

Effect of Dissolved Nitrogen Gas on the Density of Di-2-Ethylhexyl Sebacate: Working Fluid of the NIST Oil Ultrasonic Interferometer Manometer Pressure Standard

J. H. Hendricks, J. R. Ricker, J. H. Chow and D. A. Olson

Abstract: The National Institute of Standards and Technology (NIST) Low Pressure Manometry Laboratory maintains national pressure standards ranging from 1 mPa to 360 kPa through the operation of four ultrasonic interferometer manometer (UIM) pressure standards. NIST's newest UIM standard operates with Di-2-ethylhexyl sebacate (DEHS) oil as the working fluid over the range of 1 mPa to 140 Pa in absolute mode. The relative change in density of DEHS oil as a function of nitrogen gas pressure was determined using a vibrating-tube densimeter with measurement repeatability of 1×10^{-6} g/cm³ and measurement accuracy of 5×10^{-6} g/cm³ given by the instrument manufacturer. The densimeter was modified to operate at pressures below one atmosphere. The density of DEHS oil was observed to follow a linear dependence with the pressure of nitrogen gas exposure. The difference or change in density of DEHS oil after vacuum exposure ($\leq 8 \times 10^{-4}$ Pa) and pressures ranging from 138 Pa to 101 kPa was evaluated. For the pressures up to 1.367 kPa, there was no statistically significant change in the oil density observed. However, exposure to pressures between 10 kPa and 101 kPa showed significant density changes. The density of DEHS oil decreased by 46 ppm \pm 5 ppm after 2 h of nitrogen gas exposure at 101 kPa. The density of DEHS oil decreased by 42 ppm \pm 3 ppm after more than 24 h air exposure at 101 kPa. The results of this study show that the effect of dissolved gas on the density of DEHS oil does not contribute significantly to the pressure dependent uncertainty of the NIST oil UIM when operated over its range of 1 mPa to 140 Pa in absolute mode. Additionally, the results demonstrate that the oil density change is small enough that an oil manometer with an extended range of 1.4 kPa (10 torr) would not be adversely impacted by this gas density effect.

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1. Introduction

The National Institute of Standards and Technology (NIST) Low Pressure Manometry Laboratory provides national pressure standards ranging from 1 mPa to 360 kPa through the operation of four ultrasonic interferometer manometer (UIM) pressure standards. The NIST 13 kPa, 160 kPa and 360 kPa UIMs operate with mercury as the working fluid. The fourth and newest UIM operates with Di-2-ethylhexyl sebacate (DEHS) oil as the working fluid. The designed operational range of the oil UIM is 1 mPa (7.5×10^{-6} torr) to 140 Pa (≈ 1 torr). This NIST standard is currently used to provide traceability to the International System of Units (SI) for customer low pressure transducer capacitance diaphragm gauges (CDGs) with full scale

(FS) ranges of 13 Pa (0.1 torr), 133 Pa (1 torr), and the bottom range (0.01 FS and 0.1 FS) of 1.3 kPa (10 torr) CDGs.

The oil manometer standard was developed to provide accurate measurements at pressures where the effect of room temperature mercury vapor pressure (≈ 0.2 Pa) limits the resolution and accuracy of the NIST mercury UIMs in absolute mode. One advantage of using mercury in UIMs is that nitrogen calibration gas is insoluble in mercury and does not change the density of the mercury, which is critical to the measurement performance of the UIM standard. Nitrogen calibration gas, however, is soluble in DEHS oil; a glass beaker filled with this gas-saturated oil, and placed under a bell-jar is observed to “bubble” when the bell-jar is evacuated. The NIST oil UIM relies on the density of the oil being stable, or measurably unchanged within the UIM uncertainty budget. The question is then posed as to what effect does the dissolved nitrogen gas have on density of the DEHS as a function of gas pressure? Is the effect large enough to impact the uncertainty budget of the NIST 140 Pa UIM over its operational pressure range of 1 mPa to 140 Pa with typical operational exposure times of several hours? Additionally, NIST has considered building a new oil UIM standard with an extended range of 1.4 kPa in absolute mode. If this new standard is built, would exposure to this higher gas pressure lead to unacceptably large oil density changes? Finally, while the current NIST 140 Pa UIM is used in absolute mode only, what would be the impact on the pressure measurement uncertainty if it was operated in gauge mode or was not adequately degassed prior to use in absolute mode after exposure to atmospheric pressure? This paper details the results of a study to answer these questions.

Liquid column manometers have been used to measure pressure since the middle of the seventeenth century when Evangelisti Torricelli discovered that a glass tube filled with mercury could be used to measure atmospheric pressure. [1] The modern manometers today operate on the same basic principle that pressure can be determined if one knows the density, the acceleration of gravity,

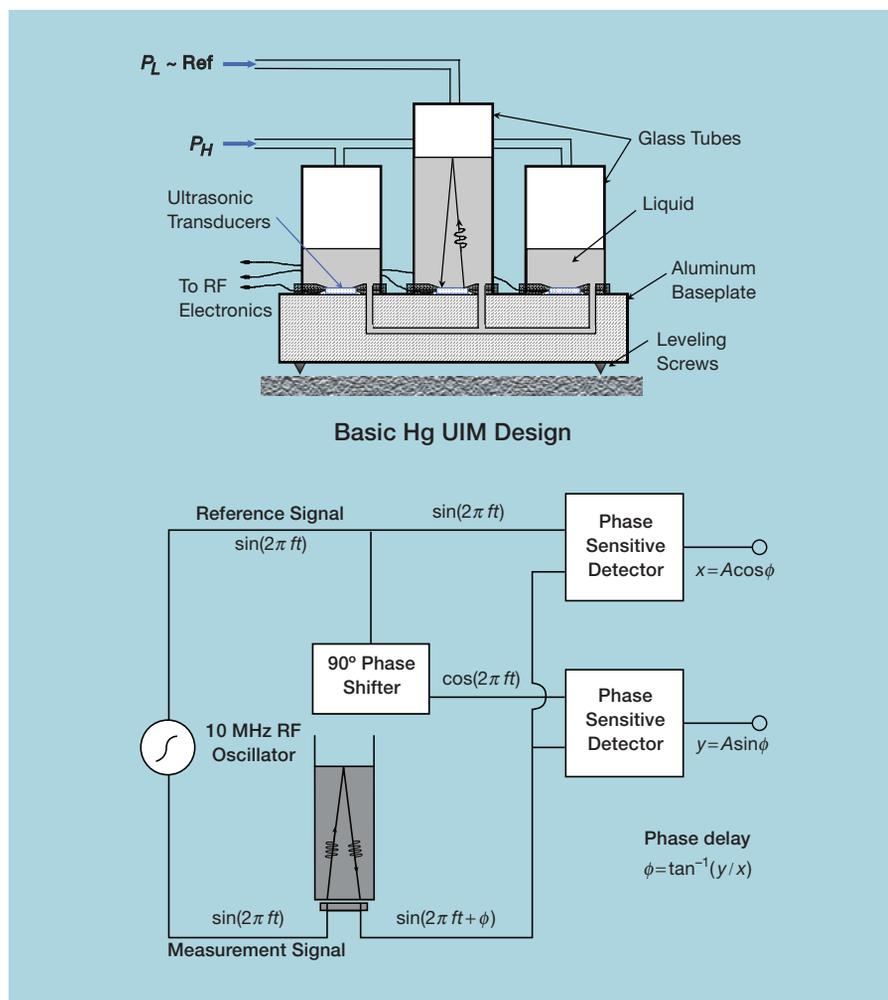


Figure 1. Schematic illustrating the method of determining column height of a liquid column manometer using ultrasound. The liquid is either mercury (Hg) or oil (DEHS). In liquid column UIMs, pulsed ultrasound emitted from the transducer disk transverses the column, is reflected from the liquid-gas interface, and returns to the transducer disk that also serves as a detector/receiver.

and differential height of a liquid column manometer.

The NIST UIM design is unique in that the column heights are determined by using a pulsed ultrasound technique (see Fig. 1). Knowing the time-of-flight, speed-of-sound, and by detecting the change in phase between sent and received signals enables the column heights to be accurately determined when at least four different, but closely spaced frequencies are used. For mercury UIMs 10 MHz ultrasound is used, while for the oil UIM, 5 MHz ultrasound is required for better ultrasound transmission. Both the speed-of-sound in the manometer fluid and the density must be accurately known for the NIST UIMs to operate with a high degree of accuracy. The standard uncertainty ($k = 1$) for the NIST mercury UIMs is

$[(3 \times 10^{-3} \text{ Pa})^2 + (2.6 \times 10^{-6} P)^2]^{1/2}$, where P is the measured pressure in Pa. References [2-7] give a full description of the NIST UIM technique and NIST oil and mercury UIM pressure measurement uncertainties. The density of mercury was accurately determined by Cook and by numerous relative density determinations done since Cook's original determination in 1961. [8, 9] With the speed-of-sound in mercury determined by Tilford [4], the NIST UIMs have best-in-the-world pressure measurement capabilities, with the lowest stated uncertainties over their operating pressures as was shown in international key comparisons of pressure. [10-11] However, the room temperature vapor pressure of mercury (≈ 0.2 Pa) ultimately limits the lowest absolute pressure that can be accurately measured. The

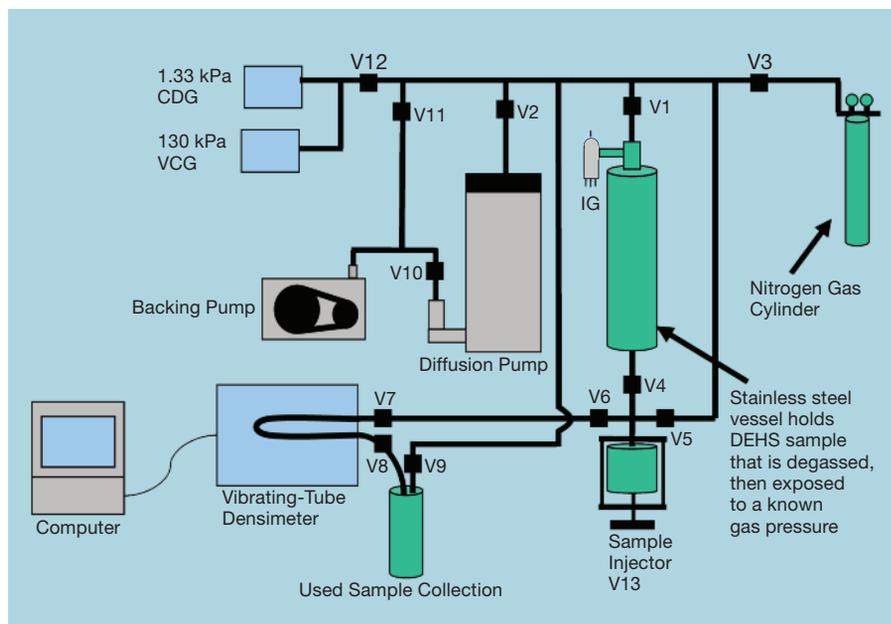


Figure 2. Schematic of the experimental apparatus to measure density under vacuum conditions. A stainless-steel vessel was charged with DEHS and evacuated to 8×10^{-4} Pa or lower. The degassed oil was then transferred under vacuum to a vibrating u-tube densimeter (DMA 5000¹). A 1.33 kPa capacitance diaphragm gauge (MKS 690) and a 130 kPa vibrating cylinder gauge (Ruska 6200B) measured the calibration gas pressure prior to density measurement with the densimeter.

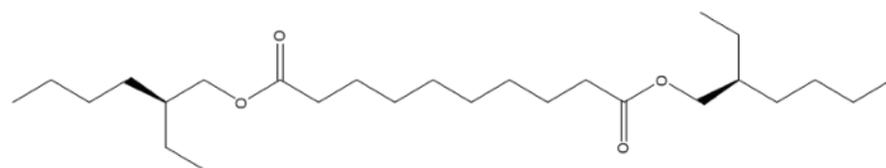
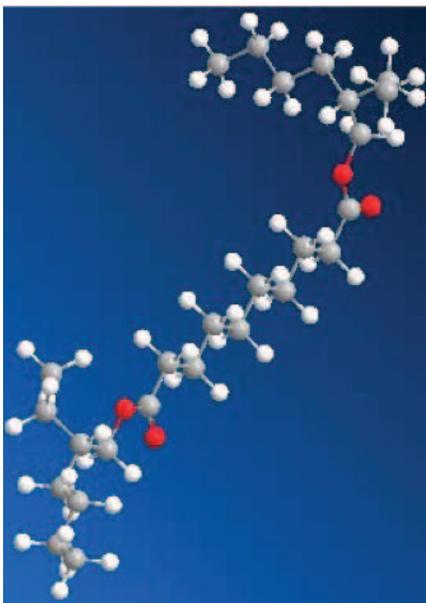


Figure 3. Di (2-ethylhexyl) Sebacate (DEHS) has the chemical structure shown above, and a chemical abstract service number (CAS No) 122-62-3. Common synonyms¹ include Invoil-s, Octoil-s, Difoil-s, dioctyl sebacate, decanedionic acid, bis (2-ethylhexyl) ester, octyl sebacate, sebacic acid bis (2-ethylhexyl) ester, Bis (2-ethylhexyl) sebacate, Bisoflex DOS, and DOS, etc. DEHS is a high molecular weight (426.68) straight chain synthetic ester that was chosen due to its relatively low room temperature vapor pressure of 4×10^{-5} Pa (3×10^{-7} torr). It is typically used as diffusion pump oil and has acceptable ultrasound transmission to be used in the NIST 140 Pa Oil UIM.

measure the change in density of DEHS oil as a function of pressure between 8×10^{-4} Pa (6×10^{-6} torr) and 101 kPa (atmospheric pressure) using a vibrating-tube densimeter. By tracking the measured changes in density, the effect of nitrogen gas on the density of DEHS oil was established, and while the effect is measurable at pressures beyond the range of the of the oil UIM, it does not exceed the uncertainty budget of the NIST 140 Pa UIM.

2. Apparatus Design

The primary goals of this experiment were to measure the relative change in density between oil that had been exposed to a known pressure of gas and oil that had been fully degassed, and to evaluate what effect the change in density would have on the NIST oil UIM uncertainty statement. The apparatus, shown in Fig. 2, was designed such that oil could be loaded into the main stainless steel sample vessel and then be fully degassed by pumping with a diffusion pump. Additionally, the design allowed for the degassed oil sample to be subsequently exposed to a known pressure of nitrogen calibration gas for a specific period of time, and then transferred to a vibrating-tube densimeter to measure density while still under conditions ranging from vacuum (8×10^{-4} Pa) to atmospheric pressure (nominally 101 kPa). A stainless steel sample vessel was constructed from a standard copper-gasket flanged nipple with an internal diameter of 40 mm. The vessel approximately mimics one of the NIST UIM pressure-side manometer columns geometry. The DEHS oil used in this study was taken from a batch of oil, lot 1202 obtained from Inland Vacuum Products sold under the product name of Invoil-s¹, a synonym for DEHS. The structure of DEHS, along with other common synonyms is shown in Fig. 3. Important features of the oil are low room temperature vapor pressure of 4×10^{-5} Pa and acceptable ultrasound transmission.

¹ Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply endorsement by NIST nor does it imply that the equipment or materials are necessarily the best for the purpose.

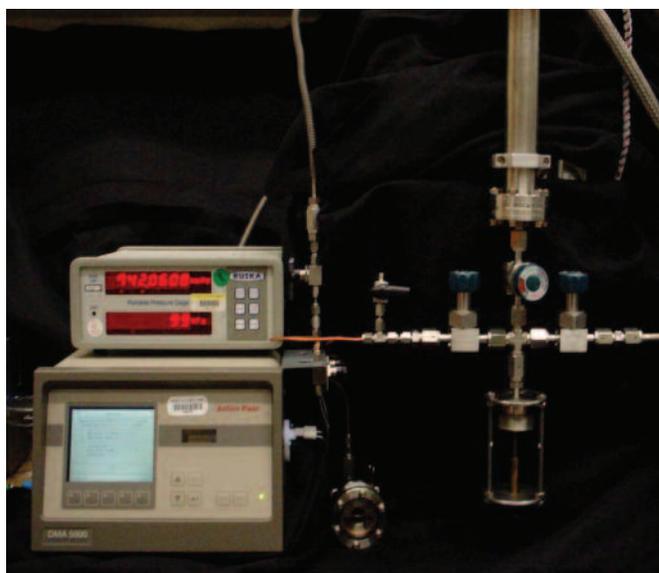


Figure 4. Photograph of the experimental apparatus. The densimeter, DMA 5000, has manufacturer specifications ($k = 1$) for repeatability: 1×10^{-6} g/cm³, uncertainty: 5×10^{-6} g/cm³, temperature control: ± 0.001 °C. The densimeter instrument measurement accuracy was checked with air and water density standards, and the stability of repeat measurements was consistent with the repeatability specification. The densimeter accuracy was not strictly evaluated for the measurement of DEHS which has a different density and viscosity than that of water. Calibration drift due to u-tube pressurization to 1 atmosphere changed the instrument reading by ≤ 2 ppm, which is essentially within the resolution of the instrument/measurement technique.

To measure the applied pressure, the system was equipped with a 130 kPa vibrating cylinder gauge (Ruska series 6200¹) and a high accuracy 1.33 kPa (10 torr) capacitance diaphragm gauge (MKS model 690¹). These gauges were calibrated against NIST UIM pressure standards [12] and at the time of use had NIST uncertainties of less than 0.5 % of reading for the CDG for pressures near 138 Pa (≈ 1 torr) and less than 0.05 % of reading for the resonance gauge at pressures near 101 kPa. The zero pressure indication of the CDG and VCG gauges were checked with a hot cathode ionization gauge (IG). The vacuum system was designed with all-metal construction to reduce outgassing from polymer based materials. All valves were either stainless-steel diaphragm type (V4, V5, V6), bellows with copper tipped seals (V1, V2, V3, V11, V12), or stainless steel body ball valves (V7, V8, V9). Vacuum seals were either silver-plated nickel gaskets or copper gaskets with a few exceptions. One area where metal gasket sealing was not feasible was the interconnecting oil lines to the vibrating-tube densimeter. In this location, the glass to metal-tube seal was made with Viton gaskets². The vacuum system was leak-checked with a helium leak detector to ensure that no physical helium leaks (non-permeation) exceeded 2.7×10^{12} molecules/sec (1×10^{-7} scc/sec). The system was pumped with an oil-diffusion pump (135 l/s for nitrogen) outfitted with a chilled-water cooled baffle. The diffusion pump was operated with the same oil being studied to

avoid any issue with diffusion pump oil cross-contamination. An ultimate (base-line) pressure of 1.3×10^{-5} Pa (1×10^{-7} torr) was measured with an ionization gauge when the sample chamber was empty (no oil) valves V6, V9 closed and valves V12, V2, V1, V4, V5 open (see Fig. 2). When the empty system was connected to the densimeter with valves V6, V7, V8, V9 open, a system base pressure of 1.3×10^{-4} Pa (1×10^{-6} torr) was measured. This higher base-line pressure is not surprising given the small diameter, 3.2 mm (1/8 inch) outer diameter (OD), copper tubing between V6 and V7 and 1.5 mm OD stainless steel tubing between V7 and V8 which limits pumping conductance, and the Viton² seals which are known to outgas and are permeable to gases such as nitrogen, water, and carbon dioxide.

An Anton Parr vibrating u-tube densimeter, model DMA5000¹, was modified by replacing Teflon-to-glass seals with Viton-to-glass seals.^{1, 2} The Viton seals enabled the use of the 1.5 mm OD stainless steel tubing necessary to connect to the rest of the vacuum system. These modifications were necessary so that the density measurements could be made under vacuum conditions, see Fig. 4. The calibration of the vibrating-tube densimeter was set and verified by following manufacturer's recommended procedure employing degassed distilled water and air to ensure that the densimeter calibration was within manufacturer specifications. A water density sample (distilled and degassed by boiling) was measured at $20.000 \text{ °C} \pm 0.001 \text{ °C}$ prior to all oil density measurements and found to be $(0.9982028 \pm 8.3 \times 10^{-7})$ g/cm³ and in agreement with the value given by the manufacturer of $(0.998203 \pm 1 \times 10^{-6})$ g/cm³ referenced to published ITS-90 tables.³ [13] Upon completion of all oil density measurements, the u-tube was carefully cleaned and the density of water (same density sample) was re-measured and found to be $(0.9982004 \pm 1.5 \times 10^{-6})$ g/cm³, or a value that was within 3 ppm of the original value including the combined uncertainty of the observations. The densimeter measurement accuracy of 5×10^{-6} g/cm³ was not strictly evaluated for the measurement of DEHS which has a different density and viscosity than that of water. The repeatability of the measurements was determined by taking multiple measurements under identical conditions. Results were found to agree with the manufacturer's stated repeatability of 1×10^{-6} g/cm³. In this study, all oil density measurements were performed at 20.000 °C , which was controlled by the densimeter. The manufacturer's stated temperature uncertainty of $\pm 0.001 \text{ °C}$ was not independently verified but is based upon two integrated Pt 100 platinum thermometers.

3. Experimental

Initially, to fully degas the oil when it came from the manufacturer, oil was exposed to vacuum conditions for over 10 days at room temperature to ensure impurities found in air, such as water were removed from the density sample. To return the oil to a degassed state after exposure to pure nitrogen, the oil was exposed to vacuum conditions until the ionization gauge indica-

³ More recent work gives a value of $(0.99820648 \pm 2.2 \times 10^{-7})$ g/cm³ at 20.001431 °C see C. H. Wolf, H. Bettin, and A. Gluschko, "Water Density Measurement by a Magnetic Flotation Apparatus," *Meas. Sci. Technol.*, vol. 17, pp. 2581–2587, 2006.

² Teflon and Viton are registered trademarks of DuPont.

Pressure (Pa) ($k = 1$)	Pressure (torr)	Gas	n-data	Batches	Exposure Time (h)	Density (g/cm ³) 20.000 °C	s. d. ⁴ of all data (g/cm ³)
$8 \times 10^{-4} \pm 2 \times 10^{-4}$ Fully degassed	6×10^{-6}	Nitrogen	57	5	>24	0.914415	2×10^{-6}
138 ± 0.5	1.035	Nitrogen	27	2	6, 23	0.914415	2×10^{-6}
435 ± 1	3.26	Nitrogen	12	1	5	0.914412	1×10^{-6}
1367 ± 0.5	10.25	Nitrogen	103	3	1, 6, 20	0.914413	1×10^{-6}
10000 ± 2.5	75	Nitrogen	107	1	19	0.914410	1×10^{-6}
50529 ± 12.5	379	Nitrogen	56	1	>24	0.914390	2×10^{-6}
101325 ± 25	760	Nitrogen	42	1	2	0.914373	4×10^{-6}
101325 ± 25	760	Air	51	1	>24	0.914377	2×10^{-6}
1367 ± 0.5	10.25	Nitrogen	10	1	1	0.914413	1×10^{-6}
1367 ± 0.5	10.25	Nitrogen	72	1	6	0.914413	1×10^{-6}
1367 ± 0.5	10.25	Nitrogen	21	1	20	0.914412	1×10^{-6}

Table 1. DEHS density shifts upon exposure to the calibration gas.

tion was generally less than 8×10^{-4} Pa (6×10^{-6} torr) which could typically be achieved after 20 h of pumping or less. The initial goal was to establish the maximum density change by comparing the fully degassed density to the fully air and nitrogen saturated values. Using the CDG and VCG pressure sensors to measure the fill pressure, nitrogen gas was introduced to the oil sample held in the stainless steel vessel (see Fig. 2) for a minimum exposure time of 1 h. Operation of the NIST oil manometer involves setting a pressure, waiting for the manometer to settle, and then recording both the gauge under test and the 140 Pa UIM pressure standard reading. Typically, this time interval is 15 min to 25 min for setting and recording one pressure. A typical calibration data collection run spanning 1 mPa to 140 Pa requires about 8 h to complete, with a series of ≈ 20 increasing pressures being sequentially set. Pressures greater than the current upper limit of the NIST oil manometer were also examined. At a pressure of 1.367 kPa (10 torr) a series of density measurements were made after 1 h, 6 h, and 20 h of exposure to evaluate if a measurable change in density could be detected as a function of time due to the process of the dissolving gas not reaching equilibrium after one hour of exposure. Samples of different exposure times were created by loading exposed oil into the sample injector by opening V4 (with V6 and V5 closed). The sample was then injected into the densimeter

and the density measured (V4 closed and V6 opened and sample injector V13 rotated). All density measurements were performed with a temperature setting of $20.000 \text{ °C} \pm 0.001 \text{ °C}$. The density was measured using the “equilibrium slow” setting, which is the highest accuracy reading procedure that ensures full equilibrium of sample temperature inside the densimeter. This procedure takes several minutes to complete after sample injection. Typical wait times after sample injection were five to ten minutes to ensure temperature equilibrium. Ten repeat measurements were generally taken before another sample was injected. A group of samples taken from the same pressure/exposure-time constituted a “batch”. Multiple batches were prepared and then analyzed at certain key pressures including fully degassed at a pressure of less than 8×10^{-4} Pa ($< 6 \times 10^{-6}$ torr), 138 Pa (1 torr) and 1.367 kPa (10 torr). The effect of possible calibration shift of the densimeter due to u-tube pressurization was checked by first measuring the density of a sample of degassed oil with vacuum conditions on both sides of the densimeter u-tube and then quickly repeating the measurements with 1 atmosphere of pressure on both sides of the densimeter u-tube. The observed result was that 1 atmosphere of u-tube pressurization changed the instrument reading by ≤ 2 ppm, which is within the resolution of the instrument/measurement technique.

4. Results and Analysis

Table 1 shows the measured density of DEHS after being fully degassed, and then exposed to various pressures of nitrogen gas for periods of time ranging from 1 h to more than 24 h. Five

⁴ s. d. is the standard deviation (Type A) uncertainty in measurement which does not include accuracy specification (Type B) given by the manufacturer ($k = 1$) of 5×10^{-6} g/cm³.

batches of fully degassed oil (see row 1 in Table 1) were prepared and measured resulting in 57 data points. The average of the five batch averages yielded a density value of 0.914415 g/cm^3 with a standard deviation of $1.3 \times 10^{-6} \text{ g/cm}^3$ (standard deviation of the mean of five averages). Alternatively, a simple average of all 57 data points yielded the same density value of 0.914415 g/cm^3 and an overall standard deviation of $1.6 \times 10^{-6} \text{ g/cm}^3$. This indicates that even between different batches, all readings appeared to come from the same parent population and that there was no systematic batch-to-batch variation. Therefore, to simplify analysis, all densities presented in Table 1 are simple averages of all data points taken at a given pressure. At a pressure of 138 Pa (1 torr) and an exposure time of 6 h to 23 h, the average density was 0.914415 g/cm^3 with a standard deviation $1.8 \times 10^{-6} \text{ g/cm}^3$. Therefore, no measurable density change was observed between fully degassed and 138 Pa exposed samples. Also shown in Table 1 are the results at 1.367 kPa (10.25 torr). This pressure is of interest because NIST has considered extending the range of the oil UIM to this pressure, which represents the maximum oil column length through which a useable ultrasound signal can be detected after reflection. At 1.367 kPa, three batches were prepared with exposure times of 1 h, 6 h, and 20 h resulting in 103 data points with an average density value of 0.914413 g/cm^3 and a standard deviation of $1.4 \times 10^{-6} \text{ g/cm}^3$. Shown in Table 1 (arrow) are data for 1 h, 6 h, and 20 h exposure time batches with average values of 0.914413 g/cm^3 , 0.914413 g/cm^3 , and 0.914412 g/cm^3 , respectively, showing no significant density change between exposure times. Thus, exposure to a pressure of 10 times the current maximum pressure range of the NIST 140 Pa UIM yielded no change in density within the type A uncertainty in the measurement (error bars). Therefore, building an extended range 1.367 kPa oil UIM is feasible in terms of negligible density change of the manometer fluid. Nitrogen exposure density data was also recorded at 10 kPa, 50 kPa, and 101 kPa with the clear trend emerging that increasing the pressure of nitrogen gas exposure

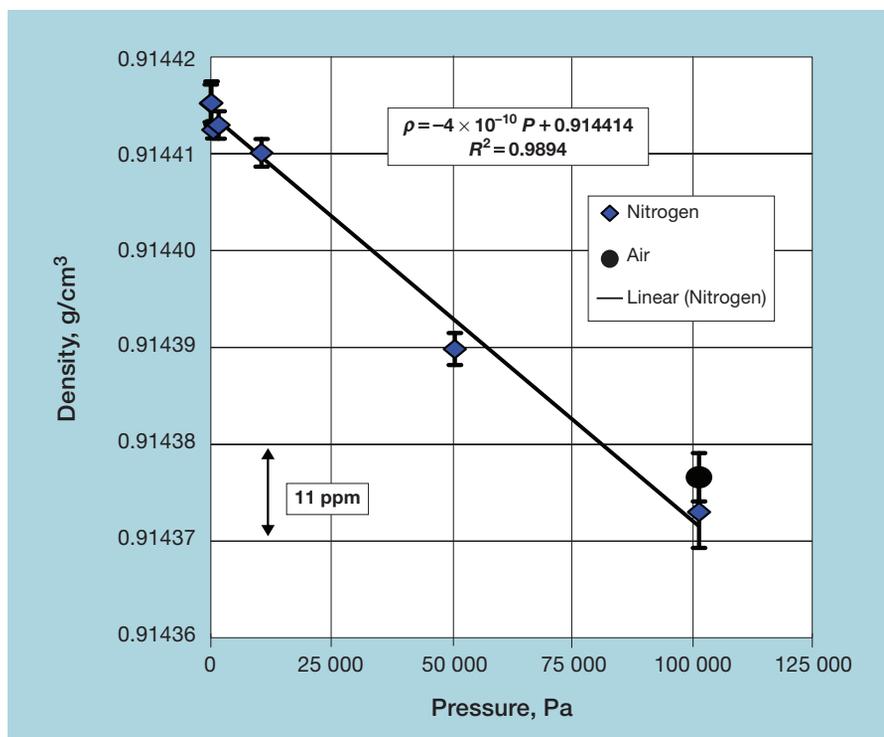


Figure 5. Linear plot shows density of DEHS after exposure to nitrogen gas at pressures ranging from $8 \times 10^{-4} \text{ Pa}$ to 1.367 kPa for periods of time ranging from 1 h to 20 h. All data at a given pressure were averaged and the error bars are the resulting standard deviation. The DEHS density decreased linearly as the partial pressure of nitrogen gas was increased. The error bars on the plot are the type A uncertainty ($k = 1$) of the measurement and do not include the densimeter measurement accuracy specification of $5 \times 10^{-6} \text{ g/cm}^3$.

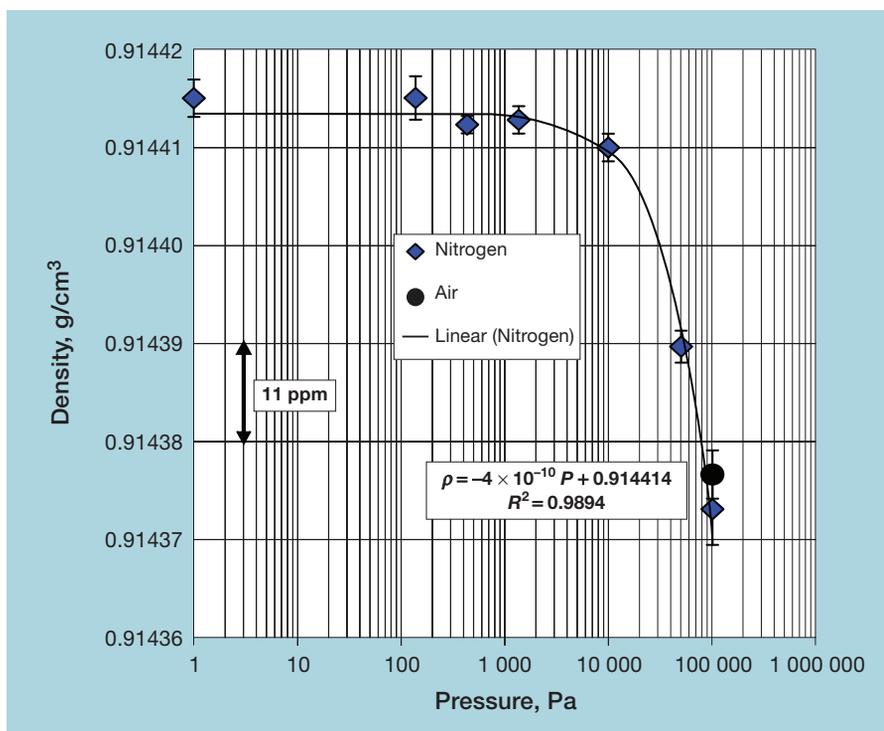


Figure 6. The log plot shows the density of DEHS as partial pressure of nitrogen gas was increased from $8 \times 10^{-4} \text{ Pa}$ to 1367 Pa (note that lowest pressure or “vacuum” data set is plotted at 1 Pa). At a pressure of 1367 Pa there was no significant difference in the measured density between 1 h and 20 h of exposure. All data at a given pressure were averaged and the error bars reflect the resulting standard deviation. The error bars on the plot are the type A uncertainty ($k = 1$) of the measurement and do not include the densimeter measurement accuracy specification of $5 \times 10^{-6} \text{ g/cm}^3$.

Pressure (Pa)	P (torr)	Gas	Pressure Limit for Change in Density	Change in Density (g/cm ³)	Change in Density* (g/cm ³)
$8 \times 10^{-4} \pm 2 \times 10^{-4}$	0.0075	Nitrogen	8×10^{-4} Pa = 0 Pa N ₂	–	–
138 ± 0.5	1.035	Nitrogen	0 Pa to 138 Pa N ₂	0.000 000	0 ± 3
435 ± 1	3.26	Nitrogen	0 Pa to 435 Pa N ₂	0.000 003	3 ± 2
1367 ± 0.5	10.25	Nitrogen	0 Pa to 1.37 kPa N ₂	0.000 002	2 ± 2
10000 ± 2.5	75	Nitrogen	0 Pa to 10.0 kPa N ₂	0.000 005	5 ± 2
50529 ± 12.5	379	Nitrogen	0 Pa to 50.5 kPa N ₂	0.000 025	28 ± 3
101325 ± 25	760	Nitrogen	0 Pa to 101.3 kPa N ₂	0.000 042	46 ± 5
101325 ± 25	760	Air	0 Pa to 101.3 kPa Air	0.000 038	42 ± 3

* Standard uncertainty ($k = 1$) due to taking a difference between two measured values each with its own standard uncertainty.

Table 2. DEHS density shifts upon exposure to calibration gas.

resulted in a decrease in the density of the oil. This is likely due to nitrogen dissolving into the DEHS and is consistent with other studies of similar oils. [14] Additionally, the density of oil exposed to 101 kPa air was measured and found to be $(0.914377 \pm 2 \times 10^{-6})$ g/cm³ which is the same within the error bars of the experimental method as the value for a similar pressure of nitrogen with a density of $(0.914373 \pm 4 \times 10^{-6})$ g/cm³.

Figure 5 is a plot of the data from Table 1 showing a linear dependence of DEHS density on the exposure pressure of nitrogen. Figure 6 shows the same data on a log-plot in order to more clearly show the low pressure data, which is clustered together in Fig. 5. The error bars in Figures 5 and 6 are the Type A uncertainty of the measurement, and do not include the densimeter accuracy specification of 5×10^{-6} g/cm³. As seen in Fig. 5 the density of DEHS at 20.000 °C \pm 0.001 °C can be expressed by a linear fit:

$$\rho_{(20.000 \text{ }^\circ\text{C})} = -4 \times 10^{-10} (\text{g/cm}^3 \text{ Pa}) P + 0.914414 \text{ g/cm}^3, \quad (1)$$

where P is the pressure of nitrogen in units of Pascal (Pa) for exposure times ≥ 1 h.

Table 2 lists the change in density of DEHS after vacuum exposure ($\leq 8 \times 10^{-4}$ Pa) and pressures ranging from 138 Pa to 101 kPa. For the pressures up to 1.367 kPa, no statistically significant change in the oil density was observed. However, exposure to pressures between 10 kPa and 101 kPa showed significant density changes. The Type A measurement uncertainty ($k = 1$) in the net change in density between fully degassed oil and oil at a given pressure is given as:

$$U_{\Delta\rho} = [U_{\rho \text{ degassed}}^2 + U_{\rho \text{ at } P}^2]^{1/2}, \quad (2)$$

where $U_{\Delta\rho}$ is the uncertainty in the change in density, $U_{\rho \text{ degassed}}$ is the uncertainty in the density measurement of the fully

degassed sample, and $U_{\rho \text{ at } P}$ is the uncertainty in the density measurement at a given pressure P . The density of DEHS decreased by $46 \text{ ppm} \pm 5 \text{ ppm}$ after 2 h of nitrogen gas exposure at 101 kPa. The density of DEHS decreased by $42 \text{ ppm} \pm 3 \text{ ppm}$ after ≥ 24 h air exposure at 101 kPa.

5. Discussion

The standard uncertainty ($k = 1$) of the NIST 140 Pa UIM for pressures $P \geq 3$ Pa is: $[(1.5 \times 10^{-3} \text{ Pa})^2 + (18 \times 10^{-6} P)^2]^{1/2}$ where P is the pressure being measured in Pa. The oil UIM measurement uncertainty is traceable to the NIST mercury UIMs through pressure comparisons to determine the product of the speed-of-sound and oil-density. [5] This method depends upon the density of the DEHS oil being stable as a function of calibration gas pressure and exposure time. In any manometer, pressure is given by eq. (3):

$$P = \rho g \Delta h, \quad (3)$$

where, P is the pressure, ρ is the density of fluid, g is the acceleration due to local gravity, and Δh is the difference in height between the reference and pressure sides of the manometer. The pressure generated by a manometer depends directly on the density of the fluid and therefore the uncertainty of the pressure is directly linked to uncertainty in the fluid density, in addition to the uncertainties in local gravity and fluid column height. Equation (4) shows how uncertainty in density relates to the uncertainty in pressure:

$$U_{\rho}(P) = g \Delta h U(\rho), \quad (4)$$

where $U(\rho)$ is the uncertainty in manometer fluid density, and $U_{\rho}(P)$ is the uncertainty in pressure due to the uncertainty in density.

Table 2 shows that there was no statistically significant change in the measured density of DEHS between vacuum and 138 Pa. This is important, because it means that the uncertainty of the NIST 140 Pa oil UIM due to density-dependence on dissolved gas does not change as a function of pressure. Additionally, even an extended range, 1.367 kPa (10 torr) oil UIM, would only have a dissolved gas density induced change of $2 \text{ ppm} \pm 2 \text{ ppm}$ as is shown in Table 2 and is not statistically significant.

The large density change of $46 \text{ ppm} \pm 5 \text{ ppm}$ between vacuum and 101 kPa nitrogen gas exposure shows that gauge mode operation NIST 140 Pa UIM would introduce oil density changes that exceed oil UIM uncertainty budget. This confirms that the NIST 140 Pa UIM shall be used in absolute mode only. For low differential pressure calibrations, NIST operates a 13 kPa mercury UIM primary pressure standard that was designed for gauge mode operation. [6]

Because the oil density change is large after exposure to atmospheric conditions, it is clear that pumping on the oil UIM for an extended period of time (>24 hours) is required should the oil UIM be exposed to atmospheric conditions for any reason, such as turbo pump repair. The NIST oil UIM is stored under vacuum conditions when not in use to ensure that the oil is fully degassed prior to use.

6. Conclusions

The relative change in density of DEHS oil as a function of nitrogen gas pressure was determined using a vibrating-tube densimeter. A linear effect was found to exist between the measured densities of DEHS at vacuum and atmospheric pressure. The results of this study show that the effect of dissolved gas on the density of DEHS does not contribute significantly to the pressure dependent uncertainty of the NIST 140 Pa oil UIM over its operating range of 1 mPa to 140 Pa in absolute mode. Additionally, the results demonstrate that the oil density change is small enough that an oil manometer with an extended range of 1.4 kPa (10 torr) would not be adversely impacted by this gas density effect. The density of DEHS was determined to be $(0.914415 \pm 2 \times 10^{-6}) \text{ g/cm}^3$ at vacuum ($8 \times 10^{-4} \text{ Pa}$) and $(0.914373 \pm 4 \times 10^{-6}) \text{ g/cm}^3$ after exposure to 101 kPa of nitrogen gas, where the uncertainty is the standard deviation (type A) in the repeated measurements. This large density change between vacuum and 101 kPa nitrogen gas exposure of $46 \pm 5 \text{ ppm}$ confirms that the NIST 140 Pa UIM must be operated in absolute mode only, and shall be stored under vacuum conditions when not in use.

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