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Thickness of Glass Electrodes

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A nondestructive magnetic method has been developed for the measurement of the thickness of glass electrode bulbs. It involves the use of the Brenner Magne-Gage as the measuring instrument and carbonyl iron powder as the backing material. Each of the four glasses investigated was found to have a characteristic "departure thickness," ranging from 54 to 130 microns. A glass electrode whose minimum thickness was equal to or less than this departure thickness was found to give the full 59 millivolts per pH unit electrode response. Bulbs of increasingly greater thickness showed increasing departures from this theoretical response. The departure thicknesses of the glasses investigated were found to be a function of their hygroscopicities.

1. Introduction

The effect of the thickness of the membrane of a glass electrode on its electrode function is of interest in connection with a continuing study of the glass electrode [10, 12, 13, 16].[1] Kratz [18] made the statement that the theoretical variation of potential with pH can be obtained only with thin-walled membranes. Kahler and DeEds [17] found that there was roughly a linear relationship between the "average electrical thickness" of an electrode and the difference, in millivolts per pH unit, between its electrode response and that of a hydrogen electrode. This difference approached zero as the membrane thickness approached zero. Dole [7], however, quotes von Steiger [20] to the effect that glass electrode potential is completely independent of the thickness of the glass. The present study has been made in order to clarify the matter.

MacInnes and Dole [19] determined the thickness of their thin membranes by weighing a measured area of uniform thickness, this uniformity being determined by the use of interference colors. Knowing the glass density, they calculated their films to be about 1μ thick. Von Steiger [20] measured the thickness of his Cremer-Haber electrodes [5, 9] by bringing a glowing glass rod up to a selected distance from the glass surface. By observing the reflection against a black background, he observed interference fringes and then calculated thicknesses. Yoshimura [22], in his study of the effect of thickness on asymmetry potential, assumed the thicknesses of his electrodes were in the order of their electrical resistances and had no direct knowledge of the thicknesses involved. Kahler and DeEds [17] measured the thicknesses of their electrodes by using a microscope with a calibrated fine focus adjustment to focus on the two surfaces of the membrane. The difference in setting, corrected for the refractive index of the glass, gave the thickness.

For the purpose of this study, a nondestructive, magnetic method for the measurement of the glass membrane thickness has been developed. It involves the use of the Magne-Gage [2] [1], developed by Brenner [2, 3], for the measurement of electroplated coatings on metals, and is also used for measurements on paint, porcelain enamel, plastic, and other films or coatings that are or can be backed by iron or steel plates.

The adaptation made by us is the use of carbonyl iron powder as the backing material and the use of a corresponding direct calibration procedure.

2. Experimental Work

2.1. Method of Measuring Thickness

The operation of the Magne-Gage is based on the decrease in magnetic attraction resulting from the interposition of a nonmagnetic material between a magnet and a magnetic material. The apparatus, shown in figure 1, consists of a lever arm that is connected to a coiled spring, which is in turn connected to a dial and knob. Suspended from the end of the lever arm is one of several interchangeable permanent bar magnets of different weights and pole strengths. Two of the magnets available have been found to cover the range of thicknesses of interest in this study.

In use, the steel-backed specimen is placed in position under the magnet, and the knob is rotated counterclockwise until the presser arm, which is slip-mounted on the assembly, brings the rounded tip of the magnet into contact with the surface of the specimen. The counterclockwise rotation is continued until the built-in stop is reached, or until a trial or previous experience indicates that the tension on the spring has been released sufficiently so that the magnet will remain in contact with the specimen when the knob is rotated clockwise, taking the presser arm off the lever arm and magnet. The knob is then rotated clockwise, increasing the tension on the spring until the force is sufficient to pull the magnet away from the specimen surface. The dial reading at this point is a function of the thickness of the nonmagnetic material. When the instrument is properly calibrated with material of known thickness, the dial reading can be converted to a thickness reading.

A Cremer-Haber type glass electrode is typically a thin glass bulb about 10 to 20 mm in diameter blown on one end of a glass tube a few millimeters in diameter. Since it is impossible to use a steel plate as a backing material, for a thickness measurement on an

[1] Figures in brackets indicate the literature references at the end of this paper.
[2] Manufactured by the American Instrument Co., Silver Spring, Md.

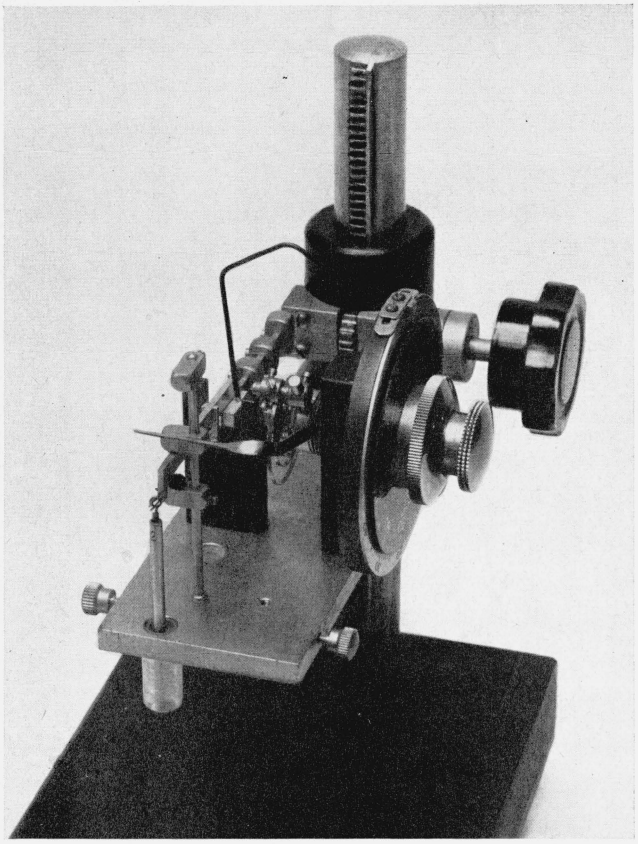

FIGURE 1. *Aminco-Brenner Magne-Gage.*
An instrument for the measurement of film thickness.

object of this shape, carbonyl iron powder is used instead. The powder is placed in the clean, dry electrode by a standard procedure, and its open end is stoppered. After adjusting the magnet to the appropriate height by means of the rack and pinion, the bulb is placed in contact with the plastic guard around the magnet, and the measurement is made. Contact with the guard serves to steady the specimen during measurement, and, if maintained during multiple measurements made to obtain a precise value for the dial reading, will insure that the readings are being made on the same spot. This is important, as all such glass bulbs are quite nonuniform in thickness. One additional precaution must be observed in handling the instrument when making measurements on powder-backed, thin membranes. It is easy for the magnet tip to dent soft or thin metal or to puncture a thin glass membrane unless contact is made gently and no pressure is exerted on the specimen by further counterclockwise rotation of the instrument knob. But in the usual case, the spring tension must be decreased to insure that the magnet will remain in contact with the specimen when the presser arm is lifted. This is accomplished before contact is made and without removing the specimen from contact with the guard, by rotating the knob counterclockwise, while using the thumb to prevent the presser arm from also rotating.

When used for the measurement of steel-backed

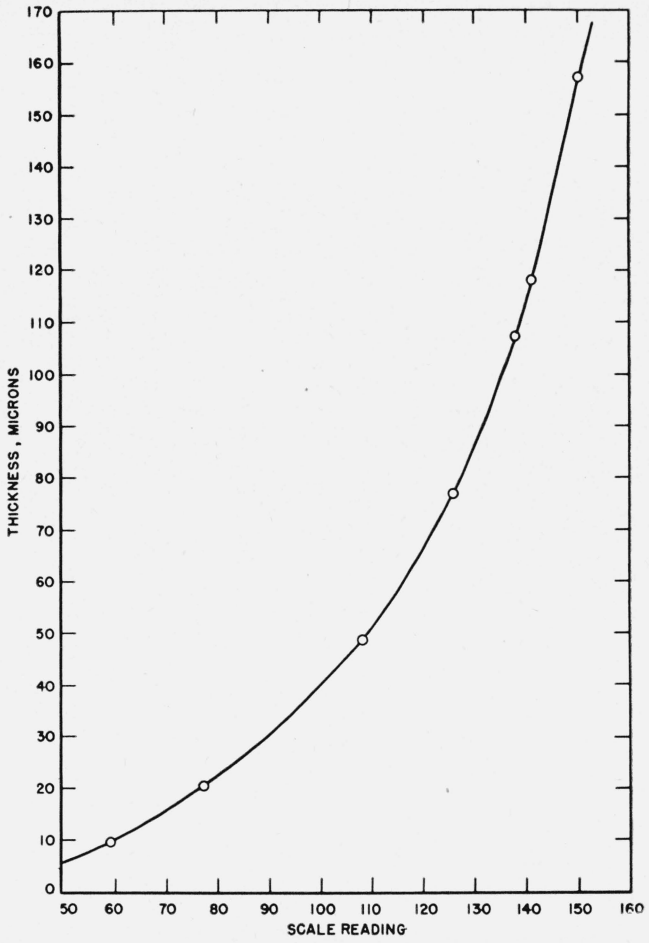

FIGURE 2. *Calibration curve showing scale reading as a function of thickness for magnet 2 of the Magne-Gage.*
Carbonyl iron powder L (20 μ average particle size), vibration-packed to equilibrium, used as backing material.

films or coatings, the Magne-Gage is calibrated against thickness standards supplied by the manufacturer. These standards are squares of steel electroplated with known thicknesses of a nonmagnetic metal. The resulting calibration curves are useless for interpreting dial readings obtained with powder-backed samples. We use instead thickness standards made by cementing aluminium or platinum foils of known and uniform thickness [3] over the open ends of glass tubes of about 9-mm diameter. These simulated electrodes are filled with carbonyl iron and measured in the same manner as the electrodes. The calibration curves resulting for magnets 2 and 3 are shown in figures 2 and 3.

In his work on the thickness of electroplated metals, Brenner [2, 3] found that the geometry of the specimen may have an appreciable effect on the scale reading obtained. In order to prove that no serious errors are introduced by the difference in shape between the Cremer-Haber electrode and the straight-tube standards, the following experiment was performed. A thick-walled bulb 15.5 mm in outside

[3] Foil-thickness measurements made by A. G. Strang.

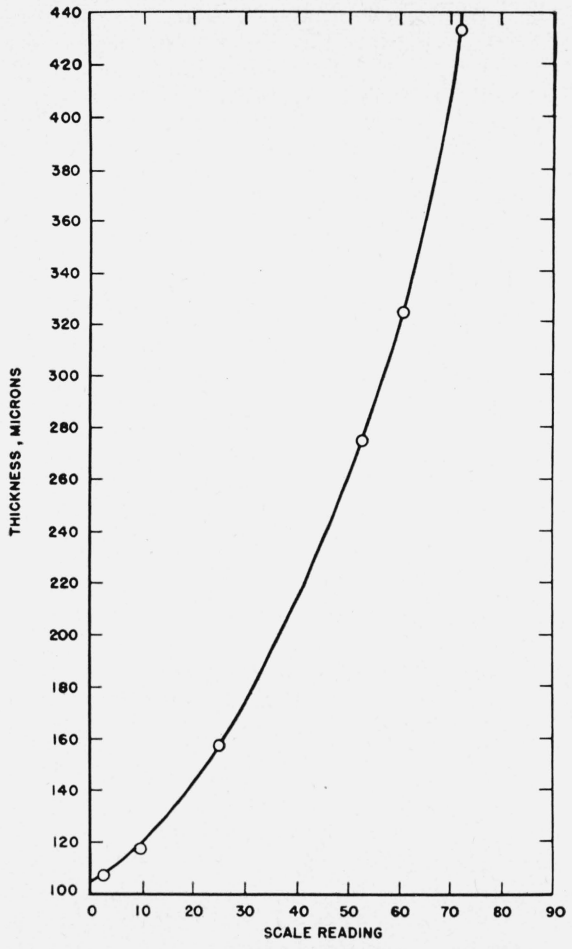

FIGURE 3. *Calibration curve showing scale reading as a function of thickness for magnet 3 of the Magne-Gage.*

Carbonyl iron powder L (20 μ average particle size), vibration-packed to equilibrium, used as backing material.

diameter was blown at the end of a piece of 6-mm tubing. A second similar electrode was prepared with a 19.0-mm bulb. The ends of the bulbs were ground off to leave holes about 2 to 3 mm in diameter. Pieces of aluminum foil 118 μ in thickness were then cemented over these holes. These simulated electrodes were filled with powder, the foil thicknesses measured with the Magne-Gage, and the readings compared with that obtained from the 118-μ straight-tube standard. Scale readings of 141, 141, and 142 were obtained, the higher reading for the 15.5-mm bulb. This is of the order of the experimental errors involved.

From the very nature of a powder, it seemed likely that the dial reading obtained on the Magne-Gage would depend on the degree of compacting of the powder, as well as on its particle size. Experiments were accordingly made on four of the five sizes available.[4] They were performed on the 118-μ straight-tube thickness standard and essentially duplicated on a typical glass electrode. The powder

[4] Available from Antara Division, General Aniline and Film Corp.

TABLE 1. *Magne-Gage scale reading as affected by vibration time and partial size*

Vibration time	Iron powder grade			
	SF (3 μ)	TH (5 μ)	E (8 μ)	L (20 μ)
118 μ straight-tube thickness standard Average scale reading (magnet 3)				
min				
0.5	------	------	------	11.5
1	30	21.5	15	10.5
1.5	------	------	------	10
2	28	20.5	14	10
2.5	------	------	------	10
3	27	20	13.5	------
4	26.5	19.5	13.5	------
5	------	19.5	13.5	------
6	26	19.5	------	------
8	25.5	------	------	------
10	26	------	------	------
Typical Cremer-Haber type glass electrode Average scale reading (magnet 2)				
1	------	------	127	120.3
2	138.5	------	125.5	120.2
3	------	------	125	------
4	136	------	125	------
6	135	------	------	------
8	134.5	------	------	------
10	134.5	------	------	------

was packed by holding the filled electrode in the normal bulb-down position and running a mechanical vibrator up and down the outside of the glass tube. In these experiments, a Sargent Ideal electric marker, set for a fairly high vibration amplitude, was used. Preliminary experiments indicated that vibration time required to reach equilibrium and Magne-Gage scale reading at equilibrium both depended on the energy of vibration. No quantitative data were obtained on this point, but it must be emphasized that the method and energy of vibration selected must be the same during measurement as during standardization.

From the data summarized in table 1, several facts are evident. For each of the four grades of carbonyl iron powder tried, vibration will result in packing to an equilibrium condition. The time needed to reach equilibrium decreases with increasing particle size. Figure 4, from the data for the straight-tube standard in table 1, illustrates this tendency. In addition, the scale readings at equilibrium decrease numerically with increasing particle size, as illustrated in figure 5. As can be seen from the calibration curves shown in figures 2 and 3, the sensitivity of measurement, as microns per scale division, decreases with increasing scale reading. Partially to keep this sensitivity as high as possible for any given thickness, but mainly to take advantage of the saving in vibration time involved, we selected 20-μ iron powder (grade L) as standard. Measurements were made after vibrating for 1.5 minutes.

The data, table 2, indicate the precision possible. Measurements were made on two electrodes, using magnet 2, filling with iron powder L, and vibrating for 1.5 minutes. After every reading, the electrode was held bulb up, still stoppered, vibrated for about 30 seconds until the powder separated from the

TABLE 2. *Multiple measurements of the thickness of two glass electrode bulbs*

	Scale readings	
	Electrode 1	Electrode 2
	121.2	131.0
	120.1	131.0
	120.1	130.7
	120.1	130.9
	120.1	130.2
	120.0	131.0
	120.2	131.0
	120.1	130.9
	121.0	131.0
	120.5	131.1
	120.2	
	121.0	
$\bar{X}$=Average	120.4	130.9
S=Standard deviation, $\sqrt{\Sigma D^2/N-1}$	0.43	0.26
$S_{\bar{X}}$=Standard error of mean, $S/\sqrt{N}$	.12	.08
Limits for true average (statistical probability=0.99)	±.12	±.09

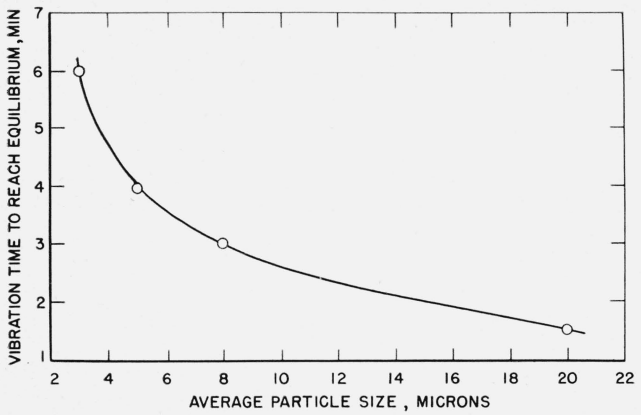

FIGURE 4. *Duration of vibration required to reach equilibrium state of packing, as a function of average particle size of the carbonyl iron powders.*

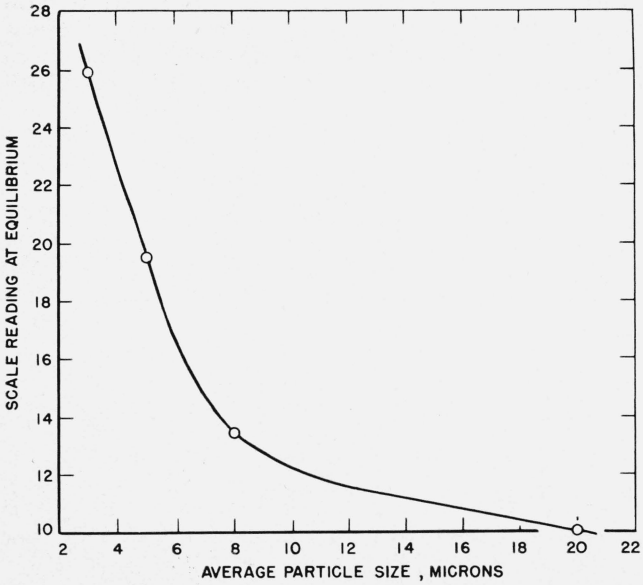

FIGURE 5. *Scale reading after packing to equilibrium as a function of average particle size of the carbonyl iron powders.*

electrode tip and then held bulb down and repacked for 1.5 minutes before the next reading was taken.

With ordinary care, scale readings can easily be reproduced to within one unit. From an examination of the calibration curves shown in figures 2 and 3, it can be seen that one scale unit amounts to about 2 to 3 percent of the thickness measured, for thicknesses down to about 30 μ. For thinner membranes, this percentage increases somewhat, but measurement to 1 μ is easily obtained.

2.2. Measurement of Electrode Response

Each electrode was prepared for voltage response measurement by soaking in distilled water overnight or longer. It was then filled with mercury [21], into which the measurement lead was dipped. A Beckman model G pH meter was used to measure the differences in potential developed in a series of Britton universal buffer solutions [4] between the experimental electrode and a well-conditioned commercial glass electrode (Beckman 1190) serving as a reference electrode. The difference between the measured potentials for the buffer solutions of pH 4 and 8, divided by four, gave the departure of the electrode from the theoretical, in millivolts per pH unit. This departure subtracted from the theoretical 59 mv per pH unit, gave the electrode response of the experimental electrode.

3. Results

3.1. Thickness Profile of a Glass Electrode

It is obvious from the nature of the glass blowing process that a bulb blown at the end of a glass tube will be nonuniform in thickness. Many measure-

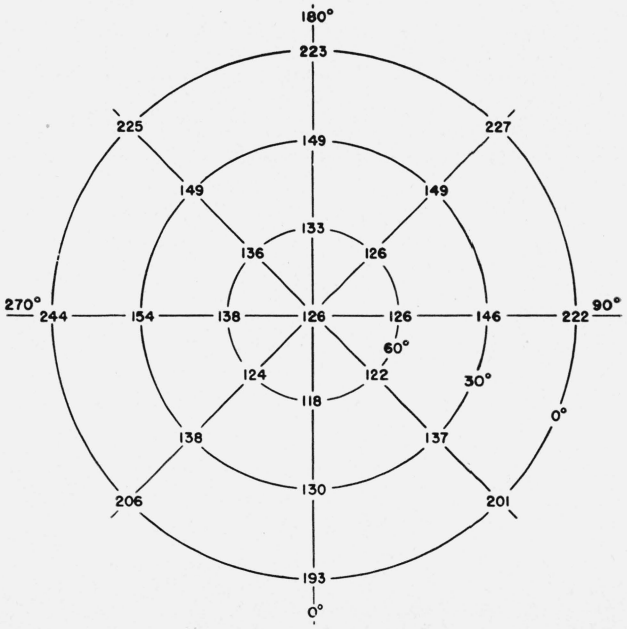

FIGURE 6. *Thickness profile of a commercial glass electrode*

Azimuthal equidistant projection, with bulb tip taken as central point. Thicknesses in microns.

ments of the thickness of glass electrode bulbs, using the powder-backed magnetic method, have shown that only in very unusual cases will the thin spot be where it might be expected, at the tip of the bulb in line with the axis of the tube. Almost invariably, it is 15 to 30 degrees off this spot.

In order to fully illustrate the range of thickness in a glass electrode bulb, a typical commercial electrode (Beckman 1190) was emptied, cleaned and dried, and its thickness profile taken by means of measurements at 25 points on the lower half of the bulb. For presentation of the data, the bulb was treated as a geographic globe with the tip as a pole, and thickness measurements were taken along the circles of latitude and longitude. The great circle passing through the thin spot of the electrode was selected as the prime meridian. The data are plotted in figure 6 on an azimuthal equidistant projection [6] of the bulb, where the tip is taken as the central point.

3.2. Electrode Response versus Thickness

The dependence of electrode response on bulb thickness was investigated for four different glasses, two of which were purported to be identical. They are (1) 9-mm, thin-walled Corning 015 glass electrode tubing, recently purchased for this investigation, (2) Corning 015 glass slab purchased about 20 years ago, (3) Kimble soft glass tubing, and (4) glass A, a single length of 9-mm, thick-walled tubing included in the shipment of Corning 015 tubing, but differing from it in appearance and in all properties investigated.

The electrode bulbs were blown on tubes of the same glass for all except the Corning 015 slab glass. Bulbs of that glass were blown on the thin-walled 015 tubing, the only available glass tubing from which it would not crack away on cooling.

The electrode responses obtained for bulbs of various thicknesses of the four glasses are shown in figure 7. The thickness given is that of the thin spot of the glass bulb. The area of this thin spot is estimated to vary from perhaps 2 to 10 mm^2, and would in any case be no smaller than the 0.75 mm,^{2} which MacInnes and Dole found to be large enough to give full electrode response with their thin-membrane electrodes [19].

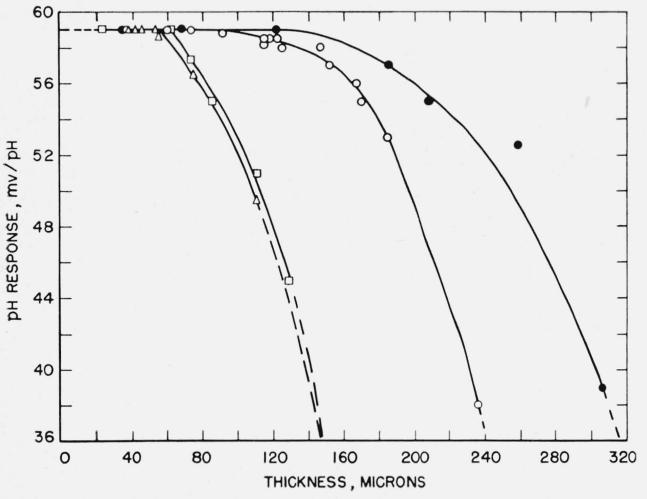

FIGURE 7. *Electrode response as a function of the thickness of the thinnest part of the electrode bulb, for four glasses.*

●, Corning 015 glass tubing; ○, Corning 015 glass slab; □, Kimble soft glass tubing; △, glass A.

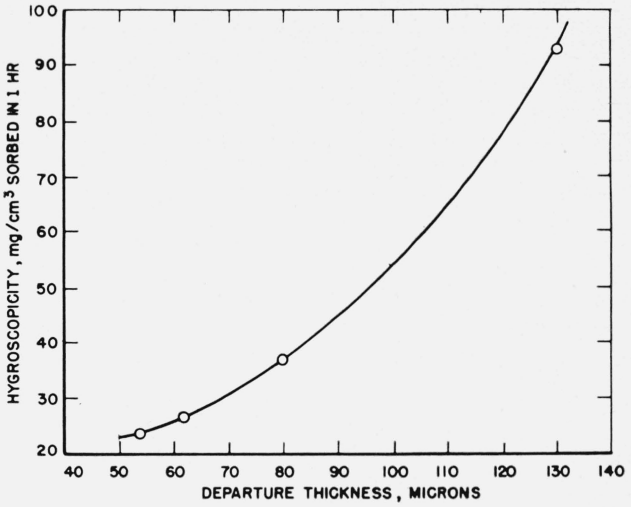

FIGURE 8. *"Departure thickness" of four glasses as a function of their hygroscopicities*

The data show that, for each of the four glasses investigated, relatively thin bulbs give the full theoretical 59 mv/pH electrode response. For each glass there is a characteristic "departure thickness", the maximum thickness that will permit full theoretical response. Beyond this point, increasingly thick bulbs show increasing voltage departures, as well as increasing difficulties and uncertainties of voltage measurement. From the data it is also evident why the two batches of Corning 015 glass were considered as different glasses. This bears out the earlier findings of others [8] that this glass may be somewhat variable in composition.

When the hygroscopicities of the four glasses were compared by the method of Hubbard [11, 16], it was found that the higher the hygroscopicity of the glass, the greater was its departure thickness. This is shown in figure 8, and is consistent with previous findings that it is impossible to get full electrode response with glasses of very low hygroscopicity [14, 15]. It is also of interest to note that the logarithm of the hygroscopicity appears to be a linear function of the departure thickness.

4. Conclusions and Summary

1. A magnetic method, employing iron powder, has been developed for the simple, rapid, and accurate determination of the thickness of glass electrode bulbs. The procedure has the additional advantage of not destroying the specimen. The method as given could be used with equal facility for thickness measurements on odd-shaped envelopes made of any nonmagnetic material.

2. A Cremer-Haber electrode bulb is nonuniform in thickness and has a thin spot that is usually 15 to 30 degrees from the tip of the bulb. The tip is usually not, therefore, the weakest spot on the bulb, as has been supposed.

3. Thin glass electrodes made of any of the glasses investigated will give full theoretical electrode response.

4. For each glass investigated there is a characteristic departure thickness. A glass electrode whose minimum thickness is equal to or less than this departure thickness will give full theoretical electrode response, whereas a thicker one will not.

5. For the glasses investigated, the departure thickness is a function of the hygroscopicity. Those of greater hygroscopicity will therefore permit the manufacture of electrodes of thicker and hence more rugged construction.

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