SPECTROFLUOROMETRIC METHOD FOR THE DETERMINATION OF COBALT, COPPER AND CADMIUM

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Numerous compounds expressed by the following general equation can be produced by the condensation of aromatic aldehydes and dithiocarbazic acid esters [1—5]:

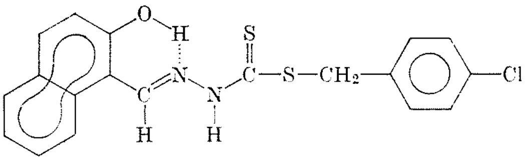
$$R\ R_1\ C = N—NH — CSSR_2$$

where R is an aromatic aldehyde.

Part of these compounds have luminescent characteristic and in the case when the aromatic aldehyde contains OH-group in ortho-position, they even have a complex forming characteristic. Thereby a possibility is given of using these compounds for the spectrofluorometric determination of the corresponding metal ions [6—8].

The fluorescent characteristic as well as the application for spectrofluorometric determination of Co, Cu, Cd ions of the reagent produced by the condensation of 2 hydroxy-1-naphtaldehyde and dithiocarbazic acid p-chlorobenzyl ester, were investigated.

The formula of the reagent (I) produced is as follows:



Reagent (I) was found to be solid, insoluble in water, slightly soluble in ethanol and well soluble in dimethylformamide (DMF).

Both in solid state in solution, the reagent fluoresces upon the effect of UV-rays.

Experimental

Apparatus

The spectrofluorometric investigations were carried out by means of a spectrofluorometer (Type HITACHI MPF-2A). The excitation and emission spectra reported here are without correction.

Stock solutions

Reagent solution: 50 mg of the reagent was solved in DMF and filled up to 100 ml in a flask.

Metal salt solutions: The Cd^{2+}, Co^{2+}, Cu^{2+} solution of 1 mg metal ion/ml concentration were produced from their appropriate sulphate salts by solving them in twice distilled water. The other metal salts were produced similarly.

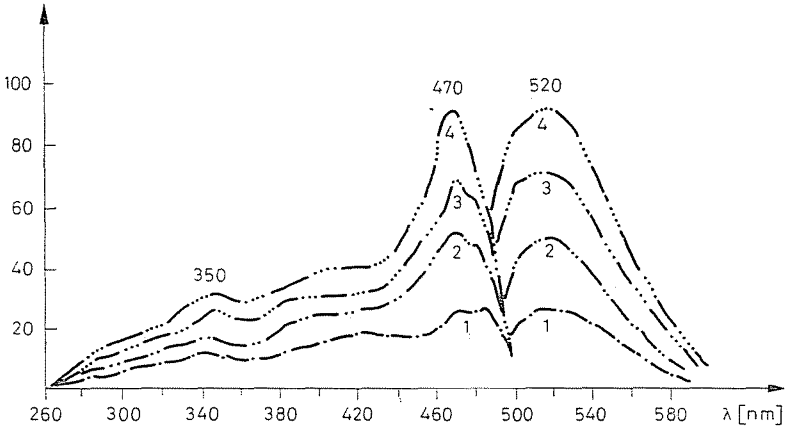


Fig. 1. Excitation and emission spectra of the reagent in different mixtures of DMF and water 1 DMF : H_2O = 90 : 10; 2 DMF : H_2O = 75 : 25; 3 DMF : H_2O = 60 : 40; 4 DMF : H_2O = = 50 : 50

Results and discussion

The intensity of fluorescence is considerably increasing when using the mixture of DMF and water as solving material. In this case the intensity of the fluorescent light is also increasing by increasing the water dosage, while in fact the spectral composition does not change. Fig. 1 shows the excitation and emission spectra recorded in DMF-water mixture of different concentrations. The additional increasing of the water amount in the DMF-water mixture is limited by the solubility of the reagent. According to our measurements the optimal mixture ratio was found to be 1 : 1, a concentration where the light intensity is sufficiently high and separation does not follow either.

By adding Co or Cu ions to the solution a non-lighting complex is forming. Consequently the concentration of the above mentioned ions can be determined by means of a calibration curve from the decrease of the light intensity.

Applying a Cd complex the case is quite different. This complex still has some fluorescence, however in a smaller degree than the stock solution, but the intensity maximum of the fluorescent light is shifted towards the shorter wave lengths. (Figs 2, 3).

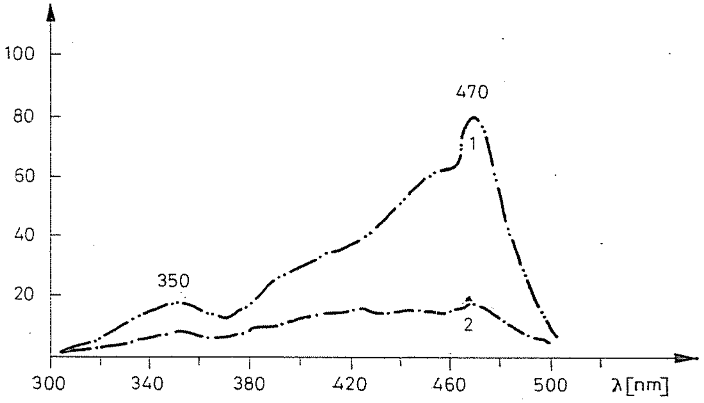


Fig. 2. The excitation spectrum of the reagent (1) and cadmium complex (2) in the 1 : 1 mixture of DMF — water

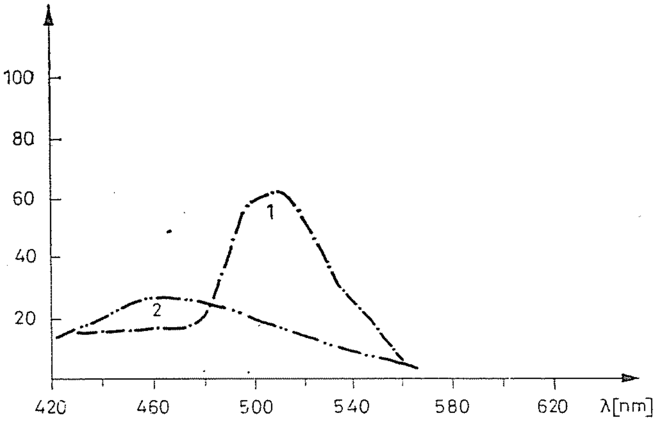


Fig. 3. The emission spectrum of the reagent (1) and cadmium complex (2) in the 1 : 1 mixture of DMF — water

Thereby the Cd ions can be determined too, if the excitation and emission wave lenghts are properly chosen.

The intensity of the fluorescent light is directly proportional to the concentration of the reagent in a concentration range about 2 to 12 μg/ml in the 1 : 1 mixture of DMF : H_2O. (Fig. 4). For our determinations the concentration of the reagent was chosen to be 10 μg/ml.

Calibration diagrams were recorded and the Cd, Co and Cu ions of unknown concentrations determined as follows.

An amount of 0,4 ml of the reagent stock solution and 9,6 ml of DMF were filled into a flask of 20 ml. Then the solution of 10 μg/ml concentration, prepared from the stock solution containing Cd, Co or Cu ions was added in an amount to cause the final metal ion concentration to be between 0,1 and

1,1 μg/ml. Afterwards the flask was filled up to the mark with twice distilled water. Before the measurement it is advisable to cool the solution to room temperature, since it is slighty heated upon being filled up with water.

Then the intensity of the fluorescent light was measured at an emission wave length 520 nm, for an excitation wave length 470 nm.

The calibration diagram is seen in Fig. 5.

A similar method was applied for determining Cd, Co, Cu ions of unknown concentration. The concentration can be read off the calibration diagram at the intensity value measured.

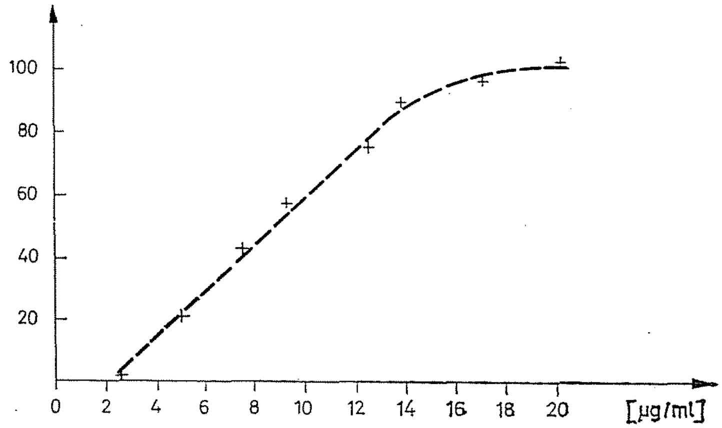


Fig. 4. Correlation between the intensity and concentration of the reagent in a 1 : 1 mixture of DMF and water. $\lambda_{\text{exc}} = 470$ nm; $\lambda E_m = 520$ nm

In Cu and Co determination on the basis of intensity — concentration data measured, the ratio between the reagent molecule and metal ion is 1 : 1. In the case of cadmium, however, the linearity subsits only to the ratio 2 : 1. This fact can be explained as follows. While the Cu- and Co-complexes have no fluorescent characteristics, i.e. these two metal-ions almost perfectly quenching for a mol ratio 1 : 1, the Cd-complex fluoresces though to a smaller degree, with band shifting (Fig. 3). Consequently the light intensity does not decrease to zero, but it is nearly parallel with the concentration axis from about 2 : 1 mol ratio (Fig. 5).

Stability of the fluorescent light

In the determination of the stability in time of the intensity, quinine hydrogen sulphate was used as reference substance. Accordingly the intensity of the fluorescent light is invariable for several hours, and even after 24 hours, the light intensity was found to slightly decrease.

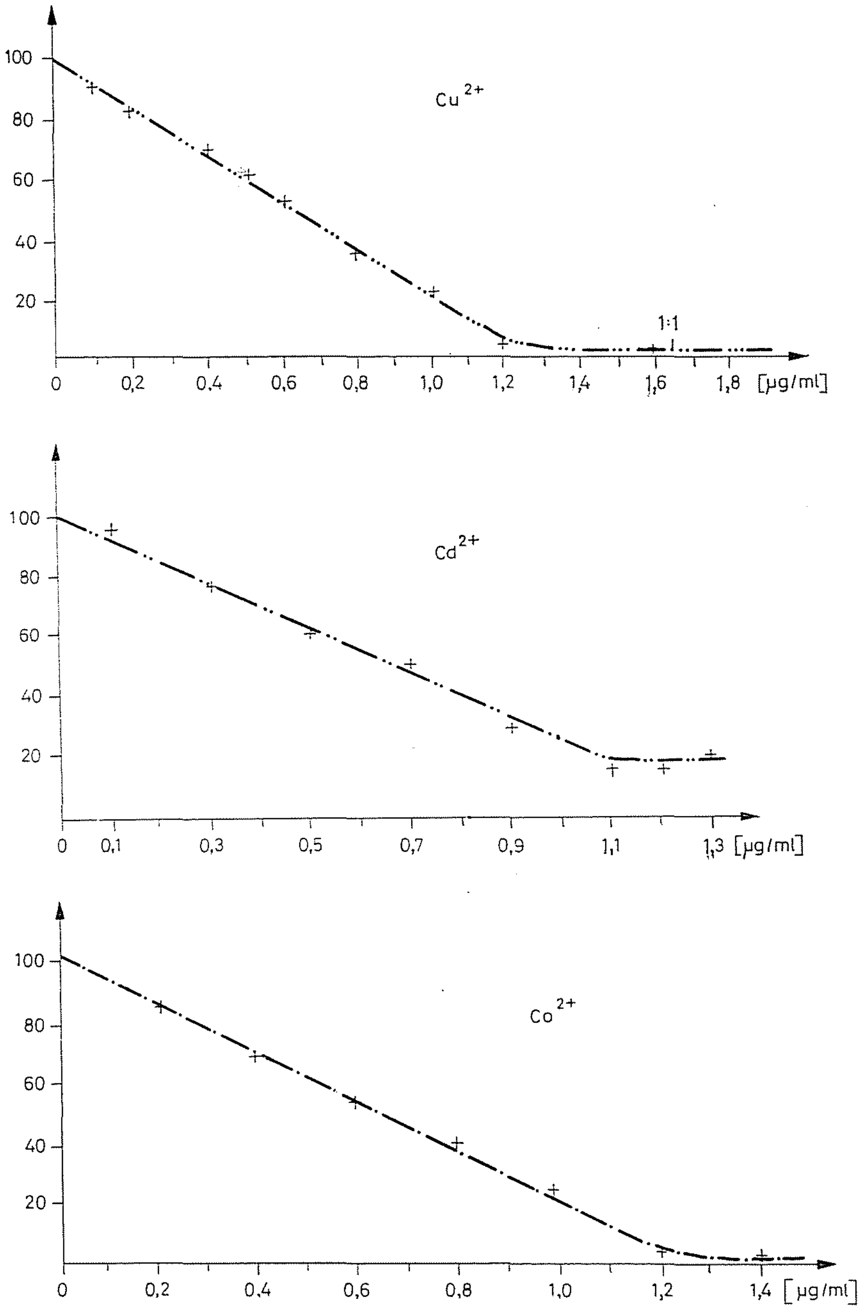


Fig. 5. Calibration curve for the quantitative determination of Cd-, Co-, Cu-ions. $\lambda_{\text{exc}} = 470$ nm; $\lambda E_m = 520$ nm

Disturbance by alien ions

Measurements showed the alkali-metals, alkali-earth metals and aluminium not to disturb the determination. This method is unsuitable if two of the three ions investigated are simultaneously present, neither on the presence of silver, zinc and nickel ions. The presence of mangane(II)-, chrom(III), iron(III)-ions is only disturbing over 0,7 μg/ml concentration.

Accuracy of the determination

The standard deviation from 10 co determinations was found to be $9{,}5 \cdot 10^{-3}$ μg, the standard deviation of the mean value was $\pm 3{,}2 \cdot 10^{-3}$ μg, for copper ions these values were $1{,}23 \cdot 10^{-2}$ μg and $\pm 4{,}1 \cdot 10^{-3}$ μg, resp., and for cadmium ions $2{,}02 \cdot 10^{-3}$ and $\pm 6{,}7 \cdot 10^{-3}$ μg, resp.

Summary

The condensed reagent of 2-hydroxy-1-naphtaldehyde and dithiocarbazic acid p-chlorobenzyl ester solved in a 1 : 1 mixture of dimethylformamide and water emits an intensive light upon the effect of ultraviolet light. The solution shows a most intensive fluorescence for an excitation wave length of 470 nm, at an emission wave length of 520 nm. In the presence of copper(II)-, cobalt(II)-, and cadmium(II)-ions a complex is forming and the intensity of the fluorescent light emitted is decreasing proportionally to the metal-ion concentration.

On this basis method has been elaborated for the spectrofluorometric determination of the above mentioned ions in the 0,1 to 1,1 ppm concentration range.

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