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COMMISSION ON ANALYTICAL NOMENCLATURE

RECOMMENDED NOMENCLATURE FOR TITRIMETRIC ANALYSIS

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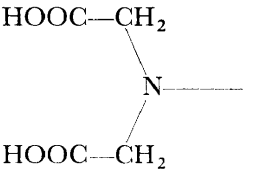
Introduction. This report was prepared by E. B. Sandell (U.S.A.) and T. S. West (U.K.) on behalf of the commission. It was circulated to all members of the division and, following moderation, was presented for further comment in the IUPAC Information Bulletin No. 26. This final version is presented in the light of all comments received.

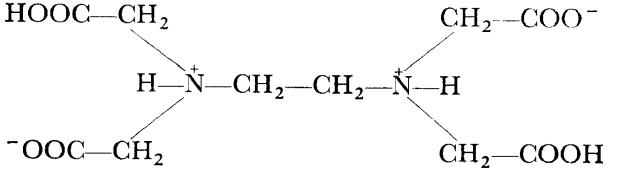
1. Acidimetry. Determination of a substance by titration with an acid†.

2. Alkalimetry. Determination of a substance by titration with a base.

3. Aminopolycarboxylic acids. Compounds containing the group



which comprise the most important class of chelate-forming titrants for the determination of metals. The most widely used compound of this type is *ethylenedinitrilotetraacetic acid*



† The term acidimetry has opposite meanings in different countries. For instance, in Britain and the U.S.A. it is used in both senses, i.e. determination *of* acid and determination *with* acid. In France acidimetry generally means measurement *of* acid, and this appears to be the original meaning of the term. However, all other usages of similar terms imply titration *with*, e.g. argentimetry; accordingly, to maintain consistency it is recommended that acidimetry means titration *with*. The same remarks apply to alkalimetry.

It is recommended that terms ending in "-metry" should end in "-*i*metry" where possible, but it is appreciated that not every term can be standardised in this way.

known as EDTA (and by various trade names). In practice the disodium salt of ethylenedinitrilotetraacetic acid (Na_2H_2Y) is used in place of the acid itself and it may also be designated EDTA.†

4. Back-titration. Titration of unreacted standard solution which has been added in excess to a sample.

5. Blank titration. A titration carried out on a solution identical with the sample solution (i.e. in volume, acidity, amount of indicator, etc.) except for the sample itself, which has been omitted.

6. Buffer capacity or buffer index. The capacity of a solution to resist changes in pH on addition of acid or base, which may be expressed numerically as the number of moles of strong acid or strong base required to change the pH by one unit when added to one litre of the specified buffer solution.

7. Comparison solution. (a) A solution having the same volume and indicator concentration as the solution being titrated, and of appropriate composition, which is used to detect the point at which the colour (or other property) of the solution being titrated begins to deviate from its initial colour (or other property), thus allowing the end-point to be found more precisely than otherwise. (b) More specifically, a solution having the same composition as the solution being titrated at the equivalence-point, used to locate the equivalence-point as accurately as possible by matching some property of the two solutions; the entire composition of the comparison solution need not be the same as that of the solution being titrated (although this is desirable), the essential requirement being that the concentration of the substance determining the colour (or other property) of the indicator is the same in the comparison solution as in the solution being titrated at the equivalence-point.

8. Complexímetry (complexometry). Titration with, or of, a substance forming a slightly dissociated soluble complex.

9. Control titration. A titration of a known amount of substance with a standard solution, made to determine the effect of variable factors and foreign substances on the accuracy of the titration.

10. Designated volume. The designated volume is the volume at the particular temperature at which the volumetric glassware was calibrated; this temperature is usually taken as 20°C, but may be 25°C or 27°C (as in some tropical countries).

11. End-point. The point in a titration at which some property of the solution (as, for example, the colour imparted by an indicator) shows a pronounced change, corresponding more or less closely to the equivalence-point. The end-point may be represented by the intersection of two lines or curves in the graphical method of end-point determination (see *End-point detection*).

† The term *complexone* appears to be a registered trade name and slight alterations in the original term as for example in *complexan*, bear the same restrictions in usage.

12. End-point detection

12.01. AMPEROMETRIC. The course of the reaction is monitored by means of a dropping mercury, rotating platinum or other (concentration polarized) polarographic microelectrode as the indicator electrode in conjunction with a suitable reference electrode. The potential of the indicator electrode is set so as to register a diffusion current for the monitored ion and a plot is made of diffusion current against amount of titrant added. End-points are generally located by extrapolation at changes in slope in the titration curve. *Polarimetric* is regarded as synonymous with *Amperometric*, but is not recommended because of possible confusion with terms used for the measurement of polarization (optical and electrochemical).

12.02. BI-AMPEROMETRIC.† The course of the reaction is monitored by observing the current flowing between two similar (usually platinum) electrodes to which a small potential difference has been applied. The virtual removal of one component of a reversible redox couple from the system (or the appearance of a redox couple) at the end-point causes the current to cease abruptly (or appear suddenly).

12.03. CHRONOPOTENTIOMETRIC. The course of the reaction is monitored by means of a relatively large concentration-polarized electrode (usually Hg or Pt) in conjunction with a suitable reference electrode. A source of constant current is applied to the electrodes and the time required for the potential of the indicator electrode to transit from a predetermined value to a higher one is observed. A plot is made of the square root of transition time against titrant added. End-points are generally located by extrapolation at changes in slope in the titration curve.

12.04. CONDUCTIMETRIC. The course of the reaction is monitored by measuring the conductance (reciprocal of ohmic resistance) of the titration medium between two inert electrodes (usually platinized platinum) immersed in the reaction medium. A plot is made of conductance against titrant added. End-points are generally located by extrapolation at changes in slope in the titration curve.

12.05. FLUORIMETRIC (FLUOROMETRIC). The course of the reaction is monitored by means of changes in fluorescence of the reacting system either visually or photometrically while the solution is irradiated by a suitable activating source such as a mercury lamp. Where instrumental detection is used, a plot is made of instrument response against titrant added. End-points are generally located by extrapolation at changes in slope in the titration curve.

12.06. HIGH-FREQUENCY. The course of the reaction is monitored by a modification of a.c. conductimetric technique in which the frequency of oscillation is in the megacycle per second (MHz) range. Changes in grid or anode current of the oscillating valve, or changes in frequency induced by chemical change, may be monitored and normally the electrodes (or tuned coil) are located outside the titration vessel. A plot is made of instrumental response against titrant added. End-points are generally located by extra-

† The term *bi-amperometric* is now recommended instead of *dead-stop* (see recommended classification and nomenclature of electroanalytical methods by P. Delahay, G. Charlot and H. A. Laitinen. Information Bulletin No. 26, p. 55).

polation at changes in slope in the titration curve. (*Radio-frequency* is regarded as synonymous with *High-frequency*.)

12.07. NEPHELOMETRIC. The course of the reaction in a precipitation system is monitored by measuring the light scattered at right angles to an incident beam. A plot is made of instrument response against titrant added. End-points are generally located by extrapolation at changes in slope in the titration curve.

12.8. PHOTOMETRIC. The course of the reaction is monitored by measuring the (optical) absorption of the titration medium within the selected narrow waveband. A plot is made of absorbance against titrant added. End-points are generally located by extrapolation at changes in slope in the titration curve. The monitor waveband is selected to match an absorption band of the titrant, titratable solute, reaction product or added indicator.

12.09. POTENTIOMETRIC. The course of the reaction is monitored by means of an indicator electrode (polarizable by one or more of the reacting ions) measured against a suitable reference electrode. The potential difference between the two electrodes is recorded. A plot is made of potential difference against titrant added. End-points are located at points of maximal slope on the titration curve.

12.10. RADIOMETRIC. The course of the reaction is monitored radiochemically by adding a radioactive indicator which may be precipitated, or dissolved, at the equivalence-point, thus changing the activity of the solution phase. A plot is made of instrumental response against titrant added. End-points are generally located by extrapolation at changes in slope in the titration curve. (In some instances the titratable solute or the titrant may be radioactive in which case no added indicator may be required.)

12.11. THERMOMETRIC. The course of the reaction is monitored by means of a sensitive temperature measuring device (thermistor, thermocouple or thermometer) immersed in the reaction medium in a thermally isolated vessel. A plot is made of the response of the monitor device against titrant added. End-points are generally located by extrapolation at changes in slope in the titration curve. (*Enthalpimetric* is regarded as synonymous with *Thermometric*.)

12.12. TURBIDIMETRIC. This is a technique similar to nephelometric titration in that it involves a precipitation system, but the course of the reaction is monitored by measurement of transmitted rather than scattered radiation.

12.13. VISUAL. The course of the reaction is monitored by visual observation of the colour (or other) change of an added indicator on neutralization, oxidation–reduction, precipitation or complexation. (In some instances the titratable solute or the titrant may be sufficiently coloured not to require addition of an indicator.)

13. Equivalence-point. The point in a titration at which the amount of titrant added is chemically equivalent to the amount of substance titrated. (*Stoichiometric* (*stoicheiometric*)*-point* and *Theoretical end-point* are synonymous with *Equivalence-point*.)

14. Factor weight. A weight of sample such that the titration volume in

millilitres represents the percentage of constituent or a simple multiple or fraction of the percentage.

15. Formality. The number of gram formula weights of the reacting substance in one litre of solution, the formula being specified whenever there is a possibility of ambiguity.

16. Indicator (visual). A substance which exhibits a visible change at or near the equivalence-point of a titration and which is, ideally, present in sufficiently small concentration not to consume an appreciable amount of the titrant in passing through its transition range.

17. Indicators (visual), types of

17.01. ONE-COLOUR. An indicator which exhibits a colour on only one side of its transition interval and is colourless on the other, or which exhibits a deeper or less intense shade of the same colour on one side of the interval.

17.02. TWO-COLOUR. An indicator exhibiting two different colours, one on each side of its transition interval.

17.03. ACID-BASE. An indicator which is itself an acid or base and which exhibits a colour change, on neutralization by a base or acid at or near the equivalence-point of a titration.

17.04. ADSORPTION. An indicator which is adsorbed or desorbed, with concomitant colour change, by a precipitation system at or near the equivalence-point of a precipitation titration.

17.05. CHEMILUMINESCENT. An indicator (acid–base or other type) exhibiting chemiluminescence, or a quenching of chemiluminescence, at or near the equivalence-point of a titration.

17.06. EXTRACTION. An indicator (acid–base or other type) which is abruptly extracted from one liquid phase into another at or near the equivalence-point of a titration. The indicator need show no colour change in the process. In some instances a titrant may serve as its own indicator.

17.07. FLUORESCENT. An indicator (acid–base or other type) which, while being activated by radiation of a suitable wavelength, exhibits a change in fluorescence emission at or near the equivalence-point of a titration.

17.08. METALLOCHROMIC. An indicator which is itself a complexing agent and which exhibits a colour change when it reacts with metal ions or has them removed from its complex at or near the equivalence-point of a complexiметric or precipitation titration.

17.09. METALLOFLUORESCENT. A special type of metallochromic indicator which is itself a complexing agent and which whilst undergoing suitable irradiation exhibits a change in its fluorescence emission when it reacts with metal ions or has them removed from its complex at or near the equivalence-point of a complexiметric or precipitation titration.

17.10. MIXED. A mixture of indicators of the same function chosen so that their transition intervals are approximately coincident and of such a composition that the resultant overall colour change of the mixture is more easily distinguished visually than that of either indicator used separately.

17.11. OXIDATION–REDUCTION (REDOX). An indicator which is

capable of being oxidized or reduced and which undergoes a colour change in the process at or near the equivalence-point.
17.12. PRECIPITATION. An indicator precipitating from solution in a readily visible form at or near the equivalence-point of a titration.
17.13. SCREENED. A mixture of an indicator (acid–base or other type) and a suitable indifferent dyestuff chosen so as to screen out unwanted parts of the visible range spectrum transmitted by the indicator in one of its forms.

18. Indicator blank or indicator correction. The amount of titrant (usually in terms of volume) required to produce the same change in the indicator as that taken to mark the end-point in the titration of the sample under the same conditions. It is not necessarily the same as the total blank (covering all the steps of an analysis), which may include the effect of other factors, such as the presence of small amounts of reacting substances in the water (or other solvent) or reagents.

19. Indicator, radioactive. A radioactive substance which functions as an adsorption, precipitation or extraction indicator.

20. Level of titration. The order (10^{-x}) of concentration (normality or formality) at which the solution of the titrant is used, e.g., 10^{-1}, 10^{-2}, or 10^{-3}. . .

21. Masking agent. A substance preventing the interfering reaction of one or more foreign substances in a determination by conversion into soluble complexes, different oxidation states, or other unreactive forms.

22. Standardization. The process of finding the concentration or an active agent in a solution, or the reacting strength of a solution in terms of some substance, usually by titration of a known amount of the substance which is pure or has a known reaction value.

23. Standard solution. A solution having an accurately known concentration of the active substance, or an accurately known titre.
23.01. PRIMARY. A standard solution prepared from a primary standard substance whose concentration is known from the weight of that substance in a known volume (or weight) of the solution.
23.02. SECONDARY. A solution whose concentration or titre has been obtained by standardization, or which has been prepared from a known weight of a secondary standard substance.

24. Standard substance
24.01. PRIMARY. A substance of high purity which, by stoichiometric reaction, is used to establish the reacting strength of a titrant, or which itself can be used to prepare a titrant solution of accurately known concentration.
24.02. SECONDARY. A substance used for standardizations, whose content of the active agent has been found by comparison against a primary standard.

25. Titrant. The solution containing the active agent with which a titration is made.

26. Titration. The process of determining a substance A by adding increments of substance B (almost always as a standardized solution) with provision for some means of recognizing the point at which all of A has reacted, thus allowing the amount of A to be found from the known amount of B added up to this point, the reacting ratio of A and B being known from stoichiometry or otherwise. The reverse process—incremental addition of A to B—is seldom applied, except in standardization titrations.

27. Titrations, types of

27.01. ACID-BASE. A titration involving the transfer of protons (Brønsted–Lowry) or electron-pairs (Lewis) from one of the reacting species to the other in solution.

27.02. ACIDIMETRIC. An acid–base titration in which a base is titrated *with* a standard solution of an acid.

27.03. ALKALIMETRIC. An acid–base titration in which an acid is titrated *with* a standard solution of an alkali.

27.04. CHELATOMETRIC. A titration in which a soluble chelate complex is formed; this is a special type of complexiметric titration.

27.05. COMPLEXIMETRIC (COMPLEXOMETRIC). A titration involving the formation of a soluble complex between a metal ion and a complexing agent.

27.06. COULOMETRIC. A titration technique in which the titrating agent (acid–base or other type) is generated electrolytically *in situ* or externally and is not added as a standard solution in the conventional manner. Time and current measurements are generally made in place of volume and mass.

27.07. INDIRECT. A titration (acid–base or other type) in which the entity being determined does not react directly with the titrant, but indirectly *via* the intermediacy of a stoichiometric reaction with another titratable entity.

27.08. IODIMETRIC. Titration with, or of, iodine (usually I_3^-). (Some authors restrict *iodimetry* to titration *with* a standard solution of iodine, and *iodometry* to titration *of* iodine; such restrictions are not recommended.)

27.09. NON-AQUEOUS. A titration (acid–base or other type) in which the solvent medium is one other than water and in which the concentration of the latter is minimal (say less than 0·5 per cent).

27.10. OXIDATION–REDUCTION (REDOX). A titration involving the transfer of one or more electrons from a donor ion or molecule (the reductant) to an acceptor (the oxidant).

27.11. PHASE. A titration in which the entity being titrated is present in a two-phase (liquid) system and which is caused to become a single phase at or near the equivalence-point, or in which a monophase containing two miscible components is caused to separate into a two-phase system by addition of a third component.

27.12. PRECIPITATION. A titration in which the entity being titrated is precipitated from solution by reaction with the titrant.

27.13. WEIGHT. A titration in which the amount of titrant is found from the weight of the standard solution required to reach the end-point.

28. Titration error. The difference in the amount of titrant, or the

corresponding difference in the amount of substance being titrated, represented by the expression:

(End-point value — Equivalence-point value)

29. Titre (titer). The reacting strength of a standard solution, usually expressed as the weight of titrated substance equivalent to 1 ml of the standard solution. (The term titre must not be used to denote the volume of titrant consumed in a particular titration.)

30. Titrimetric analysis. Analysis based on titration. Sometimes called *volumetric analysis* from the common method of measuring the titrant. This latter term is not recommended.

31. Titrimetric conversion factor. The factor giving the amount (usually weight) of the titrated substance corresponding to a unit amount (usually millilitre) of the standard solution. This factor may be the formality, etc. of the standard solution multiplied by the milliequivalent value of the substance titrated or the titre of the standard solution.

32. Transition interval. The range in concentration of hydrogen ion, metal ion, or other species over which the eye is able to perceive a variation in hue, colour intensity, fluorescence or other property of a visual indicator arising from the varying ratio of two relevant forms of the indicator. The range is usually expressed in terms of negative logarithm of the concentration (e.g. pH). For an oxidation–reduction indicator the transition interval is the corresponding range in oxidation–reduction potential.