Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Laboratory of fuels, oils and lubricants

Laboratory exercise

Density measurement and determination of the temperature coefficient of density of petroleum products

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Szczecin

EXERCISE SHEET

<table>
<tr><td rowspan="3">1</td><td colspan="3">Relation to subjects: Marine Power Plant Operation/28</td></tr>
<tr><td>Specialty/Subject</td><td>Learning outcomes for the subject</td><td>Detailed learning outcomes for the subject</td></tr>
<tr><td>MPPO – Chemistry of fuels and lubricants.</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP12 – Determination of selected quality indicators of petroleum products.</td></tr>
<tr><td>2</td><td colspan="3">Purpose of the exercise:
teaching the student to independently perform density measurement and determination of the temperature coefficient of density for petroleum products, conversion of density from a given temperature to the desired temperature with the use of the temperature density coefficient and with the use of normative density conversion tables;</td></tr>
<tr><td>3</td><td colspan="3">Prerequisites:
the student is trained in the field of health and safety regulations on a laboratory workplace, which he confirms with his signature on the appropriate form, knows - types and units of density, measurement methods, operational significance of the parameter, dependence of density on temperature;</td></tr>
<tr><td>4</td><td colspan="3">Description of the laboratory workplace:
ultrathermostat, set of hydrometers, thermometer, special cylinder used for density measurements, stand for washing laboratory glass with extraction gasoline, samples of petroleum products;</td></tr>
<tr><td>5</td><td colspan="3">Risk assessment*:
contact with extraction gasoline used for cleaning measuring instruments and laboratory glass – probability of a fire hazard due to the presence of flammable gasoline vapour – very low risk due to efficient ventilation and low concentration of volatile gasoline vapours.
Final assessment – SMALL THREAT
Safety measures required:
a. lab coats,
b. health and safety cleaning products, cleaning cloths, paper towels,
c. petroleum products waste container (for disposal),
d. container for waste gasoline beakers (for regeneration);</td></tr>
<tr><td>6</td><td colspan="3">The course of the exercise:
a. Read the workplace manual (appendix 1) and the laboratory kit for the exercise,
b. Measure the density of the crude oil product at ambient temperature and carry out an additional 6 consecutive density measurements after each increase in the temperature of the tested product in the ultrathermostat by 3°C;</td></tr>
<tr><td>7</td><td colspan="3">Exercise report:
a. Develop an exercise in accordance with the instructions contained in the workplace manual,
b. On the basis of the measurements of density at the lowest and highest temperatures, calculate the temperature density coefficient α,
c. On the basis of the obtained results of measurements of the determined density at different temperatures, prepare a graph of the dependence of density on temperature, using for this purpose a linear approximation;</td></tr>
<tr><td>8</td><td colspan="3">Archiving of research results:
Submit a written report on the performed exercise to the teacher.</td></tr>
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<tr><td>9</td><td>Assessment method and criteria:
a. EKP1, EKP2 – tasks given for independent solution and development:
mark 2.0 – has no basic physicochemical and operational knowledge concerning the density of petroleum products and the ability to solve simple tasks in this field;
mark 3.0 – has basic physicochemical and operational knowledge regarding the density of petroleum products and the ability to calculate and solve simple tasks in this field;
mark 3.5-4.0 – has extended physicochemical and operational knowledge regarding the determined performance parameter of the analysed petroleum products and the ability to solve complex tasks in this field;
mark 4.5-5.0 – has the ability to apply complex physicochemical and operational knowledge to partial evaluation of the quality and operational suitability of the analysed petroleum products due to the determined performance parameter and the ability to make operational decisions on this basis.
b. EKP3 – control works:
mark 2.0 – does not have the ability to analyse and evaluate the results of the performed analyses and determinations and to draw conclusions;
mark 3.0 – has the ability to analyse the obtained results, interpret the laws and phenomena, transform formulas, and interpret charts and tables;
mark 3.5-4.0 – has the ability to broaden the analysis of results, apply laws, construct monograms and charts;
mark 4.5-5.0 – has the ability to comprehensively analyse the obtained results, make generalizations, detect cause-effect relationships and make the right operational decisions.</td></tr>
<tr><td>10</td><td>Literature:
1. Krupowies J., Wiznerowicz Cz.: Pomiar gęstości oraz wyznaczanie temperaturowego współczynnika gęstości produktów naftowych. Instrukcja stanowiskowa do ćwiczenia, AM, Szczecin 2013.
2. Barcewicz K.: Ćwiczenia laboratoryjne z chemii wody, paliw i smarów. Wyd. AM w Gdyni, Gdynia 2006.
3. Podniało A.: Paliwa oleje i smary w ekologicznej eksploatacji. WNT, Warsaw 2002.
4. Przemysłowe środki smarne. Poradnik. TOTAL Polska Sp. z o.o., Warsaw 2003.
5. Urbański P.: Paliwa i smary. Wyd. FRWSzM w Gdyni, Gdańsk 1999.
6. PN/EN/ISO standards for the testing of petroleum products.
7. Oil product catalogs of oil companies.
8. Dudek A.: Oleje smarowe Rafinerii Gdańskiej. „MET-PRESS”, Gdańsk 1997.
9. Baczewski K., Biernat K., Machel M.: Samochodowe paliwa, oleje i smary. Leksykon, Wydawnictwa Komunikacji i Łączności, Warsaw 1993.
10. Herdzik J.: Poradnik motorzysty okrętowego. Wydawnictwo TRADEMAR, Gdynia 1995.</td></tr>
<tr><td>10</td><td>Notes</td></tr>
</table>

Appendix 1 – Manual

1. Scope of the exercise

- getting acquainted with the workplace instructions for the exercise,
- independent measurement of the density of lubricating oil samples at different temperatures,
- preparation of a graph of the dependence of density on temperature based on the measurements carried out and determination of the temperature density coefficient,
- calculating the volume of fuel or oil to be taken onto the ship, if its density at the standard temperature is known and it is known at what temperature the delivery to the ship takes place.

2. Theoretical introduction to the exercise

2.1. Principle of density determination

One of the characteristics of crude oil and its products is density. In practice, the relative density $d_{t_1}^{t_2}$ is usually determined:

$$d_{t_1}^{t_2} = \frac{\rho_{t_2}}{\rho_{t_1}}$$

where:

ρ_{t_2} – the density of the test product at the temperature t_2 [g/cm^3],

ρ_{t_1} – the density of distilled water at a temperature t_1 [g/cm^3].

The most commonly used reference temperatures are:

t_2 = 15°C, 20°C, 60°F;
t_1 = 4°C, 15°C, 60°F; (60°F = 15.6°C)

Where the density d_4^{15} and d_4^{20} is numerically equal to the density (specific mass) [g/cm^3].

Note!

In Anglo-Saxon countries, oil companies still frequently use the Fahrenheit thermometric scale.

It is assumed that: $d_{15}^{15} \cong d_{60^\circ F}^{60^\circ F}$:

$$d_4^{15} = 0.99915\ d_{15}^{15}$$

In simplified terms, it is often defined as:

$$d_4^{20} \approx d_4^{15} \approx d_{15}^{15} \approx d_{60^\circ F}^{60^\circ F}$$

World oil companies often use the determination of the density of contractual, dimensionless units, the so-called °API (*American Petroleum Institute*).
Conversion to °API can be made using the following formula:

$$^{o}\text{API} = \frac{141{,}5}{d^{60^{o}F}_{60^{o}F}} - 131{,}5$$

Petroleum products are characterized by a large change in density with a simultaneous change in temperature, which is of significant practical importance. For most petroleum products, it can be assumed with sufficient accuracy that this relationship is a linear function expressed by the equation:

$$\rho_4^{t_1} = \rho_4^{t_0} - \alpha(t_1 - t_0)$$

where:

$\rho_4^{t_1}$ – oil product density at temperature t_1 [g/cm^3],

$\rho_4^{t_0}$ – oil product density at temperature t_0 [g/cm^3],

α – temperature coefficient of density [g/cm^3 · °C] (the value by which the density changes if the temperature changes by 1°C).

NOTE !

Since the density of distilled water at 4°C is 1 g/cm^3, then $\rho_4^{t_1}$ and $\rho_4^{t_0}$ are numerically equal to the absolute density of a given petroleum product.

Table 1 shows the values of the temperature coefficient of density depending on the density.

Table 1

Values of the average temperature coefficient of density

Density range ρ [g/cm^3]	Density temperature coefficient values α [g/cm^3 · °C]	Density range ρ [g/cm^3]	Density temperature coefficient values α [g/cm^3 · °C]
0.6900÷0.6999	0.000910	0.8500÷0.8599	0.000699
0.7000÷0.7099	0.000897	0.8600÷0.8699	0.000686
0.7100÷0.7199	0.000884	0.8700÷0.8799	0.000673
0.7200÷0.7299	0.000870	0.8800÷0.8899	0.000660
0.7300÷0.7399	0.000857	0.8900÷0.8999	0.000647
0.7400÷0.7499	0.000844	0.9000÷0.9099	0.000633
0.7500÷0.7599	0.000831	0.9100÷0.9199	0.000620
0.7600÷0.7699	0.000818	0.9200÷0.9299	0.000607
0.7700÷0.7799	0.000805	0.9300÷0.9399	0.000594
0.7800÷0.7899	0.000792	0.9400÷0.9499	0.000581
0.7900÷0.7999	0.000778	0.9500÷0.9599	0.000567
0.8000÷0.8099	0.000765	0.9600÷0.9699	0.000554
0.8100÷0.8199	0.000752	0.9700÷0.9799	0.000541
0.8200÷0.8299	0.000738	0.9800÷0.9899	0.000528
0.8300÷0.8399	0.000725	0.9900÷1.0000	0.000515
0.8400÷0.8499	0.000712		

Density can be determined by several methods. The choice of method depends on the quantity of the petroleum product, its viscosity, the required accuracy of the determination and the time spent on the analysis.

The simplest instrument for determining the density of liquid petroleum products is a hydrometer, which is characterized by the density of distilled water at 4°C, so its indications correspond to d_4^t. The hydrometer can determine the density only with an accuracy of 0.001 g/cm^3, for low-viscosity products and with an accuracy of 0.005 g/cm^3 – for products with high viscosity. To determine the density of a highly viscous petroleum product (over 200 mm^2/s at 50°C), the kerosene dilution method should be used.

For small amounts of petroleum product (drops) or for substances (lubricants, paraffins, asphalts), the density equalization method or the suspended drop method (operational method – approximate) can be used. However, the most accurate results are obtained when determining the density with a pycnometer (up to 0.00005 g/cm^3). Depending on the aggregate state of the petroleum product, its quantity and the required weighing accuracy, pycnometers of various shapes and volumes are used.

The most frequently used types of the above-mentioned instruments are shown in figures 1 and 2, further in the instruction for the exercise.

2.2. Determination of density with a thermoareometer

The density of petroleum products with a viscosity not exceeding 200 mm^2/s, is performed using a thermoareometer or hydrometer (Fig. 1) as follows:

Pour about 170 cm^3 of the test sample into a 250 cm^3 measuring cylinder. Carefully immerse the hydrometer in such a range that the expected value falls in the middle of the scale of the instrument and, after fixing its position, read (at equal intervals, e.g. after 2, 4, 6 minutes) the instrument's graduation (according to the upper meniscus) the density and temperature for when using a hydrometer, measure the temperature with a thermometer.

When determining the density of used or dark oils, when reading the temperature, the thermometer should be slightly raised so that the scale of the thermometer is visible and the mercury reservoir remains immersed in the tested product or use a separate thermometer.

Carry out three measurements at the given temperature.

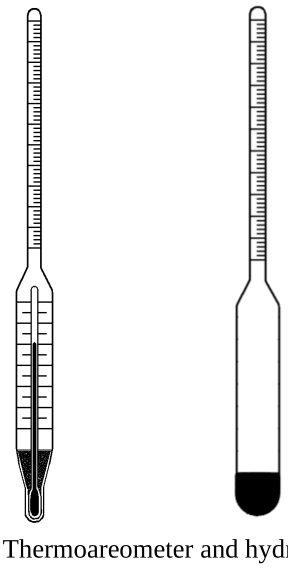

Fig. 1. Thermoareometer and hydrometer

Elaboration of the results

Calculate the average value of the density from the obtained measurements.

2.3. Determination of the density of petroleum products by the suspended drop method

Pour 200 cm^3 of the liquid with a density $\rho < 1.0 g/cm^3$ (e.g. isopropyl alcohol) into a beaker with a capacity of 300 cm^3 and add a drop of the tested oil.

When determining the density of solid grease, make a ball of the smallest possible diameter and place it in a beaker. Then add sodium chloride solution from a pipette to the beaker in such an amount that the tested sample hangs in the liquid. In this case, the density of the petroleum product is equal to the density of the solution, which must be determined with a hydrometer. To do this, pour the contents of the beaker into a 250 cm^3 measuring cylinder, insert a hydrometer and measure the density three times.

Elaboration of the results

Calculate the average value of the density from the obtained measurements.

2.4. Determination of the density of petroleum products with a pycnometer

If necessary, a sample of the petroleum product is dehydrated prior to the essential determination by adding anhydrous sodium sulphate and filtered through filter paper. If the tested petroleum product is in solid form, it should be crushed before performing the determination. A clean, dried pycnometer (Fig. 2) with a known constant, carefully fill with a pipette the test petroleum product at a temperature of 20 ± 5ºC. In the case of a pycnometer with a mark (fig. 2) - fill it slightly above the mark, and in the case of a pycnometer with a capillary hole - fill it completely. Close the pycnometer with a stopper, place it in the thermostat and keep it at 20ºC for 30 minutes. After this time, remove the pycnometer from the thermostat and in the first case remove excess liquid with a pipette, and in the second (capillary pycnometer) the excess sample will flow out automatically, then quickly wipe the pycnometer and weigh it on an analytical balance. Repeat the measurement three times. Ignore results that differ by more than 0.0004 g/cm^3.

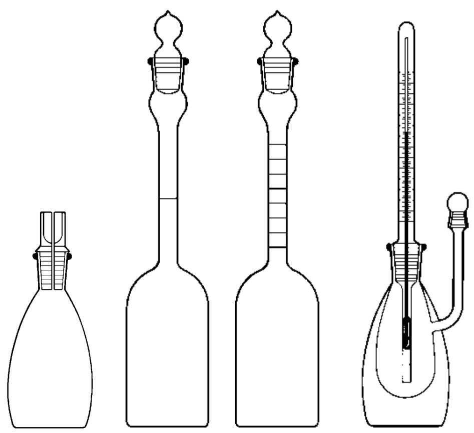

Fig. 2. Pycnometers

Elaboration of the results

Calculate the approximate value of the density of the test sample at 20ºC from the equation:

$$\rho = \frac{m_2 - m_1}{k}$$

where:

ρ – approximate density of the test sample [g/cm^3],
k – constant of the pycnometer [cm^3] (this value is given by the instructor),
m_1 – empty weight of the pycnometer [g],
m_2 – mass of the pycnometer with the test sample [g].

The calculated value from the equation is approximate as the measurement was made in air, not in a vacuum. In addition, the pycnometer constant was determined in relation to distilled water at 20°C, and the density was calculated in relation to the density of water at 4°C:

$$\rho_4^t = \rho + R$$

where:

ρ_4^t – density of the test sample at temperature tºC [g/cm^3],
ρ – approximate density determined from the equation [g/cm^3],
R – correction read from table 2 [g/cm^3].

Table 2

Corrections for determining the density value ρ_4^{20}

Approximate density value ρ [g/cm^3]	Correction R [g/cm^3]	Approximate density value ρ [g/cm^3]	Correction R [g/cm^3]
0.6900÷0.6999	– 0.0009	0.8500÷0.8599	– 0.0013
0.7000÷0.7099	– 0.0009	0.8600÷0.8699	– 0.0014
0.7100÷0.7199	– 0.0009	0.8700÷0.8799	– 0.0014
0.7200÷0.7299	– 0.0010	0.8800÷0.8899	– 0.0014
0.7300÷0.7399	– 0.0010	0.8900÷0.8999	– 0.0015
0.7400÷0.7499	– 0.0010	0.9000÷0.9099	– 0.0015
0.7500÷0.7599	– 0.0010	0.9100÷0.9199	– 0.0015
0.7600÷0.7699	– 0.0011	0.9200÷0.9299	– 0.0015
0.7700÷0.7799	– 0.0011	0.9300÷0.9399	– 0.0016
0.7800÷0.7899	– 0.0011	0.9400÷0.9499	– 0.0016
0.7900÷0.7999	– 0.0012	0.9500÷0.9599	– 0.0016
0.8000÷0.8099	– 0.0012	0.9600÷0.9699	– 0.0017
0.8100÷0.8199	– 0.0012	0.9700÷0.9799	– 0.0017
0.8200÷0.8299	– 0.0013	0.9800÷0.9899	– 0.0017
0.8300÷0.8399	– 0.0013	0.9900÷0.9999	– 0.0018
0.8400÷0.8499	– 0.0013	1.0000	– 0.0018

3. PERFORMING THE EXERCISE

Measure the density according to section 3.2 of this manual, and then place the cylinder with oil, gauge and thermometer in the thermostat. Turn on the thermostat and make 5 consecutive measurements of density with the same method, every 3 - 4 ºC increase in temperature.

4. DEVELOPMENT OF THE EXERCISE

1. Present the relationship between density and temperature in a graph.
2. From measurements at extreme temperatures (lowest and highest), calculate the temperature density coefficient (α).
3. Compare the obtained α value a with the tabular one.
4. Calculate the difference in volume that 1000 kg of oil will take at 15ºC and 50ºC.

5. THE FORM AND CONDITIONS FOR PASSING THE LABORATORY EXERCISE

1. passing the so-called "entry" before starting the exercise.
2. submission of a correct written report on the completed exercise, which should contain:

   - short theoretical introduction,
   - operational significance of the measured parameter,
   - processing of the obtained results according to the workplace manual.

3. final credit for the test at the end of the semester.

I. Example of task with solution

1000t of heavy fuel with the density ρ^{15} = 992 kg/m^3 were delivered to a ship at 15ºC. Calculate the volume of fuel taken up at the standard temperature of 15°C and how many m^3 should be taken of this fuel per ship, knowing that bunkering takes place at the temperature of 60°C. Also calculate the financial losses resulting from not taking into account the change in fuel density caused by the increase in its temperature to 60°C, assuming that 1 ton of fuel costs 600 $.

The volume of 1000 t of fuel at 15ºC is:

$$V_1 = \frac{m}{\rho^{15}} = \frac{1\,000\,000 \text{ kg}}{992 \text{ kg/m}^3} = 1\,008 \text{ m}^3$$

Then we calculate the fuel density (ρ^{60}) at the bunkering temperature of 60ºC. For this, the temperature density factor $\alpha = 0.000515$ [g/cm^3 · ºC] is required, [t/m^3 · ºC] we can read from table 1 of the manual. We use the following equation:

$$\rho^{t_1} = \rho^{t_0} - \alpha(t_1 - t_0)$$

where:

ρ^{t_1} – fuel density at temperature t_1 [g/cm^3],

ρ^{t_0} – fuel density at temperature t_0 [g/cm^3],

α – temperature coefficient of density [g/cm^3 · ºC].

After substituting the data from the task, we get:

$$\rho^{60} = 0.992 \text{ [t/m}^3] - 0.000515 \ [t/m^3 \cdot °C] \cdot (60°C - 15°C) =$$
$$= 0.992 \text{ [t/m}^3] - 0.023 \text{ [t/m}^3] = 0.969 \text{ [t/m}^3]$$

therefore $\rho^{60} = 0.969$ [t/m^3]

The volume that 1000 t of fuel will take at 60°C is calculated from the formula:

$$V_2 = \frac{m}{\rho^{60}} = \frac{1\,000\,000 \text{ kg}}{969 \text{ kg/m}^3} = 1\,032 \text{ m}^3$$

The volume difference that results between the volume that the fuel will occupy at the bunkering temperature (60°C) and its volume in (15°C) is:

$$\Delta V = V_2 - V_1 = 1032 \text{ m}^3 - 1008 \text{ m}^3 = 24 \text{ m}^3$$

corresponding to the above volume difference ΔV, the fuel mass difference Δm will be:

$$\Delta m = 24 \ m^3 \cdot 0.969 \text{ t/m}^3 = 23.26 \ t$$

hence the financial losses will be:

$$23.26 \ t \cdot 600 \ \$ = 13\ 956 \ \$$$

II. Tasks and questions to be completed by the student

Tasks

1. Calculate the volume of a heavy fuel with a mass of 1200 t at 55°C, knowing that its density at 15°C is 0.995 g/cm^3, and the temperature coefficient of density $\alpha = 0.000515$ g/cm$^3 \cdot °C$.
   Answer: 1200 tons of this fuel at 55°C will occupy a volume of 1 231.53 m^3.
2. The volume of fuel tanks on board is 960 m^3. What is the maximum quantity of heavy fuel in tonnes to be ordered, knowing that the density of this fuel at 20°C is 0.992 g/cm^3, the density temperature coefficient $\alpha = 0.000515$ g/cm$^3 \cdot °C$, and bunkering will take place at 53°C.
   Answer: A maximum of 936 tons of fuel must be ordered.
3. Calculate the temperature coefficient of density (α) of the lubricating oil, knowing that the density of this oil at 18°C is 0.882 g/cm^3, while at 36 ° C it is 0.870 g/cm^3.
   Answer: Temperature coefficient of density $\alpha = 0.000667$ g/cm$^3 \cdot °C$.

Questions

1. Define the following terms: absolute density, relative density and specific gravity and give their units.
2. What is the formula for converting the density of a petroleum product from a given temperature to a desired temperature?
3. What is the temperature dependence of density and is there a correlation between the viscosity of the petroleum product and its density?
4. What is the temperature coefficient of density of a petroleum product, in what units is it expressed and how is it determined?
5. What is the significance of the change in the density of petroleum products in the operation of marine power plant equipment and in the settlement of the consumption of these products on ships?
6. Give the methods for measuring the density of petroleum products.
7. What is the role of knowing the density of a petroleum product in its identification?