



# SCAQMD VOC Test Methodology Working Group

## Preliminary Compound Exclusion Concepts

Derived from February 27, 2014 meeting

**Objective:** Provide industry with guidance to develop a detailed test method and to reach consensus agreement amongst its members on a single test method that can be approved by SCAQMD and EPA to exclude early eluting compounds that are less volatile than methyl palmitate.

**Background:** EPA Method 24 does not adequately and accurately characterize paints, varnishes, lacquers, or other related surface coatings with low-VOC content. SCAQMD has developed and refined Method 313 with a methyl palmitate endpoint capable of accurately and reproducibly determining the VOC content of low-VOC products. SCAQMD is open to considering a procedure for identifying compounds with a Method 313 elution time prior to that of methyl palmitate that might not be volatilizing into the air during test conditions. This should be done in a manner that considers equivalency to Method 24.

For SIP and air district specific regulatory requirements, the suggested path forward is a transition to a gas chromatography (GC) method (SCAQMD Method 313), with the methyl palmitate endpoint marker for low-VOC coatings (less than 150 g/L VOC of material), and the exclusion of formulation compounds and additives that are less volatile than methyl palmitate but elute earlier on a GC. In addition, investigate further restricting the potential list of compounds for exclusion to those compounds that primarily remain in a representative film.

### 1 Pre-screening for Neat Compounds

Objective: to determine if the early eluting compound of interest is less volatile than methyl palmitate

- 1.1 Use Method 24 or alternate evaporative test method.
- 1.2 Demonstrate an alternate evaporative test method:
  - 1.2.1 Experiment with thermogravimetric analysis (TGA), as it is more controlled.
  - 1.2.2 Experiment first with different TGA parameters at 110°C, including gas flow rates, sample size, and pan configurations.
  - 1.2.3 Because air is the typical matrix for paints and coatings, it should be the default choice for evaporative testing. Other gases may be used on approval with justification.
  - 1.2.4 Demonstrate that the selected conditions generate methyl palmitate to be at an average value between 30% to 70% nonvolatile with the precision (of the generated average NV) within  $\pm 10\%$  relative.
- 1.3 Establish a single consensus method and perform laboratory repeatability tests by analyzing seven replicates of methyl palmitate over at least three days for either Method 24 or alternate test method.
- 1.4 The selected method will be reviewed, and if found to be acceptable, approved by SCAQMD/EPA.
- 1.5 Methyl palmitate must be tested under the same conditions and at the same time or within the same calibrated sequence as the candidate compound.
- 1.6 % Nonvolatile must match or exceed the average methyl palmitate result determined during sample analysis.
- 1.7 Compound of interest must be tested by independent external laboratory(s) and the raw laboratory data submitted with the exclusion request.
- 1.8 Two duplicate analyses (4 total measurements); SCAQMD/EPA will propose acceptance criteria of within  $\pm 10\%$  relative for the duplicates.
- 1.9 Early eluting candidate compounds for exclusion will be verified by SCAQMD laboratory prior to exclusion.



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### 2 Subsequent testing on fully formulated coatings<sup>1</sup>

Objective: to study if the early eluting compound of interest remains in the paint film to a greater extent than dibutyl phthalate<sup>2</sup>

- 2.1 Experiment with a laboratory formulated 'zero'-VOC paint. The test matrix should be typical of interior wall paint. The formulation is subject to SCAQMD and EPA approval. The formulation for the 'zero'-VOC paint must be included in the protocol and final test report and available for review.
- 2.2 Demonstrate the film extraction method.
  - 2.2.1 Add dibutyl phthalate in concentrations between 0.5% to 1%, which is both typical and detectable.
  - 2.2.2 Prepare paint films using ASTM D2369-10 conditions.
  - 2.2.3 If films are successively withdrawn for extraction, the dibutyl phthalate recoveries should ideally occupy the average concentration range from 50-80% with the average recovery having a precision within  $\pm 10\%$ .
  - 2.2.4 Solvents and solvent combinations, and extraction conditions may be optimized, but the final procedure should reference 1 or 2 specific solvents or solvent pairs, and only one extraction procedure. The extraction solvent must be specified for each compound of interest.
  - 2.2.5 Finalize method and perform laboratory repeatability by performing seven film preparations and extractions over at least three days.
  - 2.2.6 Method to be reviewed, and if found to be acceptable, approved by SCAQMD/EPA.
- 2.3 Add dibutyl phthalate and candidate compound to the test matrix, prepare paint films according to the approved procedure. Perform paint film extraction at 20, 40, and 60 minutes to determine if there is trend/data linearity.
- 2.4 The percent retained must match or exceed the percentage of dibutyl phthalate retained at one hour.
- 2.5 Candidate compounds to be verified by an independent external laboratory and the raw laboratory data submitted with the exclusion request.
- 2.6 Early eluting compounds will be verified by SCAQMD laboratory prior to exclusion.

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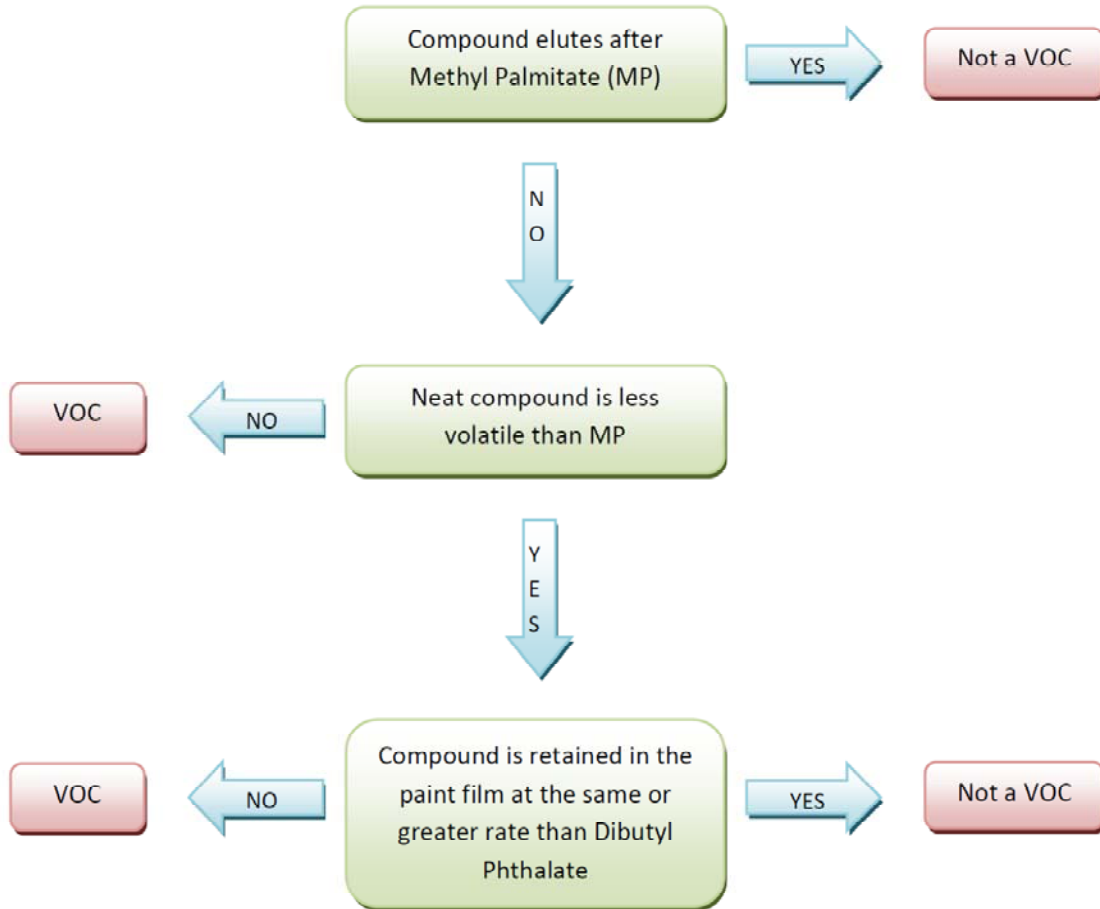
<sup>1</sup> Provided preliminary results are reproducible and validated through multi-laboratory study.

<sup>2</sup> Dibutyl phthalate was suggested as a material with a similar volatility as methyl palmitate, which elutes after methyl palmitate, and therefore is defined as a nonvolatile per SCAQMD Method 313. Dibutyl phthalate is a compound that is used in paint and coatings (unlike methyl palmitate) and therefore should be readily accepted into the coating matrix.



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3 Preliminary Compound Exclusion Concepts Flowchart



A compound will either be determined as a VOC or non-VOC by the method. There is no “semi-volatile or partially volatile” category for any compound. A compound must be determined as a non-VOC by both the “evaporative” and “film extraction” tests to be considered for classification as an Early Eluting Nonvolatile compound.

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