SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

Test Method Guidance Document

Rule 1168—Adhesive and Sealant Applications

FINAL

October 2018

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Introduction

During the 2017 rule amendment to Rule 1168 – Adhesive and Sealant Applications, staff was directed to work with stakeholders, manufacturers, and other regulatory agencies to develop a Volatile Organic Compound (VOC) Test Method Guidance Document to clarify which test method will be used to measure VOC content for compliance verifications.

Background

Rule 1168 was adopted in 1989 to control VOC emissions from adhesive applications. Since adoption, there have been 14 amendments to the rule. Rule 1168 was originally only applicable to adhesives and it regulated 19 types of adhesives. In 1998, the rule was expanded to regulate six types of sealants and five types of sealant primers. The current rule regulates 37 types of adhesives, five types of adhesive primers, 12 types of sealants, and five types of sealant primers. As the rule expanded and new types of adhesives and sealants were developed, the test methods in the rule also had to be updated to be applicable for the new types of regulated products.

Test methods were also included to identify and measure the concentration of VOCs classified as exempt compounds. The United States Environmental Protection Agency (U.S. EPA) exempts organic compounds with negligible atmospheric reactivity, less than or equal to ethane, from the regulatory definition of a VOC.[1] The SCAQMD further evaluates these exempt compounds for any potential adverse environmental or heath impacts prior to including an exemption in SCAQMD Rule 102 – Definition of Terms[2]. Rule 102 divides exempt compounds into two categories: Group I and Group II. Group II compounds are considered toxic, potentially toxic, upper-atmosphere ozone depleters and/or cause other environmental impacts, while Group I compounds are not currently known to be toxic. Rule 1168 includes a general prohibition against the use of Group II exempt compounds greater than 0.1 percent by weight. Test methods are needed to identify any Group I or Group II compounds in the regulated products.

The following is the history of the changes and additions to the test methods in Rule 1168.

Original Rule

- Referenced Laboratory Methods of Analysis for Enforcement Samples where the VOC test method was SCAQMD Method 304- *Determination of Volatile Organic Compounds (VOC) in Various Materials* [3], which is a straightforward, gravimetric method that determines the VOC content based on weight loss.

1992 Amendment

[1] See *Appendix B – Calculating the VOC of Product and the VOC of Material* for further information.
[2] http://www.aqmd.gov/docs/default-source/rule-book/reg-i/rule-102-definition-of-terms.pdf
[3] http://www.aqmd.gov/docs/default-source/laboratory-procedures/methods-procedures/304-91.pdf

- SCAQMD Method 305 – *Determination of Volatile Organic Compounds VOC in Aerosol Applications*[4] was included for determining the VOC content of aerosol adhesives.

- U.S. Environmental Protection Agency (EPA) Reference Method 24 (M24) - *Determination of Volatile Matter Content, Water Content, Density Volume Solids, and Weight Solids of Surface Coating*, was also included. M24 is the EPA equivalent test method to SCAQMD Method 304. Going forward, this Guidance Document will reference M24 instead of M304 as M24 is more routinely cited and employed by most stakeholders.

- SCAQMD Methods 302 – *Distillation of Solvents from Paints, Coatings and Inks*[5] and 303– *Determination of Exempt Compounds*[6] were included to determine the exempt compound concentration.

- SCAQMD Method 316A – *Determination of Volatile Organic Compounds VOC in Materials Used for Pipes and Fittings*[7] was included to measure the VOC content of PVC, CPVC, and ABS pipe cements. Method 316A was developed by industry to more closely replicate the field application of pipe cements, which traps some VOC emissions between the pipes, compared to M24 where the product is placed in an oven in an open weighing dish. The method was vetted by the SCAQMD laboratory prior to inclusion in Rule 1168.

1998 Amendment

- ASTM International (ASTM) Method D4457-85 - *Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph* was added as a viable alternate to SCAQMD Methods 302 and 303 for exempt compound analysis.

2000 Amendment

- SCAQMD Method 316B – *Determination of Volatile Organic Compounds VOC in Adhesive containing Cyanoacrylates*[8] was added as a specific test method for cyanoacrylates, which was a new category at that time. This test method was developed by Loctite Corporation and is a modification of SCAQMD Method 316A where the adhesive is applied between two substrates (heavy duty aluminum foil) instead of between two pieces of pipes as used in Method 316A. The intent of the method is to more accurately reflect how the product is applied and reacts in the field.

2017 Amendment

- Appendix A to Subpart PPPP of 40 CFR Part 63 (Subpart PPPP) – *Determination of Weight Volatile Matter Content and Weight Solids Content of Reactive Adhesives* was included for reactive adhesives. This method is similar to Method 316B for cyanoacrylates because the

[4] http://www.aqmd.gov/docs/default-source/laboratory-procedures/methods-procedures/305-91.pdf
[5] http://www.aqmd.gov/docs/default-source/laboratory-procedures/methods-procedures/302-91.pdf
[6] http://www.aqmd.gov/docs/default-source/laboratory-procedures/methods-procedures/303-91.pdf
[7] http://www.aqmd.gov/docs/default-source/laboratory-procedures/methods-procedures/316a-92.pdf
[8] http://www.aqmd.gov/docs/default-source/laboratory-procedures/methods-procedures/316b-92.pdf

adhesive is 'sandwiched' between two substrates, but a larger quantity of adhesive is used in Subpart PPPP. Cyanoacrylates (also known as instant glue, power glue or superglue) are applied in very small quantities, Subpart PPPP is appropriate for a wider variety of reactive adhesives applied at higher film thicknesses.

- SCAQMD Method 313 (M313) - *Determination of Volatile Organic Compounds VOC by Gas Chromatography-Mass Spectrometry*[9] and ASTM D6886 (M6886) - *Standard Test Method for Determination of the Weight Percent Individual Volatile Organic Compounds in Waterborne Air-Dry Coatings by Gas Chromatography* were also included in Rule 1168. These methods are an improvement to M24 for low-VOC products. M24 is a rigorous test method that provides accurate and reliable results when measuring the VOC content of many products regulated by Rule 1168 but there is inherent variability when employing M24 to analyze the VOC content of low-VOC or near-zero VOC products. M24 indirectly determines the VOC content by measuring the water, the non-volatile, and the exempt compound content and assumes everything else is a VOC. When the water, non-volatile, and exempt compound fractions approach 100 percent of the product, small errors in the measurements can lead to large errors in the final VOC result. M313 and M6886 directly measure the VOC content by diluting the product in solvent and injecting it onto a Gas Chromatography-Mass Spectrometry (GC/MS), yielding far greater precision in determining VOC content for low-VOC products. Significant drawbacks of these methods are they are time consuming and expensive to perform. For that reason, these methods are only employed where M24 loses precision, i.e. products with a VOC content of less than 150 g/L. The other limitation is these methods are only applicable to non-reactive products because the dilution step would prevent the components from reacting. For compliance purposes, the SCAQMD laboratory will rely on the more rigorous M313. Appendix A of this Guidance Document explains the differences between the two methods so a manufacturer utilizing M6886 will be aware of how their results could differ from results obtained by the SCAQMD laboratory using M313.

Looking toward future VOC test method development, the 2017 amendment included a category for foam sealants, which does not have test methods developed yet. In addition, staff was made aware of high-pressure single component adhesives that also do not have an approved test method. These products are still required to comply with the current and future VOC content limits in Rule 1168 and staff is working with industry to develop appropriate test methods. Until a test method is developed, formulation data will be used for compliance verification.

Test Method Determination

Rule 1168 applies to diverse products and chemistries, and many products are analyzed by a series of test methods to determine the most appropriate test method. The decision is based on product type (adhesive or sealant, one-part or two-part, reactive products or non-reactive), VOC content, and the specific chemistry (energy curable products, cyanoacrylate adhesives) if applicable. For

[9] http://www.aqmd.gov/docs/default-source/laboratory-procedures/methods-procedures/313-91.pdf

some products, the choice of test methods is obvious, such as PVC Welding Cement is always analyzed by SCAQMD Method 316A. For other products, however, a multi-step process is needed to determine the most appropriate VOC test method. Some test methods specifically state that a certain type of product or chemistry is not compatible or applicable for that method, then that type of product or chemistry will not be tested according to that method. Examples include SCAQMD Method 313, which specifically states it is not to be used for Ultraviolet/Electron Beam (UV/EB)-cured coatings, and Subpart PPPP of 40 CFR Part 63, which states it is not appropriate for one-part moisture cured urethane adhesives. Ultimately, there is only one VOC method that is most appropriate for each product and this Guidance Document will serve to clarify that for the regulated community.

The following discussion addresses the different types of products that are subject to this rule. It does not address each individual product category, but organizes them by their chemistry, use, and application method.

Adhesives

Pipe and fitting cements and cyanoacrylates have very specific test methods included in the rule that were developed to mimic the way these products are used in the field. Pipe cements are analyzed by SCAQMD Method 316A, which requires the adhesive to be applied to actual pipes, welded together and placed in the oven to drive off the VOCs. Cyanoacrylates are analyzed by SCAQMD Method 316B, which requires a small amount of adhesive **(Figure 1)** to be applied between two pieces of aluminum foil **(Figure 2)**, clamped together **(Figure 3)** prior to being placed in the oven.

Figure 1

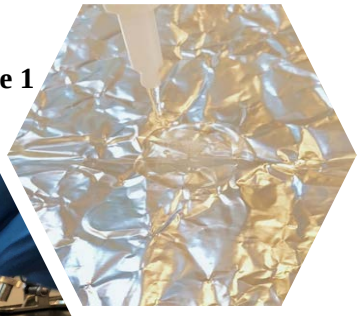
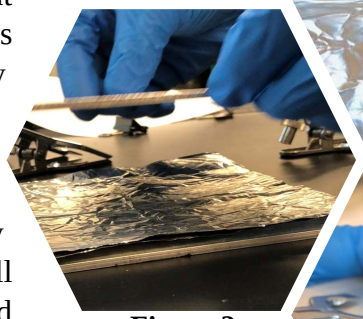


Figure 2



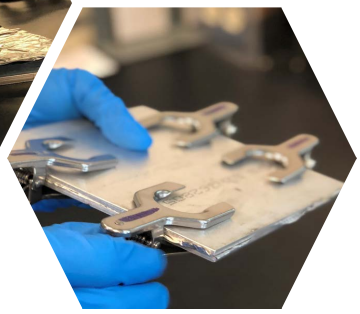


Figure 3

Energy curable adhesives are formulated with reactive components and in the case of UV or light-emitting diode (LED) applications, photoinitiators. The materials react when exposed to energy (UV/EB/LED). Unreacted, these monomers would be measured as a VOC. These types of products can be composed of a thin film or non-thin film. M24 includes ASTM D5403 - *Standard Test Methods for Volatile Content of Radiation Curable Materials*, which is a specific test method for determining the non-volatile content for non-thin film energy curable adhesives. Those adhesives are cured under a lamp prior to being placed in an oven to drive off any VOC. The loss of VOCs is determined gravimetrically (e.g. by weight loss). Unfortunately, the method cannot be used for determining VOC content of thin film energy curable products because the change of weight is too small to measure accurately. There has been a considerable effort to develop a test method for these products, but at this time, there is no method that can be used for enforcement purposes. In 2011, ASTM D7767 - *Standard Test Method to Measure Volatiles from Radiation Curable Acrylate Monomers, Oligomers, and*

Blends and Thin Coatings Made from Them was developed as a useful tool to help manufacturers determine the VOC content of thin film energy curable products. This method was included in the definition section of Rule 1168 that was approved by the Board in 2017. For non-reactive products, formulation data can be relied on to estimate the VOC of a product. It is more complicated for reactive products because it is not certain if all the reactive components will react completely. ASTM D7767 allows the manufacturer to measure the VOCs in a product by combining the reactive components, e.g. the monomers and photoinitiators. The pigments and additives are excluded so the product can be tested at a thick enough film to accurately measure the weight loss. If the pigments and additives were included, they could potentially interfere with the curing step. This method is not appropriate for compliance verification because the fully formulated (commercial) product must be tested as it is applied in the field. This is because a third party laboratory, such as the SCAQMD laboratory, cannot independently perform this analysis and have confidence that the results accurately reflect the composition of the fully formulated product. The method is not performed on the fully formulated product, but estimates the VOC by measuring the VOC content of the reactive components of the product combined with a required amount of a specified photoinitiator (2 percent by weight of ethyl-2,4,6-trimethylbenzophenylphosphinate). If the enforcement staff collected a sample of a thin film energy curable product, the manufacturer would need to supply the raw materials and a photoinitiator in order for the SCAQMD laboratory to perform the analysis. There is no mechanism to confirm the raw materials supplied are the actual raw materials used to formulate the product. This data could not be relied upon or verified as accurate to confirm compliance. If compliance staff were to discover such a product in the field, the manufacturer would need to supply formulation data, including the results of ASTM D7767 if used. SCAQMD laboratory staff could speciate the sample on the GC/MS to verify some of the raw materials contained in the formulation data and to qualitatively confirm the veracity of the formulation data. To be clear, the M313, which can be used to quantitate the VOC of certain adhesives and sealants, cannot be used for energy curable products due to their reactive nature. At this time, staff is not aware of any thin film energy curable adhesives or sealants but if these products become prevalent, staff will work with the manufacturers to develop or enhance a method for the analysis that can be used to independently verify the compliance of these products.

The test method for non-reactive adhesives depends on the VOC content. Products with a VOC content of 150 g/L material or less are analyzed by M313 and products with a VOC content above 150 g/L material are analyzed by M24.

Reactive adhesives will be analyzed by Subpart PPPP of 40 CFR Part 63, which is a sandwich method that cures the adhesive between two substrates to prevent moisture in the atmosphere from competing with the reaction taking place in the adhesive. The method uses a relatively thick layer of adhesive so it is only appropriate for products that are applied at a similar film thickness. The Applicability and Principle section of the method states it is not applicable to one part moisture cured urethanes or silicone adhesives, and EPA Method 24 should be used for those products. The challenge with those products is they require moisture to cure and the sandwich method blocks the water. These products are typically applied to wood, which is the source of the moisture. Wood presents a challenge for analytical testing because of its affinity for water so the wood substrate does not reach a stable weight in the oven. Therefore, as specified in the method, until further

method development is conducted, M24 will be used to demonstrate compliance for 1K moisture cured urethanes and silicones.

High pressure adhesives are new to the market. These products are primarily for roofing applications and the advantage over conventionally applied adhesives (e.g., trowel, brush, roller, etc.) is the speed of application. There is currently no accepted test method but staff is working with a manufacturer and an analytical laboratory to develop an appropriate test method. The analytical challenge includes obtaining a representative sample of the liquid and propellant from the large, high pressure containers and quantifying the amount of VOCs as the propellant.

Sealants

There are also many different product categories, chemistries, and application techniques for sealants, however, sealants are more straightforward than adhesives as they are not applied between substrates. Most sealants are analyzed by two test methods. All reactive sealants and non-reactive sealants with a VOC content above 150 g/L material are analyzed by M24 and non-reactive sealants with a VOC content of 150 g/L or below are analyzed with M313. As previously stated, M313 is not appropriate for reactive products since the dilution step prevents the reaction from occurring. Therefore, all reactive sealants are analyzed with M24.

Figure 4

Expanding foam sealants are a new category specifically included during the 2017 rule amendments. Foam Sealants are products used to fill and form durable, airtight seals to common building substrates. They are typically sprayed into building cavities to provide water resistance, thermal resistance, or acoustic dampening. Their use has been increasing as building owners and property managers seek to reduce building energy consumption. Rule 1168 includes two categories of expanding foam sealants: 'foam sealants' **(Figure 4)** that are typically used to fill small gaps around windows, doors, and floor and are typically supplied in aerosol cans, and 'insulating foams' **(Figure 5[10])** that are typically supplied in large canisters, applied by professionals, and sprayed into wall cavities to provide thermal insulation or minimize air infiltration.

Figure 5

The foam itself is typically a one-component or two-component polyurethane that contains little or no VOC. However, the propellants used in some of the aerosol products do contribute to the VOC content. Method development is ongoing to address the challenge of determining the VOC

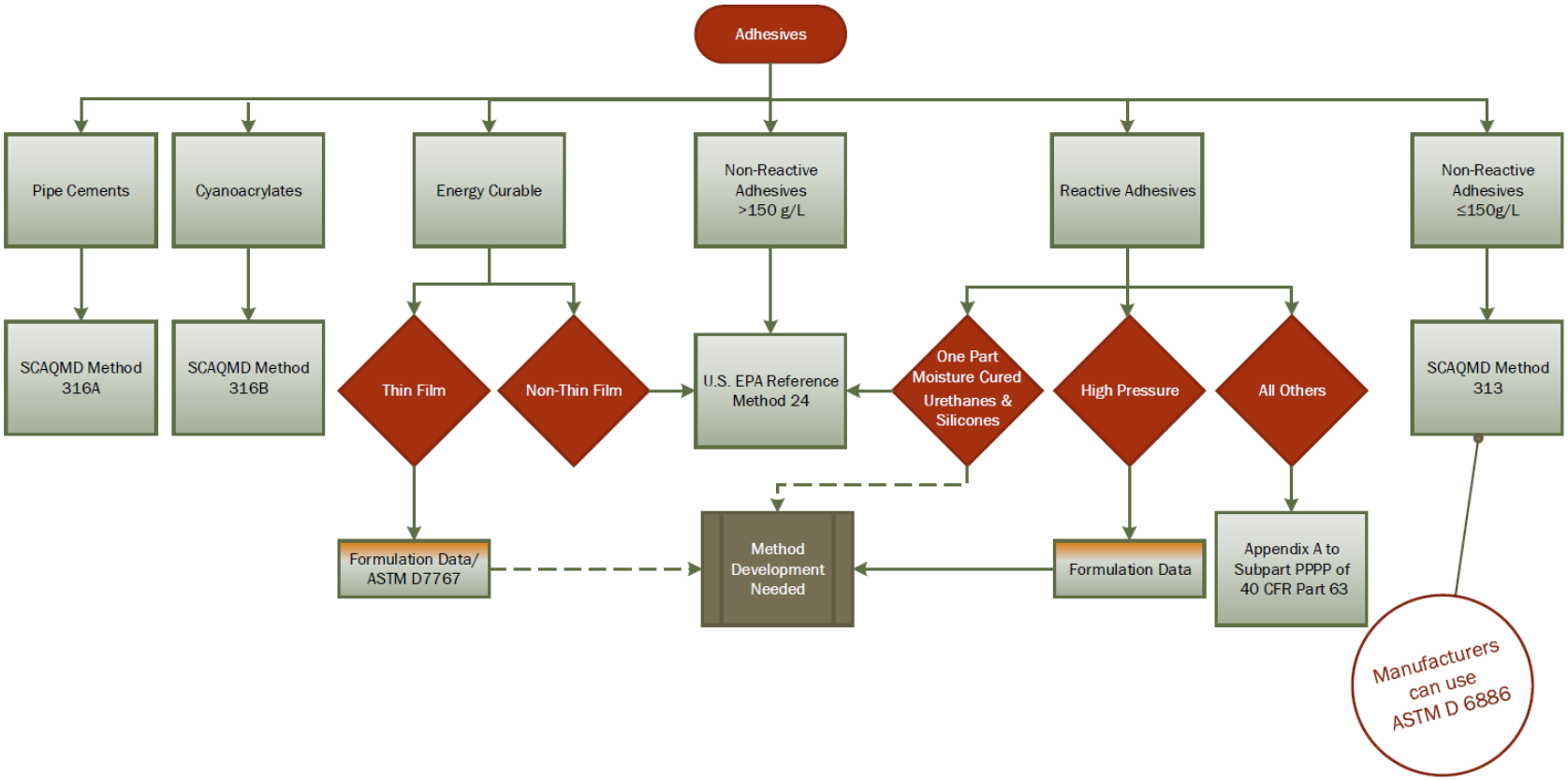
[10] Photo courtesy of Center for the Polyurethanes Industry (CPI).

content for expanding foam. The challenges are similar to high-pressure adhesives and SCAQMD laboratory staff will hopefully be able to use similar techniques.

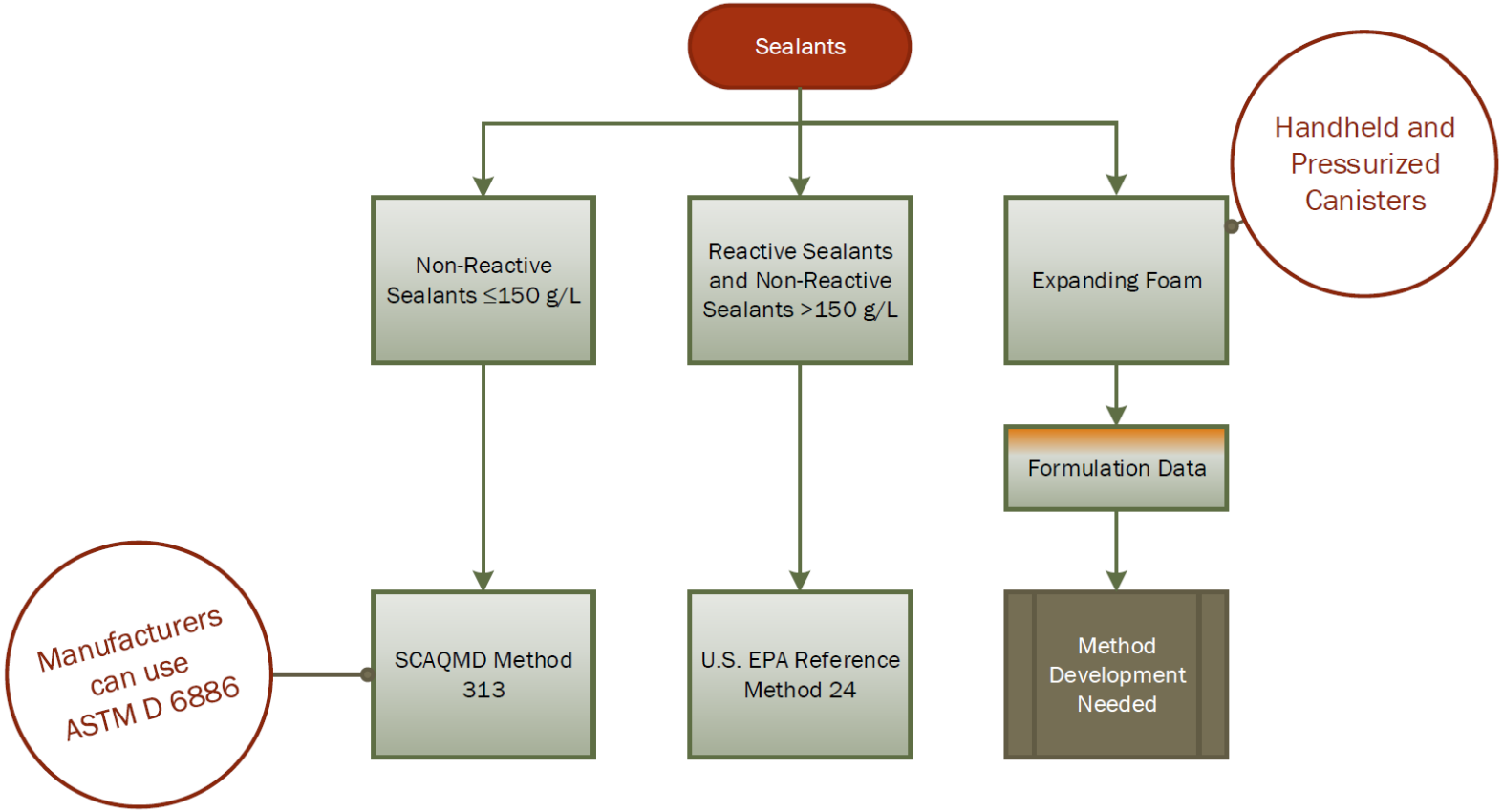
Test Method Flowcharts for Adhesives and Sealants

The following flow charts serve as guidance for determining which test method will be used for each product type.

Rule 1168 Test Method Determination: Adhesives



Rule 1168 Test Method Determination: Sealants



Conclusion

This document and flowcharts have been developed to provide clarity on how adhesives and sealants will be analyzed to demonstrate compliance with Rule 1168. There remains some product types without an appropriate test method. For those products, staff is conducting test method development. This documentation is dynamic and will be updated through a public process as method development concludes.

APPENDIX A – DIFFERENCES BETWEEN SCAQMD METHOD 313 AND ASTM D6886

The gas chromatography (GC) approach of M313 is similar to the approach developed at California Polytechnic State University, San Luis Obispo and adopted by ASTM as D6886 in 2003. ASTM is the largest developer of consensus standards, and the committee is comprised of members of industry, academia, and regulatory agencies. While ASTM D6886 places a focus on speciation of sample constituency, M313 focuses on VOC quantitation along with additional quality control (QC) requirements. M313 was the first GC method to include a marker compound to indicate when a compound should no longer be counted as a VOC, which was historically an issue with a GC-based VOC determination. The SCAQMD has participated in round robin studies (M313 versus M6886) with strong correlation between the two methods. It is staff's understanding that industry relies on M6886 for in-house or third party testing of their products. Rule 1168 includes M6886 as well as M313 since manufacturers rely on M6886 to ensure their coatings are in compliance. For compliance purposes, the SCAQMD laboratory will rely on the more rigorous M313.

The addition of Methyl Palmitate (MP) as the marker compound serves as a delineation between VOCs and semi-volatile VOCs which should not be included in the VOC calculation. This marker compound was selected to yield consistent results to M24 and the original version M313, adopted in 1991. This marker compound was further validated based on its non-volatility under ambient evaporation testing over a six month period. Prior to the use of MP as a marker compound, everything detected was measured as a VOC. This 'bright line' approach is used as a straight forward mechanism to determine if a compound should be counted as a VOC.

Differences between M313 and M6886:

	M313	M6886	Potential Difference
Marker Compound	Yes	No	Additional compounds included in the calculation could lead to higher value.
Column	624 (G43 Phase[11])	DB-5 (G27 Phase[1])	Compound elution order may differ slightly and has the potential to change which compounds are counted as VOC if using MP as a marker compound in M6886.
Default Compound	Triglyme[12]	Texanol[13]	M313 allows the relative response factor of triglyme to be used in place of target compounds for up to 5 g/L or 10 percent of sample VOC; whichever is larger. Instrument response to texanol is significantly lower and may result in an underestimation of total VOC.

[11] United States Pharmacopeia (USP) nomenclature
[12] Triethylene glycol dimethyl ether
[13] 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate

	M313	M6886	Potential Difference
Quality Control	Extensive	Limited	Extensive QC in M313 evaluates whether VOCs are completely extracted from the sample via a spike and recovery QC step. All target and spike compounds are checked for bias with continuing calibration verifications standards. Instrument inlet evaluated for molecular weight bias with instrument optimization mix that also evaluates detector method detection limit, mass spectrometer ionization capability, and separation of internal standard from commonly encountered glycols.

APPENDIX B – CALCULATING THE VOC OF PRODUCT AND THE VOC OF MATERIAL

There is sometimes confusion over the terms "VOC of adhesive/sealant" and "VOC of material." The VOC of adhesive/sealant is the same as the term "regulatory VOC," which is equivalent to the term "VOC, *less* water and exempts." The VOC of material is the same as the term "actual VOC," which is equivalent to the term "VOC, *including* water and exempts."

The regulatory VOC calculates the VOC less exempts and water, which is a more complicated calculation than the actual VOC in that it subtracts the volume of water and the volume of exempt compounds from the volume of material (see calculation below). The calculation was derived to express the VOC emitted per volume of solids in the adhesive/sealant to eliminate the effect of dilution. Dilution with water or exempt compounds would reduce the VOC-to-volume ratio while maintaining a constant VOC-to-solids ratio. This is important because those materials are applied at a certain film thickness so dilution would result in a larger volume of the material being applied to achieve the same film thickness.

For adhesives or sealants containing water or exempt compounds, the regulatory VOC is always higher than the actual VOC. For conventional solvent based products with no exempt compounds, the two VOC values are always the same. The VOC content limits listed in the rule refer to the regulatory VOC. However, low-solids products, which are defined as any regulated product that contains less than one pound of solids per gallon of material, are regulated in the rule by the actual VOC since the intent of low-solids products is not to build film thickness. VOC emissions in the inventory are also calculated based on the actual VOC.

Sample Calculations for an adhesive with the following composition:

Density= 0.99 g/mL
Water= 50% by weight
Density of water= 0.997 g/mL
Solids= 48% by weight

VOC of Adhesive/Sealant Calculation *(Regulatory VOC, less water and exempt compounds):*

Remove the *Volume Solid* from denominator

$$Volume\ Solids = \frac{Weight\ Solids}{Density}$$

$$VOC_{product} = \frac{(100 - 48 - 50)}{(\frac{100}{.99} - \frac{50}{.997})} \times 1000 \ = 39\ g/L$$

VOC of Material Calculation *(Actual VOC)*:

$$VOC_{material} = (100 - 48 - 50) \times 0.99 \times 10 = 20g/L$$