CRYOGENIC FLUIDS DENSITY REFERENCE SYSTEM:
PROVISIONAL ACCURACY STATEMENT

B.A. Younglove
J.D. Siegwarth

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

January 1977

Prepared for:
American Gas Association, Inc.
1515 Wilson Boulevard
Arlington, Virginia 22209
CRYOGENIC FLUIDS DENSITY REFERENCE SYSTEM: PROVISIONAL ACCURACY STATEMENT

B.A. Younglove
J.D. Siegwarth

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

January 1977

Prepared for:
American Gas Association, Inc.
1515 Wilson Boulevard
Arlington, Virginia 22209

U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, Secretary
Edward O. Vetter, Under Secretary
Dr. Betsy Ancker-Johnson, Assistant Secretary for Science and Technology

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Acting Director
<table>
<thead>
<tr>
<th>CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Symbols</td>
<td>2</td>
</tr>
<tr>
<td>2. DESCRIPTION OF THE BASIC MEASUREMENT PROCESS</td>
<td>4</td>
</tr>
<tr>
<td>2.1. Density</td>
<td>4</td>
</tr>
<tr>
<td>2.2. Pressure</td>
<td>10</td>
</tr>
<tr>
<td>2.3. Temperature</td>
<td>10</td>
</tr>
<tr>
<td>2.4. Composition</td>
<td>11</td>
</tr>
<tr>
<td>3. MEASUREMENT PROCESS PARAMETERS</td>
<td>12</td>
</tr>
<tr>
<td>3.1. Bounds for Systematic Errors</td>
<td>12</td>
</tr>
<tr>
<td>3.2. Random Error from Measurements on Methane</td>
<td>15</td>
</tr>
<tr>
<td>3.3. Uncertainty Statement</td>
<td>16</td>
</tr>
<tr>
<td>4. MEASUREMENT PROCESS CONTROL</td>
<td>16</td>
</tr>
<tr>
<td>5. SUMMARY</td>
<td>19</td>
</tr>
<tr>
<td>6. ACKNOWLEDGEMENTS</td>
<td>19</td>
</tr>
<tr>
<td>7. REFERENCES</td>
<td>20</td>
</tr>
<tr>
<td>8. Appendices</td>
<td>21</td>
</tr>
<tr>
<td>8.1. The Change in Volume of the Silicon Crystal from Hydrostatic Compression and Temperature</td>
<td>22</td>
</tr>
<tr>
<td>8.2. Silicon Crystal Weighings in Air</td>
<td>23</td>
</tr>
<tr>
<td>8.3. Densities of Single-Crystal Silicon</td>
<td>24</td>
</tr>
<tr>
<td>8.4. Weight Certificate</td>
<td>25</td>
</tr>
<tr>
<td>8.5. Linearity Check of the Balance</td>
<td>27</td>
</tr>
</tbody>
</table>
CRYOGENIC FLUIDS DENSITY REFERENCE SYSTEM: PROVISIONAL ACCURACY STATEMENT

B. A. Younglove and J. D. Siegwarth

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

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 argon; 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 ± 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
- $M_{bl}$: 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
silicon crystal mass
replacement mass standard used to evaluate zero of balance
apparent mass of replacement mass in gas
hanger mass, brass part
hanger mass, stainless steel wire part
hanger mass, stainless steel wire, that part of \( M_2 \) located in liquid
hanger mass, tungsten wire part
system pressure
system temperature
volume of buoy
volume of silicon
apparent mass less zero mass reading of DRS balance
density difference between DRS density and a reference density
density variation in \( \delta \) from the average value of \( \delta \), for a methane sample
density variation in \( \delta \) from a methane sample to an average methane sample
density of liquid sample
density of gas (vapor phase in equilibrium with sample liquid)
density of reference methane liquid
density of silicon
density of brass
density of stainless steel
density of tungsten
standard deviation
standard deviation of \( \epsilon \)
standard deviation of \( \eta \)
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.

\[ M_a g = (M_s - \rho V_s)g. \]  

(1)

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

\[ \rho = (M_s - M_a) \frac{1}{V_s}. \]  

(2)

Using the measured value for the silicon mass and the value for single-crystal pure silicon density, \( \rho_s \), we have

\[ M_s = \rho_s V_s. \]  

(3)

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

\[ \rho = \rho_s (1 - \frac{M_a}{M_s}). \]  

(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 counter-weight \( M_c \) 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 equivalent mass \( M_a \) (or apparent mass), and is the reading of the automatic balance. Here we have

\[ M_a + M_c = M_{rg} + M_{hg} + M_{bl}. \]  

(5)
Figure 2. Density Reference System showing small sample holder.
Figure 3. Partially disassembled Density Reference System.
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

$$M_{ao} + M_{cg} = M_{rg} + M_{wg}$$

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

$$M_a - M_{ao} = M_{hg} + M_{bo} - M_{wg}$$

or

$$\Delta M_a = M_{hg} + M_{bo} - M_{wg}.$$ (7)

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 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 $M_{ak}'$,

$$M_{ak} + M_{cg} = M_{rg} + M_{wg} + M_{kg}.$$ (7a)

Subtracting equation (6) from (7a),

$$M_{ak} - M_{ao} = M_{kg}.$$ (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

\[ \rho = \rho_s \left( 1 - f(M_1, M_2, \ldots, \rho_1, \rho_2, \ldots) \right) \]  

(8)

where the independent variables are all known. In actual practice the hanger \( M_h \), consisted of a brass part \((M_1, \rho_1)\) and a stainless steel wire suspended from this brass hanger \((M_2, \rho_2)\). 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,

\[ M_h = M_1 + M_2 - M_3 \]  

(9)

and,

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

(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 \((M_4, \rho_4)\) wrapped around the silicon crystal \((M_b, \rho_s)\) so we have

\[ M_{b,h} = M_s + M_3 + M_4 - \rho \left( \frac{M_s}{\rho_s} + \frac{M_3}{\rho_2} + \frac{M_4}{\rho_4} \right). \]  

(11)

Putting these relations into equation (7)

\[ \Delta M_a = M_1 + M_2 - M_3 - \rho g \left( \frac{M_1}{\rho_1} + \frac{M_2 - M_3}{\rho_2} \right) \]

\[ + M_s + M_3 + M_4 - \rho \left( \frac{M_s}{\rho_s} + \frac{M_3}{\rho_2} + \frac{M_4}{\rho_4} \right) - M_w + \rho g \frac{M_w}{\rho_1} \]

(12)

\[ \rho = \frac{M_s + M_1 + M_2 + M_4 - M_w - \Delta M_a - \rho g \left[ (M_1 - M_w)/\rho_1 + (M_2 - M_3)/\rho_2 \right]}{M_s/\rho_s + M_3/\rho_2 + M_4/\rho_4} \]

(13)

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

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

(14)
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.

\[
\begin{align*}
M_s &= 127.4330 \text{ g}, \quad \rho_s = 2.33078 \text{ g/cm}^3 \quad \text{the silicon crystal.} \\
M_1 &= 4.2441 \text{ g}, \quad \rho_1 = 8.5 \text{ g/cm}^3 \quad \text{the brass hanger.} \\
M_2 &= 0.2121 \text{ g}, \quad \rho_2 = 7.9 \text{ g/cm}^3 \quad \text{the stainless steel suspension wire.} \\
M_3 &= 0.026 \text{ g} \quad \text{stainless steel suspension wire submerged in liquid.} \\
M_4 &= 0.055 \text{ g}, \quad \rho_4 = 18.8 \text{ g/cm}^3 \quad \text{the tungsten wire tied about the silicon crystal.} \\
M_w &= 100.9296 \text{ g} \quad \text{the brass replacement weight.}
\end{align*}
\]

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

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

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 \(\rho_s\) 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 kPa.
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:

<table>
<thead>
<tr>
<th>Average System Temperature</th>
<th>$d\ln \rho / d\ln T$</th>
<th>$\Delta \rho / \rho$ for $\Delta T = 0.03$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>110 K</td>
<td>0.38</td>
<td>0.0038%</td>
</tr>
<tr>
<td>140 K</td>
<td>0.26</td>
<td>0.0026%</td>
</tr>
</tbody>
</table>

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 res-
ulting 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 mix-
ture 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 $\rho$ as a function of several independent variables.

$$\rho = \rho(M_1, M_2, M_3, M_4, M_w, \Delta M_a, \rho_1, \rho_2, \rho_4).$$

(15)

The uncertainty in $\rho$, arising from uncertainty in $\rho_s$, for example, can be evaluated from

$$\delta \rho = \frac{\delta \rho}{\delta \rho_s} \delta \rho_s$$

(16)

or as a dimensionless ratio,

$$\frac{\delta \rho}{\rho} = \frac{\delta \rho}{\delta \rho_s} \frac{\delta \rho_s}{\rho_s},$$

(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.

$$\frac{\delta \rho}{\rho} = \sqrt{\sum \left(\frac{\delta \rho}{\delta \rho_s} \frac{\delta \rho_s}{\rho_s} x_i \right)^2}^{1/2}.$$  

(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 $\chi$ 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 $\delta x/\chi$ is the ratio of the estimated worst possible uncertainty of that variable.

The systematic error, $\delta x/\chi$, 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 buoyancy 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

<table>
<thead>
<tr>
<th>Variable</th>
<th>Total Logarithmic Partial Derivative</th>
<th>$\delta x/\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_1$</td>
<td>$x_1$</td>
<td></td>
</tr>
<tr>
<td>$M_2$</td>
<td>$x_2$</td>
<td></td>
</tr>
<tr>
<td>$M_3$</td>
<td>$x_3$</td>
<td></td>
</tr>
<tr>
<td>$M_4$</td>
<td>$x_4$</td>
<td></td>
</tr>
<tr>
<td>$M_w$</td>
<td>$x_w$</td>
<td></td>
</tr>
<tr>
<td>$\Delta M_a$</td>
<td>$x_o$</td>
<td></td>
</tr>
<tr>
<td>$\rho_1$</td>
<td>$x_{\rho_1}$</td>
<td></td>
</tr>
<tr>
<td>$\rho_2$</td>
<td>$x_{\rho_2}$</td>
<td></td>
</tr>
<tr>
<td>$\rho_4$</td>
<td>$x_{\rho_4}$</td>
<td></td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Variable, x</th>
<th>$\partial \rho / \partial \ln x$</th>
<th>$\delta x / x$</th>
<th>$\delta \rho / \rho$ in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicon crystal mass</td>
<td>$(\rho_s - \rho)M_s / \rho \rho_s V$</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$\pm 0.0062$</td>
</tr>
<tr>
<td>brass hanger mass</td>
<td>$(\rho_1 - \rho_g)M_1 / \rho \rho_1 V$</td>
<td>$2.4 \times 10^{-4}$</td>
<td>$\pm 0.0043$</td>
</tr>
<tr>
<td>steel wire mass</td>
<td>$(\rho_2 - \rho_g)M_2 / \rho \rho_2 V$</td>
<td>$4.7 \times 10^{-3}$</td>
<td>$\pm 0.00042$</td>
</tr>
<tr>
<td>steel wire mass in liquid</td>
<td>$(\rho - \rho_g)M_3 / \rho \rho_2 V$</td>
<td>$3.8 \times 10^{-4}$</td>
<td>--</td>
</tr>
<tr>
<td>tungsten wire mass</td>
<td>$(\rho_4 - \rho_g)M_4 / \rho \rho_4 V$</td>
<td>$1.8 \times 10^{-2}$</td>
<td>--</td>
</tr>
<tr>
<td>apparent mass</td>
<td>$\Delta M_a / \rho V$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$\pm 0.010$</td>
</tr>
<tr>
<td>silicon density</td>
<td>$M_s / \rho_s V$</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$\pm 0.0016$</td>
</tr>
<tr>
<td>metal densities</td>
<td>$(M_1 - M_w) / \rho / \rho_1 V$</td>
<td>$2.3 \times 10^{-2}$</td>
<td>$\pm 0.0046$</td>
</tr>
<tr>
<td>gas density</td>
<td>$\rho_g ((M_1 - M_w) / \rho_1 + $</td>
<td>$1.0 \times 10^{-1}$</td>
<td>$\pm 0.022$</td>
</tr>
<tr>
<td>temperature gradient</td>
<td>$d \ln \rho / d \ln T$</td>
<td>$3.8 \times 10^{-1}$</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

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 uncertainty 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 experimen-
tally 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 tem-
perature [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

\[ y(T)_{ij} - H(T) = \nu(T) + \alpha_i + e_{ij} \]

where \( y(T)_{ij} \) is the \( j \)th density determination by the DRS on the \( i \)th methane
sample for temperature \( T \); \( H(T) \) is the corresponding density value derived
from the Haynes-Hiza relationship, \( \nu(T) \) represents the long term relative
bias, \( \alpha_i \) is the random contribution to all measurements made using the \( i \)th
sample, and \( e_{ij} \) is the random contribution to the \( j \)th measurement made on
the \( i \)th sample. The standard deviation (SD) for the \( \alpha_i \) 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 preceding 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 affected 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.
- Haynes and Hiza [9].
- Chui and Canfield [10].
△ Terry, et al. [12].
— Gosman, et al. [13].
□ Pan, et al. [14].
▲ Goldman and Serase [15].
× Saji and Kobayashi [16].
□ Mathias, et al. [17].
• Street and Staveley [18].
★ Dobrovolskii and Golubev [19].
work rather than periodically because of the expense of making density measurements.

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, $\alpha_i$ (see 3.2), will be tested for any change in their variability or for signs of non-random behavior (e.g., drifting). 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 $+0.21\%$. The contribution from the estimated systematic error in density was $+0.026\%$. The estimated uncertainty caused by random error is three times the standard deviation of $+0.062\%$ 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

Special acknowledgement is given to John LaBrecque of the NBS Statistical 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.
7. REFERENCES


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

\[ V = V_0(1 - kP) \]

where \( V_0 \) 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;

\[ k = -\left(\frac{1}{V_0}\frac{\partial V}{\partial P}\right)_T. \]

This correction was found to be negligible since \( k = 1.01 \times 10^{-6} \text{ bar}^{-1} \) and at 110 K and \( P = 6 \text{ bar}, \frac{\Delta V}{V} = 6 \times 10^{-6} \). 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

<table>
<thead>
<tr>
<th>Date</th>
<th>Silicon Weight in Air (gram)</th>
<th>Temperature (Celsius)</th>
<th>Pressure (mm Hg)</th>
<th>Silicon Weight in Vacuum (gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-10-74</td>
<td>127.3947</td>
<td>21</td>
<td>633</td>
<td>127.4335</td>
</tr>
<tr>
<td>01-15-74</td>
<td>127.3950</td>
<td>20</td>
<td>631</td>
<td>127.4339</td>
</tr>
<tr>
<td>01-27-74</td>
<td>127.3941</td>
<td>20</td>
<td>625</td>
<td>127.4335</td>
</tr>
<tr>
<td>02-28-74</td>
<td>127.3945</td>
<td>21</td>
<td>620</td>
<td>127.4334</td>
</tr>
<tr>
<td>04-02-74</td>
<td>127.3926</td>
<td>21</td>
<td>628</td>
<td>127.4320</td>
</tr>
<tr>
<td>04-05-74</td>
<td>127.3941</td>
<td>20</td>
<td>630</td>
<td>127.4338</td>
</tr>
<tr>
<td>10-27-74</td>
<td>127.3930</td>
<td>23</td>
<td>625</td>
<td>127.4319</td>
</tr>
<tr>
<td>10-28-75</td>
<td>127.3927</td>
<td>21</td>
<td>620</td>
<td>127.4316</td>
</tr>
</tbody>
</table>

Average: 127.4330 ± 0.0003

Std. dev.
8.3. Densities of Single-Crystal Silicon

<table>
<thead>
<tr>
<th>Densities of Silicon</th>
<th>Temperature</th>
<th>Preparation</th>
<th>Std. Deviation, 10 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.328932*</td>
<td>22-27°C</td>
<td>Grown in Vacuum</td>
<td>1 ppm</td>
</tr>
<tr>
<td>2.329021*</td>
<td>22-27°C</td>
<td>Grown in Argon</td>
<td>1 ppm</td>
</tr>
<tr>
<td>2.32904**</td>
<td>25°C</td>
<td>Not known</td>
<td>+ 9 ppm</td>
</tr>
</tbody>
</table>

* 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 \( \rho = 2.3291 \text{ g/cm}^3 \), as compared to \( \rho = 2.3289 \) from the above after correction for thermal expansion. This is a difference of about 0.009\%. 

24
Voland Corporation
27 Centre Ave.
New Rochelle, N. Y. 10802
Attn: Robert C. Luce
Order 1695

This is to certify that the weights furnished on your referenced order have been calibrated to Class S of the National Bureau of Standards tolerances under our N.B.S. Certificate No. as follows:

Weight Set 5 kg - 1 g
5 Kg. 2 kg. 2 kg. 1 kg
500 g, 200 g, 200 g, 100 g
50 g, 20 g, 20 g, 10 g
5 g, 2 g, 2 g, 1 g

Dated: March 28, 1974

By: Wilbert D. Abele
Vice President and General Manager
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 buoyancy has been considered negligible.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>APPARENT MASS CORRECTION</th>
<th>UNCERTAINTY</th>
<th>CLASS S ADJUSTMENT TOLERANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 gram</td>
<td>-0.0080 mg</td>
<td>0.022 mg</td>
<td>0.074 mg</td>
</tr>
<tr>
<td>20 .</td>
<td>+0.016</td>
<td>0.020</td>
<td>0.074</td>
</tr>
<tr>
<td>10</td>
<td>+0.009</td>
<td>0.0134</td>
<td>0.054</td>
</tr>
<tr>
<td>5</td>
<td>-0.0403</td>
<td>0.0134</td>
<td>0.054</td>
</tr>
<tr>
<td>2 .</td>
<td>+0.0216</td>
<td>0.0134</td>
<td>0.054</td>
</tr>
<tr>
<td>2 .</td>
<td>+0.0431</td>
<td>0.0093</td>
<td>0.054</td>
</tr>
<tr>
<td>1</td>
<td>+0.0229</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 Brzotky, 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 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.

<table>
<thead>
<tr>
<th>Independent Variable</th>
<th>Dependent Variable</th>
<th>Predicted Values</th>
<th>Standard Deviation of Predicted Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.000</td>
<td>4.000</td>
<td>4.001</td>
<td>.20E-03</td>
</tr>
<tr>
<td>15.998</td>
<td>15.998</td>
<td>15.998</td>
<td>.16E-03</td>
</tr>
<tr>
<td>10.999</td>
<td>10.997</td>
<td>11.000</td>
<td>.12E-03</td>
</tr>
<tr>
<td>2.000</td>
<td>2.001</td>
<td>2.001</td>
<td>.24E-03</td>
</tr>
<tr>
<td>6.999</td>
<td>7.000</td>
<td>7.000</td>
<td>.16E-03</td>
</tr>
<tr>
<td>1.000</td>
<td>1.002</td>
<td>1.001</td>
<td>.26E-03</td>
</tr>
<tr>
<td>8.999</td>
<td>9.000</td>
<td>9.000</td>
<td>.14E-03</td>
</tr>
<tr>
<td>17.998</td>
<td>17.998</td>
<td>17.999</td>
<td>.22E-03</td>
</tr>
<tr>
<td>8.999</td>
<td>9.000</td>
<td>9.000</td>
<td>.14E-03</td>
</tr>
<tr>
<td>18.998</td>
<td>18.999</td>
<td>18.998</td>
<td>.24E-03</td>
</tr>
<tr>
<td>10.999</td>
<td>11.000</td>
<td>11.000</td>
<td>.13E-03</td>
</tr>
<tr>
<td>11.999</td>
<td>11.999</td>
<td>12.000</td>
<td>.14E-03</td>
</tr>
<tr>
<td>14.998</td>
<td>14.999</td>
<td>14.999</td>
<td>.17E-03</td>
</tr>
<tr>
<td>19.998</td>
<td>18.998</td>
<td>19.998</td>
<td>.26E-03</td>
</tr>
<tr>
<td>4.000</td>
<td>4.000</td>
<td>4.000</td>
<td>.20E-03</td>
</tr>
<tr>
<td>12.999</td>
<td>12.997</td>
<td>12.999</td>
<td>.15E-03</td>
</tr>
<tr>
<td>4.999</td>
<td>5.000</td>
<td>5.001</td>
<td>.19E-03</td>
</tr>
<tr>
<td>12.999</td>
<td>12.999</td>
<td>12.999</td>
<td>.15E-03</td>
</tr>
<tr>
<td>1.000</td>
<td>1.002</td>
<td>1.001</td>
<td>.26E-03</td>
</tr>
<tr>
<td>11.999</td>
<td>12.000</td>
<td>12.000</td>
<td>.14E-03</td>
</tr>
<tr>
<td>18.998</td>
<td>18.999</td>
<td>18.998</td>
<td>.24E-03</td>
</tr>
<tr>
<td>13.998</td>
<td>14.000</td>
<td>13.999</td>
<td>.16E-03</td>
</tr>
<tr>
<td>19.998</td>
<td>19.999</td>
<td>19.998</td>
<td>.26E-03</td>
</tr>
<tr>
<td>17.998</td>
<td>17.999</td>
<td>17.999</td>
<td>.22E-03</td>
</tr>
<tr>
<td>7.999</td>
<td>8.000</td>
<td>8.000</td>
<td>.15E-03</td>
</tr>
<tr>
<td>15.998</td>
<td>15.999</td>
<td>15.999</td>
<td>.19E-03</td>
</tr>
<tr>
<td>1.999</td>
<td>2.002</td>
<td>2.001</td>
<td>.24E-03</td>
</tr>
<tr>
<td>5.999</td>
<td>6.001</td>
<td>6.000</td>
<td>.17E-03</td>
</tr>
<tr>
<td>9.998</td>
<td>10.000</td>
<td>10.000</td>
<td>.13E-03</td>
</tr>
<tr>
<td>14.998</td>
<td>15.000</td>
<td>14.999</td>
<td>.17E-03</td>
</tr>
<tr>
<td>6.999</td>
<td>7.001</td>
<td>7.000</td>
<td>.16E-03</td>
</tr>
<tr>
<td>3.000</td>
<td>3.001</td>
<td>3.000</td>
<td>.22E-03</td>
</tr>
<tr>
<td>16.998</td>
<td>17.000</td>
<td>16.999</td>
<td>.20E-03</td>
</tr>
<tr>
<td>5.999</td>
<td>6.002</td>
<td>6.000</td>
<td>.17E-03</td>
</tr>
<tr>
<td>3.000</td>
<td>3.001</td>
<td>3.001</td>
<td>.22E-03</td>
</tr>
<tr>
<td>9.999</td>
<td>10.000</td>
<td>10.000</td>
<td>.13E-03</td>
</tr>
<tr>
<td>16.998</td>
<td>16.999</td>
<td>16.999</td>
<td>.20E-03</td>
</tr>
<tr>
<td>7.999</td>
<td>8.001</td>
<td>8.000</td>
<td>.15E-03</td>
</tr>
<tr>
<td>13.998</td>
<td>13.998</td>
<td>13.999</td>
<td>.16E-03</td>
</tr>
<tr>
<td>4.999</td>
<td>5.000</td>
<td>5.001</td>
<td>.19E-03</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>-----------------------------</td>
<td>-----------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>4. TITLE AND SUBTITLE</td>
<td>NBSIR 77-852</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRYOGENIC FLUIDS DENSITY REFERENCE SYSTEM:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PROVISIONAL ACCURACY STATEMENT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. AUTHOR(S)</td>
<td>B. A. Younglove and J. D. Siegwarth</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. PERFORMING ORGANIZATION NAME AND ADDRESS</td>
<td>NATIONAL BUREAU OF STANDARDS</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DEPARTMENT OF COMMERCE</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>WASHINGTON, D.C. 20234</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP)</td>
<td>American Gas Association, Inc.</td>
<td>1515 Wilson Boulevard</td>
<td>Arlington, Virginia 22209</td>
</tr>
<tr>
<td>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.)</td>
<td>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 (+ 0.062)% (at 0.4 g/cc). Using three times this standard deviation as a limit for 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 (+ 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.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>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)</td>
<td>Densimeters; density reference system; liquid methane; LNG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18. AVAILABILITY</td>
<td>[X] Unlimited</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[X] For Official Distribution. Do Not Release to NTIS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[X] Order From National Technical Information Service (NTIS) Springfield, Virginia 22151</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19. SECURITY CLASS</td>
<td>UNCLASSIFIED</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(THIS REPORT)</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20. SECURITY CLASS</td>
<td>UNCLASSIFIED</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(THIS PAGE)</td>
<td>22. PRICE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21. NO. OF PAGES</td>
<td>$4.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22. Price</td>
<td>$4.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>