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CRYOGENIC FLUIDS DENSITY REFERENCE SYSTEM: PROVISIONAL ACCURACY STATEMENT
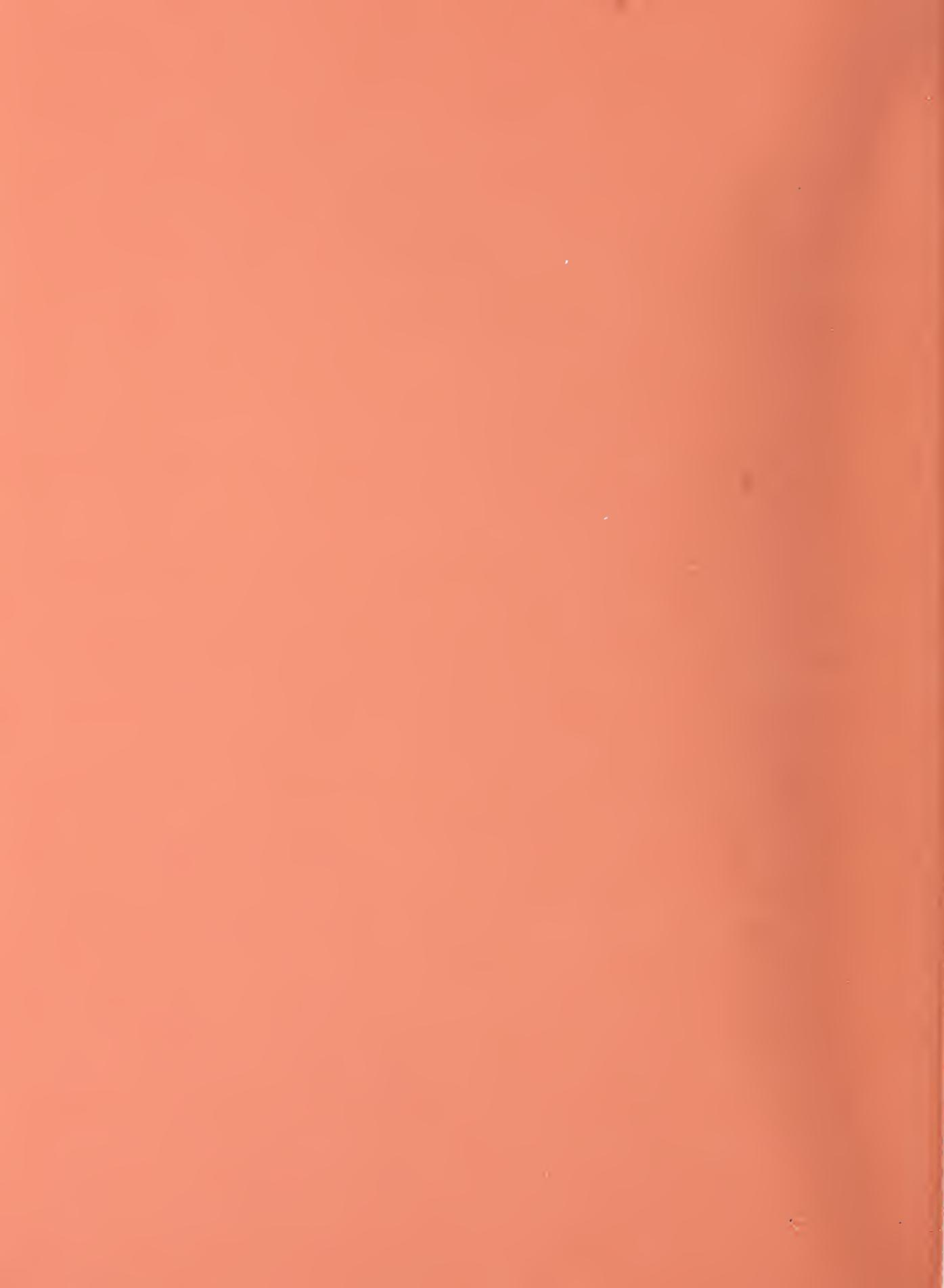
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January 1977

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B. A. Younglove and J. D. Siegwarth

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The measurement capability of the density reference system (DRS) of the National Bureau of Standards, Cryogenics Division, is described. This system measures density, pressure, and temperature of LNG mixtures for the purpose of testing densimeters which are contained in the liquid sample. Sample composition is determined by weighing the gas samples separately before condensing them into the sample. The DRS measures density by weighing a single-crystal of silicon immersed in the LNG mixture. This process is described and the equations used in the computation of density are discussed.

At this time the estimate of sample standard deviation for a single density measurement made on this system is $\pm$ 0.062% (at 0.4 g/cc). Using three times this standard deviation as a limit for random error and adding $\pm$ 0.026% as an upper bound for known sources of possible systematic error, the uncertainty of a single determination by this system is $\pm$ 0.21%. This statement of accuracy applies for the density range 380 to 430 kg/m^3 and 1200 to 1400 kg/m^3, pressures to 7 bar, and temperatures from 80 K to 140 K. This statement is expected to be correct in the intermediate density range and for all temperatures up to 300 K.

Measurement uncertainties for temperature, pressure, and composition are discussed. Comparison of measurements for liquid argon densities with the results of other laboratories is given.

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 we covered densities of 390-500 kg/m^3, a range normally found in LNG work. Some additional density measurements were made on liquid argon. Only methane density measurements were used in the determination of the system uncertainty.

At this time the value of the sample standard deviation for a single density measurement made on this system is $\pm$ 0.062% (at 0.4 g/cc), based on measurements made using samples of liquid methane (99.97%). Using three

times the standard deviation as a limit for the random error, and adding 0.026% as an upper bound for known sources of possible systematic error, the uncertainty of a single determination by this system is $\pm$ 0.21%.

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 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, reasonably 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 a 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_{ak}	apparent mass as read by balance during calibration
M_{ao}	apparent mass as read by balance for zero mass load
M_b	buoy mass, silicon crystal + tungsten wire + stainless steel wire immersed in liquid
M_{bg}	apparent mass of buoy in gas
$M_{b\ell}$	apparent mass of buoy in liquid
M_c	counterweight mass
M_{cg}	apparent mass of counterweight in gas
M_h	hanger mass
M_{hg}	apparent mass of hanger in gas
M_k	calibration mass
M_{kg}	apparent mass of calibration mass in gas
M_r	range mass
M_{rg}	apparent mass of range mass in gas

M_s	silicon crystal mass
M_w	replacement mass standard used to evaluate zero of balance
M_{wg}	apparent mass of replacement mass in gas
M_1	hanger mass, brass part
M_2	hanger mass, stainless steel wire part
M_3	hanger mass, stainless steel wire, that part of M_2 located in liquid
M_4	hanger mass, tungsten wire part
P	system pressure
T	system temperature
V	volume of buoy
V_s	volume of silicon
ΔMa	apparent mass less zero mass reading of DRS balance
δ	density difference between DRS density and a reference density
ε	density variation in δ from the average value of δ, for a methane sample
η	density variation in δ from a methane sample to an average methane sample
ρ	density of liquid sample
ρ_g	density of gas (vapor phase in equilibrium with sample liquid)
ρ_h	density of reference methane liquid
ρ_s	density of silicon
ρ_1	density of brass
ρ_2	density of stainless steel
ρ_4	density of tungsten
σ	standard deviation
σ_ε	standard deviation of ε
σ_η	standard deviation of η
μ	density difference bias

2. DESCRIPTION OF THE BASIC MEASUREMENT PROCESS

2.1. Density

The density reference system determines density via the Archimedes principle, which is that a body submerged wholly or partially in a liquid is buoyed by a force equal to the weight of the fluid displaced. The net force on the object is the difference between its weight and the buoyant force.

The basic arrangement of the silicon crystal, the weighing balance, and sample holder can be seen in figure 1. Figures 2 and 3 are photographs of the partially disassembled reference system. 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 more elaborate and is developed in the following sections.

Density from actual readings using a balance.

In practice we measure density using an automatic balance. This balance uses magnetic force to achieve balance. It has the advantage of speed and convenience of operation. On one side of the balance we have a movable counterweight M_c which can be initially adjusted to put the system in balance. Ordinarily one would adjust its moment arm to precisely balance the system. Here we leave a slight unbalance so that the automatic system will always react in one direction initially. For purpose of clarity we take the small initial unbalance of the system as being M_c, however this will subtract out subsequently as seen below. The force generated by the magnetic balancing system is considered to be an equivalant mass M_a (or apparent mass), and is the reading of the automatic balance. Here we have

$$M_a + M_{cg} = M_{rg} + M_{hg} + M_{b\ell}. \tag{5}$$

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CRYOGENIC FLUIDS DENSITY REFERENCE SYSTEM

Automatic Balance

Vent

Silicon Crystal

Sample

Sample Holder

Test Densimeters

Sample Fill Line
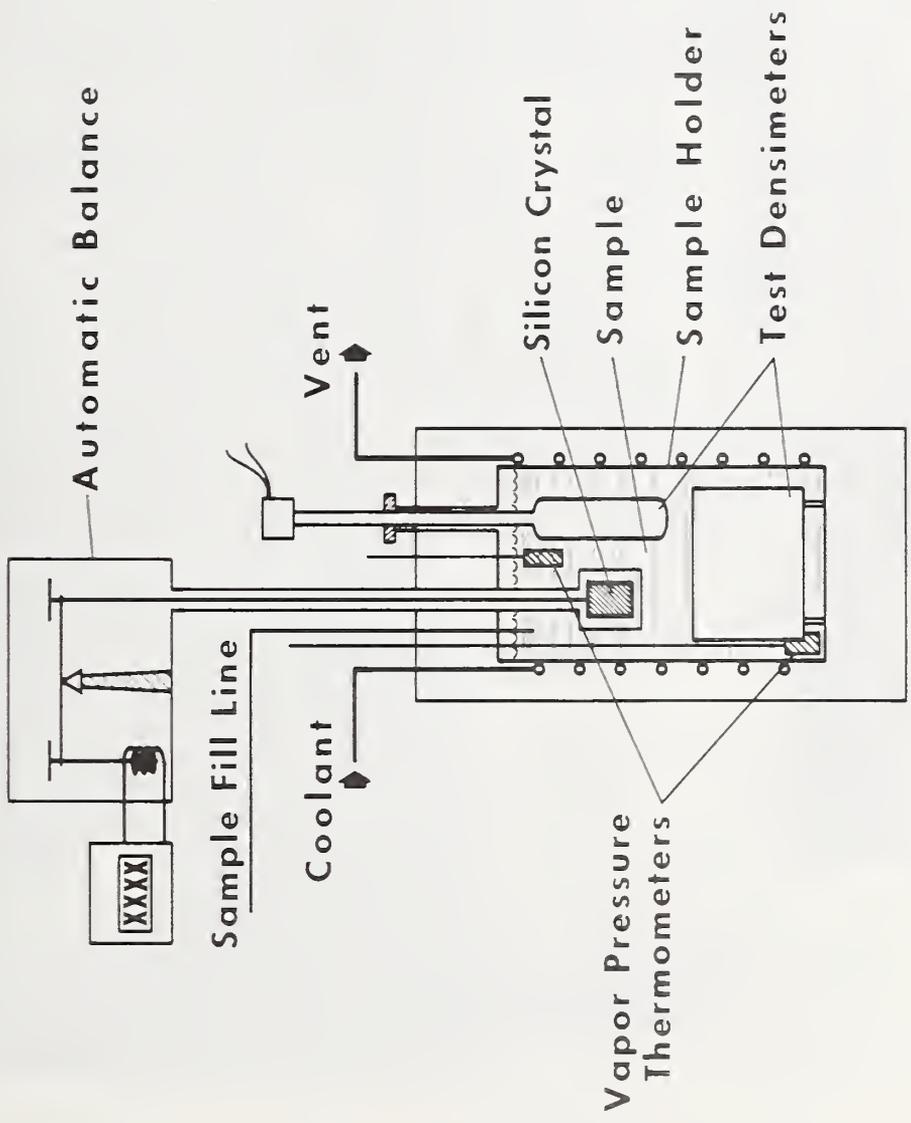
Coolant

Vapor Pressure
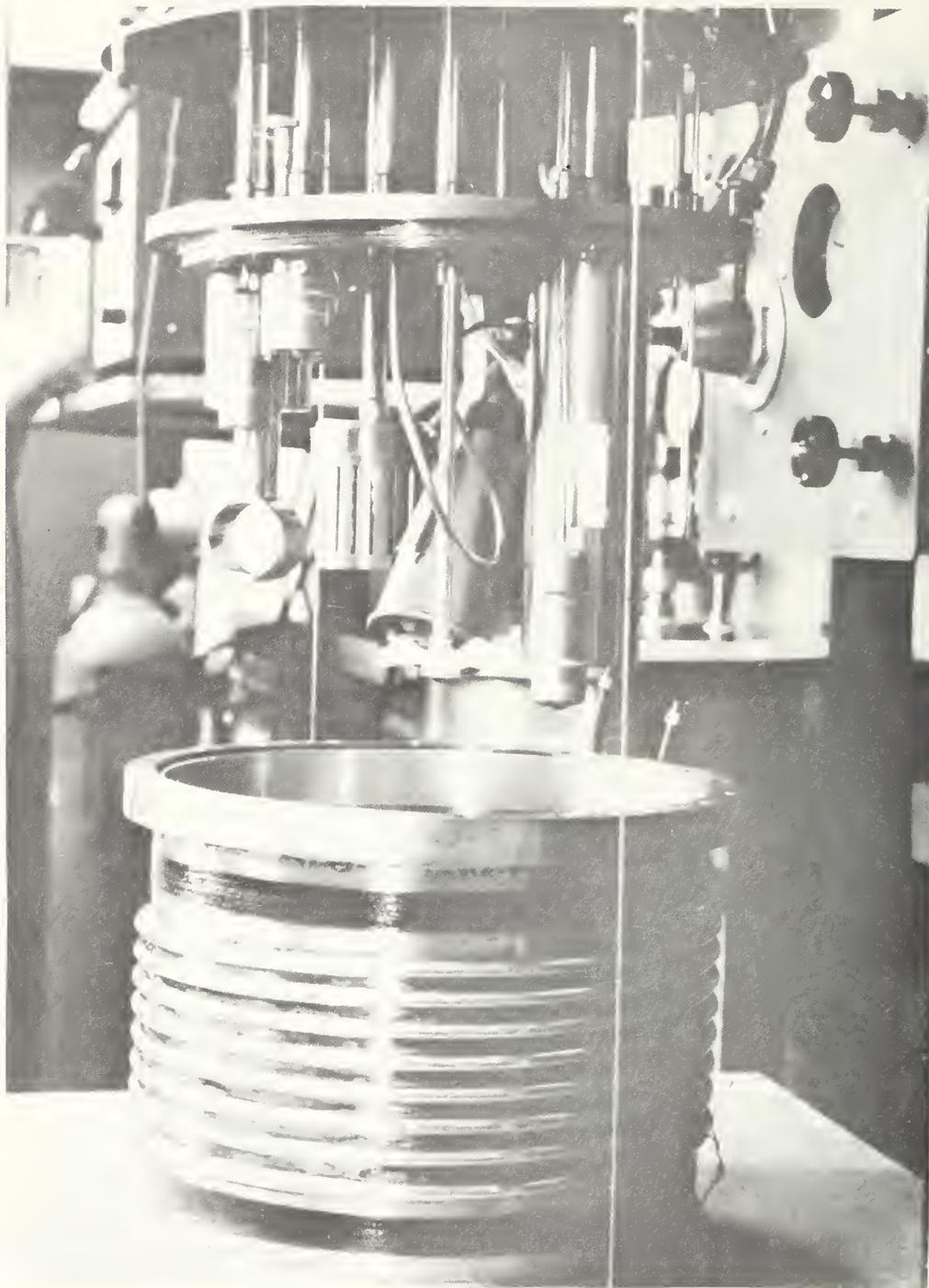Thermometers

XXXX

Figure 1.

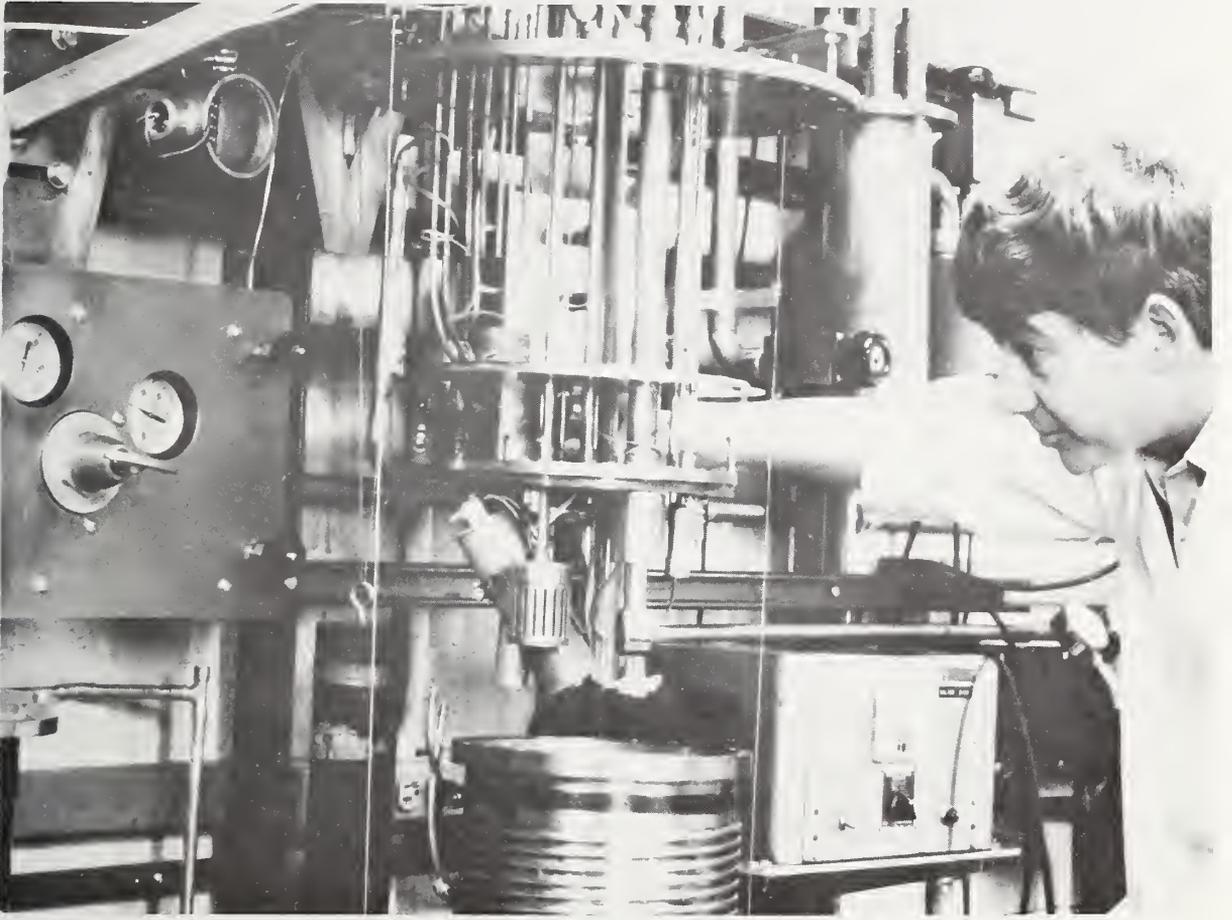Figure 2.   Density Reference System showing small sample holder.

Figure 3. Partially disassembled Density Reference System.

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Notice that M_c is now M_{cg}, as we have a buoyant effect of the gas pushing upwards on the masses in the gas.

The value of M_r was chosen for a given M_h and M_s to be large enough to give a reading on-scale (0 to 20 grams) for the automatic balance for the range of densities of LNG under consideration. When more dense liquids were measured, for example liquid argon, a heavier range weight was used.

Zeroing the balance.

Experience with the balance showed that the zero would change although the calibration did not. In order to zero the balance the silicon crystal and its wire hanger and brass support piece were lifted off manually via a mechanical contrivance that could be operated outside the enclosure through a sliding vacuum seal.

This decrease in weight was compensated for by placing the weight M_w on the balance pan, again with a mechanical device such that

$$M_{ao} + M_{cg} = M_{rg} + M_{wg} \tag{6}$$

where M_{ao} is the zero reading of the balance. Here the range weight is still on the pan as before. Since this measurement occurs just before the measurement described by equation (5) then we may subtract out M_{cg} and M_{rg} giving

$$M_a - M_{ao} = M_{hg} + M_{b\ell} - M_{wg}$$

or

$$\Delta M_a = M_{hg} + M_{b\ell} - M_{wg}. \tag{7}$$

Calibration of the balance.

The linearity was verified using a procedure recommmended by the Statistical Engineering Laboratory of NBS. See appendix 8.5. A continual check of the calibration was performed using a 10 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 precise method of placing this weight onto the balance pan.

The calibration was checked under the zero check procedure. Immediately after checking the zero, as described by equation (6), the calibration weight, M_k, was placed on the balance pan so that the apparent mass (the M_{ao} in equation (6)) is now M_{ak},

$$M_{ak} + M_{cg} = M_{rg} + M_{wg} + M_{kg}. \tag{7a}$$

Subtracting equation (6) from (7a),

$$M_{ak} - M_{ao} = M_{kg}. \tag{7b}$$

As long as equation (7b) holds, no adjustment was needed for the balance. In practice it was found that adjustment of the balance was rarely needed.

The measurement equation.

As in equation (4), the final measurement equation can be put in the form

$$\rho = \rho_s (1 - f(M_1, M_2, \ldots \rho_1, \rho_2 \ldots)) \tag{8}$$

where the independent variables are all known. In actual practice the hanger M_h, consisted of a brass part (M_1, ρ_1) and a stainless steel wire suspended from this brass hanger (M_2, ρ_2). However, part of the stainless steel wire was immersed in the liquid. The part in the gas is $M_2 - M_3$ and the part in the liquid is M_3. Therefore,

$$M_h = M_1 + M_2 - M_3 \tag{9}$$

and,

$$M_{hg} = (M_1 + M_2 - M_3) - \rho_g \left(\frac{M_1}{\rho_1} + \frac{M_2 - M_3}{\rho_2} \right) . \tag{10}$$

Also the mass M_b breaks down into

$$M_b = M_s + M_3 + M_4,$$

where M_4 is a short length of tungsten wire (M_4, ρ_4) wrapped around the silicon crystal (M_b, ρ_s) so we have

$$M_{b\ell} = M_s + M_3 + M_4 - \rho \left(\frac{M_s}{\rho_s} + \frac{M_3}{\rho_2} + \frac{M_4}{\rho_4} \right) . \tag{11}$$

Putting these relations into equation (7)

$$\Delta M_a = M_1 + M_2 - M_3 - \rho_g \left(\frac{M_1}{\rho_1} + \frac{M_2 - M_3}{\rho_2} \right)$$

$$+ M_s + M_3 + M_4 - \rho \left(\frac{M_s}{\rho_s} + \frac{M_3}{\rho_2} + \frac{M_4}{\rho_4} \right) - M_w + \rho_g \frac{M_w}{\rho_1} \tag{12}$$

$$\rho = \frac{M_s + M_1 + M_2 + M_4 - M_w - \Delta M_a - \rho_g [(M_1 - M_w)/\rho_1 + (M_2 - M_3)/\rho_2]}{(M_s/\rho_s + M_3/\rho_2 + M_4/\rho_4)} \tag{13}$$

the form of equation (8) may be obtained by factoring out ρ_s and M_b to obtain

$$\rho = \rho_s \frac{1 + \dfrac{M_1 + M_2 + M_4 - M_w - \Delta M_a}{M_s} - \dfrac{\rho_g}{M_s} [(M_1 - M_w)/\rho_1 + (M_2 - M_3)/\rho_2]}{\left(1 + \dfrac{M_3}{M_s} \dfrac{\rho_s}{\rho_2} + \dfrac{M_4}{M_s} \dfrac{\rho_s}{\rho_4} \right)} . \tag{14}$$

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The following are the measured values of the masses used in equation (13). Literature values of the densities were used, the possible effect this could have on measurement accuracy is discussed below.

M_s = 127.4330 g, ρ_s = 2.33078 g/cm^3 the silicon crystal.

M_1 = 4.2441 g, ρ_1 = 8.5 g/cm^3 the brass hanger.

M_2 = 0.2121 g, ρ_2 = 7.9 g/cm^3 the stainless steel suspension wire.

M_3 = 0.026 g   stainless steel suspension wire submerged in liquid.

M_4 = 0.055 g, ρ_4 = 18.8 g/cm^3 the tungsten wire tied about the silicon crystal.

M_w = 100.9296 g   the brass replacement weight.

The denominator of equation (13), $M_s/\rho_s + M_3/\rho_2 + M_4/\rho_4$ is the total volume of the submerged material. From the above it is

$$V = 54.674 + 0.00329 + 0.00293 \text{ cm}^3$$

$$V = 54.680 \text{ cm}^3.$$

The total equation (13) becomes

$$\rho = \frac{31.0146 - \Delta M_a + \rho_g (11.351)}{54.6802} \text{ g/cm}^3 .$$

The value for the silicon mass is an average of several weighings in air, corrected to weight in vacuum. (See appendix 8.2, page 23).

The density of silicon 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).

2.2. Pressure

The system pressure was measured using a quartz-spiral bourdon tube. During the first series of measurements (data taken before December 1975), the system used a 500 psi* gage, the data after that used a 200 psi gage. The calibration of all pressure gages used was checked at this laboratory using an air-dead weight gage, which is accurate to 0.015%, with the accuracy traceable to NBS. Pressure uncertainty was found to be within the 0.015% of full scale pressure specified by the manufacturer.

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 about 5 cm^3 of liquid methane. Pressure

* 1 psi = 6.895 k Pa.

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communicates from the thermometers to a quartz-spiral bourdon tube (100 psi maximum) via 1/16" O.D. stainless capillary tubing. The temperature range was 100 K to 140 K. Sensitivity and precision of this device is the same as specified for the gages in section 2.2. This pressure uncertainty is equivalent to 0.03 K at 100 K and 0.003 K at 140 K for the 100 psi gage used to measure vapor pressure.

Temperature gradients as measured by the vapor pressure thermometers were generally 0.030 K and on rare occasions approached 0.3 K. The density difference resulting from this temperature difference can be calculated by using methane properties [3,4]. Here we can use the dimensionless derivative $d\ln\rho/d\ln T$ at saturation:

Average System Temperature	$d\ln\rho/d\ln T$	$\frac{\Delta\rho}{\rho}$ for $\Delta T = 0.03$ K
110 K	0.38	0.0038%
140 K	0.26	0.0026%

In the worst instance the difference was only 0.04%. The densimeters under test were actually physically closer to the DRS density probe (the silicon crystal) than were the two vapor pressure thermometers, implying a lower density difference.

2.4. Composition

When mixtures were used for the density measurements, the compositions (mole fractions) were determined by accurate measurement of the mass of the separate constituents and subsequently applying corrections for the effect of gas phase to the total system composition to obtain liquid phase compositions.

The samples were weighed in metal cylinders. After transfer to the DRS cryostat, the cylinders were again weighed and the amount transferred computed from the difference.

The balance used for this purpose is a high-resolution and high-capacity balance (resolution better than 0.01 g, with maximum capacity of 20 kg). Class S weights were used (see appendix 8.4).

Upon condensation in the cryostat the sample separates into a liquid and gas phase. The volume of the gas phase was two to four times the volume of the liquid. The large volume of the gas phase was required to house the automatic balance used in weighing the silicon crystal which measured the liquid density.

The composition of the liquid phase was calculated from the total composition by subtracting the amount of the vapor phase. The total composition is that computed from the amounts of sample gas transferred into the system. If the composition of the gas and liquid phase were the same, then the liquid composition would be the same as the total composition.

For mixtures of methane with ethane, propane and butane the vapor phase was assumed to be methane. The vapor phase densities in the balance volume sample chamber and interconnecting tube are computed from a virial equation of state [3] using the system pressure and temperatures. The calculated quantities of methane are then subtracted from the total amount of methane in the system and the result is used to compute the liquid phase composition.

For mixtures with nitrogen, the vapor phase is assumed to be methane and nitrogen. The densities of the vapor phase were computed from a mixture virial equation which included terms to the second virial coefficient. Since this equation used the mixture second virial coefficient, it was computed from the second virial coefficients of the pure components and the interaction second virial coefficient for the mixture, as well as the vapor phase compositions. The vapor phase compositions were estimated from phase-equilibria data for methane-nitrogen of this laboratory [5] using enhancement factors. The resulting computation of vapor densities allows a first estimate of the amount of nitrogen and methane in the vapor phase. From this, a corresponding first estimate of the liquid phase composition is made. The estimate is improved by iterating the computation using the results of the preceding evaluation.

In the instance of a binary mixture the composition could be computed from another approach. Dielectric constant density measurements of the liquid and with the assumption that the polarizability of the methane-nitrogen mixture could be computed from ideal mixing, allows one to compute the mole fraction of the binary mixture. Agreement between the calculation described in the above paragraphs and the dielectric constant calculation was found to be about 0.2 to 0.4 mole percent when the nitrogen composition was less than 2 mole percent.

Because of the additional uncertainties of mixtures discussed above, only pure methane results were used in the random error determination.

3. MEASUREMENT PROCESS PARAMETERS

3.1. Bounds for Systematic Errors

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

However, until experimental evidence of the actual effect is obtained by introducing an offset in these factors, both singly and jointly, this analysis is just that, an estimate of undemonstrated validity.

Equation (13), the measurement equation, has the density ρ as a function of several independent variables.

$$\rho \;=\; \rho(M_s, M_1, M_2, M_3, M_4, M_w, \Delta M_a, \rho_s, \rho_1, \rho_2, \rho_4) \;. \tag{15}$$

The uncertainty in ρ, arising from uncertainty in ρ_s, for example, can be evaluated from

$$\delta\rho \;=\; \frac{\delta\rho}{\delta\rho_s}\,\delta\rho_s \tag{16}$$

or as a dimensionless ratio,

$$\frac{\delta\rho}{\rho} \;=\; \frac{\partial\ln\rho}{\partial\ln\rho_s}\,\frac{\delta\rho_s}{\rho_s}\;, \tag{17}$$

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

$$\frac{\delta\rho}{\rho} \;=\; \sum\left[\left(\frac{\partial\ln\rho}{\partial\ln x_i}\,\frac{\delta x_i}{x_i}\right)^2\right]^{1/2}\;. \tag{18}$$

This is the propagation of error relationship for systematic error [6] when the variables are independent and the magnitudes of the relative errors are small so that second order terms are negligible.

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. 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 is required for bouyancy corrections, contains all gas pressure, temperature and composition uncertainties and is the leading systematic error for mixtures containing LN_2. The uncertainties 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

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being compared. When density measurements are being compared with those of
other workers, however, there is an 0.01% maximum contribution to the systematic
error at the lowest temperature that decreases to less than 0.001% at the
highest temperatures.

Table 1. Systematic errors.

Variable, x	$\partial\ell\rho/\partial\ell nx$		$\delta x/x$	$\delta\rho/\rho$ in %
silicon crystal mass	$(\rho_s - \rho)M_s/\rho\rho_s V$ 3.9		1.6×10^{-5}	± 0.0062
brass hanger mass	$(\rho_1 - \rho_g)M_1/\rho\rho_1 V$..1.8 $\times 10^{-1}$		2.4×10^{-4}	± 0.0043
steel wire mass	$(\rho_2 - \rho_g)M_2/\rho\rho_2 V$..8.9 $\times 10^{-4}$		4.7×10^{-3}	± 0.00042
steel wire mass in liquid	$(\rho - \rho_g)M_3/\rho\rho_2 V$...6.0 $\times 10^{-5}$		3.8×10^{-4}	--
tungsten wire mass	$(\rho_4 - \rho_g)M_4/\rho\rho_4 V$..5.4 $\times 10^{-5}$		1.8×10^{-2}	--
apparent mass	$\Delta M_a/\rho V$.....................		1.0×10^{-4}	± 0.010
silicon density	$M_s/\rho_s V$.....................		1.6×10^{-5}	± 0.0016
metal densities	$(M_1 - M_w)\rho_g/\rho_1\rho V$..2.0 $\times 10^{-3}$		2.3×10^{-2}	± 0.0046
gas density	$\rho_g((M_1 - M_w)/\rho_1 +$			
	$(M_2 - M_3)/\rho_2)/\rho V$..2.2 $\times 10^{-3}$		$1.0 \times 10^{-1*}$	± 0.022
temperature gradient	$d\ell n\rho/d\ell nT$........3.8 $\times 10^{-1}$		1.0×10^{-4}	± 0.0038

Total, from equation (18) ... $\pm$ 0.026%.

*The large uncertainty for gas density results from the large uncertainty of
the methane-nitrogen vapor densities. The uncertainty due to gas density is
only 0.002% for methane and the total from equation (18) is $\pm$ 0.014%.

Some of the systematic errors listed above will be eliminated in
future measurements. By moving the point the silicon float disconnects
from the balance down into the liquid such that the float disconnects from
all suspension hardware, all systematic errors associated with the brass
hanger and the steel and tungsten hanger wires will be eliminated. The un-
certainty of the silicon mass was determined from the uncertainty of the
measuring weights and the density uncertainty comes from literature values
of the density. The uncertainty in apparent mass is due to the balance and
has been determined experimentally (see appendix 8.2). The temperature
gradient was measured to determine that uncertainty. Only the uncertainty
due to the density of the replacement weight and the gas density correction
has yet to be examined experimentally. This can be done by using a more
dense mass for the replacement weight. However, any effect due to changing

this weight should be very small compared to the random error. If any change in the estimated systematic error is warranted after experimentally checking for replacement weight buoyancy effects, this correction will be made in the updated uncertainty statements.

3.2. Random Error from Measurements on Methane

The random error of the density reference system was determined experimentally by measurements on liquid methane.

Density measurements on pure methane 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 densities as described.

The present estimates of the precision for density determinations made using the DRS are based on measurements of the density of eight different samples (fillings) of liquid methane. For the eight samples there was a total of seventy-one density measurements of saturated methane in the temperature range 100 K to 140 K -- for the last four samples the temperatures were 110 K, 125 K, and 140 K.

The model used to analyze the methane data is

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

where $y_{(T)ij}$ is the jth density determination by the DRS on the ith methane sample for temperature T; $H_{(T)}$ is the corresponding density value derived from the Haynes-Hiza relationship, $\mu_{(T)}$ represents the long term relative bias, α_i is the random contribution to all measurements made using the ith sample, and e_{ij} is the random contribution to the jth measurement made on the ith sample. The standard deviation (SD) for the α_i is called the between sample SD, and the SD for the e_{ij} is called the within sample SD. The SD of measurements $y_{(T)ij}$ is the square root of the sum of the squares of these two SD.

There were seventy-one least squares estimates of the e_{ij} for the liquid methane measurements. The variability among the estimate samples -- the last twenty-two, e.g. -- is less than among the preceeding forty-nine. The point estimate for the within SD for the first six samples is $\pm$ 0.074% (using 400 kg/m^3 as reference) and that for the last two is $\pm$ 0.034%. The corresponding 99% confidence intervals are (0.057, 0.101) and (0.024, 0.055). This change in variability is attributed to the cleaning of the knife edges on the DRS's balance. The point estimate for the between samples SD for the eight samples is $\pm$ 0.052%, a 99% confidence interval is (0.029, 0.13). The cleaning of the knife edges has not effected this component of the variability. The estimated SD for a single measurement made on the DRS

previous to the cleaning of the balance is ± 0.090%. For measurements made after that time the SD is estimated to be ± 0.062%.

Only the within SD's after the knife edges were cleaned are taken to correctly reflect the precision of the within sample density measurements. A comparison of these data with the Haynes-Hiza densities is shown in Figure 4 as well as a comparison to the work of Goodwin [3].

For the methane data the DRS measurements of density shows a bias with the Haynes-Hiza relationship which is a linear function of density. For a density of 0.38 g/cc the bias is -0.062% with an estimated SD of 0.021%; a 99% confidence interval is (-0.12%, -0.006%). For a density of 0.43 g/cc the bias is -0.11% with an estimated SD of 0.018%; a 99% confidence interval is (-0.16%, -0.062%).

Figure 5 shows a comparison of densities for two samples of liquid argon as measured by the density reference system to those measured by the Haynes-Hiza apparatus, as well as other laboratories as indicated in the caption. As can be seen in this figure, the agreement with Haynes and Hiza is generally within 0.1%.

3.3. Uncertainty Statement

While the use of three times the estimated SD is commonly used in reporting the limits of random error, because of the small number of observations (eight) relating to the sample-to-sample error, the limits using 3 x 0.062% will provide a 98% confidence interval rather than one of 99%. When the samples of liquid methane measured by the DRS exceed fifteen, the use of the factor 3 will give confidence intervals of better than 99%. The limit of possible sources of systematic error has been judged to be ± 0.026% (see section 3). This systematic limit of 0.026% plus 3 x 0.062% gives the present estimated limit of total uncertainty for a single density measurement made on the DRS as ± 0.21%.

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.

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, 125 K, 130 K and 140 K. Three measurements will be made at each temperature in random order. The remeasured methane densities can 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

16
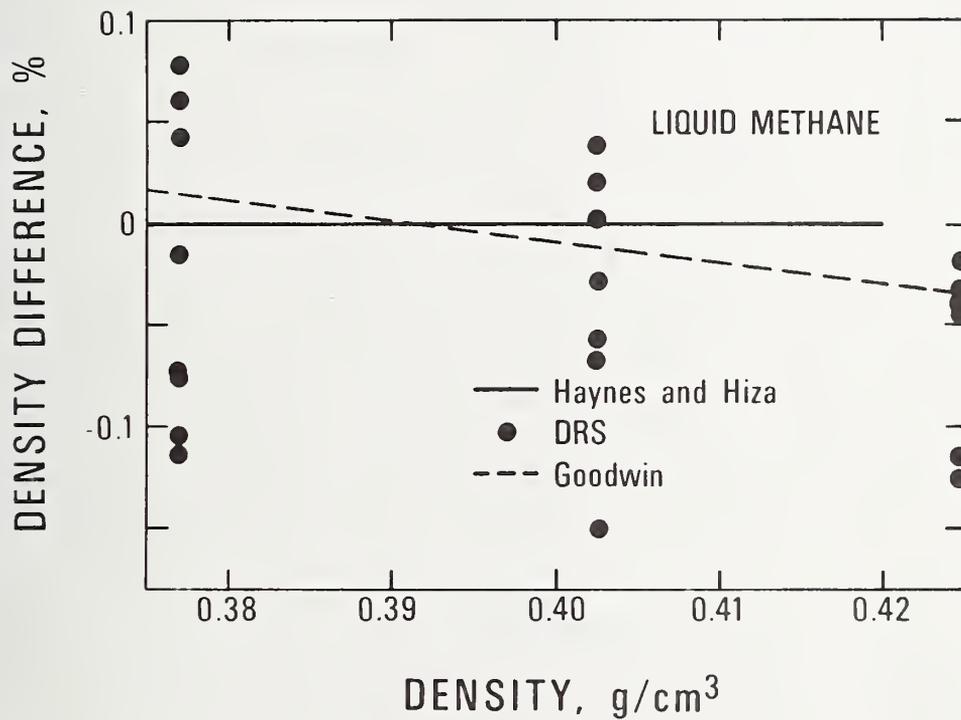
Figure 4. Liquid methane density results of this work relative to the work of Haynes, et al.[4]. The data are the 22 points taken after the knife edges were cleaned.
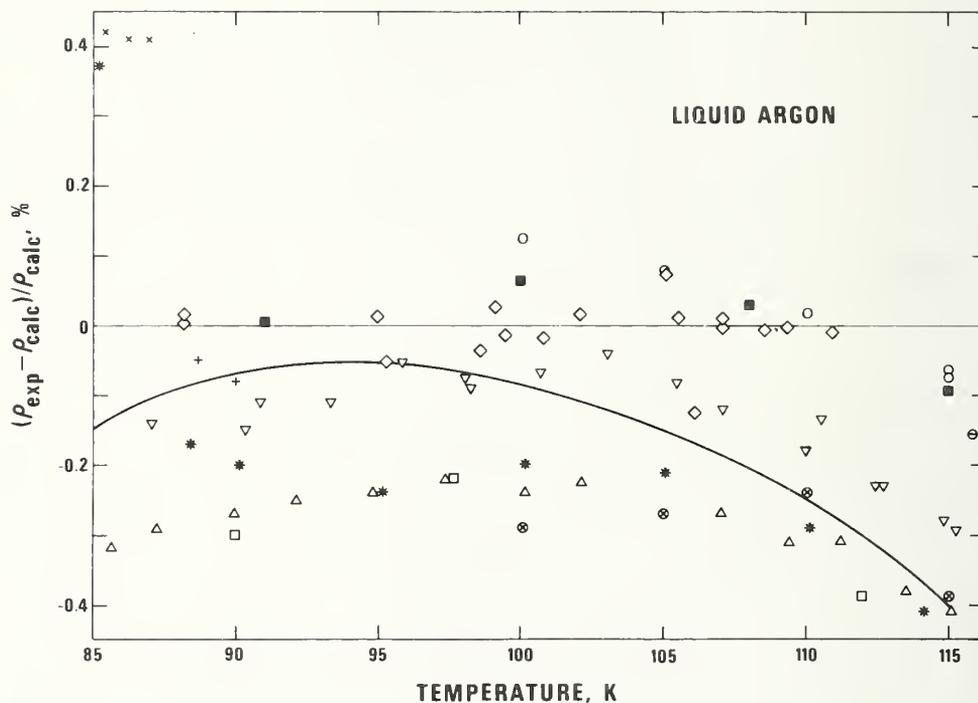
Figure 5. Liquid argon densities of other workers compared to a least squares
fit to this work.

◇	Younglove, this work.	■	Pan, et al. [14].
○	Haynes and Hiza [9].	▽	Goldman and Serase [15].
⊖	Chui and Canfield [10].	×	Saji and Kobayashi [16].
+	Van Itterbeek and Verbeke [11].	□	Mathias, et al. [17].
△	Terry, et al. [12].	⊗	Street and Staveley [18].
—	Gosman, et al. [13].	✳	Dobrovolskii and Golubev [19].

work rather than periodically because of the expense of making density mea-
surements.

For these occasions the within SD's will be compared statistically to
those of previous occasions for any change in this measure of precision,
and the occasion-to-occasion shifts, α_i (see 3.2), will be tested for any
change in their variability or for signs of non-random behavior (e.g., drift-
ing). If there is no apparent change, 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. A revised uncertainty statement will be presented
as further calibration measurements are completed.

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 $\pm$ 0.21%. The contribution
from the estimated systematic error in density was $\pm$ 0.026%. The estimated un-
certainty caused by random error is three times the standard deviation of
$\pm$ 0.062% and is based on the measurements of the densities [4] of liquid
methane taken on eight samples and on 22 independent measurements. The total
density uncertainty was taken to be the sum of the systematic and random errors.

6. ACKNOWLEDGEMENTS

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Engineering Laboratory for the considerable help and advice given this project
during its various phases. Acknowledgement is also given to Janet Donaldson
of the same group for her recommendations on the method of acquiring data from
the automatic balance.

Jim Holste contributed very heavily in the construction and start up phase
of this project. He designed and built several important features of the DRS.

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8. APPENDICES

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

The buoyant force of the liquid on the silicon crystal will be reduced by the effect of its volume being decreased by 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;

$$k = -\frac{1}{v}\frac{\partial v}{\partial P}\bigg)_t .$$

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 [7] using the usual relations for bulk modulus and elastic constants as evaluated from sound velocities.

The change in volume was computed from the thermal contraction of silicon values from Corruccini and Gniewek [8]. 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.

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

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

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

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	127.4320
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 $\pm$ 0.0003 std. dev.

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	$\pm$ 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 weighed in water and in air. Using averages of four weighings in air and water the density computed at 30 °C was ρ = 2.3291 g/cm^3, as compared to ρ = 2.3289 from the above after correction for thermal expansion. This is a difference of about 0.009%.

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June 9, 1976

REPORT OF TEST

OWNER: National Bureau of Standards   Certification No. 3087
Cryogenic Laboratory
Boulder, Colorado

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 0.0008 g based on 37 degrees of freedom.   The linearity coefficient was 0.99960.

A summary of these measurements are shown below.

Independent Variable	Dependent Variable	Predicted Values	Standard Deviation of Predicted Values
4.000	4.000	4.001	.20E-03
15.998	15.998	15.998	.19E-03
10.999	10.997	11.000	.12E-03
2.000	2.001	2.001	.24E-03
6.999	7.000	7.000	.16E-03
1.000	1.002	1.001	.26E-03
8.999	9.000	9.000	.14E-03
17.998	17.998	17.999	.22E-03
8.999	9.000	9.000	.14E-03
18.998	18.999	18.998	.24E-03
10.999	11.000	11.000	.13E-03
11.999	11.999	12.000	.14E-03
14.998	14.999	14.999	.17E-03
19.998	18.998	19.998	.26E-03
4.000	4.000	4.000	.20E-03
12.999	12.997	12.999	.15E-03
4.999	5.000	5.001	.19E-03
12.999	12.999	12.999	.15E-03
1.000	1.002	1.001	.26E-03
11.999	12.000	12.000	.14E-03
18.998	18.999	18.998	.24E-03
13.998	14.000	13.999	.16E-03
19.998	19.999	19.998	.26E-03
17.998	17.999	17.999	.22E-03
7.999	8.000	8.000	.15E-03
15.998	15.999	15.999	.19E-03
1.999	2.002	2.001	.24E-03
5.999	6.001	6.000	.17E-03
9.998	10.000	10.000	.13E-03
14.998	15.000	14.999	.17E-03
6.999	7.001	7.000	.16E-03
3.000	3.001	3.000	.22E-03
16.998	17.000	16.999	.20E-03
5.999	6.002	6.000	.17E-03
3.000	3.001	3.001	.22E-03
9.999	10.000	10.000	.13E-03
16.998	16.999	16.999	.20E-03
7.999	8.001	8.000	.15E-03
13.998	13.998	13.999	.16E-03
4.999	5.000	5.001	.19E-03

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15. SUPPLEMENTARY NOTES

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 measurement capability of the density reference system (DRS) of the National Bureau of Standards, Cryogenics Division, is described. This system measures density, pressure, and temperature of LNG mixtures for the purpose of testing densimeters which are contained in the liquid sample. Sample composition is determined by weighing the gas samples separately before condensing them into the sample. The DRS measures density by weighing a single-crystal of silicon immersed in the LNG mixture. This process is described and the equations used in the computation of density are discussed.

At this time the estimate of sample standard deviation for a single density measurement made on this system is $\pm$ 0.062% (at 0.4 g/cc). Using three times this standard deviation as a limit for random error and adding $\pm$ 0.026% as an upper bound for known sources of possible systematic error, the uncertainty of a single determination by this system is $\pm$ 0.21%. This statement of accuracy applies for the density range 380 to 430 kg/m^3 and 1200 to 1400 kg/m^3, pressures to 7 bar, and temperatures from 80K to 140 K. This statement is expected to be correct in the intermediate density range and for all temperatures up to 300 K.

Measurement uncertainties for temperature, pressure, and composition are discussed. Comparison of measurements for liquid argon densities with the results of other laboratories is given.

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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