# NBS TECHNICAL NOTE 1055

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

# Tests of Commercial Densimeters for LNG Service

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# Tests of Commercial Densimeters for LNG Service

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# Tests of Commercial Densimeters for LNG Service

J. D. Siegwarth and J. F. LaBrecque

Densimeters for liquefied natural gas (LNG) from four manufacturers were tested in liquid methane and an LNG-like mixture of methane, propane, and nitrogen in the density reference system (DRS). The calibration and performance of one type tested for the first time are reported. The stability of the calibrations and performances of three densimeters of a type previously tested have been examined and are also reported here.

Key words: density; densimeter; liquefied natural gas; methane.

## 1. INTRODUCTION

Four different densimeter designs by four manufacturers were tested for use in liquefied natural gas (LNG) in the density reference system [1,2] and the results were presented in earlier reports [2,3]. The densimeters tested in this first study were two vibrating types, a dielectric cell type and an Archimedes or displacement type. Though all proved capable of density measurement in cryogenic liquids, all suffered from the same problem; they did not have a suitable calibration for LNG service. Though the calibration of the displacement densimeter tested was within specifications [2,3], subsequent tests showed the calibration method applied to this densimeter inadequate.

To eliminate the calibration problem, NBS offered to provide transfer standards to the various manufacturers and users. The manufacturer or user would choose the instrument he prefers for a standard and NBS would calibrate it against the DRS densimeter. The DRS was rebuilt [4] to permit installation of different densimeters, to improve its reliability and to decrease the time required to acquire sufficient density data to calibrate the transfer standards. Later, the densimeter in the DRS was also rebuilt. The complete rebuild has been described in a new uncertainty statement [4].

## 2. TEST METHOD

The densimeters under test are compared to the DRS densimeter at a number of temperatures between about 109 and 128 K along the saturation line in liquid methane, occasionally in methane and nitrogen, and in LNG-like mixtures composed of methane, propane, and nitrogen. The pressures have thus far been limited to the range from 0.8 to 4 bars. The liquid temperature is changed by an electric heater or a liquid-nitrogen cooling coil while the sample is stirred. Stirring continues after the heating or cooling stops until the temperatures measured near the top and bottom of the sample are stable and indicate the sample is nearly isothermal. The temperature difference for most measurements was less than 10mK. The stirrer is stopped and the instrument readings are recorded. These include temperatures, pressure and the various densimeter outputs. The sample liquid is stirred again and a second set of data is recorded. The sample temperature usually increases perhaps by as much as one tenth degree between data sets depending on the amount of stirring. Then the sample is heated or cooled to the next chosen temperature. Normally, eight measurements at separate temperatures are made. To obtain the mixture samples, the additional components were condensed into the methane sample.

The present DRS densimeter has an apparent uncertainty for one reading of $\pm 0.055\%$ at 425 kg/m$^3$ density [3]. This is composed of a systematic uncertainty of 0.022% and 3 times the estimated standard deviation of 0.011%. A schematic of the rebuilt DRS is shown in figure 1 illustrating the relative positions of the densimeters within the liquid sample. A more detailed description of the DRS is contained in [3].

Because the two sets of data taken at one sample temperature setting are highly correlated, only one of the sets of data is used in the subsequent statistical analysis. Usually, no difference is observed in the statistical results obtained from using only the first or only the second set of data in the analysis. This implies that sufficient time has passed to establish equilibrium conditions in the liquid before the data are recorded.

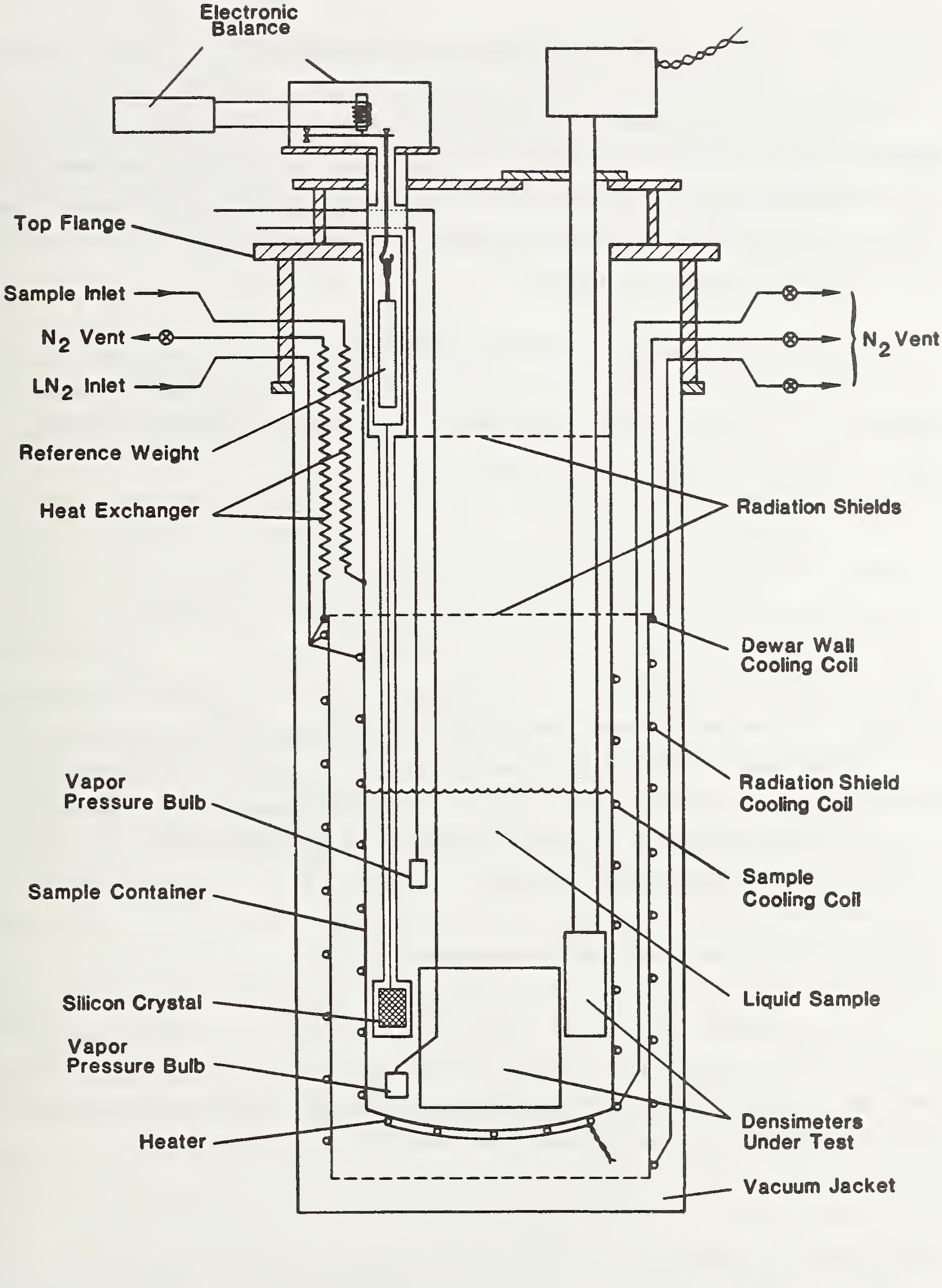

Figure 1. Schematic diagram of the improved Density Reference System.

# 3. THE COMMERCIAL DENSIMETERS

Three of the densimeter types tested and reported earlier [2,3] have undergone some additional testing. The three are the displacement densimeter, the vibrating cylinder densimeter and the vibrating plate densimeter. A second vibrating cylinder type has been tested for the first time.

## 3.1 Vibrating Element Densimeters

A vibrating element in these densimeters is locked in oscillation at one of its lower resonant frequencies. When this harmonically vibrating element is immersed in a fluid of variable density, the resonant frequency shifts with the fluid density such that, in the ideal case,

$$\rho = A + B\tau^2$$

where $\rho$ is the fluid density, $\tau$ is the period of vibration and A and B are constants. The constants A and B are derived from frequency measurements in fluids of known density. Since temperature can affect the structural properties hence the frequency of the vibrating element, such a densimeter should be calibrated in the fluid or in fluids as near as possible in temperature and density to those in which the instrument will be used.

## 3.2 Displacement or Archimedes Densimeter

This densimeter employs the Archimedes principle: an object immersed in a quiescent fluid experiences an upward force proportional to the mass of fluid it displaces. If the mass and volume of the object are known, the density of the fluid is determined by the relation

$$\rho = \rho_0 (M-M_a)/M \ . \tag{2}$$

The density of the float $\rho_0$ is given by M/V where M is the float mass in vacuum and V is its volume. The quantity $M_a$ is the apparent mass of the float when completely immersed in the liquid whose density is being measured. These densimeters require calibration in fluids of known density to determine $\rho_0$ and M for the float since the volume and mass are not known. Also, the force balance employed may not read mass directly. Some temperature effects exist also though not included in the simple eq (2). The float density $\rho_0$ is temperature dependent as is $M_a$ if the balance output is affected by temperature.

## 4. DENSIMETER TEST RESULTS

### 4.1 Vibrating Cylinder Densimeter -- First Kind

Three newer models of the vibrating cylinder densimeter reported in [3] were calibrated against the DRS densimeter for use as transfer standards. The instruments were calibrated and returned to the manufacturer who uses them to calibrate the densimeters he markets. These three densimeters are designated below as numbers 1, 2, and 3. Numbers 1 and 2 were retested in the DRS about a year and a half later.

For the first tests, the data were acquired in four separate fillings of the DRS. In the first filling, liquid methane was used as the sample liquid in which the vibrating cylinder densimeter frequencies and the DRS densimeter densities were recorded. Approximately 1% liquid nitrogen was then added and another series of data taken. Finally, about 5% liquid propane was added and a third series taken. Fillings 2, 3, and 4 were similar except that no separate series of data were taken with a methane-nitrogen mixture. Densimeter No. 3 was not tested in the first filling, but all three meters were inserted for subsequent fillings.

The data for the first three fillings contained many values well outside the bounds considered reasonable for normal deviation. All three densimeters showed outlying data and not always on corresponding readings. This problem was apparently caused by bubbles trapped in the vicinity of the vibrating spool. When the filter screens were removed from the densimeters for the fourth filling this problem disappeared. The suspected outlying data points of the first three fillings were not used in the data analysis.

The data were fit to eq (1) for each of the three densimeters under test for the methane, methane plus nitrogen, and the LNG-like mixture. Figure 2 shows the residuals from this fit for densimeter No. 1 versus temperature; the pattern of the points suggest at least a linear dependency on temperature. The methane and the LNG-like mixture data cover essentially one temperature range but different density ranges. A plot of the residuals versus density shows parallel lines rather than a continuous line, indicating a predominant temperature effect rather than a density effect. The behavior of the other two densimeters is similar. The relationship that gives a better fit to the density data than eq (1) is:

$$\text{density} = A + B/f^2 + CT \tag{3}$$

where T is temperature in Kelvins, A, B, and C are constants, and f, the frequency, is $1/\tau$.

The residuals obtained from fitting the above relationship in f and T to the data are shown versus chronological order in figures 3, 4, and 5 for densimeters Nos. 1, 2, and 3, respectively. The different symbols represent different fillings. Since the four sets of data taken for the four fillings represent roughly replicated conditions, the mean level of the residuals from filling to filling should be the same within the random uncertainty. To the extent this is not the case, shifts in the mean level of the residuals may indicate shifts in calibration. The shifts for meters No. 1 and No. 3 appear nonsystematic and may be due to random effects. Meter No. 2, however, shows a decided drift downward for the first three fillings. The filling-to-filling effects were removed before estimating the values of A, B, and C in eq (3). The estimated coefficients for eq (3) for the three densimeters are shown in table 1.

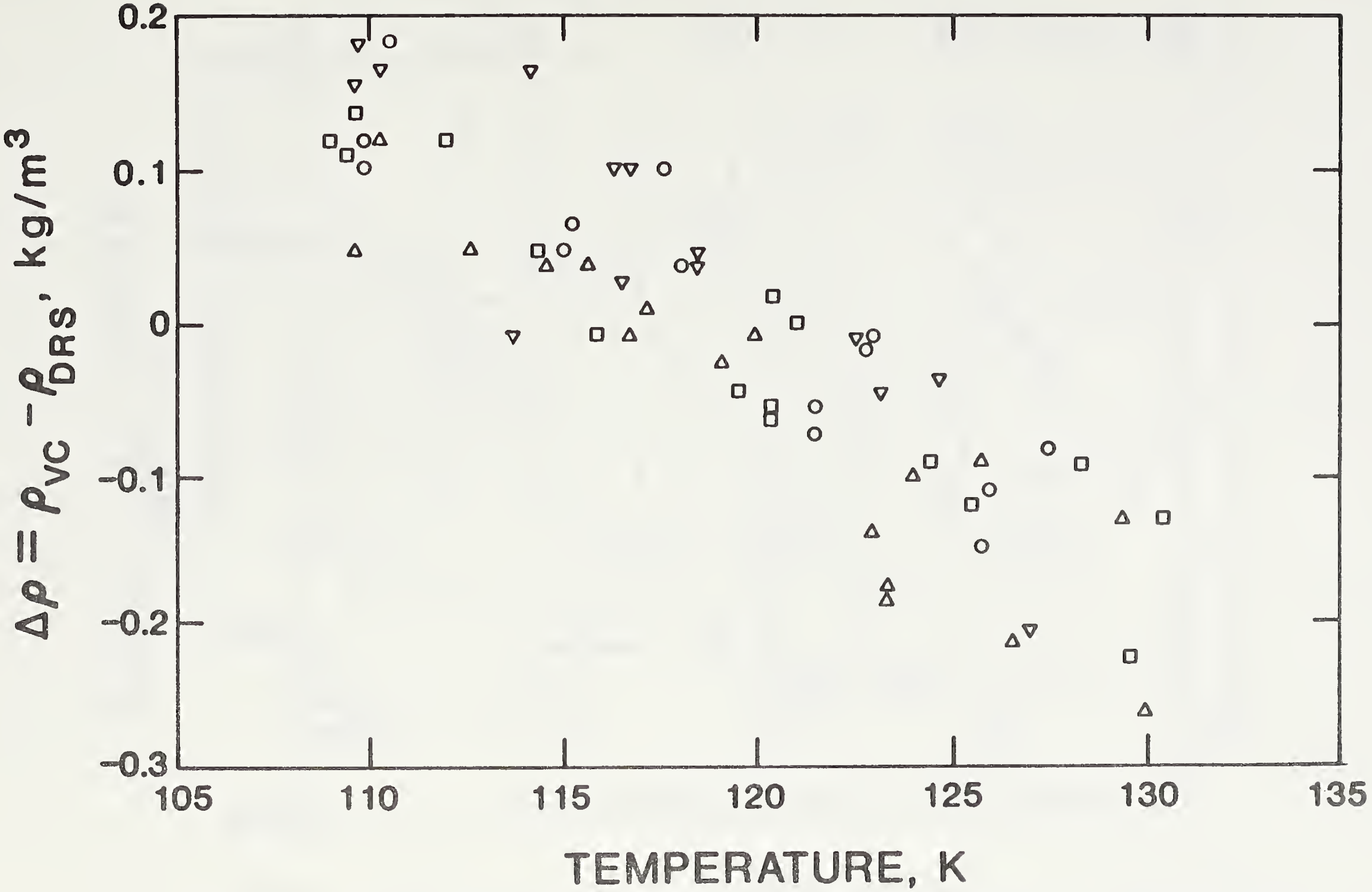

Figure 2. Δρ as a function of temperature for the first vibrating cylinder densimeter. $\rho_{vc} = A + B\tau^2$ where A and B are constants and τ is the period of vibration. The different symbols are for different fillings.

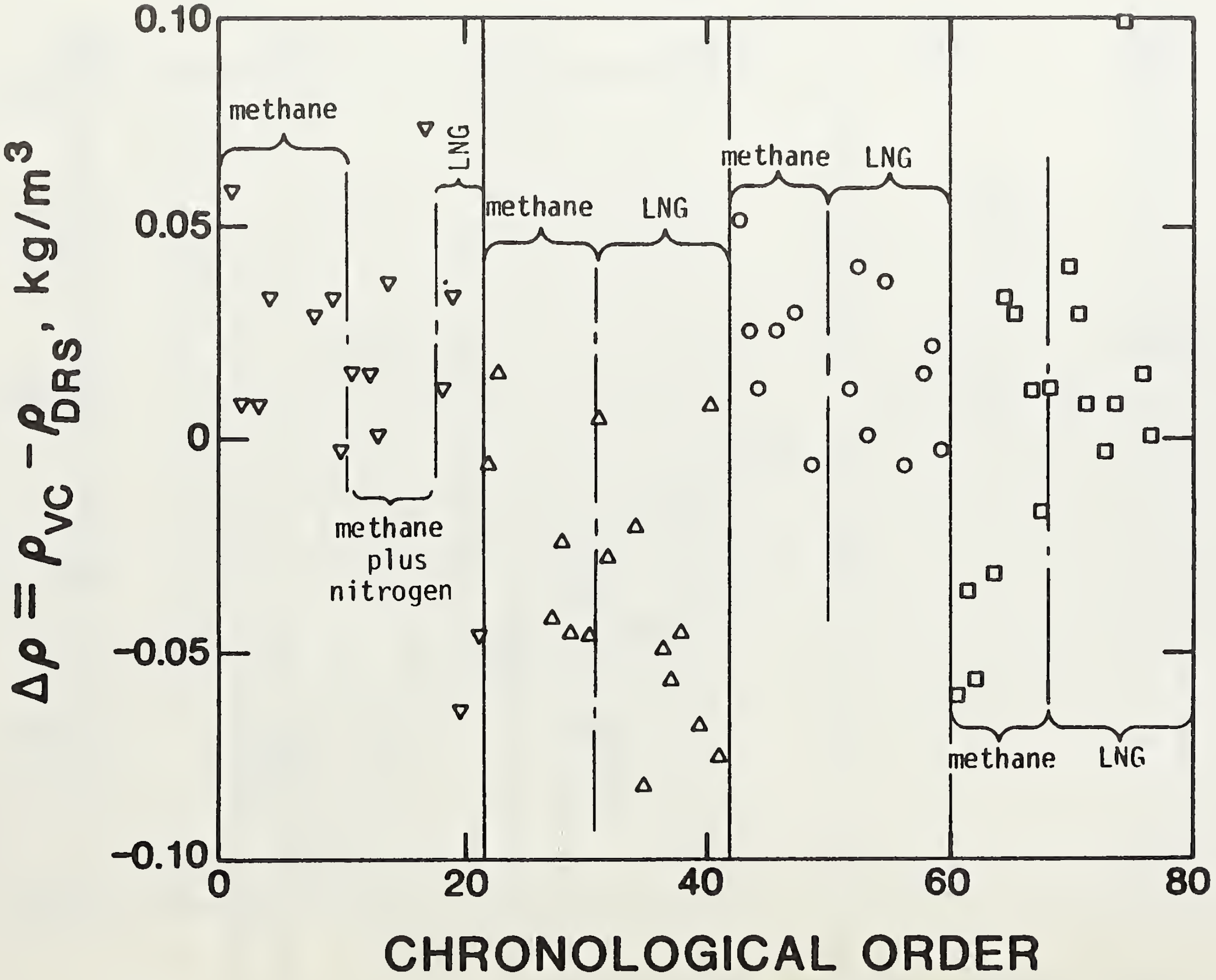

Figure 3. Δρ as a function of the order in which the data were taken for the first vibrating cylinder densimeter. $\rho_{vc} = A+B\tau^2+CT$ where A, B, and C are constants, τ is the period of vibration and T is the test liquid temperature. The different symbols are different fillings.

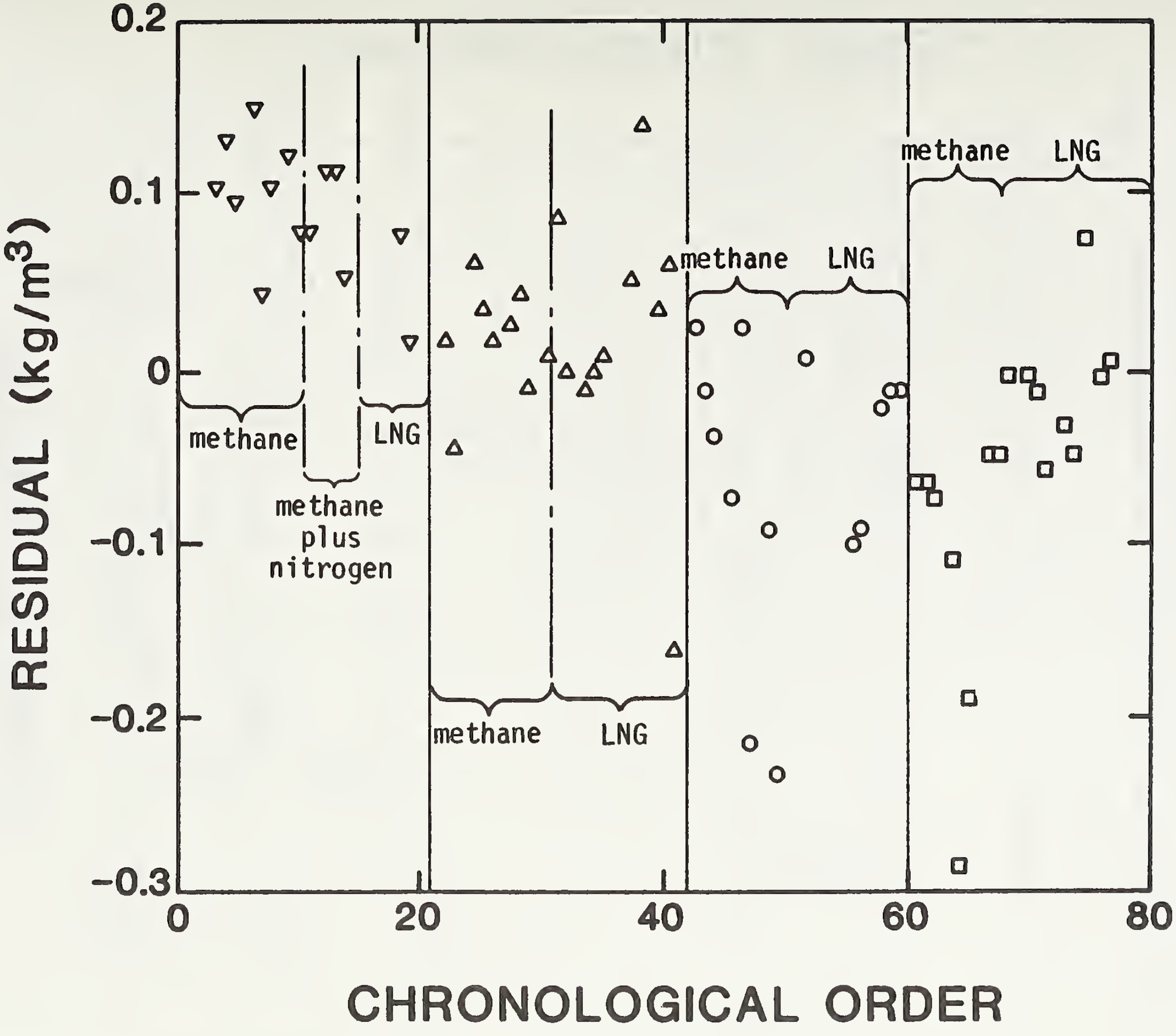

Figure 4. Residual densities for vibrating cylinder No. 2 as a function of order using the relation $\rho = A + B\tau^2 + CT$ where $\rho$, $\tau$ and T are the DRS density, No. 2 densimeter period and sample temperature, respectively.

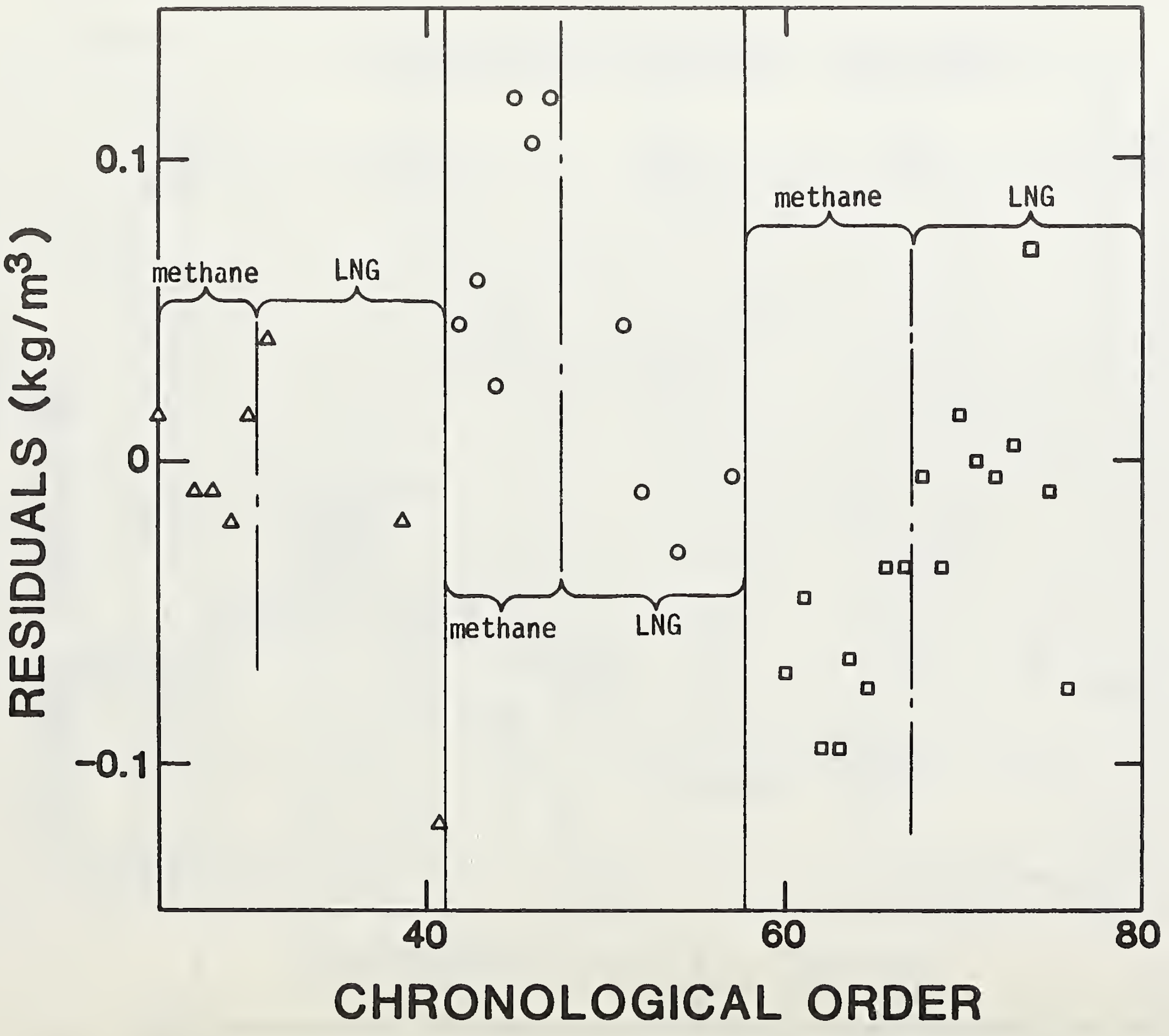

Figure 5. Residual densities for vibrating cylinder densimeter No. 3 as a function of order using the relation $\rho = 4 + B\tau^2 + CT$ where $\rho$, $\tau$ and T are DRS density, No. 3 densimeter period and sample temperature, respectively.

Table 1. Coefficients for equation 3

| | A | | B | | C | |
|---|---|---|---|---|---|---|
| Meter | Constant | SD | Coef of $\tau$ or $1/f^2$ | SD | Coef of T | SD |
| No. 1 | -189.46 | .15 | 5633.98 | .85 | -.01737 | .00071 |
| No. 2 | -193.89 | .32 | 5757.6 | 1.8 | -.0281 | .0015 |
| No. 3 | -192.88 | .33 | 5635.9 | 1.8 | -.0150 | .0016 |

These results apply to saturated methane or saturated methane + nitrogen (1%) + propane (5%) from 109 K to 130 K.

These equations contain three uncertainties: the uncertainty in the coefficients, the uncertainty because of instability in the frequency value, and uncertainty because of shifting of the mean level of the meter. When possible, these uncertainties are expressed in terms of standard deviations (SD). The table below gives a summary of the estimated standard deviations. The shifting for densimeters Nos. 1 and 3 is assumed random; however, for densimeter No. 2 such an assumption does not seem appropriate because for the first three fillings the mean level of this meter drifts downward.

Table 2. Uncertainties in predicing density values expressed in standard deviations ($kg/m^3$)

| Meter | SD for Eq. | 95% Upper Bound | SD for Measurement | 95% Upper Bound | SD for Mean Shift | 95% Upper Bound |
|---|---|---|---|---|---|---|
| No. 1 | .012 | .014 | .032 | .038 | .025 | .062 |
| No. 2 | .025 | .029 | .067 | .078 | * | -- |
| No. 3 | .024 | .030 | .055 | .069 | .043 | .102 |

*Meter drift nonrandom

The standard deviations in table 2 are estimates based on the data excluding the outlying data points. The 95% upper bounds give a more conservative value which takes into account the uncertainties in the data. The 95% upper bounds are combined by squaring, adding, and taking the square root of the sum to obtain an overall standard deviation value. Three times this value is assumed to be the random uncertainty for using the calibration equation. For densimeter No. 1 this is ±0.22 $kg/m^3$ or ±0.05% based on 425 $kg/m^3$. For densimeter No. 3 this value is ±0.38 $kg/m^3$ or ±0.09% based on 425 $kg/m^3$. No overall uncertainty has been calculated for densimeter No. 2. An additional 0.022% should be added because of systematic uncertainty in the DRS densimeter. The equations and uncertainties apply specifically to measurement in the DRS. So, the equation for densimeter No. 1 predicts a value for density based on 1/f and T with an uncertainty of ±0.07%; and the prediction for densimeter No. 3 has an uncertainty of ±0.11%.

In the fifth filling, the sample was liquid nitrogen from a storage tank. The source liquid has an impurity level < 0.01% according to the supplier. Some additional impurities may have been added by the time the sample has been placed in the DRS. The accuracy of the DRS densimeter in $LN_2$ has not been established. No present evidence suggests, however, that DRS determined $LN_2$ density is any less accurate than the methane density determination.

No prediction equation was estimated for liquid nitrogen, nor was the nitrogen data combined with the previous data to estimate a new equation. However, the above equations were used to predict the nitrogen densities based on the observed 1/f and T from the nitrogen data. The extrapolated liquid nitrogen densities disagree with measured densities by zero to -0.25% depending on the densimeter and the temperature of the liquid nitrogen.

Both the shifts between fillings and the random scatter within fillings are smaller for these densimeters than the similar densimeter tested and reported earlier [3]. No statistically significant difference is evident between the methane and LNG results as was observed in the measurements reported in [3].

When densimeter numbers 1 and 2 were retested about a year and a half later, the calibrations from the original tests were used to analyze the retest data. The residuals for densimeter No. 1,

$$R = \rho_{DRS} - (-189.46 + 5633.98/f^2 - .01737T),$$

are plotted against $\rho_{DRS}$ in figure 6. A different symbol is used for each filling of the DRS. The residuals for the retest data are slightly higher than those for the calibration data. They have a mean of 0.08 kg/m$^3$. Three times the upper bound of the standard deviation for mean shifts from table 1 is 0.19 kg/m$^3$; so the 0.08 kg/m$^3$ figure is well within this value. New calibration coefficients based on the original calibration data and the retest data are:

| Meter | Constant | SD | Coef of $1/f^2$ | SD | Coef of T | SD |
|---|---|---|---|---|---|---|
| No. 1 | -189.37 | .11 | 5633.72 | .66 | -.01770 | .00056 |

The new data showed negligible change in the coefficients.

The new upper bounds for the standard deviations (kg/m$^3$) are:

| Meter | Stand.Dev. for Eq. | 95% Upper Bound | SD for Measurement | 95% Upper Bound | SD for Mean Shift | 95% Upper Bound |
|---|---|---|---|---|---|---|
| No. 1 | .010 | .012 | .029 | .034 | .052 | .109 |

The estimated SD for mean shift is about twice the value of the original tests.

The residuals for densimeter No. 2,

$$R = \rho_{DRS} - (-193.89 + 5737.6/f^2 - .0281T), \qquad (5)$$

are plotted against $\rho_{DRS}$ in figure 7. These residuals show densimeter No. 2 to be out of calibration. If the original calibration equation were used, a -0.7 kg/m$^3$ error at 425 kg/m$^3$ and a 1.2 kg/m$^3$ error at 460 kg/m$^3$ results. Also the meter shows an increased sensitivity to the liquid in which it is used. Refitting equation (3) to the retest data for densimeter No. 2 can produce the residuals shown in figure 8.

Meter No. 1 shows good stability and good accuracy. Meter No. 2 shows much poorer stability and, consequently, poorer accuracy.

Based on the performance of meter No. 1, these results suggest that selected meters can have good accuracy. Field testing is the next step. Periodic recalibration is presently necessary to maintain accuracy at

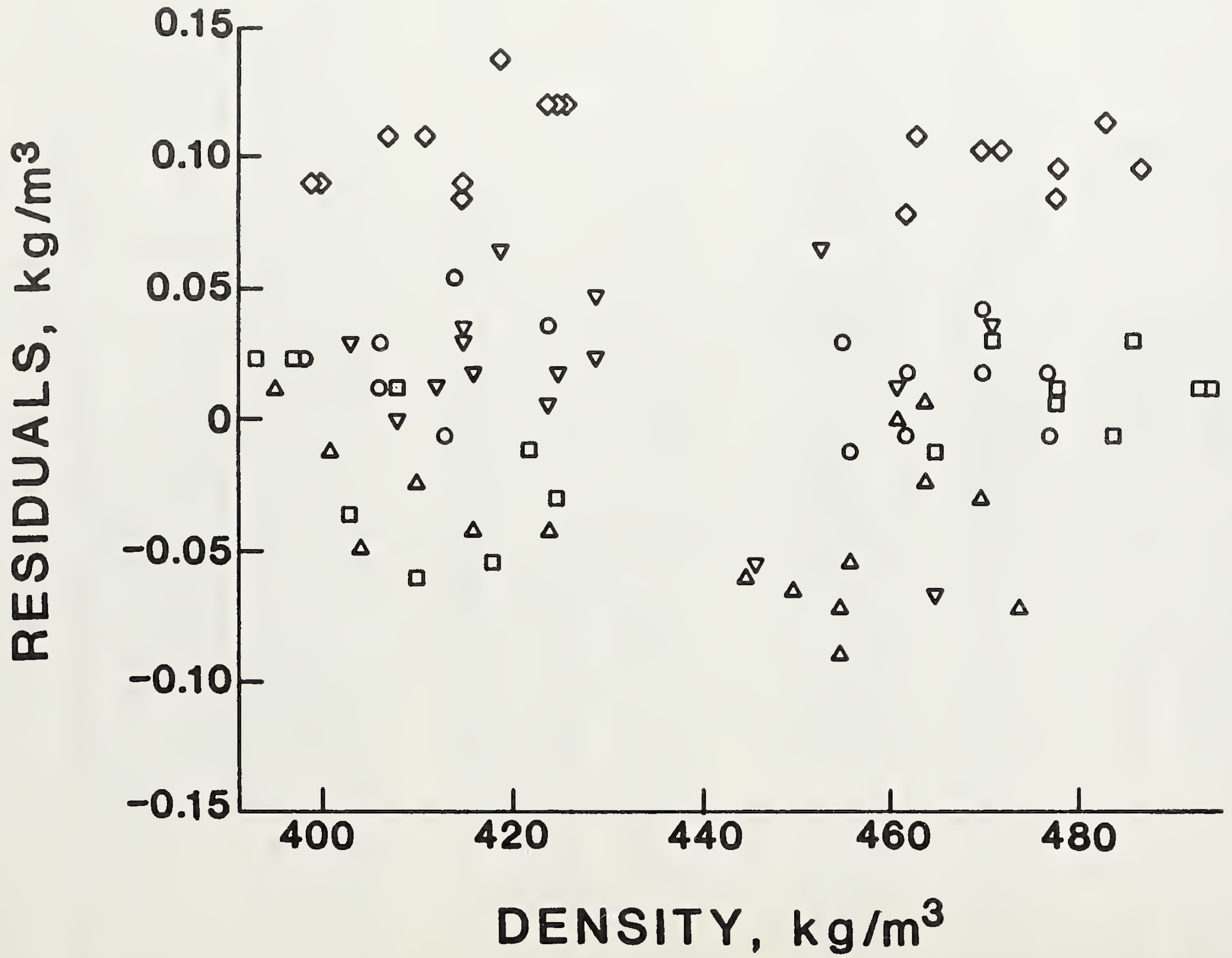

Figure 6. Residuals for vibrating cylinder no. 1, calculated from equation (4) versus density. The symbol ◇ represents the retest data. The other symbols correspond to those used in figure 3.

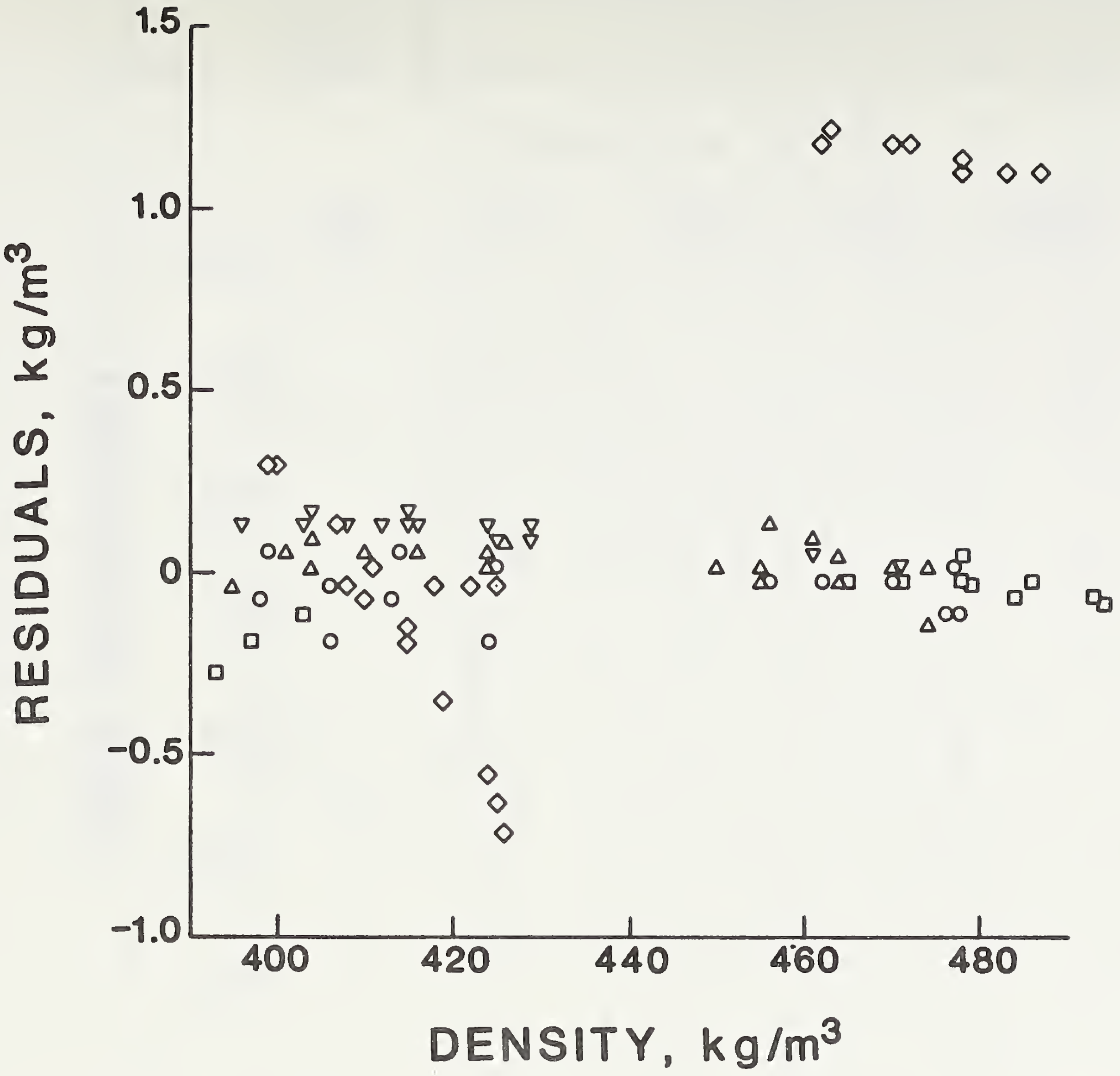

Figure 7. Residuals for vibrating cylinder no. 2 as calculated from equation (5) versus density. The symbol ◇ represents the retest data. The other symbols correspond to those used in figure 4.

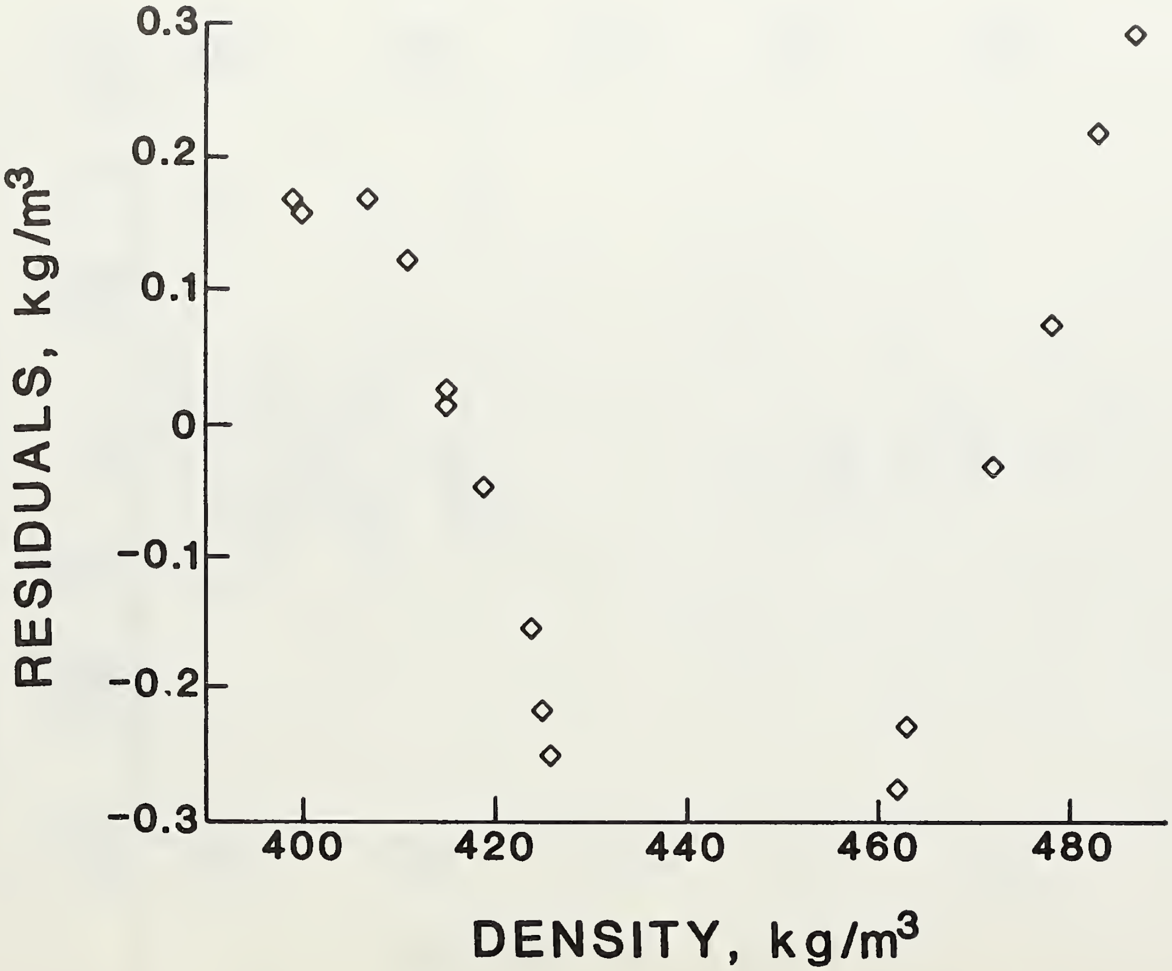

Figure 8. Residuals for vibrating cylinder no. 2 from fitting retest data to equation (3).

least until the stability of a number of meters has been established in field use over long periods of time.

If the commercial densimeters are not to exceed the random uncertainties reported here (for instance those of table 2), the filter screens must be removed from the sensing unit. In subcooled liquid there may be no problem.

### 4.2 Vibrating Cylinder Densimeter - Second Kind

This densimeter has not been previously tested. The vibrating cylinder consists of a tube forming the hole portion of a doughnut-shaped closed metal case. This case, containing the driving and sensing elements, excludes the liquid whose density is being measured from the outside wall of the vibrating cylinder. This entire unit is immersed in the liquid, but can be supported by bolting a flanged stem protruding from one side of the instrument to a support stem passing through the liquid container wall. The electrical leads are contained within this stem. For the measurements reported here, the density sensor was supported on its outer surface on a curved wood block. The axis of the vibrating cylinder was horizontal with neither end near any solid object.

The manufacturer supplied a calibration for this instrument with correction terms for the velocity of sound, pressure and temperature of the sample liquid. The calibration equation provided is:

$$\rho_b = 2221.2363 + .010101521 \times \tau^2 \ (\mathrm{kg/m^3}) \qquad (6)$$

where $\tau$ is the period of oscillation in μs and $\rho_b$ is the basic density. The density, $\rho_1$, corrected for the liquid velocity of sound is:

$$\rho_1 = \rho_b \frac{1 + 17273.47/\tau^2}{1 + 3.38610^{10}/\tau^2 C^2} \qquad (7)$$

where $\tau$ is the same as above and C is the sound velocity of the liquid in m/s. An appropriate expression for C is discussed below.

The density with the pressure effect correction is:

$$\rho_2 = \rho_1 \, [1-6.77 \times 10^{-6} \times \Delta P] - 0.0151 \times \Delta P \qquad (8)$$

where $\Delta P$ is the absolute operating pressure in bars less 1 bar. Finally, the true density $\rho$ is $\rho_2$ corrected for temperature:

$$\rho = \rho_2 \, [1-1.38 \times 10^{-5} \times \Delta T] - 0.08892 \times \Delta T \qquad (9)$$

where $\Delta T = (T - 23.14°C)$ and T is the liquid sample temperature in °C.

Since the densimeters were tested primarily in pure methane and an LNG like mixture of methane, propane and nitrogen, appropriate velocities of sound for both are needed. From the velocities of sound for methane given by Goodwin [5], the approximate expression for C(T) is:

$$C(T) = -10.316 \times T + 2490.4 \ (\mathrm{m/s}) \qquad (10)$$

where T is temperature in Kelvins.

The LNG-like mixture consisted of methane with about 4 to 6% propane and 1 to 2% nitrogen. The concentrations vary both from filling to filling and with temperature since nitrogen and methane preferentially leave the solution to fill the vapor space as the liquid temperature is raised. Since velocities of sound for liquid mixtures are not readily available, the sound velocity was estimated to be $0.95C_C + 0.05C_{C3}$ at both 110 and 126 K, where $C_C$ and $C_{C3}$ are the methane and propane sound velocities respectively. Assuming a dependence linear in T, the mixture sound velocity is:

$$C(T) = -10.44T + 2550 \text{ (m/s)}. \tag{11}$$

The model used to analyze the density data is:

$$\Delta\rho = \rho - \rho_{DRS} = \mu + a\,\rho_{DRS} + \alpha_i + e_i \tag{12}$$

where $\rho$ is the density determined by eq (9) for the vibrating cylinder densimeter, $\rho_{DRS}$, the density determined by the DRS densimeter, $\mu$ and a are the constants of a linear fit, the $\alpha_i$ are the offsets attributable to composition differences in the case of the LNG like mixture and also to filling-to-filling shifts in the densimeter calibrations, and the $e_i$ are unspecified random errors.

This densimeter was tested in eight fillings of the DRS. For the first two fillings, only the resonant frequency was recorded; for the remaining six, both frequency and period were recorded on separate counters. The period reading had a factor of 20 greater resolution than the frequency reading, an offset between density determined by frequency and that determined from period was observed. This offset corresponds to less than 0.1 Hz, the resolution of the frequency counter for a 10 second counting interval, and the count always read low by

<0.1 Hz as would be expected for a resolution limitation. The period data were used where available because of the increased resolution.

Figure 9 shows the $\Delta\rho$ for methane versus DRS density ($\rho_{DRS}$). Symbols 1 through 8 represent the first through eighth fillings, respectively.

Offsets in the density data due to the frequency counter resolution is apparent in the results of the first and second filling. Figure 10 shows $\Delta\rho$ versus $\rho_{DRS}$ for the LNG liquid mixture results. The pure methane velocity of sound, eq (10) was used. Any offset in the density values for fillings 1 and 2 is completely masked by the much larger filling-to-filling shifts shown in figure 10. This tendency for the density data to lie on separate but parallel curves implies the presence of a liquid composition dependency in the densimeter.

Figures 9 and 10 both show a linear dependence of $\Delta\rho$ on $\rho$ and the slopes are similar. However, the $\Delta\rho$ versus $\rho$ curve for the liquid methane density is offset from the average of the LNG density by approximately 12 kg/m$^3$ at 430 kg/m$^3$ when the liquid methane velocity of sound is used to calculate density. This offset is reduced to about 8 kg/m$^3$ by using eq (11) for C. The slope in the $\Delta\rho$ versus $\rho$ probably results from the increase in temperature, pressure, or both that accompanies the decrease in density of the liquid sample. The offset between the curve for the two different liquids must be caused by the composition change, possibly through differences in velocity of sound.

Equation (12) was fit to the methane data excluding the first two fillings, and the results are shown in the first line of table 5. We have assumed that the $\alpha_i$ are random shifts from filling-to-filling, and a standard deviation $\widehat{\sigma_\alpha}$, has been estimated for them. Combining the upper 99% confidence limit for $\sigma_\alpha$ and the upper 99% confidence limit for $\widehat{\sigma_e}$, we get $(0.14^2 + 0.07^2)^{1/2} = 0.16$ kg/m$^3$.

Three times this value represents the random uncertainty of a single density measurement made using this densimeter in the DRS. Part of the random error is due to the DRS densimeter, but this contribution is relatively small [3].

The equation was fit twice to the LNG data, excluding the first two fillings, once using the methane velocity of sound and once using the approximation (eq (11) and fig. 10) for a 95% methane, -5% propane mixture; i.e., 95% velocity

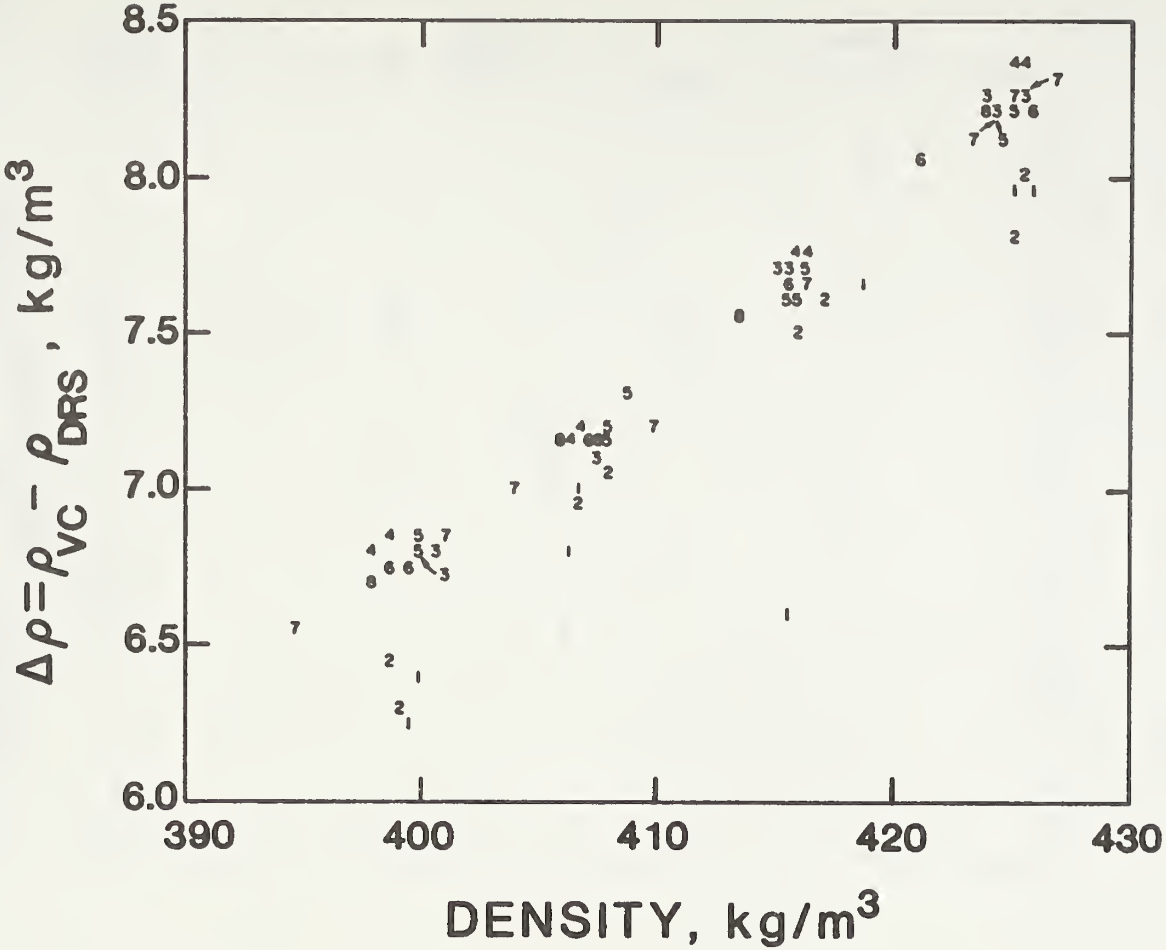

Figure 9. Difference in density measured by the DRS densimeter and the vibrating cylinder densimeter for liquid methane. Each symbol is a different filling.

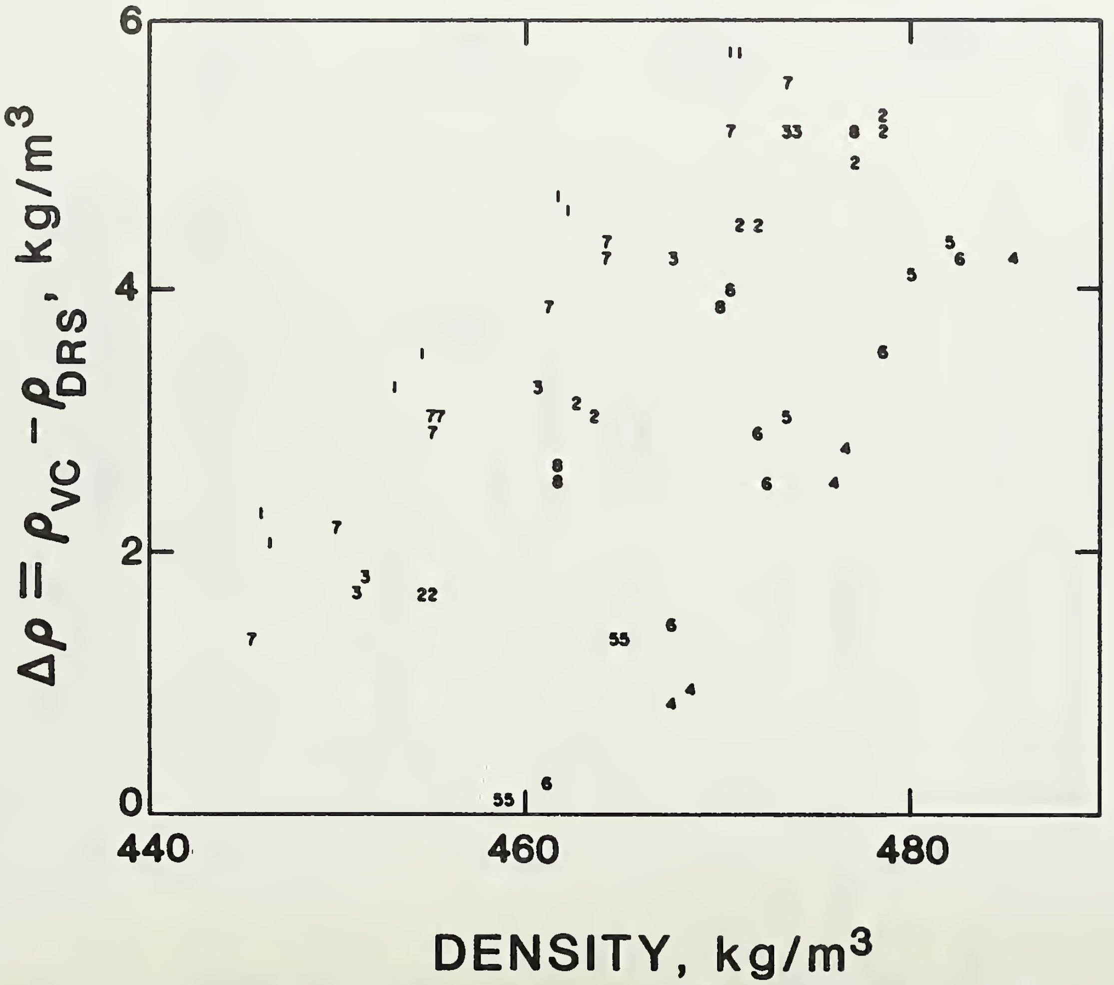

Figure 10. Difference in density measured by the DRS densimeter and the vibrating cylinder densimeter for various LNG-like mixtures of methane and 4 to 6% propane both with and without nitrogen. The different symbols indicate different fillings.

of methane + 5% velocity of propane. The results are given respectively, in lines 2 and 3 of table 5. As would be expected, the estimated standard deviations $\hat{\sigma}_\alpha$ and $\hat{\sigma}_e$ are about the same in both cases. Now estimating a standard deviation for the $\alpha_i$ in this case is misleading. Most of the variation in the $\alpha_i$ results not from random shifts associated with densimeter, but from the varying amounts of propane and nitrogen added to the methane. The scatter in the LNG data from any one sample is comparable to the scatter seen in the pure methane data. About six times $\hat{\sigma}_\alpha$ might roughly represent the sensitivity of the meter to the 4% to 6% range of the propane content in the mixture. This amounts to 0.4% spread for the average density value of the range 445 kg/m$^3$ to 491 kg/m$^3$.

Table 5. Results from filling data to equation
$\Delta\rho = \mu + a_{DRS} + \alpha_i + e_{ij}$

| | $\mu$(kg/m$^3$) 99% C.I.* | a(kg/m$^3$) 99% C.I.* | $\sigma_\alpha$(kg/m$^3$) | | $\sigma_e$(kg/m$^3$) | |
|---|---|---|---|---|---|---|
| | | | Est | Upper 99% C.B.+ | Est | Upper 99% C.B.+ |
| Methane | -16.25 ± 0.77 | .0576 ± .0019 | .045 | .14 | .052 | .070 |
| LNG (methane velocity of sound) | -73.6 ± 3.7 | .1634 ± .0080 | .64 | --- | .17 | .23 |
| LNG (LNG velocity of sound) | -57.8 ± 3.4 | .1346 ± .0073 | .61 | --- | .15 | .20 |

* Confidence interval
\+ Confidence bound

The factory calibration relation for LNG was extrapolated from measurements in other liquids. The temperature and velocity of sound corrections were calculated from other liquids. The corrections determined in the factory calibration for velocity of sound and temperature and/or pressure are obviously too small but can be adjusted to greatly improve agreement between the measured and actual density. The poor calibration of the densimeter disclosed by these tests once again emphasizes the desirability of calibrating densimeters in the liquid in which it will be used.

### 4.3 Vibrating Plate Densimeter

Since the original tests on the plate type densimeter, one additional unit has been tested in the DRS. This unit, in three attempts to calibrate it, suffered first from oil and water leaking into the stem and later from unexplained shifts in calibration between fillings of the DRS and sometimes during a filling. This unit was especially constructed to permit installation in the DRS and the calibration shifts may be unique to this instrument. The first vibrating plate densimeter tested behaved satisfactorily in cryogenic liquids. The original unit tested showed only small variations from filling to filling and functioned quite satisfactorily in liquid methane and LNG like mixtures.

Because problems arose during the tests of the one unit studied subsequent to the first, we can add, at this writing, no additional information concerning the accuracy, repeatability, and long term reliability of this vibrating plate densimeter of a more recent design.

## 4.4 Displacement Densimeter

The calibration of the original densimeter tested agreed well with the density reference system. This calibration was obtained after the densimeter had been returned once, at least, to the manufacturer for recalibration. Tests of subsequent instruments showed calibration errors up to 1/2%.

An alternate method of calibration for these densimeters was suggested. Liquid methane and LNG rather than liquid nitrogen and ambient temperature liquid would be used. Since the DRS was the only available calibration device using these liquids, the calibrations were done in it. Pure methane liquid and a mixture containing about 5% propane and 0 to 2% pure nitrogen were the calibration fluids.

In the first reported examination of a densimeter of this design, we noted a shift in the densities measured of about 0.1% relative to the DRS for the second filling but observed no corresponding shifts in the densities measured by the other densimeters present. During some later tests of other densimeters of the same manufacture, such a shift was noted again. The densimeter design subsequently was modified to eliminate this shift. We then tested three of the modified units in the DRS. Since these modified units did not have a factory calibration, they were calibrated in the DRS and tested for stability. They were first calibrated then returned to their packing boxes. Transporting and handling were simulated by hauling the densimeters in an automobile distances of 300 to 800 km. The calibration constants derived from the initial data were entered into the readout electronics and each of the densimeters were retested in the DRS to determine whether calibration shifts had resulted from the simulated handling and transport.

The following calibration equation was fit to the $\rho$, V, T data:

$$\rho = [a+b*V*(1+C*T)]/[1+d*T] \tag{13}$$

where $\rho$ is the density given by the DRS, V is the lift voltage of the displacement densimeter under test, T is its temperature readout, and a, b, c, d are the calibration constants. Since this equation is not linear in its coefficiencies, the data were fit by an iterative least squares method.

Table 6 gives the values of these coefficients, their estimated standard deviations, and the residual standard deviations for each of the three displacement densimeters based on the first set of tests.

The first of each of the two sets of readings taken at a particular temperature setting was used in most instances.

As these were the first tests with the rebuilt DRS, we experienced some minor problems during the course of these tests. The stirrer failed during the latter part of the first tests of No. 2, so equilibrium was obtained using only the heater and cooling coils. Noisy readings from occasional internal disturbances or exterior circuit noise was experienced. If a point looked suspiciously high or low, the second set of readings was used. When both sets shows the same behavior, the point was eliminated entirely. Since each temperature setting is repeated twice in a test series, an outlying point is usually obvious. For the initial test series on the three densimeters, only two points were eliminated entirely and these were for densimeter No. 2.

As explained above, after the simulated hauling, a second set of data was taken. For meters No. 1 and No. 3, one outlying point each was removed from this second set. Using the coefficients from the first series of tests, density values were computed from the lift voltage and temperature for both the first and second series of tests. The corresponding DRS values were substracted from the values predicted by eq (13) and the results are shown in figures 11, 12, and 13 for densimeters No. 1, No. 2, and No. 3, respectively.

For densimeter No. 1, figure 11 shows an upward shift of about 0.025%. In the case of meter No. 2, figure 12 indicates a slope change as well as a shift. Using the calibration equation from the first tests, the second test series predicts 0.03% low for methane and about 0.01% low for the LNG-like mixture. The least change from the first to the second test series occurred for densimeter No. 3. Figure 13 shows the predicted methane values for the second test series to be about 0.01% high for methane to about half that high for the LNG-like mixture.

The estimated standard deviations for these meters ranged from 0.006% for the first two to 0.01% for the third. However, the four outliers removed were in error from about 0.05% to 0.2%.

The calibration procedure used produced a calibration that, when combined with whatever effects handling might have had between the first and second tests, agreed with the DRS to ± 0.03% or better. The tests of these three indicate that

Table 6. Densimeter Calibration Coefficients

| Densimeter | a (S.D.)* | b (S.D.)* | c (S.D.)* | d (S.D.)* | Residual std dev (d.f.)† |
|---|---|---|---|---|---|
| No. 1 | 478.39 (.16) | -0.6525 (.0022) | $-1.055\text{x}10^{-4}(.26\text{x}10^{-4})$ | $2.93\text{x}10^{-5}(.29\text{x}10^{-5})$ | 0.018 kg/m$^3$ (11) |
| No. 2 | 477.01 (.22) | -0.7414 (.0038) | $-1.39\text{x}10^{-4}(.39\text{x}10^{-4})$ | not significant | 0.028 kg/m$^3$ (12) |
| No. 3 | 472.51 (.36) | -0.7328 (.0058) | $-2.26\text{x}10^{-4}(.60\text{x}10^{-4})$ | not significant | 0.050 kg/m$^3$ (12) |

*(S.D.) - estimated standard deviation of coefficient

†(d.f.) - degrees of freedom

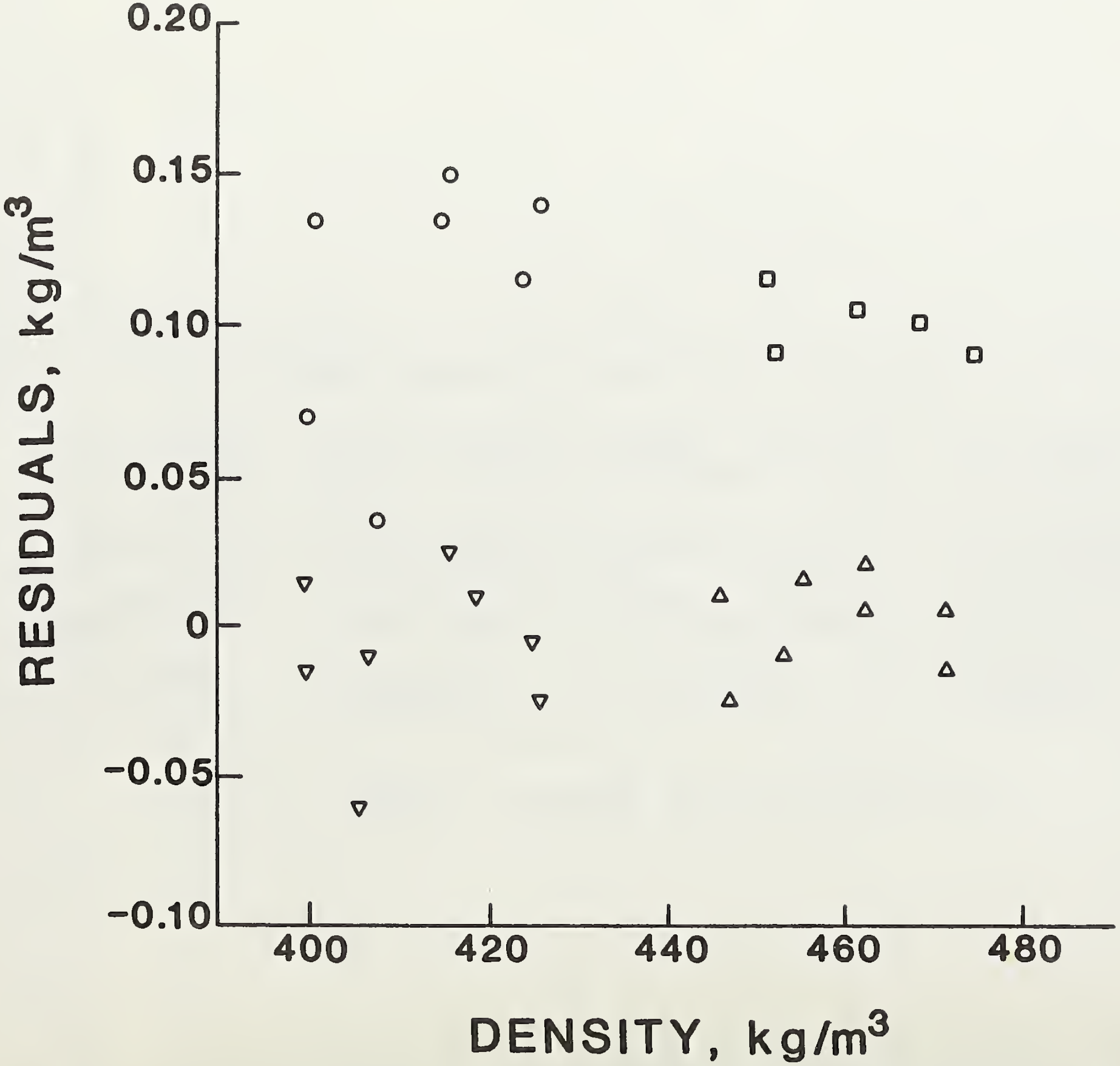

Figure 11. Residuals for displacement densimeter #1 obtained from subtracting $\rho_{DRS}$ from predicted $\rho$ based on eq (13) and first test series.
▽, 1st series, $CH_4$. △ , 1st series, LNG. ○ , 2nd series, $CH_4$.
□, 2nd series, LNG.

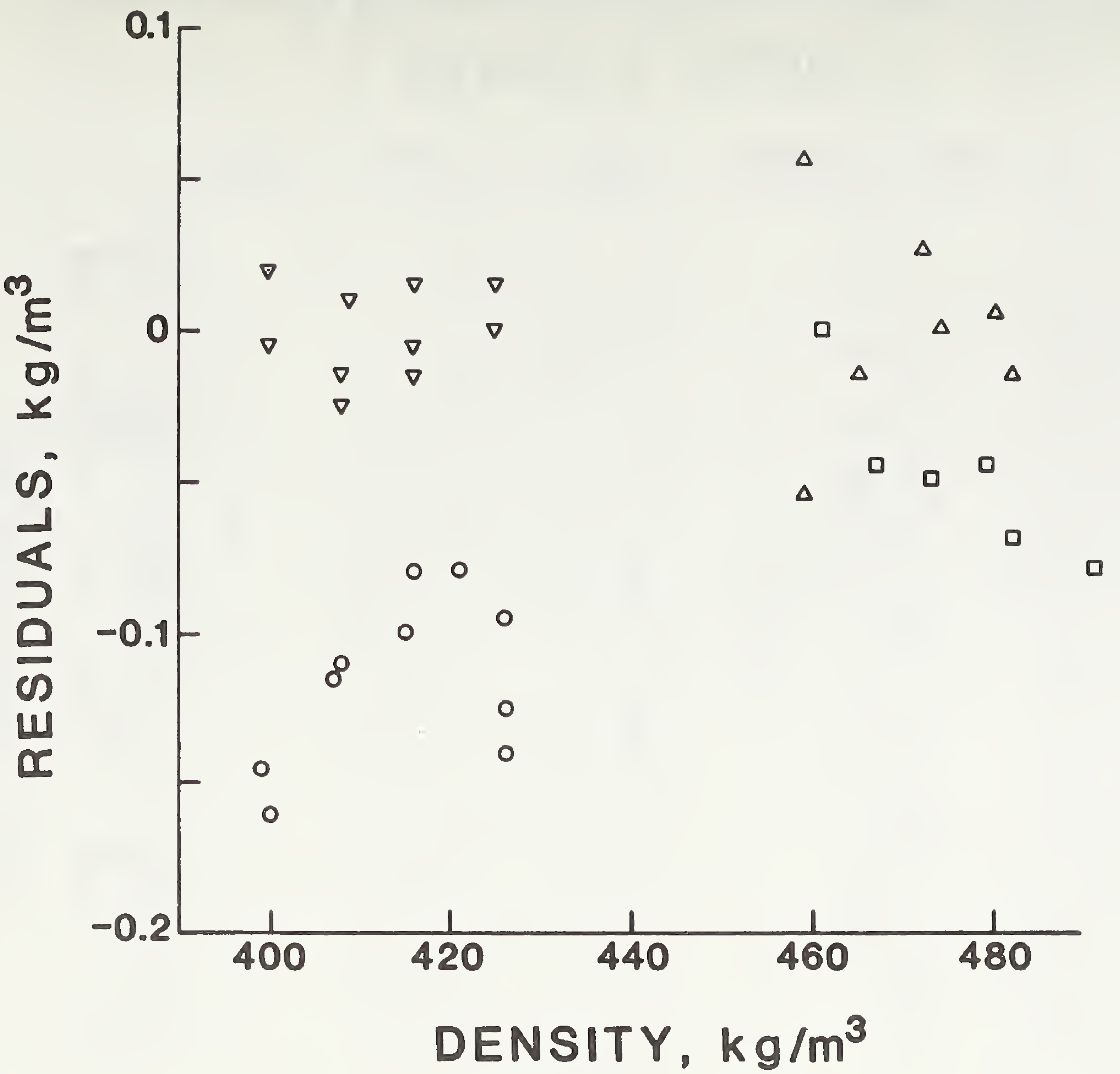

Figure 12. Residuals for displacement densimeter #2 obtained from subtracting $\rho_{DRS}$ from predicted $\rho$ based on eq (13) and first test series. ▽, 1st series, $CH_4$. △, 1st series, LNG. ○, 2nd series, $CH_4$. □, 2nd series, LNG.

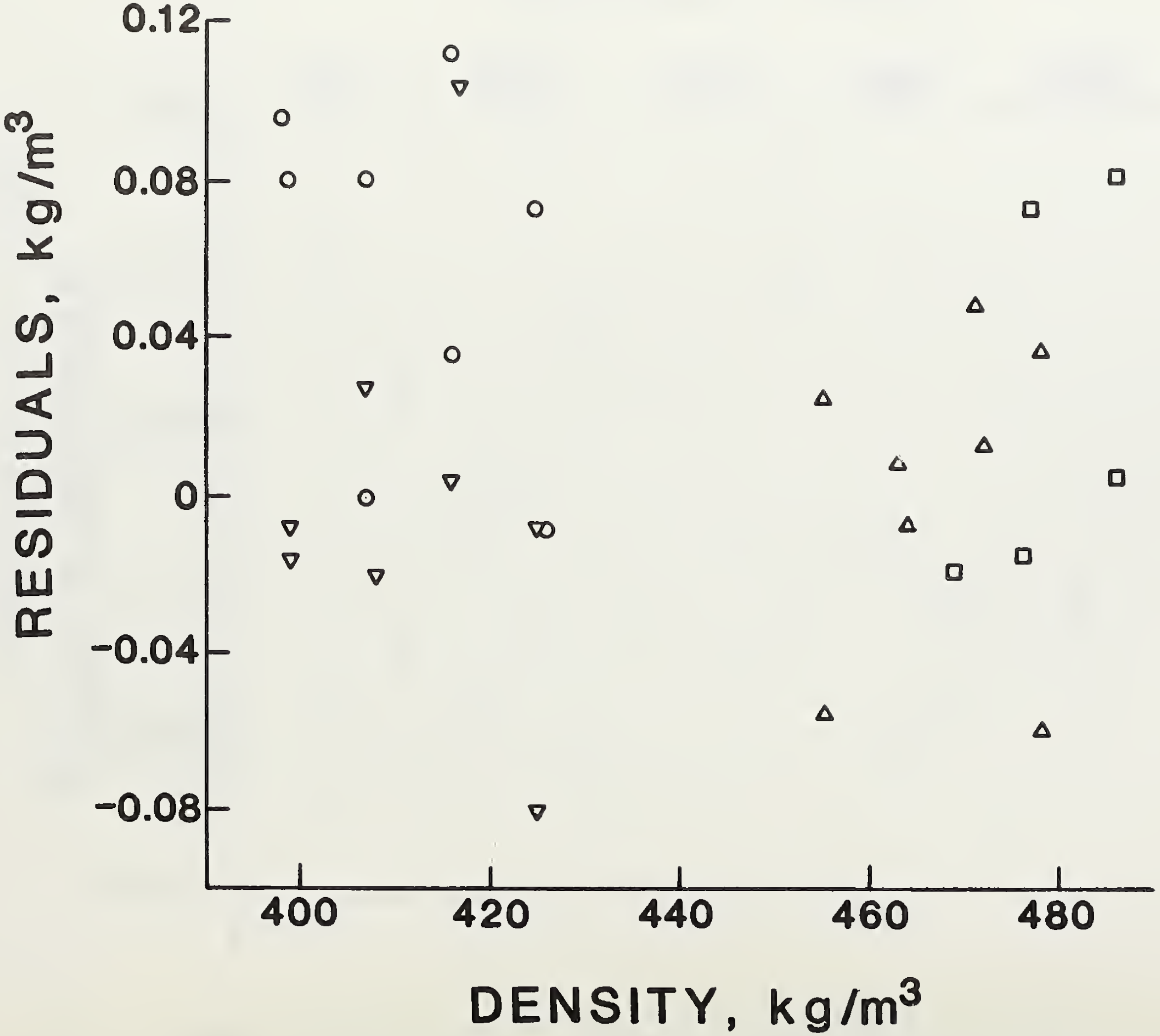

Figure 13. Residuals for displacement densimeter #3 obtained from subtracting $\rho_{DRS}$ from predicted $\rho$ based on eq (13) and first test series. ▽, 1st series, $CH_4$. △, 1st series, LNG. ○, 2nd series, $CH_4$. □, 2nd series, LNG.

the calibration method is adequate and the shift in calibration appears to be eliminated by the design changes incorporated into these densimeters. The occasional larger shifts observed apparently were probably associated with the equilibrium in the DRS. These were the first tests with the rebuilt DRS and some learning is required before the best results are obtained consistantly with a new apparatus. In any case, the largest shift is still small and repeated readings possible in a stable temperature environment, such as a tank, would eliminate occasional large deviations if associated entirely with the displacement densimeter.

This densimeter now needs some testing in field environments to determine its reliability and calibration stability over long periods of service.

## 5. CONCLUSIONS

For the vibrating cylinder sensimeter of the first kind, three essentially identical units calibrated by NBS for transfer standards were tested. All three units showed similar temperature dependence. Calibration equations for two of the units were estimated to be good to ±0.1%. The third unit gave evidence of drift and no prediction for its accuracy was provided. Two of the units were retested approximately eighteen months later. One of the units showed good agreement with the previous test results; the second unit was the one that had showed evidence earlier of drift, and the results for it were relatively large changes of calibration.

The vibrating cylinder densimeter of the second kind showed a marked dependency on composition. Repeatability for this meter when used on methane was about 0.1%, but when used on the LNG-like mixtures, which differed in small percentages of the amounts of propane and nitrogen, repeatability was about 0.4% if composition was not taken into account.

As is explained in the text, the vibrating plate densimeter tested would not maintain a calibration.

Three displacement type densimeters of the same design were tested that had no previous calibration. The meters were calibrated and showed good precision (better than ±.05%); although for one of the meters two points were removed as outliers. The meters were removed from the DRS and subject to simulated hauling as described in the text, and then retested. The retesting showed from 0.025% high for one meter to 0.03% low for another. This difference includes both the shifts of calibration from calculating and entering the calibration constants into the electronics and any shifts resulting from handlng the densimeter between tests.

All the instruments tested over a span of time have shown improved ability to measure LNG densities. More testing is necessary to establish accuracy and reliability over long periods of use. Field installations are the place to do that. Calibration systems are necessary for periodic calibration testing of these densimeters.

The DRS will remain available for tests on a cost basis into the future. A portable version of the DRS densimeter called the portable reference densimeter (PRD) also is available for testing other densimeter calibration facilities [6,7].

Results of comparison measurements between the DRS and the densimeter test system at Gaz de France [9] via the PRD [6] show that even in the laboratory, the density determined from compositional analysis and sampling is uncertain by about ±0.25%. The field measurement accuracy for liquid sampling and gas analysis is much poorer than laboratory measurement based on the heating value studies by NBS personnel [8]. Thus, ±0.25% is probably a lower uncertainty limit for density calculated from compositions obtained by liquid sampling and analysis. This should be easily improved by direct density measurement with densimeters.

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Densimeters for liquefied natural gas (LNG) from four manufacturers were tested in liquid methane and an LNG-like mixture of methane, propane, and nitrogen in the density reference system (DRS). The calibration and performance of one type tested for the first time are reported. The stability of the calibrations and performances of three densimeters of a type previously tested have been examined and are also reported here.

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