Spectrochemical Study of Microscopic Crystals. I.
Application of Microscopes in Spectrography.

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For the purpose of studying absorption spectra of insoluble substances it is necessary to deal with them in solid state. As for soluble substances solid spectroscopy is also important from the viewpoint of avoiding solvent effects, specially for unstable compounds which would undergo change on dissolution. In most cases, however, fine transparent crystals which would yield sections large enough to be subjected to ordinary spectrophotometry are rarely obtained, and moreover, it is extremely difficult to prepare by polishing such crystals thin plane-parallel sections which have desired angular relations with crystal axes. Application of substances in powdery form which has been one of the most popular practices in solid spectroscopy is more favourable in procuring experimental materials, but it defies quantitative determination of absorption and even qualitative observation in the ultra-violet regions, because of the undesirable effect of light scattering. The authors could overcome these difficulties by simply making use of microscopes. In this new method microscopic crystals which are readily obtained in pure state may be directly used for spectrographic measurements. Extensive application of this method is expected in studying various pigments, lake colours and other insoluble substances as well as unstable compounds which would decompose on dissolution or in solutions. Pleochroism of microscopic crystals may also be measured by making use of a polarizing microscope. Especially pleochroism in the ultra-violet regions which can be investigated by means of a quartz optical system is expected to be of considerable importance in stereochemistry as well as in spectrochemistry. Further this method may find its application in micro-identification as has been proposed by I. Okada⁽¹⁾ whose chief purpose was to introduce into chemical researches petrographical methods of microscopic determination of refractive indices.

In the present paper is shown an example of this method. *cis*-Dichloro-tetrammine-cobaltic chloride readily undergoes aquotization in aqueous solution, as can be easily expected from the spectrochemical

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(1) I. Okada, *J. Chem. Soc. Japan*, **47** (1926), 720.

series⁽²⁾ in which the ligand Cl^- is far more bathochromic than H_2O. The absorption spectra of this unstable compound have been determined by means of a usual polarizing microscope.

Experimental. *cis*-Dichloro-tetrammine-cobaltic chloride was prepared by the method of R. Weinland.⁽³⁾ Microscopic observation revealed that the salt thus obtained consists of rhombic prismatic crystals as shown in Fig. 1. The crystal shows straight extinction. Most crystals lie on their prismatic plane (110). Dichroism on the prismatic plane is violet and brownish red: when the crystal is oriented with its length parallel to the vibration direction of white rays it appears violet, whereas it is red when the vibrations are perpendicular to the c-axis. In other words one of the axial colours is violet and the resultant in the prismatic plane of the other two axial colours is brownish red.

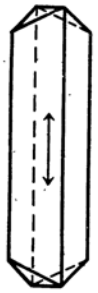
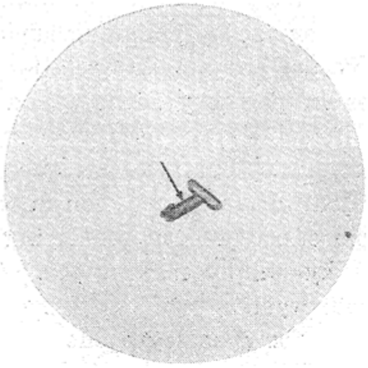


Fig. 1.



×165 $d = 0.0042$ cm.

Fig. 2.

The spectrographic experiments were carried out as follows. The most suitable crystal on a slide glass was chosen in the microscopic field. The crystal used for the measurements is shown by an arrow in the microphotograph in Fig. 2. The polarizing microscope was introduced between a light source of 200 watt incandescent lamp and a glass spectrograph. The position of the crystal was so adjusted that its image focused on the slit of the spectrograph is oriented with its c-axis parallel to the slit. The nicol was set also parallel to the c-axis. The spectrum was photographed, the time of exposure being t seconds. Next the crystal was

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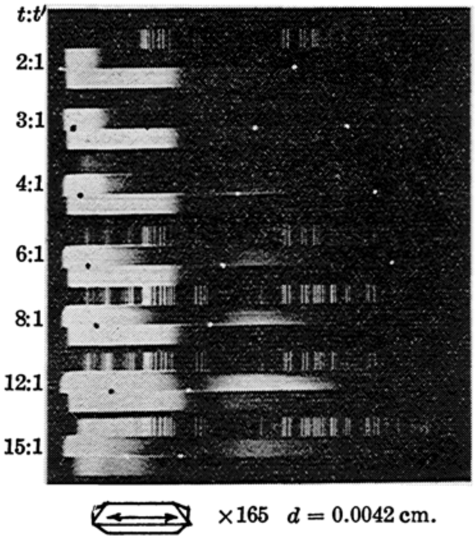
(2) R. Tsuchida, this Bulletin, **13** (1938), 445.

(3) Compare the manual by S. Shinoda and K. Harai on quantitative analysis and preparation of metallic complex salts, p. 151, Tokyo (1933).

slipped aside by a micrometer-screw on the microscope stage, so that the light traversed all the optical system except the crystal. The spectrum was taken, the exposure being t' seconds. The extinction coefficient ε in $I=I_0\times10^{-\varepsilon d}$ (d in cm.) for the wave-length at which the two spectra have equal opacity can be calculated by the following relation:

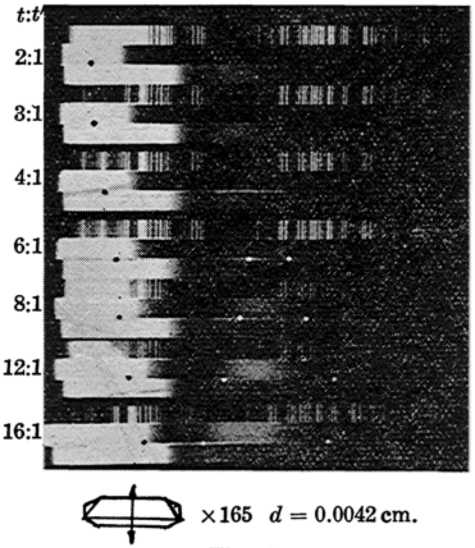
$$\varepsilon = \frac{0.9}{d} \log \frac{t}{t'} .$$

The thickness of the crystal was measured microscopically and for the purpose of finding wave-lengths, a spectrum of an iron arc was photographed side by side with the spectrum of the crystal. Extinction coefficients for various wave-lengths were measured by repeating the procedure for various combinations of t and t'. The absorption spectra thus obtained are shown in Fig. 3.



×165 $d = 0.0042$ cm.

Fig. 3.



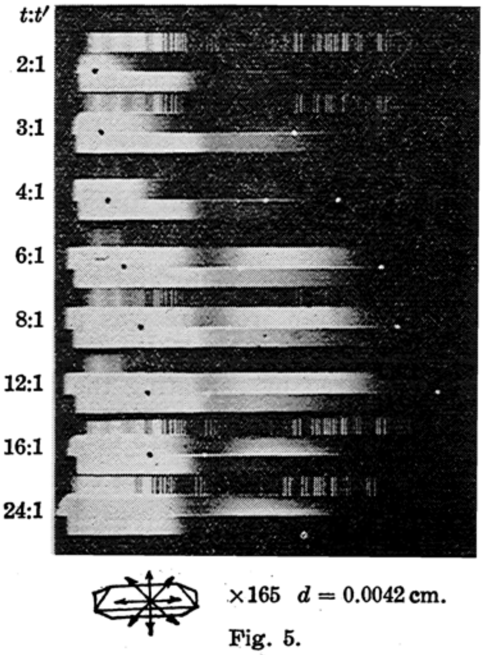
×165 $d = 0.0042$ cm.

Fig. 4.

Next the nicol was set perpendicular to the c-axis, while the crystal was kept in the same position parallel to the slit. The spectra was photographed just as in the former case. The set of the spectra are shown in Fig. 4.

Finally the nicol was removed and the procedure was repeated as in the former two cases. The spectra are shown in Fig. 5.

As is evident from the procedure, the size of the crystal sufficient for the measurements can be so small that its magnified image just covers the slit of the spectrograph.



×165 $d = 0.0042$ cm.

Fig. 5.

The absorption curves of the complex salt are given in Fig. 6, in which I shows the absorption giving rise to the facial colour on the prismatic plane (110) and II gives the absorption corresponding to the axial colour in the c-axis. The curve III is the resultant absorption in the plane containing the other two crystal axes. The facial extinction coefficients may be calculated as the mean values of those in the curves II and III. The maximal facial extinction coefficient thus calculated is $\log^{-1} 2.48$ at 57.3×10^{13} sec.$^{-1}$ and coincides with the maximum of the curve I. The axial colours of the crystal axes, a and b, have not been determined. Nevertheless the additive nature(4) of the first bands of complex compounds has been confirmed.

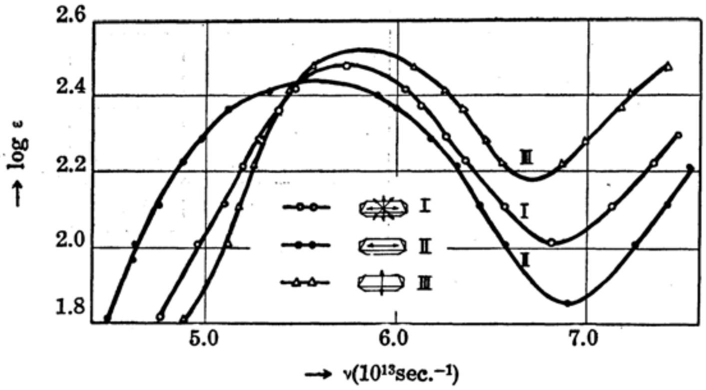


Fig. 6.

Summary.

A new method of measuring absorption spectra of microscopic crystals has been introduced. Application of a polarizing microscope

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(4) R. Tsuchida, this Bulletin, **13** (1938), 396.

renders it possible to measure pleochroism of microcrystalline substances. An example is shown of *cis*-dichloro-tetrammine-cobaltic chloride.

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