-1}$ , pH 4.6 (acetate buffer), cell 1 cm

of  $63 \mu\text{mol l}^{-1}$  using thiosulphate in a concentration of  $24 \text{ mmol l}^{-1}$  (a special calibration graph must be plotted).

Fluoride, up to a concentration of  $100 \text{ mmol l}^{-1}$ , does not affect appreciably the fluorescence of the zinc complex, and so with the help of this agent, zinc can be determined in the presence of aluminium and iron unless their concentrations exceed  $10 \mu\text{mol l}^{-1}$  (Al) and  $650 \mu\text{mol l}^{-1}$  (Fe).

#### *Extraction of the Complexes*

The aluminium and zinc complexes of SSC can only be extracted into ethyl acetate in the presence of the anionic tenside, sodium lauryl sulphate. This indicates that the complexes possess a positive charge to form ionic associates with the tenside. The optimum conditions for the extraction and the fluorescence intensity are given in Table I. In butyl acetate the fluorescence intensity is about 15 times lower than in ethyl acetate. The fluorescence intensity decreases with increasing ionic strength ( $\text{NaNO}_3$ ), probably owing to a competition of the nitrate ion with the tenside anion. A white precipitate appears in the presence of potassium ions. The reproducibility of the fluorescence intensity measurements on the extracts is poorer than on the aqueous-alcoholic solutions; the limit of determination of aluminium is about  $0.4 \mu\text{g ml}^{-1}$ .

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