[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMERICAN UNIVERSITY]

THE USE OF ORTHO,PARA-DIHYDROXY-AZO-PARA-NITROBENZENE AS A TEST FOR THE MAGNESIUM ION

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The azo dye *o,p*-dihydroxy-azo-*p*-nitrobenzene has been reported by K. Suitsu and K. Okuma[1] as rendering a very sensitive test for the magnesium ion. A recently published note by Ruigh[2] gives the method of preparation and use. A 0.5% solution of the dye in 1% sodium hydroxide solution is stated to be the proper concentration to employ. The test depends upon the formation of a blue lake with the azo dye in dilute sodium hydroxide solution. It is also stated that ammonium salts render the test less sensitive, while the presence of nickel or cobalt, cations which form similar lakes with the dye, invalidates or confuses the test.

Numerous tests with this reagent have been made in this Laboratory, and it is believed that a more sensitive and more convenient method for its use has been developed. In addition, this usage has the advantage of being very simply conducted and, with very few exceptions, can be carried out, if desired, without the preliminary, time-consuming removal of interfering anions or cations. The classical magnesium ammonium phosphate method of determining magnesium is often confusing, inasmuch as aluminum hydroxide, silicic acid, strontium phosphate and calcium phosphate often precipitate at this point in the ordinary qualitative analysis schemes. Methods of removing these substances usually involve several time-consuming separations which are, in addition, generally not very sensitive.

The method which was found to be the most practicable, involves the evaporation of the unknown solution to a small volume, or to dryness if the quantity of magnesium is very small and if substances such as organic material (which would char under such treatment) are absent. A clean porcelain crucible is essential for this test and the evaporation should be conducted within it. Five or ten ml. of 6 N sodium hydroxide is now added to the porcelain crucible or casserole and finally one drop of the dye reagent. In about ten seconds or more, depending upon the concentration of the magnesium ion, a light blue stain will appear upon those portions of the casserole which had been in contact with the solution containing magnesium. This stain adheres quite tenaciously to the surface of the casserole. If the supernatant liquid is now poured from the casserole and the stain washed twice with 5 to 10 ml. of water, the stain turns green in color but does not disappear. If the same test is carried out with nickel alone, the stain does not form as rapidly, adheres less tenaciously and turns red-

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[1] Suitsu and Okuma, *J. Soc. Chem. Ind. Japan*, **29**, 132–138 (1926); *C. A.* **20**, 3000 (1926).

[2] Ruigh, THIS JOURNAL, **51**, 1456–1457 (1929).

brown in color upon washing with water. If a similar procedure is followed with cobalt, no stain whatever forms, although a blue lake will appear.

Treatment of the stains with concentrated ammonium hydroxide is also characteristic. In the case of magnesium, the stain is not affected, but in the case of nickel the stain dissolves readily. If desired, this solution could be tested for nickel in the usual manner, that is, by the addition of dimethylglyoxime to the solution with the formation of a precipitate of nickel dimethylglyoxime.

Quantitative investigation indicates that in the absence of de-sensitizing material, 3×10^{-6} g. of magnesium can be readily detected with this technique. If, therefore, the magnesium test is applied in its customary place in the fourth or fifth group of the commonly employed qualitative analysis schemes, this small quantity of magnesium will be capable of detection.

Experiments were also conducted to determine the validity of this test in the presence of the cations commonly met with in qualitative analysis either tested singly or in any possible combination. In the presence of these cations, tested individually, no interference in any case was obtained. A great many combinations were tested, and, in general, any grouping of cations which form colored precipitates (particularly blue precipitates) upon the addition of sodium hydroxide, renders the test somewhat uncertain. Fortunately, however, only a few such conflicting combinations were found. Copper and aluminum illustrate a case in point, the cupric hydroxide apparently being absorbed by the aluminum hydroxide, thereby forming a confusing lake not readily soluble in concentrated ammonium hydroxide.

Further investigation indicates that acetates, tartrates and ammonium salts render the test less sensitive but that if magnesium be present in sufficient quantity (and in the case of organic material such as tartrates) evaporation is not carried to complete dryness (to prevent charring), the test is still valid. The quantity of these conflicting substances determines, quite naturally, the amount of detectable magnesium. Quantitative tests show that with 1 g. of these substances present only 3×10^{-4} g. of magnesium can be detected. Consequently, when great sensitivity is required, organic matter and ammonium salts should be first removed and the solution then evaporated to dryness before applying the stain method technique.

Summary

A new technique for the use of *o,p*-dihydroxy-azo-*p*-nitrobenzene as a test for the magnesium ion has been described.

With this technique the test is valid in the presence of any one of all of the common cations met with in qualitative analysis and in a great many combinations of these cations.

Nickel, cobalt or both do not confuse the test.

Acetates, tartrates and ammonium salts do not interfere but decrease the sensitivity of the test.

The test can be used most efficiently as a substitute for the classical magnesium ammonium phosphate test commonly employed in qualitative analysis procedures. Used in this way, 3×10^{-6} g. of magnesium can be detected.

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THE INTERPRETATION OF THE COLLIGATIVE PROPERTIES OF WEAK ELECTROLYTES

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Introduction

Although the importance, in the study of solutions, of the activities or activity coefficients[1,2] of the components has been most emphasized in the field of strong electrolytes, these quantities are, of course, of no less importance to the study of weak electrolytes and of non-electrolytes. Moreover, although the methods of determining the activity coefficients[1,2] have been most widely studied in the case of strong electrolytes, these methods are, of course, equally applicable to weak electrolytes and non-electrolytes. The application of these methods is illustrated by the work of Randall and Failey[3] in determining the activity coefficients of gases, of non-electrolytes, and of the undissociated part of weak electrolytes in solutions of electrolytes.

In the study of electrolytes it has been customary to regard as strong those completely or practically completely dissociated in dilute aqueous solution, and as weak those incompletely dissociated at finite concentrations. The question as to the actual extent of dissociation of a strong electrolyte in a given solution is of importance from a kinetic standpoint and has received considerable attention. To account for apparent evidences of incomplete dissociation of strong electrolytes consisting of small ions or those having "un-centrally located charges," Bjerrum[4] suggested a modification of the inter-ionic attraction theory of Debye and Hückel[5] whereby such ions, of opposite charge, when closer together than a certain minimum distance (dependent upon the dielectric constant of the medium and the absolute temperature) would be regarded as associated—behaving

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, Chapters XXII to XXVIII.

[2] Randall, *Trans. Faraday Soc.*, **23**, 498, 502 (1927).

[3] (a) Randall and Failey, *Chem. Reviews*, **4**, 271, 285, 391 (1927); see also (b) Livingston, THIS JOURNAL, **48**, 45 (1926).

[4] Bjerrum, *Det. Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **7**, No. 9 (1926).

[5] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).