

**Methanol for Industrial Use —
Specification**

PUBLIC REVIEW DRAFT MARCH 2013

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PREFACE

This Kenya Standard was prepared by the Technical Committee on Industrial Solvents and Chemicals under the authority of Kenya Bureau of Standards.

Methanol, with a chemical formula, CH_3OH is a light, volatile colourless simple flammable liquid with a distinctive odor. It is used as an antifreeze, as fuel, solvent and as a denaturant for ethanol. It also finds use in producing biodiesel through transesterification.

Its similarity to ethanol in terms of appearance and odour and its relative low price to ethanol makes it prone to misuse. It has adverse health effects including causing permanent blindness and even death,

The standard has addressed safety concerns, test methods including determination of sulphur compounds. It has captured marking requirements as well.

During the development of this standard, reference was made to the following publications:

- BS 506-1:1987 Methanol for industrial use- Part 1: Specification for methanol
- BS 506-2 1984 – Methanol for industrial use – Part 2: Methods of test

Assistance from these sources is greatly acknowledged.

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Methanol for Industrial Use – Specification

1. Scope:

This Kenyan Standard specifies requirements and methods of test for methanol for industrial use.

2. Requirements

	Requirements		
i.	Appearance	Clear and free from matter in suspension	Visual
ii.	Colour in Hazen Units	15 maximum	KS 1180
iii.	Density at 20°C, g/ml	0.791-0.794	KS 1180
iv.	Distillation range at 1013mbar, °C	Initial 64.0 Dry point 65.0	KS 1180
v.	Residue on evaporation %m/m	0.001 maximum	KS 1180
vi.	Miscibility with water	Shall not show opalescence when mixed with distilled water.	Annex A
vii.	Acidity %m/m	0.003 maximum and shall not be alkaline to phenolphthalein	Annex B
viii.	Aldehydes and ketones %m/m as acetone CH ₃ COCH ₃	0.005	Annex E
ix.	Sulphur compounds % m/m	0.0001 maximum	Annex D
x.	Permanganate test	Shall not cause potassium permanganate solution to fade in 30 minutes to match or be lighter than matching solution	Annex C
xi.	Water content% m/m of water	0.1maximum	KS 1180

Marking and packaging

Methanol shall be packed in suitable and serviceable containers and marked indelibly with the following information.

- (i) Name of product
- (ii) Manufacturer's name and/or registered trade mark; and address.
- (iii) Net content
- (iv) The word 'flammable' plus its international symbol.
- (v) Country of origin.
- (vi) Batch/Lot number
- (vii) The precautionary measures do not inhale or ingest

Annex A

Test for miscibility with water

A.1 Principle

Addition of water to a test portion, under specified conditions and examination for opalescence.

A.2 Reagent

During the analysis, use only distilled water.

A.3 Apparatus

Ordinary laboratory apparatus and two matched Nessler cylinders, of capacity 100ml.

A.4 Procedure

Test portion: of the sample, place the test portion in one of the nessler cylinders and dilute with water to the 100ml mark. Mix and adjust the temperature to about 20°C. Place 100ml of water in the other nessler cylinder.

Examine the cylinder containing the test solution vertically for opalescence, against a black background with side illumination, using the second nessler cylinder containing water as the standard.

Report the dilution-ratio of the test portion and the presence of or absence of opalescence.

Annex B

Detection of Alkalinity or determination of acidity to phenolphthalein

B.1 Principle

Dilution of a test portion with carbon dioxide-free water. Checking whether the test portion is alkaline or acidic to phenolphthalein, and if appropriate, determination of acidity by titration with standard volumetric sodium hydroxide solution.

B.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity, carbon dioxide-free, recently prepared.

B.2.1 *Water*, carbon dioxide-free. Boil distilled water and allow it to cool in a flask fitted with a stopper carrying a soda-lime guard-tube.

B.2.2 *Sodium hydroxide*, standard volumetric solution, $c(\text{NaOH}) = 0,1 \text{ mol/l}$.

B.2.3 *Phenolphthalein*, 5 g/l ethanolic solution. Dissolve 0,5 g of phenolphthalein in 100 ml of 95 % (V/V) ethanol and add the sodium hydroxide solution until a pale pink coloration is obtained.

B.3 Apparatus

Ordinary laboratory apparatus, and

B.3.1 *Conical flask*, of borosilicate glass, of capacity 500 ml, fitted with a ground glass stopper carrying a soda-lime guard-tube.

B.3.2 *Burette*, of capacity 10 ml, graduated in 0.02 ml.

B.4 Procedure

B.4.1 *Test portion*

Take $100 \pm 0,1$ ml of the laboratory sample.

B.4.2 *Determination*

Place 100 ml of the water in the conical flask add 0.5 ml of the phenolphthalein solution and restore the pale pink coloration by the addition of 1 or 2 drops of the sodium hydroxide solution. Add the test portion and a further 0.5 ml of the phenolphthalein solution and note whether the solution is alkaline; if acid, titrate the test solution with the sodium hydroxide solution stoppering the flask and swirling its contents after each addition, until a pink coloration, persisting for about 15 s, is obtained. Shake the contents of the flask, with the stopper in position, after each addition of sodium hydroxide solution.

B.4.3 *Alkaline products*

Indicate whether the product is alkaline to phenolphthalein.

B.4.4 *Acidic products*

The acidity, expressed as a percentage by mass of formic acid (HCOOH), is given by the formula where

$$\frac{0,0046 \times V}{\rho}$$

V is the volume, in millilitres, of the sodium hydroxide solution used for the determination;

ρ is the density, in grams per millilitre, of the sample at 20 °C

0.0046 is the mass, in grams, of formic acid corresponding to 1.00 ml of sodium hydroxide solution, $c(\text{NaOH}) = 0.100 \text{ mol/l}$.

NOTE: If the concentration of the standard volumetric solution used is not exactly as specified in the list of reagents, an appropriate correction should be made.

Annex C

Determination of Permanganate time

C.1 Permanganate time is the number minutes required, after adding 2ml of 0.2g/l potassium permanganate solution to 50ml of the sample, for the colour to match that of a colour standard [(cobalt(II) chloride and Uranyl nitrate colour standard)].

C.2 Reagents

C.2.1 Potassium Permanganate, 0.2g/L solution. Use water previously boiled for 30min with sufficient dilute potassium permanganate solution to give a stable faint pink coloration . Cool the water to ambient temperature before preparation of the solution. Prepare this solution immediately before use and protect from light.

C.2.2 Cobalt(II) Chloride and Uranyl nitrate, colour standard.

To 5ml of a 50g/l solution of cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), add 7ml of a 40g/l solution of Uranyl nitrate hexahydrate [$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], and dilute with water to 50ml. Prepare this solution on the day of use.

C.3 Apparatus

C.3.1 Ordinary laboratory apparatus

C.3.2 Water bath, capable of being controlled at $15 \pm 0.2^\circ\text{C}$

C.3.3 Two matched cylinders, of capacity 100ml, of transparent and colourless glass, graduated at 50ml and fitted with ground glass stoppers

C.3.4 Burette of capacity 10ml, graduated at 50ml divisions

C.4 Procedure

C.4.1 Carry out the test as soon as possible after receiving the sample. Rinse one of the cylinders first with 15-20ml of hydrochloric acid, approximately 1.19g/ml, about 38%(m/m) solution, then six times with tap water, twice with distilled water and finally with some of the laboratory sample.

Immediately fill the cylinder to the mark with more of the laboratory sample at 15°C

Fill the second cylinder to the mark with the colour standard.

Place the cylinder containing the test portion in the water bath controlled at 15 ± 0.2 °C so that the water level in the bath is approximately 25mm below the neck of the cylinder. After 15 min, remove the cylinder from the water bath and using the burette, add 2ml of potassium permanganate solution. Note the time. Immediately, stopper the cylinder, shake and replace it in the water bath.

Remove the cylinder from the water bath, at intervals of 1min and compare the colour, viewing vertically downwards against a white background with the colour of the colour standard. Avoid exposing the test solution to strong daylight.

Note the time at which the colour of the test solution matches that of the colour standard.

Report the time in minutes from the addition of the potassium permanganate solution for the colour of the test solution to match that of the colour standard.

Annex D

Determination Of Sulphur Compounds

D.1 Applicability

The method determines all sulphur compounds normally encountered in methanol for industrial use. It does not determine alkyl sulphones and other oxygen bounded sulphur compounds.

D.2 Principle

Reaction with Raney nickel of sulphur compounds in a test position to form nickel sulphide which is then decomposed with hydrochloric acid; the hydrogen sulphide evolved is absorbed in sodium hydroxide solution before being titrated with standardized mercury [11] acetate solution in the presence of dithizone as indicator.

D.3 Apparatus

D.3.1 Ordinary laboratory apparatus and reduction apparatus as shown in figure 1. Burette, of capacity 10ml, graduated in 0.02ml

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

D.3.2 Nitrogen, gas free from carbon dioxide.

D.3.3 Acetone,

D.3.4 Raney nickel

WARNING-Raney nickel is spontaneously flammable in air. After use, it is essential to dispose of it immediately by dissolving in dilute hydrochloric acid.

Treat 10g of 50/50 nickel/aluminium alloy with 100ml of 100g/l sodium hydroxide solutions, cooling with ice while the reaction proceeds. Wash the Raney nickel three times with water, remove the water by decantation and store the Raney nickel under 100ml of propan-2-ol. Raney nickel prepared in this way retains its activity for about 3 days. 5ml of this suspension will reduce quantitatively 1,0 to 1,5mg of organic sulphur to hydrogen sulphide.

D.3.5 A stabilized form of Raney nickel is available commercially in pellet form.

D.3.6 Sodium hydroxide, approximately 40 g/l solution.

D.3.7 Hydrochloric acid solution.

Dilute 3 volumes of concentrated hydrochloric acid, approximately 1.19 g/ml, with 2 volumes of water

D.3.8 Mercury[11] acetat solutions

WARNING-mercury compounds are very toxic. It essential that adequate precautions are taken including a voidance of inhalation of mercury oxide dust. The disposal of mercury compounds may be subject to local restrictions.

Dissolve 0,200g of mercury (II) oxide in 25 ml of water containing 1 ml of glacial acetic acid, and dilute to 1 000 ml with water.

D.3.9 *Methanol, sulphur-free.*

Into a 2 litre round bottom flask with two necks, measure 10 ml of the Raney nickel suspension; alternatively, measure 20 ml of acetone into the flask, add 0.5 g (1 pellet) of Raney nickel, warm until the pellet has disintegrated and decant the acetone. Add 1 500 ml of methanol, place the flask into a heating mantle and fix it with reflux condenser. Insert the nitrogen lead into the second neck and pass in gas at the rate of two bubbles per second.

Heat until slight effervescence is observed on the methanol surface and continues for 30 min. Turn off the gas flow and the heating, and allow the nickel to settle. Decant the methanol into a flask, and distil. reject the first 250 ml and collect the next 1 000 ml, rejecting the remainder.

D.3.10 *Dithizone, 1 g/l solution in acetone.*

D.4 Procedure

D.4.1 Transfer 5ml of the Raney nickel suspension to the flask of reduction apparatus; alternatively, measure 10ml of the acetone into the flask, add 0.25g(½ pellet)of Raney nickel and warm until the pellet has disintegrated and decant the acetone. Add 100ml of the sample, place the flask into a heating mantle and pass the nitrogen through at the rate of about 31h. Adjust the temperature of the heating mantle until

slight effervescence appears on the surface (just below boiling point). Continue for **30** min, swirling the flask at intervals.

Transfer **10** ml of the sodium hydroxide solution and **10** ml of the acetone to the absorber. Add two drops of the dithizone solution and, by means of the burette, one drop of the mercury (II) acetate solution to the absorber.

NOTE: The colour change should be from yellow to pink. Liberation of hydrogen sulphide will reverse this colour change.

D.4.2 Transfer **15** ml of the hydrochloric acid solution to the dropping funnel, switch off the heating mantle, and attach a second nitrogen lead to the glass tube in the top of the dropping funnel so as to apply a slight gas pressure. Admit the acid, a few millimetres at a time, to the flask and begin titrating the contents of the absorber with the mercury (II) acetate solution, as necessary to restore the pink colour. When all the acid has been added disconnect the nitrogen supply to the top of the dropping funnel, increase the nitrogen flowrate to about 12 l/h, switch on the heating mantle again and continue heating for a further 20 min. When all the hydrogen sulphide has apparently been titrated, switch off the heating mantle, divert the flow of nitrogen momentarily, cool the flask by blowing on it, allow the absorbent to travel up the delivery tube in the absorber (to recover any hydrogen sulphide which may be absorbed on its surface) and complete the titration.

D.4.3 Carry out a blank test by following the same procedure and using the same quantities of reagents as in the determination but using **100** ml of the sulphur-free methanol in place of the test portion.

D.4.4 Standardization of the mercury(II) acetate solution

Add a known amount of an aliphatic sulphur compound (e.g. di-isoamyl sulphide), equivalent to **0.65** mg to **0.85** mg of sulphur-free methanol. Carry out a determination by the method using **100** ml of this solution. From the volume of the mercury(II) acetate solution required in the titration, calculate the mass, in micrograms, of sulphur equivalent to **1** ml of the mercury(II) acetate solution.

D.5 Expression of results

The sulphur compound content expressed as a percentage by mass of sulphur (S) is given by the formula.

$$\frac{m \times (T_1 - T_2) \times 100}{10^6 \times 100 \times \rho}$$

i.e.

$$\frac{m \times (T_1 - T_2)}{10^6 \times \rho}$$

Where m is the mass in micrograms, of sulphur equivalent to 1 ml of mercury(II)acetate solution.

T1 is the volume, in millilitres of the mercury (II) acetate solution required in the test determination;

T2 is the volume, in millilitres, of mercury(II) acetate solution required in the blank test;

ρ is the density, in grams per millilitre, of the sample at 20°C.

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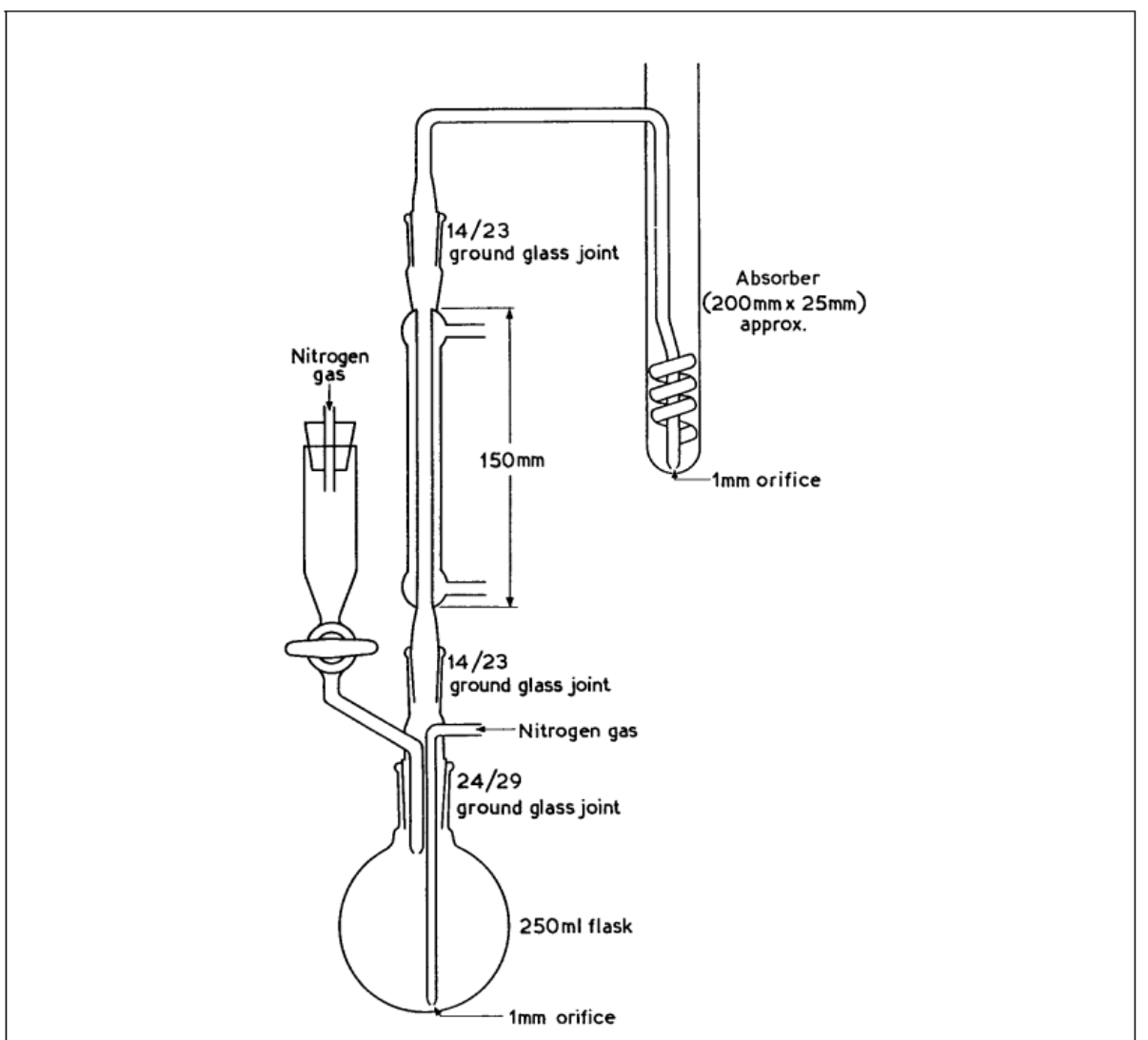


Figure 1 — Reduction apparatus for the determination of sulphur compounds

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Annex E

Estimation of content of carbonyl compounds present in small amounts — Spectrometric method

E.1 Applicability

The method is applicable to products having carbonyl compounds contents, expressed as formaldehyde, between 0.000 2 and 0.01 % (*m/m*). Reaction in acid medium of the carbonyl compounds in a test portion with 2,4-dinitrophenylhydrazine. Formation of the corresponding 2,4-dinitrophenylhydrazones, which, after

making the solution alkaline, take on a yellowish-red coloration. Spectrometric measurement of this red coloration at a wavelength of about 445 nm.

E.2 Reagents

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

E.2.1 Methanol, free from carbonyl compounds, purified as follows.

Boil under reflux 1 000 ml of methanol with 10 g of 2,4-dinitrophenylhydrazine and 10 drops of the hydrochloric acid solution for 2 to 3 h. Distil the methanol slowly using a Widmer distillation column, about 300 mm long and about 25 mm in diameter, or any other suitable column. Reject the first 75 ml of distillate and collect the next 850 ml, rejecting the remainder. If the distillate is coloured, redistil it.

E.2.2 2,4-Dinitrophenylhydrazine, saturated solution in the methanol (**11.3.1**) at ambient temperature [about 0,06 % (*m/m*) solution].

WARNING. 2,4-dinitrophenylhydrazine is harmful if inhaled, if in contact with skin or eyes, or if swallowed and carries the risk of explosion by shock, friction, heat or by other sources of ignition, particularly when dry. Inhalation of dust and contact with skin and eyes should be avoided. Particular care should be taken when using the dry material.

E.2.3 Hydrochloric acid, Q approximately 1.19 g/ml, about 38 % (*m/m*) solution.

E.2.4 Potassium hydroxide, 100 g/l solution in a 70 % (*V/V*) solution of the methanol

E.2.5 Carbonyl compounds, standard solution corresponding to 0.030 g of carbonyl compounds, expressed as formaldehyde, per litre. Weigh, to the nearest 0.000 1 g, 1.200 g of acetophenone, and dissolve it in a little of the methanol. Transfer quantitatively to a 100 ml one-mark volumetric flask, dilute to the mark with the methanol and mix. Take 5.0 ml of this solution, transfer it to a 500 ml one-mark volumetric flask, dilute to the mark with the methanol and mix. 1 ml of this standard solution contains 30 4g of carbonyl compounds, expressed as Formaldehyde.

E.3 Apparatus

Ordinary laboratory apparatus, and

E.3.1 Water bath, capable of being controlled at 50 ± 2 °C.

E.3.2 Test tubes, fitted with ground glass stoppers.

E.3.3 Spectrometer with a radiation selector for continuous variation, fitted with cells of optical path length 1 cm, or

E.3.4 Spectrometer with a radiation selector for discontinuous variation, fitted with filters providing maximum transmission at a wavelength of about 445 nm.

E.4 Procedure

E.4.1 Test portion

Take 1.0 ml of the laboratory sample and place it in one of the test tubes

E.4.2 Blank test

Carry out a blank test at the same time as the determination, following the same procedure and using the same quantities of all the reagents used for the determination, but replacing the test portion by 1.0 ml of the methanol

E.4.3 Preparation of the calibration graph

E.4.3.1 Preparation of dilute standard solutions, with a view to preparation of standard colorimetric Solutions Into a series of seven 25 ml one-mark volumetric flasks, introduce the volumes of the standard carbonyl compounds solution indicated in the following table and dilute to the mark with the methanol

Standard Carbonyl Compounds Solution	Corresponding mass of carbonyl compounds, expressed as HCHO	Mass of carbonyl compounds in 1 ml of dilute standard solution
ml	µg	µg
0 ^a	0	0
1.5	45.0	1.8
2.5	75.0	3.0
5.0	150.0	6.0
7.5	225.0	9.0
10.0	300.0	12.0
12.5	375.0	15.0
^a Compensation solution.		

E.3.3.2 Preparation of standard colorimetric solutions, for spectrometric measurements carried out in cells of optical path length 1 cm place 1.0 ml of each of the dilute standard solutions and treat the contents of each tube according to the procedure **E.3.3.3**.

E.3.3.3 Colour development

Add 1.0 ml of the 2,4-dinitrophenylhydrazine solution and one drop of the hydrochloric acid solution Stopper the tubes and heat for 30 min using the water bath controlled at 50 ± 2 °C. Allow to cool, add 5.0 ml of the potassium hydroxide solution mix, and allow to stand for 5 min.

E.3.3.4 Spectrometric measurements

Immediately carry out the spectrometric measurements on each of the standard colorimetric solutions, using either the spectrometer set at a wavelength of about 445 nm, or the spectrometer fitted with appropriate filters, after having first adjusted the instrument to zero absorbance against the methanol

E.3.3.5 Plotting the graph

Deduct the absorbance of the compensation solution from those of the standard colorimetric solutions. Plot a graph having, for example, the masses, in micrograms, of carbonyl compounds, expressed as HCHO, in 1 ml of each dilute standard solution as abscissae, and the corresponding corrected values of absorbance as ordinates.

E.4 Determination**E.4.1 Colour development**

Treat the test portion in the test tube, following the procedure specified in **E.3.3.3**.

E.4.2 Spectrometric measurements

Immediately carry out the spectrometric measurements on the coloured test solution and the blank test solution following the procedures specified in **E.3.3.4**, after having adjusted the instrument to zero absorbance against the methanol

NOTE If the absorbance exceeds the maximum of the calibration graph, repeat the determination using as the test portion 1.0 ml of a test solution prepared by diluting 1.0 ml of the laboratory sample with an appropriate volume (not more than 4.0 ml) of the methanol

E.5 Expression of results

By means of the calibration graph determine the masses of carbonyl compounds corresponding to the values of the spectrometric measurements. The carbonyl compounds content, expressed as a percentage by mass of formaldehyde (HCHO), is given by the formula

$$\frac{(m_1 - m_0) \times 100}{1,0 \times \rho \times 10^6} \times r_D$$

$$= \frac{m_1 - m_0}{\rho \times 10^4} \times r_D$$

where

m_0 is the mass, in micrograms, of carbonyl compounds found in the blank test solution

m_1 is the mass, in micrograms, of carbonyl compounds found in the test solution;

ρ is the density, in grams per millilitre, of the sample at 20 °C

r_D is the ratio of the volume of the diluted test solution to the volume of the aliquot portion taken for the determination (if the test portion was not diluted, r_D is equal to 1);

1,0 is the volume, in millilitres, of the test portion. The results can also be expressed as a percentage by mass of acetone [(CH₃)₂CO] by multiplying the above results by 1,93.