Determination of Aluminum in True Solution in the Presence of Colloidal Hydrated Alumina

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For lack of a cenvenient method of determining small amounts of aluminum, few attempts have been made to differentiate between the aluminum in true solution and that in the colloidal form (or better, large hydroxoaquoaluminum ions[1]), except Tanaka's work[2], who separated ionic aluminum from waters containing colloidal hydrated alumina, using an ion-exchange technique.

On the other hand, a simple and accurate method, involving a chloroform extraction of aluminum as 8-hydroxyquinolate and subsequent determination of the absorbance of the extract, was recently developed by Gentry and Sherrington[3] and also by other workers.[4,5] This method was later modified by Motojima[6] to be used for the simultaneous determination of iron and aluminum, and by Goto[7,8] to prevent iron from being extracted.

It has been reported by Motojima[6] that while the extraction of aluminum 8-hydroxyquinolate is complete at pH 4.5 to 9.5, the recovery of aluminum is low when the pH of the sample is adjusted prior to the addition of 8-hydroxyquinoline. This statement seems to indicate the applicability of the above extraction method to the differentiation between the two forms of aluminum in water.

The extraction method was somewhat modified in the present investigation and actually applied to the determination of aluminum in true solution.

Method. *Reagents.—8-Hydroxyquinoline (oxine) solution.*—Dissolve 2 g. of pure 8-hydroxyquinoline in 5 ml. of glacial acetic acid and dilute to 200 ml. with distilled water. *Sodium acetate solution,* 1 M. *Chloroform. Sodium sulfate, anhydrous.*—Purest grade of commercial product often contains substances which produce a considerable blank color. Purify by recrystallization from water.

Procedure.—Take approximately 10 ml. of distilled water in a separatory funnel. Add to this 2 ml. of 8-hydroxyquinoline solution and 2 ml. of sodium acetate solution, and mix well. Pour slowly from a buret 10.0 ml. of chloroform into the separatory funnel. Do not shake at this step. Add, as rapidly as possible, 20 ml. of sample (containing less than 4 mg./l. of extractable aluminum) to the separatory funnel. The pH value must be within the range 4.5 to 9.5. Shake vigorously for about 10 sec., and allow the mixture to separate into two layers. Stable emulsions will be produced in the presence of colloidal form of hydrated alumina. It is important in

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[1] See H. Tanabe, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **74**, 253, 866 (1954); **77**, 33, 37 (1957).

[2] M. Tanaka, This Bulletin, **27**, 98 (1954).

[3] C. H. R. Gentry and L. G. Sherrington, *Analyst*, **71**, 432 (1946).

[4] S. E. Wiberley and A. G. Bassett, *Anal. Chem.*, **21**, 609 (1949).

[5] J. L. Kassner and K. A. Ozier, ibid., **23**, 1453 (1951).

[6] K. Motojima, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 903 (1955).

[7] K. Goto, *Chem. and Ind.*, **1957**, 329.

[8] T. Okura, K. Goto and H. Suzuki, *Industrial Water* (*Kogyo Yosui*) **2**, 338 (1956).

such a case that the emulsions are broken with a glass rod. Run the chloroform layer into a test tube containing a small amount of anhydrous sodium sulfate, which serves to remove droplets of water in the chloroform. Measure the absorbancy at 420 mμ.

Discussion.—In the usual procedure, 8-hydroxyquinoline, sodium acetate and chloroform are added to the sample in this order, and then the mixture is skaken to extract aluminum 8-hydroxyquinolate into the chloroform layer. The usual procedure can not be applied when the sample contains colloidal hydrated alumina of a very low degree of polymerization, since such colloidal hydrated alumina is also extracted to a considerable extent into the chloroform layer because of its rather rapid depolymerization. This interference from colloidal alumina, however, will be minimized by carrying out the extraction very rapidly. The procedure described in the present paper may meet this requirement. A 10 second's shaking is sufficient for the complete extraction of aluminum in a true solution at 20°C, as will be clear from Table I.

The form of aluminum available for the present method is not known strictly. However, it may be ionic or, if not, of a very low degree of polymerization, since a clear solution containing much unextractable aluminum can be easily obtained.

It has been shown by the above method that when an acidic solution of the aluminum ion is neutralized to a pH between 5 and 8, the concentration of extractable aluminum approaches the solubility very rapidly (Fig. 1) while the solution remains clear for more than 30 min. No other methods may be able to determine such a rapidly dercreasing concentration of aluminum in a true solution. Total aluminum can be determined after decomposing colloidal alumina by boiling with a small amount of hydrochloric acid. A larger amount of sodium acetate is required in this case to obtain a suitable extraction pH.

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TABLE I
EFFECT OF SHAKING TIME ON THE EXTRACTION OF ALUMINUM AT 20°C
(Concn. of Al^{3+}: 2.55 mg./l.)

Shaking time (sec.)	Recovery of Al (%)
5	102
10	99
20	99
30	99
60	100

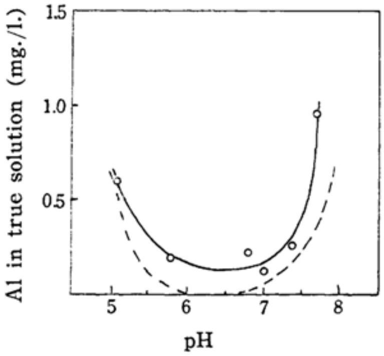

Fig. 1. Very rapid disappearance of Al^{3+} at various pH values. (25.0°; pH adjusted with NaOH)

-○-○- Al in true solution 1 min. after neutralization.
----- Solubility (see Ref. 8)
Initial concentration of Al^{3+}: 2.42 mg/l