AEROSPACE RECOMMENDED PRACTICE

ARP5088™ **REV. C**

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Superseding ARP5088B

Test Method for the Determination of Total Acidity in Polyol Ester and Diester Gas Turbine Lubricants by Automatic Potentiometric Titration

RATIONALE

As a part of the SAE Five-Year Review process, several modifications have been incorporated including ASTM water purity, autosampler carousel language, and reduced solvent size.

1. SCOPE

The test method describes the procedure for determination of the total acid number (TAN) of new and degraded polyol ester and diester-based gas turbine lubricants by the potentiometric titration technique. The method was validated to cover an acidity range of 0.05 to 6.0 mg KOH g^{-1}. The method may also be suitable for the determination of acidities outside of this range and for other classes of lubricants.

1.1 Purpose

The TAN can be used to assist in the assessment of a lubricant during condition monitoring and for quality assurance/specification verification.

WARNING: This document may involve hazardous materials, operations, and equipment. This document does not purport to address all safety-related concerns associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. REFERENCES

2.1 Applicable Documents

The following publications form a part of this document to the extent specified herein. The latest issue of SAE publications shall apply. The applicable issue of other publications shall be the issue in effect on the date of the purchase order. In the event of conflict between the text of this document and references cited herein, the text of this document takes precedence. Nothing in this document, however, supersedes applicable laws and regulations unless a specific exemption has been obtained.

2.1.1 ASTM Publications

Available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, Tel: 610 832-9585, www.astm.org.

ASTM D1193	Standard Specification for Reagent Water

TO PLACE A DOCUMENT ORDER: **Tel: 877-606-7323 (inside USA and Canada)**
Tel: +1 724-776-4970 (outside USA)
Fax: 724-776-0790
Email: CustomerService@sae.org
SAE WEB ADDRESS: http://www.sae.org

For more information on this standard, visit
https://www.sae.org/standards/content/ARP5088C/

2.1.2 ISO Publications

Copies of these documents are available online at https://webstore.ansi.org/.

ISO 3696	Water Purity

2.2 Definitions

2.2.1 TOTAL ACID NUMBER (TAN)

The quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, is required to titrate the sample potentiometrically to an aqueous pH 11 end point.

2.2.2 CLEAN OIL/LUBRICANT

A sample of oil with a TAN less than 1.5 mg KOH g^{-1}. Most new oils and lightly stressed used oils will fall into this category. It is highly recommended that a sample size of 20 g is used for samples falling into this TAN range. However, it is recognized that the volume of samples available from service or laboratory tests may make this impractical, in which case the 2.5 g sample size may be used. Based on the 2013 round robin, the 2.5 g sample size resulted in higher variability and slightly lower TAN values (~0.1 mg KOH g^{-1}) compared to using a 20 g sample size.

2.2.3 DEGRADED OIL/LUBRICANT

A sample of oil with a TAN of 1.5 mg KOH g^{-1} or greater. Most highly stressed oils will fall into this category, particularly samples from laboratory oxidation tests and static engine tests. A sample size of 2.5 g shall be used for samples falling into this TAN range.

3. TEST REQUIREMENTS

3.1 Outline of Method

The test sample is dissolved in a mixture of toluene and propan-2-ol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a silver/silver chloride reference electrode. The cell voltage corresponding to the aqueous pH 11 buffer is taken as the end point.

3.2 Apparatus

3.2.1 Potentiometric Titration Apparatus

An automatic titrimeter capable of titrating to a fixed end point using either variable or fixed titrant increments.

The burette shall have a maximum size of 10 mL and a dispensing accuracy of ±0.01 mL.

3.2.2 Glass Indicating Electrode

Pencil type; a glass electrode specifically designed for nonaqueous titrations is recommended.

3.2.3 Reference Electrode

Pencil type; silver/silver chloride electrode filled with the lithium chloride electrolyte (see 3.3.4). Other electrodes, which can be shown to give equivalent performance on the samples to be tested, may be used provided they are filled with the lithium chloride electrolyte (see 3.3.4).

The electrode shall be made of glass and shall be provided with a movable joint in the form of a sleeve or plug to facilitate easy washing of the reference electrolyte cell. A double junction design is preferable with the electrolyte cells filled with the lithium chloride electrolyte (see 3.3.4).

3.2.3.1 Combination Electrodes

The glass indicating electrode and the silver/silver chloride reference electrode may be contained in one housing. The combination electrode requires only one electrode to be maintained instead of two. The combination electrode shall be suitable for nonaqueous titrations, shall have a sleeve diaphragm/junction on the reference compartment, and shall be filled with the lithium chloride electrolyte (see 3.3.4).

3.2.4 Titration Vessel

The vessel shall have a capacity of 100 to 250 mL and be inert to the reagents. Vessel size maybe dependent on the titration solvent amount utilized for blank and sample analysis in 5.5.

3.2.5 Stirrer

A stirrer with variable speeds and fitted with a propeller or paddle of chemically inert material. The stirrer must be electrically grounded (earthed).

NOTE: Some types of apparatus may be sensitive to interference by static electricity when the apparatus is approached by the operator. In these cases, the titration vessel should be surrounded with a close-fitting cylinder of copper gauze which is electrically grounded (earthed). Refer to the equipment manufacturer if in doubt.

3.2.6 Autosampler Carousel (Optional)

An autosampler carousel-type titration stand may be used for staging multiple samples for analysis. The number of sample vessels that can be utilized by an autosampler varies, depending on the volume capacity of the vessels being used. The use of an autosampler can increase the throughput and efficiency in the analysis of multiple samples in a given set.

3.3 Reagents/Materials

Use only reagents of recognized analytical grade (where available) and water conforming to ISO 3696 Grade 3 or ASTM D1193 Type I, II, or III.

3.3.1 Aqueous pH 4, pH 7, and pH 11 buffer solutions.

NOTE: These solutions must be replaced at regular intervals consistent with their stability or when contamination is suspected. Information relating to their stability should be obtained from the manufacturer.

3.3.2 Ethanol [98% min v/v] (C_2H_5OH).

3.3.3 Lithium chloride (LiCl).

3.3.4 Lithium chloride reference electrolyte.

Prepare a 1 M or 2 M solution of the lithium chloride (see 3.3.3) in the ethanol (see 3.3.2). Commercially available solutions may be used where available.

NOTE: Potassium chloride electrolyte must not be used to fill single junction reference electrodes or to fill the outer cell of a double junction reference electrode. The use of other electrodes could affect the precision. It is desirable to reserve the electrode for nonaqueous titrations.

3.3.5 Potassium hydrogen phthalate ($KHC_8H_4O_4$).

3.3.6 Potassium hydroxide (KOH).

3.3.7 Potassium hydroxide standard volumetric alcoholic solution, c(KOH) = 0.1 M.

Add 6.5 g ± 0.5 g of the potassium hydroxide (KOH) (see 3.3.6) to 1000 mL ± 10 mL of the propan-2-ol (see 3.3.8) in a 2-L flask. Boil gently under reflux for 10 minutes and then shake to ensure it dissolves completely. Cool and stopper the flask.

Allow the solution to stand in the dark for 2 days and then filter the supernatant liquid through a 5-µm PTFE membrane filter. Store in a suitable amber glass bottle. During dispensing, the solution must be protected from atmospheric carbon dioxide (CO_2) by means of a guard tube containing soda lime or soda nonfibrous silicate absorbent. The solution must not come in contact with cork, rubber, or saponifiable stopcock grease.

Standardize frequently enough to detect concentration changes of 0.001 M by potentiometric titration against 0.1 to 0.15 g of the potassium hydrogen phthalate (see 3.3.5). The latter should be dried for 2 hours at 105 °C, weighed to an accuracy of 0.0002 g, and dissolved in approximately 100 mL of carbon-dioxide-free water.

NOTE: Commercial methanolic, ethanolic, or propanolic-based potassium hydroxide solution may also be used.

3.3.8 Propan-2-ol (C_3H_7OH).

3.3.9 Titration Solvent

Add 500 mL ± 5 mL of the toluene (see 3.3.10) and 5 mL ± 0.2 mL of the water to 495 mL ± 5 mL of the propan-2-ol (see 3.3.8). The titration solvent should be made up in large quantities and its blank value determined daily by titration prior to use.

3.3.10 Toluene ($C_6H_5CH_3$).

3.3.11 Ammonium peroxodisulfate ($(NH_4)_2S_2O_8$).

3.3.12 Sulfuric acid (H_2SO_4), 95 to 98%.

3.3.13 Ammonium peroxodisulfate cleaning solution.

Weigh 8 g of the ammonium peroxodisulfate (see 3.3.11) into a glass beaker. Carefully add 100 mL of the concentrated sulfuric acid (see 3.3.12) and gently stir. Before use, the solution should be left overnight for the solid to dissolve completely.

4. PREPARATION AND MAINTENANCE OF THE ELECTRODE SYSTEM

Although the electrodes are not particularly fragile, they should be handled carefully at all times. The following procedures are very important because pH measurements will only be as good as the condition of the electrodes.

4.1 Preparation of Electrodes for Calibration

4.1.1 Glass Electrode

The glass electrode (see 3.2.2) should be wiped dry with a clean, soft absorbent tissue before use.

4.1.2 Reference Electrode

Remove the reference electrode (see 3.2.3) from the storage solution. Wipe the electrode with clean, soft absorbent tissue taking care not to disturb the lower sleeve/plug. Uncover the filling aperture(s) to allow the electrolyte (see 3.3.4) to diffuse freely during use. Gently release the lower sleeve or plug and drain a few drops of electrolyte to flush the glass joint. Check the electrolyte level(s) and refill as necessary. Immerse the electrode in water for 5 minutes to remove any surplus electrolyte adhering to the outside of the electrode and allow water to drain off.

4.1.2.1 If using a combination electrode (see 3.2.3.1), prepare it the same as in 4.1.2.

4.2 Testing of Electrodes

4.2.1 Prepare the electrodes as detailed in 4.1.

4.2.2 Immerse the electrodes in the aqueous pH 4, pH 7, and pH 11 buffer solutions (see 3.3.1) consecutively to establish electrode response, washing all the electrodes with water after each buffer. This should be performed daily and recorded permanently. The meter/electrode combination is suitable for use when the mV reading for the pH 7 buffer (see 3.3.1) and the relative slope for the pH buffers (see 3.3.1) are within the electrode manufacturer's tolerances.

4.3 Calibration Requirements

4.3.1 Determine the cell potential of the pH 11 buffer solution (see 3.3.1) daily. The reading obtained is taken as the end point for the titrations and must be entered into the instrumental program where this is not done automatically.

NOTE: The use of temperature correction is recommended. Due to the significant effect of temperature on the pH of the pH 11 buffer (see 3.3.1), it is desirable to keep this as close to the buffer manufacturer's calibration temperature as possible.

4.3.2 Conditioning of the Electrodes for Nonaqueous Titrations

Immerse the electrode assembly in the titration solvent (see 3.3.9) for a period of 10 minutes. Rehydrate the glass electrode by immersing the bulb in water for 2 minutes and then allow excess to drain off.

4.4 Storage of Electrodes

When the electrodes are not in use, immerse the lower half of the glass electrode (see 3.2.2) in water and the lower half of the reference electrode (see 3.2.3) in the reference electrolyte (see 3.3.4). Cover the filling aperture(s) of the reference electrode during storage.

Do not allow either electrode to dry out, especially the glass electrode.

If a combination electrode is used, store the electrode as stated by the manufacturer. Common storage solutions are water or the reference electrolyte (see 3.3.4). Cover the filling aperture(s) during storage.

4.5 Cleaning of Electrodes

4.5.1 Glass Electrode

When in regular use, clean the glass electrode (see 3.2.3) weekly by immersing the tip in 0.1 M hydrochloric acid for a minimum period of 12 hours. If more aggressive cleaning is required, immerse the electrode tip in the ammonium peroxodisulfate cleaning solution (see 3.3.13) for 5 minutes followed by a thorough wash with water. The ammonium peroxodisulfate treatment should be carried out routinely at monthly intervals when the electrode is in regular use.

4.5.2 Reference Electrode

Clean the reference electrode (see 3.2.3) as necessary by flushing with the propan-2-ol (see 3.3.8) followed by the reference electrolyte (see 3.3.4).

5. PROCEDURE

5.1 Test the electrodes and calibrate the automatic titrimeter (see 3.2.1) as detailed in 4.1, 4.2, and 4.3.

5.2 Prepare the electrodes for nonaqueous titration as detailed in 4.3.2.

5.3 Set up the apparatus in accordance with the manufacturer's instructions. It is suggested to limit the overall titration rate to less than 0.35 mL min^{-1} to not cause hydrolysis of the ester base stock by the hydroxyl ion. If the titration unit is only capable of performing fixed-rate titrations, set the titration rate to 0.1 mL min^{-1}.

Examples of suitable titrimeter methods are given in Appendix A.

5.4 The burette should be filled with the 0.1 M alcoholic potassium hydroxide solution (see 3.3.7) and the tip immersed approximately 25 mm in the titration solvent (see 3.3.9).

5.5 Perform a "blank" determination in duplicate on 125 mL ± 2 mL of the titration solvent (see 3.3.9) daily or immediately after changing to a fresh batch of the titration solvent (see 3.3.9). Take the mean of the two determinations as the "blank" titration. Alternatively, the "blank" determination can use 60 mL ± 1 mL of titration solvent rather than 125 mL ± 2 mL. The same titration solvent volume used for the "blank" determination must be used for the sample determination.

NOTE: The titration solvent amount used for analysis is either 125 mL or 60 mL. The alternative use of 60 mL was necessitated by modifications of available equipment. Two samples were tested using both titration solvent amounts by 11 laboratories between 2018 ("clean" sample) and 2020 ("degraded" sample). Based on these results, the 60 mL titration solvent amount has been included in this revision.

5.6 Ensure that the test sample is representative. Weigh (to the nearest 0.001 g) into the titration vessel, either 20 g ± 1 g of clean lubricants or 2.5 g ± 0.1 g of degraded lubricants and add 125 mL ± 2 mL (or 60 mL ± 1 mL) of the titration solvent (see 3.3.9).

5.7 Perform the titration using the procedure prescribed for the equipment taking care to limit the speed of stirring to avoid spattering or stirring air into the solution.

5.8 On completion of the titration, rinse the electrodes and burette tip with the titration solvent (see 3.3.9). Rehydrate the glass electrode (see 3.2.2) by immersing the bulb in water for 2 minutes and then allow excess to drain. If either of the electrodes require further cleaning proceed with the appropriate cleaning procedure detailed in 4.5.

5.9 As an additional option, steps 5.4 through 5.8 may be facilitated with the use of an autosampler carousel (see 3.2.6). Most autosamplers can be programmed to rinse the burette tip, stirrer, and electrode with titrant solvent, utilizing a built-in rinse ring, after each analysis is complete. A specified position on the carousel may be assigned for use as a "condition" vessel, containing water, to rehydrate the electrode bulb for 2 minutes in-between samples.

Store the electrodes for short periods (less than 0.25 hour) in the titration solvent (see 3.3.9) and for longer periods as detailed in 4.4.

NOTE: Do not allow the electrodes to remain immersed in the titration solvent (see 3.3.9) for longer than is necessary between titrations. This will keep the dehydration of the glass electrode (see 3.2.2) to a minimum.

5.10 If the resulting TAN falls outside the range for the sample size used (see 2.2.2 and 2.2.3), repeat the determination using the correct sample size.

6. EXPRESSION OF RESULTS

Most modern automatic titrimeters have integral calculation methods or can be programmed for a specific application. In either case, check that the calculation used is as detailed in 6.1.

6.1 Calculate the TAN, expressed in milligrams of KOH per gram of sample, using Equation 1:

$$\text{Total acid number} = \frac{(V_1 - V_0) \times c \times 56.1}{m} \qquad \text{(Eq. 1)}$$

where:

V_1 = volume, in milliliters, of the alcoholic KOH solution (see 3.3.7) used to titrate the test portion to the end point

V_0 = volume, in milliliters, of the alcoholic KOH solution (see 3.3.7) used for the blank titration

c = actual concentration, in moles per liter, of the alcoholic KOH solution (see 3.3.7)

m = mass, in grams, of the test sample

7. PRECISION

7.1 Clean Oils (20 g and 2.5 g Sample Size)

Repeatability: The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal, and correct operation of the test, exceed the following value only in one case in 20.

$$20\text{ g sample size} = 0.066(x)^{0.35} \qquad \text{(Eq. 2)}$$

$$2.5\text{ g sample size} = 0.047(x+1.447) \qquad \text{(Eq. 3)}$$

Reproducibility: The difference between two single and independent results obtained by different operators working in different laboratories on identical materials would, in the long run, exceed the following value only in one case in 20.

$$20\text{ g sample size} = 0.158(x)^{0.21} \qquad \text{(Eq. 4)}$$

$$2.5\text{ g sample size} = 0.45 \qquad \text{(Eq. 5)}$$

where:

x = mean of the two TAN results obtained

NOTE: Reproducibility for the 2.5 g sample size was found not to be dependent on the TAN result. This is only true for TAN values greater than 0.05 mg KOH g^{-1} and less than 1.5 mg KOH g^{-1}.

7.2 Degraded Oils (2.5 g Sample Size)

Repeatability: The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal, and correct operation of the test, exceed the following value only in one case in 20.

$$0.060(x-0.174) \qquad \text{(Eq. 6)}$$