Supplemental Data and Statistical Analysis in Support of Method Equivalence of ASTM D7575 Solventless Oil and Grease and EPA Method 1664A

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Introduction

I am a professional statistician with over 30 years of experience in applying statistics to the environmental and biotechnology fields. In the early 1990s I was a statistical consultant to the US EPA Office of Water and provided statistical and data analyses of laboratory measurement data for Oil and Grease in the EPA Freon Replacement studies, including the Phase 1(US EPA, 1993), Phase 2(US EPA, 1995) and Validation (US EPA, 1995) studies that led to EPA Method 1664A (US EPA, 2000), in work done through SRI International and Dyncorp/VIAR (EPA Sample Control Center). These analyses formed the basis for the statistical tests of equivalence between analytical methods that is presented in the Analytical Method Guidance for EPA Method 1664A Implementation and Use (40 CFR part 136) (US EPA, 2000).

I was recently asked to examine data and analyses performed by Orono Spectral Solutions comparing their proposed new method ASTM D7575 Solventless Oil and Grease (ASTM International, 2010) to EPA Method 1664. A validation study was performed analyzing 14 environmental samples from a variety of facilities, with a minimum of 3 replicate analyses on each sample by each method (2 of the samples had 7 replicates each). The breadth of the samples [though not as many] is consistent with the intent of the samples of the previous EPA oil and grease development studies. Per EPA Office of Water's request for as much comparability information as possible even beyond that used to develop the ASTM D7575 method, OSS also provided 3 additional samples from additional sample sources analyzed in triplicate by each method. During the ASTM development process, these data were statistically analyzed by OSS and submitted previously. After identifying and removing 2 outlier values in deviation using the Grubbs statistical outlier test (per ASTM E178 Standard Practice for Dealing with Outlying Observations (ASTM International, 2008)), the test of method equivalence showed no significant difference between the results of the two methods.

I have reviewed the statistical analyses performed by OSS and their calculations are a correct implementation of the equivalence test given in the Guidance. While the use of the Grubbs test is not specified in the Guidance, the implementation used by OSS is formally correct.

I have performed additional statistical analyses which support the acceptance of the ASTM D7575 method as equivalent to EPA method 1664, and which do not rely on

outlier removals based on deviation to demonstrate method equivalence between the two methods.

Additional Data

The ASTM D7575 validation study data show very small relative precision in the Method 1664 results reported by the laboratory performing the study analyses of just over 5% relative standard deviation. These could reflect the performance of an experienced lab performing all analyses sequentially in a single session, but are far more precise than all previous reports of Method 1664 performance, as reported in the EPA Phase 1, Phase 2 and Validation studies. Basing the method equivalence test solely on these data makes the test of equivalence of the new method unduly difficult.

Accordingly, data from the 3 EPA studies (Phase 1, Phase 2, and Validation) on Method 1664 as made publically available from EPA were incorporated into the analysis in order to provide a more representative estimate of the precision of EPA Method 1664.

Notes on the data are included in an Appendix below. No data from the ASTM D7575 studies were excluded in this analysis. Two samples in the EPA Phase 1 study had their results removed from analysis based because of extreme within-sample variation of the Method 1664 results, as discussed in the Appendix, but this makes the results shown below more stringent in testing ASTM D7575 for method equivalence.

Analysis

Relative precision estimates for each data source and method were computed based on the Root Mean Standard Error (RMSE) of the natural logarithm of replicate concentration analyses for each sample for each method. The results are shown in Table 1, which shows the RMSE and the associated degrees of freedom (DF) for each estimate, plus the derived estimate of Relative Precision for that method calculated as

$$\sqrt{e^{RMSE^2}-1}.$$

The variability estimated for EPA Method 1664 is much higher in previous studies than in the ASTM Validation studies. The statistical significance of this difference can be tested with an F-test based on the ratio of the squares of the corresponding RMSEs, and deriving significance with an F-table with the corresponding numerator and denominator degrees of freedom. Results are shown in Table 2, which shows the F-ratio for each comparison and the associated 2-sided achieved significance level (p-value). With or without the auxiliary ASTM samples, the relative precision on Method 1664 is highly statistically significantly different (less) in the ASTM studies from that reported in prior EPA studies.

Table 1. Relative Precision Estimates

Study	Method	RMSE	DF	Relative Precision
ASTM Validation Study	ASTMD7575	0.115565	34	11.60%
ASTM Validation Study	EPA1664	0.052842	34	5.29%
ASTM Validation Study + Auxiliary Samples	ASTMD7575	0.108972	40	10.93%
ASTM Validation Study + Auxiliary Samples	EPA1664	0.051248	40	5.13%
EPA Prior Studies	EPA1664	0.170952	143	17.22%

Table 2. Comparison of Precision for EPA1664 Between Studies

Comparison	F-ratio	2-sided p-value	Significance
ASTM Validation Study vs EPA Prior Studies	10.466	1.93E-11	Highly Significant
ASTM Validation Study + Auxiliary Samples vs EPA Prior Studies	11.127	1.35E-13	Highly Significant

The estimates of method precision from each method form the denominator of the method equivalence test, and therefore use of this unrepresentative low estimate for Method 1664 precision leads to an unfair basis of comparison between the two methods. In order to perform a method equivalence test for ASTM D7575 based on a more representative estimate of Method 1664 precision, data from the EPA prior studies were used to supplement the ASTM data as the basis for the method equivalence test.

The test of method equivalence given in the Guidance is, statistically, an ANOVA test for the interaction term in the 2-way ANOVA of method and sample on the logarithms of the measured concentrations. Results of this ANOVA can be computed despite the absence of ASTM D7575 data on the EPA samples, those samples contribute solely to the residual root mean square error of the model, which is used to calculate the denominator in the F-test for interaction. The numerator is based only on the comparisons between the methods shown in the ASTM data sets, and is unchanged by the inclusion of the EPA data. Analyses were performed using model-fitting procedures in the JMP statistical software package (SAS Institute Inc., 2009), which, while producing results compatible with the calculations given in the Guidance for complete data with equal numbers of measurements across samples and methods, also allows the appropriate accounting for data where different

numbers of measurements are available for different samples or measurements are available only for one method on some samples.

Results of the analyses of the extended data sets are shown in Table 3, including the numerator Sum of Squares (SS) for Interaction, the model residual root mean square error (RMSE), the associated degrees of freedom in each term, and the F-ratio and achieved p-value for each analysis.

Table 3. Tests of Equivalence of ASTM D7575 and EPA Method 1664

	ASTM Validation Study + EPA Prior Study	ASTM Validation Study + Auxiliary Samples + EPA Prior Study
SS (Interaction)	0.327931	0.486488
DF (Interaction)	12	15
RMSE	0.149694	0.146088
DF (Error)	211	223
F-ratio	1.2195	1.5197
p-value	0.2711	0.0995
Significance	Not Significant	Not Significant

With or without the Auxiliary Samples, ASTM D7575 is not found to show significant method variation from EPA Method 1664 and therefore passes the Method Equivalence Test.

Conclusion

The analysis presented here shows that the ASTM D7575 Solventless Oil and Grease method is statistically equivalent to EPA Method 1664A when considered in light of previous well-known precision data reported for EPA Method 1664A.

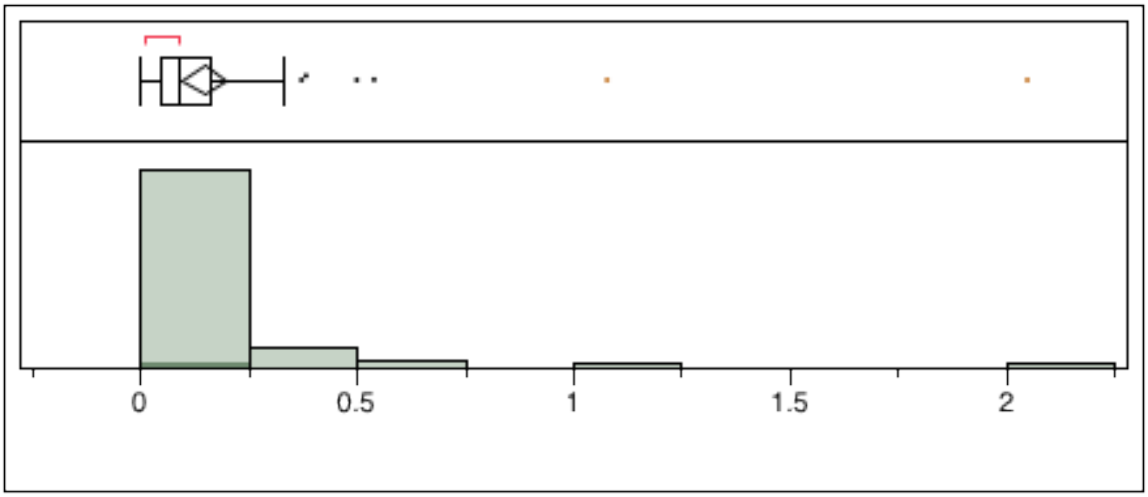
In my interest as a concerned citizen I would hope that that, given equivalence, EPA can provide users a solventless / greener alternative to the use of environmentally unfriendly and hazardous n-hexane as specified in Method 1664. Especially since the current solid-phase extraction version of EPA 1664 was adopted WITHOUT ANY comparability data because of the positive attributes it would provide (time savings, solvent use) over the liquid – liquid extraction procedure of EPA 1664.

Appendix – Notes on Data

Data for the EPA Validation study consisted of analysis of multiple splits of two physically pooled samples, one from the Petroleum industry and one from other industries (Non-Petroleum). For purposes of the statistical analysis here, each sample split was treated as a separate sample, each with 3 replicate analyses.

Two of the EPA samples in the Phase 1 study (22232 and 23111) had extremely large standard deviations among their Method 1664 analyses, as shown in the histogram in Figure 1. Data for these samples were removed from the analysis. (Note this makes the tests performed here more stringent.)

Figure 1. Distribution of Std Dev(Log_Conc, EPA1664)



One of the ASTM Validation samples (sample 7) consistently showed results well below the Method DL using both methods, and was excluded from the analysis.

Results shown in the EPA studies as "-" were excluded from the analysis.

All Method 1664 results analyzed here, both ASTM and EPA studies, were obtained using the liquid – liquid extraction version of the method.

Data were analyzed using the JMP statistical software package, version 9, produced by SAS Institute, Inc.

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