Application of Ion-Selective Electrodes in the Beet Sugar Industry

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Introduction

Attempts to determine specific ions potentiometrically have been reported nearly half a century ago. Lacking technology, however, prevented development of suitable electrodes, with the exception of the pH electrode, until about 1960. Since that time a large variety of ion-selective electrodes have been developed and introduced on the market with varying claims of success.

The objective of this report does not include theoretical consideration which is reported elsewhere (4,10)[3], but shall be limited to the practical applications of some ion-selective electrodes in the laboratory and in process control. An excellent treatise on ion-selective electrodes has been prepared by the Department of Commerce (2) to which the reader is referred.

Some applications of ion-selective electrodes in the sugarbeet industry have been previously reported by McCaslin, et al (7) and Schoenrock (12).

General

Some ions of common interest in the sugarbeet industry are sodium, potassium, calcium, magnesium, chloride, sulfate, and nitrate. Present methods for these ions are time consuming or give poor precision due to vague endpoint determinations resulting from the highly colored solutions. The use of ion-selective electrodes not only decreases analysis time, but is more precise and usually as accurate as existing methods presently being used.

Since all the solutions dealt with in the sugar industry are complex, ion-selective electrodes have limited application for measuring the concentration of ions directly from electrode response by comparison to a calibration curve. These electrodes respond not only to the ion for which they were specifically designed, but also to other ions in solution to a varying degree. The observed potential is related to ionic activity, rather than to concentration. For simple or standard solutions which are very dilute, the concentration and ionic activity are nearly syn-

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[3] Numbers in parentheses refer to literature cited.

onymous, but differ significantly as the solutions become increasingly complex. Therefore, any changes in ionic strength between standard solutions and samples would result in errors. The applications described here for laboratory use involve either a potentiometric or a precipitation titration depending upon the analysis, with the exception of the nitrate and potassium determinations. The electrode response is therefore not dependent upon the initial EMF developed by the electrode when placed in solution but to the change in electrode potential at the endpoint. There are some inherent errors in the endpoint determination in precipitation titrations using ion-selective electrodes which are described by Carr (1) and Schultz (13).

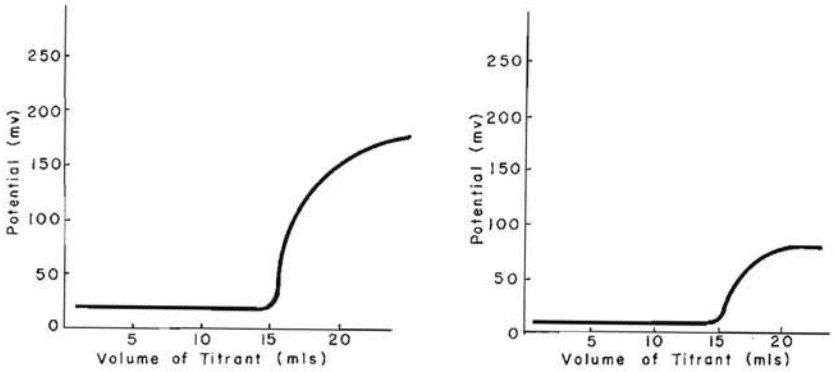
Laboratory Methods and Materials

Determination of Chlorides

The recent paper of Hozumi and Akimoto (6) describes a method for the micro-determination of chloride in organic compounds after oxygen-flask combustion. The absorption liquid, diluted with acetone to give a 90% organic medium, is titrated with standard silver nitrate. The endpoint is detected by means of a sodium sensitive electrode which is 150 times more sensitive to silver than to sodium.

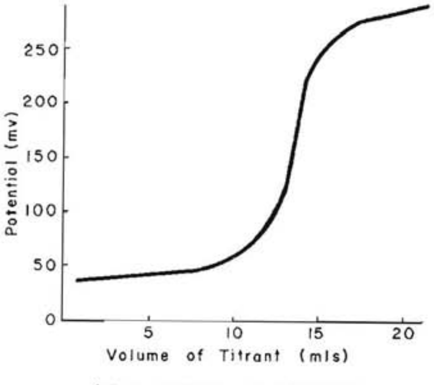
The method developed in this laboratory relates closely to the method of Hozumi and Akimoto. It involves, however, the macro-determination of chloride in an aqueous medium with the endpoint of the precipitation titration being detected by either a sodium, a glass, or a platinum electrode.

Two separate sets of equipment were successfully used for the potentiometric determination of chlorides with equal success: A Metrohm E-436 Automatic Titrator capable of plotting a first derivative titration curve and a modular assembly consisting of a Beckman Expandomatic pH Meter with 10 mv output, Beckman Potentiometric Recorder, and an Aminco Automatic Buret. The potential change at the endpoint varies from 50 to 200 mv, depending upon the electrode used (Figure 1). The amplification system must be capable of expanding this range full scale in order to obtain a sharp break in the titration curve. Figure 2 illustrates a typical titration curve obtained by proper scale expansion using a Beckman No. 39278 sodium ion electrode. The Beckman glass pH electrode No. 41263 gives a curve similar to the sodium ion electrode, while the platinum electrode gives a symmetrical S-shaped curve (Figure 1). An Orion reservoir reference electrode, Model No. 90-04, was used in conjunction with these electrodes because the filling solution contained no chlorides to contaminate the sample by electrode bleeding. A standard calomel fiber junction can also be used, but care must be taken to prevent contamination of the sample from the electrode filling solution as well as plugging of the fiber junction.



(a) SODIUM ION ELECTRODE

(b) GLASS pH ELECTRODE



(C) PLATINUM ELECTRODE

Figure 1.—Potentiometric titration curves of Cl^- with $AgNO_3$ using various electrodes in combination with an Orion reference electrode.

This method is subject to the same interferences as those encountered in other methods for the determination of chloride by precipitation with silver nitrate. Although the sodium and glass electrodes show maximum response at pH 7.6, the sample must be made slightly acidic (approximately pH 5–6) to eliminate possible interferences. These electrodes are also sensitive to the hydrogen ion which will mask the response to silver ion at the endpoint if the solution is strongly acidic.

Reagents: A silver nitrate solution standardized potentiometrically with dry reagent grade sodium chloride. The concentration of the silver nitrate solution is dependent upon the sample requirements. Concentrations from 1.0 to 0.05*N* have been used and work well. The potential change in the area of the endpoint is not as abrupt with the more dilute solutions, however.

Procedure: Transfer a sample aliquot into a 250 ml beaker, adjust the pH so the sample is slightly acidic, and add sufficient water to allow the tips of the electrodes to be adequately immersed. Place the beaker on a mag-mix and immerse the electrodes in the solution. Allow to stir for a few minutes to condition the electrodes. Zero the recorder pen at 10-20% on the recorder chart with the electrodes in the solution and actuated. A slight but steady drift in baseline is observed during the titration, either up or down scale, due to sample dilution and electrode conditioning. If the electrodes are allowed to condition for several minutes before beginning the titration, the drift is stabilized. Samples which contain little or no sodium ions have a tendency to drift during the titration resulting in a poor break in the titration curve. This can readily be overcome by adding a few crystals of sodium nitrate before beginning the titration. Titrate with standard silver nitrate to the first break in the titration curve. With proper scale expansion, an 'L" shaped curve will be obtained with either sodium ion or glass electrodes. The exact endpoint is determined by extending both legs of the curve until they intersect. The point of intersection is taken as the endpoint (Figure 2). If the platinum electrode is used, the endpoint must be taken at the point of inflection.

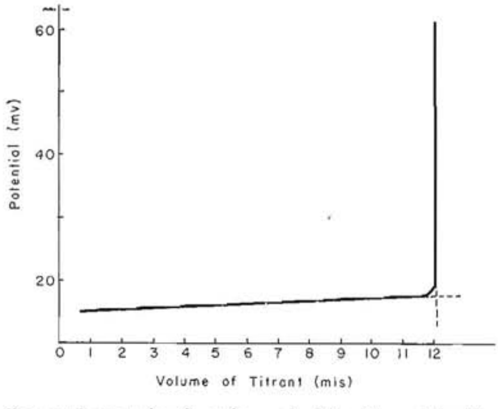


Figure 2.—Potentiometric titration of chloride with silver nitrate using a sodium ion electrode.

The precision obtained with the potentiometric method in standard sodium chloride solutions is comparable to the Mohr titration method (Table 1). The accuracy is slightly better if the first derivative of the potential curve is used for the endpoint determination rather than the first break in the titration curve. Both methods correlate better than 99.9% with the theoretical chloride concentration with a high degree of confidence. In highly colored solutions where the endpoint in the Mohr method is difficult to determine, the potentiometric method shows a much higher precision (Table 2) and the average difference between methods becomes quite pronounced.

Table 1.—Statistical comparison of methods to theoretical chloride concentration.

	Theoretical Cl^-	Mohr	Sodium electrode		Glass electrode	
			1	2	1	2
Avg. of ten samples (mg)	41.58	41.59	41.82	41.53	41.15	41.40
Difference from theoretical (%)		0.02	0.57	—0.12	—1.03	—0.43
Standard deviation		0.21	0.28	0.26	0.54	0.26
Correlation		.9993	.9999	.9997	.9997	.9998
Confidence limit			Greater than 99%			

Two methods were used for the determination of endpoint in the potentiometric method: Column 1, the endpoint was taken at the first break in the curve; Column 2, at the point of inflection found by taking the first derivative of the titration curve.

Table 2.—Comparison of the Potentiometric method of the Mohr titration method in highly colored solutions.

	Potentiometric method	Mohr method
Avg. of samples (mls)	6.63	6.79
Standard deviation	0.041	0.118
Difference between methods (%)	2.41	

The potentiometric titration of chlorides works well for molasses, raw juice, CSF, and other highly colored solutions encountered in the beet sugar industry.

Determination of Sulfate

The determination of sulfate has long been carried out gravimetrically by recovery of the sulfate as barium sulfate. This method is both tedious and time consuming and can result in errors due to incomplete precipitation, coprecipitation, or reduction of the sulfate to sulfide by carbon and high temperatures during ignition. A recent method developed by Ross and Frank (11) for sulfate uses a lead selective electrode and lead perchlorate as a titrant. In order to decrease the solubility of the lead sulfate, the titration is carried out in 50% dioxane. A number of cations and anions interfere with this method, however.

The following method essentially involves a precipitation titration of sulfate with barium chloride in an aqueous medium. The excess barium at the equivalence point is detected by means of a divalent cation electrode sensitized for barium.

This particular electrode is sensitive to a number of divalent cations to which it shows a greater selectivity than to barium. The relative selectivity of some of the ions is listed below:

Zn^{++}, Fe^{++} = 3.5
Cu^{++} = 3.1
Ni^{++} = 1.35
Ca^{++}, Mg^{++} = 1.0
Ba^{++} = 0.94
Sn^{++} = 0.54

The effect of these ions is of no great consequence as long as they are not present in excessive quantities which would mask the electrode response to barium. The endpoint is determined by an increase in electrode response resulting from excess barium in solution after the equivalence point is reached. The divalent cation electrode also is sensitive to the hydrogen ion and should therefore not be used in strongly acidic solutions. The greatest response is at a pH above 7.0, but to eliminate interferences in the precipitation method, it should be run in a slightly acidic solution. To increase the sensitivity of the method, the electrode filling solutions have been conditioned for barium. This procedure greatly increases the electrode selectivity for barium.

As with all precipitation titrations, there are errors due to ionic strength and chemical activity (1,13) as well as dependence upon the solubility product of the precipitate formed. For micro-determinations of sulfate, the solubility product of barium sulfate is too large and the electrode sensitivity too low to give reliable results. Macro-determinations work well with good precision.

Equipment: The same potentiometric set-ups employed for the chloride determination were used for sulfate except for the electrodes. An Orion divalent cation electrode No. 92-90 conditioned for barium was used in conjunction with a fiber junction standard calomel electrode.

Conditioning of the Divalent Cation Electrode: Dissolve the ion exchanger in 100 mls of chloroform. Shake with two 60 ml portions of 0.1M barium chloride. Wash twice with 100 mls water. Remove the chloroform and traces of water by heating until the temperature of the exchanger reaches 115°C. Cool and use to charge the electrode. Replace the internal reference solution supplied by Orion with a $10^{-2}M$ solution of barium chloride.

Reagents: A 1.0N barium chloride solution is standardized with reagent grade magnesium sulfate.

Procedure: A sample containing 5—50m*M* of sulfate is placed in a 250 ml beaker, the solution made slightly acidic, and sufficient water is added to just cover the tip of the electrodes. The recorder is adjusted as in the chloride procedure. Titrate with standard barium chloride to the inflection point. The endpoint is taken at the first break in the curve and read directly from the chart. The titration curve is nearly identical to the chloride titration curve in Figure 2. Use of this method was very helpful in determining regeneration profiles and resin capacities from ion exchange effluents.

Determination of Calcium and Magnesium

Several procedures described in the literature have been successfully applied to sugarbeet liquors. These include the determination of calcium and magnesium by the method of van't Riet and Wynn (14) and by the potentiometric titrations described by Orion Research, Inc. (8).

The method of van't Riet and Wynn was preferred since it required no special electrodes and gave the best results when used in complex solutions which were impossible by conventional methods. The sample is first titrated for calcium with Na_4-EGTA in the presence of sodium citrate, then for magnesium with Na_4-EDTA. The titration is monitored by means of an expanded scale pH meter using a standard glass and calomel electrode. Each endpoint corresponds to a sharp change in pH (Figure 3). The optimum pH range for the titration is from 8.0—8.6. The citrate is added to complex the magnesium preventing it from interfering with the calcium determination and also to keep it from precipitating out of solution as the hydroxide.

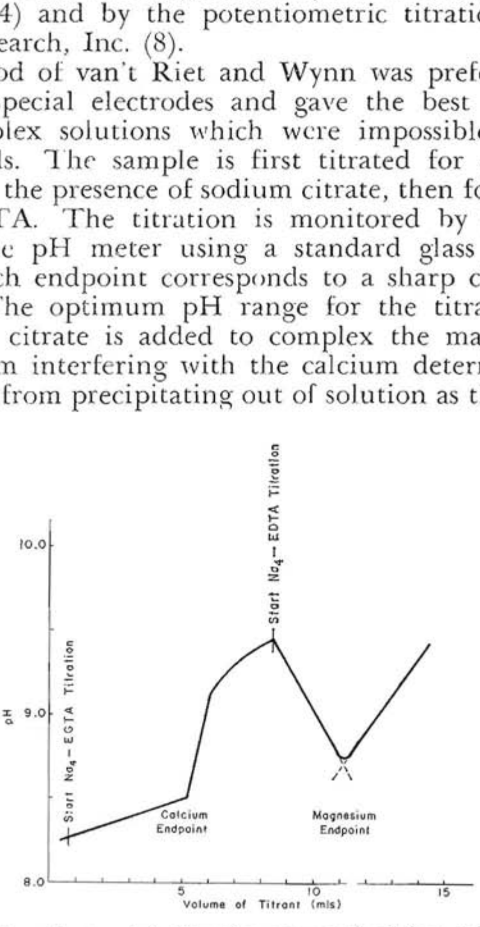


Figure 3.—Complexometric titration curve of calcium with Na_4—EGTA and magnesium with Na_4—EDTA using pH electrodes.

The method taken from Orion Research, Inc., uses Na_2-EDTA as a titrant and employs two ion-selective electrodes, one selective for calcium and the other a divalent cation electrode. Calcium endpoint is first determined by means of a calcium sensitive electrode in combination with a standard calomel electrode. The calcium electrode is then replaced by a divalent cation electrode and the titration continued slightly beyond the second inflection (Figure 4). The endpoint of the titration curve is at the point of maximum slope, or center point of the segment of greatest slope. The titrations are carried out at pH 11 and the magnesium determined by difference.

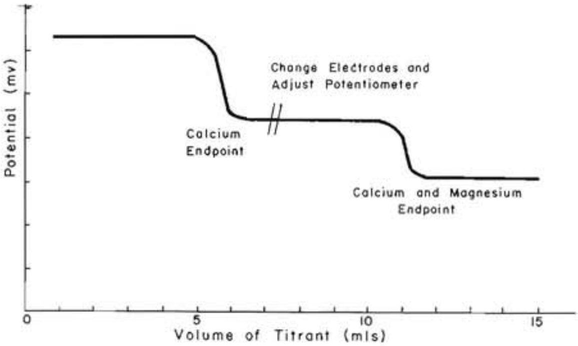


Figure 4.—Complexometric titration curve of calcium and magnesium with Na_4—EDTA using two specific ion electrodes.

Determination of Nitrate

The nitrate ion can be readily determined by the method of McCaslin, Franklin and Dillon. The nitrate concentration is measured directly as electrode response using a nitrate sensitive electrode by comparison to a standard calibration curve. The proper precautions must be taken to eliminate interfering ions and to correct for variations in ionic strength between the samples and standards. Careful and repeated standardization of the equipment is essential. This method is much less time consuming and shows a greater accuracy than the phenoldisulfonic acid method.

Determination of Potassium

The development of a new electrode by Frant and Ross (4) holds promise for the determination of potassium. The electrode is much more sensitive to potassium than sodium and has been used to determine potassium directly in solution rather than by difference. This method uses a standard curve for calibration so precautions similar to those described in the nitrate method must be taken to insure reliable results.

Factory Applications

For the past few years various ion-selective electrodes have been employed in process streams to determine their usefulness as continuous on-stream monitors. The Beckman No. 39047 monovalent cation electrode and the Orion divalent cation electrode No. 92-32 have been used to indicate cell exhaustion and cell regeneration in the Quentin process (12). In addition, a divalent cation electrode has been used to monitor limesalts in second carbonation (12). In all applications these electrodes work very well. However, since complex solutions are involved and the electrodes measure ionic activity rather than concentration, careful consideration must be given to the design of a flow-through system when incorporated in process control upon installation. Fluctuation in flow, brix, and temperature can cause changes in the electrode response.

Monitoring Ion Exchange Effluents

A monovalent cation electrode was used to monitor cell exhaustion in the Quentin process (Figure 5). The electrode and pH meter were calibrated so that untreated syrup gave a 90% reading on the chart. As the syrup was placed on the cell, the response dropped to a very low point showing a high percentage of exchange at first (point A). As the cell exhausts, the percent exchange decreases until the processed syrup approaches the concentration of unprocessed syrup (point B). In the case of cell channeling (point C), the curve takes a different appearance. Low exchange profiles over a long time period indicate incomplete removal of monovalent cations during the exhaustion steps.

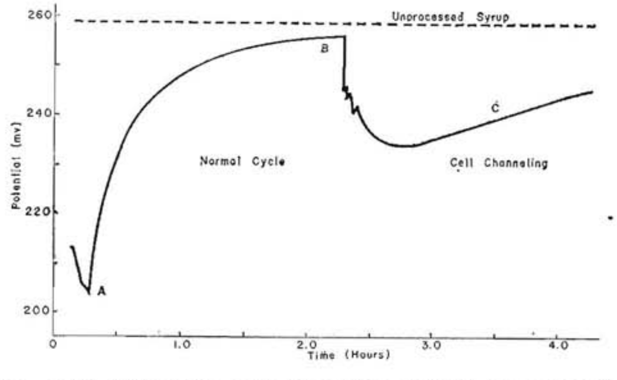


Figure 5.—Cell exhaustion and channeling profile from Quentin process —monovalent cation electrode.

Two divalent cation electrodes were employed on the regeneration cycle of the ion exchange system. Figure 6 is an actual recording showing the response of each electrode and the cut-off point. One electrode was used to monitor the cell effluent going to the sewer (6A) during the initial stages of regeneration and indicates the point at which the regenerant could be recovered in a useful concentration to be reused in the next regeneration cycle. A second divalent cation electrode (6B) monitors the effluent being recycled to the used regenerant tank during the regeneration and cell rinse. As the excess regenerant is removed from the cell, the electrode response drops and the water is returned to the rinse recovery system.

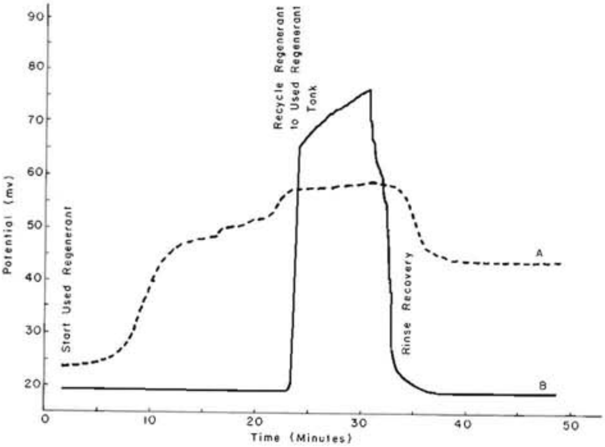


Figure 6.—Regeneration profile, Quentin process, using a divalent cation and a reference electrode to monitor separate regenerant streams.

Limesalts in Second Carbonation Juice

The divalent cation electrode gives nearly a linear millivolt output with respect to limesalts except at very low concentrations (Figure 7). It is therefore very useful for the determina-

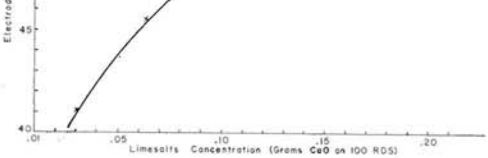


Figure 7.—Divalent cation electrode response vs. limesalts concentrations.

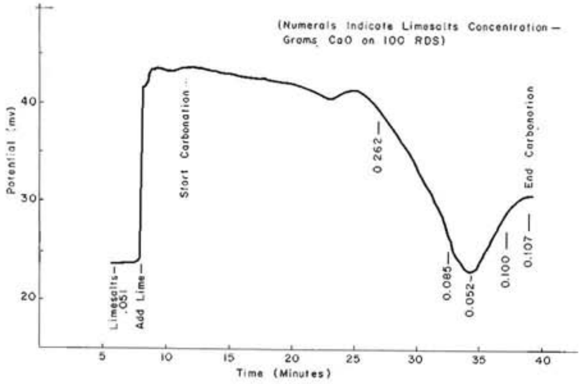


Figure 8.—Determination of second carbonation endpoint with divalent cation electrode.

tion of minimum limesalts in second carbonation as shown in Figure 8. In this carbonation profile, the limesalts decrease to a minimum value as CO_2 is added and then rapidly increases again as the sample is over-carbonated.

A divalent cation electrode and a standard calomel reference electrode were used as a monitor of second carbonation juice giving a continuous record showing fluctuations in limesalts. In conjunction, a glass and a standard calomel electrode were also employed to determine the relationship of pH with these limesalts fluctuations. Figure 9 through 11 are actual recordings of limesalts measurements determined with a divalent cation electrode. Figure 9 shows that electrode response with respect to actual laboratory analysis. Periods of high limesalts occur which are not observed by the laboratory analysis (Figure 10) and are of sufficient duration to cause serious scaling problems. Figure 11 shows the relation of pH to limesalts. The simple alkalinity

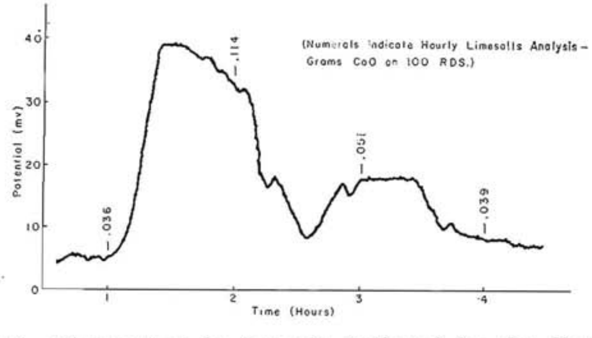


Figure 9.—Fluctuations in limesalts indicated by the divalent cation electrode with the corresponding hourly laboratory results.

titrations normally used to follow the limesalts concentration may pick up these fluctuations, but do not indicate the cause or means of correcting the problem. A record showing both limesalts and pH could indicate whether there was over or under carbonation or changes in soda ash addition. The problem could properly be corrected eliminating long periods of operation at high limesalts levels and maintaining a more uniform level of operation.

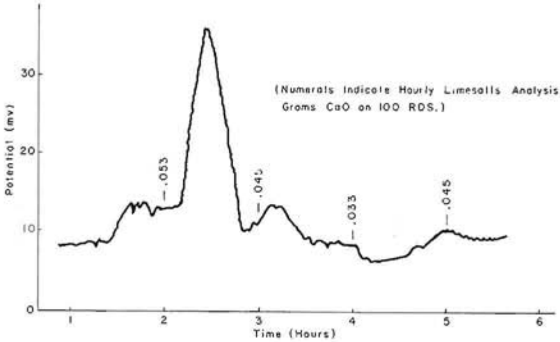


Figure 10.—Period of high limesalts detected by divalent cation electrode but completely missed by hourly laboratory analysis.

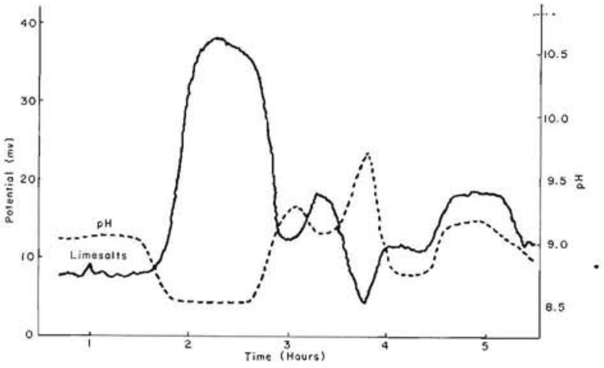


Figure 11.—Limesalts profile showing corresponding pH changes.

Summary

Ion-selective electrodes have been used successfully in process control as well as in devising new analytical procedures for the laboratory. In the Quentin process, control of the cell exhaustion, cell channeling, resin fouling, etc., can be determined with the monovalent cation electrode. This allows termination of the exhaustion cycle at the correct moment. During the regeneration cycle, monitoring regeneration effluents allows better control and utilization of regenerants.

Limesalts can be more effectively controlled by use of the divalent cation electrode. A continuous monitor of limesalts may permit second carbonation control by measurement of the actual concentration rather than pH. In conjunction with pH a good insight into the cause of certain changes in limesalts can be determined and more quickly corrected.

In process control, these electrodes encounter complex solutions. Electrode response is dependent upon ionic activity, and therefore, to the ionic strength of the solution. Drastic changes in brix will result in changes in electrode response. Other factors such as flow rate, pH, gas entrainment, and temperature all affect the electrode response and must be regulated in order to maintain reliable results. Although the membrane type electrode is capable of operating at 50°C, it is recommended that the temperature of 25° ± 5° be maintained with as little fluctuation as possible. Entrained air must be removed. Good housekeeping is essential at all times, and an occasional standardization of the instrument and replacement of ion exchanger and membranes in the electrode must be carried out to insure good response and changes due to aging.

Ion-selective electrodes have been found to be especially useful for potentiometric titrations. They are now routinely used for the determination of Cl^-, Ca^{++}, Mg^{++}, and $SO^=_4$.

The application of specific enzyme electrodes shows real promise in the biological and biochemical fields. The employment of enzymes and biological materials in membrane electrodes has resulted in the development of a number of new sensors for analysis of such species as blood glucose and lactate (15), amygdalin (9), and urea (5). At present an electrode specific for lactic acid is being developed in this laboratory and appears to be promising. Some engineering problems are yet to be overcome before routine use can be made.

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