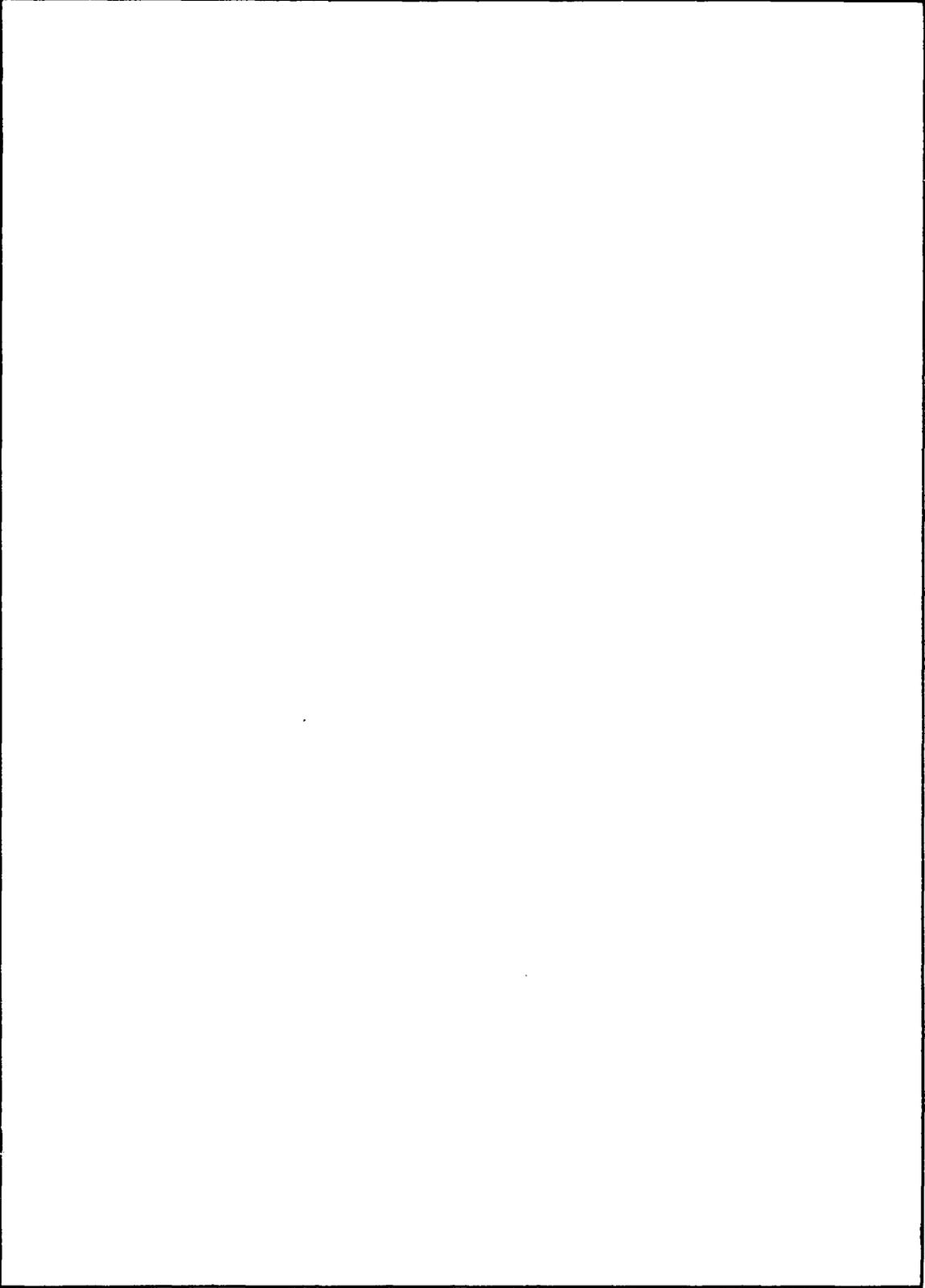


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TESTS AND PROCEDURES FOR DETERMINING THE PURITY OF TETRASODIUM ETHYLENEDIAMINETETRAACETATE (EDTA)

INTRODUCTION

Tetrasodium ethylenediaminetetraacetate (Na_4EDTA) is currently being investigated by the Navy for use as a boiler water treatment chemical. Three Navy laboratories (Naval Research Laboratory; Naval Ship Research and Development Center, Annapolis Laboratory; and Naval Ships Engineering Center, Philadelphia) and a ship (USS *Harry E. Yarnell*, DLG-17) are participating in research, testing, and evaluation of the proposed treatment. If tests at the various Navy installations are run on chemicals of different purity, erroneous and conflicting conclusions may result.

The purpose of this investigation was to test various analytical methods and establish suitable procedures for determining the purity of commercially available Na_4EDTA . Because a Military Specification for Navy procurement of Na_4EDTA would be based on the results reported herein, procedures using stable reagents and simple, readily available instrumentation were sought.

MANUFACTURE OF Na_4EDTA

Na_4EDTA , supplied by various manufacturers in the United States, is prepared by the reaction of either sodium cyanide or hydrogen cyanide with ethylenediamine and formaldehyde. When sodium cyanide is used, the resulting basic solution is evaporated to give a technical grade product containing a variety of impurities. In contrast, the use of hydrogen cyanide leads to the precipitation of the acid H_4EDTA , which is removed by filtration from the majority of reaction impurities; the desired salt of H_4EDTA is subsequently prepared from the acid by addition of the appropriate base. Na_4EDTA prepared by the second method tends to be purer and is surprisingly comparable in price to the available technical grade compound prepared by the first method. Typical specifications of Na_4EDTA as supplied by several manufacturers are listed, with current costs, in Table 1. Na_4EDTA in various states of purity is listed in catalogs of many chemical supply houses. The cost per pound through these outlets is ten to twenty times that listed by manufacturers for bulk quantities.

EXPERIMENTAL PROCEDURES

Solid Na_4EDTA samples used in this investigation were obtained directly from manufacturers. On occasion, Na_4EDTA received from chemical supply houses was also tested. The following tests were run on each sample:

1. Water content
2. Differential thermal analysis (DTA) run on original and dried sample

Note: Manuscript submitted October 31, 1973.

Table 1
Representative Manufacturers' Specifications for Na₄EDTA

Appearance or Physical Form	Chelating Activity mgCaCO ₃ /g Chelant	Solubility g/100g H ₂ O at 25°C	Properties of Aqueous Solution		Cost*	
			pH (1% soln.)	Max. Color, APHH of (%) solution	1 lb (cents)	To Chelate 1g CaCO ₃ (cents)
White and free of foreign particles†	215 minimum	90	10.5 – 11.5	500 (30)	40	0.41
White, granular powder	239 – 244	48	10.7 – 11.7	NS	51	0.46 – 0.47
White powder	215 – 220	50	10.5 – 11.5	NS	46	0.46 – 0.48
White powder	236 – 243	NS‡	10.2 – 10.8¶	35 (10)	48	0.43 – 0.46
White powder	215	NS	11.0	NS	43	0.44
Granular, non-hygroscopic powder	215	Completely soluble	10.5 – 11.5 (%NS)	35 (NS)	43	0.44

*Based on prices quoted January, 1973.

†Manufacturer also reported: (a) 20 ppm of heavy metals, as lead; and (b) no ammonia odor detected from a 30% aqueous solution.

‡The information was not specified by the manufacturer.

¶Reported for a 10% solution.

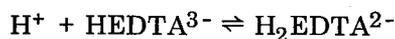
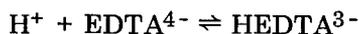
3. Nuclear magnetic resonance spectrum of aqueous solution
4. pH of aqueous solution
5. Potentiometric titration using hydrochloric acid
6. Chelating activity using calcium oxalate method
7. Atomic absorption and emission spectra for calcium and heavy metals.

The Na₄EDTA, as received, is weighed (approximately 5 g ±0.2 mg) in a clean, dry, weighing bottle (50 mm diam., 30 mm height). With the stopper ajar to allow the water to escape, the weighing bottle and sample are heated to various temperatures (±2.0°C) in a laboratory oven. Period of heating is measured from the time the specified temperature is again reached after the samples are placed in a preheated oven. Because the hot, dried sample is extremely hygroscopic, the hot weighing bottle is stoppered and allowed to cool in a desiccator over Drierite before reweighing. When a constant weight is observed (±0.5 mg), the percentage of water in the original sample is calculated.

Differential thermal analyses (DTA) are run on a du Pont 900 DTA instrument. The solid samples (3mm measured into the small DTA capillary tubes) are heated at a rate of 15°C/min in a stream of nitrogen (1 liter/min).

Potentiometric titrations and pH values of the aqueous solutions are determined with an Orion Model 801 digital pH meter and a combination glass electrode (Fisher Scientific Co., Cat. No. 13-639) standardized with a pH 10 buffer solution. The pH values are determined on stirred solutions of approximately 1 g of the solid sample dissolved in 100 ml of distilled water. The solution is allowed to reach the desired temperature (25° ±0.5°C), and the pH value determined. Then the basic solution is titrated with approximately 0.1N hydrochloric acid standardized against primary standard quality sodium carbonate.

The first two inflection points observed in the titration correspond to the reactions



The volumes of acid needed to reach these equivalence points are estimated by an initial rapid titration. Precise volumes are determined when 1-ml increments of acid are added, and the pH or potential for each increment is recorded in the neighborhood of the equivalence points. For a 1-g sample of $\text{Na}_4\text{EDTA} \cdot 2\text{H}_2\text{O}$ and 0.1N hydrochloric acid, the two inflection points will occur when approximately 20 ml and 45 ml of acid, respectively, are added.

The two equivalence points of the acid titration are determined by a computer program INFLCT* which locates the inflection point near the center of a table of equispaced data using the second differences (1). The program also gives the chelating activity and the percent of anhydrous Na_4EDTA . The chelating activity (mg CaCO_3 per gram of sample) is calculated as follows: chelating activity = (ml of HCl added between first two equivalence points, V_2) \times (normality of HCl) \times 100.09 \div (wt. of sample titrated).

The calcium oxalate method for determining the chelating activity of a sample is used by several manufacturers of Na_4EDTA to specify the quality of their chelant (2). The chelant solution is titrated with a standard solution of calcium in the presence of oxalate ions at a pH of 11.0 or slightly higher. When an excess of unchelated calcium is present in the titration, a white precipitate of calcium oxalate signals the endpoint. The advantages of this method are: (a) needed materials and apparatus are readily available, (b) solutions used are stable and may be stored over long periods, and (c) the chelation of calcium under the conditions of titration occurs quantitatively in a definite 1:1 molar ratio.

Reagents — 1. Ammonium oxalate, saturated solution: Dissolve 60 g of calcium-free ammonium oxalate in 1l of hot distilled water and allow to cool to room temperature.

2. Calcium chloride, standard solution: Add 50.05 g of primary standard calcium carbonate to 300 ml of distilled water and dissolve by slowly adding 86 ml of concentrated hydrochloric acid. Heat to boiling to remove carbon dioxide and completely dissolve the solid. Cool to room temperature, neutralize excess acid with ammonium hydroxide until slightly alkaline to litmus, and dilute to exactly 1l. One milliliter of this solution contains the equivalent of 50 mg of calcium carbonate. Other grades of calcium carbonate may be used to prepare this standard solution; however, in that case, the exact calcium content must be determined by titration with a standard solution of disodium ethylenediaminetetraacetate with murexide indicator (3).

Titration — The sample to be titrated is weighed into a suitable beaker, 85 ml of distilled water and 5 ml of saturated ammonium oxalate solution are added, and the mixture stirred with a Teflon-coated stirring bar, until the solid is dissolved. The pH of the solution is adjusted to 11 or more by the addition of 1M or 50% sodium hydroxide

*Available upon request from Chemistry Division, NRL.

solution. With some samples, the use of concentrated ammonium hydroxide, as suggested in some procedures, fails to bring the pH to the required value. The sample is titrated with standard calcium chloride solution until the first permanent turbidity is detected. The pH of the solution is again checked with a pH meter after this endpoint is reached and the pH adjusted, if necessary, to 11 or above. If the precipitate dissolves, the titration is completed by further addition of calcium chloride until a permanent turbid solution is formed. The chelating activity (mg CaCO₃ per gram of sample) is calculated as follows:

$$\text{chelating activity} = \frac{(\text{ml CaCl}_2 \text{ soln}) \times 50}{\text{grams of sample}}.$$

Atomic absorption and emission spectra were run by the Analytical Chemistry Branch, Central Materials Research Activity, NRL. Aqueous solutions of Na₄EDTA and solid samples, as received, were submitted for analysis.

RESULTS AND DISCUSSION

Content of water, which is an inert and inexpensive diluent for commercial Na₄EDTA, is determined by a simple drying technique. Although this is an easy assay of the Na₄EDTA quality, the water content of a Na₄EDTA sample determined by this method is only useful if the temperature, period of heating, and composition of the dried product are specified.

The upper limits for thermal decomposition of the solid Na₄EDTA are estimated by examining the thermograms obtained from differential thermal analysis (DTA). Typical thermograms of as-received samples consist of two or more endotherms (Fig. 1a). In most cases, thermograms of dried samples (120°C for 3 hr) exhibit just two endotherms: one at about 180°C (uncorrected) and one about 220°C (uncorrected) (Fig. 1b). The first peak is attributed to molecularly bound water that is not removed by ordinary heating, whereas occluded water is removed at lower temperatures. Weight changes observed when the original samples are dried and chelating activities determined on dried samples corroborate this conclusion. For example, a sample labeled 99.5% Na₄EDTA·2H₂O loses only 6.6% of its weight on drying at 165°C, and the dried sample has a chelating activity (254 mg CaCO₃ per gram of sample) consistent with Na₄EDTA·0.5 H₂O or (Na₄EDTA)₂·H₂O (Table 2). The bonding between Na₄EDTA and water which appears to form under the drying conditions reported herein is under investigation.

The high-temperature endotherms of the Na₄EDTA·XH₂O thermograms are attributed to the melting and subsequent decomposition of the organic compound. The decomposition temperature increases when polyvalent metal ions such as iron and calcium are chelated to the organic ligand (Fig. 2) in place of sodium ions.

Although differential thermal analysis could not be used directly to monitor the purity and composition of the many Na₄EDTA samples investigated, it did enable upper limits to be set for drying temperatures. Thus, 165°C was chosen because of the definite composition of the final product (Na₄EDTA)₂·H₂O, and the apparent lack of thermal degradation of the pure solid at this temperature.

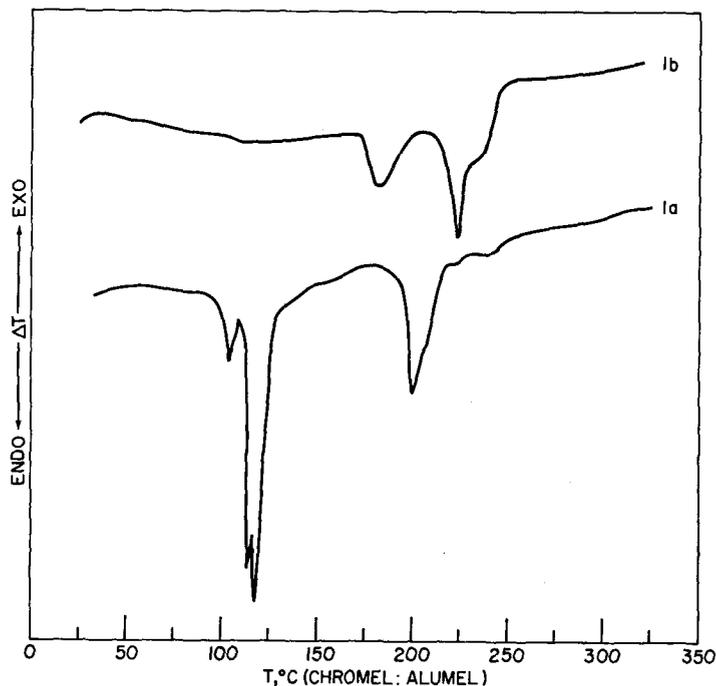


Fig. 1 — Differential Thermal Analysis (DTA) of tetrasodium ethylenediaminetetraacetate. Heating rate: 15°C/min. Atmosphere: Nitrogen at 1 l/min; (a) Original sample, (b) Dried sample. Sample size: 3 mm

Table 2
Calculated Composition of Anhydrous and Commonly Found Hydrates of Tetrasodium Ethylenediaminetetraacetate (Na₄EDTA)

Compound	Formula	Molecular Weight	Anhydrous %	Water Content %	Chelation Activity (mg CaCO ₃ per g)
Na ₄ EDTA	C ₁₀ H ₁₂ O ₈ N ₂ Na ₄	380.174	100.00	0	263.27
(Na ₄ EDTA) ₂ ·H ₂ O	C ₂₀ H ₂₆ O ₁₆ N ₄ Na ₈	778.364	97.69	2.31	257.18
Na ₄ EDTA·H ₂ O	C ₁₀ H ₁₄ O ₉ N ₂ Na ₄	398.189	95.48	4.52	251.36
(Na ₄ EDTA) ₂ ·3H ₂ O	C ₂₀ H ₃₀ O ₁₉ N ₄ Na ₈	814.392	93.37	6.63	245.80
Na ₄ EDTA·2H ₂ O	C ₁₀ H ₁₆ O ₁₀ N ₂ Na ₄	416.205	91.34	8.66	240.48
Na ₄ EDTA·3H ₂ O	C ₁₀ H ₁₈ O ₁₁ N ₂ Na ₄	434.220	87.55	12.45	230.50
Na ₄ EDTA·4H ₂ O	C ₁₀ H ₂₀ O ₁₂ N ₂ Na ₄	452.235	84.07	15.93	221.32

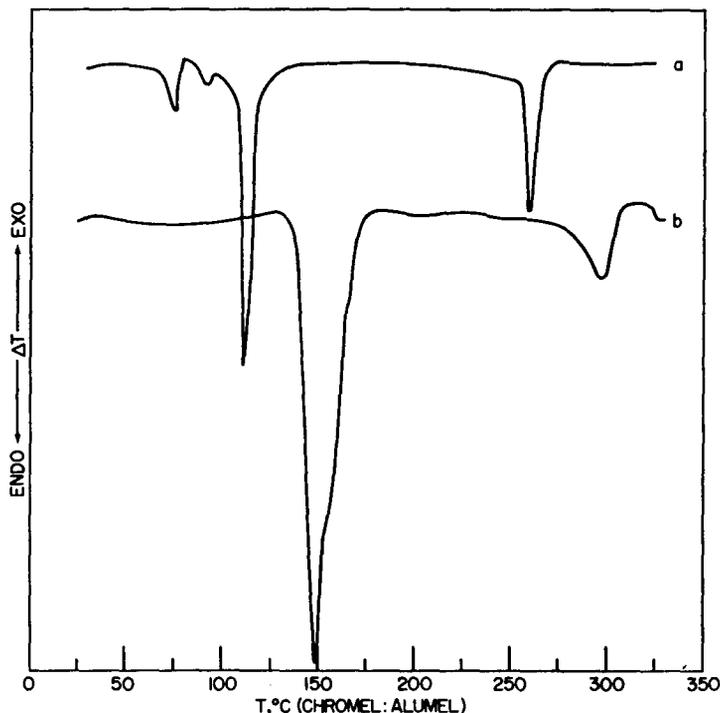
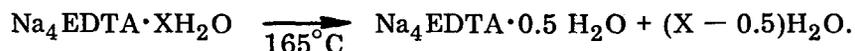


Fig. 2—Differential Thermal Analysis (DTA) of calcium (a) and iron (b) ethylenediaminetetraacetate. Heating rate: 15°C per min. Atmosphere: Nitrogen at 1 l/min; (a) Na₂CaEDTA, (b) NaFeEDTA. Sample size: 3mm

Data obtained when 5-g portions of the original Na₄EDTA sample were heated at various temperatures for a period of 3 hr are shown in Table 3. Again, 165°C (±2°C) is indicated as the best heating temperature. At lower temperatures, the water content fluctuates; at higher temperatures impure samples show evidence of decomposition by weight and color (white to tan) changes. Because the composition of the dried product heated at 165°C is not that of the anhydrous material (Table 2), the observed water contents are approximately 2.3% low according to the following equation:



No attempt was made to use vacuum drying and/or a desiccant to form the anhydrous material.

The chelating activities of the various Na₄EDTA samples were determined by two methods: (a) calcium oxalate titration, and (b) potentiometric (pH) titration. The theoretical chelating activities of various hydrates and anhydrous Na₄EDTA are listed in Table 2, and chelating activities determined on various commercial products of Na₄EDTA are summarized in Table 4. In addition to EDTA⁴⁻, other organic as well as inorganic

Table 3
Weight Loss as a Function of Temperature*

Product	Percent H ₂ O Loss						
	120°	140°	155°	165°	170°	175°	180°
A	—	6.40	6.62	6.59	6.41	6.73	6.61
B	12.72	14.01	15.05	15.00	—	—	15.13
C	—	—	—	5.81	5.68	5.81	5.83
D	—	—	—	8.57	—	—	—
E c	4.27	5.80	6.50	6.59	—	—	6.79
F	3.00	4.39	5.21	5.50	5.20	5.98	6.38

*Na₄EDTA·XH₂O (5-g samples) heated for 3 hr after oven came to temperature. Blanks indicate data not determined.

Table 4
Major Impurities Found in Commercial Na₄EDTA and Pertinent Equilibrium Constants* Compared to EDTA⁴⁻ and Oxalate Ions

Impurity	H ⁺				Ca ²⁺	
	K ₁	K ₁₂	K ₁₃	K ₁₄	K ₁	(K _{so})
Nitrilotriacetate (NTA ³⁻)	9.7	2.5	1.9	—	6.4	—
Iminodiacetate (IDA ²⁻)	9.3	2.6	—	—	2.6	—
Glycolate	3.8	—	—	—	1.1	—
Carbonate	10.2	6.6	—	—	—	(-8.0)
Hydroxide	14.0	—	—	—	1.4	—
Ethylenediamine-tetraacetate (EDTA ⁴⁻)	10.2	6.2	2.7	2.0	10.7	—
Oxalate	—	—	—	—	—	(-7.9)

*Convention for equilibrium constants and values (10^Kn) are as reported in Ref. 4.

anions may be titrated if their equilibrium constants with calcium and hydrogen ions are similar to those of EDTA⁴⁻. For the discussion that follows, pertinent equilibrium data for the major impurities detected in Na₄EDTA by other analytical methods are listed in Table 4.

The oxalate method for determining chelating activity is a simple technique that depends on a seemingly vague endpoint. However, multiplicate runs on the same sample,

but with varying sample weights, are usually within ± 0.05 ml of the theoretical titrant. The precision is well within the experimental error. A black background and a light projected through the side of the solution aid in determining the endpoint. Typical variation between operators was found to be $\pm 2\%$ of the average value.

NTA³⁻ is the only organic impurity listed in Table 4 that will cause high chelating activities when samples are analyzed by the calcium oxalate method. In the presence of a large excess of oxalate ions and at a pH greater than 11, the other impurities will not interfere because they only form weak complexes with any uncomplexed calcium ions. If the calcium oxalate method is used as the only criterion of Na₄EDTA purity, samples containing undesirable Na₃NTA may show an acceptable chelating activity.

A typical potentiometric (pH) titration curve is shown in Fig. 3. Two inflection points occur at pH values between 7.5 to 8 and 4.5 to 5. The first inflection or equivalence point represents the addition of one hydrogen ion to the tetraanion:



Addition of a second hydrogen ion,



is completed at the second equivalence point. If the sample of Na₄EDTA is pure, the volume of acid V₁, added to reach the first equivalence point will be equal to the volume of acid V₂, added between the first and second equivalence points. A significant difference (greater than ± 0.5 ml of 0.1N HCl) between V₁ and V₂ is caused by the presence of impurities or the lack of sufficient sodium hydroxide to convert the acid completely to Na₄EDTA.

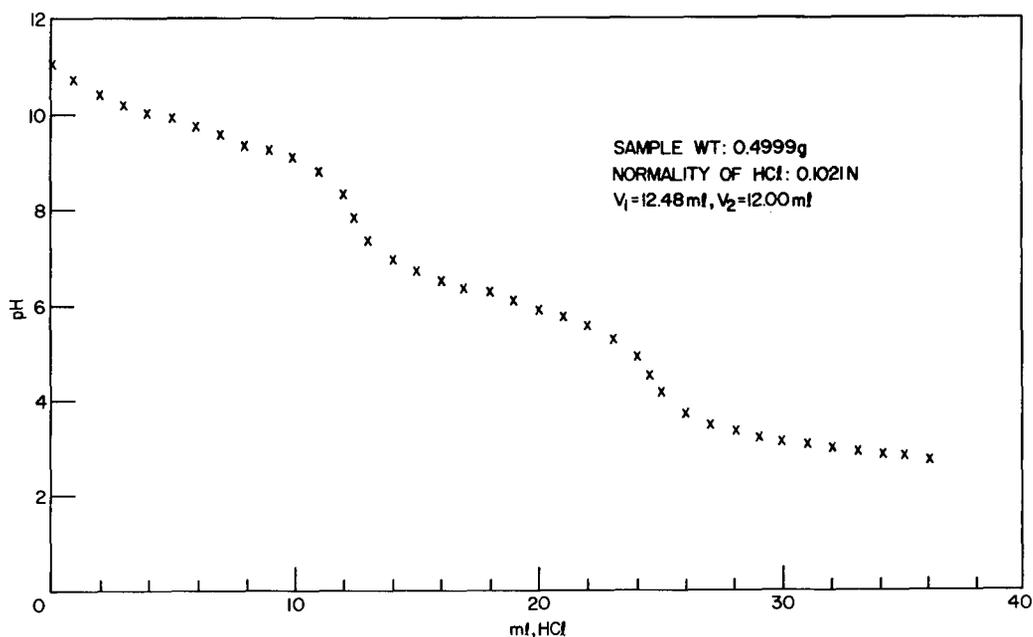


Fig. 3 — Titration of Na₄EDTA with hydrochloric acid

The equilibrium data for expected impurities (Table 4) indicate that NTA^{3-} , IDA^{2-} , CO_3^{2-} , and OH^- will be titrated, in addition to EDTA^{4-} , before the first equivalence point is reached. Thereafter, only HEDTA^{3-} and HCO_3^- will be titrated until the second equivalence point is reached. Glycolate ion, also a common impurity, is not titrated under our experimental conditions. Consequently, the difference between the volumes of acid needed to reach the two equivalence points ($V_1 - V_2$), and the chelating activities determined by the potentiometric titration and the calcium oxalate method can serve as criteria of purity for commercial Na_4EDTA . The chelating activities of several commercial Na_4EDTA products are listed in Table 5.

Table 5
Chelating Activities of Commercial Samples of $\text{Na}_4\text{EDTA} \cdot \text{XH}_2\text{O}$
(mg CaCO_3 per gram of sample)

Product	Oxalate Method		Potentiometric Titration		
	No. of samples	Chelating Activity	No. of samples	Chelating Activity	Acid Difference* (mequiv/g sample)
A	6	240	2	247	0.062
B	2	220	2	226	0.012
C	2	242	2	244	-0.108†
D	2	207	2	217	0.121
E a	4	205	4	202	0.130
E b	2	213	2	213	0.170
E c	2	215	2	214	0.161
F	2	243	2	246	-0.262
G	1	215	1	208	-0.165
H	2	210	—	—	—

* Calculated by $(V_1 - V_2) \times (\text{acid normality}) \div \text{wt of sample}$. V_1 and V_2 are volumes of acid added to reach the first and second inflection points, respectively.

† A negative quantity indicates a deficiency in base content.

For pure Na_4EDTA , the chelating activities obtained from the potentiometric titration should be in agreement with those determined by the oxalate method. Such agreement provides restrictions to the nature and amounts of impurities contained in a sample. In addition, the volumes of acid added to reach the two equivalence points provide further information concerning impurities. Some chelating agents which are present as impurities have K_1 values less than K_{12} of EDTA^{4-} (see glycolate, Table 4) and will not be determined by the methods discussed herein. Consequently, only an estimate of the nature and amounts of impurities can be made in the discussion to follow.

Although the chelating activities for product E, as determined by the potentiometric and oxalate methods, are in agreement, the large acid-difference of 0.130 to 0.170 milliequivalents (mequiv) per gram of sample, as shown in Table 5, suggests the presence of organic impurities. Because the weighted average equivalent weight of the impurities is

not known, a value of 250 mg/mequiv was chosen for an approximation. An estimated percentage of organic impurities is calculated from the following expression:

$$\text{Estimated percentage of organic impurity} = (\text{milliequivalent/g of sample}) \times (250 \text{ mg of impurity/milliequivalent}) \times (10^{-3} \text{ g/mg}) \times 10^2.$$

For product E, the calculation indicates 3% to 5% impurity. As discussed previously, this value excludes material such as glycolate ion.

The accuracy of the above method was checked by analyzing a 1% solution of Product E by nuclear magnetic resonance (5) and by a concentration/esterification/gas chromatography method (6). The sample was found to contain approximately 10% to 12% organic impurities consisting of the sodium salts of iminodiacetic, nitrilotriacetic and glycolic (3% to 4%) acids. Consequently, the organic impurities, excluding the glycolate, estimated by the method above are low and should be used only as a semiquantitative analysis. As a guide to the purity of a commercial product, the results do provide the necessary quality restrictions.

When the chelating activity determined by the potentiometric method is greater than that determined by the oxalate method, sodium carbonate is the most likely impurity. In addition, a positive value of the acid difference (V_1 is greater than V_2) indicates an excess of base, such as sodium hydroxide (Products A and B, Table 5). An estimate of the carbonate and hydroxide content of a sample may be calculated as follows:

- a. Carbonates as sodium carbonate, Na_2CO_3 (105.99 mg/mmole)
 Estimated percentage of Na_2CO_3 = [(Chelating Activity, Potentiometric method) - (Chelating Activity, Oxalate method)]
 $\times (105.99/100.09) \times 10^{-3} \text{ g/mg} \times 10^2$
- b. Hydroxides as sodium hydroxide (40.00 mg/mequiv)
 Estimated percentage of NaOH = (Acid difference, mequiv/g of sample, see Table 5) $\times 40.00 \text{ mg/mequiv} \times 10^{-3} \text{ g/mg} \times 10^2$

If V_1 is smaller than V_2 , the acid difference listed in Table 5 is negative and insufficient alkali is present to neutralize all of the acid or acids present in a commercial Na_4EDTA product. The estimated deficiency is calculated as above for an excess of base.

When the chelating activity determined by the oxalate method is greater than that determined by the potentiometric method (Product G, Table 5), the data suggest a chelating impurity, such as nitrilotriacetate ion (Table 4), that is titrated in the oxalate method but not in the potentiometric method. The percentage of organic impurity can be estimated in terms of trisodium nitrilotriacetate by the following calculation:

$$\text{Estimated percentage of organic impurity} = [(\text{Chelating activity, oxalate method}) - (\text{Chelating activity, potentiometric method})] \times (257.10/100.09 \text{ mg/mmole}) \times 10^{-3} \text{ g/mg} \times 10^2.$$

Estimated amounts of impurities calculated from the data in Table 5 are shown in Table 6. Information obtained from chelating activities and the criteria of purity determined from the data are summarized in Appendix A.

Table 6
Estimated Percentage of Inorganic and Organic Impurities
in Various Na₄EDTA Products*

Product	Average pH Value†	NaOH	Na ₂ CO ₃	Organics
A	11.17	0.25	0.74	—
B	11.01	0.05	0.64	—
C	10.70	-0.43‡	0.21	—
D	10.64	0.49	1.06	—
Ea	10.76	0.52	—	3.3
b	10.71	0.68	—	4.3
c	10.75	0.64	—	4.0
F	10.27	-1.05	0.32	—
G	10.69	-0.66	—	1.8

* Data from Table 5, and methods of calculation given in the text.

† 1% solutions used in the determination.

‡ A negative value indicates deficiency in base.

The pH values (Table 6), often cited as a measure of Na₄EDTA purity, show that the purity of the products does bear some relationship to the pH values. Thus a pure material (Product A) has a value closer to the calculated pH (11.4) of a 1% solution than that of a relatively impure material (Product E). However, this latter value is identical to that of a relatively pure Na₄EDTA sample (Product C) which contains a deficiency of base. Consequently, pH alone is not a valid criterion of purity.

Because excess base is detrimental to boiler operation, addition of unwanted base with Na₄EDTA must be avoided. A chelant formulation approaching the salt Na₃HEDTA could effectively guard against this situation. The test methods described in this report can be readily adapted to provide the proper quality limits for such a formulation.

Chelating activities were also determined on dried samples. The results are listed in Table 7. As noted from the table, in all cases except one (Product F heated at 160°C), the chelating activities determined by the potentiometric titration are greater than those determined by the oxalate method. Thermal decomposition of Na₄EDTA, liberation of volatile products, and formation of sodium carbonate explain the observed results. The chelating activities determined by the oxalate method and associated with samples considered to be only Na₄EDTA (Table 7, Products A and B) or Na₄EDTA + Na₃HEDTA (Product C and F), were close to the value calculated for a sample having the formula (Na₄EDTA)₂·H₂O (Table 2, 257 mg CaCO₃ per gram of sample).

Table 7
 Chelating Activities of Dried Samples of Na₄EDTA·XH₂O
 (mg CaCO₃ per gram of sample)

Product	Drying Temperature (°C)	Oxalate Method	Potentiometric Titration	
		Ave.* Activity	Ave. Activity*	Acid-mequiv/g of sample†
A	160	254	265	0.070
	175	254	268	0.008
	180	253	267	0.036
B	160	257	268	-0.079
	180	250	262	-0.020
C	160	256	257	-0.067
	175	254	257	0.055
D	160	226	238	0.085
E c	160	226	226	0.208
	180	226	225	0.242
F	160	254	252	0.180
	175	255	259	-0.228
	180	251	256	-0.100

* Average based on two or more determinations.

† Calculated by $(V_1 - V_2) \times (\text{acid normality}) \div \text{weight of sample}$. V_1 and V_2 are the volumes of acid at the first and second inflection points, respectively.

Decomposition of the commercial Na₄EDTA products is also evidenced by an amine-like odor detected when the buff-colored, dried sample is dissolved in water. However, solid state decomposition must not be confused with the hydrolysis that occurs in solution at high temperatures and pressures. The extensive research needed to determine the nature of these solid state decomposition products is not warranted at this time.

Although not a critical factor in the quality of Na₄EDTA, the calcium and magnesium contents of several representative specimens of Na₄EDTA were determined. Samples were analyzed by flame emission (calcium) and atomic absorption (Mg) spectroscopy. A standard addition technique was used in both procedures to overcome interference by sodium. Strontium was used as a releasing agent. The results are in Table 8. None of the samples analyzed have a weight percent of calcium or magnesium that appears to be significant (0.004 wt% to 0.029 wt%) in comparison with the amount that may be introduced into a boiler by the feedwater and makeup water.

Table 8
Atomic Absorption and Flame Emission Analyses of
Na₄EDTA Samples*

Product	Ca(ppm)†	Mg(ppm)‡	Others(ppm)
A	20	5	Fe < 50
B	20	4	Fe < 50
E a	240	53	Fe < 50
c	30	8	
F	290	58	Fe < 50

* Analytical results are as weight in original solid salt. Due to interference effects, ±20% of amounts reported must be allowed.

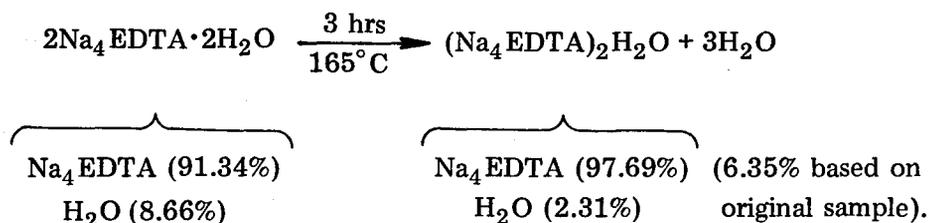
† Flame emission spectroscopy.

‡ Atomic absorption spectroscopy.

SUMMARY

Procedures requiring readily available, stable reagents and simple instrumentation were established to test the quality of commercially available Na₄EDTA. The specific tests and procedures are now contained in a Military Specification.* Should a chelant be preferred having less sodium ions than Na₄EDTA for boiler water treatment (for example, Na₃HEDTA), the methods and test procedures may be readily modified for a new Military Specification.

Na₄EDTA·XH₂O dried in an oven at 165° C forms a lower hydrate, (Na₄EDTA)₂·H₂O, and not the anhydrous compound. Consequently, for the dihydrate (Na₄EDTA·2H₂O) preferred for boiler water treatment, a restriction on the water content of 6.4% is consistent with the equation,



However, such factors as sampling, heating time and temperature (type of oven), cooling, weighing, and the hygroscopic nature of some samples require the acceptable limit of the contained water to be more realistically set at the theoretical value (8.6%).

The comparison of the chelating activities determined by the oxalate method and by the potentiometric titration with standard hydrochloric acid provides the necessary

*Available upon request from Chemistry Division, Naval Research Laboratory.

information to detect unwanted organic chelants and inorganic bases. Based on pure $\text{Na}_4\text{EDTA}\cdot 2\text{H}_2\text{O}$, the chelating activity is 240.48 mg CaCO_3 per gram of sample. A lower limit of 239 mg CaCO_3 per gram of sample provides adequate quality restrictions on the samples.

Although the chelating activity determined by the two procedures may be within 2% of each other, the acid-milliequivalent difference or volumes of standard acid needed to reach the first (V_1) and second (V_2) equivalence points of the potentiometric titration must also be examined. For calculated chelating activities that are equal ($\pm 2\%$): (a) if the two volumes of acid are equal ($V_1 = V_2$), the product does not contain excess inorganic bases or other organic chelating agents; (b) if V_1 is less than V_2 , the sample quality is acceptable, but insufficient base has been added to neutralize all of the acid, H_4EDTA ; (c) if V_1 is greater than V_2 , the product contains an excess of sodium hydroxide.

Based on the tests and procedures described, criteria of purity for commercial Na_4EDTA products are readily established. Furthermore, the chelating activities determined by the two methods described provide information that shows the nature and estimates the amounts of impurities contained in commercial Na_4EDTA . A summary of this information is included as Appendix A. For more precise analyses of Na_4EDTA and other chelants, the Naval Research Laboratory uses nuclear magnetic resonance spectroscopy and an esterification/gas chromatography method (6).

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Appendix A

INFORMATION OBTAINED FROM EXPERIMENTAL RESULTS AND ITS USE AS CRITERIA OF PURITY

1. Summary of Information Obtained from Chelating Activities Determined by the Calcium Oxalate Method and Potentiometric Titration.

I. Chelating activities in milligrams CaCO_3 per gram of sample:

- A. Values determined by each method agree within $\pm 2\%$.
 1. Sample is pure Na_4EDTA if chelating activity is $\pm 2\%$ from theoretical value.
 2. Sample contains other organic chelating agents with equilibrium constants similar to EDTA^{4-}
- B. Value obtained by oxalate method is less than that determined by the potentiometric titration.
 1. Sample contains carbonate (possibly Na_2CO_3).
- C. Value obtained by oxalate method is greater than that determined by the potentiometric titration.
 1. Sample contains organic chelating agent(s) with ionization constant(s) such that the anion does not affect the pH titration.

II. Volumes of standard acid used to reach the first two inflection points in the potentiometric titration:

- A. $V_1 = V_2$, or milliequivalents of acid used between the two inflection points are equal ($\pm 2\%$).
 1. Sample is pure Na_4EDTA .
 2. Sample does not contain excess inorganic base.
 3. Sample contains carbonate (see IB).
- B. V_1 is greater than V_2 , that is — milliequivalents of acid used to reach the first inflection point are greater than that needed for the second point. Sample contains:
 1. Excess inorganic base (possibly NaOH).
 2. Organic chelating agent with K_1 similar to EDTA^{4-} , but K_{12} much less than that of EDTA^{4-} (for example, NTA^{3-} , IDA^{2-}).
- C. V_1 is less than V_2 , that is — milliequivalents of acid used to reach the second inflection point are greater than that for the first.
 1. Insufficient sodium hydroxide used to neutralize the H_4EDTA .
 2. Sample may or may not contain other organic chelating agents.
 - a. If condition IA also holds, the material contains only EDTA^{4-} and HEDTA^{3-} .
 - b. If condition IC also holds, the material contains other organic chelating agents.

2. Criteria of Purity Determined from Data Obtained From Chelating Activities:

CA(OM) = Chelating activity by the oxalate method

CA(PT) = Chelating activity by potentiometric titration

V_1 and V_2 = Volumes (ml) of acid used to reach the first and second inflection points of potentiometric titration, respectively.

Product is of suitable quality for a desired theoretical chelating activity equal to CA(OM) if

A. CA(OM) = CA(PT) within $\pm 2\%$, and $V_1 = V_2$ within ± 0.5 ml.

B. CA(OM) = CA(PT) within $\pm 2\%$, but V_1 is less than V_2 . Although quality may be acceptable, insufficient NaOH has been added for complete conversion of H_4EDTA to Na_4EDTA .