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**THE EQUIVALENCE OF GRAVIMETRIC AND
VOLUMETRIC TEST MEASURE CALIBRATION**

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INTRODUCTION

Recently the Mass and Volume Section began taking steps toward modernizing the calibration program for volumetric test measures, devices used to contain or deliver known volumes of water. A review of the procedures used indicated a need for improvement in the following areas.

1. Methods of data reduction
2. Data analysis
3. Closure which we define as follows: when the values assigned by different calibration methods do not disagree by an amount larger than can be explained by measurement uncertainties, closure is said to exist.

The first two of these concerns have been attacked by improved models for data reduction and application of statistical techniques.

In this study, we have addressed our attention to the closure of values assigned to our working standards by different methods. As reported earlier [1]* there are two practical methods in use by which test measures are usually calibrated. The gravimetric method establishes the mass of water either contained or delivered from a test measure and hence the associated volume. The volumetric method employs a known volume from which water is transferred to an unknown volume and thereby the contained or delivered volume can be derived.

It can be argued that both methods of calibration are equally correct or that one is more correct than the other. We shall not pursue these arguments in this report but will demonstrate closure for the NBS processes, regardless of the calibration method, from 1 to 830 gallons.

* The numbers in brackets refer to similarly numbered references at the end of this paper.

TEST MEASURES

There are several basic types of test measures, many of which were used to obtain our closure data. Almost all test measures, regardless of design, have some characteristics in common. The majority have nominal volumes ranging from 1 to 1,000 gallons in increments of 5 gallons. Those most frequently encountered are the 1, 5, 50 and 100 gallon vessels.

Another common feature is that nearly all test measures are fabricated from mild steel or 304 stainless steel. Their respective thermal coefficients of expansion (cubical) are $18.6 \times 10^{-6}/^{\circ}\text{F}$ [2] and $26.5 \times 10^{-6}/^{\circ}\text{F}$ [3]. Various organizations by agreement report the volumes of test measures at 60°F, although in use the temperature span may be quite large. The advantage of dealing with only two materials whose thermal coefficients are well known is obvious.

All test measures have at least one reference point (end point) from which volume is defined and in many vessels there are two points. These may be valves, graduated necks, slicker plates, or various combinations of them. Spirit levels are also an important part of defining some end points as well as drainage characteristics.

MAINTENANCE AND DISSEMINATION OF VOLUME STANDARDS

NBS calibrates volumetric test measures as a service for the public. These measures vary in design and size from 1 to 1,000 gallons, the vast majority of which are between 1 and 100 gallons.

Our working standards (1, 5, 30, 50, 100 gal) are now maintained by both the gravimetric and volumetric transfer methods of calibration. Both of these methods are described with adequate detail in NBSIR 73-287. In essence any working standard or combination thereof can be transferred to the 100 gallon standard. Thus we can demonstrate what we call within-group closure, the internal consistency of our standards regardless of calibration method. However, in practice we must exceed the 100 gallon level to include our expected working range of 1,000 gallons. In doing so, we face a dilemma unless we have the secure foundation of closure, that is we could unknowingly propagate two volume scales, one based on gravimetric calibrations and the other based on volumetric calibrations which might not necessarily agree with each other.

Not only should we provide within-group closure of the standards, but also we should extend this property to include the range of their usage in our calibration program. The remainder of this report describes the measurements and data collected over the past few years to demonstrate closure up to 830 gallons.

CLOSURE MEASUREMENTS

To simplify following the procedure used to demonstrate closure, the reader is referred to figure 1. For convenience we have assumed the calibration process begins with 5 gallon vessels whose volumes are well defined by gravimetric calibration. This volumetric information is transferred to other vessels which in turn are also calibrated gravimetrically and the two outcomes are then compared. The blocks indicate a gravimetric calibration, and the arrows are volume transfers from that vessel. Dotted blocks indicate areas of calibration where both methods are routinely used for control chart surveillance of the calibration process. Blocks marked as 5 gallon summations are separated from the 5 gallon blocks only to aid in clarity.

The 5 gallon vessels have not been transferred to all vessels calibrated gravimetrically, the reason being the conservation of time and energy as anyone familiar with the process will recognize.

DATA

In comparing the performance of one measurement system to another, we must know the uncertainty associated with the measurements produced by each process. For the gravimetric process the random errors of the process are associated with the operation of filling and subsequent weighing, so that a standard deviation based on a sequence of independent fillings provides a measure of the effect of random errors. The error arising from the weighing operation is negligible so the discrepancies between successive fillings arise from the following: varying amounts of liquid retained on vessel walls when drained, erratic meniscus behavior detrimental to end point determination and failure to achieve an isothermal condition before measuring the liquid temperature, etc.

If there are n independent measurements, X_1, X_2, \dots, X_n of the same vessel, the standard deviation of the average, \bar{X} , is given by s/\sqrt{n} where s is the standard deviation of a single value from the mean computed from the formula

$$s = \sqrt{\sum (X_i - \bar{X})^2 / (n - 1)}$$

This value of s is a measure of the process standard deviation, σ_1 , associated with the gravimetric method for the volume and type of vessel being measured.

The uncertainty of the gravimetric value is then $\pm U_1$ where

$$U_1 = 3s_1/\sqrt{n} \quad \text{Eq. (1)}$$

Assuming that errors from the weighing process are negligible, the value of σ_1 will be dependent on the nominal size and type of measure being calibrated.

For a test measure calibrated by volume transfer using a reference test measure calibrated by the gravimetric method, there will be two sources of error in the value determined for the larger vessel. The first of these arises from random errors in the filling operation introduced at each of the K transfers required to fill the larger vessel. The second source depends on similar errors associated with the larger vessel such as reading the end point, drainage, temperature, etc. The errors from these two sources will combine in quadrature to give a standard deviation of σ_v for the random errors¹ associated with a single filling of the larger vessel. For n_1 determinations, the standard deviation of the average will be $\sigma_v/\sqrt{n_1}$. The uncertainty, U_1 , assigned to the value of the reference measure will be repeated K times, therefore the total uncertainty, $\pm U_2$, for the average of n_1 determinations for the larger vessel is

$$U_2 = 3s_v/\sqrt{n_1} + KU_1 \quad \text{Eq. (2)}$$

The second term on the right-hand side of the above equation is usually called the systematic component because it cannot be reduced in magnitude unless the reference measure is recalibrated or more than one standard is used. In our work this term is much smaller than the other term because of repeated calibrations of the reference measure. The first term can, of course, be reduced by additional work (i.e. by increasing n_1).

The difference between a value X based on the average of M gravimetric determinations and a value Y based on n_1 volume transfer measurements, each consisting of K transfers from a reference measure with n gravimetric determinations will have a standard deviation of the difference as follows:

$$\text{Standard Deviation of } (Y - X) = \sqrt{\frac{s_v^2}{n_1} + \frac{s_M^2}{M}}$$

where s_M is the standard deviation of the gravimetric values at a volume M level of K times the volume of the reference measure.

¹ The standard deviation, σ_v , has a component from the filling operation of size $\sigma_1\sqrt{K}$ plus the component contributed by the larger vessel which results from variation of the end point determination and other errors previously mentioned. If the same type of end point determination is used in both vessels, then σ_v would be nearly equal to $\sigma_1\sqrt{K}$.

The difference (Y - X) will have a possible systematic error of

$$3K \frac{s_1}{\sqrt{n}} = KU_1$$

One regards the measurement system as having the property of closure if the following inequality test is satisfied:

$$Z = \frac{|Y-X| - K(3s_1/\sqrt{n})}{\sqrt{\frac{s_v^2}{n_1} + \frac{s_M^2}{M}}} < 3 \quad \text{Eq. (3)}$$

This formula assumes that the standard deviations are known, which means that they are based on a large number of observations.

The data presented in the tables, except for the 1 gallon vessel, are for delivered volume reduced to 60 °F and to a zero scale reading where applicable. The closure test is inserted in the tables for ease in comparing pertinent values and is summarized in table 11.

Figures 2 and 3 are control charts produced by routine calibrations. Each point on the chart is a measurement produced by transferring a test measure calibrated gravimetrically to a check standard of known volume. The check standard is another test measure of the same nominal volume that is well defined. This one-to-one transfer recalibrates the check standard each time a gravimetric calibration is performed. Closure is demonstrated because each new value is within predicted limits.

Initially estimates of the standard deviation (s) like those of tables 1 and 2 are necessary to establish starting limits on the control charts. The limits become better known as more data is collected and plotted on the control chart.

The data of tables 1 through 8 is straightforward and no difficulties were encountered in demonstrating closure. However the calculation of U_2 for table 5 requires a modification of Eq. (2). This results from the use of eight identical reference test measures, each calibrated once. Each reference measure was then transferred K times to complete a calibration of the larger vessel. In a more general sense, when n_1 reference standards are each used K times to calibrate a larger vessel n_1 times, the uncertainty will be

$$U_2 = \pm 3 \sqrt{\frac{s_v^2 + Ks_1^2}{n_1}} \quad \text{Eq. (2a)}$$

Likewise a similar modification of Eq. (3) is necessary to test for closure.

$$Z = \frac{|X - Y|}{\sqrt{\frac{s_V^2 + Ks_1^2}{n_1} + \frac{s_M^2}{M}}} < 3 \quad \text{Eq. (3a)}$$

Ordinarily, we can weigh vessels up to 30 gallons on one of several equal-arm balances at our disposal. Beyond 30 gallons and up to 100 gallons we use a load cell as a mass comparator for gravimetric calibration and, beyond this point, a multiple-lever platform scale. However, most test measures larger than 100 gallons are not structurally sound enough to be lifted when filled with water. To demonstrate closure between the two methods of calibration near the 1,000 gallon capacity, we used a rigid steel tank with a useful capacity of 830 gallons.

The tank did not have a reference scale appropriate to this work, so the data shown below are at the test temperature. We simply filled the tank by transferring known volumes of water into it and then measured the accumulated volume gravimetrically.

<u>Temperature</u>	<u>Transfer</u>	<u>Gravimetric</u>
t ₁	829.940 gal	829.863 gal
t ₂	829.873	829.867
	U ₂ ± 0.024	U ₁ ± 0.060

The uncertainty, U₁, is calculated by a different but well known method not discussed in this report. For such a small data set, closure is considered to be demonstrated when the error bands overlap as is the case here.

CONCLUSIONS

Based on our data, we conclude that closure does in fact exist and that the two methods of test measure calibration may be regarded as equivalent.

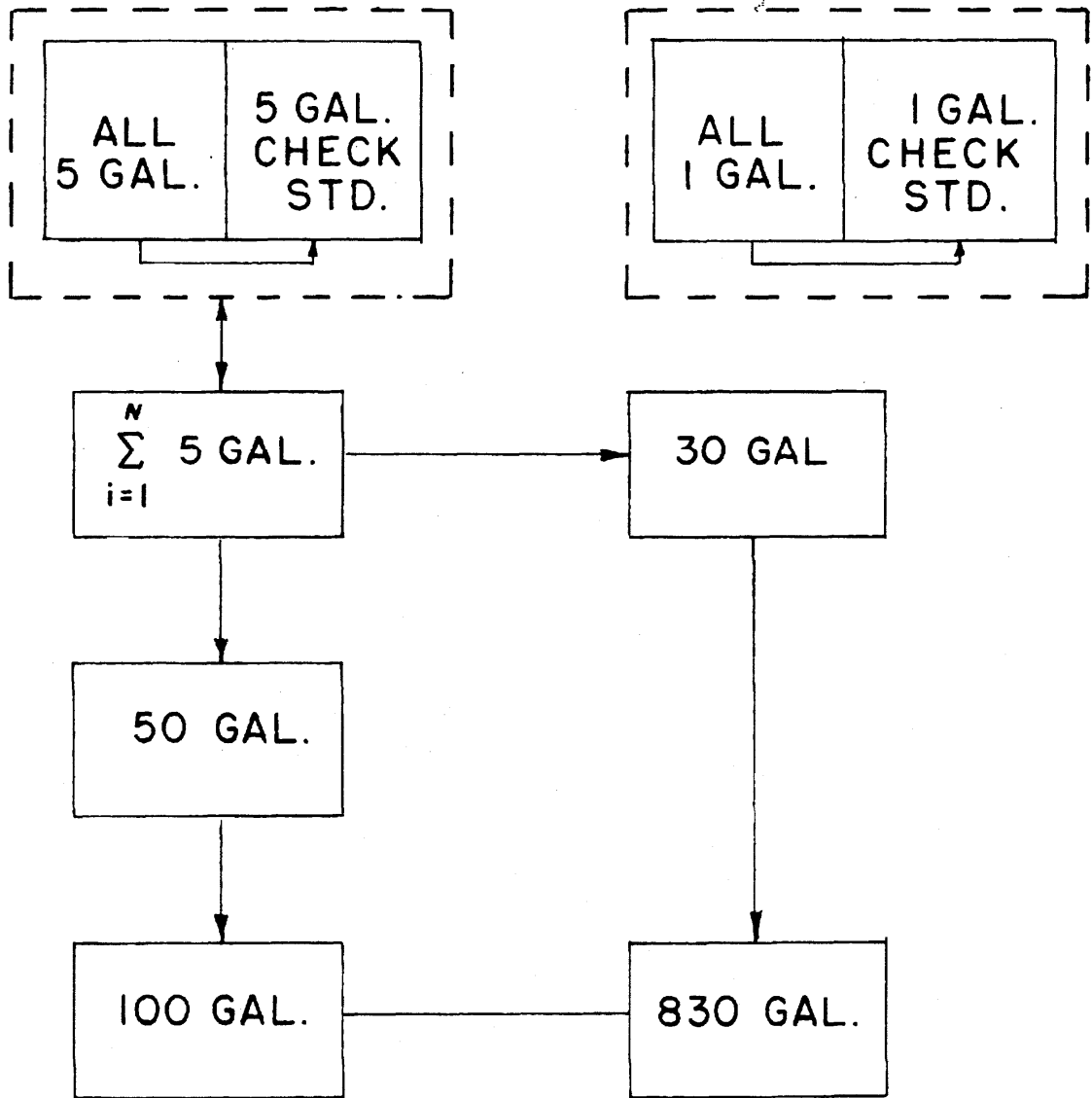
ACKNOWLEDGMENTS

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REFERENCES

- [1] Houser, John F., Procedures for the Calibration of Volumetric Test Measures, Nat. Bur. Stand. (U.S.), NBSIR 73-287 (Aug. 1973).
- [2] Tables for Positive Displacement Meter Prover Tanks, ASTM D1750-62 (API 2541), ASTM Manual (1962).
- [3] American Institute of Physics Handbook, Third Edition (1972).

MEASUREMENT DIAGRAM



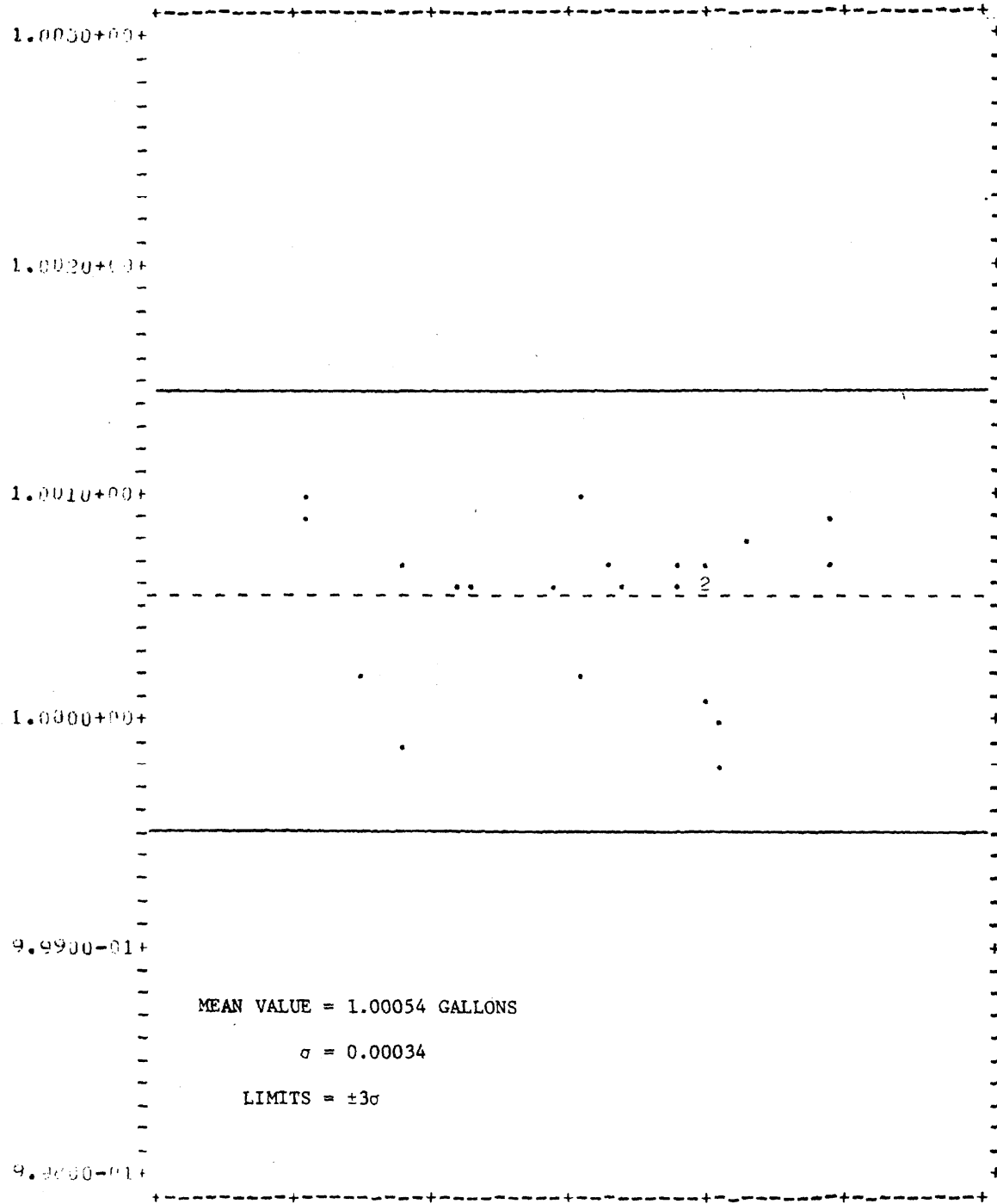
Blocks indicate gravimetric calibration

—————> Volumetric transfer

----- Check std. control chart operation

FIGURE 1

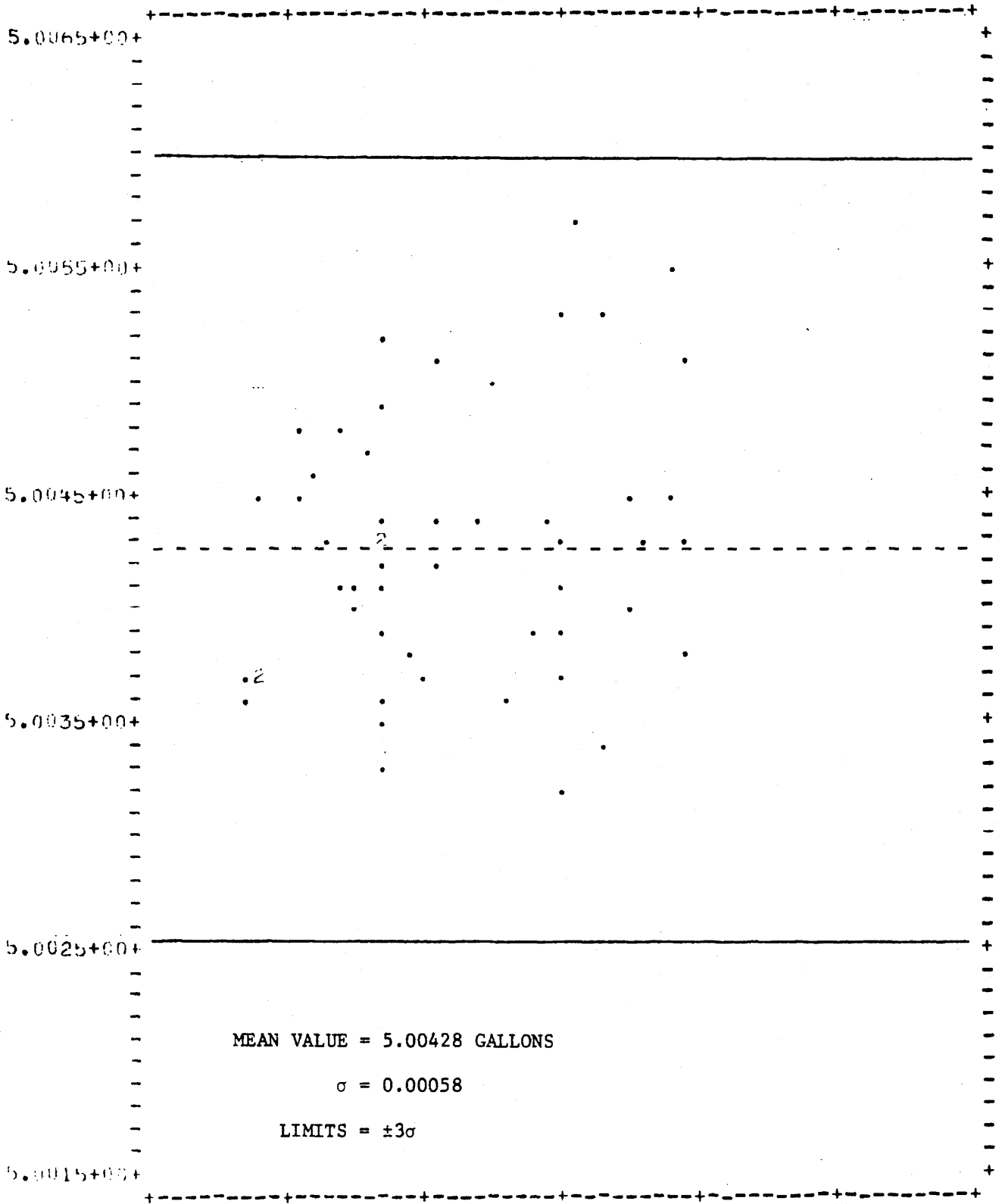
1 GALLON CHECK STANDARD



COMPLETED FROM 10-70 TO 11-73

FIGURE 2

5 GALLON CHECK STANDARD



COMPLETE FROM 2-70 TO 8-73

FIGURE 3

TABLE 1: Values for Two 5 Gallon Graduated Neck Test Measures Assigned by Repeated Gravimetric Calibration.

A	B
5.00078 gallons	5.00450 gallons
5.00154	5.00228
5.00116	5.00242
5.00104	5.00318
5.00097	5.00295
5.00119	5.00375
5.00035	5.00365
5.00080	$\bar{X} = 5.00323$
$\bar{X} = 5.00098$	$S_1 = 0.00078$
$S_1 = 0.00035$	$U_1 = \pm 0.00088$
$U_1 = \pm 0.00037$	

TABLE 2: Repeated Gravimetric Calibrations of a 5 Gallon Slicker Plate Measure and a 1 Gallon Graduated Neck Pyrex Check Standard.

5 GALLON MEASURE	1 GALLON MEASURE
5.00063 gallons	1.00063 gallons
5.00069	1.00062
5.00081	1.00042
5.00029	$\bar{X} = 1.00056$
5.00034	$S_1 = 0.00012$
$\bar{X} = 5.00055$	$U_1 = \pm 0.00021$
$S_1 = 0.00023$	Contained Volume @ 60°F
$U_1 = \pm 0.00031$	

TABLE 3: Transfer Calibrations of 30 Gallon Graduated Neck Measure Based on the 5 Gallon Slicker Plate Measure Shown in Table 2.

STARTING STANDARD	30 GALLON VALUES
5.00063 gallons	30.0048 gallons
5.00069	30.0031
5.00081	30.0047
5.00029	30.0007
5.00034	30.0049
$\bar{X} = 5.00055$	$\bar{Y} = 30.0036$
$S_1 = 0.00023$	$S_Y = 0.00180$
$U_1 = \pm 0.00031$	$U_2 = \pm 0.00428$

TABLE 4: Gravimetric Calibrations of the 30 Gallon Measure.

30 GALLON MEASURE	CLOSURE
30.00218 gallons	<u>Gravimetric Value</u>
30.00205	$\bar{X} \quad 30.00150 \pm 0.00134$
30.00153	
30.00023	<u>Transfer Value</u>
$\bar{X} = 30.00150$	$\bar{Y} \quad 30.00360 \pm 0.00428$
$S_M = 0.00089$	
$U_1 = \pm 0.00134$	$Z = 0.261 < 3$

TABLE 5: The 50 Gallon Measure Transfer Calibration Based on 8 Different Slicker Plate Measures Calibrated Gravimetrically.

STARTING STANDARDS	50 GALLON MEASURE
5.00109 gallons	50.0098 gallons
5.00078	50.0051
4.99952	50.0033
4.99937	50.0086
5.00073	50.0020
5.00090	50.0100
5.00089	50.0079
4.99903	50.0037
$S_1 = 0.00023$	$\bar{Y} = 50.0063$
$U_1 = \pm 0.00069$	$S_V = 0.0032$
	$U_2 = \pm 0.0035$

TABLE 6: 50 Gallon Measure Gravimetric Calibration via Load Cell Mass Comparator.

50 GALLON MEASURE	CLOSURE
50.0097 gallons	<u>Gravimetric Value</u>
50.0023	$\bar{X} = 50.0048 \pm 0.0027$
50.0025	
50.0037	<u>Transfer Value</u>
50.0072	$\bar{Y} = 50.0063 \pm 0.0035$
50.0073	
50.0066	$Z = 1.02 < 3$
50.0079	
50.0030	
50.0026	
50.0003	
$\bar{X} = 50.0048$	
$S_M = 0.0030$	
$U_1 = \pm 0.0027$	

TABLE 7: 100 Gallon Transfer Calibration Using the 50 Gallon Measure
As the Reference Standard. See Table 6 for 50 Gallon Data.

STARTING STANDARD	100 GALLON MEASURE
	100.012 Gallons
	100.013
	100.013
\bar{X} = 50.0048 Gallons	\bar{Y} = 100.0127
S_1 = 0.0030	S_V = 0.0006
U_1 = ± 0.0027	U_2 = ± 0.0064

TABLE 8: 100 Gallon Gravimetric Values Assigned by Load Cell Weighings.

100 GALLON GRAVIMETRIC	CLOSURE
100.012 Gallons	<u>Gravimetric Value</u>
100.010	\bar{X} 100.0096 \pm 0.0028
100.008	
100.011	<u>Transfer Value</u>
100.007	\bar{Y} 100.0127 \pm 0.0064
\bar{X} = 100.0096	
S_M = 0.0021	$Z = 2.40 < 3$
U_1 = ± 0.0028	