Quantitative Determination of NTA and Other Chelating Agents in Detergents by Potentiometric Titration with Copper Ion Selective Electrode

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Quantitative analysis of nitrilotriacetate (NTA) in detergents by titration with Cu²⁺ solution using a copper ion selective electrode was achieved. This method tolerates a wide range of pH and ingredients in detergents. In addition to NTA, other chelating agents, having relatively lower stability constants toward Cu²⁺, were also qualified with sufficient accuracy by this analytical method for model detergent formulations. The titration process was automated by automatic titrating systems available commercially.

Keywords Chelating agents, detergents, titration, copper ion selective electrode, NTA

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Introduction

Chelating agents are a major ingredient in detergents, among which salts of nitrilotriacetic acid (NTA), especially, are largely used in detergents for automatic dishwasher and in other detergents because of its properties such as high chelating value (low molecular weight), relatively low price, and reasonable complex stability constants. In order to develop the formulation of such detergents it is important to know the quantity of those compounds in commercial products to evaluate their properties and easier methodologies to determine their amounts are desired. Titration is not quite sophisticated but is very versatile, and also does not require expensive equipment, time-consuming pretreatment, and skills for operation compared to other methods, such as ion chromatography and gas chromatography. It is therefore very useful and effective, especially in the industrial sector. However, there seems to be no official method to quantify NTA by titration unlike ethylenediamine tetraacetate (EDTA). The Japanese Industrial Standard (JIS) describes a method to titrate EDTA by using Zn²⁺ as a titrant and Eriochrome black T (BT) as a chromophore under a basic condition, while the combination of Cu²⁺ and 1-(2-pyridylazo)-2-naphthol (PAN) with an acetate buffer (pH 4.65) is provided by the International Organization of Standardization (ISO) focusing mainly on EDTA. It has been reported that both systems are unsuitable for titration of NTA. Another titration system by using Cu²⁺ with Chrome Azurol S (CAS) has been known to be suitable for titration of NTA, but requires strict pH control. These colorimetric titration methods are based on the difference of stability constants between the metal ion/chelating agent and metal ion/chromophore and sometimes even with proton when pH control is critical. Therefore it would become much simpler if chromophores were not required. From this point of view, potentiometric titration is one of the promising ways to run a quantitative analysis of NTA roughly and quickly. It has already been briefly reported that NTA can be titrated by use of a copper ion selective electrode under a basic condition (pH 9.5), demonstrating that only a couple of inorganic salts are compatible with the titration. There has also been a somewhat related example of a titration method by use of a copper ion selective electrode commercially available, which mainly focused on a fractional titration between Cu²⁺ and Zn²⁺ with 3,6-dioxo-octane-1,8-diaminetetraacetate (EGTA) as a titrant. Another potentiometric titration method of using iron(III) chloride in the presence of ferroin with a purpose-made electrode under an acidic condition (pH 4.7) has also been reported, where quantitative determination of EDTA and NTA in a detergent formulation was carried out. In this case, the successful fractional titration of EDTA and NTA is favorable for the determination of chelating agents in detergent formulations. However the necessity of removing tripolyphosphate is unfavorable at the same time.

More than 30 years have already passed since those titration techniques were reported and many new chelating agents have been put to practical use since then, being currently available commercially. Furthermore, formulations of detergents have also become much more complex as the requirements for the properties of detergents from both environmental circumstances and consumers’ needs have become increasingly varied. Therefore, the optimum titration techniques for chelating agents used in detergent compositions, especially for NTA and new ones, are somewhat ambiguous nowadays. We describe herein a study of potentiometric titration to quantify NTA and other chelating agents in detergent formulations as well as the scope and limitation of the system.

Experimental

Reagents and chemicals
All commercially available materials were reagent grade and used as purchased. Deionized water was prepared using an
Aquarius RFP 542HA supplied from Advantec Toyo Kaisha, Ltd. The purity of EDTA was determined according to the method described in the Japanese Industrial Standard (JIS K 8107).

**Instruments and accessories**

Titrations were conducted using an automatic potentiometric titrator supplied from Metrohm, consisting of 905 titrando, dosino, 807 dosing unit, 772 pump unit, 814 USB sample processor with a sample rack, and 802 propeller stirrer, which was controlled by Tiamo Ver. 2.3. The titration system was equipped with a 6.0502.140 copper ion selective electrode, 6.0508.110 calcium ion selective electrode, 6.0726.100 double-junction Ag/AgCl reference electrode (bridge electrolyte KNO₃ sat.), and 6.0258.010 pH glass electrode.

**Typical titration procedures**

For the chelating agent, about 0.15 g of a chelating agent was dissolved into approximately 100 mL of deionized water and then an aqueous solution (10%) of hexamethylenetetramine was added to the solution. The sample solution prepared was neutralized by an aqueous solution (0.1 mol/L) of H₂SO₄ with a pH electrode until the pH of the solution reached about 7. The titration of the sample solution with a 0.1 mol/L solution of CuSO₄ was conducted by using a copper ion selective electrode and the endpoint of the titration was determined at the inflection point of the titration curve.

For detergent compositions, about 3.0 g of a detergent composition was used instead of a chelating agent. The other steps were quite similar to those for the chelating agent.

All experiments were conducted at room temperature. These procedures were automated by use of the automatic titration system mentioned above.

**Results and Discussion**

**Preliminary survey**

NTA³⁻ reacts with Cu²⁺ in a 1 to 1 ratio to form a [Cu(NTA)]⁻ complex. In the presence of excess NTA over Cu²⁺, almost all Cu²⁺ are bound to NTA, which is a cage-like structure containing Cu²⁺, thereby isolating it from the solvent molecule. The copper ion selective electrode which measures the electrode potential of the free Cu²⁺ in the solution records changes in the electrode potential corresponding to the Cu²⁺ concentration in the solution. The initial addition of Cu²⁺ to a sample solution of NTA produced a slow and steady increase in electrode potential reading until about 5.5 mL of Cu²⁺ was added (see Fig. 1). Then the electrode potential abruptly increased with a point of inflection, which means the equivalence point of the titration. After that, the addition of excess Cu²⁺ resulted in an almost steady decrease in electrode potential reading, which may be caused by dilution. A typical titration curve with an obvious endpoint was obtained by a simple titration of NTA trisodium in an aqueous solution (5.4 mmol/L) with a solution of CuSO₄ (0.1 mol/L) by using a copper ion selective electrode without any buffer solutions, resulting in the pH value of the system decreasing from approximately 10 to around 6 during the course of titration. A very similar titration curve was also obtained by using a CuCl₂ solution (0.1 mol/L) in spite of the information from the manufacturer suggesting that chloride ion might interfere with the titration. On the other hand, a titration system by using a solution of CaCl₂ (0.1 mol/L) with a calcium ion selective electrode under the same condition was also examined, but the slope of the titration curve was not large enough, showing an ambiguous endpoint. Since these preliminary results demonstrated that the potentiometric titration of NTA with a copper ion selective electrode would be promising, the optimum condition for this system was studied in detail.

**Effect of pH**

Several experiments to know the effect of pH on this titration were conducted because detergent compositions containing NTA can be varied with a wide range of pH. After partial neutralization of the sample solution of NTA trisodium to pH = 7 with a solution of H₂SO₄ (0.1 mol/L), the endpoint of the titration curve was somewhat ambiguous. This is probably due to the decrease of pH value to approximately 3 at the end of titration caused by somewhat acidic CuSO₄, having a stability constant that is not high enough to detect the endpoint properly. In fact, the titration curve did not show any clear endpoint under an acidic condition (pH ≈ 2) adjusted by the H₂SO₄ solution.

In order to investigate the effect of pH further, various buffer solutions were examined, revealing that the titration can be conducted successfully in a range of pH value from 4.0 (phthalate buffer solution), through 6.9 (phosphate buffer solution) and 9.2 (tetraborate buffer solution), to 10.0 (carbonate buffer solution). In contrast to carbonate buffer, NH₃/NH₄Cl buffer (pH 10) common for EDTA/Zn²⁺/BT system, is not suitable for this method, which might be ascribed to high coordination tendency of NH₃ to copper cation. However, a previous paper reported that NTA can be determined by titration method using Cu ISE with Cu(NO₃)₂ in a buffer of NH₃/NH₂NO₃ at pH ~9.6. As is mentioned above, when pH = around 2, the titration by this method was unsuccessful and a similar result was obtained when pH 12 by addition of NaOH, which should be due to the formation of insoluble Cu(OH)₂ in the latter case. Compared to methods in literature noted earlier, the titration method less affected by pH that does not require strict control of pH is advantageous to determine the quantities of ingredients in detergent formulations. According to these results, pH should be controlled to some degree but very strict control is not necessarily needed. In addition, hexamethylenetetramine (HMTA) has been used in studies as a weak buffer. For this purpose, HMTA was adequate enough to keep the pH value of the solution in that range among the several compounds and...
buffers tested. Therefore, 10 w/w% solution of HMTA was employed as a weak buffer solution in this study hereafter. Finally, a suitable titration condition was decided and a typical titration experiment for NTA was conducted as follows: NTA trisodium (0.1500 g) was dissolved into approximately 100 mL of deionized water and then an aqueous solution (10%) of hexamethylenetetramine (10 mL) was added to the solution. The sample solution prepared was neutralized by an aqueous solution (0.1 mol/L) of H2SO4 with a pH electrode until the pH of the solution reached around 7. The titration of the sample solution with a 0.1 mol/L solution of CuSO4 (factor: 0.987) was conducted by using a copper ion selective electrode and the endpoint of the titration was determined at the inflection point of the titration curve, where 5.50 mL of CuSO4 solution was consumed. Figure 1 shows the typical titration curve of electrode potential (vertical axis) against the volume of Cu2+ solution added (horizontal axis) for this particular experiment. The electrode potential (mV) corresponds to the concentration of Cu2+ in the solution. Those for different experiments are quite similar to this figure. Figure 2 shows a linear calibration curve thus obtained for NTA, which demonstrates NTA can be safely determined by titration with a copper solution using a copper ion selective electrode.

Effect of ingredients in detergents

Usually, detergent formulations contain several ingredients other than NTA salts such as surfactants, organic solvents, and alkaline agents. These ingredients may sometimes interfere with the titration. However, the following compounds have been found not to interfere with our titration systems: sodium octanoate and polyoxyethylene monoalkyl ether (both surfactants), diethylene glycol monobutyl ether (organic solvent), and sodium and potassium hydroxide (alkaline agents). It should be pointed that total amounts of NTA and sodium silicate, which is also a common alkaline agent in detergents, were determined without neutralization, though the titration after neutralization showed only the amount of NTA. Similarly,
Detected without neutralization (pH 10). This is another notable complex of DTPA formed
monoca point in comparison with the fact that tripolyphosphate acts as NTA after neutralization, although no apparent endpoint was used for the experiment, which should be due to the copper sufficient accuracy (Figs. S2 – S6, Supporting Information). In this titration system using Fe(III) i an inhibitor for the Cu²⁺/CAS system⁴ and for the potentiometric also known as bicine or DHEG, was not quantified by this chelating agents shown in Fig. 3, bis(2-hydroxyethyl)glycine, the case of diethylenetriaminepentaacetate (DTPA), the amount to DHEG, glycine was not determined. These are both amino-phosphonates (also shown in Fig. 3) can be quantified by this method as well (Figs. S8 and S9, Supporting Information). In contrast to these results suggest that neutralization is also recommended especially for unknown samples with high pH value for appropriate titration.

Other chelating agents
In addition to NTA, other chelating agents, listed in Fig. 3, were also examined. The compounds are being increasingly utilized and put to practical use in the detergent industry these days. This method is applicable to EDTA as expected (Fig. S1, Supporting Information). Other amino-carboxylate type chelating agents listed in Fig. 3 were also quantified with sufficient accuracy (Figs. S2 – S6, Supporting Information). In the case of diethylenetriaminepentacetic acid (DTPA), the amount determined by this titration was twice more than the amount used for the experiment, which should be due to the copper complex of DTPA formed by the 2:1 ratio of Cu²⁺ and DTPA (Fig. S7, Supporting Information).⁵ In contrast to these chelating agents shown in Fig. 3, bis(2-hydroxyethyl)glycine, also known as bicine or DHEG, was not quantified by this method, presumably explained by its lower stability constant toward Cu²⁺ ion compared to the compounds in Fig. 3. Similar to DHEG, glycine was not determined. These are both amino-monocarboxylates. As yet another type of chelating agent, amino-phosphonates (also shown in Fig. 3) can be quantified by this method as well (Figs. S8 and S9, Supporting Information). On the other hand, this titration method was not suitable for phosphonates without nitrogen atoms illustrated in Fig. 3. It is noteworthy that citrate can be detected by this method in spite of its lack of nitrogen atoms (Fig. S10, Supporting Information).

| Ingredient in A (%(w/w)) | Ingredient in B (%(w/w)) |
|--------------------------|--------------------------|
| NTA trisodium monohydrate (1.0) | EDTA disodium dihydrate (5.0) |
| Linear alkylbenzene sulfonic acid (1.0) | Alkyl glucoside (40% aq.) (4.0) |
| Sodium silicate pentahydrate (3.0) | Diethyleneglycol monobutyl ether (3.0) |
| Alkyl ethoxylate (1.0) | Linear alkylbenzene sulfonic acid (2.0) |
| NaOH (48% aq.) (2.0) | NaOH (48% aq.) (1.0) |
| Water (92.0) | Water (85.0) |
| Total (100.0) | Total (100.0) |
| Quantitative value = 1.0%(w/w) | Quantitative value = 5.0%(w/w) |
| Standard deviation (0.014) | Standard deviation (0.021) |
| Coefficient of variation (0.015) | Coefficient of variation (0.004) |

| Ingredient in C (%(w/w)) | Ingredient in D (%(w/w)) |
|--------------------------|--------------------------|
| N-(2-Carboxyethyl)iminodiacetic acid (3.0) | Disodium iminodiacetate monohydrate (3.0) |
| KOH (48% aq.) (5.0) | Ethanol (10.0) |
| Cocamidopropyl betaine (1.0) | Benzalkonium chloride (50% aq.) (4.0) |
| Sodium octanoate (1.0) | Alkyl ethoxylate (4.0) |
| Water (90.0) | Sodium carbonate (4.0) |
| Total (100.0) | Water (75.0) |
| Quantitative value = 3.0%(w/w) | Total (100.0) |
| Standard deviation (0.005) | Quantitative value = 3.0%(w/w) |
| Coefficient of variation (0.002) | Standard deviation (0.011) |
| Coefficient of variation (0.004) | Coefficient of variation (0.004) |

Each determination was repeated 5 times. Each sample was adjusted at pH = approximately 7 and included HMTA as described in the text.

Sodium tripolyphosphate did not interfere with the titration of NTA after neutralization, although no apparent endpoint was detected without neutralization (pH 10). This is another notable point in comparison with the fact that tripolyphosphate acts as an inhibitor for the Cu²⁺/CAS system⁴ and for the potentiometric titration system using Fe(III) in the presence of ferroin.⁶ These results suggest that neutralization is also recommended especially for unknown samples with high pH value for appropriate titration.

**Conclusions**
Quantitative determination of NTA and other chelating agents in detergents
According to the results discussed above, this titration method appears to be favorable for quantitative analysis of NTA and other chelating agents used in practical detergents. Several model detergent compositions were prepared in accordance with the formulations (A, B, C, D) shown in Table 1 and then a series of quantitative analyses by using this titration method was conducted (Figs. S11 - S14, Supporting Information). The simple procedure is as follows: (1) addition of HMTA solution, (2) neutralization, (3) titration with a CuSO₄ solution by using a copper ion selective electrode. This process is easily automated by automatic titrating systems available commercially. Each composition was titrated five times repeatedly and the results are also summarized in Table 1, showing repeatability with values of the coefficient of variation in a range from 0.002 to 0.015, as well as sufficient accuracy with differences of less than 1% between the amounts titrated and the amounts formulated. According to these results, this titration method is adequate enough for the practical use for analysis of detergent compositions to quantify chelating agents contained. More practically, this method could be used to measure the chelating value in the unit of mgCaCO₃/g of an unknown sample under investigation to determine the total amount of chelating agents.
phosphonates, were also quantified by this method. It is important to have not only fine quantification but also "rough and quick" quantification methods available to evaluate detergent compositions and commercial products. Therefore, the present procedure provides an analytical method for detergent compositions and other products containing chelating agents. Fractional titration of two or more chelating agents in a mixture in detergents is currently under investigation.

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Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/

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