

ELECTRODES FOR NONDESTRUCTIVE HIDE EVALUATION*

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ABSTRACT

Among the many specific ion electrodes now available a few are capable of determining concentrations in the surface layers of materials in sheet form. Tests have been made to determine the reliability of a surface glass electrode and an antimony billet electrode to measure hydrogen ion concentration or pH, and a silver billet electrode to measure chloride or sulfide concentrations on the surface of hides under a variety of conditions. With certain precautions the electrodes perform well for equilibrium systems. When suitably connected to a recorder they may provide an additional method for studying the time course of nonequilibrium systems.



INTRODUCTION

Recent improvements in electrodes for the determination of specific ions have led to renewed interest in the use of electrical methods for the detection and control of processing variables. Among the many electrodes now available there are a few which are capable of determining concentrations in the surface layers of materials in sheet form. Several of these might be useful in the research and control of tannery processes especially where a nondestructive measurement would be desirable.

Stubbings (1) has described the theory and practice of pH measurements in the tannery, including observations on the use of a regular glass pH electrode to determine the pH of hide surfaces. In these experiments the leather slices had to be carefully cupped around the electrode bulb to obtain reliable results. Glass electrodes are now available in which the measuring surface is flat. These facilitate measurement of the pH of a surface.

The measurement of potentials (voltages) developed at metallic electrodes can be traced back to the discovery of the voltaic cell. The magnitude of the potential depends upon the chemical reaction occurring at the surface of the electrode and a theoretical value can be calculated. The thermodynamic aspects

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of metallic electrodes are adequately treated by Lingane (2), MacInnes (3), and Kolthoff and Furman (4). The silver electrode reaction is $\text{Ag} \rightleftharpoons \text{Ag}^+ + e^-$ and the thermodynamic potential for this reversible reaction is given by the equation $E = E^\circ + \frac{RT}{F} \log (\text{Ag}^+)$. E° is the potential when the activity of

the silver ion surrounding the electrode is unity. $\frac{RT}{F}$ has a value of 0.0591 at 25°C. Therefore, the potential of the silver electrode depends upon the activity or related concentration of the silver ions surrounding the electrode.

In the presence of chloride ions the concentration of silver ions is controlled by the solubility product constant, $K_{sp} = (\text{Ag}^+) (\text{Cl}^-)$. If the silver electrode is electrolytically plated with chloride ions, the potential of the electrode will now depend upon the concentration of the chloride ions surrounding the electrode. Similarly the electrode can be made responsive to the sulfide ion.

The antimony electrode reaction is $2\text{Sb} + 3\text{H}_2\text{O} \rightleftharpoons \text{Sb}_2\text{O}_3 + 6\text{H}^+ + 6e^-$. Therefore, the antimony electrode when coated with antimony oxide will be responsive not only to hydrogen ions or acidity but also to water content. Except in very concentrated solutions the response to changes in the water content is negligible.

These theoretical potentials exist between the electrode and the solution surrounding it. Therefore, a reference electrode is required to complete the electrical circuit from the solution to the measuring device. The standard saturated calomel electrode is a suitable reference electrode. However, where prolonged studies are undertaken the potassium chloride electrolyte diffusing from the electrode will change the chloride content of the solution. A mercurous sulfate electrode in which potassium sulfate is the electrolyte can be used to prevent contamination with chloride ions.

Because of the exponential relationship between the concentration of the ion and the potential of the electrode, relatively large changes in concentration produce relatively small changes in the potential. Theoretically a ten fold change in concentration of a monovalent ion produces a potential change of 59 millivolts. A good high impedance meter will measure accurately to a tenth of a millivolt. However, the variability of measurements is about ± 1 to 2 mv. depending upon the electrode system used. Therefore, an error of from 5 to 10 percent can be expected. This is reasonable if the measurement cannot be efficiently made in another manner. The purpose of these experiments was to test the response of these electrodes when placed upon a hide surface.

EXPERIMENTAL

A Beckman‡ Research pH meter with a Moseley 7100B strip chart recorder

‡Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

attached and a Beckman Electroscan 30 were used interchangeably for measuring and recording pH and millivolt potentials. The surface glass, antimony and mercurous sulfate electrodes were made by Radiometer, Inc. The silver billet and fritted junction calomel electrodes were made by Beckman. Standard buffers were used to calibrate the pH scales. The silver billet electrodes were plated with chloride by immersing in saturated potassium chloride solution and applying alternately for 20 second intervals three volts of positive or negative potential. Another silver or a platinum electrode can act as the second electrode for this plating. A sulfide plating is applied in the same manner except that a one percent sodium sulfide solution is used.

A center split of a limed and bated hide was neutralized to pH 7.0 with acetic acid, washed thoroughly, dehydrated thoroughly with acetone and air dried. One inch squares were cut with a die, gaged for thickness, identified with punch marks, weighed, immersed in the test solutions kept at 25°C. and agitated gently to speed equilibrium with the solution. Samples were removed, drained a few moments to remove excess solution, weighed, and placed under the appropriate electrodes. The electrodes were suspended so that they could move freely in a vertical direction and only their own weight was pressing them against the hide. After a measurement on a wet sample had been completed the piece was either pressed between blotters or between glass plates using weights of 100, 1000 or 2000 grams to obtain samples with different solution contents. When the glass plates were used the expelled solution was removed from the edges of the pieces with blotters. The pieces were weighed to determine the solution content and placed under the appropriate electrode.

After a series of measurements the hide pieces were returned to the same solution for reequilibration and remeasurement or were returned to the same solution which was then treated with an additional amount of acid to develop a lower pH. In all cases the supernatant solution was tested with the same electrodes used to measure the samples.

Salt solutions of 1.0, 2.0, 3.0, 4.0 and 5.0 molar concentrations were made by dilution of the 5.0 molar solution which was made from a weighed amount of analytical grade sodium chloride. Various pH values were obtained by adding a few drops of 6.0 N sulfuric acid solution to the 100 ml of salt solution used. Three drops of a one percent solution of BSM-11 preservative in 50 percent aqueous acetone were added to each test solution.

Sodium sulfide solutions of 1, 2, 3, 4 and 5 percent concentration were made from fused technical flake sodium sulfide by weighing individual samples for each concentration and diluting to the required volume.

RESULTS AND DISCUSSION

The surface glass and antimony billet electrodes respond well to pH changes in solutions. The surface glass electrode gave very stable readings in standard

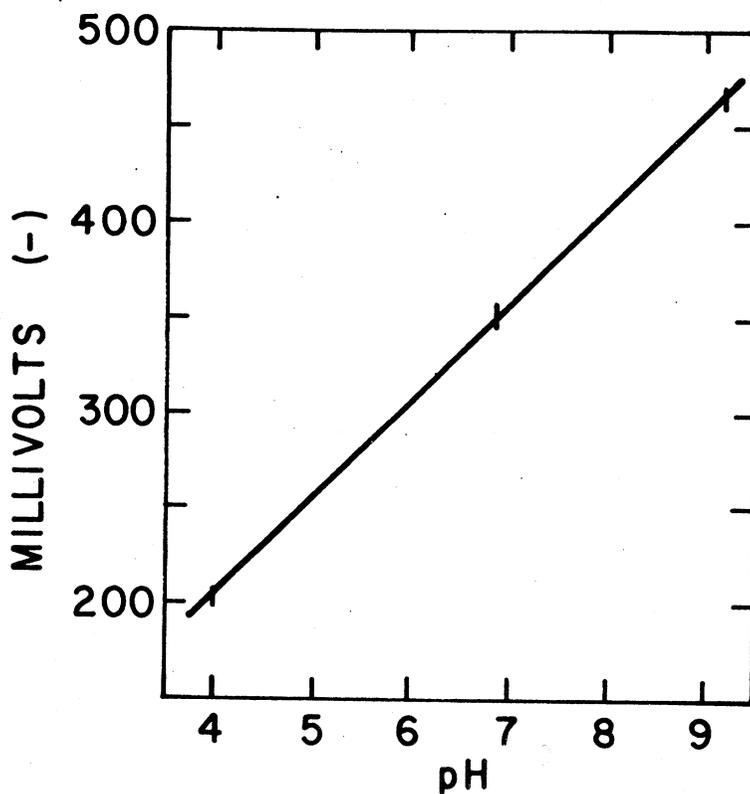


FIGURE 1.—Millivolt potential of antimony electrode in standard buffer solutions. The height of the bars indicates the spread of the values.

buffer solutions and in the acid-salt mixtures studied. An equilibrium value to a thousandth of a pH unit was usually obtained within two minutes. The antimony electrode is not as stable as the glass electrode and repetitive measurements have more scatter than those obtained with the glass electrode. The spread of the values from the trend line given by the antimony electrode for a number of measurements with each of three standard buffer solutions is shown in Figure 1.

Since standard pH buffers of different values may have different components and their salt contents do not approach the levels used for preservation or pickling of hides, salt solutions containing different amounts of acid were used to prepare the center split hide pieces for measurement. The hide pieces are ampholytes and can be expected to alter the pH and salt content of the solution into which they are put. Therefore, a minimum of 16 hours was allowed for the pieces to come to equilibrium with the solution before measurements were made. To simulate different levels of solution content in the hides, the wet hides were pressed to expel some of the solution. Since the pieces were at or close to equilibrium

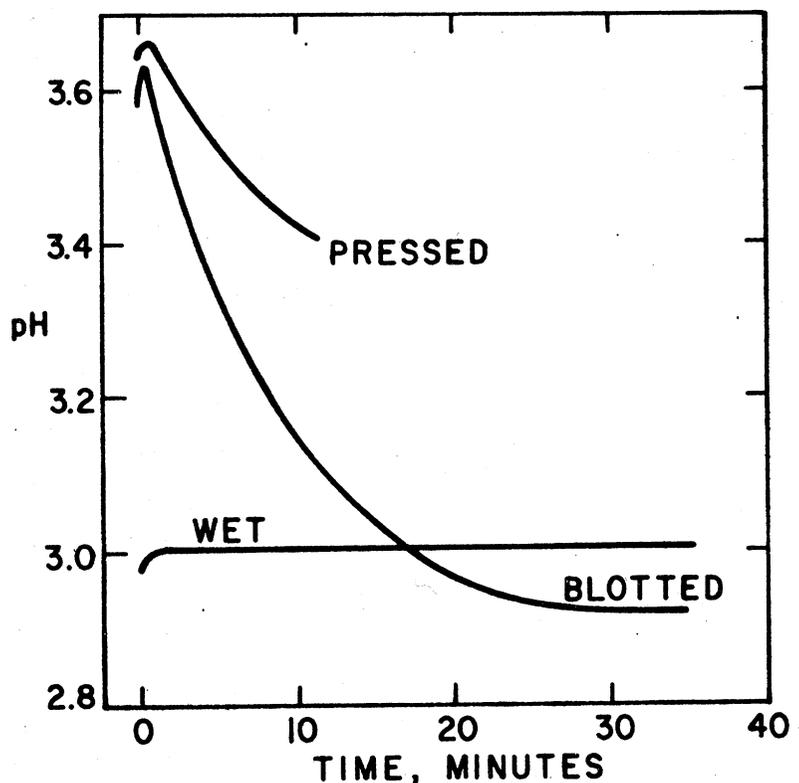


FIGURE 2.—Effect of blotting and pressing between blotters upon the pH of a hide surface determined with the surface glass electrode.

with the solution, the expulsion of some of the free solution would not be expected to change the acid or salt concentration of the free solution left within the hide. Early attempts to remove solution from the hide piece by blotting and pressing between blotters led to results like those shown in Figure 2. The pH of this 2.5 M (15 percent) supernatant salt solution was 2.99 and the glass surface electrode on the hide surface read 3.01. This value was constant for 35 minutes. After the hide piece had been blotted between electrophoresis strip blotting papers, it showed an initial pH value of about 3.63 which gradually decreased to an equilibrium value of 2.92 pH which is 0.07 unit more acid than the supernatant solution. After pressing between blotting papers under a 2000 gram weight, the hide surface showed an initial pH of 3.66 which decreased very slowly. A similar piece required over three hours to attain the equilibrium value which was also a lower pH than that given by the corresponding supernatant solution. The amounts of solution present for each gram of the dry hide sample were: wet 2.88 g, blotted 2.06 g, and pressed 1.72 g. The changing values obtained with the blotted and pressed samples do not represent a malfunction

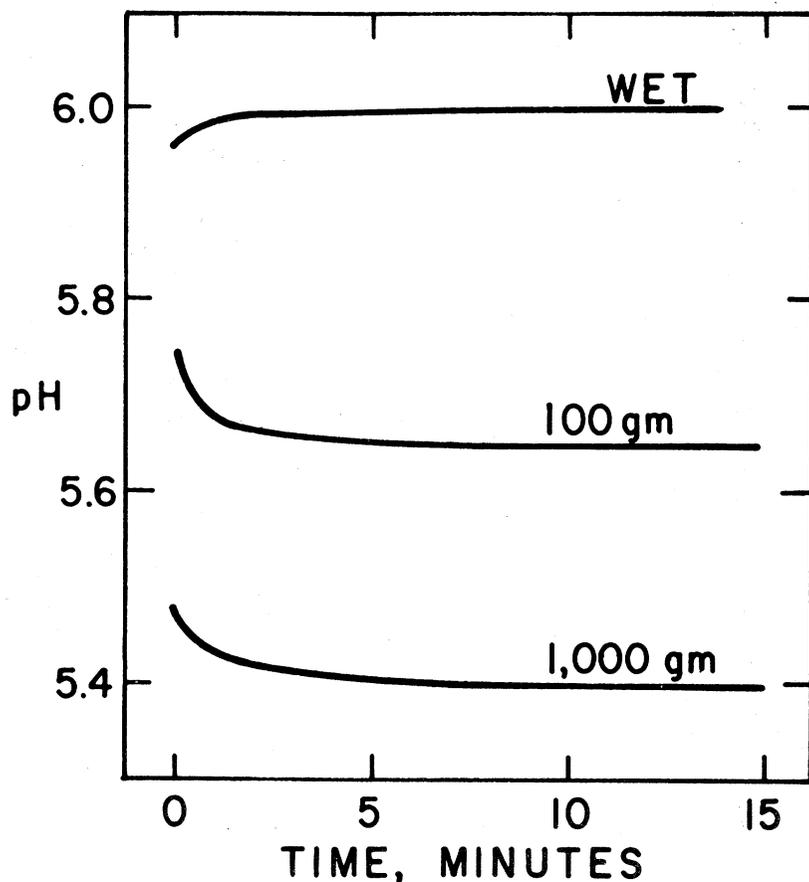


FIGURE 3.—Effect of squeezing between glass plates on the pH of a hide surface determined with the surface glass electrode.

of the electrode system. When the electrodes are not making sufficient contact the recorder track is very erratic. The tracks obtained for these experiments were extremely smooth, indicating that the electrodes were measuring an actual change occurring in the hide pieces.

When a piece of hide was pressed between glass plates and only the solution extruded from the edges was removed with a blotter, the results shown in Figure 3 were obtained. The surface glass electrode attained an equilibrium value within five minutes. There was a decrease in the equilibrium pH value from 6.00 for the wet sample and the supernatant solution to 5.65 for the sample pressed under a 100 gram weight, and to 5.40 for the sample pressed under the 1000 gram weight. This solution contained 4.0 N (24 percent) salt and the amounts of solution present in the hide piece for each gram of dry hide were: wet 3.09 gm., pressed under 100 gm. weight 2.94 gm., and pressed under 1000 gm. weight

2.55 gm. Because the small change of solution content caused by the pressing with the 100 gm. weight produces such a large change in pH value, it appears that the surface glass electrode is capable of measuring some specific property of the hide and not just the pH of the solution with which it is soaked. Additional studies are in progress to determine whether the physical structure or some previously undescribed acid equilibria are involved. The difference in rate of equilibration between samples pressed between blotters and samples pressed between glass plates indicates that the blotters remove or neutralize some of the acid present at the surface and time is required for the surface to become re-equilibrated with the remainder of the hide piece. This, however, does not explain why the observed equilibrium pH decreases when the sample is pressed.

The antimony billet electrode also detected this change in pH due to pressing solution from the hide. Because of the difference in the size and composition of

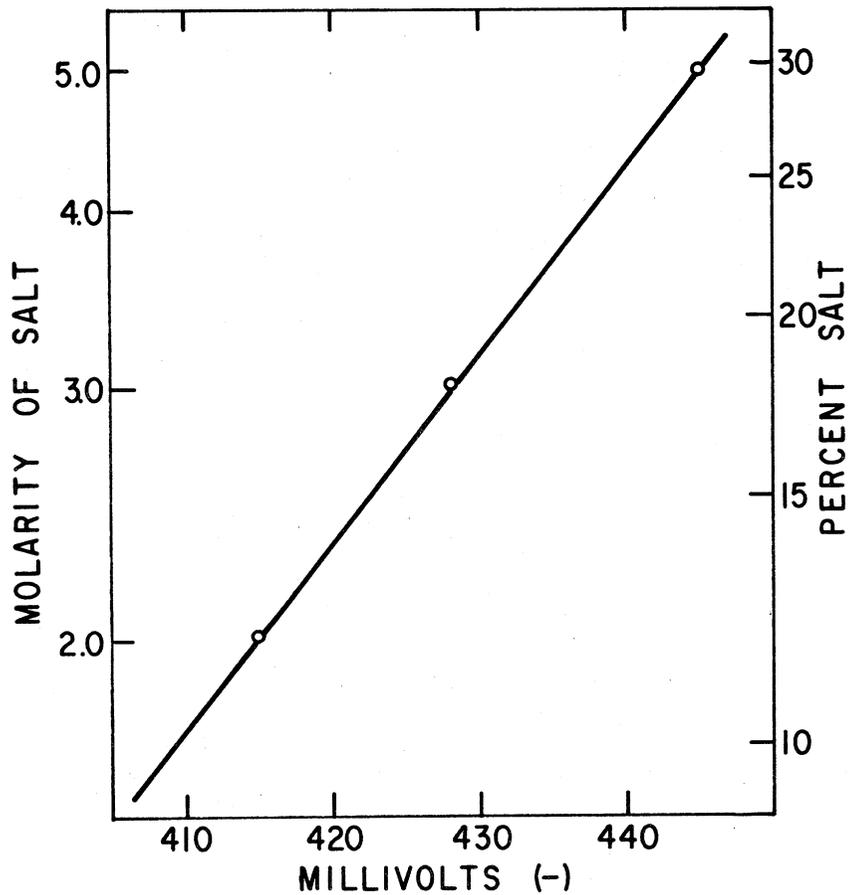


FIGURE 4.—Potential of the silver chloride electrode in salt solutions.

the sensing surface that exists between the surface glass electrode and the antimony electrode, it is doubtful that the observed pH change due to pressing can be an electrode phenomena. It is more likely that the electrodes are capable of detecting a change in hide composition previously not known to exist.

Measurements with the silver chloride plated electrode were made simultaneously with the measurements by the glass electrode. Figure 4 shows the potential of the silver chloride electrode immersed in solutions containing from 10 to 30 percent salt. The electrode responds readily if the silver chloride plating is not too thick, and sufficient electrolytically deposited silver is present among the silver chloride particles to maintain the chemical equilibrium. In all of the experiments the silver chloride electrode gave the same potential (within ± 2 millivolts) when pressed against the hide surface as when suspended in the supernatant solution. Measurements on the blotted and pressed samples gave the same reading that was obtained on the sopping wet samples. This indicates that the silver chloride electrode when placed on the surface of a hide can give an accurate measure of the concentration of the salt present within the hide. This concentration determined by the silver chloride electrode should be comparable with the

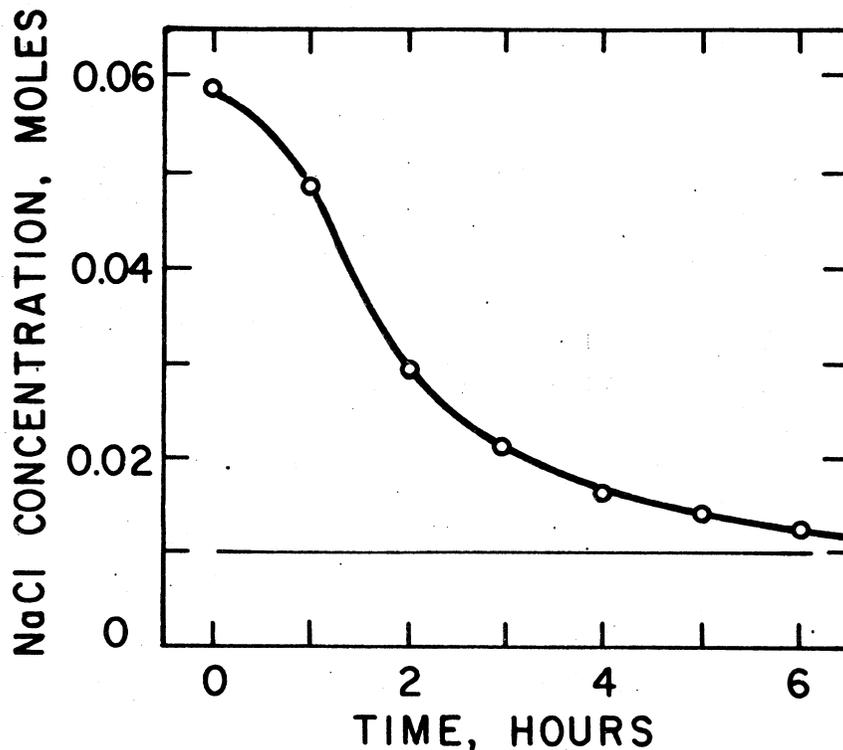


FIGURE 5.—Static diffusion of salt from the center split of cured hide into 0.01 molar salt solution.

ash to moisture ratio proposed by the Technical Committee of the Hide Bureau of the Tanners Council (5), as an adequate measure of the degree of cure. Therefore, the silver chloride electrode may provide a simpler means of measuring the degree of cure.

This silver chloride electrode has also been used to measure the rate of diffusion of salt from the center split of a hide. With a 0.01 molar salt solution against the bottom side of the split and the silver chloride electrode resting on top of the split, the drop in concentration of the salt at the top surface can be measured with the passage of time. A curve of this data is shown in Figure 5. The silver chloride electrode appears to be accurately following the changes of salt concentration at the hide surface.

If the silver billet electrode is coated with silver sulfide instead of with silver chloride it should become responsive to the sulfide ion. Figure 6 shows the poten-

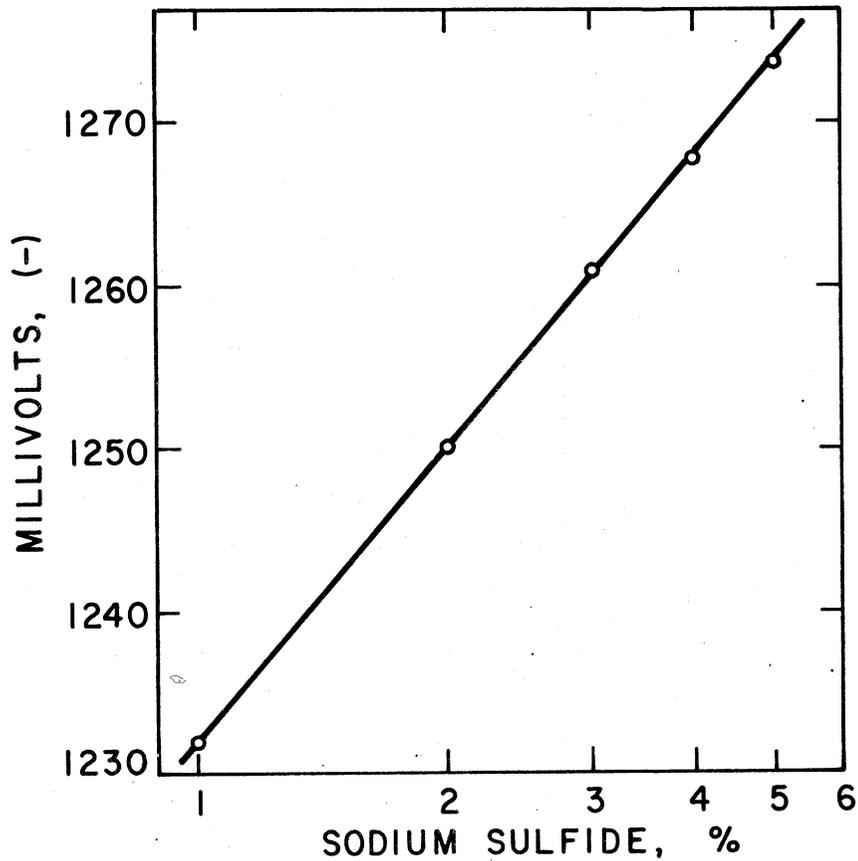


FIGURE 6.—Potential of the silver sulfide electrode in sodium sulfide solutions.

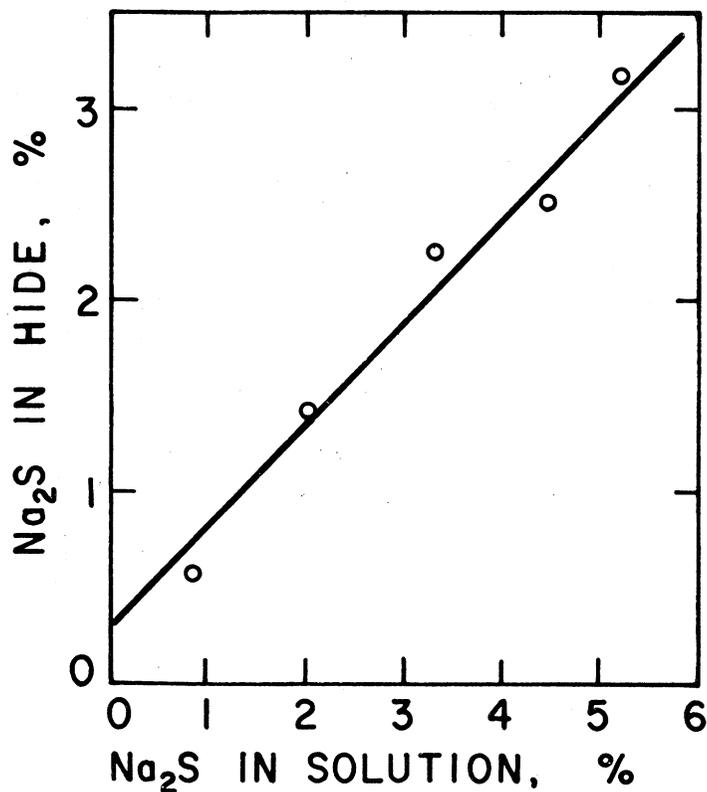


FIGURE 7.—Relationship between concentration of Na_2S in hide surface and surrounding solution determined by the same silver sulfide electrode.

tial of the silver sulfide electrode in concentrations of technical sodium sulfide from one to five percent. A very good linear relationship exists.

The center split pieces of hide soaked overnight in the sodium sulfide solutions were measured with the silver sulfide electrode on their surfaces. Very stable readings were obtained and pressing had very little effect upon the values obtained on these very turgid pieces. The concentration measured at the surface of the hide piece was about one half of the concentration measured for the supernatant solution. The spread of these values is shown in Figure 7. Although the sulfide electrode appears to give a consistent reading when against the hide surface an explanation of the difference between this reading and the reading of the supernatant solution must be found before this electrode can be considered a reliable measure of the sulfide content of hides. This should not affect its value for comparing or monitoring sulfide solutions.

CONCLUSIONS

These experiments have shown that the surface glass, antimony, silver chloride

and silver sulfide electrodes are capable of measuring the concentration of hydrogen ions, chloride ions and sulfide ions in solutions and upon the surface of hides. Although electrode measurements will never be as accurate as most chemical analyses, they can be highly specific and may enable measurements which cannot be made by other means. They could be valuable where a nondestructive test is essential.

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DISCUSSION

MR. MEO: Leader of discussion of this paper will be Dr. Thomas Thorstensen of Thorstensen Laboratory.

DR. THORSTENSEN: The paper that Ed Mellon has presented represents some very interesting work. He has given us some new procedures and some new techniques, and so often, when something like this happens, more questions are raised than we get answers. The first thing that struck me in reading the paper was that we must emphasize that we are measuring here the log of the concentration of the various ions in question, not the concentrations of the ions themselves. Consequently, there is a tenfold change in concentration to give a 59 millivolt change. I think we lose sight of this in our routine pH measurements quite often. Of immediate practicality is the fact that we can now have a pCl meter or a pS meter in addition to a pH meter. We should be able to use a pCl meter as is suggested, as a means of measuring the salt content in a hide, for routine control purposes. We could also use this in a cure house to measure the take-up of salt or the salt present in the brines. In tannery process control you can routinely measure salt content.

The possibility of measuring the pS or the sulfide concentration brings about other possible practical ideas. We could use this to monitor and control an automatic feed system to maintain a particular sulfide ion concentration in a drum unhairing system. You may be able to get by with considerably less sulfide and a better control for better quality of leather by such a system.

The possibility of using this as quality control in the washing of skins during bating is also, I think, quite evident. There is also the possibility of hooking this electrode system up to your effluent stream and putting a recorder on to measure the rate of flow of sulfide as it is being discharged.

We have been presented with a true challenge, and it is a question of whether we as leather technologists, can take up this challenge for practical application.

I'd like to ask Dr. Mellon a question about these electrodes. Do you feel that these electrodes could be prepared and maintained by the usual tannery technician?

DR. MELLON: I think that this would be possible, and I think that in a very few years we are going to have a tremendous line of much more efficient electrodes than we have at the present time. It is one of the things that motivated me to see what these electrodes could do.

DR. THORSTENSEN: Are there some questions from the floor, please?

MR. AL JAMISON (Seton Leather Co.): Dr. Mellon, I believe you stated that with this type of analysis, there is an inherent error of 5 to 10 percent. Would you say that this error is due to the fact that you are measuring the activity of the ion instead of its concentration?

DR. MELLON: Some of the error is inherent in the contact in the reference electrode. This has always been a source of difficulty with pH measurements. I would guess that 90 percent of the time, that the people in our laboratory have had trouble with pH measurements, the trouble has always been traced back to the calomel electrode. If it becomes unsaturated or becomes plugged up a little bit, you get extra resistances and potentials which cause a little variation.

We are also limited a little bit at the present time in the ability of our pH meters to record accurately what is there. The ordinary pH meter is probably good to 1/100 pH unit. The meter that I am using is good to 1/1000 pH unit. This is a little bit of a fictitious accuracy because there is no buffer accurate enough to standardize the meter to 1/1000 pH unit, but you can tell the difference between two solutions to 1/1000 pH unit.

Part of the high error is due to not being able to make sufficient contact with the solution at the calomel electrode. The one that I am using has a fritted junction which must be prevented from plugging up. I put a sidearm onto the electrode and used roughly a foot of hydrostatic pressure to increase the flow of solution through the electrode. The electrode does not plug up nearly as fast as it did without it.

DR. THORSTENSEN: There being no further questions, I would like to again thank Dr. Mellon and his co-workers. I think that he has given a major contribution to our field of tremendous practical application. Thank you very much.