National Institute of Standards & Technology

Report of Investigation

Reference Material 8507

Moisture in Mineral Oil

Reference Material (RM) 8507 is intended for use in developing and validating methods for the determination of moisture in mineral oil or similar matrices. A unit of RM 8507 consists of five ampoules per unit with each ampoule containing 10 mL of petroleum lubricating oil.

Analytical Results

The reference value for the moisture content of RM 8507 is given below. It is based on a NIST modification to the volumetric method in ASTM Standard D 1533-88, Standard Test Methods for Water in Insulating Liquids (Karl Fischer Method) [1]. However, because the coulometric method in ASTM Standard D 1533-88 is widely used in industry, a consensus result obtained from the combined results two interlaboratory round robin studies conducted among 14 laboratories based on the coulometric method in ASTM Standard D 1533-88, is also included below. This consensus coulometric result, which was confirmed by NIST, also using the coulometric method, is biased low because the solvents used do not adequately dissolve the oil matrix [2].

Reference Mass Concentration Value of Moisture: 76.8 mg/kg ± 2.3 mg/kg[a]

(Consensus Coulometric Result of Moisture: 47 mg/kg ± 4 mg/kg)[b]

[a]The uncertainty of the reference value is an expanded uncertainty at the 95 % level of confidence, computed according to the ISO Guide [3].
[b]The uncertainty of the consensus result is also an expanded uncertainty at the 95 % level of confidence, computed according to the ISO Guide [3] and includes the differences between laboratories, differences within laboratories, and uncertainties associated with replicate measurements.

Expiration of Reference Value: The reference value of RM 8507 is valid, within the measurement uncertainty specified, until 31 December 2027, provided the RM is handled in accordance with instructions given in this Report of Investigation (see Instructions for Use). This reference value is nullified if the RM is damaged, contaminated, or modified.

The coordination of the technical measurements was under the direction of S.A. Margolis and S.A Wise of the NIST Analytical Chemistry Division.

The support aspects involved in the preparation, analysis, and issuance of this RM were coordinated through the Standard Reference Materials Program by T.E. Gills and B.S. MacDonald.

Gaithersburg, MD 20899
Certificate Issue Date: June 13, 1997*
3/27/92 (original certificate date); 5/7/96 (updated recommended value)
*This revision reports an expiration date and editorially changed "recommended" to "reference" value

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Standard Reference Materials Program

Consultation on the statistical design of the experimental work and evaluation of the data were provided by S.B. Schiller and R.C. Paule of the NIST Statistical Engineering Division.

The round robin exercises were conducted with the assistance of P.J. Griffin, H.C. Manger, and ASTM Committee D 27 on Electrical Insulating Liquids and Gases. Analytical measurements made by NIST were performed by S.A. Margolis of the NIST Analytical Chemistry Division.

INSTRUCTIONS FOR USE

Handling: This material should be used with caution around heat, sparks, pilot lights, static electricity, and open flame. Proper disposal methods should also be used. The ampoules are sealed under dry argon. After opening the ampoules, exercise care to avoid contamination with moisture (e.g., dry measuring devices and containers must be used). The Material Safety Data Sheet (MSDS) that accompanies this RM provides additional information on the material.

Storage and Use: Ampoules should be stored in the dark at room temperature. For the reference value to be valid within the stated uncertainty, samples of the material for analysis should be withdrawn from the ampoules immediately after opening and used without delay. The reference value is not applicable to material left in ampoules that have been stored after opening, even if they are resealed.

PREPARATION AND ANALYSIS

Preparation of RM 8507: The oil used in the preparation of RM 8507 was obtained from Tilley Chemical Co., Baltimore, MD as CORAY 22 oil manufactured by Exxon Corporation, Houston, TX. At NIST, the material was drawn from a barrel into a clean, dry bottle under an argon atmosphere. Aliquots of 10 mL were dispensed automatically from the bottle into argon-filled, dry ampoules, which were then sealed. The reference value therefore reflects the moisture content after processing at NIST and not the content as received from the manufacturer.

Analytical Methods: The reference value was established by a NIST modification to the volumetric Karl Fischer Method in ASTM Standard D 1533-88. The consensus value obtained in the round robin exercise is based on the coulometric Karl Fischer Method also contained in ASTM Standard D 1533-88. This ASTM standard permits the analyst to saturate the vessel solvent with oil before making any measurements and states that the oil layer needs to be reduced periodically to prevent the accumulation of a large upper layer of oil that is not completely suspended in the vessel solvent. Thus the moisture being titrated is in suspension rather than in a single phase solution

The process of titrating moisture in an oil suspension either coulometrically or volumetrically, leads to a large negative bias. This bias has been characterized in a study by NIST and is described in a recent publication [2]. The results of this study demonstrate that the accurate measurement of moisture in oil requires that the oil be completely dissolved in the vessel solvent; otherwise, when the solution in the titration vessel begins to undergo the transition from a single phase to a suspension, as much as 40 % to 50 % of the moisture (depending on the composition of the oil) is sequestered and is no longer accessible to the Karl Fischer reagent. To achieve complete solubilization of an oil-water mixture, adequate amounts of nonpolar solvents such as chloroform or toluene must be present. If they are not present in sufficient amounts, then only a fraction of the moisture present will be titrated.

The problem of the incomplete dissolution of the oil sample is not unique to coulometric solvents. The method of volumetric titration also requires the presence of chloroform or another suitable nonpolar solvent to measure all the moisture available for titration.

The coulometric method in ASTM D 1533-88 is the most common method used by industry for moisture determination in oil; therefore, a consensus value obtained from two round robin studies using this method was also established. The laboratories participating in these studies are listed below. All analyses in the round robin exercises were performed using coulometric Karl Fischer instrumentation and reagents routinely used in the participating laboratories. In the first exercise, each of the six participating laboratories analyzed single samples from four ampoules of the RM. In the second exercise, each of the 14 participating laboratories analyzed single samples from two ampoules of the RM. The results from both round robin exercises were combined and the consensus value calculated by an analysis of variance of the results. Analyses made at NIST using the coulometric method in ASTM D 1533-88 confirmed the consensus coulometric value.

Participants in RM 8507 Round Robin Exercises:

J. Angelo, Exxon Research & Engineering Co., Baytown, TX
R.A. Cherrillo, Shell Development Co., Houston, TX
G. Gauger, McGraw-Edison Power System, Franksville, WI
J. Greer, United Power Services Inc., Nashville, TN
P. Griffin, Doble Engineering Co., Watertown, MA
D. Jordon, Bonneville Power Administration, Vancouver, WA
J.P. Kinney, General Electric, Rome, GA
L. Leward, MET Testing Co., Baltimore, MD
C. Manger, Baltimore Gas & Electric Co., Baltimore, MD
D. Myers, Transformer Consultants, Talmadge, OH
L. Talarico, Cosa Instrument Co., Norwood, NJ
W. Teubert, Photovolt, Indianapolis, IN
J. Thomas, Big River Electric Corp., Henderson, KY
P. von Guggenberg, Massachusetts Institute of Technology, Cambridge, MA

REFERENCES

[1] ASTM D 1533-88 "Standard Test Methods for Water in Insulating Liquids (Karl Fischer Method)," ASTM Annual Book of Standards, **Vol. 10.03**, 189, (1993).

[2] Margolis, S.A., Amperometric Measurement of Moisture in Transformer Oil Using Karl Fischer Reagents, *Anal. Chem.*, *67*, pp. 4239-4246, (1995).

[3] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, (1993).