

Analysis of Chloride in Milk with a Specific Ion Electrode

A chloride selective electrode is used as well for very accurate determinations of chloride in milk as for rapid determinations with an acceptable accuracy. Several defecating agents are dis-

cussed. The best results were obtained by measurement after defecation with Folin-Wu reagent or zinc-acetate + potassium ferrocyanide.

One of the tests which is often carried out in the analysis of milk is the determination of chloride. This determination, combined with other tests, permits the detection of mastitic or abnormal milk. The classical method is the chloride titration according to Volhard.

Recently, the use of a chloride specific ion electrode was described by Muldoon and Liska (1971). The authors measure against a calibration curve obtained with 0.001 *M* to 1 *M* chloride, which is said to be a straight line. Because the specific electrode measures activities and not concentrations, this statement sounded rather improbable. Actually, no straight line was obtained in our experiments covering the 0.001 *M* to 0.1 *M* concentration range. The slope is smaller in the high concentration range than in the lower concentration range, as is predicted from theory. Furthermore, no information is included on the precision and accuracy of the method. Therefore, it seemed necessary to undertake a systematic analytical study of the method in question. The results are reported here.

EXPERIMENTAL SECTION

Apparatus. Beckman solid state membrane electrode no. 39604. Single junction reference electrode, Orion 90-01. Radiometer pH meter 26. All measurements were carried out in a cell, thermostated at $25.0 \pm 0.1^\circ$.

Reagents. All chemicals were reagent grade. Ionic strength adjustment buffer (ISAB) as proposed by Parthasarathy *et al.* (1972): dissolve 170 g of sodium nitrate and 57 ml of anhydrous acetic acid in 500 ml of distilled water. Adjust the pH to 5.4 with 5 *M* sodium hydroxide, and dilute the solution to 1 l. with water.

Defecation. I. Folin and Wu reagent: 1 part of milk, 1 part of sodium wolframate (10%), 1 part of H_2SO_4 , $\frac{2}{3}$ N, and 7 parts of water. II. Ten parts of milk, 1 part of zinc acetate (30%), 1 part of potassium ferrocyanide (15%), and 88 parts of water. III. One part of milk and 1 part of nitric acid (6%). IV. One part of milk and 1 part trichloroacetic acid (20%). V. One part of milk and 1 part of Esbach reagent (10 g of picric acid and 20 g of citric acid/l. of distilled water).

Procedure for Potentiometric Measurements. A 25-ml aliquot of the sample (milk or the filtrate of defecated milk) was pipetted into a 100-ml polyethylene beaker, the same volume of ISAB was added, the solution magnetically stirred, and the steady state potential (180-300 sec) recorded. The chloride ion activity was determined from a calibration plot of potential *vs.* log of chloride - concentration.

RESULTS AND DISCUSSION

As also stated by one of the precited authors (Muldoon, personal communication), direct measurement is not possible. For milk containing 1095 ± 11 ppm of Cl^- (according to the Volhard titration) results of 1500-1600 ppm were found. This error is caused in part by casein, as is shown by experiments in which the potential is measured of mixtures containing constant casein and varying chloride concentrations. As is shown in Figure 1, casein causes a potential increase. However, only about $\frac{1}{10}$ of the error

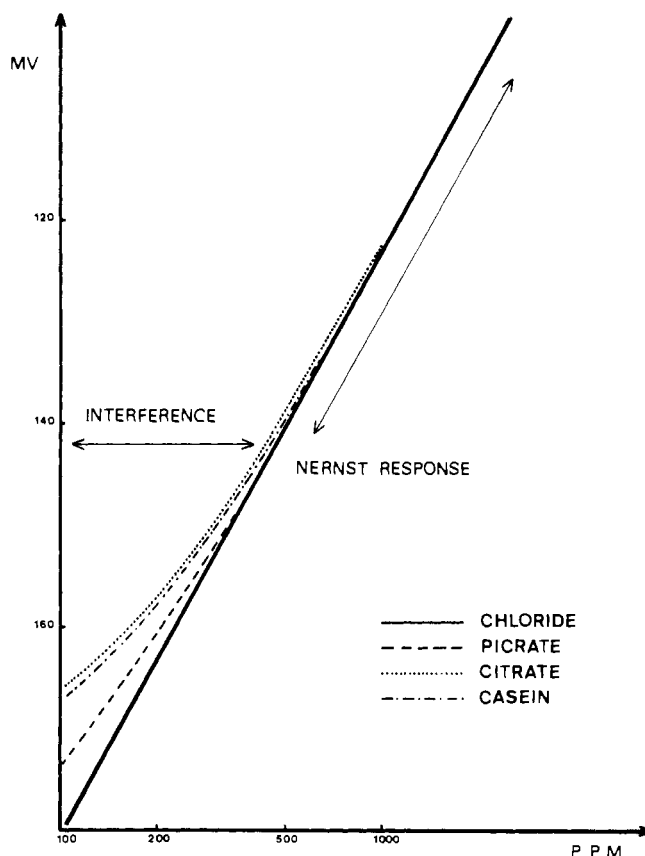


Figure 1. Effect of picrate, citrate, and casein on the response of a chloride electrode.

is due to this interference. Lactose does not interfere. The reason for the other interferences is probably an ionic strength effect, since it is found that the addition of an equal volume of ISAB to the milk sample eliminates the error to a large degree. Multireplicate analysis (five samples) gave as a result 1146 ± 23 ppm. The difference between the results obtained by this method and the Volhard titration is significant and is completely accounted for by the casein error. If one multiplies with a correction factor of 0.95, the accuracy is, however, more than sufficient for routine application.

To try and obtain still better accuracy, several defecation methods were carried out (see Experimental Section). Preliminary experiments showed that impossibly high results were obtained with defecating agents IV and V. The error found with defecating agent V is due to the presence of citrate. Picrate is found to interfere to a much smaller degree (see Figure 1). In Table I the results obtained with the other three defecating agents are compared with results obtained without defecation and by potentiometric titration using the classical Volhard method. The results are the mean of ten separate analyses.

A statistical analysis of all results presented in Table I reveals highly significant differences. A significant but not highly significant difference is detected among the results

Table I. Comparison of Direct Potentiometric Methods with Volhard Titration

Method	Result, ppm	Precision as standard deviation on each measurement
Volhard	1142	5
No defecation	1205	35
Defecating agent I	1157	20.3
Defecating agent II	1168	16.1
Defecating agent III	1130	30.8

obtained after defecation. No statistically significant difference appears when comparing the potentiometric titration and the measurements after defecation with reagents I or III.

Another way to obtain accurate results is the use of Gran's plots. One proceeds by adding increments, V , of solution containing a concentration, C , of the ion to be determined to the original solution (volume, V_0) and by measuring the potential E after each addition. By plotting $(V + V_0) 10^{-E/0.059}$ vs. V , a straight line should be obtained which intercepts the abscissa at a value of $V = V_e$. The original concentration C_0 is then computed from $C_0 = -(CV_e/V_0)$.

Gran's plots have been used with specific electrodes by several authors (Brand and Rechnitz, 1970; Liberti and Mascini, 1969; Parthasarathy *et al.*, 1972) and are generally considered as a method which should yield very accurate results. Our own experience with fluoride and nitrate electrodes has shown that this is not necessarily true, be-

cause the accuracy depends to a very large degree on the correctness of the factor 0.059. Very often the slope in the Nernst equation is somewhat lower in practice (0.056–0.058), which leads to systematic errors of several percent (Mertens and Massart, 1973).

With the measurement of chloride in milk this is not the case. It is found that the precision and the accuracy are of the order of a few pro mille.

GENERAL CONCLUSION

Chloride specific electrodes can be used as well for very accurate determinations of chloride in milk as for rapid determinations with an acceptable accuracy.

LITERATURE CITED

- Brand, M. J. D., Rechnitz, G. A., *Anal. Chem.* **42**, 1172 (1970).
 Gran, G., *Analyst* **77**, 661 (1952).
 Liberti, A., Mascini, M., *Anal. Chem.* **41**, 676 (1969).
 Mertens, J., Massart, D. L., *Bull. Soc. Chim. Belg.* **82**, 179 (1973).
 Muldoon, P. J., Liska, B. J., *J. Dairy Sci.* **54**, 117 (1971).
 Parthasarathy, N., Buffle, J., Monnier, D., *Anal. Chim. Acta* **59**, 447 (1972).

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