AN INVESTIGATION OF ETHYLENEDIAMINETETRA-ACETIC ACID AND ITS SALTS AS PRIMARY STANDARDS IN VOLUMETRIC ANALYSIS. APPLICATIONS TO THE ANALYSIS OF MINERALS.

by

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ABSTRACT

The introduction to this work is divided into two sections. The first section is a very short outline of the theory of complexometry with the emphasis on ethylenediaminetetra-acetic acid, E.D.T.A., as titrant. Detailed reviews of previous work related to the subject investigated and some theoretical background accompany each part of the thesis. The practical section contains detailed information about the techniques adopted throughout this work and about reagents and apparatus used.

The thesis consists of four parts.

The first part describes an investigation of properties of ethylenediaminetetra-acetic acid and of its lithium, potassium, ammonium and sodium salts with a view to establishing whether these compounds can be used as primary standards in metal-ion titrations.

In the second part, different aspects of titrations of several metals by E.D.T.A. are investigated. The metals considered are lead, zinc, bismuth and manganese. Here are compared results obtained by using different compounds of the same metal as standard solutions and by applying to the same standard solution different methods of titration with different indicators. The effect of heating the titrant before titration, of approaching the end-point from different sides, of interferences, masking and of other miscellaneous changes of conditions are described. Especially carefully examined are the neutralization of bismuth solutions by ammonia and the conditions of manganese titration. Finally, results obtained by titration of standard solutions prepared from various metals by the same E.D.T.A. are compared.

The third part describes exclusively complexometric titrations of tin. Also here from the variety of methods found in the literature only a few are chosen for investigation and only two are recommended for use. Conditions for distilling tin and of titrating tin in the distillate are carefully examined. Interferences and masking effects with special emphasis on the determination of tin in the presence of antimony are examined.

The fourth part deals with the analysis of certain complex materials. Tin and lead contents are determined in an alloy and in ores by applying successfully the methods of titration investigated in previous parts and found suitable.

The final pages contain the bibliography.

CONTENTS

INTRODUCTION

1. The origin of this investigation.

Work in this laboratory on the use of ethylenediaminetetra-acetic acid as a titrant in volumetric analysis gave rise to the opinion that the dihydrated disodium salt of this acid, the form in which that reagent is generally available commercially, is not a sound primary standard for work of the highest accuracy. Even after purification and drying under closely controlled conditions, the substance still seemed to fall short of a desirable standard.

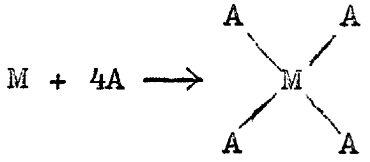
In view of the widespread use and many applications of this reagent in analysis, it seemed worthwhile testing this opinion by means of a critical investigation of this question of standardisation of so important a reagent.

The ready availability in modern times of many metals of a purity better than 99.9 or even 99.99 per cent. suggested that the metals themselves might well provide excellent standards on which to base the standardisation of the complexometric reagent. This led to an investigation of zinc, lead, bismuth, manganese, and tin as standards.

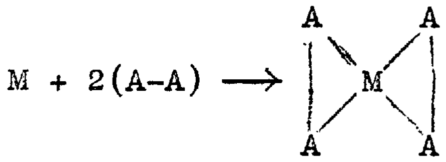
Finally, the application of the E.D.T.A. titration to the determination of tin, which has always been one of difficulty and uncertainty in accurate work, to the determination of lead in galena and of manganese in pyrolusite seemed to be desirable extensions of the use of complexometric titrations and were accordingly investigated.

2. General.

When a metal ion combines with an electron pair donor, a complex or co-ordination compound is formed. If the substance contains more than one donor group able to combine with the same metal ion, so that rings are formed, the resulting compound is called a chelate compound or metal chelate. The term is derived from the Greek "chele" for a claw, because the ligand grasps the central ion from at least two sides. The electron pair link here can be ionic as well as covalent.



complex



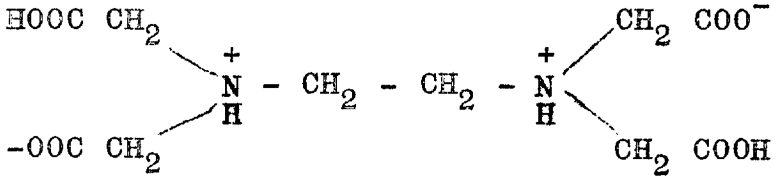
chelate

Usually, the donor atoms which combine with metals are non-metallic elements of the fifth and sixth group of periodic system, e.g. nitrogen, sulphur, oxygen etc. Chelates form a specific group with characteristic behaviour and properties, one of which is a comparatively great stability. The most stable are known to be chelates containing 5- or 6-membered rings. Rings of smaller number of members are subjected to a considerable strain, so they are less stable; rings of larger number of members, having too long a chain, are exposed to the entropic effect, and that decreases the stability of the chelate as well. Various methods of detection of chelate structure exist. Metal chelates give no chemical reactions characteristic for the said metal. They are usually coloured or have a specific absorption spectr~~a~~um, have a lower conductance, show a drop of pH and often show a decreased aqueous solubility. The stability of a chelate is expressed by a formation or stability constant

$$K = \frac{[\text{Me chelate}]}{[\text{Me}][\text{chelating agent}]}$$

The greater is the value of K, the more stable is the chelate. There are various ways of determining the stability constant: measurement of pH, ion-exchange method, polarographic measurements of pM etc. An apparent formation constant, used sometimes to characterize a chelate, is related to the stability at a particular pH. It is calculated from known ionization constants. The pH produces a considerable effect on the formation of a chelate. At low pH the chelate ionizes, while at high pH a hydrolysis of a metal ion occurs. A very large number of applications is found for water-soluble chelates, formed by some aminopolycarboxylic acids with metals. In 1930, I.G. Farben marketed a few aminopolycarboxylic acids as metal-chelating agents for industrial applications. In the early 1940's various workers characterized metal complexes of certain of these acids. But only in 1945-46 did Schwarzenbach publish results of fundamental studies of their complex-forming abilities and created a sound theory of a new branch of titrimetric analysis, based on chelate formations between titrant and the titrated metal, and called complexometry, chelatometry or sometimes chelometry. If a titration is to be successful as a method and to give acceptable results, several conditions must be observed. The reaction between titrant and the titrated substance must proceed immediately and stoichiometrically, no decomposition of the reaction product should occur, no intermediate reaction products should be produced and the end-point should be easy to detect either by visual or by instrumental methods. The said aminopolycarboxylic acids fulfil these requirements. Soon metal indicators were introduced, which permitted visual detection of the end of titrations. After the first publications of Schwarzenbach various workers investigated different compounds as possible titrants for metals. Schwarzenbach[1] used di-(2-aminoethyl)ether-NNN'N'-tetra-acetic acid. or ETHENTA and di-(2-aminoethyl)ethyleneglycol-NNN'N'-tetra-acetic acid or GLENTA for titrations of alkaline-earth metals. Bernejo Martinez and co-workers[2] determined successfully copper and zinc by back titration by 1:2-di-(2-aminoethoxy)ethane-NNN'N'-tetra-acetic acid or AEGT at pH 11 to 12 in the presen~~t~~ce of murexide as indicator. The same authors used 1:2-diaminocyclohexane-NNN'N'-tetra-acetic acid or ADCT for titrations of iron, aluminium, copper and zinc. Sanderson and West[3] found that calcium can be determined in the presence of magnesium by 1,2-bis[2-di(carboxymethyl)-aminoethoxy]ethane or EGTA which is unreactive towards magnesium. The same authors succeeded in titrating calcium in the presence of a large excess of barium by 1,2-diaminocyclohexane-NNN'N'-tetra-acetic acid, calcichrome being used as indicator, and Cu^{2+} ions by ethylenediamine-NNN'N'-tetropropionic acid or EDTP at pH 9 with Ponceau 3R as indicator, while no interference from alkaline-earth metals, magnesium and other metals in limited concentrations was observed. Přibil and Vesely[4] used triethylene tetramine hexaacetic acid or TTHA for titration of bivalent and tervalent metals. They investigated also the possibility of using 1,2-diaminocyclohexane tetra-acetic acid or DCYTA, 1,2-diaminopropane tetra-acetic acid or MEDTA, diethylene triamine-penta-acetic acid or DTPA, ethyleneglycol-bis(β-aminoethyl ether)-tetra-acetic acid and nitrilotriacetic acid or NITA.

Genkichi Nakogawa and co-workers[5] investigated the use of EGTA for the titration of calcium in the improved conditions. Many other compounds of this group were investigated as possible titrants, but the best of all as titrant for metals proved to be ethylenediaminetetra-acetic acid introduced by Schwarzenbach or shortly, E.D.T.A., used mostly in the form of its disodium salt dihydrate and known under various trade names as Complexone, Sequestric acid, Trilon B, Versene, Nullapon, Nervanaid, Iminol D, Calsol, Chelaton, Idranol, Titra Ver and others. Besides its use as a titrant in analytical chemistry, E.D.T.A. has found many varied applications worthy of mention[6]. It is used for softening the water; in negative catalysis; as anti-oxidant; as a boiler scale remover; for clarification of liquids, in particular of wines; for cleaning of metal objects from rust, scale, etc.; as a detergent additive; for dyeing; in polymerization-emulsion systems; in germicides; as an agent preventing side-reactions in chemical syntheses; for purification of chemicals and lubricating oils; in crystallization processes; for stabilization of peroxides and of vitamin C; and for decontamination of equipment from traces of radioactive metals. The applications of E.D.T.A. in research cover the control of metal ions concentration (acting as metal buffer), elimination of metal ions from animals, separation of metals by elution of cation exchangers, fractional precipitation, colorimetric determination of metals forming coloured complexes with E.D.T.A., etc. Ethylenediaminetetra-acetic acid is a diamino dicarboxylic acid of a typical betaine structure, with two strongly acidic protons, which ionize in the acid range, and two ammonium complex-forming protons, the first of which ionizes in the pH region of about 6.3 and the second at a pH of 11.5 only[7]. Thus the acid has four ionization points characterized by equilibrium constants of $pK_1 = 2.0$, $pK_2 = 2.7$, $pK_3 = 6.2$ and $pK_4 = 10.3$.



The general tendency of acetate anions towards complex formation added to the chelate effect produced by 6 ligand atoms (which number corresponds to the co-ordination number most frequently encountered among the metals) makes E.D.T.A. an excellent complexing agent forming 5-membered rings. E.D.T.A. forms complexes of various stability with nearly all metals of the periodic system. Even the complexes with alkali metals are known[1,8], but the very low stability makes impossible their use in analysis. The complexes are usually very soluble, but some of these with bi- or tervalent metals can also be separated in a solid state. Usually, E.D.T.A. complexes are colourless, except these formed with few coloured cations, e.g. nickel, cobalt, chromium and tervalent manganese, which are also highly coloured. As a rule, one gram-ion of E.D.T.A. reacts with one gram-ion of most cations while two gram-ions of H^+ are produced, independent of the valency of the metal, according to the reactions:

$$M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{--} + 2H^+$$

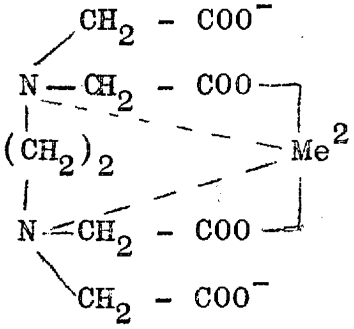
$$M^{3+} + H_2Y^{2-} \rightleftharpoons MY^{-} + 2H^+$$

$$M^{4+} + H_2Y^{2-} \rightleftharpoons MY + 2H^+$$

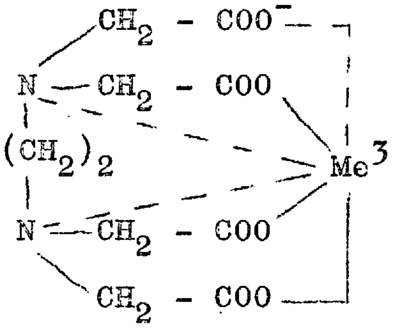
where Y is the anionic part of E.D.T.A.

This is why the solutions in complexometric titrations must be carefully buffered: if they are not, a considerable drop of pH, sometimes by several units, may occur owing to the liberated hydrogen ions.

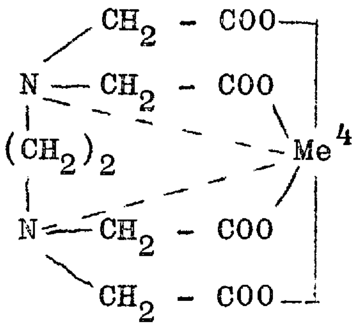
The metal complexes have the following structures[9]:



Complex with bivalent metal ion.



Complex with tervalent metal ion.



Complex with quadrivalent metal ion.

At pH < 3 hydrogen complexes MHY^{3-} are known. In strongly alkaline solutions hydroxy-complexes $M(OH)Y^{5-}$ or $M(OH)_2Y^{4-}$ can be formed. Ter- and quadrivalent metals (aluminium, iron, thorium) can form hydroxy-complexes even in neutral solutions. Some quadrivalent metals have a tendency to form complexes in which the ratio metal:Y is 1:2[1]. But all these complexes are usually not formed and have no analytical significance.

It can be seen from the above that all the metal complexes have the same composition. They differ only by charge, which depends on the valency of metal ion. The stability of metal-E.D.T.A. complexes depends on the metal valency and on the pH of solution. At low pH the stability of complexes decreases because more H^+ ions are present in the system and the equilibrium tends to shift to the left, e.g. the dissociation of the complex occurs. Thus, the more stable is the complex, the lower is the pH at which the E.D.T.A. titration is still possible. In general bivalent ion complexes are stable in more basic solutions, at pH 5 to 14, while complexes of tervalent ions exist at pH 2 to 14 and those of quadrivalent ions at pH 1 to 14. But, except for the alkaline-earth metals, the complexing efficiency does not decrease appreciably unless the pH is very low. As it was pointed out above, E.D.T.A. is used mainly as titrant for metals over a wide range of concentrations. In direct titration the metal ion in solution is titrated by E.D.T.A. until the visual or physical method indicates the end of the titration. When the complex is formed too slowly or a metal cannot be kept in solution at the pH needed to form a complex or when no suitable indicator for direct titration is available, the introduction of back titration is an advantage. E.D.T.A. is then added in excess and the part not used to complex the metal ions is back titrated by another metal ion, usually magnesium or zinc. When the above difficulties are encountered it is sometimes advantageous to introduce substitution or replacement titrations. Thus, the cation is treated with an excess of E.D.T.A. complex of other metal (usually magnesium, but sometimes also zinc, cadmium or copper), provided that the said complex is less stable than the E.D.T.A. complex of the titrated metal. Magnesium, liberated from its complex with E.D.T.A. by the titrated metal is then titrated by E.D.T.A. solution, according to the reaction

$$M + MgY \longrightarrow MY + Mg$$

Indirectly also anions and metals which do not form complexes with E.D.T.A. can be determined. As an example can serve determination of phosphate by E.D.T.A. titration. Phosphate is precipitated as $MgNH_4PO_4$, the precipitate is dissolved, magnesium is titrated by E.D.T.A. and the amount of PO_4 is calculated from the formula. A special kind of E.D.T.A. titrations is based on a pH effect[10]. To a metal solution an excess of E.D.T.A. is added and the H^+ ions liberated during the formation of complex are titrated either by a basis, potentiometrically or with the use of an ordinary acid-base indicator, or iodometrically. However, this method has several disadvantages. Its use is limited to the pH > 7; weak acids and their salts produce some influence; there is a need of careful neutralization before titration if an acceptable end-point is to be obtained. The method is good when bivalent and rare-earth metals are titrated and the use of titrants other than E.D.T.A. is preferable. This method is recommended mostly as a preliminary determination, when a back titration is to be done and it is desirable to know approximately the amount of E.D.T.A. to be added.

The end-point of a complexometric titration can be detected in various ways. At pH 5 to 6 good results are obtained by conductometric titration[11], and still more accurate results are seen when a low-frequency conductometric method is applied. High frequency titrations[12,13] are very sensitive and even 0.0002 M solutions can be titrated in this way. Spectrophotometric titrations, introduced first by Sweetser et al.,[14] are especially useful when a solution has a large volume and a small concentration (up to 0.0001 M)[15]. They are very sensitive and give a sharp end-point in the presence of an indicator. They can be applied also in the ultraviolet region without indicators. The thermochemical effect[16] found application especially in the detection of end-point of bivalent metal~~s~~ titrations. A graph is constructed where the change of temperature is plotted against amount of E.D.T.A. added. Chronopotentiometric titrations are useful when the titrated solution has a small volume and a low concentration and while stirring is undesirable. A graph is constructed where square roots of transition times are plotted against amount of E.D.T.A. added. Also coulometric, potentiometric and amperometric determinations of end-point found wide applications. Visual end-point detection, based on the use of indicators, is most frequently used. For this purpose Schwarzenbach introduced so-called metal indicators. They are dyestuff chelating agents with several ligand atoms, able to form complexes (exactly as E.D.T.A. does) with specific cations. The colour of these complexes differs from the colour of dyestuff itself and so the change of colour indicates the change of pM, e.g. the presence or absence of the cation in solution. Generally in those complexes the ratio metal:indicator is 1:1, but complexes of a ratio 1:2 or 2:1 are known. Some of them can also take up protons and serve as pH indicators. Metal indicator added in small amounts should make the solution strongly coloured near the end-point, when nearly all the metal is complexed by E.D.T.A. It must be sensitive enough to produce a sharp colour change as near the equivalence point as possible. The reaction should be specific or at least selective. Indicator-metal complex must be sufficiently stable, but always less stable than the E.D.T.A.-metal complex, otherwise blocking of the indicator occurs before the end of the reaction. The difference between stability constants of indicator-metal and E.D.T.A.-metal complexes must be at least 4[17]. All the above requirements should be fulfilled at the pH needed for the reaction. Chemically, metal indicators are mainly divided into azo-dyes, phthaleins and sulphonphthaleins, triphenylmethane dyestuffs and phenolic substances. Besides some indicators of structure different to the above, some red-ox and some acid-base indicators are occasionally used in complexometric titrations.

In analysis of complex materials containing several cations the effect of some of them on E.D.T.A. or indicator must be prevented. This is done by control of pH of the solution, prior isolation of the undesired cations before titration, by use of selective indicators or by masking. A cation can be masked by complexing, provided the complex is more stable than that with E.D.T.A., by precipitation or by transforming to a different valency state. A variety of masking agents are described. It would be useful to mention the best known of them. Cyanide ions complex cobalt, nickel, copper, mercury, zinc, cadmium, silver, platinum and bivalent iron. Tiron is used to mask aluminium and quadrivalent titanium. Triethanolamine forms complexes with aluminium, quadrivalent titanium and with small amounts of tervalent iron, with manganese in strongly alkaline medium and with tin. Iodide ion forms a soluble complex with mercury. Some heavy metals can be precipitated by sulphide, thioacetamide[18] or diethyldithiocarbamate. Other metals can be precipitated as hydroxides. Fluoride ions mask by precipitation or complex formation aluminium, titanium, quadrivalent tin and thorium, rare-earth elements, alkaline-earth metals and magnesium. BAL, which is the trade name of 2:3-mercapto-1-propanol, behaves similarly towards silver, mercury, cadmium, zinc, arsenic, antimony, tin, lead, bismuth, copper, cobalt and nickel. Thiourea is known as a masking agent for copper and tervalent thallium; thiosulphate for bivalent copper and silver in slightly acidic medium;

tartrate - for titanium, hexavalent uranium, tervalent antimony, quadrivalent tin, aluminium and other heavy metals; citrate behaves similarly. Oxalate is known as masking agent for quadrivalent tin; carbonate - for uranyl ion; nitroso-R salt - for cobalt; o-phenanthroline[7,76] - for copper, nickel, cobalt, iron, chromium, aluminium and calcium; cystein[19] - for copper and mercury; thioglycollic acid[20] - for lead, bismuth, cadmium, silver, mercury, zinc, thallium, indium, tin and iron in alkaline solutions; acetylacetone[21] - for tervalent iron, uranium, aluminium, beryllium, palladium, molybdenum and partly copper, mercury, chromium and titanium; salicylic acid[22] - for aluminium in acidic medium. Ascorbic acid is used to reduce tervalent thallium, bivalent copper, tervalent iron and manganese of higher oxidation states. Hydrazine reduces quinquivalent arsenic and tervalent iron. Hydroxylamine hydrochloride can be used instead of ascorbic acid as a reducing agent.

When a suitable method is chosen and interfering ions are removed or masked a complexometric titration can be performed.

3. Practical.

This thesis is concerned with only one aminopolycarboxylic acid used as complexometric titrant - with ethylenediaminetetra-acetic acid, E.D.T.A. - and only methods with a visual end-point detection are described. With the exception of part I, where several salts of this acid as well as the acid itself are examined, in all other parts the disodium salt dihydrate only was used. Although the name "E.D.T.A." is used by various authors for any one of the above-mentioned compounds, throughout this work, for the sake of clearness, this abbreviation is reserved only for the disodium ethylenediaminetetra-acetate dihydrate. When other salts or the acid form are concerned, their full name is given. In part II, standards prepared from different metals were compared and their use investigated. Part III is reserved for the investigation of tin determinations and part IV is concerned with the analysis of complex materials containing tin and lead.

Before beginning the main part of this thesis some notes concerning details of the work, adopted throughout all the further stages, must be made.

The water used, if not stated otherwise, is always distilled water, obtained from the general laboratory ~~m~~still. "Purified" solids means solids of analar purity grade, which were subjected to an additional purification by recrystallization or by other means. Their purity is thus probably higher than that of analar reagents. All the reagents used were, if available, of analar purity grade. E.D.T.A. used to prepare solutions in parts I and II was of analar grade and purified additionally according to the method of Blaedel and Knight[33]. E.D.T.A. used in parts III and IV, where its solutions were always standardised by metals, was of analar grade only. Its solutions were stored in Pyrex bottles. Blank determinations for the purity of reagents were always carried out and the necessary corrections, if any, were applied in the calculations. All the volumetric apparatus, e.g. burettes, pipettes and volumetric flasks were calibrated. When preparing standard solutions, titrating and also each time immediately before taking an aliquot from a flask the temperature of the solution was noted and the temperature correction applied to the volume taken. Thus all the molarities and volumes cited in this work were reduced to values at 20°C. All weighings were made on an Oertling air-damped aperiodic balance, the readings being reproducible to two or three units in the fifth decimal place. Although the balance was read to the fifth decimal place, there is, of course, a doubt as to the significance of this last figure. It is given mainly as a support for that of the fourth decimal place. The set of brass weights was calibrated and the corrections found applied to the weights. When substances used as standards were weighed, their density was either found in papers or, if necessary, determined and buoyancy corrections per gram were calculated according to the formula[7]:

$$\text{correction} = \frac{1 \times 0.0012}{\text{density of the substance weighed}} - 0.000143$$

These corrections were added to the weights of the substances and thus all the accurate weighings are related to vacuo. When no suitable indicator could be found or applied, the narrow-range indicator-paper was used with the aid of which changes of pH with the accuracy to 0.3 unit could be easily seen. If the concentration of acids or ammonia is not mentioned, it is understood that concentrated reagents are concerned.

A. <u>De-ionized water</u>.

For some determinations the ordinary distilled water is not pure enough and if it is used, some impurities can be introduced. This is particularly important when E.D.T.A. is used as standard. Then even very small amounts of heavy metals present usually in distilled water coming from a laboratory ~~p~~still with metal tubings could react with E.D.T.A. and therefore should be absent.

In that case the use of de-ionized water is necessary. De-ionized water was prepared by passing the ordinary distilled water through a column filled with "Bio-deminrolit" N7 Permutit ion-exchange mixed-~~l~~bead resin at a flow rate of about 5 ml per min. The column yields 1000 times its own volume of water. The resin was discarded after use. The resulting de-ionized water contains only 0.02 to 0.04 p.p.m. of solid residue and its specific conductivity is about 0.2×10^{-6} to 0.05×10^{-6} mho. This water, stored in polyethylene bottles, can be used in very accurate determinations.

B. Purifying of ammonia and acids.

For very accurate determinations the usual acids or ammonia of analar grade, which contain some amount of foreign ions, may not be pure enough. The additional purification is done by means of isopiestic distillation described by Irving and Cox[24]. A polythene beaker containing a needed amount of de-ionized water with exposed liquid area of about 30 cm^2 is placed in a very large desiccator on a grill of glass rods used instead of the metallic net. To the bottom of the desiccator are poured carefully large amounts of the reagent to be purified. The lid (grease-free) is replaced and the apparatus is left at room temperature for several days.

It is desirable to rock the desiccator occasionally or to expose it to changes of temperature, to assist mixing of solutions. Under these conditions the vapours of the reagent are absorbed in de-ionized water and a solution of a very great purity is obtained. In that way pure hydrochloric acid and ammonia were prepared, which were then used mostly in experiments described in parts I and II of this thesis, whenever stated. From 500 ml of hydrochloric acid (sp.gr. 1.18) and 125 ml of de-ionized water about 10N pure acid solution was obtained after 3 days of exposure. From 500 ml of aqueous ammonia (sp.gr. 0.88) and 250 ml of de-ionized water about 7N pure ammonia solution was obtained after 3 days of exposure. The purified reagents were stored in polythene bottles.

C. Calibration of volumetric apparatus.

The method applied to calibrate the volumetric glassware was that described by Kolthoff and Stenger[25]. Volumes of the apparatus were calculated according to the weight of water delivered (pipettes, burettes) or contained (volumetric flasks), to which temperature corrections supplied by the ~~National Bureau of Standards~~ British Standards Institution were applied. Burettes were first tested for leakage after 30 min. The water was delivered drop by drop and no outflow time was considered. Pipettes were held at an angle against the side of the beaker, touching the glass during the delivering. The outflow time of pipettes was checked. All the calibrated volumetric glassware was cleaned with a mixture of chromic-nitric acids when necessary. Values obtained from calibrations are quoted in the following tables.

Volumetric flasks

Nominal value in ml	Calibrated value in ml.	Mean deviation in ml.	Number of calibrations
1000	999.83	± 0.051	3
500	499.90	± 0.015	2
250	249.82	± 0.008	2
100 (AAL 7)	99.95	± 0.012	2
100 (AAL 7(1))	99.90	± 0.003	2
50 (8606)	49.95	± 0.001	2
50 (5200)	50.01	± 0.001	2

Pipettes

Nominal value in ml.	Calibrated value in ml.	Mean deviation in ml.	Outflow time in sec.	Number of calibrations.
50 A	50.06	± 0.001	27	3
50 B	50.04	± 0.001	37	3
25	24.99	± 0.001	20	3
25^{x}	25.01	± 0.003	29	3
25^{xx}	24.93	± 0.003	19	3
10	10.01	± 0.002	18	3
5	5.00	± 0.002	15	3

Burettes

	Nominal value in ml	Calibrated value in ml	Mean deviation in ml.	Number of calibrations
	0-5	5.02	± 0.003	2
Large burette	0-10	10.01	± 0.003	2
Leakage after	0-15	15.03	± 0.005	2
30 min. = 0	0-20	20.04	± 0.008	2
	0-25	25.06	± 0.005	2
	0-30	30.07	± 0.001	2
	0-35	35.08	± 0.011	2
	0-40	40.08	± 0.009	2
	0-45	45.09	± 0.007	2
	0-50	50.09	± 0.004	2
Small burette	0-1	1.01	± 0.002	2
AAL 7	0-2	2.00	± 0.001	2
Leakage after	0-3	3.00	± 0.002	2
30 min. = 0	0-4	3.99	± 0.003	2
	0-5	4.97	± 0.003	2
	0-6	5.97	± 0.002	2
	0-7	6.98	± 0.002	2
	0-8	7.98	± 0.001	2
	0-9	8.98	± 0.004	2
	0-10	9.98	± 0.001	2

	Nominal value in ml	Calibrated value in ml.	Mean deviation in ml.	Number of calibrations
Small burette AAL 7(1) Leakage after 30 min. = 0	0-1	1.03	< 0.001	2
	0-2	2.01	< 0.001	2
	0-3	3.01	± 0.001	2
	0-4	4.04	± 0.002	2
	0-5	5.05	± 0.005	2
	0-6	6.05	< 0.001	2
	0-7	7.05	± 0.002	2
	0-8	8.07	± 0.003	2
	0-9	9.05	± 0.006	2
	0-10	10.06	± 0.005	2

D. Calibration of weights.

The weights used were of brass and were calibrated on the Oertling balance by the substitution method described by Richards[26]. They were compared with an exact 10-g weight, calibrated by the National Physical Laboratory, and thus the corrections are absolute. The calibration of the weights was done once, at the beginning of the two years period of research. ~~During the time of research weighings were not done very frequently~~. Clements[27] repeated calibration of a set of brass weights every 6 months. Although he used the weights quite frequently, no change in the corrections was found after 2.5 years. The corrections found are quoted in the following table.

Nominal value of weight in grams	Correction in mg	Nominal value of weight in grams.	Correction in mg
0.01^{x}	+ 0.02	0.01 rider	0.00
0.01^{xx}	- 0.03	0.02 rider	+ 0.04
0.02	+ 0.02	0.03 rider	+ 0.04
0.05	+ 0.03	0.04 rider	+ 0.06
0.10	+ 0.02	0.05 rider	+ 0.03
0.10^{x}	+ 0.06	0.06 rider	+ 0.01
0.20	- 0.03	0.07 rider	+ 0.07
0.50	+ 0.03	0.08 rider	+ 0.03
1.00	+ 0.03	0.09 rider	+ 0.07
1.00^{x}	+ 0.03	0.10 rider	- 0.01
1.00^{xx}	+ 0.03	0.20 rider	- 0.05
2.00	+ 0.08	0.30 rider	- 0.04
5.00	+ 0.09	0.40 rider	- 0.01
10.00	+ 0.16	0.50 rider	- 0.10
10.00^{x}	+ 0.19	0.60 rider	- 0.09
20.00	+ 0.35	0.70 rider	- 0.16
50.00	+ 0.82	0.80 rider	- 0.21
		0.90 rider	- 0.20

PART I

ETHYLENEDIAMINETETRA-ACETIC ACID AND ITS SALTS

As has been pointed out, E.D.T.A., which forms the most stable complexes with metal ions, proved to be the best of all chelate-forming titrants investigated until now. Disodium ethylenediaminetetra-acetate is a white crystalline powder, moderately soluble in water, insoluble in organic solvents, and decomposed by oxidizing agents with the formation of cyclic ureides, especially in hot solutions. Its 0.1 M solution has a pH of about 5. The solubility in water increases with a rise in temperature from 10.6 per cent. at 0.5°C to 11.1 per cent. at 21°C and 27 per cent. at 98°C[23]. The salt is stable over a wide range of humidities, but can absorb up to 0.3 per cent. of moisture[23]. Solutions, about 0.01 M, stored in a soft-glass container, showed a 1 per cent. loss of strength after 4 months[23], but in borosilicate glass or polyethylene containers the loss of strength was only 0.05 per cent. after 5 months[23] and no significant change was noticed after 8 months. If a prolonged storage is required, the borosilicate glass bottles should be previously boiled in 1 to 2 per cent. alkaline E.D.T.A.

solution. Schwarzenbach[28,29,30] and Flaschka[31] used the disodium ethylenediaminetetra-acetate dihydrate as a primary standard at the 1 per cent. error level. Usually, the product of analytical reagent purity grade has an assay value of 98 to 100 per cent. Blaedel and Knight[23] have purified this salt by recrystallization from ethanol and dried it at room temperature overnight. The pure product thus obtained had an assay figure of 99.5 per cent. The authors reported that, after 4 days of drying at 80°C, constant weight was attained. An assay value of this sample was found to be 100.03 to 100.05 per cent. The sample was used as a primary standard in titrations of metals. The results obtained were at the 0.1 per cent. error level. The authors found that the salt can be dried to its anhydrous form at 120 to 150°C, but this form is too hygroscopic to be safely used. It must be weighed in closed containers and stored over phosphorus pentoxide. Duval[32] investigated the thermal stability of the salt while it was heated on a thermobalance with photographic registration. He found that the number of water molecules in the salt was rather unstable and suggested dehydration before using it as a standard.

Besides the disodium dihydrate other salts of ethylenediaminetetra-acetic acid, as well as the acid itself, are known and used. The acid is not hygroscopic and crystallizes without water. It can be easily dried to constant weight and easily weighed. However, the low solubility in water (only 0.02 g in 100 ml at 22°C)[16] makes the preparation of solutions more complicated. The compound dissolves easily in sodium hydroxide and ammonia and is precipitated again by acidifying the solution, especially to pH below 1. Mono-, di-, tri-, and tetra-potassium as well as mono-, tri-, and tetra-sodium ethylenediaminetetra-acetates are known and have been isolated[16]. The best-known is the tetra-sodium salt. It is stable, has a high solubility in water (60 g in 100 ml)[8], does not decompose at elevated temperatures and is inert towards most chemical compounds, except strong oxidizing agents. This salt is recommended especially when the end-point determination is based on pH effect, owing to the considerable basicity of the solutions. The tetra-lithium salt has also been isolated[8]. Brintziger and Hesse[33] mentioned the isolation of a highly insoluble uranyl ethylenediaminetetra-acetate. Suk and Malat[34] prepared tetra-ammonium ethylenediaminetetra-acetate.

When a carbonate, a hydroxide or an oxide of a polyvalent metal is allowed to react with an equivalent amount of E.D.T.A., complex salts, in which a part of the metal is bounded ionically as a simple cation and another part is complexed, can be crystallized from concentrated solutions by addition of acetone or alcohol. Brintziger and co-workers[33,35,36] isolated and investigated some of them. Also complex salts containing two or more metals, one complexed and another one bounded only ionically, are known. They found application in the substitution titrations.

In this chapter, investigation of the properties of ethylenediaminetetra-acetic acid and some of its salts is described with the view to finding out which of these compounds can be obtained in a form that is stable, pure, non-hygroscopic, homogeneous and easy enough to deal with to be recommended as a primary standard.

1. Potassium ethylenediaminetetra-acetate.

An attempt was made to obtain this salt pure, and its properties were investigated. The reagents used were:-

Ethylenediaminetetra-acetic acid prepared from the disodium salt, which was previously purified according to the method of Blaedel and Knight, potassium hydroxide pellets of analar grade and absolute alcohol.

Two ways of preparation of the salt were tried.

a) Recrystallization.

To a suspension of ethylenediaminetetra-acetic acid in a minimum amount of water heated nearly to boiling washed potassium hydroxide pellets were added in an amount just sufficient to dissolve the solid matter. They were followed by a small excess of the acid, added to avoid the presence of an excess of alkali. The pH of the suspension was 7 to 8. The whole was filtered while hot and the filtrate was cooled rapidly. Fine crystals of potassium ethylenediaminetetra-acetate appeared on cooling.

b) Precipitation from alcohol.

A solution of potassium ethylenediaminetetra-acetate was prepared as above, but this time the procedure was carried out at room temperature. The excess of undissolved ethylenediaminetetra-acetic acid was filtered off. To the filtrate alcohol was added slowly with stirring until no more crystals seemed to appear. The volume of alcohol required exceeded 10 times that of the initial solution.

In both cases the resultant precipitate consisted of very thin crystals, which appeared in larger quantity only after a prolonged standing, but even then the yield was surprisingly low. Carbon tetrachloride and ether, tried successively instead of alcohol, did not produce any precipitate. The precipitation must be carried out with a minimum amount of water, otherwise any salt can be hardly isolated. From more diluted solutions hydrochloric acid does not precipitate the ethylenediaminetetra-acetic acid even at pH below 1. Further investigations of potassium ethylenediaminetetra-acetate were abandoned. The salt was too difficult to prepare and to deal with because of its very high solubility.

2. Lithium ethylenediaminetetra-acetate.

The pure salt was obtained and its properties were investigated.

Preparation.

Lithium hydroxide of G.P.R. grade was purified in the following way.

A filtered saturated aqueous solution of the lithium hydroxide was evaporated to dryness in a porcelain dish under an infra-red lamp. The residue was dissolved in hot water, filtered and re-evaporated. Instead of the hydroxide, lithium carbonate can be used in the synthesis. However, the latter was not available in analar grade of purity. It could be purified by precipitation from boiling solution, but the yield was very low, so the idea of using this reagent was given up.

A suspension of ethylenediaminetetra-acetic acid, prepared as previously described (p.30), in a minimum quantity of water was just dissolved by the addition of a small amount of lithium hydroxide. A small excess of ethylenediaminetetra-acetic acid was added to avoid the presence of an excess of alkali. The undissolved acid was filtered off. The filtrate was treated slowly with ethanol until a permanent precipitate just appeared.

This precipitate was removed by filtration and discarded. The filtrate was diluted with ethanol, with stirring, until no more precipitate seemed to appear. The volume of ethanol required exceeded 7 to 8 times that of the initial solution. The precipitate thus obtained was filtered through a sintered-glass funnel, washed with acetone and then with ether, and finally dried in air overnight at room temperature. The yield was satisfactory.

Two portions of about 1 g of the salt each were dried at 80°C to see if constant weight can be obtained and how much time is required for drying. The samples were weighed in closed weighing bottles after cooling in a desiccator over silica gel for 45 min. before each~~ing~~ weighing. The figures of drying are seen from the following table:

Table I. Drying of lithium ethylenediaminetetraacetate.

Time of drying	Sample N1 weight in grams	Sample N2 weight in grams
0	18.49600	17.50867
+ 5 hrs.	18.47516	17.47761
+ overnight	18.46012	17.46223
+ overnight	18.45807	17.45998
+ overnight	18.45656	17.45748
+ 3 days	18.44301	17.44461
+ 5 hrs.	18.44429	17.44604
+ overnight	18.44460	17.44622
+ overnight	18.44400	17.44570

The dried samples were then weighed at intervals of 3 to 4 min. in a closed balance case, the containers being open, over a period of 25 min., to see if they were hygroscopic. The increase of weight after 25 min. was 0.00290 g for sample N1 and 0.00273 g for sample N2. The hygroscopicity of the glass container was shown to be negligible.

Thus we see that after a period of drying exceeding 1 week, constant weight could not be attained. In addition, the salt proved to be fairly hygroscopic. For these reasons, further investigations concerning the purity and composition of the salt were abandoned.

3. Ethylenediaminetetra-acetic acid.

The acid was prepared and purified and the purity of the obtained product was checked. The density of the pure compound was found. Then the acid was dried to see if constant weight could be obtained and under what conditions. Finally, the pure dry acid was dissolved and its molecular weight was determined by titrations with standard metal solutions to see if a good agreement with the theoretical value could be obtained, e.g. whether the compound is stable and homogenous..

Reagents used:

Disodium ethylenediaminetetra-acetate, purified according to the method of Blaedel and Knight, disodium ethylenediaminetetra-acetate of analar purity grade, and ethylenediaminetetra-acetic acid, analar hydrochloric acid and aqueous ammonia, hydrochloric acid and aqueous ammonia purified by isopiestic distillation.

A) Purification and testing the purity.

Sample N1.

Two grams of disodium ethylenediaminetetra-acetate, purified previously, were placed in a Pyrex beaker, dissolved in 25 ml of water and the solution filtered from dust. To the filtrate 10 to 11 ml of N-HCl were added dropwise, with constant stirring, to precipitate the ethylenediaminetetra-acetic acid. The mixture, whose pH was 2.5 to 2.8, was filtered through a sintered-glass funnel and the precipitate was washed 5 times with 0.01N HCl and then with deionized water until the washings were chloride-free. The ethylenediaminetetra-acetic acid thus obtained was dried for 1 hr. at 140°C, weighed, transferred to a previously ignited and weighed platinum crucible and then ignited. The ignition was started at the lowest possible temperature and continued at dull red for a short time after the main part of the substance had been destroyed. The crucible containing the non-volatile residue was cooled for 25 min. in a desiccator over silica gel and weighed.

Sample N2.

Disodium ethylenediaminetetra-acetate analar was used for this preparation. The procedure was the same as that followed for the sample N1. This time the precipitate was filtered through a sintered-silica crucible to avoid possible contaminations from glass, washed with three 10 ml portions of alcohol before drying and dried for 1 hr at 100°C before weighing. The dry weighed sample was then ignited to find the amount of residue remaining. The non-volatile residue, when tested in the Bunsen flame on a platinum wire showed the presence of sodium.

Sample N3.

This sample was prepared in the same way as sample N2.

Sample N4.

Ten grams of analar disodium ethylenediaminetetraacetate were placed in a Pyrex beaker and dissolved in 125 ml of water and the solution was filtered to remove the dust. To the filtrate heated nearly to boiling, 28 ml of a filtered 2N HCl were added dropwise, with constant stirring. The contents of the beaker were digested for several minutes, while being stirred. After a quick cooling to the room temperature, 2 to 3 drops of 2N HCl were added to make sure that the precipitation was complete, and the solution was filtered through a sintered-glass funnel. The main part of the precipitate was first washed by decantation with hot 0.02N HCl, then transferred to the funnel and washed 10 times with 10-ml portions of cold, 0.02N HCl. The washing was continued with de-ionized water until all chloride ion was removed and then with two 10-ml portions of alcohol. The resultant ethylenediaminetetraacetic acid was dried at 110 to 130°C for 1 hr. and a weighed portion was ignited to find the amount of the residue remaining. The residue, when tested in flame on a platinum wire, showed the presence of sodium.

Sample N5.

This time the ethylenediaminetetra-acetic acid containing a large amount of impurity (about 1.1 per cent.) was purified. A suspension of the compound in a minimum amount of water was nearly dissolved in a minimum amount of aqueous ammonia. The small amount of ethylenediaminetetra-acetic acid left undissolved to make sure that no excess of ammonia was present, was filtered off. The ethylenediaminetetra-acetic acid was re-precipitated from the filtrate by dropwise addition of hydrochloric acid until the supernatant liquid attained a pH of 2 to 3 when tested by a universal indicator-paper. Now the whole was digested and the procedure was continued as for sample N4. The dried ethylenediaminetetra-acetic acid was ignited to find the amount of residue remaining.

Sample N6.

The ethylenediaminetetra-acetic acid was prepared from the disodium salt of analar grade in the same way as the sample N4. The humid product thus obtained was transferred to a polythene beaker by a small amount of de-ionized water to make a thin paste. Then the ethylenediaminetetra-acetic acid was dissolved in purified ammonia, re-precipitated and washed by purified hydrochloric acid, the procedure being the same as for sample N5, but the digestion having been omitted, while polythene beakers were used to avoid the possible contamination from glass. After drying for 2 hrs. at 120°C two portions of this sample were ignited to find the amount of residue remaining. This time no residue was seen.

Table II. Purification of ethylenediaminetetra-acetic acid.

Sample	Weight of dry acid in grams	Weight of non-volatile residue in grams	Per cent. of non-volatile residue
N1	1.26185	0.00034	0.03
N2	0.90578	0.00031	0.03
N3	0.95386	0.00063	0.07
N4	1.00783	0.00033	0.03
N5	1.00382	0.00012	0.01
N6	0.96686	None	0
N6	1.00607	None	0

The ethylenediaminetetra-acetic acid is thus easy to prepare and to purify. The main impurity is sodium when disodium ethylenediaminetetra-acetate is used for the preparation. A sample of ethylenediaminetetra-acetic acid free from sodium can be obtained only by a double precipitation. Purified aqueous ammonia and purified acid, de-ionized water and polythene containers must be used.

B) Drying.

Two portions each of about 1 g of the pure ethylenediaminetetra-acetic acid were dried in weighing bottles at a temperature range from 100 to 150°C. Having obtained an acid of high purity, the next step was to determine whether it could be easily dried to constant weight and whether the dried sample was hygroscopic. When a constant weight at one temperature was attained, the temperature was raised. The samples, after cooling in a desiccator over silica gel for 45 min. were weighed in closed weighing bottles. The figures for the drying are shown in the following table.

Table III. Drying of ethylenediaminetetra-acetic acid.

Temp. of drying	Time of drying	Sample N1 weight in grams	Sample N2 weight in grams
-	-	17.61010	19.97991
100°C	1 hr.15 min.	17.41456	19.80122
110°C	+ 3 hrs.	17.41426	19.80100
110°C	+ 1 hr.	17.41423	19.80099
120°C	+ 1 hr.	17.41417	19.80098
120°C	+ 1 hr.	17.41417	19.80100
130°C	+ 1 hr.	17.41392	19.80080
130°C	+ 1 hr.30 min.	17.41396	19.80071
140°C	+ 1 hr.15 min.	17.41381	19.80076
140°C	+ 1 hr.	17.41382	19.80068
150°C	+ 2 hr.30 min.	17.41349	19.80040*
150°C	+ overnight	17.41233	19.79901

*The colour of the sample turned from white to yellowish.

Hygroscopicity.

Both samples, dried to constant weight at 110°C, were weighed in the closed balance case, the weighing bottles being open, every 3 to 4 min., over a period of about 25 min. to see if they were hygroscopic.

	Sample N1	Sample N2
Weight after drying for 4 hr. at 110°C.	17.41423	19.80099
Weight after 25 min. exposure to air of the balance case.	17.41476	19.80155

Both samples attained again their constant weight after drying for 1 hour at 110°C.

The temperature recommended for drying is 120°C. When the acid is dried at 110°C, results are practically the same. Above 120°C, a small but increasing loss of weight is noticed. At 150°C, the loss of weight becomes considerable and the sample changes colour: probably at this point decomposition begins. A sample freshly prepared by re-precipitation should be dried at the recommended temperature for 2 to 3 hrs. If a once-dried sample is to be used after a prolonged storage, 1 hr. is enough to dry it completely. The substance is only very slightly hygroscopic and the change of weight during weighing is negligible.

C) Determination of density.

It was necessary to find the density of ethylenediaminetetra-acetic acid in order to calculate the buoyancy correction to be applied to the weighings. This was done with sufficient accuracy by means of a 25-ml specific-gravity bottle and absolute alcohol, in which the substance is insoluble. The temperature (about 20°C) does not interfere significantly with the determination.

Purified ethylenediaminetetra-acetic acid, dried for 2 hrs. at 120°C was used. Two parallel determinations were made. The values obtained for d were 1.53 and 1.52, mean 1.52(5), g/ml. This gives a buoyancy correction of + 0.00064 g per gram to be applied to weighings of the pure acid when it is used as a standard.

D) Determination of the molecular weight.

This was done by means of titration of pure, dried, weighed portions of the substance by standard metal~~s~~ solutions. Since 1 gram-ion of the cation in solution reacts with 1 gram-molecule of the ethylenediaminetetra-acetic acid and if the exact amount of metal used for titration and the weight of the acid are known, the molecular weight of the latter can be easily calculated. Solutions of lead and of zinc were chosen as standards;

they give good end-points and reproducible results that agree well for each solution, under conditions easy to establish. The detailed investigation of these methods of titration, however, done before this determination was performed, is described for the sake of completeness in part II of this thesis.

Titrations by lead.

Standard lead solutions were prepared from lead foil of analar grade. The preparation of these solutions is described in detail in part II (p. 85). E.D.T.A. used to prepare the diluted solutions was of analar grade, purified additionally according to the method of Blaedel and Knight. Ammonia and hydrochloric acid used here were purified by isopiestic distillation. Other reagents, except hexamine, were of analar grade and the blank determination carried out on them to check the purity was zero. De-ionized water was used throughout.

Method.

A portion of ethylenediaminetetra-acetic acid, equivalent approximately to a pipetted volume of standard lead solution, dried for 1 hr. at 120°C before weighing and placed in a beaker containing about 70 ml of water, was dissolved in a minimum amount of ammonia. The contents of the beaker were neutralized by 2N-hydrochloric acid and then by a few drops of 2N-sodium hydroxide just to the red colour in the presence of 0.1 ml of 0.1 per cent. xylenol orange solution. The solution was diluted with water to 100 ml and 1 ml of 2N-nitric acid, followed by 1.5 g of hexamine, dissolved in a minimum amount of water, was added. After the addition of a pipetted 50-ml. aliquot of standard lead solution of suitable molarity the titration was completed either by diluted (1 + 3) standard lead solution from a burette or, if lead was present in excess, by diluted (1 + 3) E.D.T.A. solution of molarity very close to that of the lead solution, standardized previously against the same standard lead.

The titration completed, the molecular weight of the ethylenediaminetetra-acetic acid was calculated according to the formula:

$$\text{Mol.wt.} = \frac{\text{weight of the acid taken x 1000}}{\text{molarity of Pb x ml.of Pb used}}$$

and compared with the molecular weight, 292.25, of ethylenediaminetetra-acetic acid calculated from the formula. The results are shown in the following table and can be compared with each other from the values of the molecular weight found or from those of the percentage ratio (Molecular weight found - Molecular weight of E.D.T.A.)/Molecular weight of E.D.T.A.

Table IV. Determination of molecular weight of ethylenediaminetetra-acetic acid.

Weight of sample taken in grams	Molarity of Pb soln.	Ml. of Pb used	Mol.wt. found	$\frac{[\text{Mol.wt.found}-292.25]}{292.25}\times 100$
0.36393	0.02436	50.93	293.34	+ 0.4
0.37066	"	51.83	293.57	+ 0.5
0.36567	"	51.14	293.47	+ 0.4
0.36783	"	51.46	293.32	+ 0.4
0.27965	0.03824	24.88	293.94	+ 0.6
0.27899	"	24.88	293.24	+ 0.3

The method was slightly modified. The ethylenediaminetetra-acetic acid was dried for 3 hrs. at 120°C to make sure that drying was complete, and was then dissolved in ammonia and diluted with water to 100 ml. This solution was neutralized with 2N-nitric acid and ammonia just to the red colour in the presence of 0.1 ml of xylenol orange. [It was tried to neutralize the solution in the presence of 2:4-dinitrophenol as indicator. However, the titration cannot be carried out. No end-point at all can be obtained in the presence of this indicator, so the idea was abandoned.] Then 1 ml of 2N-nitric acid followed by 1 g of hexamine in solution and a pipetted aliquot of standard lead were added.

The titration was completed from a burette by a pendulum method, in which the diluted (1 + 3) lead solution was alternated with the diluted E.D.T.A. solution of molarity very close to that of the lead, prepared from a weighed amount of ethylenediaminetetra-acetic acid dissolved in ammonia, neutralized, and standardized against the same diluted lead solution. Three readings were taken and the mean amount of lead solution used was found. Then the molecular weight of the ethylenediaminetetra-acetic acid was calculated. The results are shown in Table V.

Table V. Determination of molecular weight of ethylenediaminetetra-acetic acid.

Weight of sample taken in grams	Molarity of Pb soln.	Ml. of Pb used	Mol.wt. found	$\frac{[\text{Mol.wt.found}-292.25]}{292.25}\times 100$	
0.43438	0.02995	49.44	293.30	+ 0.4	
0.43720	"	49.77	293.23	+ 0.3	
0.43809	"	49.87	293.23	+ 0.3	
0.43506	"	49.54	293.17	+ 0.3	
0.43676	"	49.67	293.52	+ 0.4	*
0.43676	"	49.67	293.52	+ 0.4	
0.43676	"	49.67	293.52	+ 0.4	
0.43676	"	49.67	293.52	+ 0.4	

*A weighed portion of ethylenediaminetetra-acetic acid was dissolved in ammonia and the solution was diluted with water to the mark in a 250-ml volumetric flask. Four aliquots of this solution were taken for titration, the weight of the acid in the aliquot having been calculated.

Titrations by zinc.

Standard zinc solutions were prepared from granulated zinc of analar grade. The preparation of these solutions is described with details in part II of this work. Other reagents used were the same as in lead titrations.

Method:

A portion of the ethylenediaminetetra-acetic acid, equivalent approximately to a pipetted aliquot of standard zinc solution and dried for 1 hr. at 120°C before weighing, was placed in a beaker containing about 70 ml of water and dissolved in a minimum amount of ammonia. The solution was neutralized in the presence of 0.2 ml of xylenol orange with 2N-hydrochloric acid and then with ammonia just to the red colour. It was diluted with water to 200 ml. and 2 ml of 2N-hydrochloric acid followed by 3 g of hexamine, dissolved in a minimum amount of water, were added. After the addition of a pipetted aliquot of zinc solution the titration was completed by diluted (1 + 3) standard zinc solution added from a burette. The molecular weight of ethylenediaminetetra-acetic acid was calculated and compared with the theoretical, as before.

Table VI. Determination of molecular weight of ethylenediaminetetra-acetic acid.

Weight of sample taken in grams	Molarity of Zn soln.	Ml.of Zn used	Mol.wt. found	$\frac{[\text{Mol.wt.found}-292.25]\times 100}{292.25}$
0.39049	0.02622	50.84	292.93	+ 0.2
0.40072	0.02716	50.30	293.35	+ 0.4
0.39495	"	49.67	292.77	+ 0.2
0.45251	"	56.79	293.45	+ 0.4
0.45888	"	57.53	293.59	+ 0.5

Then the method was slightly modified. The sample was dried for 3 hrs. at 120°C to ensure complete dryness, dissolved in ammonia and diluted with water to 200 ml. The neutralization was carried out in the presence of 2:4 dinitrophenol as indicator. Then 2 ml of 2N HCl followed by 3 g of hexamine in solution and a pipetted aliquot of standard zinc solution were added. The titration was completed in the presence of xylenol orange from a burette by a pendulum method, while the diluted (1 + 3) zinc solution was alternated with the diluted E.D.T.A. solution of molarity very close to that of the zinc solution, and prepared from weighed amount of the ethylenediaminetetra-acetic acid, dissolved in ammonia, neutralized and standardized against the same diluted zinc solution.

Three readings were taken and the mean amount of zinc solution used for titration was found. Then the molecular weight of the ethylenediaminetetra-acetic acid was calculated.

Table VII. Determination of molecular weight of ethylenediaminetetra-acetic acid.

Weight of sample taken in grams	Molarity of Zn soln.	Ml.of Zn used	Mol wt. found	$\frac{[\text{Mol.wt.found}-292.25]\times 100}{292.25}$
0.42844	0.02944	49.74	292.65	+ 0.2
0.43232	"	50.42	291.39	- 0.3
0.43431	"	50.17	294.05	+ 0.6
0.43369	"	50.33	292.64	+ 0.2
0.43026	"	50.09	291.51	- 0.3
0.43179	"	49.93	293.74	+ 0.5
0.43179	"	49.93	293.74	+ 0.5 [x]
0.43179	"	49.93	293.74	+ 0.5

[x] A weighed portion of the acid was dissolved in ammoni~~um~~a and the solution was diluted with water to the mark in a 250-ml volumetric flask. Three aliquots of this solution were taken for titration, the weight of the acid in an aliquot having been calculated.

Here large differences in results, which are either too high or too low, are seen. It is supposed that this could be caused by the presence of the dinitrophenol, which affected so badly the titrations by lead.

In the next series of determinations 2:4-dinitrophenol was eliminated. The solutions were neutralized in the presence of xylenol orange and the titrations were completed by a pendulum method.

Table VIII. Determination of molecular weights of ethylenediaminetetra-acetic acid.

Weight of sample taken in grams	Molarity of Zn soln.	Ml. of Zn used	Mol. wt. found	$\frac{[\text{Mol.wt.found} - 292.25] \times 100}{292.25}$
0.46527	0.03176	49.95	293.36	+ 0.4
0.46403	"	49.83	293.13	+ 0.3
0.46140	"	49.56	293.13	+ 0.3
0.46570	"	50.03	293.08	+ 0.3
0.46418	"	49.78	293.59	+ 0.5
0.46418	"	49.78	293.59	+ 0.5
0.46418	"	49.78	293.59	+ 0.5 [x]
0.46418	"	49.78	293.59	+ 0.5

[x] A weighed portion of the acid was dissolved in aqueous ammonia and the solution was diluted with water to the mark in a 250-ml volumetric flask. Four aliquots of this solution were taken for titration, the weight of the acid in one aliquot having been calculated.

The last four results quoted in table VIII show that when aliquots are taken the precision of the titrations is perfectly satisfactory. Only when different samples of the ethylenediaminetetra-acetic acid are taken for a determination do the differences in the values for the molecular weight of the acid appear. This shows that the factor causing the differences lies in the acid itself.

Status of ethylenediaminetetra-acetic acid as a primary standard in volumetric analysis.

In spite of the fact that the ethylenediaminetetra-acetic acid has been carefully purified, is free from non-volatile inorganic matter and can be dried to constant weight, that the weighings are accurate to 0.02 to 0.04 per cent. and that the titrations of aliquots show no variation, the precision obtained between different determinations of the molecular weight is variable and poor, being of the order of 0.3 to 0.5 per cent. For a satisfactory standard, the precision should be equal to or better than 0.1 per cent. The cause of the observed variations is unknown, but the conclusion can be drawn that carefully purified ethylenediaminetetra-acetic acid is not a satisfactory primary standard for E.D.T.A. titrations in volumetric analysis.

This being so, attention was next directed to the possibility of using the ammonium salt~~s~~ of E.D.T.A. as a satisfactory standard~~s~~. The dihydrated disodium salt, often recommended as a standard, was also investigated.

4. Ammonium ethylenediaminetetra-acetate.

Pure ammonium ethylenediaminetetra-acetate was prepared and its purity checked. The density of the compound was found and the conditions of drying were controlled with a view to seeing if the salt can be dried to constant weight. Finally, the molecular weight was determined by titrations of the dissolved salt with standard metal solutions. The composition of the salt was also checked by determination of its ammonia content.

The reagents used were:

Purified ethylenediaminetetra-acetic acid, absolute ethanol, acetone, ether, ammonia and hydrochloric acid of analar grade.

A) Preparation and purity test.

A suspension of ethylenediaminetetra-acetic acid suspended in a minimum amount of water, was dissolved by the dropwise addition of aqueous ammonia with constant stirring. A small excess of ethylenediaminetetra-acetic acid, left undissolved, was filtered off. To the filtrate a 7- to 8-fold excess of ethanol was added until no more precipitate was produced. The resulting precipitate was filtered through a sintered-glass funnel, washed with acetone and then with ether, and air-dried. Samples prepared in this way were taken for further investigation. Two portions of the salt, each of about 1 g, were dried to constant weight at 80°C and ignited in a platinum crucible to check the impurity. The percentage of non-volatile residue, composed mainly of sodium, was the same as that found previously in the ethylenediaminetetra-acetic acid taken to prepare the salt.

B) Drying.

Two portions of the prepared ammonium ethylenediaminetetra-acetate of high purity were dried in glass containers until constant in weight. Then the temperature was raised and the drying was continued to see how the salt behaved at various temperatures and which one can be recommended for drying. The samples were cooled for 45 min. in a desiccator over silica gel before being weighed.

Table IX. Drying of ammonium ethylenediaminetetraacetate.

Temp. of drying	Time of drying	Sample N1 weight in grams (+ container)	Sample N2 weight in grams (+ container)
-	-	19.96200	16.52100
80°C	3 hrs.	19.73904	16.32583
80°C	+ 3 hrs.	19.73872	16.32536
80°C	+ 90 min.	19.73865	16.32538
90°C	+ 90 min.	19.73820	16.32494
90°C	+ 1 hr.	19.73829	16.32500
100°C	+ 5 hrs.	19.73587	16.32176
100°C	+ 3 days	19.72238	16.30187
100°C	+ 1 hr.	19.72234	16.30190
110°C	+ 2 hrs.	19.71179	16.29741
110°C	+ 2 days	19.69771	16.28393[x]

[x] The colour turned from white to pinkish.

Both samples, dried to constant weight at 80°C, were weighed at the intervals of 3 to 4 min. in a closed balance case, the weighing bottles being open, over a period of about 25 min. to see if they were hygroscopic.

	Sample N1 weight in grams	Sample N2 weight in grams
After drying for 7 hrs. at 80°C.	19.73865	16.32538
After 25 min. exposure to the air of the balance case.	19.73938	16.32630

The figures show that the substance after drying at 80°C is hygroscopic but both samples attained again their constant weight after 1 hr. of drying at 80°C. Then two portions of the freshly prepared salt were dried to constant weight directly at 100°C. After 7 days of drying, they continued to lose weight, while the colour changed to pinkish. The experiment was repeated - with the same results.

The temperature recommended for drying of the ammonium ethylenediaminetetra-acetate is therefore 80°C. The time needed is about 6 hrs. When heated at higher temperatures, a constant loss of weight occurs. After prolonged drying at 100°C or after a less prolonged drying at 110°C the substance changes colour, probably as a result of partial decomposition. If a once-dried sample has been stored for a long time, 1 hr. of drying at 80°C is enough to attain a constant weight again. The substance is only slightly hygroscopic.

c) Determination of density.

The density of the compound was needed to calculate the buoyancy correction to be applied to the weighings. The determination was done with sufficient accuracy by means of a 25-ml specific gravity bottle and absolute alcohol in which the substance is insoluble. The salt used here was previously dried to constant weight at 80°C. Two parallel determinations were made. The values obtained for d were 1.37 and 1.34, mean 1.35(5) g/ml. This makes a buoyancy correction of + 0.00074 g. per gram to be applied to weighings of the salt when it is used as a standard.

D) Determination of the molecular weight.

This was done, as for the ethylenediaminetetra-acetic acid, by titration of weighed portions of the dry pure salt with standard solutions of lead and zinc.

Titration by lead.

Standard lead solutions were prepared from lead foil of analar grade. E.D.T.A. used to prepare the solutions was of analar grade, purified additionally according to the method of Blaedel and Knight. Aqueous ammonia was purified by isopiestic distillation. Other reagents, except hexamine, were of analar grade and the blank determination carried on them to check the purity was zero. De-ionized water was used throughout. Standard lead solutions were prepared in the same way as those used in the titrations of ethylenediaminetetra-acetic acid.

Method:

Portions of ammonium ethylenediaminetetra-acetate, dried to constant weight at 80°C before weighing, were dissolved in water, transferred to volumetric flasks and the solutions were diluted with water to their marks. Aliquots of these solutions, containing known amounts of the salt, were titrated by standard metal solutions. Then the molecular weight was calculated.

To an aliquot of the ammonium ethylenediaminetetra-acetate, prepared as is described above, 0.1 ml of xylenol orange was added and the solution was neutralized with ammonia to the red colour. The solution was then diluted with water to 100 ml and 1 ml of 2N-nitric acid, followed by 1.5 g of hexamine in solution, was added. The solution was titrated by the standard lead solution up to the approximate end-point, the titration being completed by diluted (1 + 4) lead solution for greater accuracy.

Table X. Determination of molecular weight of ammonium ethylenediaminetetra-acetate.

Weight in grams of the salt in aliquot	Molarity of Pb	Ml.of Pb soln. used	Mol.wt. found	$\frac{[\text{Mol.wt.found}-335.33]100}{335.33}$	
0.78819	0.04793	48.90	336.28	+0.3	aliquots from soln.1
0.78819	0.04793	48.92	336.14	+0.3	" " " 1
0.37754	0.03824	29.45	335.25	<-0.05	" " " 2
0.37754	0.03824	23.45	335.25	<-0.05	" " " 2
0.36654	0.03824	28.63	334.87	-0.2	" " " 3
0.36654	0.03824	28.63	334.87	-0.2	" " " 3

The molecular weights found suggest that the formula of the salt should be that of di-ammonium ethylenediaminetetra-acetate hemihydrate, which has the molecular weight of 335.33. The accuracy was calculated in relation to this molecular weight.

Titration by zinc.

Standard zinc solutions were prepared from granulated zinc of analar grade. Other reagents were the same as those used in the lead titrations. Zinc solutions were prepared in the same way as those used in titrations of ethylenediaminetetra-acetic acid.

Method:

Portions of ammonium ethylenediaminetetra-acetate, dried to constant weight at 80°C before weighing, were dissolved in water, transferred to volumetric flasks and the latter were filled with water to their marks. Aliquots of these solutions, containing a known amount of the salt were titrated by standard zinc solutions. Then the molecular weight of the ammonium ethylenediaminetetra-acetate was calculated.

Each aliquot of the salt solution was neutralized in the presence of 0.2 ml of xylenol orange with hydrochloric acid and ammonia just to the red colour and diluted with water to 200 ml. ~~Thus~~ Then 2 ml of 2N-hydrochloric acid followed by 3 g of hexamine and 50 ml of standard zinc solution were added and the titration was completed by diluted(1 + 4) solutions for the sake of greater accuracy.

Table XI. Determination of molecular weight of ammonium ethylenediaminetetra-acetate.

Weight of the salt in aliquot in grams	Molarity of Zn soln.	Ml.of Zn soln. used	Mol.wt. found	$\frac{[\text{Mol.wt.found}-335.33]}{335.33}100$	
0.41433	0.02466	50.06	335.49	<+0.05	aliquots from soln.1
0.41433	0.02466	51.50	335.56	<+0.05	" " " 1
0.44565	0.02622	50.80	334.45	-0.3	" " " 2
0.44565	0.02622	50.80	334.45	-0.3	" " " 2
0.44725	0.02622	50.97	334.72	-0.2	" " " 3
0.44725	0.02622	50.97	334.72	-0.2	" " " 3

The molecular weights obtained are nearly the same as those found by titration by lead solution.

E) Determination of ammonia in the ammonium salt.

The ammonia contents in the ammonium ethylenediamine-tetra-acetate, needed to establish the composition of the salt, was determined by distillation in the Parnas[37] apparatus. Samples, dried at 80°C to constant weight before weighing, were dissolved in 5 ml. of water and transferred to the apparatus with the help of about 6 ml. of water. Then 8 ml of a 40% sodium hydroxide solution were added and the apparatus was set in action. The distilled ammonia was absorbed either in 50 ml of 4% boric acid solution and then titrated directly by standardized hydrochloric acid in the presence of screened methyl red, or in 50 ml of standardized hydrochloric acid, the excess of the acid being then titrated by standardized sodium hydroxide in the presence of the same indicator. Blank determinations were carried out and the appropriate corrections were applied.

Table XII. Nitrogen content in ammonium ethylenediaminetetra-acetate.

Weight of sample in grams	Absorbed in	Ml.of 0.1N -HCl used	N found in grams	% of N	Deviation
0.40016	HCl	22.55	0.03159	7.89	-0.47
0.40940	"	22.62	0.03169	7.74	-0.62
0.39411	"	22.07	0.03092	7.60	-0.76
0.39997	"	22.94	0.03213	8.03	-0.33
0.46375	boric acid	26.48	0.03709	8.00	-0.36
0.41512	" "	24.31	0.03405	8.20	-0.16
0.40376	" "	23.61	0.03307	8.19	-0.17
0.30199	" "	17.58	0.02462	8.15	-0.21
0.41423	" "	23.91	0.03359	8.11	-0.25

The calculated theoretical ammonia content in the diammonium ethylenediaminetetra-acetate hemihydrate is 8.36% of nitrogen. The figures obtained for the nitrogen contents are rather lower and varying.

The conclusion as to the composition of the salt was drawn from the results of the titrations as well as from the per cent. of nitrogen present. The salt obtained should be diammonium ethylenediaminetetra-acetate hemihydrate of molecular weight 335.33. The results obtained from titrations by metals are near to the theoretical calculated value with good accuracy. The tendency to obtain lower figures both for molecular weights and for the ammonium contents indicates the tendency, however small, of the salt to lose ammonia.

5. Sodium ethylenediaminetetra-acetate dihydrate.

This compound is, until now, the best-known and the most widely used of all the salts of ethylenediaminetetra-acetic acid. The salt supplied by manufacturers was purified according to the method of Blaedel and Knight[23], and the purity of the obtained product was examined. The density of the pure compound was found in order to calculate the necessary buoyancy correction. Then the salt was dried to see if a constant weight can be obtained and under what conditions. Finally, the molecular weight of the pure dry salt was determined by means of titrations with standard metal solutions to see if the compound is suitable as a primary standard.

A) Purification and purity tests.

The reagents used were disodium ethylenediaminetetra-acetate dihydrate of laboratory-reagent grade and absolute alcohol.

To a solution of disodium ethylenediaminetetra-acetate saturated at room temperature and containing about 10 g of the salt per 100 ml, alcohol was added slowly, with stirring, until a permanent precipitate began to appear. This precipitate was filtered off and discarded. The filtrate was diluted with an equal volume of alcohol. The resulting precipitate was filtered through a sintered-glass funnel, washed with acetone and then with ether and air-dried at room temperature overnight. This product was tested for purity according to instructions given for analar materials[38].

pH.

A 5 per cent. solution of the salt, prepared in carbon dioxide-free water was tested with a narrow-range indicator-paper. Then colorations produced by addition of a drop of methyl orange and methyl red to aliquots of the solution were checked. The pH found was about 5.

Chlorides.

To a solution containing 1.25 g of the substance in 20 ml of warm water, 1.5 ml of nitric acid (8 + 17) were added. After cooling, the solution was diluted with water to 25 ml and treated with 0.5 ml of 0.25-M silver nitrate. The produced opalescence was considerably smaller than that produced by 0.05 mg of chloride under similar conditions. Thus the chlorides content in the tested sample was below the limit of 0.004 per cent.

Iron.

A 1.5-g portion of the salt was ignited in a porcelain crucible. The substance remaining after ignition was treated with 2.5 ml of hydrochloric acid. The whole was evaporated to dryness and the residue was dissolved by warming with 15 ml of hydroohloric acid (43 + 957). A 10 ml aliquot was retained for heavy metals test. To the remaining 5 ml, 1 drop of 0.05-N potassium permanganate was added with stirring, followed by 2.5 ml of 7.5-M ammonium thiocyanate and 5 ml of a mixture containing equal volumes of amyl alcohol and amyl acetate. The solution was shaken vigorously. The coloration of the upper layer was less intensive than that produced by 0.005 mg of iron under similar conditions. Thus the iron contents were below the limit of 0.001 per cent.

Heavy metals.

To 10 ml of the solution, retained from previous test, were added 12.5 ml of water and 2.5 ml of ammonia (7 + 18). Hydrogen sulphide under pressure was passed through the mixture. The aliquot became less opalescent than that containing 0.01 mg of lead and 0.005 mg of iron under similar conditions and treated in the same way. So the heavy metals contents were below the limit of 0.001 per cent.

The product obtained by purification had quite a satisfactory standard of purity.

B) Drying.

Before drying the substance, the hygroscopicity of weighing bottles was controlled. Two empty clean glass weighing bottles were heated at 80°C for about 100 min. cooled in a desiccator over silica gel for 45 min. and weighed, while closed, every 3 to 4 min. over a period of 20 min. to check their capacity for adsorbing moisture.

	N1.	N2.
Initial weight, in grams	19.65421	20.14269
Weight after 20 min., in grams	19.65429	20.14267
Weight, in grams, after 1 day of exposure in the balance case, while the containers were open	19.65430	20.14259

Thus, the glass containers do not adsorb moisture significantly and the eventual changes in weight during weighing, if any, can be attributed to the dried substances.

Two portions of disodium ethylenediaminetetra-acetate, each of about 0.5 g, were dried at 80°C in glass weighing bottles until constant in weight. The samples were allowed to cool for 45 min. in a desiccator over silica gel before weighing.

Table XIII. Drying of disodium ethylenediamine-tetra-acetate.

Time of drying at 80°C	Sample N1 weight in grams	Sample N2 weight in grams
8 days	20.11172	20.67210
+ 1 day	20.11202	20.67230
+ 1 day	20.11200	20.67223
1 day of storage in a desiccator over silica gel with the weighing bottles closed	20.11317	20.67322
1 day of exposure in a closed balance case with the weighing bottles open	20.11380	20.67318
1 day as above	20.11378	20.67307
1 day (dried again)	20.11088	20.67106

Table XIV

Another two, 0.5-g portions of the substance, which had been dried at 80°C for 10 days, were taken.

Time of drying	Sample N1 weight in grams	Sample N2 weight in grams
-	20.73430	20.06488
+ 4 hrs.	20.73156	20.06373
+ 16 hrs.	20.73088	20.06348
+ 4 hrs.	20.73076	20.06341
+ 16 hrs.	20.73073	20.06352

Hygroscopicity.

Both samples were weighed in a closed balance case, the containers being open, every 3 to 4 min. over a period of about 20 min. to see if they were hygroscopic.

Weight after 20 min.	20.73175	20.06435

Samples were dried again at 80°C with a view to attaining constant weight.

+ 1 day	20.73140	20.06370
+ 1 day	20.72920	20.06268
+ 3 days	20.72904	20.06250
+ 1 day	20.72754	20.06187

Table XV

Two more 0.5-g portions of the substance which, after purification, were dried for 3 days at 80°C, were dried to see if constant weight could be attained.

Time of drying at 80°C	Sample N1 weight in grams	Sample N2 weight in grams
-	16.02244	17.96141
+ 2 hrs.	16.02260	17.96170
+ 3 days	16.02306	17.96200
+ 2 hrs.	16.02300	17.96195
+ 1 day	16.02287	17.96177
+ 1 day	16.02262	17.96146
+ 1 day	16.02191	17.96073

The figures given in the tables above show that drying of the disodium ethylenediaminetetra-acetate is very tedious and fraught with uncertainty. Sometimes after days of drying the constant weight seems to be attained, but when the drying is continued, a new loss of weight is noted. Sometimes even an increase in weight during the drying was observed. In addition the salt is slightly hygroscopic, more than are ammonium ethylenediaminetetra-acetate and ethylenediaminetetra-acetic acid. It picks up moisture even when stored in a desiccator over a desiccant. All the moisture is absorbed in the first day of exposure.

c) Determination of density.

The determination of the density was done with sufficient accuracy by means of the 25-ml specific gravity flask and the absolute alcohol in which the substance was insoluble. A portion of analar grade disodium ethylenediaminetetra-acetate was used and 3 parallel determinations were done.

The values obtained for d were 1.60, 1.64 and 1.63, mean 1.62 g/ml. This makes a buoyancy correction of + 0.00060 g per gram to be applied to weighings of the salt when it is used as a standard.

D) Determination of the molecular weight.

This was done, as for ethylenediaminetetra-acetic acid and ammonium ethylenediaminetetra-acetate, by titrating weighed portions of the salt with standard solution of lead.

Standard lead solution was prepared from purified, recrystallized lead nitrate by dissolving a weighed portion dried previously for 2 hrs. at 120°C, in a known volume of water. Ammonia was purified by isopiestic distillation. Other reagents, except hexamine, were of analar grade and the blank determination carried out to check their purity was zero. De-ionized water was used throughout.

Method:

A portion of the salt, dried previously for 4 days at 80°C, was weighed and dissolved in water. The solution thus obtained was neutralized with aqueous ammonia in the presence of 0.1 ml of xylenol orange just to the red colour and diluted with water to 100 ml. Then 1 ml of 2N-nitric acid followed by 1.5 g of hexamine in solution and by a pipetted aliquot of standard lead solution was added and the titration was completed from a 10-ml burette by a pendulum method, while the diluted (1 + 3) lead solution was alternated with a diluted, separately prepared, E.D.T.A. solution of a molarity very close to that of the lead solution and standardized against the same lead. Three readings were taken and the amount of lead solution used was calculated. Then the molecular weight of the disodium ethylenediaminetetra-acetate was found.

Table XVI. Determination of molecular weight of disodium ethylenediaminetetra-acetate dihydrate.

Weight of the sample in grams	Molarity of Pb	Ml.of Pb used	Mol.wt. found	$\frac{[\text{Mol.wt.found}-372.25]100}{372.25}$	
0.55915	0.03006	49.83	373.26	+ 0.3	
0.56010	"	49.95	373.15	+ 0.2	
0.56301	"	50.22	372.85	+ 0.2	
0.56029	"	49.90	373.53	+ 0.3	*
0.56029	"	49.90	373.53	+ 0.3	
0.56029	"	49.91	373.53	+ 0.3	

*A weighed portion of the salt was dissolved in 250 ml of water and three 50-ml aliquots were taken for titration, the weight of the acid in an aliquot having been calculated. The last three results show that the precision of the titration is satisfactory.

The molecular weight obtained in all cases was too high: possibly the drying was not completed.

Conclusions

The substance considered an ideal primary standard in volumetric analysis should possess several properties.

a) It must be easy to obtain.

b) It must be easy to purify.

c) It must be easy to dry.

d) It must be easy to preserve in a pure state: the composition should remain unchanged during the storage.

e) It should remain unaltered in air during weighing: no absorption of carbon dioxide, or water, or oxygen should take place.

f) It should be capable of being tested for impurities by tests of known sensitivity and the total amount of impurities should not, in general, exceed 0.01 to 0.02 per cent.

g) It should have a high equivalent weight, so that errors introduced by weighing are at a minimum.

h) It should be readily soluble under the conditions in which it is to be used.

i) The reaction with the standard should be stoichiometric and instantaneous.

j) The titration error should be negligible or easy to determine accurately by experiment.

The anion of ethylenediaminetetra-acetic acid is a very good titrant; the more valuable as it can be used, under adjusted conditions, for titration of many different cations. Indicators that enable the end-point of the titration to be seen even within a fraction of a drop have been described. But can it be safely used as a primary standard, and in combination with which cation? As far as the four investigated salts and the acid itself are concerned, the requirements of d), e), g) and (i), except for the potassium ethylenediaminetetra-acetate, which can be obtained and purified only with a very small yield, are fully satisfied. The experience of many investigators is the same about the requirement j). The requirement (h) is also fulfilled; all except one of the investigated compounds are readily soluble in water. The only insoluble one, the ethylenediaminetetra-acetic acid, can be quite readily dissolved in ammonia and neutralized, so the solutions of a known strength can easily be prepared. All the above compounds are easy to obtain and to purify apparently. Their non-volatile impurities are very small and if great care is taken, even compounds approaching 100 per cent. purity as far as non-volatile impurities and cations are concerned can be obtained. However, we know little or nothing of the purity of the organic content of these substances. The only uncertainty seems to be in the drying. The writer has not succeeded in drying the lithium salt to constant weight: even after a period of drying of 1 week at 80°C the weight still changed. Besides, the salt showed the highest hygroscopicity of all the compounds tested: after an exposure to air over a period of 25 min. the weight of this salt increased nearly at a ratio of 3 mg per gram.

The acid itself can be dried quite well and in a relatively short period at 110°C to 120°C. After 25 min. of exposure to air it absorbed only 0.5 mg of moisture per gram, which is not much. Being apparently pure and dry it was expected to be an ideal standard. However, the determination of the molecular weight done by titrations by two metals from several freshly prepared standards, proved that no stable figure can be obtained. The deviation was nearly +0.3 to 0.5 per cent. A possible explanation of this phenomenon is that the composition of this compound was uncertain.

The ammonium salt can be dried to constant weight quite easily and quickly at 80°C. After 25 min. of exposure to air it absorbed about 1 mg of moisture per gram. The determination of molecular weight made by titrations by two metals and the determination of the ammonia contents indicated that the composition of this salt should be diammonium ethylenediaminetetra-acetate hemihydrate. However, also here no stable figure was obtained. The deviation varied from 0.05 to 0.3 per cent. The tendency to obtain figures for the ammonia contents as well as for the molecular weight lower than the theoretical indicates that **the salt may lose** ammonia.

The most complicated was the drying of the sodium salt. In spite of some hopeful impressions a constant weight, that does not change after a prolonged drying, was never attained. After 25 min. of exposure to the air the salt absorbed nearly 2 mg per gram of moisture. However, for rough drying 4 days at 80°C can be recommended. The determination of molecular weight done by titration by lead solution showed the deviation of about 0.2 to 0.3 per cent.

Thus none of the investigated compounds is satisfactory as a primary standard. However, when only rough accuracy of the determination is required the sodium or ammonium salts, properly purified and dried can be used as such at an error level up to 0.3 per cent.

PART II

TITRATION OF DIFFERENT METAL SOLUTIONS BY E.D.T.A.

COMPARISON OF METALS STANDARDS.

As ethylenediaminetetra-acetic acid and its salts proved not to be suitable for use as primary standards in work where high accuracy is required, it is clear that E.D.T.A. solutions have to be standardized by some other method. The substances that suggest themselves for the preparation of standard solutions are metals. Nowadays aluminium, antimony, bismuth, cadmium, copper, gallium, germanium, gold, indium, iron, lead, magnesium, manganese, mercury, nickel, silver, tin, tungsten and zinc are available in sufficient grade of purity. However, the low molecular weight of some of them and the difficulty of keeping others from oxidation are disadvantages. That is why analysts were looking for metal compounds suitable to use as standards. Several of these compounds can be easily purified and dissolved and, of course, they always have higher molecular weight than the metals themselves. From many recommended compounds few deserve a special mention, being of particular interest. Blaedel and Knight[12] found zinc oxide, calcium carbonate and magnesium sulphate heptahydrate to be satisfactory. Zinc oxide was ignited at red heat before use.

Malincrodt standard luminescent calcium carbonate reached 99.95 per cent. of purity after drying for 2 hrs. at 130°C; the same compound manufactured by other firms gave too high results. Magnesium sulphate heptahydrate was dried at 110°C, ground and ignited at 650°C to form anhydrous magnesium sulphate, a needed amount of which could be weighed. Lott and Cheng[39] investigated drying possibilities of some hydrated salts available in a reagent grade purity. They found that magnesium sulphate heptahydrate and zinc ammonium sulphate hexahydrate, both dried in a desiccator over a solid desiccant, can be used to standardize the E.D.T.A. with the error of 0.05 per cent. when compared to metallic zinc. Toschitake Iwamoto[40] recommends the use of lead chloride as a standard for E.D.T.A. titrations. Coltman[41] prepared a stable pure manganese oxalate which can be used as standard. Lindstrom and Stephens[42] found that magnesium iodate tetrahydrate, a stable, fairly soluble in water compound of high molecular weight, is an excellent standard. Budesinsky[43] recommended dipyridinozinc thiocyanate. Powell et al.[44] used cadmium N-hydroxyethyl-(ethylenediamine)-NN'N'-triacetate, which is easy to prepare and purify, stable and non-hygroscopic. Other authors recommended many other metal compounds as good standards. However, for some of the metal ions satisfactory and easy in performing methods of complexometric titrations are not yet elaborated; others can be determined only by back titrations, which complicates the procedure and makes impossible checks on both sides of the end-point. In this thesis only methods based on visual end-point detection were considered, reviewed and investigated. Four metals, which do not suffer from the above-mentioned disadvantages and for which methods easy to perform and showing a sharp and accurate end-point exist, were selected as standards to investigate various aspects of E.D.T.A. titrations. Results obtained by titrating one E.D.T.A. solution by standards prepared from all selected metals were compared. Conclusions were drawn as to a choice of methods which can be applied with good accuracy in the analysis of complex materials also.

1. Lead.

Two lines of approach exist in all the methods of lead determination. It can be titrated in alkaline or in slightly acid medium. The most used method of lead titration uses Eriochrome Black T as indicator in the alkaline medium. First Schwarzenbach[28] determined lead by addition of an excess of E.D.T.A. and back titration of this excess by standard zinc solution at pH 10 in the presence of Eriochrome Black T. Flaschka[46] recommended direct titration of lead solutions containing tartrate ion by E.D.T.A. at pH 8 to 10 in the presence of the same indicator. Kinnunen and Merikanto[47] titrated the excess of added E.D.T.A. by zinc at pH 10, in the presence of zincon as indicator. Suk and Malat[34], and Vřešťal and Havíř[45] titrated lead directly in slightly alkaline medium in the presence of catechol violet. Peng Young Sun[48] titrated lead at pH 5.5 to 6 in pyridine or hexamine buffered solutions in the presence of gallein as indicator. The same indicator can be used also at pH 10, but then more cations interfere. Karakasevic et al.[49], Korbl and Přibil[50], and Budevski et al.[51] applied lead titrations in neutral solutions with methylthymolblue as indicator. Erdley and Polos[52] titrated lead in the presence of variamine blue. Flaschka and Abdine[53] back titrated the E.D.T.A. added in excess to lead solution by copper sulphate in acid solution in the presence of PAN. Flaschka and Franschitz[54] titrated the excess of E.D.T.A. added by zinc solution at pH 5 in the presence of dimethylnaphthidine-ferro-ferricyanide as indicator. Přibil et al.[56,55] recommended direct titration of lead in solutions buffered by hexamine at pH5 in the presence of xylenol orange as indicator. Lead can also be titrated directly in solution buffered by sodium acetate in the presence of pyrogallol red.

Titrations performed in alkaline medium, most frequently in the presence of Eriochrome Black T, leave the end-point not very well pronounced. Back titrations are never recommended for very accurate determinations, if not strictly necessary. In direct titrations xylenol orange seems to be the indicator giving the best and most sensitive end-point. The conditions of the titration are easy to observe. Thus, this method was chosen to investigate the lead titrations by E.D.T.A.

Xylenol orange, which is 3:3'-bis-di(carboxymethyl)-aminomethyl-o-cresol-sulphonphthalein, was described by Pribil et al.[55,56] The indicator is prepared by condensation of cresol red with formaldehyde and iminodiacetic acid. Besides the metal indicator properties it is also an acid-base indicator with colour change from yellow to violet at pH about 6. The table below shows the exact colour changes of the indicator with the changes of pH.

To 100 ml of de-ionized water 0.1 ml of 0.1 per cent. xylenol orange solution was added. The pH, adjusted with aqueous ammonia, was controlled ~~in~~ by a pH-meter and the colour change following the change of pH was noted.

Table XVII. Xylenol orange colour changes at various pH.

pH	Colour
4.8	yellow
5.5	yellow
5.7	orange
6.6	dirty violet
7.8	purple red

The aqueous solutions of xylenol orange are stable for many months. In acidic medium coloured complexes with thorium (pH 2.5 to 3.5), bismuth (pH 1 to 3), tervalent thallium (pH 4 to 5), lanthanum, scandium, lead, zinc (pH 5), cadmium and bivalent mercury (pH 6) are formed which can be titrated by E.D.T.A. Cobalt, copper, iron and aluminium block the indicator. Complexes with metals in alkaline medium are of no analytical use. The end-point of titrations is seen within a fraction of a drop, because the colour change is extremely sharp.

A) Comparison of lead standard solutions.

Standard lead solution was prepared initially from lead foil of analar grade. The foil was etched by warming with

2N-nitric acid and rinsed twice with 2N-nitric acid and then with water. The following washing twice with ethanol and twice with ether assisted drying. If the weight remains unchanged during the weighing, the metal is accepted as dry. A weighed portion of a dry lead foil was placed in a 250-ml round-bottomed, long-necked flask and covered with 10 ml. of 2N-nitric acid for each gram of lead. A small funnel was placed in the mouth of the flask, the contents of which were gently heated to assist dissolution of the metal. When all the lead had dissolved, the solution was diluted with 75 ml of water, the funnel was replaced by an anti-bump tube and the whole was boiled gently to expel nitrous fumes until a moistened starch-potassium iodide paper, held in the vapour, showed no signs of darkening. The solution was cooled, transferred to a calibrated volumetric flask and neutralized by aqueous ammonia, added dropwise, in the presence of methyl red. Then a few drops of 2N-nitric acid were added just to dissolve any precipitate formed and the flask was filled with water to the mark, the molarity being calculated.

Another, more simple, method of preparation of standard lead solution involved lead nitrate. However, although this compound is marketed in a quite pure grade, an additional purification was applied. From the lead nitrate, moistened with nitric acid, a hot saturated solution was prepared. This solution was filtered quickly, while hot, and the filtrate was cooled with stirring. The resulting pure crystalline salt was filtered through sintered-glass and dried at 100°C. The dry powder was crushed well in an agate mortar and transferred into a labelled bottle. A portion of about 1 g was dried at various temperatures. It was found that in the range of temperatures 110° to 140° the weight remains constant. The recommended temperature of drying is then 120°C and the time 2 hrs.

The purified recrystallized lead nitrate was tested for purity according to the instructions laid down for analar reagents[38]. A 10 per cent w/v solution in water was completely clear. The pH of a 5 per cent. solution in carbon dioxide-free water was about 3.8. The salt contains no alkali metals: heated in a flame on a platinum wire produced no colouration. There were no traces of chloride found by the silver nitrate test. No iron was found by the thiocyanate test and no copper was found by shaking with zinc dibenzyldithiocarbamate.

Standard lead solutions were prepared by dissolving weighed portions of the purified lead nitrate, dried previously for 2 hrs. at 120°C, in a known volume of water. All the lead solutions were stored in Pyrex bottles.

Both lead standard solutions, one prepared from metal foil and the other from purified lead nitrate were compared by titration with E.D.T.A. solution of unknown molarity. The molarity of E.D.T.A., calculated from results of titration in both cases, was compared.

Method:

A solution containing an aliquot of standard lead solution and an aliquot of E.D.T.A. was neutralized with aqueous ammonia in the presence of 0.1 ml of xylenol orange just to the red colour. One ml of 2N-nitric acid followed by 1.5 g of hexamine in solution was added.. The solution was diluted with water to 150 ml and the titration was completed from burettes by the pendulum method, while the diluted (1 + 3) lead solution was alternated with the diluted (1 + 3) E.D.T.A. solution. Three readings were taken and a volume of E.D.T.A. equivalent to a volume of lead ~~were~~ as noted. Then the molarity of E.D.T.A. was calculated. De-ionized water, analar grade reagents and purified by isopiestic distillation ammonia were used throughout. Blank carried out for the reagents was zero. Two sets of standard lead solution were compared. Three aliquots of each standard were titrated.

Table XVIII. Comparison of lead standard solutions.

Molarity of Pb	Soln.prepared from	Ml.of Pb used	Ml.of EDTA used	Molarity of EDTA found
0.02995	lead foil	50.03	50.27	0.02984
"	" "	"	"	"
"	" "	"	"	"
0.03008	lead nitrate	50.03	50.43	0.02984
"	" "	"	"	"
"	" "	"	"	"

Table XVIII (Contd.)

Molarity of Pb	Soln.prepared from	Ml.of Pb used	Ml.of EDTA used	Molarity of EDTA found
0.05906	lead foil	25.01	25.66	0.05756
"	" "	"	"	"
"	" "	"	"	"
0.05901	lead nitrate	25.01	25.64	0.05756
"	" "	"	"	"
"	" "	"	"	"
0.05904	" "	"	25.65	0.05757
"	" "	"	"	"
"	" "	"	"	"

The molarity of E.D.T.A. obtained by titration by both kinds of standards, those prepared from metal foil and those prepared from purified lead nitrate, was always the same. Thus there is no difference whether a standard is prepared from one or other substance. The colour change at the end-point of the titrations was quite good. The purified and dried lead nitrate, which is more simple to handle, is recommended for using.

B) Effect of heating on the E.D.T.A. solution.

Sometimes methods of E.D.T.A. titrations involve heating of the solution. The behaviour of the E.D.T.A. solutions when subjected to heating to various temperatures and under various conditions was controlled. Aliquots of

E.D.T.A. solution were titrated with standard lead under various conditions to see if temporary previous heating caused any change of molarity. The titrations were completed by the pendulum method with the use of diluted solutions. Every figure is the mean obtained from titration of three aliquots.

I. The solution was titrated as usual, without any heating or change in pH, which was equal to about 4.7.

II. The solution was heated to boiling and cooled to room temperature before titration. The pH was about 4.7.

III. The pH was adjusted by 2N-sodium hydroxide to 7.0. The solution was then heated to boiling and cooled to room temperature before titration.

IV. The pH was adjusted by 2N-sodium hydroxide to 7.0. The solution was boiled for 5 min. and cooled to room temperature before titration.

V. The pH was adjusted to 7.0 by 2N-NaOH. The solution was digested for 10 min. at 90°C and cooled to the room temperature before titration.

Table XIX. Effect of heating on E.D.T.A.

Titration	Molarity of Pb	Ml.of Pb used	Ml.of EDTA used	Molarity of EDTA found
I	0.03006	50.05	50.54	0.02977
II	"	"	50.53	0.02977
III	"	"	50.53	0.02977
IV	"	"	50.53	0.02977
V	"	50.31	50.78	0.02978

All the results were the same. The strength of the E.D.T.A. did not change, when a solution was a subject to previous heating to boiling or near boiling for the period up to 10 min. over a range of pH from 4.7 to 7.0. If the conditions of any particular determination require this, the E.D.T.A. solution can be safely heated.

2. Zinc.

This metal can be titrated in alkaline as well as in neutral and weakly acidic medium. The first titration of zinc was introduced by Biederman and Schwarzenbach[28]. They titrated the metal ions directly at pH 10 with Eriochrome Black T as indicator. Kinnunen and Merikanto[47] titrated zinc in similar conditions with zincon, which is more specific as indicator. Malat, Suk and Jenickova[57] used catechol violet as indicator in direct titrations of zinc in weakly alkaline medium. Cheng and Bray[58] titrated zinc directly at pH 5 to 7 in the presence of PAN as indicator. Finally, Körös and Remport-Horvath[59] recommended direct titration at pH 5 with xylenol orange as indicator.

In general, titrations with the use of xylenol orange are known to be very good: they have an excellent end-point and the conditions of the titrations are easy to observe. However, also the use of Eriochrome Black T as indicator in the alkaline medium is highly recommended by many analysts. The end-point here is perhaps the best that can be obtained with this indicator in metal titrations. These two methods were chosen to be applied in the titrations of zinc and compared one with another and both with other metals.

Eriochrome Black T, sodium(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate, was one of the first metal indicators introduced by Schwarzenbach in the first complexometric titrations. Until now it is also one of the most widely used. At present it is marketed in various countries by different manufacturers under several trade names as Eriochromeschwarz T, Pontachrome Black TA, Potting Black C, Diamond Blue Black EBS, Omega Chrome Black S, Chromogen Black Special ETOO and other. Its main disadvantage is a certain lack of selectivity. Its main advantage is a high sensitivity, up to the concentrations of 10^{-7} gram-ions of metal per litre. Having two ionizable phenolic hydrogen atoms, it can be regarded as an acid-base indicator, wine red at pH up to 6.3, blue at pH 6.3 to 11.5 and orange above pH 11.5. Its complexes with metals are wine-red coloured. Thus the titrations are possible only at a pH range in which the indicator itself is blue. The sharpest colour change was observed in buffered solutions at pH 10 to 11. The indicator is readily irreversibly oxidised in alkaline medium with the formation of a brown product. This is done by oxidizing agents as well as by manganese and cerium ions, if present in solutions without a reducing agent. Some metals, which either precipitate as hydroxides in alkaline medium, as lead, mercury, gallium and rare earths or otherwise block the indicator as do nickel, aluminium, cobalt, or do not show any colour with the indicator at all, can be successfully determined by back titration. Sometimes an additional complexing agent helps to keep the metals in solution, as does tartrate with lead, indium and some rare earths. Zinc, cadmium, bivalent mercury, lead, manganese (a reducing agent must be present), indium, lanthanum, calcium, magnesium, barium and strontium can be titrated direct. Aluminium, iron, cobalt, nickel, copper, silver and platinum block the indicator and must be absent or masked in all direct titrations. Solutions of the indicator in aqueous buffers, alcohols and triethanolamine, of various periods of stability, usually not very long, can be prepared. But the most stable, although sometimes difficult to measure is a mixture with the solid sodium chloride, which can be stored indefinitely.

A) Comparison of zinc standard solutions.

Standard zinc solution was prepared initially from a granulated zinc of analar grade by dissolving it in bromine[60]. A piece of zinc was etched with (1 + 5) hydrochloric acid to remove any film of oxide. After etching, the metal was washed with water and then 2 times with ethanol and twice with ether in order to assist drying. It is accepted as dry if it does not change the weight during weighing. A weighed piece of dry zinc was placed in a 250-ml round-bottomed long-necked flask and covered with 100 ml of water. A small funnel was inserted in the mouth of the flask and redistilled analar bromine was added from a glass dropper, drop by drop, with shaking until all the metal dissolved. To the dissolved zinc 2 ml of HCl were added and the solution was gently warmed to expel the excess of bromine. The funnel was replaced by an anti-bump tube and the contents of the flask were boiled until the bromine was completely expelled and a moistened starch-potassium iodide paper, held in the vapour~~s~~, showed no signs of darkening. After cooling, the solution was neutralized with purified isopiestic ammonia and hydrochloric acid in the presence of methyl red just to the red colour, transferred to a calibrated volumetric flask and diluted to the mark with water, the molarity being calculated.

Another method of prepara~~tion~~ing a standard zinc solution, involved zinc oxide. The zinc oxide of analar grade was taken as a basic material, subject to further purification. The powder was dissolved in a minimum quantity of hydrochloric acid. To the solution diluted ammonia (1 + 2), containing a small amount of ammonium carbonate to eliminate eventually present impurities, was added dropwise, with stirring, until a small amount of precipitate appeared, which was filtered off and rejected. Then a diluted pure ammonia (1 + 2) was added dropwise until the precipitation was complete. The precipitate was filtered through a sintered-glass funnel and washed with water until chloride-free. The zinc hydroxide thus prepared was dissolved in purified by isopiestic distillation hydrochloric acid, diluted with de-ionized water and re-precipitated by purified by isopiestic distillation ammonia (1 + 2). The precipitate was filtered on a sintered-glass funnel, washed with de-ionized water until chloride-free and dried overnight at 140°C. Then the substance was heated for 15 min. in a platinum crucible over the full bunsen flame, cooled for 25 min. in a desiccator over silica gel, weighed and re-ignited for another 15 min. to check if the ignition is complete. However, the complete washing out of hydrochloric acid is a long and tedious procedure. If traces of hydrochloric acid are left, they affect the platinum crucible on igniting. Thus it was decided to adopt another method, replacing the hydrochloric acid by nitric acid.

The zinc oxide of analar grade was dissolved in nitric acid. The impurities were precipitated, as above, by ammonia (1 + 2), containing a small amount of ammonium carbonate, and filtered off. The filtrate was saturated with washed carbon dioxide and zinc hydroxide was precipitated by diluted (1 + 2) ammonia. The precipitate was filtered through a sintered-glass funnel, washed with water many times, dissolved in nitric acid and diluted with de-ionized water. The solution was saturated with washed carbon dioxide, zinc was re-precipitated with purified by isopiestic distillation ammonia, filtered through a sintered-glass funnel, washed many times with de-ionized water, dried overnight at 140°C and ignited in a platinum crucible over a full bunsen flame. After 15 min. of ignition the substance attained a constant weight. Zinc oxide thus prepared did not affect the platinum crucible used, therefore this procedure is preferable to the one involving dissolution in hydrochloric acid. The ignited zinc oxide was weighed in a closed balance case in a covered platinum crucible over a period of 30 min. The gain in weight after 30 min. was 0.35 mg per gram, showing that the substance is not very hygroscopic.

The purity of the purified zinc oxide was tested according to the specification for analar reagents[38].

The solution obtained by dissolving 2.5 g in 20 ml of 5N-hydrochloric acid and 5 ml of water was clear. No sulphate, alkalis, or iron and only traces of chloride were found. The product was purer than the ordinary zinc oxide of analar grade.

To prepare a standard zinc solution a portion of zinc oxide, previously ignited in a platinum crucible over a full bunsen flame for 15 min. and cooled in a desiccator over silica gel for 25 min., was weighed and dissolved in a minimum amount of purified isopiestic hydrochloric acid. The solution was neutralized in the presence of methyl red with isopiestic ammonia just to the red colour and diluted to a known volume. The molarity was then calculated. The standard zinc solutions were stored in Pyrex bottles.

Both zinc standard solutions, the one prepared from the granular metal and the other from the purified zinc oxide, were compared by titration with an E.D.T.A. solution of unknown strength. The molarity of that E.D.T.A., calculated from results of titration in both cases, was compared. In addition, a standard zinc solution prepared from an ordinary zinc oxide of analar grade was compared with the other two standards in the same way. Two methods of titration were adopted.

Method I.

A pipetted aliquot of unknown E.D.T.A. solution was neutralized in the presence of 0.2 ml. of xylenol orange by 2N-hydrochloric acid and ammonia just to the red colour. The solution was then diluted with water to 200 ml, 2 ml of 2N-hydrochloric acid followed by 3 g of hexamine in solution and 50 ml of standard zinc were added and the titration was completed by a pendulum method, while the diluted zinc solution (1 + 3) was alternated with the diluted (1 + 3) E.D.T.A. solution. Three readings were taken and the volume of zinc used was noted. Then the molarity of E.D.T.A. was calculated.

Method II.

To a 50-ml aliquot of E.D.T.A. were added 5 ml of a freshly prepared buffer (containing 6.75 g of ammonium chloride and 57 ml of ammonia in 100 ml), followed by 50 ml of water, 50 ml of standard zinc solution and 0.15 ml of 0.5 per cent. Eriochrome Black T solution in methanol. The titration was completed by a pendulum method, as above.

De-ionized water, analar grade reagents and isopiestic hydrochloric acid and ammonia were used throughout.

Two solutions of E.D.T.A. of unknown strength were used. Every result is a mean of 3 titrations performed, whose figures were always very close and very often identical.

Table XX. Comparison of zinc standard solutions.

Zn.soln. prepared from	Method	Molarity of Zn soln.	Ml.of Zn used	Ml.of EDTA used	Molarity of EDTA found
ZnO purified	I	0.03090	50.79	50.44	0.03112
Zn metal	I	0.03176	50.04	51.09	0.03111
ZnO purified	II	0.03090	50.52	50.27	0.03105
Zn metal	II	0.03176	50.30	51.48	0.03103
ZnO purified	I	0.03051	51.01	50.42	0.03087
Zn metal	I	0.03168	50.01	51.36	0.03085
ZnO analar	I	0.03066	50.50	50.21	0.03084
ZnO purified	II	0.03051	50.75	50.24	0.03082
Zn metal	II	0.03168	50.01	51.44	0.03080
ZnO analar	II	0.03066	50.50	50.27	0.03080

The molarity of E.D.T.A. obtained by titrations based on zinc metal and zinc oxide, when the same method of titration was applied, in all the cases was nearly equal. The non-purified analar zinc oxide proved to be as good as the metal. Thus both zinc metal and zinc oxide can be used equally safely for the preparation of standard solutions. However, in further use, the metal was preferred because it is more easy to handle and less hygroscopic during the weighing.

B) Comparison of the two methods of titration, with xylenol orange and Eriochrome Black T as indicators.

The method applying xylenol orange as indicator is quite satisfactory and gives quite good and sharp end-point even when the diluted solutions are used. However, the method applying Eriochrome Black T has an end-point less easy to detect. When the metal is titrated by E.D.T.A. the change of colour occurs from purple red and a blue with a red tint to a pure blue of various shades, from dark at the beginning to azure when an excess of E.D.T.A. is added. The same phenomenon was observed by the writer when other metals were titrated, whenever the Eriochrome Black T indicator was used. The choosing of the correct end-point of the titration with the use of Eriochrome Black T as indicator is rather a matter of personal preference. The difference in results calculated with the dark blue and azure end-point amounted to 0.14 per cent. After several discussions the writer decided to base the observations on the point, when any trace of red tint is no more visible and the colour of the solution is dark blue.

A small, but constantly appearing difference is always seen between the results of titrations, obtained by two methods. This is seen clearly from the following table illustrating the results from titrations of various solutions, while in each pair of aliquots of the same solution one aliquot was titrated by first method and the other aliquot by second method. Various solutions of zinc and E.D.T.A. were taken. All these solutions were titrated in triplicate and each figure is a mean of the three titrations.

<u>Table XXI. Comparison of xylenol orange and Eriochrome Black T methods.</u>

Method	Molarity of Zn soln.	Ml.of Zn used	Ml.of EDTA used	Molarity of EDTA found	Difference %
XO	0.03090	50.79	50.44	0.03112	0.2
ErioT	"	50.52	50.27	0.03105	
XO	0.03176	50.04	51.09	0.03111	0.3
ErioT	"	50.30	51.48	0.03103	
XO	0.03051	51.01	50.42	0.03087	0.2
ErioT	"	50.75	50.24	0.03082	
XO	0.03168	50.01	51.36	0.03085	0.2
ErioT	"	50.01	51.44	0.03080	
XO	0.03066	50.50	50.21	0.03084	0.1
ErioT	"	50.50	50.27	0.03080	
XO	0.02690	50.27	50.45	0.02680	0.2
ErioT	"	50.01	50.27	0.02676	
XO	0.02410	50.02	51.36	0.02347	0.1
ErioT	"	50.03	51.42	0.02345	

On the whole, the method in which xylenol orange is used as indicator is found to have a better end-point and is recommended to be used whenever possible. The difference in results obtained by the two methods amounts to 0.1 to 0.3 per cent.

C) End-point in metal titrations attained by different ways.

This investigation was done in order to find out whether the results of titrations depend on the way in which the end-point is approached, e.g. if there is any difference when a metal is titrated by E.D.T.A. or E.D.T.A. by a metal.

An E.D.T.A. solution was titrated by standard zinc and lead solutions. The methods of titrations were the same as these mentioned in the sections describing lead and zinc titrations (p.85, 95), xylenol orange being used as indicator in both cases. Titrations were completed by the usual pendulum method, while diluted solutions were used. First, end-point was found by a titration by E.D.T.A. Then an excess of E.D.T.A. was added and the solution was titrated back by metal. This was repeated twice for all the aliquots and the mean values were shown in table. Calculations of the E.D.T.A. molarity were done for both the end-points: this when the titration was completed by metal and that with the titration completed by E.D.T.A. The results were compared. De-ionized water was used throughout, as well as isopiestic hydrochloric acid and ammonia. Each result is a mean of 2 figures obtained while 2 aliquots were titrated. The first result and the latter two are related to 2 different E.D.T.A. solutions.

Metal soln.	Molarity of metal soln.	Molarity of E.D.T.A. solns.from titrn. completed by metal	Molarity of E.D.T.A.solns. from titrn. completed by E.D.T.A.
zinc	0.02466	0.02481	0.02480
zinc	0.02716	0.02489	0.02489
lead	0.02436	0.02489	0.02489

The results are the same whether the titration is completed by a metal solution or by E.D.T.A. However, it is recommended, whenever possible, to complete the titrations by E.D.T.A.; the colour change from red to pure yellow is a little more easy to detect.

3. Bismuth.

Complexes of bismuth with E.D.T.A. are stable even at a very low pH. Nearly all the titrations of bismuth are performed in acid solutions, because the metal hydrolyses already at low pH and cannot be kept in solution, even if previously complexed by E.D.T.A. Working at lower pH has another advantage: it increases the selectivity and is less subject to interferences. Only Landgren[61] determined bismuth at higher pH by back titration of an excess of added E.D.T.A. with magnesium sulphate, and Eriochrome Black T as indicator, while the solution was buffered with ammonia and borax. All other analysts determined bismuth in acid solutions. K. ter Haar and Bazen[62] determined bismuth by back titrating an excess of E.D.T.A. by thorium at a pH 2 to 2.8 with Alizarin S as indicator. Gronkvist[63] used gentian violet as indicator while the titrated solution was buffered with potassium acid phthalate and contained a large amount of thiourea. Malat, Suk and Ryba[64] used catechol violet as indicator at pH 2 to 2.5 when solutions were neutralized with ammonia. Cheng[65] determined bismuth by back titrating an excess of E.D.T.A. by standard bismuth solution at pH 1.5 to 2.0 with potassium iodide as indicator. Fritz[66] titrated bismuth directly and used thiourea as indicator. Suk, Malat and Jenickova[67] used pyrogallol red or bromopyrogallol red as indicator in bismuth titrations at a pH 2 to 3. Přibil et al.[55,56] recommended direct titration at a pH 1 to 3 with xylenol orange as indicator. Peng Young Sun[68] titrated bismuth at pH 1.5 in the presence of gallein as indicator. Other indicators used in bismuth titration include PAN, recommended by Busev[69], naphthol violet applied by Budesinsky[70], methylthymolblue used by Korbl and Přibil[71], as well as PAR, glycinthymolblue, hematoxylin and thoron.

The best end-points and the easiest conditions of titrations can be obtained when catechol violet and xylenol orange are used as indicators and titrations are performed in nitric acid solutions. Those two methods were chosen for further investigations.

Catechol violet, whose full name is pyrocatecholsulphonphthalein, besides its metal indicator properties is also an acid-base indicator. Its solution is stable for a long period of time. At pH below 1.5, the indicator is red; between 2 and 6 - yellow; at pH 7, the colour changes to violet and at pH 10 - to blue. Complexes formed with metals are usually blue, so the most successful titrations are carried out between the pH limits 2 to 6, when the colour change is particularly sharp. In highly alkaline solutions the indicator is not very stable. Several bivalent metals, as magnesium, manganese, zinc, cadmium and lead, which form complexes with the indicator only in alkaline medium, can be also titrated in weakly basic buffered solution, but the colour change from blue to violet is less satisfactory. However, in the acid solutions ter- and quadrivalent metals can be easily titrated. Procedures have been described for the determination of bismuth, thorium, copper, iron, aluminium, titanium, lead, gallium, nickel, palladium, cobalt, manganese, zinc, magnesium, cadmium and indium[34].

A) Comparison of bismuth standard solutions.

Standard bismuth solutions were prepared initially from the metal of high purity, better than 99.99 per cent., supplied by Mining and Chemical Products Ltd. The pure metal was etched quickly with diluted (1 + 1) nitric acid to clean the surface. Then it was washed several times with 2N-nitric acid, water and finally with ethanol and ether to dry it. The drying was completed by pressing between 2 sheets of a filter-paper. A weighed portion of a metal was placedin a 250-ml long-necked round-bottomed flask and covered with 15 ml of (1 + 2) nitric acid. A small funnel was inserted in the mouth of the flask and the solution was warmed to assist dissolution. When the metal was completely dissolved, 15 ml of 2N-nitric acid were added, the funnel was replaced by an anti-bump tube and the solution was boiled to expel nitrous fumes, until a moistened starch-potassium iodide paper, held in vapours, showed no sign of darkening.

After cooling, the solution was transferred quantitatively to a 250-ml volumetric flask, the flask and the anti-bump tube being rinsed by 55 ml of 1N-nitric acid to avoid hydrolysis. Then the flask was filled to the mark with water and the molarity of the solution was calculated. As the bismuth titrations depend on the molarity in nitric acid of the solution and the adjustment of the acid concentration can be done only by dilution with water, the amount of the acid present in the standard bismuth solution must be strictly controlled.

Another method of preparation of standard bismuth solution involved the use of bismuth oxide. This compound was prepared from bismuth nitrate pentahydrate of analar grade. The yield was a little above 50%. Twenty grams of the salt were moistened with 7 ml of nitric acid, dissolved in water and diluted to 500 ml. To the cold solution, saturated with washed carbon dioxide, ammonia (1 + 1) was added dropwise, with stirring, until a turbidity began to appear. After 1 hr. this small precipitate was filtered off through a sintered-glass funnel and rejected. To the filtrate ammonia (1 + 1) was added drop by drop, until the precipitation was completed, and a few ml of supernatant solution were just red when tested with methyl red. The precipitate was washed three times with water by decantation, filtered through a sintered-glass funnel and washed three times with water. It was then transferred to a beaker, dissolved in 7 ml of nitric acid and de-ionized water, diluted with de-ionized water to 500 ml and re-precipitated as above, de-ionized water and aqueous ammonia purified by isopiestic distillation being used. The filtered precipitate was washed 10 times with de-ionized water and dried at 120° to 130°C for about 8 hrs. Then about 1 g of the dried substance was ignited in a vitreosil crucible at increasing temperatures until constant in weight. The crucible was cooled in a desiccator over silica gel for 45 min. before each weighing. The necessary temperature of ignition was established. The results are shown in table XXII.

Table XXII. Ignition of bismuth trioxide.

Time of ignition	Temp. of ignition	Weight in grams	
3 hrs.	520°C	12.35979	
overnight	520°C	12.35860	
2 hrs.	575°C	12.35848	
1 hr.	575°C	12.35844	
2 hrs.30 min.	620°C	12.35843	
overnight	660°C	12.35844	
2 hrs.	800°C	12.35842	fused to the crucible

The substance, ignited to constant weight, was weighed in a covered crucible in a closed balance case over a period of 30 min. The gain in weight after 30 min. was 1 mg per gram. Ignited again, it attained the constant weight after 30 min. of ignition. The recommended temperature of ignition is then 575° to 620°C and the time, if once ignited before, is 30 min.

The purified bismuth trioxide was tested for purity according to the specification for analar reagents[38]. Traces of chloride and of lead, but no sulphate, copper, iron or alkali metal were found by these tests.

To prepare a standard bismuth solution the oxide, ignited to constant weight and weighed, was dissolved in a calculated amount of nitric acid and diluted with water to a known volume, so that the solution was 0.5N in nitric acid. The molarity of the solution was calculated.

All the bismuth solutions were stored in Pyrex bottles.

A solution of E.D.T.A. was titrated by both bismuth standard solutions, the one prepared from a metal and the other prepared from bismuth oxide, and the molarities of E.D.T.A., calculated according to the results obtained from both titrations, were compared.

Method:

The final solution, when titrated, must be 0.1 to 0.2N in nitric acid. This condition is fulfilled if the method of preparing the standard bismuth solution and that of the titration are strictly observed. To a 50-ml aliquot of a standard bismuth solution were added 200 ml of water, 0.2 ml of xylenol orange and 50 ml of the E.D.T.A. solution. The titration was completed by a pendulum method while the diluted (1 + 3) bismuth solution was alternated with the diluted (1 + 3) E.D.T.A. solution. Three readings were taken and the amount of bismuth used was calculated. Every figure in the table is the mean obtained by the titration of three aliquots. These were in almost exact agreement.

Table XXIII. Comparison of Bi standard solutions.

Soln.prepd. from	Molarity of Bi soln.	Ml of Bi soln. used	Ml of E.D.T.A. soln.used	Molarity of E.D.T.A. found
Bi_2O_3	0.02685	50.01	50.27	0.02671
Bi metal	0.02688	50.02	50.31	0.02673

The difference between the molarities obtained by using both standards for titrations is very small, so both substances, the metal and the oxide, can be used as standards with the same security. The oxide is very hygroscopic and therefore less easy to weigh than the metal. Besides, the procedure of preparation is rather long and tedious. Bismuth metal is therefore recommended for the preparation of standard solutions.

B) Investigation of the method involving the use of xylenol orange.

Effect of changing the volume.

As the first step the relation between the total volume of the titrated solution, the normality in nitric acid and the results of titration was investigated. The standard bismuth solution was about 0.28N in nitric acid. Three aliquots were titrated in duplicate. The figures quoted are the mean values of 2 titrations in close agreement. The first titrated solution contained 50 ml of bismuth, 50 ml of E.D.T.A., and 0.1 ml of xylenol orange; the total volume was thus 100 ml.

The second contained 50 ml of standard bismuth solution, 50 ml of E.D.T.A. solution, 50 ml of water and 0.1 ml of xylenol orange; the total volume of the titrated solution was then 150 ml.

The third contained 50 ml of bismuth solution, 50 ml of E.D.T.A., 350 ml of water and 0.2 ml of xylenol orange; the total volume of the titrated solution was 450 ml. The molarity of E.D.T.A. was calculated from the results of the titration.

Table XXIV. Effect of the volume changes in bismuth titrations.

Total volume in ml	Normality in HNO_3	Molarity of Bi soln.	Molarity of E.D.T.A. soln. found
100	0.14	0.02330	0.02321
150	0.09	"	0.02321
450	0.03	"	0.02321

The results do not depend on the volume of the titrated solution. Only the acid concentration must be within the prescribed limits.

C) Neutralization by ammonia.

Usually the published methods recommend a neutralization of the excess of nitric acid in the bismuth solutions by aqueous ammonia in order to attain the acid concentration suitable for titration. First Gattow and Schott[72,73] observed, that in all cases, when such neutralization was done, faulty results were obtained. The cause of this was a formation of polycations, hardly soluble bismuthyl compounds and other hydrolysis products in the presence of the base. These products dissolve slightly, with the liberation of the bound metal, so the end-point of the titration is unstable and turns back as a new portion of metal appears in the solution. The same effect is produced by other bases such as sodium hydroxide and pyridine. Sodium carbonate and acetate do not produce this error, but they affect otherwise the end-point and hence they are not recommended for use. Otherwise the error can be avoided if an excess of E.D.T.A. is added. The solution is then neutralized and back titrated. The error, smaller at the lower pH and proportional to the amount of ammonia present, was observed by the authors with all the indicators used.

It was decided to test the statement of Gattow and Schott. Solutions of bismuth were neutralized with ammonia to various pH. The end-points and the results of titrations were compared with an aliquot which contained no ammonia and whose pH was adjusted only by dilution with water. The amount of ammonia required to adjust solutions to a needed pH was previously determined in the pH meter and the pH of the solutions tested was checked once more by a narrow-range indicator-paper. All the titrations were completed by the pendulum method.

I. The solution contained 50 ml of bismuth, 50 ml of E.D.T.A. and 200 ml of water. The total volume was 300 ml. No adjustment by ammonia was made. Two aliquots were titrated and the figure quoted below is the mean value.

II. The solution contained 50 ml of bismuth and 50 ml of E.D.T.A. No adjustment by ammonia was made. The end-point of titration was not clearly seen: a reddish tint persisted.

III. The solution contained 50 ml of bismuth and 50 ml of E.D.T.A. It was adjusted with ammonia. The end-point was not seen well.

IV-VII. The solution contained 50 ml of bismuth and 50 ml of E.D.T.A. It was adjusted with ammonia. The end-point was seen well.

VIII. The solution, containing 50 ml of bismuth and 50 ml of E.D.T.A. was adjusted with ammonia. The end-point cannot be attained; the solution remained red all the time owing to the red colour of the indicator at this pH.

The results of the titrations are seen from the table.

Table XXV. Neutralization of bismuth solution by ammonia.

Soln.N	Molarity of Bi soln.	Normality in HNO_3	Adjustment with ammonia	pH	Molarity of E.D.T.A. found	End-point
I	0.03001	0.07	no adjustment	1.16	0.02997	seen well
II	"	0.21	" "	0.60	"	seen not well
III	"	0.21	adjusted	0.80	"	" "
IV	"	0.21	"	1.00	0.03002	seen well
V	"	0.21	"	1.10	"	" "
VI	"	0.21	"	2.00	"	" "
VII	"	0.21	"	3.00	"	" "
VIII	"	0.21	"	6.70	---	no colour change

The above experiments confirmed the statements of Gattow and Schott. The molarity of E.D.T.A. found from the titrations of solutions whose pH was adjusted by ammonia was higher (e.g. that of the bismuth solutions was lower) than the molarity found by titrations of solution where no ammonia was present. The limits of pH for the titration with xylenol orange are 1 to 3: below as well as above these limits, the end-point cannot be seen.

D) Evaporation of bismuth solutions.

As the adjustment of pH in bismuth titrations cannot be done by neutralization and is not always possible to do by simple dilution with water, especially if solutions of high acid concentrations are concerned, the next logical step would be to try to remove the excess of nitric acid by evaporation.

Four 50-ml aliquots of bismuth solution were evaporated to dryness to remove all the nitric acid present. The residue was dissolved in 1.8 ml of nitric acid (1 + 2) and the solution was diluted with water. After the addition of 50 ml of E.D.T.A. and the dilution with water to 100 ml, the solution had an acid content suitable for the titration. The titration was completed in the presence of xylenol orange. The molarity of E.D.T.A. found as a mean of the four titrations was 0.02996. The molarity of E.D.T.A., found as a mean of three titrations of solutions which did not undergo the evaporation and where the acid contents were adjusted by dilution only was 0.02996. Both results are the same. The excess of nitric acid can safely be removed by evaporation to dryness.

E) Investigation of the method involving the use of catechol violet.

Bismuth forms pure blue complexes with catechol violet in the pH range 2 to 4[72]. The end-point of the titration is usually very sharp; the colour change from blue through violet and purple to yellow is easy to detect within a fraction of a drop. The colour of the indicator, as known, depends on the pH of the solution. As pointed out above, bismuth forms complexes with the indicator in the pH range 2 to 4. At pH values below 1.8, the solution acquires a violet tint. At pH greater than 2.5 the precipitate of basic bismuth nitrate appears very soon, so it is desirable not to titrate solutions above this pH limit. Thus the real pH required for bismuth titrations must be not lower than 2 and not higher than 2.5. Various authors adjust the pH in this titration by ammonia. The next experiment shows how the addition of ammonia to bismuth solutions affects the results. All the results shown in the table are the means of two titrations having a very close agreement. Solutions containing bismuth, E.D.T.A. and 0.2 ml of 0.1 per cent. aqueous solution of catechol violet were diluted with water to various volumes, quoted in column 2 of table XXVI, and thus had various normalities in nitric acid, as quoted in column 3 of the same table. Then all these solutions were neutralized to pH 2 with ammonia and the titration was completed by diluted E.D.T.A. Of course, solutions of higher concentration of nitric acid required larger amounts of ammonia to be neutralized.

Table XXVI. Effect of the increasing amounts of ammonia on the titration results.

Molarity of Bi soln	Total volume in ml	Normality in HNO_3	Molarity of E.D.T.A. found
0.02902	300	0.11	0.02896)
"	100	0.33	0.02899)
0.02330	450	0.03	0.02323)
"	100	0.14	0.02326)
0.02306	400	0.04	0.02349)
"	100	0.14	0.02352)
"	150	0.09	0.02346)

The above table shows that the results depend directly on the amount of ammonia needed for neutralization. Where larger amounts of ammonia were introduced, the molarity of E.D.T.A. was found higher, indicating that some bismuth did not take part in the reaction.

Now a question arose, was it due to the NH_4^+ ion or to the OH' ion of the ammonia molecule. To clear this point to neutralized by ammonia solutions were added various amounts of ammonium nitrate, prepared from analar nitric acid and purified by isopiestic distillation ammonia.

The results obtained are shown in the table.

Table XXVII. Effect of ammonium nitrate on the results of titration.

Molarity of Bi	Total volume in ml	Normality in HNO_3	Weight of NH_4NO_3 added in grams	Molarity of E.D.T.A. found	End-point
0.03001	400	0.07	-	0.03007	good
"	"	"	1.5	"	"
"	"	"	2.5	"	"
"	"	"	5.0	"	not very good
"	"	"	10.0	"	" " "

It follows that the addition of ammonium nitrate does not affect the results of the titration, however a large excess of this salt can slightly decrease the sharpness of the end-point. The effect is probably due only to the OH' ions.

F) Comparison of methods involving the use of xylenol orange and catechol violet.

Bismuth solutions were titrated by E.D.T.A. solutions of unknown strength. Each pair of solutions was titrated by two methods, with the use of the two indicators. The acidity of solutions was adjusted by dilution with water only, to avoid errors caused by ammonia. Each result is a mean of at least two titrations in close agreement.

Table XXVIII. Comparison of xylenol orange and catechol violet methods.

Molarity of Bi solns.	Indicator	Total volume in ml	Normality in HNO_3	Molarity of E.D.T.A. found	Difference,%
0.02902	xylenol orange	300	0.11	0.02892	0.1
0.02902	catechol violet	300	0.11	0.02896	
0.02330	xylenol orange	100	0.14	0.02321	0.1
"	catechol violet	450	0.03	0.02323	
0.02306	xylenol orange	150	0.09	0.02346	0.1
"	catechol violet	400	0.04	0.02349	

A small but persistent difference of 0.1 per cent., larger than the difference between the replicate titrations, was found between two methods of titration with the use of two indicators. Here the conditions of titration were strictly the same and the difference is due only to the colour change of the indicators. It confirms other statements of Gattow and Schott, who found also that all the different indicators give results which are not equal, although the difference was always small.

4. Manganese.

Electrolytic manganese of a purity suitable for volumetric standardizations now being available, an investigation of its possibilities as a standard in E.D.T.A. titrations seemed to be worth while. Nearly all the determinations of manganese are performed in alkaline media. Manganese was first determined by Schwarzenbach[28] in an alkaline solution of pH 10, the excess of E.D.T.A. added being back-titrated by standard zinc or magnesium solutions to avoid blocking of the Eriochrome Black T indicator. Later, Flaschka[74] found that manganese can be also titrated directly at the same pH and in the presence of the same indicator, provided that tartrate, which prevents the precipitation of hydroxide and ascorbic acid which prevents the oxidizing action of manganese on the indicator, are present in the solution. However, Kinnunen[75] found that the presence of tartrate is not only unnecessary, but even leads to error. Ascorbic acid is enough to keep manganese ions in solution and to prevent their oxidizing action. Kinnunen and Merikanto[47] determined manganese in alkaline solution of pH 10, the excess of E.D.T.A. added being back-titrated by standard zinc solution with zincon as indicator. Suk et al.[34] titrated manganese directly in the presence of hydroxylamine hydrochloride as reducing agent in a weakly alkaline medium with catechol violet as indicator. Flaschka and Abdine[53] determined manganese in acid solutions by titrating back the excess of E.D.T.A. added with standard copper solution in the presence of PAN as indicator. Přibil and Kopanica[77], Morris[78], and Studlar[79] titrated manganese directly in ammoniacal solutions in the presence of hydroxylamine hydrochloride with thymolphthalexone as indicator.

After careful consideration, the method recommended by Kinnunen[75] with the use of Eriochrome Black T and those recommended by Suk and co-workers[34] and Přibil and Kopanica[77] with the use of catechol violet and thymolphthalexone as indicators were chosen for further investigation.

A) Preparation of standard manganese solutions and comparison of methods.

The standard solution of manganese was prepared from electrolytic manganese metal flakes supplied by Hopkin and Williams by dissolving them in bromine[60]. The corroded surface of the metal was etched in 2N-nitric acid until it became quite bright, washed with water and ether, dried by pressing between two sheets of filter-paper and weighed. The weighed portion was introduced into a long-necked round-bottomed flask and covered by 10 ml of 2N-hydrochloric acid. A small funnel was inserted in the mouth of the flask and analar re-distilled bromine was added from a glass dropper, drop by drop, with shaking, until all the metal dissolved.

Then the funnel was replaced by an anti-bump tube and the excess of bromine was removed by gentle boiling until a moistened starch-potassium iodide paper, held in the vapours, showed no signs of darkening. After cooling, the solution was transferred to a calibrated volumetric flask, which was then filled with water to the mark, and a molarity of the solution was calculated. Manganese solution thus prepared was tested for the presence of impurities, according to the specification for analar reagents[38]. Only traces of iron, much below the standard requirements, were found. The tests for heavy metals, calcium, barium, nickel, and sulphate were negative.

The etched metal flakes consisted of manganese of a high purity. Aliquots of the standard manganese solution were titrated by the same E.D.T.A. solution according to the method of Kinnunen and to that of Suk and co-workers and the results were compared.

Method I:

To a 50-ml aliquot of manganese 0.4 g of ascorbic acid was added and the solution, diluted with water to 100 ml, was neutralized with ammonia or sodium hydroxide in the presence of methyl red to the yellow colour. Then 3 ml of triethanolamine followed by 2 ml of ammonia buffer (containing 6.75 g of ammonium chloride and 57 ml of ammonia in 100 ml) and 0.15 ml of 0.5 per cent. Eriochrome Black T solution in methanol were added and the whole was titrated by E.D.T.A. The change of colour at the end of the titration from wine red to pure blue is quite well seen. Ascorbic acid can be replaced by hydroxylamine hydrochloride and the neutralization can be done by means of ammonia or sodium hydroxide with the same effect. Metal solutions of a molarity 0.01 to 0.05 can be safely used.

Method II:

To a 50-ml aliquot of the manganese solution, diluted with water to 100 ml, was added 0.4 g of hydroxylamine hydrochloride and the solution was neutralized with ammonia or sodium hydroxide. Then 10 ml of a buffer (containing equal volumes of 1M ammonia and 1M ammonium chloride) followed by 0.2 ml of 0.1 per cent. aqueous catechol violet solution were added and the solution was titrated by E.D.T.A. The colour change from pure blue to purple red was difficult to detect. When the excess of E.D.T.A. added was back-titrated with standard manganese solution the colour change from purple red to pure blue was seen better, but was still difficult to detect.

The mean titre in the method I was 40.30 ml of E.D.T.A.
" " " " " " II " 39.50 " " "

From all the points of view the method with the applying of catechol violet is not recommended for use. Besides the difficulties in the detection of the end-point the results obtained are too low. It was observed, as in zinc titrations, that the end-point which manganese gives with Eriochrome Black T has several steps. The blue colour changes from deep dark blue to the azure. The difference in results between the 2 steps is 0.24 per cent. It was decided also here to rely on the first pure dark blue shade.

As the next step the Kinnunen method, including the use of Eriochrome Black T as indicator, was compared with the Přibil and Kopanica method involving the use of thymolphthalexone.

Method III:

To 50 ml of manganese solution were added 2.4 g of hydroxylamine hydrochloride followed by 10 ml of triethanolamine. The solution was diluted to 125 ml with water, 0.30 ml of 0.5 per cent. solution of thymolphthalexone in ethanol followed by 50 ml of E.D.T.A. were added and the titration was completed by E.D.T.A. The pH of the solution was about 8. The end-point, from blue to colourless, was seen not very well. When the ammonia was added to the solution, the colour change was from deep blue to light blue, but seen still less satisfactorily.

The molarity of E.D.T.A. obtained by Eriochrome Black T method was 0.03001.

The molarity of E.D.T.A. obtained by thymolphthalexone method was 0.02999.

Although the results obtained by both methods are very close, the use of the thymolphthalexone method is not recommended because of the difficulties in detecting the end-point. So it was decided to apply the Eriochrome Black T method for the titrations of manganese in comparing it with other metals standard solutions and in trying to apply it to the analysis of complex materials. Results obtained by complexometric titration of manganese can be controlled by running a parallel determination by Lang's[80] method for manganese determination.

B) Interferences and masking.

Further investigations of manganese titration by E.D.T.A. with Eriochrome Black T as indicator were carried out with the view to applying the direct titration to a solution of manganese ores, especially pyrolusite, which contain other metals as impurities. In particular, the interference by and the possibility of masking of calcium, magnesium, aluminium and iron were examined. Calcium and magnesium are co-titrated under normal conditions, and so an attempt was made to mask these two metal ions by precipitation with fluoride ion. Aluminium and iron both block the indicator. Aluminium can be masked by fluoride as well as by triethanolamine. According to many published methods, iron can be masked either by triethanolamine or, even if present in large amounts, by potassium cyanide. Manganese itself forms with small amounts of cyanide only a weak complex, from which it is extracted by E.D.T.A. Nearly the same occurs with triethanolamine. The behaviour of the solution after the addition of various amounts of triethanolamine and potassium cyanide was studied.

Method:

To 50 ml of the standard manganese solution about 0.4 g of ascorbic acid was added. The solution was diluted with water to 100 ml and neutralized with ammonia in the presence of methyl red to the yellow colour. Then 2 ml of the ammonia buffer, mentioned before, followed by 0.15 ml of 0.5 per cent. methanol solution of Eriochrome Black T and 50 ml of E.D.T.A. were added and the titration was completed by E.D.T.A. from a burette by a pendulum method. Each of the cited results is a mean of two titrations.

Solution I - titrated as mentioned above.

" II - 0.5 ml of triethanolamine added before the buffer; the solution should not be allowed to stand, because the indicator oxidizes quickly.

" III - 2 ml of the triethanolamine added before the buffer.

" IV - 3 ml of triethanolamine added before the buffer.

Solution V - 12 ml of triethanolamine added before the buffer.

" VI - 0.1 g of potassium cyanide added before the buffer.

" VII - 0.2 g of potassium cyanide added before the buffer.

" VIII - 0.3 g of potassium cyanide added before the buffer.

" IX - 0.6 g of potassium cyanide added before the buffer.

" X - 0.1 of potassium cyanide and 3 ml of triethanolamine added before the buffer.

" XI - 0.2 g of potassium cyanide and 3 ml of triethanolamine added before the buffer.

Table XXXII. Effect of masking agents on manganese solution.

Soln.	Molarity of Mn soln.	Ml of E.D.T.A. used	Molarity of E.D.T.A. found	End-point
I	0.03043	50.24	0.03032	good
II	"	"	"	"
III	"	"	"	"
IV	"	"	"	" , becomes worse.
V	"	"	"	hardly visible
VI	"	"	"	good
VII	"	"	"	"
VIII	"	about 49.00	too high	"
IX	"	about 46.00	still higher	"
X	"	50.24	0.03032	"
XI	"	50.24	"	"

The maximum amount of potassium cyanide which can be added to 50ml of about 0.03 M manganese solution with good results is 0.2 g. Above this figure a loss of manganese is seen. Probably the complex of manganese with cyanide is not entirely destroyed by E.D.T.A. End-points in the presence of cyanide are always good, better than those seen when cyanide is not added. The presence of triethanolamine, even in very small amounts, affects the end-point. The solutions must be titrated at once. The indicator oxidizes quickly. When an aliquot of manganese solution is titrated by the pendulum method, while the diluted metal solution is alternated three times with a diluted E.D.T.A. solution, the first titration has a good end-point, the end-point of the second titration is worse, and the third one still worse. When a large amount of triethanolamine is added, even the first end-point is quite bad. The recommended amount of triethanolamine is 3 ml. So the titrated solution can contain 0.2 g of potassium cyanide and 3 ml of triethanolamine.

The behaviour of foreign metal~~s~~ ions present in the solution and the effect of masking were studied. The cations were added in proportions likely to be met in pyrolusite, e.g. 2 per cent. of calcium and iron and 1 per cent. of magnesium and aluminium. Calcium solution was prepared from analar calcium carbonate; magnesium - from magnesium sulphate heptahydrate; aluminium - from aluminium sulphate and iron - from ferric ammonium sulphate. As pointed out above, calcinm and magnesium are titrated along with manganese and aluminium and iron block the indicator.

I. To 50 ml of about 0.03M manganese solution, about 0.4 g of ascorbic acid was added. The solution was diluted with water to 100 ml and neutralized with ammonia in the presence of methyl red to the yellow colour. Then 2 ml of the ammonia buffer followed by 0.15 ml of Eriochrome Black T and 50 ml of E.D.T.A. were added and the titration was completed from a burette by a pendulum method.

The titre was 51.70 ml of E.D.T.A.

II. Masking of calcium and magnesium.

To the manganese solution were added 1 ml of 0.03M calcium solution and 0.5 ml of 0.03M magnesium solution.

a) Before the neutralization with ammonia 2.5 g of ammonium fluoride in solution were added. The colour change was very bad: a greyish tint persisted and the pure blue colour could not be attained.

Very approximate titre was 51.00 ml of E.D.T.A.

b) Before the neutralization with ammonia 1.25 g of ammonium fluoride in solution were added. The colour change was as above.

Very approximate titre was 51.00 ml of E.D.T.A.

c) Before ascorbic acid 2.50 g of ammonium fluoride were added. A small amount of precipitate appeared. The ~~f~~colour change was not seen well because of the presence of the precipitate. Probably some manganese co-precipitated.

Very approximate titre was 50.50 ml of E.D.T.A.

III. Masking of iron.

To the manganese solution 1 ml of 0.03M iron solution was added.

a) The solution on titration remained brownish, no change of colour could be seen.

b) Three ml of triethanolamine were added before the buffer. The colour change could hardly be seen, because the colour turned immediately back to red.

c) Six millilitres of triethanolamine were added before the buffer. The colour change was as above.

d) Before the buffer 0.2 g of potassium cyanide were added. The violet tint persisted. The colour turned back to red. The end-point could be hardly seen.

e) Before the buffer 0.2 g of potassium cyanide and 6 ml of triethanolamine were added. The colour change was as above.

f) Before ascorbic acid 0.4 g of tartaric acid was added. The solution remained red, no change at all was seen.

g) Before ascorbic acid 1 g of the citric acid was added. The solution remained green, no colour change at all was seen.

IV. Masking of aluminium.

To the manganese solution 0.5 ml of 0.03M aluminium solution was added.

a) The solution conserved a violet tint and became again red on standing. The end-point was not clear.

b) Before the ascorbic acid 0.2 g of tartaric acid was added. The colour change was as above.

c) Before the buffer 6 ml of triethanolamine were added. The colour change was better than above, but still not quite clear.

d) Before the buffer 0.2 g of potassium cyanide and 6 ml of triethanolamine were added. The colour change was quite clear.

The titre was 51.71 ml of E.D.T.A.

From all the interfering metals only aluminium could be successfully masked by triethanolamine in the presence of cyanide. Calcium and magnesium were precipitated by fluoride, but a little manganese was co-precipitated and the results were never satisfactory. Iron can be partially masked by the addition of cyanide and triethanolamine, but the colour change was never quite satisfactory. The above experiments were carried out to find a good method of masking for the elements present usually in pyrolusite to make possible a direct titration of the one solution without previous tedious separations. However, except for aluminium, no success was obtained. The end-point was never seen very well. The next logical step would be to try to overcome the interferences of foreign metals by using other indicators and methods. Endo and Koroki[81] determined manganese in the presence of several foreign metals ions and masking agents with thymolphthalexone as indicator. However, the writer found that this indicator, as well as catechol violet, had a very poor end-point even when solutions of pure manganese only were titrated. Therefore the use of these methods for sure and accurate determinations of manganese in complex materials cannot be recommended.

5. Comparison of standard solutions prepared from various metals.

Standard solutions prepared from four metals were titrated by the same E.D.T.A. solutions, different methods and indicators being used. The results, expressed as the molarity of E.D.T.A. found, are compared in table XXXIII. The methods of titrations are those described in foregoing sections above, where the description of particulars concerning each metal is given. Each of the figures quoted in the tables below is a mean obtained from a minimum of two titrations that agreed closely. De-ionized water was used throughout for the preparation of metal standards as well as for the titrations. These were completed by the pendulum method. The acidity of the bismuth solutions was adjusted by dilution with water only; no ammonia was present.

Table XXXIII. Comparison of various metal solutions.

Metal	Molarity of metal	Indicator	Ml. of metal soln. used	Ml. of EDTA used	Molarity of E.D.T.A. found	Difference %
Zn	0.02716	xylenol orange	50.08	54.65	0.02489	Zn and
Pb	0.02436	" "	51.34	50.25	0.02489	Pb = 0

Table XXXIII (Contd).

Metal	Molarity of metal	Indicator	Ml.of metal soln. used	Ml.of EDTA used	Molarity of E.D.T.A. found	Difference %
Zn	0.02690	xylenol orange	50.27	50.45	0.02680	
Zn	"	Erio T	50.01	50.27	0.02676	Zn and Pb=0.2
Pb	0.02691	xylenol orange	50.03	50.32	0.02676	Zn and Bi=0.3
Bi	0.02688	" "	50.02	50.31	0.02673	Bi and Pb=0.1
Mn	0.03043	Erio T	50.06	50.24	0.03032	
Pb	0.03044	xylenol orange	50.04	50.26	0.03031	Mn and Pb=0.03
Pb	0.02896	xylenol orange	50.00	50.24	0.02882	Bi and Pb=0
Bi	0.02899	" "	50.01	50.30	0.02882	Bi and Mn=0
Mn	0.02896	Erio T	50.28	50.52	0.02882	Mn and Pb=0
Bi	0.02306	catechol violet	51.55	50.60	0.02349	
Bi	"	xylenol orange	51.05	50.18	0.02346	Zn and Bi<0.05
Zn	0.02410	Erio T	50.03	51.42	0.02345	Zn and Pb=0.1
Zn	"	xylenol orange	50.02	51.36	0.02347	Pb and Bi=0.1
Pb	0.02305	" "	51.03	50.07	0.02349	

It will be seen that the values obtained by means of different metals for the molarities of the different solutions of E.D.T.A. are in good agreement, but small differences, some of them larger probably than the experimental errors involved, do occur. These should be considered in the most accurate work.

Conclusions.

Standard solutions, prepared from a metal and a suitable compound of this metal usually behave similarly. When solutions prepared from bismuth were compared to those prepared from bismuth oxide, from zinc to those from zinc oxide and from lead to those from lead nitrate, the results obtained by both under the same conditions of the reaction were the same for all metals. Sometimes it is easier to use the compound, as with lead nitrate, whilst at other times the use of metal itself is more advantageous, as with bismuth and zinc. When one metal ion is titrated by two different methods always a small difference in results seems to persist. This was observed by the comparison of results obtained by titration of zinc by the method with xylenol orange as indicator at pH 5 and by that with Eriochrome Black T as indicator at pH 10, as well as by the comparison of results obtained by the titration of bismuth with catechol violet and xylenol orange used as indicators and by titration of manganese with Eriochrome Black T and thymolphthalexone as indicators. Even if all the other conditions of titration including pH and volume are the same, it is enough to change the indicator only to obtain a slightly different result. It should be emphasized that when an E.D.T.A. solution has to be standardized, this should be done always against the same metal ion and as nearly as possible under the same conditions as are to be used in the determination. If E.D.T.A. solutions are to be used for titration of different cations, a new standardization should be done for each of the cations involved.

PART III

THE APPLICATION OF THE E.D.T.A. TITRATION TO THE DETERMINATION OF TIN.

Gravimetric methods for the determination of tin are often long and tedious and volumetric methods based mostly on the reduction of tin and titrimetric oxidation[82,83,84] are subject to considerable uncertainty and error. A new volumetric method that could be applied to a solution of tin obtained by distillation would constitute an advance and would be valuable. The E.D.T.A. titration of such a solution appeared to be a likely and desirable possibility.

Tin in both its oxidation states forms stable complexes with E.D.T.A. at pH1 to 6[85]. Bivalent tin forms also a weak complex with E.D.T.A. in the alkaline region. Since tin cannot be kept in solution in a not very acid medium, usually an excess of E.D.T.A. has to be added and the unused part back-titrated. The first to introduce the complexometric titration of tin was Kubista[86]. His method was based on the property of bivalent tin forming in alkaline medium a weak complex with E.D.T.A. He treated the bivalent tin solution with E.D.T.A., the excess of which was back-titrated by a standard magnesium solution in the presence of Eriochrome Black T after the pH had been adjusted to 10.

However, the end-point was not good owing to the hydrolysis of the complex near the equivalence point and adsorption of the indicator on the product of hydrolysis. The complex of quadrivalent tin is completely hydrolyzed in alkaline solution under these conditions. Only one method of direct titration of tin was reported. It was that of Dubsky[87] who titrated bivalent tin directly by E.D.T.A. at a pH adjusted by pyridine-acetic acid buffer to 5.5 to 6 in the presence of methylthymolblue as indicator. Quadrivalent tin was masked by fluoride and tervalent antimony by tartaric acid. Jankovsky[88] treated a mixture of bi- and quadrivalent tin with E.D.T.A., the excess of which was titrated by standard zinc solution in the presence of catechol violet in a solution whose pH was adjusted by ammonium acetate to 5. Catechol violet forms no coloured complexes with zinc at this pH, but it forms a blue one with quadrivalent tin. Zinc ions extract E.D.T.A. from the complex with tin, which is weaker in these conditions. Thus the indicator changes colour with the appearance of free Sn^{4+} ions in the solution. The excess of E.D.T.A. was titrated under similar conditions and at similar pH by zinc solution in the presence of 3,3'-dimethylnaphthidine-ferro-ferricyanide system by Kinnunen and Wennerstrand[85] and Sajo[89]. Sajo[90,91] introduced successfully the use of benzidine-ferro-ferricyanide system in similar conditions. Ottendorfer[92] titrated the amount of E.D.T.A. freed from the complex with quadrivalent tin by the addition of fluoride, by standard lead solution at pH 5 to 6 in hexamine buffered solutions in the presence of xylenol orange. Yurist and Korotkova[93] titrated the excess of E.D.T.A. added to tin by ferric trichloride at pH 5 in acetate buffered solution in the presence of sulfosalicylic acid as indicator. Takamoto[94] titrated the excess of E.D.T.A. added to bivalent tin solution by cobalt chloridein ammonium acetate medium in the presence of thiocyanate as indicator. This method is subject to limited interferences only, as cobalt ions, owing to the extreme stability of Co-E.D.T.A. complex, decompose complexes of E.D.T.A. with many metals, but not that with bivalent tin. Kinnunen and Wennerstrand[85] and Körbl and Přibil[95] titrated the excess of E.D.T.A. added to tin solution by thorium nitrate, while the pH was adjustedby ammonium acetate to 2, in the presence of xylenol orange or methylthymolblue. Kinnunen et al.[96] improved this method. He introduced titration at pH 2.5 to 3.5 in the presence of xylenol orange. Dixon[97] added to the Sn-E.D.T.A. complex, buffered to pH 2.5 by ammonium acetate, a bismuth solution to complex the unused part of E.D.T.A. The excess of bismuth was then titrated by E.D.T.A. as described above. Tin is unlikely to be present in its solutions, as well as in the solutions of complex materials, completely in the bivalent state. To introduce a reduction process was highly undesirable. That is why only methods dealing with quadrivalent tin were taken into consideration. As most of the methods practically differ only by a choice of indicator or in small particulars, it was decided to investigate only the methods of Jankovsky, Kinnunen et al. and of Yurist and Korotkova and to choose the best of them.

The best method of complete separation from heavy metals and nearly complete separation from arsenic and antimony, which usually are most likely to accompany tin, is distillation, described in detail by Mogerman[98], Scherrer[99,100] and also by De Bruyne and Hoste[101], who succeeded in separating these metals even from a solid material. The upper limit of the amount of tin which can be distilled is 240 mg. The upper limit for antimony is 100 mg. Antimony and arsenic, if present, are reduced before distillation to the tervalent state by hydrazine sulphate in sulphuric acid solution. Arsenic is distilled from nearly 11N-hydrochloric acid at 110°C. Antimony, in amount proportional to the amount of hydrochloric acid used, is distilled at 155 to 165°C, while tin is retained by ortho-phosphoric acid. Tin is distilled as the tetrabromide at 140°C or 180°C. The temperature of distillation depends on the composition of hydrobromic acid mixture used. In further investigations only the method of Mogerman was followed. The elements which may co-distil, although in small amounts only, with the fraction of tin are antimony, germanium, boron and molybdenum. Antimony can be eliminated, if desired, by using a larger amount of hydrochloric acid for the distillation of the 160°C fraction. Molybdenum can be removed by repeated distillation. The other two elements are not likely to be present in complex materials containing tin. The distillate obtained in the Mogerman method contains mainly tin tetrabromide and hydrobromic acid in high concentration. From here tin is to be recovered. Mogerman does it by means of a precipitation by cupferron from solutions about 5 per cent. in sulphuric or hydrochloric acid. Under these conditions tin is precipitated as a complex compound with cupferron, which is then dried, decomposed by ignition and weighed as tin dioxide. Besides tin in both valency states cupferron can also precipitate molybdenum and tervalent antimony. The latter must then be oxidized to quinquevalent form by permanganate. The acidity of the solution exposed to precipitation by cupferron must be well controlled. If too acid, the solution must be diluted with water to a needed concentration, but must not be neutralized by a base. In that case ammonium bromide is formed, which is very difficult to be later washed out, and, if present, volatilizes with some tin on ignition. For the same reason the precipitate with cupferron should be very well washed out in order to remove even traces of bromide. The amount of cupferron should be controlled. The solution should be well cooled and the precipitate with tin should be filtered at once; otherwise decomposition of cupferron occurs, some soluble organic compounds are formed and tin is liberated back into solution. The drying and igniting of the precipitate, which is extremely light in weight, requires more than usual care. It should be done very slowly and carefully in order to prevent particles from escaping.

The determination of tin in the distillate by precipitation with cupferron, like most gravimetric methods, is a tedious and time-consuming procedure, which takes nearly 2 working days. Therefore an attempt was made to determine tin by complexometric titration. As pointed out before, besides tin can be present in the distillate four other elements in very small amounts. Boron would not interfere with E.D.T.A. titrations. From all the mentioned elements only antimony is likely to interfere. It forms complexes with E.D.T.A. and indicators in acid medium. However, the complexometric behaviour of antimony is not much investigated. It was ensured that it can be determined only by back titrations. Kinnunen and Wennerstrand[102] made an attempt to determine tervalent antimony at pH 4 in ammonium acetate buffered solution by back titrating the excess of E.D.T.A. by zinc solution in the presence of xylenol orange as indicator. Dubsky[87] contemplated the possibility of using methylthymolblue as indicator and Takamoto[94] titrated back the excess of E.D.T.A. by cobalt solution in the presence of thiocyanate as indicator. However, all these methods gave rather poor results, but they show that in the range of acidities and in the presence of indicators used in tin titrations, antimony is likely to interfere. Therefore, the possibility of the presence of antimony in the distillate, its effect on the titration and eventual possibilities of masking were carefully investigated.

1. Preparation of standard tin solution. Examination of the titration methods.

Standard tin solution was prepared from granular analar tin by dissolving it in bromine[60]. After etching in 2N-hydrochloric acid to clean the surface, the metal was washed with water, with ethanol and with ether to assist drying. It was accepted as dry if it did not change weight during weighing. A weighed piece of dry tin was placed in a 250-ml long-necked round-bottomed flask and covered with 30 ml of (1 + 5) hydrochloric acid. A small funnel was inserted in the mouth of the flask and analar re-distilled bromine was added from a glass dropper, drop by drop, with shaking, until all the metal dissolved. Then the funnel was replaced by an anti-bump tube and the contents of the flask were gently boiled until the bromine was completely expelled and a moistened starch-potassium iodide paper, held in vapours, showed no signs of darkening. The solution should be boiled only as little as possible in order to avoid possibilities of the loss of tin. After cooling, the contents were transferred to a volumetric flask and diluted to the mark with (1 + 5) hydrochloric acid, the molarity of the solution being calculated. When the presence of bromide is not desirable, the metal can be dissolved in hydrochloric acid only, but the time required to prepare the solution is longer. The etched, dried and weighed piece of tin was placed into a beaker or conical flask and covered with hydrochloric acid. The beaker was covered with a watch glass and set aside overnight. In that time, the tin dissolved gently and completely. The solution was transferred to a calibrated volumetric flask and diluted to the mark by water and hydrochloric acid, the molarity being calculated. The final concentration of the solution should be not less than (1 + 9) in hydrochloric acid. When solutions of lower acidity were prepared, after 2 weeks a small precipitate of hydrolyzed tin appeared.

Three chosen methods of tin titration were investigated.

Method I:[93]

The solution containing 25 ml of about 0.03M standard tin and 25 ml of a little stronger E.D.T.A. and having a volume of 150 ml was neutralized with ammonium acetate until the Congo Red paper changed colour. Then 15 ml of a buffer (containing 54 g of sodium acetate and 100 ml of 2N-acetic acid in 200 ml) followed by 1 ml of 20 per cent. sulfosalicylic acid were added and the excess of E.D.T.A. was titrated by ferric chloride. The colour change was from green-yellow to yellow-orange. The reaction is reversible.

Method II:[88]

A solution containing 50 ml of about 0.03M tin and 50 ml of a little stronger E.D.T.A. was neutralized in the presence of thymolblue with ammonium acetate. Then 10 ml of 3M-sodium acetate were added to bring the pH to 5 and the whole was heated to 70 to 80°C. After the addition of 0.15 ml of 0.1 per cent. catechol violet solution the excess of E.D.T.A. was titrated, while hot, by standard zinc solution prepared by dissolving zinc in bromine (see part II). The colour change, irreversible, was from yellow to blue.

Method III:[96]

The solution containing 50 ml of about 0.03M tin and 50 ml of a little stronger E.D.T.A. and having a volume of 200 ml was neutralized with ammonium acetate in the presence of 0.25 ml of 0.1 per cent. 2:4 dinitrophenol solution in 70 per cent. ethanol until the colour turned just to slightly yellow and the pH was within limits of 2.5 to 3.5. After the addition of 0.15 ml of xylenol orange the excess of E.D.T.A. was titrated by thorium nitrate. Hydrated thorium nitrate, which has somewhat unstable number of water molecules and then rather uncertain composition, cannot be used as standard. The relation thorium: E.D.T.A. must be determined by a separate titration of

E.D.T.A. aliquot by thorium nitrate solution under the conditions stated above and the volume of thorium nitrate used in titration of tin must be converted to a volume of E.D.T.A. The colour change, from yellow to red, is reversible and very good.

Method I was abandoned. The medium and the pH are very similar to those of method II, but the colour change was not very good and sensitive.

The only inconvenience of method III is a need of an additional titration to standardize the thorium solution against E.D.T.A. This can in some way affect the accuracy of results. But the advantages here are lower pH, which reduces the risk of over-neutralization and precipitation of tin, a good internal indicator to show exactly the point of neutralization and a very good reversible colour change, which enables a control on both sides of the end-point of the titration.

Method II requires rather an experienced eye to detect the colour change at the end-point, which can be from yellow to blue, green bluish-green or even reddish or dirty violet which slowly change to blue on standing. Solutions should be titrated hot, to accelerate the destruction of the Sn-E.D.T.A. complex by zinc: in the cold this reaction is rather too slow. But the possibility of basing results on one titration only tends to produce more accurate results.

Both methods II and III present a common problem of neutralization. Many experiments were carried out to solve this problem. Tin hydroxide precipitates from solutions even from Sn-E.D.T.A. complex at a low pH. However, if E.D.T.A. is present in an excess of 15 to 20 per cent. it helps to keep tin in solution when neutralized by ammonium acetate. The safest way to neutralize tin solutions containing an excess of E.D.T.A. is to do it by ammonium acetate: thus tin solutions can be neutralized even to pH as high as 5 to 6 without any danger of precipitating. As far as only standard solutions of tin, containing relatively small amounts of free acid are concerned, this works well. But as soon as tin containing distillate with large amounts of hydrobromic acid is to be titrated, the neutralization requires extremely large amounts of the salt. This is both uneconomic, increases the volume of the solution under test, which should be kept constant and possibly small, and, worse still, decreases the sharpness of the end-point of titration by affecting indicators. Sodium hydroxide, ammonia or sodium acetate cannot be used to neutralize tin solutions to the necessary pH without precipitation. The method of Jankovsky[88], who suggests neutralization by aqueous ammonia in the presence of a little acetic acid proved ineffective: the precipitation was not avoided. The best way found was to neutralize most of the acid in a solution under test by adding solid sodium hydroxide, pellet by pellet, until a small amount of precipitate appeared, which dissolved on stirring, and then to complete the neutralization by means of solid ammonium acetate. This reduced considerably the amount of the latter in solution. Solid substances were used in order to avoid the increase of volume of the solutions under test. The above modification solved any problem concerning method III, where the colour change of the dinitrophenol indicated the end of neutralization. Where the method II was concerned, a new problem arose. Jankovsky brought the pH to the needed value of 5 by buffering the solution by a small amount of sodium acetate. It worked well, when only small amount of acid and consequently of ammonium acetate were present in solution. When a solution contains large amounts of acid and of ammonium acetate needed for neutralization in the presence of thymol blue to the pH of about 2.8, the amount of sodium acetate required to adjust the pH to 5 is very large. Thus the pH cannot be adjusted simply by an addition of a specified amount of sodium acetate. It is much better to complete the pH adjustment by solid ammonium acetate. In that case an indicator is needed, which changes colour at pH about 5. The use of thymol blue can be eliminated, as there is no point in detecting an intermediate pH. Several indicators were examined. Methyl orange showed too low an end-point. Methyl red showed one too high. An indicator consisting of one part of methyl red solution and 3 parts of bromocresol green solution showed a sharp colour change from red to yellow at pH 5.1 when a solution of acid was neutralized by sodium hydroxide, but no positive colour change could be observed in neutralization by ammonium acetate. A mixed indicator consisting of 1 part of 0.1 per cent. bromocresol green solution and 1 part of 0.02 per cent. methyl orange solution did not show any change of colour from green at the desired pH when the solution was neutralized with ammonium acetate. Another indicator tried, 4-phenylazo-1-naphthylamine(0.1 per cent.solution in ethanol), showed a very good colour change from red to yellow at pH of about 5 when a solution of acid was neutralized by sodium hydroxide or ammonia. But any colour change was hardly seen if ammonium or sodium acetate was present in the solution. Unfortunately, the presence of ammonium acetate in the solution makes impossible the use of many indicators. For the moment no indicator helping with the adjustment of pH to 5 in the presence of ammonium acetate was found. The adjustment was controlled **only by** a narrow-range indicator-paper, the approximate amount of ammonium acetate needed having been calculated before.

Thus the modified method II is:

To a solution containing a 50-ml aliquot of about 0.03M tin and a 50-ml aliquot of a little stronger E.D.T.A. solid sodium hydroxide was added, pellet by pellet, until a small amount of precipitate appeared, which dissolved on stirring. The neutralization was completed by the addition of a calculated amount of solid ammonium acetate, the pH, which should be 5, being controlled by narrow-range indicator-paper. The solution was then heated to 70 to 80°C and after the addition of catechol violet the excess of E.D.T.A. was titrated by standard zinc solution.

Comparison of methods II and III.

The two methods were compared by performing titrations with the use of the same E.D.T.A. solution, whose molarity was then calculated according to the results obtained in both cases. Each result is a mean of three titrations. Blank determinations, carried out on reagents only, were for both methods zero. The E.D.T.A. molarity found according to results obtained by method II was 0.03052. The E.D.T.A. molarity found according to results obtained by method III was 0.03040. Thus a small difference amounting to 0.4 per cent. exists between the results from the two above methods.

2. Interferences and masking in the method of Jankovsky.

In the distillate obtained by Mogerman's method besides tin, hydrobromic acid in large amounts and possibly very small amounts of antimony are present. The titration of tin in the presence of various amounts of these substances was investigated. Results are expressed as volume of zinc solution used to back titrate the excess of E.D.T.A.

a) The tin solution was titrated in duplicate.

The titre was 0.72 ml of Zn soln.

b) To the tin solution 16 ml of hydrochloric acid were added. The end-point of the titration was a little diffuse ~~offused~~, probably because of a large amount of ammonium acetate needed for neutralization.

The titre was 0.82 ml of Zn soln.

c) To the tin solution 17 g of sodium chloride were added. End-point was good.

The titre was 0.75 ml of Zn soln.

d) To the tin solution 15 g of sodium bromide were added. End-point was good.

The titre was 0.76 ml of Zn soln.

e) To the tin solution 15 g of potassium bromide were added. End-point was good.

The titre was 0.76 ml of Zn soln.

The presence of chlorides, bromides and alkali metals, even if added in large amounts, does not interfere with the titrations. Hydrobromic acid itself may contain traces of bromine, which attacks the indicator and makes titration impossible. To avoid this it is recommended to boil the tin solution before the titration for a few minutes in order to remove traces of bromine possibly present. If this is done, the large amount of hydrobromic acid, present in tin distillate, does not affect the titration.

Another important interfering agent is antimony. The behaviour of its ions, both ter- and quinquevalent, was examined.

a) The tin solution was titrated in duplicate.

The titre was 1.17 ml of Zn soln.

b) To the tin solution 16 mg of tervalent antimony were added. End-point was good.

The titre was 1.18 ml of Zn soln.

c) To the tin solution 24 mg of tervalent antimony were added. During the neutralization antimony precipitated much below the needed point. The pH of titration could not be attained and the solution could not be titrated because the colour change was not well seen in the presence of the large amount of precipitate. The same happened when larger amounts of tervalent antimony were added to the solution.

d) To the tin solution 20mg of quinquevalent antimony were added. End-point was good.

The titre was 1.15 ml of Zn soln.

e) To the tin solution 40 mg of quinquevalent antimony were added. During the neutralization antimony precipitated much before the correct pH was reached. The pH of titration could not be attained and the solution could not be titrated because the colour change was not well seen in the presence of the large precipitate. The same happened in the presence of larger amounts of quinquevalent antimony.

f) To the tinsolution 20 mg of quinquevalent antimony and 16 mg of ~~tri~~tervalent antimony were added. The end-point was good.

The titre was 1.15 ml of Zn soln.

The titration by the Jankovsky method can be carried out in the presence of small amounts of ter- or quinquevalent antimony. The upper limit for both valency states is 20 mg of antimony in the solution containing about 180 mg of tin and having a volume of 100 ml. If present in larger amount, the antimony precipitates on neutralization causing probably a partial co-precipitation of tin and making the titration impossible. Masking of antimony by tartaric acid is not possible because it masks tin as well.

3. Interferences and masking in the method of Kinnunen.

The behaviour of the same substances during a titration of tin by this method was examined by carrying out a series of experiments which are described below.

a) In all cases when a large amount of ammonium acetate was present in the solution the end-point was not good. The effect of an excess of ammonium acetate was here much more marked than in Jankovsky's method. If a large amount of acid is present, the bulk of it must be neutralized first by sodium hydroxide and only the final neutralization should be completed by ammonium acetate.

b) A large amount of bromide present as hydrobromic acid or sodium bromide (85 g) does not affect the end-point. Results do not change with various amounts of acids present and neutralized. Important is only the right pH of the solution and no large excess of ammonium acetate present.

c) Thymol blue cannot be used as indicator for neutralization instead of dinitrophenol, since the end-point is not good.

d) The range of pH between 2,5 to 3.5 must be observed, otherwise the end-point could not be well seen.

e) The method has shown a good reproducibility of results, the maximum deviation being within 0.3 per cent. when solutions containing various amounts of tin in a range of 36 to 180 mg and large amounts of acids were titrated.

The reproducibility is expressed as volume of E.D.T.A. solution used to titrate 1 ml of tin solution.

Amt.of Sn in soln. in mg	Ml.of E.D.T.A. soln. used for 1 ml of Sn soln.
90	0.886
90	0.883
36	0.883
180	0.885

f) To the tin solution 30 mg of quinquevalent antimony were added. During the neutralization antimony precipitated much below the needed point. The pH of titration could not be attained without a large amount of precipitate which makes impossible carrying on the titration. The same happened when larger amounts of quinquevalent antimony were present.

g) To the tin solution 20 mg of quinquevalent antimony were added. Now the solution could be neutralized without precipitation. When the excess of E.D.T.A. was titrated by thorium nitrate, the colour changed to red very early, much below the real end-point, but turned back to yellow. The same happened when the next portion of thorium nitrate was added. The final end-point could not be seen clearly. The same happened in the presence of 10 mg of quinquevalent antimony, but the first colour change was seen later.

h) To the tin solution 24 mg of tervalent antimony were added. During the neutralization antimony precipitated much below the needed point. The pH of titration could not be attained without a large ammount of precipitate which made impossible carrying on the titration.

i) To the tin solution 16 mg of tervalent antimony were added. The solution could be neutralized to the necessary pH without precipitation, but antimony precipitated on titration by thorium nitrate. The same was observed when only 3 mg of tervalent antimony were present in solution.

j) The solution did not contain tin. Only 20 mg of quinquevalent antimony and an excess of E.D.T.A. were present. When the excess of E.D.T.A. was titratedby thorium nitrate, the colour changed to red very early, much below the point of equivalence when only E.D.T.A. would be concerned, but turned back to yellow at once. Here happened the same as in the previous titration in the presence of tin.

k) Antimony could not be masked by tartaric and citric acids, since both of them not only mask tin as well, but also make complexes with thorium.

l) To the tin solution 20 mg of quinquevalent antimony and 5 ml of acetylacetone were added. The presence of acetylacetone did not improve the end-point of titration nor did it prevent a precipitation when larger amounts of antimony were present.

m) An attempt to mask antimony by Rhodamine B was made. A drop of 0.4 per cent. aqueous Rhodamine B added to an antimony containing solution under test produced a very intensive red-violettish colouration which persisted also after neutralization and any change of colour produced by xylenol orange could not be seen.

n) Removal of antimony by precipitation by pyrogallol was also tried. This can be done if the solution containing antimony after the addition of not less than 2 g of pyrogallol in solution per 20 mg of antimony is heated nearly to boiling and then rapidly cooled with stirring. The white crystalline precipitate with antimony of both valency states can be easily filtered off and tin can then be titrated in the filtrate in the usual way. Tin alone does not form any precipitate under the same conditions but can co-precipitate partially with antimony with a loss of up to 2 per cent. The end-point of titration in the presence of pyrogallol is seen well, but the colour is not very stable. The solution cannot be titrated in the presence of the precipitate; the end-point then cannot be seen. In the presence of hydrobromic acid pyrogallol forms a yellow-coloured solution, probably of a bromine derivative, and does not precipitate antimony.

The titration by the Kinnunen method cannot be carried out in the presence of antimony of either valency state. Even small amounts interfere and thus all the antimony must be absent. Tervalent antimony has a tendency to precipitate during the titration. Quinquevalent antimony probably forms a weak complex with E.D.T.A., which is gradually decomposed in the presence of thorium with the extraction of E.D.T.A. Therefore, when a new portion of unbound E.D.T.A. appears in the solution, the colour turns back to yellow. Antimony could not be masked by tartaric and citric acids, which seem to make complexes with tin and thorium as well. Neither acetylacetone has any masking effect on antimony. Rhodamine B, owing to its intense colouration, cannot be present in the solution. Pyrogallol helps to remove antimony from the solution but cannot be used in the presence of hydrobromic acid, which is always found in large amounts in the tin containing distillate. Thus further investigation of the effect of this masking agent were abandoned.

Thus if the titration by Kinnunen's method is expected to give good results, antimony must be absent in the solution under test. The pH limits of 2.5 to 3.5 must be observed and the amount of ammonium acetate in the solution must be as small as possible: otherwise the end-point is unsatisfactory. The effect produced here by ammonium acetate is worse than in titrations by Jankovsky's method.

The disadvantages of Kinnunen's method are a very limited amount of ammonium acetate which could be present in solution and a necessity of total absence of antimony. Another inconvenience is the additional titration to be made to find the ratio E.D.T.A.:thorium nitrate. The disadvantages of Jankovsky's method are the changing colour of the end-point and lack of a suitable indicator for neutralization. But the Kinnunen method has a very good end-point and the Jankovsky method is not so sensitive to the presence of larger amounts of ammonium acetate and small amounts of antimony.

4. Distillation of tin.

Tin is best separated from impurities by distillation with hydrobromic acid and then determined in the distillate. Aliquots of standard tin were distilled and tin in the distillate was determined gravimetrically by precipitation with cupferron and ignition to tin dioxide to control the reproducibility of the results obtained by distillation itself. When the trustworthiness of the distillation procedure was ascertained, tin was determined in distillates by titration and the results obtained were compared with those expected from calculations.

Method:

About 25 ml of 0.03M standard tin solution containing about 90 mg of tin were pipetted into the distillation apparatus described by Mogerman[98] and followed by 80 ml of (1 + 1) hydrochloric acid. Washed carbon-dioxide or nitrogen was passed through the solution ~~at a~~ rate of 2 to 3 bubbles per sec., to prevent bumping. The rate of passing the gas should not be too high because of possible mechanical loss or of entrainment of undistilled particles of liquid. A beaker containing 100 ml of water, which served as a receiver and was isolated from the flame by an asbestos board and cooled in ice, was connected to the apparatus, while the tip of the condenser was dipped in the water. The distillation was done over a Bunsen flame. When the temperature reached 110°C, 12 ml of orthophosphoric acid were added dropwise at a rate of 30 to 40 drops per min. to fix tin and the distillation at this temperature was continued until only a very small volume of solution remained in the flask and the temperature started to rise slowly. When the temperature reached 155°C, 25 ml of hydrochloric acid were added at a rate of 30 to 40 drops per min., while the temperature was maintained between 155 and 165°C. When all the hydrochloric acid was added, the distillation was discontinued. The contents of the distillation flask were cooled to 150°C and a new receiver with 100 ml of water, covered by a moistened quantitative filter-paper with a hole for the condenser stem, to prevent any loss by misting, was connected. The heating was started again at 150°C and the temperature was raised quickly to 180°C, while 90 ml of hydrobromic acid mixture [consisting of (1 + 2) hydrobromic acid and 5 ml of hydrochloric acid per every 100 ml of solution] were added dropwise, at a rate of 30 to 40 drops per minute. The temperature of 180 to 185°C, at which tin was distilled as tetrabromide, was maintained until all the hydrobromic acid mixture was added and the distillation was finished. To make sure that all the tin is distilled another receiver containing 100 ml of water can be connected and another small volume of hydrobromic acid mixture can be distilled. The volume of the distillate was about 190 ml and the concentration of the acid needed no adjustments. If other amounts of hydrobromic acid mixture were distilled, the volume of the distillate should be adjusted so that the hydrobromic acid concentration should be not over 6 per cent.v/v. The distillate was titrated with 1M-potassium permanganate to an amber colour to oxidize any antimony possibly present in the solution to quinquevalent state. The filter-paper used as cover was added to the solution to assist filtration. Tin was precipitated from the solution cooled to at least 10°C by the addition of 70 ml of freshly prepared, 6 per cent. aqueous solution of cupferron, also cooled previously to 10°C. The reagent was added by small portions at a time with continual stirring. Then the solution was acidified by sulphuric acid until the concentration of this acid was about 4 per cent. v/v. The precipitate was filtered at once through a Whatman N41 filter-paper under a small suction with the use of a paper cone and washed with (1 + 40) cooled cupferron solution until the filtrate was chloride-free, as shown by silver nitrate. Then the filter-paper with the precipitate was transferred to a large silica crucible, previously ignited and weighed. The precipitate was dried cautiously under an infra-red lamp and then ignited, while covered, over a small Bunsen flame. The ignition was completed by heating for 1 hr at 1000°C. After cooling in a desiccator over silica gel for 45 min., the precipitate was weighed as tin dioxide. Usually tin dioxide attains the constant weight under these conditions and re-ignition is not necessary. When also antimony was present, before being transferred to the distillation apparatus the solution containing tin was boiled with 0.5 g of hydrazine sulphate for 5 min.

The recovery of tin after distillation was examined on 20 aliquots distilled.

a) Aliquots of standard tin tetrabromide solution distilled and precipitated by the above method showed a loss of tin of about 2 to 5 per cent.

b) When antimony was present and the solution was reduced by boiling with hydrazine sulphate the loss amounted to 10 to 17 per cent. No tin was detected by qualitative tests in the fraction distilled at 160°C.

c) The accuracy was not good also when larger volumes amounting up to 165 ml of hydrobromic acid mixture were distilled.

d) When before distillation solutions were evaporated with sulphuric acid to reduce the volume, the loss of tin amounted to above 80 per cent. This was not due to the distillation or to the precipitation because

e) the aliquots evaporated and precipitated without distillation showed the same loss of tin, while

f) the aliquots precipitated directly without evaporation or distillation showed a very good recovery with the positive error of 0.3 mg.

g) Aliquots of standard tin chloride solution, prepared by dissolving tin in hydrochloric acid only, to which 12 ml of sulphuric acid were added, were transferred to the distillation apparatus and tin was distilled and precipitated as above. The recovery was very good, with a small positive error of 0.6 mg only.

h) The presence of antimony in moderate amounts did not affect the determination, provided that the solution has been evaporated to fumes and the latter was reduced by boiling with hydrazine sulphate. Tin chloride aliquots distilled in the presence of 25 mg of reduced antimony showed the same good recovery with a very small negative error of 0.2 mg only. The results were good even when only 90 ml of hydrobromic acid mixture were distilled.

i) The same tin chloride aliquots, distilled in the presence of hydrochloric acid only, with no sulphuric acid added to the solution, showed a loss of 25 per cent.

It was probably the presence of bromide ions which caused the losses.

j) Tin was precipitated from the tetrabromide solution as hydroxide, filtered and dissolved in sulphuric acid. This solution, containing no bromide ions, was distilled in the usual way.

An aliquot of tin tetrabromide solution, containing about 90 mg of tin, was neutralized in the presence of methyl orange by (1 + 1) ammonia. To the neutralized solution 24 g of ammonium nitrate dissolved in a little water were added, the solution was diluted with water to about 300 ml and heated to boiling. As soon as the precipitate settled it was filtered through a Whatman N41 filter-paper under slight suction and washed by 2 per cent. ammonium nitrate solution until the filtrate was halide-free. The filter-paper containing the precipitate was transferred to a Kjeldahl flask and treated cautiously by 12 ml of sulphuric acid. After 15 min., 25 ml of nitric acid were added and the contents of the flask were heated for 15 min. on steam and then on flame to expel nitrogen oxides. If the solution darkens, more nitric acid should be added and the heating should be continued until dense fumes of sulphuric acid appear and the liquid is quite clear and light. After a short cooling 10 ml of water were added to remove the last traces of nitric acid and the solution was evaporated to fumes of sulphuric acid again.

Then 0,5 g of hydrazine sulphate was added and the solution was boiled for 5 min. After cooling 25 ml of water and 10 ml of hydrochloric acid were added. The solution was transferred to the distillation apparatus with the aid of 80 ml of (1 + 1) hydrochloric acid and tin was distilled and precipitated by cupferron as described before. Only 90 ml of hydrobromic acid mixture were used in distillation. The recovery of tin was quite good, with a small positive error of 0.5 mg only.

k) The same procedure as above was carried out in the presence of 25 mg of antimony. The recovery of tin was quite good with a very insignificant negative error of 0.2 mg only.

l) A blank determination was carried out on the reagents put through the whole procedure and the obtained value of 0.11 mg was taken into account in calculations.

Tin evaporated or distilled in the presence of bromide ions is partially lost. If sulphuric acid is present, the loss is very large. This confirms statements in the literature to this effect. Thus, tin tetrabromide cannot be distilled if bromide ions have not been previously removed by separating tin as hydroxide. In any case tin should be distilled in the presence of sulphuric acid. If sulphuric acid is absent, the distillation proceeds with a tendency to misting and bumping, the amount of hydrochloric acid mixture required is larger and even if a large excess of it is used, tin is not completely removed. When tin was distilled in the presence of hydrochloric acid only, even the addition of as much as 155 ml of hydrobromic acid mixture did not remove tin entirely (see o), while in the presence of sulphuric acid 90 ml were quite enough to remove completely the same amount of tin (see g, h, j and k). Reduction by hydrazine sulphate in the boiling concentrated sulphuric acid affects only antimony and does not concern tin. Standard solution of tin chloride can be safely evaporated, reduced and distilled in the presence of sulphuric acid without any loss and an amount of 90 ml of hydrobromic acid mixture is enough to bring all 90 mg of tin to the distillate. The addition of 25 mg of antimony has no effect on distillation and precipitation of tin. The blank carried out on the reagents, which were of laboratory reagents grade only, was negligible. Later on carbon dioxide was substituted by washed nitrogen, which proved to be equally good and was used in all the future determinations.

5. Titration of the tin-containing distillate.

Tin in the tetrabromide aliquots was precipitated by ammonia, the precipitates were dissolved in sulphuric acid, as described above, and the solutions were distilled. To the distillates, which were boiled out for 5 min. while covered by a watch glass to expel any traces of bromine and had a volume of about 200 ml, were added aliquots of E.D.T.A. Solutions were neutralized to pH 5 and the excess of E.D.T.A. was titrated by standard zinc solution according to the Jankovsky method. The volume of zinc used in titrations of the distillates was compared with volume of zinc required in titrations of undistilled aliquots of standard tin solution having the same volume as the distillate. The possibility of presence of any tin on a filter-paper, used as cover on receivers, as a result of eventual misting was considered. To remove the traces of tin possibly present, filter-papers were heated to boiling with (1 + 1) hydrochloric acid. The resulting solutions were filtered with washing by hydrochloric acid. The filtrates, having a final concentration (1 + 9) in hydrochloric acid and volumes of about 100 ml were titrated to see if there was any tin present.

a) Two undistilled 25-ml aliquots of standard tin solution about 0.03M, were titrated.

The titres were 0.60
0.62 ml of Zn soln.

b) Undistilled 25-ml aliquot of standard 0.03M tin solution, to which 90 ml of hydrobromic acid mixture were added, was boiled out for 5 min. while covered with a watch glass and then titrated.

The titre was 0.65 ml of Zn soln.

c) Two distilled 25-ml aliquots of the same 0.03M tin solution were titrated.

The titres were $\begin{matrix}0.58\\0.62\end{matrix}$ ml of Zn soln.

d) To each of two solutions obtained from extraction of filter-papers used as a cover were added 3 ml of E.D.T.A. These solutions were neutralized and titrated, as above. Even after an addition of 3.5 ml of standard zinc solution the colour did not change in both cases. There was no tin on the papers.

The distillate containing tin can be safely titrated complexometrically and shows a very good recovery. The deviation between the distilled and undistilled aliquots titrated is only 0.08 per cent. No tin was found on filter-papers used as covers: thus when the distillate is to be titrated and not precipitated by cupferron and the filter-paper is not needed as a filtration aid, it is not necessary to use the filter-paper cover at all. The volume of distillates should be the same as the volume of undistilled standard solution with which the distillate is compared; otherwise the results slightly differ.

6. Distillations of tin in the presence of antimony.

Results obtained when various amounts of tin and various amounts of antimony were present in solutions under test were investigated.

a) A solution containing about 90 mg of tin as tin chloride, 25 mg of antimony as antimony chloride and 12 ml of sulphuric acid was evaporated in a Kjeldahl flask to fumes of sulphuric acid, re-evaporated after the addition of 10 ml of water, reduced by boiling with 0.5 g of hydrazine sulphate and transferred to the distillation apparatus. Tin was distilled as usual, and the distillate was titrated according to the Jankovsky method. The recovery was quite good. There was only a small loss of tin amounting to 0.15 per cent.

b) The solution contained 90 mg of tin as chloride and 90 mg of antimony. The same conditions as for a) were observed. During the evaporation with sulphuric acid large amounts of white and orange deposit appeared on the upper part of the flask neck. Here the loss of tin amounted to 13 per cent.

c) The solution contained 90 mg of tin as chloride and 270 mg of antimony. The same conditions as for a) were observed. The same deposit appeared on the flask neck during the evaporation. The loss of tin amounted to 42 per cent.

In all the above cases, the fraction distilled at 160°C did not contain any tin, as shown by qualitative tests.

d) The solution contained 90 mg of tin as chloride,100 mg of antimony and both 12 ml of sulphuric acid and 12 ml of orthophosphoric acid to retain tin. The same conditions as for a) were observed. A very small amount of deposit was seen on the neck of Kjeldahl flask during the evaporation. For the distillation of the first fraction at 160°C only 25 ml of hydrochloric acid were used. The titration of the tin containing distillate could not be performed, because on neutralization with ammonium acetate a white precipitate, indicating the presence of more than 20 mg of antimony, appeared much below the pH needed for titration.

d) The solution contained 90 mg of tin as chloride, 100 mg of antimony, 12 ml of sulphuric acid and 12 ml of orthophosphoric acid to retain tin. The same conditions as for a) were observed. A very small amount of deposit was seen on the neck of Kjeldahl flask during the evaporation. For the distillation of the first fraction at 160°C, 150 ml of hydrochloric acid were used to remove possibly much antimony. The titration of the distillate could be performed well, but a loss of tin amounted to about 2.8 per cent.

f) From the solution containing 90 mg of tin and 50 mg of antimony, tin and antimony were precipitated as hydroxides, dissolved in sulphuric acid and distilled (see Section 4, paragraph j). For the distillation of the first fraction at 160°C, 100 ml of hydrochloric acid were used to remove the antimony. The titration of the distillate could be performed well. A loss of tin amounted to about 0.6 per cent.

g) From the solution containing 90 mg of tin and 100 mg of antimony, tin and antimony were precipitated as hydroxides, dissolved in sulphuric acid and distilled. For the distillation of the first fraction at 160°C, 175 ml of hydrochloric acid were used to remove the antimony. The titration of the distillate could be performed well. A loss of tin amounted to 0.4 per cent.

h) From the solution containing 36 mg of tin and 100 mg of antimony, tin and antimony were precipitated as hydroxides, dissolved in sulphuric acid and distilled. For the distillation of the first fraction at 160°C, 100 ml of hydrochloric acid were used to remove the antimony. The titration of the distillate could be performed well. A loss of tin amounted to 1.9 per cent.

i) From the solution containing 11 mg of tin and 100 mg of antimony, tin and antimony were precipitated as hydroxides, dissolved in sulphuric acid and distilled. For the distillation of the first fraction at 160°C, 100 ml of hydrochloric acid were used to remove the antimony. The titration of the distillate could be performed well. A loss of tin amounted to 4 per cent.

j) Solution containing about 90 mg of tin and small amount of antimony, not reduced by hydrazine sulphate, was distilled. Traces of antimony were detected by Rhodamine B test in the fraction containing tin as well as in those distilled at 110°C and 160°C, but the bulk of antimony remained undistilled.

The above experiments permit some conclusions as to the behaviour of tin in the presence of various amounts of antimony to be drawn. If antimony is not reduced previously by hydrazine sulphate to the tervalent state, the main part of it is not distilled, but some traces can be found in all the fractions of the distillation. In that case antimony seems to slip a little out of control. As pointed out before, tin as well as antimony are lost during the evaporation in the presence of bromides. The loss of tin is always larger if antimony is present in the solution. Tin can be safely evaporated in the presence of chlorides and sulphuric acid without any loss if the amount of antimony present in the solution does not exceed 25 mg. Antimony, however, is completely lost during the evaporation in the presence of sulphuric acid and chlorides. If the amount of antimony exceeds 25 mg and the solution is evaporated in the presence of sulphuric acid and chlorides, some tin also is lost from the solution. Probably the vanishing antimony carries on some tin. The loss of tin is proportional to the amount of antimony present in solution. When the evaporation of the solution can be omitted no large loss of tin occurs in the presence of large amounts of antimony which can be distilled off at 160°C, provided that sufficient amount of hydrochloric acid is used to distil it. Small loss of tin occurring in this case indicates that the use of large amounts of hydrochloric acid to distil antimony is undesirable, since some tin is probably co-distilled at that step with antimony. If the amount of hydrochloric acid used to distil the 160°C fraction is not sufficient to remove all the antimony, the remainder of the latter distils at 180°C together with tin, which is highly undesirable and can even make the titration impossible. Orthophosphoric acid present in the evaporating solution retains tin as well as antimony if the temperature is sufficiently low. However, it does not retain antimony quantitatively. A small loss of tin occurring under these conditions is due probably to the excess of hydrochloric acid used for distillation of the 160°C fraction. When small amounts of tin and larger amounts of antimony are present together, the accuracy of the determination is always lower.

Summary.

The tedious and time-consuming gravimetric determination of tin in the tin distillate by cupferron can be replaced by a simple complexometric titration. This reduces the time of determination of the tin in the distillate from two days to a matter of minutes, the time required for a titration. The agreement between the gravimetric determination and the complexometric titration of tin is good and the accuracy of the titration compared to theoretical figures remains within 0.08 per cent. Two methods of complexometric titration were proved to be equally successful and both can be applied in the presence of large amounts of acid. One of them enables the determination of about 90 mg of tin in solution in the presence of as much as 20 mg of antimony, both ter- and quinqu~~e~~ivalent. If the other method is applied, although it may seem more convenient in use, antimony must be absent. A great part of the work was done to investigate the problem of antimony which may be present in complex materials containing tin and possibly under certain conditions accompany it in the distillate, especially if the amount of antimony is large. Masking of antimony was not successful. It should not be removed by evaporation in the presence of hydrochloric acid and sulphuric acid nor distilled off by

a large amount of hydrochloric acid, as in both cases some loss of tin occurs. Some 20 mg of antimony are permitted to be present in the tin containing distillate and some more can be removed by distillation at 160°C with a small amount of hydrochloric acid which does not affect tin, but if larger amounts of antimony are present in the aliquot to be distilled, they must be separated.

PART IV

ANALYSIS OF COMPLEX MATERIAL.

1. Determination of tin in an alloy.

The complexometric titrations described in the previous section were applied to the determination of tin in an alloy.

A copper-base alloy "Glacier LB 10" was selected for analysis. As the specification indicated that in addition to tin the alloy contained about 15 per cent. of lead as well as iron and antimony in small quantities and traces of nickel and zinc, it was decided to attack the alloy by nitric acid, which by precipitating tin as metastannic acid, separates it from lead and iron, but all the antimony is co-precipitated. Antimony is then separated from tin by distillation.

Method:

To a weighed alloy sample, containing about 90 mg of tin, placed in a beaker covered by a watch-glass, were added 70 ml of (1 + 1) nitric acid, and the beaker was set aside until nearly all the alloy was dissolved, then gentle warming completed the attack. The solution was boiled to expel the nitrous oxides, diluted with hot water to a volume 3 times larger than its own and heated on the steam overnight. Under these conditions, if no excess of iron is present, all the tin is precipitated. After the addition of macerated filter-paper, the precipitated metastannic acid was filtered through a Whatman N42 filter-paper while a gentle suction was applied, washed a few times with hot (1 + 99) nitric acid and transferred with the filter-paper to a Kjeldahl flask. Then 12 ml of sulphuric acid were added and the filtered metastannic acid, carrying on the co-precipitated antimony, was treated in the same way as the precipitated tin hydroxide (see part III, paragraph 4, j), e.g. dissolved by evaporating to fumes of sulphuric acid and then distilled. To the boiled-out tin-containing distillate 25 ml of about 0.03M E.D.T.A. were added and the solution was titrated according to the Jankovsky method. The percentage of tin in alloy was calculated according to the formula

$$\%\mathrm{Sn} = \frac{(\text{ml of EDTA} \times M_{\mathrm{EDTA}} - \text{ml of Zn} \times M_{\mathrm{Zn}}) \times \text{at.wt.of Sn} \times 100}{1000 \times g}$$

where M_{EDTA} is the molarity of E.D.T.A. solution used, calculated from the results of titration of standard tin solution,

M_{Zn} is the molarity of zinc solution used and

g is the weight of the sample taken.

Four samples of alloy were weighed, attacked by nitric acid, distilled and titrated as above. The results obtained for the percentage of tin were 8.17, 8.12, 8.18, and 8.21 and the mean deviation amounted to 0.025 per cent. These results were in good agreement with the results obtained by other analysts applying the gravimetric ending of tin determination with precipitation by cupferron.

2. Determination of tin in tin ores.

A) Tin Ore "Z".

The ore taken for analysis was ground in an agate mortar to pass a 120-mesh nylon bolting cloth. As the qualitative test showed, besides tin present probably in the form of oxide, which was the main component, the ore contained also considerable amounts of iron and silica, some antimony and small amounts of nickel, magnesium and aluminium. The first difficulties arose with the opening up of the ore. To do this portions of the ore were fused successively with potassium hydroxide, with a (1 + 1) mixture of sodium peroxide and sodium hydroxide, with a (1 + 1) mixture of sodium carbonate and sulphur, with potassium persulphate and with a (5 + 2) mixture of sodium carbonate and sodium hydroxide, but in all the cases the attack of the ore was not complete. Also sintering with sodium peroxide at 480°C for 20 min. proved ineffective. Finally, the problem was solved by removing first the silica by evaporation with hydrofluoric acid in the presence of sulphuric acid and then by fusing the remaining residue with sodium peroxide. The tin-containing solution was distilled with hydrobromic acid mixture to separate tin from other metals and the tin in distillate was titrated by E.D.T.A.

Method:

First moisture contents were determined. About 1.5 g of the ore were dried for 6 hrs. in a glass weighing bottle at 110°C, then cooled for 45 min. in a desiccator over silica gel and weighed. The percentage of moisture was calculated. Then as soon as possible after weighing of samples for the moisture determinations another 1.5-g portion of the air-dried ore was weighted (the calculated moisture per cent. being subtracted from the weight) and placed in a platinum dish. The ore in the platinum dish, to which 20 ml of (1 + 1) sulphuric acid and 25 ml of hydrofluoric acid were added, was heated on a sand-bath over a very low flame, with occasional stirring to prevent caking, until dense fumes of sulphuric acid appeared. The slow fuming was continued for 5 min. After cooling, the sides of the basin were rinsed with water and the solution was re-evaporated until fumes of sulphuric acid appeared again. The slow fuming was continued for 10 min. After cooling, the solution was diluted with 40 ml of water and digested on the steam-bath, while the dish was covered with a watch glass, to dissolve the soluble sulphates. After cooling, a macerated filter-paper was added and the solution was filtered through a 9-cm Whatman N40 filter-paper while the filtrate was collected in a calibrated

250-ml volumetric flask. The platinum dish was rinsed with three 5-ml portions of 5 per cent. ammonium sulphate solution and wiped with a piece of quantitative filter-paper to remove traces of residue. The paper was added to the filtered residue and the dish was rinsed again. The residue was washed by three 10-ml portions of 5 per cent. ammonium sulphate. The filter-paper containing the residue was transferred to a thick-walled nickel crucible and ashed. The ash was mixed well with 3 g of sodium peroxide and the mass was fused at a temperature of dull redness for 10 min. in the covered crucible, while rocking the crucible from side to side to assist the attack. The lid was open at the beginning to allow moisture to escape. After cooling, the crucible was placed in a 150-ml beaker containing 40 ml of water and the fused mass was extracted by heating and dissolving in water. When all the fused mass had dissolved, the crucible was removed from the solution and rinsed with water. The crucible was heated with a little (1 + 1) sulphuric acid to remove any traces of material remaining and the acid was added to the water extract. The water extract was acidified with (1 + 1) sulphuric acid until the reaction ceased. Then the solution was heated with 10 ml of hydrochloric acid. On this heating any precipitate present dissolved completely, but some ore remained unattacked. The solution was filtered into the same 250-ml volumetric flask containing the previous filtrate. The residue was ashed in nickel crucible and re-fused with a small amount of sodium peroxide as above. The melt was extracted with water, neutralized with (1 + 1) sulphuric acid and dissolved by heating with 8 ml of (1 + 1) hydrochloric acid. This time the solution was quite clear and no ore remained unattacked. The solution was added to the previous filtrate and after mixing the volume was adjusted to the mark with water. The temperature of the solution has been noted, the volume at 20°C was calculated and a weight of the ore corresponding to a unit of volume was calculated. An aliquot of the ore solution was pipetted into the distillation apparatus, 12 ml of sulphuric acid followed by 80 ml of (1+1) hydrochloric acid were added and the tin was distilled as usual. The reduction with hydrazine sulphate was omitted here. The ratio of antimony to tin in the ore was so small that the amount of antimony which could be present in the tin-containing fraction would have no effect on the titration.

Four 50-ml aliquots and one 25-ml aliquot were distilled as described above. In two distillates tin was titrated according to the method of Jankovsky, while the percentage of tin in the ore was calculated according to the same formula as that applied for the alloy (see paragraph 1) where g is the weight of the ore in the aliquot taken. The results obtained for the percentage of tin were 28.24 and 28.22 per cent. In the other two distillates, tin was titrated according to the method of Kinnunen, while the percentage of tin in the ore was calculated according to the formula

$$\%\text{Sn} = \frac{\text{at.wt.of Sn(ml of EDTA} - \text{a} \times \text{ml of Th)} \times M_{EDTA} \times 100}{1000 \times g}$$

where a is the ratio E.D.T.A. : thorium nitrate obtained by titration of an aliquot of E.D.T.A. by thorium nitrate,
M_{EDTA} is the molarity of E.D.T.A. used calculated from the results of titration of standard tin solution,
g is the weight of the ore in aliquot taken.
The results obtained were 28.16 and 28.18 per cent. of tin. The difference in results obtained by the two methods of titration amounted to 0.2 per cent.

To control results obtained by titration, tin in the distillate obtained from the 25 ml aliquot of the original ore solution was determined gravimetrically by precipitation with cupferron. The percentage of tin in the ore was calculated according to the formula

$$\%\text{Sn} = \frac{\text{atomic weight of Sn} \times b \times 100}{\text{mol.wt. of } SnO_2 \times g}$$

b was the weight of the ignited residue

g was the weight of the ore in aliquot of the ore solution taken.

The result obtained was 28.42 per cent. of tin.

Another 1.5-g portion of the tin ore was converted into solution as described above. Four 50-ml aliquots of the ore solution were distilled. Tin in two distillates was determined by titration according to the method of Jankovsky and in the other two distillates gravimetrically by means of precipitation by cupferron.

Percentage of tin in the ore obtained by titration was 28.32 and 28.27 per cent. of tin.

Percentage of tin in the ore obtained gravimetrically was 28.26 and 28.24 per cent. of tin.

B) Bolivian tin ore.

It was desirable to try out the method on a higher-grade ore and a Bolivian tin ore containing about 70 per cent. of tin was chosen. The ore was ground in an agate mortar to pass a 120 mesh nylon bolting cloth. As the qualitative test showed, besides tin present probably in the form of oxide, which was the main component, the ore contained also considerable amounts of copper and iron, moderate amounts of silica, lead, aluminium and sulphides and small amounts of nickel and tellurium. Also here only the fusion with sodium peroxide proved to be a satisfactory method to open the ore, but before this sulphides had to be converted into sulphates by evaporation with nitric acid.

Method:

First moisture contents were determined. About 1.2 g of the ore were dried to constant weight in a glass weighing bottle at 110°C, then cooled in a desiccator over silica gel for 45 min. and weighed. The percentage of moisture was calculated. Then as soon as possible after weighing out this sample another 1.2 g of the air-dried ore were weighed (the calculated moisture per cent. being subtracted from the weight) and placed in a platinum dish. The ore in the covered platinum dish was warmed with 20 ml of nitric acid until no more effervescence was seen. Then the solution was evaporated to dryness on the steam-bath. To the dry residue were added 20 ml of (1 + 1) sulphuric acid and 25 ml of hydrofluoric acid and the further procedure was exactly the same as in the case of ore 'Z". After the removal of silica by evaporation with hydrofluoric acid the solution was filtered and the residue was fused with 3 g of sodium peroxide in a nickel crucible. One fusion was enough to attack the ore completely. The ore solution was collected in a calibrated 500-ml volumetric flask and the volume was filled to the mark with water. The temperature of the solution was noted, the volume corrected to 20°C was calculated and a weight of the ore corresponding to a unit of volume was calculated. Six 50-ml aliquots were distilled to separate tin from other metals, while the reduction by hydrazine sulphate was omitted because no antimony was found to be present in ore. In two distillates tin was determined by titration according to the Jankovsky method. The percentage of tin found was 69.51 and 69.36 per cent. In two other distillates tin was determined by titration according to Kinnunen method. The percentage of tin was found to be 69.38 and 69.27 per cent. In the last two distillates tin was determined gravimetrically by precipitation with cupferron. The percentage of tin found was 69.40 and 69.26 per cent. of tin.

In general the results obtained by titration by both methods and by precipitation with cupferron are in good agreement. A great advantage of the titration method is a considerable saving of time and labour.

c) Appendix.

A typical example of the experimental figures obtained in the determination of tin contents in complex material is given below. The figures are taken from the determination of tin in the Bolivian ore by the method of

Jankovsky. First standard tin and zinc solutions are prepared from pure metals. They are used to determine the molarity of E.D.T.A. under the same conditions as those applied in determination. Then the tin contents are determined, the calculations being based on the standardised E.D.T.A. and standard zinc solution.

<u>Preparation of standard tin solution</u>:

3.56405 g	initial weight of tin
+ 2 g	correction for weights
+ 7 g	buoyancy correction
3.56414 g	weight of tin "in vacuo"

The tin solution was transferred quantitatively to the 1000-ml volumetric flask, having the volume of 999.83 ml at 20.0°C. The flask was filled to the mark at 20.0°C.

999.83 ml	
0 ml	temp. correction for the solution
999.83 ml	at 20.0°C

$$\text{Molarity of Sn soln. at } 20^{\circ}\text{C} = \frac{\text{weight of tin}}{\text{vol. x at.wt.}} =$$

$$\frac{3.56414}{999.83 \text{ x } 118.7} = 0.03003$$

Preparation of standard zinc solution:

1.98320 g initial weight of zinc
\- 14 g correction for weights
\+ 5 g buoyancy corrections

1.98311 g weight of zinc "in vacuo"

The dissolved zinc solution was transferred quantitatively to the 1000-ml volumetric flask having the volume of 999.83 ml at 20.0°C and filled to the mark at 19.1°C.

999.83 ml
\+ 15 ml temp. correction for the solution

999.98 ml at 20.0°C

Molarity of zinc soln. at 20.0°C =

$$\frac{\text{weight of Zn}}{\text{vol. x at.wt.}} = \frac{1.98311}{999.98 \times 65.38} = 0.03033$$

Standardization of E.D.T.A. solution:

About 0.03M E.D.T.A. solution was prepared and its molarity was determined by running titration of 2 parallel aliquots.

Sn: 25-ml aliquots, measured by a pipette, were taken at 16.0°C.

24.93 ml volume of the pipette at 20.0°C
\+ 2 ml temp. correction for the solution

24.95 ml at 20.0°C

E.D.T.A. : 25-ml aliquots, measured by a pipette, were taken at 16.0°C

25.01 ml volume of the pipette at 20.0°C
\+ 2 ml temp. correction for the solution

25.03 ml at 20.0°C

Zinc solution was added from a burette.

Ml of Zn soln. used in 2 parallel titrations were:

$$\begin{matrix} 4.05 \\ 4.08 \end{matrix} \text{ after calibration corrections } \begin{matrix} 4.12 \\ 4.09 \end{matrix} \text{ mean } 4.11$$

$$M_{EDTA} = \frac{\text{ml of Sn} \times M_{Sn} + \text{ml of Zn} \times M_{Zn}}{\text{ml of E.D.T.A.}} =$$

$$\frac{24.95 \times 0.03003 + 4.11 \times 0.03033}{25.03} = 0.03491$$

Preparation of a solution from the ore:

The ore was weighed, the moisture contents of 0.14 per cent., previously determined, being subtracted.

1.19824 g initial weight of the ore
\+ 9 g correction for weights

1.19833 g weight of the ore.

Here buoyancy corrections are not applied.

$$1.19833 - \frac{0.14}{100} \times 1.19833 = 1.19665 \quad \text{weight of the dry ore.}$$

The solution resulting from the decomposition of the ore was transferred quantitatively to the 500-ml volumetric flask, having the volume of 499.90 ml at 20.0°C and filled to the mark at 23.3°C.

499.90 ml
\- 32 ml temp.correction for the soln.
499.58 ml at 20.0°C

From this solution a 50-ml aliquot was pipetted at 23.4°C for titration.

50.06 ml vol. of the pipette at 20.0°C
\- 3 ml temp.correction for the solution
50.03 ml at 20.0°C

Weight of the dry ore in the aliquot taken for titration:

$$\frac{50.03 \times 1.19665}{499.58} = 0.11983 \text{ g}$$

<u>Titration of the tin-containing aliquot:</u>

A 25-ml aliquot of a 0.03491M E.D.T.A. solution was pipetted at 22.5°C.

25.01 ml vol. of the pipette at 20.0°C
\- 1 ml temp.correction for the solution
25.00 ml at 20.0°C

Zinc solution was added from a burette.

Ml of zinc solution used were 5.59, after calibration corrections 5.64.

The temperature corrections were negligible here.

The percentage of tin in the ore was calculated according to the formula:

$$\% \text{ of Sn} = \frac{\text{at.wt. x } 100(\text{ml of EDTA x } M_{EDTA} - \text{ ml of Zn x } M_{Zn})}{1000 \text{ x weight of the ore}}$$

$$\% \text{ of Sn} = \frac{118.7 \text{ x } 100(25.00 \text{ x } 0.03491 - 5.64 \text{ x } 0.03033)}{1000 \text{ x } 0.11983}$$

$$= 69.51$$

Another aliquot of tin solution can be titrated as above and the mean tin percentage in the ore can be calculated.

3. Determination of lead in galena.

When lead is to be determined by complexometric titrations in lead ores, it is desirable to get it separated as the numerous other components of the ore usually interfere. Mahr and Otterbein[103] separated lead by means of solid thiourea at 0°C. After being dissolved, lead was titrated by E.D.T.A. at pH 10 in the presence of Eriochrome Black T. Other authors separated lead mainly as lead sulphate. Welcher[9] recommended dissolution of the lead sulphate in ammonia buffer containing tartaric acid and titration at pH 10 in the presence of Eriochrome Black T. Osborn[104] suggested dissolution of the lead sulphate by prolonged shaking with an ion-exchange resin. Fainberg[105] decomposed the ore by nitric acid, separated lead as lead sulphate and titrated it later at pH 10 in the presence of Eriochrome Black T. Amin and Farah[106] dissolved the separated lead sulphate in an acetate buffer. Karakasevic et al.[49] dissolved it in ammonium acetate and titrated lead at pH 6.3 in the presence of methylthymolblue. Thus most authors finally determined lead in ores by titration in alkaline solution in the presence of Eriochrome Black T as indicator. This makes possible the use of cyanides as masking agents, if necessary. But the end-point in the presence of Eriochrome Black T is never very sharp, so another method of titration is desirable. Xylenol orange[55,56] was suggested as indicator, as it is known to give a very sharp end-point and to be more selective. However, this method requires a weakly acid medium, which makes the use of cyanide as a masking agent impossible. The separation, however, provides lead in a nearly pure state and the amounts of impurities present are usually negligible and have no serious effect.

Various aspects of the determination of lead in galena, based on titration in the presence of xylenol orange, were investigated. The ore was decomposed by nitric acid with the conversion of sulphide into sulphate. Then silica was removed by evaporation with hydrofluoric acid in the presence of sulphuric acid. This is necessary as the end-point of a titration in the presence of precipitated silica is not clear. The same operation separated lead as lead sulphate. The precipitated lead sulphate was filtered, dissolved in ammonium acetate buffer and titrated by E.D.T.A.

A) Interferences and masking.

Method of titration:

Fifty ml of about 0.03M standard lead solution to which were added 15 ml of acetate buffer (containing 20 g of ammonium acetate and 3 ml of acetic acid in 100 ml and having pH of 5.8) or otherwise an appropriate amount of lead sulphate dissolved in the necessary amount of acetate buffer were diluted with water to 150 ml. After the addition of 50 ml of about 0.03M E.D.T.A. and 0.15 ml of xylenol orange, the titration was completed by E.D.T.A. In the presence of the ammonium acetate buffer the pH of solutions is always about 5.8, i.e. within the limits required for titration with xylenol orange as indicator, and no further adjustment is needed. The results obtained from titration in the presence of the acetate buffer, compared with those obtained when the solution was buffered by hexamine (see part II, p.85) were the same. In the presence of the acetate buffer, the end-point of the titration was sharp to within 1 drop. The presence of tartaric acid or a small amount of o-phenanthroline does not affect the end-point. The effect of a few metal ions, likely to accompany lead in galena, was studied. Cadmium and zinc were co-titrated; silver had no effect on the titration; aluminium, copper and iron in both valency states blocked the indicator, and must therefore be absent or masked. The masking effect of o-phenanthroline was examined. Cadmium, copper, zinc and aluminium were unaffected by this reagent: as far as cadmium and zinc were concerned, an excess of E.D.T.A. was still needed to titrate them and copper and aluminium produced very bad end-points. In the presence of about 2 mg of iron, even in the tervalent state, an intense red colouration was produced and any further proceedings were impossible. The above metals cannot be masked by cyanide. To mask metal ions effectively an excess of cyanide is needed and this raises the pH of the solution which cannot be back adjusted by the addition of acid. After the separation of lead as sulphate only insignificant traces of these foreign ions are likely to be present.

B) Titrations of lead sulphate solutions.

Lead was precipitated from standard lead solutions as lead sulphate and dissolved in acetate buffer and the solution was titrated by E.D.T.A. Results were compared with those obtained by titrations of aliquots of standard lead nitrate when no precipitation took place.

An aliquot of 25 ml of about 0.06M lead nitrate was evaporated on the steam-bath in a porcelain dish with 4 ml of (1 + 1) sulphuric acid. When the volume ceased to diminish, the evaporation was continued on a very slightly heated sand-bath until fumes of sulphuric acid appeared. After cooling, the sides of the dish were rinsed with 10 ml of water and the solution was evaporated to fumes again. The slow fuming was continued for 10 min. After cooling again, 40 ml of water were added and the whole was stirred well. Then 40 ml of ethanol (or water) were added and the solution was allowed to stand overnight to complete precipitation. The next day lead sulphate was filtered through a Whatman N42 filter-paper and washed with (1 + 39) sulphuric acid solution in 50 per cent. ethanol. The washed precipitate was dissolved in hot acetate buffer. After cooling the solution was diluted with water and titrated by E.D.T.A. as described above under A).

1) A 25-ml aliquot of standard lead nitrate solution, unprecipitated, was titrated in duplicate.

The titres were $\begin{matrix}25.92\\25.88\end{matrix}$ ml of E.D.T.A.

2) A 25-ml aliquot of lead solution was precipitated as lead sulphate, filtered, dissolved and titrated. After the evaporation the solution was diluted with 80 ml of water.

The titre was 25.60 ml of E.D.T.A.

3) A 25-ml aliquot of lead solution containing iron, cadmium, zinc, copper and aluminium (each in the amount equal to 1 per cent. of lead contents) and taken in duplicate was precipitated, filtered, dissolved and titrated. After the evaporation the solution was diluted with 80 ml of water.

The titres were $\begin{matrix}25.60\\25.57\end{matrix}$ ml of E.D.T.A.

4) A 25-ml aliquot of lead solution was precipitated, filtered, dissolved and titrated. After the evaporation the solution was diluted with 80 ml of 25 per cent. ethanol.

The titre was 25.70 ml of E.D.T.A.

5) As above. After the evaporation the solution was diluted with 80 ml of 37.5 per cent. ethanol.

The titre was 25.66 ml of E.D.T.A.

6) As above. After the evaporation the solution was diluted with 80 ml of 50 per cent. ethanol.

The titre was 25.65 ml of E.D.T.A.

7) As above. After the evaporation the solution was diluted with 80 ml of 62.5 per cent ethanol.

The titre was 25.71 ml of E.D.T.A.

8) A 25-ml aliquot of lead solution containing iron and zinc ions (each in the amount equal to 10 per cent. of the lead content) was precipitated, filtered, dissolved and titrated. After the evaporation the solution was diluted with 80 ml of 12 per cent. ethanol.

The titre was 25.45 ml of E.D.T.A.

A small loss of lead is seen when the solution is subjected to precipitation and dissolution in acetate buffer. It seems that lead is not recovered completely. It is recommended to dilute the fumed out solution with 80 ml of ethanol, preferably 50 per cent., instead of water: the solubility of lead sulphate is a little higher in water. Several foreign cations present in amount equal to 1 per cent. of the lead content each do not affect the results. They are probably removed when the precipitate is washed. Foreign cations present in larger amounts cause a small loss.

C) Determination of lead in lead nitrate.

E.D.T.A. solution was standardized against a standard lead solution prepared from analar lead foil. Samples of analar recrystallized lead nitrate, called "lead J", were weighed, dissolved in water and titrated by the standardized E.D.T.A. In the samples dried at 120°C the amount of lead found was equal to the theoretically calculated, e.g. to 62.56 per cent.

In three air-dried samples the amount of lead found by titration was successively 62.51, 62.51 and 62.53 per cent., the mean value being 62.52 per cent. The lead contents in the sample having been known once, the effect of precipitation as lead sulphate was studied. Portions of the lead J were weighed and dissolved in water, the lead was precipitated as lead sulphate, the precipitate was filtered and the lead percentage was determined either gravimetrically or by dissolving the precipitate and titrating the solution by E.D.T.A. Results obtained were compared with those obtained previously by simple titration.

1) The precipitated lead sulphate was filtered through previously ignited and weighed sintered silica crucibles. After drying, the precipitates were ignited at 500 to 600°C for 15 min., cooled in a desiccator over silica gel for 45 min.. and weighed, the amount of lead being calculated.

Then lead sulphate was dissolved as carefully as possible in hot acetate buffer and after cooling the solution was titrated by E.D.T.A., the percentage of lead obtained in that way being calculated. Three portions of lead J were treated as above. The lead contents obtained gravimetrically were successively 62.48, 62.53 and 62.45 per cent. When these precipitates were dissolved and titrated by standardized E.D.T.A., the contents of lead were found successively 62.29, 62.22 and 62.24 per cent.

2) Four portions of precipitated lead sulphate were filtered through a Whatman N42 filter-paper. The filtrate was neutralized to a suitable pH and tested by E.D.T.A. for the presence of lead. No lead was found in the filtrate. Then the bulk of the precipitate was washed down into a beaker and a small amount remaining on the paper was dissolved by washing many times with hot acetate buffer. The whole was dissolved and titrated by standardized E.D.T.A. The contents of lead found were successively 62.25, 62.28, 62.21 and 62.26 per cent.

3) Three portions of precipitated lead sulphate were filtered through a sintered silica crucible instead of paper, dissolved as carefully as possible, with many washings, in hot acetate buffer and titrated with standardized E.D.T.A. Contents of lead found were successively 62.14, 62.30 and 62.27 per cent.

4) The effect of the process of precipitation itself was examined. A larger amount of solution was prepared from lead J. To 25-ml aliquots of that solution 2 ml of 2N-sulphuric acid were added to precipitate the lead. After the precipitation was complete, the solution was not filtered, but neutralized with a little ammonia and acetic acid in the presence of xylenol orange just to yellow colour. Then the acetate buffer was added to establish the right pH and the whole was heated to obtain a clear solution. After cooling, the solution was titrated by E.D.T.A. Results were compared with those obtained from a simple titration of an aliquot of the same solution which was not a subject to precipitation.

Titres of the solutions in which lead was not precipitated were 25.88 and 25.90 ml of E.D.T.A.

Titres of the solutions in which lead was precipitated were 25.85, 25.91, 25.88 and 25.91 ml of E.D.T.A.

5) Four 25-ml aliquots of a solution (other than the above) prepared from lead J were pipetted into porcelain dishes and precipitated as lead sulphate. Two of these precipitates were neutralized and dissolved without filtering in hot acetate buffer (see 4). The remaining two precipitates were filtered through N42 Whatman filter-paper, as usual. After the dissolution of the precipitate

in the usual way the filter-paper was digested on the steam-bath in the original porcelain dish for 30 min. with acetate buffer. Then the liquid was removed by decantation and added to the main solution. The 30 min. digestion with fresh portions of acetate buffer was repeated 3 times. The last portion was neutralized and tested for the presence of lead by passing hydrogen sulphide. No lead was found, its complete removal being indicated. Results obtained from titration of the four aliquots were compared.

Titres of the solutions in which lead sulphate was not filtered were 25.55 and 25.58 ml of E.D.T.A.

Titres of the solutions in which lead sulphate was filtered and filter-papers were digested were 25.55 and 25.62 ml of E.D.T.A.

As found before, a small but persisting difference in results was found between the lead solution aliquots simply titrated by E.D.T.A. as such and the same aliquots in which lead was precipitated as lead sulphate, filtered, dissolved and titrated. The fact that the lead was completely precipitated from the solution was ascertained both by the absence of lead in the filtrate and the full recovery of lead, with the accuracy of about 0.06 per cent., when the precipitate was ignited and weighed, When the same weighed precipitate was dissolved and titrated, the usual loss in lead of about 0.4 per cent was noted. Another indication in favour of the statement that it was not the process of precipitation itself which caused the errors were the good recoveries obtained when the precipitated lead sulphate was dissolved in the beaker, but not filtered. Thus the cause of the loss was probably the incomplete dissolution of lead sulphate, small particles of which, adsorbed on the surface of filter-paper or on the porous surface of the sintered silica, can be difficult to remove. Indeed when the filter-paper was kept in contact with hot acetate buffer for a long enough time, all the lead sulphate was dissolved and the results showed no more loss. It is recommended after removing the bulk of the precipitate to digest the filter-paper for about 1 hr. with a hot acetate buffer to ensure the full removal of lead sulphate. When this requirement is satisfied, lead can be separated from other ions and fully recovered by precipitation as lead sulphate, dissolving the precipitate and titrating.

D) Determination of lead in galena.

The ore taken for analysis was ground to pass a 90-mesh sieve. As the qualitative tests showed, besides lead present as sulphide, which was the main component, the ore contained also considerable amounts of zinc and iron, some silica and traces of antimony, chromium and cadmium. The presence of large amounts of zinc and iron made necessary the separation of lead. The ore was attacked by **nitric** acid.

A portion of galena, preferably of small weight (about 0.57 g) was weighed and placed in a platinum dish. After the addition of a few ml of water to the covered dish, nitric acid was cautiously added in small portions at the time. The attack was completed by gentle boiling, while covered, on a very slightly heated sand-bath until no black particles were visible. When the attack was complete, the cover was removed. Four ml of (1 + 1) sulphuric acid and 10 ml of hydrofluoric acid were added and the solution was evaporated on the sand-bath until fumes of sulphuric acid appeared. This removed both the silica and most of the nitric acid. After cooling, the sides of the dish were rinsed with water and the whole was re-evaporated to fumes of sulphuric acid, a slight fuming being maintained for 10 min. After cooling, the solution was diluted with 40 ml of water, heated to dissolve soluble sulphates, cooled, diluted with 40 ml of ethanol and set aside overnight to promote complete precipitation of lead sulphate. The next day the precipitate was filtered through a Whatman N42 filter-paper under a slight suction, washed with (1 + 39) sulphuric acid solution in 50 per cent. ethanol and then dissolved in hot acetate buffer. The filter-paper was digested on the steam-bath with acetate buffer for 1 hr. to ensure the complete dissolution of any traces of precipitate absorbed and the extract was then added to the main solution. The solution was diluted with water to 150 ml, 25 ml of E.D.T.A. were pipetted and the titration of lead was completed in the presence of xylenol orange by E.D.T.A. added from a burette. The percentage of lead in the ore was calculated according to the formula

$$\%\text{Pb} = \frac{\text{at.wt.of Pb x ml EDTA x } M_{\text{EDTA}} \text{ x } 100}{1000 \text{ x weight of the ore}}$$

where M_{EDTA} was the molarity of E.D.T.A. previously determined by titrating standard lead solution.

Two portions of galena were weighed and treated as above and the results obtained were 54.10 and 54.10 per cent. of lead. Then a larger portion of galena was weighed and treated as above. The solution obtained by dissolving lead sulphate was transferred to a calibrated 250-ml volumetric flask which was then filled with water to the mark and a weight of the ore in a unit of volume was calculated. Two 50-ml aliquots of this solution were titrated by E.D.T.A., as usual, and the contents of lead were calculated. However, this method is less recommended, because a larger amount of the ore requires larger amounts of acids and considerably more time and effort to complete the attack. The completeness of the attack can be ascertained with difficulty, because a small amount of unattacked black particles is not always visible in the presence of large amounts of the residue. The results obtained by titration of two 50-ml aliquots of the ore solution by E.D.T.A. were successively 54.05 and 53.99 per cent. of lead. They were in good agreement with the results obtained by other workers in the laboratory who have determined lead in this ore gravimetrically.

Conclusion.

The work reported in this thesis has shown that the substances usually recommended as primary standards for ethylenediaminetetra-acetic acid titrations, namely the dihydrated disodium salt and the acid itself, are not the best primary standards for this purpose. The ammonium potassium, and lithium salts of E.D.T.A., are also unsatisfactory.

Satisfactory standards are provided by the pure metals zinc, lead, and bismuth and one or two of their compounds and when possible the E.D.T.A. solution used should be standardized against the same metal and indicator as is used in the determination that is made.

After separation by distillation, tin can be determined in its alloys and ores by an E.D.T.A. titration instead of a gravimetric procedure with much saving of time and effort. Lead in galena can with advantage be determined by a similar titration after its separation as sulphate.

REFERENCES

1. G. Schwarzenbach, Complexometric Titrations, Methuen and Co. Ltd., 1957.
2. F. Bernejo Martinez, M. Paz Castro and R. Rey Mendoza, Inf.Quim.Anal., 1960, 14(2), 34.
3. I. P. Sanderson and T. S. West, Talanta, 1963, 10, 247.
4. R. Přibil and V. Vesely, Talanta, 1962, 9, 939.
5. Genkichi Nakogawa, Hiroko Wada and Motoharu Tanaka, Talanta, 1963, 10, 325.
6. A. E. Martell and M. Calvin, Chemistry of the Metal Chelate Compounds, Prentice Hall Inc., 1953.
7. A. J. Vogel, A Textbook of Quantitative Inorganic Analysis, 3rd Edition, Longmans, 1961.
8. T. S. West and A. S. Sykes, Analytical Applications of Diamino-ethane-tetra-acetic Acid, B.D.H.Ltd.
9. F. J. Welcher, Analytical Uses of Ethylenediaminetetra-acetic Acid, Van Nostrand Co.Inc., 1957.
10. F. L. Hahn, Anal.Chim.Acta, 1950, 4, 583.
11. J. L. Hall, J. A. Gibson Jr., P. R. Wilkinson and H. O. Philips, Anal.Chem., 1954, 26, 1484.
12. W. J. Blaedel and H. T. Knight, Anal.Chem., 1954, 26, 743.
13. W. J. Blaedel and H. V. Malmstadt, Anal.Chem., 1952, 24, 455.

14. P. B. Sweetser, E. Clark, C. E. Bricker, Anal.Chem., 1953, 25, 253.

15. D. C. Burtner, Univ.Microfilms, Ann Arbor, Mich., Publ.No.8094.

16. C. L. Wilson and D. W. Wilson, Comprehensive Analytical Chemistry, Vol,1B, Elsevier, 1960.

17. H. Flaschka, A. J. Barnard Jr., and W. C. Broad, Chemist-Analyst, 1956, 45, 83.

18. G. C. Krijn, Chem.Weekbl, 1962, 58, 127.

19. W. Berndt and J. Sara, Talanta, 1961, 8, 653.

20. R. Přibil, and V. Vesely, Talanta, 1961, 8, 880.

21. W. Z. Jablonski and E. A. Johnson, Analyst, 1960, 85, 297.

22. R. Přibil and V. Vesely, Talanta, 1963, 10, 383.

23. W. J. Blaedel and H. T. Knight, Anal.Chem., 1954, 26, 741.

24. H. Irving and J. J. Cox, Analyst, 1958, 83, 526.

25. I. M. Kolthoff and V. A. Stenger, Volumetric Analysis, Vol.II, 2nd revised edition, Interscience Publishers Ltd., 1947.

26. T. W. Richards, J.Am.Chem.Soc., 1900, 22, 144.

27. J. A. Clements, Ph.D.Thesis, University of London, 1962.

28. W. Biedermann and G. Schwarzenbach, Chimia, 1948, 2, 56.

29. W. Biedermann and G. Schwarzenbach, Helv.Chim.Acta, 1948, 31, 459.

30. W. Biedermann, G. Schwarzenbach and F. Bongerter, Helv.Chim.Acta, 1946, 29, 811.

31. H. Flaschka, Mikrochemie ver Mikrochim.Acta, 1952, 39, 38.

32. C. Duval, Anal.Chim.Acta, 1957, 16, 545.

33. H. Brintziger and J. Hesse, Z.Anorg.Chem., 1942, 249, 113.

34. V. Suk and M. Malat, Chemist-Analyst, 1956, 45, 30.

35. H. Brintziger et al., Z.Anorg.Chem., 1943, 251, 285.

36. H. Brintziger et al., Z.Anorg.Chem., 1948, 256, 65.

37. J. K. Parnas, Z.Anal.Chem., 1938, 114, 275.

38. Analar Standards for Laboratory Chemicals, 5th Edition, Published by B.D.H. and Hopkin and Williams, 1957.

39. P. F. Lott and K. L. Cheng, Chemist-Analyst, 1958, 47, 8.

40. Toschitake Iwamoto et al., Anal.Chim.Acta, 1962, 26(2), 167.

41. R. W. Coltman, Ind.Eng.Chem., 1924, 16, 606.

42. F. Lindstrom and B. G. Stephens, Anal.Chem., 1962, 34(8), 993.

43. B. Budesinsky, Chem.Listy., 1955, 49, 1726 or Coll.Czech Chem.Comm., 1956, 21, 255.

44. J. E. Powell, J. S. Fritz and D. B. James, Anal.Chem., 1960, 32(8), 954.

45. J. Vřešťal and J. Haviř, Chem.Listy., 1956, 50(11), 1851.

46. H. Flaschka, Mikrochemie, 1952, 39, 315.

47. J. Kinnunen and B. Merikanto, Chemist-Analyst, 1955, 44, 50.

48. Peng Young Sun, J.Chinese Chem.Soc., Taiwan, 1961, 8(3), 181.

49. M. Karakasevic, K. Daca and S. Bencina, Kem.u Ind., Zagreb, 1961, 10(2), 50.

50. J. Korbl and R. Přibil, Chem.Listy., 1957, 51, 1067.

51. O. Budevski and C. Simova-Filippova, Compt.Rend.Acad. Bulg.Sci., 1961, 14, 179.

52. L. Erdey and L. Polos, Anal.Chim.Acta, 1957, 17, 458.

53. H. Flaschka, H. Abdine, Chemist-Analyst, 1956, 45, 2.

54. H. Flaschka, W. Franschitz, Z.Anal.Chem., 1955, 144, 421.

55. R. Přibil, Analyst, 1958, 83, 188.

56. J. Korbl, R. Přibil, A. Emř, Coll.Czech.Chem.Comm., 1957, 22, 961.

57. M. Malat, V. Suk and A. Jenickova, Coll.Czech.Chem.Comm., 1954, 19, 1156.

58. K. L. Cheng and A. H. Bray, Anal.Chem., 1955, 27, 782.

59. E. Körös and Z. Remport-Horvath, Chemist-Analyst, 1957, 46, 91.

60. L. S. Theobald and J. P. Stern, Analyst, 1952, 77, 99.

61. O. Landgren, Svensk.Farm.Tid., 1952, 56, 241.

62. K. ter Haar and J. Bazen, Anal.Chim.Acta, 1954, 10, 108.

63. K. E. Grönkvist, Farmac.Revy., 1953, 52,305.

64. M.Malat, V. Suk and O. Ryba, Coll.Czech.Chem.Comm., 1954, 19, 258.

65. K. L. Cheng, Anal.Chem., 1954, 26, 1977.

66. J. S. Fritz, Anal.Chem., 1954, 26, 1978.

67. V. Suk, M. Malat and A. Jenickova, Coll.Czech.Chem.Comm., 1956, 21, 418.

68. Peng Young Sun, J.Chinese Chem.Soc., Taiwan, 1961, 8(4), 314.

69. A. Busev, Zhur.Anal.Khim., 1957, 12, 386.

70. B. Budesinsky, Chem.Listy., 1957, 51, 726.

71. J. Korbl and R. Přibil, Chem.Listy., 1957, 51, 1061.

72. G. Gattow and D. Schott, Z.Anal.Chem., 1962, 188(1), 10.

73. G. Gattow and D. Schott, Z.Anal.Chem., 1962, 188(2), 81.

74. H. Flaschka, Chemist-Analyst, 1953, 42, 56.

75. J. Kinnunen, Chemist-Analyst, 1954, 43, 93.

76. R. Přibil and F. Vyara, Coll.Czech.Chem.Comm., 1959, 24, 3103.

77. R. Přibil, M. Kopanica, Chemist-Analyst, 1959, 48, 35.

78. A. G. Morris, Chemist-Analyst, 1960, 49, 105.

79. K. Studlar, Chemist-Analyst, 1960, 49, 106.

80. R. Lang, Z.Anal.Chem., 1935, 102, 8.

81. Y. Endo and C. Koroki, Japan Analyst, 1960, 9(12), 992.

82. D. Wood and R. Clark, Analyst, 1957, 82, 624.

83. H. Challis and J. Jones, Analyst, 1957, 82, 658.

84. R. K. Mittal, J. P. Tandon and R. C. Mehrotra, Z.Anal. Chem., 1962, 189(5), 406.

85. J. Kinnunen and B. Wennerstrand, Chemist-Analyst, 1957, 46, 34.

86. Z. Kubista, Chemicky Prumysl, 1954, 4, 175.

87. J. Dubsky, Coll.Czech.Chem.Comm., 1959, 24(12), 4045.

88. J. Jankovsky, Coll.Czech.Chem.Comm., 1957, 22, 1052.

89. I. Sajo, Acta Chim.Acad.Sci.Hung., 1955, 6, 251.

90. I. Sajo, Z.Anal.Chem., 1957, 155, 202.

91. I. Sajo, Magyar Kem.Folyoirat, 1956, 62, 56.

92. L. J. Ottendorfer, Chemist-Analyst, 1958, 47(4), 96.

93. Y. M. Yurist and O. I. Korotkova, Zav.Lab., 1962, 28(6), 660.

94. S. Takamoto, J.Chem.Soc.Japan, Pure Chem.Section, 1955, 76(12), 1342.

95. J. Körbl and R. Přibil, Chemist-Analyst, 1956, 45, 102.

96. J. Kinnunen and B. Wennerstrand, Chemist-Analyst, 1957, 46, 92.

97. M. Dixon, P. J. Heinle, D. E. Humlicek and R. L. Miller, Chemist-Analyst, 1962, 51(2), 42.

98. W. D. Mogerman, Journal of Research of the Nat.Bureau of Standards, 1944, 33, 307 (U.S.Dept. of Commerce).

99. J. A. Scherrer, J.of Res.of Nat.Bureau of Standards, 1936, 16, 253.

100. J. A. Scherrer, J.of Res.of Nat.Bureau of Standards, 1938, 21, 95.

101. P. de Bruyne and J. Hoste, Bull.Soc.Chim.Belg., 1961, 70(5-6), 221.

102. J. Kinnunen and B. Wennerstrand, Chemist-Analyst, 1958, 47, 38.

103. C. Mahr and H. Otterbein, Z.Anal.Chem., 1955,144, 28.

104. G. H. Osborn, Analyst, 1953, 78, 220.

105. S. Y. Fainberg, Zavod.Lab., 1958, 24(1), 18.

106. A. M. Amin and N. Y. Farah, Chemist-Analyst, 1955, 44, 62.