# INTERNATIONAL STANDARD 3771

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# Petroleum products — Total base number — Perchloric acid potentiometric titration method

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

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It has been approved by the Member Bodies of the following countries :

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# Petroleum products — Total base number — Perchloric acid potentiometric titration method

## 1 SCOPE AND FIELD OF APPLICATION

**1.1** 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.[1)]

**1.2** 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 polyacidic bases, and salts of heavy metals.

## 2 DEFINITION

For the purpose of this International Standard the following definition applies.

**total base number :** The quantity of perchloric acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide (or alternatively in millequivalents of hydroxide per gram), that is required to neutralize all basic constituents present in 1 g of sample when titrated under the prescribed conditions.

## 3 PRINCIPLE

**3.1** The test portion 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 with a potentiometric titrimeter. A glass indicating electrode and a calomel reference electrode are used, the latter being connected with the test portion solution by means of a salt bridge. The meter readings are plotted against the corresponding volumes of titrating solution, and the end-point is taken at the last inflection in the resulting curve.

**3.2** Occasionally certain used oils give no inflection when titrated according to 3.1, in which case a back-titration modification with a standard volumetric acetous sodium acetate solution titrant is employed. (See clause 10.)

## 4 REAGENTS

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

**4.1 Acetic acid**, glacial (CAUTION, see below)

CAUTION — Acetic acid, acetic anhydride, and chlorobenzene are toxic and irritant. Carry out all operations involving the use of these materials in a well-ventilated area, preferably under a hood (fume cupboard).

**4.2 Acetic anhydride.** (CAUTION, see 4.1.)

**4.3 Chlorobenzene.** (CAUTION, see 4.1.)

**4.4 Potassium hydrogen phthalate** ($KHC_8H_4O_4$).

**4.5 Sodium carbonate**, anhydrous ($Na_2CO_3$).

**4.6 Sodium perchlorate** electrolyte.

Prepare a saturated solution of sodium perchlorate ($NaClO_4$) (CAUTION, see below) in the glacial acetic acid (4.1). An excess of undissolved sodium perchlorate should always be present at the bottom of the solution.

CAUTION — Sodium perchlorate is toxic and an irritant. It is also a powerful oxidizing agent when heated. Great care should be taken to avoid contact with organic matter under conditions that may result in subsequent drying or heating, and spillage should be washed immediately and thoroughly with water.

**4.7 Titration solvent.**

Add 1 volume of the glacial acetic acid (4.1) to 2 volumes of the chlorobenzene (4.3) (CAUTION, see 4.1).



1) For many materials, this method gives similar results to those obtained for total base number by using ASTM D 664, *Neutralization number by potentiometric titration*, but with products containing certain compounds such as strongly overbased oil additives and nitrogenous polymeric compounds, higher results than those obtained using method ASTM D 664 may be obtained.

**4.8 Perchloric acid,** 0,1 N standard volumetric acetous solution.

4.8.1 *Preparation*

Mix 8,5 ml of 70 to 72 % (*m/m*) perchloric acid ($HClO_4$ 70 to 72 % (*m/m*)) (or 10,2 ml of 60 to 62 % (*m/m*) perchloric acid, or 11,8 ml of 57 % (*m/m*) perchloric acid) with 500 ml of the glacial acetic acid (4.1) and 30 ml (or 35 ml if the 60 to 62 % (*m/m*) perchloric acid is used, or 40 ml if the 57 % (*m/m*) perchloric acid is used) of the acetic anhydride (4.2) (see note). Dilute to 1 *l* with the glacial acetic acid (CAUTION, see below). Allow the solution to stand for 24 h before standardization.

CAUTION — This perchloric acid solution is not hazardous under the conditions of this test. However, concentrated perchloric acid is a powerful oxidizing agent when heated and forms explosive mixtures when heated with organic matter. Great care should be taken to avoid contact with organic matter under conditions that may result in subsequent drying or heating, and spillage should be washed immediately and thoroughly with water.

NOTE — Excess acetic anhydride must be avoided to prevent acetylation of any primary or secondary amines which may be present in the sample under test.

4.8.2 *Standardization*

Dry a quantity of the potassium hydrogen phthalate (4.4) in an oven at 120 °C for 2 h and allow it to cool. Take 0,1 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 the warm glacial acetic acid. Add 80 ml of the chlorobenzene (4.3), cool, and titrate with the perchloric acid solution (4.8.1), using the electrode system and procedures given in 7.1 to 7.4 and 8.3 to 8.5. Detect the end-point by the same procedure as will be used for base number determination (see 9.2). Carry out a blank titration on 40 ml of the glacial acetic acid plus 80 ml of the chlorobenzene (see 8.6).

4.8.3 *Calculation*

Calculate the normality $T_0$ of the perchloric acid solution from the formula

$$T_0 = \frac{1\,000\,m}{204{,}23 \times (V_1 - V_0)} \qquad \ldots (1)$$

where

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

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

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

NOTES

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

2 The perchloric acid solution should be re-standardized at least once a week and more often if there is any reason to suspect that the normality has changed.

**4.9 Sodium acetate,** 0,1 N standard volumetric acetous solution (for back-titration, see clause 10).

4.9.1 *Preparation*

Dissolve 5,3 g of the anhydrous sodium carbonate (4.5) in 300 ml of acetic acid. Dilute to 1 *l* with acetic acid after dissolution is complete.

4.9.2 *Standardization*

Use the 120 ml of the titration solvent (4.7) and 8,00 ml of the standard volumetric acetous perchloric acid solution (4.8). Titrate with the sodium acetate solution (4.9.1) using the electrode system and procedure given in 7.1 to 7.4 and 8.3 to 8.5. Detect the end-point by the same procedure as will be used for base number determination (see 9.2).

4.9.3 *Calculation*

Calculate the normality $T_1$ of the sodium acetate solution from the formula

$$T_1 = \frac{(8{,}00 - V_0)\,T_0}{V_2}$$

where

$T_0$ and $V_0$ are as defined for equation (1);

$V_2$ is the volume, in millilitres, of acetous sodium acetate solution used in the standardization.

NOTE — The sodium acetate solution should be re-standardized at least once a week and more often if there is any reason to suspect that the normality has changed.

## 5 APPARATUS

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

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

**5.3 Reference electrode,** sleeve-type saturated calomel electrode with non-aqueous salt bridge as described in clause 7.

NOTE — 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.

**5.4 Stirrer,** either mechanical or electrical, with variable speeds and with propeller or paddle of chemically inert material. If an electrical stirrer is used, it must 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.

**5.5 Burette,** of capacity 10 to 20 ml, graduated in 0,05 ml divisions and calibrated with an accuracy of ± 0,02 ml, or an **automatic burette,** of similar accuracy.

**5.6 Titration beaker,** of capacity 250 ml, made of borosilicate glass. A tall-form beaker is particularly suitable.

**5.7 Titration stand,** suitable to support the beaker, electrodes, stirrer, and burette. An arrangement that allows for the removal of the beaker without disturbing the electrodes, burette, and stirrer is desirable.

NOTE — 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).

## 6 PREPARATION OF TEST PORTION

It is essential to ensure that the test portion is representative, as any sediment may be acidic or basic or have adsorbed acidic or basic material from the liquid phase. If necessary, laboratory samples may be warmed to aid mixing. Used oils should be vigourously shaken to ensure homogeneity before preparing the test portion.

## 7 PREPARATION OF ELECTRODE SYSTEM

### 7.1 Preparation of electrodes

If the calomel electrode (5.3) is to be changed from aqueous bridge to non-aqueous, drain out the aqueous solution, wash out all crystals of potassium chloride with water, then rinse the outer jacket (salt bridge) several times with the sodium perchlorate electrolyte (4.6). 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 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 the chlorobenzene (4.3). When in use, the electrolyte level in the calomel electrode should be kept above that of the liquid in the titration beaker (5.6) to prevent entry of contaminants in the salt bridge. When not in use, fill the calomel electrode with the sodium perchlorate electrolyte, leave the bung in the filling orifice, and immerse both electrodes in water, keeping the level of the electrolyte above that of the water.

### 7.2 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 : Dip the electrodes into a well-stirred mixture of 100 ml of the glacial acetic acid (4.1) plus 0,2 g of the potassium hydrogen phthalate (4.4) and record the titrimeter reading. Rinse the electrode with the chlorobenzene (4.3) and immerse in 100 ml of the glacial acetic acid plus 1,5 ml of the standard volumetric acetous perchloric acid solution (4.8). The difference between readings should be at least 0,30 V.

NOTE — The electrodes should be tested at least once a week and more often if there is any reason to suspect that they have changed.

### 7.3 Cleaning of electrodes

Following a titration, first wash the electrodes with the titration solvent (4.7) 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. Before starting a series of sample titrations, follow this rinsing procedure, then run one or two blank titrations on the solvent to condition the electrodes. Repeat the blank titration if necessary.

### 7.4 Maintenance of electrodes

If there is reason to believe that the glass electrode (5.2) has become contaminated, it may be cleaned by immersing in cold chromic acid cleaning solution for 5 min, followed by thorough washing in water. After this cleaning treatment, test the electrode as described in 7.2. The calomel electrode can be cleaned by draining and refilling with fresh sodium perchlorate solution (4.6). 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 (4.7) 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.

## 8 PROCEDURE

### 8.1 Test portion

Calculate the quantity of test portion required from its expected total base number (TBN) from the equation

$$\text{Approximate mass, in grams, of test portion} = \frac{28}{\text{expected TBN}} \qquad \ldots (3)$$

NOTES

1 For a possible exception, see note to 10.2.

2 If the expected TBN is unknown, it can be readily approximated by a simple procedure. Weigh 0,2 to 0,3 g of the test portion and titrate to a 570 mV end-point. Calculate this value as an inflection point and divide the result into 28 to obtain the correct mass of the test portion.

Weigh the test portion into the titration beaker, applying the limits shown as follows :

| Mass of test portion | Precision of weighing |
|---|---|
| g | g |
| more than 10 to 20 | 0,05 |
| more than 5 to 10 | 0,02 |
| more than 1 to 5 | 0,005 |
| more than 0,25 to 1,0 | 0,001 |
| 0,1 to 0,25 | 0,000 5 |

A maximum of 20 g should be taken for analysis.

### 8.2 Preparation of test solution

Add 120 ml of the titration solvent (4.7), place the beaker (5.6) on the titration stand (5.7) and stir the solution (see 5.4) until the test portion has dissolved.

NOTE — If dissolution of the test portion proves difficult, dissolve in 80 ml of the chlorobenzene (4.3) in the titration beaker, then add 40 ml of the glacial acetic acid (4.1). Many used oils contain some solid material which will not dissolve. The presence of this undissolved material is a normal condition.

### 8.3 Preparation of apparatus

Prepare the electrodes as directed in 7.1, 7.2 and 7.3. Position the electrodes in the 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; for example, 700 mV. 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 (5.5) with the standard volumetric acetous perchloric acid solution (4.8) and place the burette in position in the titration assembly (5.6 and 5.7), taking care that the tip is immersed below the level of the surface of the liquid in the beaker (5.6). Record the initial burette and titrimeter (cell potential) readings.

### 8.4 Titrations

#### 8.4.1 *Manual titration*

Titrate with the standard volumetric acetous perchloric acid solution (4.8), added in suitable small portions. After each addition, wait until a constant cell potential has been established, that is 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 the 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 standard volumetric acetous perchloric acid solution in 0,05 ml portions.

In the intermediate regions (plateaux) where 0,1 ml increments change the potential by less than 0,03 V, add the standard volumetric acetous perchloric acid solution in portions sufficient to produce a total potential change approximately equal to, but not greater than, 0,03 V.

Stop the titration when the addition of 0,1 ml of the standard volumetric acetous perchloric acid solution produces a change of potential less than 0,005 V.

#### 8.4.2 *Automatic recording titration*

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

### 8.5 Cleaning of apparatus

On completion of the titration, remove the beaker and rinse the electrodes and burette tip with the titration solvent (4.7), then with water, then again with solvent (see 7.3). Store the electrodes in water when not in use (see 7.1).

### 8.6 Blank test

#### 8.6.1 *Manual titration*

For each set of samples, make a blank titration on 120 ml of the titration solvent. Add the standard volumetric acetous perchloric acid solution (4.8) in 0,05 ml increments, waiting after each addition until a constant cell potential is established (see 8.4.1). Record titrimeter and burette readings after each increment.

#### 8.6.2 *Automatic titration*

For each series of samples, make a blank titration on 120 ml of the titration solvent (4.7). Follow the procedure in 8.4.2.

## 9 EXPRESSION OF RESULTS

**9.1** For a manual titration, plot the volumes of the acid added against the corresponding titrimeter readings.

**9.2** Read the end-point from the graph obtained from the manual or automatic titration. The end-point is the mid-point of the inflection, i.e. that point at which the curve changes from concave to convex. A useful but not mandatory guide is that the end-point should be preceded and followed by a deflection of at least 50 mV/ml of titrant.

**9.3** If there is no inflection point or only a very poor one, proceed to clause 10. The inflection obtained during back-titration should preferably meet the criteria described in 9.2.

**9.4** Calculate the total base number (TBN) from the formula

$$\frac{(V_4 - V_3)\, T_0 \times 56{,}1}{m} \qquad \ldots (4)$$

where

$V_3$ is the volume, in millilitres, of the standard