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Precise Complexometric Coulometric Titration of Disodium Dihydrogen Ethylenediaminetetraacetate Dihydrate and Aluminium[†]

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The purity of recrystallized disodium dihydrogen ethylenediaminetetraacetate dihydrate was determined accurately by titration with zinc ion coulometrically generated from an amalgamated zinc anode. The reagents used were of 99.446%±0.002% homogeneity when the sample was dehydrated and stored in a hygrostat (relative humidity, *ca.* 58% at 20 °C) over 1 year. Aluminium of high purity (99.99%) was coulometrically titrated with the purified reagent. Aluminium was allowed to react with a certain amount of the reagent, excess of the reagent being titrated with zinc ion anodically generated. The end point was determined potentiometrically using a mercury electrode. The purity was found to be 99.976% with a standard deviation of 0.010% for 6 degree of freedom. Cause of the lower result (0.01%) is discussed.

Marinenko reported on an accurate coulometric determination of gallium for the measurements of the stoichiometric composition of gallium arsenide and of the atomic weight of Ga.[1] The sample containing gallium was allowed to react with excess disodium dihydrogen ethylenediaminetetraacetate dihydrate (Na_2H_2edta) of known composition and the excess of the reagent was back-titrated with coulometrically generated zinc ion. The method requires standard Na_2H_2edta (as a solid) of sufficient purity and homogeneity. However, no mention was given on the quality of Na_2H_2edta.

H_4edta (free acid) of high purity (J. T. Baker Chemical Co., U.S.A.)[2] is insoluble in water and inadequate for the present investigation. Dihydrated disodium salt of the acid of high purity is not available owing to the uncertainty of the content of water of crystallization.

The purity of Na_2H_2edta has been determined by acidimetric[3] or complexometric[1,4–10] coulometry. Several electrogenerated metallic ions, zinc(II),[1,4] lanthanum(III),[5] bismuth(III),[6,7] lead(II),[8] mercury(II),[9] and copper(II)[10] ions, were used as complexometric titrants. The current efficiency for the generation of the titrants, except zinc(II), has not been measured accurately, some electrode materials of high purity not being available. On the other hand, metallic zinc of high purity is available and the current efficiency for the generation of zinc(II) ion has been measured accurately.[11] Moreover, zinc(II) ion is useful as a back-titrant for the determination of metallic ions which have a larger stability constant with edta than that of zinc–edta complex.

The Analytical Methods Committee in the U.K. reported recently the procedure for accurate standardization of Na_2H_2edta by spectrophotometric titration with the use of pure bismuth[12] or zinc[13] metal. However, it gives no satisfactory accuracy because of the difficulty in the detection of the end point.

Only the complexometric procedure can be applied to determine aluminium by coulometric titration. Several coulometric investigations with use of 8-quinolinol complex have been reported.[14–18] The precision attained was higher than 0.1%(as standard deviation), not being sufficient for determining the aluminium content in pure aluminium metal. On the other hand, Na_2H_2edta has high equivalent weight and its use is particularly advantageous for precise determination of metals of small atomic weight such as aluminium. So far, however, it has not been used for complexometric coulometric determination of aluminium.

In this investigation, Na_2H_2edta was purified by recrystallization from ethanolic solution,[19] and by storage in a hygrostat for a long time. Its purity was determined by coulometric titration, and the purity of metallic aluminium was coulometrically determined with the purified Na_2H_2edta.

Experimental

Apparatus and Reagents. Apparatus for coulometric generation of the titrant and for measurement of the time interval of the electrolysis as well as precautions in the weighing of sample were the same as reported.[20] As the Faraday constant, 96484.6 C mol^{-1} was used.

A tall lipless beaker (*ca.* 200 ml) made from quartz plugged with a silicone rubber stopper was used as the electrolytic cell. The generator anode was an amalgamated zinc rod (*ca.* 6 cm^2 in area), and the generator cathode a platinum plate (1×1 cm). The zinc rod was prepared from zinc metal (99.999%, guaranteed by the Industrial Inspection Institute of Japan as a standard reference material for titrimetric analysis). The diaphragm under the cathodic compartment was prepared as follows: the bottom of a polyethylene tube was closed with a polyethylene plate with many fine holes. An agar-agar gel saturated with potassium nitrate was plugged on the bottom, the thickness of the agar layer being about 2 cm.

The end point for titration of Na_2H_2edta was determined by an amperometric procedure using a mercury-plated platinum electrode[21] (applied voltage −1.25 V *vs.* SCE), and that for aluminium was determined potentiometrically with a mercury cup electrode[22] and an "Expandomatic" pH meter (Beckman Instruments, Inc.). A salt bridge of potassium nitrate–agar was used for connection of the electrolytic cell with a saturated calomel electrode in an outside compartment, since chloride ion interferes with the indication of the potential of mercury cup electrode.

All reagents were of analytical grade, and were used (except Na_2H_2edta) without further purification. A 0.5 mol dm^{-3} acetate buffer of pH 6.2 was used as the anolyte for the determination of purity of Na_2H_2edta. Small amounts

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of solid tungstic acid and 1 mol dm^{-3} potassium nitrate solution (*ca.* 15 ml) were placed in the cathodic compartment.

Procedure. *Coulometric Titration of Na_2H_2edta*: Residual oxygen in the anolyte specified above was removed by passing oxygen-free nitrogen gas for *ca.* 2 h under vigorous stirring. The gas was then allowed to flow over the anolyte throughout the titration.

As pretitration, *ca.* 50 mg of Na_2H_2edta was added to the cell and titrated with anodically generated zinc ion at a constant current of *ca.* 150 mA. Near the end point of titration, the generating current was cut off, the indicator current being measured with a microammeter (full-scale deflection: 10 μA). This was repeated after the end point had been determined. The end point was determined graphically. An Na_2H_2edta sample (*ca.* 400 mg accurately weighed) was then transferred to the cell. After dissolution, it was titrated with coulometrically generated zinc ion by the same procedure as above. The time interval of titration was measured from the two titration curves.

Preparation of Solution of Aluminium Sample: Small pieces of aluminium metal (99.99%) were dipped into hot 7% sulfuric acid for a few minutes, washed successively with water and ethanol, dried *in vacuo* and stored in a desiccator containing magnesium perchlorate. *Ca.* 150 mg of the sample was weighed into a decomposition flask (*ca.* 50 ml) fitted with a reflux condenser[23] to prevent loss by spitting, and dissolved in 10 ml of 6 mol dm^{-3} nitric acid in the presence of platinum wires as a catalyst. The solution was then transferred to the electrolytic cell and evaporated to a small volume (*ca.* 20 ml). A weighed amount of the Na_2H_2edta (solid, standardized) was added in slight excess and the pH of the solution was adjusted to 3.5 by gradual addition of solid sodium acetate trihydrate. The solution was heated nearly to boil for *ca.* 15 min on a hot plate to ensure the complete complexation reaction of aluminium ion with edta. After cooling, the pH of the solution was adjusted to 6.2 by the dropwise addition of 20% sodium hydroxide solution. The solution was finally diluted to *ca.* 150 ml with deaerated water.

Coulometric Titration of Aluminium: After deoxygenation of the solution of aluminium, the solution was cooled below 3 °C in an ice bath. Excess edta was back-titrated with electrogenerated zinc ion. Because of sluggish attainment of the equilibrium condition near the end point of the titration, the constant current was cut off near the end point, and the potential of the indicator electrode was measured after it became stable. This was repeated in order to obtain the titration curve. The end point was determined by means of the differential titration curve. A blank experiment was carried out throughout the procedure.

Results and Discussion

Standardization of Na_2H_2edta. The purity and pretreatment of commercial Na_2H_2edta were first investigated by the procedure described previously. Three different lots of analytical-grade Na_2H_2edta A, B, and C were analyzed (a) without any treatment and (b) after drying, the assay values being given in Table 1.

The results for both (a) and (b) indicate low purity and considerable inhomogeneity. Wendlandt pointed out that the composition of crystalline water among commercial Na_2H_2edta is not stoichiometric.[24] The results (Table 1) indicate similar phenomena. Duval found the evolution of water at 60 °C on heating Na_2H_2edta.[25] However, Blaedel and Knight recommended 80 °C as the optimum temperature for air-drying of the hydrated salt without decomposition.[19] The values of relative standard deviation seem to support 80 °C, since constant weight of Na_2H_2edta was obtainable by heating at the temperature for 4 d. JIS(Japanese Industrial Standard) recommends heating of the reagent at 80 °C for 5 h,[26] but the time is not sufficient to attain constant weight.

TABLE 1. ASSAYS OF ANALYTICAL-GRADE Na_2H_2edta

Sample	No. of detns.	Purity (%)	s_R %
A	3	99.280	0.061
	3	99.653[a)]	0.024
B	3	99.585	0.076
	3	99.961[a)]	0.063
C	3	99.629	0.049
	3	99.728[a)]	0.022
	10	99.697[b)]	0.009[c)]

a) Dried at 80 °C for 4 d. b) Stored in hygrostat (*ca.* 58% rel. humidity) for 6 months. c) $\sqrt{V}$ value.

TABLE 2. ASSAYS OF Na_2H_2edta RECRYSTD. FROM REAGENT B

Method of pretreatment	No. of detns.	Purity %	s_R %
Without drying	5	97.607	0.054
Dried at 80 °C for 4 d	6	98.981	0.080
Dried at 80 °C for 4 d[a)]	4	99.211	0.017
Stored in hygrostat[b)] for 6 months	4	99.268	0.010
Dehydrated *in vacuo* and stored in hygrostat[b)]			
for 12 months	1	99.445	—
for 15 months	6	99.446	0.002

a) Ground prior to drying. b) About 58% rel. humidity.

The hydrated salt is stable over a wide range of humidity.[19] The weight of the reagent left under ordinary atmospheric conditions (35—60% relative humidity) changed from −0.017% to +0.025%. Thus, one of the reagents (Sample C, Table 1) was gently ground with an agate mortar, dried at 80 °C for 4 d, and stored in the hygrostat containing a saturated solution of sodium bromide at ordinary temperature (relative humidity *ca.* 58%) with frequent mixing. The results of assay of the Na_2H_2edta stored for 6 months in the hygrostat (Table 1) indicate that the reagent shows sufficient homogeneity.

Na_2H_2edta(Sample B, Table 1) of analytical grade was purified by recrystallization from ethanolic solution[19] in order to obtain pure Na_2H_2edta. The results obtained for the recrystallized reagent (Table 2) are somewhat lower than those of the original material. This may be mainly due to the contamination from glassware and distilled water. Since the recrystallized reagent may contain occluded water, it was dehydrated completely in a vacuum oven overnight at 120 °C,[19] and rehydrated by being kept in the hygrostat (relative humidity *ca.* 58%) until the purity became constant.

TABLE 3. DETERMINATION OF HIGH-PURITY ALUMINIUM (99.99%)[a)]

Sample taken (mg)	Al found (mg)	Purity %
137.611	137.576	99.975
150.915	150.871	99.971
156.859	156.836	99.985
169.583	169.512	99.958
143.749	143.725	99.983
127.214	127.182	99.975
150.650	150.624	99.983
		Mean = 99.976±0.009%[b)]
		R = 0.027%
		s_R = 0.010%

a) Value estimated by the manufacturer. b) The 95% confidence interval for the mean.

Excellent homogeneity could be attained by storing for more than 1 year.

In conclusion, the recrystallized reagent is suitable for use as a complexometric standard, when it is once dehydrated and then stored in a hygrostat, for example a desiccator containing a saturated solution of sodium bromide, for more than 1 year with frequent mixing.

Assay of Aluminium. The purity of the metallic aluminium (99.99%) was determined by the procedure described previously. When the electrolyte was not cooled, the aluminium content exceeded 100%. This may be caused by the displacement reaction of aluminium–edta complex to zinc–edta complex with the electrogenerated zinc ion, since the stability constant of aluminium–edta complex is similar to that of zinc–edta complex. The electrolyte was, therefore, cooled below 3 °C during the course of titration in order to prevent the displacement reaction. The results for the aluminium sample obtained by the proposed method are given in Table 3.

The purity was somewhat less than 99.99% (estimated by the manufacturer), though the standard deviation was small. The cause of this result was investigated.

Impurities in the sample were first examined. Semi-quantitative spectrographic analysis indicates that the sample contains in total *ca.* 30 ppm of metallic impurities, iron, copper, manganese, magnesium, silicon, and antimony. Oxygen was determined by bromine–methanol dissolution followed by spectrophotometric measurement (8-quinolinol extraction method),[27)] the content being *ca.* 40 ppm. Thus, the purity of this sample can be evaluated as 99.99%.

Marinenko and Foley reported that the anodic oxidation of zinc proceeds at 100.000% current efficiency with current density between 10^{-2} and 10^3 mA cm^{-2}.[11)] In the present investigation, the current density was *ca.* 25 mA cm^{-2}, no error due to the current efficiency being present. The error due to the location of end point was considered. Sharp potential breaks were usually obtained at the end point (*ca.* 12 mV per 1 μg of aluminium). The difference of 0.1 s in the duration of electrolysis corresponds to *ca.* 15 ppm of aluminium. Thus, the uncertainty of the graphical location of the end point is below several ppm. The standard deviation in the measurement of the generating current was not greater than 0.005%. Thus, the titration error can not be the cause of the lower result. Some displacement reaction between aluminium- and zinc–edta complexes might be the main source of *ca.* 0.01% error.

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