

PAINT MATERIAL ODOR ASSESSMENT - OLFACTOMETRY

GM9709P

1 SCOPE. This specification covers the requirements for assessing the relative odor potential of automotive paint materials. It includes liquid paint materials that are applied by spraying, electrodeposition primers and solvents. It also includes 3 methods for sample collection and the appropriate use of these methods. Reference GM9832P if a simple "can test" for odor acceptability is required.

1.1 RESTRICTED AND REPORTABLE CHEMICALS (GM1000M). All materials supplied to this specification must comply with the requirements listed in GM1000M, **Restricted and Reportable Chemicals**.

2 REFERENCED STANDARDS.

GM1000M	9984090	AWMA E6
GM9832P	ASTM 679	
9984032	ASTM E544	

3 EQUIPMENT. Equipment requirements are separated into 4 categories: General, Method A, Method B and Method C.

3.1 GENERAL EQUIPMENT.

- Triangular dynamic dilution Olfactometer -- capable of supplying regulated concentrations of sample to the test port at calibrated flow rates.
- Butanol sample bottles from 15 to 2000 ppm with a step factor of 2 for each intensity (8 point scale).
- Tedlar sampling bags with a 10 to 40 L volume capacity or as determined by olfactometer set-up.
- Volumetric flow rate measurement equipment capable of measuring to ± 0.01 L/minute.
- Teflon Tubing - 1/8 and 1/4 inch O.D.
- Thermometer (for ambient temperature).
- Barometer.
- Stop watch.
- Ultrasonic Cleaner.
- Pure nitrogen cylinder.
- Matheson Dual Stage Regulator with 0 to 200 psig delivery pressure range.

3.2 METHOD A EQUIPMENT.

- Dry filter spraybooth.
- Cup guns or pressure pots (.8 to 2 L).
- Rigid container odor sampling lung and evacuation pump.
- Sampling probe with minimum 1/4 inch ID.
- 100 x 300 mm phosphated plain steel panels.

NOTE: Use any 9984032 or 9984090 phosphate.

3.3 METHOD B EQUIPMENT.

- Force-dry, gas-fired oven capable of 200°C (400°F).
- 100 x 300 mm phosphated plain steel panels.

NOTE: Use any 9984032 or 9984090 phosphate.

3.4 METHOD C EQUIPMENT.

- Oven for liquid evaporation - Varian Aerograph Series 1200 Chromatograph or equivalent.
- Digital flowmeter capable of measuring 1 to 2 L/minute with a resolution of 0.001 L/minute (Gilian Primary Standard Airflow Calibrator (Giliblator) or equivalent).
- Teflon tubing with internal diameter of 1/8 inch (0.3 cc).
- Analytical balance capable of weighing 20 grams within 0.0001 g.
- Syringes - 10 and 250 μ L with spare needles. (Hamilton Model 1801RN and Model 1825RN Gastight Syringes or equivalent).
- Ultrasonic Cleaner.
- Septa for GC injection port.

4 TEST PROCEDURE. Basic methodology for sample collection and odor measurement protocol is per guidelines set forth in the AWMA E6 Odor Committee Standard (for Method A). Exceptions and clarifications for GM testing and data reporting are contained in this procedure.

All testing is to be done using a **side-by-side** relative comparison approach. For example, new materials should be compared to the existing materials they intend to replace.

4.1 SAMPLE COLLECTION. All odor samples must be collected using odor-free, chemically inert, nonreactive, low permeability, smooth materials. Line lengths from sampling probe to the sampling bag must be kept to a minimum.

4.1.1 Sample Bags. Bags must be Tedlar with a 10-40 L capacity unless otherwise agreed upon prior to start of test.

4.1.2 Conditioning. Preconditioning must be done with both inert gas and sample gas. Use an agreed upon method.

4.1.3 Replication. Three (3) runs per sample must be done for each collection method.

4.1.4 Documentation. Information requirements are shown in Table 1A and B.

4.2 COLLECTION METHODS. There are 3 methods for collecting odor samples based on the type of material being evaluated.

4.2.1 Method A - Paint Spray Application. This method is used for simulation of relative odor potential of liquid paints that are spray-applied. Sampling for this method is done in the exhaust stack from the booth per Figure 1. Typical materials evaluated are liquid basecoats, clearcoats or primers.

4.2.1.1 Sample Preparation. Reduce paint as required to simulate production or use a production sample at spray viscosity.

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Determine initial paint properties (VOC, weight solids, etc.) and the amount of paint sprayed by both weight and volume.

4.2.1.2 Replication. Spray three 100 x 300 mm panels per run. There should be 3 runs per sample unless otherwise agreed upon.

4.2.1.3 Sampling Time is One Minute. Initiate sampling simultaneously with the initiation of spraying. Sample the exhaust stack continuously during spraying. Specify draw rate in L/minute.

4.2.1.4 Paint Colors. Odor analysis for a new topcoat technology must be done with a minimum palette of White, Medium Red Mica and Light Metallic plus clearcoat. Odor analysis for a new primer-surfacer technology must be done on a minimum of Gray and Red. Specific WAXXXX codes will be agreed upon at test initiation. Testing of additional colors may be required prior to plant implementation, depending on color-to-color solvent variation and plant location.

4.2.2 Method B - Oven Bake. This method is typically used for electrodeposition primer, powder paint, liquid paints that may give off odorous by-products, sealers and adhesives. Materials are baked at upper bake limits and samples are collected from the oven exhaust air per Figure 2.

4.2.2.1 Sample Preparation. Apply target films of Electrodeposition primer or powder. A minimum of 6 panels per run must be used.

4.2.2.2 Sampling Time. Heat oven to upper limit of bake schedule and insert test specimens. Bake for 30 minutes and sample continuously at constant flow rate to the bag.

4.2.3 Method C - Head Space. This method should be used for determining odor threshold of solvents and for screen testing liquid paints for impact of formulation changes. See Figure 3 for equipment layout.

4.2.3.1 Sample Preparation. Paint samples must be at spray viscosity and thoroughly mixed.

4.2.3.2 Test Conditions. For paint samples, the following settings of the gas chromatograph should be used.

Program Mode -- ISO

Injector Temperature -- 45°C (113°F)

Column oven -- oven & fan

Oven Temperature -- 45°C (113°F)

Other Settings -- not used

4.2.3.3 Sample Size. Use 50 µL for paint unless otherwise agreed upon. Quantity of sample should be such that the resulting odor threshold (D/T) is between 50 and 500 OU (odor units). Select a clean syringe in the proper size (250 µL for 50 to 500 µL liquid volume, 10 µL for 10 µL liquid volume) and flush the syringe with the liquid sample at least 3 times.

4.2.3.4 General Procedure. Connect a clean, dry Teflon tube to the gas chromatograph (approximately 0.3 cm OD by 100 cm long). With power on, turn nitrogen cylinder on and adjust the regulator for delivery pressure of about 100 psig. Extract the exact appropriate volume of liquid. Weigh the filled syringe and record the weight as the initial weight.

4.2.3.4.1 Measure the flow rate at the sample line outlet using the Gilibrator. Adjust the cylinder regulator to give a steady flow rate of 0.8 - 1.2 L/minute. Record this as the initial flow rate.

4.2.3.4.2 Connect a cleaned and labeled 30-L Tedlar bag to the outlet of the sample line. Collect some nitrogen and flush the bag. Reconnect the bag to the sample line outlet and start timing immediately. Collect the nitrogen for approximately 2 minutes and inject the liquid sample into the injection port. Allow the needle to reside in the injector port for at least 1 minute to evaporate the droplet at the tip. Re-weigh the syringe and record as the final weight.

4.2.3.4.3 Continue running for 30 minutes with the nitrogen on. Remove the Tedlar bag at the end of the sampling period and record the sampling time.

4.2.3.4.4 Measure the flow rate immediately and record this as the final flow rate. If the difference between initial and final flow rate is greater than 10%, the sample must be discarded and the cause of variance must be ascertained.

4.2.3.4.5 Remove the sample line and flush it with acetone and then distilled water. Then clean it in an ultrasonic cleaner for at least 15 minutes. Reclean with distilled water and dry with clean, dry air.

4.2.3.5 Calculations. The volume of nitrogen used to fill the sample bag is calculated using the average of the initial and final flow rates multiplied by the total sampling time, correcting for temperature and pressure. The concentration of liquid in the sample bag is calculated by dividing the weight of the liquid injected in milligrams by the volume of nitrogen in cubic meters. This concentration, divided by the threshold odor value gives the threshold concentration in mg/m³.

4.3 ODOR TEST PROTOCOL. The time interval between sample collection and odor panel evaluation must be no more than 24 h. As a general practice, analysis should be conducted within 8 h of sample collection.

4.3.1 Panel Selection. Panelists must be screened for sensitivity to n-butanol, which is the reference standard, and trained in the use of olfactometer equipment. Report average sensitivity for each group.

4.3.2 Olfactometer. A dynamic olfactometer should be used in accordance with ASTM 679. Any deviations must be discussed with the appropriate engineer for approval prior to testing.

4.3.3 Flow Rate. The sample gas flow rate must be between 5 and 10 L/minute per sniff port.

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4.3.4 Sample Dilution. The maximum step factor between subsequent concentrations is 2. The same dilution factor must be used for each replicate. Report any variance in step factor from concentration to concentration.

4.3.5 Odor Measurements. The following odor parameters will be determined by measurement or calculation and reported.

4.3.5.1 Dilution to Detection Threshold (D/T_d) Where the Detection Threshold (T_d) is the lowest concentration of an odorant at which an odorized sample can be distinguished from non-odorous air by 50% of the group of observers. NOTE: This may also be referred to as ED_{50} .

4.3.5.2 Dilution to Recognition Threshold (D/T_r) Where the Recognition Threshold, T_r is the lowest concentration of an odorant at which the odor character can be described/characterized by 50% of the group of observers.

4.3.5.3 Odor Unit (OU). An odor unit is the amount of odor produced by a given DILUTION at DETECTION THRESHOLD (D/T_d) by the volume or weight of paint sprayed. Report OU_v and OU_w when using collection Method A. Report ppm by volume when using collection Methods B and C.

4.3.5.3.1 OU_v - Odor units based on volume of paint sprayed in mls for odor sample collection in the stack.

4.3.5.3.2 OU_w - Odor units based on weight in g of paint sprayed for odor sample collection in the stack.

4.3.5.4 Intensity (I). Intensity is the comparison of the odorant strength, T_r of n-butanol in water. Butanol samples are prepared per ASTM E544, Method B on an 8-point scale which starts at a concentration of 15 ppm and goes to 2000 ppm. See Figure 4 for the relationship between the rating scale and the concentration level of n-BUTANOL in water.

4.3.5.5 Odor Character Description. This is a general description of odor using Harper's Scale of odor-quality descriptors as a guide. See Figure 6.

4.4 OTHER DEFINITIONS AND CALCULATIONS.

4.4.1 Dilution Air. The odor-free air used to dilute the odor sample and serve as the blanks against which the samples are judged. The quality of the dilution air must be judged to be odor-free by all panel members and the panel moderator. A typical procedure for obtaining odor-free air is to filter it through a charcoal filter.

4.4.2 Dilution Factor (D). The dimensionless factor based on the ratio of sample flow of an odorous substance into the total flow of a non-odorous substance is introduced into the test chamber. Flows are usually measured in L/minute.

$$D = \frac{\text{Dilution air flow Rate} + \text{Sample air flow Rate}}{\text{Sample air flow rate}}$$

where flow rate is L/minute to the sniff ports.

4.4.3 Dose Response Function. The relationship between odor concentration and intensity as expressed by

Steven's Law is $I = aC^b$, where

I = odor intensity expressed in ppm of butanol in the air using butanol scale units (1 - 8) or equivalent

$C = D/T_r$, where D is the dilution factor and T_r is the odor recognition threshold

a, b = constants specific to each odor, where

a = Y-axis intercept, and

b = Slope of the Dose Response Line

Both a and b are determined by the $\log_{10}$ plot of ODOR INTENSITY (I) in ppm butanol vs. ODOR CONCENTRATION (C) = D/T_r . The dilution to threshold ratio is derived from the olfactometry measurements with the odor panelists. Recognition threshold is determined, compared with butanol concentration and then plotted. To obtain additional points for the plot, concentration of the sample is increased at regular intervals and compared with butanol concentration by the panelists. A minimum of 3 points must be obtained for the plot. A typical plot is shown in Figure 7. The Dose Response Function variables would thus be defined for the material and process under evaluation.

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

6 GENERAL INFORMATION. This is a new specification issued by NAO Paint Engineering in cooperation with Worldwide Facilities Group in December 1997.

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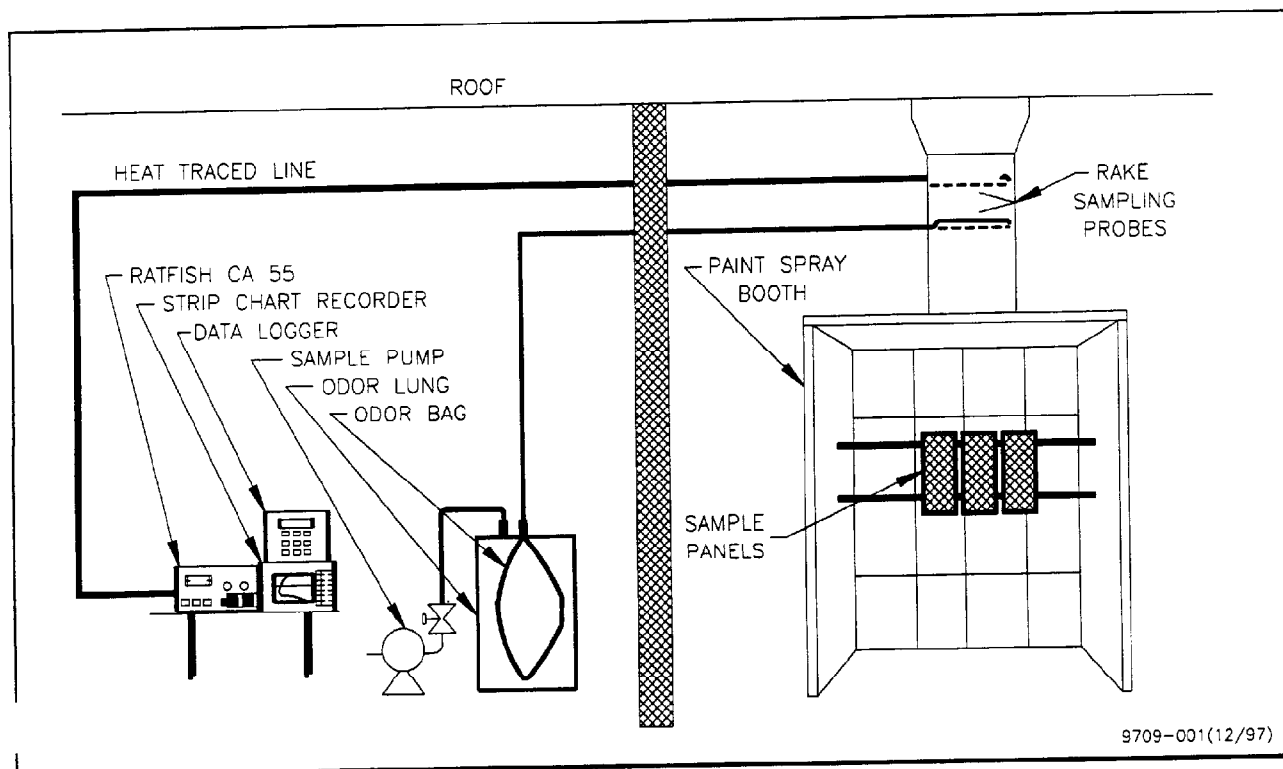


FIGURE 1 - SPRAY BOOTH SAMPLING SCHEMATIC