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since the publication of the dry ash method (1,2). For several years the results of each batch have been controlled by the simultaneous determination of standard control sera. This continuous experience has enable an adequate comparison of modifications resulting in the one-day method. The typical results presented in Table I point out the similar values obtained by both methods using control sera with different PBI levels and patients sera. The recovery experiments in Table II were designed to check every procedure in the method that would retain added inorganic iodide. It can be seen from these experiments that iodine was not lost in the more rapid drying process at 106° C.

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## Sulfonation of Bathophenanthroline and Bathocuproine

RICHARD L. CRYBERG AND HARVEY DIEHL<sup>1</sup>

4,7-Diphenyl-1, 10-phenanthroline, introduced in 1952 as a spectrophotometric reagent for iron by Smith, McCurdy and Diehl (1), has proved useful and popular; some twenty papers (2) have now appeared detailing its application to the determination of iron in sea water, wine, serum, urine, various metals, and other materials. This reagent was given the common name Bathophenanthroline. The great sensitivity of the reagent is made peculiarly useful by virtue of the solubility of its red, ferrous derivative in isoamyl alcohol, for extraction of the red compound from water into the immiscible solvent provides a concentration method making possible the determination of iron in concentrations as low as 0.002 parts per million, and even more important, provides a method of removing the iron contaminants from the various reagents used in the analysis.

The one disadvantage bathophenanthroline suffers is the occasional appearance of a turbidity when the analysis is performed entirely in the aqueous solution, especially when perchlorate is present. The English chemist Trinder (3) solved this problem by sulfonating bathophenanthroline by treatment with chlorosulfonic acid, the sulfonated product being completely water soluble, even in the presence of perchlorate. Later Blair and Diehl (4) isolated and characterized the sulfonated

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product showing it to be a disulfonic acid. The material was isolated as the disodium salt and the spectrophotometric properties of the ferrous derivative were shown to be only slightly different from that of the unsulfonated material. Adoption of this sulfonated reagent, particularly by clinical chemists, has created a demand for the material and efforts to prepare it in fair quantity have revealed certain shortcomings in the synthesis methods of Trinder and of Blair and Diehl. The merest traces of iron in the water, chemicals, glassware, and even the air of the laboratory, are collected during the synthesis and are concentrated in the final disodium salt, rendering it pink. Also, the quality of the product is erratic, the equivalent weight occasionally being far from the theoretical, sometimes higher and sometimes lower.

From repetitions of the Blair and Diehl synthesis we concluded that the difficulties arise in part from the use of chlorosulfonic acid and the necessity of subsequently removing hydrochloric acid by evaporation. It is quite possible that sulfones are formed during these operations. Hot, fuming sulfuric acid proved an adequate sulfonating agent and the subsequent steps using it proved simpler. By adopting high standards of cleanliness and by testing the alkalines used for iron with phenyl-2-pyridyl ketoxime, it became possible to obtain uniformly a product light tan in color and free of iron.

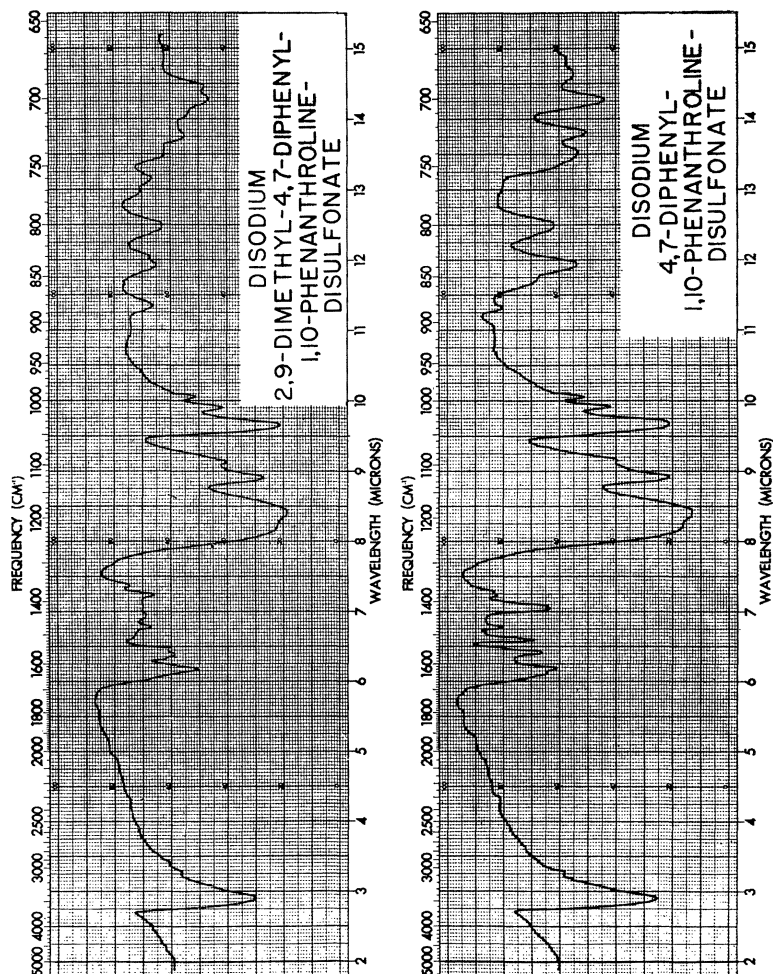
The identical procedure can be applied to the sulfonation of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine), a highly sensitive reagent for copper (5, 6, 4).

Procedure for the Sulfonation of Bathophenanthroline or Bathocuproine. Clean all glassware used in the following work by rinsing it with 20 per cent fuming sulfuric acid containing 0.1 g. of bathophenanthroline (or bathocuproine), then rinsing twice with 20 per cent fuming sulfuric acid, then rinsing with deionized water, and finally draining dry.

Check the ammonium hydroxide and sodium hydroxide to be used by dissolving a sample in deionized water and adding a little phenyl-2-pyridyl ketoxime and a crystal of hydroxylammonium chloride; if no red color is detected, the materials are pure enough to use directly..

Purify the ion exchange resin to be used, Amberlite IR-120, by washing it with concentrated hydrochloric acid to remove iron and following with deionized water until the eluate is free of chloride.

To 150 ml. of reagent grade, 20 per cent fuming sulfuric acid in 1-liter, round bottom flask equipped with a still head and a dropping funnel, add 15 g. of bathophenanthroline. Heat the mixture on a steam bath with occasional shaking. After 15



minutes all the solid will have dissolved and the solution will be deep brown in color. After two hours, cool the solution in an ice bath and slowly add concentrated, reagent-grade ammonium hydroxide, keeping the solution below  $70^{\circ}$  until the solution is basic, pH above 7 as indicated by placing a drop of the mixture on indicator paper. A considerable amount of brown viscous material separates during the neutralization. Heat this alkaline mixture on a steam bath to remove most of the excess ammonia. Then replace the dropping funnel with a capillary bubbler tube and distill the water away under vacuum using a steam bath for heat. Without attempting to remove the salt from the flask extract the residue five times with 250-ml. portions of boiling 95 per cent ethanol which dissolves the ammonium salt of the

bathophenanthroline disulfonic acid. Filter the combined ethanol extracts through a coarse, fritted glass funnel. Pass the solution through a 3.5 x 40 cm.-column of cation exchange resin, IR-120, in the hydrogen form. Evaporate away the ethanol on a steam bath and take up the residue in 25 ml. of water. Neutralize the resulting solution with an approximately 1 N solution of iron-free, reagent grade sodium hydroxide, bringing the pH to 8.5, as measured with a pH meter. Evaporate this solution to dryness on a steam bath. Grind the residue in a mortar.

For bathophenanthroline: yield: 23.5 g, 97.5 per cent; equivalent weight found 268, 273, calculated for  $C_{24}H_{14}N_2(SO_3Na)_2$  268.2 (one-half the molecular weight). For bathocuproine: yield: 23 g., 97.5 per cent; equivalent weight found 278, 280, calculated for  $C_{26}H_{18}N_2(SO_3Na)_2$  282.2.

The infrared spectra of the sulfonated materials, are shown in the accompanying figures. The bands expected for the sulfonic groups (7) are present at  $9.65\mu$  and at  $8.40\mu$ . The spectra of the unsulfonated materials is found in the work of R. C. Smith (8).

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## Application of Guggenheim's Short Formula to the Calculation of Dipole Moments<sup>1</sup>

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*Abstract.* By substituting the actual physical constants of benzene into Guggenheim's short formula for orientation polarization, a simple relation for the dipole moment was obtained. The accuracy of this equation was tested with empirical data of some one hundred dipole moment measurements and the relation was found to agree within 0.02 debyes with calculations made using the Kumler-Halverstadt equations.

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