POTENTIOMETRIC DETERMINATION OF CHLORIDES IN MOLASSES

By G. W. COMRIE

Technical Services Division
Hulett's South African Sugar Mills and Estates Ltd.

Abstract

A method for the determination of chlorides using the potentiometric technique is described. The method is compared with the classical Mohr titration on analytical reagents. Analysis of molasses showed that high concentrations of carbohydrates did not interfere. The possibility of various inorganic anions interfering is discussed and it appears that errors caused by the presence of the more common anions is negligible.

1. Introduction

Volumetric determinations of chloride ions using classical visual end point techniques are unsuited to analysis of coloured solutions such as molasses. Potentiometric determination of chloride was initially reported by Behrend[1] and a comprehensive study of this technique is given by Kolthoff & Furman[2]. Methods using an automatic chloride titrator[3] as well as methods using sophisticated and extensive procedures[4] in sugar products have been described. The adoption of the potentiometric method to molasses solutions was found to give accurate and rapid results in the direct titration of chloride.

2. Experimental

2.1 *Reagents*

(a) Sodium chloride M & B reagent of assay min. 99.5%
(b) Silver nitrate AE & CI reagent of assay min. 99.9%
(c) Potassium nitrate Merck reagent of assay min. 99.0%
(d) Agar No. 3 Oxoid reagent.

2.2 *Measuring equipment*

Titrations were performed automatically using a Metrohm Potentiograph (EA 436) in conjunction with a Multi-Titration set (EA 436 E). These are shown in Figure 1. Titration curves (i.e. potential against volume) produced by the apparatus (Figure 2) were used to calculate the end point. The potentiograph was capable of supplying plots of the first differential but this mode was not used.

2.3 *Electrodes*

The indicator electrode was in the form of a silver rod of approximately 3 mm diameter and 127 mm length. Care was taken to keep the electrode free of AgCl precipitate (and grease free) by extensive rinsing between determinations and occasional immersion in dilute ammonia solution.

The reference was a general all purpose saturated calomel electrode connected to the titration cell by means of a KNO_3—agar salt bridge. The electrolyte was a 1N KNO_3 solution.

2.4 *Salt bridge*

The salt bridge consisted of a glass U-tube of approximately 6 mm internal diameter (Figure 3) filled with a KNO_3—agar gel. The gel was prepared by heating 3 g of agar with 30 g of KNO_3 in 100 ml water until all had dissolved and the solution became viscous. The arms of the U-tube were filled with the solution by suction and allowed to cool. The solution sets to a gel. The salt bridge, when not in use, was kept in a saturated KNO_3 solution to prolong its life.

2.5 *Quality of water*

For obvious reasons the quality of the water used throughout is of importance. Water used in this laboratory was prepared using a mixed ion-exchange resin.

2.6 *Procedure*

An approximately 0.1N $AgNO_3$ solution was made up and standardised against a 0.1N NaCl solution. Pipetting of solutions was performed using a Metrohm Piston Burette (E.274). Initially a flow rate of 1.2 ml per minute was set for the addition of $AgNO_3$ however the potentiograph was able to sense the end point in terms of potential change and the flow rate decreased as the end point was reached. The total potential change over the entire determination was in the order of 500 mV and the sensitivity of the potentiograph was adjusted accordingly.

The sample to be analysed was prepared as follows. A solution of 40 g of molasses in 1000 ml of water was prepared, 20 ml of this solution was used for analysis. The resultant plot of potential against volume $AgNO_3$ added was used to calculate the end point in the usual manner.

3. Results

3.1 *Comparison with classical methods*

Comparison of the potentiometric with the classical Mohr titration was made on analytical reagents. From the results given in Table 1 it can be seen that the potentiometric method gave results which were consistently lower than those of the classical titration. Since the end point of the Mohr titration is given by a colour change it can be assumed that there are two end points, a "true" value when all Cl^- has been precipitated as AgCl and there is no excess Ag^+ present, and an "observed" end point when there is a slight excess of Ag^+ which is necessary for the colour change. The "observed" end point will give a greater Cl^- concentration than the "true" value. If it is assumed that the difference between the "true" and "observed" is independent of the Cl^- concentration being deter-

mined, then the following equations can be established:

$$a + b = c \quad \ldots\ldots (1)$$
$$2a + b = d \quad \ldots\ldots (2)$$

where

a = $[Cl^-]$ given by "true" end point (x
b = difference between "true" and "observed" $[Cl^-]$
c = $[Cl^-]$ given by "observed" end point (x moles Cl^- present)
2a = $[Cl^-]$ given by "true" end point (2x moles Cl^- present)
d = $[Cl^-]$ given by "observed" end point (2x moles Cl^- present)

Subtracting (2) − (1)

$$a = d - c \quad \ldots\ldots (3)$$

The results of the application of (3) are shown in Table 2. There is good agreement between the "corrected" Mohr and the potentiometric results.

3.2 *Application to molasses*

The potentiometric method was applied to the sample of molasses. These results appear in Table 1. The standard deviation of these results compared favourably with that of the analytical reagents.

3.3 *Recovery tests*

After analysis on the original molasses a known amount of Cl^- was added and the total Cl^- concentration determined. It can be assumed from these results (Table 3) that large concentrations of carbohydrates do not interfere in the determination.

3.4 *Inorganic interference*

Two types of errors can be considered as a result of inorganic interferences. The errors may arise from co-precipitation of the interfering anion with AgCl or, if co-precipitation does not take place, errors may be introduced by adsorption of Cl^- on the precipitated foreign anion.

In the case of $CO_3^=$, $PO_4^{\equiv}$, $SO_3^=$ and $SO_4^=$, AgCl precipitates first and hence the second type of interference does not occur. The degree of co-precipitation must be considered but can be shown to be negligible by calculation (Appendix I). Table 4 shows the percentage Cl^- remaining in solution as the foreign anion starts to precipitate. For this reason these anions will not interfere in the determination. These conclusions were confirmed experimentally.

Considerable errors were experienced in the presence of Br^-. Co-precipitation does not take place but the second type of error appears to be evident. The AgBr precipitates before the AgCl and, because of the nature of the AgBr, Cl^- appears to be adsorbed thus depressing the end point. This is not evident in the case of I^- although AgI is precipitated prior to AgCl. The presence of Br^- in molasses is not to be expected and the interference from this anion was not considered to be of great importance.

4. Conclusions

It is possible to determine Cl^- in molasses with considerable accuracy in the presence of $CO_3^=$, $PO_4^{\equiv}$, $SO_3^=$, $SO_4^=$, and I^-. Interferences from Br^{-4} can cause considerable errors but this cannot be considered as a serious drawback to the method.

Acknowledgements

The author wishes to thank Mr. R. P. Jennings and Mr. D. M. Oosthuizen for their advice and Mr. A. E. Dixon for his help in the laboratory investigations. The author also wishes to thank Optical Instruments (Pty) Ltd., for their permission to reproduce Figure 1 from the potentiograph manual.

References

1. R. Behrend. Z.physik Chem., 11, 485 (1893).
2. I. M. Kolthoff, N. H. Furman, Potentiometric Titrations. 1931. John Wiley & Sons, inc., New York.
3. M. D. Peiperl, F. G. Carpenter and V. R. Deitz. 1959. The automatic chloride titrator in the analysis of some ionic constituents. Proc. Tech. Sess. Bone Char 1959, 53.
4. C. A. Browne, F. W. Zerban. 1955. Physical and Chemical Methods of Sugar Analysis. John Wiley & Sons, Inc., New York. 1070p.

Appendix I

Calculation of the extent of interference of the presence of $CO_3^=$, in the determination of Cl^-. The two anions are assumed to be present in equimolar quantities (O.1M).

Solubility product S_p (AgCl) = 1.7×10^{-10} ....(1)

Solubility product S_p (Ag_2CO_3) = 8.2×10^{-12} ...(2)

i.e. for AgCl to begin to precipitate

$$[Ag^+] = \frac{1.7 \times 10^{-10}}{0.1} = 1.7 \times 10^{-9}$$

and for Ag_2CO_3:

$$[Ag^+] = \sqrt{\frac{8.2 \times 10^{-12}}{0.1}} = 9.1 \times 10^{-6}$$

i.e. AgCl will be precipitated first.

Assume that $AgNO_3$ is added until Ag_2CO_3 is just beginning to precipitate. At this stage both (1) and (2) will hold.

i.e. $$\frac{1.7 \times 10^{-10}}{[Cl^-]} = \sqrt{\frac{8.2 \times 10^{-12}}{[CO_3^=]}}$$

i.e. $$[Cl^-]^2 = \frac{2.89 \times 10^{-20}}{8.2 \times 10^{-12}} \times [CO_3^=]$$

hence $[Cl^-] = 1.88 \times 10^{-5}$

i.e. percentage Cl^- remaining in solution:

$$= \frac{1.88 \times 10^{-5}}{0.1} \times 100$$
$$= 1.88 \times 10^{-2}\%$$

Hence errors due to presence of $CO_3^=$ are negligible.

TABLE 1

	Potentiometric Determination on Analytical Reagents	Mohr Determination on Analytical Reagents	Potentiometric Determination on Molasses
No. of determinations	25	7	25
Mean (g Cl^-)	1.82×10^{-2}	1.85×10^{-2}	2.04×10^{-2}
Standard deviation	3.30×10^{-5}	3.52×10^{-5}	2.94×10^{-5}
% deviation from the mean	0.18%	0.19%	0.14%

TABLE 2

'Observed' [Cl^-] due to x moles Cl^-	1.85×10^{-2}
'Observed' [Cl^-] due to 2x moles Cl^-	3.67×10^{-2}
Difference ('True' [Cl^-])	1.82×10^{-2}
[Cl^-] from potentiometric titration	1.82×10^{-2}

TABLE 3

	Determination on Molasses	Determination on Molasses $+Cl^-$	Determination on Cl^-	% Recovery
Mean (g Cl^-)	1.03×10^{-2}	2.11×10^{-2}	1.08×10^{-2}	100
% deviation from mean	0.17%	0.14%	0.17%	—

TABLE 4

Interfering Anion	% Cl^- Remaining in Solution
$CO_3^{=}$	1.88×10^{-2}
$PO_4^{=}$	2.43×10^{-3}
$SO_4^{=}$	1.55×10^{-5}
$SO_3^{=}$	1.23×10^{-2}

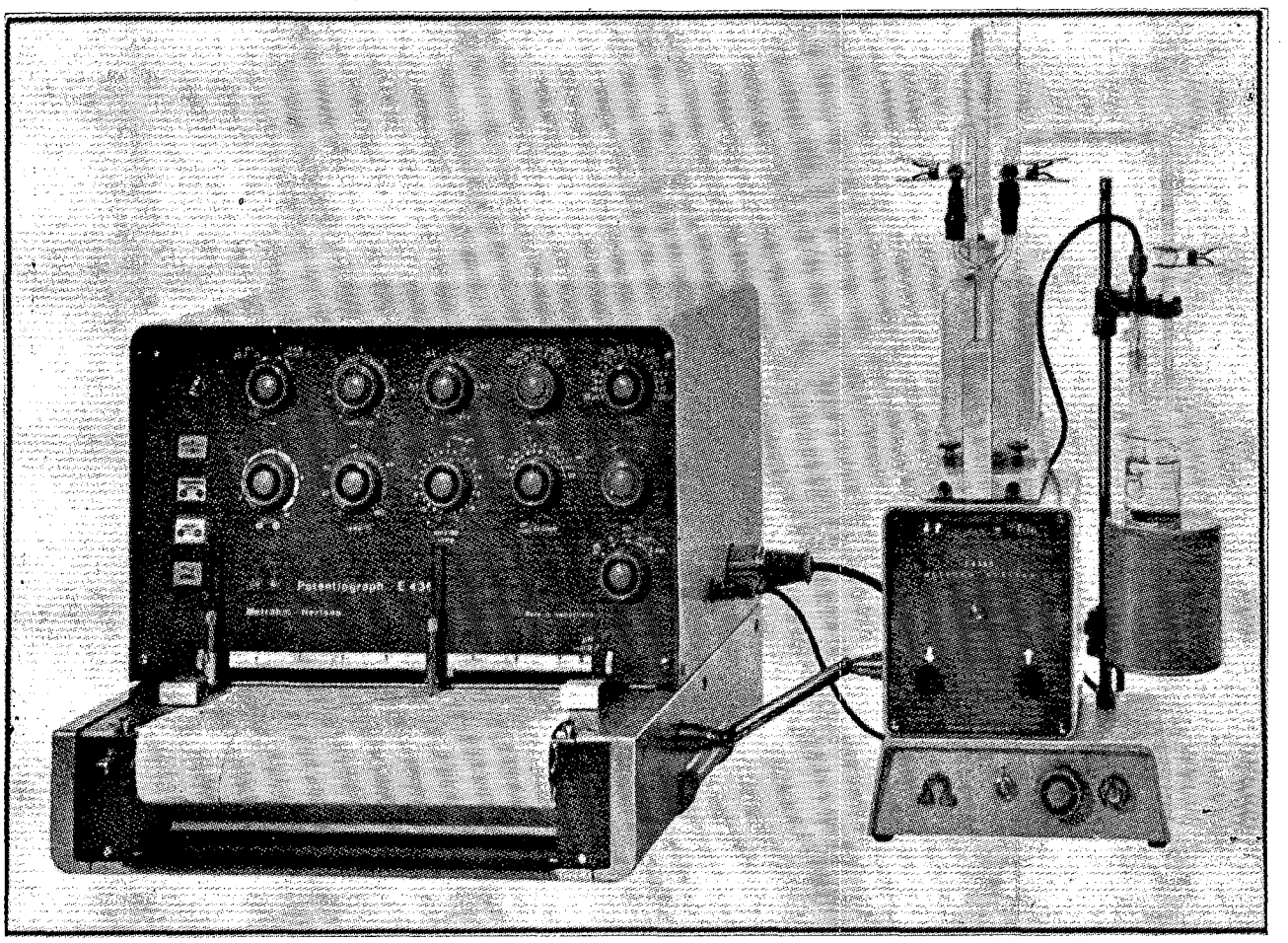

FIGURE 1: Metrohm potentiograph and titration set.

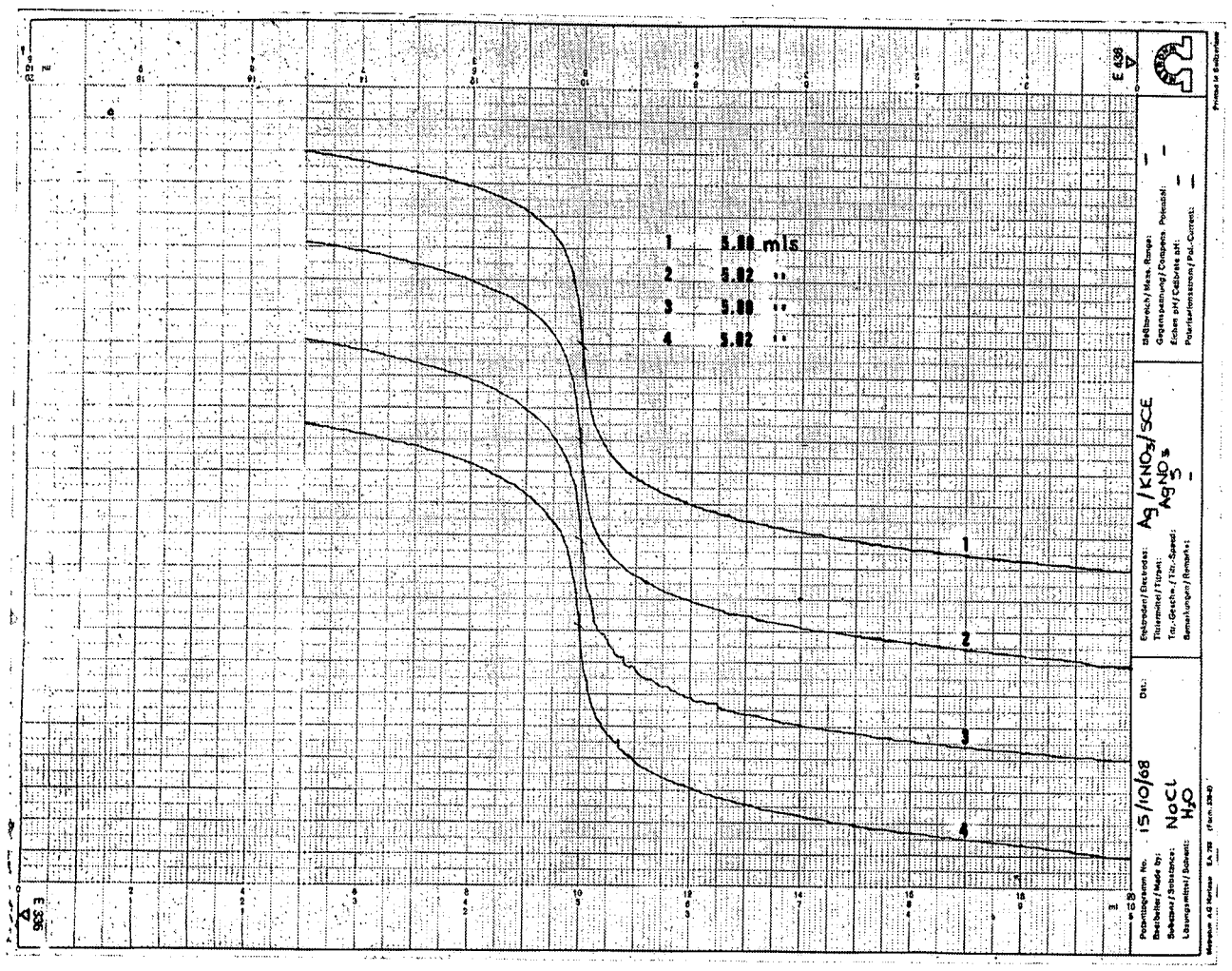

FIGURE 2: Potentiometric curves produced by the potentiograph in four consecutive determinations.

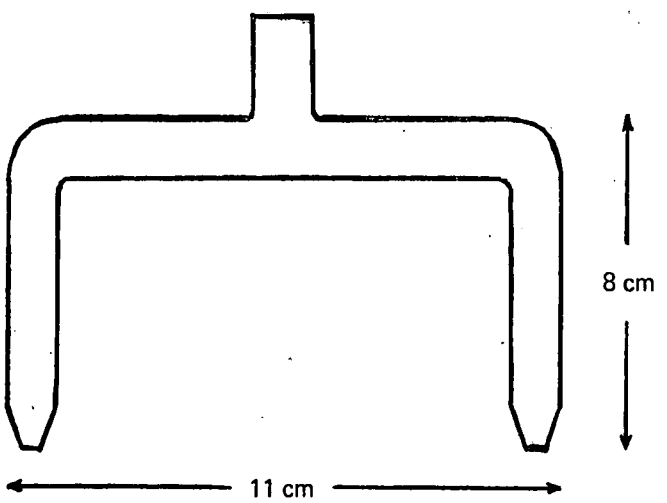

FIGURE 3: Salt bridge.

Discussion

Mr. Alexander (in the chair): Various uses for chloride determination have been mentioned in the paper but a further one has been recently discovered.

Enzymes are being tested for the removal of starch and one of the factors affecting the stability of the starch-removing enzyme is its chloride content.

Most of the enzymes are supplied with an additional amount of sodium chloride.

Our juices and syrups already have more than sufficient chloride to protect the enzyme.

Mr. van Hengel: For a long time the industry has been seeking a better definition of purity — the ratio of sucrose to non-sucrose.

It might be possible to express purity as a ratio in which sucrose is available in solutions to an ion which is chemically inert and is not added or removed by any of our normal clarification processes. If chloride was such an ion and could be determined accurately it would be possible to draw up a more correct mass balance in a factory and so detect losses.

Is Mr. Comrie's method accurate in sucrose solutions other than molasses and could it be used in a factory laboratory?

Mr. Comrie: I see no reason why this method cannot be applied to all sugar products. On raw sugars and refined sugars the same standard deviations have been achieved.

The addition of lime in a factory could cause problems with the mass balance. The factory laboratory staff should have no difficulty with the method.

Mr. MacGillivray: To what levels of chloride is this method sensitive, as a much lower percentage of chloride would be present in juice compared to molasses?

The S.M.R.I. has been using the same method on juices and when the juice had been preserved with mercuric chloride, apart from this additional chloride which could be allowed for, there was interference from a silver mercuro complex which was insoluble and precipitated very early in the titration.

Mr. Comrie: It has been reported that chlorides may be determined polentiometrically in analytical reagents down to .001 normal solutions.

After this the precipitated silver chloride is decomposed by light.

In connection with mercuric chloride, I cannot comment as I did not use a preservative. This should present no problem, however, if the complex is insoluble and does not interfere.

Mr. Oosthuizen: These methods are usually worked with .01 normal solution. The volume of the titration solution determines the amount to be titrated, usually about 15 ml so that the error, the reproducibility on volume, is negligible.

A .001 normal solution will bring problems because of the electrometric detection of an end point.

Mr. Alexander: As Mr. Comrie was able to determine chloride in both molasses and refined sugar the method should be able to determine it in juice.

Mr. Francis: A refinery in Toronto is attempting to use chloride as a standard for computer control of the factory.

Mr. Jennings: The application for the determination of the maximum angle for minimum recirculation (Mamrec), would be interesting.

Mr. Prince: At Empangeni, for the determination of Mamrec, we introduced dye into the juice in the diffuser and tried to obtain the juice after it had filtered through the bed, in order to determine the amount of dye in the relative portions from the different sampling points below the diffuser bed.

We could not pick up the dye so chloride was used as a tracer.

About ten gallons of concentrated chloride were run into the diffuser and chlorides were determined conductometrically, a similar method to that used by Mr. Comrie, and the test was very successful.

Mrs. Swart: Although I am not in favour of the Mohr titration, because of difficulty with the end point, the effect of overtitration should be cancelled out by standardisation, assuming both determinations are performed by the same analyst.

Mr. Bruijn: In the official Mohrs titration the silver nitrate is standardised with a standard chloride. The bottle in which you have standardised must be kept and then you titrate the sample to the same colour. In this case the error due to overtitration cancels out.

This is not normally done in practice as the standardisation may have been done a week before and errors can be made by not titrating to exactly the same final colour.

Mr. Comrie: I did keep the solution as a standard. However, you must go past the end point to see the colour change and this will vary with each person.