Feb. 20th, 2020 Draft

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

1. **Scope and Application**:
   1.1. This method is used to determine whether a compound can be excluded from the Volatile Organic Carbon (VOC) calculation of film-forming coatings when it 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) (M313).
   1.2. This method is intended to discern the film retention and exclusion status of individual compounds, not mixtures of multiple compounds (e.g. mineral spirits).
   1.3. This method uses a range of 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 excluded from VOC characterization during M313 analysis.
   1.4. This method does not exhaustively cover the health and safety concerns of each compound that may be utilized with 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 determination. All non-exempt compounds which elute prior to methyl palmitate are deemed to be volatile and are calculated as VOC. No chromatographic endpoint marker will perfectly analogize volatility taking place during product cure in film-forming products. South Coast AQMD 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. Dibutyl Phthalate (DBP) is utilized as a surrogate for methyl palmitate (MP) for Method 319 as MP is not miscible with most coatings or resins. DBP is less volatile than MP and elutes after MP in Method 313.
   2.3. Candidate compounds for which the measured or selected modeled vapor pressure (based on the US EPA EPI Suite) is below the threshold listed in Section 3.1, but which are retained in a film-forming coating under ASTM D2369 conditions (110°C in a forced air oven for one hour) may be evaluated for exclusion from VOC classification within M313.
   2.4. Exclusion consideration is granted for a given, tested coating chemistry. Retainment in film must be demonstrated by stakeholders for each candidate compound in at least 3 appropriate matrices per chemistry, as listed in Appendix 1.
   2.5. Exclusion testing is to be performed first by a requestor external to South Coast AQMD using the "M319 Exclusion 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).

2.6. 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 to not overload the matrix with a component which is already present in high concentration.

2.7. Multiple candidate compounds can be analyzed contemporaneously; however, each candidate compound must be spiked independently to accurately determine which compounds are uniquely retained.

2.8. Compounds granted 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.

2.9. Exclusions for coating chemistries not represented on the list of acceptable matrices in Appendix 1 will not be granted until M319 is validated for these materials. Chemistries for which this method is currently not suitable include alkyd and polyurethane coatings.

2.10. Due to potential changes in sales trends and/or product formulations, South Coast AQMD may re-evaluate testing matrices for ongoing suitability. Re-evaluation may result in replacement of old matrices with more matrices more appropriate for current sales and technology trends. Matrix changes may necessitate confirmation testing to determine whether new product formulations reduce film retainment of previously excluded compounds.

2.11. The "M319 Exclusion Nomination" spreadsheet and candidate compound pass/fail exclusion status 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. Before any candidate compounds are analytically evaluated ensure that the candidate compound's measured vapor pressure is less than or equal to $1.0x10^{-4}$ mmHg at 25 °C. If no measured vapor pressure is available for the candidate compound, the "selected" modeled vapor pressure from the U.S. EPA EPI Suite may instead be utilized. The candidate compound must have a "selected" modeled vapor pressure below $1.0x10^{-3}$ mmHg at 25 °C. If the candidate compound exceeds the vapor pressure limit for either the measured or modeled vapor pressure, the candidate compound is rejected from further testing. See appendix 4 for a flowchart of the candidate compound exclusion process.

3.2. Mixtures containing 1%, 3%, and 5% by weight of the candidate compound are prepared in an approved 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).

3.3. 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 candidate compound mixtures.
3.4. 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.
3.5. 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.
3.6. 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 candidate compound will be further evaluated for potential exclusion at the South Coast AQMD Laboratory. If the candidate compound is shown to be more volatile than DBP at any test level, the candidate compound shall no longer be considered for exclusion and should not be referred to South Coast AQMD for confirmation testing, though it is appreciated if the failure can be passed along to South Coast AQMD so that stakeholder efforts are not duplicated elsewhere.

4. **Interferences:**
4.1. Use ACS reagent 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. This test is not applicable for solid and semi-solid candidate compounds or compounds that cannot otherwise be mixed evenly throughout the sample 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. Candidate compounds should not be mixed with a matrix with which it is incompatible or reactive. 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.

5. **Safety**:
   5.1. Eye protection, a lab coat, closed toe shoes, gloves, and all other appropriate PPE should be utilized while handling chemicals.
   5.2. Perform all candidate 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, 58 mm 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 candidate 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#: 84-74-2. 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 candidate compound. (Please see notes in Appendix 1).

8. **Procedure:**
   8.1. Place approximately 5 new 3 mm 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 candidate 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. (see 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 oven within 2 hours of preparation.
   8.5. After matrix spiking 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 candidate 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 is necessary. If vortex mixing is insufficient to homogenize the mixture, then room-temperature bath sonication should be employed at three-minute intervals until sample is homogeneous.
   8.6. Clearly label a preconditioned aluminum pan (see Section 6.2) by lightly 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 Exclusion 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 coating over the pan as this could potentially lead to adverse matrix effects which may negatively impact data reproducibility.
8.11. Record the mass of the syringe to the nearest 0.1 mg after dispensing mixture.
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 blank and 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. 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 candidate compound.
8.21. Repeat steps 8.1 through 8.18 (omitting the addition of a candidate 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 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	30.0000 ± 0.0200
Mass of candidate 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:

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

where
V_A = % volatiles (first determination),
W_1 = weight of dish plus specimen,
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.

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

$$\%\, NV = (N_A + N_B + N_C)/3 \quad (2)$$

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 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 determination.

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. These matrix disruptions include, but are not limited to beading, bi-layer formation, gross separation from the pan, etc.

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.

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

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, candidate 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 are physical deviations from the matrix blank or between candidate concentration levels.

11.3. Comparison to DBP:

11.3.1. The average %NV of each concentration level of a candidate compound will be compared to the % NV for the corresponding concentration of the DBP-spiked matrix. If the % NV for a candidate compound is higher than or equal to the average % NV of DBP for every spike level in every matrix, then this compound will be viewed as a potentially excluded compound and may be referred to South Coast AQMD for confirmation testing.

11.3.2. Candidate compound % NVs can fall below that of DBP and be referred to the South Coast AQMD Laboratory so long as the determined % NV value in each test matrix is within 1.5% RPD of DBP for each spike level.

11.3.3. If the candidate compound average % NV is lower than DBP and exceeds 1.5% RPD for any spike concentration in any of the tested matrices, the compound will not be considered for exclusion 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. It is requested that data for both passing and failing candidates be submitted to South Coast AQMD to make failures public and prevent duplication of effort by stakeholders.

12. **Sources**:

- ASTM D2369 Standard Test Method for Volatile Content of Coatings
- ASTM D2369-81, 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

Approved matrices and matrix selection guidelines

Acceptable Emulsion Coating Matrices [1]:

1. 100% Acrylic Resin: Rhoplex VSR 5102 Resin
2. 100% Acrylic Formulated Non-Flat: Behr Marquee Exterior Semi-Gloss Enamel (Ultra-Pure White 5450)
3. PVA: Sherwin Williams PVA Drywall Primer & Sealer (White B28 W 8010 • 6510-83263)

This space is reserved for additional coating families, pending their validation.

Matrix selection guidelines

Matrices should be selected based upon current sales trends within each coating family. Selected matrices should include a representative from the highest-selling resin chemistry, that same resin type in isolation, and a second fully formulated product that sells in high volume but contains a different resin chemistry.

Resins are also desirable for this process as they are likely to be available for longer periods of time than fully formulated products. When selecting between multiple viable matrices, the preferable selections will have a solid content between 40 - 60% by weight, and a neutral pH to not produce incompatibilities with the aluminum pans used during testing. Matrices should have material VOC concentration of 150 g/L or less, as higher VOC products will not be reflective of those analyzed by M313.

When possible, it is best to avoid matrices that already contain a meaningful concentration of potential candidate compounds. Special consideration should be given to tinting either of the two fully formulated products in the matrix set, as colorants may also contain candidate compounds which make analysis results more difficult to assess.

Please contact South Coast AQMD if a required matrix is no longer available for purchase so that a suitable replacement may be identified.

[1] Approved emulsion exclusions will be applied to acrylic and acrylic-vinyl blends. 100% acrylic, styrene acrylic, vinyl acetate, and vinyl acetate ethylene are included in these categories.

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 Vial + Beads+ matrix + Compound:		

Appendix 3

Example Candidate compound Analysis Sheet:

Analyst Name: _____
Date: _____

Lab Number: _____
Test Counter: _____

Time In: _____
Time Out: _____

Method: _____

Matrix Description: _____
Test Compound Identification: _____

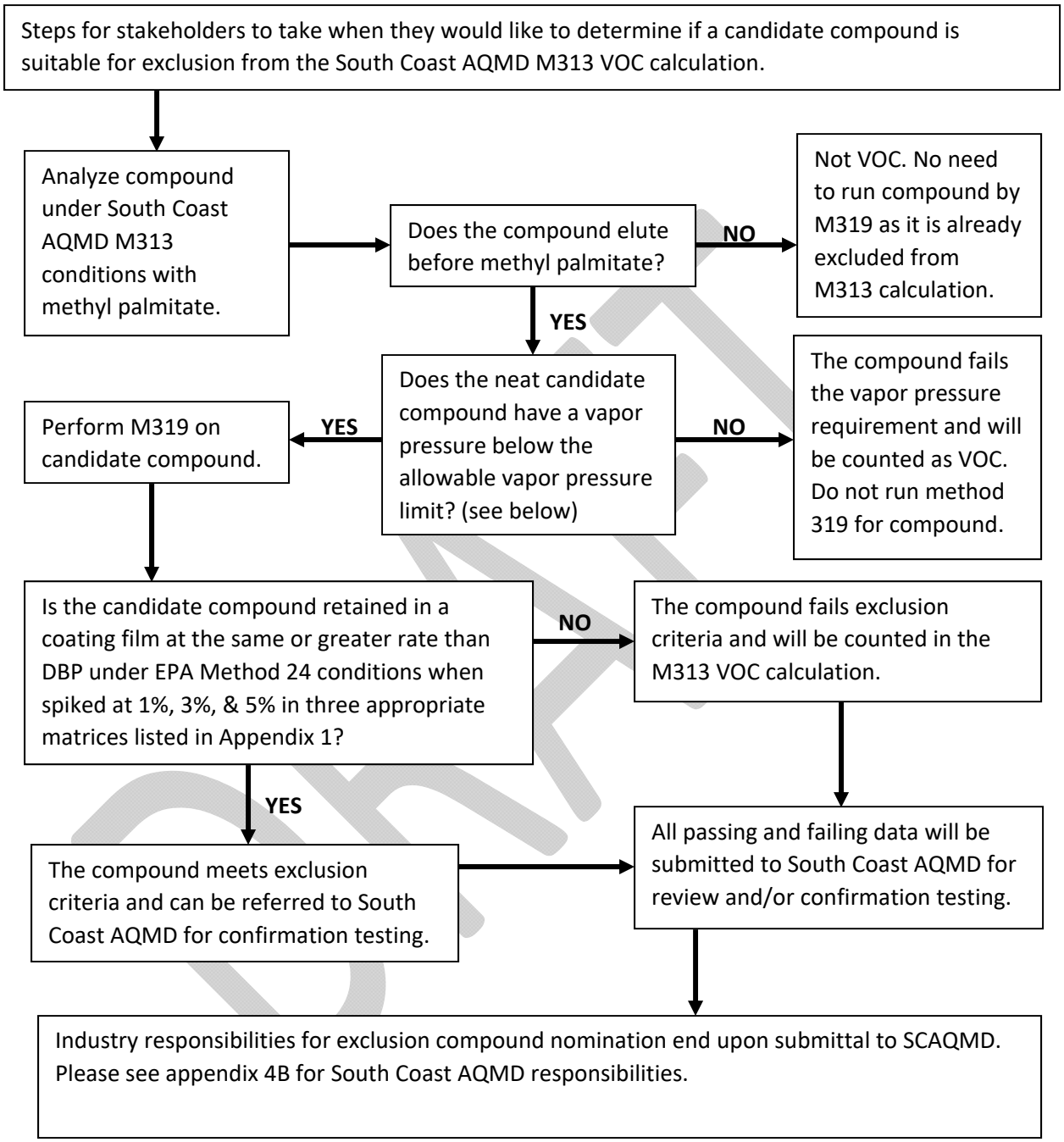
Instruments: _____
_____
_____

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:			

Appendix 4A: Industry Responsibilities



1. Vapor Pressure limits:
    a. Measured vapor pressure threshold: 1.0×10^{-4} mmHg at 25 ˚C.
    b. Modeled vapor pressure threshold: 1.0×10^{-3} mmHg at 25 ˚C.
    c. Measured threshold takes priority when measured and modeled values are both available.
2. SCAQMD will provide an excel calculation template named “M319 Exclusion Pathway Template” on the VOC working group webpage: here.

Appendix 4B: South Coast AQMD Responsibilities