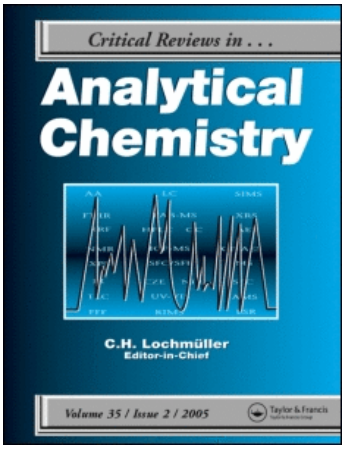

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ANALYTICAL APPLICATIONS OF CHLORAMINE-*T*

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I. INTRODUCTION

Chloramine-*T*, the sodium salt of *N*-chloro-*p*-toluenesulfonamide, was first prepared by F. D. Chattaway in 1905.[1] In 1924, A. Noll[2] proposed its use as a substitute standard reagent in place of the more expensive iodine standard. Since 1924, there have been more than one hundred papers published on its application in analytical chemistry.

It is the chief purpose of this review to consider the current and potential status of chloramine-*T* as a titrimetric reagent. To achieve this objective, the material gathered for this review is presented under a number of specific headings given in the table of contents.

II. LITERATURE ON CHLORAMINE-*T*

The literature on titrimetric analysis with chloramine-*T* up to about 10 years ago has been surveyed in a number of books and papers.[3-5] The use of chloramine-*T* in a number of colorimetric reactions, among which the determinations of cyanide and iodide would seem to be the most important, are reported in books by L. Meites[6] and F. Feigl.[7]

The literature on reported titrimetric determinations with chloramine-*T* during about the past 10 years is summarized in Table 1.

III. PURITY OF SOLID CHLORAMINE-*T*

Chloramine-*T* may be prepared by crystallization from alkaline solution, either after the alkaline reaction of dichloramine-*T* with sodium hydroxide, or after the alkaline reaction of *p*-toluenesulfonamide with sodium hypochlorite. The possible likely impurities are, therefore, *p*-toluenesulfonamide, sodium chloride, and dichloramine-*T*. Commercially available, chloramine-*T* is said to contain up to 1.5% sodium chloride and to be more than 98% pure. The latter figure is calculated on the "available chlorine" obtained from the trihydrate (relative molecular mass, 281.7).

It is claimed that the possible dichloro contaminant may be removed by washing the solid with carbon tetrachloride (see, for example, Reference 26), and that the purity may be increased to 99.5% by recrystallization from an aqueous solution.[3]

Presumably, some increase in purity is due to a decrease in the content of sodium chloride.

IV. STANDARDIZATION OF CHLORAMINE-*T* SOLUTIONS

Since chloramine-*T* cannot be obtained in the solid state with a purity of greater than about 99.5% for precision titrimetry, its solutions must be standardized by titration with a known standard solution.

Bishop and Jennings[3] have extensively investigated three possible methods. The first method is based on a direct titration with standard solution of arsenic(III) in 2 *M* hydrochloric acid, containing 0.1 *M* bromide. The endpoint may be found either by using *p*-rosaniline hydrochloride as a specific bromine indicator or by potentiometric titration, using a bright platinum indicator and a SCE reference electrode. The second method is based on the titration of iodine, liberated in the reaction of chloramine-*T* with potassium iodide and with standardized sodium thiosulfate solution. It is possible to carry out this titration in either hydrochloric or acetic acid solution using excess potassium iodide. The third method is based on the reaction of chloramine-*T* with arsenic(III) in 0.2 to 0.4 *M* bicarbonate medium in the presence of 0.0005 to 0.05 *M* iodide. The latter is required as a chemical catalyst, and the endpoint is detected by the observation of free iodine in the solution, using starch as an indicator.

The accuracy and precision of these methods have been examined extensively and are better than the limiting accuracy and precision (0.1%) attained by the use of grade A glassware.

As this work is of fundamental importance to the use of chloramine-*T* in titrimetry, the details of the methods employed and of the results obtained are given in Table 2.

V. STABILITY OF CHLORAMINE-*T* AS A SOLID AND IN LIQUID SOLUTIONS

A. Solid

Chloramine-*T* is obtained in the form of a white crystalline solid which is a trihydrate. One manufacturer, R. W. Greef and Co. Inc. (U.S.A.), reports that a typical particle size analysis of their product gives 85% of the crystals lying within the range of 0.05 to 0.5 mm.

TABLE 1

Recent Reported Titrimetric Determinations Using Chloramine-*T*

a	b	c	d	e	f	g	h
Compound	Quantity, milligrams (mg) or millimoles (m*M*)	Ref. No.	Direct (D) or excess (E)	If E, period of standing, min.	Medium for reaction	Oxidation product	Precision as percentage
triphenyl phosphine and its metal complexes e.g., cadmium (II)	0.3–0.5 m*M*	8	E	1	0.2M H_2SO_4	$(C_6H_5)_3PO$	0.5
thiosemi-carbazide	4–40 mg	9	E	30	acetate buffer pH 4	CO_2, N_2, NH_4^+, SO_4^{2-}	0.5
dimethyl sulfoxide	0.2–1 m*M*	10	E	1	acetate buffer pH 4	$(CH_3)_2SO_2$	0.5
Polythio-nates $S_{3-8}O_6^{2-}$	0.03–0.5 m*M*	11	E	few	about 0.5 *M* CH_3COOH	SO_4^{2-}	0.7
ammonium ferrous sulfate	1–210 mg (as CAT)	12	D	–	1–5 *M* H_3PO_4 (OsO_4 as catalyst)	ferric ion	0.2
thiosemi-carbazide complexes e.g., zinc (II)	2–20 mg	13	E	5	acetate buffer pH 4	as 9	1.0
hypophos-phite	0.2–0.5 m*M*	14	E	300	0.5–1.0 *M* H_2SO_4	H_3PO_3	1.0
nitrite	25 mg	15	E	5	0.6 *M* CH_3COOH separate CU^{2+} and NH_4^+ by prior ion exchange	NO_3^-	0.4
sodium borohy-dride	8–20 mg	16	E	1-2	1 *M* NaOH	$H_2BO_3^-$	0.1
thiourea metal complexes e.g., zinc (II)	21–44 mg	17	E	15	0.5 *M* NaOH	NH_2CONH_2, SO_4^{2-}	–
thiourea	0.1–0.3 m*M*	18	E	2	pH 10 (NaOH)	NH_2CONH_2, SO_4^{2-}	0.5

TABLE 1 (continued)

Recent Reported Titrimetric Determinations Using Chloramine-*T*

a	b	c	d	e	f	g	h
Compound	Quantity, milligrams (mg) or millimoles (m*M*)	Ref. No.	Direct (D) or excess (E)	If E, period of standing, min.	Medium for reaction	Oxidation product	Precision as percentage
indigo carmine	0.04 – 0.14 m*M*	19	E	20	1 *M* HCl	isatin sulfonate	1.0
thioglycolic acid	0.05–0.25 m*M*	20	E	180	0.2 *M* HCl	$CH_2SO_2OH{\cdot}COOH$	1.0
rongalite	0.02–0.06 m*M*	21	E	30	1 *M* HCl	$NaHSO_4$	2
cobalt (II)	0.3–30 mg	22	D	–	pH 2.0–6.5; add excess EDTA to cobalt II	Co(III)	1
ascorbic acid	0.7–7.0 mg (as CAT)	23	D	–	neutral $NaHCO_3$	dehydro-ascorbic acid	2 to 6
thioacetamide	0.5 m*M*	24	E	30 (60°C)	0.2 *M* NaOH	CH_3COO^-, NH_3, SO_4^{2-}	2
2-ethylanthraquinone (reduce to quinol)	30–60 mg	25	D	–	60:40 isopropyl alcohol: water; 0.5 *M* H_2SO_4, 1 *M* HCl, 0.05 *M* KBr	2-ethylanthraquinone	0.1

The key to the vertical columns in this table is as follows:

a is the name of the compound.
b expresses quantity in either milligrams (mg) or millimoles (m*M*) of compound determined in column a. Occasionally chloramine-*T* (CAT) is determined.[12,23]
c gives reference number to references in this review.
d indicates whether a direct (D) or indirect excess (E) method of titration was used. In all cases where excess chloramine-*T* was used, the excess of chloramine-*T* was determined by acidifying the solution (if necessary), adding potassium iodide, and titrating the liberated iodine with standard sodium thiosulfate solution.
e indicates the period of standing with excess chloramine-*T*. Presumably, the percentage excess is important, but this is often difficult to determine from the original paper.
f states the medium for the reaction.
g states the oxidation product formed during the reaction with chloramine-*T*.
h indicates the precision attained. It is difficult sometimes to assess this figure.

TABLE 2

A Comparison of Methods for the Standardization of Chloramine-*T* Solutions

Method	Factor of 0.05 *M* chloramine-*T* solution			
Against oxygen-sublimed As_2O_3				
in 2*M* HCl, 0.1 *M* KBr, rosaniline	1.0022	1.0021	1.0021	1.0021
ditto, potentiometric	1.0021	1.0020	1.0021	1.0021
in 0.5 *M* $NaHCO_3$, 0.005 *M* KI, starch	1.0021	1.0022	1.0021	1.0022
ditto, potentiometric	1.0022	1.0021	1.0021	1.0021
in 2 *M* HCl, potentiometric	1.0022	1.0020	1.0021	1.0021
excess $As^{(III)}$, back-titrated with bromate	1.0021	1.0022	1.0021	1.0021
Against ultimate standard $KBrO_3$ through pure As_2O_3				
2 *M* HCl, 0.1 *M* KBr, rosaniline	1.0021	1.0023	1.0021	1.0021
0.5 *M* $NaHCO_3$, 0.005 *M* KI, starch	1.0021	1.0021	1.0020	1.0021
Against ultimate standard KIO_3 through $Na_2S_2O_3$ using 4 equivalents of acid and 3 equivalents of iodide				
H_2SO_4 starch	1.0021	1.0023	1.0021	1.0020
HCl, starch	1.0021	1.0019	1.0021	1.0022
HOAc, starch	1.0021	1.0022	1.0018	1.0021

Standardization of chloramine-T

In the recommended methods below, the quantities actually used in the experiments reported in Table 1 are given in parentheses.

Method 1(a). Against arsenic(III) in acid solution using rosaniline hydrochloride as indicator. Pipette an aliquot (50 ml) of standard 0.05 *M* arsenic(III) solution into a titration bottle (250 to 300 ml bottle with a well-ground glass stopper), add sufficient hydrochloric acid (40 ml of 10 *M*) and potassium bromide (20 ml of 1.0 *M*) to give concentrations of 2 *M* and 0.1 *M*, respectively, in the expected endpoint volume (200 ml) and dilute appropriately (90 ml – volume of washings). Titrate with 0.05 *M* chloramine-*T* to within 0.1 ml of the endpoint. Add 2 drops (0.1 ml) of 0.1% aqueous rosaniline hydrochloride per 100 ml of solution, and complete the titration split-dropwise till the very pale yellow color changes to bright purple. The purple color develops over a period of 5 to 10 sec. On each addition of titrant, rinse down, stopper the bottle, immediately shake vigorously and allow to stand for 15 sec. Rinse down the stopper and repeat. Any delay in shaking, or too large an increment of titrant will allow premature bromination of the indicator and lead to reddening of the solution. Warning of the endpoint is given by a purple tint in the foam.

So that the endpoint will be clean and brilliant, it is necessary to delay addition of the indicator till within 0.05 to 0.1 ml before the endpoint. To locate this point, a preliminary titration may be done to the first faintly perceptible smell of free bromine, or with a reversible indicator such as quinoline yellow or *o*-dianisidine and 0.1 ml deducted from the result. However, premature bromination of the rosaniline does not prevent observation of the endpoint, and this indicator will serve for rough titration if its addition is delayed as long as possible, and the titration solution mixed vigorously as quickly as possible, after each increment of titrant. As the red color develops, more indicator is added, 4 drops at a time. At the endpoint, the red color will suddenly deepen to a much more intense purplish-red. To check the endpoint, a further addition of indicator

Footnote (continued)

is made. If the color does not change, or becomes more intense, the endpoint has been reached, but if the color reddens to orange-red, the titration is incomplete.

Method 1(b). Against arsenic(III) in neutral buffer, using starch as indicator. Pipet an aliquot (50 ml) of standard 0.05 *M* arsenic(III) solution into a conical flask, add sufficient sodium bicarbonate (100 ml of 1.0 *M* solution) and potassium iodide (10 ml of 0.1 *M* solution) to give concentrations of about 0.5 and 0.005 *M*, respectively, in the expected endpoint volume (200 ml), and titrate with 0.05 *M* chloramine-*T* solution, adding 1 ml of freshly prepared 1% starch solution about 0.5 ml before the endpoint. Finish slowly to a permanent clear very pale blue color.

Method 2. Against potassium iodate through thiosulfate. Pipet an aliquot (25 ml) of 0.05 *M* chloramine-*T* into a titration bottle, add three equivalents (15 ml of 0.5 *M*) potassium iodide, and four equivalents (10 ml of 1.0 *M*) hydrochloric acid, and titrate with 0.1 *M* thiosulfate, adding 1 ml of freshly prepared 1% starch solution as indicator 0.5 ml before the endpoint.

Standardize the thiosulfate by substituting an aliquot of standard 0.01667 *M* iodate for the chloramine-*T* in the above process.

A direct comparison of the various methods on a 5-l batch of chloramine-*T* solution is given in Table 2 and illustrates the excellence of the standardization, particularly against, or through, arsenic(III).

The stability behavior of a solid may be examined by considering the effects (among others) of light, temperature, humidity, and the presence of additives. These four effects are relevant to chloramine-*T* and are listed below.

1. **Light** – Chloramine-*T* is unstable when exposed to visible radiation.[3] When stored in a clear glass bottle exposed to sunlight, surface layers in the radiation path darkened to a pale creamy yellow color and decreased in strength as an oxidation reagent by about 0.5% per month. However, when stored in a brown glass bottle in diffuse laboratory daylight, the rate of decrease of strength was only about 0.02% per month.

2. **Temperature** – The behavior of chloramine-*T* has been examined thermogravimetrically.[27] It is reported to lose its water of crystallization gradually from above 40°C and give the anhydrous salt at 150°C. A further increase of temperature results in a violent explosion somewhere around 200°C.

Bishop and Jennings[3] reported that heating in an air oven above 40°C, or on a water or a steam bath, produced a sintered yellow substance, believed to be dichloramine-*T*, which decomposed on further heating. They suggest that the decomposition becomes violent at 120°C.

3. **Humidity** – Solid chloramine-*T*, being a trihydrate, presents both the possibilities of efflorescence and of deliquescence. Bishop and Jennings[3] found no change in the percentage purity when a sample of chloramine-*T* was stored for 10 weeks in an open dish in the absence of light. This observation would seem to rule out efflorescence. They also reported that a sample of chloramine-*T*, which had been partially dehydrated over sulfuric acid in a desiccator and then rehydrated in a hygrostat, absorbed water in excess of that required by the trihydrate. The initial conclusion that might be drawn is that chloramine-*T* is deliquescent. This is not necessarily correct, because the particle size and the surface area must be of importance in the ability of a solid to absorb water, and the sample after rehydration was said to be in the form of a fine powder, which would have a relatively large surface area for moisture absorption.

4. **Additives** – Chloramine-*T* is said by one manufacturer, R. W. Greef and Co. Inc., to be incompatible with most organic substances, acids, and ammonium compounds. One would expect it to be incompatible with other reducing substances, such as iodides and bromides, as well.

B. Liquid Solutions

The stability of a liquid solution may be considered in connection with the effects of solvent, light, pH, and temperature.

With rare exception, solutions of chloramine-*T* are prepared using water as the solvent. Bishop and Jennings[3] showed conclusively and in agreement

with Noll[2] that when stored in brown glass bottles 0.05 *M* solutions decreased in strength by only 0.02% per month. In a clear glass bottle, however, the strength had decreased by 0.4% after one week. Thus, solutions are stable in the absence of light but not in its presence. The pH of an 0.05 *M* solution is found to be 7.7.[3,28] However, there have been other claims that it is around 10.[4,15] This suggests that there is some significant difference in the quality of commercial samples available.

Recently Rao et al.[28] have reported results concerning the effect of pH on the stability of a chloramine-*T* solution. They found a pronounced decrease in room temperature stability, corresponding to a maximum loss in titer of about 2%, when solutions of chloramine-*T* were kept for up to 60 min in acetate-buffered solutions in the pH range 3 to 6. As will be discussed later, it may be deduced that there is a significant shift over this range of pH-values in the position of the equilibrium involving the $RNCl^-$ anion and dichloramine-*T* ($RNCl_2$) and *p*-toluenesulfonamide (RNH_2).

Rao et al. also conclude that at 60 to 80°C solutions of chloramine-*T* are stable only if they are highly acidic (except, of course, in the presence of acids such as hydrochloric acid) or highly alkaline. No experimental results are given, though these were said to be not reproducible.

There is little information available on the stability of chloramine-*T* in solvents other than water. Martindale, the Extra Pharmacopoeia,[29] states that chloramine-*T* is soluble to the extent of 1 part in 12 of alcohol (which is about half of the solubility found for water), and that the solution decomposes on standing.

Tomicek et al.[30] have described titrations of reducing agents in glacial acetic acid with, among other substances, chloramine-*T*. Recently, Jacob and Nair[31] have described the titration of dichloramine-*T* dissolved in anhydrous glacial acid with ascorbic acid in glacial acetic acid.

VI. NATURE OF MOLECULAR AND IONIC SPECIES PRESENT IN CHLORAMINE-*T* SOLUTIONS

The current view of the behavior of chloramine-*T* in aqueous solution is listed in the following equations.[32-34]

Chloramine-*T* is a strong electrolyte which first dissociates:

$$RNCl\,Na \rightleftharpoons RNCl^- + Na^+ \quad (1)$$

(The *p*-toluenesulfonyl, part of the molecule, $CH_3C_6H_4SO_2$, is designated by the symbol R.)

The anion then takes up hydrogen ion to form the free acid:

$$RNCl^- + H^+ = RNHCl \quad (2)$$

(The dissociation constant K_a for this acid has been calculated to be 2.38×10^{-3}, though the acid itself has never been isolated.)

The free acid disproportionates to give *p*-toluenesulfonamide and sparingly soluble dichloramine-*T*:

$$2RNCl \rightleftharpoons RNCl_2 + RNH_2 \quad (3)$$

The equilibrium constant for this reaction is said to be 6.1×10^{-2}.[32]

The dichloramine-*T* and the free acid hydrolyze:

$$RNCl_2 + H_2O \rightleftharpoons RNHCl + HOCl \quad (4)$$

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl \quad (5)$$

The hydrolysis constants for these two reactions are 8×10^{-7} and 4.88×10^{-8}.

Finally, hypochlorous acid dissociates ($K_a = 3.3 \times 10^{-8}$).

$$HOCl \rightleftharpoons H^+ + OCl^- \quad (6)$$

From these results it may be deduced[3] that the free acid and dichloramine predominate in strongly acidic solutions pH < 1, but that as the pH rises, the anion of the acid $RNCl^-$ assumes importance, reaching predominance in weakly acidic (pH 5) solutions. The concentrations of $RNCl^-$ and $RNCl_2$ are equal at pH 2.6.

Recently,[35] the equilibrium constant of reaction 3 has been reported to be 5.8×10^{-2} over the range of pH-values between 2 and 4. At pH 3.70 and 25°C the rate constant k_d of the forward reaction is given as 10.10 l mol^{-1} s^{-1} and the rate

constant k_{-d} of the reverse reaction is given as 215 $l\ mol^{-1}\ s^{-1}$; these values correspond to one of 4.7×10^{-2} for the equilibrium constant of reaction 3. The authors observe that the rate of disproportionation of RNHCl is not a particularly fast reaction. They suggest that the mechanism of disproportionation of the free acid probably involves only the reaction between the ionized and unionized species, the former acting as the donor and the latter the acceptor of the transferred positive chlorine.

Rao et al.[28] conclude from this paper that the formation of dichloramine-*T* involves the formation and eventual combination of free radicals:

$$RNCl + Cl^{\cdot} \rightarrow RNCl_2 \quad (7)$$

with minor side reactions

$$2\ Cl^{\cdot} \rightarrow Cl_2 \quad (8)$$

$$2\ RNCl^{\cdot} \rightarrow R-\underset{Cl}{N}-\underset{Cl}{N}-R \quad (9)$$

Very recently, Rao et al.[36] have attempted to confirm the existence of the dimeric compound supposed to be formed by reaction 9. They claimed that when large amounts of iron(II) and chloramine-*T* were allowed to react at pH 4.7, a yellow-white solid was precipitated. The latter appeared to be a mixture of substances. Its infrared spectrum revealed bands mostly characteristic of a *p*-toluenesulfonamide, but the solid was found to liberate iodine very slowly from acidified potassium iodide solution, and it also contained chlorine. There was a gradual loss of both chlorine and the weak oxidizing action on keeping the solid for several days. This evidence was considered to demonstrate the existence of a product like R–NCl–NCl–R.

The yellowish-white solid may be similar to that reported as being formed when chloramine-*T* solutions are exposed to visible light.[33] According to Engfeldt,[37] during the formation of this solid, there is a slow evolution of gas which had the composition 96.7% nitrogen, 2.1% carbon dioxide, and 1.2% hydrogen.

The liberation of gas has not been reported again. However, it may be noted that C. M. da Silva Cornea and W. A. Waters have reported the existence and behavior of free toluene-*p*-sulfonyl radicals[38] which are easily produced by the thermolysis or photolysis of $p\text{-}CH_3C_6H_4SO_2I$. The formation of these radicals in chloramine-*T* solutions could account for the liberation of nitrogen gas.

VII. QUANTITATIVENESS OF CHEMICAL REACTIONS INVOLVING CHLORAMINE-*T*

Bishop and Jennings have made detailed studies of a number of titrimetric reactions using chloramine-*T*. From their work, it may be concluded that arsenic(III),[3] iodide,[39] and antimony(III)[40] may be quantitatively titrated with chloramine-*T*. Titrations of a number of other substances, such as with hydrazine and nitrite, give either poor or unsatisfactory results:[41] accuracies and precisions better than 1% are probably impossible to achieve in titrations of these substances with chloramine-*T*, and this falls far short of the ±0.1% usually sought.

The mechanisms of the reactions that occur in titrations of various reductants with chloramine-*T* are almost completely unexplored. In this field there is only one publication, and that is an early one (1936); it deals with the reaction of hydrogen peroxide with chloramine-*T*.[42] Chloramine-*T* is obviously a strong oxidant, and one whose strength increases with decreasing pH. For example, it will oxidize chloride to chlorine, bromide to bromine, and iodide to iodine at pH values less than 0.3, 5.0, and 9.0, respectively. Some workers[43] have attempted to measure the redox potential of the chloramine-*T*-sulfonamide system. However, unless a reversible redox couple is established at an indicator electrode, the results of such measurements are dubious, to say the least, and the chloramine-*T*-*p*-toluenesulfonamide system does not behave reversibly at a platinum electrode.

The rate of free halogen formation is apparently very fast. This reviewer was unable to determine the rate of formation of bromine in acetate buffer by measuring the absorbance due to the formation of bromine on mixing chloramine-*T* and bromide ions at low concentrations, around 10^{-4} to 10^{-5} mol dm^{-3}, for the reaction attained completion in less than a few seconds.

VIII. METHODS OF ENDPOINT DETECTION IN CHLORAMINE-*T* TITRATIONS

Chemical Indicators

Bishop and Jennings have examined the behaviors of a number of indicators for use in titrations of arsenic(III) with chloramine-*T*.[44] In addition to *p*-rosaniline, which is specific for bromine, amaranth and bordeaux are recommended as irreversible indicators. Reversible indicators such as quinoline yellow, tartrazine, and *p*-ethoxychrysoidine have been used successfully, though sometimes they give an appreciable indicator error. In excess titrations, where an excess of chloramine-*T* is added to the solution being analyzed, this excess is usually determined by acidifying and adding potassium iodide. The liberated iodine is then titrated with standard sodium thiosulfate solution, using starch as an iodine indicator.

Instrumental Endpoints

The most widely used method has been that of potentiometric titration, using a bright platinum indicator electrode whose potential is measured with respect to a saturated calomel reference electrode (see, for example, References 12, 23, and 45). Other methods used have included differential electrolytic potentiometry[46] and amperometry[22] using two polarized electrodes. A rotating platinum electrode has also been used for amperometric titrations of arsenic(III),[52] tin(II), and ascorbic acid.[53]

IX. ASSESSMENT OF THE CURRENT AND FUTURE USAGE OF CHLORAMINE-*T* AS A TITRIMETRIC REAGENT

Current Usage

The current usage of chloramine-*T* is limited. In Table 3, I have attempted to give a critical comment on each of the recent papers listed in Table 1. However, if I adopted the standard of 0.1% accuracy and further required that all proposed methods should be subjected to some statistical test for measurement of precision, few if any of the recently proposed methods would be acceptable.

Earlier work, referred to in References 3, 4, 5, and 41 has established some useful chloramine-*T* titrimetric methods such as those for arsenic(III), iodide, and antimony(III). Its proposed use as a replacement for iodine, as recommended by A. Noll,[2] has been amply justified.

(An asterisk reference is given to a paper that I regard as one having analytical significance rather than one describing a chemical reaction.)

Future Usage

A pessimistic view of the future use of chloramine-*T* would be that it has no future. This view is based on the obvious fact that in only a very few redox titrations does it behave with some advantage over, say, standard solutions of iodine, bromate, or iodate. Further, the last three reagents are easily available at a purity of 99.9% compared to the 99.0% purity of chloramine-*T*.

A more optimistic view of the future would be as follows: chloramine-*T* is an extraordinarily versatile redox titrant. It can be used in both strongly acidic and strongly alkaline media. In many applications it will satisfactorily replace a number of other redox titrants such as iodine, bromine, *N*-bromosuccinimide, iodine monochloride, hypochlorite, bromate, and iodate. Its stabilities, both in the solid state and in aqueous solutions, are adequate for precision titrimetry at the 0.1% level, provided of course, that it is stored in the absence of light. In addition it may be standardized accurately using arsenic(III).

In the course of preparing the review a few questions have arisen which concern the use of chloramine-*T* in titrimetry and upon which further work is needed. These relate to:

1. The use of chloramine-*T* in alkaline solution and the use of catalysts.
2. The reaction of chloramine-*T* with p-toluenesulfonamide.

The Use of Chloramine-*T* in Alkaline Solutions and the Use of Catalysts

A number of chloramine-*T* titrations have been reported to be feasible in alkaline solutions (for recent examples, see References 16, 17, and 24). There is also a paper on the titration of stannous chloride dissolved in glycerol with chloramine-*T* in bicarbonate media.[50]

TABLE 3 (continued)

19	*Indigocarmine* The paper states that both chloramine-*T* and iodine in alkaline medium ruptured the carbon-carbon double band in indigocarmine. This conclusion was based, for example, on the finding that four equivalents of chloramine-*T* are required to oxidize 1 mol of indigocarmine.
20	*Thioglycolic acid* The direct titration in the presence of iodide gave the product $(S\ CH_2\ COOH)_2$, while with excess chloramine-*T* 3 mol of chloramine-*T* were required for each mol of CH_2 SH COOH; suggesting the formation of the sulfonic acid CH_2 (SO_2OH) COOH. This method gives poor titrimetric precision.
21	*Rongalite* Rongalite recrystallized from aqueous solution gave crystals having the formula $Na\ HSO_2 \cdot HCHO \cdot 2H_2O$. One mol of the latter required 2 mol of chloramine-*T*. It was confirmed that added formaldehyde was not oxidized by chloramine-*T* under the chosen experimental conditions. Iodine behaved similarly to chloramine-*T*. The results presented are sparse.
22	*Cobalt* The redox potential of the cobalt(III) to cobalt(II) couple is lowered by adding EDTA. This makes it possible for chloramine-*T* to oxidize cobalt(II) in the pH range 2.0 to 6.5. The method of attaining such a pH range is not stated. More results would be needed to confirm this as a method for cobalt(II).*
23	*Ascorbic acid* In this method, excess ferrocyanide is added to chloramine-*T* in the presence of iodide in bicarbonate medium. The ferrocyanide formed is titrated potentiometrically with ascorbic acid. Since ascorbic acid has been reported to be oxidized directly by chloramine-*T* this seems to be an odd way of determining chloramine-*T*.
24	*Thioacetamide* In order to oxidize thioacetamide quantitatively the temperature must be at least 60°C and the solution must be alkaline. At room temperature (28°C), the reaction appears to be very incomplete. This paper does not contain enough data to define a titrimetric method.
25	*2-Ethylanthraquinone* In this method 2-ethylanthraquinone is reduced to its hydroquinone by passing through a Jones (zinc-amalgam) reductor column. The hydroquinone is titrated potentiometrically in the presence of bromide with chloramine-*T*. It was found and reported elsewhere[47] that potassium bromate would not oxidize the hydroquinone without large-scale side reactions.

*Chloramine-*T* has been reported to react with EDTA.[15]

There are papers on the use of osmium tetroxide as a catalyst for titrations with chloramine-*T* in alkaline media[48,49] as well as in orthophosphoric acid in the presence of chloride.[12]

One must therefore conclude that chloramine-*T* behaves as an oxidizing agent in alkaline media, but the mechanism by which it does so seems to be quite unknown, as does the effect of osmium tetroxide. These questions need to be investigated, as indeed does the entire question of the rates and mechanisms of the reactions of chloramine-*T*.

The Reaction of Chloramine-*T* With *p*-Toluenesulfonamide

p-Toluenesulfonamide is supposed to be the final product that is formed when chloramine-*T* acts as an oxidizing agent. Clearly, when chloramine-*T* is used in excess both it and the sulfonamide are present in solution. If a stoichiometric reaction is to take place between chloramine-*T* and the substance titrated, no further reaction is allowable. It is surprising that there are no reports of any recent investigation to determine whether there is any further reaction between these two com-

pounds, for H. D. Dakin reported,[51] in 1917, that benzaldehyde *p*-sulfonamide is formed when they are heated together in aqueous solution.

In view of the considerable number of titration methods using excess chloramine-*T*, the effect of the presence of *p*-toluenesulfonamide should be examined.

APPENDIX

Toxicity of Chloramine-*T*

Chloramine-*T*, listed in *Chemical Abstracts* as Sodium *N*-chloro-*p*-toluenesulfonamide has a number of uses in addition to those in analytical chemistry, for example in water purification.[54] Its relative cheapness has apparently been due to the availability of the ortho- and paratoluenesulfonylchlorides. The former is used in the production of saccharin, and the latter is a by-product for the production of chloramine-*T*.[55] Possible methods of preparation are given in Reference 56.

The toxic hazard rating code lists the hazard analysis of chloramine-*T*, as either slight or unknown.[57] However, some recent analytical papers concerned with the colorimetric detection of around 25 ppm chloramine-*T* (added as a preservative) in dairy products[58] and in minced meat and farinaceous foods[59] have repeated previous statements that chloramine-*T* may be highly toxic in a dose of 500 mg.[60] The toxicity is ascribed to the reaction between chloramine-*T* and split products of proteins in ingested foods producing toxic nitriles. For example, Serin showed that the reaction between chloramine-*T* and glycine produced cyanogen chloride.[60] Much earlier, Dakin had reported[61] that traces of hydrocyanic acid were produced in this reaction though, at that time, apparently he had no analytical method which would have determined cyanogen chloride.

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