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**Committee D27 on Electrical Insulating Liquids and Gases
Subcommittee D27.03 on Analytical Tests**

Research Report RR #D27-1013

**Inter-Laboratory Study to Establish Precision Statements for ASTM
D4059, Standard Test Method for Analysis of Polychlorinated
Biphenyls in Insulating Liquids by Gas Chromatography**

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1998 ASTM D 1533 ROUND ROBIN COLLABORATIVE STUDY

A. PROGRAM DESIGN

Statistical calculations were performed on round robin data obtained by Method D 1533, "Water-in-Insulating Liquids by Coulometric Karl Fischer Titration", from a collaborative ASTM program conducted in 1998. A precision statement was developed using these data which included repeatability, reproducibility and the method detectability limit (MDL). The bias for the mineral oil data was not determined since there was no suitable reference standard for which the exact water content was known.

In addition, the precision and "estimated" bias of the round robin results for the three groups of water-in-alcohol (octanol or butanol) standards used in the collaborative program were determined. One standard was NIST SRM 2890 (SRM-1), water saturated octanol. The other two standards, water saturated octanol (INH-1) and water saturated butanol (INH-2), were prepared as in-house standards by the participants in the program. These standards were run before the water-in-oil round robin samples were measured, and then again after the water-in-oil samples were measured.

The original round robin data collected for the oil samples were reported in µg water/g oil, and that for the standards in µg water/10 µL of water saturated alcohol. The results from the statistical analysis of the oil samples are reported in units of µg/g (mg/kg, ppm), and that for the standards in mg/mL.

A.1 Laboratories

A total of 36 laboratories participated in this program and they are listed in Appendix B. Each laboratory was given a code number A, B, C, etc. A copy of the letter and data reporting forms (A and B) that were sent to the round robin participants are included in Appendix C.

A. 2 Samples

A total of nine oils were selected for the program as shown below. Six new oils and three used oils were selected for the collaborative program. The matrix of approximate concentrations is shown below. The oil samples were randomly coded so that each laboratory ran replicates of each sample for a total of 18 samples per laboratory.

Water, µg/g	New Oil-Shell Diala A			New Oil-Univolt 60			Used Oil ⁽¹⁾		
	S1	S2	S3	E1	E2	E3	U1	U2	U3
5 - 15	X, X			X, X			X, X		
25 -35		X, X			X, X			X, X	
35 -50			X, X			X, X			X, X

Note: (1) Doble Engineering provided the used oil. The new oils were provided by Exxon, USA and Shell Oil.

B. STATISTICAL ANALYSIS

Separate statistical analyses were performed on each of five data sets using the new ASTM D 6300 method (Release 3.0) which was obtained from David Lawrey of Committee D 02. The five data sets included the following:

1. SRM 2980 water saturated octanol data (Table 1)
2. In-house water saturated octanol data (Table 3)
3. In-house water saturated butanol data (Table 5)
4. Low water concentration data (Table 7)
5. All sample and lab water in mineral oil data (Table 9)

The low concentration data set (< 20 µg/g water) was the one used to calculate a Method Detection Limit (MDL). When laboratories did not report data, it was considered "missing", and therefore, could not be used in the analysis. The round robin data and the results of the statistical calculations are shown in Tables 1 to 10.

B. 1 Outlier Tests

Outlier tests are concerned with establishing uniformity in the repeatability and reproducibility estimates. Cochran's criterion at the 1% significance level was used to detect a *discordant result in a pair of repeat results*. Hawkins' test at the 1% significance level was used to detect either a discordant pair of results from a *laboratory on a particular sample* or a *discordant set of results from a laboratory on all samples*. These outlier tests are discussed in detail in ASTM D 6300.

C. PRECISION OF WATER SATURATED OCTANOL: SRM 2890

Table 1: contains the round robin data for replicate measurements made on each SRM water-saturated-octanol standard before running the oil samples, and again on a second SRM sample after running all the oil samples.

Table 2: contains missing or rejected outliers removed at the 1% level (99% probability) and the final statistics for precision and bias.

The ASTM repeatability for SRM 2890 was 2.43 mg/mL and the reproducibility was 7.47 mg/mL. The bias, based on a NIST certified reference value of 39.24 mg/mL was 0.65 mg/mL.

D. PRECISION OF IN-HOUSE WATER SATURATED OCTANOL: INH-1

Table 3: contains round robin data for duplicate measurements made on an in-house INH-1 water saturated octanol sample before and after running all the oil samples.

Table 4: contains missing or rejected outliers removed at the 1% level (99% probability) and the final statistics for precision and bias.

The ASTM repeatability for this sample was 4.39 mg/mL, twice the value measured for the SRM 2890 octanol standard. The reproducibility of the in-house standard was 7.30 mg/mL, about the