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SOUTH COAST AQMD Method 319: Determination of Exclusion Status for Compounds in Film-Forming Coatings

1. **Scope and Application**:
   1.1. This method describes a procedure to determine whether a compound should be excluded from the Volatile Organic Carbon (VOC) calculation of film-forming coatings when VOC is determined to be present in a sample using South Coast AQMD Method 313 – Determination of Volatile Organic Compounds (VOC) by Gas Chromatography-Mass Spectrometry/Flame Ionization Detection (GC-MS/FID).
   1.2. This method is intended to discern the film retention of individual compounds, and not mixtures of multiple compounds (e.g. mineral spirits), for exclusion from South Coast AQMD Method 313 (M313) determination.
   1.3. This method uses a range individual candidate compounds from 1% - 5% by weight to determine volatility. Candidate compounds are spiked into individual test matrices and compared to a relative marker. Compounds formulated beyond 5% by weight in products will not be granted exclusion status during M313 analysis.
   1.4. This method does not exhaustively cover the health and safety concerns of each compound that may be determined from this method. Proper laboratory practices for hygiene should be used when handling chemicals of any kind.

2. **Background**:
   2.1. South Coast AQMD Method 313 (M313) utilizes methyl palmitate as a chromatographic endpoint marker for VOC determinations. All compounds which elute prior to methyl palmitate are included in VOC calculations, less any exempted compounds. No chromatographic endpoint marker will perfectly analogize volatility demonstrated during product curing in which a film is formed. AMQD Method 319 is intended to correct discrepancies between chromatographic and gravimetric testing in instances where this discrepancy can be demonstrated to originate from film retainment of a candidate compound.
   2.2. Candidate compounds for which the measured or modeled vapor pressure (based on the US EPA EPI Suite) is lower than or equal to that of Methyl Palmitate, and which also elute before methyl palmitate but are retained in a film-forming coating under current ASTM D2369 conditions (110°C in a forced air oven for one hour) are candidates for exclusion from VOC calculation.
   2.3. Exclusion consideration is granted for a given, tested, coating chemistry. Retainment in film must be demonstrated for at least 3 appropriate matrices, as listed in Appendix 1.
   2.4. Exclusion testing is to be performed first by a requestor external to South Coast AQMD using the "M319 Exemption Nomination" spreadsheet found on South Coast AQMD's website. Once submitted to South Coast AQMD, testing will be confirmed within 90 days and the requestor will be made aware of the status of the nominated compound(s).

2.5. Multiple candidate compounds can be compared at once, but each candidate compound must be spiked independently so as to accurately determine which compounds are uniquely retained.
2.6. South Coast AQMD testing will be conducted on coatings purchased at retail locations, collected from the field, or formulated to AQMD specification by an independent formulator. Samples will be screened for the candidate compound to be evaluated so as to not overload the matrix with a component which is already present in high concentration.
2.7. Compounds granted with exclusion status will receive no changes in treatment during EPA Method 24 (M24) analysis. Excluded compounds will be ignored during M313 analysis. Since these compounds will not be considered *exempt* they will not affect the regulatory VOC concentration of a fully-formulated sample.
2.8. Since exclusions are intended solely to reconcile measurements between M24 and M313 in instances wherein M313 meaningfully "overcounts" VOC respective to M24, exclusions may not be applied in instances where film-retainment is not demonstrated during M24 screening.
2.9. Exemptions for specialty coatings not represented on the list of acceptable matrices in Appendix 1 will be handled on a case-by-case basis as needed. Examples of specialty coatings include, but are not limited to, alkyd and polyurethane based chemistries. Evaluation of special matrices may require that a small amount of un-spiked sample matrix be shipped to South Coast AQMD to confirm results.
2.10. Due to potential changes in formulation, South Coast AQMD will re-evaluate excluded compounds using store-bought matrices at least every ten years to confirm that new formulations are not causing an unforeseen effect on candidate compound evaporation.
2.11. The "M319 Exemption Nomination" spreadsheet and candidate compounds which meet all requirements for M313 VOC determination exclusion will be posted on SOUTH COAST AQMD's VOC website: http://www.aqmd.gov/home/rules-compliance/compliance/vocs

3. **Summary of Method**:
3.1. Mixtures containing 1%, 3%, and 5% by weight of the candidate compound are prepared in an acceptable matrix (see Appendix 1). The reference compound, dibutyl phthalate (DBP) will be prepared in the same manner. The mixtures are prepared in 40 mL glass vials with PTFE lined caps suitable for trace level volatile organic analysis (VOA).
3.2. A matrix blank will be prepared by transferring the sample matrix into a 40 mL VOA vial, and subjecting it to the same handling and procedure as the reference compound and test compound mixtures.
3.3. A preconditioned aluminum pan (Section 6.2) is tared and 0.4000 ± 0.0100 grams of the above prepared mixture is dispensed into the pan via a syringe (see Section 6.5). The mass of the sample mixture dispensed into the pan is obtained by the mass difference of the syringe before and after dispensing prepared mixture. Each mixture level is run in triplicate.

3.4. The pan containing the mixture is then placed in an appropriate forced-air oven (see Section 6.4) where it is heated at 110°C (± 5°C) for 1 hour (± 2 minutes). The pan is subsequently removed from the oven, placed in a desiccator, allowed to reach room temperature, and weighed. The percent Non-Volatile (% NV) is calculated from the mass difference between the sample mixture before and after heating. See Section 10 for detailed calculations.

3.5. Calculated % NV results obtained for the prepared mixtures are evaluated against a mixture containing the reference compound, DBP. If a compound is demonstrated to be less volatile than DBP in the evaluation matrix, the test compound will be further evaluated for potential exclusion at the South Coast AQMD Laboratory. If the test compound is shown to be more volatile than DBP at any test level, the test compound shall no longer be considered for exclusion and should not be sent to South Coast AQMD for confirmation.

4. **Interferences:**

4.1. Use ACS-grade, or equivalent, standards to eliminate variability due to impurities.

4.2. Ensure balance is properly calibrated and capable of providing accurate mass readings within the mass range employed in this analysis. Balance calibration should be performed annually at minimum, and should be QC-checked on each day of use with NIST-traceable weights.

4.3. Ensure that the oven utilized to heat the coatings is within the temperature and flow specifications put forth by ASTM D2369. A properly calibrated thermometer (see Section 6.3) must be used to determine the temperature of the oven. Do not assume that a factory calibration for a thermometer is accurate.

4.4. As this is a weight-by-difference gravimetric test, the use of good laboratory practices is crucial to ensure analytical transfer of the prepared mixtures. Any mixture loss to gloves, bench tops, dripping, etc. will result in highly variable and inaccurate data.

4.5. Candidate compounds must be able to be capable of mixing throughout the test matrix. For instance, extremely hydrophobic compounds in a predominantly water matrix may not remain dispersed evenly enough to dispense the prepared mixture into the pans in a way that will meet reproducibility criteria.

4.6. Test compounds should not be mixed with a matrix with which it is incompatible. For instance acetic anhydride should not be mixed with a sample matrix that contains ethylene glycol, or other hydroxyl-group-containing compounds, as a principle component.

4.7. This test is not applicable for solid and semi-solid compounds that cannot be mixed evenly throughout the sample matrix.

5. **Safety**:

5.1. At a minimum, personal protective equipment. Eye protection, a lab coat, closed toe shoes, and gloves should be utilized while handling chemicals.

5.2. Perform all test compound mixture preparation procedures listed in Section 8 in a properly-operating laboratory fume hood, or equivalent, to avoid exposure to volatile reagents.

5.3. Follow SDS statements and a Chemical Hygiene Plan and/or Laboratory Safety Manual for additional safe handling procedure and disposal requirements.

6. **Apparatus:**
    6.1. Analytical Balance, capable of weighing ± 0.1000 mg.
    6.2. Aluminum Foil Pans, 58mm in diameter by 18 mm in height with a smooth (planar) bottom surface. Pans with inconsistent flatness may lead to sample pooling and irreproducible values. Precondition the pans for 30 minutes in an oven at 110°C (± 5°C). Transfer pans to a desiccator to allow the pans to cool to room temperature before weighing. Preconditioned pans can be stored in the desiccator prior to use. Do not handle pans with bare hands.
    6.3. A calibrated NIST traceable thermometer, or a thermometer calibrated against a NIST traceable thermometer that can accurately read 110°C to with a minimum 0.5 °C graduation.
    6.4. A Forced Draft Oven, Type IIA or Type IIB as described in the current approved version of ASTM E145. The oven must be operating in accordance with Specification ASTM E145 as proper air flow and adequate temperature control ensure satisfactory precision.
    6.5. Disposable 10 mL plastic syringe with cap. A needle and cap may be used if the matrix or test compound viscosity permits.
    6.6. 40 mL glass vials with PTFE lined caps certified to be used for trace level volatile organic analysis.
    6.7. 3 mm glass or ceramic mixing beads.

7. **Reagents**:
    7.1. Dibutyl phthalate (DBP) reference compound, CAS#: 1102-60-7. ACS reagent grade or better.
    7.2. Candidate compounds, ACS reagent grade or better. Compounds must be stored under appropriate conditions to minimize absorption of atmospheric water. Verify that compounds are not expired. It is recommended that compounds that are not freshly purchased for this testing be evaluated for purity by GC-MS prior to use to confirm that compounds have not deteriorated during storage.
    7.3. An acceptable matrix, representative of the product type formulated with the test compound. (Please see notes in Appendix 1).

8. **Procedure:**
    8.1. Place approximately 5 new 3mm glass or ceramic beads into a new, clean 40 mL VOA vial in order to aid in sample homogenization. Seal with a PTFE lined cap and record the mass to the nearest 0.1 mg.
    8.2. Ensure that the matrix is completely homogenized via a mechanical shaker, manual mixing, or a combination of both.
    8.3. Prepare 1%, 3%, and 5% mixtures of the single test compound in the chosen matrix according to preparation instructions outlined in table 9.1.1. Accurate knowledge of the spiked compound concentrations is crucial. Great care must be taken during sample spiking to ensure an accurate mass is obtained. Keep the mixture vial capped at all times, only removing the cap for short periods of time for the addition of the matrix or spiking compound. Prepare only a single set of mixtures for a single compound at a

time in order to minimize sample settling or other loss of spiked mixture homogeneity. (Please see worksheet in Appendix 3.)

8.4. Mixtures must be analyzed the same day that they are prepared in order to minimize random variation due to sample settling and/or loss to headspace. To ensure agreement between labs, re-prepare samples if they are not placed in the over within 2 hours following preparation.

8.5. After mixture preparation is complete, place the capped vial on a vortex shaker (or equivalent high-speed shaker) for a minimum of 1 minute. Shake mixture vial vigorously by hand for 30 seconds to ensure mixing beads do not trap trace amounts of the test compound. Place vial on a vortex shaker for an additional minute. Inspect the spike mixtures for evidence of clumps, layers, or other non-homogeneity. If non-homogeneity is observed, additional mixing may be necessary. If vortex mixing is insufficient to homogenize the mixture, then room-temperature bath sonication should be employed at three minute intervals to homogenize the sample.

8.6. Clearly label a preconditioned aluminum pan (see Section 6.2) in by scribing a unique identifier into the base of the pan. Care must be taken not to add mass to the pan with this identification. Do not puncture or warp the flatness of the pan bottom. Ensure the label will be clearly readable following the addition of the mixture to the pan and subsequent time in the oven. Record the mass of the pan to the nearest 0.1 mg. Remove the aluminum pan from the balance and place on a clean surface free of lint, dust, and particulates. (Example M319 Exemption Nomination Worksheet provided in Appendix 3.)

8.7. Fill a plastic syringe (see Section 6.5) with the 1% mixture and remove any dried or lingering mixture from the syringe tip with a lint free wipe. Recap the tip of the syringe. Withdraw a new aliquot in a new syringe if sample remains in syringe for more than 10 minutes prior to completion of spike level.

8.8. Obtain the mass of the mixture filled syringe to the nearest 0.1 mg and record this mass on the data entry sheet.

8.9. Analytically transfer 0.4000 ± 0.0100 g of mixture into pan from Section 8.5. Note that this is a tighter specimen weight than what is listed in ASTM D2369 in an attempt to limit interferences from small deviations in sample mass added to replicate pans. The mass of the dispensed mixture is obtained by difference in the syringe mass prior to and post mixture dispensing. Do not obtain mixture mass using pan mass differences before and after mixture addition.

8.10. Use the tip of the syringe to continuously and evenly disperse the mixture over the entire flat area inside the pan. An even coating is essential to produce reproducible data. Do not add water or any other solvent to disperse the matrix over the pan as this could potentially lead to adverse matrix effects which negatively impact data reproducibility.

8.11. Record the mass of the syringe after dispensing mixture to the nearest 0.1 mg.

8.12. Set complete pan aside and repeat steps 8.5-8.10 for two additional pans (totaling three pans per mixture percent level). Wipe the tip of the syringe between replicates to remove any dried or lingering mixture.

8.13. After completing preparation of all 3 replicates for a single mixture level, place all 3 pans in the 110°C (± 5°C) oven (see Section 6.4). Record the time the pans were placed into the oven.

8.14. Remove pans from the oven after 1 hour (± 2 minutes). Place pans in a clean desiccator, and allow pans to cool to room temperature (approximately 10 minutes). Record the time the pans were removed from the oven.
8.15. After the pans have been cooled to room temperature, record the mass of each individual pan containing the mixture residue. Record the time and date of mass collection.
8.16. Repeat steps 8.5-8.15 for the remaining 3% and 5% levels.
8.17. Calculate the % NV for all pans following the equations in Section 10. Record the calculated values for each pan.
8.18. Calculate the average % NV for each weight percent mixture as well as the matrix blank, and record these values.
8.19. Perform statistical analysis described in Section 11.
8.20. Repeat steps 8.1 through 8.18 for each individual candidate compound. DBP is the reference standard and is therefore a required test compound.
8.21. Repeat steps 8.1 through 8.18 (omitting the addition of a test compound to the matrix used in step 8.3) to perform the analysis on an unspiked matrix blank.

9. **Standards**:

9.1. Prepare test mixtures according to the following table. Only a single compound is used to prepare the test mixtures. A list of the appropriate test matrices can be found in found in Appendix 1.

Table 9.1.1 Spiked Mixture Preparation Criteria

	1% Mix	3% Mix	5% Mix	Matrix Blank
Mass of matrix (g):	29.7000 ± 0.0100	29.1000 ± 0.0100	28.5000 ± 0.0100	30 ± 0.0200
Mass of test compound (g):	0.3000 ± 0.0100	0.9000 ± 0.0100	1.5000 ± 0.0100	0

10. **Calculations**:

10.1. Calculate the percent volatile matter, *V*, in the samples as follows:

$$V_A = 100\left[\left((W_1 - W_2)/S_A\right) \times 100\right] \quad (1)$$

where
V_A = % volatiles (first determination),
W_1 = weight of dish,
W_2 = weight of dish plus specimen after heating in the oven,
S_A = specimen weight (this is the difference in sample syringe weight)
V_B = % volatiles (duplicate determination, calculate in same manner as V_A), and
V_C = % volatiles (triplicate determination, calculate in same manner as V_A and V_B.

$$V = (V_A + V_B + V_C)/3 \quad (2)$$

10.2. The percent of non-volatile matter, % *NV*, in the coating may be calculated by difference as follows:

$$\% NV = (N_A + N_B + N_C)/3 \quad (3)$$

where:
$N_A = 100 - V_A$,
$N_B = 100 - V_B$, and
$N_C = 100 - V_C$

N_A represents first determination, N_B represents duplicate determination, and N_C represents triplicate determination.

10.3 Report *N*, the mean of the triplicate determination if relative percent difference (see Section 11.1) of the highest and lowest value is 1.5 % or less. If the relative difference between these values is greater than 1.5 %, repeat the triplicate determinations.

11. **Quality Control and Statistical Evaluation**:

11.1. Disruption of film formation: prior to collecting final weights for each spiked pan, the analyst must check each pan to determine if spiking has caused a matrix disruption that creates deviations from the film-formation demonstrated in the blank matrix.

11.2. Relative Percent Difference (RPD) calculation: The calculation of the relative percent difference is the absolute value of the difference of the highest and lowest % NV divided by the average of the highest and lowest % NV. This ratio is then multiplied by 100 to generate a percent value.

$$RPD = \left[\frac{|N1 - N2|}{\left(\frac{(N1 + N2)}{2}\right)}\right] * 100$$

Where:
N1 = Highest % NV value of triplicate.
N2 = Lowest % NV value of triplicate.

11.2.1. Data is acceptable for the triplicate analysis of DBP, test compounds, and the method blank if the RPD is less than or equal to 1.5%.

11.2.2. If any QC failure occurs for a given test level, the level must be re-made and re-analyzed. If there are multiple RPD failures for a candidate compound then a root cause for the failure should be investigated.

11.2.3. Record physical observations if there is physical deviations from the matrix blank or between candidate concentration levels.

11.3. Comparison to DBP:

11.3.1. After the RPD is calculated for each triplicate run and passes RPD requirements, the test compounds will be compared to DBP. If all of the test compound percent levels have a higher average % NV than DBP then this compound will be viewed as a potentially excluded compound and can be nominated as an excluded compound for South Coast AQMD to further evaluate.

11.3.2. Test compounds can fall below concentration of DBP and also be a candidate to pass, so long as the determined % NV value is within 1.5% RPD of DBP for each spiked level.

11.3.3. If the test compound average % NV is lower than DBP and outside of 1.5% RPD for any spike concentration for any of the tested matrices, the compound will not be considered for exclusions status and will remain designated as VOC content.

11.4. The spreadsheet containing all data and results can be emailed to the South Coast AQMD Laboratory email address, after which staff will contact the requestor to confirm the submittal. A list of compounds evaluated by South Coast AQMD will be placed on South Coast AQMD's website, along with each compound's exclusion assessment. AQMD's VOC website can be found at the following address: http://www.aqmd.gov/home/rules-compliance/compliance/vocs

12. **Sources**:

- ASTM D2369 Standard Test Method for Volatile Content of Coatings
- ASTM D 2369-81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.
- EPA Method 24: Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings.
- ASTM E145-94(2011) Standard Specification for Gravity-Convection and Forced-Ventilation Ovens

Appendix 1

Acceptable Matrices:

a. Flat latex paint
b. Non-flat latex paint
c. Emulsion resin (formulation requirements forthcoming)

Appendix 2

Example Prep sheet:

Analyst Name: _____
Date: _____

Lab Number: _____
Test Counter: _____

Matrix Description: _____
Test Compound Description: _____

Instruments: _____
_____
_____

References: _____

Description	Actual Mass (g)	Net Mass
Mass of 40 mL VOA Vial + Beads:		
Mass of VOA vial + Beads + matrix:		
Mass of VOA + Beads+ matrix + Compound:		

Appendix 3

Example Test Compound Analysis Sheet:

Analyst Name: _____
Date: _____

Lab Number: _____
Test Counter: _____

Time In: _____
Time Out: _____

Method: _____

Matrix Description: _____
Test Compound Identification: _____

Instruments: _____
_____
_____

References: _____

Oven Temperature: 110 °C
Dispersant solvent: None

Pan ID:	Pan #1	Pan #2	Pan#3
Syringe + Sample (g):			
Syringe - Sample (g):			
Sample Mass(g):			
Pan + Residue (g):			
Pan mass(g):			
Dried Residue (g):			
Non-Volatile (wt%):			
Average NV (wt%):			
QC Check:			
QC allowances:			
Test Status:			