Comparison of Density Instruments for Use in Commodity Package Testing

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Abstract

For commodity packaging enforcement, the National Institute of Standards and Technology, Weights and Measures Division currently require the density of products to be tested using gravimetric methods and calculating the volume contained using the acquired results. Density is the measure of mass per unit volume of a material. Research is focused on finding an alternative method for field workers to measure product density by comparing current gravimetric methods to electronic densitometers. A sample of various liquid compositions and densities from the same products that the Weights and Measures officials use were tested for repeatability assessment. Various restrictive factors that affect the quality of the density measurement will be described as part of this research. An assessment of the measurement results, proposed changes to NIST Handbook 133, identification of limiting factors, measurement issues, and general instructions to minimize potential damage to field devices will be incorporated.

INTRODUCTION

The National Institute of Standards and Technology (NIST) Weights and Measures Division oversees each state Weights and Measures Divisions throughout the country. NIST Handbook 133 gives the guidelines for determining and checking the net contents of packages goods, in which each state must follow. The method used for testing volumetric net contents uses density to determine the net contents in a given package.

Currently, the field gravimetric method for testing density is a time consuming, yet very important process for state weights and measures divisions throughout the country. State field inspectors use this method to test the volumetric density of goods in order to calculate and determine the net quantity of volumetric packaged commodities. According to NIST Handbook 133, "Gravimetric testing is the preferred method of testing most products because it reduces destructive testing while maximizing inspection resources." The current processes take a longer amount of time than other methods currently available on the market and have many aspects for error.

The goal of this research is to find an alternative method for measuring commodity density measurements. Time, accuracy, and repeatability are carefully researched before a final conclusion was made for possible changes to NIST Handbook 133.

Five different methods of determining density were used throughout the research to compare values and repeatability in each instrument. The current gravimetric method used in the field today was primarily compared with two separate electronic handheld density meters (densitometers). Two lab methods of determining density were also used as a comparison and should have given the best accuracy and precision for density.

The final conclusion will come from whether or not the handheld densitometers are sufficient for field inspectors to use during their liquid density measurements. It is important for the instrument to be lightweight, fairly cheap, easy to use, quick, and give good measurements.

INSTRUMENT INSTRUCTION

The following describes some basic instrument instructions for each method of testing density used during this experiment. Table 1 describes the reference temperature that should be used for the testing of a chosen sample. Depending on the sample, a different temperature must be used for the density testing, according to the NIST standards for commodity testing. This reference temperature must be held stable throughout the entire experiment and only has a five degree Fahrenheit refinement period. It is very important for the field inspector to make sure the sample is at the desired temperature both before the testing is begun and after all measurements have been made. There are different reference temperatures depending on the type of commodity being tested.

Table 1: Reference Temperatures for Liquids*

	Liquid Commodity	Reference Temperature (C)
1	Frozen food labeled by volume (e.g., fruit juice)	-18
2	Beer	3.9
3	Food that must be refrigerated (e.g., milk, dairy products, some juice. Usually labeled "Keep Refrigerated")	4.4
4	Distilled Spirits or petroleum	15
5	Unrefrigerated products (e.g., includes products sold unchilled, such as soft-drinks and wine)	20

*Taken from NIST Handbook 133

A. Mettler Toledo DE 51 Density Meter

After turning on the instrument (switch in the left hand side on the back of the machine) the display will read, “Wait for Ready” until the cell temperature reaches the desired temperature. If the “No Calibration” message appears, then either the cell has not been calibrated or memory clear has been performed, requiring a calibration. This machine must be calibrated before any measurements are made. Be sure to allow the instrument enough time to boot up before starting the cleaning and calibration process described below. Calibration and an initial DI water test must be done before proper measurement results are shown on the display.

Cleaning

Calibration includes performing a full cleaning of the instrument. The sampling tube should be inserted into either ethanol or acetone. High purity ethanol is preferred because it is inexpensive and readily available in most labs. Flush the measuring cell with ethanol for approximately 10 s using the <PUMP> key on the main keyboard display. During the cleaning, remove the sampling tube from the liquid in the beaker and insert it back multiple times to create air bubbles for further cleaning. Press <PUMP> to stop the machine. To dry the cell, press the <PUMP> key for approx. 2 s until the “Purge Checking” display appears. This is an automatic pump cycle and the unit will stop the pump when the cell is completely dry.

Calibration

Check with the DE51 instruction manual for a complete explanation of how to calibrate the machine using proper DI water. Calibration must be done for each change in temperature and when the machine says “No Calibration” after it is turned on. Before any measurements are made, it is necessary to wait for a minimum of 20 minutes before measurements can be properly recorded.

Measurement

After the instrument is ready, the method of testing must be chosen and the measurement parameters must be set for the chosen method. Chose the method by pressing the <Sample> key and the arrows to find which method is wanted. After the method is chosen, the <Measurement Parameters> key should be chosen and changed according to the tables found in the appendix. The measurement parameters tell the instrument the temperature to test the sample at and tell the instrument how much time is needed for the sampling rates, cleaning rate, and purge time. It is important to double check the temperature used in the measurement parameters, with Table 1.

After the method is all set according to the designated tables, the green <Measure> key should be pressed while the sample tubing is inserted into the sample needing to be tested. The machine will work as needed for the designed set parameters. Follow the directions on the display for further instruction. For rinse 1, use proper DI water for cleaning; rinse 2 requires the user to use ethanol for all liquids other than oil. Acetone must be used on the DE51 machine for proper cleaning during rinse 2 of the measuring cell while using oil products. Sugary products require hot water (50C) to run through the machine during rinse 1, for the break down of sugar in the tubing.

This lab machine makes testing the density easy and fairly quick. However, this method is awkward, and not to be used in the field. This is a piece of equipment used for comparison only. It should be giving precise results.

Uncertainty

The digital density meter DE51 has a measuring range over 0.00001 to 3 g/cm^3 and a limit of error of $2*10^{-5}$. The value of repeatability for this machine is $1*10^{-5}$, a rather good number to use as a machine for comparison.

Some change was found while using different alcohol concentrations. A test was done using different amounts of DI Water and Ethanol for a change in concentration for comparability. There were changes in the density found at a higher concentration of alcohol using this machine. Further information can be seen in excel documents. not included in this document.

B. Anton Paar DMA 35N Density Meter Handheld

The following is a list of the wetted materials in the DMA 35N density meter handheld.

Glass: glass cell and cylinder of pump
PTFE: suction tube, and piston of pump
PVDF: manifold (part where the glass cell and the cylinder is mounted on)
Viton: o-ring sealing the gap between manifold and glass cylinder (only standard version)
KALREZ: o-ring sealing the gap between manifold and glass cylinder (only EX and EX Petrol version)

Because of the materials used in the machine, acetone cannot be used as a cleaning product for this device because it will attack the Vitron o-ring. Another ring, the Kalrez o-ring, can be purchased if acetone is a necessity for cleaning (ie: most petroleum products). However, throughout this research, the Kalrez o-ring was not tested nor used. Other chemicals that should be not be used are MEK, HF and strong bases above a pH of about 9. Because of these requirements, the choice of alcohol cleaning product is high purity ethanol for rinsing.

Before Measurement

Turn the densitometer on and clean the sensing tube with DI water and ethanol by using the plunger to extrapolate the product. Hot water (50C) should be run through the densitometer 3 or more times followed by at least 2 ethanol rinses before initial measurements are made if sugar was used as a prior sample. If it is unknown, use DI water for the initial rinse, (in place of the hot water) using the same procedure. After making sure most of the ethanol is pushed out of the handheld, the commodity density may now be measured.

Measurement

After making sure the sample is at the correct reference temperature for testing and the handheld is cleaned, extrapolate the sample into the densitometer for readings. It is a simple syringe type process, made easy for any user. There is no need to clean the densitometer between each measurement, so multiple measurements can be made in a shorter amount of time. The display will give the temperature of the sample along with the density in g/cm^3. After the final measurements are made, be sure to clean the handheld completely so it is ready for future use and is clean of bacteria.

Uncertainty

The Anton Paar handheld has a density uncertainty of ±0.001g/cm^3 and a temperature uncertainty of ±0.2 g/cm3. The error is going to be ±0.00025 g/cm^3. The density repeatability value is ±0.0005 g/cm^3, with a temperature repeatability value of ±0.1 g/cm^3. The density measuring range on this instrument is from 0 to 1.999 g/cm^3, allowing for a fairly good range of samples to be tested.

C. Mettler Toledo Densito 30PX Handheld

The Mettler Handheld densitometer is a simple and easy to use instrument for measuring density and testing the temperature of a pure liquid sample. It is unknown whether acetone can be used in the machine. Throughout the research, ethanol was the only alcohol used to clean the densitometer thoroughly. If acetone is a necessity, the manufacturer should be called for prior verification.

Before Measurement

Turn the handheld on and clean the sensing tube with at least 3 rinses of DI water followed by at least 2 rinses of high purity ethanol. If a sugary product was used prior to the next measurement, replace the DI water with hot water (50C) and follow the same procedure for a full cleaning. After the cleaning is finished, measurement can be made on DI water making sure that the density value corresponds to the density standard (0.998203 g/cm^3).

Measurement

Making sure the sample is at the correct measuring temperature (Table 1) extrapolate the sample into the handheld using the fill button until the measuring cell is full. It is necessary to ensure that no air bubbles are contained within the measuring cell due to improper results. The instrument will automatically execute a measurement result for density and temperature. The temperature tool can be used as a final test for the desired temperature of the sample.

Push the drain button down completely to deplete the sample from the measurement cell. There is no need to clean the cell between each measurement if the same sample is being tested over a 10-sample time period. After all the values are taken, a complete cleaning must be done to prepare for the next measurement or storage.

Uncertainty

The accuracy of measurement for technical data using the Mettler Toledo handheld is ±0.001 g/cm^3. There is a standard deviation (error) factor of 0.00025 g/cm3 for this device, which is used to compare with all of the values received from the research.

D. Gravimetric Test (Field Device)- Balance "SB32000"

This gravimetric test, using balance "SB32000," is currently the device that field inspectors use to make density measurements in stores and warehouses. The balance must be calibrated prior to use, usually in a lab, before any measurements are made.

Before Measurement

Using NIST calibrated weights, the balance must be tested and recorded to make sure the calibration is set correctly.

The graduated cylinder being used needs to be clean and dry of water/alcohol before the flask is chosen for testing. Making sure the flask was calibrated as "to deliver" water at the reference temperature needs to be poured in making sure the line of reference is wet down. Using the NIST standard 30-second empty, 10-second drain, the water should be emptied out. Using the flask at wet down, it should be put onto the balance and tarred before the sample should be poured in. A flask should be chosen that has either the exact amount as in the sample bottle (ie: 1 pint) or slightly less than the bottle.

If the sample is required to be mixed before poured, then carefully roll the bottle because shaking causes the sample to entrap a high number of air bubbles, where rolling the bottle causes less air entrapments. If carbonated beverages are being tested, the measurement should be done as fast as possible, creating as little air pockets as necessary for the final measurement. During this research, no carbonated beverages were tested.

Before filling the graduated cylinder with the product, a thermometer should be used to check that the product is at the desired testing temperature (see Table 1 for reference temperatures). Using the meniscus as a reading for how much liquid is in the flask, carefully fill to the neck of the measure using a surface at eye level. Use a black color outside the flask directly below the point of measure for correct reading, making sure to read the bottom of the meniscus for clear liquids and the volume from the center top rim of the liquid surface for opaque liquids.

Measurement

Weigh the filled flask on the balance and carefully record the measurement. Determine the density mathematically using the standard density equation of mass per unit volute equals density. The net content of the bottle can then be calculated after the density is recorded and calculated. Follow NIST Handbook 133 for more instructions on finding the net content.

E. Gravimetric Test - Balance "Sartorius"

This gravimetric test, using balance "Sartorius," is used in the laboratory metrology lab at NIST. This balance was used to compare densities with the field balance and the handheld densitometers. This balance has more of an accurate display of a balance and is highly sensitive to measurements compared to the field device used by field inspectors. The instrument instruction is the same procedure than the field device; however this balance is not carried throughout warehouses and grocery stores for measurements.

LIMITING FACTORS

A. Mettler Toledo DE 51 Density Meter

This densitometer is not able to properly test carbonated beverages, nor any product with a large amount of air. The air bubbles create an inaccurate indication, which is not repeatable. Some juices also have a large amount of air bubbles inside, such as Welch's juice, thus creating a terrible repeatability. The repeatability is bad because the amount of air bubbles inside the instrument changes for each sample, creating a different density for each test.

Testing has also proven that certain mixtures of alcohol and water concentrations do not give a repetitive result survey. The results for this experiment can be found in the appendix page. According to testing, 50% alcohol and water mixture gives the largest standard deviation values. Products with solids cannot be used in the DE-51 machine because of the sample tubing. The solids get stuck in the tubing creating a blockage, not allowing the sample to draw completely into the machine for cleaning or measuring.

Oil can be tested, however the cleaning process needs to be much more thorough. Compared to some other samples, the cleaning process used with oil takes much longer and will sometimes need to be done twice before another sample can be tested. The only way to tell the machine is clean is by eye and by testing the density of water first, making sure it is correct. Most likely, if the density of water is not correct (for 20C the value should be 0.99820) the machine is either dirty or needs to be recalibrated before more measurements can be made.

B. Mettler Toledo Densito 30PX Handheld

Carbonated beverages cannot be properly tested using this device. Similar to the DE 51 Densitometer, the air bubbles from the sample create an inaccurate indication for density measurement. Either repeatability will be bad, or an error will show up on the display due to the air intake.

Any samples which have solids included cannot be tested because of the possibility of the device lodging, causing error and possibly the handheld to break.

Oils can be tested in this handheld, but is difficult to clean using solely ethanol. A thorough cleaning is necessary before the next sample measurement can be taken place.

C. Anton Paar DMA 35N Density Meter Handheld

This handheld machine is used similarly to the Mettler-Toledo Handheld instrument and has the same limiting factors associated. Using the Anton Paar machine, acetone cannot be used as a cleaning product for this device because it will attack the Vitron o-ring. As described, a substitute ring can be bought if acetone is necessary. Other chemicals that should be not be used for cleaning are MEK, HF and strong bases above a pH of about 9 or so.

D. Gravimetric Test - Balance "Sartorius"

This balance is only used in a laboratory setting and is not a practical piece of equipment to use during field study. Some limiting factors associated with this method have to do with human error. The human eye must read the exactness of the meniscus and there can be many factors of human error associated.

These gravimetric methods take a longer time than the handheld instrument while in the field. There is little room for human error using the handheld compared to the balance method. From the research, it took about double the amount of time for the balance methods compared to the handheld methods.

E. Gravimetric Test (Field Device)- Balance "SB32000"

Compared to the handheld devices, the balance is a semi-awkward device to carry around while doing testing around the field and seems to have a low accuracy and sensitivity to measurement. As seen by the recorded values, the accuracy changes by only 0.005 lb. at a time, making it hard for even a slight change in weight measurement. Because of the low accuracy and low measurement sensitivity, there is never a standard deviation higher than zero, which is a value known to not be exact. A higher error is given to this instrument because no change is noticed in the density measurements throughout the procedure.

Because the balance must be calibrated before any measurements are made, the calibration is usually done in a lab, before the metrologist uses it for measurements. After the field worker takes the balance, the balance goes through sometimes long travel and can be in the extreme heat/cold for a long period of time. From all of the changes in temperature and rough handling, the calibration may easily change, resulting in untrue results.

It is necessary for the field inspector to follow all procedures correctly in order to have true measurements. Because the meniscus should be very carefully read, using a magnifying glass especially, most field workers are too busy or lazy to sit and read the meniscus properly.

RESULTS

A. Samples Tested

Table 2 names the samples used throughout the experiment and the said amount of net contents each bottle contains. (e.g. the net content value on the outside of the bottle) These samples were chosen from an initial matrix including all possible combinations of samples that have sugar, alcohol content, and viscosity variants.

Product Name	Content on Bottle (mL)
Windex no drip	946
Vegetable Oil	709
Tilex	946
Witch Hazel	473
Febreze	500
Hydrogen Peroxide	473
Lemon Juice	236
Sea Breeze	295
Alcohol	473
White Vinegar	473
Gatorade	946
Listerine	500
Lemonade	946
Strawberry Daiquiri Mix	1000
SunnyD	1890
Vitamin Water	591
Snapple	473
Welch's	1890

B. Mean Density Results

Table 3: Method and Number Correlations

Number	Method
1	Mettler Toledo DE51
2	Mettler Toledo PortableLab
3	Anton Paar DMA 35n
4	Balance "Sartorius"
5	Balance "SB32000"

The graphs given in the appendix represent the mean density in g/cm^3 versus the method represented by numbers 1-5. Table 3 describes the method number correlations. The results show a good correlation between the methods and the average density. Overall, the average difference between the comparisons in the field method and the handheld methods are not a large difference for field comparisons. When looking at the mean density graphs, it is important to take a look at the numbers on the axis, as they change from graph to graph. The error reported in the graphs is the standard deviation between the ten-recorded values for each sample per each method. These graphs can be found in the appendix.

C. Median Density Results

The median density in g/cm^3 was recorded and compared versus the method used. The graphs can be found in the appendix. Similar to the Mean Density graphs, it is necessary to pay attention to the axis values.

D. Repeatability Results

Each graph recorded was taken per ten measurements taken for each sample in each method. The graphs can be found in the appendix for analysis.

DISCUSSION AND CONCLUSIONS

The handheld densitometers were found to be a good alternative method for the current gravimetric method; however, change in Handbook 133 will not be made until further experimentation is taken place. Throughout the experiment, the net contents for each sample should have been calculated and determined using each method separately. Not enough information was gathered in this experiment to be able to compare this conclusion. Two bottles of the same sample should have been researched for more information to be available for comparison between the methods and the determination of whether field inspectors would start to fail more commodities if they were to change the method of density determination. A Table of the Pros and Cons for the handheld method and the gravimetric field method is given below in Table 4. From this table, one could come to the conclusion that it does not make much sense for each state to buy these handheld densitometers because of the price and the usage of the balances for other measurements throughout the procedure.

Handheld Densitometers

Pros	Cons
Easy to use	Sample restrictions
Quick measurements	Sometimes difficult to clean
Good accuracy	Some cleaning products restricted
Practical for field use	Extra expenditure

Gravimetric Field Test - Balance

Pros	Cons
Very few restrictions	Calibration can easily be offset
Already have the equipment	Long preparation and cleaning times
Equipment is used for other things	Takes longer to test sample density

Further investigation can be made using a wider variety of commodities before any changes are made to the Handbook 133. Possibly a list of target commodities to study further can be tested; such as: carbonated products, different alcohol concentrations, and change in viscosity. Since there are limitations on the chosen sample for the handheld densitometers, this investigation might prove there to be fewer limitations.

Overall, with the information gathered in this study, the handheld densitometer seems to work well for field measurements and seem to give similar results to the current methods. It s a much quicker process and could be a valuable purchase if the state has enough funds for purchasing.

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RESOURCES

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