NBS TECHNICAL NOTE 698

U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

CRYOGENIC FLUIDS DENSITY REFERENCE SYSTEM: PROVISIONAL ACCURACY STATEMENT

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CRYOGENIC FLUIDS DENSITY REFERENCE SYSTEM: PROVISIONAL ACCURACY STATEMENT

technical note no 698

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The density reference system of the Cryogenics Division of the National Bureau of Standards is described. This system is used in making density measurements of cryogenic liquids. The methods of computation and the accuracy to which the density of the liquid can be measured are discussed in detail.

At this time the estimate of sample standard deviation for a single density measurement made using this system is 0.016% (at 422.63 kg/m^3). Using three times this standard deviation as a limit for random error and using 0.028% as the bound for known sources of possible systematic error, the uncertainty of a single determination with this system is ± 0.076%. This provisional statement of accuracy applies for the density range 400 to 480 kg/m^3, pressures from 0 to 3 bar, and temperatures from 110 K to 125 K. Because of the densimeter design, this accuracy statement is expected to apply to the density range from 400 to 1000 kg/m^3 and to the temperature range of 77 to 300 K at least, and to pressures of 7 bar, though these ranges of application have yet to be verified.

Key Words: Densimeters, density reference system; liquid methane; LNG.

1. INTRODUCTION

The density reference system (DRS) was evolved to determine the uncertainty of measurements made by several field type densimeters capable of operating at cryogenic temperatures in liquefied natural gas (LNG). The project was performed under a grant from the American Gas Association, Inc. (A.G.A.) on behalf of its membership.

This system has the capability at present of operating from room temperature to near the boiling point of liquid nitrogen (300 K to 80 K), and at pressures of 7 bar (100 psi) to vacuum. In this work densities of 400-480 kg/m^3 were covered.

At this time the value of the standard deviation for a single density comparison measurement made on this system is 0.016% (at the methane normal boiling point density of 422.63 kg/m^3), based on measurements made using samples of cryogenic liquids. Using three times this standard deviation as a limit for the random error, and adding 0.028% as the bound for known sources of possible systematic error, the uncertainty of a single determination by this system is taken to be ± 0.076%.

Density is determined in the DRS by weighing an extremely pure (semiconductor grade) single-crystal of silicon in the liquid whose density is to be determined. The density of the liquid is calculated from the apparent weight of the silicon submerged in the liquid using the Archimedes principle.

It is appropriate that silicon was used in this work as its density has been recommended by Bowman [1] of NBS as the primary standard for solid densities. His work, which uses Archimedes principle, discusses the several advantages that this type of silicon has for accurate measurements of liquid densities: relatively low density (compared to other solids), high thermal conductivity, low electrical resistance, and low compressibility. Of course, Bowman's work and others [2] provide accurate values for silicon density.

1.1. Symbols

g	acceleration of freely falling body
k	compressibility factor
L	length
L_{298}	length at reference temperature 298 K
L_T	length at absolute temperature T
M_a	apparent mass
M_{ao}	apparent mass as read by balance for zero mass load
M_c	counterweight mass
m_c	bouyancy correction to M_c
M_s	silicon crystal mass
M_w	reference mass standard used to evaluate zero of balance
m_w	bouyancy correction to M_w
P	system pressure
T	system temperature
V_s	volume of silicon
ρ	density of liquid sample
ρ_g	density of gas (vapor phase in equilibrium with sample liquid)
ρ_s	density of silicon
ρ_w	density of brass
$Y_{(T)ij}$	jth density determination by the DRS on the ith methane filling
$H_{(T)}$	corresponding density value from average T using Haynes-Hiza relationship
$\mu_{(T)}$	systematic difference between $Y_{(T)}$ and $H_{(T)}$
α_i	shift in the mean for measurements made on ith filling
e_{ij}	random contribution to jth measurement on ith filling

2. DESCRIPTION OF THE BASIC MEASUREMENT PROCESS

2.1 System Description

The density reference system consists of a vacuum insulated cryogenic fluid sample container with an integral densimeter. Provision is made to insert other densimeters into this container so that simultaneous measurements of the density of an isothermal fluid can be made with the reference and test densimeters. It is desired that the density reference system be able to test density measurements of other instruments to 0.1%.

The liquid sample, test densimeters, and measuring devices are contained in a closed system, as shown schematically in figure 1. An automatic balance is in the upper gas space which is an integral part of the sample space. From the balance arm is suspended the silicon crystal, whose apparent mass when immersed is directly related to the liquid density. Two vapor pressure thermometers are used to measure the liquid temperature at the top and bottom of the sample. Pressure of the liquid sample is measured by a quartz-spiral bourdon gauge.

Cryogenic temperatures are achieved by flowing cold nitrogen gas through a coiled tube attached to the outside of the sample holder. These coils are used to cool the sample, and resistance heaters are used to heat it when changing temperatures between data points. Each data point is taken with the sample and container as nearly as possible at isothermal conditions. During the period of time data are being recorded, the thermal inertia of the sample is used to keep the temperature constant. The heat leak to the sample has been minimized by surrounding the sample container with a nitrogen gas cooled shield. This shield temperature is maintained near that of the sample by controlling the flow of the nitrogen gas passing through the shield cooling coil. To obtain temperature equilibrium rapidly in the 14 liter vessel, a 5-cm diameter turbine pump is used to mix the sample. The sample fluid is pumped through a 3.5-cm diameter intake line from the bottom of the sample vessel and is exhausted into the top of the vessel through a discharge line of the same size. This stirrer, capable of mixing the fluid very rapidly at full speed, is operated at reduced speed during the actual measurements, since rapid circulation of the fluid sample affects the densimeter readings. The stirring speed used, is well below the disturbance threshold.

CRYOGENIC FLUIDS DENSITY REFERENCE SYSTEM

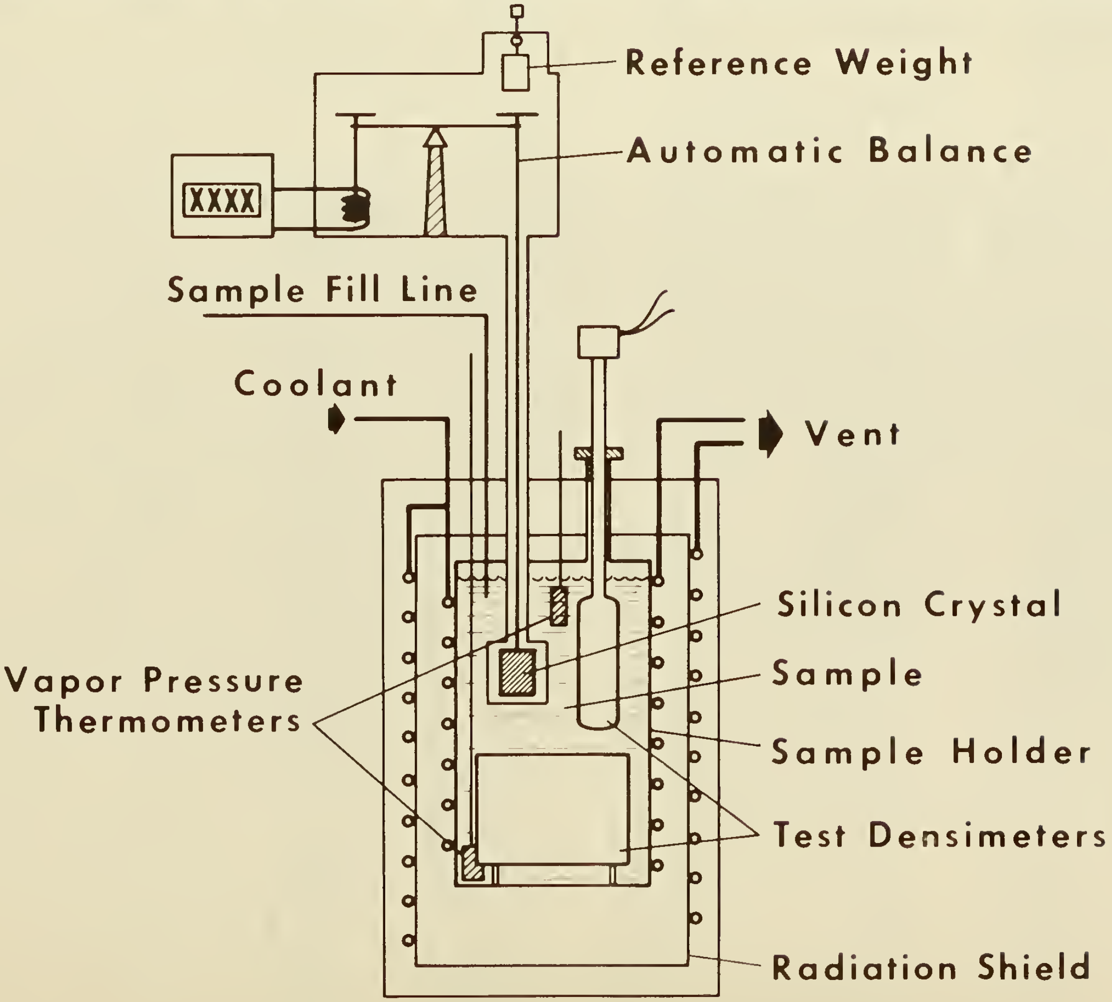

Figure 1.

2.2. Density

The density reference system densimeter uses the Archimedes principle; that is, a body immersed wholly or partially in a liquid experiences a lifting force equal to the weight of the fluid displaced. The net force on the body is the difference between its weight and this buoyant force.

The basic arrangement of the silicon crystal, the weighing balance, and sample holder can be seen in figure 1. A silicon crystal is weighed immersed in the test liquid. Its apparent weight is the difference in its true weight and the buoyant force exerted by the liquid.

$$M_a g = (M_s - \rho V_s) g. \tag{1}$$

In the following relations we have removed the factor, g, as it is common in all terms. Solving for density

$$\rho = (M_s - M_a) \frac{1}{V_s} . \tag{2}$$

Using the measured value for the silicon mass and the value for single-crystal pure silicon density, ρ_s, we have

$$M_s = \rho_s V_s . \tag{3}$$

Combining equations (2) and (3) to eliminate V_s,

$$\rho = \rho_s (1 - M_a/M_s). \tag{4}$$

This is the basic form of the measurement equation. The one actually used is developed below.

It is desired to weigh the 127 g silicon crystal to about 1 mg. The electronic balance used weigh the crystal only weighs to 1 mg on a zero to 20 g range. This is sufficient to measure the buoyancy change of the crystal in the fluids over the density ranges of interest. A counter weight on the balance beam is adjusted so that the weight reading of the crystal is less than 20 g for the lowest density liquid. Then equation 2 can be written:

$$M_a + M_c - m_c = M_s - \rho V_s . \tag{5}$$

The M_a of equation (2) has been replaced by $M_a + M_c - m_c$ where m_c is the counterweight buoyancy correction due to the sample vapor which has free access to the vessel containing the balance. Since M_c cannot be measured directly another weighing is required. Before or after weighing the silicon crystal, the crystal is disconnected and a reference weight M_w is placed on the balance pan. This reference weight is chosen so that it is approximately two grams heavier than M_c. This insures that the balance reading will remain well above 0 g as the balance does not read negative weights. The balance condition for the electronic balance with only the reference weight on the pan is;

$$M_{ao} + M_c - m_c = M_w - m_w. \qquad (6)$$

Subtracting equation (5) from (6) and solving for ρ gives an equation for ρ that excludes M_c and m_c:

$$\rho = \frac{M_s - M_w + m_w + M_{ao} - M_a}{M_s/\rho_s} \qquad (7)$$

Like M_c and m_c, all other components of the balance and the crystal suspension are weighed in both measurements and cancel out when equations (5) and (6) are subtracted.

All the quantities in equation (7) are measured separately from the density measurements except for m_w and of course $M_{ao} - M_a$. The density at room temperature of the gas vapor in the balance volume, ρ_g, is calculated from the vapor pressure of the sample and m_w is calcuated using the relation:

$$m_w = M_w \, \rho_g/\rho_w \, .$$

The quantity m_w may be measured by weighing a plastic weight in the gas in the sample space when the gas composition is unknown.

The measured values of the various masses in equation (7) are:

$M_s = 127.4330$ g, $\rho_s = 2.33078$ gm/cm^3

$M_w = 100.9296$ g, $\rho_w = 8.5$ gm/cm^3 .

so equation (7) becomes:

$$\rho = \frac{26.5034 + M_{ao} - M_a + \rho_g(11.9)}{54.674} \text{ g/cm}^3$$

The value for the silicon mass is an average of several weighings in air, corrected to weight in vacuum (see appendix 8.2).

The density of 2.33078 g/cm^3 has been corrected for thermal contraction to LNG temperatures (appendix 8.3) from the literature values (appendix 8.1). Pressure dependence of ρ_s is negligible (appendix 8.1).

Calibration of the balance.

The linearity was verified using a procedure recommended by the Statistical Engineering Laboratory of NBS. See appendix 8.5. A continual check of the calibration was performed using a 5 gram weight. Provision was made for lowering this calibration weight onto the balance pan by a thermally actuated bi-metallic strip. This allowed a very gentle and repeatable placement of this weight upon the balance pan.

The calibration of the electronic balance was checked periodically during the course of the run both while reading the reference weight and while reading the silicon float weight. The calibration has never required adjusting.

A scale factor correction of 1.0002 has been applied to the scale readings even though a 99% confidence interval for this scale factor is 1.0002±.00045.

2.3. Temperature

Temperature was measured using vapor pressure thermometers. One thermometer bulb was located at the bottom of the sample volume and the other near the top. Each thermometer contains a few cm^3 of liquid methane. Pressure communicates from the thermometers to a quartz-spiral bourdon tube pressure gage (200 psi maximum)* via 1/16" O.D. stainless capillary tubing. The temperature range was 110 K to 126 K. All the quartz-spiral pressure gages used in this work were calibrated using an air dead weight gage. The air dead weight gage has an accuracy of ± 0.015%. The accuracy of the quartz-spiral gages was found to be better than ± 0.015% of full-scale pressure. This pressure uncertainty is equivalent to 0.03 K at 110 K and 0.01 K at 125 K for the 200 psi gage used to measure the vapor bulb pressures.

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*1 psi = 6.895 k Pa.

Temperature gradients as measured by the vapor pressure thermometers have shown a median value of 0.06 K with 17% of the measurements larger than 0.1 K and a maximum gradient of 0.29 K. The densimeters under test are closer to the DRS density probe than are the two vapor pressure thermometers. It is assumed for the purposes of error estimation that ΔT is no larger than 0.05 K. The density difference resulting from this temperature difference can be calculated by using methane properties [3,4]. Here we use the dimensionless derivative $\partial \ln\rho/\partial \ln T$ at saturation:

Average System Temperature	$\partial \ln\rho/\partial \ln T$	$\frac{\Delta\rho}{\rho}$ for $\Delta T = 0.05$ K
110 K	0.38	.017%
127 K	0.5	.02%

An additional temperature uncertainty, usually less than 30 mK, results from the temperature of the sample drifting slightly during the course of a density measurement.

2.4 Vapor Pressure

The liquid sample vapor pressure was measured using a quartz-spiral bourdon tube pressure gage. Most of the measurements were made using a 0 to 100 psi unit that was calibrated against the air dead weight gage.

3. MEASUREMENT PROCESS PARAMETERS

3.1. Bounds for Systematic Errors

The primary sources of uncertainty in the density measurements can be obtained from examination of the measurement equation. The knowledge of the basic uncertainties of the separately measured quantities such as the masses and densities, can be combined to give an estimate of the systematic errors in the density as measured by the density reference system.

Equation (7), the measurement equation, has the density ρ as a function of several independently measured variables.

$$\rho = \rho(M_s, M_w, M_a, M_{ao}, \rho_s, \rho_w) \quad . \tag{8}$$

The uncertainty in ρ, arising from uncertainty in some variable x, for example, can be evaluated from

$$\delta\rho = \frac{\delta\rho}{\delta x}\,\delta x \tag{9}$$

or as a dimensionless ratio,

$$\frac{\delta\rho}{\rho} = \frac{\partial\ell n\rho}{\partial\ell nx}\,\frac{\delta x}{x}\quad, \tag{10}$$

which has the advantage of expressing the independent and dependent variables as dimensionless ratios. The total uncertainty in density is taken to be the square root of the sum of the squares of the various contributions.

$$\frac{\delta\rho}{\rho} = \left\{\sum\left(\frac{\partial\ell n\rho}{\partial\ell nx_i}\,\frac{\delta x_i}{x_i}\right)^2\right\}^{\frac{1}{2}}. \tag{11}$$

This is the propagation of error relationship for systematic error when the variables are independent and the magnitudes of the relative errors are small so that second order terms are negligible [5].

Table 1 is a summary of the most significant contributions to the total systematic uncertainty in density as estimated from the various contributing sources. The first column, labelled x identifies the variable for which the uncertainty is calculated. The second column is the total logarithmic partial derivative of the liquid density with respect to the variable of the first column and the magnitude. The column labelled $\delta x/x$ is the ratio of the estimated worst possible uncertainty of that variable.

The systematic error, $\delta x/x$, due to mass determinations is estimated from the uncertainty generated by the balance and weights used to determine the masses. The estimate of the systematic error of the apparent mass is the uncertainty of the electronic balance reading as specified by the manufacturer. Linearity measurements (appendix 8.5) indicate this number is conservative. The error estimate of the silicon crystal density covers uncertainties due to the temperature and pressure effects (appendix 8.1) as well as uncertainties in published densities (appendix 8.3). The metal density uncertainties of which M_W is the dominant term are estimated from volume and weight. The gas density, required for bouyancy corrections, contains all gas pressure, temperature and composition uncertainties when calculated. This quantity is also determined experimentally by weighing a

Table 1. Systematic errors.

Variable, x	$\partial \ell n\rho/\partial \ell nx$ and max magnitude		$\delta x/x$	$\delta\rho/\rho$ in %
silicon crystal mass	$(\rho_s - \rho)M_s/\rho\rho_s V$	5	1.6×10^{-5}	±0.0080
apparent masses	$M_a/\rho V$	$M_a/22$	$.001/M_a$	±0.0046
	$M_{ao}/\rho V$	$M_{ao}/22$	$.001/M_{ao}$	±0.0046
Silicon density	$M_s/\rho_s V$	1	3.0×10^{-5}	±0.003
ref. wt density	$M_w\rho_g/\rho_w\rho V$	2×10^{-3}	.006	±0.0012
gas density	$M_w\rho_g/\rho_w\rho V$	2×10^{-3}	.05	±.01
temperature gradient	$\partial \ell n\rho/\partial \ell nT$	.5	4×10^{-4}	±.02
temperature drift over course of measurement	$\partial \ell n\rho/\partial \ell nT$	.3	4×10^{-4}	±.012
total, from equation (11)		=		.028%

low density weight of known mass and volume in the gas. The only significant uncertainty is then in the balance readings. The uncertainty due to temperature gradients is discussed in section 2.3. An additional systematic error results from the uncertainty in the absolute value of T. This is not included in the table since it makes no contribution to the systematic error when densimeters are being compared. When density measurements are being compared with those of other workers; however, there is this 0.01% contribution to the systematic error at the lowest temperature that decreases to less than 0.001% at the highest temperature.

3.2 Random Error from Measurements on Methane

The random error of the density reference system was determined experimentally by measurements on cryogenic liquids.

In order to observe the DRS over several periods of operation, measurements were taken on saturated liquid methane for five separate fillings of the system. For these five fillings there was a total of 53 density measurements. The temperatures at which the saturated methane was measured were nominally 110 K, 115 K, 120 K, and 126 K. These density measurements were compared to densities computed from the Haynes-Hiza relation for density versus temperature for saturated liquid methane [4]. The vapor pressure measurements were converted to temperature [3] and the resulting temperature converted to density. The percent deviations of the Haynes-Hiza values from the DRS are shown in figure 2 in chronological order, in figure 3 as a function of density, and in figure 4 as a function of temperature.

The model used to analyze the methane data is

$$H_{(T)} - Y_{(T)ij} = \mu_{(T)} + \alpha_i + e_{ij}$$

where $Y_{(T)ij}$ is the jth density determination by the DRS on the ith methane filling for temperature T; $H_{(T)}$ is the corresponding density value derived from the Haynes-Hiza relationship, $\mu_{(T)}$ represents any systematic difference between the two methods at temperature T, α_i represents a shift in the mean for measurements on the ith filling, and e_{ij} the random contribution to the jth measurement made on the ith sample.

Figure 2, $100\cdot(H-Y)/Y$ as a function of chronological order, provides a look at shifts, α_i, in the mean of the Y_{ij} from one filling to the next, each filling having a different symbol. The statistical analysis of the data, however, does not indicate the presence of any shift not accounted for by the within sample variability of the data.

The percentage differences, plotted in figure 4 as a function of temperature, show what appears to be a second degree effect. It would not be surprising to find apparent systematic differences between the two methods. The DRS data can be reasonably fit as a second order polynomial in temperature as discussed below; and the Haynes-Hiza relationship relating temperature and density for saturated methane may also be fairly well

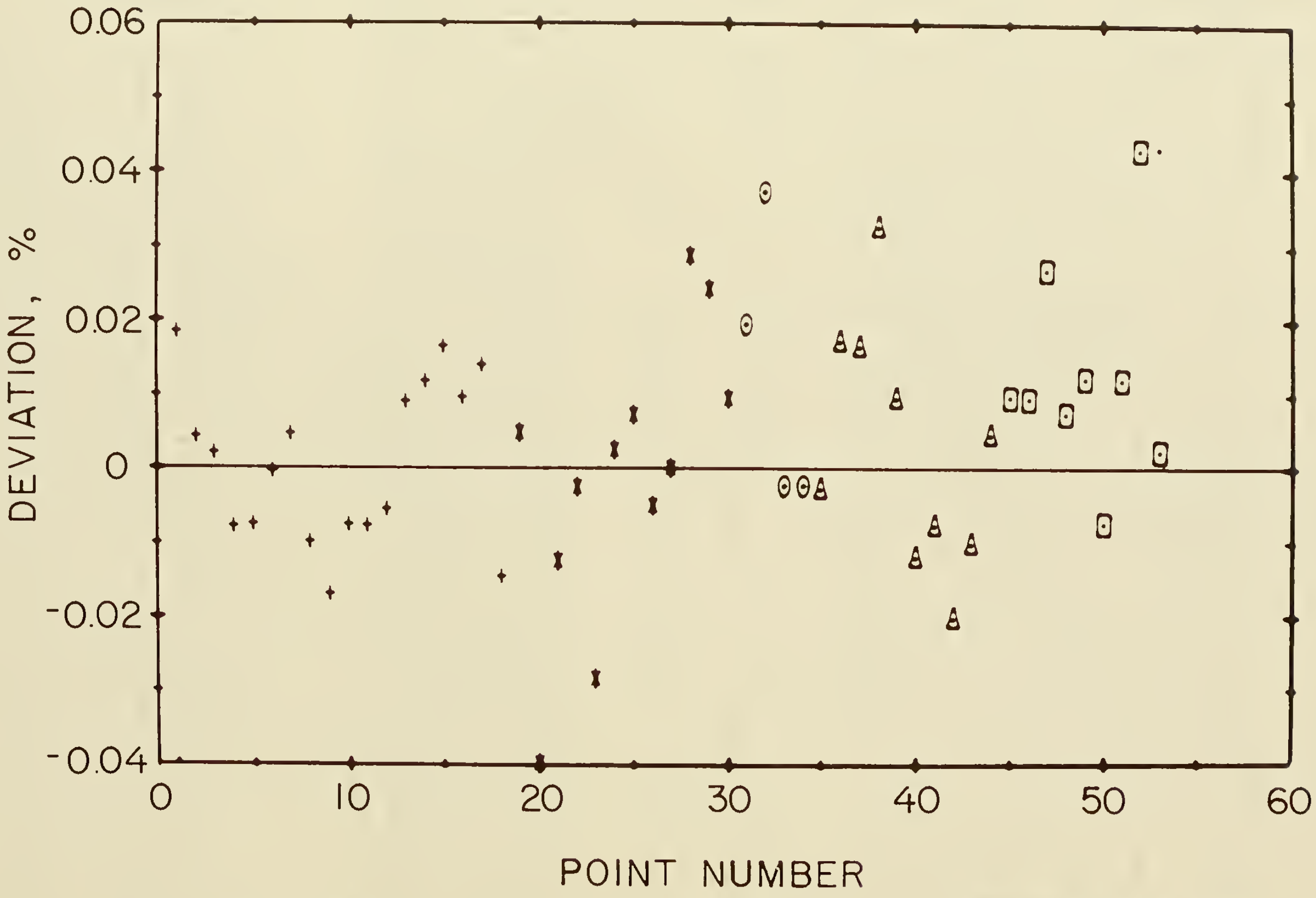

Figure 2. Deviation of the density of liquid methane calculated from temperature using Haynes-Hiza results from the corresponding DRS density as a function of the chronological order of the measurement. Different symbols identify different fillings.

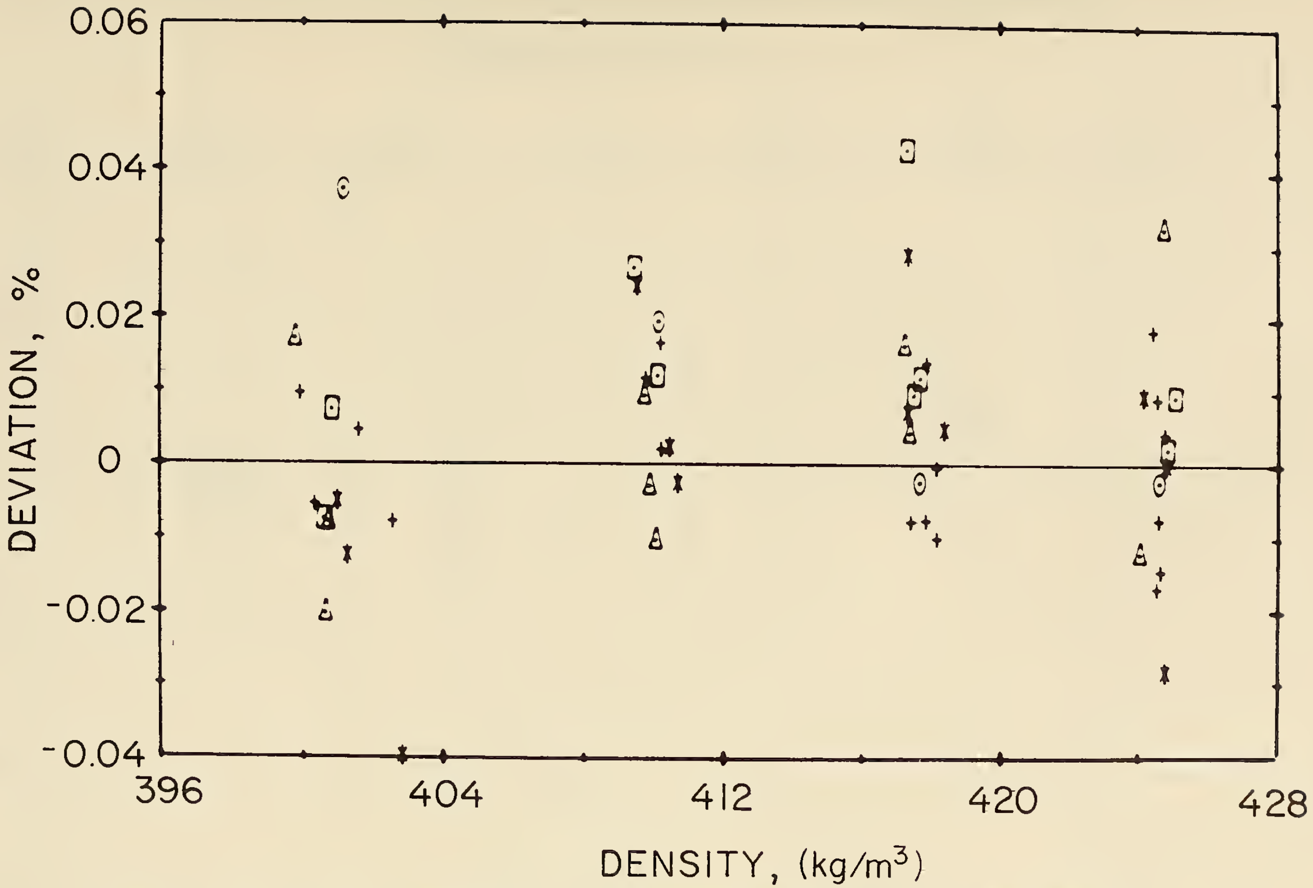

Figure 3. Deviation of the density of liquid methane calculated from temperature using Haynes-Hiza results from the corresponding DRS density as a function of the density. Different symbols identify different fillings.

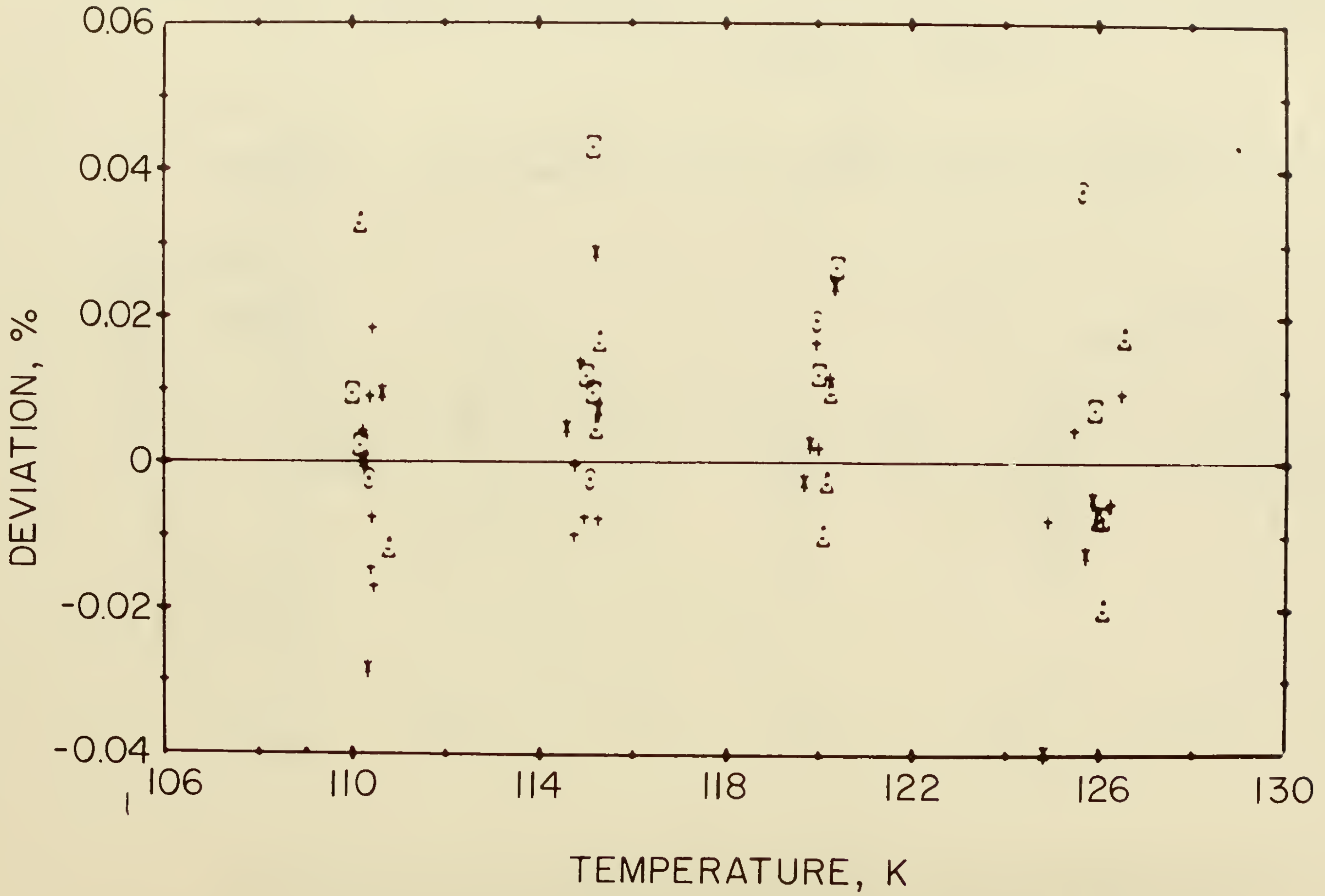

Figure 4. Deviation of the density of liquid methane calculated from temperature using the Haynes-Hiza results from the corresponding DRS density as a function of temperature.

represented by a second order polynomial. Therefore, unless the two functions were identical, their difference would also look like a second degree polynomial—see figure 5. However the differences among the four group means are small enough to be due to the imprecision in the data without having to resort to systematic difference as an explanation. Hence the subscript (T) can be dropped from the $\mu_{(T)}$ in the model and an overall mean μ can be considered. A 99% confidence interval for this systematic difference between the DRS and the Haynes-Hiza determinations is 0.024±0.026 kg/m^3; i.e., not distinguishable from 0 at the 1% significance level.

On the basis of the data, a new model can be written:

$$Y_{(T)ij} - H_{(T)} = \mu + e_{ij} ,$$

where μ is considered to be small, if not zero. The estimated standard deviation (SD) of the $Y_{(T)ij}$ based on this model is 0.065 kg/m^3 for 52 degrees of freedom (d.f.). An upper 99% confidence limit for this value is 0.084 kg/m^3.

Tests were also made with other liquids: Methane plus 1% nitrogen, methane plus 2% nitrogen, LNG, LNG plus 2% nitrogen. The LNG mixture contained 88½% of CH_4, 6½% C_2H_6, 3% C_3H_8 and 2% n-C_4H_{10}. The LNG data covers a density range from 445 to 480 kg/m^3. The method of least squares was used to fit each of these four sets of data as functions of temperature. The estimated deviation obtained from these fits are

liquid	standard deviation (kg/m^3)
C_1 + 1% N_2	.075 (11 d.f.)
C_1 + 2% N_2	.066 (6 d.f.)
LNG	.062 (11 d.f.)
LNG + 2% N_2	.052 (5 d.f.)

These estimated standard deviations are not statistically different from the estimated standard deviation of 0.065 kg/m^3 (52 d.f.) obtained for the pure methane data. An estimate for the standard deviation based on the data for all liquids is 0.065 kg/m^3 (85 d.f.). The estimated systematic error applies to these mixtures also.

A least squares fit of the DRS density to the temperature of the saturated methane resulted in the following equation:

$$D(T) = 533.074 - 0.51138T - 0.0042734T^2 ,$$

where D(T) is the predicted density in kg/m^3 for T in Kelvin. The residual standard deviation was 0.065 kg/m^3 (50d.f.). The range for T was 110 K-126 K. The standard deviation for predicted value of D in this temperature range went from about 0.01 kg/m^3 near the middle to 0.02 kg/m^3 at the ends.

The percentage deviation, 100(H(T) - D(T))/D(T), between the Haynes-Hiza relationship [4] and the one above is shown in Figure 5. A similar comparison is also shown for the above relationship and that determined by Goodwin [3]. In this figure the limits of random error (99% confidence interval) associated with the empirical fit of the DRS data are shown in percent as the shaded area. No systematic errors associated with any of these three methods are included. As can be seen, the percent deviation for the Haynes-Hiza relationship is almost entirely within the shaded area.

3.3 Uncertainty Statement

The use of three times the estimated standard deviation is commonly used in reporting the limits of random error. This derives partly from simplicity and partly from the fact that if the true standard deviation were being used,

$$m_{(T)} \pm 3 \text{ SD}$$

would contain 99.7% (almost all) of the measured $Y_{(T)ij}$, where $m_{(T)}$ is the systematic difference from the true density. Considering $m_{(T)}$ as the percentage systematic error, section 3.1 gives bounds to this value of ±.028%. Transforming the estimated standard deviation of ± 0.065 kg/m^3 to percent at 422.63 kg/m^3, the normal boiling point density of methane, gives a value of ± 0.016%. The sum of 3 x 0.016% plus 0.028% gives the present estimated limit of total uncertainty for a single density measurement made on pure methane with the DRS as ±.076%. This uncertainty is smaller for LNG mixtures because of the increased density.

4. MEASUREMENT PROCESS CONTROL

As future measurements are made, the random errors will be continually checked and the systematic error estimates will be confirmed experimentally or the error source eliminated where possible as described below.

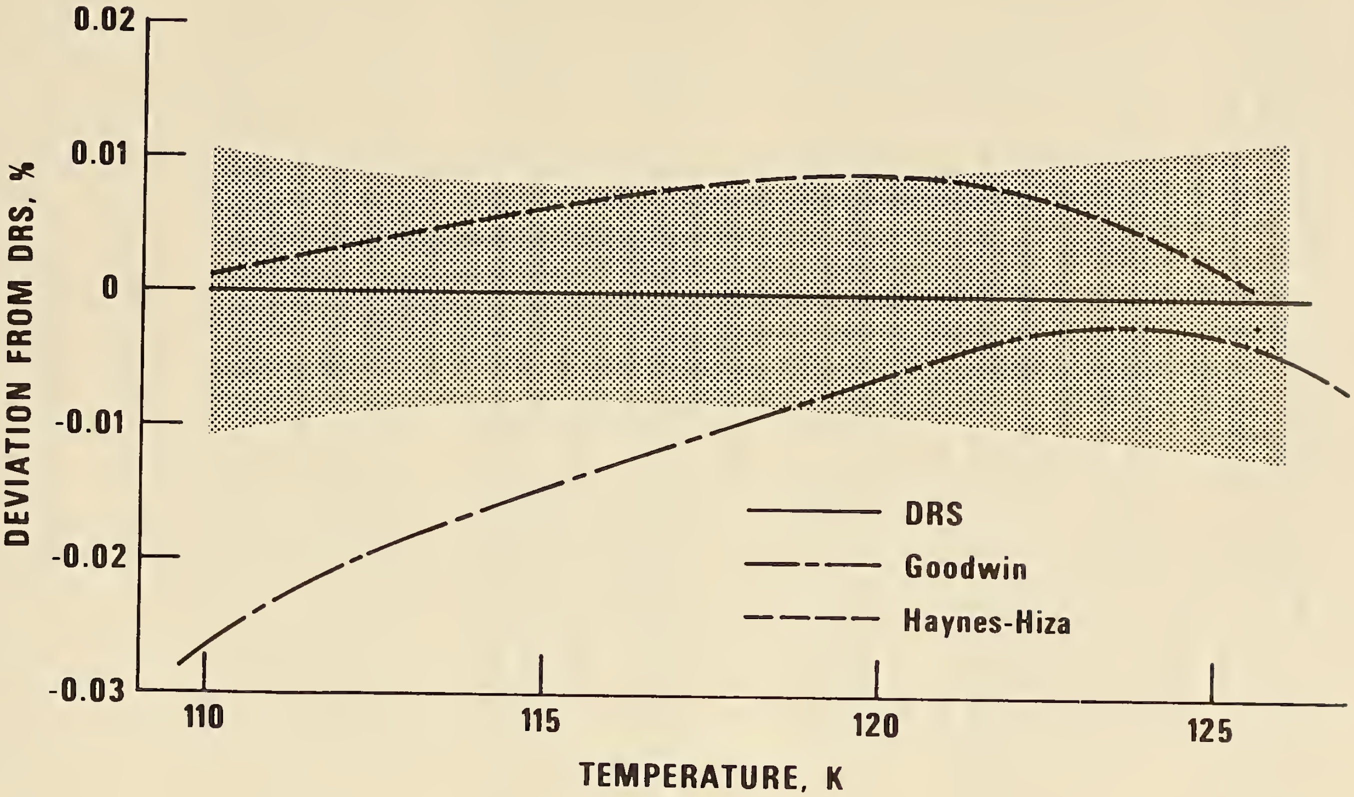

Figure 5. Methane densities along saturation curves from measurements of Haynes and Hiza[4] and from correlations of Goodwin[3] compared to DRS density measurements.

Each time a set of density reference measurements are made using the system, measurements on at least two separate fillings of pure liquid methane will be included in the tests. Density measurements will be made at temperatures around 110 K, 115 K, 120 K and 125 K. These measurements will be made at each temperature in random order. The remeasured methane densities will be compared to the Haynes-Hiza results and to the earlier reference system measurements to determine whether the system has shifted. This reliability of the system will be checked only in conjunction with density comparison work rather than periodically because of the expense of making density measurements.

For these occasions the within standard deviations will be compared statistically to those of previous occasions to test for any change in this measure of precision and the presence of occasion-to-occasion shifts or signs of non-random behavior (e.g., drifting) will be tested. If there are no apparent changes, the data from previous occasions will be combined with the new data to obtain updated estimates. Any statistically verifiable changes in the DRS process will call for corrective action with respect to the process. Revised uncertainty statements will be presented as needed.

5. SUMMARY

The density reference system of the National Bureau of Standards, Cryogenics Division is described. Since the density determination by the DRS is basically a weighing process, the details of calculation of this process are described in detail. The procedure for determining the density from weighing, zeroing and calibrating the balance is discussed.

The uncertainty of the density reference system is ± 0.076%. The contribution from the estimated systematic error in density was ± 0.028%. The estimated uncertainty caused by random error is three times the standard deviation of 0.016% and is based on a hundred measurements of the densities [4] of various cryogenic liquids. The total density uncertainty was taken to be the sum of the systematic and random errors.

6. ACKNOWLEDGEMENTS

The authors wish to especially thank Dr. J. C. Holste who contributed heavily to the construction and start-up of the density reference system. The authors also wish to thank Janet Donaldson of the NBS Statistical Engineering Laboratory for her recommendations on the method of acquiring data from the automatic balance and Milton Loeb for his help with the data analysis.

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8. APPENDICES

8.1. The Change in Volume of the Silicon Crystal from Hydrostatic Compression and Thermal Contraction

The buoyant force of the liquid on the silicon crystal will be reduced by the decrease in volume due to hydrostatic compression. This is described by

$$V = V_o(1 - kP)$$

where V_o is the volume at the reference pressure, in this case about one atmosphere or one bar. P would be the pressure in excess of this and k the compressibility;

$$k = - \frac{1}{V} \left.\frac{\partial V}{\partial P}\right)_T .$$

This correction was found to be negligible since $k = 1.01 \times 10^{-6}$ bar^{-1} and at 110 K and $P \simeq 6$ bar, $\frac{\Delta V}{V} = 6 \times 10^{-6}$. In this case k was computed from silicon data on velocity of sound by McSkimmin [6] using the usual relations for bulk modulus and elastic constant as evaluated from sound velocities.

The change in volume was computed from the thermal contraction of silicon values from Corruccini and Gniewek [7]. We have

$$\frac{L_{298} - L_T}{L_{298}} = 25.5 \times 10^{-5}$$

for the change from 298 K to 100 K. This value is essentially unchanged over the temperature interval 100 K to 140 K.

$$\frac{\Delta V}{V} = 3 \frac{\Delta L}{L} ,$$

$$\rho_s = 232.90 \ (1.000765) \ \text{kg/m}^3$$

$$= 233.08 \ \text{kg/m}^3 .$$

8.2. Silicon Crystal Weighings in Air

Date	Silicon Weight in Air gram	Temperature Celsius	Pressure mm Hg	Silicon Weight in Vacuum gram
01-10-74	127.3947	21	633	127.4335
01-15-74	127.3950	20	631	127.4339
01-27-74	127.3941	20	625	127.4335
02-28-74	127.3945	21	620	127.4334
04-02-74	127.3926	21	628	128.4320
04-05-74	127.3941	20	630	127.4338
10-27-74	127.3930	23	625	127.4319
10-28-75	127.3927	21	620	127.4316
		Average		127.4330

The estimated uncertainty including uncertainties associated with the calibration weights is taken to be ±.002 gm.

8.3. Densities of Single-Crystal Silicon

Densities of Silicon	Temperature	Preparation	Std. Deviation, 1σ
2.328932*	22-27°C	Grown in Vacuum	1 ppm
2.329021*	22-27°C	Grown in Argon	1 ppm
2.32904**	25°C	Not known	± 9 ppm

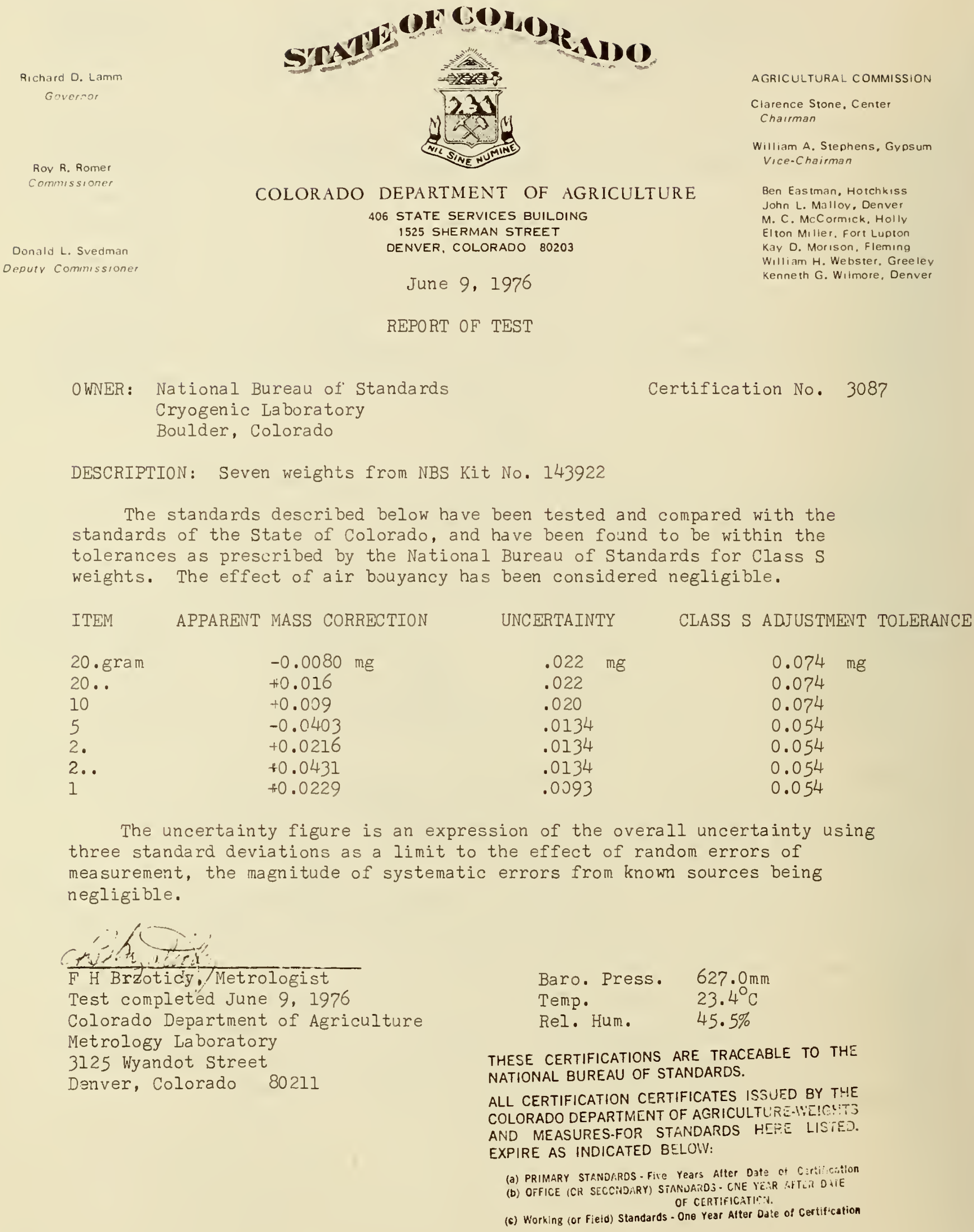
* Each are average of 12 measurements, Bowman, Schoonover, and Jones [1].

** An average of about 75 measurements, Henins and Bearden [2].

Reference density for silicon was taken to be 2.3290 at 25°C.

A 14 g portion of the same crystal was weighted in water and in air. Using average of four weighings in air and water the density computed at 30°C was $\rho = 2.3291$ g/cm^3, as compared to $\rho = 2.3289$ from the above after correction for thermal expansion. This is a difference of about 0.009%. The density used here is 2.3290 gm/cm^3. The uncertainty, taken to be ±0.0007 gm/cm^3, includes the vacuum grown crystal density since the atmosphere in which this crystal was grown is unknown.

8.4. Weight Certificate



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June 9, 1976

REPORT OF TEST

OWNER: National Bureau of Standards
Cryogenic Laboratory
Boulder, Colorado

Certification No. 3087

DESCRIPTION: Seven weights from NBS Kit No. 143922

The standards described below have been tested and compared with the standards of the State of Colorado, and have been found to be within the tolerances as prescribed by the National Bureau of Standards for Class S weights. The effect of air bouyancy has been considered negligible.

ITEM	APPARENT MASS CORRECTION	UNCERTAINTY	CLASS S ADJUSTMENT TOLERANCE
20.gram	-0.0080 mg	.022 mg	0.074 mg
20..	+0.016	.022	0.074
10	+0.009	.020	0.074
5	-0.0403	.0134	0.054
2.	+0.0216	.0134	0.054
2..	+0.0431	.0134	0.054
1	+0.0229	.0093	0.054

The uncertainty figure is an expression of the overall uncertainty using three standard deviations as a limit to the effect of random errors of measurement, the magnitude of systematic errors from known sources being negligible.

F H Brzoticy, Metrologist
Test completed June 9, 1976
Colorado Department of Agriculture
Metrology Laboratory
3125 Wyandot Street
Denver, Colorado 80211

Baro. Press. 627.0mm
Temp. 23.4°C
Rel. Hum. 45.5%

THESE CERTIFICATIONS ARE TRACEABLE TO THE NATIONAL BUREAU OF STANDARDS.

ALL CERTIFICATION CERTIFICATES ISSUED BY THE COLORADO DEPARTMENT OF AGRICULTURE-WEIGHTS AND MEASURES-FOR STANDARDS HERE LISTED. EXPIRE AS INDICATED BELOW:

(a) PRIMARY STANDARDS - Five Years After Date of Certification
(b) OFFICE (OR SECONDARY) STANDARDS - ONE YEAR AFTER DATE OF CERTIFICATION.
(c) Working (or Field) Standards - One Year After Date of Certification

8.5. Linearity Check of the Balance

The linearity of the balance was verified by weighing 1, 2, 2, 5, 10, and 20 g class S weights (see weight certificate in appendix 8.4) in combinations to produce weights of 1, 2, 3, 4, 5, 6, . . .20 g in a random order. These weighings were analyzed by the Statistical Engineering Laboratory of NBS.

Their interpretation was that the residual standard deviation is 0.0009 g based on 36 degrees of freedom. The linearity coefficient was 1.00014.

A summary of these measurements is shown below.

Weight (g)	Balance Reading (g)	Predicted Reading (g)	Standard Deviation of predicted Values (g x 10^3)
3.9996	3.9995	3.9997	.27
15.9981	16.0015	15.9998	.19
10.9987	11.0005	10.9997	.14
1.9998	2.000	1.9996	.25
6.9992	6.999	6.9997	.16
.9999	0.999	0.9996	.27
8.9990	8.9995	8.9997	.14
17.9979	18.001	17.9999	.23
8.9990	9.000	8.9998	.14
18.9978	18.999	18.9999	.25
10.9987	11.000	10.9997	.14
11.9986	12.0005	11.9998	.14
14.9982	15.0015	14.9998	.18
19.9976	20.0005	19.9999	.27
3.9996	4.000	3.9997	.21
12.9985	12.999	12.9998	.15
4.9994	5.000	4.9996	.19
12.9985	12.9995	12.9998	.15
.9999	1.000	.9996	.27
11.9986	11.999	11.9998	.14
18.9978	19.001	18.9999	.25
13.9984	14.000	13.9999	.16
19.9976	19.998	19.9999	.27

Weight (g)	Balance Reading (g)	Predicted Reading (g)	Standard Deviation of predicted Values (g x 10^3)
17.9979	17.998	17.9999	.23
7.9991	8.000	7.9997	.15
15.9981	16.001	15.9998	.19
1.9998	2.000	1.9996	.25
5.9993	5.999	5.9996	.18
9.9988	10.000	9.9997	.14
14.9982	15.000	14.9998	.18
6.9992	6.9995	6.9997	.16
2.9997	2.9995	2.9996	.23
16.9980	17.0005	16.9999	.21
5.9993	5.999	5.9996	.18
2.9997	2.9995	2.9996	.23
9.9988	10.0005	9.9997	.14
16.9980	16.999	16.9999	.21
7.9991	7.999	7.9997	.15
13.9984	13.998	13.9999	.16
4.9994	4.9995	4.9996	.19

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The density reference system of the Cryogenics Division of the National Bureau of Standards is described. This system is used in making density measurements of cryogenic liquids. The methods of computation and the accuracy to which the density of the liquid can be measured are discussed in detail.

At this time the estimate of sample standard deviation for a single density measurement made using this system is 0.016% (at 422.63 kg/m^3). Using three times thi standard deviation as a limit for random error and using 0.028% as the bound for know sources of possible systematic error, the uncertainty of a single determination with this system is $\pm$ 0.076%. This statement of accuracy applies for the density range 400 to 480 kg/m^3, pressures from 0 to 3 bar, and temperatures from 110 K to 125 K. Because of the densimeter design, this accuracy statement is expected to apply to the density range from 400 to 1000 kg/m^3 and to the temperature range of 77 to 300 K at least, and to pressures of 7 bar, though these ranges of application have yet to be verified.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Densimeters; density reference system; liquid methane; LNG.

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