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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

Reference number
ISO 3771:1994(E)

Foreword

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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.

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

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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 standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this 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 may be considered to have basic characteristics include organic and inorganic bases, amino compounds, salts of weak acids (for example soaps), basic salts of polyacid bases, and salts of heavy metals.

Two variations of the method are described, Procedures A and B, using different titration solvent volumes and test sample masses.

NOTE 1 Round-robin tests on a series of unused and used oils and additive concentrates have shown the Procedures A and B to give statistically equivalent results.

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

unused oils — base numbers from 6 to 70;

additive concentrates — base numbers from 5 to 300;

used oils on which were employed the forward titration — base numbers from 5 to 27.

NOTE 2 During the development of the original test method (Procedure A) and the test method using reduced titration solvent volume (Procedure B), cooperative testing was done on samples covering a wide range of types of oils, of additive concentrates which are used to prepare these oils, and of service conditions of the oils. Nevertheless it was not possible to cover the complete range of base numbers. It is reasonable to suppose that interpolation within and extrapolation from the ranges actually tested will not introduce serious errors in the precision.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

3 Definition

For the purposes of this International Standard, the following definition applies.

3.1 base number: The 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

4.1 The test sample is dissolved in an essentially anhydrous mixture of chlorobenzene and glacial acetic acid and titrated with a standard volumetric solution of perchloric acid in glacial acetic acid using a potentiometric titrimeter. A glass indicating electrode and a calomel reference electrode are used, the latter being connected with the test sample solution by means of a salt bridge. 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.

4.2 Procedure A uses 120 ml of titration solvent; Procedure B uses 60 ml of titration solvent. In addition, the two procedures use different equations for the calculation of appropriate sample masses. Many portions of Procedures A and B are identical. Only the unique portions are described separately for the two procedures.

4.3 Occasionally certain used oils give no inflection when titrated according to 4.1, in which case back-titration with a standard volumetric acetous sodium acetate solution titrant is carried out (see clause 11).

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 Chlorobenzene, C_6H_5Cl.

5.4 Potassium hydrogen phthalate, $KHC_8H_4O_4$.

5.5 Sodium carbonate, Na_2CO_3, anhydrous.

5.6 Sodium perchlorate, $NaClO_4$, electrolyte.

Prepare a saturated solution of sodium perchlorate in the acetic acid (5.1). An excess of undissolved sodium perchlorate shall always be present at the bottom of the solution.

5.7 Titration solvent.

Add 1 volume of acetic acid (5.1) to 2 volumes of chlorobenzene (5.3).

5.8 Perchloric acid, $HClO_4$, 0,1 mol/l standard volumetric acetous solution.

5.8.1 Preparation

Either mix 8,5 ml of perchloric acid (70 % to 72 % mass fraction) with 500 ml of acetic acid (5.1) and 30 ml of acetic anhydride (5.2) or, if the titrant is prepared using 60 % to 62 % mass fraction perchloric acid, use 10,2 ml of 60 % to 62 % mass fraction perchloric acid and 38 ml of acetic anhydride or, if the titrant is prepared using 57 % mass fraction perchloric acid, use 11,8 ml of 57 % mass fraction perchloric acid and 40 ml of acetic anhydride.

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

Dilute to 1 000 ml with acetic acid (5.1) and allow the solution to stand 24 h before standardization.

5.8.2 Standardization

5.8.2.1 Procedure A

Dry a quantity of potassium hydrogen phthalate (5.4) in an oven at 120 °C for 2 h and allow it to cool. Take 0,1 g to 0,2 g of the potassium hydrogen phthalate weighed to the nearest 0,1 mg, and dissolve it with care in 40 ml of warm acetic acid (5.1). Add 80 ml of chlorobenzene (5.3), cool, and titrate with the perchloric acid solution (5.8.1), using the electrode system and procedures given in 8.1 to 8.4 and 9.4. Detect the endpoint by the same procedure used for the base number determination (see 10.2). Carry out a blank titration on 40 ml of acetic acid plus 80 ml of chlorobenzene (see 9.6).

5.8.2.2 Procedure B

Dry a quantity of potassium hydrogen phthalate (5.4) in an oven at 120 °C for 2 h and allow it to cool. Take 0,05 g to 0,1 g of the potassium hydrogen phthalate weighed to the nearest 0,1 mg and dissolve it with care in 20 ml of warm acetic acid (5.1). Add 40 ml of chlorobenzene (5.3), cool, and titrate with the perchloric acid solution (5.8.1) as described in 5.8.2.1. Carry out a blank titration on 20 ml of acetic acid plus 40 ml of chlorobenzene (see 9.6).

5.8.3 Calculation of concentration

Calculate the concentration, C_0, in moles per litre, of the perchloric acid solution from the formula:

$$C_0 = \frac{1\,000m}{204{,}23\,(V_1 - V_0)} \qquad \ldots (1)$$

where

m is the mass, in grams, of potassium hydrogen phthalate;

V_0 is the numerical value of the volume, in millilitres, of perchloric acid solution used for the blank titration;

V_1 is the numerical value of the volume, in millilitres, of perchloric acid solution used for the titration.

Because of the relatively large coefficient of cubic expansion of organic liquids, use the acetous perchloric acid solution either within 5 °C of the temperature at which it was standardized or, if used at a temperature more than 5 °C higher, multiply the volume used by the factor $[1 - (t \times 0{,}001)]$, or if used at a temperature more than 5 °C lower, multiply by the factor $[1 + (t \times 0{,}001)]$, where t is the difference, in degrees Celsius, between the temperatures of standardization and use (and is always positive).

Restandardize the perchloric acid solution at least once a week, or more often if there is any reason to suspect that the concentration has changed.

5.9 **Sodium acetate, $NaC_2H_3O_2$**, 0,1 mol/l standard volumetric acetous solution.

5.9.1 Preparation

Dissolve 5,3 g of anhydrous sodium carbonate (5.5) in 300 ml of acetic acid (5.1). Dilute to 1 l with acetic acid after dissolution is complete.

5.9.2 Standardization

5.9.2.1 Procedure A

Use 120 ml of titration solvent (5.7) and 8,00 ml of the perchloric acid solution (5.8). Titrate with sodium acetate solution (5.9) using the electrode system and procedure given in 8.1 to 8.4 and 9.4. Detect the endpoint by the same procedure used for the base number determination (see 10.2).

5.9.2.2 Procedure B

Use 60 ml of titration solvent (5.7) and 4,00 ml of perchloric acid (5.8). Titrate as described in 5.9.2.1.

5.9.3 Calculation of concentration

Calculate the concentration, C_1, in moles per litre, of sodium acetate from the formulae:

$$C_1 = \frac{(8{,}00 - V_0)\,C_0}{V_2} \quad \text{for Procedure A} \qquad \ldots (2)$$

$$C_1 = \frac{(4{,}00 - V_0)\,C_0}{V_2} \quad \text{for Procedure B} \qquad \ldots (3)$$

where

C_0 and V_0 are as defined for equation (1);

V_2 is the numerical value of the volume, in millilitres, of sodium acetate (5.9) used in the standardization.

Restandardize the sodium acetate solution at least once a week, or more often if there is any reason to suspect that the concentration has changed.

5.10 **Cleaning solution**, strongly oxidizing acid, e.g. chromiumsulfuric acid.

WARNING — When using chromiumsulfuric acid cleaning solution, eye protection and protective clothing are essential. Never pipette the cleaning solution by mouth. After use, do not pour cleaning solutions down the drain, but neutralize them with great care owing to the concentrated sulfuric acid present, and dispose of them in accordance with standard procedures for toxic laboratory waste (chromium is highly dangerous to the environment).

6 Apparatus

Ordinary laboratory apparatus, and in particular the following are required.

6.1 **Potentiometric titrimeter**, either automatic recording or manual.

6.2 **Glass electrode**, pH 0 to pH 11, general-purpose type.

6.3 **Reference electrode**, sleeve-type saturated calomel electrode with non-aqueous salt bridge as described in clause 8.

NOTE 3 Some reference electrodes with fritted or fibre diaphragms and some combined glass plus reference electrode systems are commercially available, such as the single-rod glass plus silver/silver chloride electrode assembly. During the development of this method, the use of electrodes of these types gave problems in some laboratories, but not in others. Accordingly, these electrodes are permitted in this method, provided that the sodium perchlorate bridge is used; however, if stability or other problems arise with their use, the sleeve-type electrode should be used.

6.4 Stirrer, either mechanical or electrical, with variable speeds and with 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 will not produce a permanent change in meter reading during the course of a titration. A magnetic stirrer with stirring bar may be used provided that it meets the above conditions.

6.5 Burette, manual or automatic, conforming to the requirements of ISO 385-1, 10 ml or 20 ml capacity, graduated in 0,05 ml divisions, calibrated with an accuracy of ± 0,02 ml.

6.6 Titration beaker, tall-form, made of borosilicate glass or plastic that is inert to the reagents listed in clause 5.

For Procedure A, use a beaker of 250 ml capacity, and for Procedure B, use a beaker of approximately 150 ml capacity such that 60 ml of titration solvent will cover the electrodes.

6.7 Titration stand, suitable to support the beaker, electrodes, stirrer and burette.

NOTES

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

5 Some apparatus may be sensitive to interference by static electricity, shown by erratic movements of recorder pen or meter indicator, when the titration assembly (beaker and electrodes) is approached by the operator. In this case, surround the beaker closely with a cylinder of copper gauze which is electrically grounded (earthed).

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 6 If necessary, laboratory samples may be warmed to aid mixing. Shake used oils vigorously to ensure homogeneity before preparing the test sample.

8 Preparation of electrode system

8.1 Preparation of electrodes

If the calomel electrode (6.3) is to be changed from aqueous bridge to non-aqueous, drain out the aqueous solution, wash out crystals of potassium chloride with water, then rinse the outer jacket (salt bridge) several times with the sodium perchlorate electrolyte (5.6). Finally, fill the outer jacket with the sodium perchlorate electrolyte up to the filling hole. When using the sleeve-type electrode, carefully remove the ground-glass sleeve and thoroughly wipe both ground-glass surfaces. Replace the sleeve loosely and allow a few drops of electrolyte to drain through to flush the ground-glass joint and to wet the ground surfaces thoroughly with electrolyte. Set the sleeve firmly in place, refill the outer jacket with the sodium perchlorate electrolyte and rinse the electrode with chlorobenzene (5.3). When in use, keep the electrolyte level in the calomel electrode above that of the liquid in the titration beaker (6.6) to prevent entry of contaminants in the salt bridge. When not in use, fill the calomel electrode with sodium perchlorate electrolyte, leave the stopper in the filling orifice, and immerse both electrodes in water, keeping the level of the electrolyte above that of the water.

8.2 Testing of electrodes

Test the titrimeter electrode combination when first put into use or when new electrodes are installed, and retest at intervals thereafter as follows.

8.2.1 Procedure A

Dip the electrodes into a well-stirred mixture of 100 ml of acetic acid (5.1) plus 0,2 g of potassium hydrogen phthalate (5.4) and record the titrimeter reading. Rinse the electrode with chlorobenzene (5.3) and immerse in 100 ml of acetic acid plus 1,5 ml of perchloric acid (5.8). The difference between readings shall be at least 0,30 V for satisfactory electrode performance.

8.2.2 Procedure B

Dip the electrodes into a well-stirred mixture of 50 ml of acetic acid (5.1) plus 0,1 g of potassium hydrogen phthalate (5.4) and record the titrimeter reading. Rinse the electrode with chlorobenzene (5.3) and immerse in 50 ml of acetic acid plus 0,75 ml of perchloric acid (5.8). The difference between readings shall be at least 0,30 V for satisfactory electrode performance.

8.3 Cleaning of electrodes

Before starting a series of sample titrations, follow the rinsing procedure below:

First wash the electrodes with the titration solvent (5.7) to remove any adhering oily material from the previous titration, then with water to dissolve any sodium perchlorate that may have formed around the sleeve of the calomel electrode and to restore the aqueous gel layer of the glass electrode. Rinse again with the titration solvent. Repeat before the blank titration if necessary.

8.4 Maintenance

If there is reason to believe that the glass electrode (6.2) has become contaminated, clean it by immersing in room-temperature cleaning solution (5.10) for 5 min, followed by thorough washing in water.

After a cleaning treatment, test the electrode as described in 8.2.

The calomel electrode can be cleaned by draining and refilling with fresh sodium perchlorate solution (5.6).

Maintain the electrolyte level in the calomel electrode above that of the liquid in the titration beaker at all times. Do not allow the electrodes to remain immersed in titration solvent (5.7) for longer than is necessary between titrations.

Although the electrodes are not extremely fragile, handle them carefully at all times and particularly avoid scratching the glass electrode.

9 Forward titration

9.1 Test sample amount

9.1.1 Calculate the approximate mass, m, in grams, of test sample required from its expected base number (BN) using either equation (4) or equation (5).

$$m_A = \frac{28}{\text{expected BN}} \quad \text{for Procedure A} \qquad \dots (4)$$

or

$$m_B = \frac{10}{\text{expected BN}} \quad \text{for Procedure B} \qquad \dots (5)$$

A maximum of 20 g shall be taken for Procedure A, and 10 g for Procedure B.

For possible exceptions involving back-titration, see 11.2.

9.1.2 If the expected BN is unknown, it can be readily estimated by a simple procedure: either weigh 0,2 g to 0,3 g of the test sample for Procedure A, or 0,1 g to 0,2 g of the test sample for Procedure B, and titrate to a 570 mV endpoint. Calculate this value as an inflection point and divide the result into 28 for Procedure A, or 10 for Procedure B, to obtain the correct mass of the test sample.

It is especially important for Procedure B that great care be exercised in obtaining accurate test masses, particularly for high base-number petroleum products which require small test sample masses.

9.1.3 Weigh the test sample into the titration beaker, applying the precision limits shown in table 1.

Table 1 — Test sample masses and weighing precision

Test sample mass, m g	Precision of weighing g
$10 < m \leqslant 20$	0,05
$5 < m \leqslant 10$	0,02
$1 < m \leqslant 5$	0,005
$0,25 < m \leqslant 1$	0,001
$0,1 < m \leqslant 0,25$	0,000 5

9.2 Preparation of test sample solution

To the test sample add 120 ml (Procedure A) or 60 ml (Procedure B) of the titration solvent (5.7), place the beaker (6.6) on the titration stand (6.7) and stir the solution (see 6.4) until the test sample has dissolved. If dissolution of the test sample proves difficult, dissolve using 80 ml (Procedure A) or 40 ml (Procedure B) of chlorobenzene (5.3) in the titration beaker, then add 40 ml (Procedure A) or 20 ml (Procedure B) of acetic acid (5.1).

NOTE 7 Many used oils contain some solid materials which will not dissolve. The presence of this undissolved material is a normal condition.

9.3 Preparation of apparatus

Prepare the electrodes as directed in 8.1 to 8.3. Position the electrodes in the test solution so that they are immersed as far as possible. Continue the stirring throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution. Adjust the titrimeter so that it reads in the upper part of the millivolt scale: e.g. 700 mV.

NOTE 8 For simple titrimeters without this adjustment, it may be necessary to incorporate a source of potential in series with the electrode. A 1,5 V dry cell and potential divider is suitable.

Fill the burette (6.5) with perchloric acid (5.8) and place the burette in position in the titration assembly (6.6 and 6.7), taking care that the tip is immersed below the level of the surface of the liquid in the beaker (6.6). Record the initial burette and titrimeter (cell potential) readings.

9.4 Titration

9.4.1 Manual titration

Titrate the test sample solution (9.2) with perchloric acid (5.8), added in suitable small portions. After each addition, wait until a constant cell potential has been established, i.e. when the rate of change of cell potential is less than 0,005 V/min, and record the burette and titrimeter readings. At the start of titration and in any subsequent regions (inflections) where 0,1 ml of titrant consistently produces a total change of more than 0,03 V (corresponding to 0,5 pH scale unit) in the cell potential, add the perchloric acid in 0,05 ml portions.

In the intermediate regions (plateaus) where 0,1 ml increments change the potential by less than 0,03 V, add the perchloric acid solution in portions sufficient to produce a potential change approximately equal to, but not greater than, 0,03 V. Stop the titration when the addition of 0,1 ml of perchloric acid produces a change in potential of less than 0,005 V.

9.4.2 Automatic recording titration

Adjust the instrument in accordance with the manufacturer's instructions and set the maximum titration speed at 1,0 ml/min.

9.5 Cleaning of apparatus

On completion of the titration, remove the beaker and rinse the electrodes and burette tip with the titration solvent (5.7), and then with water, then again with titration solvent (see 8.3). Store the electrodes in water when not in use (see 8.1).

9.6 Blank test

9.6.1 Manual titration

For each series of test samples, carry out a blank titration on 120 ml (Procedure A) or 60 ml (Procedure B) of the titration solvent (5.7). Add the perchloric acid (5.8) in 0,05 ml increments, waiting after each addition until a constant cell potential is established (see 9.4.1). Record titrimeter and burette readings after each increment.

9.6.2 Automatic titration

For each series of test samples, carry out a blank titration on 120 ml (Procedure A) or 60 ml (Procedure B) of the titration solvent (5.7). Follow the procedure given in 9.4.2.

10 Calculation of base number

10.1 For manual titration, prepare a graph by plotting the volumes of the acid added against the corresponding titrimeter readings.

10.2 Read the endpoint from the graph (10.1) obtained from the manual titration or from the automatic titration recording. The endpoint is taken as the midpoint of the inflection, i.e. the point at which the curve changes from concave to convex.

NOTE 9 A useful but not mandatory guide is that the endpoint should be preceded and followed by a deflection of at least 50 mV per 0,1 ml of titrant.

10.3 Calculate the base number, BN, in milligrams KOH per gram test sample, using equation (6):

$$\mathrm{BN} = \frac{56{,}1\ [C_0\,(V_4 - V_3)]}{m} \qquad \ldots (6)$$

where

V_3 is the volume, in millilitres, of perchloric acid (5.8) used to titrate the blank test solution (9.6) to the inflection point on the titration curve;

V_4 is the volume, in millilitres, of perchloric acid (5.8) used to titrate the test sample to the inflection point on the titration curve;

C_0 is the concentration of the perchloric acid (5.8) [as defined for equation (1)];

m is the mass, in grams, of the test sample.

10.4 If there is no inflection point, or a very poor one, proceed to clause 11. The inflection obtained during back-titration shall meet the criteria described in 10.2.

11 Back-titration

11.1 When there is no inflection point, or only a very poor one, from the procedure described in clause 9, follow the modified method described in 11.2 to 11.7, in which excess perchloric acid (5.8) is added to the test sample, and the excess is back-titrated with sodium acetate (5.9). This modified method applies to both Procedure A and Procedure B of the forward titration method.

11.2 Either weigh accurately the amount of test sample specified in 9.1 into the titration beaker (6.6) and proceed in accordance with 11.3, or use the test sample being titrated as in 9.1 to 9.4.2 provided that the test sample mass does not exceed that in note 18. If it is apparent from the forward titration that a satisfactory inflection will not be obtained, note the volume of perchloric acid (5.8) used, then proceed with 11.6. Modify the standardization (5.9.2) to take account of the volume of perchloric acid used.

The test sample mass for the back-titration modification should not exceed 5 g for Procedure A or 2,5 g for Procedure B. If, with this test sample, no inflection point is found, reduce the test sample mass by a half and repeat the analysis. Reducing the test sample mass generally improves the clarity of the inflection point.

NOTE 10 The cooperative work which led to the precision statement (see 13.1) employed a test sample mass of 5 g max.

11.3 Dissolve the test sample in 80 ml (Procedure A) or 40 ml (Procedure B) of chlorobenzene (5.3) (see note 12), and add 40 ml (Procedure A) or 20 ml (Procedure B) of acetic acid (5.1).

11.4 Add 8,00 ml (Procedure A) or 4,00 ml (Procedure B) of perchloric acid (5.8) to the beaker using the burette (6.5) (an excess of perchloric acid is required). If necessary, add more, and correct accordingly (see 11.2).

11.5 Stir the contents of the beaker for 2 min.

11.6 Titrate the unneutralized perchloric acid (5.8) in accordance with 9.4, using sodium acetate (5.9) instead of perchloric acid as titrant.

NOTE 11 For the back-titration, the starting point will be in the range 0 mV to 100 mV.

11.7 Calculate the base number, BN, in milligrams KOH per gram test sample, using equation (7):

$$\mathrm{BN} = \frac{56{,}1\,[C_1\,(V_2 - V_5)]}{m} \qquad \ldots (7)$$

where

C_1 and V_2	are as defined for equation (2) or equation (3);
V_5	is the volume, in millilitres, of sodium acetate (5.9) used in the back-titration;
m	is the mass, in grams, of the test sample.

12 Expression of results

Report the base number calculated in 10.3 or 11.7 to the nearest 0,1 BN for values below 100, and to the nearest whole integer BN for values of 100 and above. Indicate (Procedure A) or (Procedure B) following the result, and annotate the result if the back-titration modification has been used.

13 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as follows:

13.1 Repeatability, r

The difference between successive 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 values below only in one case in 20.

For BN (Procedure A), forward titration: $r = 0{,}03x$

For BN (Procedure A), back-titration: $r = 0{,}24x$

For BN (Procedure B), forward titration: $r = 0{,}05x$

where x is the mean of the base numbers being considered.

13.2 Reproducibility, R

The difference between two single and independent results, obtained by different operators working in different laboratories on nominally identical test ma-