

AN ELECTRODIALYSIS CELL FOR THE DETERMINATION OF TOTAL ELECTROLYTE IN CURED OR PICKLED HIDES*

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ABSTRACT

An electro dialysis cell has been designed so that a one inch square of hide may be inserted into the center compartment without disassembling the cell. The two electrode compartments are arranged for continuous flushing with water to prevent accumulation of high concentrations of electrolyte or gases within these chambers and to provide cooling for the cell.

The conditions necessary to obtain quantitative recoveries of electrolyte are discussed and some applications to pickled hide analysis are presented.



INTRODUCTION

Studies of variations of the salt and acid content of pickled hides are limited by the practicality of the techniques available. Usually the salt content is determined by ashing the sample but this makes the same sample unavailable for other studies. A pressing technique was developed by Cameron *et al.* (1) to remove free water and electrolyte from protein samples. This removes the greater portion of the free water and electrolytes so that pH and salt determinations can be made upon a solution but this technique does not remove all of the free electrolyte (2); therefore, it yields high values for the bound electrolyte.

An effective method for obtaining a reproducible pH value (active acidity) of pickled stock developed by M. H. Battles was reported by O'Flaherty and Tancous (3). In this method equal parts by weight of finely cut pickled stock and saturated brine are mixed and allowed to stand overnight before the pH is determined. This value is a measure of the concentration of the free dissociated acid in equilibrium with the hide but gives no evidence of the total amount of acid present or the amount bound by the protein.

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In 1934 Elod and Siegmund (4) described an electro dialysis apparatus for the complete removal of electrolytes from textile and leather samples. They also described the possibility of obtaining separate values for the anions and cations by separating the electrode compartments with paper membranes. Their technique, unfortunately, was never developed into a useful method.

Studies of electrolyte migration during the early stages of the pickling process were hindered by a lack of knowledge of the total amount of electrolyte in the hide before it reaches complete equilibrium with the pickle solution. Electro dialysis of hides pieces in a commercially available electro dialysis cell indicated that this technique could give a measure of the total anions and cations contained in a piece of hide but the structure of the cell could be improved to increase the efficiency of the determination.

EXPERIMENTAL

The Cell

The electro dialysis cell was constructed of three plates of Plexiglas[®]‡, each one half inch thick, and two plates each one eighth of an inch thick. These plates were three and one quarter inches square. One of the half inch thick pieces was cut into the form of a U by removing a one and one quarter inch wide section from the center of one edge to within one inch of the opposite edge as shown in Figure 1.

The other two half inch thick pieces had chambers routed out of one side to a depth of three eighths of an inch. These chambers were shaped as shown in Figure 1 so that water pumped into the bottom corner of one side would flow diagonally across the chambers and out from the top on the opposite side. Small holes were drilled from the sides into the upper and lower points of these chambers to accommodate small bore (approximately five sixty fourths of an inch in outside diameter) Teflon tubing. The fit must be close to prevent leakage. The outside of this tubing was lubricated with silicon vacuum grease to facilitate introduction into the hole and to seal the junction so that there would be no leakage.

An additional hole was drilled through the center of the top to be a tight fit for the platinum wire lead to the electrode. The lead wire was spot welded to a perforated platinum sheet which covered about half of the area of the chamber. The electrode lead was sealed into the cell with a Plexiglas cement. The outside ends of the leads were connected to binding post terminals which were cemented to the top of the cell with Plexiglas cement.

The two thin plastic sheets had one and one quarter inch square holes cut in their centers to correspond with the openings in the center section and the end compartments.

‡Reference to brand or firm name does not constitute an endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

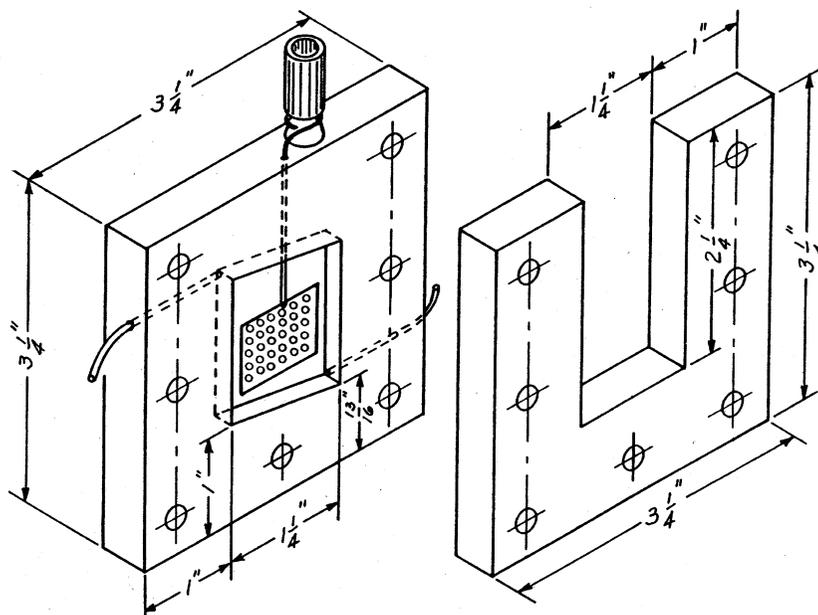


FIGURE 1.—Diagram of the center and electrode sections of the electrolysis cell.

Cellulose dialysis tubing of one and seven eighths inch internal diameter was cut to make the two membranes to isolate the electrode chambers from the center compartment. The membrane on the anode side of the cell was protected on the electrode side with a fine polyethylene filter to act as a barrier to keep the liberated chlorine gas from the dialysis membrane.

The cell was assembled with seven bolts to provide even tension on the cellulose diaphragms. One of the thin plastic sheets was placed on each side of the center compartment to seal the dialysis membrane at the top where there is no support from the center compartment. The mating surfaces of each of the plastic sheets were coated with silicon vacuum grease to help seal the joints against leakage.

Cold water was pumped through each of the electrode chambers and the solution emerging from each chamber was collected separately. The receiver for the anode solution should contain from 40 to 100 ml. of a standard alkaline solution to trap the chlorine which is evolved at the anode when salt is present in the central compartment.

To enable the cell to be run at high current the center compartment may be cooled by inserting a coil of small diameter Teflon tubing through which cold water is pumped.

Testing the Cell

The cell was tested and calibrated by inserting measured amounts of salt solution into the center compartment, filling the compartment with water at least to the level of the top of the electrodes, and electrolyzing the solution. The liquid and gas from the anode chamber were trapped in a measured volume of standard alkali in the anion receiver. The cation receiver contained no additions. The anion solution was back titrated with standard acid only to pH 8.7 so that the weak acids that were present would not be liberated from their alkali salts. The amount of the originally added alkali which was not titrated is equivalent to the anions produced in the electro dialysis. The cationic solutions were titrated with standard acid to pH 5.0 so that any carbonates formed by carbon dioxide from the air would not affect the results. This titration gives directly the amount of cations formed in the electro dialysis.

Between 40 and 100 ml. of standard tenth normal alkali will be needed in the anion receiver, depending upon the type of sample under investigation. If insufficient alkali is used, some of the chlorine produced will not be trapped and the results will be low.

Hide Studies

When a hide piece is to be studied, it is suspended in the center compartment with a fine nylon thread so that it may be kept upright and be more easily removed from the cell after the dialysis is completed.

The cell was tested with samples of pickled hide prepared from the center split of cattle hides. These had been split out of lime in a commercial tannery and then delimed with acetic acid to the isoelectric region and, after thorough washing, they were dehydrated thoroughly with acetone and air-dried to remove all the acetone. The material was then die cut into one inch squares. The ash content was about three tenths of a percent and the air-dried moisture content was seventeen and one half percent.

Several squares were marked and weighed individually, then placed in a quart jar with 100 ml. of a ten percent salt solution which contained sufficient sulfuric acid to give a pH of about two and ten parts per million of BSM 11® as a preservative. The samples were shaken for various lengths of time, removed from the solution, and pressed between two glass plates with a 100 gram weight on top. The exuded solution was removed from the exposed edges with blotters. The pH of the surface was determined with a flat-surfaced glass electrode (5); then the piece was weighed and placed in the electro dialysis cell.

The pH of the solution was determined with the same electrode and a sample of it was run in the electro dialysis cell to determine the amount of anions and cations present. The difference between the air-dried weight and the weight just before electro dialysis was taken as a measure of the amount of solution absorbed.

This weight divided by the specific gravity of the solution gave the milliliters of the solution which were absorbed. From the adjusted (Figure 4) electro dialysis values on the supernatant solution the milliequivalents of anions and cations which could have been absorbed as the piece was wetted by the solution were determined. The analysis of the piece gives the actual amount of the anions and cations absorbed. For these calculations the excess of anions over cations was taken as the amount of sulfuric acid absorbed, although there is no evidence that the anions are not absorbed in a random fashion.

The amount of anions and cations found in the piece, subtracted from the amount of anions and cations that could have been present in the amount of solution absorbed, was determined and calculated on the basis of a gram of dry hide. A negative sign was used if the piece contained less than the absorbed solution indicated should be present.

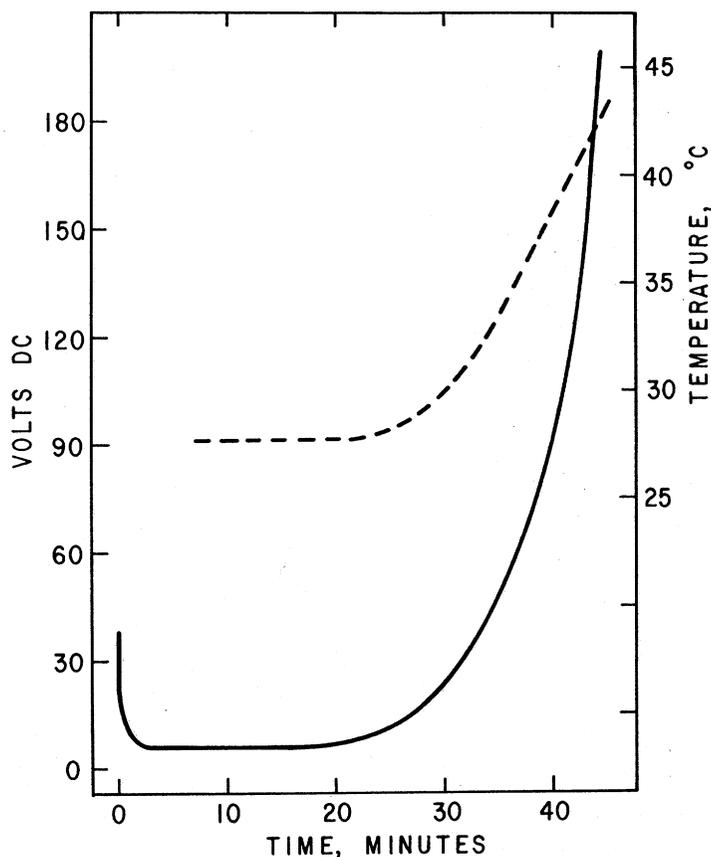


FIGURE 2.—The variation of voltage and temperature during operation of the cell. Solid line shows the voltage; dashed line shows the temperature.

Some of the electrodialyzed pieces were ashed to determine the extent of salt removal. Less than one tenth of a percent ash on the oven-dried weight was found in all cases.

RESULTS AND DISCUSSION

A typical voltage variation across the cell at constant electrical current flow of 60 milliamperes with a salt solution in the center compartment and a liquid flow of two milliliters per minute through the electrode chambers is shown in Figure 2. The voltage starts at about 30 volts and decreases rapidly as ions are drawn into the electrode chambers, increasing their conductivity. When the number of ions migrating into the electrode compartments equals the number being removed by the solution flow, the voltage remains constant at about seven to ten volts.

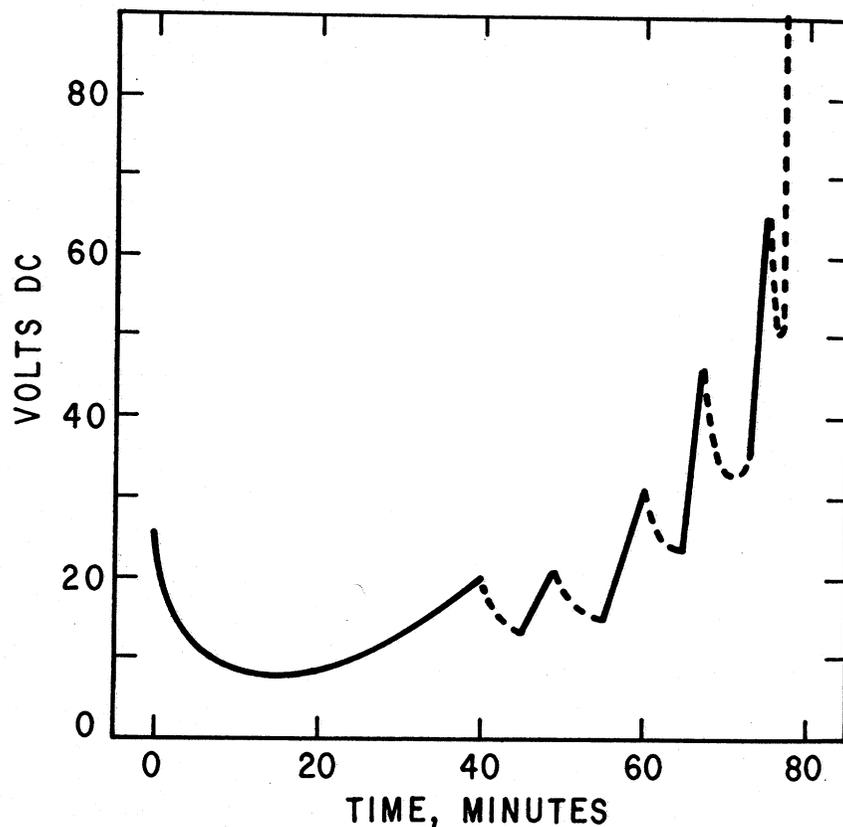


FIGURE 3.—Effect of flow through the electrode chambers upon the voltage curve. Solid line for pumps on; dashed line for pumps off.

When the ions in the center compartment become depleted, the conductivity of the solution decreases and a higher voltage is required to maintain the constant current. Soon after the voltage begins to rise, the temperature in the center compartment also begins to rise as more electrical energy is dissipated in the cell. This temperature rise is not desirable because it will increase the thermal diffusion of ions through the membranes and reduce the recovery of the anions and cations.

Figure 3 shows that the increase in voltage rise can be delayed by stopping the flow of solution through the electrode chambers and allowing the concentration of ions in the chambers to increase, thus raising the conductivity of the cell and lowering the voltage. It is simpler to reduce the pumping rate and it was found that a pumping rate of one half milliliter per minute through the cation chamber and one milliliter per minute through the anion chamber gave the best performance.

After the voltage reached about 75 volts, the current was gradually reduced so that the temperature in the center cell did not exceed 35°C. When the voltage reached 200 volts at a current flow of five milliamperes, the center cell was practically free of electrolyte and the run was stopped.

Figure 4 shows the percent recovery of the anions and cations as a function

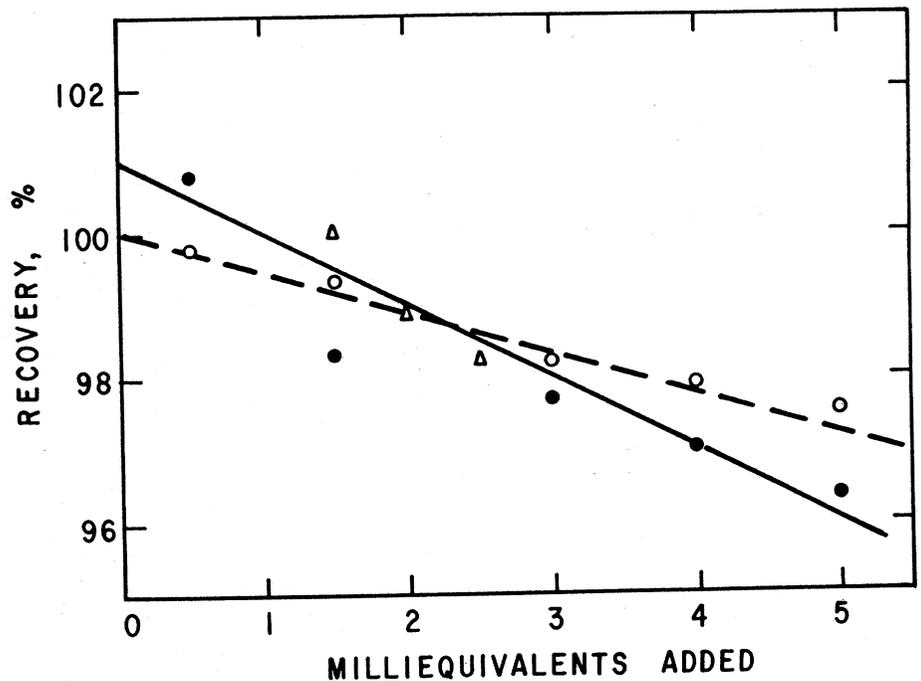


FIGURE 4.—Variation of percent recovery of anions and cations with the total electrolyte content. ○ cations, ● anions, △ cation and anion points falling in same place.

of the electrolyte content of the sample of saline solution. For these runs measured amounts of a standard salt solution were placed in the center cell and the electro dialysis started at 150 milliamperes. The pumps for flushing the electrode chambers were started three minutes after the current was turned on. This delay is necessary to recover ions which have thermally diffused through the membrane in the few minutes before the current is turned on.

The anion recovery curve has a greater slope than the cation curve and has an intercept at zero concentration of approximately 101 percent. The intercept is believed to be due to the small amount of carbon dioxide which dissolves in the boiled flushing water before it is pumped through the cell. The greater slope which indicates a greater loss of anions is believed due to the reaction of the chlorine produced at the anode with the membrane and the components of the cell. The loss of the cations is believed to be due to the small amount of salt which is thermally diffusing through the membrane and is being flushed out by the flushing solution. The larger the electrolyte content of the sample, the longer the electro dialysis takes and, therefore, the greater the amount of diffusion that can take place. If these curves are used to correct the titration values, then an accuracy of about one percent can be achieved independent of sample size.

The data obtained when an acetone dehydrated corium split was pickled by immersing in a salt-acid pickle are shown in Table I. It appears that about 80 percent of the electrolyte absorbed is absorbed within the first hour. This is not surprising because a large amount of solution must be absorbed just to wet the hide. There is a slow increase after this for several hours and then a decrease to the equilibrium value. The amount of acid absorbed increases more rapidly than the amount of salt, so that the amount of anions absorbed appears to be greater than the amount of cations absorbed. The difference between the electrolyte content of the solution absorbed and the electrolyte content of the hide indicates that in the first hour both the acid and salt are absorbed from the solution more slowly

TABLE I
VARIATION OF THE ELECTROLYTE CONTENT OF
PICKLED HIDES WITH THE TIME IN THE PICKLE

Time in Pickle (Hours)	Total Electrolyte Found in Hide Piece			Difference from Theoretical Based on Grams of Solution Absorbed	
	Anions (Meq.*)	Cations (Meq.)	Acid (Meq.)	Anions (Meq.)	Cations (Meq.)
1	2.58	2.46	0.12	-0.10	-0.15
3	2.92	2.55	0.37	+0.30	+0.02
4.5	3.14	2.75	0.39	+0.28	-0.03
40.0	2.75	2.32	0.43	+0.28	-0.10

*Milliequivalents per gram of dry hide.

than the water. During the second and third hours, both the acid and salt appear to have been absorbed from the solution more rapidly than the water, and the acid absorption appears to be increasing more rapidly than the salt absorption. During the next few hours the amount of the absorbed acid, salt, and water are all increasing, but the salt does not seem to be increasing as rapidly as the water. By the time equilibrium is reached, the salt absorption has decreased, while the acid absorption has increased slightly and salt appears to have been returned to the solution.

Additional data obtained during the study of pickled hides are shown in Table II. The difference between the pH values of the solution and the pH values measured on the surface of the hide decreased with time and eventually became equal at equilibrium time.

TABLE II
THE pH AND MOISTURE RELATIONSHIPS IN PICKLED HIDES

Time in Pickle (Hours)	pH Solution	pH Hide	Increases in*		
			Weight	Water	Electrolyte
1	1.78	2.43	1.87	1.73	0.14
3	1.87	2.24	1.85	1.69	0.16
4.5	1.81	2.00	1.98	1.80	0.18
40.0	2.16	2.15	1.74	1.59	0.15

*Grams per gram of dry hide.

This indicates that the hide is binding acid as rapidly as, or more rapidly than, it is being absorbed from the solution, so that it is not present to contribute a higher acidity to the hide surface. The variations in the increases of weight and water in the hide would indicate that the absorption rates of the three components of the solution are not equal. The acid penetrates more rapidly than the salt and causes a swelling which draws in more solution than is needed at equilibrium when the salt penetration is completed and the initial acid swelling is reduced. The loss of this swelling water is taking out some of the absorbed salt, so that the equilibrium salt content is lower than the intermediate values obtained before equilibrium.

The unequal migration rates of the water, acid, and salt indicated here would create stratigraphic variations in the content of these materials during the non-equilibrium period. Experiments now in progress are showing that these variations in concentration do exist sometimes with very startling results.

CONCLUSIONS

An electro dialysis cell was constructed into which a hide piece can be easily inserted without dismantling the cell.

The separated anions and cations can be determined to an accuracy of about one percent by applying a correction depending upon the amount of electrolyte found.

Electro dialysis of pickled hide pieces, which were made by immersing dehydrated corium in a salt-acid pickle for different times, indicated that the water, acid, and salt were absorbed from the solution at different rates at different times, probably producing stratigraphic variations in their distribution within the hide. At equilibrium, these variations appear to disappear.

ACKNOWLEDGMENT

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DISCUSSION

MR. MALCOLM H. BATTLES: The discussion will be led by Dr. William Prentiss of Rohm and Haas.

DR. PRENTISS: Each of us at one time or another has very likely been faced with a problem of not having a proper instrument or tool to handle a very specific problem. The rapid growth of the instrument development companies in the U. S. and abroad certainly is a testament to the fact that instruments are needed in our research to obtain more fundamental information or to improve our knowledge about various processes. I think that we are indebted to Dr. Mellon and his associates for the innovation that they have shown in taking a basic concept in electro dialysis and applying it with a simple modification to develop this electro dialysis cell. It certainly will be helpful in studying many of the processes, as Dr. Mellon has already indicated in his paper. Are there any questions from anyone at this time?

Dr. Mellon, I have one. In your abstract you have commented that the apparatus would be useful for cured hide as well as pickled, and the data you presented have been principally for a study on pickled stock. Do you feel that this instrument will have the same applicability in studying a curing process as it has in a pickling process?

DR. MELLON: I believe that the cell would be useful for the cured hides although in most cases a simple ash determination will adequately determine the total amount of salt. In studies of the initial stages of curing, the cell might be very helpful because we have found in some of our electrode studies that the salt concentration on the surface of the hide does not equal the salt concentration in the solution. In some cases the salt concentration on the surface of the hide was very much higher than the salt concentration in the solution. This was one reason why we developed this electro dialysis cell. We felt that the chloride ion specific ion electrode was telling us something but we needed additional data to interpret exactly what it was. We had difficulty seeing how the salt concentration on the surface of the hide could be higher than in the solution that it was in contact with, but we know that this is a certainty and we will be publishing on this fairly soon. The cell will probably never be a tool for use as control in the industry. It is mainly a research tool which will help us to add up and interpret the values we will obtain by other methods. It is these other methods which we hope to develop into control instruments for the tannery, but in order to do this we have to be quite sure what these electrodes are telling us.

DR. PRENTISS: Thank you Dr. Mellon. You answered one of the other questions I had in mind as to whether it could be used for quality control, since certainly we are becoming more conscious about quality control in our operations. Are there any other questions from the floor? If not, we thank you very much, Dr. Mellon, for an excellent paper.