AEROSPACE RECOMMENDED PRACTICE

ARP5991™ **REV. A**

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Superseding ARP5991

(R) Test Method for the Determination of Water Concentration in Polyol Ester and Diester Aerospace Lubricants by Coulometric Karl Fischer Titration

RATIONALE

The determination of the water content of polyol ester and diester aerospace lubricants is of importance in assessing the possibility of water corrosion of lubricant system components. Excessive amounts of water in these lubricants may also lead to hydrolysis of the lubricant, resulting in corrosion and wear of lubricated components and degradation of the lubricant properties. This SAE Aerospace Recommended Practice (ARP) has been tailored for determination of the water content in these types of lubricants. Revision A includes: (1) Incorporation of a rationale statement. (2) Removal of specific revision numbers in the reference ASTM standards. (3) Addition of ASTM D1193 reference in Section 2 (Applicable Documents). (4) Inclusion of the use of commercially available water standards for validation of the Karl Fischer apparatus/reagent system. (5) Revision of the repeatability criterion in 8.4. (6) Editorial changes for clarification of the procedure.

1. SCOPE

The test method describes the procedure for the direct determination of water concentration in polyol ester and diester based aerospace lubricants by commercially available automated coulometric Karl Fischer titration instruments. The method was validated to cover the water concentration range of 150 to 3500 µg/g. The method may also be suitable for the determination of water concentrations outside this range and for other classes of fluids; however, the precision statement shall not be applicable for such uses.

1.1 Purpose

Knowledge of the water concentration in polyol and diester aerospace lubricants is required to assess the possibility of water corrosion of lubricant system components. The presence of excess amounts of water may also result in hydrolysis of the lubricant, resulting in corrosion and wear of the lubricated components and degradation of the lubricant properties. Significant variability observed in inter-laboratory Karl Fischer test results for these lubricants highlighted the need for a standardized Karl Fischer test procedure, specifically suited for these lubricants.

2. 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.

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2.1 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 D6304	Standard Test Method for the Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration
ASTM D6300	Standard Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
ASTM D1193	Standard Specification for Reagent Water

3. TEST REQUIREMENTS

3.1.1 Outline of Method

An accurately weighed aliquot of the fluid sample is injected into the titration vessel of a coulometric Karl Fischer apparatus in which iodine for the Karl Fischer reaction is generated coulometrically at the anode. Upon the completion of the titration of the water in the sample, the electrometric end point sensor detects excess iodine, and the titration is terminated. The quantity of water is determined by the integration of the total amount of current consumed by the reaction, which, based on the stoichiometry of the reaction, is proportional to the molar concentration of water in the sample.

4. APPARATUS

4.1 Coulometric Karl Fischer Apparatus (Using Electrometric End Point)

A number of automated coulometric Karl Fischer apparatus consisting of a titration cell, platinum electrodes, magnetic stirrer, and a control unit are commercially available. The instructions for the operation of these devices are provided by the respective manufacturers and are not discussed in this document.

4.1.1 Syringes

Fine glass syringes with luer fittings and hypodermic needles are recommended. Disposable plastic precision syringes can be used for routine sample analysis but not for the validation. The bores of the needles shall be kept as small as possible but large enough to avoid problems arising from excessive back pressure or blocking while obtaining a sample. Suggested syringe sizes are as follows:

4.1.2 Ten microliters fine glass syringe graduated for readings to the nearest 0.01 µL or better. This syringe is used in the standardization step.

4.1.3 One and five mL capacities, accurate to the nearest 0.01 mL. A quality gas-tight glass syringe with a PTFE fluorocarbon plunger and luer fitting is recommended. Disposable plastic precision syringes can be used.

NOTE: Rinse all glass syringes and needles with anhydrous acetone (or equivalent) after cleaning. Then dry in an oven at 100 °C and store immediately in a desiccator.

4.2 Balance

An analytical balance with a resolution of 0.0001 g.

5. REAGENTS/MATERIALS

Reagent grade chemicals, conforming to the specifications of the Committee on Analytical Reagents of The American Chemical Society shall be utilized in all tests, unless indicated otherwise.

5.1 Karl Fischer Reagent

Standard commercially available reagents for coulometric Karl Fischer titration.

5.2 Cathode Solution

Standard, commercially available cathode Karl Fischer solution.

5.3 Octan-1-ol

ACS grade, >99% pure, <1% mass percent of water, <0.4% mass percent of evaporation residue. See Appendix A for the preparation of water saturated octan-1-ol.

5.4 Water

Reagent grade water as defined by Type IV of ASTM D1193.

5.5 Xylene

Reagent grade, <0.05% water.

5.6 Acetone

Reagent grade, <0.05% water.

6. PREPARATION OF APPARATUS

6.1 Follow the manufacturer's direction for the preparation and operation of the titration apparatus.

Table 1 - Test sample size based on water concentration

Expected Water Concentration (µg/g)	Sample Size (g)	Water Titrated (µg)
100 to 500	2.0	200 to 1000
500 to 1000	1.0	500 to 1000
>1000	0.5	>500

6.2 Turn on the apparatus and start the magnetic stirrer for a smooth stirring action avoiding the formation of a vortex. Allow the residual moisture in the titration vessel to be titrated until the end point is reached and the background current (or background titration rate) is constant and less than the value recommended by the manufacturer.

NOTE: High background current for a prolonged period may be due to moisture on the inside wall of the titration vessel. Gentle swirling of the vessel will wash the inside with electrolyte. Keep the titrator on to allow stabilization to a low background current.

7. VALIDATION

7.1 Validate the operation of the apparatus/reagent system by injecting a 10 µL sample of water saturated octan-1-ol (see Appendix A) or 1000 µg or 1 µL of water in the titration vessel as outlined in 8.3.1 for the test sample. Suitable, commercially available reference water standards in the 0.01 to 0.1% water content range may also be used for the validation of the apparatus/reagent. Suggested intervals for the validation are each time the apparatus is turned on and initially with fresh reagent.

7.1.1 The water concentration of the water saturated octan-1-ol should be within 47300 µg/g ± 1000 µg/g. The result of 1000 µg or 1 µL injection of water should be within 1000 µg ± 10 µg. The result for a commercial water standard should be within the limits specified by the manufacturer.

NOTE: If the fluid being analyzed is suspected to interfere with the titration, a water-spiked sample of the fluid can be utilized for the validation as outlined in Appendix A, Section A.9.

8. PROCEDURE

In case of referee samples, requirements outlined in Appendix B are to be applied in addition to the following:

8.1 Examine the fluid sample for the presence of free water droplets or emulsified water as evidenced by a hazy to milky appearance of the fluid. If free water droplets are observed, withdraw sample for titration avoiding free water droplets as per 8.3.1. If emulsified water is observed, shake the sample bottle vigorously by hand followed by ultrasonication in a bath at high frequency for 15 minutes, followed by shaking by hand before withdrawing a sample for titration as per 8.3.1.

8.2 Shake the sample bottle vigorously by hand prior to opening for sampling.

NOTE: Open the sample only to withdraw sample, otherwise keep the sample bottle tightly closed.

8.3 Add the test aliquot to the titration vessel using the following method:

8.3.1 Starting with a clean, dry syringe of suitable capacity (see Table 1 and the note below), withdraw and discard to waste at least one portion of the sample to rinse the inside of the syringe. Immediately afterwards, withdraw an additional portion of the sample, withdraw the syringe above the fluid surface and pull the plunger slightly to prevent the sample from dripping. Wipe the needle clean with dry paper tissue and weigh the syringe to the nearest 0.1 mg. Insert the needle through the inlet port septum, start the titration and inject the test specimen above the reagent surface. Before withdrawing the syringe through the septum, pull the syringe plunger back slightly to draw back any droplet of sample fluid that might have remained on the tip of the needle. Withdraw and weigh the syringe to the nearest 0.1 mg, to obtain the weight of the sample injected.

8.3.2 After the end point is reached, record the micrograms of water titrated from the digital readout of the instrument.

NOTE: In case the water concentration of the sample cannot be estimated, use a small trial portion of the sample initially and then adjust the aliquot size as needed for subsequent trials. If the water concentration can be estimated, then withdraw enough volume in the syringe for two trials. If the sample contains volatile materials, consideration must be given to the possibility of evaporation of these materials from the sample between runs. It may be necessary to withdraw a sample just prior to each run.

8.4 When the background current or titration rate returns to a stable reading as discussed in 6.2, withdraw an additional specimen into the syringe (or use the sample left from the previous withdrawal) and add to the titration vessel as per 8.3.1.

NOTE: If the difference in the results of the two trials is >5%, withdraw an additional (third) specimen and add to the titration vessel as per 8.3.1 and obtain a third data point for the water concentration. If the difference in the results of any one of the three trials differs by more than 5% from the average of the three trials, validate the equipment as per Section 7.

8.5 Replace the anode and cathode reagents when one of the following occurs and then repeat the preparation of the apparatus as in Section 6.

8.5.1 Persistently high and unstable background current.

8.5.2 Phase separation in the titration vessel or oil coating the electrodes.

NOTE: Phase separation and oil coating the electrodes can be due to insufficient solubility of the fluid in the anode reagent. Thirty percent xylene (by volume) mixed with the anode reagent has shown improved solubility for polyol ester based fluids.

8.5.3 The fluid level in the titration vessel reaches the maximum recommended by the manufacturer.

8.5.4 The instrument displays an error message that directly or indirectly suggests replacement of the electrolytes, as per the instrument's operating manual.

8.5.5 The reagents in the titrator are over 1 week old.

8.5.6 The result of validation with 1000 µg pure water is outside of 1000 µg ± 10 µg, with saturated octan-1-ol is outside of 47300 µg/g ± 1000 µg/g, or with a commercial water standard is outside of the allowed range.

8.6 Thoroughly clean the anode and cathode compartments with xylene if the vessel becomes contaminated.

9. CALCULATION OF RESULTS

Most automatic Karl Fischer apparatus have integral calculation methods or can be programmed for a specific application. Calculate the water concentration in µg/g of the sample as follows:

$$\text{Water, µg/g} = W_1/W_2 \tag{Eq. 1}$$

where:

W_1 = mass of water titrated, µg

W_2 = mass of sample used, g

10. REPORT

Report the water concentration to the nearest whole µg/g based on the average of the two (or three) trials for a fluid sample. The test report shall contain at least the following information relating to the analysis:

1. Identification of the fluid sample evaluated
2. Reference to the method
3. Results of the test
4. Date of the test

NOTE: The presence of free or emulsified water in the sample shall be mentioned in the report with a note indicating that the result does not take into account the free water in the sample.

11. PRECISION AND BIAS

The precision of this test method as determined by the statistical examination of the inter-laboratory test results is as follows:

11.1 Repeatability

The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials, would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$\text{Repeatability} = 0.003875\ (x)^{1.287}$$

where:

x = mean value of duplicate measurements

11.2 Reproducibility

The difference between the results obtained by different operators, working in different laboratories on identical test materials, would, in the long run exceed the following values in only one case in twenty:

$$\text{Reproducibility} = 0.02187\ (x)^{1.287}$$

where:

x = mean value of duplicate measurements

12. NOTES

12.1 Revision Indicator

A change bar (l) located in the left margin is for the convenience of the user in locating areas where technical revisions, not editorial changes, have been made to the previous issue of this document. An (R) symbol to the left of the document title indicates a complete revision of the document, including technical revisions. Change bars and (R) are not used in original publications, nor in documents that contain editorial changes only.

PREPARED BY SAE E-34 PROPULSION LUBRICANTS COMMITTEE

APPENDIX A - HELPFUL HINTS FOR COULOMETRIC KARL FISCHER WATER ANALYSIS

Following are some suggestions to obtain accurate and precise results by this test method. Some of these suggestions are also described in the test method but are reiterated here for easy reference.

A.1 All equipment should be thoroughly cleaned of moisture. Rinse all glass syringes and needles with anhydrous acetone (or equivalent) after cleaning. Then dry in an oven at 100 °C and store immediately in a desiccator until needed for use.

A.2 Keep the sample bottles tightly sealed before and after withdrawing a sample aliquot with a dry hypodermic needle.

A.3 Although standardization is not necessary in coulometric titrations, reagent performance can deteriorate with use, hence it should be monitored by accurately injecting either 1000 µg of pure water, 10 µL water saturated octan-1-ol, or a suitable, commercially available water standard, after the starting up of the equipment and after each reagent change. If the fluid is suspected to interfere with the titration, utilize the procedure in Section A.9 for the validation of the apparatus with the fluid.

A.4 Rinse the internals of the clean and dry syringe at least once with the sample and discard the aliquot before taking an aliquot for injecting in the titration vessel.

A.5 High background current for a prolonged period may be due to moisture on the inside wall of the titration vessel. Gentle swirling of the vessel will wash the inside with electrolyte. Keep the titrator on to allow stabilization to a low background current.

A.6 The frit separating the vessel compartments may get clogged with sample residue. Disassemble the apparatus and acid clean the frit per the manufacturer's recommendations. The reassembled apparatus should be prepared for use as in 6.2 and validated per Section 7.

A.7 Replace the anode and cathode reagents when one of the following occurs and then repeat the preparation of the apparatus as in 6.2 and validate per Section 7.

A.7.1 Persistently high and unstable background current.

A.7.2 Phase separation in the titration vessel or oil coating the electrodes.

NOTE: Phase separation and oil coating the electrodes can be due to the insufficient solubility of the fluid in the anode reagent. Thirty percent xylene (by volume) mixed with the anode reagent has shown improved solubility for polyol ester and diester based fluids.

A.7.3 The fluid level in the titration vessel reaches the maximum recommended by the manufacturer.

A.7.4 The instrument displays an error message that directly or indirectly suggests replacement of the electrolytes, as per the instrument's operating manual.

A.7.5 The reagents in the instrument are over 1 week old.

A.7.6 The result of validation with 1000 µg pure water is outside of 1000 µg ± 10 µg, with saturated octan-1-ol is outside of 47300 µg/g ± 1000 µg/g, or with a commercial water standard is outside of the allowed range.

A.7.7 Thoroughly clean the anode and cathode compartments with xylene or other solvent recommended by the manufacturer if the vessel becomes contaminated.

A.8 Procedure for the preparation of water saturated octan-1-ol (WSO) for the validation of the apparatus:

A.8.1 Mix five parts octan-1-ol with one part distilled water in a clean glass container over a magnetic stirrer using a Teflon stirring bar for 24 hours at room temperature. Let the mixture stand un-stirred for 3 days.