Revision of the Regulation of the Quality Control of Gas oil

Petroleum Distribution and Retail Division,
Natural Resources and Fuel Department,
Agency for Natural Resources and Energy

The second interim report (July 2004) of the Fuel Policy Sub-committee, Petroleum Committee, and Advisory Committee for Natural Resources and Energy pointed out that quality regulations for BDF(Bio Diesel Fuel)-blended gas oil was necessary.

In response to the indication, at the Fuel Policy Sub-committee, the draft standards were compiled to set the upper limit for BDF to be blended with gas oil in June 2006. Based on the results of the conformity tests, it was proposed that six properties(FAME(Fatty Acid Methyl Ester) content, Triglyceride, methanol, oxidation stability, Total acid number (TAN), and total content of individual organic acids) were added to the current gas oil regulation (see below Chart) in order to specify the BDF (FAME) mixture (mixture up to 5 mass % is allowed) and the properties of the fuel satisfying the aspects of ①, ② and ③ in the Regulation of the Quality Control of Gas oil.

① FAME sufficiently refined (purity is high) should be blended.
② FAME in fresh condition (not degraded with time) should be blended.
③ Properties should be such that generation of acid and sludge from the heat load and oxidative degradation is controlled (oxidative stability is established).

(Note) The second interim report by the Fuel Policy Sub-committee, Petroleum Committee, and Advisory Committee for Natural Resources and Energy (July 2004):

"Characteristics of BDF-blended gas oil that are not harmful from safety and environmental perspective, when used with ordinary diesel vehicle, shall be studied, and appropriate specifications shall be reflected in the fuel regulation."

Chart: The draft of amended item and test methods

Regulatory Item		BDF-Blended Diesel oil	Diesel oil(BDF is not blended)	Test methods
Existing Items	Sulfur	0.005 mass % ore less	0.005 mass % ore less	JIS K 2541-1, -2,-6 or-7
	Cetane Index	45 or more	45 or more	JIS K 2280
	Distillation Temperature 90%	360℃ or less	360℃ or less	JIS K 2254
Additional Items	FAME Content	5.0 mass % or less	0.1 mass % or less	See Exhibit 1
	Triglyceride Content	0.01 mass % or less	0.01 mass % or less	
	Methanol Content	0.01 mass % or less	—	See Exhibit 2
	TAN	0.13 mgKOH/g or less	—	JIS K 2501
	Formic Acid, Acetic Acid and Propionic acid	0.003 mass % or less in total	—	See Exhibit 3
	Oxidation Stability (Acid Value Growth)	0.12 mgKOH/g or less	—	See Exhibit 4

Exhibit 1: Determination of Fatty Acid Methyl Ester and triglyceride contents in Diesel Fuels (Draft)

Exhibit 2: Determination of Methanol Content in FAME-Blended Diesel Fuels (Draft)

Exhibit 3: Determination of Formic Acid, Acetic Acid and Propionic Acid Contents in FAME - Blended Diesel Fuels (Draft)

Exhibit 4: Determination of Oxidation Stability of FAME - Blended Diesel Fuels (Draft)

Exhibit 1

Determination of Fatty Acid Methyl Ester and triglyceride contents in Diesel Fuels

(Draft)

- High Performance Liquid Chromatography -

(WARNING – The use of this 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 to determine the applicability of regulatory limitations prior to use.)

1. Scope

This standard specifies a test method for the determination of concentrations of Fatty Acid Methyl Ester (hereinafter referred to as "FAME") and triglycerides in diesel fuels. This standard allows the determination of the concentrations of FAME and triglyceride in a concentration range of 0.1-10 mass percentage and of 0.01-0.1 mass percentage, respectively.

In case the concentration of a sample is beyond the scope of this standard (such as FAME), the test may be performed by diluting the sample to suitable levels and complying with this standard.

2. Normative reference

The standards cited at the appropriate places in this standard are as follows. For these reference standards, their latest version (including the Supplements) shall be applied.

JIS K 0124 General rules for high performance liquid chromatography

JIS K 2249 Crude petroleum and petroleum products - Determination of density and petroleum measurement tables based on a reference temperature (15 °C)

JIS K 2251 Crude petroleum and petroleum products - Sampling

JIS Z 8401 Guide to the rounding of numbers

JIS Z 8402-6 Accuracy (trueness and precision) of measurement methods and results - Part 6: Use in practice of accuracy values

3. Terms and definitions

For the purposes of this standard, the following terms and definitions used herein shall be applied.

3.1 FAME (Fatty acid methyl esters)

Fatty acid methyl esters are used for diesel fuels. They are produced from vegetable oils, animal fats and other fatty oils through methyl-esterification and purification processes.

3.2 Triglycerides

Triglycerides are the fats and oils that are mainly composed of fatty acids from 16 to 18 carbon atoms.

4. Summary of test method

A sample is injected from the sample injection port into High Performance Liquid Chromatograph (hereinafter referred to as "HPLC"), which has been first adjusted to predetermined conditions, as the sample and an elution fluid of 0.4 % 2-propanol/n-hexane pass through a silica gel column, because of the difference of the partition coefficient between Solid- and Liquid-Phase, three eluates containing diesel fuel, FAME, and triglycerides are separated in this order. Each eluate is detected by a differential refractive index detector.

FAME concentration (mass percentage) and triglyceride concentration (mass percentage) are calculated by both density of the sample and a value obtained from their calibration curves that have been already prepared using methyl stearate and trilinolein as their standard, respectively.

5. Reagents

5.1 2-Propanol Shall be for HPLC and 99 or more % in purity.

5.2 n-Hexane Shall be for HPLC and 96 or more % in purity.

5.3 Methyl stearate 99 or more % in purity.

5.4 Trilinolein 95 or more % in purity.

5.5 Diesel fuel Commercially available diesel fuel that does not contain both FAMEs and triglycerides.

5.6 Eluent A mixture of 0.4 vol% 2-propanol and 99.6 vol% n-hexane.

6. Apparatus

6.1 System configuration

The testing apparatus of HPLC shall be as follows:

A schematic diagram example of this system is shown in **Fig. 1**. General information for all types of HPLC shall be based on **JIS K 0124.**

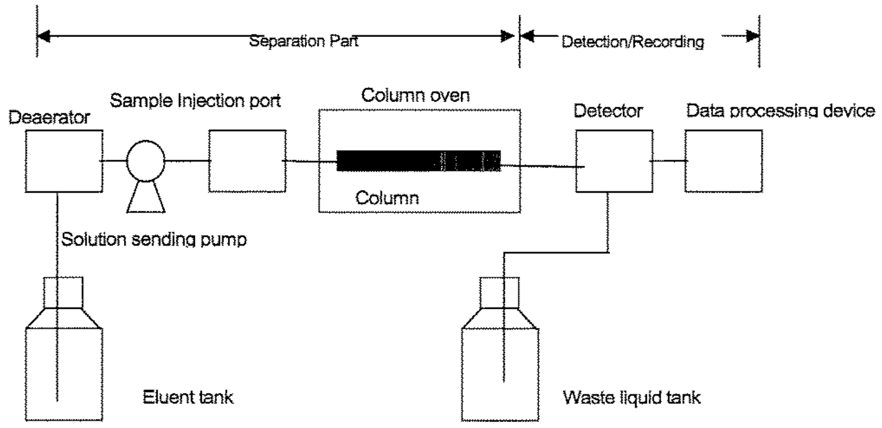


Fig. 1 Schematic Diagram Example for HPLC System

6.2 Separation unit

a) Eluent tank Shall be made of materials that do not contaminate the elutent solution.

b) Deaerator Shall be capable of removing gases dissolved in the eluent. Such deaerator is installed in front of the solution-sending pump in order to prevent the generation of pulsating flow during the solution-sending process by the pump. However, there is no need to do so when the solution can be sent without generating pulsating flow by using an ultrasonic device for deaeration.

c) Solution sending sump Shall be a pump for HPLC and capable of adjusting a flow rate to 1.0mL/min ± 0.01mL/min.

d) Sample injection port Shall be capable of injecting 5 μL-10 μL of sample into the system in a good reproducible manner.

e) Column Oven Shall be capable of controlling the column temperature within a range of 40°C ± 0.5°C.

f) Column Shall be a silica gel column (4.6 mm in internal diameter, 250 mm in length, and 5 μm in particle size) meeting the conditions shown in **Section 7.5** in terms of "Retention iime" and "Separation degree."

g) Waste liquid tank Shall be capable of storing effluents generated from the testing apparatus.

6.3 Detector Shall be capable of detecting the difference in refractive index between a sample solution and a reference solution. In testing the samples, the temperature of cells in the detector is kept constant.

6.4 Recorder Shall be not only capable of drawing chromatograms and indicating the retention time and peak area values but also capable of processing data.

7. Preparation

7.1 Conditioning of HPLC

a) Set each test condition, using **Table 1** as reference data. Also, set the data processing device to boot.

Table 1 Test Conditions of HPLC

Items	Conditions
Column	Silica Gel: Internal diameter (4.6 mm), Length (250 mm), Particle size (5 μm)
Column Temperature	40 °C ± 0.5 °C
Eluent	0.4 Vol% 2-propanol/n - hexane solution
Flow Rate	1.0 mL/min ± 0.01 mL/min
Injected Volume	10 μL

NOTE If the signal of methyl stearate (stock standard solution) on a chart goes beyond the threshold, then the injection volume can be changed to 5 μL.

b) By sending the eluent into the system, check if the state of the base line is set stable.

7.2 Eluent preparation

Place 4 mL of 2-propanol into 1000 mL volumetric flask using a transfer pipette. Next, pour n-hexane into the flask up to the marked line.

7.3 Preparation of stock standard solution (5 g/50 mL of methyl stearate + 0.05 g/50 mL of trilinolein)

Weigh 5.0g of methyl stearate and 0.05g of trilinolein to the nearest 0.1mg and place them into 50 mL volumetric flask. After dissolving them with some amount of diesel fuel, pour more diesel fuel into the flask up to the marked line.

7.4 Preparation of standard solution for calibration curve

Prepare a set of four 10mL volumetric flasks (labeled No. 1 through No. 4). Weigh 1 mL, 2 mL, and 5 mL of the stock standard solution for three standard solutions for calibration curve (No. 2, No. 3, and No. 4), respectively. After dissolving them with diesel fuel, pour more diesel fuel into each flask up to the marked line to give the three standard solutions. Prepare standard solution No.1 by the following these steps: Firstly, weigh 1 mL of standard solution No. 2 and place it into the flask labeled "No. 1". Secondly, dissolve it with some amount of diesel fuel and pour diesel fuel into the flask up to the marked line. The analyte concentrations of each calibration curve solution are as in **Table 2**.

Table 2 Concentration of the Standard Solution for Calibration Curve

Unit μg/10 μL

Standard Solution for calibration curve	Methyl stearate	Trilinolein
1	10	-
2	100	1
3	200	2
4	500	5
5 (Stock Standard)	1000	10

7.5 Determination of retention time and peak resolution

By using calibration curve solution No.5 under the measurement conditions shown in **Table 3**, measure the retention time of methyl stearate and the peak resolution of methyl stearate and/or trilinolein. Such retention time and peak resolution have to be within the range of **Table 4**. **Fig. 2** shows an example of the chromatogram. The peak resolution of methyl stearate and trilinolein are calculated by the following formula:

$$R = \frac{1.18 \times (T_2 - T_1)}{W_1 + W_2}$$

Where: R : peak resolution of methyl stearate and trilinolein

T_1 : Retention time of methyl stearate (min.)

T_2 : Retention time of trilinolein (min.)

W_1 : FWHM* of methyl stearate (min.)

W_2 : FWHM of trilinolein (min.)

FWHM*: Full Width at Half-Maximum

Table 3 Measurement Conditions (to be checked)

Items	Conditions
Column Temp.	40 °C ± 0.5 °C
Eluent	0.4 vol% 2-propanol/n-hexane solution
Flow Rate	1.0 mL/min ± 0.01 mL/min
Injected Volume	5 μL

Table 4 Performance of the Column

Checking items	Conditions
Retention time of methyl stearate (min.)	3.5 or more
Peak resolution of methyl stearate and trilinolein	3 or more

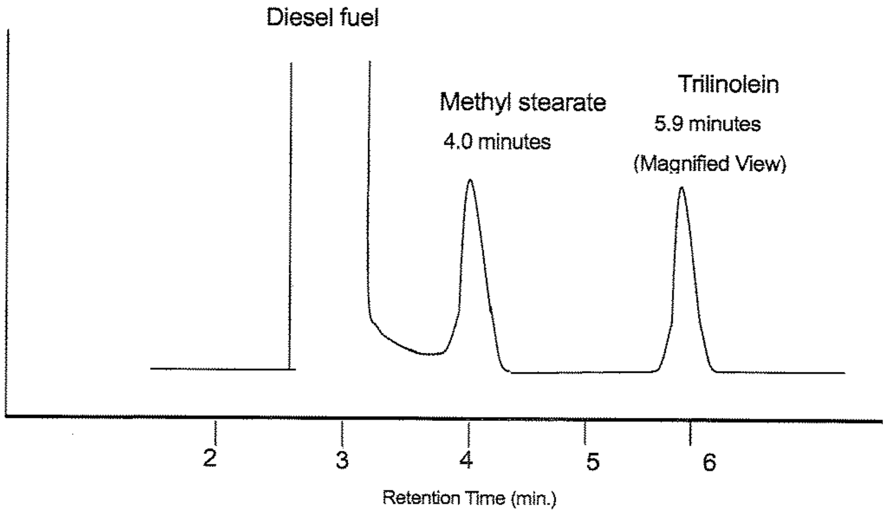


Fig. 2 Example of the Chromatogram for Analytes in Standard Samples

7.6 Calibration Curve Preparation

Measure the five standard solutions for calibration curve solutions by HPLC twice for each solution. If the difference between area values of the two tests is within 15% of the average value, the average value is recorded.

By plotting the concentration value of each analyte (x axis) (μg/10 μL) versus the average area value (y axis), prepare a calibration curve.

8. Sampling and Preparation

A sample is collected and prepared according to the collection method for the primary sample and the preparation method for the secondary sample specified in **JIS K 2251** or an equivalent method.

9. Procedures

Procedures for the test shall be as follows:

a) After setting the test conditions as same as in **Section 7.6,** inject 10 µL of the sample so that the chromatogram can be recorded.

b) Calculate the area of FAME by using the peak group corresponding to the retention time of methyl stearate that has been eluted through the process in **Section 7.5.** In the same way, calculate the area of triglycerides by using the peak group corresponding to the retention time of trilinolein that has been also eluted through the process in **Section 7.5.**

When multiple peaks are superimposed upon each other, the peaks of FAME and triglyceride is separated by "Tangent method."

Fig. 3 shows an example of the chromatogram for a FAME-containing diesel fuel.

Reference In general, FAME is a mixture of various kinds of methyl caboxylates while waste edible oils are a mixture of many types of triglycerides. Therefore, broad peaks can usually be observed in such cases.

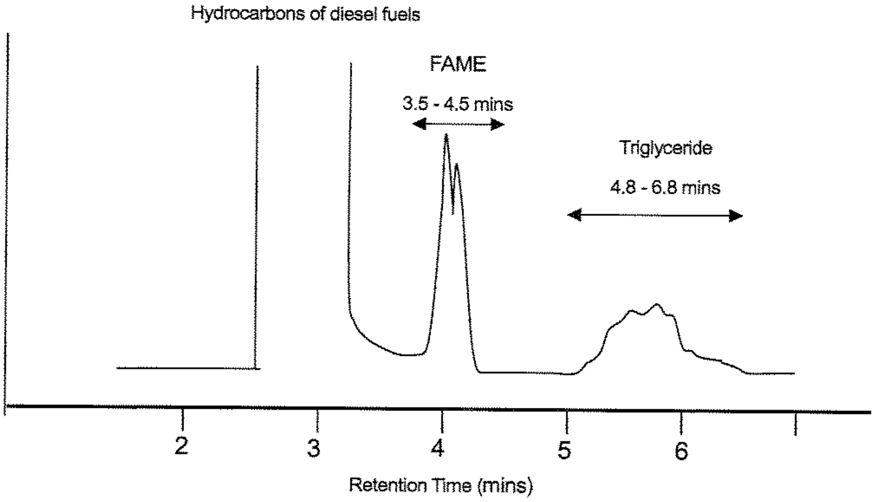


Fig. 3 Separation Example of Overlapped Peak Areas (FAME & Triglyceride)

c) Calculate the mass (µg) of FAMEs and triglycerides in the injected sample by using the calibration curve.

d) Determine the density of the sample in accordance with **JIS K 2249.**

10. Calculation

The concentrations of FAMEs and triglycerides in the sample are calculated by the following formula:

$$S = \frac{B}{D \times 10 \times 1000} \times 100$$

Where : S : Concentration of FAME or triglyceride (mass percentage)

B : Mass of FAME or of triglyceride calculated in **Section 9. c)** (µg)
D : Density of the sample calculated in **Section 9. d)** (g/cm^3 at 15°C)
10 : Injected sample volume (µL)
1000 : Coefficient for conversion into the Unit "µg"

11. Expression of Results

Test results shall be expressed as follows:

a) For FAMEs, the result value is rounded off to two decimal places (in this case, the rounding unit is 0.01) as stipulated in **JIS Z 8401**. If the result value is 0.10 or lower, such value shall be reported as " 0.1 or lower."

b) For triglycerides, the result value is rounded off to three decimal places (in this case, the rounding unit is 0.001) as stipulated in **JIS Z 8401**. If the result value is 0.010 or lower, such value shall be reported as " 0.01 or lower."

12. Precision

12.1 The tolerance in test results obtained by this test method (0.95: Probability) shall be as follows:

RemarksNOTE If the test result is not within the following tolerance range, such result shall be treated as specified in **JIS Z 8402-6.**

a) Repeatability

Repeatability shown in Table 5 is defined as a tolerance of the difference between test results obtained from two replicated tests, either of which is conducted in the same laboratory by the same person using the same test equipment and the same sample within a short period of time.

b) Reproducibility

Reproducibility shown in Table 5 is defined as a tolerance of the difference between two test results obtained from a couple of different tests, either of which is conducted in a different laboratory by a different person using different test equipment and the same sample.

Table 5 Precision

Unit Mass%

	Repeatability	Reproducibility
FAME	$0.02X+0.03$	$0.08X+0.04$
Triglyceride	$0.219X$	$0.587X$

NOTE X : Average value of the two test results

13. Test report on

The following information shall be included in the test report:

a) Name of sample, name of sampling location, and sampling date
b) Name of test method
c) Results obtained from the process of **Section 11**
d) Special remarks

Exhibit 2

Determination of Methanol Content
in FAME-Blended Diesel Fuels
(Draft)
- Using Gas Chromatograph with Oxygen Detector -

(WARNING – The use of this 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 to determine the applicability of regulatory limitations prior to use.)

1. Scope

This standard specifies a test method for the determination of methanol content in diesel fuels and/or diesel fuels in which Fatty Acid Methyl Ester (hereinafter referred to as "FAME") is mixed at a rate up to 5% using a Gas Chromatograph with an oxygen detector.

Note The concentration range in this standard shall vary 0.01 to 0.5 mass percentage.

2. Normative reference

The standards cited at the appropriate places in this standard are as follows. For these reference standards, their latest version (including the Supplements) shall be applied.

JIS K 0114 General rules for high performance liquid chromatography
JIS K 0512 Hydrogen
JIS K 1107 High Purity Nitrogen
JIS K 2251 Crude petroleum and petroleum products - Sampling
JIS K 8101 Ethanol (99.5% reagent grade)
JIS K 8891 Methanol (reagent)
JIS Z 8401 Guide to the rounding off of numbers
JIS Z 8402-6 Accuracy (trueness and precision) of measurement methods and results - Part 6: Use in practice of accuracy values

3. Terms and definitions

For the purpose of this standard, the following terms and definitions shall be applied.

a) FAME (Fatty acid methyl esters)

Fatty acid methyl esters are used for diesel fuels. They are produced from vegetable oils, animal fats and other fatty oils through methyl-esterification and purification processes.

b) Oxygen compound

General term for oxygen-containing organic compounds such as alcohols and esters in diesel fuels.

4. Summary of test method

A sample is injected into a gas chromatograph equipped with an oxygen detector to separate and elute each component, and then chromatograms corresponding to oxygen concentration profiles are recorded on each oxygen compound basis. Next, the chart peak of methanol is identified and methanol concentration is calculated from the prepared calibration curve by using the compounds of concern and an internal standard (Internal Standard Method).

NOTE 1. An example of the Gas Chromatograph with an oxygen detector would be GC-AED, which is equipped with an atomic emission detector.

NOTE 2. Generally, methyl n-decanoate (caprate) or methyl dodecanoate (laurate) is used as an internal standard. And the methyl esters of carboxylic acids which do not exist in the sample analyzed and which remains stable in the solvent can also be used for this purpose.

5. Apparatus

The testing device and testing equipment shall be as follows:

a) Gas chromatograph (GC)

A GC equipped with an oxygen detector shall be used. General information for all types of GC is based on the provisions specified in **JIS K 0114.**

b) Automatic sample Injectior

Automatic sample injector is capable of sampling and/or injecting a desired volume of test sample (0.1 -1.0 μL).

6. Reagents and materials

The reagents and materials used herein shall be as follows.

a) Methanol Specified in **JIS K 8891**.

b) Ethanol Specified in **JIS K 8101**.

c) Methyl decanoate (caprate) 99 or more mass percentages in purity.

d) Diesel fuel for dilution Commercially available diesel fuel that does not contain methanol.

e) Hydrogen Specified in **JIS K 0512**.

f) Helium 99.99 or more volume percentages in purity.

g) Nitrogen Specified in **JIS K 1107**.

h) Air Dried air is used.

i) 10 % Methane/Nitrogen Specified in the instruction manual of the testing device.

j) Sample for calibration curve The sample for making calibration curve shall be prepared as follows:

1) Weigh 0.25 g of methanol to the nearest 0.1 mg and add ethanol to it to give 25 mL of solvent mixture (Mother Solution A).
2) Using pipettes, transfer 5 mL, 1 mL, and 0.5 mL of Mother Solution A into a set of three 10mL volumetric flasks, respectively. After that, add 0.1g of methyl decanoate (caprate) as an Internal Standard (first

weighed to the nearest 0.1mg) into each flask to give 10 mL of standard sample by adding ethanol.

3) With a pipette, place 0.5mL of Mother Solution A into 50mL volumetric flask. Then, add 0.5g of methyl decanoate (caprate) (first weighed to the nearest 0.1 mg) into the flask to give 50 mL of standard sample by adding ethanol.

4) The approximate concentrations of methanol in each standard sample for calibration curve preparation are shown in **Table 1**.By using actual measured values, concentrations (mg/mL) of both methanol and methyl dodecanoate (caprate) in these standard are calculated and rounded off to two decimal places.

NOTE Methanol is not very soluble in diesel fuel; therefore, ethanol shall be used as a diluent solvent.

Table 1 Standard Samples for Calibration Curve Preparation (Methanol)

Compound Name	Concentration mg/mL			
	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
Methanol	5	1	0.5	0.1
Methyl decanoate (Caprate) (Internal Standard)	10	10	10	10

7. Preparation

Preparation for the test shall be as follows.

7.1 Conditioning of gas chromatograph

The gas chromatograph shall be conditioned as follows:

a) An example for setting the operating conditions of the gas chromatograph is shown in Table 3. The automatic sample injector shall be equipped with microsyringes and also, the data processing device shall be set to boot.

Table 3 Example of gaschromatograph conditons

Column	Liquid phase		Poly ethylene glycol (PEG)
	Internal diameter	mm	0.25
	Length	m	30
	Film Thickness of the liquid phase	μm	0.25
Column Oven Temperature	Initial temp.	°C	50
	Holding time for keeping initial temp.	min	2
	Ramp rate	°C/min	4
	Final temp.	°C	270
	Holding time for keeping final temp.	min	3
Detector	Type		Atomic Emission Detector
	Wave length of the monitor	nm	171
	Gas		10 % methane/nitrogen, hydrogen
	Cavity temp.	°C	300
Others	Carrier gas		Helium

	Flow rate of carrier gas mL/min	1.3
	Split ratio	30 - 100 : 1
	Temp. of the injection port °C	270
	Injection volume of sample μL	1

b) Start the heating system of column oven and data processing devicesin order to verify that the state of a base line in a blank operation isstable.

c) By using a suitable concentration methanol solution diluted with ethanol and diesel fuelfor dilution, check the peak area where each component is eluted. Also, make sure that the peaks of such analytes are not superimposed on each other.

7.2 Preparation of **Calibration Curve**

Preparation for the calibration curve shall be as follows:

a) Inject the standard sample used for calibration curve into the column by using automatic injector. Immediately , start the heating system and data processing device to record the chromatogram and peak area. All standard samples shall be sequentially measured.

b) Make the calibration curve using the peak area obtained through theprocess **a)** above and the calculated concentrations of **Section 6. j)**. By selecting concentration ratio of methanol to the Internal Standard (C/Cin) as a horizontal axis versus peak area ratio (A/Ain) as a vertical axis, a calibration curve expressing the relation between concentration ratio and peak area ratio shall be prepared.

Where: C : Concentration of methanol in the standard sample used for calibration curve preparation [mg/mL]

C_{in} : Concentration of internal standard in the standard sample used for calibration curve preparation [mg/mL]

A : Peak areaof methanol in the standard sample used for calibration curvepreparation

A_{in} : Peak area of internal standard in the standard sample used for calibration curve preparation

NOTE Calibration curves shall be prepared prior to a series of test operations. Of course, when any of test conditions is changed (such as the replacement of column and/or of microsyringes), the calibration curve shall be prepared as well.

8. Sampling and preparation

a) A sample is collected and prepared according to the collection method for the primary sample and the preparation method for the secondary sample specified in **JIS K 2251** or an equivalent method.

b) Weigh 0.1 g of methyl decanoate (caprate) of internal standard to the nearest 0.1 mg. Place it into 10 mL volumetric flask, which has been first measured empty weight, and then add the test sample to give 10 mL of mixture solution. Again, weigh the 10 mL volumetric flask containing such solution to the nearest 0.1 mg. By using the measured values of the internal standard, concentration of methyl decanoate (caprate) (mg/mL) in the prepared sample solution is calculated and rounded off to two decimal places.

NOTE For the sample containing methanol of which concentration is beyond the determination limit, the sample shall be diluted to the level within the determination limit using diesel fuel.

9. Procedures

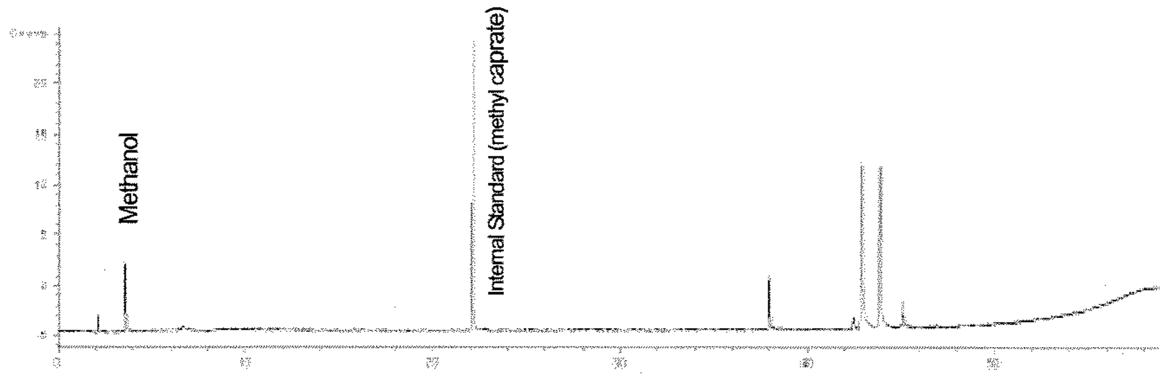
Procedures for the test shall be as follows:

a) Start the test injecting the amount of test sample into the injection port of the gas chromatograph system under the same conditions as in **Section 7.2 a)**.

b) Record the chromatogram and peak area of each analyte.

c) Identify the peak positions of methanol and of methyl decanoate (caprate) respectively.

Reference An example of the chromatogram is shown in **Reference Figure 1**.



Reference Figure 1 Chromatogram of methanol

10. Calculation

A calculation method shall be as follows.

a) The content of methanol is calculated according the following equation and the value is round off with a round off error of 0.01 according to the specifications in **JIS Z 8401**. The value is, however, reported as less than 0.01 mass percentage when found less than 0.01 mass percentage.

$$C_S = \frac{(A_s - Y \times A_{in-s}) \times C_{in-s} \times 10}{A_{in-s} \times K \times 1000 \times (M - m_{in})} \times 100$$

Where: C_s : Concentration of methanol in the test sample [mass%]

A_s : Peak area of methanol in the prepared sample containing internal standards

$A_{in\text{-}s}$: Peak area of methyl caprate in the prepared sample containing internal standards

Y : y axis intercept of the calibration curve (as a area ratio)

$C_{in\text{-}s}$: Concentration of methyl caprate in the prepared sample containing internal standards [mg/mL]

K : Coefficient of the calibration curve

M : Mass of the prepared sample containing internal standards [g]

m_{in} : Mass of methyl decanoate (caprate) [g]

10 : Sample volume [mL]

1000 : Coefficient for conversion into the Unit " mg"

11. Precision

The tolerance in test results obtained by this test method (0.95: Probability) shall be as follows:

NOTE If the test result is not within the following tolerance range, such results shall be treated as specified in **JIS Z 8402-6**.

a) Repeatability

Repeatability shown in **Table 4** is defined as a tolerance of the difference between test results obtained from two replicated tests, either of which is conducted in the same laboratory by the same person using the same test equipment and the same sample within a short period of time.

b) Reproducibility

Reproducibility shown in **Table 4** is defined as a tolerance of the difference between two test results obtained from a couple of different tests, either of which is conducted in a different laboratory by a different person using different test equipment and the same sample.

Table 4 Precision

Unit Mass%

Content	Concentration range	Repeatability	Reproduciblity
Methanol	0.01-0.5	$0.094X+0.003$	$0.94X+0.015$

NOTE X: Average value of the two test results

12. Test Report

The following information shall be included in the test report:.

- **a)** Name of sample, name of sampling location, and sampling date
- **b)** Name of test method
- **c)** Results obtained from the process of **Section 10**
- **d)** Special remarks

Exhibit 3

Determination of Formic Acid, Acetic Acid and Propionic Acid Contents in FAME - Blended Diesel Fuels

(Draft)

– Water Extraction – Ion Chromatography Method –

(WARNING – The use of this 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 to determine the applicability of regulatory limitations prior to use.)

1. Scope

This standard specifies a quantitative method for determination of of formic, acetic and propionic acids in a diesel fuel alone and its blends with up to 5% of fatty acid methyl esters (hereinafter referred to as "FAME") by the ion chromatography.

NOTE This standard can quantify 1-20 mass ppm of each component.

2. Normative reference This standards cited at the appropriate places of this standard are as follows. For these reference standards, their latest version (including the Supplements) shall be applied.

JIS K 0127	General rules for ion chromatographic analysis
JIS K 0557	Water used for industrial water and wastewater analysis
JIS K 8267	Sodium formate
JIS K 8372	Sodium acetate
JIS K 2251	Crude petroleum and petroleum products—Sampling
JIS Z 8401	Guide to the rounding of numbers
JIS Z 8402-6	Accuracy (trueness and precision) of measurement methods and results—Part 6: Use in practice of accuracy values

3. Terms and definitions

For the purpose of this standard, the following terms and definitions shall be applied.

a) FAME (Fatty acid methyl esters)

Fatty acid methyl esters used for diesel fuels. They are produced from vegetable oils, animal fats and other fatty oils through methyl-esterification and purification processes.

4. Summary of of test method

A sample is mixed with water and shaken to extract formic, acetic and propionic acids into the water. The separated aqueous phase is injected into an ion chromatograph to separate and elute each component, of which a chromatogram corresponding to each acid ion is recorded. The concentration of each acid component is determined by comparing with a pre-determined calibration curve.

5. Apparatus

The testing device and equipment used herein shall be as follows.

a) Ion chromatograph

An ion chromatograph is equipped with a separation column and a detector to enable separation and quantification of the formic, acetic and propionic acid ions. A general information for the ion chromatography shall be based on the provisions specified in **JIS K 0127**.

b) Separatory funnel

Separatory funnel is washed off with water and then dried before use.

c) Shaker

Shall be capable of securing the separatory funnel and shaking it.

6. Reagents and Materials

The reagents and materials used herein shall be as follows.

a) **Water** Specified **in JIS K 0577**.

b) **Sodium formate** Specified in **JIS K 8267**.

c) **Sodium acetate** Specified in **JIS K 8372**.

d) **Propionic acid** 99 or more % in purity.

e) **Formic acid standard solution (1000 mg/L)** Weigh 0.1478 g of sodium formate and dissolve it in water. Then transfer the solution to a 100 mL volumetric flask, to which water is added up to the marked line.

f) **Acetic acid standard solution (1000 mg/L)** Weigh 0.1367 g of sodium acetate and dissolve it in water. then transfer the solution to a 100 mL volumetric flask, to which water is added up to the marked line.

g) **Propionic acid standard solution (1000 mg/L)** Weigh 0.1000 g of propionic acid and dissolve it in water. Then transfer the solution to a 100 mL volumetric flask, to which water is added up to the marked line.

7. Preparation

Preparation for the test shall be as follows.

7.1 Conditioning of ion chromatograph

The ion chromatograph shall be conditioned as follows.

a) The ion chromatograph is installed according to the instruction manual. An automatic sample injector and data processing equipment are ready to operate.

b) Run a blank test to confirm a stable base line.

c) Confirm the retention time for each acid by introducing each acid solution that is diluted to a proper concentration into the ion chromatograph And also confirm no overlapping of peaks of the acids. Examples of the analytical conditions are given in **Table 1** and **Table 2**.

Table 1 Example 1 of Analytical Condition

Separation column (inner diameter x length)	Anion exchange column (4 mm x 200 mm)
Guard column (inner diameter x length)	Anion exchange column (4 mm x 50 mm)
Eluant	1 m mol/L KOH
Flow rate	1.2 mL/min
Detector	Electric conductance detector
Amount injected	50 µL
Others	Suppressor in use

Table 2 Example 2 of Analytical Condition

Separation column (inner diameter x length)	Ion-exclusion column (9 mm x 250 mm)
Eluant	1.0 mmol/L Octanesulfonic acid
Flow rate	1.0 mL/min
Detector	Electric conductance detector
Amount injected	25 µL
Others	Suppressor in use (regeneration fluid 5.0 mmol/L TBAOH)

7.2 Preparation of Calibration Curve

Preparation for the calibration curve shall be prepared as follows.

a) Mixture for dilute standard solutions (an example) Transfer one mL of each standard solution of formic, acetic and propionic acids (1000 mg/L for each acid) into a 100 mL volumetirc flask, and add water up to the marked line. Dilute this solution (10 mg/L) stepwise with water to use as samplea for preparation of the calibration curve. The concentration range of each acid for the calibration curve is from 0.5 mg/L to 10 mg/L.

b) Inject the sample for the preparation of the calibration curve into the sample injection port by the automatic sample injector or in a manual manner. Immediately, activate the data processing equipment to record the chromatogram and the peak area. All samples are successively injected for the measurement of chromatograms in the preparation of the calibration curve.

c) Using the values obtained in **b)**, the concentration of each acid and the peak area are taken in the x-axis and y-axis of the calibration curve respectively, to prepare the calibration curve based on the relation of the concentration with the peak area for each acid.

NOTE The calibration curve is prepared before a series of the tests is operated. The calibration curve is also prepared again when the test conditions are changed - such as replacement of the column or its parts.

8. Sampling and preparation

A sample is collected and prepared according to the collection method for the primary sample and the preparation method for the secondary sample specified in **JIS K 2251** or an equivalent method.

9. Procedures

The test ing procedures shall be as follows.

a) Take 10 mL of a sample into a separatory funnel.

b) Add 10 mL of water to the funnel, which is plugged with a stopper.

c) Hold the separatory funnel with a shaker, and shake for 10 minutes.

d) After being allowed to settle, transfer the aqueous phase into a 25 mL volumetic flask.

e) Repeat the operations **b)**, **c)** and **d)** (extract twice) and then add water up to the marked line of the 25 mL volumetric flask. This sample is used as the water extract sample.

f) Inject a specified amount of the water extract sample into the sample injection port of the ion chromatograph under the same condition as in **Section 7.2 b)** to initiate the test.

g) Record the chromatogram and the peak area for each component.

h) Identify the peaks of the formic acid, acetic acid and propionic acid ions.

i) Determine the density of the test sample according to **JIS K 2249**.

j) Calculate the concentration of each acid in the water extract sample corresponding to the peak area using the calibration curve.

NOTE 1. When the acid concentration in the sample is high, the separation of the aqueous phase may become poor.

NOTE 2. When the concentration of each acid in the water extract sample exceeds the concentration range in the calibration curve, the water extract sample is diluted with water to adjust the concentration of each acid within the concentration range of the calibration curve.

NOTE An example of the chromatogram is shown in **Reference Figure 1**.

Reference Figure 1 A chromatogram example of ions of formic, acetic and propionic acids.

10. Calculation

A calculation method shall be as follows.

a) The content of each acid identified is calculated according the following equation and the value is round off with a round off error of 0.1 according to the specifications in **JIS Z 8401**. The value is ,however, reported as less than 1 mass ppm when found less than 1 mass ppm.

$$C = \frac{C_S \times 25}{10 \times d}$$

where, C : Concentration of each acid in the test sample (mass ppm)
C_S : Concentration of each acid in the water extract sample determined by the calibration curve (mg/L)
25 : Volume of the volumetric flask (mL)
10 : Sample content (mL)
d : Density of the test sample (g/mL)

11. Precision

The tolerance in test results obtained by this test method (0.95: Probability) shall be as follows.

NOTE If the test result is not within the following tolerance range, such result shall be treated as specified in **JIS Z 8402-6** .

a) Repeatability

Repetability shown in **Table 3** is defined as a tolerance of the difference between test results obtained from two replicated tests, either of which is conducted in a same laboratory by the same person using the same test equipment and the same sample during a short period of time.

b) Reproducibility

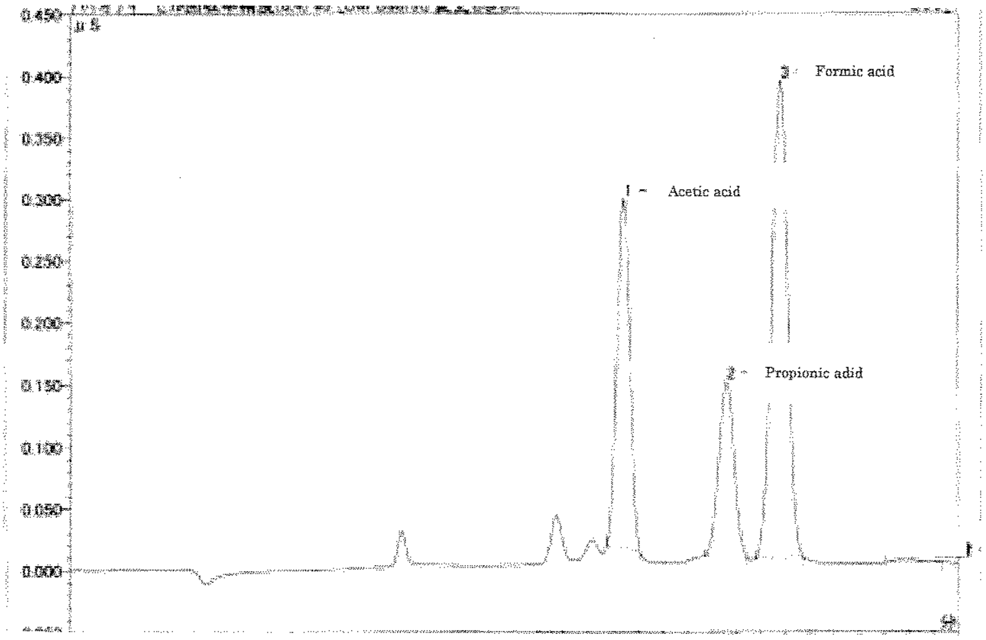
Reproducibility shown in **Table 3** is defined as a tolerance of the difference between two test results obtained from a couple of different tests, either of which is conducted in a different laboratory by a different person using a different test equipment and the same sample.

Table 3 Precision

Unit: mass ppm

Component	Concentration range	Repeatability	Reproducibility
Formic acid	1-20	0.01 X + 0.3	0.3 X
Acetic acid	1-20	0.03 X + 0.2	0.2 X + 1.1
Propionic acid	1-20	0.04 X + 0.3	0.2 X + 0.6

Remarks *X*: Average value of the two test results.



12. Test **report**

The following information shall be included in the test report.

a) Name of the sample, name of sampling location, and sampling date

b) Name of test method

c) Results obtained from the process of **Section 10**

d) Special remarks

Exhibit 4

Determination of Oxidation Stability of FAME - Blended Diesel Fuels

(Draft)

(WARNING – The use of this 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 to determine the applicability of regulatory limitations prior to use.)

1. Scope

This standard specifies a method for determination of the acid value increase (hereinafter referred to as "Δ acid value") in the oxidation stability test under the accelerated oxidation condition for diesel fuel and its blends with fatty acid methyl esters (hereinafter referred to as "FAME") up to 5% .

Remarks This test method was prepared with referring to **ISO 12205**, 1995, "Petroleum products - Determination of the oxidation stability of middle-distillate fuels" and **JIS K 2501**, 2003, "Petroleum products and lubricants – Potentiometric titration (acid value) in the test method of the neutralization value.

2. Normative reference

The standards cited at the appropriate places in this standard are as follows. For these reference standards, their latest version (including the Supplements) shall be applied.

JIS K 8034	Acetone (reagent)
JIS K 8680	Toluene (reagent)
JIS K 8891	Methanol (reagent)
JIS K 0557	Water Used for Industrial Water and Wastewater Analysis
JIS K 2251	Crude petroleum and petroleum products – Sampling
JIS K 2501	Petroleum products and lubricants – Determination of neutralization value
JIS Z 8401	Guide to the rounding of numbers
JIS Z 8402-6	Accuracy (trueness and precision) of measurement methods and results – Part 6: Use in Practice of accuracy values
ISO 3171	Petroleum liquids – Automatic pipeline sampling

3. Terms and definitions

For the purpose of this standard, the following terms and definitions herein shall be applied.

a) **FAME** (Fatty acid methyl esters)

Fatty acid methyl esters are used for diesel fuels. They are produced from vegetable oils, animal fats and other fatty oils through methyl-esterification and purification processes .

b) Δ acid value

Δ acid value **is an** acid value increase in the oxidation stability test, namely the difference in acid values between before and after the test.

4. Summary of test method

A test fuel filtered beforehand is oxidatively degraded by injecting oxygen at 115°C for 16 hours. The acid values before and after this oxidation stability test are determined by the acid value-potentiometric titration method according to **JIS K 2501**.

NOTE Although the test temperature in **ISO 12205** is 95°C, the temperature in this standard shall be 115°C.

5. Reagents and materials

The reagents and materials used herein shall be as follows.

a) Acetone Specified in **JIS K 8034**.

b) Toluene Specified in **JIS K 8680**.

c) Methanol Specified in **JIS K 8891**.

d) Trisolvent (TAM) Mixture of equal volumes of acetone, toluene and methanol.

e) Oxygen Purity of higher than 99.5% as specified in **JIS K 1101**

f) Water Type A3 specified in **JIS K 0557**.

6. Apparatus

The test apparatus and devices shall be calibrated, validated and properly maintained according to the instruction manuals of the manufacturers.

a) Oxidation cell

As shown in **Fig. 1**, the apparatus is composed of a test tube, a condenser, and an oxygen delivery tube made of borosilicate glass.

NOTE The test apparatus used in this test is identical with the one using copper and steel coils specified in the test method for the oxidation stability of the turbine oil in the test method for the lubricants-oxidation stability in **JIS K 2514**. The apparatus is therefore thoroughly washed before the test to eliminate these residual metals.

b) Constant-temperature bath

The bath is filled with a bath fluid which can maintain the temperature of samples in the oxidation cells at 115°C ± 0.2°C. The bath is equipped with an agitator to make the fluid temperature uniform, where the oxidation apparatus can be immersed about 350 mm deep. The sample shall be shielded from light during the oxidation test. The minimum volume of the bath fluid is 6 L per for the oxidation apparatus.

Reference A metal bath of the same volume equipped with a control equipment can be also used.

c) Flow meters

Shall be those to adjust a flow rate of 3.0 L/h ± 0.3 L/h and installed on every oxidation cells.

d) Constant-temperature bath for drying the glassware

Shall be those capable of drying the glassware at 105°C ± 5°C.

e) Filter assembly

Shall be, as shown in **Fig. 2**, capable of holding the filter.

f) Filter

Shall be a PTFE (polytetrafluoroethylene) membrane filter with a pore diameter of 0.8 µm and a diameter of 47 mm. Single sheet of the filter is used for preliminary filtration before the test, whereas two stacked sheets are used for the measurement of the insoluble fraction in filtration.

NOTE A cellulose ester filter cannot be used because of poor chemical resistance to acids, alcohols, and esters, etc.

g) Other apparatus

A forceps with a spade shaped tip to handle filters, and stopwatch.

7. Preparation

Preparation for the test shall be as follows.

7.1 Preparation of glassware besides the oxidation cells

All glassware is washed with the trisolvent mixture and then rinsed with water. After that, the glassware is washed with either an alkaline or neutral detergent, rinsed three times with the water specified in **JIS K 0557** and once with acetone, and then dried.

7.2 Preparation of oxidation cell and accesories

After completion of **Section 7.1**, the test tube of the oxidation cell is filled with either weak alkaline or neutral detergent in water specified in JIS K 0577. After the test tube is attached to the oxygen delivery tube, to the top of which the condenser is attached, the system is soaked for at least two hours. After being washed with the aqueous detergent, the system is rinsed five times with a tap water and then three times with the water specified in **JIS K 0557**. After washed with acetone, both the oxidation cell and the oxygen delivery tube are dried.

8. Preparation of sampling

Preparation of sampling shall be as follows.

8.1 A sample is collected and prepared according to the collection method for the primary sample and the preparation method for the secondary sample specified in **JIS K 2251** or an equivalent method.

8.2 After thorough agitation, a sample is collected from the sample container at the place kept away from direct sunlight. Storage of the sample before oxidation, oxidation itself and cooling of the sample after oxidation is carried out in a dark place. The sample after oxidation is cooled using a method described in **Section 10.5** "Cooling of sample".

8.3 A metal container lining with the epoxy resin or with similar material,or borosilicate glass container can be used after rinsed with the test sampler twice. A soda glass or plastic container cannot be used because of possible elution of the plasticizer.

8.4 The test is performed immediately after receiving the sample.

NOTE When the test cannot be run within a day, the sample is sealed with an inert gas such as oxygen free nitrogen, argon or helium and stored below 10°C.

9. Sampling

The sample shall be prepared as follows.

9.1 When the sample is kept in a tank, drum or container larger than 19 L in volume, it is collected according to the procedure in **Section 8.2**.

9.2 When the quantity is small, the sample is shaken or rolled for mixing and then poured or collected with a pipette or other means.

9.3 All of the tubes, sealed containers and pipettes exposed to the received sample are washed with the trisolvent and then with the sample itself. The sample stored below 10°C is allowed to the ambient temperature and collected with stirring after confirming there is no insoluble wax.

10. Procedures

Procedures the test shall be as follows.

10.1 Filtration of sample

A sheet of the filter is attached to the filter holder of the filter assembly in **Fig. 2** and suctioned under a pressure of approximately 80 kPa. 450 mL of the sample is filtered into a 500 mL pre-washed suction flask. This filtration is performed for every sample.

NOTE Do not reuse the filter already used for a different sample, because deposit of the previous sample left on the filter may remove more solid of the next sample.

10.2 Collection of sample

50 ml ± 0.5 ml of the sample is collected, tilting the suction flask.

10.3 Determination of acid value

The sample collected in **Section 10.2** is immediately subjected to the determination of the acid value by the potentiometric titration method according to **JIS K 2501**. When the immediate measurement cannot be performed, the sample is sealed with an inert gas, kept under a dark place and used for the measurement as soon as possible.

10.4 Assembling of oxidation apparatus

The clean oxygen delivery tube is attached to the clean test tube, to which 350 mL ± 5 mL of the filtered sample is added. Within 60 minutes, the oxidation apparatus is immersed in the bath such that the sample is positioned below the fluid level of the constant-temperature bath. During this work, the oxidation cell is kept under a dark place. The condenser is attached to the top of the oxygen delivery tube and the oxidation cell, and connected to the cooling water. The oxygen supply tube is connected via a flow meter to the oxygen delivery tube. The flow rate of oxygen is set at 3.0 L/h±0.3 L/h. The sample is protected from exposure to the sunlight. The time when the oxidation apparatus is placed in the constant-temperature bath is recorded to set as zero. The oxidation apparatus is kept at 115°C ± 0.2°C for 16 hours ± 0.25 hour. Positions of the oxidation cells in the constant-temperature bath are recorded. When the number of the oxidation cells immersed in the constant-temperature bath does not reach a fixed number, a dummy tube(s) without the oxygen delivery tube and the condenser is placed with 350 mL of a certain sample to fill empty position(s)..

10.5 Cooling of sample

The sample is removed from the constant-temperature bath and the opening of the oxidation cell is covered with an aluminum foil or plastic film to prevent from the dust contamination. The sample is immediately placed in ice-cold water (approximately 0°C) for five hours.

10.6 Collection of sample

50 mL ± 0.5 mL of the supernatant portion is collected, tilting the oxidation cell.

10.7 Determination of acid value

The sample collected in **section 10.6** is immediately subjected to the determination of the acid value by the potentiometric titration method according to **JIS K 2501**. When the sample cannot be immediately used for the measurement, it is sealed with an inert gas, kept in a dark place, and analyzed as soon as possible.

11. Calculation

The calculation shall be as follows.

11.1 Δ acid value is calculated by the following formula.

$$\Delta TAN = TAN_i - TAN_0$$

Where, ΔTAN : Δ acid value (mg KOH/g)

TAN_i : Acid value (mg KOH/g) obtained in **Section 10.7** after the oxidation stability test,

TAN_0 : Acid value (mg KOH/g) obtained in **Section 10.3** before the oxidation stability test.

12. Expression of Results

The results can be expressed according to **JIS K 2501**.

13. Precision

The tolerance in test results obtained by this test method (0.95: Probability) shall be as follows .

NOTE If the test result is not within the following tolerance range, such result shall be treated as specified in **JIS Z 8402-6** .

a) Repeatability

Repeatability shown in **Table 4** is defined as a tolerance of the difference between test results obtained from two replicated tests, either of which is conducted in a same laboratory by the same person using the same test equipment and the same sample during a short period of time.

b) Reproducibility

Reproducibility shown in **Table 4** is defined as a tolerance of the difference between two test results obtained from a couple of different tests, either of which is conducted in a different laboratory by a different person using a different test equipment and the same sample.

Table 4 Precision of Calculation

	Repeatability	Reproducibility
Acid value (unit: mg KOH/g)	Y = 0.24X + 0.015	Y = 1.10X + 0.024

NOTE *X*: Average of the two test results.

14. Test report

The following information shall be included in the test report.

a) Name of the sample, name of sampling location, and sampling date.

b) Name of test method

c) Results obtained from the process of **Section 11**

d) When the immersion time of the oxidation cells in the constant-temperature bath is not 16 hours ± 0.25 hour, the time used is reported.

e) Special remarks

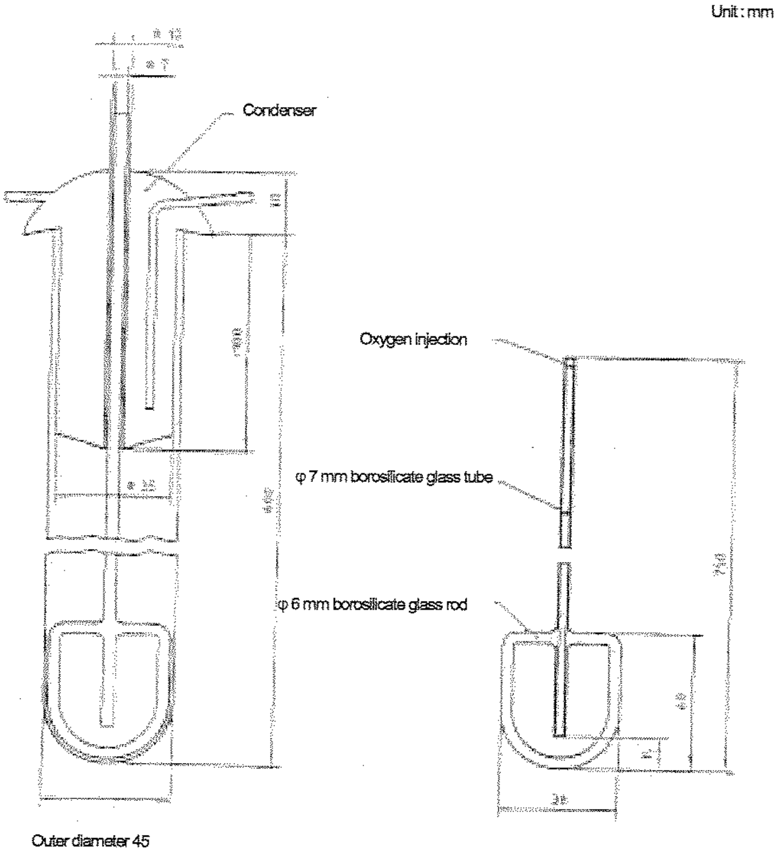


Fig. 1 Oxidation apparatus

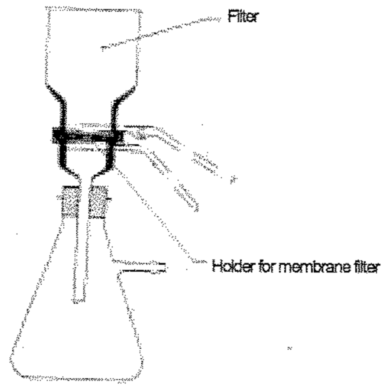


Fig. 2 Filter apparatus