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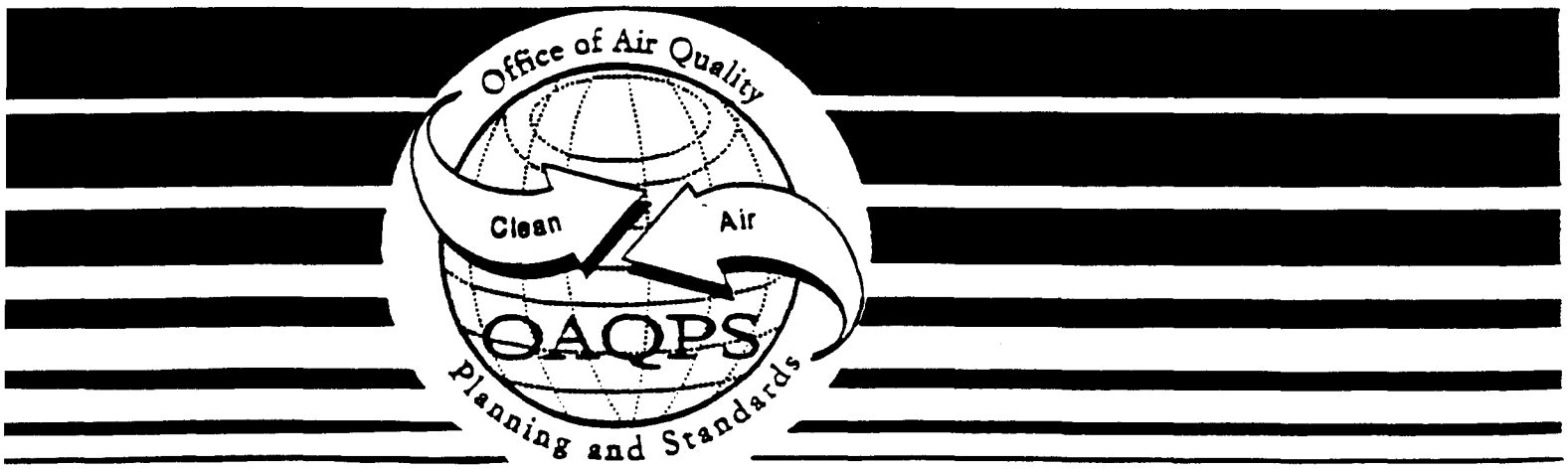
Round Robin Study



FINAL SUMMARY REPORT
ON
EVALUATION OF THE WATER-BASED COATING METHOD (ATD-FID)

by

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TABLE OF CONTENTS

Page

Section 1. Introduction 1

Section 2. Summary and Conclusions 3

Section 3. Recommendations 6

Section 4. Procedures 8

- Selection of Laboratories 8
- Selection of Test Paints 11
- Laboratory Kick-Off Meetings 13
- Overview of ASTM E691 16

Section 5. Results and Discussion 19

- Equipment Performance 19
- Laboratory Performance 21
- QA Activities 24
- Problems Encountered With Draft Method 27
- Comments from Laboratories 28
- ASTM E691 Results 31

References 43

APPENDIX A. MSDS SHEETS FOR STUDY PAINTS AND AVERAGE RELATIVE SENSITIVITY CALCULATIONS

APPENDIX B. LABORATORY KICK-OFF MEETING HANDOUT

APPENDIX C. ASTM STANDARD PRACTICE E691-92

APPENDIX D. LABORATORY DATA SHEETS

LIST OF TABLES

Table 4.1. Six Participating Laboratories 10

Table 4.2. Coatings Purchased for Interlaboratory Study 12

Table 4.3. Wt% VOC Results for Paint Samples 12

LIST OF TABLES
(Continued)

Page

Table 4.4. Materials Supplied to Participating Laboratories 15

Table 5.1. GC and Integrator Systems Used in Interlaboratory Study 20

Table 5.2. Laboratory QC Check Results 22

Table 5.3. Average Paint Relative Sensitivities Used by Laboratories 24

Table 5.4 Comparison of Wt% VOC_c Calculated Using Lab and Battelle RS_{avg} 24

Table 5.5. Results of Audit Paint 1403-0100, Ultra Egshell White 26

Table 5.6. Results from M24 Audit Samples 26

Table 5.7. Laboratory Comments on Draft Method 28

Table 5.8. Paint 4020-1000 Wt% VOC_c Results 32

Table 5.9. Paint 1403-0100 Wt% VOC_c Results 33

Table 5.10. Paint 4206-0100 Wt% VOC_c Results 33

Table 5.11. Paint MS1-6659A Wt% VOC_c Results 34

Table 5.12. Precision Statistics 40

Table 5.13. Precision Statement 42

LIST OF FIGURES

Figure 5.1. Mean Wt% VOC_c Results from Paint 4020-1000 by Laboratory 34

Figure 5.2. Mean Wt% VOC_c Results from Paint 1403-0100 by Laboratory 35

Figure 5.3. Mean Wt% VOC_c Results from Paint 4206-0100 by Laboratory 35

Figure 5.4. Mean Wt% VOCc Results from Paint MS1-6659A by Laboratory 36

LIST OF FIGURES
(Continued)

Page

Figure 5.5. h - Laboratories within Paints 38

Figure 5.6. h - Paints within Laboratories 38

Figure 5.7. k - Laboratories within Paints 39

Figure 5.8. k - Paints within Laboratories 39

Figure 5.9. Standard Deviations of Repeatability and Reproducibility Versus Mean Wt% VOC_c 41

Section 1
Introduction

To reduce the formation of ozone, the Environmental Protection Agency (EPA) regulates volatile organic compounds (VOC) from a number of facilities and materials. One category of materials is coatings and inks. The current EPA regulations require the use of EPA Method 24 to determine the VOC content of coatings and inks.

Method 24 indirectly determines the VOC content of a coating by measuring the coatings volatile content using the American Society for Testing and Materials (ASTM) method D 2369, water content by ASTM methods D 3792 or D 4017 and exempt compounds content by ASTM D 4457. The VOC content is calculated as the difference of the volatile content minus the water content and exempt content. The precision of Method 24 is poor if the water content is much larger than the VOC content.

Under a previous contract with Entropy (EPA contract 68D20163, work assignment Numbers 3-05 and 4-02), EPA developed a method for measuring the VOC content of water-based coatings directly rather than indirectly as in EPA Method 24. In this method, a Perkin-Elmer Model ATD-400 automated tube desorber is used to thermally desorb the volatiles from a weighed sample of coating, and a flame ionization detector on a gas chromatograph (GC) is used to estimate the total amount of VOCs in the volatilized material.

The purpose of this project was to conduct an interlaboratory study to evaluate the draft water-based coating method. A total of six laboratories participated in the interlaboratory study. Each of the laboratories was required to analyze four different water-based coatings following

the procedure described in the draft method. The results from the participating laboratories were analyzed using the statistical procedures described in ASTM E 691, Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.

Section 2
Summary and Conclusions

The four paints chosen as samples for the interlaboratory study included the following types of water-based coating: one automotive paint, one wall and trim enamel, one interior/exterior architectural paint, and one interior/exterior primer. The water contents of these paints ranged from 30% to 54% and the weight percent VOC levels ranged from 2.9% to 15.4%. The weight percent VOC content of the test paints was stable during the course of the study.

A total of six laboratories participated in the interlaboratory study of the draft water-based coating method. In the search for these laboratories, no laboratories were found that had the Perkin-Elmer ATD-400 which is the required instrument for the draft method. The many laboratories that plan to perform this method in the future will need to lease or buy the ATD-400. Presently, Perkin-Elmer is the only firm that leases ATD-400 instruments.

Mechanically, the single Perkin-Elmer ATD-400 system used for the interlaboratory study proved to be very reliable. The automated tube loading system mis-loaded only one tube during the entire study. After the ATD-400 focusing trap was packed with Tenax GR and Carbopak B sorbent as required by the draft method, it was found to be very difficult to install into the instrument. At one of the laboratories, the sorbent bed migrated so that it was no longer inside the cooled region of the trap; however, this migration did not have any significant affect on the test results. The laboratory personnel were able to learn how to operate the ATD-400 with only one or two hours of training.

In general, all six of the laboratories were able to follow the analytical portion of the draft method with a minimum amount of additional instruction from Battelle. All of the laboratories were able to prepare the standards and samples and to perform the paint analyses without any major difficulties. Blank levels were not found to be a problem during the course of the interlaboratory study. All of the laboratories achieved valid calibrations on the first try. The %RSD limits in the draft method were found to be reasonable.

The data analysis and calculations section was found to be the area of the method where errors were made by the laboratories. In particular, the various calculations necessary to compute the corrected weight percent VOC (Wt% VOC_c) led to the most errors by the laboratories. Laboratory personnel who did not have chemistry backgrounds, such as quality assurance personnel, had a difficult time with these calculations and required additional guidance from Battelle. Laboratory 1 did find an error with equation 13.2 in the draft method. The weight percent conversion in this equation is not correct.

The mean Wt% VOC_c measured by the six laboratories were very consistent for each of the four test paints. There was also good agreement between the laboratory Wt% VOC_c values and those measured by Battelle. Since the Battelle measurements were made on a separate ATD-400 instrument from the one used by the laboratories, these results indicated there was no evidence of any instrument bias with the draft method. The consistency of the Wt% VOC_c results suggest that the use of different gas chromatographs and chromatographic data systems in the study did not have a significant affect on the results.

The Wt% VOC_c results were analyzed using the statistical procedures described in ASTM E 691. None of the laboratories were found to have *h* statistic (a measure of between-laboratory consistency) above the critical values; therefore, there was not any evidence to show that any one of the laboratories produced biased data relative to the other laboratories in the study. For the *k* statistic (a measure of within-laboratory consistency), only one paint at laboratory 5 was found to be above the critical value. No calculation errors or physical evidence

of any instrument or procedures problems were found for this paint, so it was retained in the precision analysis of the method.

From the ASTM E 691 analysis of the study data, precision statistics were determined for the draft method. The 95% repeatability limit for the method ranged from 0.15 - 1.32, while the 95% reproducibility limit ranged 0.49 - 3.57. These limits represent the difference between any two measurements at the same laboratory (repeatability) and the difference between any two measurements taken at different laboratories (reproducablity) with a 95% confidence. A precision statement was drafted for the water-based coating method.

Section 3
Recommendations

The largest source of errors and questions in the draft method were the portions involving the calculation of the correction factor (RS_{avg}) for the corrected weight percent VOC (Wt% $VOC_{c)}$. These calculations require some knowledge of chemistry, because functional groups in the chemical structure of the VOC paint components have to be identified and counted. In the interlaboratory study, it was found that laboratory personnel, who did not have a chemistry background, had a difficult time with these calculations. Considering the errors found with this portion of the draft method, all laboratories should be required to submit these calculations along with their data. Only by checking these calculations will it be possible to assure the draft method is being applied consistently. With the number of calculations performed in the draft method, more guidance needs to be included on the number of significant figures that should be reported.

One way to simplify the calculations would be to tabulate the relative sensitivity (RS_i) for the most common VOC components in water-based coatings and put them in a database. From this database, the laboratories performing the draft method could select the RS_i values that they need and calculate the final RS_{avg} value for the water-based coating. The calculation of the RS_{avg} is a calculation that every laboratory should be able to perform. Constructing the RS_i database would free the laboratories from having to make the chemical calculations and eliminate a source of error in the method.

The draft method does not give any guidance on how to apply the approximately 25 µL of coating to the PTFE (polytetrafluorethylene - type of Teflon®) liners. For this study, a procedure involving a disposable 1 mL syringe with a luer tip and a 22 gauge luer hub needle

was used by the laboratories to load the paints onto the PTFE liners. This method of loading the PTFE liners worked well enough that it should be added to the method.

In the kick-off meetings, it was found that pass levels for the standard calibration and quality control check standard were scattered over several pages of the draft method. The draft method would be easier to follow if all of this information were combined into the same section of the method. Also, a table showing the pass levels of the standards would make the method much easier to follow.

Section 4
Procedures

In this section, the key procedures that were used to conduct the interlaboratory study are discussed. These include the procedures used to select the laboratories and the test paints. The training and instructions given to the participating laboratories in the kickoff meeting are described. A brief overview of the ASTM standard practice (E691) that was used to evaluate the results of the interlaboratory study is given.

Selection of Laboratories

A search was conducted to identify six laboratories that would participate in the interlaboratory study. Three different sources were used to identify laboratories. The first was a list of laboratories that had participated in a previous round robin study (1995 U.S. EPA Report) of coating samples for U.S. EPA. The second source was the yellow page listings of paint laboratories, testing laboratories, and paint manufacturers in the Columbus, Cleveland, Cincinnati, and Dayton, Ohio metropolitan areas. The third source was an Internet search of paint laboratories and paint manufacturers. Battelle attempted to identify laboratories to participate in the interlaboratory study based on an evaluation of the following factors, in decreasing order of importance:

- Experience in analyzing paint samples - Laboratories with more demonstrated experience were preferred

- Cost to participate - Laboratories willing to participate at their own expense were preferable to laboratories requiring reimbursement for participation
- Access to ATD-400 - Laboratories with an ATD-400 system would be preferable to laboratories without
- Proximity to Battelle - To save travel/equipment shipment expenses

Initially eight laboratories were identified that would be willing to participate. None of these laboratories nor any of the other laboratories that were contacted had the Perkin-Elmer ATD-400 system that is necessary to perform the draft method. To resolve this problem, a search was done to determine if an ATD-400 could be leased for use in the interlaboratory study. The only lease source found for the ATD-400 was Perkin-Elmer itself. Arrangements were made to lease an single ATD-400 system from Perkin-Elmer that could be used by the laboratories to perform the draft method.

The list of laboratories was reduced to six as a result of scheduling conflicts and a desire to minimize shipping costs for the ATD-400 system. The final list of participating laboratories is shown in Table 4.1. Each laboratory was sent a letter describing the interlaboratory study in more detail. In this letter, the laboratories were told that their anonymity would be protected. In reporting the results to U.S. EPA, each laboratory would be assigned a number (1 - 6). The participation of the laboratories would be recognized in the report, but the results would only reference the number assigned to the laboratories. Also included with the letter was a Memorandum of Agreement that the laboratories had to sign and return.

Table 4.1. Six Participating Laboratories

Participating Laboratory	Laboratory Type
South Coast Air Quality Management District 21865 East Copley Drive Diamond Bar, California 91765-4182 Contact: Rudy Edden Phone: 909-396-2391 Joan Niertit Phone: 909-396-2174	District Air Quality Laboratory
Dexter Coating Systems 1 East Water Street Waukegan, Illinois 60085 Contact: Roger Brown Phone:847-625-3320	Coating and Adhesive Manufacturer
Yenkin-Majestic Paint Corporation 1920 East Leonard Ave Columbus, Ohio 43236 Contact: Phillip Boadt Ron Ducker – ext 323 Phone: 614-253-8511	Paint Manufacturer
CTL Engineering 2860 Fisher Rd. Columbus, Ohio 43204 Contact: Richard Herrold Phone: 614-276-8123	Engineering and Product Testing Laboratory
PPG Industries, Inc. 4325 Rosanna Dr. Allison Park, PA 15101 Contact: Joseph Benga Phone: 412-492-5511	Paint Manufacturer
Wilson Environmental Laboratories, Inc. 410 Venture Drive Columbus, Ohio 43081 Contact: Eric Layman Phone: 614-431-0010	Environmental Service Laboratory

Selection of Test Paints

Battelle was required by U.S. EPA to obtain at least six water-based coatings with varying water concentrations that could be used as test coatings for the interlaboratory study. The EPA work assignment manager (WAM) supplied Battelle with a list of coatings that had been used in a previous round robin study (1995 U.S. EPA Report) and a draft report on the development of the draft water-based coating method that also listed several coatings. A number of these coatings were not found to be available anymore. Several of the manufacturers were reluctant to provide information to Battelle on the ingredients of the coatings when they found out the study was being sponsored by U.S. EPA. The search for the paint samples then turned to local paint suppliers in Columbus, Ohio. These paint suppliers were much more willing to share information about their products. Material safety data sheets (MSDS) were obtained on a number of different types of water-based paints such as automotive paints, architectural paints, primers, and wall paints. A total of six water-based paints were chosen to represent a wide variety of paint types as well as varying water concentrations. These paints were purchased in one gallon cans from two suppliers in Columbus, Ohio. Table 4.2 lists the six paints that were purchased as well as a description of the paints and the paint manufacturers. An MSDS sheet was obtained for each paint. These MSDS sheets can be found in Appendix A. Also shown in Appendix A are the calculations for the average relative sensitivities (RS_{avg}) used in the draft method to calculate the corrected weight percent VOC of the coatings. For these calculations, if the weight percent of a particular VOC was given as a range on the MSDS sheet, the middle value of the range was used for the average relative sensitivity calculations.

Of the six candidate paints, U. S. EPA had instructed that four were to be chosen for actual use in the interlaboratory study. As part of the decision making process in selecting the study paints, all six of the water-based paints were analyzed at Battelle following the procedures described in the draft method. The Perkin-Elmer ATD-400 thermal tube desorber leased for the study was used for these analyses. Table 4.3 lists the uncorrected weight percent VOC (Wt% VOC_u), the corrected weight percent VOC (Wt% VOC_c) measured for each paint, and the RS_{avg} from Appendix A used to calculate the Wt% VOC_c. Battelle and the WAM chose four paints that would be represent the range of Wt% VOC_c found in the paint analyses. The coatings that

were selected for use in the interlaboratory study were: MS1-6659A, 1403-0100, 4206-0100, and 4020-1000.

Table 4.2. Coatings Purchased For Interlaboratory Study

Coating ID (% water)	Identity	Product Use	Manufacture
MS1-6659A (54.0%)	Silver Waterborne Industrial Enamel	Automotive Paint	Martin Senour Paints
MS1-6660A (43.9%)	Gray Waterborne Industrial Enamel	Automotive Paint	Martin Senour Paints
1403-0100 (30-40%)	Ultra Eggshell White Acrylic	Wall and Trim Enamel	ICI Dulux Paints
4206-0100 (30-40%)	White Devflex Waterborne Semi-gloss Enamel	Interior/exterior Architectural Paint	Devoe Coatings
4020-1000 (30-40%)	White DTM Waterborne Primer	Flat Interior/Exterior Primer	Devoe Coatings
25524 (39.1%)	White Water-Reducible Acrylic	Traffic Paint	ICI Performance Coatings

Table 4.3. Wt% VOC Results for Paint Samples

Coating ID	Sample Number	Wt% VOC_u	RS_{avg}	Wt% VOC_c
MS1-6659A	4	13.7	1.019	13.4
MS16660A	4	17.1	1.022	16.7
1403-0100	14	3.28	0.837	3.91
4206-0100	4	10.4	1.239	8.43
4020-1000	4	3.28	1.359	2.41
25524	4	2.43	0.649	3.74

For the interlaboratory study, the four test paints were transferred from the one gallon cans into smaller vials that would be provided to the participating laboratories. This transfer procedure involved first shaking the gallon of each paint on a commercial paint shaker. Next 60 cc polypropylene disposable syringes were used to transfer each paint from the one gallon cans to 4 dram glass vials. These syringes had a large opening (8 mm) in the syringe tip and were used without a needle to minimize the chances of causing separation between the solid and liquid portions of the paint. Each syringe was filled by immersing the syringe tip approximately four inches below the surface of the paint before the paint was drawn into the syringe. After the syringe was removed from the paint, it was wiped off with a paper towel to remove any paint on the outside surfaces of the syringe. The paint in the syringe was discharged into each 4 dram vial so that the vial was filled as full as possible to minimize the headspace left in the vial. The vials were sealed with screw-top caps that had a Teflon liner on the sealing surface of the cap. After the cap was tightened, it was wrapped with Teflon tap to give added protection from leakage. Once all of the vials were filled, they were placed in a box and stored in a refrigerator prior to being sent to the participating laboratories. The laboratories were also asked to refrigerate the paints samples prior to analyzing them.

Laboratory Kick-off Meetings

Since the six laboratories had to share one Perkin-Elmer ATD-400 thermal tube desorber, a schedule was established that allowed each laboratory to have possession of the system for two weeks. In order to perform the analyses described in the draft method, the ATD-400 transfer line needs to be connected to a gas chromatograph (GC) with a flame ionization detector (FID). Also, the output of the FID needs to be monitored with an integration system (integrator or PC based chromatographic system) that allows the total peak area to be measured.. Several of the participating laboratories also required a GC and integration system to perform the testing either because they did not have this equipment or because they did not want to take their systems out of production. In these cases, Battelle provided a Hewlett Packard 5890 GC with a FID and a Chromperfect data system.

After the ATD-400 was received at each laboratory, a one day kick-off meeting was held. In this meeting, Battelle personnel helped the laboratory personnel connect the ATD-400 to the GC and data system and made sure the system was operating properly. The laboratory personnel were given training on how to operate the ATD-400. The tube conditioning parameters and tube analysis parameters required by the draft method were programmed into the ATD-400 as two separate methods by Battelle personnel prior to shipping it to the laboratories. At the kickoff meeting, the ATD-operators were shown where these parameters were located in each method and how to load the methods. The ATD operators used these two programs in sequential fashion to first clean the PTFE liners and then to analyze the paint samples and standards. The only information that the ATD-400 operators had to input into the two methods were the start tube number and the stop tube number. The draft method requires a carrier gas flowrate through the sample tube of 100 mL/min for tube cleaning and 5 mL/min for tube analysis. The ATD-operators were left a flowmeter and shown how to adjust the carrier gas flowrate.

Each laboratory was also given all of the materials that would be needed to perform the draft method. These materials are listed in Table 4.4. The 2-butoxyethanol used for the standard preparation in the study came from a single one liter bottle of Aldrich 99^{+}% spectrophotometric grade 2-butoxyethanol (Lot 01139DR). Prior to each kickoff meeting, the one ounce bottle was emptied and refilled by Battelle personnel with fresh 2-butoxyethanol to avoid any cross contamination from laboratory to laboratory.

At the kick-off meeting, each participating laboratory was given a packet of information. This packet of information is shown in Appendix B. Included in the packet was the draft test method that the laboratories were to follow in performing their work. The details of the draft method such as sample volumes, loading techniques and standard preparation were reviewed with each laboratory. Special emphasis was place on the calibration and quality control check standard accuracy and precision requirements of the draft method.

The laboratories were given information about the paints that they would need to compute the correction factors for the Wt% VOC_c calculations. This information included the

ingredients of each paint and the chemical structure of specific VOC components. Examples of the calculations used to determine the correction factor were supplied as well as the Jorgensen, et al. reference cited in the draft method. Each laboratory was instructed to treat the ingredients mineral spirits and solvent naphtha as a $C_{10}H_{22}$ alkane. In cases where the weight percent of the ingredients were given as a range, the laboratories were instructed to use the middle value of the range for the average relative sensitivity calculations.

Table 4.4. Materials Supplied to Participating Laboratories

	Material
1.	One ounce of 2-butoxyethanol in an amber screw cap bottle
2.	Thirty PTFE liners for sample tubes (Perkin-Elmer Part No. L407-1596)
3.	Sixteen stainless steel tubes, 1/4 inch OD, 5mm ID, 3.5 inches long with end caps (Perkin-Elmer Part No. L427-0123)
4.	Silanized glass wool for packing PTFE liners (Alltech Pesticide Grade Glass Wool, Part #: 4034)
5.	Twelve 1 mL polypropylene syringes with a luer tip with 20 gauge luer hub needles for loading the sample paints into the liners (Becton-Dickinson 309602 Tuberculin syringe)
6.	One Hamilton #805, 50 µl syringe for loading the standards onto the glass wool
7.	Four sample paints in 4 dram vials labeled with one of the following sample codes • 1403-0100 • MS1-6659A • 4206-0100 • 4020-1000
8.	Logbook to record information while performing the draft method

Data sheets were provided to record the various calibration and QC/QA measurements required by the draft method and the test results from the four sample paints. Each laboratory was instructed to analyze the four water-based paints in triplicate for this study. The laboratories were also asked to submit hard copies of their chromatograms and calculations so Battelle could determine if they were applying the draft method correctly.

Overview of ASTM E 691

The statistical methodology used to evaluate the interlaboratory study of the water-based coating method, as recommended by standard practice ASTM E 691, is detailed below. A copy of ASTM E 691 can be found in Appendix C.

An interlaboratory study evaluates the precision of laboratory results by measuring within laboratory and between laboratory variability. These types of variability are referred to as repeatability and reproducibility, and are defined below:

Repeatability: Precision under the following conditions: independent test results are obtained with the same method on identical test materials in the same laboratory by the same operator using the same equipment within short periods of time.

Reproducibility: Precision under the following conditions: test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

The following statistical model for laboratory results is considered when evaluating these two types of laboratory precision:

$Y_{jL} = \mu + \gamma_L + \varepsilon_{jL}$, L = 1 to p, where p = total number of laboratories in the study.
j=1 to n_L, where n_L is the number of observations made per lab.

μ = true paint sample result

γ_L = the measurement error associated with different laboratories with different operators using different equipment. Considered a $N(0,\sigma^2_L)$ random variable, with σ^2_L being the measurement error due to different laboratory conditions.

ε = error under reproducibility conditions. Considered a $N(0,\sigma^2_r)$ random variable, with σ^2_r being the measurement error.

Note that in this model the four laboratories in which the analysis was done are considered to be a random sample from the population of all possible combinations of labs, operators, and equipment. The model has two sources of variability. σ^2_r is the residual error attributable to measurement error (e.g. sampling and analytical variability) and effects left unexplained by the model, and σ^2_L is the additional error that results from different laboratory conditions.

The interlaboratory study takes an Analysis of Variance approach to evaluate repeatability and reproducibility. Error under repeatability conditions (σ^2_r) is estimated by the model Mean Squared Error. The estimate of σ^2_L is also estimated by the model, and error under reproducibility conditions is estimated in the following manner:

σ^2_R (reproducibility error) = $\sigma^2_r + \sigma^2_L$

Two consistency statistics are used to evaluate the performance of laboratories involved in the study. The first is a *between-lab consistency statistic*, which is used to determine if a laboratory is obtaining average sample results that are significantly different from other laboratories in the study. The statistic is calculated as follows:

$h = (y - y^*) / s_y$

y = average result for the laboratory in question.
y* = overall average of all p laboratories considered in the study.
s_y = standard deviation of the p average laboratory results

The distribution of *h* can be equated to a t distribution with p-2 degrees of freedom, and from this fact critical values for *h* can be determined. A value for *h* exceeding the given critical value means the laboratory in question is producing biased results. In other words, the average measurement from that laboratory is significantly higher or lower than the measurements obtained from the other laboratories.

The second statistic is a *within-lab consistency statistic*, which is used to determine the variability of laboratory results as compared to other labs in the study. This statistic is calculated as follows:

$k = s / s_r$

s = the standard deviation of the n measurements taken in the laboratory in question.
s_r = the estimated study-wide measurement error (an estimate of σ_r)

The distribution of *k* can be equated to an F distribution with (n-1) and (n-1)(p-1) degrees of freedom, and from this fact critical values for *k* can be determined. A value for *k* exceeding the given critical value means the laboratory in question is producing data that is highly variable as compared to other laboratories in the study. In other words, the lab in question is producing data that is not as precise as the data from other labs.

Section 5
Results and Discussion

In this section, the results from the various activities conducted as part of the interlaboratory study are discussed. Comments are made on the performance of the Perkin-Elmer ATD-400 system and the performance of the laboratories in applying the draft method. The various quality assurance (QA) activities that occurred before and during the study are reported. Finally, the results from the laboratories and the ASTM E 691 analysis are reported and discussed.

Equipment Performance

All six of the participating laboratories were able to complete the testing in the two weeks that they were scheduled to used the Perkin-Elmer ATD-400 system. Table 5.1 shows the gas chromatograph (GC) and integrator systems that were used with the ATD-400 system at each laboratory. None of the laboratories reported any difficulties in operating the ATD-400 system. The only ATD-400 installation problem that was experienced was at laboratory 3. Problems were encountered in getting the ATD-400 to trigger the data system. The communication cable linking the ATD-400 to the data system had to be rewired so that the data system was triggered properly. During the course of the interlaboratory study, Battelle personnel did all of the maintenance on the ATD-400 unit leased for this study.

After analyzing the GC chromatograms from laboratories 1, 2, and 3, it was determined that there was a decrease in the peak resolution of the 50% standard at laboratories 2 and 3. Prior to shipment to laboratory 4, the ATD-400 system was assembled at Battelle, and the system performance was evaluated. In this evaluation, the sorbent bed in the focusing trap was found to

Table 5.1. GC and Integrator Systems Used in Interlaboratory Study

Laboratory	GC System	Integrator System
1	Battelle provided Hewlett-Packard 5890	Battelle provided Chromperfect data system (3.52)
2	Battelle provided Hewlett-Packard 5890	Battelle provided Chromperfect data system (3.52)
3	Laboratory provided Varian 3400	Laboratory Provided Varian Star Chromatography data system (Version 4.0)
4	Battelle provided Hewlett-Packard 5890	Battelle provided Chromperfect data system (3.52)
5	Laboratory provided Hewlett-Packard 5890	Battelle provided Chromperfect data system (3.52)
6	Laboratory provided Hewlett-Packard 5890	Laboratory provided Chromperfect data system (Version3.5)

have migrated so that is was no longer in the region of the trap cooler. This migration had little affect on the overall performance of the system, since all of the laboratories (1, 2, and 3) passed the calibration and quality control check standard (QCCS) tests required in the draft method. The only effect was some peak broadening, especially for the 50 % standard. Since the method requires the total area to be used, these broader peaks would not be expected to cause any significant errors in the measurements. None the less, a new focusing trap was installed in the ATD-400 system so that the sorbent bed was located properly within the trap cooler. To guard against a reoccurrence of this problem, the location of the sorbent was checked during the installation of the ATD-400 system at laboratories 4, 5, and 6.

The replacement of the focusing trap did not completely improve the peak resolution problem. After performing several tests, it was found that peak resolution was regained by

replacing the fused silica transfer line between the ATD-400 system and the GC. The old 0.32 mm internal diameter (I.D.) fused silica transfer line was replaced with a 0.53 mm I.D. transfer line because it was felt that a larger transfer line may prevent this problem in the future. The draft method does not specifically address what I.D. this transfer line should be. All three standards (0.5%, 5%, and 50%) as well as a QCCS standard were analyzed on the ATD-400 using the new transfer line. Peak resolution was excellent, and the instrument passed all of the calibration and QCCS requirements of the draft method.

The leased ATD-400 system proved to be very reliable in this interlaboratory study. The unit was rugged enough that it could be shipped to all six laboratories and operate normally after it was reattached to the GC. The automated tube loading system mis-loaded only one tube during the whole course of the study. The only maintenance difficulty experienced was installing the focusing trap. This trap consists of a 3 mm I.D. fused silica tube that is sealed in the system with two graphite ferrules. The middle section of this tube is packed with a 10 mm long section of Tenax GR and a 10 mm section of Carbopak B as required by the draft method. The focusing trap had to be installed twice during the study: once when the unit was originally received from Perkin-Elmer and once after laboratory 3 had completed their testing. Both times it was found to be very difficult to seal the graphite ferrules well enough to pass the ATD-400 internal leak test. Likewise, it was very easy to break the fused silica tube while tightening the ferrules. Eventually, Battelle personnel implemented the use of a helium leak detector to aid in getting the focusing trap leak free.

From time to time in the interlaboratory study, some of the laboratories obtained split GC peaks or peaks with a trailing tail. These types of occurrences came and went with no apparent explanation. Again, since total peak area was being measured, these chromatographic features did not affect the results.

Laboratory Performance

All of the laboratories were able to prepare the standards and samples and to perform the paint analyses without any major difficulties. Blank levels were not found to be a problem

during the course of the interlaboratory study. The blank levels ranged from below the detection limit to 0.2 Wt%. All of the laboratories achieved valid calibrations on the first analysis of the 0.5%, 5%, and 50 % standards. Only one laboratory (laboratory 3) did not pass the percent accuracy and percent relative standard deviation (%RSD) requirements of the quality control check standard (QCCS) on the first try. Table 5.2 lists the %RSD of the calibration response factor, as well as the %RSD and % accuracy of the QCCS. These results show there was some variability in the %RSD for both the calibration response factor and the %RSD of the QCCS. The present %RSD limits in the draft method appear to be reasonable. If the limits were tightened by even 5%, the calibrations and QCCS of some of the laboratories would not have been acceptable.

Table 5.2. Laboratory QC Check Results

Laboratory	%RSD of Calibration Response Factor (Limit: %RSD<30%)	%RSD of Quality Control Check (Limit: %RSD<20%)	% Accuracy of Quality Control Check Standard (Limits: 90%<%Accuracy<110%)
1	8.36	1.40	102
2	24.6	15.6	99.3
3	25.3	4.01	103
4	14.1	10.1	103
5	6.40	3.23	100
6	22.7	1.17	101

The draft method requires a number of calculations to compute the average relative sensitivity (RS_{avg}) in order to calculate the corrected weight percent VOC (Wt% $VOC_{c)}$ from the Wt% VOC_u value. The laboratories were found to make several errors in performing these calculations. For instance, one laboratory initially used a C_6 for the mineral spirits and solvent naphtha instead of a C_{10} alkane. Another laboratory left out one step in calculating the RS_{avg} values. When errors such as these were made, the laboratories were informed and asked to recalculate the RS_{avg} values. The laboratories (1,3,4,5, and 6) in which personnel with a

chemistry background performed these calculations required the least assistance from Battelle in order to make these computations. At laboratory 2, the person performing the draft method, including the calculations, had a quality assurance background. This laboratory required much more additional assistance from Battelle to complete the calculations.

One common error involved the calculation of the relative sensitivity (RS_i) value for mineral spirits and solvent naphtha for the paints that contained these components. As mentioned earlier, all of the laboratories were told to treat mineral spirits and solvent naphtha as a $C_{10}H_{22}$ alkane. According to Jorgensen, et al., 0.08 should be subtracted from the carbon number of an hydrocarbon in calculating the effective carbon number (ECN) of the hydrocarbon. This ECN value is then used to compute the RS_i of the hydrocarbon. The ECN for a $C_{10}H_{22}$ alkane should be 9.92 (10-.0.08 = 9.92). Laboratories 3, 4 and 5 failed to make this correction and used 10 as the ECN for mineral spirits and solvent naphtha. Table 5.3 lists the final RS_{avg} values that were calculated by the laboratories after any gross errors were corrected, as well as the RS_{avg} values computed by Battelle . With the exception of the values shown in bold print in Table 5.3, any variation in the values from laboratory to laboratory is due to rounding differences. The bold print values represent the errrors that resulted from the use of an ECN value of 10 for mineral spirits or solvent naphtha instead of 9.92.

To investigate the effect that this error in the RS_{avg} for Laboratories 3, 4 and 5 had on the final Wt% VOC_c values, the Wt% VOC_c for paints MS1-6659A, 4206-0100, and 4020-1000 was also calculated using Battelle's RS_{avg}. The % Difference between the laboratory Wt% VOC_c and the Battelle Wt% VOC_c was calculated for each paint. These values are shown in Table 5.4. As can be seen, the error resulting from using an ECN of 10 instead of 9.92 for mineral spirits and solvent naphtha resulted in a less than 1% error in the final Wt% VOC_c. To assure that the final database was consistent, the affected Wt% VOC_c from laboratories 3, 4 and 5 were corrected before they were entered into the database.

Table 5.3. Average Paint Relative Sensitivities Used by Laboratories

Laboratory	Paint Average Relative Sensitivity (RS_{avg})			
	MS1-6659A	1403-0100	4206-0100	4020-1000
1	1.019	0.837	1.239	1.359
2	1.019	0.838	1.24	1.362
3	**1.020**	0.838	**1.245**	**1.368**
4	**1.018**	0.838	**1.233**	**1.369**
5	**1.021**	0.838	**1.246**	**1.368**
6	1.019	0.838	1.241	1.361
Battelle	1.019	0.837	1.239	1.359

Table 5.4. Comparison of Wt% VOC_c Calculated Using Lab and Battelle RS_{avg}

Paint	% Difference Between Wt% VOC_c Calculated Using Lab RS_{avg} and Wt% VOC_c Calculated Using Battelle RS_{avg}		
	Lab 3	Lab 4	Lab 5
MS1-6659A	-0.098	0.098	-0.196
4206-0100	-0.482	0.487	-0.562
4020-1000	-0.658	-0.730	-0.658

QA Activities

At the beginning of the study, Battelle was required to analyze an audit paint sample according to the draft method to demonstrate to the Work Assignment Manager (WAM) the ability of Battelle to conduct the method. The audit paint sample was chosen by the WAM from one of the six paints purchased for the interlaboratory study (see Table 4.2). The coating chosen was 1403-0100, utlra eggshell white. Battelle performed the method using a Perkin-Elmer ATD-400 that was located in Battelle's Hazardous Materials Laboratory (HML). This Perkin-Elmer

ATD-400 was a separate instrument from the leased ATD-400 instrument that was used by the six participating laboratories. After modifying the ATD-400 to meet the specifications of the draft method, it was found to meet all of the calibration and QC checks required by the draft method. Battelle analyzed the audit sample on March 3, 1999 in triplicate and submitted the results to the WAM on March 6. These results are shown in Table 5.5. After reviewing the audit results, the WAM was satisfied that Battelle could perform the draft method.

The sample of paint 1403-0100 used for the audit analysis was taken from the original one gallon can on March 3, 1999. On April 12, the paints samples that would be given to the six participating laboratories were taken from the one gallon cans of the four test paints, which included paint 1403-0100, and loaded into the 4 dram sample vials. As each laboratory performed their portion of the study, the paints were distributed to them. As mentioned in Section 4, the 4 dram vials were kept refrigerated prior to their distribution to the laboratories. After laboratory 3 finished their testing on June 30, Battelle collected the four paint samples supplied to them and archived them in a refrigerator. On August 25, 1999, the paint samples collected from laboratory 3 were analyzed on the ATD-400 at the HML. A Hewlett-Packard 5890 GC was used for these analyses. The results from the analyses on the 1403-0100 done on August 25 are also shown on Table 5.5. A comparison of the March 3 and August 25 results on paint 1403-0100 show that the paint samples in the 4 dram vials remained very stable during the course of the study.

The leased Perkin-Elmer ATD-400 that was used for the interlaboratory study was received by Battelle on March 18, 1999. The unit was installed on one of Battelle's Hewlett-Packard 5890 GCs to meet the specifications of the draft method. The performance of the ATD-400 system was evaluated by analyzing samples from the six candidate paints. It was at this time that the results shown in Table 4.3 were obtained. After analyzing a number of samples of the six candidate paints, the WAM was concerned that the Wt% VOC_c values being measured with the instrument were low; therefore the the WAM submitted four additional audit paint samples for analysis with the ATD-400 system. These samples were labeled M24-003-A, M24-003-B, M24-003-C, and M24-003-D and had previously been characterized for Wt% VOC. The purpose

for analyzing these samples was to evaluate the accuracy of the Wt % VOC values measured with the ATD-400. Samples M24-003-A and M24-003-B were duplicates of one paint, while samples M24-003-C and M24-003-D were duplicates of another paint. Battelle analyzed aliquots from samples M24-003-A, M24-003-B, and M24-003-C. The results from these samples are shown in Table 5.6. All of the VOC content in each of the paints was assumed to be hexane. When the results were reported to U.S. EPA, the WAM was satisfied that the instrument was working properly and that it was ready for use in the interlaboratory study.

Table 5.5. Results of Audit Paint 1403-0100, Ultra Eggshell White

Analysis Date	Sample #	Wt% VOC_c	Mean Wt% VOC_c	% RSD
3/03/99	1	4.89	4.55	6.43
	2	4.34		
	3	4.44		
8/25/99	1	4.29	4.46	3.25
	2	4.57		
	3	4.51		

Table 5.6. Results from M24 Audit Samples

Sample	Wt% VOC_u (uncorrected)	Wt% VOC_c (corrected)
M24-003-A	46.4	26.2
M24-003-B	48.6	27.4
M24-003-C	51.0	28.8

To assure the quality of the data reported by the participating laboratories, a thorough QC/QA audit was made of all of the information submitted by each laboratory. The chromatograms were checked to determine if the individual laboratory was using the total peak

areas and if they were summing the peak areas from the two desorptions performed for each analysis. The RS_{avg} calculations were examined to assure that the laboratories had derived this number correctly. The data from the standard preparation, system calibration, QCCS, and paint analyses were entered into Excel spreadsheets to check the calculations made by each laboratory. Any errors found were noted on the data sheets submitted by each laboratory. The data sheets from each of the laboratories can be found in Appendix D.

Problems Encountered With Draft Method

The draft method states that approximately 25 μL of a coating sample should be applied to the PTFE liner prior to analysis. The method does not give very detailed instructions on how to apply this small amount of paint to the liner. When Battelle initially performed the method, pipets or syringes with needles did not work well for these measurements because the paint samples were too thick to draw through the small opening of a needle or pipet. The best procedure that Battelle found to load the 25 μL of paint onto the liners was to use a 1 mL syringe with a luer tip. First the syringe was filled with paint without attaching a needle. The syringe tip was immersed approximately 2.5 cm into the 4 dram vial containing the paint, before the paint was drawn into the syringe with the plunger. The syringe was then removed from the paint and wiped off with a paper towel. Next a luer hub 22 gauge needle was placed on the tip of the syringe, and the plunger was depressed until paint was discharged from the tip of the needle. The liner was loaded by inserting the needle into the glass wool packing. The smallest divisions on the 1 mL syringe represented 10 μL. By moving the syringe plunger three small divisions, approximately 30 μL of paint was loaded onto the glass wool. Disposable syringes were used for this paint loading, because it was so difficult to clean the paint off the syringe and plunger.

All six of the laboratories were given 1 mL disposable syringes and 22 gauge needles as part of the materials supplied to them. The laboratories were told at the kick-off meeting that they could use the syringes to load the PTFE liners or a method of their own if they felt it would work better. All of the laboratories chose to use the syringes supplied to them to load the paint samples. The mean weight of paint applied to the PTFE liners in the interlaboratory study using

the 1 mL syringes was 31 mg with a %RSD of 28%. Considering the difficulty in accurately delivering such a small volume of paint (25 μL), these results are very good.

Laboratory 1 found a problem in applying equation 13.2 in the draft method. Equation 13.2 is shown below. This equation fails to show that the weight percent of 2-butoxyethanol in the standard solution ($Wt.\%_s$) needs to be divided by 100 to convert the percentage back into a fraction. Laboratory 1 followed this equation strictly and results showed a mass value that was one hundred times too large. Equation 13.2 needs to be revised to include the Wt% conversion.

$$mass_s = (Mass_{ss})\,(Wt.\%_s)$$

Comments from Laboratories

At the kickoff meeting, the laboratories were asked to give written comments on the draft method if they desired. The comments received can be found in Table 5.7.

Table 5.7. Laboratory Comments on Draft Method

Laboratory	Comments:
1	The method was very straightforward and no problems were encountered in the actual preparation and analyses. The instrumentation worked well and required very little extra attention. The only item that was unclear was the use of the "%" factor in the calculations. Although it works itself out because it is used at the front-end and the back-end of the calculations, our numbers in the middle of the calculations were off by a factor of 100.
3	Since many material data safety sheets (MSDS) are prepared with limited individual component and concentration data, determination of accurate average relative sensitivity values may be difficult.
4	• From the QCCS Data Sheet and the test method, it was a bit unclear how to calculate the 2-BE Mass (mg). No instructions were included in the test method explaining the calculation of this step (R_{fid}/average RF). • Since there are many calculations in the test method using both very small numbers and very large numbers, it may be useful to include in the test method guidelines as far as either significant figures or decimal place values.

Table 5.7. Laboratory Comments on Draft Method
(Continued)

Laboratory	Comments:
4 (Cont.)	• In general, the calculations in the test method were sometimes confusing, and often a bit too complex and time-consuming. • During the addition of the coatings to the liner, it was a little difficult in the beginning to obtain consistent weight numbers among the triplicate preparations. The technique did improve with each sample. However, base on the data, it appears that achieving consistent sample weights among the replicates could be a critical factor for achieving acceptable data. • Since the test method relies on the composition of the coating, it would appear that the availability of a complete MSDS would be a critical factor for the calculations. Since not all companies are willing to divulge certain information, the absence of this information may affect the results. For example, the MSDS for sample MS1-6659A essentially listed only 3 solvents. An actual GC compositional analysis of this sample detected the presence of 10 solvents. Also, most MSDS information lists only ranges for the concentrations. Depending on whether each component is at the low or high end of the range, then using only the middle number could affect the calculations. The MSDS for sample 4206-0100 listed 3 solvents, each with a range of 1-5%. The calculations for the EPA method specify using a value of 3 for each. An actual compositional analysis of this sample detected that one solvent was in the 3 % range, but that another was in the 1% range, and the third was near 5%. • This test method relies on the analyst having a good knowledge of chemistry. The calculations for the effective carbon number involve knowing the complete structure of the solvent including the molecular weight, carbon number, and ester, alcohol, and ether linkages. Mistakes in any of these will result in erroneous calculations. • The general consensus of the personnel in our lab was that this particular test method uses 2 (three, if you include the computer) rather expensive pieces of equipment to generate data that must be extensively manipulated using calculations based on information that may be inaccurate or incomplete. For the cost of one piece of the equipment, an analysis can be performed to determine the total VOC content using gas chromatography, generating accurate data more easily.

Table 5.7. Laboratory Comments on Draft Method
(Continued)

Laboratory	Comments:
6	• The proposed method shows a great deal of promise in measuring the VOC content of coatings directly rather than indirectly as is currently done in the gravimetric ASTM, EPA and SCAQMD methods. However, the proposed method may require modification and tighter QC requirements in order to make it applicable to the wide range of samples received for compliance analysis. Comparing the current and proposed methods might also yield useful results. Potential problems in applying this method to compliance samples are as follows: • The proposed method requires formulation data to calculate average FID sensitivity and corrected VOC content. This is a problem for compliance samples, which almost never have accompanying formulation data. Even when the data is available, it may be irrelevant because of "field modification" of the coating, or the data itself may be in dispute. Because of these issues, the proposed method may need to be modified to make it applicable to coatings that are completely unknown. • The proposed method calculates VOC as weight percent of material injected into the instrument. The calculation should be modified to exclude exempt solvents. Also, since the EPA and SCAQMD require VOC "of coating", these should be included in the calculations. • The acceptable calibration error (+/- 30% RSD) allows too much error for compliance purposes. The calibration range of the proposed method is from 0.5% to 50% VOC (w/w) of material, which translates to about 5 to 500 g/L VOC. SCAQMD method has a repeatability of about 10 grams per liter of VOC over 50-500 g/L. However, the accuracy of the gravimetric method is unknown. Direct comparison might have revealed a method bias. • The proposed method may not be suitable for multi-package coating that require special curing conditions. It would be useful in distinguishing between water or ammonia emissions and VOC emissions, which the current gravimetric method can't differentiate. • The lowest standard appears to be too low to yield repeatable results.

ASTM E691 Results

The corrected weight percent VOC (Wt% VOC_c) values were the test results analyzed using the statistical procedures described in ASTM 691. This is the final result that is obtained from the draft method once all of the measurements and calculations have been completed. The Wt% VOC_c results were arranged in tables by paint. The three Wt% VOC_c results reported by each laboratory were entered into the tables and the following statistics were calculated following the equations in ASTM 691. The calculations were performed using the PROC GLM procedure in SAS:

x = individual Wt% VOC_c test result

$\bar{x}$ = the mean of the three test results from each laboratory

$\bar{x}'$ = the mean of the $\bar{x}$s calculated for each laboratory

s = standard deviation of the three test results from each laboratory

d = cell deviation = $\bar{x}-\bar{x}'$

$s_{\bar{x}}$ = standard deviation of the laboratory means

s_r = repeatability standard deviation

s_R = reproducibility standard deviation

$h = d/s_{\bar{x}}$

$k = s/s_r$

Tables 5.8-5.11 show the individual Wt% VOC_c results measured by each laboratory. As mentioned earlier, the results from laboratory 3, 4, and 5 were corrected before they were entered into the tables, so that all of the laboratories were using the same correction factors. Also shown in these tables are the results of the calculations for $\bar{x}$, s, d, *h*, and *k*. The results for $\bar{x}'$, $s_{\bar{x}}$, s_r, and s_R are shown in Table 5.12.

As mentioned in the QA Activities, Battelle retrieved the paint samples that were used by laboratory 3 and analyzed them with a separate ATD-400. For comparison of Wt% VOC_c

values, the Battelle results have been included in Tables 5.8-5.11. However, the Battelle results were not used in any of the ASTM E691 precision calculations.

The mean Wt% VOC_c values ($\bar{x}$) from Tables 5.7-5.10, have been plotted by paint in Figures 5.1-5.4. The Battelle values have also been included in these figures. The laboratories show very good agreement on each of the four paints. The mean Wt% VOC_c from the Battelle measurements also compare very well with the laboratory results. In general, the Battelle results are in the middle of the range of mean Wt% VOC_c reported by the six laboratories. Since Battelle used a different ATD-400 from the laboratories, the good agreement between the Battelle and six laboratory results indicates there is not any evidence of instrument bias with the draft method. The consistency of the paint results shows that the draft method was very insensitive to the GC and chromatographic data system that were used.

Table 5.8. Paint 4020-1000 Wt% VOC_c Results

Lab Number	Test Results, x			$\bar{x}$	s	d	*h*	*k*
	1	2	3					
1	3.13	3.12	3.09	3.113	0.0208	0.2378	1.42	0.38
2	2.64	2.62	2.60	2.620	0.0200	-0.2556	-1.52	0.37
3	2.96	2.97	3.01	2.980	0.0265	0.1044	0.62	0.49
4	2.74	2.82	2.80	2.787	0.0416	-0.0889	-0.53	0.76
5	2.97	2.89	2.74	2.867	0.1168	-0.0089	-0.05	2.14
6	2.92	2.86	2.88	2.887	0.0306	0.0111	0.07	0.56
Battelle	2.81	2.82	2.78	2.80	0.0241			

Table 5.9. Paint 1403-0100 Wt% VOC_c Results

Lab Number	Test Results, x			$\bar{x}$	s	d	*h*	*k*
	1	2	3					
1	5.92	5.95	6.07	5.980	0.0794	1.0422	1.56	1.46
2	4.94	4.84	4.87	4.883	0.0513	-0.0544	-0.08	0.94
3	3.81	3.92	3.89	3.873	0.0569	-1.0644	-1.59	1.05
4	4.94	4.92	5.01	4.957	0.0473	0.0189	0.03	0.87
5	5.03	4.99	5.10	5.040	0.0557	0.1022	0.15	1.02
6	4.89	4.91	4.88	4.893	0.0153	-0.0444	-0.07	0.28
Battelle	4.30	4.57	4.51	4.460	0.1450			

Table 5.10. Paint 4206-0100 Wt% VOC_c Results

Lab Number	Test Results, x			$\bar{x}$	s	d	*h*	*k*
	1	2	3					
1	9.50	9.68	9.74	9.640	0.1249	-0.1372	-0.27	0.75
2	8.87	8.69	9.14	8.900	0.2265	-0.8772	-1.72	1.36
3	9.81	9.59	10.0	9.800	0.2052	0.0228	0.04	1.23
4	10.5	10.5	10.3	10.43	0.1155	0.6561	1.29	0.69
5	9.87	9.72	9.94	9.843	0.1124	0.0661	0.13	0.67
6	9.85	10.2	10.1	10.05	0.1790	0.2694	0.53	1.07
Battelle	9.19	9.47	8.40	9.353	0.1421			

Table 5.11. Paint MS1-6659A Wt% VOC_c Results

Lab Number	Test Results, x			$\bar{x}$	s	d	*h*	*k*
	1	2	3					
1	17.3	16.1	16.0	16.47	0.7234	1.0656	0.88	1.53
2	14.0	13.9	14.0	13.96	0.0700	-1.4411	-1.19	0.15
3	15.6	15.5	15.2	15.43	0.2082	0.0322	0.03	0.44
4	15.5	16.7	16.4	16.20	0.6245	0.7989	0.66	1.32
5	13.5	14.5	13.5	13.86	0.5860	-1.5378	-1.27	1.24
6	16.5	16.3	16.6	16.48	0.1716	1.0822	0.89	0.36
Battelle	14.3	14.4	14.5	14.39	0.1055			

Figure 5.1. Mean Wt% VOC_c Results from Paint 4020-1000 by Laboratory

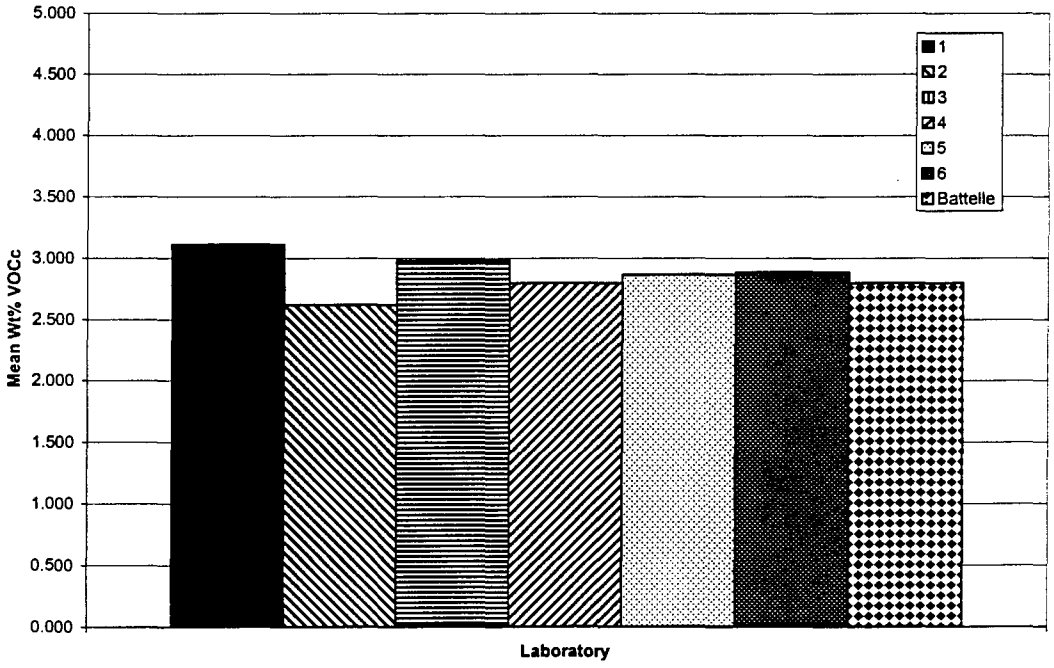


Figure 5.2. Mean Wt% VOC_c Results from Paint 1403-0100 by Laboratory

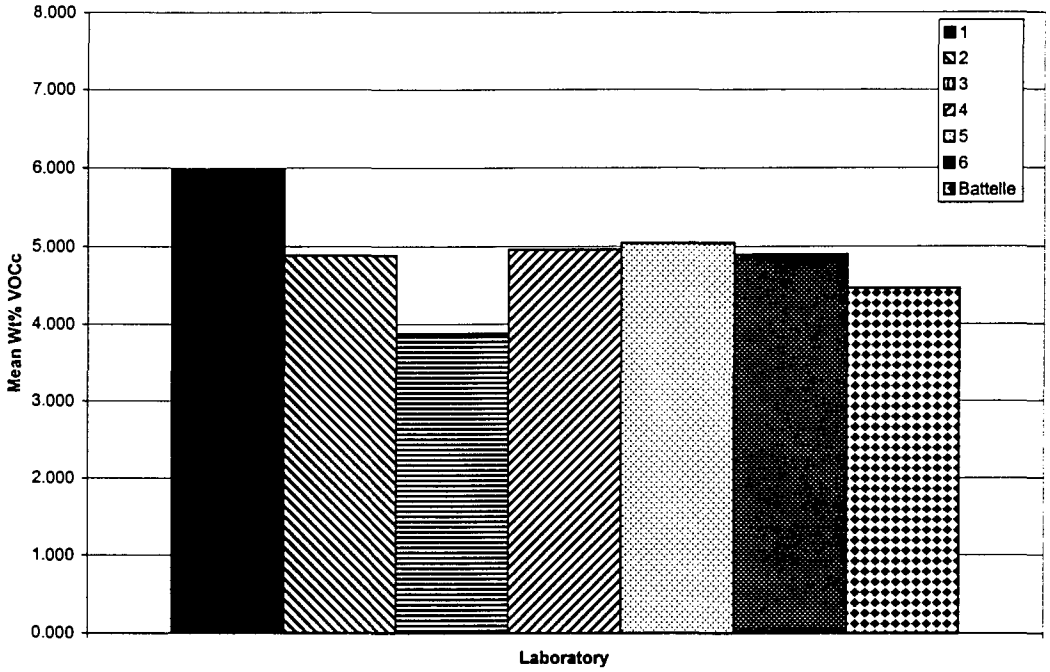


Figure 5.3. Mean Wt% VOC_c Results from Paint 4206-0100 by Laboratory

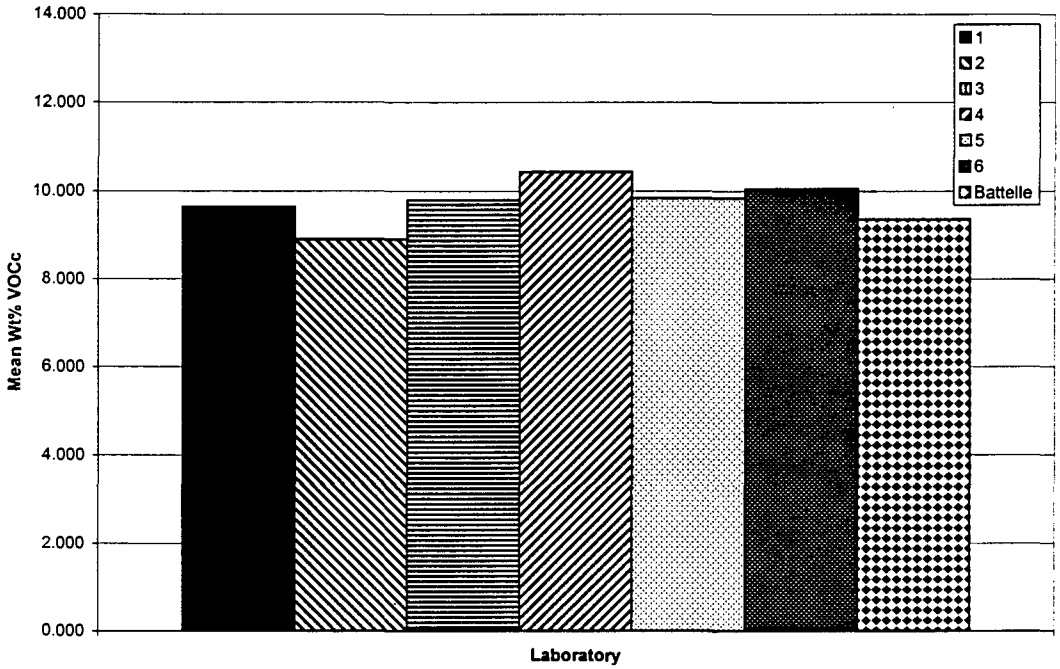
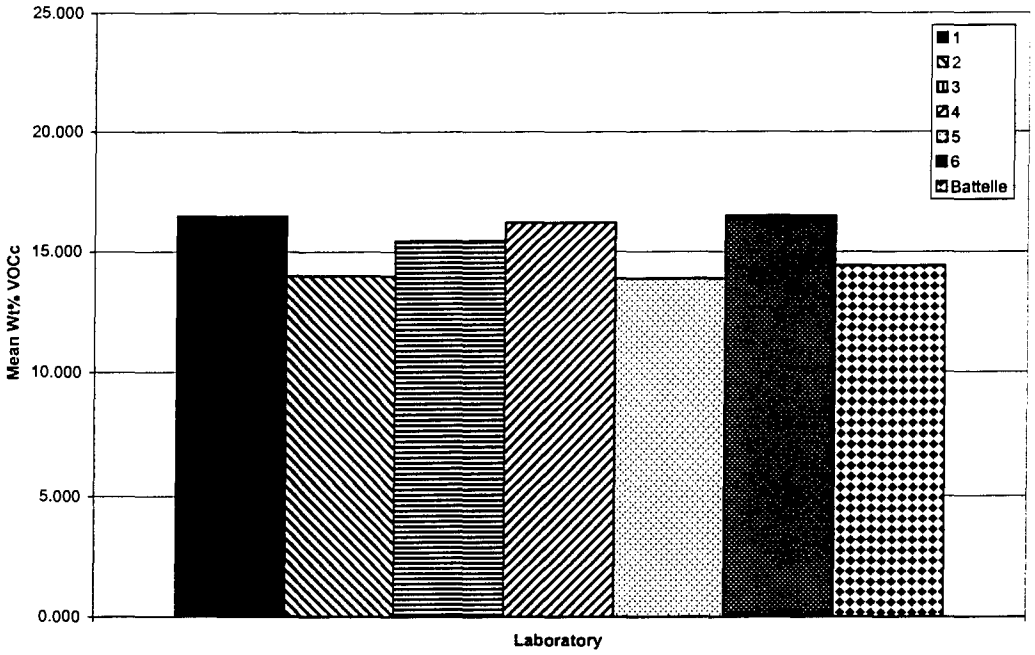


Figure 5.4. Mean Wt% VOC_c Results from Paint MS1-6659A by Laboratory



The *h* and *k* values reported in Tables 5.8-5.11 are consistency statistics. The *h* statistic is a between-laboratory consistency statistic. A large value of this statistic indicates that a laboratory produces data that yields significantly different Wt% VOC_c results from the other laboratories. The *k* statistic is a within-laboratory consistency statistic. A large value of this statistic indicates a laboratory that produces data that is significantly more variable than data from the other laboratories.

As directed in ASTM E 691, the values of *h* and *k* consistency statistics in Tables 5.8-5.11 were plotted on bar graphs in two ways: paints grouped by laboratory (Figure 5.6 and 5.8) and laboratories grouped by paint (Figures 5.5 and 5.7). On Figures 5.5-5.8, the paints were arranged in order of increasing mean Wt% VOC_c ($\bar{x}$) and the laboratories were arranged in order of their code number (1-6). For plotting purposes on Figures 5.5-5.8, the paints have been given the following codes:

- Paint 4020-1000 = A
- Paint 1403-0100 = B
- Paint 4206-0100 = C
- Paint MS1-6659A = D

The critical values of the *h*and *k* consistency statistics at the 0.5% significance level (α = 0.005) were also plotted as recommended in ASTM E 691. These values are shown as the horizontal dashed lines in Figures 5.5-5.8. The critical values of *h* depend on the number of laboratories participating in the interlaboratory study (six for this study), and the critical values of *k* depend both on the number of laboratories and on the number of replicate test results per laboratory per paint (three for this study). The critical values were obtained from Table 12 in ASTM E 691. The critical value for *h* is ±1.92 and for *k* is 1.98.

An examination of Figures 5.5 and 5.6 show none of the h statistics from the interlaboratory study exceeded the critical value; therefore, there is not enough evidence to show that any one of the laboratories produced biased data relative to the other laboratories in the study. Figure 5.7 and 5.8 show that laboratory 5 exceeded the critical *k* value for paint 4020-1000 (A). The result means that laboratory 5 produced a mean Wt% VOC_c whose standard deviation was significantly higher than that of the other laboratories in the study.

The k statistic for the other three paints analyzed by laboratory 5 were not out of line with the values from the other laboratories even though these paints had higher mean Wt% VOC_c . A review of the data did not reveal any calculation errors. The %RSD for laboratory 5, paint 4020-1000 was 4.07%. Since no physical evidence indicated a problem with the laboratory 5 paint 4020-1000 results, the data was retained in the analysis.

Figure 5.5. h - Laboratories within Paints

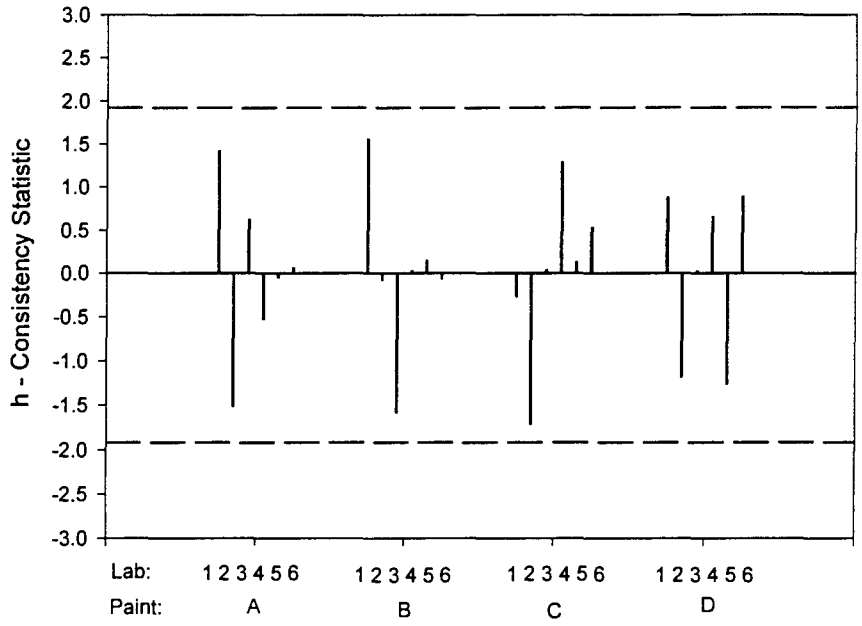


Figure 5.6. h - Paints within Laboratories

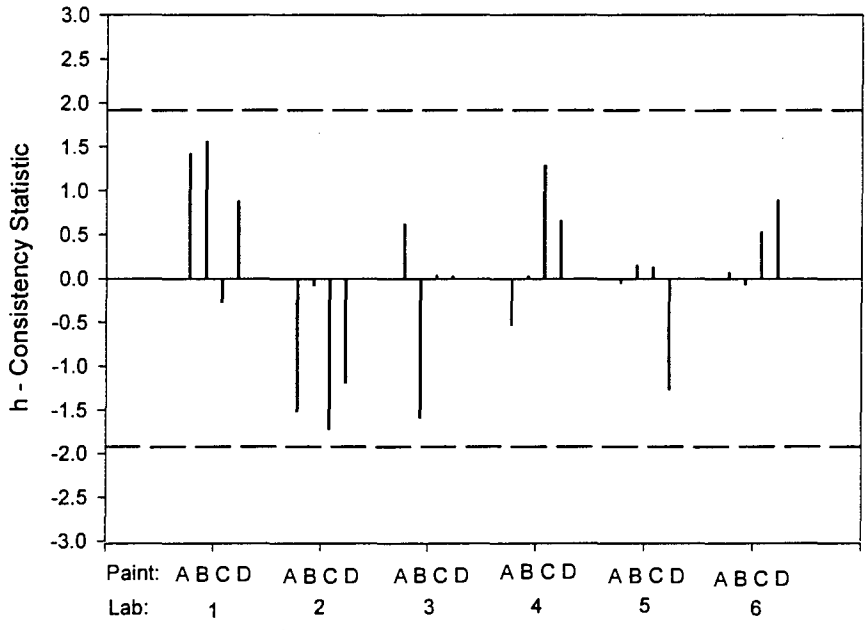


Figure 5.7. k - Laboratories within Paints

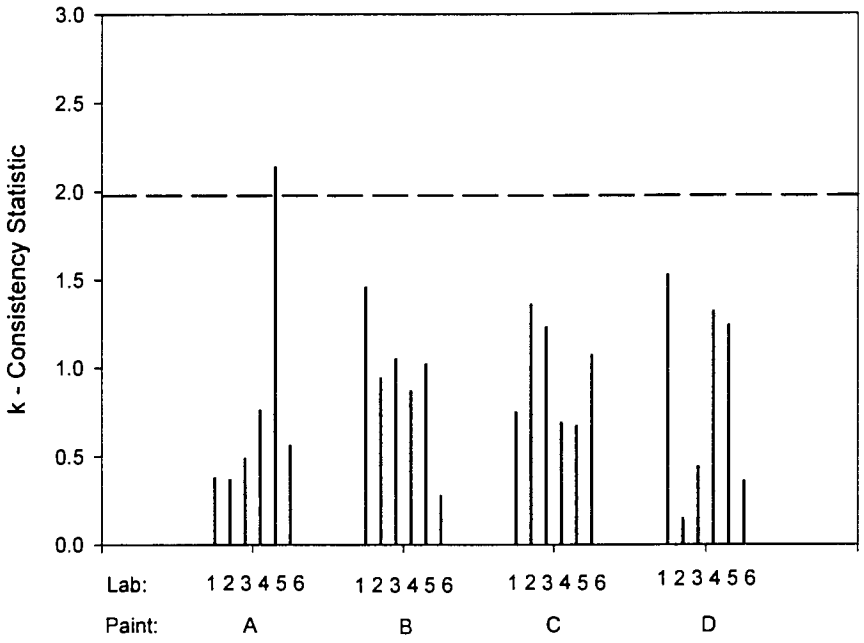


Figure 5.8. k - Paints within Laboratories

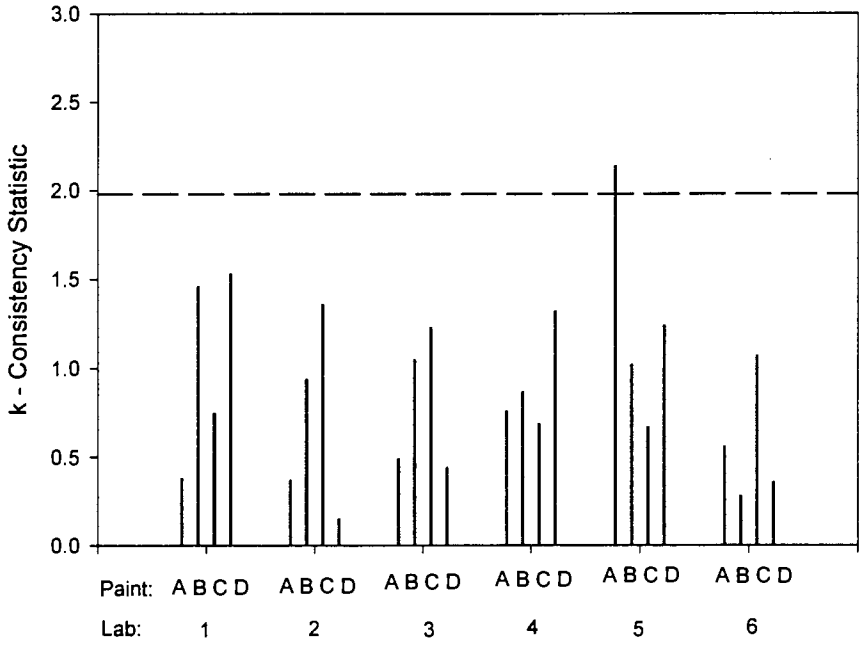


Table 5.12 summarized the precision statistics for the interlaboratory study of draft water-based coating method as recommended by ASTM E 691. As defined earlier, $\bar{x}'$ is the overall measured mean Wt% VOC_c for the eighteen observations reported for each paint (six laboratories, each making three measurements). The standard deviation of the six different laboratory means is reported as $s_{\bar{x}}$. The repeatability standard deviation (within a laboratory) and the reproducibility standard deviation (between laboratories) are reported as s_r and s_R respectively. Figure 5.9 shows s_r and s_R plotted at a function of $\bar{x}'$.

Table 5.12. Precision Statistics

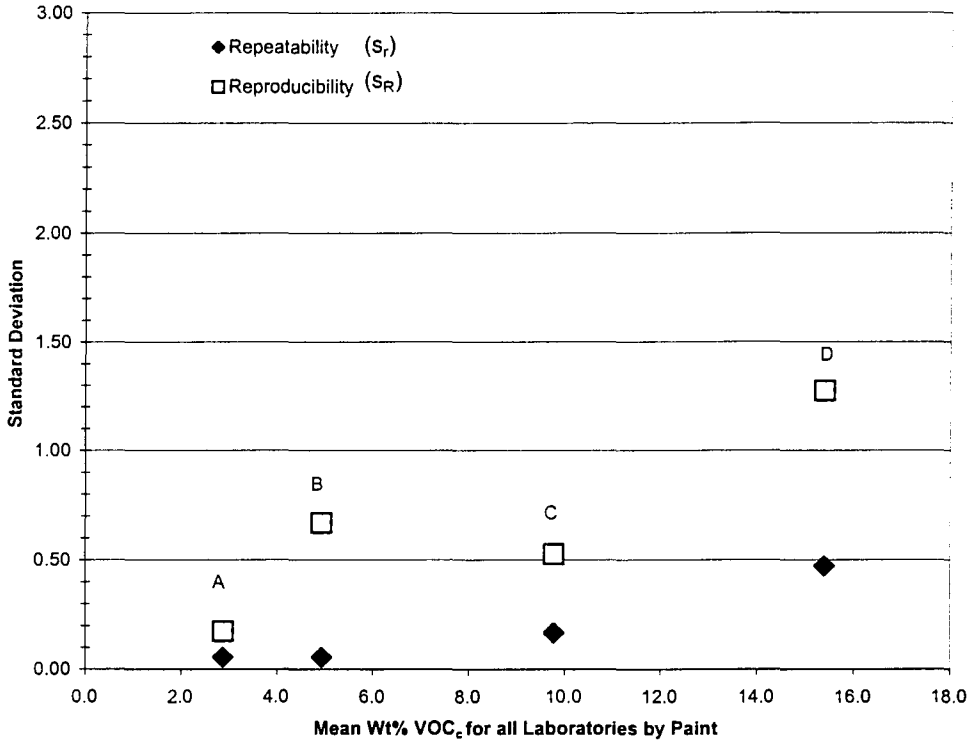
Paint	$\bar{x}'$	$s_{\bar{x}}$	s_r	s_R	r	R
4020-1000	2.8756	0.1678	0.0545	0.1736	0.15	0.49
1403-0100	4.9378	0.6686	0.0544	0.6701	0.15	1.88
4206-0100	9.7772	0.5092	0.1668	0.5271	0.47	1.48
MS1-6659A	15.4011	1.2155	0.4716	1.2751	1.32	3.57

As stated in ASTM E 691, the 95% repeatability (r) and reproducibility (R) limits were calculated with the following equations and are reported in Table 5.12.

$r = 2.8\ s_r$

$R = 2.8\ s_R$

Figure 5.9. Standard Deviations of Repeatability and Reproducibility Versus Mean Wt% VOC_c



The repeatability limit is a 95% upper confidence bound of the difference between two measurements under repeatability conditions. For two measurements taken in the same lab, same operator, etc., the difference between them would be no more than r. This would be true about 95 times out of 100. The reproducibility limit represents the same confidence bound, only with reproducibility conditions (different lab, operator, etc.). For example, if r = 0.15 as for paint 4020-1000, the difference between any two measurements taken at the same lab, same operator, etc., would be expected to be no more than 0.15. Similarly, if R = 0.49, the difference between two measurements taken at different labs, different operators, etc., would be expected to be no more than 0.49 with 95% confidence.

Table 5.13 lists the precision statement that was prepared with precision information obtained in this interlaboratory study. The final form of this statement is prepared in accordance

with ASTM E 177, Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods.

Table 5.13. Precision Statement[A]

Paint	Wt % Average	Repeatability Standard Deviation (Wt %)	Reproducibility Standard Deviation (Wt %)	Repeatability Limit (Wt %)	Reproducibility Limit (Wt %)
4020-1000	2.8756	0.0545	0.1736	0.15	0.49
1403-0100	4.9378	0.0544	0.6701	0.15	1.88
4206-0100	9.7772	0.1668	0.5271	0.47	1.48
MS1-6659A	15.4011	0.4716	1.2751	1.32	3.57

[A] The table was calculated using the relationship: limit = 2.8 × standard deviation

Interlaboratory Test Program - An interlaboratory study of weight percent volatile organic chemicals in water-based coatings was conducted in accordance with Practice ASTM E 691 in six laboratories with four paints, with each laboratory obtaining three test results for each material

References

1. ASTM E-177, Standard for Use of the Terms Precision and Bias in ASTM Test Methods, 1990, 79-90.

2. ASTM E 691, Standard Practice for Conducting a Interlaboratory Study to Determine the Precision of a Test Method, 1992, 425-443.

3. Jorgensen, A.D., Picel, K.C., Stamoudis, V.C., Prediction of Gas Chromatography Flame Ionization Detector Response Factors from Molecular Structures, Analytical Chemistry, 1990, 62: 683-689.

4. Peterson, M.R., Howe, G.B., Jayanty, R.K.M. Development and Evaluation of a Procedure to Measure Total VOC in Paints and Coatings Using an Automated Thermal Desorption Device and a Gas Chromatorgaphy Detector, Draft Report to U.S. Environmental Protection Agency, Contract No. 68D20163, Research Triangle Institute, Research Triangle Institute, Research Triangle Park, North Carolina, September 1996.

5. Evaluation of the Water-based Coating Method, U.S. Environmental Protection Agency Report, August 30, 1995.

APPENDIX A

MSDS SHEETS FOR STUDY PAINTS AND AVERAGE RELATIVE SENSITIVITY CALCULATIONS

MSDS for Paints MS1-6659A and MS1-6660A

MATERIAL SAFETY DATA SHEET

SI-6660A
4 00

ANUFACTURER'S NAME
MARTIN SENOUR PAINTS
101 Prospect Avenue
Cleveland, OH 44115

EMERGENCY TELEPHONE NO.
(216) 566-2917

ATE OF PREPARATION
07-SEP-99

INFORMATION TELEPHONE NO.
(216) 566-2902

Section I -- PRODUCT IDENTIFICATION

RODUCT NUMBER
MSI-6660A

HMIS CODES

Health	3*
Flammability	0
Reactivity	0

RODUCT NAME
MSI* Waterborne Industrial Enamel, Gray (Ford)
RODUCT CLASS
Water-reducible Acrylic Coating

Section II -- HAZARDOUS INGREDIENTS

NGREDIENT CAS No.	% by WT	ACGIH TLV	OSHA PEL	UNITS	V.P.
-Propoxyethanol 2807-30-9	4	Not Established			1.30
-Butoxyethanol 111-76-2	7	25	25	PPM (Skin)	0.60
Cobalt 2-Ethylhexanoate. 136-52-7	0.2	Not Established			0.00
Triethylamine. 121-44-8	2 STEL	1 3	25 100	PPM (Skin) PPM (Skin)	54.00
Titanium Dioxide. 13463-67-7	14	10	10(5)	MG/M3 as Dust ***	
	*** Total Dust (Respirable Fraction)				
Carbon Black. 1333-86-4	0.4	3.5	3.5	MG/M3	0.00

pH - 8.7

Section III -- PHYSICAL DATA

PRODUCT WEIGHT -- 9.37 lb./gal.
SPECIFIC GRAVITY -- 1.13
BOILING POINT -- 185-343 F
VOLATILE VOLUME -- 68 %
OC (Theoretical) -- 2.77 lb.

EVAPORATION RATE -- Slower than Ether
VAPOR DENSITY -- Heavier than Air
MELTING POINT -- N.A.
SOLUBILITY IN WATER -- N.A.
332 gm. (less Federally Exempt Solvents)

Section IV -- FIRE AND EXPLOSION HAZARD DATA

FLASH POINT	LEL	UEL
Not Applicable	N.A.	N.A.

FLAMMABILITY CLASSIFICATION
Not Applicable

Continued on page 2

XTINGUISHING MEDIA
Carbon Dioxide, Dry Chemical, Alcohol Foam
NUSUAL FIRE AND EXPLOSION HAZARDS
Closed containers may explode (due to the build-up of pressure) when xposed to extreme heat.
PECIAL FIRE FIGHTING PROCEDURES
Full protective equipment including self-contained breathing apparatus hould be used. Water spray may be ineffective. If water is used, fog ozzles are preferable. Water may be used to cool closed containers to revent pressure build-up and possible autoignition or explosion when xposed to extreme heat.

Section V -- HEALTH HAZARD DATA

OUTES OF EXPOSURE
Exposure may be by INHALATION and/or SKIN or EYE contact, depending on onditions of use. Alcohols and acetates can be absorbed through the skin. ollow recommendations for proper use, ventilation, and personal protective quipment to minimize exposure.
CUTE Health Hazards
FFECTS OF OVEREXPOSURE
Irritation of eyes, skin and upper respiratory system. In a confined rea vapors in high concentration may cause headache, nausea or dizziness.
IGNS AND SYMPTOMS OF OVEREXPOSURE
Redness and itching or burning sensation may indicate eye or excessive kin exposure.
EDICAL CONDITIONS AGGRAVATED BY EXPOSURE
None generally recognized.
MERGENCY AND FIRST AID PROCEDURES

If INHALED:	If affected, remove from exposure. Restore breathing. Keep warm and quiet.
If on SKIN:	Wash affected area thoroughly with soap and water. Remove contaminated clothing and launder before re-use.
If in EYES:	Flush eyes with large amounts of water for 15 minutes. Get medical attention.
If SWALLOWED:	Get medical attention.

HRONIC Health Hazards
Carbon Black is classified by IARC as possibly carcinogenic to humans group 2B) based on experimental animal data, however, there is nsufficient evidence in humans for its carcinogenicity.
Cobalt and cobalt compounds are classified by IARC as possibly arcinogenic to humans (group 2B) based on experimental animal data, owever, there is inadequate evidence in humans for its carcinogenicity.
Prolonged overexposure to solvent ingredients in Section II may cause dverse effects to the liver, urinary and blood forming systems.
Rats exposed to titanium dioxide dust at 250 mg./m3 developed lung ancer, however, such exposure levels are not attainable in the workplace.

Section VI -- REACTIVITY DATA

TABILITY -- Stable
ONDITIONS TO AVOID
None known.
NCOMPATIBILITY
None known.

Continued on page 3

AZARDOUS DECOMPOSITION PRODUCTS
By fire: Carbon Dioxide, Carbon Monoxide
AZARDOUS POLYMERIZATION
Will not occur

Section VII -- SPILL OR LEAK PROCEDURES

TEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Remove all sources of ignition. Ventilate and remove with inert bsorbent.
ASTE DISPOSAL METHOD
Waste from this product is not hazardous as defined under the Resource onservation and Recovery Act (RCRA) 40 CFR 261.
Incinerate in approved facility. Do not incinerate closed container. ispose of in accordance with Federal, State, and Local regulations egarding pollution.

Section VIII -- PROTECTION INFORMATION

RECAUTIONS TO BE TAKEN IN USE
Use only with adequate ventilation. Avoid breathing vapor and spray ist. Avoid contact with skin and eyes. Wash hands after using.
This coating may contain materials classified as nuisance particulates listed "as Dust" in Section II) which may be present at hazardous levels nly during sanding or abrading of the dried film. If no specific dusts re listed in Section II, the applicable limits for nuisance dusts are CGIH TLV 10 mg./m3 (total dust), 3 mg./m3 (respirable fraction), OSHA PEL 5 mg./m3 (total dust), 5 mg./m3 (respirable fraction).
ENTILATION
Local exhaust preferable. General exhaust acceptable if the exposure to aterials in Section II is maintained below applicable exposure limits. efer to OSHA Standards 1910.94, 1910.107, 1910.108.
ESPIRATORY PROTECTION
If personal exposure cannot be controlled below applicable limits by entilation, wear a properly fitted organic vapor/particulate respirator pproved by NIOSH/MSHA for protection against materials in Section II.
When sanding or abrading the dried film, wear a dust/mist respirator pproved by NIOSH/MSHA for dust which may be generated from this product, nderlying paint, or the abrasive.
ROTECTIVE GLOVES
Wear gloves which are recommended by glove supplier for protection gainst materials in Section II.
YE PROTECTION
Wear safety spectacles with unperforated sideshields.

Section IX -- PRECAUTIONS

OL STORAGE CATEGORY
Not Applicable
RECAUTIONS TO BE TAKEN IN HANDLING AND STORING
Keep container closed when not in use. Transfer only to approved ontainers with complete and appropriate labeling. Do not take internally. eep out of the reach of children.

Continued on page 4

Section X -- OTHER REGULATORY INFORMATION

ARA 313 (40 CFR 372.65C) SUPPLIER NOTIFICATION

CAS No.	CHEMICAL/COMPOUND	% by WT	% Element
121-44-8	Triethylamine.	2	
	Cobalt Compound.	0.2	0.0
	Glycol Ethers	12	

ALIFORNIA PROPOSITION 65

WARNING: This product contains a chemical known to the State of alifornia to cause cancer.

SCA CERTIFICATION

All chemicals in this product are listed, or are exempt from listing, n the TSCA Inventory.

The above information pertains to this product as currently formulated, nd is based on the information available at this time. Addition of educers or other additives to this product may substantially alter the omposition and hazards of the product. Since conditions of use are utside our control, we make no warranties, express or implied, and assume o liability in connection with any use of this information.

MATERIAL SAFETY DATA SHEET

SI-6659A
3 00

ANUFACTURER'S NAME
MARTIN SENOUR PAINTS
101 Prospect Avenue
Cleveland, OH 44115

EMERGENCY TELEPHONE NO.
(216) 566-2917

ATE OF PREPARATION
25-AUG-99

INFORMATION TELEPHONE NO.
(216) 566-2902

Section I -- PRODUCT IDENTIFICATION

RODUCT NUMBER

MSI-6659A

HMIS CODES

Health	2*
Flammability	0
Reactivity	1

RODUCT NAME
MSI* Waterborne Industrial Enamel, Silver
RODUCT CLASS
Water-reducible Acrylic Coating

Section II -- HAZARDOUS INGREDIENTS

NGREDIENT CAS No.	% by WT	ACGIH TLV	OSHA PEL	UNITS	V.P.
ineral Spirits. 64742-88-7	1	100	100	PPM	2.00
-Propoxyethanol 2807-30-9	5	Not Established			1.30
-Butoxyethanol 111-76-2	6	25	25	PPM (Skin)	0.60
obalt 2-Ethylhexanoate. 136-52-7	0.2	Not Established			0.00
pH - 8.7					

Section III -- PHYSICAL DATA

PRODUCT WEIGHT -- 8.50 lb./gal. EVAPORATION RATE -- Slower than Ether
SPECIFIC GRAVITY -- 1.02 VAPOR DENSITY -- Heavier than Air
BOILING POINT -- 212-395 F MELTING POINT -- N.A.
VOLATILE VOLUME -- 69 % SOLUBILITY IN WATER -- N.A.
OC (Theoretical) -- 2.76 lb. 330 gm. (less Federally Exempt Solvents)

Section IV -- FIRE AND EXPLOSION HAZARD DATA

LASH POINT	LEL	UEL
Not Applicable	N.A.	N.A.

LAMMABILITY CLASSIFICATION
Not Applicable
XTINGUISHING MEDIA
Carbon Dioxide, Dry Chemical, Alcohol Foam
NUSUAL FIRE AND EXPLOSION HAZARDS
Closed containers may explode (due to the build-up of pressure) when xposed to extreme heat.

Continued on page 2

PECIAL FIRE FIGHTING PROCEDURES
Full protective equipment including self-contained breathing apparatus hould be used. Water spray may be ineffective. If water is used, fog ozzles are preferable. Water may be used to cool closed containers to revent pressure build-up and possible autoignition or explosion when xposed to extreme heat.

Section V -- HEALTH HAZARD DATA

OUTES OF EXPOSURE
Exposure may be by INHALATION and/or SKIN or EYE contact, depending on onditions of use. Alcohols and acetates can be absorbed through the skin. ollow recommendations for proper use, ventilation, and personal protective quipment to minimize exposure.
CUTE Health Hazards
FFECTS OF OVEREXPOSURE
Irritation of eyes, skin and upper respiratory system. In a confined rea vapors in high concentration may cause headache, nausea or dizziness.
IGNS AND SYMPTOMS OF OVEREXPOSURE
Redness and itching or burning sensation may indicate eye or excessive kin exposure.
EDICAL CONDITIONS AGGRAVATED BY EXPOSURE
None generally recognized.
MERGENCY AND FIRST AID PROCEDURES

If INHALED:	If affected, remove from exposure. Restore breathing. Keep warm and quiet.
If on SKIN:	Wash affected area thoroughly with soap and water. Remove contaminated clothing and launder before re-use.
If in EYES:	Flush eyes with large amounts of water for 15 minutes. Get medical attention.
If SWALLOWED:	Get medical attention.

HRONIC Health Hazards
Cobalt and cobalt compounds are classified by IARC as possibly arcinogenic to humans (group 2B) based on experimental animal data, owever, there is inadequate evidence in humans for its carcinogenicity.
Prolonged overexposure to solvent ingredients in Section II may cause dverse effects to the liver, urinary and blood forming systems.

Section VI -- REACTIVITY DATA

TABILITY -- Stable
ONDITIONS TO AVOID
None known.
NCOMPATIBILITY
None known.
AZARDOUS DECOMPOSITION PRODUCTS
By fire: Carbon Dioxide, Carbon Monoxide
AZARDOUS POLYMERIZATION
Will not occur

Section VII -- SPILL OR LEAK PROCEDURES

TEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Remove all sources of ignition. Ventilate and remove with inert bsorbent.

Continued on page 3

ASTE DISPOSAL METHOD
Waste from this product is not hazardous as defined under the Resource onservation and Recovery Act (RCRA) 40 CFR 261.
Incinerate in approved facility. Do not incinerate closed container. ispose of in accordance with Federal, State, and Local regulations egarding pollution.

Section VIII -- PROTECTION INFORMATION

RECAUTIONS TO BE TAKEN IN USE
Use only with adequate ventilation. Avoid breathing vapor and spray ist. Avoid contact with skin and eyes. Wash hands after using.
This coating may contain materials classified as nuisance particulates listed "as Dust" in Section II) which may be present at hazardous levels nly during sanding or abrading of the dried film. If no specific dusts re listed in Section II, the applicable limits for nuisance dusts are CGIH TLV 10 mg./m3 (total dust), 3 mg./m3 (respirable fraction), OSHA PEL 5 mg./m3 (total dust), 5 mg./m3 (respirable fraction).
ENTILATION
Local exhaust preferable. General exhaust acceptable if the exposure to aterials in Section II is maintained below applicable exposure limits. efer to OSHA Standards 1910.94, 1910.107, 1910.108.
ESPIRATORY PROTECTION
If personal exposure cannot be controlled below applicable limits by entilation, wear a properly fitted organic vapor/particulate respirator pproved by NIOSH/MSHA for protection against materials in Section II.
When sanding or abrading the dried film, wear a dust/mist respirator pproved by NIOSH/MSHA for dust which may be generated from this product, nderlying paint, or the abrasive.
ROTECTIVE GLOVES
Wear gloves which are recommended by glove supplier for protection gainst materials in Section II.
YE PROTECTION
Wear safety spectacles with unperforated sideshields.

Section IX -- PRECAUTIONS

OL STORAGE CATEGORY
Not Applicable
RECAUTIONS TO BE TAKEN IN HANDLING AND STORING
Keep container closed when not in use. Transfer only to approved ontainers with complete and appropriate labeling. Do not take internally. eep out of the reach of children.

Section X -- OTHER REGULATORY INFORMATION

ARA 313 (40 CFR 372.65C) SUPPLIER NOTIFICATION

CAS No.	CHEMICAL/COMPOUND	% by WT	% Element
	Cobalt Compound.	0.2	0.0
	Glycol Ethers	12	

SCA CERTIFICATION
All chemicals in this product are listed, or are exempt from listing, n the TSCA Inventory.

Continued on page

The above information pertains to this product as currently formulated, nd is based on the information available at this time. Addition of educers or other additives to this product may substantially alter the omposition and hazards of the product. Since conditions of use are utside our control, we make no warranties, express or implied, and assume o liability in connection with any use of this information.

964 — SECTION I — PRODUCT IDENTIFICATION

MATERIAL SAFETY DATA SHEET

THE MARTIN-SENOUR CO.
101 PROSPECT AVE. N.W.
CLEVELAND, OH 44115

Automotive Finishes

EMERGENCY TELEPHONE NO. (216) 566-2917
INFORMATION TELEPHONE NO. (216) 566-2902
DATE OF PREPARATION 1-Nov-96

©1996, The Martin-Senour Co.

MSI™ Waterborne Industrial Enamel

6655A 6660A

MSI/N2

— SECTION II — CAS No.	HAZARDOUS INGREDIENT (percent by weight)	ACGIH TLV <STEL>	OSHA PEL <STEL>	Units	Vapor Pressure (mm Hg)	MSI-6651D Red (PH)	MSI-6654B Med. Yellow (Cat #2)	MSI-6656C Orange (Alfa Chalmers)	[redacted]	[redacted]	MSI-6661B Industrial Dark Grey	MSI-6720 Primer Grey	MSI-6721 Primer Red Oxide
8742-88-7	Mineral Spirits	100	100	PPM	2.0				1				
[illegible]	2-Propoxyethanol	Not Established			1.3	5	4	5	5		5		
[illegible]	[illegible]-methanol	25	25	PPM (Skin)	0.6	8	6	7	[illegible]			11	[illegible]
	[illegible]ne	10 <15>	10 <15>	PPM	54.0								
	[illegible]-Ethylhexanoate	Not Established				0.1	0.1	0.1	[illegible]		0.2		
	[illegible]	2	2	Mg/M3	as Resp. Dust							8	9
	[illegible]arbonate	10	15[5]	Mg/M3 [Resp.	as Dust Fraction]							23	22
	[illegible]nium Dioxide	10	10[5]	Mg/M3 [Resp.	as Dust Fraction]	1	5			14	4	3	
	[illegible] Black	3.5	3.5	Mg/M3						0.4	0.2	0.1	
Weight per Gallon (lbs.)						8.50	9.33	8.46	8.50	9.36	8.67	10.72	10.86
Percent Water						53.4	47.3	54.4	54.0	[illegible]3.9	51.8	38.1	35.9
VOC (Volatile Organic Compounds) Total - lbs./gal.						1.21	1.26	1.18	1.22	[illegible]	1.24		
VOC Less Water & Federally Exempt Solvents - lbs./gal.						2.66	2.69	2.67	[illegible]	2.[illegible]			
[illegible]hotochemically Reactive						No	No	[illegible]	[illegible]	No			
[illegible]sh Point (°F)						None	None	[illegible]	None	None			
HMIS (NFPA) Rating (health - flammability - reactivity)						2 0 0	2 0 0	2 0 0	2 0 1	3 0 0			

[illegible]ingredient subject to the reporting requirements of the Superfund Amendments and Reauthorization Act (SARA) Section 313, 40 CFR 372.65 C

→→→ *MSDS Text Page Follows* →→→

MSI™ Waterborne Industrial Enamel

MSI/N

Section III — PHYSICAL DATA

PRODUCT WEIGHT -	See TABLE	EVAPORATION RATE -	Slower than Ether
SPECIFIC GRAVITY -	1.01 1.31	VAPOR DENSITY -	Heavier than Air
BOILING RANGE -	185-395 °F	MELTING POINT -	N.A.
VOLATILE VOLUME -	64-72 %	SOLUBILITY IN WATER -	N.A.
pH -	8-9		

Section IV — FIRE AND EXPLOSION HAZARD DATA

FLAMMABILITY CLASSIFICATION FLASH POINT see TABLE LEL N.Ap UEL N.Ap.
Not Applicable
EXTINGUISHING MEDIA
Carbon Dioxide, Dry Chemical, Alcohol Foam
UNUSUAL FIRE AND EXPLOSION HAZARDS
Closed containers may explode (due to the build-up of pressure) when exposed to extreme heat.
SPECIAL FIRE FIGHTING PROCEDURES
Full protective equipment including self-contained breathing apparatus should be used. Water spray may be ineffective. If water is used, fog nozzles are preferable. Water may be used to cool closed containers to prevent pressure build-up and possible autoignition or explosion when exposed to extreme heat.

Section V — HEALTH HAZARD DATA

ROUTES OF EXPOSURE
Exposure may be by INHALATION and/or SKIN or EYE contact, depending on conditions of use. Alcohols and acetates can be absorbed through the skin. To minimize exposure, follow recommendations for proper use, ventilation, and personal protective equipment.
ACUTE Health Hazards
EFFECTS OF OVEREXPOSURE
Irritation of eyes, skin and respiratory system. In a confined area vapors in high concentration may cause headache, nausea or dizziness.
SIGNS AND SYMPTOMS OF OVEREXPOSURE
Redness and itching or burning sensation may indicate eye or excessive skin exposure.
MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE
None generally recognized.
EMERGENCY AND FIRST AID PROCEDURES
If INHALED: If affected, remove from exposure. Restore breathing. Keep warm and quiet.
If on SKIN: Wash affected area thoroughly with soap and water. Remove contaminated clothing and launder before re-use.
If in EYES. Flush eyes with large amounts of water for 15 minutes. Get medical attention.
If SWALLOWED: Get medical attention.
CHRONIC Health Hazards
Carbon Black is classified by IARC as possibly carcinogenic to humans (group 2B) based on experimental animal data, however, there is insufficient evidence in humans for its carcinogenicity.
Cobalt and cobalt compounds are classified by IARC as possibly carcinogenic to humans (group 2B) based on experimental animal data, however, there is inadequate evidence in humans for its carcinogenicity.
Prolonged overexposure to solvent ingredients in Section II may cause adverse effects to the liver, urinary, and blood forming systems.
Rats exposed to titanium dioxide dust at 250 mg /m3 developed lung cancer, however, such exposure levels are not attainable in the workplace.

Section VI — REACTIVITY DATA

STABILITY - Stable
CONDITIONS TO AVOID
None
INCOMPATIBILITY
None known.
HAZARDOUS DECOMPOSITION PRODUCTS
By fire: Carbon Dioxide, Carbon Monoxide
HAZARDOUS POLYMERIZATION - Will Not Occur

Section VII — SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Remove all sources of ignition. Ventilate and remove with inert absorbent.
WASTE DISPOSAL METHOD
Waste from these products is not hazardous as defined under the Resource Conservation and Recovery Act (RCRA) 40 CFR 261.
Incinerate in approved facility. Do not incinerate closed container. Dispose of in accordance with Federal, State, and Local regulations regarding pollution.

Section VIII — PROTECTION INFORMATION

PRECAUTIONS TO BE TAKEN IN USE
Use only with adequate ventilation. Avoid breathing vapor and spray mist. Avoid contact with skin and eyes. Wash hands after using.
These coatings may contain materials classified as nuisance particulates (listed "as Dust" in Section II) which may be present at hazardous levels only during sanding or abrading of the dried film. If no specific dusts are listed in Section II, the applicable limits for nuisance dusts are ACGIH TLV 10 mg./m3 (total dust), 3 mg./m3 (respirable fraction), OSHA PEL 15 mg./m3 (total dust), 5 mg./m3 (respirable fraction).
VENTILATION
Local exhaust preferable. General exhaust acceptable if the exposure to materials in Section II is maintained below applicable exposure limits. Refer to OSHA Standards 1910.94, 1910.107, 1910.106.
RESPIRATORY PROTECTION
If personal exposure cannot be controlled below applicable limits by ventilation wear a properly fitted organic vapor/particulate respirator approved by NIOSH/MSHA for protection against materials in Section II.
When sanding or abrading the dried film, wear a dust/mist respirator approved by NIOSH/MSHA for dust which may be generated from this product, underlying paint, or the abrasive.
PROTECTIVE GLOVES
Wear gloves which are recommended by glove supplier for protection against materials in Section II.
EYE PROTECTION
Wear safety spectacles with unperforated sideshields.

Section IX — PRECAUTIONS

DOL STORAGE CATEGORY - Not Applicable
PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
Keep container closed when not in use. Transfer only to approved containers with complete and appropriate labeling. Do not take internally. Keep out of the reach of children.

Section X — OTHER REGULATORY INFORMATION

CALIFORNIA PROPOSITION 65
WARNING: MSI-6622A, MSI-6720 and MSI-6721 contain a chemical(s) known to the State of California to cause cancer. MSI-6646C and MSI-6654B contain chemicals known to the State of California to cause cancer and birth defects or other reproductive harm.

TSCA CERTIFICATION
All chemicals in these products are listed, or are exempt from listing, on the TSCA Inventory.

The above information pertains to these products as currently formulated, and is based on the information available at this time. Addition of reducers or other additives to these products may substantially alter the composition and hazards of the products. Since conditions of use are outside our control, we make no warranties, express or implied, and assume no liability in connection with any use of this information.

covers MSDS pages MSI/N1 to MSI/N2

MSDS for Paint 1403-0100

Physical Data

Product Code	Description latex enamel flat	Wt./Gal.	VOC gr./ltr.	% Volatile by Volume	Flash Point	Boiling Range	HMIS	DOT, proper shipping name
1403-0100	dulux ultra interior acrylic eggshell, white ✓	11.12	111.51	59.12	none	212-477	*110	paint ** protect from freezing **
1403-0110	white tint base	11.12	111.55	59.12	none	212-477	*110	paint ** protect from freezing **
1403-0120	pure brilliant white	11.12	111.55	59.12	none	212-477	*110	paint ** protect from freezing **
1403-0300	intermediate tint base	10.41	65.19	65.77	none	212-477	*110	paint ** protect from freezing **
1403-0400	deep tint base	9.69	62.88	67.96	none	212-477	*110	paint ** protect from freezing **
1403-0500	accent base	9.73	58.38	66.38	none	212-477	*110	paint ** protect from freezing **
1403-1000	white-high hiding	11.12	111.36	59.12	none	212-477	*110	paint ** protect from freezing **
	antique white	11.13	111.33	59.12	none	212-477	*110	paint ** protect from freezing **
1403-1050	cielo blanco	11.12	111.52	59.12	none	212-477	*110	paint ** protect from freezing **

Ingredients

Product Codes with % by Weight

	1403-0100	1403-0110	1403-0120	1403-0300	1403-0400	1403-0500	1403-1000	1403-1020	1403-1050
ethanol, 2,2'-oxybis-	1-5	1-5	1-5				1-5	1-5	1-5
limestone						5-10			
nepheline svenite	5-10	5-10	5-10				5-10	5-10	5-10
kieselguhr	1-5	1-5	1-5				1-5	1-5	1-5
quartz				10-20	10-20	10-20			
propanoic acid, 2-methyl-, monoester with 2,2,4-trimethyl-1,3-pentanediol	1-5	1-5	1-5	1-5	1-5	1-5	1-5	1-5	1-5
titanium oxide	20-30	20-30	20-30	10-20	1-5	20-30	20-30	20-30	20-30
vinyl acrylic copolymer	10-20	10-20	10-20	10-20	10-20		10-20	10-20	10-20
water	30-40	30-40	30-40	40-50	50-60	50-60	30-40	30-40	30-40
2-propenoic acid, 2-methyl-, methyl ester, polymer with butyl 2-propenoate and ethenylbenzene	1-5	1-5	1-5	1-5	1-5		1-5	1-5	1-5

Chemical Hazard Data

CHEMICAL NAME	COMMON NAME	CAS. NO.	ACGIH-TLV 8-HOUR TWA	ACGIH-TLV STEL	OSHA-PEL 8-HOUR TWA	OSHA-PEL STEL	OSHA-PEL C	OSHA-PEL S	S.R. STD.	S 2	S 3	C C	N	I	O
ethanol, 2,2'-oxybis-	diethylene glycol	111-46-6	ne	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n
limestone	natural calcium carbonate	1317-65-3	10 mg/m³	ne	5 mg/m³	ne	ne	ne	ne	n	n	n	n	n	n
nepheline svenite	same	37244-96-5	10 mg/m³	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n
kieselguhr	silica, diatomaceous earth	61790-53-2	10 mg/m³	ne	6 mg/m³	ne	ne	ne	ne	n	n	n	n	n	n
quartz	quartz	14808-60-7	0.1 mg/m³	ne	0.1 mg/m³	ne	ne	ne	ne	n	n	n	y	y	
propanoic acid, 2-methyl-, monoester with 2,2,4-trimethyl-1,3-pentanediol	texanol	25265-77-4	ne	ne	ne	ne	ne	ne	ne	n	n	n	n		
titanium oxide	titanium dioxide	13463-67-7	10 mg/m³	ne	5 mg/m³	ne	ne	ne	ne	n	n	n	n	n	n
vinyl acrylic copolymer	vinyl acrylic copolymer	sup. conf.	ne	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n
water	water	7732-18-5	ne	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n
2-propenoic acid, 2-methyl-, methyl ester, polymer with butyl 2-propenoate and ethenylbenzene	butyl acrylate-methyl methacrylate-styrene cop	27136-15-8	ne	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n

Footnotes:

C = Ceiling - Concentration th exceeded, even instantaneously

S = Skin - Additional above airborne expos absorption

save, over and ay result from skin

R.STD = Supplier Recommend

ppm = parts per million

mg/m³ = milligm ubic meter

S2 = Sara Section 302 EHS

Sara Sec Chemical

CERCL Ilemical

Carcinogenicity Lis By:
N = NTP, I = IARC = OSH
y = yes, n = no

FIRE AND EXPLOSION HAZARD DATA

Extinguishing media : Dry chemical or foam water fog. Carbon dioxide.

Unusual fire and explosion hazards : Closed containers may burst if exposed to extreme heat or fire. In closed tanks, water or foam may cause frothing or eruption.

Special fire fighting procedures : Water may be used to cool and protect exposed containers. Firefighters should use full protective clothing, eye protection, and self-contained breathing apparatus.

HEALTH HAZARD DATA

Primary route(s) of exposure : Inhalation, skin contact, eye contact, ingestion.

Effects of overexposure :

Inhalation : Irritation of respiratory tract, lungs. Prolonged inhalation may lead to dizziness and/or lightheadedness, headache, nausea, vomiting, coughing, sneezing, central nervous system depression, anesthetic effect or narcosis, difficulty of breathing, pneumoconiosis.

Skin contact : Irritation of skin. Prolonged or repeated contact can cause dermatitis, defatting.

Eye contact : Irritation of eyes. Prolonged or repeated contact can cause conjunctivitis.

Ingestion : Ingestion may cause fatigue, drowsiness, dizziness and/or lightheadedness, nausea, vomiting, diarrhea, gastro-intestinal disturbances, severe abdominal pain, central nervous system depression, central nervous system damage, liver damage, kidney damage, bladder damage, pulmonary edema, loss of consciousness, cyanosis, death.

Supplemental health information : Contains a chemical that is moderately toxic by ingestion. Other effects of overexposure may include toxicity to liver, kidney. May be absorbed through skin. Contains crystalline silica which is considered a hazard by inhalation. IARC has classified crystalline silica as probably carcinogenic for humans (2a). This classification is based on the findings of laboratory animal studies that were considered sufficient and data from epidemiological studies that were considered limited for carcinogenicity. Crystalline silica is also a known cause of silicosis, a noncancerous lung disease. NTP has classified crystalline silica a reasonably anticipated human carcinogen. A study conducted by NTP, using a continuous breeding protocol, demonstrated that diethylene glycol in drinking water at a concentration of 3.5% (6.1 g/kg/day) resulted in decreased fertility and reproductive performance in mice. These effects were not seen in the lower dose levels evaluated. Since the exposure resulting from incidental contact is likely to be lower by several degrees of magnitude and the route of exposure used in this study does not reflect a likely route from occupational or consumer use the significance of these findings to humans is uncertain.

Medical conditions aggravated by exposure : Eye, skin, respiratory disorders kidney disorders liver disorders nervous system disorders

FIRST AID PROCEDURES

Inhalation : Remove to fresh air. Restore and support continued breathing. Get emergency medical attention. Have trained person give oxygen if necessary. Get medical help for any breathing difficulty. Remove to fresh air if inhalation causes eye watering, headaches, dizziness, or other discomfort.

Skin contact : Flush from skin with water. Then wash thoroughly with soap and water. Remove contaminated clothing. Wash contaminated clothing before re-use.

Eye contact : Flush immediately with large amounts of water, especially under lids for at least 15 minutes. If irritation or other effects persist, obtain medical treatment.

Ingestion : If swallowed, obtain medical treatment immediately.

REACTIVITY DATA

Stability : Stable

Incompatibility : Oxidizers, acids, bases, aluminum, zinc, magnesium, sodium, potassium.

Conditions to avoid : Elevated temperatures, contact with oxidizing agent, contact with aluminum or zinc, high concentration of dust, freezing, sparks, open flame.

Hazardous decomposition products : Carbon monoxide, carbon dioxide, oxygen.

Hazardous polymerization : Will not occur

SPILL OR LEAK PROCEDURES

Steps to be taken in case material is released or spilled : Comply with all applicable health and environmental regulations. Eliminate all sources of ignition. Ventilate area. Spills may be collected with absorbent materials. Evacuate all unnecessary personnel. Place collected material in proper container. Vacuum clean spillage. Large spills - shut off leak if safe to do so. Dike and contain spill. Pump to storage or salvage vessels. Use absorbent to pick up excess residue. Keep salvageable material and rinse water out of sewers and water courses. Small spills - use absorbent to pick up residue and dispose of properly.

Waste disposal : Dispose in accordance with all applicable regulations. Avoid discharge to natural waters.

SPECIAL PROTECTION INFORMATION

Respiratory protection : Control environmental concentrations below applicable standards. Where respiratory protection is required, use only NIOSH/MSHA approved respirators in accordance with OSHA standard 29 CFR 1910.134.

Ventilation : Provide dilution ventilation or local exhaust to prevent build-up of vapors.

Personal protective equipment : Eye wash, safety shower, safety glasses or goggles. Impervious gloves, impervious clothing, face shield.

SPECIAL PRECAUTIONS

Handling and storage : Store below 100f(38c). Keep away from heat, sparks and open flame. Keep from freezing.

Other precautions : Use only with adequate ventilation. Do not take internally. Keep out of reach of children. Avoid contact with skin and eyes, and breathing of vapors. Wash hands thoroughly after handling, especially before eating or smoking. Keep containers tightly closed and upright when not in use. Avoid conditions which result in formation of inhalable particles such as spraying or abrading (sanding) painted surfaces. If such conditions cannot be avoided, use appropriate respiratory protection as directed under special protection information.

The information contained herein is based on data available at the time of preparation of this data sheet which ICI Paints believes to be reliable. However, no warranty is expressed or implied regarding the accuracy of this data. ICI Paints shall not be responsible for the use of this information, or of any product, method or apparatus mentioned and you must make your own determination of its suitability and completeness for your own use, for the protection of the environment, and the health and safety of your employees and the users of this material.

Complies with OSHA hazard communication standard 29CFR1910.1200.

925 Euclid Avenue
Cleveland, Ohio 44115

EMERGENCY TELEPHONE NO. (800)545-2643

MSDS for Paint 4020-1000

Physical Data

primer

Product Code	Description	Wt./Gal.	VOC gr./ltr.	% Volatile by Volume	Flash Point	Boiling Range	HMIS	DOT, proper shipping name
4020-1000	white	11.72	77.48	55.57	none	212-453	*310	paint ** protect from freezing **
4020-7100	red	11.29	81.58	58.13	none	212-453	*310	paint ** protect from freezing **

Ingredients

Product Codes with % by Weight

	4020-1000	4020-7100
carbonic acid calcium salt	20-30	20-30
quartz	5-10	5-10
solvent naphtha (petroleum), medium aliphatic	1-5	1-5
ethanol, 2-(2-butoxyethoxy)-	1-5	1-5
titanium oxide	5-10	
lead		.01-.1
quartz	.1-1.0	.1-1.0
silica	1-5	
iron oxide		5-10
2-propenoic acid, polymer with butyl 2-propenoate and ethenylbenzene	10-20	10-20
water	30-40	30-40

			ACGIH-TLV		OSHA-PEL				S.R.	S	S	C			
CHEMICAL NAME	COMMON NAME	CAS. NO.	8-HOUR TWA	STEL	8-HOUR TWA	STEL	C	S	STD.	2	3	C	N	I	O
carbonic acid calcium salt	calcium carbonate	471-34-1	10 mg/m³	ne	5 mg/m³	ne	ne	ne	ne	n	n	n	n	n	n
quartz	quartz	14808-60-7	0.1 mg/m³	ne	0.1 mg/m³	ne	ne	ne	ne	n	n	n	y	y	n
solvent naphtha (petroleum), medium aliphatic	hydrotreated light distillate (petroleum)	64742-88-7	100 ppm	ne	100 ppm	ne	ne	ne	ne	n	n	n	n	n	n
ethanol, 2-(2-butoxyethoxy)-	diethylene glycol monobutyl ether	112-34-5	ne	ne	ne	ne	ne	ne	ne	n	y	n	n	n	n
titanium oxide	titanium dioxide	13463-67-7	10 mg/m³	ne	10 mg/m³	ne	ne	ne	ne	n	n	n	n	n	n
lead	lead	7439-92-1	0.15 mg/m³	ne	0.05 mg/m³	ne	ne	ne	ne	n	y	y	n	y	n
quartz	quartz	14808-60-7	0.1 mg/m³	ne	0.1 mg/m³	ne	ne	ne	ne	n	n	n	y	y	n
silica	amorphous silica	7631-86-9	10 mg/m³	ne	6 mg/m³	ne	ne	ne	ne	n	n	n	n	n	n
iron oxide	ferric oxide	1309-37-1	5 mg/m³	ne	10 mg/m³	ne	ne	ne	ne	n	n	n	n	n	n
2-propenoic acid, polymer with butyl 2-propenoate and ethenylbenzene	sytrene/acrylate copolymer	25586-20-3	ne	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n
water	water	7732-18-5	ne	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n

Footnotes:

Ceiling - Concentration that should not be exceeded even instantaneously

Supplier Recommended Standard

S = Skin - Additional exposure over and above airborne exposure may result from skin absorption

n/a = not applicable

ne = not established

ppm = parts per million

mg/m³ = milligrams per cubic meter

S2 = Sara Section 302 EHS

S3 = Sara Section 313 Chemical

CC = ERCLA Chemical

Carcinogenicity Listed By:
N = NTP, I = IARC, O = OSHA

FIRE AND EXPLOSION HAZARD DATA

Extinguishing media : Dry chemical or foam water fog. Carbon dioxide.

Unusual fire and explosion hazards : Vapors are heavier than air and may travel long distances to a source of ignition and flash back. Closed containers may burst if exposed to extreme heat or fire. May decompose under fire conditions emitting irritant and/or toxic gases.

Special fire fighting procedures : Water may be used to cool and protect exposed containers. Firefighters should use full protective clothing, eye protection, and self-contained breathing apparatus. Self-contained breathing apparatus recommended.

HEALTH HAZARD DATA

Primary route(s) of exposure : Inhalation, skin contact, eye contact, ingestion.

Effects of overexposure :

Inhalation : Irritation of respiratory tract. Prolonged inhalation may lead to mucous membrane irritation, drowsiness, dizziness and/or lightheadedness, headache, nausea, coughing, difficulty with speech, central nervous system depression, anesthetic effect or narcosis, difficulty of breathing, bronchitis, pneumoconiosis.

Skin contact : Irritation of skin. Prolonged or repeated contact can cause dermatitis, defatting.

Eye contact : Irritation of eyes. Prolonged or repeated contact can cause conjunctivitis, blurred vision, tearing of eyes, redness of eyes, severe eye irritation or burns.

Ingestion : Ingestion may cause lung inflammation and damage due to aspiration of material into lungs, drowsiness, dizziness and/or lightheadedness, headache, uncoordination, nausea, gastro-intestinal disturbances, apathy, intoxication.

Supplemental health information : Other effects of overexposure may include toxicity to liver, kidney, blood. May be absorbed through skin. Excessive exposure to lead, including ingestion, can result in lead poisoning. Early symptoms are fatigue, disturbance of sleep, constipation, with more severe exposure followed by colic, anemia, and neuritis (nerve inflammation). Prolonged overexposure can severely damage red blood cell formation, kidneys, nervous and reproductive systems. Other symptoms include loss of appetite, metallic taste in mouth, anxiety, nausea, pallor, headache, irritability, muscle and joint pain, tremors, numbness, dizziness and hypertension. Excessive inhalation of fumes may lead to metal fume fever characterized by a metallic taste in mouth, excessive thirst, coughing, weakness, fatigue, muscular pain, nausea, chills and fever. Notice - reports have associated repeated and prolonged occupational overexposure to solvents with permanent brain and nervous system damage. Intentional misuse by deliberately concentrating and inhaling the contents may be harmful or fatal. Contains crystalline silica which is considered a hazard by inhalation. IARC has classified crystalline silica as probably carcinogenic for humans (2a). This classification is based on the findings of laboratory animal studies that were considered sufficient and data from epidemiological studies that were considered limited for carcinogenicity. Crystalline silica is also a known cause of silicosis, a noncancerous lung disease. NTP has classified crystalline silica a reasonably anticipated human carcinogen.

Medical conditions aggravated by exposure : Eye, skin, respiratory disorders lung disorders

FIRST AID PROCEDURES

Inhalation : Remove to fresh air. Restore and support continued breathing. Get emergency medical attention. Have trained person give oxygen if necessary. Get medical help for any breathing difficulty.

Skin contact : Flush from skin with water. Then wash thoroughly with soap and water. Remove contaminated clothing. Wash contaminated clothing before re-use.

Eye contact : Flush immediately with large amounts of water, especially under lids for at least 15 minutes. If irritation or other effects persist, obtain medical treatment.

Ingestion : If swallowed, obtain medical treatment immediately

REACTIVITY DATA

Stability : Stable

Incompatibility : Oxidizers, acids, bases. Alkalis aluminum, metals, peroxides, nitric acid, magnesium.

Conditions to avoid : Elevated temperatures, contact with oxidizing agent, high concentration of dust, freezing, sparks, open flame. Ignition sources

Hazardous decomposition products : Carbon monoxide, carbon dioxide, lead oxide, toxic gases

Hazardous polymerization : Will not occur

SPILL OR LEAK PROCEDURES

Steps to be taken in case material is released or spilled : Comply with all applicable health and environmental regulations. Eliminate all sources of ignition. Ventilate area. Place collected material in proper container. Complete personal protective equipment must be used during cleanup. Large spills - shut off leak if safe to do so. Dike and contain spill. Pump to storage or salvage vessels. Use absorbent to pick up excess residue. Keep salvageable material and rinse water out of sewers and water courses. Small spills - use absorbent to pick up residue and dispose of properly.

Waste disposal : Dispose in accordance with all applicable regulations. Avoid discharge to natural waters.

SPECIAL PROTECTION INFORMATION

Respiratory protection : Control environmental concentrations below applicable standards. Where respiratory protection is required, use only NIOSH/MSHA approved respirators in accordance with OSHA standard 29 CFR 1910.134.

Ventilation : Provide dilution ventilation or local exhaust to prevent build-up of vapors. Use explosion-proof equipment.

Personal protective equipment : Eye wash, safety shower, safety glasses or goggles. Impervious gloves, impervious clothing, apron.

SPECIAL PRECAUTIONS

Handling and storage : Store below 100f. Keep away from heat, sparks and open flame. Keep from freezing. Do not store in aluminum containers. Keep container tightly closed in a well-ventilated area.

Other precautions : Use only with adequate ventilation. Do not take internally. Keep out of reach of children. Avoid contact with skin and eyes, and breathing of vapors. Wash hands thoroughly after handling, especially before eating or smoking. Keep containers tightly closed and upright when not in use. Contains lead. Dried film of this product may be harmful if eaten or chewed. Do not use on toys, furniture, or surfaces of other articles which might be chewed by children. Do not apply on exterior surfaces of dwelling units, such as windowsills, porches, stairs, or railings to which children may be commonly exposed. Avoid conditions which result in formation of inhalable particles such as spraying or abrading (sanding) painted surfaces. If such conditions cannot be avoided, use appropriate respiratory protection as directed under special protection information. Empty containers may contain hazardous residues. Ground equipment when transferring to prevent accumulation of static charge.

The information contained herein is based on data available at the time of preparation of this data sheet which ICI Paints believes to be reliable. However, no warranty is expressed or implied regarding the accuracy of this data. ICI Paints shall not be responsible for the use of this information, or of any product, method or apparatus mentioned and you must make your own determination of its suitability and completeness for your own use, for the protection of the environment, and the health and safety of your employees and the users of this material.

MSDS for Paint 25524

Page: MATERIAL SAFETY DATA SHEET Printed 07/24/9
For Coatings, Resins and Related Materials
Revised : 03/15/91

SECTION I - PRODUCT IDENTIFICATION

Manufacturer: AEXCEL CORPORATION
7373 PRODUCTION DRIVE
MENTOR, OH 44061

Information Phone: (216) 974-3800
Emergency Phone: (800) 424-9300
CHEMTREC Phone: (800) 424-9300

Product Class: WATER BASE
Trade Name : 22683-25524
Product Code : 72W-A035
C.A.S. Number: NONE

! Hazard Ratings: Health - 1
! none -> extreme Fire - 1
! 0 ---> 4 Reactivity - 0
!
!

SECTION II - HAZARDOUS INGREDIENTS

Ingredients	CAS #	Weight %	--- Exposure Limits ---- ACGIH/TLV	OSHA/PEL	VP mm HG
WATER	NONE	39.134	ppm	0	ppm 0
TEXANOL	25265-77-4	1.108	Undetermined		0
TITANIUM DIOXIDE	13463-67-7	8.520	15 mg/M3	0	mg/M3 0
CALCIUM CARBONATE	471-34-1	19.170	0 mg/M3	0	mg/M3 98
PROPRIETARY PIGMENT	(SEE SECTION	14.910	Undetermined		0
ACRYLIC RESIN	UNKNOWN	13.683	Undetermined		0
METHANOL (SARA)	67-56-1	1.704	200 ppm	200	ppm 97.7
		STEL=		250	

THE WORD SARA AFTER AN INGREDIENT IN THIS SECTION MEANS THAT IT IS SUBJECT TO THE REPORTING REQUIREMENTS OF SECTION 313 OF TITLE III OF THE SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT OF 1986.

-> These items are listed on the SARA TITLE III Section 313 inventory

SECTION III - PHYSICAL DATA

Boiling Range: 147 - 477 Deg. F
Vap. Rate: 0.08 x n-Butyl Acetate
Volatiles volume: 61.5 %
Appearance: HEAVY WHITE LIQUID

Vapor Density: Heavier than Air.
Liquid Density: Heavier than Water.
Wgt per gallon: 11.74 Pounds.

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

Flammability Class: IIIB Flash Point: >200 DEG F LEL N/A

EXTINGUISHING MEDIA:
NONE

SPECIAL FIREFIGHTING PROCEDURES:
NONE.

NUSUAL FIRE & EXPLOSION HAZARDS:
KEEP CONTAINERS TIGHTLY CLOSED. ISOLATE FROM HEAT, SPARKS AND OPEN FLAME. CLOSED CONTAINERS MAY EXPLODE WHEN EXPOSED TO EXTREME HEAT. IN A TEST "EVALUATION OF THE FIRE HAZARD OF WATER-BORNE COATINGS" [FACTORY MUTUAL RESEARCH CORPORATION SCEINTIFIC CIRCULAR 804 DECEMBER 1977] FOUR WATER-BORNE COATINGS "PRESENTED NO [FIRE] HAZARD". "IT WAS ALSO CONCLUDED THAT RESULTS OBTAINED FROM LABORATORY [FLASH
(cont.)

AEXCEL CORPORATION / Latex Traffic Paint
Material Safety Data Sheet for: 22683-22524 (72W-A036

SECTION IV - FIRE AND EXPLOSION HAZARD DATA (cont.)

-UNUSUAL FIRE & EXPLOSION HAZARDS: (cont.)
POINT] TESTS ARE NOT A REPRESENTATIVE INDICATION OF THE FIRE HAZARD OF WATER-BORNE COATINGS".

SECTION V - HEALTH HAZARD DATA

-PERMISSIBLE EXPOSURE LEVEL:
SEE SECTION II FOR INFORMATION ABOUT INDIVIDUAL INGREDIENTS.
-EFFECTS OF OVEREXPOSURE:
SEVERE EYE IRRITATION. EXCESSIVE INHALATION MAY CAUSE HEADACHES, DIZZINESS AND/OR NAUSEA. SKIN CONTACT MAY CAUSE IRRITATION OR RASH.

THE SPECIFIC CHEMICAL IDENTITY OF THE PROPRIETARY PIGMENT(S) IN SECTION II IS WITHHELD AS A TRADE SECRET.

SKIN ABSORPTION MAY POTENTIALLY CONTRIBUTE TO THE OVERALL EXPOSURE TO METHANOL. APPROPRIATE MEASURES SHOULD BE TAKEN TO PREVENT ABSORPTION SO THAT THE TLV IS ALWAYS MET.
-
NIOSH RECOMMENDS A LIMIT OF 200 ppm, 8 HOUR TWA; 800 ppm 15 MINUTE CEILING FOR METHANOL.
-
OVEREXPOSURE TO METHANOL (OR ITS COMPONENTS) HAS BEEN SUGGESTED AS A CAUSE OF EYE DAMAGE IN HUMANS.
-

-FIRST AID:
IN ALL SUCH CASES, CONTACT A PHYSICIAN FOR PROPER MEDICAL ATTENTION, AND TAKE THIS INFORMATION TO THE PHYSICIAN.

SECTION VI - REACTIVITY DATA

STABILITY: [ ] Unstable [x] Stable
HAZARDOUS POLYMERIZATION: [ ] May occur [x] Will not occur
-INCOMPATIBILITY
N/A
-CONDITIONS TO AVOID:
N/A
-HAZARDOUS DECOMPOSITION PRODUCTS:
CO,CO2

SECTION VII - SPILL OR LEAK PROCEDURES

-STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
COLLECT IN A RETAINING AREA OR CONTAINER. THEN TRANSFER TO A CLOSED CONTAINER. AVOID EXPOSURE TO HEAT, SPARKS, FIRE OR OPEN FLAME. AVOID HOT METAL SURFACES.

MSDS for Paint 4206-0100

Physical Data DevFlek Devoe Coating - Acrylic Sem gloss Catchetechnical)

Product Code	Description	Wt./Gal.	VOC gr./ltr.	% Volatile by Volume	Flash Point	Boiling Range	HMIS	DOT, proper shipping name
4206-0100	white X	10.54	189.53	57.83	none	212-453	310	paint ** protect from freezing **
4206-0110	white tint base	10.23	195.70	59.32	none	212-453	310	paint ** protect from freezing **
4206-0300	intermediate tint base	9.29	215.22	64.06	none	212-453	310	paint ** protect from freezing **
4206-0400	deep tint base	9.03	217.81	64.76	none	212-453	310	paint ** protect from freezing **
4206-1000	white-high hiding	10.39	191.29	58.64	none	212-453	310	paint ** protect from freezing **
4206-9990	black	8.78	222.15	65.69	none	212-453	*310	paint ** protect from freezing **

Ingredients

Product Codes with % by Weight

	4206-0100	4206-0110	4206-0300	4206-0400	4206-1000	4206-9990
titanium oxide			1-5	1-5		
solvent naphtha (petroleum), medium aliphatic	1-5	1-5	1-5	1-5	1-5	1-5
ethanol, 2-butoxy-	1-5	1-5	1-5	1-5	1-5	1-5
ethanol, 2-(2-butoxyethoxy)-	1-5	1-5	1-5	1-5	1-5	1-5
titanium oxide	10-20	10-20	5-10	1-5	10-20	
silica	1-5	1-5			1-5	
carbon black						1-5
water	30-40	30-40	40-50	40-50	30-40	50-60
2-propenoic acid, polymer with ethenylbenzene and (1-methylethenyl)benzene, ammonium salt	5-10	5-10	5-10	5-10	5-10	5-10
aluminum hydroxide	5-10	5-10	5-10	1-5	5-10	5-10
2-propenoic acid, 2-methyl-, methyl ester, polymer with ethenylbenzene and 2-ethylhexyl 2-propenoate	5-10	5-10	10-20	10-20	5-10	10-20
2-ethylhexyl ester, acrylic acid polymer with styrene	5-10	5-10	10-20	10-20	5-10	10-20

Chemical Hazard Data

			ACGIH-TLV		OSHA-PEL				S.R.	S	S				
			UR TWA	STEL	8-HOUR TWA	STEL	C	S	STD.	2	3		N		
			/m³	ne	10 mg/m³	ne	ne	ne	ne	n	n		n		
			pm	ne	100 ppm	ne	ne	ne	ne	n	n		n		
			5 ppm	ne	25 ppm	ne	ne	skin	ne	n	y	n	n		
				ne	ne	ne	ne	ne	ne	n	y	n	n		
			/m³	ne	10 mg/m³	ne	ne	ne	ne	n	n	n	n		
			/m³	ne	6 mg/m³	ne	ne	ne	ne	n	n	n	n	n	n
carbon black		1333-86-4	3.5 mg/m³	ne	3.5 mg/m³	ne	ne	ne	ne	n	n	n	n	n	n
water	water	7732-18-5	ne	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n
2-propenoic acid, polymer with ethenylbenzene and (1-methylethenyl)benzene, ammonium salt	acrylic copolymer	89678-90-0	ne	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n
aluminum hydroxide	same	21645-51-2	10 mg/m³	ne	5 mg/m³	ne	ne	ne	ne	n	n	n	n	n	n
2-propenoic acid, 2-methyl-, methyl ester, polymer with ethenylbenzene and 2-ethylhexyl 2-propenoate	styrene copolymer	25750-06-5	ne	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n
2-ethylhexyl ester, acrylic acid polymer with styrene	styrene copolymer	25153-46-2	ne	ne	ne	ne	ne	ne	ne	n	n	n	n	n	n

Footnotes:

C = Ceiling - Concentration that should not be exceeded, even instantaneously.

S.R.STD. = Supplier Recommended Standard

S = Skin - Additional exposure, over and above airborne exposure, may result from skin absorption.

ne = not established

ppm = parts per million

mg/m³ = milligrams per cubic meter

S2 = Sara Section 302 EHS

S3 = Sara Section 313 Chemical

CC = CERCLA Chemical

Carcinogenicity Listed By:
N = NTP, I = IARC, O = OSHA
y = yes, n = no

ICI Paints

MATERIAL SAFETY DATA SHEET

prepared 07/01/97

DEVFLEX 4205 INTERIOR/EXTERIOR WATERBORNE ACRYLIC

4205

FIRE AND EXPLOSION HAZARD DATA

Extinguishing media : Dry chemical or foam water fog. Carbon dioxide.

Unusual fire and explosion hazards : Vapors are heavier than air and may travel long distances to a source of ignition and flash back. Closed containers may burst if exposed to extreme heat or fire. May decompose under fire conditions emitting irritant and/or toxic gases.

Special fire fighting procedures : Water may be used to cool and protect exposed containers. Firefighters should use full protective clothing, eye protection, and self-contained breathing apparatus. Self-contained breathing apparatus recommended.

HEALTH HAZARD DATA

Primary route(s) of exposure : Inhalation, skin contact, eye contact, ingestion.

Effects of overexposure :

Inhalation : Irritation of respiratory tract. Prolonged inhalation may lead to mucous membrane irritation, drowsiness, dizziness and/or lightheadedness, headache, nausea, vomiting, chest pain, coughing, difficulty with speech, central nervous system depression, anesthetic effect or narcosis.

Skin contact : Irritation of skin. Prolonged or repeated contact can cause dermatitis, defatting. Skin contact may result in dermal absorption of component(s) of this product which may cause headache, nausea, vomiting.

Eye contact : Irritation of eyes. Prolonged or repeated contact can cause conjunctivitis, blurred vision, tearing of eyes, redness of eyes, severe eye irritation, severe eye irritation or burns, corneal injury.

Ingestion : Ingestion may cause lung inflammation and damage due to aspiration of material into lungs, fatigue, drowsiness, dizziness and/or lightheadedness, headache, uncoordination, nausea, vomiting, diarrhea, apathy, intoxication, loss of consciousness.

Supplemental health information : Contains a chemical that is moderately toxic by ingestion. Other effects of overexposure may include toxicity to liver, kidney, lungs, blood. May be absorbed through skin. Notice - reports have associated repeated and prolonged occupational overexposure to solvents with permanent brain and nervous system damage. Intentional misuse by deliberately concentrating and inhaling the contents may be harmful or fatal. The international agency for research on cancer (IARC) has classified carbon black as possibly carcinogenic to humans (group 2b) based on sufficient evidence in animals and inadequate evidence in humans.

Medical conditions aggravated by exposure : Eye, skin, respiratory disorders lung disorders asthma-like conditions kidney disorders

FIRST AID PROCEDURES

Inhalation : Remove to fresh air. Restore and support continued breathing. Get emergency medical attention. Have trained person give oxygen if necessary. Get medical help for any breathing difficulty. Remove to fresh air if inhalation causes eye watering, headaches, dizziness, or other discomfort.

Skin contact : Flush from skin with water. Then wash thoroughly with soap and water. Remove contaminated clothing. Wash contaminated clothing before re-use. Dispose of contaminated leather items, such as shoes and belts.

Eye contact : Flush immediately with large amounts of water, especially under lids for at least 15 minutes. If irritation or other effects persist, obtain medical treatment.

Ingestion : If swallowed, obtain medical treatment immediately.

REACTIVITY DATA

Stability : Stable

Incompatibility : Oxidizers, acids, bases. Alkalis aluminum, zinc, magnesium. Nitrates

Conditions to avoid : Elevated temperatures, contact with oxidizing agent, freezing, sparks, open flame. Ignition sources

Hazardous decomposition products : Carbon monoxide, carbon dioxide, toxic gases, unidentified organic compounds.

Hazardous polymerization : Will not occur

SPILL OR LEAK PROCEDURES

Steps to be taken in case material is released or spilled : Comply with all applicable health and environmental regulations. Eliminate all sources of ignition. Ventilate area. Spills may be collected with absorbent materials. Use non-sparking tools. Evacuate all unnecessary personnel. Place collected material in proper container. Complete personal protective equipment must be used during cleanup. Large spills - shut off leak if safe to do so. Dike and contain spill. Pump to storage or salvage vessels. Use absorbent to pick up excess residue. Keep salvageable material and rinse water out of sewers and water courses. Small spills - use absorbent to pick up residue and dispose of properly.

Waste disposal : Dispose in accordance with all applicable regulations. Avoid discharge to natural waters.

SPECIAL PROTECTION INFORMATION

Respiratory protection : Control environmental concentrations below applicable standards. Where respiratory protection is required, use only NIOSH/MSHA approved respirators in accordance with OSHA standard 29 CFR 1910.134.

Ventilation : Provide dilution ventilation or local exhaust to prevent build-up of vapors. Use explosion-proof equipment.

Personal protective equipment : Eye wash, safety shower, safety glasses or goggles. Impervious gloves, impervious clothing, apron.

SPECIAL PRECAUTIONS

Handling and storage : Store below 100f(38c). Keep away from heat, sparks and open flame. Keep from freezing. Do not store in aluminum containers. Keep container tightly closed in a well-ventilated area.

Other precautions : Use only with adequate ventilation. Do not take internally. Keep out of reach of children. Avoid contact with skin and eyes, and breathing of vapors. Wash hands thoroughly after handling, especially before eating or smoking. Keep containers tightly closed and upright when not in use. Avoid conditions which result in formation of inhalable particles such as spraying or abrading (sanding) painted surfaces. If such conditions cannot be avoided, use appropriate respiratory protection as directed under special protection information. Empty containers may contain hazardous residues. Ground equipment when transferring to prevent accumulation of static charge.

The information contained herein is based on data available at the time of preparation of this data sheet which ICI Paints believes to be reliable. However, no warranty is expressed or implied regarding the accuracy of this data. ICI Paints shall not be responsible for the use of this information, or of any product, method or apparatus mentioned and you must make your own determination of its suitability and completeness for your own use, for the protection of the environment, and the health and safety of your employees and the users of this material.

Complies with OSHA hazard communication standard 29CFR1910.1200.

925 Euclid Avenue
Cleveland, Ohio 44115

EMERGENCY TELEPHONE NO. (800)545-2643

Average Relative Sensitivity Calculations

Compound	Other names	CAS No.	Carbon Number	Ester Linkage (-1.27 each)	Alcohol Linkage (-0.64 each)	Ether Linkage (-0.78 each)	Amine Linkage (-0.58 each)	Effective Carbon Number	MW	Relative Sensitivity
2-butoxyethanol		111-76-2	6		-0.64	-0.78		4.58	118	1.000
2-propoxyethanol	ethylene glycol monopropyl ether	2807-30-9	5		-0.64	-0.78		3.58	104	0.887
Mineral Spirits and Solvent Naphtha		64742-88-7	10					9.92	142.29	1.796
Hexane		110-54-3	6					5.92	86.18	1.770
triethylamine		121-44-8	6				-0.58	5.42	101.19	1.380
ethanol, 2,2'-oxybis	diethylene glycol	111-46-6	4		-1.28	-0.78		1.94	106	0.472
propanoic acid, 2-methyl-, monester with 2,2,4-trimethyl-1,3-pentanediol	Texanol	25265-77-4	12	-1.27	-0.64			10.09	216.32	1.202
methanol		67-56-1	1		-0.64			0.36	32.04	0.289
ethanol, 2-(2-butoxyethoxy)-	diethylene glycol monobutyl ether	112-34-5	8		-0.64	-1.56		5.80	162	0.922

MS1-6659A Silver Waterborne Industrial Enamel (Automotive Paint)

Ingred. No.	Cas No.	Wt/Wt%	Ingredient	Actual VOC	Fraction of Total VOC	Rel. Sens	Contribution
1	64742-88-7	1	Mineral Spirits	1.00	0.083	1.796	0.150
2	2807-30-9	5	2-Propoxyethanol	5.00	0.417	0.887	0.370
3	111-76-2	6	2-Butoxyethanol	6.00	0.500	1.000	0.500
4	136-52-7	0.1	Cobalt 2-Ethylhexanoate				
5	7732-18-5	54.0	Water				
				12.00	1.00	**Avg RS=**	1.019

MS1-6660A Gray Waterborne Industrial Enamel (Automotive Paint)

Ingred. No.	Cas No.	Wt/Wt%	Ingredient	Actual VOC	Fraction of Total VOC	Rel. Sens	Contribution
1	121-44-8	2	Triethylamine	2.00	0.143	1.380	0.197
2	2807-30-9	4	2-Propoxyethanol	4.00	0.286	0.887	0.253
3	111-76-2	8	2-Butoxyethanol	8.00	0.571	1.000	0.571
4	136-52-7	0.2	Cobalt 2-Ethylhexanoate				
5	13463-67-7	14	Titanium Dioxide				
6	1333-86-4	0.4	Carbon Black				
7	7732-18-5	43.9	Water				
				14.00	1.00	**Avg RS=**	1.022

1403-0100 Dulux Ultra Interior Acrylic Eggshell White (Interior Wall Paint)

Ingred. No.	Cas No.	Wt/Wt%	Ingredient	Middle Est. VOC	Fraction of Total VOC	Rel. Sens	Contribution
1	111-46-6	1-5	Ethanol, 2,2'-oxybis	3.00	0.500	0.472	0.236
2	37244-96-5	5-10	Nepheline syenite				
3	61790-53-2	1-5	Silica, diatomaceous earth				
4	25265-77-4	1-5	Propanoic acid, 2-methyl-, monester with 2,2,4-trimethyl-1,3-pentanediol (Texanol)	3.00	0.500	1.202	0.601
5	13463-67-7	20-30	Titanium oxide				
6		10-20	Vinyl acrylic copolymer				
7	27136-15-8	1-5	2-Propenoic acid, 2-methyl-, methyl ester, polymer with butyl 2-propenoate and ethenylbenzene				
8	7732-18-5	30-40	Water				
				6.00	1.00	**Avg RS=**	0.837

4206-0100 Acrylic Semi-Gloss Architectural Paint

Ingred. No.	Cas No.	Wt/Wt%	Ingredient	Middle Est. VOC	Fraction of Total VOC	Rel. Sens	Contribution
1	64742-88-7	1-5	Solvent naphtha (petroleum), medium aliphatic	3.00	0.333	1.796	0.599
2	111-76-2	1-5	2-Butoxyethanol	3.00	0.333	1.000	0.333
3	112-34-5	1-5	Ethanol, 2-(2-butoxyethoxy)-	3.00	0.333	0.922	0.307
4	13463-67-7	10-20	Titanium oxide				
5	7631-86-9	1-5	Silica				
6	89678-90-0	5-10	2-Propenoic acid, polymer with ethenylbenzene and (1-methylethenyl)benzene, ammonium salt				
7	21645-51-2	5-10	aluminum hydroxide				
8	27136-15-8	5-10	2-Propenoic acid, 2-methyl-, methyl ester, polymer with ethenylbenzene and 2-ethylhexyl 2-propenoate				
9	25153-46-2	5-10	2-Ethylhexyl ester, acrylic acid polymer with styrene				
10	7732-18-5	30-40	Water				
				9.00	1.00	**Avg RS=**	1.239

4020-1000 Waterbase Primer (White)

Ingred. No.	Cas No.	Wt/Wt%	Ingredient	VOC	Middle Est.	Fraction of Total VOC	Rel. Sens	Contribution
1	64742-88-7	1-5	Solvent naphtha (petroleum), medium aliphatic	3.00		0.500	1.796	0.898
2	112-34-5	1-5	Ethanol, 2-(2-butoxyethoxy)-	3.00		0.500	0.922	0.461
3	14808-60-7	5-10	Quartz					
4	471-34-1	20-30	calcium carbonate					
5	25586-20-3	10-20	2-Propenoic acid, polymer with butyl 2-propenoate and ethenylbenzene					
6	13463-67-7	5-10	Titanium oxide					
7	7631-86-9	1-5	Silica					
8	7732-18-5	30-40	Water					
					6.00	1.00	**Avg RS=**	1.359

25524 Latex Traffic Paint

Ingred. No.	Cas No.	Wt/Wt%	Ingredient	Actual VOC	Fraction of Total VOC	Rel. Sens	Contribution
1	13463-67-7	8.52	Titanium dioxide				
2	471-34-1	19.2	Calcium Carbonate				
3	unknown	13.683	Acrylic Resin				
4	25265-77-4	1.108	Propanoic acid, 2-methyl-, monester with 2,2,4-trimethyl-1,3-pentanediol (Texanol)	1.11	0.394	1.202	0.474
5	67-56-1	1.704	Methanol	1.70	0.606	0.289	0.175
6		14.90	Proprietary Pigment				
7	7732-18-5	39.1	Water				
				2.81	1.000	**Avg RS=**	0.649

APPENDIX B

LABORATORY KICK-OFF MEETING HANDOUT

Interlaboratory Study of Draft Water-Based Coating Method (ATD-FID)

Battelle would like to thank **Laboratory Name**, Inc. for participating in an interlaboratory study of a draft method developed by U.S. Environmental Protection Agency (EPA) to measure the VOC content of water-based coatings. As a participant, you will be required to analyze four water-based coating samples in **triplicate** following the draft test method. A copy of the draft test method can be found in Attachment 1. Battelle is providing you with the four water-based paint samples. As part of the draft test method, you will be required to perform several calculations in order to compute the corrected Wt% VOC for each coating. Attachment 2 contains information on the coatings that you will need to compute the correction factors for the Wt% VOC calculations. This information includes the ingredients of each paint and the chemical structure of specific VOC components. Attachment 3 shows examples of the calculations used to determine the correction factors. Attachment 4 contains the reference cited in the draft test method on which the correction factor calculations are based.

The deliverables for this work will be the various calibration and QC/QA measurements required by the draft test method, as well as the test results from the four paint samples. Data sheets can be found in Attachment 5 to record all of the required information. Battelle is also providing a logbook to record information while performing the draft test method. Please record any special events that arise during any phase of the testing. All of the data should be reported to Battelle within two weeks after completion of the testing (**Date**). This report should include the data sheets as well as the raw data (chromatograms and calculations) generated in performing the test method. Also please provide a short narrative on specific aspects of the apparatus, reagents, calibration, or procedure that you feel were a problem and any ways you feel the method could be improved.

Battelle is providing you with various materials needed to perform the test method. Attachment 6 contains a list of the supplied materials. These materials include the Perkin-Elmer ATD-400 thermal tube desorber. Since this unit must be shared with other participating laboratories, Battelle would like you to complete the testing within two weeks.

Finally if there are any problems or concerns that arise in performing the testing, please contact Battelle at the following numbers:

Pat Callahan

Phone: 614-424-4206
Fax: 614-424-3638
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Attachment 1.

Draft Test Method

Measurement of Total VOC in Paints and Coatings Using an Automated Thermal Desorber and a Flame Ionization Detector

1. Scope and Application

1.1 Applicability. This method is applicable for determination of the total volatile organic compound (VOC) content of paints and coatings. The term "coating" used in this method shall be understood to mean paints and coatings.

1.2 Principle. The method is based on the response of a flame ionization detector (FID) to VOCs that are released from a coating that is heated at 110° C. Since the response of an FID per unit mass of VOC is compound dependent, a correction of the apparent VOC weight percent of a coating must be made based on a predicted average relative sensitivity of the coating. (Relative to the calibration standard FID response per unit mass).

2. Summary of Method

A sample of a whole coating is weighed into a PTFE liner containing a plug of silanized glass wool and then inserted into a stainless steel tube. The tube is placed in an automated thermal desorber where it is heated at 110° C while purging with helium for 30 minutes. During tube heating, volatile components are collected on a solid sorbent trap which is cooled to -30° C. After tube desorption, the trap is heated to 325° C and the desorbed compounds are transferred directly to a flame ionization detector. Tube desorption is repeated for another 30 minute period and the analysis results are summed with those from the first desorption.

3. Definitions [Reserved]

4. Interferences

4.1 Any residual VOC from the glass wool, PTFE liners, or sample tubes constitutes a positive bias for a coating analysis. In addition, residual VOC in the sorbent trap of the Automated Thermal Desorption unit will cause a positive bias.

4.2 Cross-contamination may occur if the devices used to transfer coating during the sample preparation process are not adequately cleaned between uses. All such devices should be cleaned with acetone or other suitable solvent and checked for plugs or cracks before and after each use.

5. Safety

5.1 Many solvents used in coatings are hazardous. Precautions should be taken to avoid unnecessary inhalation and skin or eye contact. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations in regards to the performance of this test method.

5.2 2-butoxyethanol is harmful if inhaled or absorbed through the skin. The user should obtain relevant health and safety information from the manufacturer. 2-butoxyethanol should be used only with adequate ventilation. Avoid contact with skin, eyes, and clothing. In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes. If eyes are affected, consult a physician. Remove and wash contaminated clothing before reuse.

5.3 User's manuals for the gas chromatograph, thermal desorber, and other related equipment should be consulted for specific precautions to be taken related to their use.

6. Equipment and Supplies

6.1 Sample Collection.

6.1.1 Sampling Containers. Dual-seal sampling containers, four to eight fluid ounce capacity, should be used to collect the samples. Glass sample bottles or plastic containers with volatile organic compound (VOC) impermeable walls must be used for corrosive substances (e.g., etch primers and certain coating catalysts such as methyl ethyl ketone (MEK) peroxide). Sample containers, caps, and inner seal liners must be inert to the compounds in the sample and must be selected on a case-by-case basis.

6.1.2 Other routine sampling supplies needed include waterproof marking pens, tubing, scrappers/spatulas, clean rags, paper towels, cooler/ice, long handle tongs, and mixing/stirring paddles..

6.1.3 Personal safety equipment needed includes eye protection, respiratory protection, hard hat, gloves, steel toe shoes, etc.

6.1.4 Shipping supplies needed include shipping boxes, packing material, shipping labels, strapping tape, etc.

6.1.5 Data recording forms and labels needed include coating data sheets and sample can labels.

NOTE: The actual requirements will depend upon the conditions existing at the source sampled.

6.2 Laboratory Equipment and Supplies.

6.2.1 Gas Chromatograph (GC). Any instrument equipped with a flame ionization detector may be used.

6.2.2 Recorder. If available, an electronic data station or integrator may be used to record the detector response and associated data. If a strip chart recorder is used, it must meet the following criteria: A 1 to 10 millivolt (mV) linear response with a full scale response time of 2 seconds or less and a maximum noise level of +0.03 percent of full scale.

6.2.3 Automated Thermal Desorber. A Perkin Elmer Model ATD-400, or equivalent, fitted with a 3 mm ID sorbent trap

containing a 10 mm long section of Tenax GR and a 10 mm long section of Carbopack B.

6.2.4 Sample analysis tubes. Stainless steel tubes, 1/4 inch OD, 5 mm ID, 3.5 inches long, with end caps. (PE Part No. L427-0123)

6.2.5 Tube liners. PTFE liners for sample tubes, 2 inches long with bevelled end. (PE Part No. L407-1596). NOTE: Liners should fit snugly to prevent slipping out of tube during processing.

6.2.6 Silanized glass wool. For packing into bevelled end of PTFE insert.

6.2.7 Disposable pipet or syringe. For transferring coating or calibration standard to tube liner.

6.2.8 Capillary restrictor. 50 cm long and 0.1 mm ID fused silica tubing for attaching thermal desorber transfer tube to FID. The restrictor is attached to the end of the transfer tube inside the GC oven with a zero volume union.

6.2.9 Tube and Tube Fittings. Supplies to connect the thermal desorber and GC to gas cylinders.

6.2.10 Pressure Regulators. Devices used to regulate the pressure between gas cylinders and the thermal desorber and GC.

6.2.11 Flow Meter. A device used to determine the carrier gas flow rate through the thermal desorber and GC. Either a digital flow meter or a soap film flow meter may be used to measure gas flow rates.

6.2.12 Balance. Used to determine the weights of standards and samples. An analytical balance capable of accurately weighing to 0.0001 g is required.

7. Reagents and Standards

7.1 Purity of Reagents. Reagent grade chemicals shall be used in all tests. Unless otherwise specified, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of determination.

7.2 Support Gases. Helium carrier gas shall have a purity of 99.995 percent or higher. Ultra-high purity grade hydrogen (99.999 percent) and zero-grade air shall be used for the flame ionization detector. Dry grade nitrogen or air shall be used for the ATD-400 Peltier cooler purge gas and for valve actuation.

7.3 2-Butoxyethanol. Compound used to calibrate the FID response.

7.4 Reagent grade water. Solvent for 2-butoxyethanol in calibration standards.

7.5 Calibration Standards. Calibration standards are used to determine the response of the detector to known amounts of 2-

butoxyethanol. Calibration standards must be prepared at a minimum of three concentration levels in water. The lowest concentration standard should contain nominally 0.5% by weight of 2-butoxyethanol in water. The mid-level standard should contain nominally 5%, and the high level standard should contain nominally 50%. Calibration standards should be stored for 1 week or less in sealed vials with minimal headspace. Calibration standards are prepared by weighing an appropriate amount of 2-butoxyethanol into a vial containing a weighed amount of water.

8. Sample Collection, Preservation, Transport, and Storage

8.1 Copies of material safety data sheets (MSDS) for each sample should be obtained prior to sampling. The MSDS contains information on the ingredients, and physical and chemical properties data. The MSDS also contains recommendations for proper handling or required safety precaution.

8.2 A copy of the blender's worksheet can be requested to obtain data on the exact coating being sampled. The manufacturer's formulation information from the product data sheet should also be obtained.

8.3 Prior to sample collection, thoroughly mix the coating to ensure that a representative, homogeneous sample is obtained. It is preferred that this be accomplished using a coating can shaker or similar device; however, when necessary, this may be accomplished using mechanical agitation or circulation systems.

8.3.1 Water-thinned coatings tend to incorporate or entrain air bubbles if stirred too vigorously; mix these types of coatings slowly and only as long as necessary to homogenize.

8.3.2 Each component of multicomponent coatings that harden when mixed must be sampled separately. The component mix ratios must be obtained at the facility at the time of sampling and submitted to the analytical laboratory.

8.4 Sample Collection. Samples must be collected in a manner that prevents or minimizes loss of volatile components and that does not contaminate the coating reservoir. A suggested procedure is as follows. Select a sample collection container which has a capacity at least 25 percent greater than the container in which the sample is to be transported. Make sure both sample containers are clean and dry. Using clean, long-handled tongs, turn the sample collection container upside down and lower it into the coating reservoir. The mouth of the sample collection container should be at approximately the midpoint of the reservoir (do not take the sample from the top surface). Turn the sample collection container over and slowly bring it to the top of the coating reservoir. Rapidly pour the collected coating into the sample container, filling it completely. It is important to fill the sample container completely to avoid any loss of volatiles due to volatilization into the headspace.

Return any unused coating to the reservoir or dispose as appropriate.

NOTE: If a company requests a set of samples for its own analysis, a separate set of samples, using new sample containers, should be taken at the same time.

8.5 Once the sample is collected, place the sample container on a firm surface and insert the inner seal in the container by placing the seal inside the rim of the container, inverting a screw cap, and pressing down on the screw cap which will evenly force the inner seal into the container for a tight fit. Using clean towels or rags, remove all residual coating material from the outside of the sample container after inserting the inner seal. Screw the cap onto the container.

8.5.1 Affix a sample label clearly identifying the sample, date collected, and person collecting the sample.

8.5.2 Prepare the sample for transportation to the laboratory. The sample should be maintained at the coating's recommended storage temperature specified on the Material Safety Data Sheet, or, if no temperature is specified, the sample should be maintained within the range of 5° C to 38° C.

8.6 The shipping container should adhere to U.S. Department of Transportation specification DOT 12-B. Coating samples are considered hazardous materials; appropriate shipping procedures should be followed.

9. Quality Control

9.1 Laboratories using this method should operate a formal quality control program. The minimum requirements of the program should consist of an initial demonstration of laboratory capability and an on-going analysis of blanks and quality control samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. When results indicate atypical method performance, a quality control check standard (see section 9.4) must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.2 Before processing any samples, the analyst must demonstrate, through analysis of a reagent blank (water), that there are no interferences from the analytical system, glassware, and reagents that would bias the sample analysis results. Each time a set of analytical samples are processed or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

9.3 Required instrument quality control parameters are found in the following sections:

9.3.1 Baseline noise must be demonstrated to be <5 percent of full scale using the procedures given in Section 11.1.

9.3.2 The GC system must be calibrated as specified in section 11.2.

9.3.3 A one-point daily calibration check must be performed as specified in section 11.3.

9.4 To establish the ability to generate results having acceptable accuracy and precision, the analyst must perform the following operations.

9.4.1 Prepare or purchase a quality control check standard (QCCS) containing nominally 5% 2-butoxyethanol in water. If prepared in the laboratory, the QCCS must be prepared independently from the calibration standards.

9.4.2 Analyze three aliquots of the QCCS according to the method beginning in section 12.6 and calculate the weight percent of 2-butoxyethanol.

9.4.3 Calculate the mean weight percent ($\overline{X}$) from the three results obtained in section 9.4.2.

9.4.4 Calculate the percent accuracy using the known concentration (T) in the QCCS using Equation 1, section 13.

9.4.5 Calculate the percent relative standard deviation (percent RSD) using equation 4, Section 13, substituting X for RF.

9.4.6 If the percent accuracy (section 9.4.4) is within the range 90 percent to 110 percent and the percent RSD (section 9.4.5) is <20 percent, system performance is acceptable and sample analysis may begin. If these criteria are not met, then system performance is not acceptable and the test must be repeated. Repeated failures indicate a general problem with the measurement system that must be located and corrected. In this case, the entire test, beginning at Section 9.4.1, must be repeated after the problem is corrected.

9.5 Great care must be exercised to maintain the integrity of all standards. It is recommended that all standards be stored at -10°C to 0°C in screw-cap amber glass bottles with Teflon liners.

9.6 Unless otherwise specified, all weights are to be recorded within 0.1 mg.

10. Tube Conditioning

Before beginning tube conditioning, load an appropriate number of liners with approximately 2 cm long plugs of silanized glass wool. (Insert the plug into the large opening and push down to bevelled end.) Insert liners into sample tubes (bevelled end first) and install tube caps. Load sample tubes into the thermal desorber and establish the following conditions:

Tube desorption temperature: 200° C
Tube desorption time: 10 min.

Carrier gas flowrate through tube: 100 cc/min. minimum
Switching valve temperature: 175° C

Condition sample tubes using a tube conditioning mode (Mode 1 on ATD-400) in which no tube flow passes through the cold trap.

11. Calibration

11.1 Detector Baseline Drift. Operate the GC at initial (i.e., before sample injection) conditions on the lowest attenuation to be used during sample analysis. Adjust the recorder pen to zero on the chart and obtain a baseline for at least one minute. Initiate the GC operating cycle that would be used for sample analysis. On the recorder chart, mark the pen position at the end of the simulated sample analysis cycle. Baseline drift is defined as the absolute difference in the pen positions at the beginning and end of the cycle in the direction perpendicular to the chart movement. Calculate the percent baseline drift by dividing the baseline drift by the chart width representing full-scale deflection and multiply the result by 100.

11.2 Calibration of GC. Bring all calibration standards to room temperature while establishing the GC and thermal desorber operating conditions.

The GC must be calibrated using a minimum of three concentration levels of 2-butoxyethanol. (See section 7.5 for instructions on preparation of the calibration standards.) Prepare calibration standard tubes following the procedure in Section 12.6. Analyze loaded tubes using the established method.

11.2.1 Tabulate the area responses and the 2-butoxyethanol masses (Equation 2, Section 13) for the calibration standards. Calculate the response factor for each mass using Equation 3, Section 13.

11.2.2 Using the RF's from the calibration, calculate the percent relative standard deviation (percent RSD) using Equation 4, Section 13. The percent RSD must be less than 30 percent. This criterion must be met in order for the calibration to be valid. If the criterion is met, the mean RF is to be used until the next calibration.

11.3 Daily Calibration Check. The response factor (section 11.2.2) must be checked and verified at least once each day that samples are analyzed. This is accomplished by analyzing the mid-level calibration standard.

Calculate the percent change in the RF since the last calibration using Equation 5, Section 13. If the percent change is less than 10 percent, the last calibration curve is assumed to be valid. If the percent difference is greater than 5 percent, the analyst should consider this a warning limit. If the percent difference exceeds 10 percent, corrective action must be taken. If no source of the problem can be determined after corrective

action has been taken, a new three-point (minimum) calibration must be generated. This criterion must be met before coating analysis begins.

12. **Coating_Analysis Procedure**

12.1 All samples and standards must be allowed to warm to room temperature before analysis.

12.2 Set the GC to the operating conditions listed below:

Column oven temperature: 150° C
FID temperature: 250° C
FID air flowrate: Per manufacturer instructions.
FID hydrogen flowrate: Per manufacturer instructions.
FID range: Set high enough to prevent exceeding data system input range.

12.3 Set the thermal desorber to the operating conditions listed below:

Tube desorption temperature: 110° C
Tube desorption time: 30 min.
Number of desorptions and injections per tube: 2
Switching valve temperature: 175° C
Transfer line temperature: 175° C
Trap low temperature: -30° C
Trap high temperature: 325° C
Trap hold time: 5 min.
Trap heating rate: 5° C/sec
Tube desorption flowrate: 5 cc/min.
Trap inlet split flowrate: 100 cc/min.
Trap outlet split flowrate: 50 cc/min.
Carrier flowrate to FID: 1 cc/min.
Helium pressure: 20 psig

12.4 Perform the daily calibration check as described in section 11.3. Samples are not to be analyzed until the criteria in section 11.3 are met.

12.5 Place the as-received coating sample on a paint shaker, or similar device, and shake the sample for a minimum of 5 minutes to achieve homogenization.

12.6 NOTE: The steps in this section must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory hood free from solvent vapors. All weights must be recorded to the nearest 0.1 mg.

12.6.1 Add approximately 25 μL of coating to a tared PTFE liner. Weigh the liner and record weight. Insert the liner into a stainless steel sample tube.

12.6.2 Cap the tube with standard storage caps.

12.7 Load tubes into the automated thermal desorber and analyze.

12.8 Measure total area of FID response during the period from 0 min. to 5.5 min. run time.

12.9 Perform two consecutive desorptions and analyses for each sample tube. Record the total area for both desorptions.

13. Data Analysis and Calculations

13.1 Calculate the percent accuracy for the QCCS (see Section 9.4) as follows:

$$\%\text{Accuracy} = 100\left(\frac{\bar{x}}{T}\right)$$

where

%Accuracy = accuracy as a percent of the true value
$\bar{x}$ = mean measured value
T = true value

13.2 Calculate the mass of 2-butoxyethanol loaded in the calibration standard tube (see Section 11.2.1) as follows:

$$mass_s = (mass_{ss})(Wt.\%_s)$$

where

$mass_s$ = mass of 2-butoxyethanol in standard solution (mg)
$mass_{ss}$ = mass of standard solution loaded into tube (mg)
$Wt.\%_s$ = weight percent of 2-butoxyethanol in standard solution

13.3 Calculate the response factor for each calibration level (see Section 11.2.1) as follows:

$$RF = \frac{R_{FID}}{mass_s}$$

where

RF = response factor for 2-butoxyethanol
R_{FID} = area response of FID between 0 and 5.5 min run time
$mass_s$ = mass of 2-butoxyethanol in standard solution (mg)

13.4 Calculate the relative standard deviation for the multilevel calibration (see Section 11.2.2) as follows:

$$\%RSD = 100\left(\frac{\sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}{(n-1)}}}{\overline{RF}}\right)$$

where

%RSD = relative standard deviation
RF_i = response factor for calibration level i
$\overline{RF}$ = mean response factor for all calibration levels
n = number of calibration levels

13.5 Calculate the percent difference between the daily calibration check standard response factor and the mean response factor (see Section 11.3) as follows:

$$\%Difference = \left(\frac{\overline{RF} - RF_{ccs}}{\overline{RF}}\right)100$$

where

$\overline{RF}$ = mean response factor for all calibration levels
RF_{ccs} = response factor for calibration check standard

13.6 Calculate the uncorrected mass of VOC in the coating sample from the total area response of both tube desorptions (see Section 12.9) as follows:

$$\text{VOC mass}_u = \frac{R_{FID}}{\overline{RF}} \quad (6)$$

where

VOC mass_u = uncorrected mass of VOC in sample (mg)
R_{FID} = area response of FID between 0 and 5.5 min run time
$\overline{RF}$ = mean response factor for all calibration levels

13.7 Calculate the uncorrected weight percent VOC in the coating sample as follows:

$$\text{Wt.\% VOC}_u = \left(\frac{\text{VOC mass}_u}{\text{sample wt.}} \right) 100$$

where

$\text{Wt.\% VOC}_u$ = uncorrected weight percent VOC
VOC mass_u = uncorrected mass of VOC in sample (mg)
sample wt. = weight of coating loaded into tube (mg)

13.8 Calculate effective carbon numbers for each compound using Jorgensen's technique (Reference 1). Use effective carbon numbers and molecular weights to calculate a relative sensitivity for each compound as follows:

$$RS_i = \frac{\left(\frac{MW_s}{ECN_s} \right)}{\left(\frac{MW_i}{ECN_i} \right)} \qquad (8)$$

where

RS_i = relative sensitivity of VOC component
MW_s = molecular weight of calibration standard compound
ECN_s = effective carbon number of calibration standard compound
MW_i = molecular weight of component i in coating
ECN_i = effective carbon number of component i in coating

13.9 Using the estimated weight percent of each VOC in the coating (from the MSDS or other source), calculate the estimated weight fraction of the total VOC for each individual VOC as follows:

$$FVOC_i = \frac{Wt.\%_i}{\sum_{i=1}^{n} Wt.\%_i} \quad (9)$$

where

$FVOC_i$ = estimated VOC component i weight fraction of total VOC
$Wt.\%_i$ = estimated VOC component i weight percentage of coating
n = number of VOC components in coating

13.10 Calculate the average relative sensitivity of the coating as follows:

$$RS_{avg} = \sum_{i=1}^{n} (FVOC_i)(RS_i) \quad (10)$$

where

RS_{avg} = average relative sensitivity of coating components that are VOC's
$FVOC_i$ = estimated VOC component i weight fraction of total VOC
RS_i = relative sensitivity of VOC component i

13.11 Calculate the corrected weight percent VOC in the coating as follows:

$$Wt.\%\ VOC_c = \frac{Wt.\%\ VOC_u}{RS_{avg}} \quad (11)$$

where

$Wt.\%\ VOC_c$ = corrected weight percent VOC
$Wt.\%\ VOC_u$ = uncorrected weight percent VOC
RS_{avg} = average relative sensitivity of coating components that are VOC's

14. **Method Performance** [Reserved]
15. **Pollution Prevention** [Reserved]

16. **Waste Management**

16.1 The coating samples and laboratory standards and reagents may contain compounds which require management as hazardous waste. It is the laboratory's responsibility to ensure all wastes are managed in accordance with all applicable laws and regulations.

16.2 To avoid excessive laboratory waste, obtain only enough sample for laboratory analysis.

16.3 It is recommended that discarded waste coating solids, used rags, used paper towels, and other non-glass or non-sharp waste materials be placed in a plastic bag before disposal. A separate container, designated "For Sharp Objects Only," is recommended for collection of discarded glassware and other sharp-edge items used in the laboratory. It is recommended that unused or excess samples and reagents be placed in a solvent-resistant plastic or metal container with a lid or cover designed for flammable liquids. This container should not be stored in the area where analytical work is performed. It is recommended that a record be kept of all compounds placed in the container for identification of the contents upon disposal.

17. **References**

1. Jorgensen, et al. Anal. Chem. 1990, 62 683-689.

Attachment 2.

Ingredients of the Four Test Paints and Structures of VOC Components

Paint Ingredients

Coating	Ingred. No.	Cas No.	Wt/Wt%	Ingredient
MS1-6659A	1	64742-88-7	1	Mineral Spirits
	2	2807-30-9	5	2-Propoxyethanol
	3	111-76-2	6	2-Butoxyethanol
	4	136-52-7	0.1	Cobalt 2-Ethylhexanoate
	5		54.0	Water

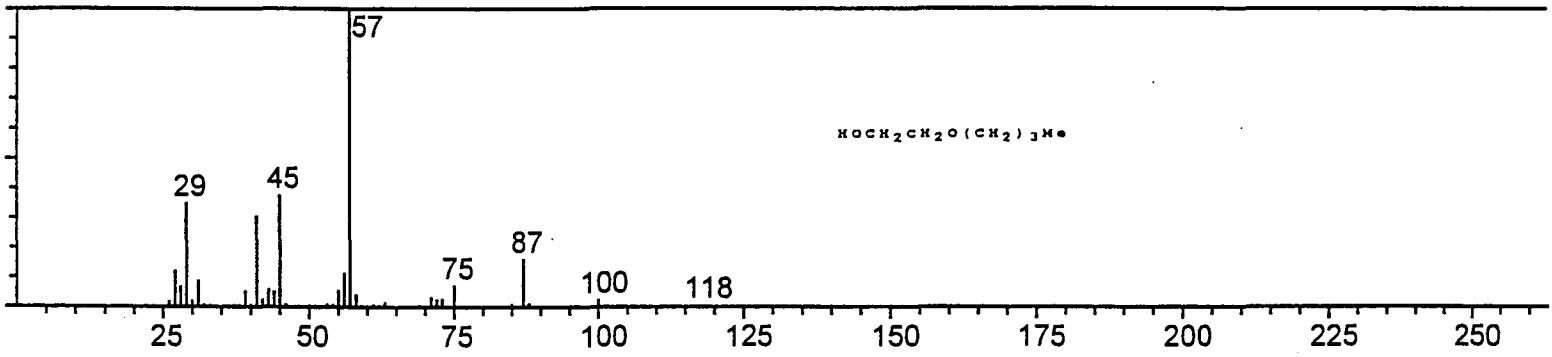
Coating	Ingred. No.	Cas No.	Wt/Wt%	Ingredient
1403-0100	1	111-46-6	1-5	Ethanol, 2,2'-oxybis
	2	37244-96-5	5-10	Nepheline syenite
	3	61790-53-2	1-5	Silica, diatomaceous earth
	4	25265-77-4	1-5	Propanoic acid, 2-methyl-, monester with 2,2,4-trimethyl-1,3-pentanediol (Texanol)
	5	13463-67-7	20-30	Titanium oxide
	6		10-20	Vinyl acrylic copolymer
	7	27136-15-8	1-5	2-Propenoic acid, 2-methyl-, methyl ester, polymer with butyl 2-propenoate and ethenylbenzene
	8		30-40	Water

Coating	Ingred. No.	Cas No.	Wt/Wt%	Ingredient
4206-0100	1	64742-88-7	1-5	Solvent naphtha (petroleum), medium aliphatic
	2	111-76-2	1-5	2-Butoxyethanol
	3	112-34-5	1-5	Ethanol, 2-(2-butoxyethoxy)-
	4	13463-67-7	10-20	Titanium oxide
	5	7631-86-9	1-5	Silica
	6	89678-90-0	5-10	2-Propenoic acid, polymer with ethenylbenzene and (1-methylethenyl)benzene, ammonium salt
	7	21645-51-2	5-10	aluminum hydroxide
	8	25750-06-5	5-10	2-Propenoic acid, 2-methyl-, methyl ester, polymer with ethenylbenzene and 2-ethylhexyl 2-propenoate
	9	25153-46-2	5-10	2-Ethylhexyl ester, acrylic acid polymer with styrene
	10		30-40	Water

Coating	Ingred. No.	Cas No.	Wt/Wt%	Ingredient
4020-1000	1	64742-88-7	1-5	Solvent naphtha (petroleum), medium aliphatic
	2	112-34-5	1-5	Ethanol, 2-(2-butoxyethoxy)-
	3	14808-60-7	5-10	Quartz
	4	471-34-1	20-30	calcium carbonate
	5	25586-20-3	10-20	2-Propenoic acid, polymer with butyl 2-propenoate and ethenylbenzene
	6	13463-67-7	5-10	Titanium oxide
	7	7631-86-9	1-5	Silica
	8	7732-18-5	30-40	Water

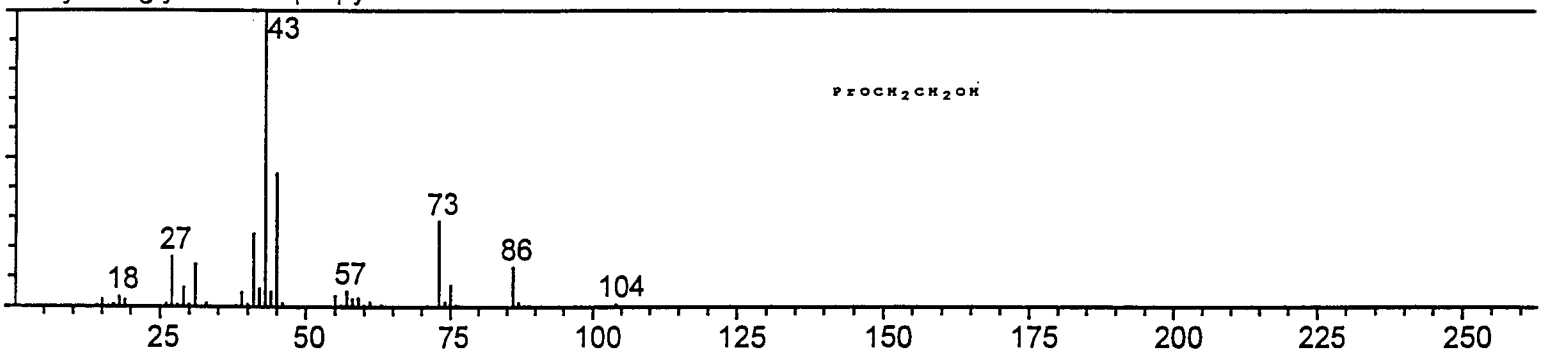
Query:
CAS: 111-76-2

Serial: 3806 CAS Reg No: 111-76-2 MW: 118 Form: C6 H14 O2
Ethanol, 2-butoxy- (CAS)
2-Butoxyethanol
2-N-BUTOXYETHANOL



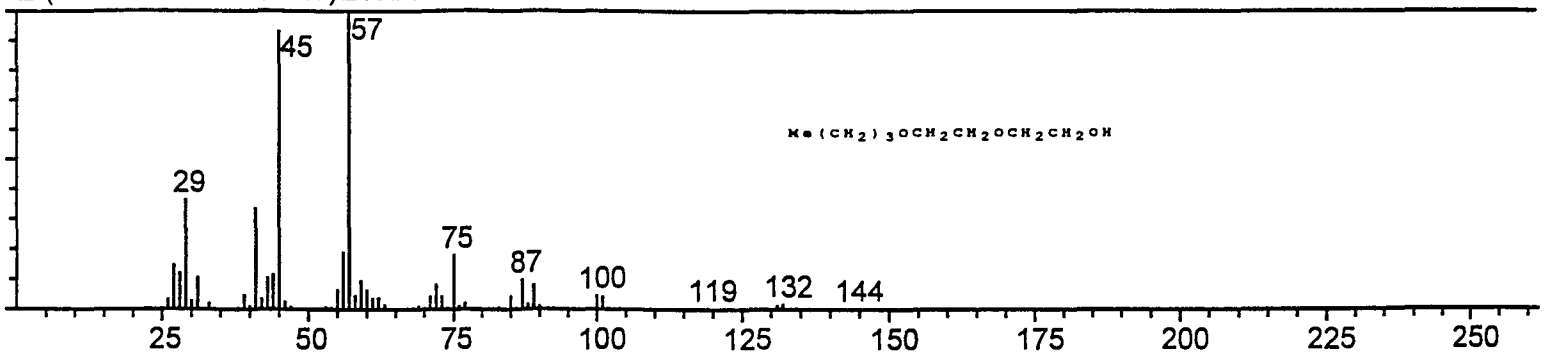
Query:
CAS: 2807-30-9

Serial: 2127 CAS Reg No: 2807-30-9 MW: 104 Form: C5 H12 O2
Ethanol, 2-propoxy- (CAS)
2-Propoxyethanol
Ethylene glycol monopropyl ether



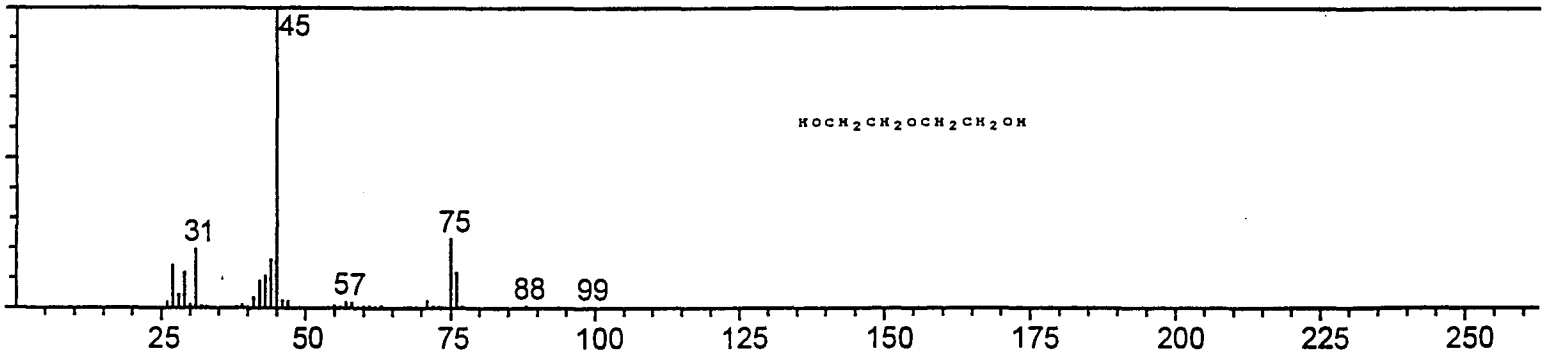
Query:
CAS: 112-34-5

Serial: 13208 CAS Reg No: 112-34-5 MW: 162 Form: C8 H18 O3
Ethanol, 2-(2-butoxyethoxy)- (CAS)
2-(2-Butoxyethoxy)ethanol
2-(2-BUTOXY-ETHOXY)ETHANOL



Query:
CAS: 111-46-6

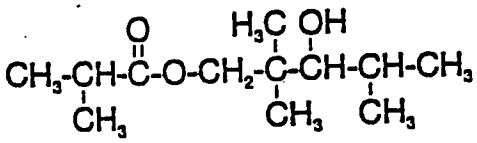
Serial: 2210 CAS Reg No: 111-46-6 MW: 106 Form: C4 H10 O3
Ethanol, 2,2'-oxybis- (CAS)
Diethylene glycol
DEG



Propanoic acid, 2-methyl-, monester with 2,2,4-trimethyl-1,3-pentanediol (Texanol)

Cas: 25265-77-4

MW: 216.32



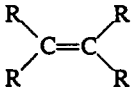
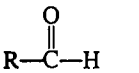
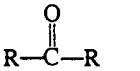
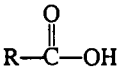
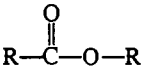
Mineral Spirits and Solvent Naphtha (petroleum), Medium Aliphatic

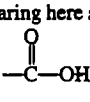
$C_{10}H_{22}$ Alkane

MW: 142.29

$Me(CH_2)_8Me$

TABLE 27-1
Some Classes of Organic Compounds

Type of compound	General structural formula	Example	Name
alkanes	R—H	$CH_3CH_2CH_2CH_2CH_3$	pentane
alkenes		$CH_3CH_2CH_2CH{=}CH_2$	1-pentene
alkynes	R—C≡C—R	$CH_3CH_2C{\equiv}CCH_3$	2-pentyne
alcohols	R—OH	$CH_3CH_2CH_2CH_2CH_2OH$	1-pentanol
alkyl halides	R—X	$CH_3CH_2\underset{\displaystyle Br}{\underset{\vert}{C}}HCH_2CH_3$	3-bromopentane
ethers	R—O—R	$CH_3CH_2OCH_2CH_2CH_3$	ethyl propyl ether
aldehydes		$CH_3CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\Vert}{C}}H$	pentanal
ketones		$CH_3CH_2\overset{\displaystyle O}{\overset{\Vert}{C}}CH_2CH_3$	3-pentanone
acids		$CH_3CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\Vert}{C}}OH$	pentanoic acid
esters		$CH_3CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\Vert}{C}}OCH_3$	methyl pentanoate
amines	$R{-}NH_2$	$CH_3CH_2CH_2CH_2CH_2NH_2$	pentylamine

Some of the functional groups appearing here and discussed later in the chapter have distinctive names: —OH, hydroxyl; , carbonyl;  , carboxyl; $-NH_2$, amino.

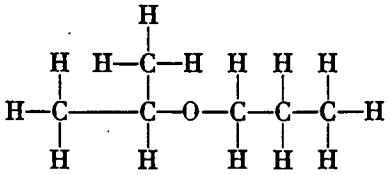
tinctive functional groups are indicated in blue. You may find it helpful to refer to this table from time to time.

Example 27-5 illustrates that when we name organic compounds we must designate the functional groups present, as well as follow the other nomenclature rules outlined in (27.1).

Example 27-5

Naming functional groups in an organic compound. Use information from Table 27-1 and from elsewhere in this section to derive an acceptable name for the compound $(CH_3)_2CHOCH_2CH_2CH_3$.

Solution. First we should convert the condensed formula into a structural formula.

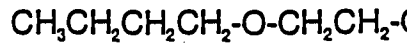


From the presence of the group C—O—C we see that this is an ether. The group shown on the left is isopropyl; the one on the right is propyl. We can call the compound isopropyl propyl ether.

SIMILAR EXAMPLE: Exercise 5.

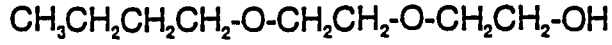
Attachment 3.

Example of Calculations for Effective Carbon Number (ECN) and VOC FID Sensitivities Relative to 2-Butoxyethanol



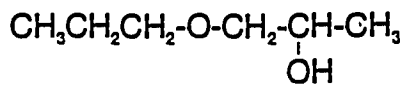
111-76-2

butyl cellosolve
ethylene glycol monobutyl ether
2-butoxyethanol



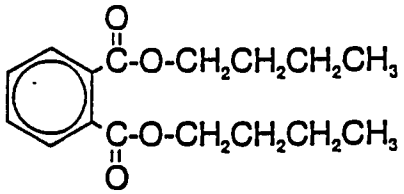
112-34-5

diethylene glycol monobutyl ether



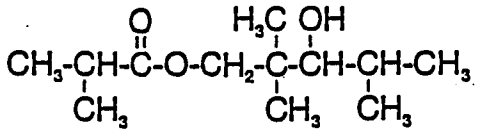
1569-01-3

n-propoxypropanol
1-propoxy-2-propanol



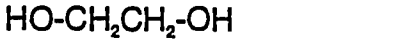
84-74-2

dibutylphthalate



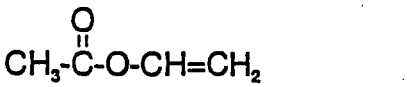
25265-77-4

texanol
texanol ester alcohol
2,2,4-trimethylpentane-1,3-diol
monoisobutyrate



107-21-1

ethylene glycol
1,2-ethanediol



108-05-4

vinyl acetate
acetic acid ethenyl ester

FIGURE 3.
STRUCTURES, SYNONYMS, AND CAS NUMBERS OF VOC's IN TEST COATINGS

concept.[9,10] Table 3 demonstrates the approach and Table 4 gives calculated values for all VOC's listed on the MSDS's for the four test coatings.

TABLE 3. CALCULATION OF EFFECTIVE CARBON NUMBERS[1]

Compound	Carbon Number	Carbon Number Corrections for: Ester Linkage(s) (-1.27 each)	Alcohol Linkage(s) (-0.64 each)	Ether Linkage(s) (-0.78 each)	Effective Carbon Number
2-butoxyethanol	6		-0.64	-0.78	4.58
diethylene glycol monobutyl ether	8		-0.64	-1.56	5.80
1-propoxy-2-propanol (mixture of isomers)	6		-0.64	-0.78	4.58
dibutylphthalate	16	-2.54			13.46
2,2,4-trimethylpentane-1,3-diolmonoisobutyrate	12	-1.27	-0.64		10.09
ethylene glycol	2		-1.28		0.72
vinyl acetate	4	-1.27			2.73

[1]Calculations based on Jorgensen, *et al.*, *Anal. Chem.*, **1990**, *62*, 683-689

TABLE 4. VOC FID SENSITIVITIES RELATIVE TO 2-BUTOXYETHANOL

Compound	CAS No.	MW	Effective Carbon Number	Calculated FID Sensitivity Relative to 2-Butoxyethanol[1]
2-butoxyethanol	111-76-2	118.18	4.58	1.000
diethylene glycol monobutyl ether	112-34-5	162.23	5.80	0.923
1-propoxy-2-propanol (mixture of isomers)	1569-01-3	118.18	4.58	1.000
dibutylphthalate	84-74-2	278.35	13.46	1.248
2,2,4-trimethylpentane-1,3-diol monoisobutyrate	25265-77-4	216.32	10.09	1.204
ethylene glycol	107-21-1	62.07	0.72	0.299
vinyl acetate	108-05-4	86.09	2.73	0.818

[1]On a mass basis

[9]Andrew D. Jorgensen, Kurt C. Picel, and Vassilis C. Stamoudis, Prediction of gas chromatography flame ionization detector response factors from molecular structures, *Anal. Chem.*, **1990**, *62*, 683-689.

[10]Magdolna Morvai, Ildikó Pályka, and Ibolya Molnár-Perl, Flame ionization detector response factors using the effective carbon number concept in the quantitative analysis of esters, *J. Chromatog. Sci.*, **1992**, *30*, 448-452.

Coating ID	CAS No.	Wt/Wt %	Ingredient	Middle VOC	ATD-FID Calculations Fraction of Total VOC	Rel. Sens.	Contri-bution
IS-91-1	7429-90-5	3%	aluminum				
IS-91-1	none		acrylic polymer				
IS-91-1	none		melamine resin				
IS-91-1	none		polyurethane polymer				
IS-91-1	112-25-4		2-hexyloxyethanol				
IS-91-1	111-76-2	4%	ethylene glycol-mono butyl ether	4.0	1.00	1.000	1.000
IS-91-1	7732-18-5		water				
IS-91-1				4.0	1.00	RS_{ave}=	1.000
CT05	111-76-2	<5%	2-butoxyethanol	2.5	0.25	1.000	0.250
CT05	112-34-5	<5%	diethylene glycol monobutyl ether	2.5	0.25	0.923	0.231
CT05	1569-01-3	<5%	n-propoxypropanol	2.5	0.25	1.000	0.250
CT05	84-74-2	<5%	dibutylphthalate	2.5	0.25	1.248	0.312
CT05	7631-86-9	<5%	silica - amorphous				
CT05	21645-51-2	<5%	aluminum hydroxide				
CT05				10.0	1.00	RS_{ave}=	1.043
CP05	111-76-2	<5%	2-butoxyethanol	2.5	0.33	1.000	0.333
CP05	7779-90-0	<5%	zinc phosphate				
CP05	25265-77-4	<5%	2,2,4-trimethyl-1-1,3-pentanediol monois	2.5	0.33	1.204	0.401
CP05	84-74-2	<5%	dibutylphthalate	2.5	0.33	1.248	0.416
CP05				7.5	1.00	RS_{ave}=	1.150
Y 4118	107-21-1	1-5%	1,2-ethanediol	3.0	0.46	0.299	0.138
Y 4118	14808-60-7	10-20%	quartz				
Y 4118	25265-77-4	1-5%	propanoic acid, 2-methyl-, monoester with 2,2,4-trimethyl-1,3-pentanediol	3.0	0.46	1.204	0.555
Y 4118	13463-67-7	10-20%	titanium dioxide				
Y 4118	108-05-4	<1.0%	acetic acid ethenyl ester	0.5	0.08	0.818	0.063
Y 4118	Trade Secret	10-20%	vinyl acrylic copolymer				
Y 4118	25035-69-2	1-5%	2-propenoic acid, 2-methyl-, polymer with butyl 2-propenoate and methyl 2-methyl-2-propenoate				
Y 4118	7732-18-5	30-40%	water				
Y 4118				6.5	1.00	RS_{ave}=	0.757

Attachment 4.

Reference for Test Method

with a vapor cell in an oven and comparing the LIF intensity I_F in the same system.

Figure 5 shows the PMT output voltage V_F as a function of the Na density n for three vapor cells with different buffer gas pressures. The Fairbank formula was used for the conversion from temperature to Na number density (*1*). V_F was proportional to n over a number density range from 10^7 to 10^{11} cm^{-3}. The detection limit 10^7 cm^{-3} is relatively high, because it is determined by stray light and no attempt to decrease it has been made. The V_F value for the vapor cell with a He gas pressure of 1 atm is 50% smaller than that of the evacuated cell because of collisional quenching by He. From Figure 5, the output PMT voltage of 1 mV corresponds to the atomic density n of 1.68×10^7 atoms/cm^3 at 1 atm.

We calculated the total number of dissociated atoms N passed through the observing region in the atomizer by the following formula:

$$N = nsvS \quad (7)$$

where s is the cross section of the discharge tube, v is the He velocity, and S is the integrated pulse form of the LIF signal in mV; consider the absolute density and the atomization efficiency for the LIF signal shown in Figure 2A obtained for a concentration of 10 ng/cm^3. The maximum number density is 1.18×10^{11} atoms/cm^3, because the peak voltage in Figure 2A is 700 mV and a 10% ND filter is used. Integration of the envelope of the LIF signal in Figure 2A provides $S = 280$ mV s; $s = 0.043$ cm^2, $v = 108$ cm/s and $n = 1.68 \times 10^7$ atoms/(cm^3 mV). Therefore, $N = 2.62 \times 10^{11}$ atoms. We define the atomizing efficiency β_a as

$$\beta_a = \frac{\text{number of dissociated atoms N}}{\text{number of atoms (ions) in sample water}} \quad (8)$$

Since the number of atoms in a 10 μL sample of water of 10 ng/cm^3 is 2.7×10^{13}, β_a is calculated to be 9.7%. However, shown in Figure 2A, since the plasma was turned on and off, the integration should not be done along the envelope but the pulse shape. In that case, the efficiency is given by $\beta_a = 1.6\%$.

The feature of this type of atomizer is that the instantaneous number density obtained in the observation region is large, because rapid injection of the sample is attained by flash heating. According to the results mentioned above, a peak density of 1.18×10^7 atoms/cm^3 is obtained for the sample of 1 pg/cm^3. Therefore, we can expect atomic detection of less than 1 pg/cm^3 by decreasing the noise sources.

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Prediction of Gas Chromatography-Flame Ionization Detector Response Factors from Molecular Structures

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The prediction of flame ionization detector response factors as a function of molecular structure components is evaluated with modern capillary column gas chromatography equipment that included an on-column injector. The effect on the standard carbon content based response by electronegative atoms is analyzed for various functional groups. This study updates much earlier work that characterized the decrease in signal response by using average correction factors for each functional group. The effective carbon number concept based on naphthalene as the internal standard was used. For 56 compounds containing a single functional group, predictions based on these average responses reproduced the actual response to within 1.7% on average. This model was then extended to bifunctional groups with similar success for several molecules. The effects of changes in temperature programming and concentration were found to be minimal within the range studied.

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INTRODUCTION

High sensitivity, uniform response to hydrocarbons, and a broad linear range have made the flame ionization detector (FID) perhaps the most widely used detector in gas chromatography. The FID response of hydrocarbons is generally proportional to the mass of carbon present in the sample, but the degree of signal reduction due to partially oxidized carbon atoms in heteroatomic compounds varies markedly with heteroatom and bond types. Compounds that contain, for example, oxygen, nitrogen, or halogens give varied responses but can be quantified by the FID if corrections are made for the usual loss of sensitivity caused by the presence of these atoms in various functional groups. Correction factors can be determined either through the analysis of authentic standards or from accurate predictions of loss of response based on measurements made for compounds of related molecular structure.

Predictive methods would be quite useful if they could accurately indicate the change in response caused by the presence of one or more heteroatomic functional groups. Correction factors have long been used for various function-

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alities. However, a comprehensive approach is needed for determining FID response precisely so that a broadly applicable system for predicting response can be developed. Modern analytical instrumentation allows highly precise response measurements to be made for the wide variety of substances that are needed for the development of such a system. Furthermore, systematic response predictions could be easily automated on computerized data systems to greatly facilitate analysis of complex organic mixtures and reduce the requirement for analyzing large numbers of authentic standards. To this end the present work has determined the response of a large number of compounds from many different chemical classes in order to critically reevaluate the conclusions of earlier reports and to begin to develop a systematic approach for predicting FID response in general on the basis of molecular structure. A system to accurately predict the response for a large number of compounds, many of them related to coal liquids, will be presented.

Although many questions about the specifies of flame chemistry in the FID remain unanswered, there is general agreement that the primary source of ions in the flame is the chemical ionization caused by the reaction of an oxygen atom with a radical containing a single carbon (*1–5*). The most commonly proposed reaction is

$$CH + O \rightarrow CHO^+ + e^- \quad (1)$$

Schaefer (*6*) has presented data suggesting that reactions other than eq 1 are also significant contributors to ion production. He based his conclusion on the temperature dependence of the ion current.

Some work has been able to distinguish the relative contribution of the ground state of CH compared to that of some excited states of the radical (*7, 8*). Although the latter are much more effective at producing ions, it was demonstrated that the reaction of the former is primarily responsible for the ion current in the FID.

The origin of CH and related radicals has been the cause for considerable speculation, and divergent views have been defended. Blades (*2, 9*) has presented data to support the theory that in most cases radicals are produced by a series of hydrogen-stripping and hydrogen-cracking reactions that occur in the reducing section of the flame. For example

$$C_2H_6 + {}^{\bullet}H \rightarrow {}^{\bullet}C_2H_5 + H_2 \quad (2)$$

$${}^{\bullet}C_2H_5 + {}^{\bullet}H \rightarrow 2{}^{\bullet}CH_3 \quad (3)$$

Sternberg (*1*) presented a table that summarized data from a variety of compounds and allowed prediction of the effective carbon number (ECN) of a compound from its structure. For example, he found that the presence of a carbonyl group reduced the effective number of carbons by one, while a primary alcohol caused a decrease of 0.6 carbon. Other researchers working at about the same time obtained similar results (*10–12*).

More recently two groups have reported on the FID response of various compounds. Tong and Karasek (*13*) determined a large number of absolute response factors for aliphatic and aromatic hydrocarbons and a few substituted species. They concluded that average response values were sufficiently accurate for the quantification of hydrocarbon compounds in many applications. A slight quantitative distinction between alkanes and aromatics was seen. However, their study included only a small number of nonhydrocarbons, and it was not possible to make a firm statement about most other classes.

Scanlon and Willis (*14*) used their own data and some results from the literature to maintain that the ECN concept is of value in checking the results from samples of known composition. The evaluation of column performance was mentioned as an example. Their instrumentation was also of modern design, and they did employ an internal standard, but some of their results were achieved by using a split rather than an on-column injection.

Frequently we need to find the approximate concentration of a large number of species in a complex mixture, such as a coal-derived liquid. Typically a gas chromatograph/mass spectrometry analysis provides the molecular structure for the components. Because hundreds of compounds may be present and because a degree of accuracy equal to a few percent is sufficient, the preparation and analysis of accurately prepared standards are not practical or required. In many cases it would also be quite difficult to obtain a substance in sufficient purity for use as a standard. We therefore concluded that it was time to expand the review of ECNs to a wider range of compounds than has been reported in the recent literature and to develop a systematic approach for predicting FID response. We wanted to confirm that the presence of a particular functional group could be characterized by a single adjustment to the ECN and to determine whether these effects could be described in a simple additive fashion for polyfunctional compounds. Our eventual aim was to develop a computer program that would query the user for structural information about each peak in a chromatogram, calculate the ECN from information in a data base, and use the area and concentration of the internal standard to calculate the concentration of the component.

EXPERIMENTAL SECTION

Instrumentation. All analyses were performed by using a Hewlett-Packard 5880A gas chromatograph equipped with an FID and a J&W Scientific on-column injector. The column was J&W Scientific's DB-5, 30 m × 0.32 mm i.d., with a 0.25-μm film thickness, purchased from Alltech Associates. The carrier gas was helium at a linear flow velocity of 40 cm/s. The detector gas flows were 35 mL/min for hydrogen, 410 mL/min for air, and 30 mL/min for nitrogen as the make-up gas. The oven was programmed for an initial hold of 2 min at 30 °C, then 10 °C/min until all peaks were eluted or a temperature of 300 °C was reached. All mass measurements were performed on a Mettler AC100 analytical balance.

Chemicals. The solvent for all mixtures was methylene chloride (HPLC grade from Baker Chemicals and Fisher Scientific). The compounds were of 98% or greater stated purity, except for two with 97% and two unstated. They were obtained from Aldrich Chemical Co., Fluka Chemicals, and Chemical Procurement Laboratories (one compound only). Naphthalene was the internal standard; it had a stated purity of 99+%. The purity of each compound was checked by performing a separate GC analysis of the substance at high concentration in methylene chloride. The final relative response factors for each compound was corrected for the total amount of chromatographable impurities that were found. The average correction was 0.6%. Only three corrections were above 2%, and 2.6% was the largest.

Procedure. An accurately weighed sample of approximately 60 mg of each compound was dissolved in solvent in a 25-mL volumetric flask to make stock solutions. A mixture of 5–10 compounds was prepared by adding 0.90 mL of stock solution for each and a like amount of the internal standard stock, using a 1.0-mL gas-tight syringe, to a second 25-mL volumetric flask to give concentrations of about 50 ppm by mass. A few compounds were also studied at 200 and 10 ppm to look for a concentration effect. At least three sets of all stock solutions, including the internal standard and mixtures, were prepared, and each mixture was analyzed 3 or more times. Solutions were usually analyzed within 24 h of preparation. Injection volumes were between 1 and 2 μL.

RESULTS AND DISCUSSION

The precision of the relative response factors (RRF) measurements was uniformly good. For the set of three or more injections of the same solution, the average variation from the

Table I. FID Response for Nitrogen Heterocycles

name	formula	RRF	ECN	ECN minus no. of carbons	% error in prediction
pyrole	C_4H_5N	0.646	3.38	−0.62	−0.2
pyridine	C_5H_5N	0.691	4.26	−0.74	2.6
2-picoline	C_6H_7N	0.727	5.28	−0.72	1.8
3-picoline	C_6H_7N	0.723	5.25	−0.75	2.4
2,3-lutidine	C_7H_9N	0.752	6.28	−0.72	1.4
3,4-lutidine	C_7H_9N	0.801	6.70	−0.30	−4.8
3,5-lutidine	C_7H_9N	0.772	6.45	−0.55	−1.1
3-ethylpyridine	C_7H_9N	0.747	6.26	−0.75	2.1
5-ethyl-2-methylpyridine	$C_8H_{11}N$	0.788	7.45	−0.55	−1.0
2-propylpyridine	$C_8H_{11}N$	0.760	7.18	−0.82	2.7
indole	C_8H_7N	0.811	7.41	−0.59	−0.5
5-methylindole	C_9H_9N	0.815	8.34	−0.66	0.4
quinoline	C_9H_7N	0.825	8.32	−0.68	0.7
4-methylquinoline	$C_{10}H_9N$	0.854	9.54	−0.46	−1.7
carbazole	$C_{12}H_9N$	0.897	11.70	−0.30	−2.8
acridine	$C_{13}H_9N$	0.973	12.21	−0.79	1.4
averages				−0.62	1.7

Table II. FID Response for Ketones

name	formula	RRF	ECN	ECN minus no. of carbons	% error in prediction
3-pentanone	$C_5H_{10}O$	0.614	4.12	−0.88	1.8
2-hexanone	$C_6H_{12}O$	0.659	5.15	−0.85	1.1
3-heptanone	$C_7H_{14}O$	0.686	6.11	−0.89	1.5
3-octanone	$C_8H_{16}O$	0.711	7.11	−0.89	1.3
3-nonanone	$C_9H_{18}O$	0.738	8.19	−0.81	0.2
cyclohexanone	$C_6H_{10}O$	0.672	5.14	−0.86	1.2
1-indanone	C_9H_8O	0.799	8.24	−0.76	−0.5
3-methylcyclopentanone	$C_6H_{10}O$	0.654	5.00	−1.00	3.9
acetophenone	C_8H_8O	0.761	7.13	−0.87	1.0
benzylacetone	$C_{10}H_{12}O$	0.790	9.14	−0.86	0.7
benzophenone	$C_{13}H_{10}O$	0.887	12.60	−0.40	−3.2
9-fluorenone	$C_{13}H_8O$	0.887	12.47	−0.53	−2.2
averages				−0.80	1.6

Table III. FID Response for Hydrocarbons

name	formula	RRF	ECN	ECN minus no. of carbons	% error in prediction
Alkanes					
n-octane	C_8H_{18}	0.854	7.61	−0.39	4.1
n-decane	$C_{10}H_{22}$	0.891	9.89	−0.11	0.3
n-dodecane	$C_{12}H_{26}$	0.928	12.34	+0.34	−3.4
n-tetradecane	$C_{14}H_{30}$	0.884	13.68	−0.32	1.8
Aromatics					
1,2,4-trimethylbenzene	C_9H_{12}	0.970	9.09	+0.09	−1.9
averages				−0.08	2.3

mean for the RRF was usually a few tenths of a percent. For the set of replicate solutions of the same compound, the average variation from the mean was 1.1% for the entire complement of 71 compounds. This number is quite consistent with an assumption that the primary sources of uncertainty are the determination of mass and the delivery of 0.90 mL of solution. The four normal hydrocarbons did exhibit an average variation for the replicate set of solutions equal to 2.6%, more than twice the value for the entire set. This may

Table IV. FID Response for Ethers and Furans

name	formula	RRF	ECN	ECN minus no. of carbons	% error in prediction
Ethers					
anisole	C_7H_8O	0.728	6.14	−0.86	1.4
diphenyl ether	$C_{12}H_{10}O$	0.859	11.41	−0.59	−1.6
xanthene	$C_{12}H_{10}O$	0.858	12.20	−0.80	0.2
Furans					
2,3-benzofuran	C_8H_6O	0.761	7.01	−0.99	3.0
dibenzofuran	$C_{12}H_8O$	0.865	11.35	−0.65	−1.1
averages				−0.78	1.5

Table V. FID Response for Alcohols and Phenols

name	formula	RRF	ECN	ECN minus no. of carbons	% error in prediction
Primary Alcohols					
1-pentanol	$C_5H_{12}O$	0.663	4.56	−0.44	−4.4
1-heptanol	C_7H_8O	0.728	6.60	−0.40	−3.6
Secondary Alcohols					
2-hexanol	$C_6H_{14}O$	0.667	5.32	−0.68	0.8
3-octanol	$C_8H_{18}O$	0.725	7.37	−0.63	−0.1
2-nonanol	$C_9H_{20}O$	0.743	8.36	−0.64	−0.0
1-indanol	$C_9H_{10}O$	0.824	8.62	−0.38	−3.1
2-indanol	$C_9H_{10}O$	0.842	8.42	−0.58	−0.7
Phenols					
phenol	C_6H_6O	0.709	5.21	−0.79	2.9
p-cresol	C_7H_8O	0.756	6.38	−0.62	−0.3
1-naphthol	$C_{10}H_8O$	0.806	9.06	−0.94	3.2
2-naphthol	$C_{10}H_8O$	0.804	9.05	−0.95	3.4
averages				−0.64	2.0

Table VI. FID Response for Amines and Esters

name	formula	RRF	ECN	ECN minus no. of carbons	% error in prediction
Amines					
aniline	C_6H_7N	0.748	5.43	−0.57	−0.3
4-aminobiphenyl	$C_{12}H_{11}N$	0.868	11.45	−0.55	−0.3
1-aminonaphthalene	$C_{10}H_9N$	0.873	9.75	−0.25	−3.4
2-aminofluorene	$C_{13}H_{11}N$	0.851	12.03	−0.97	3.2
averages				−0.58	1.8
Esters					
ethyl acetate	$C_4H_8O_2$	0.400	2.75	−1.25	−0.8
propyl acetate	$C_5H_{10}O_2$	0.462	3.68	−1.32	1.2
methyl benzoate	$C_8H_8O_2$	0.635	6.75	−1.25	−0.3
averages				−1.27	0.8

have been due to the less than ideal solvent for such nonpolar compounds. Preliminary additional work with hexane as the solvent improved precision.

Tables I–VI give the results for a set of 56 compounds. Except for the hydrocarbons, each compound contained only one functional group. The fifth column in each table gives the difference between the ECN and the actual number of carbons in a given compound, i.e., the change in ECN due to the presence of the functional group. The average value for this change is given for each class of compounds. For example, nitrogen heterocycles with one nitrogen atom (Table I) have ECN values that are, on average, 0.62 less than their actual

Table VII. Summary of ECN Changes and Prediction Errors

class	no. of compounds	av % error in prediction	average ECN change	ref 1 ECN change
nitrogen heterocycles	16	1.7	−0.62	
ketones	12	1.6	−0.80	−1.0
amines primary	4	1.8	−0.58	−0.6
alcohols and phenols	11	2.0	−0.64	−0.6 (1°) −0.75 (2°)
ethers and furans	5	1.5	−0.78	−1.0
esters	3	0.8	−1.27	−1.25
hydrocarbons	5	2.3	−0.08	0
	total 56	av 1.7		

carbon count. For this set of compounds the range is between 0.30 and 0.82 carbons.

For each class of compounds, the average ECN loss was used to calculate a predicted ECN value. The last column of each table gives the difference between this predicted ECN and the actual ECN is a percentage of the latter. A negative number indicates that the predicted ECN and therefore the RRF was lower than the observed RRF. Below this last column is the average of the absolute value of these percent errors in prediction. Note that some tables have distinctions within a group, e.g., primary and secondary alcohols and phenols. However, the statistics are calculated for the entire group. A case could be made for treating these subgroups separately. Sternberg (*1*) has done this for some classes, and we are pursuing this line of research in the case of alcohols and hydrocarbons.

Table VII summarizes the group data from Tables I–VI and gives the comparable numbers quoted by Sternberg (*1*). Note that the average difference between the predicted ECN and its experimental value was only 1.7%. Of the 56 compounds, 36 (64%) differed by less than 2% and 43 (77%) by less than 3%. These results clearly indicate that one can assume a single value for the change in ECN due to the presence of one functional group and achieve a quite reasonable degree of accuracy, at least under the conditions of these experiments. Even though the range of values for the shift in ECN seems at first glance to be rather large (e.g., −0.30 to −0.82 for the nitrogen heterocycles), one must remember that these are fractions of a single carbon out of the total number of carbons in a compound. Therefore, a difference of 0.30 between the experimental and predicted ECN is only 3% for a compound with 10 carbons.

Ironically, the poorest prediction record was found for hydrocarbons, but only a small number of these compounds were included because there are numerous reports in the literature for this class. This group's average prediction error of 2.3% is quite acceptable for the purposes of this work. The second highest percent error in prediction was found for the alcohols and phenols. This finding seems to support the need for discriminating among the three chemically different hydroxyl groups (primary, secondary, and phenol). However, the 2.0% average difference is not high enough to justify any distinction at this time.

The last column of Table VII gives the results of Sternberg as reported in 1962 (*1*). Excellent agreement is seen for primary amines, esters, and hydrocarbons. The average value for all of the alcohols and phenols is also quite reasonable, given the earlier data for primary and secondary alcohols. The observed effects of oxygen for ketones and ethers, including furans, are less than those obtained by Sternberg to a rather significant degree. This may very well reflect more efficient chromatography with modern columns and perhaps the use of higher purity standards in the present work. In fact, it is quite surprising that only these differences are found, given the significant changes that have occurred in instrumentation in the last 25 years.

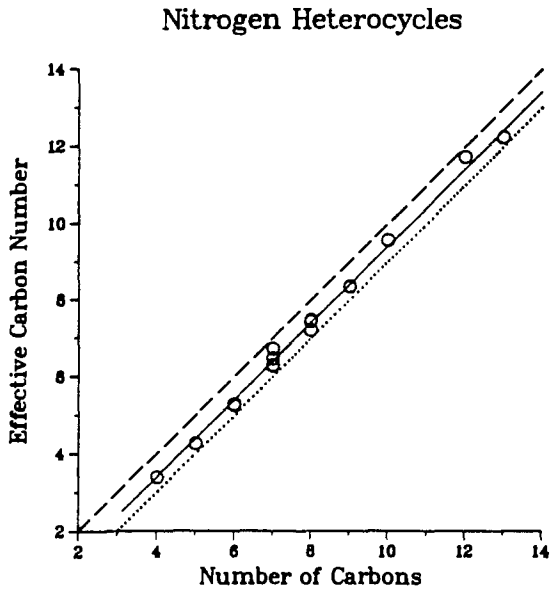


Figure 1. ECN versus carbon number of nitrogen heterocycles. Symbols indicate experimental points: (– – –) ECN equals number of carbons (no effect); (• • •) each heteroatom reduces ECN by 1.0 (full effect); (——) carbon number minus average change in ECN for group.

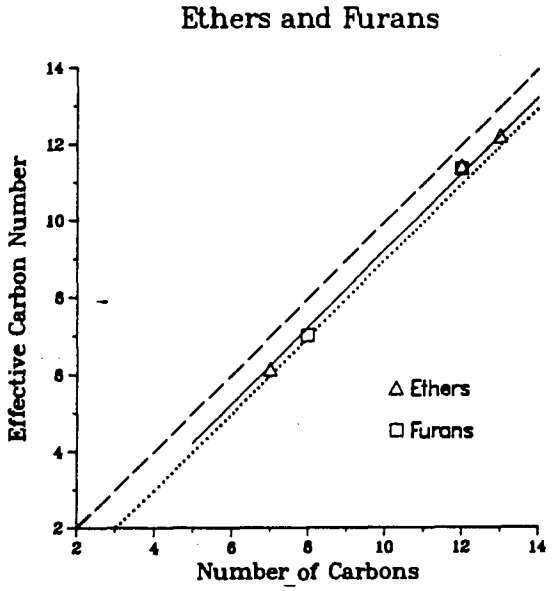


Figure 2. ECN versus carbon number for ethers and furans. Symbols and lines are as in Figure 1.

Figures 1–5 present these results in graph form for five of the compound classes studied. The plots give ECN versus the actual number of carbons. Symbols indicate experimental points, the dashed line is for the case of ECN equaling the number of carbons (no effect), and the dotted line is for the case in which each heteroatom causes as reduction of exactly one carbon in the ECN (full effect). The solid line through the symbols is not the best line in a least-squares sense but is determined by subtracting the average change in ECN for the group from the number of carbons. That is, the intercept is shifted with the data, but the slope is fixed at one. In all cases it is apparent that the solid line gives a significantly better fit to the data than either the dashed line (no effect) or the dottled line (full effect).

Table VIII includes the results from three additional groups of compounds. Two of the three sulfides studied showed very slight increases in response from what would be expected from

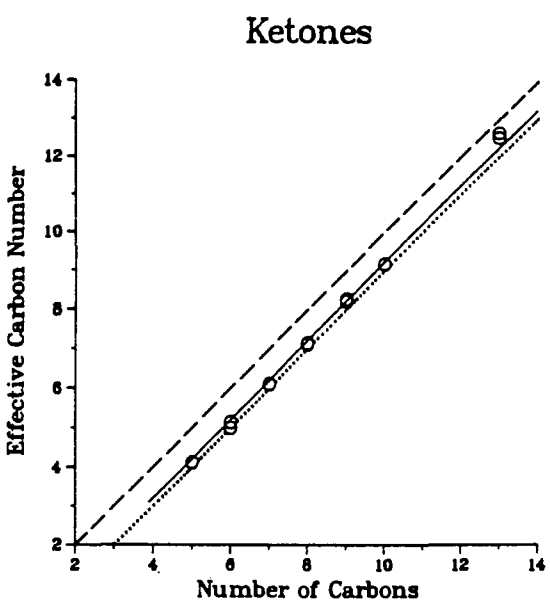


Figure 3. ECN versus carbon number for ketones. Symbols and lines are as in Figure 1.

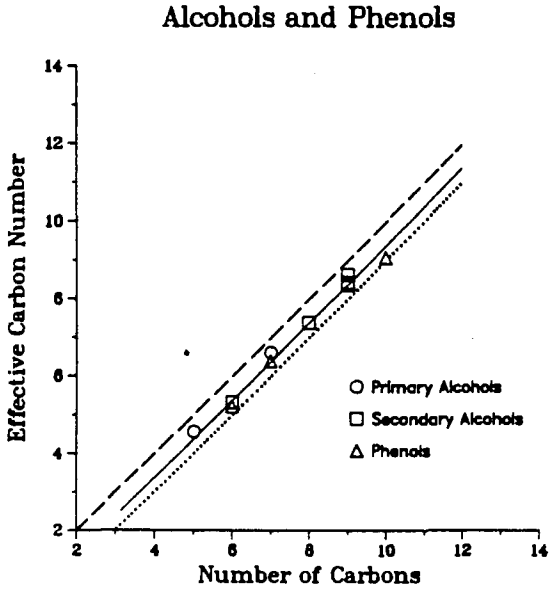


Figure 4. ECN versus carbon number for alcohols and phenols. Symbols and lines are as in Figure 1.

the analogous hydrocarbons. The third compound, thianaphthene, had a reduced response, but by only 0.21 effective carbon. These data are consistent with the commonly accepted notion that the presence of sulfur atoms does not affect the FID response in a significant way.

The second small data set in Table III contains two nitriles. They fortuitously yielded identical shifts of −0.42 carbon. This differs rather significantly from the value of −0.70 given in ref 1. We offer no suggestions for this difference, except those already noted above in the case of ketones and ethers. The agreement is striking, even if it is only for two compounds.

The addivitity of functional group effects on the ECN was addressed in a study of six additional compounds. The details of this work are given in Table IX. Each compound contained two separate functional groups. Table IX gives a predicted ECN value expected from the simple sum of the average ECN shifts given in Table VII and also the experimental ECN. In four of the six cases the agreement is excellent, with a difference of 1.5% or less. The other two compounds have an error in prediction of 3.3% and 4.4%. The latter is for catechol, which contains two hydroxyl groups on adjacent carbons

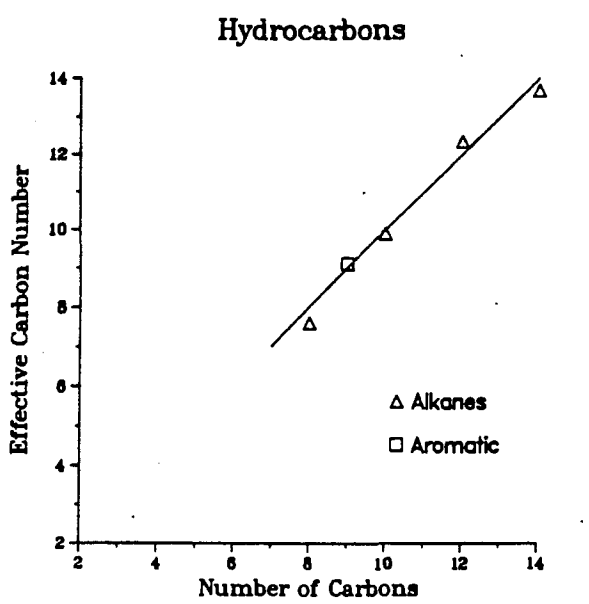


Figure 5. ECN versus carbon number for hydrocarbons. Symbols and lines are as in Figure 1.

Table VIII. FID Response

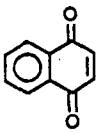
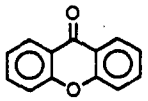
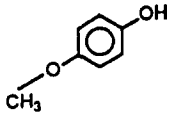
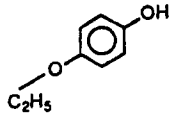
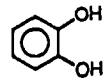
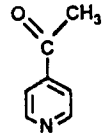
name	formula	RRF	ECN	ECN minus no. of carbons
	Sulfides			
thianaphthene (thionaphthene)	C_8H_6S	0.744	7.79	−0.21
dibenzothiophene	$C_{12}H_8S$	0.837	12.04	+0.04
thianthrene	$C_{12}H_8S_2$	0.703	12.09	+0.09
	Nitriles			
benzonitrile	C_7H_5N	0.818	6.58	−0.42
1-cyanonaphthalene	$C_{11}H_7N$	0.885	10.58	−0.42
	Aminopyridines			
4-aminopyridine	$C_5H_6N_2$	0.492	3.61	−1.39
2-(methylamino)pyridine	$C_6H_8N_2$	0.618	5.21	−0.79
2-(dimethylamino)pyridine	$C_7H_{10}N_2$	0.656	6.26	−0.74
4-(dimethylamino)pyridine	$C_7H_{10}N_2$	0.642	6.12	−0.88

of a benzene ring. The proximity of these functional groups may account for the only modest agreement in this case because the carbons involved may not be responding independently in the flame. Although only a small number of compounds have been studied in this evaluation of addivitity, a favorable preliminary conclusion is justified.

The simplest way to view the effect of an electronegative atom on a carbon atom in the FID is to assume that the bond between them survives the reducing part of the flame in a certain percent of the molecules and that the pair therefore does not undergo oxidative ionization in the oxidizing region. Although only a small fraction of all of the carbon atoms will be ionized, the heteroatom seems to have a proportional effect on that fraction.

The esters present an interesting application of this simple picture. Since the ether bond in an ester includes one carbon already bonded to an oxygen in the carbonyl, a simple addition of effects would not be expected. Table VII indicates that a carbonyl in a ketone causes a reduction of 0.80 in effective carbons and a that simple ether causes a reduction of 0.78. The overall reduction for the ester might be predicted along the following lines: the carbonyl carbon will be removed from ionization 80% of the time, the ether oxygen will remain with one of the two carbons 78% of the time, with half of this frequency, 39%, for each of the carbons. However, for the

Table IX. Compounds with Multiple Functionalities

structure	name	group(s)	no. of carbons	reduction	ECN predicted	ECN experimental	% difference
	1,4-naphthoquinone	two ketones	10	2 × 0.80	8.40	8.34	+0.8
	xanthone	ketone + ether	13	0.80 + 0.78	11.42	11.56	−1.2
	4-methoxyphenol	phenol + ether	7	0.64 + 0.78	5.58	5.50	+1.5
	4-ethoxyphenol	phenol + ether	8	0.64 + 0.78	6.58	6.37	+3.3
	catechol	two phenols	6	2 × 0.64	4.72	4.94	−4.4
	4-acetylpyridine	N in ring + ketone	7	0.62 + 0.80	5.58	5.52	+1.1

carbonyl carbon, this ether oxygen has an effect only for the 20% of the time when the carbonyl oxygen does not remain. Therefore that total reduction of carbon will be

carbonyl carbon	0.80 + 0.20(0.78/2)	= 0.88
second ether carbon	0.78/2	= 0.39
total		= 1.27

Interestingly, this is exactly the value found in the small set of three esters studied in the present work, and it is virtually identical with Sternberg's result of 1.25 (*1*). One must be cautious about over-interpreting from this quite small sample of compounds, but the agreement is quite supportive of the suggested analysis. These facts lend further weight to our working model, which does include the additivity of effects.

Additive effects were further studied by using aminopyridines. The results are summarized in Table VIII. Although three of the four compounds have quite consistent shifts in ECN, one of them gave a value almost twice that of the other three. Somewhat more disturbing is the fact that the presence of an amino group and a nitrogen in a ring would be expected to cause a change in response equal to −0.58 and −0.62, respectively. This sum of −1.20 is not too far from the 4-aminopyridine result of −1.39, but it is quite far from the approximately −0.80 found for the other three compounds. Possible sorptive losses would produce effects in the opposite direction. We have no other suggestions for these discrepancies.

We have performed some experiments to see if the numbers reported here are valid for other experimental conditions. A set of ketone mixtures was analyzed in duplicate at a temperature program rate of 4 °C/min rather than the 10 °C/min used for all of the other studies. The mean RRF values from these runs were on average slightly greater than the results in Table II, with two-thirds higher and one-third lower. The average of the absolute values of the percent deviations was 2.1%.

The concentration dependence of the results was tested with additional mixtures of these ketones at nominal concentrations of 200 and 10 ppm. At the higher concentration, five of the eight compounds differed by less than 3% from the results in Table II and seven of eight by less than 4%. At the lower concentration, the results for 3-pentanone and 1,4-naphthoquinone were above the numbers in Table II by about 6%, the 3-heptanone was low by the same amount, and 2-hexanone was low by almost 11%. The remaining four compounds differed by 2.5% or less. The analysis scheme presented in the present work must be used with caution at low concentrations. Some of the variations seen in all three of these tests of conditions must be ascribed to differences in chromatographic conditions and small data sets.

Variations in flame conditions might be expected to cause unacceptable deviations. We have begun a comprehensive study using a wide variety of hydrogen and air flow rates. Preliminary indications are that although absolute responses do vary measurably with hydrogen concentration, the relative responses as obtained by using an internal standard are sufficiently constant for the type of analysis that we propose.

If one wanted to use the RRF values reported in this work but did not want to use naphthalene as an internal standard, a simple determination of the RRF between the desired internal standard and the naphthalene would give a correction factor that could be applied to all of the needed numbers. If the new standard were one of the other compounds in this study, even that experiment would be unnecessary. Scanlon and Willis (*14*) used tridecane and tetradecane as their ECN standards and found the ECN of naphthalene to be 10.01. Therefore, our assumed value of 10 would make the present RRF values be appropriate also for the alkanes that they used.

Future work in this area is needed to more firmly establish the additivity of effects before the entire process can be accurately modeled. We would envision the automated use of RRF values from a computerized data base or from a calculation, either based on the individual contributions of all the structural groups.

One can, therefore, conclude that FID responses for a wide variety of compounds can be predicted to a good degree of accuracy, typically 2-3%. This obviates the need to obtain high-purity standards and to accurately prepare and analyze solutions of these compounds as long as one confirms that good chromatographic conditions are present. If one needs greater accuracy than this method provides, standards of actual purity greater than 98% would have to be obtained, and at least two sets of standard solutions would have to be prepared, because one can expect a single solution to differ from the mean of a set of standards by 1% or more (see text above). Although the primary use for this technique is expected to be the quantification of components in a complex organic mixture if a molecular or at least a general structural identification can been made, other uses for response prediction would be in evaluations of sample purity and column performance.

ACKNOWLEDGMENT

Victoria Vlastnik is acknowledged for assistance in data collection and Doug Hoffman for technical assistance. The preliminary work cited was performed by Maria Portellos.

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Surface-Enhanced Raman Analysis of Sulfa Drugs on Colloidal Silver Dispersion

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Surface-enhanced Raman spectrometry (SERS) of three sulfa drugs (sulfadiazine, sulfamerazine, and sulfamethazine) is reported. Silver colloidal dispersions prepared by simple borohydride reduction of silver nitrate are used as substrates. The capability of SERS for spectral fingerprinting of analytes with close structural properties using easily prepared substrates and relatively simple instrumentation is illustrated. By careful attention to the timing in the measurement, quantitative information can be obtained from silver colloids. Linearity was achieved up to 100 ng mL^{-1}. Limits of detection range in the low nanograms per milliliter level.

The discoveries of sulfonamides (sulfa drugs) and antibiotics constitute some of the most significant medical achievements of this century. They have therapeutic uses both in human and veterinary medicine and in disease prevention in livestock. In 1985, over 100×10^6 kg of these drugs were used annually. Over 5000 sulfa drugs, which have a general structure of the type $H_2NC_6H_4SO_2NHR$, have been synthesized and tested. Fewer than 30 of these have proven worthy of sustained use (*1*). Their biological activity is based on the inhibition of the biosynthesis of folate cofactors in bacteria by blocking a step in the formation of dihydrofolic acid from *p*-aminobenzoic acid (2). The sulfapyrimidines, where the R group is a pyrimidine ring, have been touted as the ultimate stage of development of sulfa drugs. Important members of this group are sulfadiazine, sulfamerazine, and sulfamethazine (*3*).

During the 1940s, these drugs enjoyed widespread use in combating bacterial infections in humans and in the treatment of diseases affecting pet and food-producing animals. Recently, the reduction of sulfa drug use in humans has been triggered by increased bacterial resistance to the drugs and the development of more effective antimicrobial agents. However, the use of sulfa drugs in veterinary medicine has persisted because the drugs are easily administered in feed and water, are economical, and have proven to be effective for the treatment of livestock diseases. The use of combinations of two or more sulfa drugs was also shown to be of therapeutic value. During treatment with sulfa drugs, the higher the concentration of drug that can be maintained in the body, the greater its effect. However, increasing the drug concentration also increases the side effects, the most common of which is crystalluria, a deposition of crystals in the renal tubules due to the limited solubility of the sulfa drugs in water. However, when used in combination, each drug acts independently. Since all of the sulfapyrimidines have been shown to have the same therapeutic effect, combination therapy allows a higher total drug concentration to be maintained in the blood while minimizing the effects of crystalluria.

The use of sulfa drugs to promote growth and treat diseases of livestock animals has been a major cause of sulfa drug tissue residue in swine marketed for human consumption. In 1973, the U.S. Food and Drug Administration set a tolerance of 100 ng of sulfonamide per gram of edible tissue. Random assays

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Attachment 5.

Data Sheets

Standard Data Sheet

Standard	Date	Vial Wt	Vial+H_2O Wt	Vial+H_2O+ 2-BE Wt	H_2O Wt (mg)	2-BE Wt (mg)	Wt % 2-BE
0.50%							
5%							
50%							
5% QCCS							

Analyst: _____

QCCS Data Sheet

Date	Sample	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	R_{fid}	2-BE Mass (mg)	Wt % 2-BE
	QCCS-1						
	QCCs-2						
	QCCS-3						
					Mean Measured Conc.($\bar{X}$)=		
					True Conc. (T)=		
					Accuracy=		
						%RSD=	

Analyst: _____

Calibration Data Sheet

Date	Nominal Std %	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	Standard Wt % 2-BE	$Mass_s$ (mg)	R_{fid}	RF (area unit/mg)	%RSD
	0.5								
	5								
	50								
						Average RF $(\overline{RF})$ =			

Analyst: _____

Paint Results Data Sheet

Date	Paint	Sample	Sample Wt (mg)	R_{fid}	$\overline{RF}$	VOC $mass_u$ (mg) ($R_{fid}/\overline{RF}$)	Wt% VOC_u (uncorrected)	Wt% VOC_c (corrected)
	MS1-6659A	1						
	MS1-6659A	2						
	MS1-6659A	3						
	1403-0100	1						
	1403-0100	2						
	1403-0100	3						
	4206-0100	1						
	4206-0100	2						
	4206-0100	3						
	4020-1000	1						
	4020-1000	2						
	4020-1000	3						

Analyst: _____

Attachment 6.

Materials

Materials Provided for Interlaboratory Study

1. One ounce of 2-Butoxyethanol for preparing standards.

2. Thirty (30) PTFE liners for sample tubes

3. Silanized glass wool for packing the PTFE liners

4. Sixteen (16) ¼ inch stainless steel tubes

5. Twelve (12) 1 cc syringes with 20 gauge needles for loading the sample paints into the PTFE liners

6. One Hamilton #805 50µL syringe

7. Four sample paints labeled with one of the following sample codes:

   A. 1403-0100
   B. MS1-6659A
   C. 4206-0100
   D. 4020-1000

6. Logbook

7. Perkin-Elmer Model ATD-400 Thermal Tube Desorber (SN 48996) with Hewlett Packard 5890 GC (BMI Tag# X-52157)

8. Chrom Perfect data system on Dell model GXL5133 Pentium Computer (SN 5X789) with Digital DEClaser 1800 printer (SN 2M42400778)

APPENDIX C

ASTM STANDARD PRACTICE E691-92

Designation: E 691 – 92

Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[1]

This standard is issued under the fixed designation E 691; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

Tests[1] performed on presumably identical materials in presumably identical circumstances do not, in general, yield identical results. This is attributed to unavoidable random errors inherent in every test procedure; the factors that may influence the outcome of a test cannot all be completely controlled. In the practical interpretation of test data, this inherent variability has to be taken into account. For instance, the difference between a test result and some specified value may be within that which can be expected due to unavoidable random errors, in which case a real deviation from the specified value has not been demonstrated. Similarly, the difference between test results from two batches of material will not indicate a fundamental quality difference if the difference is no more than can be attributed to inherent variability in the test procedure. Many different factors (apart from random variations between supposedly identical specimens) may contribute to the variability in application of a test method, including: *a* the operator, *b* equipment used, *c* calibration of the equipment, and *d* environment (temperature, humidity, air pollution, etc.). It is considered that changing laboratories changes each of the above factors. The variability between test results obtained by different operators or with different equipment will usually be greater than between test results obtained by a single operator using the same equipment. The variability between test results taken over a long period of time even by the same operator will usually be greater than that obtained over a short period of time because of the greater possibility of changes in each of the above factors, especially the environment.

The general term for expressing the closeness of test results to the "true" value or the accepted reference value is accuracy. To be of practical value, standard procedures are required for determining the accuracy of a test method, both in terms of its bias and in terms of its precision. This practice provides a standard procedure for determining the precision of a test method. Precision, when evaluating test methods, is expressed in terms of two measurement concepts, repeatability and reproducibility. Under repeatability conditions the factors listed above are kept or remain reasonably constant and usually contribute only minimally to the variability. Under reproducibility conditions the factors are generally different (that is, they change from laboratory to laboratory) and usually contribute appreciably to the variability of test results. Thus, repeatability and reproducibility are two practical extremes of precision.

The repeatability measure, by excluding the factors *a* through *d* as contributing variables, is not intended as a mechanism for verifying the ability of a laboratory to maintain "in-control" conditions for routine operational factors such as operator-to-operator and equipment differences or any effects of longer time intervals between test results. Such a control study is a separate issue for each laboratory to consider for itself, and is not a recommended part of an interlaboratory study.

The reproducibility measure (including the factors *a* through *d* as sources of variability) reflects what precision might be expected when random portions of a homogeneous sample are sent to random "in-control" laboratories.

To obtain reasonable estimates of repeatability and reproducibility precision, it is necessary in an interlaboratory study to guard against excessively sanitized data in the sense that only the uniquely best operators are involved or that a laboratory takes unusual steps to get "good" results. It is also important to recognize and consider how to treat "poor" results that may have unacceptable assignable causes (for example, departures from the prescribed procedure). The inclusion of such results in the final precision estimates might be questioned.

An essential aspect of collecting useful consistent data is careful planning and conduct of the

[1] This practice is under the jurisdiction of ASTM Committee E-11 on Statistical Methods and is the direct responsibility of Subcommittee E11.20 on Test Method Evaluation and Quality Control.

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study. Questions concerning the number of laboratories required for a successful study as well as the number of test results per laboratory affect the confidence in the precision statements resulting from the study. Other issues involve the number, range, and types of materials to be selected for the study, and the need for a well-written test method and careful instructions to the participating laboratories.

To evaluate the consistency of the data obtained in an interlaboratory study, two statistics may be used: the "*k*-value", used to examine the consistency of the within-laboratory precision from laboratory to laboratory, and the "*h*-value", used to examine the consistency of the test results from laboratory to laboratory. Graphical as well as tabular diagnostic tools help in these examinations.

1. Scope

1.1 This practice describes the techniques for planning, conducting, analyzing, and treating the results of an interlaboratory study (ILS) of a test method. The statistical techniques described in this practice provide adequate information for formulating the precision statement of a test method.

1.1.1 A computer software package for performing the calculations and producing the tables and graphs associated with Practice E 691. This software can be run on PC compatible computers, and hard copy tables and graphs can be printed on dot-matrix printers.

1.2 This practice does not concern itself with the development of test methods but rather with gathering the information needed for a test method precision statement after the development stage has been successfully completed. The data obtained in the interlaboratory study may indicate, however, that further effort is needed to improve the test method.

1.3 Since the primary purpose of this practice is the development of the information needed for a precision statement, the experimental design in this practice may not be optimum for evaluating materials, apparatus, or individual laboratories.

1.4 *Field of Application*—This practice is concerned exclusively with test methods which yield a single numerical figure as the test result, although the single figure may be the outcome of a calculation from a set of measurements.

1.4.1 This practice does not cover methods in which the measurement is a categorization, such as a go-no-go allocation (two categories) or a sorting scheme into two or more categories. For practical purposes, the discontinuous nature of measurements of these types may be ignored when a test result is defined as an average of several individual measurements. Then, this practice may be applicable, but caution is required and a statistician should be consulted.

1.5 The information in this practice is arranged as follows:

	Section
Scope	1
Referenced Documents	2
Terminology	3
Summary of Practice	4
Significance and Use	5
Planning the Interlaboratory Study (ILS)	
ILS Membership	6
Basic Design	7
Test Method	8
Laboratories	9
Materials	10
Number of Test Results per Material	11
Protocol	12
Conducting the Testing Phase of the ILS	
Pilot Run	13
Full Scale Run	14
Calculation and Display of Statistics	
Calculation of the Statistics	15
Tabular and Graphical Display of Statistics	16
Data Consistency	
Flagging Inconsistent Results	17
Investigation	18
Task Group Actions	19
Examples of Interlaboratory Studies	20
Precision Statement Information	
Repeatability and Reproducibility	21
Annexes	
Theoretical Considerations	A1
Index to Selected Terms	A2
References	
Tables and Figures	
Tables	Table
Glucose in Serum Example	1–7
Pentosans in Pulp Example	8–11
Critical Values of Consistency Statistics, h and k	12
Figures	Fig.
Glucose in Serum Example	1–5
Pentosans in Pulp Example	6–10

1.6 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[2]

E 456 Terminology Related to Quality and Statistics[2]

E 1169 Guide for Conducting Ruggedness Tests[2]

2.2 *ASTM Adjunct:*

E 691 Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

3. Terminology

3.1 *Definitions*—For formal definitions of statistical terms, see Terminology E 456.

3.2 *Descriptions of Terms Specific to This Standard:*

3.2.1 *Test Method and Protocol*—In this practice, the term "test method" is used both for the actual measurement process and for the written description of the process, while the term "protocol" is used for the directions given to the laboratories for conducting the ILS.

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[2] *Annual Book of ASTM Standards*, Vol 14.02.

[3] An adjunct is available from ASTM Headquarters. Request PCN: 12-5-6910-34 for 5¼" disk and 12-506911-34 for a 3½" disk.

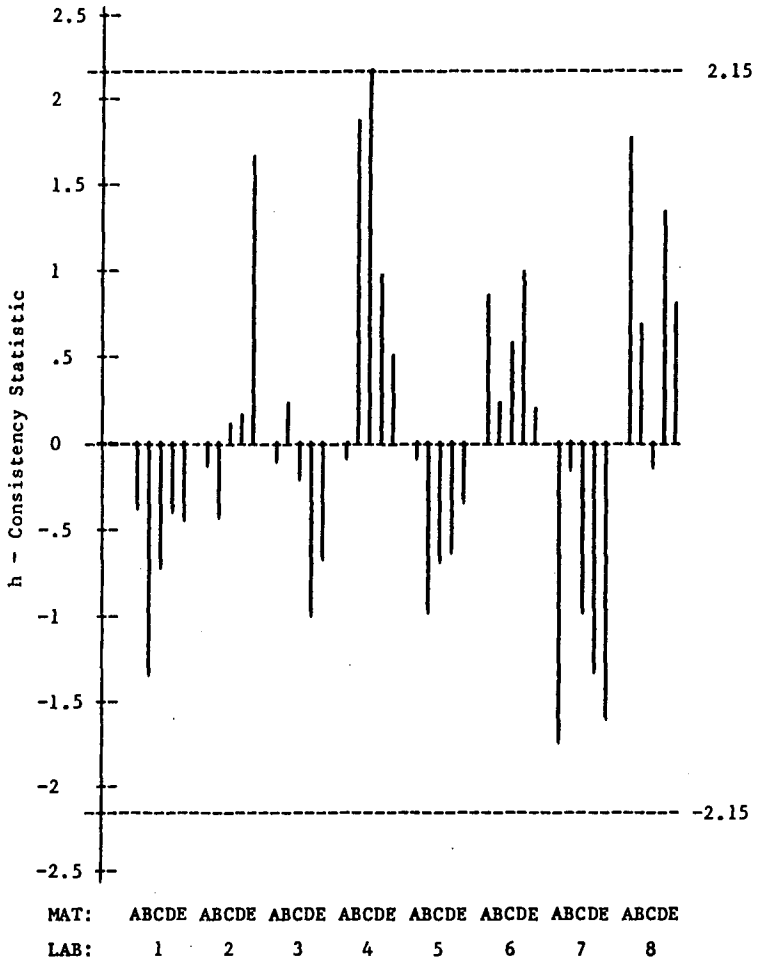

FIG. 1 Glucose in Serum: *h*—Materials within Laboratories

3.2.2 *Observations, Test Determinations and Test Results:*

3.2.2.1 A test method often has three distinct stages, the direct observation of dimensions or properties, the arithmetic combination of the observed values to obtain a test determination, and the arithmetic combination of a number of test determinations to obtain the test result of the test method. In the simplest of test methods a single direct observation is both the test determination and the test result. For example, the test method may require the measurement of the mass of a test specimen prepared in a prescribed way. Another test method may require the measurement of the area of the test specimen as well as the mass, and then direct that the mass be divided by the area to obtain the mass per unit area of the specimen. The whole process of measuring the mass and the area and calculating the mass per unit area is a test determination. If the test method specifies that only one test determination is to be made, then the test determination value is the test result of the test method. Some test methods require that several determinations be made and the values obtained be averaged or otherwise combined to obtain the test result of the test method. Averaging of several determinations is often used to reduce the effect of local variations of the property within the material.

3.2.2.2 In this practice, the term "test determination" is used both for the process and for the value obtained by the process, except when "test determination value" is needed for clarity.

3.2.2.3 The number of test determinations required for a test result should be specified in each individual test method. The number of test results required for an interlaboratory study of a test method is specified in the protocol of that study.

3.2.3 *Test Specimens and Test Units*—In this practice a test unit is the total quantity of material needed for obtaining a test result as specified by the test method. The portion of the test unit needed for obtaining a single test determination is called a test specimen. Usually a separate test specimen is required for each test determination.

3.2.4 *Precision, Bias, and Accuracy of a Test Method:*

3.2.4.1 When a test method is applied to a large number of portions of a material, that are as nearly alike as possible, the test results obtained nevertheless will not all have the same value. A measure of the degree of agreement among these test results describes the precision of the test method for that material.

3.2.4.2 Numerical measures of the variability between such test results provide inverse measures of the precision of the test method. Greater variability implies smaller (that is, poorer) precision and larger imprecision.

3.2.4.3 This practice is designed only to estimate the precision of a test method. However, when accepted refer-

TABLE 1 Glucose in Serum ILS Test Result Data

Laboratory	Material				
	A	B	C	D	E
1	41.03	78.28	132.66	193.71	292.78
	41.45	78.18	133.83	193.59	294.09
	41.37	78.49	133.10	193.65	292.89
2	41.17	77.78	132.92	190.88	292.27
	42.00	80.38	136.90	200.14	309.40
	41.15	79.54	136.40	194.30	295.08
3	41.01	79.18	132.61	192.71	295.53
	40.68	79.72	135.80	193.28	290.14
	42.66	80.81	135.36	190.28	292.34
4	39.37	84.08	138.50	195.85	295.19
	42.37	78.60	148.30	196.36	295.44
	42.63	81.92	135.69	199.43	296.83
5	41.88	78.16	131.90	192.59	293.93
	41.19	79.58	134.14	191.44	292.48
	41.32	78.33	133.76	195.12	294.28
6	43.28	78.66	137.21	195.34	297.74
	40.50	79.27	135.14	198.26	296.80
	42.28	81.75	137.50	198.13	290.33
7	41.08	79.76	130.97	194.66	287.29
	41.27	81.45	131.59	191.99	293.76
	39.02	77.35	134.92	187.13	289.36
8	43.36	80.44	135.46	197.56	298.46
	42.65	80.80	135.14	195.99	295.28
	41.72	79.80	133.63	200.82	296.12

ence values are available for the property levels, the test result data obtained according to this practice may be used in estimating the bias of the test method. For a discussion of bias estimation and the relationships between precision, bias, and accuracy, see Practice E 177.

3.2.5 *Repeatability and Reproducibility*—These terms deal with the variability of test results obtained under specified laboratory conditions. Repeatability concerns the variability between independent test results obtained within a single laboratory in the shortest practical period of time by a single operator with a specific set of test apparatus using test specimens (or test units) taken at random from a single quantity of homogeneous material obtained or prepared for the ILS. Reproducibility deals with the variability between single test results obtained in different laboratories, each of which has applied the test method to test specimens (or test units) taken at random from a single quantity of homogeneous material obtained or prepared for the ILS.

3.2.5.1 *Repeatability Conditions*—The within-laboratory conditions specified above for repeatability. The single-operator, single-set-of-apparatus requirement means that for a particular step in the measurement process the same combination of operator and apparatus is used for every test result and on every material. Thus, one operator may prepare the test specimens, a second measure the dimensions and a third measure the breaking force. "Shortest practical period of time" means that the test results, at least for one material, are obtained in a time not less than in normal testing and not so long as to permit significant changes in test material, equipment or environment.

3.3 For further discussion of the terms discussed above, see Practice E 177, and the formal definitions in Practice E 456.

TABLE 2[A] Interlaboratory Study Worksheet for Glucose in Serum Initial Preparation of Test Result Data for Material *A*

Laboratory Number	Test Results, x			$\bar{x}$	s	d	h	k
	1	2	3					
1	41.03	41.45	41.37	41.2833	0.2230	−0.2350	−0.39	0.21
2	41.17	42.00	41.15	41.4400	0.4851	−0.0783	−0.13	0.46
3	41.01	40.68	42.66	41.4500	1.0608	−0.0683	−0.11	1.00
4	39.37	42.37	42.63	41.4567	1.8118	−0.0616	−0.10	1.70
5	41.88	41.19	41.32	41.4633	0.3667	−0.0550	−0.09	0.34
6	43.28	40.50	42.28	42.0200	1.4081	0.5017	0.83	1.32
7	41.08	41.27	39.02	40.4567	1.2478	−1.0616	−1.75	1.17
8	43.36	42.65	41.72	42.5767	0.8225	1.0584	1.75	0.77

[A] Average of cell averages, $\bar{\bar{x}} = 41.5183$
Standard deviation of cell averages, $s_{\bar{x}} = 0.6061$
Repeatability standard deviation, $s_r = 1.0632$
Reproducibility standard deviation, $s_R = 1.0632$

where:

x = individual test result,

$\bar{x}$ = cell average = $\sum_1^n x/n$ where n = number of test results per cell = 3,

$\bar{\bar{x}}$ = average of cell averages = $\sum_1^p \bar{x}/p$ where p = number of laboratories = 8,

s = cell standard deviation = $\sqrt{\sum_1^n (x - \bar{x})^2/(n-1)}$

d = cell deviation = $\bar{x} - \bar{\bar{x}}$

$s_{\bar{x}}$ = standard deviation of cell averages = $\sqrt{\sum_1^p d_2/(p-1)}$

s_r = repeatability standard deviation = $\sqrt{\sum_1^p s^2/p}$

s_R = reproducibility standard deviation = larger of s_r and $\sqrt{(s_{\bar{x}})^2 + (s_r)^2(n-1)/n}$

$h = d/s_{\bar{x}}$, and

$k = s/s_r$.

4. Summary of Practice

4.1 The procedure presented in this practice consists of three basic steps: planning the interlaboratory study, guiding the testing phase of the study, and analyzing the test result data. The analysis utilizes tabular, graphical, and statistical diagnostic tools for evaluating the consistency of the data so that unusual values may be detected and investigated, and also includes the calculation of the numerical measures of precision of the test method pertaining to both within-laboratory repeatability and between-laboratory reproducibility.

5. Significance and Use

5.1 ASTM regulations require precision statements in all test methods in terms of repeatability and reproducibility. This practice may be used in obtaining the needed information as simply as possible. This information may then be used to prepare a precision statement in accordance with Practice E 177.

PLANNING THE INTERLABORATORY STUDY (ILS)

6. ILS Membership

6.1 *Task Group*[4]—Either the task group that developed the test method, or a special task group appointed for the purpose, must have overall responsibility for the ILS, including funding where appropriate, staffing, the design of the ILS, and decision-making with regard to questionable data. The task group should decide on the number of laboratories, materials, and test results for each material. In addition, it

[4] To facilitate the preparation of the final report on the ILS, the task group can obtain the Research Report format guide from ASTM Headquarters.

TABLE 3 Glucose in Serum-h[A]

Laboratory	Material				
	A	B	C	D	E
1	−0.39	−1.36	−0.73	−0.41	−0.46
2	−0.13	−0.45	0.10	0.15	1.64
3	−0.11	0.22	−0.21	−1.01	−0.68
4	−0.10	1.85	2.14	0.96	0.49
5	−0.09	−0.99	−0.71	−0.64	−0.34
6	0.83	0.21	0.55	0.97	0.17
7	−1.75	−0.16	−1.00	−1.33	−1.62
8	1.75	0.67	−0.15	1.31	0.79

[A] Critical value = 2.15.

TABLE 5[A] Glucose in Serum-h[B]

Laboratory	Material				
	A	B	C	D	E
1	−0.39	−1.36	−0.88	−0.41	−0.46
2	−0.13	−0.45	0.39	0.15	1.64
3	−0.11	0.22	−0.08	−1.01	−0.68
4	−0.10	1.85	1.59	0.96	0.49
5	−0.09	−0.99	−0.64	−0.64	−0.34
6	0.83	0.21	1.09	0.97	0.17
7	−1.75	−0.16	−1.28	−1.33	−1.62
8	1.75	0.67	0.01	1.31	0.79

[A] Recalculated values after correcting Cell C4, (see 20.1.4 and 20.1.5).
[B] Critical value = 2.15.

should specify any special calibration procedures and the repeatability conditions to be specified in the protocol (see 12.3 and 12.4).

6.2 *ILS Coordinator*—The task group must appoint one individual to act as overall coordinator for conducting the ILS. The coordinator will supervise the distribution of materials and protocols to the laboratories and receive the test result reports from the laboratories. Scanning the reports for gross errors and checking with the laboratories, when such errors are found, will also be the responsibility of the coordinator. The coordinator may wish to consult with the statistician in questionable cases.

6.3 *Statistician:*

6.3.1 The test method task group should obtain the assistance of a person familiar with the statistical procedures in this practice and with the materials being tested in order to ensure that the requirements outlined in this practice are met in an efficient and effective manner. This person should also assist the task group in interpreting the results of the data analysis.

6.3.2 When a person having adequate knowledge of both the materials and the proper statistical techniques is not available, the task group should obtain the services of a statistician who has experience in practical work with data from materials testing. The task group should provide the statistician with an opportunity to become familiar with the statistical procedures of this practice and with both the materials and the test method involved. The statistician should become a member of the task group conducting the ILS, (task group members need not be members of ASTM).

6.3.3 The calculations of the statistics (see Section 15) for each material can be readily done by persons not having statistical knowledge. (see 15.1.3 and 15.4.2.)

6.4 *Data Analyst*—This individual should be someone who is careful in making calculations and can follow the directions in Sections 15 through 17.

6.5 *Laboratory ILS Supervisor*—Each laboratory must have an ILS supervisor to oversee the conduct of the ILS within the laboratory and to communicate with the ILS Coordinator. The name of the supervisor should be obtained on the response form to the "invitation to participate" (see 9.4).

7. Basic Design

7.1 Keep the design as simple as possible in order to obtain estimates of within- and between-laboratory variability that are free of secondary effects. The basic design is represented by a two-way classification table in which the rows represent the laboratories, the columns represent the materials, and each cell (that is, the intersection of a row with a column) contains the test results made by a particular laboratory on a particular material (see Table 1).

8. Test Method

8.1 Of prime importance is the existence of a valid, well-written test method that has been developed in one or more competent laboratories, and has been subjected to a ruggedness test prior to the ILS.

8.2 A ruggedness test is a screening procedure for investigating the effects of variations in environmental or other conditions in order to determine how control of such test conditions should be specified in the written description of the method. For example, the temperature of the laboratory or of a heating device used in the test may have an effect that cannot be ignored in some cases but may be much less in others. In a ruggedness test, deliberate variations in temperature would be introduced to establish the allowable limits on control of temperature. This subject is discussed more fully in Refs (1,2 and 3) see also Guide E 1169.

8.3 As a result of carrying out the screening procedure, and of some experience with the test method in the sponsoring laboratory and one or two other laboratories, a written

TABLE 4 Glucose in Serum-k[A]

Laboratory	Material				
	A	B	C	D	E
1	0.21	0.11	0.22	0.02	0.18
2	0.46	0.89	0.79	1.78	2.33
3	1.00	0.56	0.63	0.61	0.69
4	1.70	1.85	2.41	0.74	0.22
5	0.34	0.52	0.44	0.72	0.24
6	1.32	1.09	0.47	0.63	1.03
7	1.17	1.38	0.77	1.45	0.84
8	0.77	0.34	0.36	0.94	0.42

[A] Critical value = 2.06.

TABLE 6[A,B] Glucose in Serum-k

Laboratory	Material				
	A	B	C	D	E
1	0.21	0.11	0.36	0.02	0.18
2	0.46	0.89	1.40	1.78	2.33
3	1.00	0.56	1.12	0.61	0.69
4	1.70	1.85	1.02	0.74	0.22
5	0.34	0.52	0.78	0.72	0.24
6	1.32	1.09	0.83	0.63	1.03
7	1.17	1.36	1.38	1.45	0.84
8	0.77	0.34	0.63	0.94	0.42

[A] Recalculated values after correcting cell C4, (See 20.1.4 and 20.1.5).
[B] Critical value = 2.06.

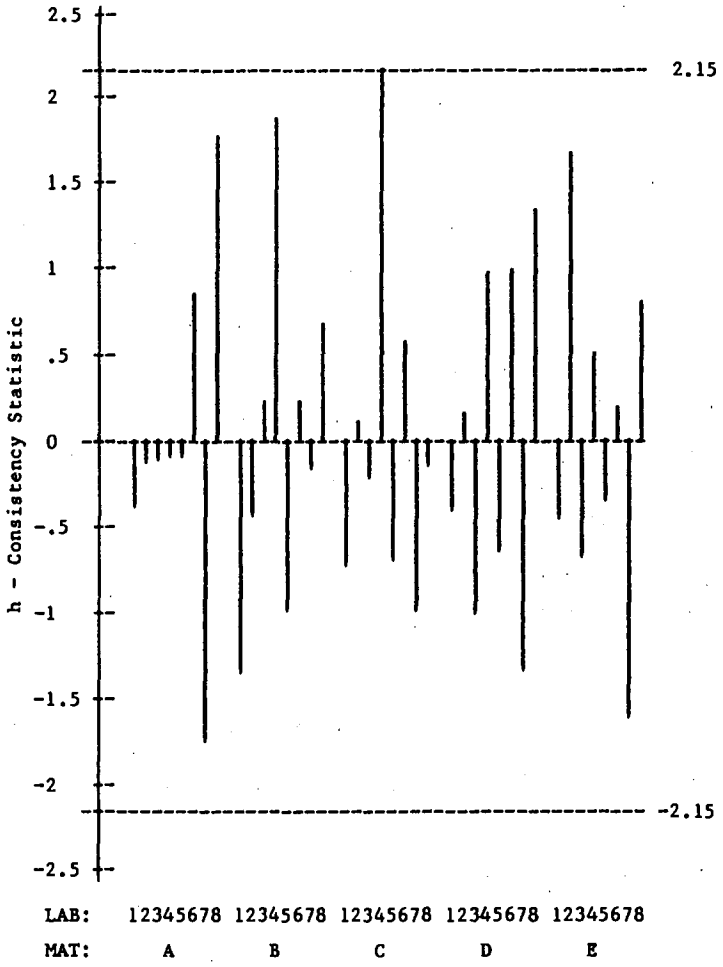

FIG. 2 Glucose in Serum: *h*—Laboratories within Materials

version of the test method must have been developed (but not necessarily published as a standard method). This draft should describe the test procedure in terms that can be easily followed in any properly equipped laboratory by competent personnel with knowledge of the materials and the property to be tested. The test conditions that affect the test results appreciably should have been identified and the proper degree of control of the test conditions specified in the description of the test procedure. In addition, the test method should specify how closely (that is, to how many digits) each observation in the test method is to be measured.

8.4 The test method should specify the calibration procedure and the frequency of calibration.

9. Laboratories

9.1 *Number of Laboratories:*

9.1.1 An ILS should include 30 or more laboratories but this may not be practical and some ILS have been run with fewer. It is important, that enough laboratories be included in the ILS to be a reasonable cross-section of the population of qualified laboratories; that the loss or poor performance of a few will not be fatal to the study, and to provide a reasonably satisfactory estimate of the reproducibility.

9.1.2 **Under no circumstances should the final statement of precision of a test method be based on acceptable test results for each material from fewer than 6 laboratories.** This would require that the ILS begin with 8 or more laboratories in order to allow for attrition.

9.1.3 The examples given in this practice include only 8 and 7 laboratories, respectively. These numbers are smaller than ordinarily considered acceptable, but they are convenient for illustrating the calculations and treatment of the data.

9.2 Any laboratory considered qualified to run the test routinely (including laboratories that may not be members of ASTM) should be encouraged to participate in the ILS, if the preparatory work is not excessive and enough suitably homogeneous material is available. In order to obtain an adequate number of participating laboratories, advertise the proposed ILS in where appropriate (for example, trade magazines, meetings, circulars, etc.).

9.3 "Qualified" implies proper laboratory facilities and testing equipment, competent operators, familiarity with the test method, a reputation for reliable testing work, and sufficient time and interest to do a good job. If a laboratory meets all the other requirements, but has had insufficient experience with the test method, the operator in that laboratory should be given an opportunity to familiarize himself with the test method and practice its application before the ILS starts. For example, this experience can be obtained by a pilot run (see Section 13) using one or two trial

TABLE 7 Glucose in Serum—Precision Statistics

NOTE—This table (with the column for $s_{\bar{x}}$ omitted) is a useful format for the presentation of the precision of a test method as required by Section A21 of the *Form and Style of ASTM Standards*.

Material	$\bar{x}$	s_x'	s_r	s_R	r	R
A	41.5183	0.6061	1.0632	1.0632	2.98	2.98
B	79.6796	1.0027	1.4949	1.5796	4.19	4.42
C	134.7264	1.7397	1.5434	2.1482	4.33	6.02
D	194.7170	2.5950	2.6251	3.3657	7.35	9.42
E	294.4920	2.6931	3.9350	4.1923	11.02	11.74

samples provided by the task group and returning the raw data and the test results to the task group. **The importance of this familiarization step cannot be overemphasized.** Many interlaboratory studies have turned out to be essentially worthless due to lack of familiarization.

9.4 Obtain written ensurance from each potential participating laboratory that it is properly equipped to follow all the details of the procedure and is willing to assign the work to a skilled operator in a timely manner. The decision of a laboratory to participate should be recorded on a response form to a written invitation. The invitation should include information covering the required time for calibrating the apparatus and for testing all of the materials, and other possible costs. The response form should include the name, address, and telephone number of the person supervising the ILS work within the laboratory, the address and other markings required to ensure the ILS sample material will be promptly delivered to the ILS supervisor, answers to brief questions concerning equipment, environment, and personnel, including previous use of the test method, upon which the apparent competence of the laboratory may be judged, and an affirmation that the laboratory understands what is involved and agrees to carry out its responsibilities with diligence.

9.5 The ILS should not be restricted to a group of laboratories judged to be exceptionally qualified and equipped for the ILS. Precision estimates for inclusion in a test method should be obtained through the efforts of qualified laboratories and personnel operating under conditions that will prevail when the test method is used in practice.

10. Materials

10.1 Material designates anything with a property that can be measured. Different materials having the same property may be expected to have different property levels, meaning higher or lower values of the property. Different dilutions of the same material or compound to be assayed are considered "different materials" for the purpose of this practice. The terminology "different levels of material" may be used, if appropriate.

10.2 The number and type of materials to be included in an ILS will depend on the range of the levels in the class of materials to be tested and likely relation of precision to level over that range, the number of different types of materials to which the test method is to be applied, the difficulty and expense involved in obtaining, processing, and distributing samples, the difficulty of, length of time required for, and expense of performing the test, the commercial or legal need for obtaining a reliable and comprehensive estimate of precision, and the uncertainty of prior information on any of these points.

TABLE 8 Pentosans in Pulp-ILS Test Results

Laboratory	A	B	C	D	E	F	G	H	I
1	0.44	0.96	1.23	1.25	1.98	4.12	5.94	10.70	17.13
	0.49	0.92	1.88	1.25	1.92	4.16	5.37	10.74	16.56
	0.44	0.82	1.24	1.42	1.80	4.16	5.37	10.83	16.56
2	0.41	0.83	1.12	1.25	1.99	4.10	5.26	10.07	16.08
	0.41	0.83	1.12	1.25	1.94	4.11	5.26	10.05	16.04
	0.41	0.84	1.12	1.26	1.95	4.10	5.26	9.82	16.13
3	0.51	0.92	1.11	1.35	2.05	4.11	5.16	10.01	16.01
	0.51	0.93	1.13	1.35	2.08	4.16	5.16	10.17	15.96
	0.51	0.92	1.11	1.35	2.03	4.16	5.21	10.17	16.06
4	0.40	0.96	1.15	1.29	2.05	4.20	5.20	10.98	16.65
	0.38	0.94	1.13	1.29	2.04	4.20	5.20	10.67	16.91
	0.37	0.94	1.13	1.29	2.04	4.22	5.20	10.52	16.75
5	0.49	0.82	0.98	1.23	1.94	4.61	5.00	10.48	15.71
	0.49	0.82	0.98	1.23	1.96	4.63	5.00	10.27	15.45
	0.49	0.84	0.98	1.23	1.96	4.53	4.96	10.38	15.66
6	0.43	0.88	1.11	1.31	2.01	3.93	4.85	9.57	15.05
	0.41	0.92	1.12	1.30	1.99	3.92	4.87	9.57	14.73
	0.40	0.88	1.11	1.31	1.98	3.84	4.91	9.62	15.04
7	0.186	0.866	1.05	1.13	1.98	4.21	5.27	11.5	18.8
	0.171	0.900	0.962	1.15	1.93	4.18	5.32	10.8	18.2
	0.153	0.831	0.927	1.15	1.98	4.16	5.10	11.5	18.1

10.2.1 For example, if it is already known that the precision is either relatively constant or proportional to the average level over the range of values of interest, a smaller number of materials will be needed than if it is merely known that the precision is different at different levels. The ruggedness test (see 8.2) and the preliminary pilot program (see Section 13) help to settle some of these questions, and may often result in the saving of considerable time and expense in the full ILS.

10.2.2 An ILS of a test method should include at least three materials representing different test levels, and for development of broadly applicable precision statements, six or more materials should be included in the study.

10.2.3 The materials involved in any one ILS should differ primarily only in the level of the property measured by the test method. When it is known, or suspected, that different classes of materials will exhibit different levels of precision when tested by the test method, consideration should be given to conducting separate interlaboratory studies for each class of material.

10.3 Each material in an ILS should be made to be or selected to be as homogeneous as possible prior to its subdivision into test units or test specimens (see 3.2.3). If the randomization and distribution of individual test specimens (rather than test units) does not conflict with the procedure for preparing the sample for test, as specified in the test method, greater homogeneity between test units can be achieved by randomizing test specimens. Then each test unit would be composed of the required number of randomized test specimens. (See Section 11 and 14.1 for the quantity of each material needed, its preparation and distribution.)

NOTE—It may be convenient to use established reference materials, since their homogeneity has been demonstrated.

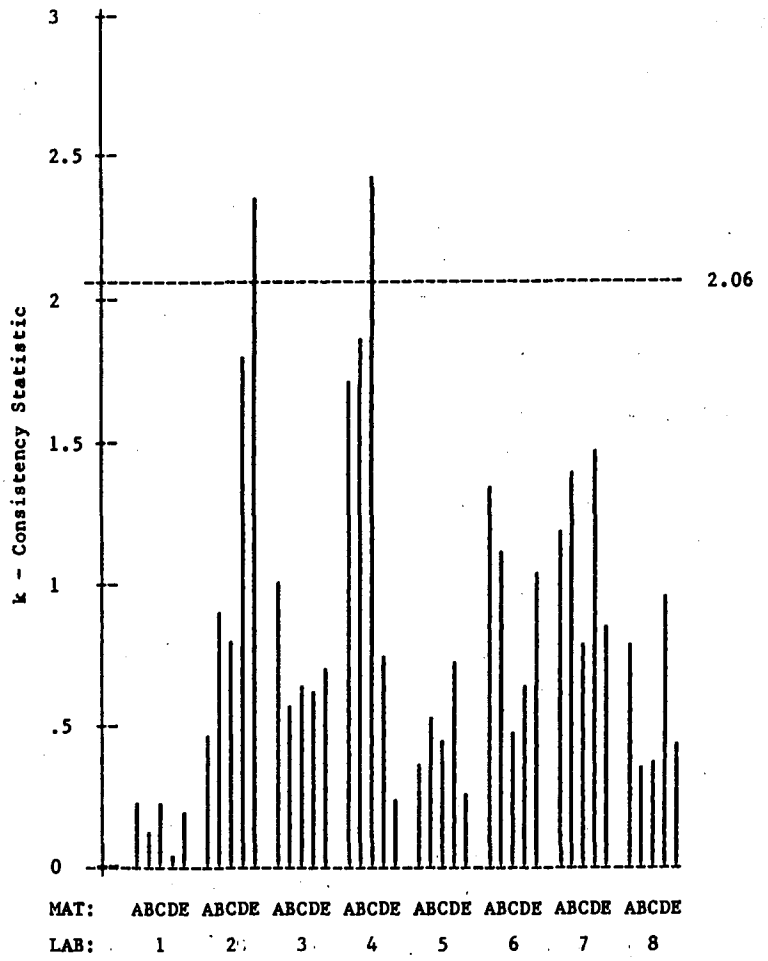

FIG. 3 Glucose in Serum: *k*—Materials within Laboratories

11. Number of Test Results per Material

11.1 In the design of an ILS a sufficient total number of test results on each material must be specified to obtain a good estimate of the measure of repeatability, generally the repeatability standard deviation. In many cases, the standard deviation in question will be a function of the property level being measured. When this occurs, the standard deviation should be determined separately for each level. It is generally sound to limit the number of test results on each material in each laboratory to a small number, such as three or four. The minimum number of test results per laboratory will normally be three for a chemical test and three or four for a physical or optical test. The number may be as small as two when there is little danger that a test unit will be lost or questionable test results obtained, or as many as ten when test results are apt to vary considerably. Generally, the time and effort invested in an ILS is better spent on examining more materials across more laboratories than on recording a large number of test results per material within a few laboratories.

12. Protocol

12.1 In the protocol, cite the name, address, and telephone number of the person who has been designated ILS coordinator (see 6.2). Urge the laboratories to call the coordinator when any questions arise as to the conduct of the ILS.

12.2 Clearly identify the specific version of the test method being studied. If the test method allows several options in apparatus or procedure, the protocol should specify which option or options have been selected for the

TABLE 9 Pentosans in Pulp-h[A]

Laboratory	Material								
	A	B	C	D	E	F	G	H	I
1	0.46	0.35	2.05	0.56	−1.51	−0.17	1.73	0.63	0.36
2	0.05	−1.14	−0.05	−0.23	−0.39	−0.38	0.35	−0.75	−0.25
3	0.93	0.88	−0.07	1.21	1.35	−0.18	−0.04	−0.50	−0.32
4	−0.19	1.40	0.05	0.32	1.16	0.12	0.07	0.57	0.38
5	0.75	−1.28	−0.94	−0.57	−0.51	1.97	−0.91	−0.04	−0.69
6	0.08	0.21	−0.09	0.56	0.23	−1.37	−1.42	−1.45	−1.30
7	−2.08	−0.41	−0.94	−1.85	−0.33	0.01	0.21	1.54	1.84

[A] Critical value = 2.05.

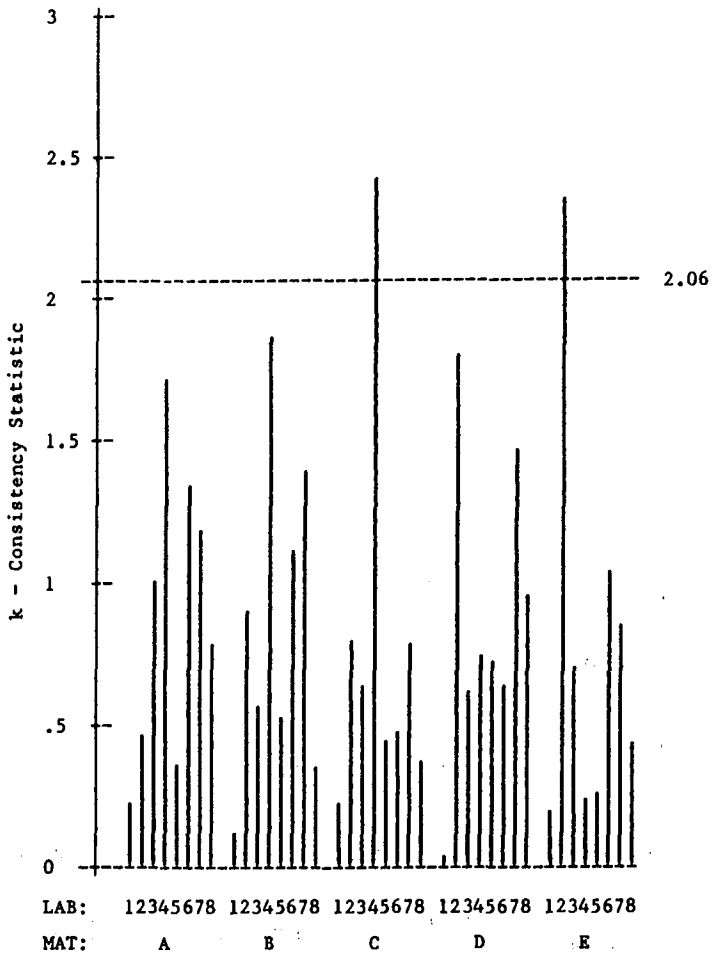

FIG. 4 Glucose in Serum: *k*—Laboratories within Materials

ILS. Test units and test data sheets must be provided for each option.

12.3 When special calibration procedures are required before every determination or every test result, they should be described specifically in the test method. If the test method specifies calibration only daily or less frequently, the ILS task group must decide whether to require recalibration before obtaining each test result. While doing so will eliminate calibration drift and help ensure relative independence of the test results, changes in calibration may increase the variability between test results.

12.4 Describe any special circumstances that must be addressed in implementing the repeatability conditions, such as the period of time between obtaining the test results for the same material; that is, not less than in normal testing and not so long as to likely permit significant changes in test material, equipment or environment.

12.5 Specify the required care, handling, and conditioning of the *materials* to be tested. Explain the coding system used in identifying the materials and the distinction between test units and test specimens, where appropriate.

12.6 Supply data sheets for each material for recording the raw data as observations are made. Give instructions on the number of significant digits to be recorded, usually one more, if possible, than required by the test method. Also, supply test result sheets on which test results can be calculated and reported. In many instances this can be combined with the raw data sheet. Specify the number of significant digits to be reported, usually two more than required by the test method. Request the laboratories send raw data and test result sheets as soon as the testing is completed, and at least weekly if testing will continue over several weeks.

12.7 Request that each laboratory keep a record (or log) of any special events that arise during any phase of the testing. This record, to be sent to the ILS coordinator, will provide a valuable source of information both in dealing with unusual data and in making improvements in the test method in future revisions.

TABLE 10 Pentosans in Pulp-*k*[A]

Laboratory	Material								
	A	B	C	D	E	F	G	H	I
1	1.93	2.24	2.61	2.62	2.32	0.71	2.47	0.34	1.53
2	0.00	0.18	0.00	0.15	0.67	0.18	0.00	0.72	0.21
3	0.00	0.18	0.08	0.00	0.64	0.89	0.22	0.48	0.23
4	1.02	0.36	0.08	0.00	0.15	0.36	0.00	1.21	0.61
5	0.00	0.36	0.00	0.00	0.29	1.63	0.17	0.54	0.64
6	1.02	0.72	0.04	0.15	0.39	1.52	0.23	0.15	0.84
7	1.10	1.07	0.44	0.31	0.73	0.77	0.87	2.09	1.76

[A] Critical value = 2.03.

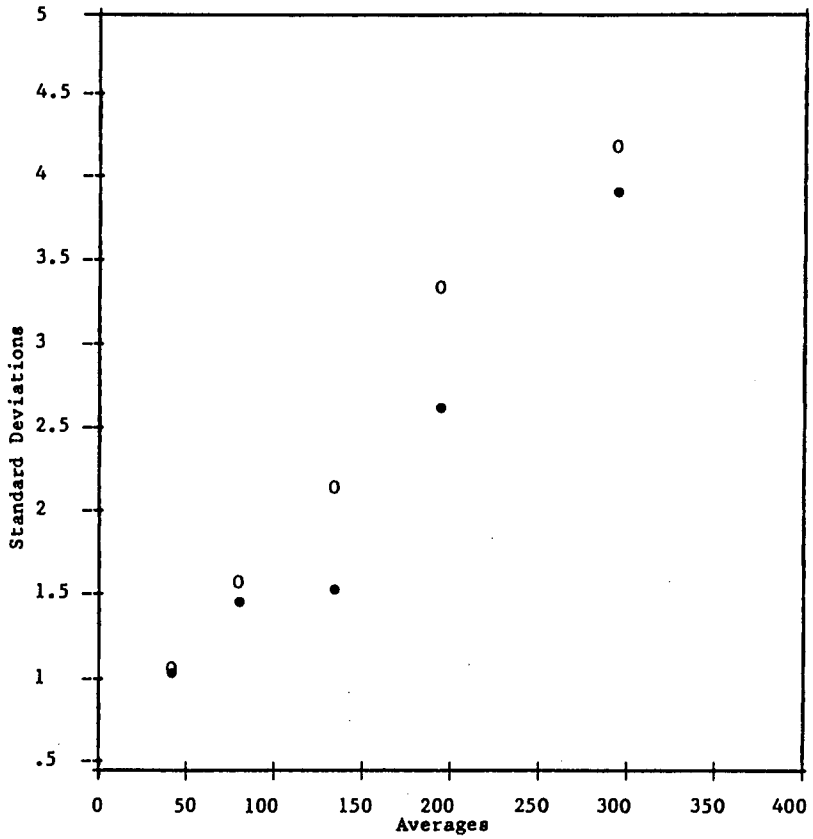

FIG. 5 Glucose in Serum: Standard Deviations of Reproducibility (O) and Repeatability (●) Versus Average

12.7.1 Instruct the laboratories to notify the ILS coordinator promptly whenever an error in test procedure arises, so that a decision can be made as to whether a new set of test units should be sent to the laboratory for a complete retest of the material.

12.8 Enclose with the protocol a questionnaire requesting information on specific aspects of the apparatus, reagents, calibration, or procedure, as well as any other information that might assist in dealing with data inconsistencies, or ensure the task group that the laboratory complied with the current requirements of the test method. Also obtain any other information that may be needed in preparing the final research report on the ILS (see Footnote 3).

CONDUCTING THE TESTING PHASE OF THE ILS

13. Pilot Run

13.1 Before investing laboratory time in the full scale ILS, it is usually wise to conduct a pilot run with only one, or perhaps two, material(s) to determine whether the test method as well as the protocol and all the ILS procedures are clear, and to serve as a familiarization procedure for those without sufficient experience with the method (see 9.3). The results of this pilot run also give the task group an indication of how well each laboratory will perform in terms of promptness and following the protocol. Laboratories with poor performance should be encouraged and helped to take corrective action.

13.2 All steps of the procedures described in this practice should be followed in detail to ensure that these directions are understood, and to disclose any weaknesses in the protocol or the test method.

TABLE 11 Pentosans in Pulp—Precision Statistics

Material	$\bar{X}$	s_R	s_r	s_R	r	R
A	0.4048	0.1131	0.0150	0.1137	0.04	0.32
B	0.8841	0.0447	0.0322	0.0519	0.09	0.14
C	1.1281	0.1571	0.1429	0.1957	0.40	0.55
D	1.2686	0.0676	0.0375	0.0742	0.11	0.21
E	1.9809	0.0538	0.0396	0.0628	0.11	0.18
F	4.1814	0.2071	0.0325	0.2088	0.09	0.58
G	5.1843	0.2172	0.1330	0.2428	0.37	0.68
H	10.4010	0.5630	0.1936	0.5848	0.54	1.64
I	16.3610	1.0901	0.2156	1.1042	0.60	3.09

14. Full Scale Run

14.1 *Material Preparation and Distribution:*

14.1.1 *Sample Preparation and Labelling*—Prepare enough of each material to supply 50 % more than needed by the number of laboratories committed to the ILS. Label each test unit or test specimen with a letter for the material and a sequential number. Thus, for ten laboratories and two test results for each laboratory the test units for material B would be numbered from B1 to B30, or, if five test specimens per test unit are required, the test specimens may be numbered B1 to B150.

14.1.2 *Randomization*—For each material independently, allocate the specified number of test units or test specimens to each laboratory, using a random number table, or a suitable computerized randomization based on random numbers. See Ref. (4) for a discussion of randomization.

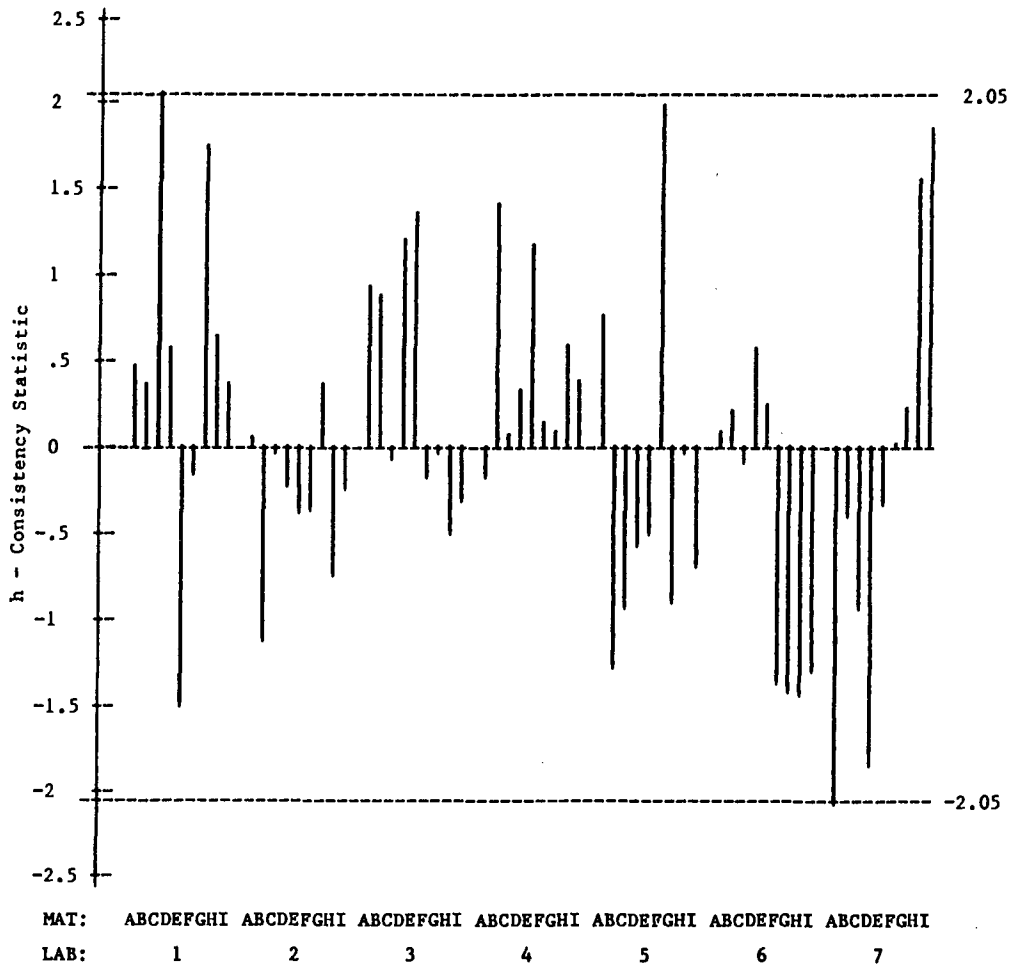

FIG. 6 Pentosans in Pulp: *h*—Materials within Laboratories

14.1.3 *Shipping*—Ensure that the test units are packaged properly to arrive in the desired condition. When the material is sensitive to the conditions to which it is exposed (light, heat, humidity, etc), place special directions for opening the package on a label outside the package. Clearly indicate the name of the person who has been designated as ILS supervisor at the laboratory on the address of each package. Follow each laboratory's instructions for ensuring prompt delivery of the package.

14.1.4 *Follow-up*—Once the test units have been shipped, the ILS coordinator should call each laboratory ILS supervisor within a week to ten days to confirm that all test units have arrived safely. If the task group has decided to intermingle test units from different materials in the order of testing, the testing should not start until all the test units have arrived at the laboratory so they can be tested in the specified order.

14.1.5 *Replacement Sets of Test Units*—As the ILS progresses, a laboratory may discover that the test method was not used properly on some test units. The laboratory ILS supervisor should discuss this with the ILS coordinator, who may send a replacement set of test units, replace the misused test units, or do nothing, as may seem desirable.

14.2 *Checking Progress*—From time to time, at intervals appropriate to the magnitude of the ILS, the coordinator should call each ILS supervisor to ascertain how the testing is progressing. By comparing the progress of all laboratories, the coordinator can determine whether some laboratories are lagging considerably behind the others and so advise these laboratories.

14.3 *Data Inspection*—The completed data sheets should be examined by the coordinator immediately upon receipt in order to detect unusual values or other deficiencies that should be questioned. Replacement sets of test units or of specific test units may be sent when there is missing or obviously erroneous data. The task group can decide later whether or not the additional data should be used in the estimation of the precision of the test method.

CALCULATION AND DISPLAY OF STATISTICS

15. Calculation of the Statistics

15.1 *Overview*—The analysis and treatment of the ILS test results have three purposes, to determine whether the collected data are adequately consistent to form the basis for a test method precision statement, to investigate and act on any data considered to be inconsistent, and to obtain the precision statistics on which the precision statement can be based. The statistical analysis of the data for estimates of the precision statistics is simply a one-way analysis of variance (within- and between-laboratories) carried out separately for each level (material). Since such an analysis can be invali-

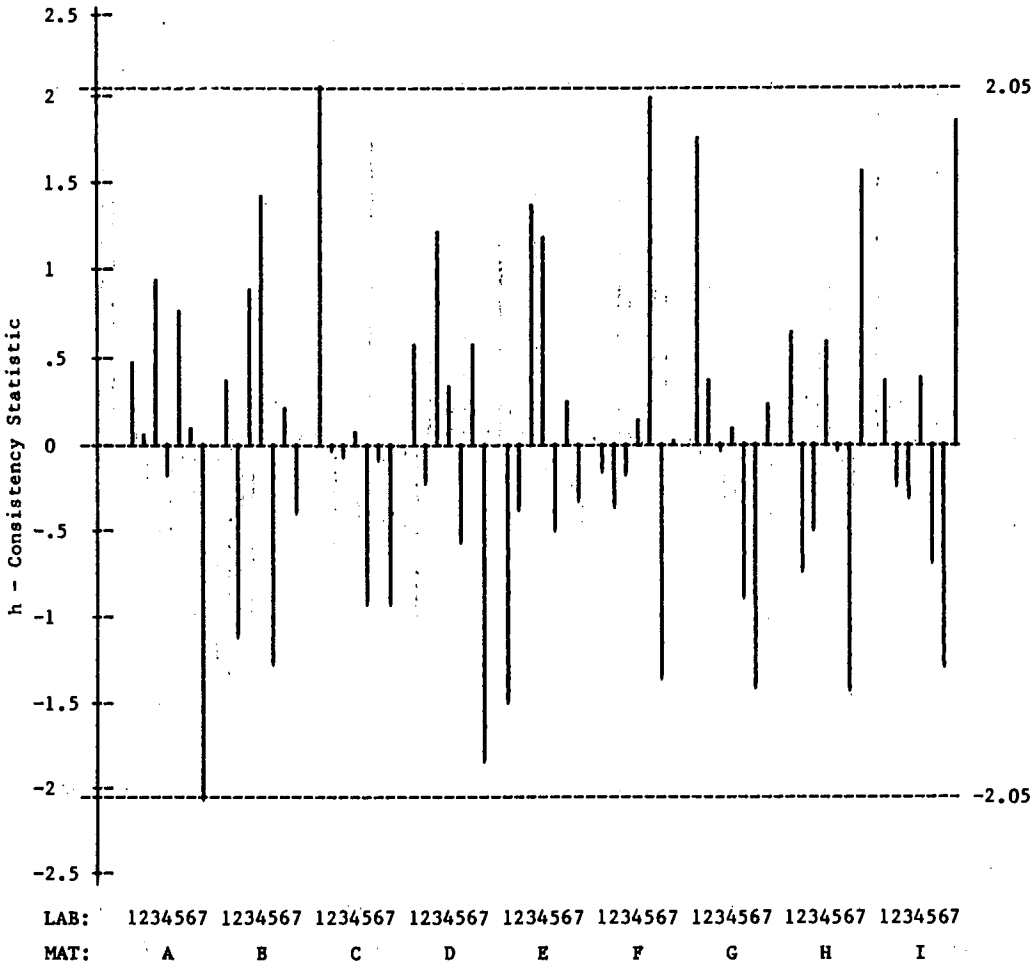

FIG. 7 Pentosans in Pulp: *h*—Laboratories within Materials

dated by the presence of severe outliers, it is necessary to first examine the consistency of the data. The following paragraphs show, in terms of a numerical example, how the entire program is carried out:

15.1.1 The calculations are illustrated with test results from an ILS in which the concentration of glucose in serum (see Table 1) was measured at five different concentration levels by eight laboratories. Each laboratory obtained three test results at each concentration level.

15.1.2 For extended calculations it is usually necessary to retain extra significant digits in order to ensure that statistically important information is not lost in calculation by rounding off too soon. As a general rule, retain at least two more digits in the averages than in the reported test results and at least three significant figures in the standard deviations.

15.1.3 While the calculations described in this section are arranged for use of a hand calculator, they also can be readily programmed for the computer. If necessary, contact Committee E-11 for advice on computational matters, (see 15.4.2).

15.2 *Table of ILS Test Results*—The test results received from the laboratories are usually best arranged in rows and columns as in Table 1. Each column contains the data obtained from all laboratories for one material, and each row contains the data from one laboratory for all materials. The test results from one laboratory on one material constitute a cell. Thus, the cell for Laboratory 2 and Material C contains the test results 132.92, 136.90 and 136.40. This cell is called C2, by material and laboratory. It helps in the interpretation of the data to arrange the materials in increasing order of the measured values.

15.3 *Worksheets*—Generally, it facilitates the calculations to prepare a separate calculation worksheet for each material, using Table 2 as a model but making appropriate changes for different numbers of laboratories, and test results per material. Enter the test result data for one material (from one column of Table 1) on a worksheet. Also enter the results of the following calculations for that material on the same worksheet, as illustrated in Table 2. Work on only one material at a time.

15.4 *Cell Statistics:*

15.4.1 *Cell Average, $\bar{x}$*—Calculate the cell average for each laboratory using the following equation:

$$\bar{x} = \sum_{1}^{n} x/n \qquad (1)$$

where:

$\bar{x}$ = the average of the test results in one cell,
x = the individual test results in one cell, and
n = the number of test results in one cell.

Thus from Table 2 for Material A, Laboratory 1 (that is, for Cell A1):

$$\bar{x} = (41.03 + 41.45 + 41.37)/3 = 41.2833.$$

15.4.2 *Cell Standard Deviation, s*—Calculate the standard deviation of the test results in each cell using the following equation:

$$s = \sqrt{\sum_{1}^{n} (x - \bar{x})^2/(n - 1)} \quad (2)$$

The symbols have the same meaning as for Eq 1. Thus for Cell A1:

$$s = \sqrt{(41.03 - 41.2833)^2 + (41.45 - 41.2833)^2 + (41.37 - 41.2833)^2]/(3 - 1)}$$
$$= 0.2230$$

While Eq 2 shows the underlying calculation of the cell standard deviation, inexpensive pocket calculators are available that calculate both the average and the standard deviation directly. Check to be sure the calculator uses $(n - 1)$ as the divisor in Eq 2, not n, and has adequate precision of calculation.

15.5 *Intermediate Statistics:*

15.5.1 *Average of the Cell Averages, $\bar{x}$*—Calculate the average of all the cell averages for the one material using Eq 3.

$$\bar{\bar{x}} = \sum_{1}^{p} \bar{x}/p \quad (3)$$

where:
$\bar{\bar{x}}$ = the average of the cell averages for one material,
$\bar{x}$ = the individual cell averages, and
p = the number of laboratories in the ILS.
Thus for material A:

$$\bar{\bar{x}} = (41.2833 + 41.4400 + 41.4500 + 41.4567 + 41.4633 + 42.0200 + 40.4567 + 42.5767)/8$$
$$= 41.5183$$

15.5.2 *Cell Deviation, d*—For each laboratory calculate the cell deviation by subtracting the cell average from the average of the cell averages using the following equation:

$$d = \bar{x} - \bar{\bar{x}} \quad (4)$$

Thus for cell A1:

$$d = 41.2833 - 41.5183 = -0.2350$$

15.5.3 *Standard Deviation of the Cell Averages, $s_{\bar{x}}$*—Calculate this statistic using the following equation:

$$s_{\bar{x}} = \sqrt{\sum_{1}^{p} d^2/(p - 1)} \quad (5)$$

Thus for material A:

$$s_{\bar{x}} = \sqrt{[(-0.2350)^2 + (-0.0783)^2 + (-0.0683)^2 + (-0.0616)^2 + (-0.0550)^2 + (0.5017)^2 + (-1.0616)^2 + (1.0584)^2]/(8 - 1)}$$
$$= 0.6061$$

15.6 *Precision Statistics*—While there are other precision statistics, introduced later in this practice, the fundamental precision statistics of the ILS are the repeatability standard deviation and the reproducibility standard deviation. The other statistics are calculated from these standard deviations.

15.6.1 *Repeatability Standard Deviation, s_r*—Calculate this statistic using the following equation:

$$s_r = \sqrt{\sum_{1}^{p} s^2/p} \quad (6)$$

where:
s_r = the repeatability standard deviation,
s = the cell standard deviation (p of them from Eq 2), and
p = the number of laboratories.
Thus for material A:

$$s_r = \sqrt{[(0.2230)^2 + (0.4851)^2 + (1.0608)^2 + (1.8118)^2 + (0.3667)^2 + (1.4081)^2 + (1.2478)^2 + (0.8225)^2]/8}$$
$$= 1.0632$$

15.6.2 *Reproducibility Standard Deviation, s_R*—Calculate a provisional value of this statistic using the following equation:

$$(s_R)^* = \sqrt{(s_{\bar{x}})^2 + (s_r)^2 (n - 1)/n} \quad (7)$$

where: $s_{\bar{x}}$ and s_r are obtained from Eqs 5 and 6. The symbol, * indicates provisional value, (for more information see A1.1.2).
Thus for Material A:

$$(s_R)^* = \sqrt{(0.6061)^2 + (1.0632)^2 (3 - 1)/3} = 1.0588$$

Enter the larger of the values obtained by the use of Eqs 6 and 7 as the final value of s_R to be used for precision statements. In this case, Eq 6 yields the larger value. Therefore, $s_R = 1.0632$.

15.7 *Consistency Statistics, h and k:*

15.7.1 For each cell, calculate a value of h using the following equation:

$$h = d/s_{\bar{x}} \quad (8)$$

where:
h = the between-laboratory consistency statistic,
d = the cell deviation (i.e., the deviation of the cell average from the average of the cell averages, from 15.5.2), and
$s_{\bar{x}}$ = the standard deviation of the cell averages (from 15.5.3).
Thus for Cell A1:

$$h = -0.2350/0.6061 = -0.39$$

Retain two decimal places in the computed values of h.

15.7.2 For each cell, use the following equation to calculate a value of k.

$$k = s/s_r \quad (9)$$

where:
k = the within-laboratory consistency statistic,
s = the cell standard deviation for one laboratory (from 15.4.2), and
s_r = the repeatability standard deviation of the material (from 15.6.1).
Thus for Cell A1:

$$k = 0.2230/1.0632 = 0.21$$

Retain two decimal places in the computed values of k.

15.8 *Other Materials*—Repeat the steps described in 15.4 through 15.7 for each material, entering the calculation results on separate worksheets.

TABLE 12 Critical Values of h and k at the 0.5 % Significance Level[A]

Critical value of h	p	Critical values of k Number of replicates, n								
		2	3	4	5	6	7	8	9	10
1.15	3	1.72	1.67	1.61	1.56	1.52	1.49	1.47	1.44	1.42
1.49	4	1.95	1.82	1.73	1.66	1.60	1.56	1.53	1.50	1.47
1.74	5	2.11	1.92	1.79	1.71	1.65	1.60	1.56	1.53	1.50
1.92	6	2.22	1.98	1.84	1.75	1.68	1.63	1.59	1.55	1.52
2.05	7	2.30	2.03	1.87	1.77	1.70	1.65	1.60	1.57	1.54
2.15	8	2.36	2.06	1.90	1.79	1.72	1.66	1.62	1.58	1.55
2.23	9	2.41	2.09	1.92	1.81	1.73	1.67	1.62	1.59	1.56
2.29	10	2.45	2.11	1.93	1.82	1.74	1.68	1.63	1.59	1.56
2.34	11	2.49	2.13	1.94	1.83	1.75	1.69	1.64	1.60	1.57
2.38	12	2.51	2.14	1.96	1.84	1.76	1.69	1.64	1.60	1.57
2.41	13	2.54	2.15	1.96	1.84	1.76	1.70	1.65	1.61	1.58
2.44	14	2.56	2.16	1.97	1.85	1.77	1.70	1.65	1.61	1.58
2.47	15	2.57	2.17	1.98	1.86	1.77	1.71	1.66	1.62	1.58
2.49	16	2.59	2.18	1.98	1.86	1.77	1.71	1.66	1.62	1.58
2.51	17	2.60	2.19	1.99	1.86	1.78	1.71	1.66	1.62	1.59
2.53	18	2.61	2.20	1.99	1.87	1.78	1.72	1.66	1.62	1.59
2.54	19	2.62	2.20	2.00	1.87	1.78	1.72	1.67	1.62	1.59
2.56	20	2.63	2.21	2.00	1.87	1.79	1.72	1.67	1.63	1.59
2.57	21	2.64	2.21	2.00	1.88	1.79	1.72	1.67	1.63	1.59
2.58	22	2.65	2.21	2.01	1.88	1.79	1.72	1.67	1.63	1.59
2.59	23	2.66	2.22	2.01	1.88	1.79	1.72	1.67	1.63	1.59
2.60	24	2.66	2.22	2.01	1.88	1.79	1.73	1.67	1.63	1.60
2.61	25	2.67	2.23	2.01	1.88	1.79	1.73	1.67	1.63	1.60
2.62	26	2.67	2.23	2.02	1.89	1.80	1.73	1.68	1.63	1.60
2.62	27	2.68	2.23	2.02	1.89	1.80	1.73	1.68	1.63	1.60
2.63	28	2.68	2.23	2.02	1.89	1.80	1.73	1.68	1.63	1.60
2.64	29	2.69	2.24	2.02	1.89	1.80	1.73	1.68	1.64	1.60
2.64	30	2.69	2.24	2.02	1.89	1.80	1.73	1.68	1.64	1.60

[A] The above critical values for the h and k consistency statistics were calculated from Student's t and the F-ratio using the following relationships:

$h = (p-1)\,t\sqrt{p(t^2+p-2)}$ t with $p-2$ degrees of freedom, and

$k = \sqrt{p/[1+(p-1)/F]}$ F with $n-1$ and $(p-1)(n-1)$ degrees of freedom.

where p = number of laboratories. See Annex A1.2 for derivations of these relationships.

16. Tabular and Graphical Display of Statistics

16.1 *Material Order*—It is often useful to arrange the worksheets in order of increasing values of $\bar{x}$, the material averages. This order may facilitate interpretation.

16.2 *Tables*—From the Table 2 results for each material, prepare tables of h and k as shown in Tables 3 and 4 for the glucose in serum example.

16.3 *Graphs*—Prepare bar graphs for h and k in two ways: materials grouped by laboratory as in Figs. 1 and 3, and laboratories grouped by material as shown in Figs. 2 and 4. Arrange the laboratories and materials within and between each grouping in the same order as used in Table 1. Thus the materials will be arranged in order of increasing $\bar{x}$ from left to right, and the laboratories in order of laboratory code number.

DATA CONSISTENCY

17. Flagging Inconsistent Results

17.1 *Critical Values of the Consistency Statistics*—Table 12 lists critical values of the h and k consistency statistics at the 0.5 % significance level. The critical values for h (first column) depend on the number of laboratories (p, second column) participating in the ILS and the critical values for k (columns headed 2 through 10) depend both on the number of laboratories (p) and on the number of replicate test results (n) per laboratory per material. The 0.5 % level was chosen based on the judgment and experience that the 1.0 % resulted in too many cells being flagged and the 0.1 % level in too few. For further discussion see Annex A1.

17.1.1 Obtain from Table 12 the appropriate critical values. For the glucose in serum example, the respective critical h and k values are 2.15 and 2.06. In Tables 3 and 4 circle those values that exceed the critical values and underline those values that approach the critical values. On each graph draw a horizontal line for each critical value: two for h, since there are both positive and negative values of h, and one for k, as shown in Figs. 1 to 4.

17.1.2 The h and k graphs and the marked tables give a picture of the overall character of the variability of the test method as well as singling out particular laboratories or cells that should be investigated.

17.2 *Plots by Laboratory*—In order to evaluate the differences between laboratories, use the following guidelines.

17.2.1 *h Graph*—There are three general patterns in these plots. In one, all laboratories have both positive and negative h values among the materials. In the second, the individual laboratories tend to be either positive or negative for all materials and the number of negative laboratories equals the number of positive laboratories, more or less. Neither of these patterns is unusual or requires investigation, although they may tell something about the nature of the test method variability. In the third pattern, one laboratory, with all h values positive (or negative), is opposed to all the other laboratories, with substantially all the h values negative (or positive). Such a pattern calls for an investigation of that laboratory.

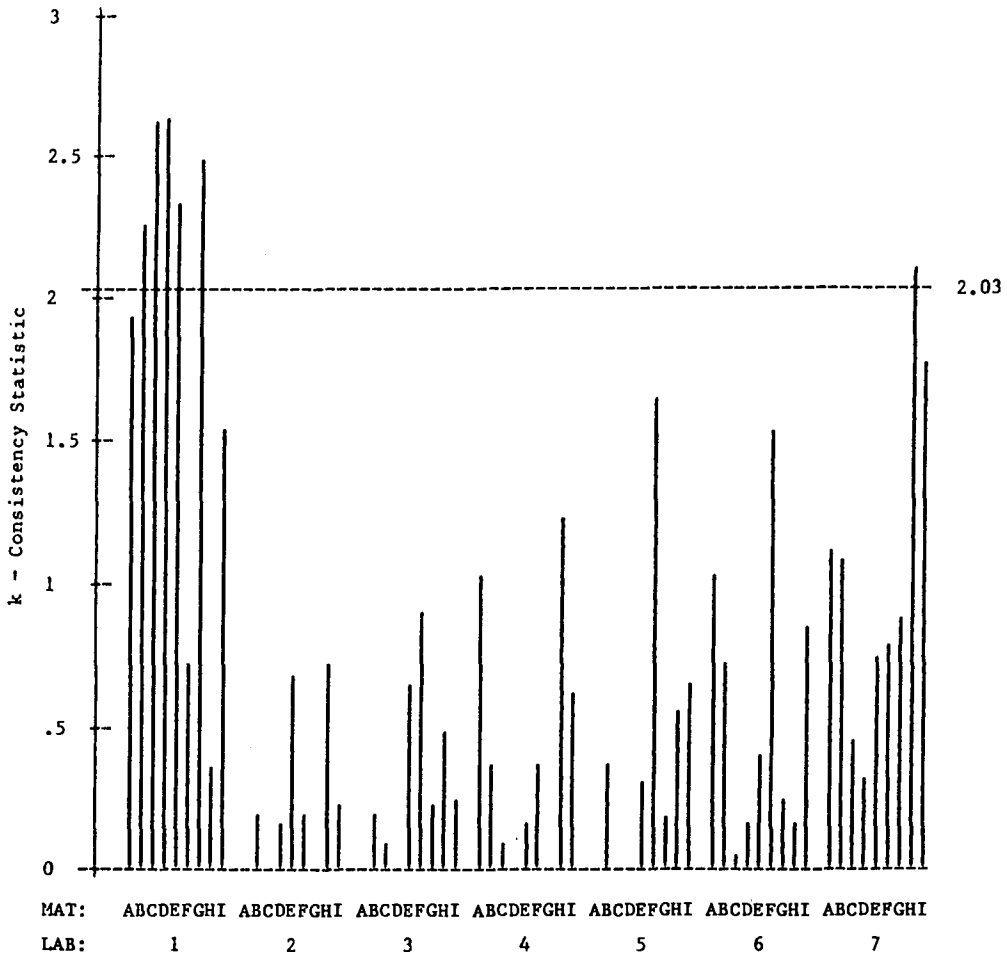

FIG. 8 Pentosans in Pulp: *k*—Materials within Laboratories

17.2.1.1 Another kind of pattern to look for occurs within one laboratory, in which the h values for low property levels are of one sign, and for high property levels are of the opposite sign. If the values are extreme, this behavior should be investigated.

17.2.2 *k Graph*—Here the primary pattern to look for is that of one laboratory having large k values (or very small k values) for all or most of the materials. High k values represent within-laboratory imprecision. Very small k values may indicate a very insensitive measurement scale or other measurement problem.

17.3 *Plots by Material*—When a plot by laboratory shows several h or k values near the critical value line, look at the corresponding plot by material to see how that laboratory differs from the rest for a given material. Often a vertical line that seems strong in the plot by laboratory, because of its relation to the lines for the other materials, will turn out to be reasonably consistent with the other laboratories for the same material. Contrarywise, the h or k value for the one laboratory may be revealed as strongly different from the values for the other laboratories in the plot by material. If so, this behavior should be investigated.

18. Investigation

18.1 *Clerical and Sampling Errors*—Examine the laboratory report for each flagged cell. Try to locate where each test result in the flagged cell begins to deviate from the others. Is it in the original observations? Are the data rounded prematurely? Are the calculations correct? Then, look for signs of mislabeling of test units such that the test result for one material was reported as belonging to another material. Check these errors with the laboratories: do not assume them to be so.

18.2 *Procedural Errors:*

18.2.1 Study the laboratory reports again looking for deviations from either the test method or the protocol. For instance, variations in the number of significant digits reported in the test results may be a sign of incorrect rounding, or that the equipment in one laboratory is different from the rest. Also, study the event log for special comments relating to the flagged cells.

19. Task Group Actions

19.1 *General*—If the investigation disclosed no clerical, sampling or procedural errors, the unusual data should be retained, and the precision statistics based on them should be published. If, on the other hand, a cause was found during the investigation, the task group has several options to consider. If the laboratory clearly and seriously deviated from the test method, the test results for that laboratory must be removed from the ILS calculations. However, despite the danger of the recalcitrant laboratory having prior knowledge,

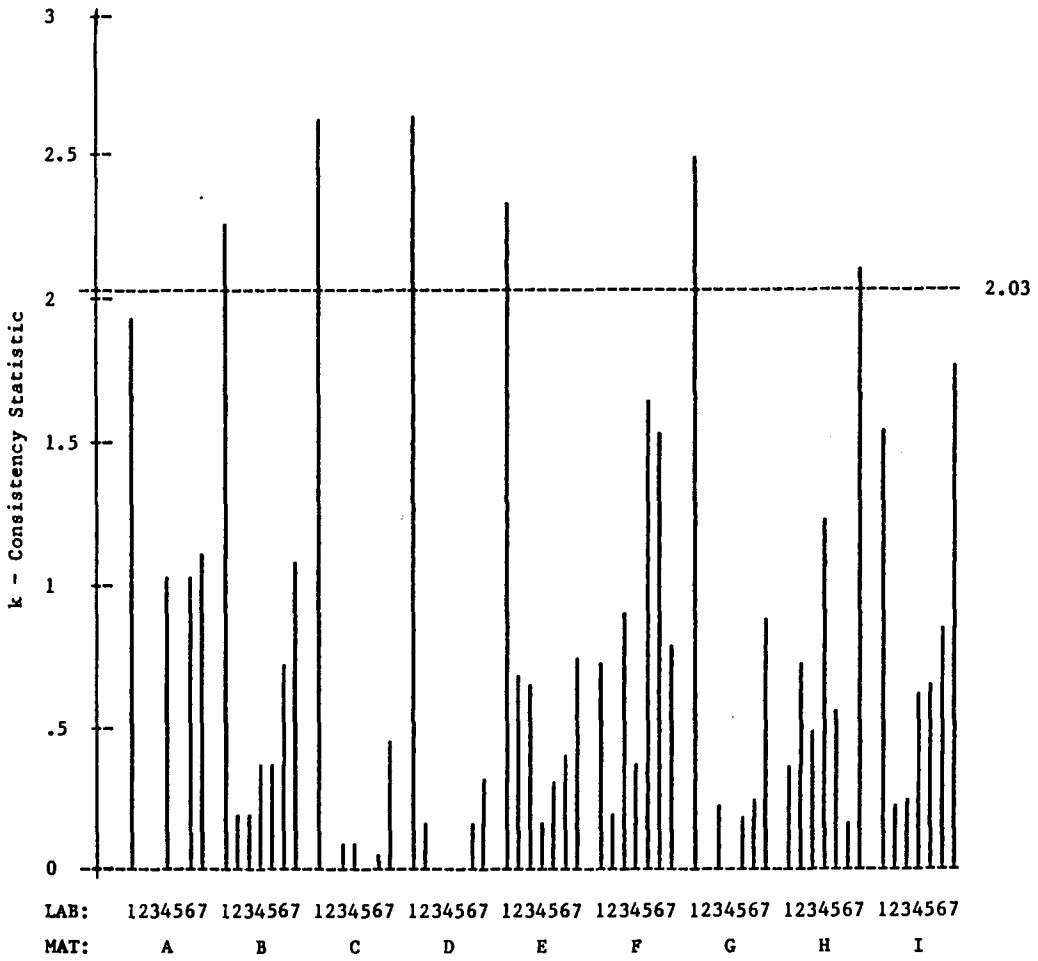

FIG. 9 Pentosans in Pulp: *k*—Laboratories within Materials

it may be appropriate to ask the laboratory to retest one or more materials following the correct procedure, and then include the new set of test results in the ILS calculations. Of course, if the data have changed, recalculation of the *h* and *k* values must be made and the data consistency examined again.

19.2 *Exception*—When a large number of laboratories have participated in the ILS and no cause for some unusual cell values have been found during the investigation, it may be appropriate to delete a cell from the study if all of the other laboratories are in substantial agreement. The number of laboratories that can be considered large enough to support deletion of data without an identified cause cannot be stated exactly. Any action which results in discarding more than five percent of the ILS data likely will lead to the presentation of precision data that the test method cannot deliver in routine application.

19.3 *Test Method Vagueness*—One of the important things to be on the alert for during a laboratory investigation is for vagueness in the test method standard that permits a wide range of interpretation leading to loss of precision. Particular elements to check are lack of measurement tolerances, diversity of apparatus and insufficient direction for operator technique. These problems can be the basis for a revision of the standard.

20. Examples of Interlaboratory Studies

20.1 *Glucose in Serum*—The ILS is described in 15.1.1.

20.1.1 *h Statistic*—The overall impression given by Figs. 1 and 2 and Table 3 is one of reasonable consistency for variation among laboratories. Only Laboratory 4 stands out with large values for Materials B and C. The graph for Material C, in Fig. 2, shows that Laboratory 4 is distinctly different from the other laboratories. The graph for Material B, however, does not single out Laboratory 4.

20.1.2 *k Statistic*—Laboratories 2 and 4 stand out in Fig. 3 and Table 4. The laboratory plot, in Fig. 3, indicates Laboratory 4 has three high values, but a look at the material plots (Fig. 4) for *A* and *B* suggests that Laboratory 4 is not out of line for these two materials. On the other hand, the plot for Material C shows Laboratory 4 is different. Similarly, the plot for Material E shows Laboratory 2 is different for this material.

20.1.3 *Cells and Test Results*—Cells C4 and E2 should be investigated. A look at Table 1 reveals that the second test results of 148.30 in C4 and of 309.40 in E2 are the particular values to be investigated.

20.1.4 *Action*—If the data from Laboratory 4 were typed, the result 148.30 in Cell C4 could have been a typographical error. We have no way of knowing this today, many years after this study was made. We will suppose, however, that the task group did indeed call the laboratory and did find that

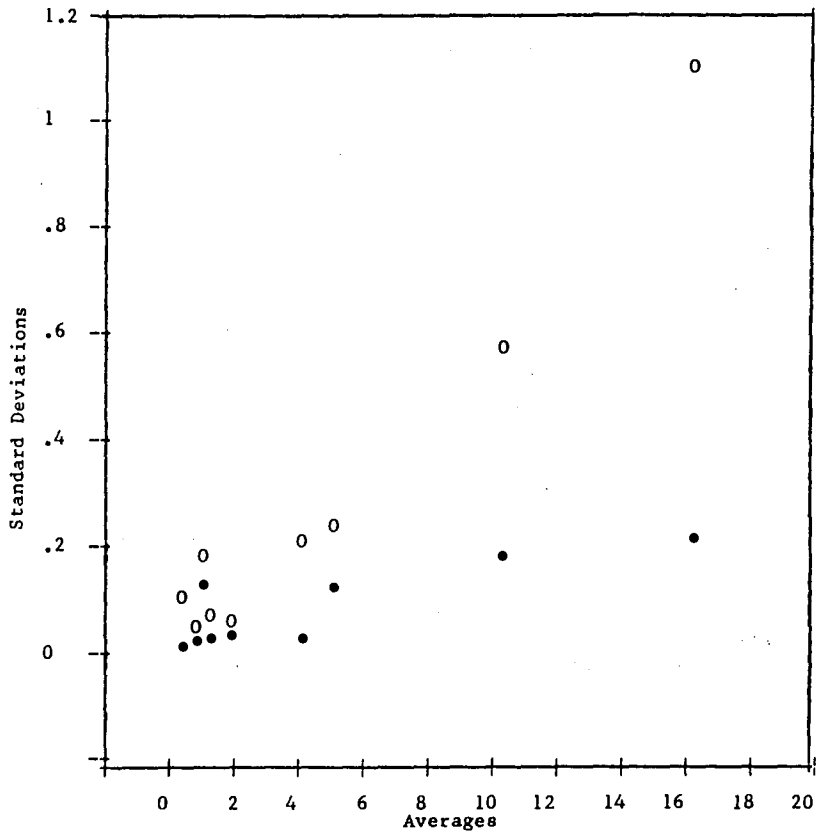

FIG. 10 Pentosans in Pulp: Standard Deviations of Reproducibility (O) and Repeatability (●) Versus Average

the number should have been 138.30. However, let us suppose that for Cell E2 the task group could find no explanation of the apparently high value of 309.40. In such a case they should retain the value.

20.1.5 *Recalculation*—Tables 5 and 6 show the recalculated consistency statistics resulting from correcting Cell C4. The discussion of the glucose in serum data is continued in Section 21.

20.2 *Pentosans in Pulp*—Seven laboratories tested nine materials, obtaining three test results per material as shown in Table 8.

20.2.1 *h Statistic*—At first glance no one laboratory is singled out for attention by Fig. 6 or Table 9. For Material A Laboratory 7 is different and for Material C, Laboratory 1. On further inspection of the laboratory plot for Laboratory 7 we note the first five materials are negative and the last four positive. Keeping in mind that the first five materials are close together in property level while the last two are much higher in property level, one can see that Laboratory 7 has a different response to property level than the other laboratories. Laboratory 6 shows the reverse response, but not as strongly.

20.2.2 *k Statistic*—From Fig. 8 and Table 10, it is obvious that Laboratory 1 is different from the rest with five materials greatly exceeding, and one near, the critical value line. In addition, Laboratory 7 is different for Material H.

20.2.3 *Cells and Test Results*—Both Laboratories 1 and 7 should be investigated in depth. Examination of the cell data for Laboratory 1 in Table 8 suggests special attention should be given to test results 2 in A, 3 in B, 2 in C, 3 in D, 3 in E, and 1 in G, but there appears to be an overall problem in within-laboratory variability. On the other hand, Laboratory 7 has a different problem in not agreeing with the other laboratories at the two extremes of property level. For Material A the Laboratory 7 test results are less than half the values obtained by the other laboratories, while for Material I the test results are about 10 % higher than the rest. This variation with property level should be explored.

20.2.4 *Action*—Note that Laboratory 7 reported test results to three significant digits for all property levels while all the other laboratories reported to two decimal places. This difference in reporting would have been a good place to start the inquiry of this laboratory. It might be the indication of apparatus differences, or perhaps a sign that the laboratory may have disregarded other requirements of the test method or interlaboratory protocol. The apparently poor within-laboratory precision of Laboratory 1, if determined to be due to improper test equipment or poor maintenance of test environment might have required omitting this laboratory's data from the analysis, but with so few laboratories in the ILS and no physical evidence, the task group should retain this laboratory's data in the analysis.

PRECISION STATEMENT INFORMATION

21. Repeatability and Reproducibility

21.1 *General*—Once the task group has concluded which cells are sufficiently inconsistent to require action, and action has been taken, the statistics of 15.4 through 15.6 are recalculated (see also 20.1.5). Using the corrected statistics,

calculate for each material the 95 % repeatability and reproducibility limits (see Practice E 177) according to the following Eqs 10 and 11:

$$r = 2.8\ s_r \quad (10)$$

$$R = 2.8\ s_R \quad (11)$$

21.2 Prepare a table for the corrected precision statistics as shown in Tables 7 and 11.

21.3 *Variation of Precision Statistics with Property Level:*

21.3.1 Quite often the values of s_r and s_R will be found to vary with the values of the property level $\bar{x}$. This type of response is the case for both examples as can be seen in Figs. 5 and 10, that are based on Tables 7 and 11 respectively. The manner in which the statistics vary with the property level should be shown in presenting the precision information in the precision statement of the test method. The statistician should recommend the most appropriate relationship to present, using Practice E 177 as a guide.

21.4 *Precision Statement*—Table 7 or 11 (with the column for $s\bar{x}$ omitted) is a useful format for the presentation of the precision statement of the test method as required by Section A21 of the "Form and Style of ASTM Standards (Bluebook)". Having obtained the required precision information in accordance with this practice, the final form of the precision statement may be prepared in accordance with Practice E 177.

21.5 *Conclusion*—The precision statistics obtained by an ILS such as described in this practice must not be treated as exact mathematical quantities which are applicable to all circumstances and uses. The small number of laboratories and of materials included in the usual ILS guarantees that there will be times when differences greater than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95 % probability limit would imply. The repeatability limit and the reproducibility limit should be considered as general guides, and the associated probability of 95 % as only a rough indicator of what can be expected. If more precise information is needed in specific circumstances, those laboratories directly involved in a material comparison must conduct interlaboratory studies specifically aimed at the material of interest.[5]

[5] Following the ASTM Research Report format guide, prepare a research report on the ILS to be filed at ASTM Headquarters.

ANNEX

(Mandatory Information)

A1. THEORETICAL CONSIDERATIONS

A1.1 Underlying Assumptions of ILS

A1.1.1 *Within-Laboratory Variability*—The cell standard deviation is a measure of the within-laboratory variability of each individual laboratory. All laboratories are assumed to have essentially the same level of variability when following the specified repeatability conditions. This assumption is not always fulfilled. However, the shorter the period of time in which the test results for a particular material are to be obtained by the laboratories the more likely the validity of this assumption. Therefore, the laboratory cell variances can generally be pooled by averaging the squares of the cell standard deviations. The square root of this average within-laboratory variance is the repeatability standard deviation s_r.

A1.1.2 *Between-Laboratory Variability:*

A1.1.2.1 *Variability of Laboratory Means*—The test results obtained on a particular material at any particular laboratory are considered part of a population having a normal distribution with a standard deviation equal to the repeatability standard deviation but with a mean that may be different for each laboratory. The laboratory means are also assumed to vary according to a normal distribution, whose mean is estimated by the average of all ILS test results for a given material, and whose standard deviation is designated by s_L. (The effect of a single outlying laboratory on this assumption will be less if there are enough laboratories.) For the ILS calculations, s_L is estimated from the standard deviation of the cell averages, $s_{\bar{x}}$, and the repeatability standard deviation, s_r is as follows:

$$(s_{\bar{x}})^2 = (s_L)^2 + (s_r)^2/n \quad (A1.1)$$

Where $(s_r)^2$ is the pooled variance for the cell averages of one material, and n is the number of test results per cell. $(s_{\bar{x}})^2$ is the observed variance of the average of the cell averages. When $(s_L)^2$ calculates to less than zero, s_L is taken equal to zero.

A1.1.2.2 *Reproducibility Standard Deviation*—The variance among individual test results obtained in different laboratories is the sum of the within-laboratory variance and the between-laboratory variance of the laboratory means. Thus, the reproducibility variance is given by Eq A1.2 as follows:

$$(s_R)^2 = (s_r)^2 + (s_L)^2 \quad (A1.2)$$

Substituting Eq A1.1 into Eq A1.2 produces Eq A1.3:

$$(s_R)^2 = (s_r)^2 + (s_{\bar{x}})^2 - (s_r)^2/n \quad (A1.3)$$

Simplifying and taking the square root gives Eq A1.4 as follows (and Eq 7):

$$s_R = \sqrt{(s_{\bar{x}})^2 + (s_r)^2\,(n-1)/n} \quad (A1.4)$$

When s_R calculates to less than s_r, s_R is set equal to s_r.

A1.2 Consistency Statistics

A1.2.1 *Critical Values*—The derivation of the equations for calculating critical values of h and k are given in A1.2.2 and A1.2.3. In each case critical values were calculated at three significance levels, 1 %, 0.5 %, and 0.1 %. Of these three only the 0.5 % critical values were chosen for flagging as described in Section 17. This choice is based on the judgment from experience that the 1 % values are too

sensitive (flag too many) and the 0.1 % values are not sensitive enough for flagging adequately in the analysis of ILS data.

A1.2.2 *Between-Laboratory Consistency:*

A1.2.2.1 The consistency statistic h is an indicator of how one laboratory's cell average, for a particular material, compares with the average of the other laboratories. The critical values for the comparison are calculated with an equation derived from an unpaired t-test as given by Eq A1.5 as follows:

$$t = (\bar{x}_c - \bar{x}^*)/s_{\bar{x}}^* \sqrt{[1 + 1/(p-1)]} \quad \text{(A1.5)}$$

where:

t = observed Student's t value,
$\bar{x}_c$ = cell average being tested,
$\bar{x}^*$ = average of all cell averages except the one being tested,
$s_{\bar{x}}^*$ = standard deviation of all the cell averages except the one being tested, and
p = number of laboratories in the ILS.

In this relationship t has p-2 degrees of freedom. Three further equations are required in order to express h in terms of t from Eq A1.5. These follow as Eqs A1.6, A1.7, and A1.8:

$$\bar{x}^* = (p\bar{x} - \bar{x}_c)/(p-1) \quad \text{(A1.6)}$$

$$(s_{\bar{x}})^2 = (p-1)(s_{\bar{x}})^2/(p-2) - p(\bar{x} - \bar{x}_c)^2/[(p-1)(p-2)] \quad \text{(A1.7)}$$

$$h = d/s_{\bar{x}} = (\bar{x}_c - \bar{x})/s_{\bar{x}} \quad \text{(A1.8)}$$

Each of these equations is derived by simple algebraic operations from the definitions of symbols accompanying Eq A1.5 and Table 2. Combining them with Eq A1.5 results in Eq A1.9 as follows:

$$h = (p-1)t/\sqrt{p(t^2 + p - 2)} \quad \text{(A1.9)}$$

A1.2.2.2 The critical values of h were calculated by Eq A1.9 using published values of Student's t at the 0.5 % two-tailed significance levels (**6**). The values obtained are given in Table 12.

A1.2.3 *Within-Laboratory Consistency:*

A1.2.3.1 The consistency statistic, k, is an indicator of how one laboratory's within-laboratory variability, under repeatability conditions, on a particular material, compares with all of the laboratories combined. Values of k larger than 1 indicate greater within-laboratory variability than the average for all laboratories. Since such variation among laboratories is expected, critical values of k have been calculated to aid in the decision of whether the cell standard deviation of one laboratory is sufficiently different from the rest of the laboratories as to require investigation.

A1.2.3.2 A valid test for determining whether a particular cell variance is inconsistent relative to the variances of the other laboratories is to calculate the F-ratio of the one cell variance to the pooled variance of all the other laboratories—excluding the variance being tested. This is shown in Eq A1.10 as follows:

$$F = s^2/[(\sum_i (s_i)^2)/(p-1)] \quad \text{(A1.10)}$$

where:

s^2 = cell variance of cell being tested,
$\sum_i$ = summation of all other variances,
$(s_i)^2$ = cell variances other than the one being tested, and
p = the number of laboratories.

The consistency statistic k is defined by Eq A1.11 and the repeatability variance by Eq A1.12 as follows:

$$k = s/s_r \quad \text{(A1.11)}$$

$$(s_r)^2 = (\sum_i (s_i)^2 + s^2)/p \quad \text{(A1.12)}$$

Combining Eqs. A1.10, A1.11 and A1.12 results in Eq A1.13 as follows:

$$k = \sqrt{[p/(1 + (p-1)/F)]} \quad \text{(A1.13)}$$

A1.2.3.3 The degrees of freedom for F in Eq A1.10 are $n - 1$ and $(p-1)(n-1)$. The upper critical values of k are calculated from the upper critical values of F at the 0.5 % significance level for selected combinations of numbers of test results and laboratories. The values of k given in Table 12 were obtained using SAS's BETAINV (inverse beta function) and using IMSL's routine MDFI (for the F cdf inverse).

APPENDIX D

LABORATORY DATA SHEETS

Laboratory 1 Data Sheets

Standard Data Sheet
6/16/99

Standard	Vial Wt. (mg)	Vial+Water Wt (mg)	Vial+Water+2-BE Wt. (mg)	Water Wt. (mg)	2-BE St. (mg)	Wt. % of 2-BE
0.50%	2206	3189.9	3195.3	983.9	5.4	0.55
5%	2185	3124.7	3169.2	939.7	44.5	4.52
50%	2167.6	2663.5	3111	495.9	447.5	47.43
5% QCCS	2191.4	3133.3	3178.2	941.9	44.9	4.55

Calibration Data Sheet
6/16/99 10:22

Nominal std.	Coating+Liner Wt. (mg)	Liner Wt. (mg)	Mass std. (mg)	Std Wt. % of 2-BE	Corrected std. mass (mg)	FID response	RF	%RSD
0.50%	507.8	483.3	24.5	0.55	0.133730921	84871.8	634646.045	
5%	497.7	472.8	24.9	4.52	1.125838244	842399	748241.592	8.35553096
50%	481.4	460.7	20.7	47.43	9.819005724	7023017.8	715247.348	

Average RF =	699378.328
Standard Dev. =	58436.7727

QCCS Data Sheet
6/16/99 10:22

Sample	Coating +liner Wt. (mg)	Liner Wt. (mg)	Mass (mg)	FID area	2-BE Mass (mg)	Wt % 2-BE
QCCS-1	515.9	496.1	19.8	643723	0.920421143	4.6485916
QCCS-2	466.4	441.5	24.9	814765	1.164983911	4.6786502
QCCS-3	475.5	450.8	24.7	786751	1.124928338	4.5543657

Mean Measured Conc. (% 2-BE)= 4.6272025

True Conc. (% 2-BE)= 4.55

Accuracy= 101.6954

%RSD= 1.4013709

Paint Results Data Sheet
6/16/99 10:22

Paint	Sample	Sample Wt (mg)	FID Area	VOC mass (mg)	Wt. % VOC(uncorrected)	RS(avg)	Wt. % VOC (corrected)
MS1-6659A	1	8.3	1023484	1.463419667	17.63156225	1.019	17.30280888
MS1-6659A	2	28	3213238.3	4.594420746	16.40864552	1.019	16.10269433
MS1-6659A	3	26.5	3027846.2	4.32933947	16.33713007	1.019	16.03251234
1403-0100	1	33.4	1156877	1.654150484	4.95254636	0.8365	5.920557513
1403-0100	2	32.7	1138307.2	1.627598618	4.977365803	0.8365	5.950228097
1403-0100	3	32.4	1149891.2	1.644161899	5.074573762	0.8365	6.066436058
4206-0100	1	34.2	2815372.8	4.025536233	11.77057378	1.239	9.500059547
4206-0100	2	33	2768373.3	3.958334408	11.99495275	1.239	9.681156376
4206-0100	3	27.1	2286739.5	3.269674521	12.06521964	1.239	9.737868955
4020-1000	1	34.2	1017972.5	1.455539097	4.255962271	1.359	3.131686734
4020-1000	2	36.5	1083998.3	1.549945511	4.246426057	1.359	3.124669652
4020-1000	3	33.1	972907.9	1.391103872	4.20273073	1.359	3.092517094

Laboratory 2 Data Sheets

Standard Data Sheet

Standard	Test Date	Vial Wt	Vial+H_2O Wt	Vial+H_2O+ 2-BE Wt	H_2O Wt (mg)	2-BE Wt (mg)	Wt % 2-BE
0.50%	6-14-99	2.2950	3.8210	3.8295	1.5260	.0085	.55%
5%	6-14-99	2.2782	3.7952	3.8750	1.5170	.0798	4.997%
50%	6-14-99	2.3149	3.0737	3.8163	.7588	.7426	49.46%
5% QCCS	6-14-99	2.2822	3.8065	3.8965	1.5243	.0900	5.58%

Analyst: _____

QCCS Data Sheet

R_{fid}/RF

Test Date	Sample	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	R_{fid}	$VOC_{mass_{ui}}$ 2-BE Mass (mg)	$\frac{VOC_{mass_{ui}}}{Mass_{ss}}$ Wt % 2-BE
6-14-99	QCCS-1			25.4	1824919.6	1.654	6.51
6-14-99	QCCs-2			25.2	1348753.5	1.222	4.85
6-14-99	QCCS-3			25.1	1459480.2	1.323	5.27

Mean Measured Conc.($\bar{X}$)=	5.54
True Conc. (T)=	5.58
Accuracy=	99.34
%RSD=	15.57

Analyst: _____

Calibration Data Sheet

Test Date	Nominal Std %	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	Standard Wt % 2-BE/ac	$Mass_s$ (mg)	R_{fid}	RF (area unit/mg)	%RSD
6-14-99	0.5			25.2	.0055	.1386	195986.5	1414044.01	
6-14-99	5			25.0	.04997	1.24925	1139258	911953.57	24.61
6-14-99	50			24.4	.4946	12.068	11871101.7	983684.26	
						Average RF ($\overline{RF}$) =		1103227.28	

Analyst: _____

Calibration used for QCCS

PATRICK J. CALLAHAN
P.J. Callahan
Battelle 8/28/99

Calibration Data Sheet

Date	Nominal Std %	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	Standard Wt % 2-BE/oc	$Mass_s$ (mg)	R_{fid}	RF (area unit/mg)	%RSD
6-17-99	0.5			25.5	.0055	.14025	195745.4	1395689.13	
6-17-99	5			25.4	.04997	1.269238	1142197.0	899907.64	25.78
6-17-99	50			24.5	.4946	12.1177	1129780.9	932339.05	
						Average RF ($\overline{RF}$) =		1075978.613	

Analyst: _____

Calibration used for Paint Samples

PATRICK J. CALLAHAN
P.J. Callahan
Battelle 8/28/99

Paint Results Data Sheet

Date	Paint	Sample	Sample Wt (mg)	R_{fid}	$\overline{RF}$	VOC $mass_u$ (mg) ($R_{fid}/\overline{RF}$)	Wt% VOC_u (uncorrected)	Wt% VOC_c (corrected)
6-17-99	MS1-6659A	1	29.1	4471592.1	1075978.613	4.156	14.28	14.01
6-17-99	MS1-6659A	2	26.1	3970975.3	1075978.613	3.691	14.14	13.88
6-17-99	MS1-6659A	3	24.2	3713052.9	1075978.613	3.451	14.26	13.99
6-17-99	1403-0100	1	25.1	1119354.9	1075978.613	1.040	4.14	4.94
6-17-99	1403-0100	2	23.7	1036683.5	1075978.613	.963	4.06	4.84
6-17-99	1403-0100	3	25.1	1103396.7	1075978.613	1.025	4.08	4.87
6-17-99	4206-0100	1	26.5	3136676.6	1075978.613	2.915	11.00	8.87
6-17-99	4206-0100	2	25.2	2918757.0	1075978.613	2.713	10.77	8.69
6-18-99	4206-0100	3	26.8	3267420.0	1075978.613	3.037	11.33	9.14
6-17-99	4020-1000	1	33.3	1287482.2	1075978.613	1.197	3.59	2.64
6-17-99	4020-1000	2	25.9	995264.0	1075978.613	.925	3.57	2.62
6-17-99	4020-1000	3	33.8	1286499.3	1075978.613	1.196	3.54	2.60

Analyst: _____

Laboratory 3 Data Sheets

Standard Data Sheet

Standard	Date	Vial Wt	Vial+H_2O Wt	Vial+H_2O+ 2-BE Wt	H_2O Wt (mg)	2-BE Wt (mg)	Wt % 2-BE
0.50%	6-21-99	Tared (25 ml)	24853.7	24985.8	24853.7	132.1	0.5287
5%	6-21-99	Tared (10 ml)	9436.4	9945.3	9436.4	508.9	5.117
50%	6-21-99	Tared (5 ml)	2221.9	4730.5	2221.9	2508.6	53.03
5% QCCS	6-21-99	Tared (25 ml)	23698.2	24873.7	23698.2	1175.5	4.726

Analyst: _____

Calibration Data Sheet

Date	Nominal Std %	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	Standard Wt % 2-BE	$Mass_s$ (mg)	(thousands) R_{fid}	RF (area unit/mg)	%RSD
6-28-99	0.5	by volume	–	25.0	0.529	0.132	191.9	1453.8	
6-28-99	5	by volume	–	24.9	5.12	1.27	1231.5	969.7	25.3
6-28-99	50	by volume	–	23.7	53.0	12.6	20562.3	1631.9	
						Average RF $(\overline{RF})$ =		1351.8	

Analyst: _____

σ_{n-1} = 352.7

QCCS Data Sheet

Date	Sample	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	(thousands) R_{fid}	2-BE Mass (mg)	Wt % 2-BE
6-28-99	QCCS-1	by volume	–	24.9	1699.2	1.26	5.06
6-28-99	QCCs-2	by volume	–	24.9	1568.9	1.16	4.66
6-28-99	QCCS-3	by volume	–	24.9	1624.3	1.20	4.83
					Mean Measured Conc.($\bar{X}$)=		4.86
					True Conc. (T)=		4.73
					Accuracy=		97% ← mistake should be 102.5%
					%RSD=		5.8 ↑ mistake should be 4.01%

Analyst: _____

PATRICK J. CALLAHAN
P.J. Callahan
8/28/99

Paint Results Data Sheet

Date	Paint	Sample	Sample Wt (mg)	(thousands) R_{fid}	(thousands) $\overline{RF}$	VOC mass$_u$ (mg) ($R_{fid}/\overline{RF}$)	Wt% VOC$_u$ (uncorrected)	Wt% VOC$_c$ (corrected)
6-28-99	MS1-6659A	1	25.5	5469.5	1351.8	4.046	15.9	15.6
6-28-99	MS1-6659A	2	24.7	5286.2	1351.8	3.910	15.8	15.5
6-28-99	MS1-6659A	3	20.0	4194.3	1351.8	3.103	15.5	15.2
6-28-99	1403-0100	1	27.3	1178.1	1351.8	0.8715	3.19	3.81
6-28-99	1403-0100	2	29.2	1295.7	1351.8	0.9585	3.28	3.92
6-28-99	1403-0100	3	26.3	1159.0	1351.8	0.8574	3.26	3.89
6-28-99	4206-0100	1	29.7	4879.8	1351.8	3.610	12.2	9.76
6-28-99	4206-0100	2	26.3	4223.7	1351.8	3.125	11.9	9.54
6-28-99	4206-0100	3	27.9	4681.5	1351.8	3.463	12.4	9.97
6-28-99	4020-1000	1	33.8	1837.7	1351.8	1.359	4.02	2.94
6-28-99	4020-1000	2	29.9	1631.9	1351.8	1207	4.04	2.95
6-28-99	4020-1000	3	26.9	1488.0	1351.8	1.101	4.09	2.99

Analyst: _____

Laboratory 4 Data Sheets

QCCS Data Sheet

Date	Sample	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	R_{fid}	2-BE Mass (mg)	Wt % 2-BE	
7/15/99	QCCS-1 (P)	NA	NA	23.6	236495.7	1.09	4.62	
7/15/99	QCCS-2 (P)	NA	NA	27.7	335728.2	1.55	5.59	
7/15/99	QCCS-3 (P)	NA	NA	22.9	269210.9	1.25	5.46	
						Mean Measured Conc.($\bar{X}$)=	5.22	
						True Conc. (T)=	5.06	
						Accuracy=	103.2	PASSED
						%RSD=	10.09	PASSED

Analyst: _____

NA = Not applicable. Our lab uses the tare function on the balance.

NOTE: Also ran 2 BLANKS: Blank 1 = Clean Liner; Blank 2 = Liner containing 25.8 mg DI water.
No areas reported for either blank.

Standard Data Sheet

Standard	Date	Vial Wt	Vial+H_2O Wt	Vial+H_2O+ 2-BE Wt	H_2O Wt (mg)	2-BE Wt (mg)	Wt % 2-BE
0.50%	7/15/99	NA	NA	NA	4974.8	24.6	0.49
5%	7/15/99	NA	NA	NA	1899.8	101.6	5.08
50%	7/15/99	NA	NA	NA	1000.3	1006.0	50.14
5% QCCS-1(P)	7/15/99	NA	NA	NA	1899.7	101.3	5.06
5% QCCS-2(B)	7/15/99	NA	NA	NA	1901.1	100.8	5.04

Analyst: _____

NA = Not applicable. Our lab uses the tare function on the balance.

Calibration Data Sheet

Date	Nomina Std %	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	Standard Wt % 2-BE	$Mass_s$ (mg)	R_{fid}	RF (area unit/mg)	%RSD
7/16/99	0.5	NA	NA	27.1	0.49	0.13	24128.0	185600.0	
7/16/99	5	NA	NA	24.6	5.08	1.25	270304.6	216243.7	14.13
7/16/99	50	NA	NA	23.5	50.14	11.78	2905986.0	246688.1	
						Average RF ($\overline{RF}$) =		216177.3	

PASSED

Analyst: _____

NA = Not applicable. Our lab uses the tare function on the balance.

ONE-POINT CALIBRATION CHECK:

Date	Nomina Std %	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	Standard Wt % 2-BE	$Mass_s$ (mg)	R_{fid}	RF (area unit mg)	**% DIFF**
7/17/99	5	NA	NA	24.7	5.04	1.24	278022.5	224211.7	**-3.72**

PASSED

QCCS Data Sheet

Date	Sample	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	R_{fid}	2-BE Mass (mg)	Wt % 2-BE	
7/15/99	QCCS-1 (B)	NA	NA	25.1	317896.0	1.47	5.86	
7/15/99	QCCS-2 (B)	NA	NA	22.8	296018.9	1.37	6.01	
7/15/99	QCCS-3 (B)	NA	NA	24.3	306215.3	1.42	5.84	
						Mean Measured Conc.($\bar{X}$)=	5.90	
						True Conc. (T)=	5.04	
						Accuracy=	117.1	FAILED
						%RSD=	1.58	PASSED

Analyst: _____

NA = Not applicable. Our lab uses the tare function on the balance.

Paint Results Data Sheet

Date	Paint	Sample	Sample Wt (mg)	R_{fid}	$\overline{RF}$	VOC $mass_u$ (mg) ($R_{fid}/\overline{RF}$)	Wt% VOC_u (uncorrected)	Wt% VOC_c (corrected)
7/16/99	MS1-6659A	1	11.4	388357.3	216177.3	1.80	**15.79**	**15.51**
7/16/99	MS1-6659A	2	25.4	933023.0	216177.3	4.32	**17.01**	**16.71**
7/16/99	MS1-6659A	3	23.7	853080.8	216177.3	3.95	**16.67**	**16.38**
7/16/99	1403-0100	1	30.7	274039.9	216177.3	1.27	**4.14**	**4.94**
7/16/99	1403-0100	2	26.2	232522.6	216177.3	1.08	**4.12**	**4.92**
7/16/99	1403-0100	3	31.4	285352.9	216177.3	1.32	**4.20**	**5.01**
7/16/99	4206-0100	1	31.6	885611.6	216177.3	4.10	**12.97**	**10.52**
7/16/99	4206-0100	2	35.8	1007103.4	216177.3	4.66	**13.02**	**10.56**
7/16/99	4206-0100	3	28.3	778731.1	216177.3	3.60	**12.72**	**10.32**
7/16/99	4020-1000	1	27.9	223743.8	216177.3	1.04	**3.73**	**2.72**
7/16/99	4020-1000	2	36.0	297978.4	216177.3	1.38	**3.83**	**2.80**
7/16/99	4020-1000	3	30.0	245374.1	216177.3	1.14	**3.80**	**2.78**

Analyst: _____

Laboratory 5 Data Sheets

QCCS Data Sheet

Date	Sample	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	R_{fid}	2-BE Mass (mg)	Wt % 2-BE
8/06/1999	QCCS-1			25.0	1470271	1.215335664	4.8613427
8/06/1999	QCCS-2			25.0	1565861	1.294350985	5.1774039
8/06/1999	QCCS-3			25.3	1518494	1.255197112	4.9612534

Mean Measured Conc.($\bar{X}$)=	5
True Conc. (T)=	5
Accuracy=	100 %
%RSD=	3.23

Analyst: _____

$\overline{RF} = 1209765.371$

Calibration Data Sheet

Date	Nominal Std %	Coating+ Liner Wt	Liner Wt	$Mass_{ss}$ (mg)	Standard Wt % 2-BE	$Mass_s$ (mg)	R_{6d}	RF (area unit/mg)	%RSD
8/06/1999	0.5			25.0	0.5%	0.125	174521.1	1396168.8	
8/06/1999	5			25.0	5.0%	1.25	1580053.0	1264042.4	18.84%
8/06/1999	50			24.9	50.0 %	12.45	11877140.0	953982.1486	
						Average RF ($\overline{RF}$) =		1204732.783	

Analyst: _____

Calibration Data Sheet

Date	Nominal Std %	Coating+ Liner Wt	Liner Wt	$Mass_{as}$ (mg)	Standard Wt % 2-BE	$Mass_s$ (mg)	R_{fid}	RF (area unit/mg)	%RSD
8/11/1999	0.5			25.2	0.50%	0.126	199424.2	1582731.746	
8/11/1999	5			25.2	5.0%	1.26	1860699.0	1476745.238	3.7 %
8/11/1999	50			25.1	50.0%	12.55	21069950.0	1678880.478	
						Average RF $\overline{(RF)}$ =		1579452.487	

mistake should be 6.4%

Analyst: _____

Paint Results Data Sheet

Date	Paint	Sample	Sample Wt (mg)	R_{6d}	$\overline{RF}$	VOC mass$_u$ (mg) ($R_{6d}/\overline{RF}$)	Wt% VOC$_u$ (uncorrected)	Wt% VOC$_c$ (corrected)
8/12/1999	MS1-6659A	1	25.8	5620253.8	1579452.487	3.5584	13.7922 %	13.51
8/12/1999	MS1-6659A	2	32.6	7627750.6	1579452.487	4.8294	14.8141 %	14.51
8/12/1999	MS1-6659A	3	25.4	5526586.1	1579452.487	3.4990	13.7756 %	13.49
8/12/1999	1403-0100	1	24.6	1638773.2	1579452.487	1.0376	4.2179 %	5.033
8/12/1999	1403-0100	2	27.2	1746860.5	1579452.487	1.1376	4.1823 %	4.991
8/12/1999	1403-0100	3	29.2	1971891.6	1579452.487	1.2485	4.2757 %	5.102
8/12/1999	4206-0100	1	27.7	5351978.8	1579452.487	3.3885	12.2328 %	12.64
8/12/1999	4206-0100	2	24.1	4582053.3	1579452.487	2.9010	12.0373 %	12.44
8/12/1999	4206-0100	3	30.1	5855259.4	1579452.487	3.7071	12.3159 %	12.72
8/11/1999	4020-1000	1	39.4	2510335.8	1579452.487	1.5894	4.0340 %	2.949
8/12/1999	4020-1000	2	25.4	1575356.1	1579452.487	0.9974	3.9268 %	2.870
8/12/1999	4020-1000	3	26.3	1547404.2	1579452.487	0.9797	3.7251 %	2.723

mistake values calculated with wrong RS_{Avg}

Values Calculated using RS_{Avg} 1.246 are 9.82, 9.66, 9.88

Analyst: _____

PATRICK J. CALLAHAN

P.J. Callahan

9/2/99

Laboratory 6 Data Sheets

Standard Data Sheet

Standard	Date	Vial Wt (gm)	Vial+H_2O Wt (gm)	Vial+H_2O+ 2-BE Wt (gm)	H_2O Wt (mg)	2-BE Wt (mg)	Wt % 2-BE
0.50%	8/19/99	2.3290	3.9156	3.9245	1,586.6	8.9	0.5578
5%	8/19/99	2.3006	3.7645	3.8473	1,463.9	82.8	5.3533
50%	8/19/99	2.2817	3.1059	3.9304	824.2	824.5	50.0091
5% QCCS	8/19/99	2.3036	3.8868	3.9673	1,583.2	80.5	4.8386

Analyst: _____

Calibration Data Sheet

Date	Nominal Std %	Coating+ Liner Wt (gm)	Liner Wt (gm)	$Mass_{st}$ (mg)	Standard Wt % 2-BE	$Mass_s$ (mg)	R_{std}	RF (area unit/mg)	%RSD
8/19/99	0.5	0.5531	0.5279	25.2	0.5578	0.1406	93,772.3	667,107.0	
8/19/99	5	0.4845	0.4594	25.1	5.3533	1.3437	952,916.4	709,184.9	8.0685
8/19/99	50	0.4790	0.4548	24.2	50.0091	12.1022	9,462,017.0	781,842.6	
						Average RF $\overline{(RF)}$ =		719,378.2	

Analyst: _____

QCCS Data Sheet

Date	Sample	Coating+ Liner Wt (gm)	Liner Wt (gm)	$Mass_{ss}$ (mg)	R_{fid}	2-BE Mass (mg)	Wt % 2-BE
8/19/99	QCCS-1	0.4787	0.4533	25.4	898,941.6	1.2496	4.9197
8/19/99	QCCS-2	0.4931	0.4677	25.4	887,825.3	1.2342	4.8589
8/19/99	QCCS-3	0.5626	0.5372	25.4	878,156.7	1.2207	4.8060
					Mean Measured Conc.(X)=		4.8615
					True Conc. (T)=		4.8386
					Accuracy=		100.4738
						%RSD=	1.1709

Analyst: _____

Calibration Data Sheet

Date	Nominal Std %	Coating+ Liner Wt (gm)	Liner Wt (gm)	$Mass_m$ (mg)	Standard Wt % 2-BE	$Mass_s$ (mg)	R_{sd}	RF (area unit/mg)	%RSD
8/20/99	0.5	0.5530	0.5277	25.3	0.5578	0.1411	73,804.6	522,979.2	
8/20/99	5	0.4846	0.4592	25.4	5.3533	1.3597	1,021,429.0	751,195.3	22.7359
8/20/99	50	0.4789	0.4547	24.2	50.0091	12.1022	10,045,310.0	830,039.8	
						Average RF ($\overline{RF}$) =		701,404.8	

Analyst: _____

QCCS Data Sheet

Date	Sample	Coating+ Liner Wt (gm)	Liner Wt (gm)	$Mass_{ss}$ (mg)	R_{fid}	2-BE Mass (mg)	Wt % 2-BE
8/25/99	QCCS-1	0.4760	0.4510	25.0	848,260.4	1.2094	4.8375
	QCCS-2						
	QCCS-3						
						Mean Measured Conc.(X)=	4.8375
						True Conc. (T)=	4.8386
						Accuracy=	99.9773
						%RSD=	

Analyst: _____

$$\% \text{ Difference} = \frac{\left(701{,}404.8 - \frac{848{,}260.4}{(0.0484)(25)}\right) \times 100}{701{,}404.8}$$

PATRICK J. CALLAHAN

P.J. Callahan

= 0.05%

Paint Results Data Sheet

Date	Paint	Sample	Sample Wt (mg)	R_{fid}	$\overline{RF}$	VOC $mass_u$ (mg) ($R_{fid}/\overline{RF}$)	Wt% VOC_u (uncorrected)	Wt% VOC_c (corrected)
8/25/99	MS1-6659A	1	36.5	4,307,566.4	701,404.8	6.1413	**16.83**	**16.50**
8/25/99	MS1-6659A	2	31.9	3,713,699.8	701,404.8	5.2947	**16.60**	**16.28**
8/25/99	MS1-6659A	3	38.8	4,615,410.2	701,404.8	6.5802	**16.96**	**16.63**
8/25/99	1403-0100	1	46.5	1,337,259.7	701,404.8	1.9065	**4.10**	**4.89**
8/25/99	1403-0100	2	39.6	1,143,124.7	701,404.8	1.6298	**4.12**	**4.91**
8/25/99	1403-0100	3	51.1	1,466,773.8	701,404.8	2.0912	**4.09**	**4.88**
8/25/99	4206-0100	1	33.1	2,835,984.2	701,404.8	4.0433	**12.22**	**9.85**
8/25/99	4206-0100	2	52.1	4,623,064.2	701,404.8	6.5911	**12.65**	**10.20**
8/25/99	4206-0100	3	41.6	3,654,292.4	701,404.8	5.2100	**12.52**	**10.09**
8/25/99	4020-1000	1	58.0	1,615,703.8	701,404.8	2.3035	**3.97**	2.92
8/25/99	4020-1000	2	52.6	1,438,136.9	701,404.8	2.0504	**3.90**	2.86
8/25/99	4020-1000	3	61.6	1,690,767.1	701,404.8	2.4105	**3.91**	2.88

Analyst: _____

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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-454/R-99-040		

4. TITLE AND SUBTITLE	5. REPORT DATE
Evaluation of the Water-based Coating Method (ATD-FID) Round Robin Study	September 1999
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7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
EMAD	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
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U.S. Environmental Protection Agency	Final Report
Research Triangle Park, NC 27711	14. SPONSORING AGENCY CODE
	EPA/200/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The purpose of this project was to conduct an interlaboratory study to evaluate the draft water-based caoting method. A total of six laboratories participated in the interlaboratory study. Each of the laboratories was required to analyze four different water-based coatings following the procedure described in the draft method. The results from the participating laboratories were analyzed using the statistical procedure described in ASTM E 691, Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.

17. Method Evaluation — KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
	Method Evaluation of Water-based Coating Method	

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