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PREPARATION OF AMMONIUM AURINTRICARBOXYLATE

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ABSTRACT

A procedure is described for the preparation of an ammonium salt of aurintricarboxylic acid which is satisfactory for use in the colorimetric determination of aluminum. The development of this procedure was necessary because a sensitive reagent could neither be prepared by existing methods nor purchased in the market.

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I. INTRODUCTION

Thirteen years ago Hammett and Sattery¹ observed that the bright-red lake formed by aluminum salts and aurintricarboxylic acid is stable in an ammoniacal solution buffered with ammonium acetate, and that under these conditions the lake can be used as a test for aluminum. Upon this observation Lundell and Knowles² developed a quantitative method for the detection and determination of small amounts of aluminum in certain nonferrous materials. More recently Scherrer and Mogerman³ utilized the reaction and applied the method to the determination of small amounts of aluminum in a variety of nonferrous materials.

The last-named authors found that a satisfactory reagent must show a definite pink color with 0.02 mg of aluminum in a volume of 50 ml, and only a slight straw color if aluminum is absent.

The reagent used by Lundell and Knowles, purchased in the market, happened to be satisfactory. When this lot was exhausted no product of similar quality could be obtained. Some of the preparations from more recent commercial sources were found to yield solutions which were unstable whereas others produced "muddy" precipitates. All of them were too deeply colored, in the absence of aluminum, to be satisfactory.

The preparation of the reagent, therefore, became necessary. A description of the method is given in this paper.

¹ J. Am. Chem. Soc. **47**, 142 (1925).

² Ind. Eng. Chem. **18**, 60 (1926).

³ J. Research NBS **21**, 105 (1938) RP1117.

II. EXISTING PROCEDURES FOR PREPARING THE DYE

The dye was first mentioned in 1889 in a German patent ⁴ based on work by K. Sandmeyer. Directions were given for its preparation by the reaction of salicylic acid with formaldehyde in a mixture of concentrated sulfuric acid and sodium nitrite.

N. Caro ⁵ prepared aurintricarboxylic acid indirectly from 5, 5'-methylenedisalicylic acid, made by condensing formaldehyde and salicylic acid. To a mixture of 13 parts of concentrated sulfuric acid and 1 part of sodium nitrite was added a mixture of 2 parts of 5, 5'-methylenedisalicylic acid and 1 part of salicylic acid. The products of this reaction were poured into cold water, and the insoluble portion was removed by filtration. After repeated digestion and washing with hot water, the residue was dissolved in alkali and precipitated by hydrochloric acid. The product was then purified by a method which F. Zulkowsky ⁶ recommended for the removal of resins in the purification of aurin.

G. B. Heisig and W. M. Lauer ⁷ prepared the dye according to one of the methods described in the Geigy patent. To a quantity of sulfuric acid, cooled in an ice bath, sodium nitrite was added, with vigorous stirring, in small portions in order to suppress the evolution of oxides of nitrogen. Salicylic acid was then added slowly in small portions, and the mixture stirred at 20° C until all solid material was dissolved. The mixture was then surrounded by an ice-salt bath, and when the temperature reached 0° C formaldehyde was slowly added, with vigorous stirring, at such a rate that the temperature did not rise above 5° C. The reaction was said to be complete a few minutes after all the formaldehyde was added.

Apparently no explanation has been suggested for the reactions which occur when aurintricarboxylic acid is formed. Possibly a nitroso compound of salicylic acid is produced first, which, in its tautomeric form of a quinoneoxime, unites with 5,5'-methylenedisalicylic acid. The =C=NOH (oxime) group is assumed to couple at the methylene linkage, and in so doing parts with nitrogen, hydrogen, and water in the proportions which are present in hydroxylamine.

Attempts to prepare the dye by the methods of Sandmeyer, Caro, and Heisig and Lauer yielded products unsatisfactory for use in the colorimetric determination of aluminum. The dyes were not very sensitive and "blank" determinations always showed a deep-yellow or orange color. It was observed that the reaction is not completed immediately after the addition of formaldehyde, and that more time than was usually allowed is necessary to form a dye of suitable characteristics. Further experimental work led to other refinements necessary to obtain a satisfactory product. The procedure, given in the following section, is based on that of Sandmeyer, but certain changes have been introduced with respect to temperature, time of reaction, and washing treatment.

⁴ D. R. P. 49970, issued to Joh. Rud. Geigy and Co.

⁵ Ber. deutsch. chem. Ges. 25, 941 (1892).

⁶ Am. Chem. Pharm. 202, 200 (1880).

⁷ Organic Syntheses 9, 8 (1929).

III. RECOMMENDED PROCEDURE

The following procedure was found to produce ammonium aurintricarboxylate suitable for use in the determination of small amounts of aluminum.

Add 4 g of sodium nitrite, in small portions and while vigorously stirring, to 44 ml of sulfuric acid (sp gr 1.84) contained in a 250-ml beaker. The nitrite should be added slowly to prevent excessive evolution of oxides of nitrogen. When all of the nitrite is dissolved, cool the solution to 10° C. Over a period of 5 to 10 minutes, next add 12 g of salicylic acid, while again stirring the solution. Cool the solution to 3° C by immersing the beaker in crushed ice, and add dropwise 3.5 ml of an approximately 37-percent solution of formaldehyde, while again vigorously stirring. Since the temperature at this stage must not exceed 5° C a small thermometer makes a convenient stirrer. When all the aldehyde has been added, allow the beaker to remain in the ice bath for about 1 hour and stir the contents every 5 minutes. The reaction is now allowed to proceed at a reduced temperature for about 20 hours. A cooling bath is conveniently made by placing a 20-lb block of ice in a tray having approximately the dimensions 12 by 12 by 3.5 inches and filling the tray with ice water. With this arrangement, when the room temperature is 20 to 25° C, the temperature of the reacting mixture will increase about 1 to 2° C during the first 7 hours and then gradually to about 20° C during the next 13 hours.

Cover the beaker containing the reacting mixture, place it in one corner of the tray, and weight it to prevent tipping. Allow the beaker to remain in the ice bath for 20 hours. At the end of this time, slowly pour the contents of the beaker into 2 liters of cold distilled water, while constantly stirring. When the solution has stood for 1 hour, filter it, using a Büchner funnel and a 15-cm paper of close texture. Wash the precipitate three times with distilled water and then return it to the beaker in which the precipitation was made. Add 1 liter of water and 50 ml of hydrochloric acid (sp gr 1.18), and boil for 2 or 3 minutes. Let the precipitate settle for 10 minutes and then wash it three times by decantation with water. Crush and break up the black mass with a stirring rod which has been flattened on one end. Repeat the boiling treatment with 1 liter of water and 50 ml of hydrochloric acid, as well as the subsequent washing with water, twice more.

Finally, dissolve the residual mass in an excess of ammonium hydroxide, and evaporate the resulting solution to dryness on the steam bath. Grind the cooled residue to a fine powder, and transfer to a bottle.

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