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The Analysis of Activators in Several Phosphors

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The activators in the zinc sulfide phosphors were analyzed by colorimetry. The reagents were *p*-dimethylaminobenzylidene-rhodanine for the determination of silver in zinc sulfide and sodium dithiocarbamate, and zinc dibenzyldithiocarbamate for copper. The analytical procedures were discussed, and the range of the activator content to which these procedures are applicable was clarified. The methods were then used to determine the activator contents in the phosphors in the form of powder and single crystals; the results obtained make it clear that the activators are dissipated during the firing process in the preparation of phosphors and that copper is incorporated during the single-crystal preparation.

It is well known that the quantity of activators in the phosphors is one of the most important factors in determining their characteristics. The quantity of activators has been analyzed by several researchers, while, because of a variety of combinations between the host lattice materials and activators, it is necessary to extend the analytical method to all phosphors. We have reported on the application of polarography to the analysis of activators in calcium silicate phosphors,[1] and Rathje[2] has published a paper on the analysis of silver in zinc sulfide phosphors by flame-photometry.

The aim of the present research is to establish the methods of analyzing silver and copper in zinc sulfide phosphors. The method consists of the preparation of a sample solution and the determination of activators by colorimetry; the results obtained make it clear that the activators are dissipated during the firing process in the preparation of phosphor and that copper is incorporated during the single-crystal preparation.

The Analysis of Silver in the Zinc Sulfide Phosphors Activated by Silver by Colorimetry.—*a) Principle.*—It is well known that the colorimetric analysis of silver is carried out by using dithizone or rhodanine derivatives. The absorption curve of silver rhodanine has a peak at ca. 470 mμ, as is shown in Fig. 1; the figure was obtained by using an interference filter and a photocell. This absorption is affected by the presence of oxidizing agent, including chloride ions, therefore, the agents should be completely removed from the sample solution.

b) Experimental.—Reagents and Materials: All reagents were of the reagent grade. Zinc sulfide phosphors were prepared by the usual procedure in our laboratory. The amounts of silver added to zinc sulfide before firing ranged from 10^{-3} to 10^{-5} mole per mole of zinc sulfide. *p*-Dimethylaminobenzylidene-rhodanine was dissolved in methanol.

Apparatus: Tokyo Koden Co.'s Photoelectric Colorimeter 7A.

Sample Preparation: Weigh 0.5—1.0 g. of the sample of phosphor, add ca. 10 ml. of a concentrated hydrogen peroxide solution and heat in a evaporating dish with watch-glass cover until the mixture has completely dried. Repeat the evaporation after adding ca. 5 ml. of concentrated nitric acid, then dissolve the residue with ca. 1 ml. of concentrated nitric acid. After cooling, add water to make the whole volume to 100 ml. Take 10 ml. of this solution out with a pipette, add 0.2 ml. of a 0.05% rhodanine solution, and agitate carefully. After 10 min., measure the absorption at 470 mμ by means of an interference filter.

Standard Preparation: The standards used to obtain the analytical absorption curve were made by dissolving in 0.1 N nitric acid various amounts of silver nitrate crystals dried previously at 110°C. Standards in the range from 0.1 to 4 p. p. m. of silver in 0.1 N nitric acid were prepared and treated in the same manner as the samples.

Absorption Curve: The absorption curve was obtained for the solution which contains 1 p. p. m. of silver and 0.2 ml. of *p*-dimethylaminobenzylidene-rhodanine in 10 ml. by means of interference filter, and is shown in Fig. 1. From the figure it is convenient to use the interference filter at 470mμ.

Color Stability: The stability of the colored solution is shown in Fig. 2, which shows that the analysis is most accurately carried out when the solution is held constant for 5 min., after the addition of rhodanine and for not longer than 15 min. When the colored solution is held for one day, there is a colored precipitate.

The Effect of the Silver Concentration on the Absorbance: The absorbance of the colored solution was obtained

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[1] Y. Kotera, M. Yonemura and T. Sekine, This Bulletin, **28**, 132 (1955).

[2] A. O. Rathje, *Anal. Chem.*, **27**, 1583 (1955).

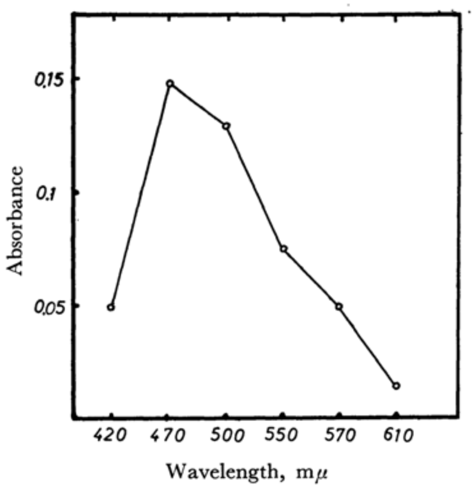

Fig. 1. Absorption curve of Ag-rhodanine.

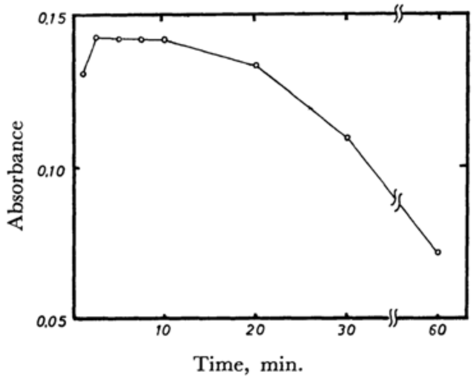

Fig. 2. Effects of standing time on the absorbance.

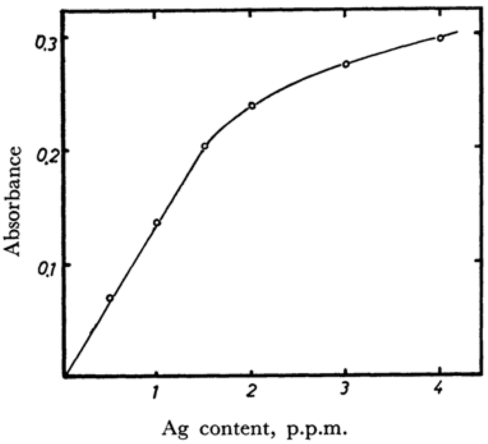

Fig. 3. Effects of silver concentrations on the absorbance.

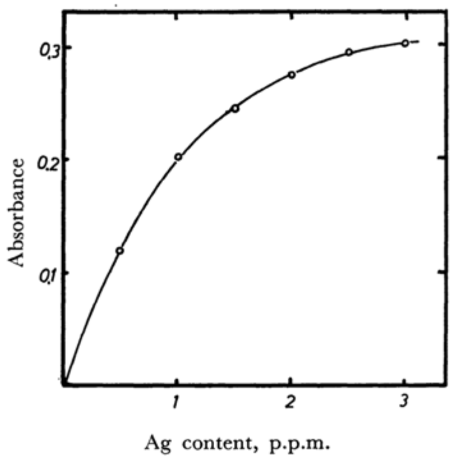

Fig. 4. Calibration curve.
Wavelength 470 mμ

in the 0.1 to 4 p.p.m. range of silver; it is shown in Fig. 3. From the figure it is possible to determine silver in the range from 0.1 to 1 p. p. m.

The Effect of the Presence of Zinc Sulfate on the Absorbance: When a sample of phosphor is treated as described above, the solution contains a certain amount of zinc sulfate prepared by the hydrogen peroxide oxidation of sulfide. It is, therefore, necessary to test the effect of zinc sulfate upon the absorbance. Various amounts of silver were added to the precipitated zinc sulfide; after they had been dried at 110°C, these samples were treated as had been the sample phosphors. The absorbance of the colored solution is shown in Fig. 4 as the function of the amount of silver. A comparison of Fig. 4 with Fig. 3 will show the effect of zinc sulfate; the colored solution was more stable in this case than without sulfate. The determination of the silver amount in sample phosphors was carried out by the use of the curve in Fig. 4.

c) Results and Discussion.—Zinc sulfide phosphors, which had been prepared by adding various amounts of silver before firing and by subsequent firing at 110°C for 2 hr., were analyzed; the results are shown in Table I. The same samples were washed after firing either by distilled water or by a potassium cyanide solution (5%), and the results for both samples were tabulated. As expected, a part of the silver dissipates during firing, while a part of the residual silver does not diffuse in the crystal lattice of zinc sulfide phosphors, but changes to silver sulfide, adhering on their crystal surface; the amount is estimated to be the difference in the results for the two washing agents. As for the analytical procedure, it was difficult to dissolve zinc sulfide phosphors without separating sulfur or its compound. This difficulty was overcome by the use of an oxidizing agent, for example, hydrogen peroxide, in our procedure; the residual oxidizing agent should be removed completely before the addition of rhodanine.

The Analysis of Copper in the Zinc Sulfide Phosphors Activated by Copper by Sodium Dithiocarbamate. — *a) Principle.* — The

TABLE I. ANALYTICAL RESULTS OF SILVER IN SILVER-ACTIVATED ZINC SULFIDE PHOSPHORS

Sample Amount of silver added to zinc sulfide before firing (g. a./mol.)	Silver content determined, wt.% treatment after firing	
	H_2O	KCN soln.
10^{-3}	0.058	0.030
6×10^{-4}	0.033	0.019
3×10^{-4}	0.014	0.016
10^{-4}	0.0051	0.0091
6×10^{-5}	0.0007	0.0017
3×10^{-5}	0.0019	—
10^{-5}	0	0

analysis of a trace of copper has been widely carried out colorimetrically. Dithiocarbamate compounds, dithizone, 1-10 phenanthroline derivatives, cuprizon, etc. are commonly used as the coloring agents. Dithiocarbamate compounds were selected for this research.

b) Experimental.—Reagents and Materials: $CuSO_4 \cdot 5H_2O$ was used; it had been prepared in the Osaka Industrial Research Institute for analytical use. The other reagents were of the reagent grade. The zinc sulfide precipitated was given by the Dai Nippon Toryo Co., while the zinc sulfide phosphors and their single crystals were prepared in our laboratory.

Apparatus: This was the same as in the case of silver determination.

Sample Preparation: Weigh ca. 0.1 g. of a sample of phosphor, and then dissolve it in concentrated hydrochloric acid. Add to this solution 10 ml. of a 10% EDTA-2Na aq. solution, 2 drops of a 0.1% Crezol Red solution, and 5 ml. of a 1 N ammonium citrate solution; then add concentrated aqueous ammonia until the color of the indicator changes. Make the total volume to 50 ml. and transfer to a separating funnel. Add 5 ml. of a 0.1% sodium diethyldithiocarbamate solution and 10 ml. of chloroform, and agitate vigorously for ca. 2 min. Take out the colored layer of chloroform in a 25-ml. measuring flask, add 10 ml. of chloroform to the residual aqueous part, and agitate for 1 min. Take out the chloroform layer in the same measuring flask, and make the total volume to 25 ml. by adding ca. 5 ml. of chloroform. Transfer the solution into the colorimeter cell and measure the absorbance by means of a 420 mμ filter.

Standard Preparation: Dissolve the precipitated zinc sulfide in hydrochloric acid, add the standard solution of copper to this solution, treat it in the manner described above, and obtain the relationship between the amount of copper and the absorbance. The results obtained, shown in Fig. 5, indicate that the determination of copper between 0.5 and 1 p. p. m. is possible by this procedure.

c) Results and Discussion.—Single crystals of zinc sulfide prepared by the vapor-transport method were analyzed. The results, shown in Table II, show that copper is easily introduced during the single crystals preparation; work is now in progress in our laboratory attempting to reduce the copper content in the single crystals. Hydrogen chloride, bromine, and iodine are used in the vapor-transport method; they are tabulated in Table II. The difference in copper content among the three samples might be explained by the volatility difference in the materials used in the crystal preparation.

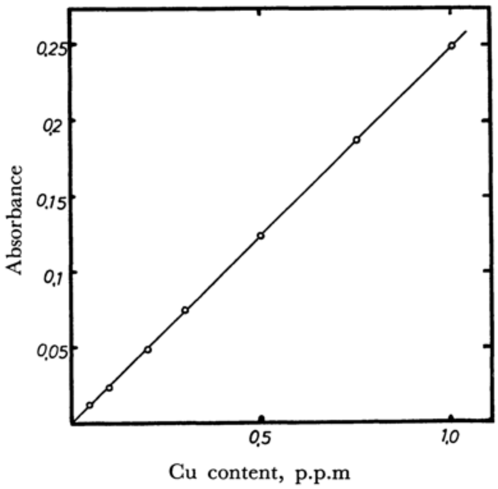

Fig. 5. Calibration curve (relation between the amount of copper and the absorbance).

TABLE II. ANALYTICAL RESULTS OF IMPURITY COPPER IN ZINC SULFIDE SINGLE CRYSTALS PREPARED BY THE VAPOR-TRANSPORT METHOD

Sample	Copper content determined wt.%
ZnS-HCl	0.017
$ZnS-Br_2$	0.007
$ZnS-I_2$	0.011

The Analysis of Copper by Zinc Dibenzyldithiocarbamate.—*a) Experimental.—Sample Preparation:* Weigh 0.5 to 1.0 g. of a sample of phosphor, and dissolve it in concentrated hydrochloric acid. After boiling this solution to remove the hydrogen sulfide, add concentrated hydrochloric acid or distilled water to make the whole volume to 100 ml. of a 1 N hydrochloric acid solution, and then transfer it into a separating funnel. Add to this exactly 10 ml. of a 0.01% zinc dibenzyldithiocarbamate solution in carbon tetrachloride, and agitate the mixture vigorously for ca. 1 min. Transfer the yellow-colored layer of carbon tetrachloride into the colorimeter cell, and measure the absorbance at 420 mμ.

The standard preparation and the other procedures are almost the same as in the case of sodium dithiocarbamate. The relation between the

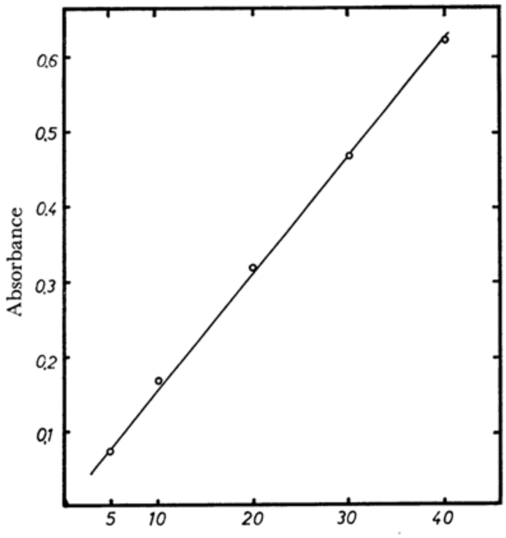

Fig. 6. Calibration curve (relation between the amount of copper and the absorbance).

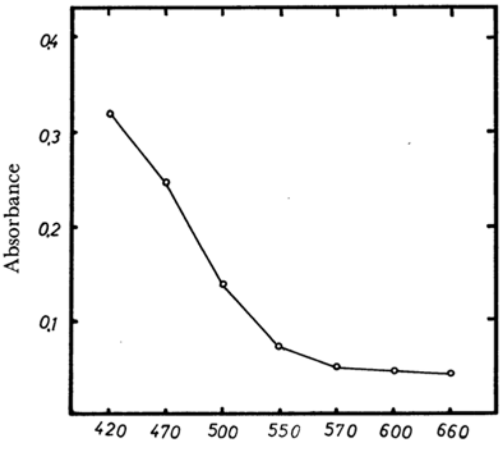

Fig. 7. Absorption curve of Cu-dithiocarbamate.

amount of copper and the absorbance, shown in Fig. 6, indicates the possibility of determining copper in the range from 5 to 40 p. p. m.

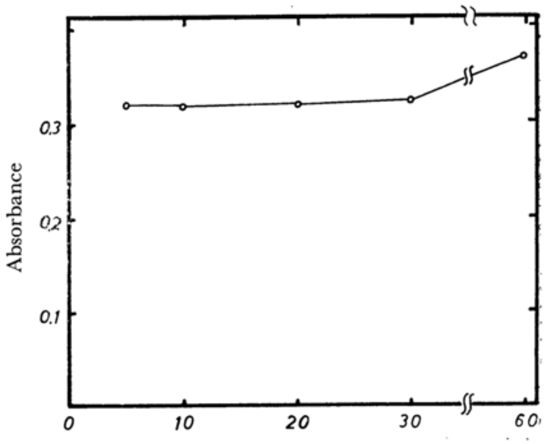

Fig. 8. Effects of standing time on the absorbance.

The absorption curve of the copper dithiocarbamate solution measured as a function of the wavelength is shown in Fig. 7, while the stability of the colored solution is shown in Fig. 8.

c) Results and Discussion.—Zinc sulfide phosphors activated by copper were prepared, and the copper content was determined by the procedure described above. The results obtained, shown in Table III, indicate that copper does not dissipate so much in the case of zinc sulfide phosphors, whose copper content is low, as does silver in zinc sulfide.

TABLE III. ANALYTICAL RESULTS OF COPPER IN COPPER ACTIVATED ZINC SULFIDE PHOSPHORS

Sample Amount of copper added to zinc sulfide before firing, g. a/mol.	Copper content determined, wt.%
10^{-4}	0.0067
10^{-5}	0.00077

It may be concluded that the analysis of copper in zinc sulfide phosphors is accurately carried out by the use of sodium diethylthiocarbamate for copper contents ranging from 0.5 to 1 p. p. m. and by the use of zinc dibenzyldithiocarbamate in the range from 5 to 40 p. p. m.

We thank Dai-Nippon-Toryo Co. for offering precipitated zinc sulfide.