

EUR 387.e

REPRINT

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

A SENSITIVE METHOD FOR END-POINT
DETECTION
IN CONSTANT CURRENT COULOMETRY

by

K. F. LAUER Y. LE DUIGOU

1963



Central Nuclear Measurements Bureau
Geel Establishment (Belgium)

Reprinted from
ANALYTICA CHIMICA ACTA
29 - 1963

LEGAL NOTICE

This document was prepared under the sponsorship of the Commission of the European Atomic Energy Community (EURATOM).

Neither the EURATOM Commission, its contractors nor any person acting on their behalf :

- 1° — Make any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this document, or that the use of any information, apparatus, method, or process disclosed in this document may not infringe privately owned rights; or
- 2° — Assume any liability with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this document.

The authors' names are listed in alphabetical order.

This reprint is intended for restricted distribution only. It reproduces, by kind permission of the publisher, an article from "ANALYTICA CHIMICA ACTA", 29 - 1963, 87-89. For further copies please apply to Elsevier Publishing Co., P.O. Box 211 — Amsterdam-C. (Netherlands).

Dieser Sonderdruck ist für eine beschränkte Verteilung bestimmt. Die Wiedergabe des vorliegenden in „ANALYTICA CHIMICA ACTA“, 29 - 1963, 87-89 erschienenen Aufsatzes erfolgt mit freundlicher Genehmigung des Herausgebers. Bestellungen weiterer Exemplare sind an Elsevier Publishing Co., P.O. Box 211 — Amsterdam-C. (Netherlands) zu richten.

Ce tiré-à-part est exclusivement destiné à une diffusion restreinte. Il reprend, avec l'aimable autorisation de l'éditeur, un article publié dans «ANALYTICA CHIMICA ACTA», 29 - 1963, 87-89. Tout autre exemplaire de cet article, doit être demandé à Elsevier Publishing Co., P.O. Box 211 — Amsterdam-C. (Netherlands).

Questo estratto è destinato esclusivamente ad una diffusione limitata. Esso è stato riprodotto, per gentile concessione dell'Editore, da «ANALYTICA CHIMICA ACTA», 29 - 1963, 87-89. Ulteriori copie dell'articolo debbono essere richieste a Elsevier Publishing Co., P.O. Box 211 — Amsterdam-C. (Netherlands).

Deze overdruk is slechts voor beperkte verspreiding bestemd. Het artikel is met welwillende toestemming van de uitgever overgenomen uit „ANALYTICA CHIMICA ACTA“, 29 - 1963, 87-89. Meer exemplaren kunnen besteld worden bij Elsevier Publishing Co., P.O. Box 211 — Amsterdam-C. (Netherlands).

EUR 387.e

REPRINT

A SENSITIVE METHOD FOR END-POINT DETECTION IN CONSTANT CURRENT COULOMETRY by K.F. LAUER and Y. LE DUIGOU.

European Atomic Energy Community - EURATOM.

Central Nuclear Measurements Bureau.

Geel Establishment (Belgium).

Reprinted from "ANALYTICA CHIMICA ACTA", 29 - 1963, pages 87-89.

A potentiometric end point detection method is described for a precise localization of the end point in constant current coulometric titration of acids and bases. The method has been applied to the titration of a boric acid solution.

EUR 387.e

REPRINT

A SENSITIVE METHOD FOR END-POINT DETECTION IN CONSTANT CURRENT COULOMETRY by K.F. LAUER and Y. LE DUIGOU.

European Atomic Energy Community - EURATOM.

Central Nuclear Measurements Bureau.

Geel Establishment (Belgium).

Reprinted from "ANALYTICA CHIMICA ACTA", 29 - 1963, pages 87-89.

A potentiometric end point detection method is described for a precise localization of the end point in constant current coulometric titration of acids and bases. The method has been applied to the titration of a boric acid solution.

EUR 387.e

REPRINT

A SENSITIVE METHOD FOR END-POINT DETECTION IN CONSTANT CURRENT COULOMETRY by K.F. LAUER and Y. LE DUIGOU.

European Atomic Energy Community - EURATOM.

Central Nuclear Measurements Bureau.

Geel Establishment (Belgium).

Reprinted from "ANALYTICA CHIMICA ACTA", 29 - 1963, pages 87-89.

A potentiometric end point detection method is described for a precise localization of the end point in constant current coulometric titration of acids and bases. The method has been applied to the titration of a boric acid solution.



A sensitive method for end-point detection in constant current coulometry

Constant current coulometric titrations of acids and bases have been described earlier¹. For high precision analysis with such a method the exact determination of the endpoint is important. Potentiometric methods of indication are very often used and we have therefore examined the sensitive detection method described elsewhere², for acid-base coulometric titrations. In the straightforward potentiometric titration, the endpoint is located by recording in the close neighbourhood of the endpoint the derivative of successive potential changes resulting from successive additions of very small quantities of titrating reagents (*e.g.* 0.010 ml of 0.1 *N* sodium hydroxide solution).

During a coulometric titration the equivalent of such successive additions can be realized by passing a current of exactly known intensity during a short time interval, *e.g.* 50 or 100 mA during 1 sec, 100 mA for 1 sec being about equivalent to the above mentioned amount of base. A similar technique has been described for a coulometric determination of phenol³. These short impulses of constant current intensity are produced by using a preset-time timer in connection with the current generator. The coulometer is calibrated by measuring the potential drop across high precision resistances that are included in the electrolysis circuit. Two resistances (R_1 and R_2 , Fig. 1) are used to control the current during the electrolysis and are themselves

calibrated during the main calibration of the whole apparatus. They are of such dimensions that currents of 50 and 200 mA can be controlled. We intend to replace the simple adjustment circuit later on by a self-regulating electronic circuit, that would keep the current automatically constant to about 0.01%.

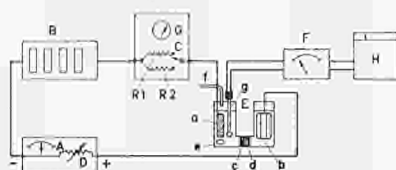


Fig. 1. Diagram of the coulometer.

- | | |
|---|--------------------------------------|
| A Constant current supplier | H Recorder (for end-point recording) |
| B Electronic timer | a Platinum cathode |
| C Potentiometer device for current adjustment control | b Silver anode |
| G Galvanometer | c Sintered glass |
| R ₁ , R ₂ Calibrated resistors | d Agar-agar plug |
| D Variable resistor for current adjustment | e Magnetic stirrer |
| E Coil | f Nitrogen entrance |
| F End-point indicator (pH meter) | g Glass-calomel electrode |

A diagram of the coulometer is shown in Fig. 1. The titration cell for acid-base titration has two cell compartments connected by a tube closed with a sintered glass disc and an agar-agar plug. The reduction of one equivalent of hydrogen occurs at the platinum gauze cathode and at the silver anode one equivalent of silver chloride is deposited. Before the beginning of a titration the current is adjusted by means of the resistance D to about 200 mA. Then the titration is started and the actual current is readjusted every 5 min so that the galvanometer G is always at zero. When the needle of the pH meter (F) begins to move rapidly, that is near the end-point, the current is switched off. Then successive impulses of 1 sec \times 100 mA are produced, and the nearer the end-point is approached, the higher becomes the resulting trace of the recorder. This is continued until the end-point has been passed by two or three impulses. In case of the boric acid titration after mannitol addition, the first and second end-points are recorded by just the same method. The total quantity of electricity (m in coulombs) that passes between the first and the second end-points corresponds to the boric acid titrated. This means that if readings are as follows:

n_0, n_1 = number of impulses after the first, and before the second end-point,

t_1 = duration of one impulse (sec),

t_2 = duration of the passage of the main current (sec),

i_1 = intensity of the current during the impulses (mA),

i_2 = intensity of the main current (mA),

then $m = (n_0 + n_1) t_1 \cdot i_1 + t_2 \cdot i_2$

The use of separate pH meter electrodes in the same titration compartment seems to be quite unsuitable. To avoid undue induction effects in the pH electrodes owing to the electric field, a standard combined glass calomel electrode is preferable to separating the calomel electrode and the platinum electrode from the titration cell by two salt bridges as in a method described earlier⁴. The exact positioning of this electrode is very important.

The method was tested for 0.1 *N* hydrochloric acid and a reproducibility of about 0.02% (relative standard deviation for a series of test results) was obtained. When this coulometric procedure was applied to the boric acid titration described previously², a reproducibility of the order of 0.065% was obtained. A comparison of the factors for the boron content obtained for the same solution of boric acid by chemical standardization and by coulometry gave the following results:

	<i>Factor</i>	<i>Relative standard deviation of the mean (95% probability level)</i>
Coulometric	30.8785	0.065%
Titrimetric	30.8562	0.04 %

The coulometric method is much faster and easier to apply than the previously described volumetric method.

In a later article complete details of the reproducibility, the accuracy and the instrumentation used will be described.

*Euratom,
Central Bureau for
Nuclear Measurements,
Steenweg naar Retie,
Geel (Belgium)*

K. F. LAUER
Y. LE DUIGOU

¹ J. K. TAYLOR AND S. W. SMITH, *J. Res. Nat. Bur. Std.* 63-A, 2 (1959) 153.

² K. F. LAUER AND Y. LE DUIGOU, *Z. Anal. Chem.*, 184 (1961) 4.

³ G. S. KOZAK AND Q. FERNANDO, *Anal. Chim. Acta*, 26 (1962) 541.

⁴ A. PARKER AND E. A. TERRY, *AERE Report AM-72*, 1961.

(Received February 25th, 1963)

CDNA00387ENC