3. Appendix A of part 63 is amended by adding Method 311 to read as follows:

## Appendix A to Part 63-Test Methods

## Method 311 - Analysis of Hazardous Air Pollutant Compounds in Paints and Coatings by Direct Injection into a Gas Chromatograph

1. Scope and Application

1.1 Applicability. This method is applicable for determination of most compounds designated by the U. S. Environmental Protection Agency as volatile hazardous air pollutants (HAP's) (See Reference 1) that are contained in paints and coatings. Styrene, ethyl acrylate, and methyl methacrylate can be measured by ASTM D 4827-93 or ASTM D 4747-87. Formaldehyde can be measured by ASTM PS 9-94 or ASTM D 1979-91. Toluene diisocyanate can be measured in urethane prepolymers by ASTM D 3432-89. Method 311 applies only to those volatile HAP's which are added to the coating when it is manufactured, not to those which may form as the coating cures (reaction products or cure volatiles). A separate or modified test procedure must be used to measure these reaction products or cure volatiles in order to determine the total volatile HAP emissions from a coating. Cure volatiles are a significant component of the total HAP content of some coatings. The term "coating" used in this method shall be understood to mean paints and coatings.

1.2 Principle. The method uses the principle of gas chromatographic separation and quantification using a detector that responds to concentration differences. Because there are many potential analytical systems or sets of operating conditions that may represent useable methods for determining the concentrations of the compounds cited in Section 1.1 in the applicable matrices, all systems that employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the prescribed quality control, calibration, and method performance requirements are met. Certified product data sheets (CPDS) may also include information relevant to the analysis of the coating sample including, but not limited to, separation column, oven temperature, carrier gas, injection port temperature, extraction solvent, and internal standard.

2. Summary of Method

Whole coating is added to dimethylformamide and a suitable internal standard compound is added. An aliquot of the sample mixture is injected onto a chromatographic column containing a stationary phase that separates the analytes from each other and from other volatile compounds contained in the sample. The concentrations of the analytes are determined by comparing the detector responses for the sample to the responses obtained using known concentrations of the analytes.

3. Definitions [Reserved]

4. Interferences.

4.1 Coating samples of unknown composition may contain the compound used as the internal standard. Whether or not this is the case may be determined by following the procedures of Section 11 and deleting the addition of the internal standard specified in Section 11.5.3. If necessary, a different internal standard may be used.

4.2 The GC column and operating conditions developed for one coating formulation may not ensure adequate resolution of target analytes for other coating formulations. Some formulations may contain nontarget analytes that coelute with target analytes. If there is any doubt about the identification or resolution of any gas chromatograph (GC) peak, it may be necessary to analyze the sample using a different GC column or different GC operating conditions.

4.3 Cross-contamination may occur whenever high-level and low-level samples are analyzed sequentially. The order of sample analyses specified in Section 11.7 is designed to minimize this problem.

4.4 Cross-contamination may also occur if the devices used to transfer coating during the sample preparation process or for injecting the sample into the GC 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 Dimethylformamide is harmful if inhaled or absorbed through the skin. The user should obtain relevant health and safety information from the manufacturer. Dimethylformamide 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 and other related equipment should be consulted for specific precautions to be taken related to their use.

6. Equipment and Supplies

**NOTE:** Certified product data sheets (CPDS) may also include information relevant to the analysis of the coating sample

including, but not limited to, separation column, oven temperature, carrier gas, injection port temperature, extraction solvent, and internal standard.

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.

6.1.1.1 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.

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

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

6.1.4 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 and capable of being temperature programmed may be used. Optionally, other types of detectors (e.g., a mass spectrometer), and any necessary interfaces, may be used provided that the detector system yields an appropriate and reproducible response to the analytes in the injected sample. Autosampler injection may be used, if available.

6.2.2 Recorder. If available, an electronic data station or integrator may be used to record the gas chromatogram 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 $\pm$0.03 percent of full scale. Other types of recorders may be used as appropriate to the specific detector installed provided that the recorder has a full scale response time of 2 seconds or less and a maximum noise level of $\pm$0.03 percent of full scale.

6.2.3 Column. The column must be constructed of materials that do not react with components of the sample (*e.g.*, fused silica, stainless steel, glass). The column should be of appropriate physical dimensions (*e.g.*, length, internal diameter)

and contain sufficient suitable stationary phase to allow separation of the analytes. DB-5, DB-Wax, and FFAP columns are commonly used for paint analysis; however, it is the responsibility of each analyst to select appropriate columns and stationary phases.

6.2.4 Tube and Tube Fittings. Supplies to connect the GC and gas cylinders.

6.2.5 Pressure Regulators. Devices used to regulate the pressure between gas cylinders and the GC.

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

6.2.7 Septa. Seals on the GC injection port through which liquid or gas samples can be injected using a syringe.

6.2.8 Liquid Charging Devices. Devices used to inject samples into the GC such as clean and graduated 1, 5, and 10 microliter ($\mu$l) capacity syringes.

6.2.9 Vials. Containers that can be sealed with a septum in which samples may be prepared or stored. The recommended size is 25 ml capacity. Mininert® valves have been found satisfactory and are available from Pierce Chemical Company, Rockford, Illinois.

6.2.10 Balance. Device 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 Carrier Gas. Helium carrier gas shall have a purity of 99.995 percent or higher. High purity nitrogen may also be used. Other carrier gases that are appropriate for the column system and analyte may also be used. Ultra-high purity grade hydrogen gas and zero-grade air shall be used for the flame ionization detector.

7.3 Dimethylformamide (DMF). Solvent for all standards and samples. Some other suitable solvent may be used if DMF is not compatible with the sample or coelutes with a target analyte. **NOTE:** DMF may coelute with ethylbenzene or p-xylene under the conditions described in the note under Section 6.2.3.

7.4 Internal Standard Materials. The internal standard material is used in the quantitation of the analytes for this method. It shall be gas chromatography spectrophotometric quality or, if this grade is not available, the highest quality available. Obtain the assay for the internal standard material

and maintain at that purity during use. The recommended internal standard material is 1-propanol; however, selection of an appropriate internal standard material for the particular coating and GC conditions used is the responsibility of each analyst.

7.5 Reference Standard Materials. The reference standard materials are the chemicals cited in Section 1.1 which are of known identity and purity and which are used to assist in the identification and quantification of the analytes of this method. They shall be the highest quality available. Obtain the assays for the reference standard materials and maintain at those purities during use.

7.6 Stock Reference Standards. Stock reference standards are dilutions of the reference standard materials that may be used on a daily basis to prepare calibration standards, calibration check standards, and quality control check standards. Stock reference standards may be prepared from the reference standard materials or purchased as certified solutions.

7.6.1 Stock reference standards should be prepared in dimethylformamide for each analyte expected in the coating samples to be analyzed. The concentrations of analytes in the stock reference standards are not specified but must be adequate to prepare the calibration standards required in the method. A stock reference standard may contain more than one analyte provided all analytes are chemically compatible and no analytes coelute. The actual concentrations prepared must be known to within 0.1 percent (e.g., 0.1000 $\pm$ 0.0001 g/g solution). The following procedure is suggested. Place about 35 ml of dimethylformamide into a tared ground-glass stoppered 50 ml volumetric flask. Weigh the flask to the nearest 0.1 mg. Add 12.5 g of the reference standard material and reweigh the flask. Dilute to volume with dimethylformamide and reweigh. Stopper the flask and mix the contents by inverting the flask several times. Calculate the concentration in grams per gram of solution from the net gain in weights, correcting for the assayed purity of the reference standard material.

**NOTE**: Although a glass-stoppered volumetric flask is convenient, any suitable glass container may be used because stock reference standards are prepared by weight.

7.6.2 Transfer the stock reference standard solution into one or more Teflon-sealed screw-cap bottles. Store, with minimal headspace, at -10°C to 0°C and protect from light.

7.6.3 Prepare fresh stock reference standards every six months, or sooner if analysis results from daily calibration check standards indicate a problem. Fresh stock reference standards for very volatile HAP's may have to be prepared more frequently.

7.7 Calibration Standards. Calibration standards are used to determine the response of the detector to known amounts of reference material. Calibration standards must be prepared at a minimum of three concentration levels from the stock reference

standards (see Section 7.6). Prepare the calibration standards in dimethylformamide (see Section 7.3). The lowest concentration standard should contain a concentration of analyte equivalent either to a concentration of no more than 0.01% of the analyte in a coating or to a concentration that is lower than the actual concentration of the analyte in the coating, whichever concentration is higher. The highest concentration standard should contain a concentration of analyte equivalent to slightly more than the highest concentration expected for the analyte in a coating. The remaining calibration standard should contain a concentration of analyte roughly at the midpoint of the range defined by the lowest and highest concentration calibration standards. The concentration range of the standards should thus correspond to the expected range of analyte concentrations in the prepared coating samples (see Section 11.5). Each calibration standard should contain each analyte for detection by this method expected in the actual coating samples (e.g., some or all of the compounds listed in Section 1.1 may be included). Each calibration standard should also contain an appropriate amount of internal standard material (response for the internal standard material is within 25 to 75 percent of full scale on the attenuation setting for the particular reference standard concentration level). Calibration Standards should be stored for 1 week only in sealed vials with minimal headspace. If the stock reference standards were prepared as specified in Section 7.6, the calibration standards may be prepared by either weighing each addition of the stock reference standard or by adding known volumes of the stock reference standard and calculating the mass of the standard reference material added. Alternative 1 (Section 7.7.1) specifies the procedure to be followed when the stock reference standard is added by volume. Alternative 2 (Section 7.7.2) specifies the procedure to be followed when the stock reference standard is added by weight.

**NOTE**: To assist with determining the appropriate amount of internal standard to add, as required here and in other sections of this method, the analyst may find it advantageous to prepare a curve showing the area response versus the amount of internal standard injected into the GC.

7.7.1 Preparation Alternative 1. Determine the amount of each stock reference standard and dimethylformamide solvent needed to prepare approximately 25 ml of the specific calibration concentration level desired. To a tared 25 ml vial that can be sealed with a crimp-on or Mininert® valve, add the total amount of dimethylformamide calculated to be needed. As quickly as practical, add the calculated amount of each stock reference standard using new pipets (or pipet tips) for each stock reference standard. Reweigh the vial and seal it. Using the known weights of the standard reference materials per ml in the stock reference standards, the volumes added, and the total weight of all reagents added to the vial, calculate the weight

percent of each standard reference material in the calibration standard prepared. Repeat this process for each calibration standard to be prepared.

7.7.2 Preparation Alternative 2. Determine the amount of each stock reference standard and dimethylformamide solvent needed to prepare approximately 25 ml of the specific calibration concentration level desired. To a tared 25 ml vial that can be sealed with a crimp-on or Mininert® valve, add the total amount of dimethylformamide calculated to be needed. As quickly as practical, add the calculated amount of a stock reference standard using a new pipet (or pipet tip) and reweigh the vial. Repeat this process for each stock reference standard to be added. Seal the vial after obtaining the final weight. Using the known weight percents of the standard reference materials in the stock reference standards, the weights of the stock reference standards added, and the total weight of all reagents added to the vial, calculate the weight percent of each standard reference material in the calibration standard prepared. Repeat this process for each calibration standard to be prepared.

8. Sample Collection, Preservation, Transport, and Storage

8.1 Copies of material safety data sheets (MSDS's) for each sample should be obtained prior to sampling. The MSDS's contain information on the ingredients, and physical and chemical properties data. The MSDS's also contain recommendations for proper handling or required safety precautions. Certified product data sheets (CPDS) may also include information relevant to the analysis of the coating sample including, but not limited to, separation column, oven temperature, carrier gas, injection port temperature, extraction solvent, and internal standard.

8.2 A copy of the blender's worksheet can be requested to obtain data on the exact coating being sampled. A blank coating data sheet form (see Section 18) may also be used. 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 (see Section 18) 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.

8.9 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 ongoing analysis of blanks and quality control samples to evaluate and document quality data. 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, 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 is 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 stability must be demonstrated to be $\leq$5 percent of full scale using the procedures given in Section 10.1.

9.3.2 The GC calibration is not valid unless the retention time (RT) for each analyte at each concentration is within ±0.05 min of the retention time measured for that analyte in the stock standard.

9.3.3 The retention time (RT) of any sample analyte must be within ±0.05 min of the average RT of the analyte in the calibration standards for the analyte to be considered tentatively identified.

9.3.4 The GC system must be calibrated as specified in Section 10.2.

9.3.5 A one-point daily calibration check must be performed as specified in Section 10.3.

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 a quality control check standard (QCCS) containing each analyte expected in the coating samples at a concentration expected to result in a response between 25 percent and 75 percent of the limits of the calibration curve when the sample is prepared as described in Section 11.5. The QCCS may be prepared from reference standard materials or purchased as certified solutions. 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 11.5.3 and calculate the weight percent of each analyte using Equation 1, Section 12.

9.4.3 Calculate the mean weight percent ($\bar{X}$) for each analyte from the three results obtained in Section 9.4.2.

9.4.4 Calculate the percent accuracy for each analyte using the known concentrations ($T_i$) in the QCCS using Equation 3, Section 12.

9.4.5 Calculate the percent relative standard deviation (percent RSD) for each analyte using Equation 7, Section 12, substituting the appropriate values for the relative response factors (RRF's) in said equation.

9.4.6 If the percent accuracy (Section 9.4.4) for all analytes is within the range 90 percent to 110 percent and the percent RSD (Section 9.4.5) for all analytes is $\leq$20 percent,

system performance is acceptable and sample analysis may begin. If these criteria are not met for any analyte, then system performance is not acceptable for that analyte and the test must be repeated for those analytes only. 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. Calibration and Standardization.

10.1 Column Baseline Drift. Before each calibration and series of determinations and before the daily calibration check, condition the column using procedures developed by the laboratory or as specified by the column supplier. 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.

10.2 Calibration of GC. Bring all stock standards and calibration standards to room temperature while establishing the GC at the determined operating conditions.

10.2.1 Retention Times (RT's) for Individual Compounds. **NOTE**: The procedures of this subsection are required only for the initial calibration. However, it is good laboratory practice to follow these procedures for some or all analytes before each calibration. The procedures were written for chromatograms output to a strip chart recorder. More modern instruments (e.g., integrators and electronic data stations) determine and print out or display retention times automatically.

The RT for each analyte should be determined before calibration. This provides a positive identification for each peak observed from the calibration standards. Inject an appropriate volume (see NOTE in Section 11.5.2) of one of the stock reference standards into the gas chromatograph and record on the chart the pen position at the time of the injection (see Section 7.6.1). Dilute an aliquot of the stock reference standard as required in dimethylformamide to achieve a

concentration that will result in an on-scale response. Operate the gas chromatograph according to the determined procedures. Select the peak(s) that correspond to the analyte(s) [and internal standard, if used] and measure the retention time(s). If a chart recorder is used, measure the distance(s) on the chart from the injection point to the peak maxima. These distances, divided by the chart speed, are defined as the RT's of the analytes in question. Repeat this process for each of the stock reference standard solutions.

**NOTE:** If gas chromatography with mass spectrometer detection (GC-MS) is used, a stock reference standard may contain a group of analytes, provided all analytes are adequately separated during the analysis. Mass spectral library matching can be used to identify the analyte associated with each peak in the gas chromatogram. The retention time for the analyte then becomes the retention time of its peak in the chromatogram.

10.2.2 Calibration. The GC must be calibrated using a minimum of three concentration levels of each potential analyte. (See Section 7.7 for instructions on preparation of the calibration standards.) Beginning with the lowest concentration level calibration standard, carry out the analysis procedure as described beginning in Section 11.7. Repeat the procedure for each progressively higher concentration level until all calibration standards have been analyzed.

10.2.2.1 Calculate the RT's for the internal standard and for each analyte in the calibration standards at each concentration level as described in Section 10.2.1. The RT's for the internal standard must not vary by more than 0.10 minutes. Identify each analyte by comparison of the RT's for peak maxima to the RT's determined in Section 10.2.1.

10.2.2.2 Compare the retention times (RT's) for each potential analyte in the calibration standards for each concentration level to the retention times determined in Section 10.2.1. The calibration is not valid unless all RT's for all analytes meet the criteria given in Section 9.3.2.

10.2.2.3 Tabulate the area responses and the concentrations for the internal standard and each analyte in the calibration standards. Calculate the response factor for the internal standard ($RF_{is}$) and the response factor for each compound relative to the internal standard (RRF) for each concentration level using Equations 5 and 6, Section 12.

10.2.2.4 Using the RRF's from the calibration, calculate the percent relative standard deviation (percent RSD) for each analyte in the calibration standard using Equation 7, Section 12. The percent RSD for each individual calibration analyte must be <u>less</u> than 15 percent. This criterion must be met in order for the calibration to be valid. If the criterion is met, the mean RRF's determined above are to be used until the next calibration.

10.3 Daily Calibration Checks. The calibration curve (Section 10.2.2) must be checked and verified at least once each

day that samples are analyzed. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint of the working range and performing the checks in Sections 10.3.1, 10.3.2, and 10.3.3.

10.3.1 For each analyte in the calibration standard, calculate the percent difference in the RRF from the last calibration using Equation 8, Section 12. If the percent difference for each calibration analyte is less than 10 percent, the last calibration curve is assumed to be valid. If the percent difference for any analyte is greater than 5 percent, the analyst should consider this a warning limit. If the percent difference for any one calibration analyte 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 quantitative analysis begins.

10.3.2 If the $RF_{is}$ for the internal standard changes by more than ±20 percent from the last daily calibration check, the system must be inspected for malfunctions and corrections made as appropriate.

10.3.3 The retention times for the internal standard and all calibration check analytes must be evaluated. If the retention time for the internal standard or for any calibration check analyte changes by more than 0.10 min from the last calibration, the system must be inspected for malfunctions and corrections made as required.

11. Procedure

11.1 All samples and standards must be allowed to warm to room temperature before analysis. Observe the given order of ingredient addition to minimize loss of volatiles.

11.2 Bring the GC system to the determined operating conditions and condition the column as described in Section 10.1. **NOTE:** The temperature of the injection port may be an especially critical parameter. Information about the proper temperature may be found on the CPDS.

11.3 Perform the daily calibration checks as described in Section 10.3. Samples are not to be analyzed until the criteria in Section 10.3 are met.

11.4 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.

11.5 **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.

11.5.1 Add 16 g of dimethylformamide to each of two tared vials (A and B) capable of being septum sealed.

11.5.2 To each vial add a weight of coating that will

result in the response for the major constituent being in the upper half of the linear range of the calibration curve. **NOTE**: The magnitude of the response obviously depends on the amount of sample injected into the GC as specified in Section 11.8. This volume must be the same as used for preparation of the calibration curve, otherwise shifts in compound retention times may occur. If a sample is prepared that results in a response outside the limits of the calibration curve, new samples must be prepared; changing the volume injected to bring the response within the calibration curve limits is not permitted.

11.5.3 Add a weight of internal standard to each vial (A and B) that will result in the response for the internal standard being between 25 percent and 75 percent of the linear range of the calibration curve.

11.5.4 Seal the vials with crimp-on or Mininert® septum seals.

11.6 Shake the vials containing the prepared coating samples for 60 seconds. Allow the vials to stand undisturbed for ten minutes. If solids have not settled out on the bottom after 10 minutes, then centrifuge at 1,000 rpm for 5 minutes. The analyst also has the option of injecting the sample without allowing the solids to settle.

11.7 Analyses should be conducted in the following order: daily calibration check sample, method blank, up to 10 injections from sample vials (*i.e.*, one injection each from up to five pairs of vials, which corresponds to analysis of 5 coating samples).

11.8 Inject the prescribed volume of supernatant from the calibration check sample, the method blank, and the sample vials onto the chromatographic column and record the chromatograms while operating the system under the specified operating conditions. **NOTE:** The analyst has the option of injecting the unseparated sample.

12. Data Analysis and Calculations

12.1 Qualitative Analysis. An analyte (e.g., those cited in Section 1.1) is considered tentatively identified if two criteria are satisfied: (1) elution of the sample analyte within ±0.05 min of the average GC retention time of the same analyte in the calibration standard; and (2) either (a) confirmation of the identity of the compound by spectral matching on a gas chromatograph equipped with a mass selective detector or (b) elution of the sample analyte within ±0.05 min of the average GC retention time of the same analyte in the calibration standard analyzed on a dissimilar GC column.

12.1.1 The RT of the sample analyte must meet the criteria specified in Section 9.3.3.

12.1.2 When doubt exists as to the identification of a peak or the resolution of two or more components possibly comprising one peak, additional confirmatory techniques (listed in Section 12.1) must be used.

12.2 Quantitative Analysis. When an analyte has been

identified, the quantification of that compound will be based on the internal standard technique.

12.2.1 A single analysis consists of one injection from each of two sample vials (A and B) prepared using the same coating. Calculate the concentration of each identified analyte in the sample as follows:

$$HAP_{wt\%} = 100 \times \frac{(A_x)(W_{is})}{(A_{is})(\overline{RRF_x})(W_x)} \qquad \textbf{Eq. (1)}$$

where:

$HAP_{wt\%}$ = weight percent of the analyte in coating.
$A_x$ = Area response of the analyte in the sample.
$W_{is}$ = Weight of internal standard added to sample, g.
$A_{is}$ = Area response of the internal standard in the sample.
$\overline{RRF_x}$ = Mean relative response factor for the analyte in the calibration standards.
$W_x$ = Weight of coating added to the sample solution, g.

12.2.2 Report results for duplicate analysis (sample vials A and B) without correction.

12.3 Precision Data. Calculate the percent difference between the measured concentrations of each analyte in vials A and B as follows.

12.3.1 Calculate the weight percent of the analyte in each of the two sample vials as described in Section 12.2.1.

12.3.2 Calculate the percent difference for each analyte as:

$$\%Dif_i = 100 \times \frac{|A_i - B_i|}{\frac{(A_i + B_i)}{2}} \qquad \textbf{Eq. (2)}$$

where $A_i$ and $B_i$ are the measured concentrations of the analyte in vials A and B.

12.4 Calculate the percent accuracy for analytes in the QCCS (See Section 9.4) as follows:

$$\% \text{ Accuracy}_x = 100 \times \frac{\overline{X}_x}{T_x} \qquad \textbf{Eq. (3)}$$

where $\overline{X}_x$ is the mean measured value and $T_x$ is the known true value of the analyte in the QCCS.

12.5 Obtain retention times (RT's) from data station or integrator or, for chromatograms from a chart recorder, calculate the RT's for analytes in the calibration standards (See Section 10.2.2.2) as follows:

$$RT = \frac{\text{Distance from injection to peak maximum}}{\text{Recorder chart speed}} \qquad \textbf{Eq. (4)}$$

12.6 Calculate the response factor for the internal standard (See Section 10.2.2.3) as follows:

$$RF_{is} = \frac{A_{is}}{C_{is}} \qquad \textbf{Eq. (5)}$$

where:

$A_{is}$ = Area response of the internal standard.
$C_{is}$ = Weight percent of the internal standard.

12.7 Calculate the relative response factors for analytes in the calibration standards (See Section 10.2.2.3) as follows:

$$RRF_x = \frac{A_x}{RF_{is}\ C_x} \qquad \textbf{Eq. (6)}$$

where:

$RRF_x$ = Relative response factor for an individual analyte.
$A_x$ = Area response of the analyte being measured.
$C_x$ = Weight percent of the analyte being measured.

12.8 Calculate the percent relative standard deviation of the relative response factors for analytes in the calibration standards (See Section 10.2.2.4) as follows:

$$\%RSD = 100 \times \frac{\sqrt{\frac{\sum_{i=1}^{n}(RRF_x - \overline{RRF_x})^2}{n-1}}}{\overline{RRF_x}} \qquad \textbf{Eq. (7)}$$

where:

n = Number of calibration concentration levels used for an analyte.

$RRF_x$ = Individual RRF for an analyte.

$\overline{RRF_x}$ = Mean of all RRF's for an analyte.

12.9 Calculate the percent difference in the relative response factors between the calibration curve and the daily calibration checks (See Section 10.3) as follows:

$$\%\ Difference = \frac{\left| \overline{RRF_x} - RRF_c \right|}{\overline{RRF_x}} \times 100 \qquad \textbf{Eq. (8)}$$

where:

$\overline{RRF_x}$ = mean relative response factor from last calibration.

$RRF_c$ = relative response factor from calibration check standard.

13. Measurement of Reaction Byproducts That are HAP. [Reserved]

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 nonglass or nonsharp 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. Clean Air Act Amendments, Public Law 101-549, Titles I-XI, November, 1990.

2. Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph. ASTM Designation D3792-79

3. Standard Practice for Sampling Liquid Paints and Related Pigment Coatings. ASTM Designation D3925-81.

4. Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph. ASTM Designation D4457-85.

5. Standard Test Method for Determining the Unreacted Monomer Content of Latexes Using Capillary Column Gas Chromatography. ASTM Designation D4827-93.

6. Standard Test Method for Determining Unreacted Monomer Content of Latexes Using Gas-Liquid Chromatography. ASTM Designation D 4747-87.

7. Method 301 - “Field Validation of Pollutant Measurement Methods from Various Waste Media,” 40 CFR 63, Appendix A.

8. "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards" by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY and the "United States Pharmacopeia."

18. Tables, Diagrams, Flowcharts, and Validation Data

Agency:_____ Inspector:_____
Sample ID#:_____ Date/Time:_____
Source ID:_____
Coating Name/Type:_____
Plant Witness:_____

Type Analysis Required:_____

Special Handling:_____

Sample Container Label

# COATING DATA

Date: _____ Source: _____

| Data | Sample ID No. | Sample ID No. |
|---|---|---|
| Coating:<br>Supplier Name | | |
| Name and Color of Coating | | |
| Type of Coating (primer, clearcoat, etc.) | | |
| Identification Number for Coating | | |
| Coating Density (lbs/gal) | | |
| Total Volatiles Content (wt percent) | | |
| Water Content (wt percent) | | |
| Exempt Solvents Content (wt percent) | | |
| VOC Content (wt percent) | | |
| Solids Content (vol percent) | | |
| Diluent Properties:<br>Name | | |
| Identification Number | | |
| Diluent Solvent Density (lbs/gal) | | |
| VOC Content (wt percent) | | |
| Water Content (wt percent) | | |
| Exempt Solvent Content (wt percent) | | |
| Diluent/Solvent Ratio (gal diluent solvent/gal coating) | | |

# STOCK REFERENCE STANDARD

Name of Reference Material:_____
Supplier Name:_____
Lot Number:_____
Purity:_____

Name of Solvent Material: Dimethylformamide
Supplier Name:_____
Lot Number:_____
Purity:_____

Date Prepared:_____ Prepared By:_____
Notebook/page no.:_____

## Preparation Information

1. Weight Empty Flask: _____,g
2. Weight Plus DMF: _____,g
3. Weight Plus Reference Material: _____,g
4. Weight After Made to Volume: _____,g
5. Weight DMF (lines 2-1+3-4): _____,g
6. Weight Ref. Material (lines 3-2): _____,g
7. Corrected Weight of Reference Material (line 6 times purity) _____,g
8. Fraction Reference Material in Standard (Line 7 ÷ Line 5): _____,g/g soln
9. Total Volume of Standard Solution: _____, ml
10. Weight Reference Material per ml of Solution (Line 7 ÷ Line 9): _____,g/ml

Laboratory ID No. for this Standard: _____

Expiration Date for this Standard: _____

# CALIBRATION STANDARD

Date Prepared: _____ Prepared By: _____
Date Expires: _____ Notebook/page: _____

Calibration Standard Identification No.: _____

## Preparation Information

Final Weight Flask Plus Reagents: _____,g
Weight Empty Flask: _____,g
Total Weight Of Reagents: _____,g

| Analyte name[a] | Stock reference standard ID No. | Amount of stock reference standard added (by volume or by weight) | | | | Calculated weight analyte added, g | Weight percent analyte in calibration standard[b] |
|---|---|---|---|---|---|---|---|
| | | Volume added, ml | Amount in standard, g/ml | Weight added, g | Amount in standard, g/g soln | | |
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[a]Include internal standard(s).

# QUALITY CONTROL CHECK STANDARD

Date Prepared: _____ Prepared By: _____
Date Expires: _____ Notebook/page: _____

Quality Control Check Standard Identification No.: _____

## Preparation Information

Final Weight Flask Plus Reagents: _____,g
Weight Empty Flask: _____,g
Total Weight Of Reagents: _____,g

| Analyte name[a] | Stock reference standard ID No. | Amount of stock reference standard added (by volume or by weight) | | | | Calculated weight analyte added, g | Weight percent analyte in QCC standard[b] |
|---|---|---|---|---|---|---|---|
| | | Volume added, ml | Amount in standard, g/ml | Weight added, g | Amount in standard, g/g soln | | |
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[a]Include Internal Standard(s).
[b]Weight percent = weight analyte added ÷ total weight of reagents.

QUALITY CONTROL CHECK STANDARD ANALYSIS

Date QCCS Analyzed: _____ Analyst: _____

QCCS Identification No. _____ QCC Expiration Date: _____

Analysis Results

| Analyte | Weight percent determined | | | Mean Wt percent | Percent accuracx | Percent RSD | Meets criteria in Section 9.4.6 | |
|---|---|---|---|---|---|---|---|---|
| | Run 1 | Run 2 | Run 3 | | | | Percent accuracy | Percent RSD |
| | | | | | | | | |
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# CALIBRATION OF GAS CHROMATOGRAPH

Calibration Date: _____ Calibrated By: _____

## PART 1. Retention Times for Individual Analytes

| Analyte | Stock standard ID No. | Recorder chart speed | | Distance from injection point to peak maximum | | Retention time, minutes[a] |
|---|---|---|---|---|---|---|
| | | Inches/min. | cm/min. | Inches | Centimeters | |
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[a]Retention time = distance to peak maxima ÷ chart speed.

# CALIBRATION OF GAS CHROMATOGRAPH

Calibration Date:_____ Calibrated By:_____

## PART 2. Analysis of Calibration Standards

Analyte Calib. STD ID No.
____ Calib. STD ID No.
____ Calib. STD ID No.
____
Name:
Conc. in STD
Area Response
RT
Name:
Conc. in STD
Area Response
RT
Name:
Conc. in STD
Area Response
RT
Name:
Conc. in STD
Area Response
RT
Name:
Conc. in STD
Area Response
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Name:
Conc. in STD
Area Response
RT
Name:
Conc. in STD
Area Response
RT
Name:
Conc. in STD
Area Response
RT
Internal Standard
Name:
Conc. in STD
Area Response
RT

CALIBRATION OF GAS CHROMATOGRAPH

Calibration Date: _____ Calibrated By: _____

PART 3. Data Analysis for Calibration Standards

| Analyte | Calib. STD ID ___ | Calib. STD ID ___ | Calib. STD ID ___ | Mean | percent RSD of RF | Is RT within ±0.05 min of RT for stock? (Y/N) | Is percent RSD <30% (Y/N) |
|---|---|---|---|---|---|---|---|
| Name:<br>RT<br>RF | | | | | | | |
| Name:<br>RT<br>RF | | | | | | | |
| Name:<br>RT<br>RF | | | | | | | |
| Name:<br>RT<br>RF | | | | | | | |
| Name:<br>RT<br>RF | | | | | | | |
| Name:<br>RT<br>RF | | | | | | | |

# DAILY CALIBRATION CHECK

Date: _____ Analyst: _____
Calibration Check Standard ID No.: _____
Expiration Date: _____

| Analyte | Retention Time (RT) | | | Response Factor (RF) | | |
|---|---|---|---|---|---|---|
| | Last | This | Difference [a] | Last | This | Difference [b] |

[a]Retention time (RT) change (difference) must be less than ±0.10 minutes.
[b]Response factor (RF) change (difference) must be less than 20 percent for each analyte and for the internal standard.

# SAMPLE ANALYSIS

Vial A ID No.: _____

Vial B ID No.: _____

Analyzed By: _____ Date: _____

Sample preparation information Vial A (g) Vial B (g)

Measured:

wt empty vial

wt plus DMF

wt plus sample

wt plus internal standard

Calculated:

wt DMF

wt sample

wt internal standard

## Analysis Results: Duplicate Samples

| Analyte | Area response Vial A | Area response Vial B | RF | Wt percent in sample Vial A | Wt percent in sample Vial B | Wt percent in sample Average |
|---|---|---|---|---|---|---|

Internal Standard