Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Laboratory of fuels, oils and lubricants

Laboratory exercise

Determination of chemical reaction of water extract and total acid number or base number of lubricating oils

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EXERCISE SHEET

<table>
<tr><td rowspan="3">1</td><td colspan="3">**Relation to subjects: M**arine **P**ower **P**lant **O**peration/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 – Performing determinations 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 the determination of the chemical reaction of water extract, the base number or the acid number of lubricating oils;</td></tr>
<tr><td>3</td><td colspan="3">**Prerequisites:**
the student is trained in the occupational health and safety regulations in a laboratory workplace, which is confirmed by a handwritten signature on the appropriate form, knows the concepts of: base number BN, total acid number TAN, methods of measuring these parameters and their operational significance and limit values, classification quality and classification symbols of lubricating oils, the method of assessing the quality and operational suitability of oils;</td></tr>
<tr><td>4</td><td colspan="3">**Description of the laboratory workplace:**
pear-shaped separator, basic laboratory glassware, indicators, typical laboratory set for potentiometric titration (pH-meter, combined electrode, magnetic stirrer, burette), 0.1 M acid and alkali solutions, samples of used lubricating oils;</td></tr>
<tr><td>5</td><td colspan="3">**Risk assessment *:**
contact with 0.1M acid and alkali – probability of chemical burn – very small, effects - slight.
Final assessment – **VERY SMALL THREAT**
Security measures required:
a. lab coats,
b. health and safety cleaning products, paper towels;</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. Determine the chemical reaction of the water extract of the tested lubricating oil,
c. Perform the determination of the base number (BN) or acid number (TAN) depending on the type of oil tested</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 determinations: the chemical reaction of the water extract and the base number or the acid number of the tested lubricating oil, determine its quality and operational suitability by comparing the marked BN or TAN with their limit values;
c. On the basis of the obtained results, determine the operational reasons for the changes in the tested parameters and propose possible corrective or remedial actions;</td></tr>
<tr><td>8</td><td colspan="3">**Archiving of research results:**
Submit a written report on the performed exercise to the acaemic teacher.</td></tr>
</table>

9	**Assessment method and criteria:** a. EKP1, EKP2 – tasks given for independent solution and development: mark 2.0 – the student has no basic chemical, physicochemical and operational knowledge concerning the chemical reaction of the water extract, the acid number and base number of lubricating oils, and the ability to solve simple tasks in this field; mark 3.0 – has basic chemical, physicochemical and operational knowledge regarding the chemical reaction of the water extract, acid number and base number, as well as the ability to calculate and solve simple tasks in this field; mark 3.5 – 4.0 – has extended chemical, physicochemical and operational knowledge regarding the determined operational parameters of lubricating oils and the ability to solve complex tasks in this field; mark 4.5 – 5.0 – has the ability to apply complex chemical, physicochemical and operational knowledge to partial evaluation of the quality and usability of the tested lubricating oils due to the determined parameters 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-and-effect relationships and make the right operational decisions.
10	**Literature:** 1. Krupowies J., Wiznerowicz Cz.: Oznaczanie odczynu chemicznego wyciągu wodnego oraz całkowitej liczby kwasowej lub liczby zasadowej olejów smarowych. 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, Warszawa 2002. 4. Przemysłowe środki smarne. Poradnik. TOTAL Polska Sp. z o.o., Warszawa 2003. 5. Urbański P.: Paliwa i smary. Wyd. FRWSzM w Gdyni, Gdańsk 1999. 6. Krupowies J.: Badania zmian parametrów fizykochemicznych silnikowych olejów smarowych eksploatowanych na statkach Polskiej Żeglugi Morskiej. WSM w Szczecinie, Studia nr 27, Szczecin 1996. 7. Krupowies J.: Badania zmian właściwości oleju obiegowego okrętowych silników pomocniczych. WSM w Szczecinie, Studia nr 40, Szczecin 2002. 8. PN/EN/ISO standards for the testing of petroleum products. 9. Oil product catalogs of oil companies. 10. Dudek A.: Oleje smarowe Rafinerii Gdańskiej. „MET-PRESS”, Gdańsk 1997. 11. Baczewski K., Biernat K., Machel M.: Samochodowe paliwa, oleje i smary. Leksykon, Wydawnictwa Komunikacji i Łączności, Warszawa 1993. 12. Herdzik J.: Poradnik motorzysty okrętowego. Wydawnictwo TRADEMAR, Gdynia 1995.
10	Notes

APPENDIX 1 – MANUAL

1. SCOPE OF THE EXERCISE

- determination of the chemical reaction of the water oil extract and its importance in the assessment of the operational usefulness of the oil,
- determination of the base or acid number of the lubricating oil depending on the type of oil,
- evaluation of the operational suitability of the tested oil on the basis of the tests and limit values.
- learning about the quality classification and classification symbols of modern lubricating oils.

2. THEORETICAL INTRODUCTION TO THE EXERCISE

Qualitative classification of engine lubricating oils according to API

Quality classification of lubricating oils - historical outline and present state.

The first version of the quality classification according to API (American Petroleum Institute), introduced in 1947, classified the oils as follows:

- **regular** – oils without additives or with a small amount of additives reducing the pour point and increasing the viscosity;
- **premium** – oils with antioxidant and anti-corrosive additives;
- **HD** (*Heavy Duty*) – oils intended for operation in harsh conditions, containing, compared to the previous groups, also cleaning additives.

The second version of the quality classification according to API, introduced in 1952, included five classes marked with symbols:

MS, MM, ML, DG, DS.

M – oils for spark ignition engines:

S – difficult working conditions,
M – average working conditions,
L – light working conditions.

D – oils for compression ignition engines:

G – relatively light operating conditions for engines in which fuel burns with sulfur content up to 0.5%,
S – heavier working conditions with high heat loads.

In 1970, a new quality classification of lubricating oils, called API-ASTM-SAE, was developed with the participation of three institutions: API, ASTM, CRC (*American Petroleum Institute, American Society for Testing Materials, Coordinating Research Council*).

It includes two main groups:

S – oils for spark ignition engines (*Service Station Oil*),
C – oils for compression ignition engines (*Commercial Oils*).

These are open classifications, i.e., they can be extended. Until 1993, there were 8 quality classes in the S group:

SA, SB, SC, SD, SE, SF, SG, SH, …

Until 1993, there were 7 quality classes in group C:
group C includes:

CA, CB, CC, CD, CD-II, CE, CF-4, …

There is a common rule that the quality of the oil is the better, as the second part of the letter designation is located further in the letter.

Currently, oils of quality classes: SA, SB, SC, SD and SE and classes: CA and CB are considered obsolete.

Contemporary classification designations of marine engine oils used by oil producers are given in Table 1:

Next to the brand name of the oil, BN and the SAE viscosity class are given:

Base Number (BN).

Viscosity grade according to SAE – American Society of Automotive Engineers.

Oil companies use a different order of notation BN and SAE in the designation of oils, as shown in Table 1.

Table 1

Classification designations of marine engine oils

Brand name of the oil	SAE	BN
RAFINERIA GDAŃSKA S.A.		
MARINOL RG 1030	30	10
MARINOL RG 1040	40	10
MARINOL RG 1230	30	12
MARINOL RG 1240	40	12
MARINOL RG 2030	30	20
MARINOL RG 2040	40	20
CASTROL MARINE OIL		
CASTROL MXD 303	30	30
CASTROL MXD 304	40	30
CASTROL MXD 403	30	40
CASTROL MXD 404	40	40
ELF LUB MARINE		
ATLANTA MARINE D 3005	30	5
ATLANTA MARINE D 4005	40	5
DISOLA M 3015	30	15
DISOLA M 4015	40	15
MOBIL MARINE LUBRICANTS		
Mobilgard 312	30	12
Mobilgard 412	40	12
EXXON MARINE LUBRICANTS		
EXXMAR 12TP 30	30	12
EXXMAR 12TP 40	40	12
EXXMAR 24TP 30	30	24
EXXMAR 24TP 40	40	24
EXXMAR 30TP 30	30	30
EXXMAR 30TP 40	40	30

2.1. Chemical reaction of water oil extract

Testing the chemical reaction of the water extract of lubricating oils is a qualitative test. It consists in mixing distilled water with a sample of the tested oil in a 1: 1 ratio and obtaining an aqueous extract after shaking this mixture in the distributor. Then, taking small amounts of this extract into two test tubes, add methyl orange to one of them, and phenolphthalein to the other.

If the methyl orange changes its colour from yellow to orange-red, it means that the reaction of the aqueous extract is acidic, i.e., the sample contains water-soluble acids (strong mineral acids). Such a result proves that the alkaline reserve of the oil has been exhausted and it has been acidified. This oil is not suitable for further operation due to the risk of sulfur corrosion and should be changed for fresh oil.

If the colour does not change (it is still yellow) – the reaction of the water extract is not acidic.

If phenolphthalein changes its colour to raspberry in the second test tube – the reaction of the water extract of the oil is alkaline. This result proves that the alkaline additives contained in the oil are water-soluble. In such a case, when centrifuging the water-soaked oil, there is a risk of washing out some of these additives.

If there is no change in the colour of phenolphthalein – the measured reaction of the water extract is not alkaline, i.e., alkaline additives (if present in the oil), – these are insoluble in water.

When no change in the colour of the indicators is found in both test tubes, the reaction of the water extract of the tested oil is neutral.

2.2. Total Acid Number TAN

The number of milligrams of potassium hydroxide needed to neutralize the acids in 1g of lubricating oil is the acid number expressed in [mg KOH/g]. This value is used to determine the acid content in both fresh and used oils. Since various types of acids can occur in lubricating oils, it is very important which acid group the given acid number applies to.

The acids found in lubricating oils can be divided into two main groups, namely the so-called "weak" acids, which do not cause corrosion of the lubricated parts, and "strong" acids, the presence of which in the lubricating oil causes or may cause corrosion. The group of "weak" acids, devoid of corrosive action, includes high-molecular organic acids, which are insoluble in water, mainly as a result of oxidation of oil components. The acid number characterizing the content of these acids is often marked with the symbol WAN (*Weak Acid Number*).

As the acid number increases due to the aging of the oil due to the oxidation of certain components, it also serves as an indicator of the degree of aging of the oil. The group of "strong" acids with corrosive properties includes, first of all, inorganic acids derived from acidic products of fuel combustion and low molecular weight organic acids resulting from oil oxidation. Both types of acids are water-soluble. The acid number describing the content of these acids is denoted by the symbol SAN (*Strong Acid Number*).

The content of all acids in a lubricating oil is determined by the total or total acid number TAN, which is the sum of the acid numbers WAN and SAN.

As fresh oils (non-motor oils) show a neutral reaction of the aqueous extract and thus are free of water-soluble corrosive acids, the given acid number value is both the WAN and TAN acid number.

2.3. Base number BN

The Base Number (BN) is a measure of the amount of alkali enriching additives contained in an engine lubricating oil. These additives include: additives neutralizing acid combustion products, corrosion inhibitors, dispersing and washing compounds. The composition of the package of enriching compounds depends on the type of engine and the type of fuel burned in it. The base number is expressed in [mg KOH/g] oil, and it is the number of milligrams of potassium hydroxide, determined to be equivalent in terms of acid neutralization capacity to the alkaline additives found in 1 g of lubricating oil. It is used to evaluate the content of alkaline additives in engine lubricating oils. The alkaline reserve of these oils neutralizes the corrosive acids formed during the combustion of sulphur compounds contained in the fuel. The neutralizing abilities of engine oils, and thus their base number, must be the higher, the higher the sulphur content in the fuel (Table 2). During operation, the base number value drops in relation to the BN value of fresh oil, because some of the alkaline additives it contains are used to neutralize the acids. The allowed decrease in the BN of oil in operation is 50% of the value of the BN of fresh oil.

Table 2

Base number (BN) of circulating oils for trunk piston engines
depending on the sulphur content of the fuel used

No.	The sulphur content of the fuel [%]	BN of fresh oil [mg KOH/g]
1.	< 1%	12 – 15
2.	1 % < S < 2 %	25 – 30
3.	2 % ≤ S ≤ 5 %	30 – 40

3. PERFORMING THE EXERCISE

3.1. Chemical reaction of water oil extract

The method of determining the reaction of water extracts is intended for obtaining extracts from liquid petroleum products and lubricants. The principle of measurement is to determine the pH of the water extract of the tested sample, acid – to methyl or basic orange – to phenolphthalein.

For a pear manifold with a capacity of 250 cm^3 pour 50 cm^3 of distilled water and 50 cm^3 of the tested oil sample. Shake the resulting mixture for 5 minutes, taking care not to form a homogeneous emulsion. Then insert the separator and let the layers separate. Remove the stopper from the funnel, fill two test tubes to 1/5 of their volume with water extract. Add 4 drops of phenolphthalein to one test tube, and the same amount of methyl orange to the other. Compare the color of the obtained solutions with the previously prepared standards.

Determination of the reaction of water extract of samples containing detergents and for oils forming an emulsion

For a manifold with a capacity of 250 cm^3, pour 50 cm^3 of the test sample at a temperature of 20 °C and add 50 cm^3 of a 1: 1 alcohol-water solution, neutralized against phenolphthalein and heated to 50 °C in a water bath under an air cooler. Gently shake the solution thus obtained for 5 minutes. Then place the funnel in a stand, and after clearly separating the mixture, pour the bottom layer into two test tubes. Add 4 drops of phenolphthalein to one, and 4 drops of methyl orange to the other. Compare the colour of the obtained solutions with the reference samples as before.

Elaboration of the results

Determine the reaction of the water extract of the tested oil, knowing that:

1. this reaction is considered to be alkaline if the tested sample of the water extract becomes raspberry coloured in relation to phenolphthalein;
2. this reaction is considered acidic if the test sample turns orange-red in the presence of methyl orange.
3. the lack of colour change in both test tubes, in relation to the standard samples prepared with distilled water, proves the neutral pH of the water extract.

Determination of the reaction of the water extract using a pH-meter

The pH of the water extract can be determined by measuring the pH of the water or hydro-alcoholic extract. The measurement is made with an instrument called a pH meter. On the basis of the values read on the scale of the pH meter, determine the reaction of the water or hydroalcoholic extract of the tested sample according to Table 3.

Table 3

The pH value of the water or hydroalcoholic extract

Reaction of the extract	pH value read	Acceptable measurement error
acidic	up to 4.0	0.2
slightly acidic	between 4.0 and 6.0	0.3
neutral	between 6.0 and 8.0	0.3
slightly alkaline	between 8.0 and 10.0	0.3
alkaline	from 10.0	0.3

3.2. Determination of the acid number

The total acid number TAN is the amount of milligrams of potassium hydroxide needed to neutralize all acid components in 1 g of oil (grease). This value is determined for both fresh and used oils.

The acid number method is used for oils and greases. The measurement principle is to extract the acids contained in the tested oil with a mixture of ethyl alcohol and benzene and titrate them with an alcoholic potassium hydroxide solution against alkaline blue 6B as an indicator of the reaction.

Performing the determination

Blank test

Pour 50 cm^3 of alkaline blue 6B into a 250 cm^3 conical Erlenmeyer flask. Fill the burette to zero with 0.1 M alcohol potassium hydroxide. Titrate the sample until the first permanent blue to pink colour change. Repeat the measurement and record the obtained results.

After completing the blank titration, proceed with the actual measurement. To this end, weigh out with an accuracy of 0.01 g to about $5 \div 10$ g of the tested oil into two clean Erlenmeyer conical flasks with a capacity of 250 cm^3 and, while stirring, add 50 cm^3 of alkaline blue 6B. Then titrate the contents of the flask with 0.1M alcoholic potassium hydroxide solution until the first permanent change of blue to pink colour is obtained.

Elaboration of the results

Calculate the acid number of the tested LK oil in [mg KOH/g] from the relationship:

$$\mathrm{LK}=\frac{(V_2-V_1)\cdot M\cdot 56{,}1}{m}$$

where:

V_2 – the amount of cm^3 of potassium hydroxide used to titrate the sample with the solvent, [cm^3],

V_1 – amount of cm^3 of potassium hydroxide used to titrate the solvent (blank test), [cm^3],

M – the molar concentration of the potassium hydroxide solution,

m – sample weight [g].

The final result should be the arithmetic mean of at least two measurements that do not differ by more than those specified in Table 4.

Table 4

Acceptable measurement error

Total acid number [mg KOH/g] of the product	Repeatability [mg KOH/g] of the product
0.05 ÷ 1.0	0.02
1.0 ÷ 5.0	0.1
5.0 ÷ 20	0.5
20 ÷ 100	2
100 ÷ 250	5

3.3. Determination of the base number by the method of potentiometric titration

The base number is the amount of hydrochloric or perchloric acid needed to neutralize all basic components contained in 1 g of the analysed petroleum product. expressed in the number of milligrams of potassium hydroxide equivalent to these acids.

Potentiometric titration is a titration at which the equivalence point (i.e.. the point where the equilibrium of the H_3O^+ and OH^- ions occur) is determined on the basis of the potential difference of the respective electrodes immersed in the test solution.

The potentiometric method is used to determine the base number of all petroleum products. including used oils. and especially for oils with a high alkaline reserve resulting from the presence of such additives as: organic bases. amine compounds. salts of weak acids and polyhydroxy salts.

In titrations. the indicator electrode and the reference electrode form a cell. The potential of the indicator electrode depends on the content of the titrated component. while the potential of the reference electrode is constant and does not depend on the composition of the solution. The titration is carried out to a more or less rapid change of the potential of the indicator electrode (up to the so-called potential jump that will occur at the equivalence point) or to a certain value of the potential of the indicator electrode (570 mV). or to a certain pH value ($pH \approx 4$). A magnetic stirrer is usually used during the titration of the test solution with a combination electrode of the SAgP-209W type. The combined electrode consists of a glass electrode. known as the indicator (measuring) electrode. and silver chloride electrode – constituting the reference electrode or the so-called reference electrode. These electrodes are located in one housing and when placed in the test solution they form the appropriate measuring cell which can be represented by the following scheme: Ag, AgCl (0.1M HCl), test solution (saturated KCl) AgCl, Ag. The electromotive force (EMF) of this cell depends on the potential change at the boundary: glass membrane - test solution.

Carrying out the determination of the base number by potentiometric titration with perchloric acid

Pour 120 cm^3 of solvent I into the samples into a 250 cm^3 beaker. Then place the beaker in a copper mesh on a magnetic stirrer. After turning on the stirrer and making the rotation so that the liquid in the vessel does not splash and air is not sucked in. insert the SAgP-209W electrode (previously washed with distilled water and solvent I) and start the titration. Fill the burette with 0.1 M perchloric acid and place it in the test solution so that its end is just below the surface of the solution. Immediately record the initial state of the burette and read the potential value on the instrument (or the pH value if using the pH scale). Add perchloric acid to the test sample in amounts of 0.05 cm^3 each. and add the next portion only after the value becomes stable on the instrument. The measurement can be started when the potential does not change more than 5 mV or o 0.1 pH within 1 minute.

The titration is considered complete when the change of potential is less than 5 mV or 0.1 pH after adding 0.05 cm^3 perchloric acid solution. You should then read and write the liquid level in the burette. and then remove the electrode and the burette tip. Wash them successively with solvent I for samples, distilled water and again with solvent. Then proceed to titration of the tested sample. For this purpose. weigh the mass of the sample calculated from the equation below into a 250 cm^3 beaker, add 120 cm^3 of sample solvent and place in a copper mesh on a magnetic stirrer.

$$m = \frac{28}{LZ_p} \cdot 10^{-3}$$

where:

m – sample weight. [g];

BN_p – predicted base number;

28 – factor (the amount of KOH corresponding to 1 cm^3 of 0.1 m perchloric acid solution. [mg]).

After turning on the stirrer and selecting the appropriate rotations for the tested sample. insert the SAgP-209W electrode. Place the end of the burette just below the surface of the test solution, read the initial state. Then proceed with the titration. Add the perchloric acid to the test sample in small portions, add another portion only after the value indicated on the device is stabilized. At the beginning of the titration and at the inflection point of the titration curve, perchloric acid should be dropped in amounts of 0.1 cm^3 each. If this addition causes a greater potential increase than 30 mV or 0.5 pH, add the acid in amounts of 0.05 cm^3 each.

The titration is considered complete when the change in potential is less than 5 mV or 0.1 pH after adding 0.1 cm^3 (0.05 cm^3) of perchloric acid solution. Read the liquid level in the burette. Then remove the electrode from the titration solution as well as the end of the burette and wash successively with: sample solvent, distilled water and again with the solvent, repeat the measurement three times.

After completing the measurements. place the electrode in a vessel with a saturated solution of potassium chloride. The immersion depth of the electrode during storage and during the measurement must not be greater than 2/3 of the length of the glass part of the electrode. Minimum immersion should reach the protective cap.

Elaboration of the results

After the measurements, plot the titration curve, placing the potentiometer readings in [mV] on the ordinate (or the potentiometer readings in pH units) and on the abscissa – the amount of 0.1M perchloric acid solution added dropwise in [cm^3]. The points of inflection of the titration curve which are generally near the potentials corresponding to the buffer solutions, are to be taken as the equivalence points.

Calculate the base number BN_c in [mg KOH/g] oil according to the formula:

$$LZ_c = \frac{(V_2 - V_1) \cdot M_1 \cdot 56{,}1}{m}$$

where:

BN_c – base number [mg KOH/g];

V_2 – volume of 0.1M perchloric acid used for titration of the test sample, up to the inflection point of the titration curve, [cm^3];

V_1 – volume of 0.1M perchloric acid used for titration of the test sample, up to the inflection point of the titration curve, [cm^3];
m – sample weight, [g];
M_1 – the molar concentration of perchloric acid [M];
56.1 – coefficient determining the number of mg of potassium hydroxide contained in 1 cm^3 of a 1M solution.

The correct result will be the mean value of the base number BN_c calculated from the equation given above. for results that do not differ more than that indicated in Table 5.

Table 5

Acceptable measurement error

Total acid number [mg KOH/g] of the product	Repeatability [mg KOH/g] of the product
0.05 ÷ 1.0	0.02
1.0 ÷ 5.0	0.1
5.0 ÷ 20	0.5
20 ÷ 100	2
100 ÷ 250	5

Determination of the base number for used oils. the titration curve of which does not show a distinct inflection point

Pour 80 cm^3 of chlorobenzene and 40 cm^3 of glacial acetic acid into a 250 cm^3 beaker. Then add from a pipette at least 8 cm^3 of a solution of 0.1 M perchloric acid dissolved in glacial acetic acid. Place the beaker in a copper mesh and place it on a magnetic stirrer. With the stirrer turned on, titrate the unreacted perchloric acid with 0.1M sodium acetate solution in dissolved acetic acid acetic acid. Record the results obtained.

After two measurements for the blank sample (the so-called blank), you should start the actual measurement.

The calculated mass of the sample from the above-mentioned relation may not exceed 5 g. If at this mass, the tested petroleum product does not show an inflection point on the titration curve, the sample should be reduced to 3 g and the determination should be repeated.

Dissolve the weighed sample in a 250 cm^3 beaker in 80 cm^3 of chlorobenzene, add 40 cm^3 of glacial acetic acid and using a pipette at least 8 cm^3 of 0.1 M perchloric acid. Turn on the stirrer and stir for 2 minutes, then titrate the unreacted perchloric acid. To do this, fill the burette with 0.1 M sodium acetate dissolved in glacial acetic acid.

Insert the washed SAgP-209W electrode into the tested solution and place the end of the filled burette in this solution, so that it is just below the surface. Then note the initial state of the burette and the potential value (or the pH value on the pH scale).

Add a solution of sodium acetate in acetic acid of 0.05 cm^3 in small portions from the burette at the beginning of the titration and at the inflection point of the curve. The titration is considered complete when the change in potential is less than 5 mV or 0.1 pH after adding more sodium acetate solution. After performing the titration, remove the electrode from the test solution, wash it and then place it in the vessel with a saturated solution of potassium chloride.

Elaboration of the results

Calculate the base number BN_c in [mg KOH/g] according to the formula:

$$LZ_c = \frac{(V_4 - V_3) \cdot M_1 \cdot 56{,}1}{m}$$

where:

BN_c – base number, [mg KOH/g];

V_4 – volume of 0.1M sodium acetate in acetic acid solution used for the "blank" titration, [cm^3];

V_3 – volume of 0.1M sodium acetate used for the titration of the test sample, [cm^3];

m – weight of the test sample [g];

M_1 – the molar concentration of perchloric acid.

The correct result will be those values of the total base number BN_c, which do not differ by more than 24% of the mean value.

Note!

In the absence of chloric acid (VII), the determination of the base number $BN_{c.}$ should be titrated with a 0.1M solution of hydrochloric acid in isopropyl alcohol.

For this purpose, weigh (with the accuracy of 0.1 g) a sample of the mass calculated according to the formula given above into a 250 cm^3 beaker, but this mass should not exceed 20 g and add 125 cm^3 of solvent to the samples. Place the vessel in a grid on a magnetic stirrer and turn it on. After the sample is completely dissolved, proceed with the measurement as described above.

Elaboration of the results

Calculate the base number BN_c in [mg KOH/g] of the oil sample according to the formula:

$$LZ_c = \frac{(V_6 - V_5) \cdot M_1 \cdot 56{,}1}{m}$$

where:

BN_c – base number, [mg KOH/g].

V_6 – volume of hydrochloric acid used to titrate the test sample to the inflection point of the titration curve, [cm^3].

V_5 – volume of hydrochloric acid used for titration of the "blank" sample to the inflection point of the titration curve, [cm^3].

m – weight of the test sample, [g].

M_1 – molar concentration of hydrochloric acid.

56.1 – coefficient determining the number [mg] of potassium hydroxide contained in 1 cm^3 of a 1M solution.

4. DEVELOPMENT OF THE EXERCISE

1. Determine the chemical reaction of the water extract of the analysed petroleum product and provide practical information about this reaction.
2. Compare your results with the acid number or base number limits for the oil under test.
3. Evaluate further operational usefulness of the tested oil.
4. In the appendices to this exercise. at the end of the manual. the cross-sections of marine engines (trunk piston engine and crossheader) are shown in Figures 1 and 2 in order to better understand the functions and utility tasks of lubricating oils.

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 performed exercise. which should include:

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

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

Tasks and questions to be completed by the student

Tasks

1. For oils: Marinol RG 1530 and Marinol RG 4040. provide:
   - BN values of fresh oil;
   - limit values BN of the oil used;
   - in which engines should these oils be used;
   - what fuels should be used in them;
   - viscosity grades of these oils;
   - what determines the selection of the oil viscosity class?
2. For oils: Castrol MXD 304 and Castrol MXD 403 provide data as in point 1:
3. For oils: Mobilgard 312 and Mobilgard 412 provide data as in point 1:
4. As a result of testing the Marinol RG 2030 oil, BN was determined, which is 12.15 mg KOH / g of oil and it was determined, that the chemical reaction of the water extract of this oil was neutral. What diagnostic conclusions follow from the given results of this analysis?
5. The Maronol RG 4040 circulating oil from a trunk piston engine was tested to determine its base number BN. For a sample of 2.12 g of this oil, 7.55 cm^3 of hydrochloric acid with a titer of 0.1 mol/dm^3 were used. Calculate the BN of the oil and determine whether the oil is fit for further service.
   Answer: BN = 18.92 mg KOH/g.
6. The Maronol RG 1530 circulating oil from a trunk piston engine was tested to determine its base number BN. For a sample of 3.28 g of this oil, 4.15 cm^3 of hydrochloric acid with a titer of 0.1 mol/dm^3 were used. Calculate the BN of the oil and determine whether the oil is fit for further service.
   Asnwer: BN = 7.10 mg KOH/g.
7. A sample of CastrolHyspinAWS68 oil was collected from the ship's hydraulic system for testing in order to determine its total acid number TAN. For a sample of 7.52 g of this oil, 1.45 cm^3 of potassium hydroxide with a titer of 0.1 mol/dm^3 were used. Calculate the TAN of the oil and determine whether the oil is suitable for further use, knowing that the acid number of the hydraulic oil should not exceed 1.8 mg KOH/g of oil.

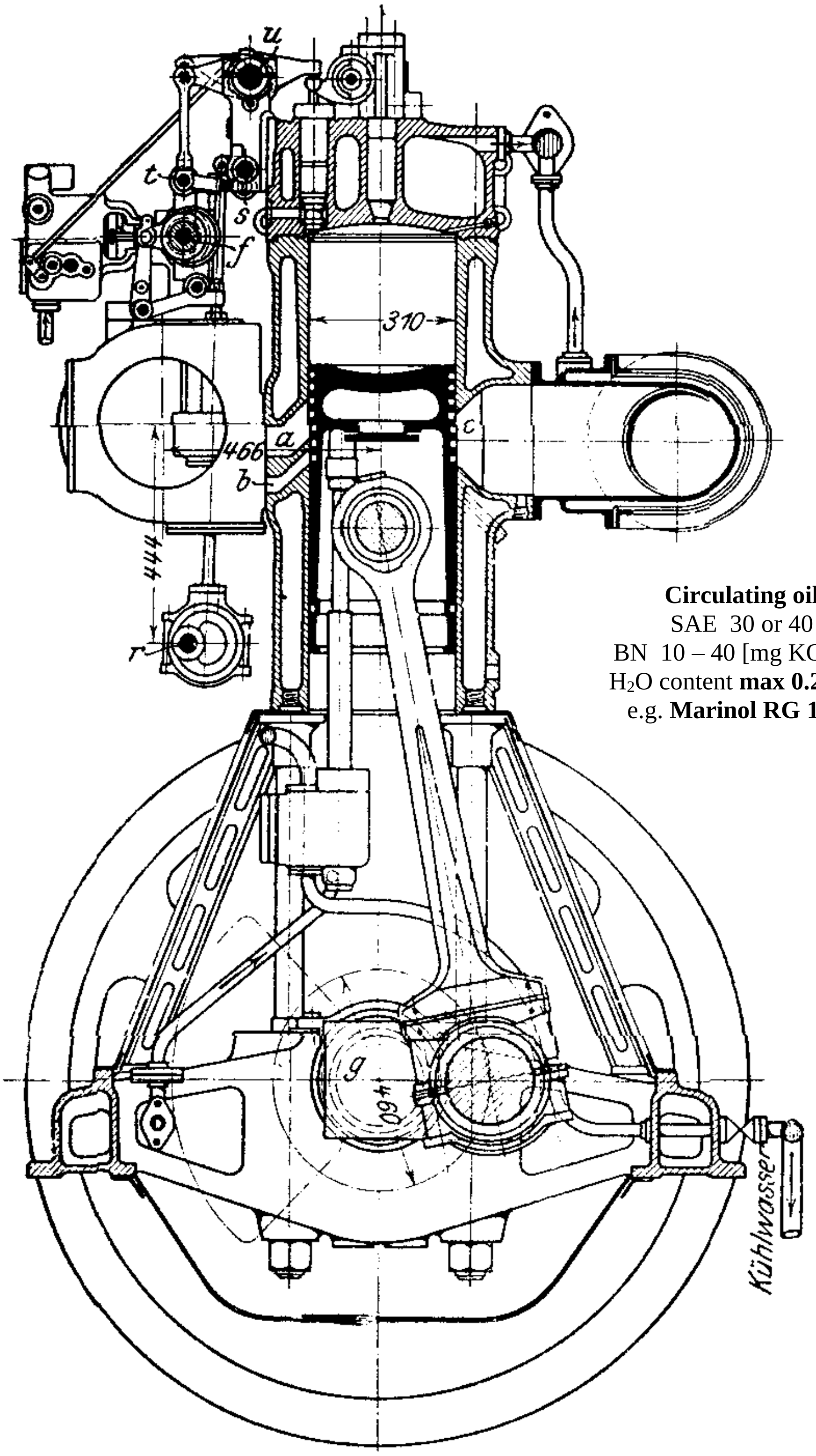
Questions

1. What is the principle of determining the chemical reaction of a water extract of lubricating oils and the evaluation of the results of this determination?
2. What practical information can knowledge of chemical reactions provide:
   a. acidic;
   b. neutral;
   c. alkaline.
3. For which oils is the acid number tested and for which the base number and why?
4. Explain the purpose of acid number determination for fresh and used oils. What are the relationships between these numbers?
5. Explain the purpose of the base number determination for fresh and used oils. What are the relationships between these numbers?
6. What is the principle of determining the base number of engine oils? What characterizes this number? What is its operational significance and what is its limit value?
7. Specify the functions performed by the components included in the so-called quality packages used as additives to lubricating oils?

8. What is the quality classification of engine oils according to API and what are its criteria?
9. When is the oil completely changed due to the chemical reaction of the water extract and because of the indicated alkaline reserve?
10. Report the ranges of numerical values of BN for fresh circulating oils for a trunk piston and crosshead engines and for cylinder oils.
11. What is the selection principle of the BN of lubricating oil depending on the type of fuel used in the engine?
12. What is the process of refreshing engine oil during its operation?

Appendix to the exercise

TRUNK PISTON ENGINE

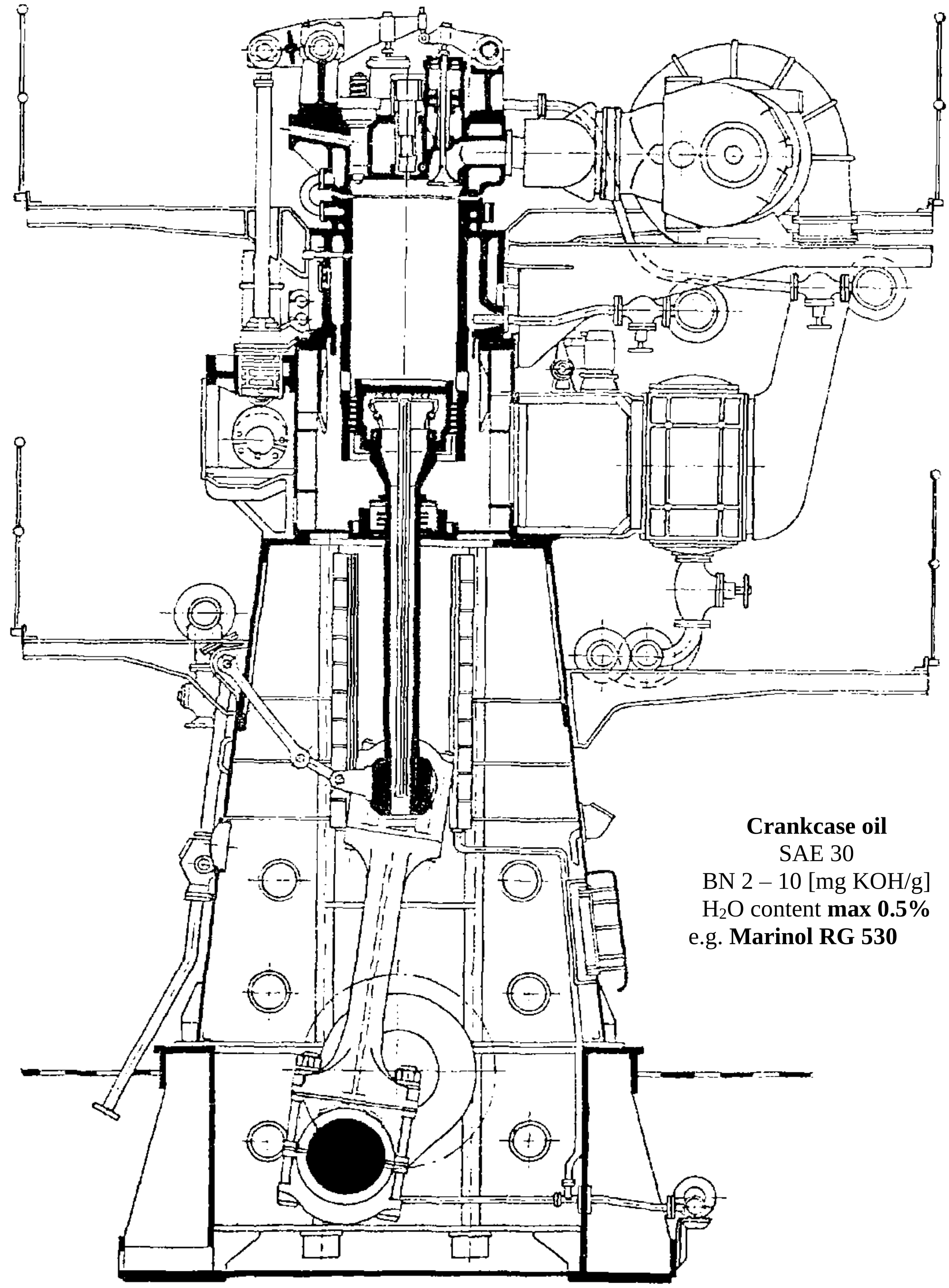


Circulating oil
SAE 30 or 40
BN 10 – 40 [mg KOH/g]
H_2O content **max 0.2%**
e.g. **Marinol RG 1530**

Fig. 1. Cross-section of a trunk piston engine (380 KM)

CROSSHEAD ENGINE

Cylinder oil
SAE ≥ 50 (50+, 60)
BN ≥ 50 [mg KOH/g]
even 120 [mg KOH/g]
e.g. **Marinol RG 7050**



Crankcase oil
SAE 30
BN 2 – 10 [mg KOH/g]
H_2O content **max 0.5%**
e.g. **Marinol RG 530**

Fig. 2. D 55 type engine – cross-section