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Petroleum products — Determination of base number — Perchloric acid potentiometric titration method

Produits pétroliers — Détermination de l'indice de base — Méthode par titrage potentiométrique à l'acide perchlorique

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 3771 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This third edition cancels and replaces the second edition (ISO 3771:1994), which has been technically revised.

Petroleum products — Determination of base number — Perchloric acid potentiometric titration method

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a method for the determination of basic constituents in petroleum products by potentiometric titration with perchloric acid in glacial acetic acid.

The constituents that can be considered to have basic characteristics include organic and inorganic bases, amino compounds, salts of weak acids (e.g. soaps), basic salts of polyacid bases, and salts of heavy metals.

The ranges of base number values for which precision values for the method have been established are:

— unused oils: base numbers from 3 to 45;

— additive concentrates: base numbers from 5 to 45;

— used oils: base numbers from 3 to 30.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
base number
w_{BN}
quantity of perchloric acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide, required to titrate 1 g of sample dissolved in the specified solvent to a well-defined inflection point, as specified in this International Standard

4 Principle

The test sample is dissolved in an essentially anhydrous mixture of toluene, acetone and glacial acetic acid, and titrated with a standard volumetric solution of perchloric acid in glacial acetic acid using a potentiometric titrimeter. A combination pH-Ag/AgCl glass electrode (6.2) is used. The meter readings are plotted against the corresponding volumes of titrating solution, and the endpoint is taken as the last inflection in the resulting curve.

5 Reagents

During the analysis, use only reagents of recognized analytical grade, and water equivalent to Grade 3 of ISO 3696.

5.1 Acetic acid (CH_3COOH), glacial.

5.2 Acetic anhydride [$(CH_3–CO)_2O$].

5.3 Toluene.

5.4 Acetone.

5.5 Tris (hydroxymethyl)-aminomethane (Tris) ($C_4H_{11}NO_3$).

5.6 Potassium hydrogen phthalate ($KHC_8H_4O_4$).

5.7 Tetraethylammoniumbromide 0,4 mol, electrolyte. Use an appropriate non-aqueous electrolyte in the electrode. Tetraethylammoniumbromide (TEABr in ethylene glycol, 0,4 mol/l) is an example of such an electrolyte. In general, follow the manufacturer's instructions for electrolyte use in the electrode. Prepare a solution (0,4 mol/l) of TEABr in ethylene glycol.

5.8 Lithium chloride (LiCl): electrode manufacturers recommend alternatively a saturated solution of LiCl in ethanol (96 % denatured). Dissolve 70 g LiCl in 500 ml ethanol at ambient temperature, stirring for several hours.

5.9 Titration solvent: add six volumes of toluene (5.3) to three volumes of acetic acid (5.1) to one volume of acetone (5.4).

5.10 Perchloric acid ($HClO_4$), 0,1 mol/l standard volumetric acetous solution.

5.10.1 A 0,1 mol/l acetic acid perchloric acid mixture may be obtained commercially. If necessary this may be prepared using concentrated perchloric acid ($HClO_4$), acetic acid and acetic anhydride. Perchloric acid is available in different concentrations, the amount of acetic anhydride required depends on the concentration. Three typical possibilities are found in Table 1. When preparing the mixture, initially dissolve the appropriate amount of perchloric acid in 500 ml of acetic acid, add the appropriate amount of acetic anhydride and dilute to 1 l with acetic acid.

Store this solution for at least 24 h before standardization.

WARNING — This perchloric acid solution is not harmful under the test conditions, but concentrated perchloric acid is a powerful oxidant when dry or heated. Take great care to avoid contact with organic matter under conditions that may result in subsequent drying or heating. Wash spills immediately and thoroughly with water.

NOTE Avoid adding excess acetic anhydride to prevent acetylation of any primary or secondary amines which may be present in the sample being tested.

Table 1 — Perchloric acid and acetic anhydride dilution volumes based on perchloric acid concentrations

Perchloric acid concentration % (*m*/*m*)[a]	**Perchloric acid addition** ml	**Acetic anhydride** ml
70 to 72	8,5	30
60 to 62	10,2	35
57	11,8	40

[a] For the purposes of this International Standard, the term "% (*m*/*m*)" is used to represent the mass fraction of a material.

5.10.2 Standardization may be conducted using either tris (hydroxymethyl)-aminomethane (5.5) or potassium hydrogen phthalate (5.6), as described below. Commercially available certified solutions may be used in place of standardization.

a) Procedure A using tris (hydroxymethyl)-aminomethane (5.5)

Dry tris (hydroxymethyl)-aminomethane over silica gel in a desiccator (minimum of 24 h at room temperature). Measure approximately 0,05 g of tris(hydroxymethyl)-aminomethane to 0,1 mg accuracy and dissolve in 60 ml of acetic acid. Titrate the solution with perchloric acid (5.10) using the electrode system and methods given in 8.1 to 8.4 and 9.3 to 9.6. Detect the end point using the same method as used for base number determination (10.1). The titer shall be adjusted each time a new titration solution is prepared or minimum once a week.

b) Procedure B using potassium hydrogen phthalate (5.6)

Dry a quantity of potassium hydrogen phthalate (5.6) for 2 h in an oven at 120 °C and allow it to cool in a desiccator. Dissolve 0,1 g to 0,2 g of potassium hydrogen phthalate weighed to the nearest 0,1 mg and in 60 ml of acetic acid (5.1). Titrate with the perchloric acid solution (5.10.1) using the appropriate method (see Procedure A above). The titer shall be adjusted each time a new titration solution is prepared or minimum once a week.

5.10.3 Calculation of the concentration is carried out as described below.

a) Calculation procedure A using tris (hydroxymethyl)-aminomethane (5.5)

Calculate the concentration, $c_{0(\mathrm{Tris})}$, expressed in moles per litre, of the perchloric acid solution from Equation (1):

$$c_{0(\mathrm{Tris})} = \frac{m_{\mathrm{Tris}} \times f_{\mathrm{c}}}{121{,}14 \times V_{\mathrm{pa}}} \tag{1}$$

where

m_{Tris}	is the mass of tris (hydroxymethyl)-aminomethane (5.5), expressed in milligrams;
f_{c}	is the correction factor calculated from the concentration given in the certificate divided by 100;
121,14	is the molar mass of tris (hydroxymethyl)-aminomethane (5.5), expressed in milligrams per millimole;
V_{pa}	is the volume of perchloric acid solution used, expressed in millilitres.

b) Calculation procedure B using potassium hydrogen phthalate (5.6)

Calculate the concentration, $c_{0(\mathrm{KHP})}$, expressed in moles per litre, of the perchloric acid solution from Equation (2):

$$c_{0(\mathrm{KHP})} = \frac{m_{\mathrm{KHP}} \times f_{\mathrm{c}}}{204{,}22 \times V_{\mathrm{pa}}} \tag{2}$$

where

m_{KHP}	is the mass of potassium hydrogen phthalate (5.6), expressed in milligrams;
f_{c}	is the correction factor calculated from the concentration given in the certificate divided by 100;
204,22	is the molar mass of potassium hydrogen phthalate (5.6), expressed in milligrams per millimole;
V_{pa}	is the volume of perchloric acid solution used, expressed in millilitres.

6 Apparatus

6.1 Potentiometric titrimeter: acceptable microprocessor-controlled titration systems with automatic burettes are available, which ensure rapid and reliable titration in routine operation. They perform the titration and the plotting and assessment of the titration curve automatically. The automatic burettes shall be at least accurate to 1/5 000 of the actual swept volume of the cylinder to ensure adequate accuracy. The titration of the 0,1 mol/l perchloric acid may be performed in equal steps in volume (incremental) or, dependent on the development of the curve, in variable volume steps (dynamic). Both dosing methods are acceptable; however, an optimum distribution of measurement points can only be achieved if the titration takes place dynamically. Follow the recommendations of the relevant manufacturer when adjusting titration parameters.

6.2 Combination pH-Ag/AgCl glass electrode for use with non-aqueous media: electrostatic effects are a frequent source of problems (interference, fluctuating signals, sluggish adjustment response) when using pH electrodes with non-aqueous media. The pH glass electrode shall fulfil the following in order to minimize the influences and at the same time to improve the measurement accuracy and reliability. Use a combination electrode with a low membrane resistance (in the order of 100 MΩ to 200 MΩ). The integrated reference electrode shall have a flexible sleeve diaphragm, to facilitate the cleaning of the diaphragm. This will ensure that the resistance of the reference electrode diaphragm is minimized and guarantee an adequate shielding of the complete electrode. The reference electrode shall also have an Ag/AgCl reference cell. Additionally, the reference electrode shall be internally shielded so that the electrostatic effects remain independent of the level of the reagent (5.7 and 5.8).

6.3 Stirrer, either mechanical or electrical, with variable speeds and with a propeller or paddle of chemically inert material. If an electrical stirrer is used, it shall be grounded (earthed) so that disconnecting or connecting the power to the motor does not produce a permanent change in the meter reading during the course of a titration. A magnetic stirrer with stirring bar may be used provided that it meets the above conditions.

6.4 Titration beaker (tall form), of an appropriate volume.

6.5 Titration stand, suitable for supporting the beaker, electrodes, stirrer and burette.

NOTE An arrangement that allows for the removal of the beaker without disturbing the electrodes, burette and stirrer is desirable.

6.6 Balance, with a resolution of 0,001 g or less for base number values up to 30 and 0,000 1 g for base number values greater than 30.

7 Preparation of test sample

Ensure that the test sample is representative, as any sediment may be acidic or basic or have absorbed acidic or basic material from the liquid phase.

NOTE If necessary, laboratory samples can be warmed up to 60 °C to aid mixing. Used oils are shaken vigorously to ensure homogeneity before preparing the test sample.

8 Preparation of electrode system

8.1 Preparation of electrodes

Remove the cap from the electrode filling neck. Ensure that the ground glass sleeve is securely in place by pushing it firmly up or down (depending on the electrode type). Turn the ground glass sleeve slightly and gently push it in again. Allow a few drops of electrolyte to flush through (to wash the diaphragm) and allow the electrolyte to spread out between the ground glass surface and the core inner cell. Top the electrolyte up to the top of the electrolyte filling neck. In addition to its basic function, the electrolyte provides an electrical shield against outside interference. pH electrodes are particularly sensitive to interference when used with non-aqueous solvents. For this reason, it is very important that the level of the electrolyte is as high as possible. Only conduct measurements and titrations with the plug removed.

Precondition new electrodes. It has been found that submerging the new electrodes in the solvent mixture for 12 h is effective. The same applies for electrodes which are used in water (see 8.3).

8.2 Maintenance of electrodes

Thoroughly clean the electrode before long-term storage and then keep in the same electrolyte that will be used to fill it. Close the electrode filling plug during storage.

8.3 Testing of electrodes

If there are any doubts about the performance of the electrode, for example when adjusting the titre, test the electrode using a buffer solution, for example with a standard pH buffer (pH 4 and pH 7). As the electrode is a pH electrode for acid/base titrations, the testing is different to a standard electrode test. Measure the potential difference (use the mV range) of the titrator (or a pH meter) between two buffer solutions with pH 4 and pH 7. Proper performance gives a difference of at least 150 mV (50 mV/dpH).

Condition the electrode after this test (see 8.1).

8.4 Cleaning of electrodes

Thoroughly wash the electrode with the solvent between titrations (washing with toluene then petroleum ether, then toluene again has been found to be effective). The electrode may not be coated with an oil film after washing. Both dipping the electrode and automatic cleaning have proved effective with the various automatic samplers on the market.

9 Performance

9.1 Sample amounts

Select the sample mass so that approximately 5 ml of perchloric acid solution are used up at the inflection. Table 2 shows the test sample mass based on total base number (3.1).

Table 2 — Test sample mass based on total base number

Total base number	Test sample mass g	Precision of weighing mg
3 to 15	2,00	1
>15 to 30	1,00	1
>30 to 45	0,25	0,1
EXAMPLE Total base number of 10 corresponds to approximately 2 g test sample.		

9.2 Preparation of test sample solution

To the test sample, add 60 ml to 100 ml of the titration solvent (5.9) and stir the solution (see 6.3) until the test sample has dissolved. Oil samples that are difficult to dissolve may be pre-dissolved using an external stirrer.

9.3 Preparation of apparatus

Prepare the electrodes as specified in 8.1. Position the electrodes far enough into the test solution that the lower rim of the ground sleeve is covered.

Position the electrode to one side of the beaker containing the solution, not in the middle, to ensure an adequate flow past the electrode. Position the tip of the burette so that the titrated medium is not directly dosed onto it. Stir vigorously without stirring air into the solution. Fill the supply bottle with 0,1 mol/l perchloric acid solution. Fill the hoses and the cylinder of the burette without air bubbles.

9.4 Titration

9.4.1 Dynamic titration

Dynamic titration (see 6.1) has been found effective in most cases. The parameters differ between manufacturers (see their recommendations). The examples given in Table 3 have been tried.

Table 3 — Examples of titrations

Example 1: Measure point interval titration		**Example 2: Dynamic titration method**	
Minimum volume increments	10 µl	Minimum ΔV	0,01 ml
Measurement drift	10 mV/min	Measurement type dE/dt	1/6 mV/s
Waiting time	20 s	Maximum waiting time, t_{max}	20 s
Maximum volume	8 ml	Volume to terminate titration	8 ml
End point criterion	15 mV	Threshold for first derivative	15 mV

9.4.2 Incremental titration

See the manufacturer’s recommendations.

9.5 Cleaning of apparatus

See the manufacturer’s recommendations for cleaning and storing the apparatus for long periods of time (see also 8.4).

9.6 Blank test

For each series of test samples, the blank volume is found with the recommended amount of titration solvent (5.9). This conditions the electrode system. A blank test is mandatory for each new batch of solvent. Normally the blank is so low that it does not need to be taken into account.

10 Calculation of base number

10.1 The end point of a potentiometric titration lies at the mid point of the inflection of the resulting titration curve. Modern titration apparatus finds the inflection automatically. Follow the manufacturer’s recommendations regarding the sensitivity and parameters. As the total base number titration records the sum of the base components, it is not necessary to differentiate between potential multiple endpoints. In order to avoid stopping the titration too early it is recommended only to stop the titration after a predefined maximum volume. If there is more than one end point then use the last clear endpoint when interpreting the titration. It helps to use the first differential; this is an option with most modern apparatus.

10.2 Calculate the total base number, w_{BN}, expressed in milligrams KOH per gram test sample, using Equation (3):

$$w_{\mathrm{BN}} = \frac{56{,}1\left[c_0\left(V_2 - V_1\right)\right]}{m_{\mathrm{S}}} \tag{3}$$

where

V_1	is the volume, expressed in millilitres, of perchloric acid (5.10) used to titrate the blank test solution (see 9.6) to the inflection point on the titration curve;
V_2	is the volume, expressed in millilitres, of perchloric acid (5.10) used to titrate the test sample to the inflection point on the titration curve;
c_0	is the concentration, expressed in moles per litre, of the perchloric acid (5.10) [as defined in Equations (1) or (2)];
56,1	is the molar mass of potassium hydroxide, expressed in milligrams per millimole;
m_{S}	is the mass, expressed in grams, of the test sample.

11 Expression of results

Report the base number, w_{BN}, as calculated in 10.2, to the nearest 0,1 mg KOH/g sample.

12 Precision

12.1 General

The precision of the method, as obtained by statistical examination of interlaboratory test results, is given in 12.2 and 12.3.

12.2 Repeatability

The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the average of the two test results by a percentage greater than those given in Table 4 (repeatability) in only one case in 20.

Table 4 — Repeatability

Test sample	**Base number**, w_{BN} mg KOH/g sample	**Repeatability** %
Fresh oils and additive concentrates	$3 \le w_{\mathrm{BN}} \le 20$	5
	$w_{\mathrm{BN}} > 20$	3
Used oils	$3 \le w_{\mathrm{BN}} \le 20$	5
	$w_{\mathrm{BN}} > 20$	5

12.3 Reproducibility

The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the average of the two test results by a percentage greater than those given in Table 5 (reproducibility) in only one case in 20.

Table 5 — Reproducibility

Test sample	**Base number**, w_{BN} mg KOH/g sample	**Reproducibility** %
Fresh oils and additive concentrates	$3 \leq w_{BN} \leq 20$	10
	$w_{BN} > 20$	6
Used oils	$3 \leq w_{BN} \leq 20$	15
	$w_{BN} > 20$	15

13 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard (ISO 3771:2011);

b) the type and complete identification of the product tested;

c) the result of the test (see Clause 11);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.

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