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METHOD AND APPARATUS FOR TITRATIONS

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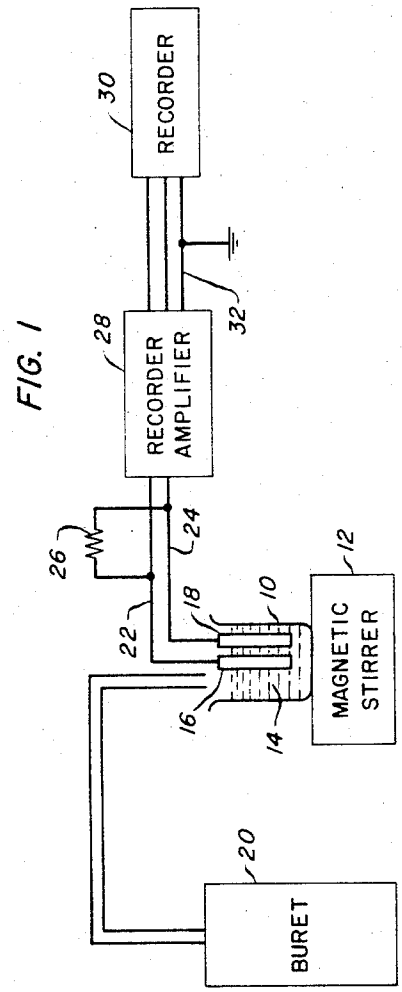


FIG. 1

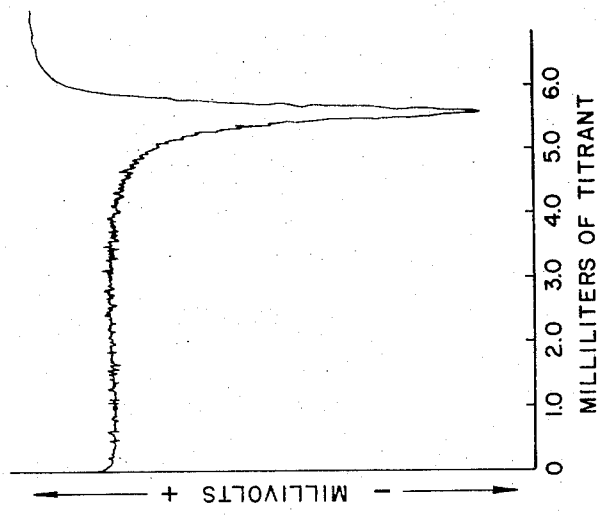


FIG. 2

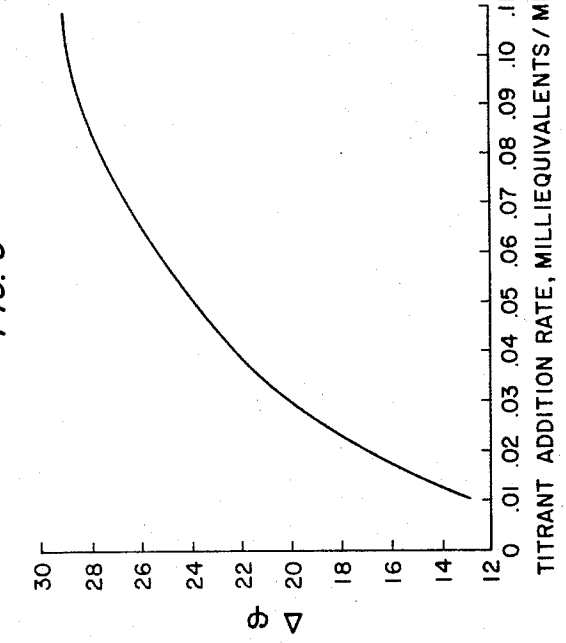


FIG. 3

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METHOD AND APPARATUS FOR TITRATIONS

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U.S. Cl. 204—1 17 Claims

ABSTRACT OF THE DISCLOSURE

An indicator electrode and a nonpolarizable reference electrode are shorted across a fixed resistance and used in the titration of a metal ion solution with EDTA or a similar chelating agent. No potential is impressed on the electrodes, and the end-point is indicated by a current flowing through the fixed resistance. This method of end-point determination is called "amperogenic." The method is effective at any pH at which a complex can form, and at very low metal ion concentrations.

This invention relates generally to a method and apparatus for performing quantitative determinations of metal ion concentrations and, more particularly, the invention relates to the "amperogenic" end-point determination of titrations carried out with titrants forming highly stable anionic complexes with the metal ion. Typical of the titrants which may be employed in the invention are chelating agents such as compounds of ethylenediamine tetracetic acid (EDTA) and 1,2-cyclohexanediamine tetracetic acid (CDTA).

By "amperogenic" is meant a system wherein the indicator electrode generates a current only when the other conditions of the titration are fulfilled, i.e., the end-point is reached. In the novel system of the invention, the potential of the indicator electrode is not measured at all, but rather the voltage developed across a "shorting" resistor is measured, which voltage results from the flow of current between the electrodes in the external circuit near the end-point.

The EDTA titration of metal ions is of great industrial importance, having been characterized even in 1956 by Barnard et al. as "probably the outstanding reagent development of the past decade" (Chemist-Analyst, 45, 86, 111, 1956; ibid., 46, 18, 46, 76, 1957). Activity in this field is attested by the fact that the above-cited review articles list more than 450 references to the technical literature. Certain of the more pertinent references are discussed hereinbelow.

Presently, the use of the EDTA titration is limited in two ways. First, the generally accepted method for end-point detection is the utilization of metallochromic indicators. These materials are generally organic complexing agents which have one color in the complexed form and a second color in the noncomplexed form. At the end-point of the titration, a distinct color change should occur in the solution. In many cases, unfortunately, the color change is not sharp and is severely affected by the presence of certain trace ions in the solution. Secondly, the titrations are only effective over a concentration range of from about 0.1 M to 10^{-3} M, and outside of this range the end-points become quite indistinct. Conditions of the titration are dictated by the metal ion being determined or the presence of other metal ions in the solution. Another critical factor is pH, each metallochromic indicator functioning only at a specific level. Thus, in order to perform an EDTA titration successfully, it is necessary to find an indicator that is specific for the metal ion to be determined, is not interfered with by any of the other metal ions that are present in the solution, and which functions at a pH appropriate for the rest of the system being titrated.

Several potentiometric end-point detection systems for the EDTA titration have been examined. The major advantage of a potentiometric detection system is that it is relatively free of the restrictions placed on the system by the metallochromic indicator. Siggia et al., Anal. Chem. 27, 1745 (1955), have described the use of platinum-calomel and tungsten-calomel electrode systems for the detection of end-points, but these have of necessity been in solvent mixtures. There is no known indication in the literature that these electrodes would function on solutions containing mixtures of ions.

The use of iron (III) and copper (II) as indicating ions with a platinum-calomel electrode pair has been well examined by Patzak et al., Z. Anal. Chem., 156, 248 (1957) and Belcher et al., Anal. Chem. Acta, 13, 226 (1955), but a low pH must be maintained to prevent the iron (III) from precipitating, and this often causes the reaction between EDTA and the metal ion being determined to be incomplete.

Reilley et al., Anal. Chem., 29, 264 (1957), examined the use of the mercury electrode with a mercury-EDTA complex as an indicating system. This system requires the complete absence of halogen, so even a calomel electrode cannot be used without a salt bridge interposed between it and the solution being titrated. There are also pH restrictions on the mercury electrode system, as it cannot be used in solutions of alkalinity exceeding pH 10, and does not function properly in the presence of any agent which will strongly complex with mercury (II).

While the term "amperogenic" has been applied to the method of end-point detection set forth herein, it is to be emphasized that this method is not related to the well-known amperometric method of end-point detection. Amperometric determinations impress a polarizing voltage on the electrodes (for example, with a Fisher Electropode), and measure results with a bridge circuit and galvanometer. Results are plotted as applied potential (volts vs. S.C.E.) vs. diffusion current, and the end-point depends on a redox reaction at the surface of the working electrode. Amperometric determinations using a mercury pool electrode have proven effective at low ion concentrations (10^{-6} M), but background currents prevent accuracy at lower concentrations. Conventional amperometric titrations, employing a dropping mercury electrode, are only effective to about 10^{-4} M. Either type of electrode, of course, requires special equipment and is not suited to rapid or automatic titration. Voltammetric, potentiometric and amperometric titrations were compared by Kolthoff, Anal. Chem., 26, 1685 (1954).

It is thus a general object of the present invention to provide an improved method and apparatus for quantitative determination of metal ions by EDTA or like titrants which overcomes the deficiencies of prior methods.

A further object of the present invention is to provide an improved method of end-point detection for EDTA-

type titrations which is effective at any pH, at which the complex will form.

A still further object of the present invention is to provide an improved method of end-point detection for EDTA-type titrations which is effective at metal ion concentrations of 10^{-6} M and lower.

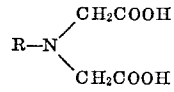
Another object of the present invention is to provide an improved method of end-point detection for EDTA-type titrations, wherein the end-point is clear and sharp even at concentrations of 10^{-6} M and lower.

Yet another object of the present invention is to provide novel apparatus for carrying out the method of the invention.

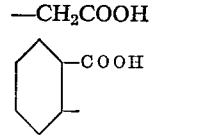
Various other objects and advantages of the invention will become clear from the following description of several embodiments thereof, and the novel features will be particularly pointed out in connection with the appended claims.

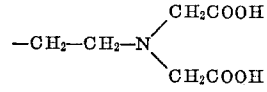
In the following discussion, reference will be made primarily to the use of EDTA compounds as titrant, but it is to be understood that while this is a preferred chelating agent, due to its excellent ability to quickly form stable complexes with almost any metal ion, this is by no means the only reagent useful with the invention. As noted above, CDTA compounds also give excellent results. In general, any chelating agent which rapidly forms a stable, anionic (i.e., negatively charged), liquid phase complex may be employed. For divalent metal ions, the complexes must thus have at least three bonds thereto; similarly, for trivalent ions, there must be at least four bonds between the ion and the complex. Compounds having carboxylic acid groups commonly meet these requirements; the bonds formed by most other anionic groups do not produce sufficiently table complexes. The criterion that the resulting complex must be anionic makes it impossible to use complexing agents containing only imino or amino groups, unless these groups are present with other negatively charged bonding groups. For example, tetraethylene-pentamine gave no end-point when used as a titrant.

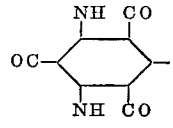
A group of titrants suitable for use with the invention may be defined as follows: compounds of amino polycarboxylic acids having more than one carboxymethyl group attached directly to the nitrogen atom. Especially suitable complexing agents are compounds of amino polycarboxylic acids of the general formula

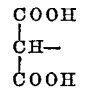


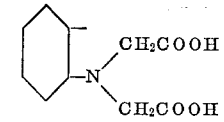
where R is selected from the following group: hydrogen,

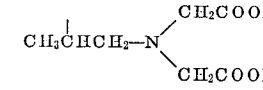




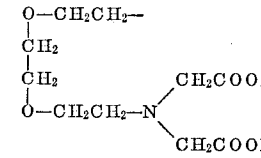








and



The listed acids are, respectively, imidodiacetic acid, nitrilotriacetic acid, anthranilic-acid diacetic acid, ethylenediamine-tetracetic acid (EDTA), uramildiacetic acid, aminomalonic acid diacetic acid, 1,2-cyclohexanediamine tetracetic acid (CDTA), 1,2-propylenediamine tetracetic acid and 1,2-bis(2-aminoethoxy)ethane-N,N'-tetracetic acid. As those skilled in the art will recognize, while reagents are normally named as the acid, it is common practice to employ the salts thereof in actual use due to limited solubility of these acids in aqueous solution.

In essence, the present invention is based, at least in part, on the discovery that when an electrode pair, for example a bright platinum indicator electrode and a saturated calomel reference electrode, are "shorted" across a fixed resistor, and the electrode pair is immersed in the unknown solution, the end-point of a titration with an EDTA compound or similar complexing agent is indicated by the potential developed across the shorting resistor just at the end-point, provided that the rate of titrant addition is slower than the rate of complexing. In accordance with the invention, current flows through the external circuit, but no external potential is applied across the shorting resistor. As the end-point is approached, there is a gradual increase in the flow of current between the electrodes in the negative direction, which becomes sharper as the end-point is neared. Immediately after the end-point, the potential drops very sharply to a potential near the initial value. The resulting curve resembles the first derivative of a poteniometric titration curve. Back-titrations work equally well with, of course, the potential change being in the opposite direction. As pointed out in more detail hereinbelow, the flow of current near the end-point is believed to be caused by the adsorption or desorption of material from the indicator electrode at this point. The novel method of connecting the electrodes results in an amperogenic end-point determination which is effective at any pH at which the complex can form, and at concentrations much lower than have heretofore been possible. In contrast to amperometric titrations, the mechanism of the invention does not depend on a redox reaction at the surface of the working electrode to determine the end-point.

Other conditions of titrations carried out in accordance with the invention are conventional. Buffers are used to keep the solution from becoming too acidic and thus causing a drift in the base line of the titration curve; acetic acid-sodium acetate mixtures and ammonium hydroxide-ammonium chloride mixtures are typical examples. Particular ions in multi-ion solutions may be determined with the use of conventional masking compounds. For example sodium cyanide will mask nickel, zinc, iron and gold, ascorbic acid will mask copper, and sodium hydroxide will mask magnesium in the presence of calcium. All of these are well known in conventional titration procedures.

Understanding of the invention will be facilitated by referring to the following detailed description thereof,

taken in conjunction with the accompanying drawings, in which:

FIGURE 1 is a simplified schematic diagram of the titration and end-point detection apparatus according to the invention;

FIGURE 2 is a chart showing a typical end-point in terms of millivolts vs. ml. of titrant (i.e., time), for a titration carried out in accordance with the invention; and

FIGURE 3 is a chart showing rate of titrant addition vs. the change in potential at the end-point.

Equipment for carrying out a titration according to the invention is illustrated in FIGURE 1. A titration beaker **10** is provided with suitable stirring means, which can be bubbles of an inert gas, a magnetic stirrer **12**, as shown, or any other suitable agitating device. A known quantity of the metal ion-containing solution **14** to be titrated is contained in beaker **10**, and an indicator electrode **16** and a reference electrode **18** are immersed therein. Any standard reference electrode, i.e., an electrode which is capable of passing an electric current without changing its potential, may be employed. A saturated calomel electrode (S.C.E.) or a silver, silver chloride electrode are typical examples. As used herein, the expression "nonpolarizable electrode" is intended to mean any such electrode, and may include the salt bridge normally associated therewith (which may be included in the physical construction of the electrode). The indicator or polarizable electrode (also called a polarographic or working electrode), must be a conductor or semiconductor, and need only be a material which is inert to chemical or electrochemical attack under the conditions of the titration. Satisfactory materials include platinum, gold, pyrolytic graphite and silicon.

Titrant is delivered to the beaker **10** by a constant delivery rate buret **20**. As discussed in more detail hereinbelow, it is most advantageous to add titrant continuously, rather than drop-wise. Burets capable of such operation are readily available.

Electrodes **16** and **18** are connected to leads **22** and **24**, respectively, across which is connected a fixed resistor **26**. Resistor **26** may have essentially any value, but results indicate that a value of about 100,000 ohms is to be preferred. As noted below, if the input impedance to the circuitry following has a suitable value, resistor **26** is not required.

Prior workers have attempted to keep the resistance between the electrodes as high as possible, and have for this reason used electrometers, vacuum tube voltmeters and Wheatstone bridges (which have infinite input resistance at balance) as measuring devices. Where the value being measured is the potential of the indicator electrode with respect to the potential of the reference electrode (i.e., a potentiometric determination), this is of course to be desired. In the method of the present invention, however, the potential of the indicator electrode is not measured at all. Rather, the potential developed across resistor **26** (or across the input of the amplifier), due to the flow of current between the electrodes, is measured. Thus, current must flow thruogh the external circuit, but no external potential may be applied across the resistor. For the latter purpose, it is necessary that amplifier **28**, or another suitable isolating device, be introduced between shorting resistor **26** and the recorder **30**. If the recorder **30** were to be connected directly across the electrodes, the balancing bridge in the input circuit thereof (necessary for zero displacement of the chart span) would impress a potential across the resistor and across the electrodes. As any appreciable current flow changes the potential of the indicator electrode by polarization, the result would be either no end-point detection or an unpredictable current pulse.

As is conventional in recorder-amplifier connections, a common ground **32** is employed.

With the above described arrangement, the unique amperogenic end-point is readily detected, in that the current increases sharply in the external circuit at the end-point of the titration. The sharpness of the end-point determination is illustrated in FIGURE 2, wherein the potential change, in millivolts, is plotted against milliliters of titrant added. The various factors affecting the slope of this curve are discussed in the examples.

The sequential determination of two ions in the same solution may be carried out by the method of the invention if the complexes formed by each ion are of such relative strength that first one forms and then the other. In such a case, two maxima occur in the titration curve. An example of this type of titration is a solution containing barium and cadmium ions.

While not wishing to be bound by any particular theory of operation, it is believed that the observed phenomena can be explained in terms of a discharge of the Helmholtz double layer at the surface of the electrode at the end-point of the titration. Such a double layer would act as a capacitor and would explain the non-equilibrium current pulses that are responsible for the end-point indication.

Let it be assumed that divalent cations are adsorbed on the surface of the indicator electrode. The result is the formation of an electrical double layer. Electrons must migrate to the surface of the electrode to compensate for the adsorbed, positively charged divalent cations. An analogy is the formation of an electrical capacitor, two charged layers, one in the metal surface and another in the solution immediately next to the surface. The concentration of metal ions on the electrode surface can be explained in terms of a Langmuir isotherm, that is, the concentration of metal ions on the surface of the electrode is a function of the concentration of the metal ions in the surrounding solution.

The multivalent metal ions are strongly attracted to the electrode. This lowers the stability constant of those particular metal ions toward EDTA as compared to those metal ions in the solution. The net result is the preferential titration of the metal ions in solution. If the titrant solution is added continuously, the rate of change of metal ion concentration in solution is essentially constant until just before the end-point of the titration, whereupon the rate of change of metal ion concentration in the solution becomes very great. At this point, the rate of removal of the metal ions from the surface of the electrode becomes very great. As this reduces the concentration of positive charges at the electrode surface, the excess of electrons within the metal electrode itself must be discharged. The electrons cannot be discharged into the solution because of their low potential, which prohibits any electrochemical reaction. The metal is negatively charged with respect to the solution, however, and can discharge through the external circuit. It is this flow of current which is measured to detect the end-point. From this it can be seen that the lack of an impressed potential on the electrodes is essential to the end-point detection.

If, on the other hand, it were to be assumed that the negative ions are adsorbed on the surface of the electrode just at the end-point of the titration, identical results would be obtained. Thus, with either assumption, desorption of cations as the end-point is approached or adsorption of anions at the same time, the result should be the same.

Understanding of the invention will be further enhanced by referring to the following specific examples. A discussion of the various factors affecting the shape and magnitude of the end-point indication is also included.

EXAMPLES

Indicator electrodes were prepared of gold, pyrolytic graphite, silicon (semicontuctor grade) and platinum. In each case a suitable plastic seal was applied so that only a controlled area (1–2 cm.^{2}) of the electrode was exposed. The reference electrode in all cases was a saturated

colamel electrode, in most cases a fiber type with a potassium chloride salt bridge and an added potassium nitrate salt bridge. While the bridge is not essential, its large contact area with the solution being titrated appreciably decreases stirring noise, compared to tests made without the bridge. The added potassium nitrate bridge is necessary when titrating metals which precipitate with chloride. Polishing of electrode surfaces prior to use was found to be helpful.

Other experimental equipment included a constant rate buret. Delivery was generally 1 ml. of solution per minute, with the delivery tip immersed in the solution. For measurements in which the impedance of the measuring circuit was held constant, a recorder amplifier was used, This has a nominal input impedance of 100K ohms, which suffices as the "shorting" resistor. A photo-chopper on the input circuit acts as an isolation device from the potentiometric recorder. The amplifier was used at an amplification of unity. For measurements in which it was desired to vary the impedance of the measuring circuit, 150 a. microvolt ammeter was employed as an isolation device. This has an input impedance of 90 megohms on the millivolt scale, and when the resistance of the external circuit was varied, the meter input was directly shorted with 10% carbon resistors. A Sargent MR recorder received the output of the amplifier or the meter.

The change of potential at the end-point, $\Delta\varphi$, varied to some extent with the "freshness" of the indicator electrode, and varied considerably with the metal ion being titrated, as shown in Table I. It can be seen from this data that there is no correlation between $\Delta\varphi$ and the pK of the metal-EDTA complex.

Table I.—Values of $\Delta\varphi$ for various metal ions

M^{+2}:	$\Delta\varphi$ (mv.)
Mg	3.7
Sr	8.9
Ca	10.2
Ba	11.0
Ni	15.1
Pb	16.1
Zn	27.1
Cd	27.1

The shape and magnitude of the titration curve also varies with the resistance of the external circuit, $\Delta\varphi$ increasing with increasing resistance. It was determined experimentally that the magnitude of $\Delta\varphi$ is a linear function of external resistance up to about 30K ohms. At resistances below about 100K the shape of the curve is not appreciably changed but at resistance values in excess of 470K ohms the trailing edge of the curves became drawn out all instances. The end-point was detectable, however, at resistances well below 30K ohms and up into the megohm range.

It was also found that Q, the number of coulombs generated in the circuit, is constant for any given electrode, and varies inversely with the ionic strength of the solution (in the tests, ionic strength was maintained with potassium chloride, and the buffer concentration, constant throughout, was taken into account in determining total ionic strength). The value of Q, and therefore of $\Delta\varphi$, also varied with the area of the electrode, Q rising with increased electrode area, sharply at first but leveling off above about 3 $cm.^2$.

The last factor effecting $\Delta\varphi$ is rate of titrant addition, and attention is drawn to FIGURE 3, where it can be seen that $\Delta\varphi$ drops appreciably at low rates of addition, varying by a factor of about two (15–30 mv. over the range). Thus, for maximum $\Delta\varphi$ at the end-point, rate of titrant addition should be relatively large. It is of course to be understood that the rate is measured in milli-equivalents of the EDTA or whatever titrant is being used, and so depends on both concentration of the titrant solution and the absolute rate of solution addition. The concentration of the metal ion solution, i.e., what is being determined, may also influence rate of titrant addition, at least in a practical sense. For example, where it is known that the metal ion solution is very dilute, it is necessary that the titrant solution also be dilute, since a concentrated solution would pass the end-point quicker than the response time of the equipment, thus reducing the accuracy of the determination. In such an instance, the rate of titrant addition will be below 0.01 milliequivalents per minute, but the end-point is still readily detetcable.

It will be noted that, on one hand, a relatively high rate of titrant addition is desirable for maximum $\Delta\varphi$ at the end-point but, on the other hand, titrant addition must be slower than the rate of complex formation. This is the reason that compounds of EDTA, CDTA and other rapid complex forming materials are preferred.

As noted hereinabove, continuous titrant addition is preferred but is not essential to the practice of the invention. Titrant may be added drop-wise, in which case a millivolt meter should be used in place of the potentiometric recorder. Under this operating arrangement, a deflection of the meter is noted after each addition just before the end-point; a drop which produces no deflection of the meter being one drop past the end-point. As those skilled in the art will recognize, such an arrangement is much less convenient than the continuous-addition-recorder combination discussed previously.

The foregoing discussion is intended only to illustrate the factors which change either the shape of the titration curve or the magnitude of $\Delta\varphi$. As should be obvious, the end-point is sharp and clear within very broad limits of these factors, and is essentially independent of the pH of the solution, temperature (up to boiling) and other factors which have been limitations on prior art techniques. Even under unfavorable conditions the signal-to-noise ratio (i.e., detectability of the end-point) was at least 10.

The above discussion has been concerned with metal ions having only a single stable valence state in solution. Metals having more than a single stable valence state in solution, either as the aquo complex or the EDTA complex, produce curves which are complicated by the oxidation-reduction couple of the ion, and back titration is therefore necessary. Metals in this category include iron, cobalt, copper and manganese. It is possible to perform a back titration of these metal ions using another metal such as cadmium or lead. In the back titration, a perfectly normal curve is obtained, but of opposite polarity to the normal curve, and the multivalent condition of the ions does not manifest itself. It will of course be understood that back titrations can be performed on any metal ion, whether it has a single or multiple valence states. It is only necessary that the ion used in the back titration form a weaker complex with EDTA than the ion being determined.

Identical shapes were obtained for all of the electrodes on both the forward and back tritrations (see FIGURE 2). In all cases the end-point occurred when the slope of the curve changed sign. No absolute value is given for the potential of the electrodes, as this is a function of pH of the solution, and the oxygen content of the solution. Due to the constant stirring, the oxygen content of the solution would sometimes change during the course of the titration causing a drift in the base line. The electrodes were found to be insensitive to moderate temperature changes during the titrations.

Results of a number of titrations carried out in accordance with the invention are set forth in Table II, and are compared therein with the results obtained by EDTA titrations with metallochromic indicators and by metal ion exchange with acid-base titration. As is clear from Table II, titration according to the invention gives an exact end-point at the maximum of the titration curve.

TABLE II.—STANDARDIZATION OF METAL SOLUTIONS

Metal solution	Normality of Solution: EDTA titration with metallochromic indicator	Metal ion exchange+acid base titration	EDTA titration with amperogenic end-point indication
Mg^{+2}	0.306	----------	0.304
Ca^{+2}	0.410	----------	0.413
Sr^{+2}	0.295	0.301	0.298
Ba^{+2}	0.288	0.295	0.297
Mn^{+2}	0.307	0.304	0.304
Co^{+2}	0.292	0.285	0.285
Ni^{+2}	0.282	----------	0.284
Cu^{+2}	0.295	0.297	0.298
Zn^{+2}	0.314	0.317	0.315
Cd^{+2}	0.296	0.294	0.297
Pb^{+2}	0.331	0.322	0.320

It will be understood that various changes in the details, steps, materials and arrangements of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims.

What is claimed is:

1. A method of determining the end-point in the titration of a metal ion-containing solution wherein said ion has a single stable valence state in solution comprising:

placing an indicator electrode and a nonpolarizable electrode in said solution;

adding to said solution at a controlled rate a titrant solution of known concentration, said titrant solution containing a chelating agent which rapidly forms a stable, anionic, liquid phase complex with said metal ion; and

in the absence of any applied potential monitoring the flow of current across a fixed external resistance between said electrodes, said end-point being indicated by a maximum negative potential across said resistance.

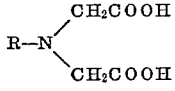
2. A method of determining the end-point in the titration of a metal ion-containing solution wherein said ion has a single stable valence state in solution comprising:

placing an indicator electrode and a nonpolarizable electrode in said solution;

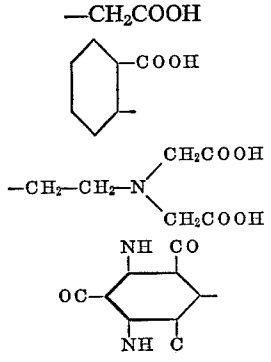
adding to said solution at a controlled rate a titrant solution of known concentration, said titrant being a compound of an amino polycarboxylic acid having more than one carboxy-methyl group attached directly to a nitrogen atom; and

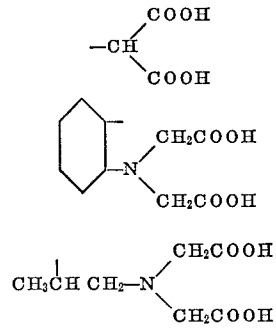
in the absence of any applied potential monitoring the flow of current across a fixed external resistance between said electrodes, said end-point being indicated by a maximum negative potential across said resistance.

3. The method as defined in claim **1**, wherein said chelating agent is a compound of an amino polycarboxylic acid of the general formula

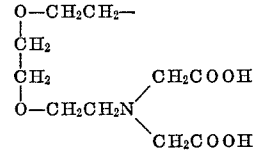


where R is selected from the group consisting of hydrogen,





and



4. The method as claimed in claim **2**, wherein said titrant solution is added continuously.

5. The method is claimed in claim **2**, wherein said monitoring step comprises:

connecting said electrodes to suitable isolating means, said isolating means having a fixed input impedance as said external resistance; and

connecting the output of said isolating means to potentiometric recording means, whereby said recording means monitors the potential across said fixed resistance without impressing a potential on said electrodes.

6. The method as claimed in claim **5**, wherein said isolating means is a recorder-amplifier.

7. The method as claimed in claim **5**, wherein said end-point is indicated by a change in the sign of the slope of the output of said recording means.

8. A method of titrating a solution for quantitative determination of a metal ion, said metal ion having a single stable valence state in solution, which method includes the steps of:

placing an indicator electrode and a reference electrode in said solution;

adding a titrant solution of known concentration at a controlled rate to said solution, said titrant solution being selected from the group consisting of compounds of ethylenediamine tetracetic acid, 1,2-cyclohexane diamine tetracetic acid, imidodiacetic acid, nitrilotriacetic acid, anthranilic acid-diacetic acid, uramildiacetic acid, aminomalonic diacetic acid, 1,2-propylenediamine tetracetic acid, and 1,2-bis(2-aminoethoxy)ethane-N,N'-tetracetic acid; and

monitoring the flow of current between said electrodes across a fixed resistance, said monitoring being carried out in the absence of any applied potential across said electrodes, said end-point being indicated by a maximum negative potential across said fixed resistance.

9. The method as claimed in claim **8**, wherein said titrant solution is added continuously.

10. A method of determining the end-point of the back titration of a metal ion-containing solution comprising:

placing an indicator electrode and a nonpolarizable electrode in said solution;

adding to said solution a known quantity of a chelating agent which rapidly forms a stable, anionic, liquid phase complex with said metal ion, the quantity of said chelating agent being in excess of the amount required to complex said ion;

adding to said solution at a controlled rate a titrant solution of known concentration, said titrant solution containing a second metal ion, said second metal ion forming a weaker complex with said chelating

agent than the metal ion being determined; and

in the absence of any applied potential monitoring the flow of current across a fixed external resistance between said electrodes, said end-point being determined by a maximum potential across said resistance.

11. A method of determining the end-point in the back titration of a metal ion-containing solution comprising:

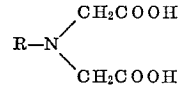
placing an indicator electrode and a nonpolarizable electrode in said solution;

adding to said solution a known quantity of a compound of an amino polycarboxylic acid having more than one carboxy-methyl group attached directly to a nitrogen atom, the quantity of said compound added being in excess of the amount required to complex said ion;

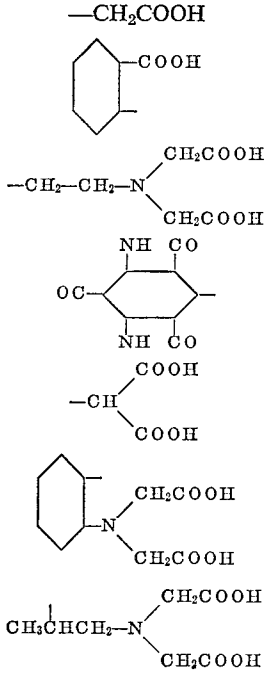
adding to said solution at a controlled rate a titrant solution of known concentration, said titrant solution containing a second metal ion, said second metal ion forming a weaker complex with said added compound than the metal ion being determined; and

in the absence of any applied potential monitoring the flow of current across a fixed external resistance between said electrodes during addition of said compound, said end-point being determined by a maximum potential across said resistance.

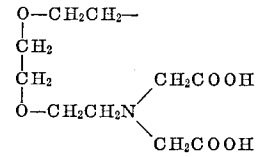
12. The method as defined in claim **10**, wherein said chelating agent is a compound of an amino polycarboxylic acid of the general formula



where R is selected from the group consisting of hydrogen,



and



13. The method as claimed in claim **11**, wherein said titrant solution is added continuously.

14. The method as claimed in claim **11**, wherein said monitoring step comprises:

connecting said electrodes to suitable isolating means, said isolating means having a fixed input impedance as said external resistance; and

connecting the output of said isolating means to potentiometric recording means, whereby said recording means monitors the potential across said fixed resistance without impressing a potential on said electrodes.

15. The method as claimed in claim **14**, wherein said isolating means is a recorder-amplifier.

16. The method as claimed in claim **14**, wherein said end-point is indicated by a change in the sign of the slope of the output of said recording means.

17. Apparatus for the ampereogenic end-point determination of EDTA-type titrations of metal-ion solutions that comprises:

means for continuously adding a titrant to said solution at a controlled rate;

means for agitating said solution;

an indicator electrode and a reference electrode immersed in said solution;

an external fixed resistance between said electrodes; and

measuring means comprising electrical isolating means and potentiometric recording means, said isolating means preventing said recording means from impressing a potential on said electrodes.

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