BRITISH STANDARD

**BS 2000-139:
1998
ISO 6618:1996**

Methods of test for petroleum and its products —

Part 139: Petroleum products and lubricants — Neutralization number — Colour-indicator titration method

(Identical with IP 139/1998)

ICS 75.080; 75.100

National foreword

This British Standard reproduces ISO 6618:1996 and implements it as the UK national standard. It supersedes BS 2000-139:1993 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

The Institute of Petroleum publishes and sells all parts of BS 2000, and all BS EN petroleum test methods that would be part of BS 2000, both in its annual publication "Standard methods for analysis and testing of petroleum and related products and British Standard 2000 parts" and individually.

Further information is available from:

The Institute of Petroleum, 61 New Cavendish Street, London W1M 8AR. Tel: 020 7467 7100. Fax: 020 7255 1472.

Cross-references

The British Standards which implement international publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled "International Standards Correspondence Index", or by using the "Find" facility of the BSI Standards Electronic Catalogue.

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Summary of pages

This document comprises a front cover, an inside front cover, pages 139.1 to 139.8, an inside back cover and a back cover.

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Petroleum products and lubricants - Determination of acid or base number - Colour-indicator 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 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 colour-indicator titration method for the determination of acid or basic constituents in petroleum products and lubricants soluble in mixtures of toluene and propan-2-ol. It is applicable for the determination of acids or bases whose dissociation constants in water are greater than 10^{-9}; extremely weak acids or bases whose dissociation constants are less than 10^{-9} do not interfere. Salts react if their hydrolysis constants are greater than 10^{-9}.

NOTE 1 In new and used oils, the constituents considered to have acidic characteristics include inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, and additives such as inhibitors and detergents. Similarly, constituents considered to have basic properties include organic and inorganic bases, amino compounds, salts of weak acids (soaps), basic salts of polyacidic bases, salts of heavy metals, and additives such as inhibitors and detergents.

The method is not suitable for measuring the basic constituents of many basic additive-type lubricating oils, for which ISO 3771 can be used.

This International Standard indicates relative changes that occur in an oil during use under oxidizing conditions. Although the titration is made under definite equilibrium conditions, the method does not measure an absolute acidic or basic property that can be used to predict performance of an oil under service conditions.

NOTES

2 No general relationship between bearing corrosion and acid or base number is known.

3 Oils, such as many cutting oils, rustproofing oils, and similar compounded oils, or excessively dark-coloured oils, that cannot be analyzed by this method owing to obscurity of the colour-indicator end-point, can be analyzed in accordance with ISO 6619. The acid or base numbers obtained by this colour-indicator method may or may not be numerically the same as those obtained by ISO 6619, but they are generally of the same order of magnitude.

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

ISO 3771 : 1994, *Petroleum products - Determination of base number - Perchloric acid potentiometric titration method.*

ISO 6619 : 1988, *Petroleum products and lubricants - Neutralization number - Poteniometric titration method.*

NOTES

1 ISO 3771 employs the use of chlorobenzene as a solvent. Alternatives to this solvent are being sought.

2 ISO 6619 is under review, and the scope will be restricted to acid number.

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 acid number: Quantity of base, expressed in milligrams of potassium hydroxide (KOH) per gram of sample, that is required to titrate the acid constituents present in 1 g of sample when titrated under prescribed conditions.

3.2 strong acid number: Quantity of base, expressed in milligrams of potassium hydroxide (KOH) per gram of sample, that is required to titrate the strong acid constituents present in 1 g of sample when titrated under prescribed conditions.

3.3 base number: Quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide (KOH) per gram of sample, that is required to titrate the base constituents present in 1 g of sample when titrated under prescribed conditions.

4 Principle

To determine the acid number or base number, the test portion is dissolved in a mixture of toluene and propan-2-ol containing a small amount of water, and the resulting single-phase solution is titrated at room temperature with standard alcoholic base or alcoholic acid solution, respectively, to the end-point indicated by the colour change of added *p*-naphtholbenzein solution (orange in acid and green-brown in base).

To determine the strong acid number, a separate portion of the sample is extracted with boiling water and the aqueous extract is titrated with potassium hydroxide solution using methyl orange as indicator.

5 Reagents and materials

During the analysis, use only reagents of recognized analytical grade, and only water in accordance with Grade 3 of ISO 3696.

5.1 Propan-2-ol, anhydrous, maximum water content 0,9 % (*V/V*) (volume fraction 0,9 %).

5.2 Toluene.

5.3 Titration solvent.

Add 500 ml of toluene (5.2) and 5 ml of water to 495 ml of propan-2-ol (5.1).

5.4 Hydrochloric acid, $c(\text{HCl}) = 0,1$ mol/l standard volumetric alcoholic solution.

Prepare in accordance with 5.4.1 or use commercially available solution. Standardize in accordance with 5.4.2.

5.4.1 Preparation

Mix 9 ml of concentrated HCl [35,4 % (*m/m*) (mass fraction 35,4 %)] with 1 l of propan-2-ol (5.1).

5.4.2 Standardization

Standardize frequently enough to detect changes of 0,000 5 mol/l, preferably by electrometric titration of approximately 8 ml (accurately measured) of the 0,1 mol/l alcoholic KOH solution (5.5) diluted with 125 ml of carbon dioxide-free water.

5.5 Potassium hydroxide, $c(\text{KOH}) = 0,1$ mol/l standard volumetric alcoholic solution.

Prepare in accordance with 5.5.1 or use commercially available solution. Standardize in accordance with 5.5.2.

5.5.1 Preparation

Add 6 g of solid KOH to approximately 1 l of propan-2-ol (5.1) in a 2-litre conical flask. Boil the mixture gently for 10 min to 15 min, stirring to prevent solids from forming a cake on the bottom.

Add at least 2 g of barium hydroxide [Ba(OH)_2] and again boil gently for 5 min to 10 min.

Allow to cool to room temperature, and then to stand for several hours. Filter the supernatant liquid through a fine sintered-glass or porcelain filtering funnel; avoid unnecessary exposure to carbon dioxide during filtration.

Store the solution in a chemically resistant dispensing bottle out of contact with cork, rubber or saponifiable stopcock lubricant and protected by a guard tube containing soda lime or nonfibrous soda silicate absorbent[1]. Glass bottles are not recommended for storage.

5.5.2 Standardization

Standardize frequently enough to detect changes of 0,000 5 mol/l, preferably against 0,1 g to 0,15 g of pure potassium acid phthalate (5.9) weighed with an accuracy of 0,000 2 g and dissolved in approximately 100 ml of carbon dioxide-free water, using phenolphthalein (5.8) to detect the end-point.

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[1] Ascarite, Carbosorb and Indecarb are examples of suitable products available commercially. This information is given for the convenience of users of this International standard and does not constitute an endorsement by ISO of these products.

NOTES

1 To simplify calculations, both the standard potassium hydroxide and hydrochloric acid solutions may be adjusted so that 1 ml is equivalent to 5 mg of KOH.

2 Because of the relatively large coefficient of cubic expansion of organic liquids such as propan-2-ol, the standard alcoholic solutions should be standardized at temperatures close to those employed in the titrations of sample, and close to 20 °C.

5.6 Methyl orange, indicator solution.

Dissolve 0,1 g of methyl orange in 100 ml of water.

5.7 *p*-naphtholbenzein indicator solution, meeting the specifications given in annexes A and B. Dissolve 1,0 g of *p*-naphtholbenzein in 100 ml of titration solvent (5.3).

NOTE - In a study in 1992, only one commercially available source of this indicator met the specification given in annex A[2]. Careful adherence to this requirement is therefore recommended.

5.8 Phenolphthalein, indicator solution.

Dissolve 0,5g of phenolphthalein in 100 ml propan-2-ol (5.1).

5.9 Potassium acid phthalate.

6 Apparatus

Ordinary laboratory apparatus and:

6.1 Burette, capacity 50 ml, graduated in 0,1 ml subdivisions, or capacity 10 ml, graduated in 0,05 ml subdivisions.

7 Preparation of used oil sample

7.1 Strictly observe the sampling procedure in 7.2 and 7.3. Failure to obtain a representative test portion causes serious errors.

NOTE - Sediment may be acidic or basic, or may have absorbed acidic or basic material from the sample.

As used oil may change appreciably in storage, samples should be tested as soon as possible after removal from the lubricating system; the dates of sampling and testing should be noted.

7.2 Heat the laboratory sample of used oil to 60 °C ± 5 °C in the original container and agitate until all of the sediment is homogeneously suspended in the oil. If the original container is a can, or if it is glass and more than three-quarters full, transfer the entire sample to a clear glass bottle having a capacity at least one-third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by violent agitation of portions of the sample in the original container.

NOTE - When laboratory samples are visibly free from sediment the heating procedure described may be omitted.

7.3 After complete suspension of all sediment, filter the test sample, or a convenient aliquot, through a 150 µm wire mesh filter to remove large contaminating particles.

8 Determination of acid number

8.1 Into a 250-ml conical flask, introduce the appropriate mass of test portion given in table 1. Add 100 ml of the titration solvent (5.3) and 0,5 ml of the indicator solution (5.7) and, without stoppering, swirl until the test portion is completely dissolved by the solvent. If the mixture assumes a yellow-orange colour, proceed as specified in 8.2; if it becomes green or green-black, proceed as specified in clause 9.

Table 1 - Mass of test portion

Type of oil	Acid or base number	Mass of test portion g	Accuracy of weighing g
New or light-coloured	≤ 3	20 ± 2	0,05
	> 3 to 25	2 ± 0,2	0,01
	> 25 to 250	0,2 ± 0,02	0,001
Used or dark-coloured	≤ 25	2 ± 0,2	0,01
	> 25 to 250	0,2 ± 0,02	0,001

NOTE - Light-coloured test portions of low acid number permit the use of 20 g test portions to obtain more precise results. The test portion size for dark-coloured oils is limited to the quantity specified to minimise possible interference by the dark colour.

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[2] Solid *p*-naphtholbenzein meeting the specification given in annex A is available from Distillation Products Industries, Eastman Organic Chemicals Dept., Rochester 3, New York, USA. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

8.2 Titrate immediately at a temperature below 30 °C. Add the potassium hydroxide solution (5.5) in increments and swirl to disperse the potassium hydroxide as necessary. Shake vigorously near the end-point but avoid dissolving carbon dioxide in the solvent. Consider the end-point definite if the colour change persists for 15 s or if it reverses on addition of two drops of the hydrochloric acid solution (5.4).

In the case of acidic oils, the orange colour changes to a green or green-brown as the end-point is approached.

To observe the end-point of dark-coloured oil, shake the flask vigorously to produce momentarily a slight foam when the colour change occurs as the last few drops of titrant are added and observe the titration under a white fluorescent lamp at bench-top level.

8.3 Carry out a blank titration on 100 ml of the titration solvent and 0,5 ml of the indicator solution, adding the potassium hydroxide in 0,05 ml or 0,1 ml increments. Record the quantity of potassium hydroxide solution required to reach the end-point (orange to green).

9 Determination of base number

9.1 If the titration solvent (5.3) containing the dissolved test portion assumes a green or greenish-brown colour after the indicator is added (8.1), carry out the titration as specified in 8.2, but use the hydrochloric acid (5.4) as titrant and titrate until the green-brown colour changes to orange.

9.2 Carry out a blank titration as specified in 8.3.

NOTE - The titration solvent usually contains weak acid impurities which react with the strongly basic components of the test portion. To correct the base number for the test portion, it is thus necessary to determine an acid number blank of the solvent.

10 Determination of strong acid number

10.1 Introduce approximately 25 g of a representative sample, weighed to within 0,05 g, into a 250 ml separating funnel, and add 100 ml of boiling water. Shake vigorously and, after phase separation, collect the aqueous phase in a 500 ml beaker. Make two new extractions from the test sample, each time with 50 ml of boiling water, and add the extracts obtained to the same beaker.

To the combined extracts add 1,0 ml of the methyl orange indicator (5.6) and, if the solution becomes pink or red, titrate with the potassium hydroxide solution (5.5) until the solution becomes golden-brown in colour. If the initial colour is not pink or red, report the strong acid number as zero.

10.2 Into a 250 ml conical flask, introduce 200 ml of the boiling water from the same source. Add 0,1 ml of the methyl orange indicator solution (5.6). If the indicator solution is yellow-orange, titrate with the hydrochloric acid solution (5.4) to the same depth and shade of colour obtained in the titration of the test portion.

If the indicator colour is pink or red, titrate with the potassium hydroxide solution (5.5) to the same end-point as that used in the test portion titration.

11 Calculation

11.1 Acid number

Calculate the acid number, AN, in milligrams of KOH per gram of the test sample, from the equation:

$$AN = \frac{(V_1 - V_0)\, c_{KOH} \times 56{,}1}{m} \qquad \ldots(1)$$

where

V_1 is the volume, in millilitres, of potassium hydroxide solution required for titration of the test portion;

V_0 is the volume, in millimetres, of potassium hydroxide solution required for titration of the blank solution;

c_{KOH} is the concentration, in moles per litre, of the standard volumetric potassium hydroxide solution;

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

11.2 Strong acid number

Calculate the strong acid number, SAN, in milligrams of KOH per gram of test sample, from either equation (2), if the blank titration is made with acid, or equation (3), if the blank titration is made with base.

$$SAN = \frac{[(V_2\, c_{KOH}) + (V_3\, c_{HCl})] \times 56{,}1}{m} \qquad \ldots(2)$$

$$SAN = \frac{(V_2 - V_4)\, c_{KOH} \times 56{,}1}{m} \qquad \ldots(3)$$

where

V_2 is the volume, in millilitres, of potassium hydroxide solution required to titrate the water extract (10.1);

V_3 is the volume, in millilitres, of hydrochloric acid solution required to titrate the blank solution (10.2);

V_4 is the volume, in millilitres, of potassium hydroxide solution required to titrate the blank solution (10.2);

c_{KOH} is the concentration, in moles per litre, of the standard volumetric potassium hydroxide solution;

c_{HCl} is the concentration, in moles per litre, of the standard volumetric hydrochloric acid solution;

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

11.3 Base number

Calculate the base number, BN, in milligrams of KOH per gram of test sample, from the equation:

$$\mathrm{BN} = \frac{[(V_5\, c_{HCl}) + (V_0\, c_{KOH})] \times 56{,}1}{m} \quad \ldots(4)$$

where

V_5 is the volume, in millilitres, of standard volumetric hydrochloric acid solution required for titration of the test portion (clause 9);

the other symbols are as described in 11.1 and 11.2

12 Expression of results

Report the results, calculated in accordance with clause 11, as acid number, strong acid number or base number as appropriate, to the nearest 0,1.

13 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as shown below.

13.1 Repeatability

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 normal and correct operation of the test method, exceed the values shown in table 2 in only one case in 20.

13.2 Reproducibility

The difference between two single and independent results, obtained by different operators working in different laboratories on nominally identical test material would, in the normal and correct operation of the test method, exceed the values shown in table 2 in only one case in 20.

14 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

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

c) the results of the test (see clause 12);

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

e) the date of the test.

Table 2 - Precision values

Acid or base number	Repeatability	Reproducibility
≤ 0,1	0,03	0,04
> 0,1 to 0,5	0,05	0,08
> 0,5 to 1,0	0,08	15 % of the level
> 1,0 to 2,0	0,12	15 % of the level

NOTES

1 This precision statement applies only to new light-coloured straight mineral oils and new and used inhibited steam turbine oils. Insufficient data are available on other oils falling within the scope of this International Standard, so no precision statement is given for such oils.

2 The precision values do not apply to oils that are so highly coloured as to obscure the end-point colour change.

Annex A
(normative)
Specification for *p*-naphtholbenzein

A.1 Appearance

Red amorphous powder.

A.2 Chloride content

Less than 0,5 % (*m/m*) (mass fraction less than 0,5 %).

A.3 Solubility

10 g shall dissolve completely in 1 l of titration solvent (5.3).

A.4 Minimum absorbance

Dissolve exactly 0,1 g of test portion in 250 ml of methanol. Make up 5 ml of this solution to 100 ml with pH 12 buffer, prepared by mixing 50 ml of 0,05 mol/l dibasic sodium phosphate solution with 26,9 ml of 0,1 mol/l sodium hydroxide solution. This final dilution shall have a minimum absorbance of 1,2 when read at the 650 nm peak using a suitable spectrometer[3], 1 cm cells, and water as the blank.

A.5 pH range

A.5.1 The indicator shall turn to the first clear green at a relative pH of 11 ± 0,5 when tested by the method for the pHr range of *p*-naphtholbenzein indicator as specified in annex B.

A.5.2 The indicator shall require not more than 0,5 ml of 0,01 mol/l potassium hydroxide solution above that for the blank to bring the indicator solution to the first clear green (see B.8).

A.5.3 The indicator shall require not more than 1,0 ml of 0,01 mol/l potassium hydroxide solution above that for the blank to bring the indicator solution to a blue colour.

A.5.4 The initial pHr of the indicator solution shall be at least as high as that of the blank.

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[3] A Beckman DU spectrometer is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

Annex B

(normative)

Determination of pHr range of *p*-naphtholbenzein indicator

B.1 Scope

This annex provides a method for determining the acceptability of *p*-naphtholbenzein indicator for use in this International Standard.

B.2 Definition

For the purpose of this annex, the following definition applies.

B.2.1 pHr: Arbitrary term which expresses the relative hydrogen ion activity in the toluene/propan-2-ol medium in a manner similar to that in which the term pH expresses the actual hydrogen ion activity in aqueous solutions.

For the purposes of this International Standard, the pHr acidity scale is defined by two standard buffer solutions which have been designated pHr 4 and pHr 11. The exact relationship between pHr and the true pH of a toluene/propan-2-ol solution is not known and cannot be readily determined.

B.3 Principle

A prescribed amount of indicator is titrated electrometrically through the various colour changes with alcoholic potassium hydroxide solution, and the results are plotted against meter readings converted to pHr units.

B.4 Reagents and materials

The requirements of clause 5 apply.

B.4.1 Potassium hydroxide, *c*(KOH) = 0,01 mol/l, standard volumetric alcoholic solution.

B.4.2 Acidic buffer solution, pHr = 4,0.

Prepare a stock solution in accordance with the procedure given in ISO 6619. Add 10 ml of buffer stock solution to 100 ml titration solvent (5.3). Use the diluted solution within 1 h.

B.4.3 Alkaline buffer solution, pHr = 11,0.

Prepare a stock solution in accordance with the procedure given in ISO 6619. Add 10 ml of buffer stock solution to 100 ml titration solvent (5.3). Use the diluted solution within 1 h.

B.4.4 Potassium chloride, electrolyte.

Prepare a saturated solution of potassium chloride (KCl) in water.

B.5 Apparatus

Meter, glass electrode, calomel electrode, stirrer, beaker and stand, as specified in ISO 6619.

B.6 Preparation of electrode system

Prepare the electrode system in accordance with ISO 6619.

B.7 Standardization of apparatus

B.7.1 Prior to each test or series of tests, set the meter to read on the pH scale, insert the electrodes into a beaker containing acidic nonaqueous buffer solution (B.4.2) at a temperature of 25 °C ± 2 °C and stir the solution vigorously. When the pH-meter reading becomes constant, adjust the asymmetry potential dial of the instrument so that the meter reads 4,0.

B.7.2 Remove the acid buffer, clean the electrodes, and immerse them in water for several minutes. Dry the electrodes and insert them in a beaker containing alkaline nonaqueous buffer solution (B.4.3) at 25 °C ± 2 °C. When the pH-meter reading has become steady, record the exact value.

B.7.3 If the reading from B.7.2 is within 0,2 pH unit of 11,0, the initial acidity, pHr, of unknown solutions may be read directly from the dial of the meter.

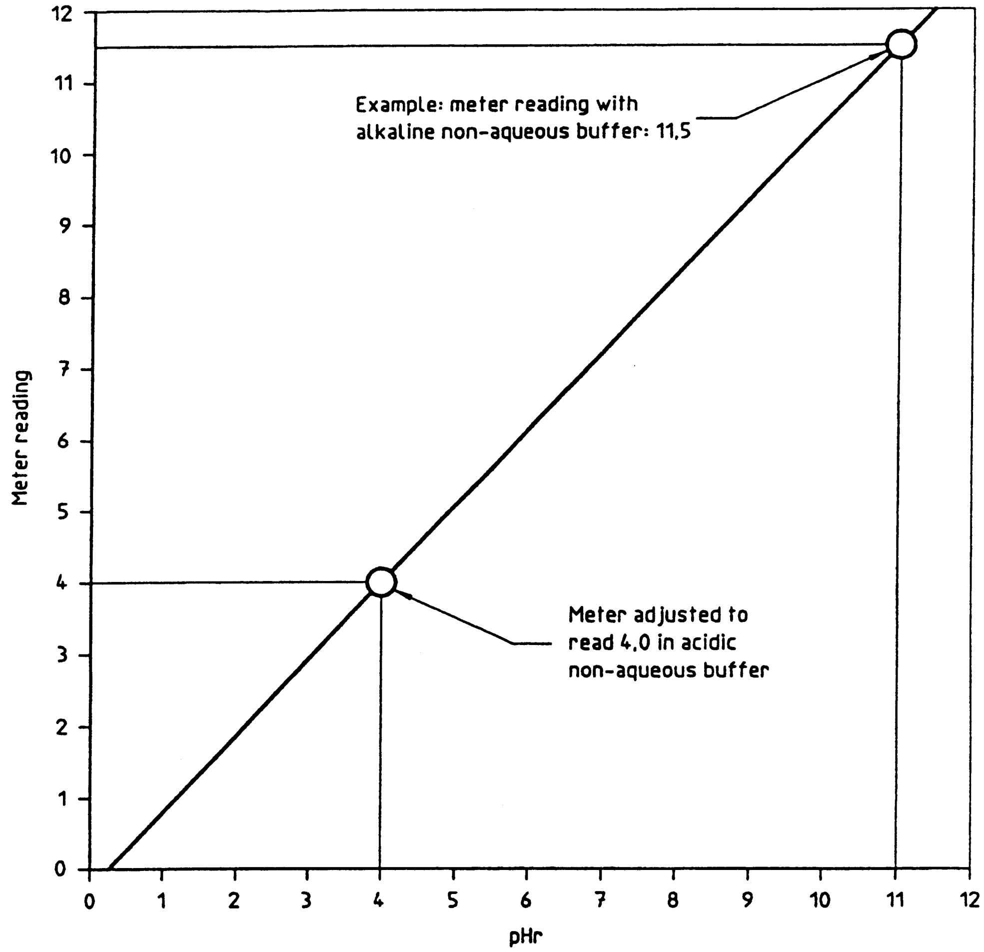

Figure B.1 - Example of calibration curve for conversion of pH meter readings to pHr

If the reading is not within 0,2 pH unit of 11,0, prepare a correction graph as shown in figure B.1. Use the graph to convert pH-meter readings to initial acidity, pHr.

B.8 Procedure

B.8.1 Titrate 100 ml of titration solvent (5.3) with potassium solution (B.4.1) until the meter indicates a pHr between 13 and 14 (see B.8.4).

B.8.2 Add 0,5 ml of the *p*-naphtholbenzein indicator solution under examination to a fresh portion of titration solvent, and after cleaning the electrodes, titrate with potassium hydroxide solution (B.4.1) until the meter indicates a pHr between 13 and 14.

B.8.3 During the titration, plot the volume of titrant against the pHr or meter reading and note on the curve the various colour changes at the corresponding pHr values.

NOTE - The following colour changes, in order, are intended as a guide:

- amber to olive green;
- olive green to clear green;
- clear green to bluish green;
- bluish green to blue.

B.8.4 Plot the results of the blank titration on the same paper as used for the indicator.

B.9 Expression of results

Subtract the volume of titrant used in the blank titration from that used for the indicator solution titration at the same pHr corresponding to the definite colour changes between 10 and 12 pHr to obtain the true pHr range of the indicator.

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