

Japan Customs Analysis Methods

No. 301

Quantitative Analysis of Petroleum Oil in Lubricating Oils

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1. Scope

This analysis method is applied to lubricating oils which are classified in heading 27.10 or 34.03 in Customs Tariff Law (Appendix Table—Customs Tariff Schedule) and which require the determination of their petroleum contents.

2. Outline of Test Method

This analysis method is generally applied for determining the petroleum oil contents in lubricating oils manufactured by adding additives to lubricant base oils. The analysis follows the processes shown in the following flow-diagram, depending on the kinds of additives contained.

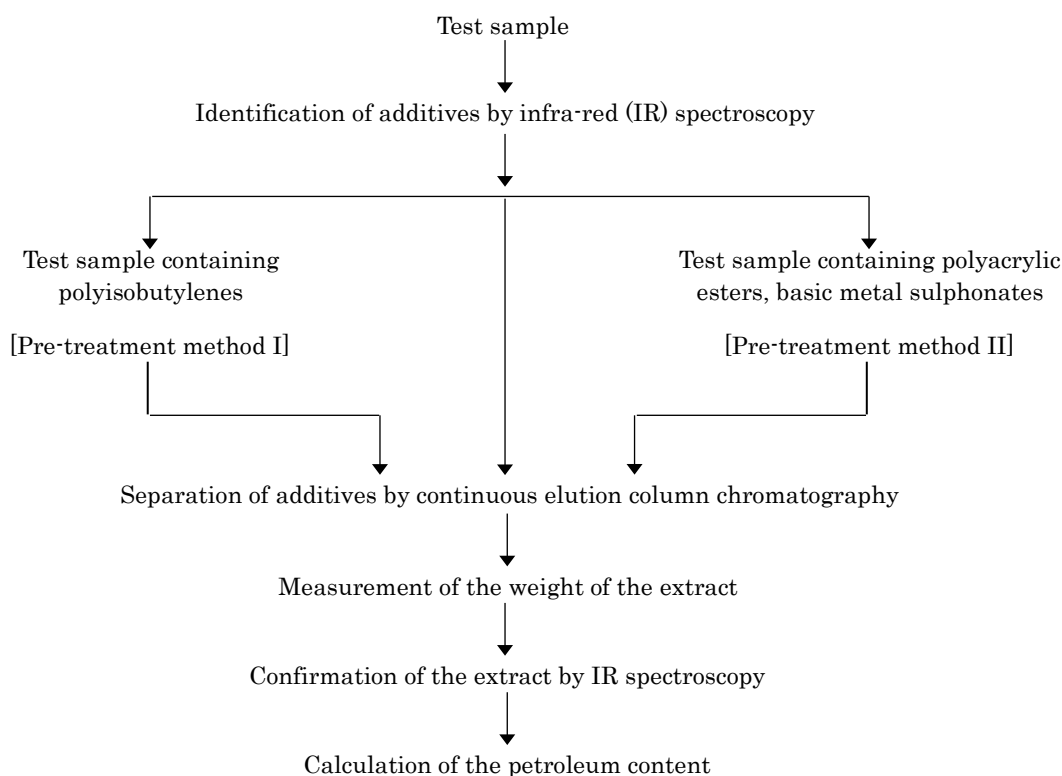


Fig. Flow diagram of this analysis method

The summary of the procedures is as follows.

- (1) Measure IR spectra of test samples and compare them with those of lubricating oil additives (reference) for identification. Based on the result of the IR identification and referring to the flow diagram on the previous page, the remaining process is determined as follows.
- (2) If expected to contain polyisobutylenes, the sample is pre-treated by the procedure in 4.1 (Pretreatment method I) for separation of those, and if expected to contain polyacrylic esters and/or basic metal sulphonates, the sample is pre-treated by the procedure in 4.2 (Pretreatment method II) for separation of those.

If expected to contain all the above additives, the sample is first pre-treated by the procedure in 4.1 and then a portion of the resulting material is pretreated by the procedure in 4.2.

- (3) For test samples which do not contain polyisobutylenes, polyacrylic esters or basic metal sulphonates, or from which such polymeric additives and basic metal sulphonates have already been removed by the procedures in 4.1 and 4.2, their petroleum oil contents will be determined by separating the other additives under continuous elution column chromatography as described in 4.3. Referring to the Appended Table, which summarized the adsorption properties of lubricating oil additives against silica-gel and alumina, either silica gel or alumina is to be used as the packing material (adsorbent) for the chromatography, depending on the additives contained in the test sample.

3. Apparatuses and Reagents

3.1. Apparatuses

- (1) Soxhlet extractor, JIS R 3503 or equivalent
- (2) Holder for aeration (see Appendix 1)
- (3) Chromatographic glass column for continuous elution column chromatography, for example, a lengthened type of JIS R 3503 Soxhlet extractor (see Appendix 1)
- (4) Rubber membrane for dialysis, JIS T 9111 grade
- (5) Extraction thimble (filter paper thimble)

3.2. Reagents

All chemicals must be JIS special grade or equivalent, unless otherwise specified.

- (1) Petroleum ether
- (2) Benzene, JIS grade 1 or above
- (3) Acetone, JIS grade 1 or above
- (4) Silica gel, for chromatography (100 to 200 mesh); Activate at 140°C for 4 hours before use.⁽¹⁾
- (5) Alumina, Activated, Activity I, for chromatography (100 to 200 mesh); Activate at 140°C for 4 hours before use.⁽¹⁾

Note 1) When using an adequately activated chemical, the heating treatment for activation can be omitted.

4. Procedure

4.1. Pretreatment method I (Removal of polyisobutylenes by fractional precipitation)

Accurately weigh about 5 g of test sample in a 200 mL Erlenmeyer flask and add 20 mL of petroleum ether to dissolve. Gradually add 20 mL of acetone to the flask, stirring continuously. Connect the flask to a reflux condenser and heat on a hot water bath for 10 minutes. Leave it to stand until the supernatant becomes clear. Transfer the mother liquor from the flask by decantation. Wash the precipitated solids in the flask with 20 mL of a mixture of petroleum ether and acetone (1:1) three times and add each of the washings to the mother liquor.

Dissolve the precipitates again in 20 mL of petroleum ether and repeat the fractional precipitation above twice.

Transfer the mother liquid and all the washings to a 200 mL Erlenmeyer flask which has been previously weighed. Recover most of the solvent from the flask, for example by a rotary evaporator, and further remove the remaining solvent by heating on a hot water bath. Place the flask in a drying oven at a constant temperature of $100 \pm 2^\circ\text{C}$ and dry to a constant weight. Calculate from the following formula the percentage of remains after the polyisobutylene removal. Use the resulting material for the procedure in 4.2 or 4.3.^(2, 3)

$$\%, \text{ remains after polyisobutylene removal} = \frac{F}{S_0} \times 100$$

Where—

S_0 : Weight (g) of test sample collected (g).

F_a : Weight (g) of remains after the removal of polyisobutylenes

Note 2) If polyisobutylenes which are not fractionally precipitated with a petroleum ether/acetone mixture (1:1) are contained, separate and quantify them using gel permeation chromatography.

Note 3) Measure an infrared spectrum of the residual matter after the removal of polyisobutylenes. If the spectrum shows no absorption peaks derived from other additives, the quantity of the residual matter is deemed to be equal to the petroleum oil content in the test sample.

4.2. Pretreatment method II (Removal of polyacrylic esters and basic metal sulphonates using a rubber membrane dialysis method)⁽⁴⁾

Accurately weigh 1–2 g of test sample in a rubber membrane distended inside an extraction thimble and attach an aeration holder to the upper side of the rubber membrane by fastening with kite string. Place the rubber membrane together with the extraction thimble in a Soxhlet extractor with the position of the knot of the rubber membrane higher than the maximum liquid level of the extractor.

Add about 120 mL of petroleum ether into a receiver flask. Connect the receiver flask to an extractor and place on a hot water bath for reflux for about 10 hours. Adjust the temperature of the bath so that the extractor siphons 6–8 times per hour. After the dialysis, remove the receiver flask and use the total amount of the petroleum ether as test material for the procedure in 4.3.

Note 4) Polyacrylic esters can be separated and quantified by gel permeation chromatography.

4.3. Determination of Petroleum Oil Content using Continuous Elution Column Chromatography

4.3.1. Preparation of Separation Column

Fill a glass column for continuous elution column chromatography with about 50 g of silica gel or alumina by the dry loading method. Put a cover of filter paper or degreased cotton on the upper end of the column. Infiltrate the adsorbents in the glass column with an excess amount of petroleum ether and then drain the solvent until the level of the solvent is just at the top of the stationary phase.

4.3.2. Continuous Chromatographic Separation

Add about 100 mL of petroleum ether into a receiver flask which has been previously weighed and connect the flask to the chromatography column prepared in 4.3.1.

Accurately weigh about 1 g of test sample (for pre-treated samples according to 4.2, use whole liquids in receiver flasks from which polyacrylic esters and basic metal sulphonates have been removed; for pre-treated samples according to 4.1, use about 1 g of those from which polyisobutylenes have been removed), dissolve in a small amount of petroleum ether, and drip the whole amount onto the top of the column.

Connect the chromatography column to a condenser and place them on a water bath. Circulate petroleum ether through the column for 16 hours, adjusting the water bath temperature so that the circulating speed at the bottom of the column is 100–120 drops per minute.

Remove the flask, recover most of the solvent from it, for example by a rotary evaporator, and further remove the remaining solvent by heating the flask on a hot water bath. Place the flask in a drying oven at a constant temperature of $100 \pm 2^\circ\text{C}$ and dry to a constant weight. Weigh the flask and calculate the content of the petroleum ether-eluted substance. Measure an IR spectrum of the petroleum ether-eluted matter. Provided that the IR spectrum shows no absorption peak derived from additives, calculate the petroleum content according to 4.5.^(5, 6, 7)

Note 5) In column chromatography using silica-gel as adsorbent, when absorption peaks derived from

additives are detected in the IR spectrum of the petroleum ether-eluted matter, take possible countermeasures, such as reduction of the amount of sample collected, use of alumina instead of silica gel, etc.

Note 6) If test samples contain additives such as metal phenates and metal sulphonates, it is desirable that 0.2–0.3 g of sample is collected for 50 g of alumina.

Note 7) When the procedure provides a petroleum oil content lower than but near classification criteria, perform the following operation after continuous elution with petroleum ether:

Replace the receiver flask with another one and perform the continuous elution with benzene or toluene⁽⁸⁾ for 8 hours. Measure an

IR spectrum of the benzene or toluene-eluted matter after determination of the quantity. If the eluted matter is identified as an aromatic substance from the IR spectrum, add the fraction for petroleum oil. The recovery rates of base oils by the continuous elution method are as follows.

Note 8) Continuous elution with toluene will require a heating mantle or other heating devices, together with a heat-retaining measure, such as covering the chromatography column with aluminum foil, etc., for a good reflux, due to insufficient heating of the water bath.

Recovery rates (%) of base oils, 16 hour-continuous elution with petroleum ether

Adsorbent	Neutral oil	Bright stock oil
Silica gel	99.4—99.8	98.1—98.5
Alumina	98.2—98.4 (99.4)*	91.7—93.6 (97.9—98.3)*

*Recoveries when an additional 8-hour continuous elution with benzene is conducted

4.4. Determination of Volatile Matter Content

This determination is to be carried out to correct the loss of base oil, when lubricating oil samples generate such losses through the procedure in 4.1 or 4.3.⁽⁹⁾

In parallel with the processes in 4.3.2, accurately weigh about 1–2 g of the original sample in a receiver flask for Soxhlet extraction and dry it in an oven at a constant temperature of 100±2°C to a constant weight. Determine loss in weight and calculate the volatile matter content from the formula below.

$$\%, \text{volatile matter} = \frac{L}{S_1} \times 100$$

Where—

S₁ : Weight (g) of test sample collected

L : Weight (g) of loss

Add the volatile matter content to the petroleum oils content, as the loss which occurred in the procedure in 4.1 or 4.3, except the case where the volatile matter is identified as a non-petroleum substance by comparing infrared spectra of the sample measured before and after this determination.

Note 9) In general, a loss of about 0.1% (volatile matter) occurs in lubricant base oils after drying at 100°C for 5 hours.

4.5. Calculation of petroleum oils content

Calculate the petroleum oils content in the original test sample from the following formula:

(1) For samples prepared by Pretreatment method I (in 4.1.)

$$\%, \text{petroleum oils} = \text{remains after polyisobutylene removal (\%)} \times \frac{P}{S} + \text{volatile matter(\%)}$$

(2) Others

$$\%, \text{petroleum oils} = \frac{P}{S} \times 100 + \text{volatile matter(\%)}$$

Where—

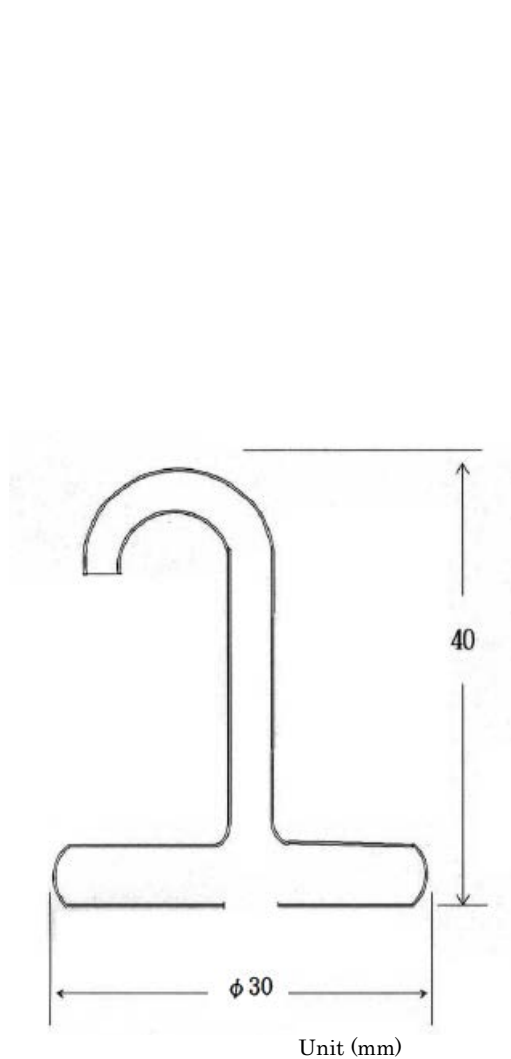
S: Weight (g) of test material collected in 4.2 or 4.3.2

P: Weight (g) of substance eluted in 4.3.2.

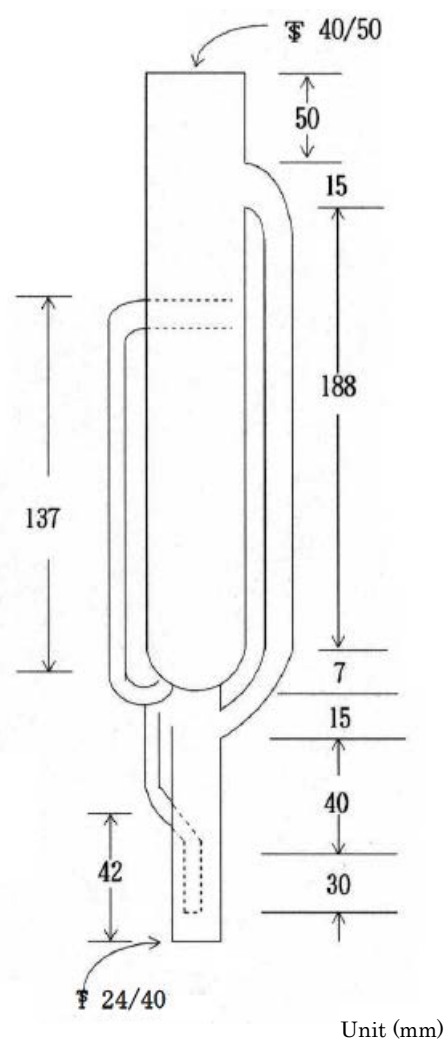
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Appendix 1



Example of aeration holder



Example of glass column for continuous elution column chromatography

Appendix 2

Table Adsorption properties of lubricating oil additives to silica-gel / alumina
(Eluent: Petroleum ether)

No.	Additives	Adsorbent	
		Silica gel	Alumina
1	Zinc dialkyl dithiophosphate	(-)	(-)
2	2,6-Di-tert.-butyl-p-cresol	(+)	(+)
3	Polyisobutylenes	(+ +)	(+ +)
4	Polymethacrylates	(+ +)	(+ +)
5	Polyalkenyl succinimides	(+)	(+)
6	Lead naphthenates	(-)	(-)
7	Chlorinated paraffins	(-)	(-)
8	Tricresyl phosphate	(-)	(-)
9	Barium, calcium phenates	(+)	(-) a
10	Barium, calcium sulphonates	(+)	(-) a
11	Basic, overbased Ba, Ca, Mg sulphonates	(+)	(-) a
12	Fatty oils	(-)	(-)
13	Sulfurised sperm oil	(+)	(-)
14	Methyl laurate	(-)	(-)
15	Polyoxyethylene nonyl phenol ether	(-)	(-)
16	Aliphatic diester oils (Dioctyl adipate)	(-)	(-)
17	Alkenyl sebacates	(-)	(-)
18	Silicone oils	(-)	(-)
19	Metallic soaps of fatty acids	(-)	(-)
20	Lauryl alcohol	(-)	(-)
21	Alkyl borates	(-)	(-)

(-) : completely adsorbed, (+) : partially eluted, (+ +) : fully eluted, a : completely adsorbed when the gel ratio is increased

* The adsorption properties shown in this table were results of testing for petroleum oil additives diluted with base oils at their typical concentrations in lubricating oils.