

Investigation on the Electrometric Method for Determination of the Chloride.

I. Use of the improved, portable pH apparatus after Itano for the determination.

By

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In the previous paper¹⁾, the author described an improved, portable pH apparatus which was originally devised and later modified. This paper deals with the use of the apparatus in electrometric determination of the chloride especially in conjunction with a method given by BEST.²⁾

Electrometrically, the analytical determination may be made by two methods, namely the conductivity and potentiometric method. The conductivity method is based upon the change of conductance in the analytical system owing to the presence or disappearance of one kind of ions or another. The potentiometric method is carried out on the principle that a certain potential difference is produced in the system in course of the analysis, and to measure the potential difference various methods are used, such as (a) in chain with the standard electrode viz. calomel electrode, (b) without the use of standard electrode but direct combination with the potentiometer and (c) the use of a definite reference cell is made so that the end of the titration is indicated by the reversed direction of a galvanometer without the use of potentiometer. The choice of method should be made according to the purpose for which the method is used.

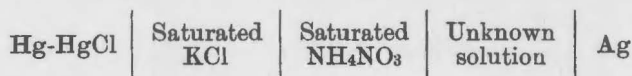
In 1914 the author with VAN SUCHTELEN³⁾, described an electrotitrametric method which employs the electric conductivity principle. That is the change of electric conductance in course of titration is indicated graphically and the end-point of titration is indicated by a sharp point where the resistance changes and the amount of silver nitrate used indicates the amount of chloride present. This method obviates such sources of error as color interference which is encountered in the ordinary titration method. However the influence of temperature is rather big and needs careful temperature adjustment.

1) ITANO, A., Berichte des Ohara Institute etc. IV, 471, 1930.

2) BEST, R. J., Jour. Agr. Science 19, 533, 1929.

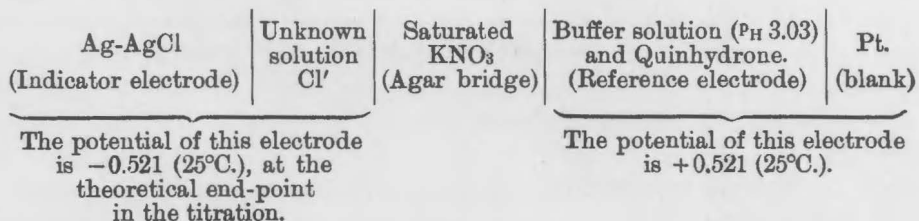
3) VAN SUCHTELEN, F. H. H. and A. ITANO, J. Amer. Chem. Soc. 36, 1793, 1914.

KAWAMURA and SAITO¹⁾ reported an electrometric method for the determination of chloride in soil by the use of potentiometer. The method is based upon the principle that when a silver electrode is immersed in a solution, the potential difference is produced which is dependent on the amount of silver ions present in the solution. In the chloride determination, as the silver nitrate is added to a sample, it forms silver chloride which is practically insoluble so that until all the chlorine ions are changed to silver chloride and an excess of silver nitrate present, there is no appreciable change in the potential difference. However a rapid change of potential difference is brought about as the silver ions increase, and it is measured by a chain given below and this point is taken as an end-point :



The amount of silver nitrate used to bring about the rapid change of potential difference is noted on a graph and the amount of chlorine is calculated. They claimed that they obtained the close, parallel results with the titration method which uses potassium chromate as an indicator. They also determined the chloride contents of various soils successfully.

BEST²⁾ reported a rapid electrometric method for determination of chloride content of soils in which the use of galvanometer and a reference electrode of known potential is made, and which gives the end-point sharply and easily. The following chain is employed in the method :



Connecting such chain in a circuit with a sensitive galvanometer viz. 2—3 milliamperes per sq. cm., the direction of E. M. F. is observed. That is the quinhydrone reference electrode forms the positive pole at the beginning of the titration when the concentration of chlorine ions is greater than 10⁻⁵, and at the theoretical end-point the E. M. F. becomes zero and as soon as the (Cl') becomes less than 10⁻⁵, the quinhydrone electrode becomes negative which is indicated by the reversed direction of galvanometer.

Since the BEST's method seemed to be very satisfactory and easily adapted to the portable p_H apparatus which is equipped with the required galvanometer and vessel for the reference electrode, this investigation was undertaken and the description of the method will be given.

1) KAWAMURA, K. and B. SAITO, *J. Soc. of Agr. Chemistry of Japan*, IV, 114, 1928.

2) BEST, R. J., *Loc. Cit.* p. 533.

Theoretical Discussion* of the Best's Method.

The E. M. F. at the metal-solution interface in this titration is given by the formula (1)

$$E = E^{\circ} - \frac{RT}{F} \ln \frac{1}{(Cl')} \quad \dots \dots \dots (1)$$

where

$E^{\circ} = -0.2245$ at 25°C. (after Lewis).

$(Cl') = 1.0 \times 10^{-5}$ at 25°C., at the theoretical end-point in the titration.

$R =$ gas constant.

$T =$ absolute temperature.

$F =$ Faraday constant.

at 25°C., the value of E is calculated from the formula (1) and is found to be -0.521 .

Therefore to obtain a zero E. M. F. at the end of titration, a reference electrode which gives $+0.521$ should be used. Through the following formula, such an electrode is found :

The E. M. F. of the chain noted previously is given by formula (2)

$$E = \underbrace{E_a^{\circ} - \frac{RT}{nF} \ln \frac{1}{(Cl')}}_{\text{E. M. F. of the indicator electrode}} + \underbrace{E_b^{\circ} - \frac{RT}{nF} \ln \frac{1}{(H^+)}}_{\text{E. M. F. of the reference electrode}} \quad \dots (2)$$

at 25°C., the formula (2) becomes

$$E = 0.4745 - 0.0591 \log \frac{1}{(Cl')} - 0.0591 \log \frac{1}{(H^+)} \quad \dots \dots (3)$$

at the end-point of the titration

$$\begin{aligned} E &= 0.4745 - 0.2955 - 0.0591 \log \frac{1}{(H^+)} \quad \dots \dots \dots (4) \\ &= 0.179 - 0.0591 \log \frac{1}{(H^+)} \end{aligned}$$

In order to have the value of E as zero,

$$0.0591 \log \frac{1}{(H^+)} = 0.179 \quad \dots \dots \dots (5)$$

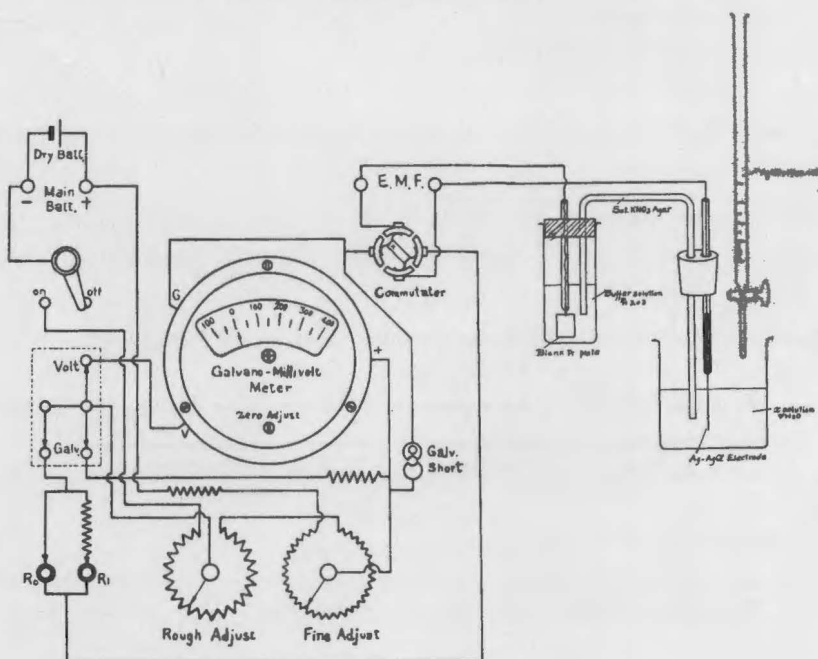
The buffer solution of P_H 3.03 gives the desired value.

* BEST, R. J., *Loc. cit.* P. 533;
MILLER, E., *Die Electrometrische Massanalyse*;
CAVANAGH, B., *J. Chem. Soc. (London)* 2207, 1927.

Preparation and Description of the Apparatus.

The apparatus is set up as shown in Fig. I. In place of the ordinary quinhydrone chain, the following parts are placed and the titration is carried out:

Fig. I.
Connection Diagram of New Type Itano's P_H Apparatus
as used in Chlorine Determination.



1. Ag-AgCl electrode:

A silver wire of 1 mm. diameter and about 5 cm. long is held in a glass tube so that 2—3 cm. is projected beyond the tip (The silver wire may be cemented to the glass tubing or a long silver wire is taken and connected directly to the lead.). The silver wire is coated with AgCl to 2—3 cm. from the tip by having it at the positive pole in N/10 NaCl solution, and a platinum electrode, at the other pole; electrolyze for one hour by passing the current 2—3 milliamperes per sq. cm.; the silver electrode becomes greyish brown color when it is coated; the electrode is immersed in water and kept in dark place to store.

2. Agar bridge:

3% agar in saturated KNO_3 is used to prepare the bridge.

3. Buffer solution (P_H 3.03) :

The buffer solution is prepared according to CLARK¹⁾ but N/5 H_2SO_4 is added to M/5 KH phthalate instead of M/5 HCl.

4. N/35.46 $AgNO_3$, N/35.46 KCl and N/100 KCl are prepared as usual.

Method of Procedure.

a. Keep the battery switch on 'off.'

b. Place the commutator at either position and both the resistance are placed on zero although it is practically immaterial where they are placed.

c. Keep the short circuit key out and use it to bring quickly the galvanometer needle to rest before the next swing.

After the apparatus is set as described above, the standardization may be carried out as follows :

d. Take a known amount of standard KCl solution (5 cc.) to which about 50 cc. distilled water is added in a beaker. The beaker is then placed so that the Ag-AgCl electrode and the end of agar bridge are immersed in the solution. Then it is titrated by adding N/35.46 $AgNO_3$ solution from the burette, and the key of galvanometer is tapped on each addition until the original direction of galvanometer is reversed. Near the turning point, a few seconds are allowed to complete the reaction otherwise the reaction is completed immediately.

If an excess $AgNO_3$ is added, titrate back with N/35.46 KCl solution although it rarely happens to pass the end-point.

Some of the results of titration of the standard solutions are given below :

Table I.
Results of Titration.

No. of experiment.	cc. N/35.46 KCl	cc. N/35.46 $AgNO_3$	cc. theoretical.
1.	5.0	5.05	5.00
2.	5.0	5.00	"
3.	10.0	10.00	10.00
4.	10.0	10.00	"
5.	10.0	10.00	"
	N/100 KCl	N/35.46 $AgNO_3$	
6.	5.0	1.8	1.78
7.	10.0	3.5	3.55
8.	10.0	3.5	"
9.	10.0	3.55	"
10.	10.0	3.5	"

As Table I. indicates, the practical results obtained agree very well with the theoretical data as far as the accuracy of the burette permits.

1) CLARK, W. M., The Determination of Hydrogen Ions (2nd edition) p. 108.

Summary.

In this paper, it was shown how the improved, portable P_H apparatus (ITANO) can be used conveniently in the method of BEST for the determination of chloride.

The advantages of this method over the others may be summarized as follows:

1. The end-point of titration is sharp and easily observed so that the personal factors are avoided.
2. It is not necessary to make a graph or any other interpretation of the results.
3. Each determination is carried out quickly.
4. This method is decidedly superior to the ordinary colorimetric method which is difficult to apply to the turbid or colored solution.

Further investigation on the use of this method in the determination of chloride in soils of various nature as well as some factors, is in progress and will be reported later.
