SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

PROTOCOL FOR DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) CAPTURE EFFICIENCY

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1. Overview and Applicability

1.1 Principle

The procedures used in this protocol are refined from an approach commonly referred to as a liquid/gas mass balance. The approach, as its name implies, involves a simultaneous measurement of liquid phase Volatile Organic Compound (VOC) usage along with a measurement of gaseous phase VOC capture as conveyed to air pollution control equipment. The VOC capture efficiency, based on these measurements, is a regulated provision under various SCAQMD rules and is independent of the control device efficiency.

For the liquid phase measurement, the mass usage rate of VOC is calculated from the measured usage of the VOC containing material along with laboratory determination of VOC and volatile carbon content. For the gaseous phase measurement, duplicate gas samples are withdrawn from the inlet of the collection device according to SCAQMD Method 25.1. VOC concentration is determined from laboratory analyses of Total Gaseous Non-Methane Organic Compounds (TGNMOC) as carbon. The VOC capture rate is calculated based on TGNMOC as carbon, the liquid phase ratio of volatile carbon to VOC, and the measured control device inlet flow rate.

This procedure does not rely on sometimes undependable VOC information often obtained from Material Safety Data Sheets (MSDS), but instead provides analytical means for determining VOC to carbon ratios. Additional requirements on existing methods are also employed for the purpose of improving precision and accuracy.

1.2 Applicability

This protocol is subject to requirements for number of sampling runs and all additional requirements specified in the United States Environmental Protection Agency's (EPA) technical guidelines document, ***Guidelines for Determining Capture Efficiency.*** This protocol is designed for use in individual sampling runs allowed under the EPA guideline's alternative protocols section. Under EPA requirements, a valid capture efficiency test must involve a minimum of three sampling runs.

This protocol is designed primarily for coating, printing, and resin operations, but can be applied to any process using liquid or solid VOC containing materials where the VOCs may evolve and become fugitive emissions. These processes generally involve the use of an open hood or other collection device used to convey VOC emissions from application and/or curing points to air pollution control equipment such as an afterburner/incinerator or carbon adsorber. For simplicity, in this protocol the VOC containing material will be referred to generically as coating.

This protocol is intended to provide guidelines by which capture efficiency may be determined in an accurate and reproducible manner. Variations in facility types, sizes, operating requirements, and other parameters make it necessary to evaluate each source test on a case by case basis. Alternative procedures for unique situations may be employed, subject to approval by the Executive Officer. As an alternative to this protocol or in cases where the protocol cannot be applied (see section 1.3 Interferences), EPA methods using total enclosures cited as EPA Methods 204 through 204F must then apply.

1.3 Definitions

The following is a list of terms and definitions that are used in the protocol:

CAPTURE EFFICIENCY is the percentage of VOCs used, emitted, evolved, or generated by an operation, that are collected and directed to an air pollution control device.

CARBON USAGE is a calculated quantity based on coating usage and coating Volatile Carbon analysis (refer to Section 4).

COATING is a generic reference to the VOC containing material in liquid or solid phase which is the source of process VOC emissions.

NONVOLATILES is the fraction of coating remaining after the volatile fraction has been expelled during analysis.

TGNMOC is Total Gaseous Non-Methane Organic Compounds and is the terminology used to express the results of SCAQMD 25.1 analysis. Due to the destructive nature of the analysis, TGNMOC is expressed as carbon in concentration units of ppmv. This protocol uses an analytical approach in converting TGNMOC as carbon to actual mass VOC. While TGNMOC does not include methane, some rule specific exempt carbon containing compounds will be included.

USAGE is the amount of coating that is consumed in the process and is expressed in units of lb/hr.

VOC is Volatile Organic Compounds which can be present in the coating or evolved in the gaseous phase as captured or fugitive emissions.

VOC CAPTURE RATE is a calculated quantity representing VOC captured and conveyed to a control device (refer to Section 4).

VOC USAGE is a calculated quantity based on coating usage and coating analysis (refer to Section 4).

VOLATILE CARBON (in Coating) is determined analytically as the mass of carbon in the volatile fraction of the coating per unit mass of coating expressed in weight percent.

1.4 Interferences

The presence of another coating line, open solvent or coating storage, or other sources of VOC in or near the building in which the operation is enclosed, may cause a positive interference. Steps should be taken to isolate the operation from any outside VOC sources.

Some oven burners or burner boxes use gases within the oven as a source of combustion air (direct firing). In most cases the combustion of VOCs within oven burners does not significantly affect the mass balances and the final results for capture efficiency. If, however, VOC combustion in the oven burners is significant and cannot be quantified, a negative interference may occur.

In the case of water wash spray booths or other applications where a water curtain may be employed, and the effect of the water's VOC retention cannot be quantified, a negative interference may occur.

Certain coatings have properties which make it difficult to determine the extent of VOC elution with laboratory simulation of the curing process (reactive diluents, heavy solvents, uncertain endpoints, VOC retention in the substrate). Although this method attempts to account for these situations, in a few cases a positive or negative interference may occur.

For some coating operations, due to design, it can be difficult to obtain accurate coating usage. A positive or negative interference may occur.

Some operations are not logistically suited for measuring flow at the control device inlet as according the SCAQMD Method 1.1. A positive or negative interference may occur.

The presence of rule exempt solvents will cause a positive interference for VOC mass emission rates; capture efficiency, however, will not be affected.

If the coating is applied to a porous substrate, a fraction of the coating solvents may temporarily or permanently be retained in the product (substrate). An interference may or may not occur. The effect of this interference is subject to a substrate retention evaluation. If applicable, substrate retention factors must be determined by direct measurement or analysis of the materials used during capture efficiency testing. Whether or not application of substrate retention factors are appropriate will depend on evaluation of the cured product's fate and chemical nature. The appropriateness for applying adjustment factors for the effect of substrate retention and the procedures by which the factors are determined are subject to approval by the Executive Officer on a case by case basis.

Procedures for minimizing the effects of any of the above interferences where applicable are not all addressed in this protocol. Alternative procedures must be evaluated on a case by case basis and are subject to approval by the Executive Officer.

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2. Field Procedures

2.1 Sampling Apparatus and Procedures

A TGNMOC sample must be taken from all VOC laden gas streams leading to the control device from curing ovens, applicator hoods etc. TGNMOC sampling must be conducted according to SCAQMD Method 25.1 heeding the following precautions:

> Due to materials used in the types of operations encountered, accumulation of residue in the sampling ports and inner duct walls is common. Extra care must be taken to ensure the Method 25.1 nozzles do not contact this accumulation causing contamination.
>
> Since the types of operations encountered are often unsteady and intermittent, it is imperative that the samples be extracted at a constant rate for proper integration. Method 25.1 tank vacuums must be recorded at five minute intervals to ensure a steady sampling rate.

> Samples must be taken at a well mixed and uniform location, i.e. far from situations causing stratification such as duct junctions, addition of dilution air, bends in the ductwork, or other flow disturbances as described in SCAQMD Method 1.1. Alternatively, an approved stratification check or multi-point sampling may be used for proper representation (refer to SCAQMD Source Test Manual Chapter X).

If the TGNMOC results of duplicate samples required under Method 25.1 do not agree within 20%, the sampling run may not be considered valid. Field observations of occurrences that may cause sample bias may be used to invalidate one of the duplicate samples should disagreement occur.

If the afterburner exhaust gases or any other VOC laden stream is introduced to the process, TGNMOC samples must be taken there as well and accounted for in calculating capture efficiency.

2.2 Flow Measurement

A velocity traverse must be conducted for all VOC laden gas streams leading to the control device according to SCAQMD Method 2.1 with the additional constraints outlined in this section.

All traverse locations must meet SCAQMD Method 1.1 requirements and not exhibit cyclonic flow. All duct cross sectional measurements must be performed and recorded to the nearest 1/8 inch. Extra attention must be given to make certain the port does not extend past the inner duct wall into the flow stream and that the build-up of material does not interfere with duct dimensions. Following these procedures is extremely important since small deviations in these cases can cause large errors in capture efficiency.

Since it is not practical to conduct a velocity traverse during Method 25.1 sampling, velocity traverses should be conducted immediately before or after Method 25.1 sampling under flow conditions similar to those encountered during sampling. Additionally, reference point velocities must be taken during Method 25.1 sampling at 2.5 minute intervals at a representative traverse point. Specifics concerning reference point velocities can be found in Chapter X, Section 2 of the SCAQMD Source Test Manual. The chosen reference point must also be recorded at regular intervals at least nine times during the pre/post sampling full traverse in order to ensure representation.

If the afterburner exhaust gases or any other VOC laden stream is introduced to the process, flow rates must be determined there as well.

2.3 Moisture

For the purpose of obtaining dry flow rates, moisture can be determined for all VOC laden gas streams leading to the control device according to Method 4.1. Alternatively, the procedure described in Section 4.1 of this protocol may be used for determining moisture.

2.4 Usage Weight

Usage rate must be determined for each VOC containing material used in the process individually by measuring the amount consumed and net elapsed time. In addition to coatings, this includes cleaning solvents, roll wash solvents, or fountain solutions used during the sampling run that become part of the VOC capture.

Usage should be determined gravimetrically during the sampling run, using calibrated on-line scales or calibrated mass or volumetric flow measuring devices and the coating density. The usage device employed must have a minimum sensitivity of 0.5% of the net usage of the coating/solvent which is being measured. Additionally the measurement device must be within the calibration period specified by the manufacturer.

Portable, low profile, electronic, platform scales, which can be rented or purchased at a minimal cost, work well for this purpose. For obtaining an instantaneous coating weight during steady state operation, these platform scales may be temporarily placed under the coating drum or reservoir from which coating is conveyed to the applicator. If the applicator has a secondary, integral coating reservoir, such as with roller coaters, dip coaters, and lithographic presses, the amount of coating in this secondary reservoir must be the same during all coating weight measurements. Recirculating systems with a constant overflow drain should be able to maintain a constant secondary reservoir level. For operations employing a continuous bulk feed system, either a smaller temporary reservoir (such as a 55 gallon drum), or the calibrated flow measuring device may be employed.

Testing should be conducted only when a single coating or set of coatings is applied. Difficulties may arise if coatings are changed during sampling.

For coatings with VOC contents that change over the sampling interval (due to effects of solvent addition and/or evaporation), net coating weight must be determined at the beginning and end of the sampling runs, accounting for the tare weights of containers and/or fixtures used to convey the coating.

For coatings with VOC contents that do not change over the sampling interval, tare weights need not be taken since they automatically drop out of the usage equation.

Alternatively, a usage procedure measuring the cured coating solids weight gain on the coated product may be employed, provided this weight gain is significant relative to the product weight. Coating usage then becomes solids gain divided by the coating solids content as applied plus the effect of added solvents.

2.5 Sampling Interval

The Method 25.1 sampling should take place over a minimum of one hour or longer, if necessary, to meet accuracy constraints in measuring usage or the following start/stop criteria. The Method 25.1 sampling should begin and end only when the process has been operating for a sufficient period and steady state operation can be assured. A steady state is defined as operating at constant oven temperature, coating application rate, etc., and that the application rate is consistent with the rate at which the product is curing and evolving VOCs throughout the oven. Coating weights should also be taken from the on-line scale(s) at the start and end of Method 25.1 sampling. The process should remain steady and, if possible, plan for a sampling interval in which no shut-downs (for coating change, coil change, sheet replacement, etc.) will occur.

If a shut-down period of more than five minutes should occur, sampling must stop and a coating weight must be taken. Sampling should be resumed as soon as the process restarts without waiting for steady state so that the shut down and start periods are encompassed within the sampling runs. A coating weight must again be taken. Net elapsed time and usage do not include periods during which sampling is interrupted. The process must be documented as operating for at least 70% of the period during which sampling is taking place.

2.6 Process Samples

One-quart (optionally one-pint for inks), zero head-space process (coating) samples must be obtained at the beginning and end of each sampling run. These samples must taken in the condition applied, that is after the addition of any supplemental solvents, thinners and diluents, and in the condition which they are conveyed to the coating mechanism and usage is measured. In addition, samples or exact formulations of any solvents added separately to the coating or during the run must be obtained.

If the sampling is interrupted by shutdown for a period of more than five minutes, samples must be taken at shutdown and start-up when there is reason for the VOC content of the coating to change during the shutdown.

2.7 Maximum Curing Temperature

The maximum curing temperature that the coating encounters during sampling must be obtained for use in process duplication for laboratory analysis.

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3. Laboratory Procedures

3.1 Apparatus

3.1.1 Thermogravimetric Analyzer (TGA)

Capable of accurately measuring the amount and rate of change in the weight of a liquid coating sample as a function of time and temperature. Balance accuracy must be plus or minus 0.1% or better with a sensitivity of ten micrograms or less. Heating rate must be programmable from ambient to 500^{0}C at 0.1 to 100^{O}C/min in 0.01^{O}C increments.

3.1.2 Gas Chromatograph with Gas Sampling Valve

Capable of resolving carbon dioxide from other fixed gases. The GC system must include a methanizer capable of reducing carbon dioxide to methane with at least 95% efficiency when using flame ionization detection (FID). A methanizer is not required if thermal conductivity detection (TCD) or infrared detection (IRD) is used.

3.1.3 Gas Chromatograph with Liquid Injection Port

Capable of resolving water from organic solvents. The GC must use thermal conductivity detection for the measurement of water.

3.1.4 Computer or Integrator

Capable of processing chromatographic data, such as, integrating areas under the response curve.

3.2 Sample Analysis

3.2.1 Determination of Weight Loss

a. A 10 to 100 mg aliquot of the liquid coating sample is placed in a pan or boat and weighed automatically by the TGA. W_i is the initial weight.

b. The sample is heated according to a predetermined temperature program up to the process maximum curing temperature and held until all the volatiles have been driven off. A continuous plot of weight vs. temperature or time is displayed and when the weight loss curve plateaus, that is, the slope or rate of change approaches an acceptably small value, the endpoint is reached and the TGA run concluded. W_f is the final weight.

The cured sample should have the same appearance as the cured product observed during field sampling. If sample appears to be burned, overcuring or oxidation may have occurred, in which case the sample should be re-run at lower 5°C increments until the desired cured appearance is achieved.

3.2.2 Determination of Volatile Carbon by TCA

a. VOCs purged from the TGA furnace are directed to the combustion furnace via a heated line (heated to at least oven temperature) where they are oxidized to carbon dioxide. Combustion efficiency shall be verified prior to analysis using methane and carbon dioxide gas standards.

b. An evacuated stainless steel intermediate collection vessel (ICV) of known volume is used to collect the carbon dioxide generated by the combustion of the VOCs. After the collection is completed, the ICV is pressurized with UHP or better nitrogen for ease of withdrawal.

c. The ICV gas sample is injected into the gas chromatograph for component separation and the measurement of carbon dioxide by either methanizer/FID or TCD or IRD. Quantification of carbon dioxide shall based on external standard calibration.

d. A blank run and a recovery standard run shall be performed prior to sample runs on the TGA. The blank run shall be used for baseline correction. The recovery standard shall contain a known amount of volatile organic carbon. A 95% or better recovery must be achieved prior to sample analysis.

3.2.3 Determination of Water by GC

The analysis of water shall be accomplished using the procedure "Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph", as described in ASTM-D-3792-79. Samples not amenable to this method may be analyzed using the procedure "Water in Paint and Paint Materials by Karl Fischer Method", as described in ASTM-D-4017-81. Water based samples can be analyzed by the Gas Chromatograph method only.

3.3 Laboratory Calculations

Volatile Carbon in Coating (% wt.) = $[W_c/W_i] * 100\%$

Nonvolatiles (% wt.) = $[W_f/W_i] * 100\%$

VOC (% wt.) = [100% - % wt. Nonvolatiles - % wt. water]

Where:

W_i = initial coating weight by TGA. (mg)

W_f = final coating weight by TGA. (mg)

W_c = volatile organic carbon weight as carbon. (mg)
= $[0.14636 \times CO_2 \times V \times (P_f/P_i) \times (1/T)]$,

Where:

CO_2 = ICV carbon dioxide concentration (ppmv)

V = ICV volume (L)

P_f = ICV final absolute pressure after pressurization (mmHg)

P_i = ICV initial absolute pressure after filling but before pressurization (mmHg)

T = ICV absolute temperature (K)

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4. Engineering Calculations and Reporting

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. For the purpose of simplification, the VOC containing material will be generically referred to as "coating" in the calculation section.

4.1 Moisture Content

As an alternative to using SCAQMD Method 4.1 to obtain moisture, the following equation may be used if the moisture in the gas stream is present primarily as a product of the combustion of natural gas. This is the case in most afterburner exhausts and most inlets that contain combustion gases or recycled exhaust streams. The following relation should not be used in processes where additional unquantifiable moisture is introduced such as with water wash spray booths or when large amounts of water based coatings are used.

Moisture Content by Combustion Equation

$$\%H_2O = \left[1 - \frac{1}{1 + 0.018\,(\%CO_2 + \%CO - 0.04)}\right] 100 + \%\text{ambient } H_2O$$

For all gas streams, regardless of weather or not other sources of moisture exist, the ambient moisture (relative humidity) must be taken into account for determining dry flow rates.

4.2 Volumetric Flow Rate

The volumetric flow rate of the control device inlet(s) and any other VOC laden streams, must be calculated in dry standard cubic feet per minute (dscfm) as in SCAQMD Methods 1.1, 2.1, and 3.1. and corrected for reference point velocities as in Chapter X, Section 2 of the SCAQMD Source Test Manual.

4.3 VOC and Carbon Usage Rate

The VOC and carbon usage rates are calculated for each coating individually by performing VOC and carbon mass balances using the following relationships:

> VOC in the coating before sampling minus VOC in the unused coating after sampling, equals VOC evolved during sampling.
>
> Volatile Carbon in the coating before sampling minus Volatile Carbon in the unused coating after sampling, equals volatile carbon evolved during sampling. Volatile Carbon is the organic carbon in the volatile or solvent portion of the coating not including solids and water expressed per unit of coating including solids and water.

Any solvents, thinners, or other VOC containing materials added to the coating or coating process must also be included in this mass balance.

These mass balances can be performed by using the calculation sheet in Figure 1. If multiple coatings are used, the mass balances in Figure 1 must be performed on each coating and then totaled for a Total VOC Rate and Total Volatile Carbon Rate.

Alternatively, if it can be assured that VOC contents of the coatings do not change over the test period, then the simplified calculation sheet shown in Figure 2 can be used to determine Total VOC Rate and Total Volatile Carbon Rate.

4.4 VOC Capture Rate

The individual VOC capture rates are determined for each stream venting to the control device using the following quantities:

C - Concentration of Total Gaseous Non-Methane Organic Compounds (TGNMOC) from the Method 25.1 sample taken at the control device inlet, reported in ppm as carbon;

Q - Control device inlet flow rate in dry standard cubic feet per minute;

Tc - Total Carbon Usage Rate in pounds per hour;

Tv - Total VOC Usage Rate in pounds per hour;

M - Molecular Weight of carbon = 12 lb/lb-mol;

The VOC capture rate in pounds per hour can then be calculated as follows:

$$\text{VOC Capture Rate} = 1.583 \times 10^{-7} \times (T_V/T_C) \times M \times C \times Q$$

These calculations can be performed by using the calculation sheet in Figure 1. If multiple streams are present, the VOC Capture Rate must be calculated separately as above and added together for a Total VOC Capture Rate. If the afterburner exhaust gases or any other VOC laden stream is introduced to the process, the VOC mass rates in these streams must be subtracted from the VOC Capture Rate since they are not part of the overall mass balance.

For applications where solvents are recovered such as with carbon adsorbers and refrigeration units, the VOC capture rate can be assumed to be the same as the amount recovered in the control device.

4.5 VOC Capture Efficiency

The percent capture efficiency is then calculated as follows:

$$\text{Capture Efficiency} = \frac{\text{Total VOC Capture Rate}}{\text{Total VOC Usage Rate}} \times 100$$

Test No.__________ Date____________

SOURCE TEST CALCULATIONS

A. Coating Identification.........................._______

B. Net Coating Weight (Pre-Test minus tare)........__________lb

C. Net Unused Coating Weight (Post-Test minus tare)__________lb

D. Solvent Added to Coating or Process............__________lb

E. Net Elapsed Time.... ....__________hr

F. Pre-Test VOC (100 - %H_2O - %Nonvolatiles).......__________%

G. Pre-Test Volatile Carbon in Coating............__________%

H. Post-Test VOC (100 - %H_2O - %Nonvolatiles)......__________%

I. Post-Test Volatile Carbon in Coating...........__________%

J. Added Solvent VOC (Most Often 100%)............__________%

K. Added Solvent Volatile Carbon..................__________%

L. Volatile Carbon Usage Rate:

$$\frac{1}{E}\left[\left(B \times \frac{G}{100}\right) + \left(D \times \frac{K}{100}\right) - \left(C \times \frac{I}{100}\right)\right]$$

= ___________lb/hr

M. VOC Usage Rate:

$$\frac{1}{E}\left[\left(B \times \frac{F}{100}\right) + \left(D \times \frac{J}{100}\right) - \left(C \times \frac{H}{100}\right)\right]$$

= ___________lb/hr

FIGURE 1
VOC AND VOLATILE CARBON USAGE RATES FOR INDIVIDUAL COATINGS WHICH VOC CONTENTS MAY CHANGE OVER THE SAMPLING PERIOD

Test No.__________ Date____________

SOURCE TEST CALCULATIONS

Coating (identification)	Coating Usage (lb/hr)	VOC (% wt.)	Volatile Carbon in Coating (% wt.)	Volatile Carbon Usage (lb/hr)	VOC Usage (lb/hr)
#1					
#2					
#3					
#4					
#5					
#6					
TOTALS		N/A	N/A		

WHERE

$$\text{Coating Usage (lb/hr)} = \frac{\text{(lb Pre-Test Coating Weight - lb Post-Test Coating Weight)}}{\text{Net Elapsed Time}}$$

VOC (% wt.) = 100 - % Water - % Nonvolatiles

Water (% wt.) - from coating analysis

Nonvolatiles (% wt.) - from coating analysis

Volatile Carbon in Coating (% wt.) - from coating analysis

Volatile Carbon Usage (lb/hr) =
(Coating Usage lb/hr) x (Volatile Carbon in Coating % wt./100)

VOC Usage (lb/hr) = (Coating Usage lb/hr) x (VOC Content % wt./100)

FIGURE 2
VOC AND VOLATILE CARBON USAGE RATES FOR COATINGS WHICH VOC CONTENTS DO NOT CHANGE OVER THE RUN AND NO SOLVENTS ARE ADDED DURING THE RUN

Test No.__________ Date____________

SOURCE TEST CALCULATIONS

Duct Identification	Flow Rate (dscfm)	TGNMOC Conc. (ppm)	VOC Capture Rate (lb/hr)
#1			
#2			
#3			
#4			
TOTALS		N/A	

WHERE:

VOC Capture Rate = 1.583 x 10^{-7} x (Flow Rate dscfm) x (TGNMOC ppm) x (12 lb/lb-mol) x (Total VOC Usage Rate lb/hr) / (Total Volatile Carbon Usage Rate lb/hr)

$$\text{Capture Efficiency} = \frac{\text{Total VOC Capture Rate}}{\text{Total VOC Usage Rate}} \times 100$$

$$= \frac{\qquad}{\qquad} \times 100 = \qquad \%$$

FIGURE 3
VOC CAPTURE RATE AND CAPTURE EFFICIENCY