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# Spray Polyurethane Foam Test Method Development

## Progress and Future Plans

July 15, 2020

# Points of Contact

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# Presentation Agenda

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- ❖ Rule 1168 History – the need for new test methodology
- ❖ Priorities and desired method characteristics
- ❖ Complementary test methods
- ❖ South Coast AQMD development approaches
- ❖ Unanswered questions and future steps

# Rule 1168 Adhesive and Sealant Operations – 2017 New Definitions

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- (35) **FOAM INSULATION** is an expanding foam that is sprayed into ceiling or wall cavities to provide thermal resistance or to minimize air infiltration.
- (36) **FOAM SEALANT** is a foam used to fill and form a durable, airtight, water-resistant seal to common building substrates, such as wood, brick, concrete, foam board, and plastic.

Category	VOC Limits (g/L) <sup>1</sup>			
	Current	Upon Adoption	1/1/2019	1/1/2023
<b>Substrate Specific Adhesives</b>				
Metal	30			
Plastic Foams	50			
Porous Material (except wood)	50			
Wood	30			
Fiberglass	80			
Reinforced Plastic Composite	250		200	
<b>Sealants</b>				
<b>Architectural Applications</b>				
Clear, Paintable, and Immediately Water-Resistant Sealant	250	380		250
Foam Insulation	250			50 <sup>3</sup>
Foam Sealant	250			50 <sup>3</sup>
Grout	250	65		
Roadway Sealant	250			
Non-Staining Plumbing Putty	250	150		50
Potable Water Sealant	250	100		
<b>Roofing</b>				
Single Ply Roof Membrane Sealant	450			250 <sup>2</sup>
All Other Roof Sealants	300			250 <sup>2</sup>

Source:

# Rule 1168 History – Adhesive and Sealant Applications

## Rule 1168

Adopted April 7, 1989

- Originally only applicable to adhesives
- 19 adhesive categories

## 1998 Amendment

Added sealants

- 6 sealants categories
- 5 sealant primer categories

## 2017 Amendment

37 adhesive categories

5 adhesive primer categories

12 sealants categories

5 sealant primer categories

# Rule 1168 – Test Method Updates

1989

Laboratory Methods of Analysis for Enforcement Samples

SCAQMD Laboratory Method 304 - *Determination of Volatile Organic Compounds (VOC) in Various Materials*

1992

SCAQMD Method 305 – *VOC in Aerosol*

U.S. EPA Reference Method 24 (M24) - *Volatile Organic Content*

SCAQMD Methods 302 – *Distillation of Solvents*

SCAQMD Methods 303– *Exempt Compounds*

SCAQMD Method 316A –*VOC in Pipes and Fittings*

1998

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*

2000

Method 316B – *VOC in Adhesive containing Cyanoacrylates*

# Rule 1168 – Test Method Updates

2017

Included 3 additional VOC test methods

1. Method for reactive adhesives
  - Adhesive placed between two substrates
2. Two methods for lower VOC products
  - SCAQMD Method 313
  - ASTM D6886
3. An undefined method for Spray Polyurethane Foam (SPF) products

# Method Development Priorities

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Now: Handheld single-component canisters

Later:

- “Propane” style single-component tanks
- Two-component tanks



# Method Characteristics for Single-Component Products

Required	Desired
High precision and accuracy	Simplicity over complication
Runs at “laboratory scale”	Minimal mess
Captures all VOC in product via direct analysis of material	Utilization of CARB/EPA-approved methodology when possible
Applicability to most products on the market	Applicability to all products on the market
Utilizes stakeholder knowledge and expertise	No chemical conversion of materials as an intermediary step
Well-characterized and predictable interferences	Zero interferences
Quantitative sub-sampling with mass balance	
High throughput	
Appropriate cure time for product	

# Potentially useful methods

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**CARB Method 310 -** Determination of VOC in Consumer Products and ROC in Aerosol Coating Products

## 3.2 Initial Testing of Aerosol Products

If the sample is an aerosol product, the aerosol propellant is separated from the non-propellant portion of the product by using ASTM D3074-94 (as modified in Appendix A for metal aerosol container) or ASTM D3063-94 (as modified in Appendix A for glass aerosol container). The propellant portion is analyzed for exempt or prohibited compounds by using US EPA Reference Method 18. The remaining non-propellant portion of the product is then analyzed as specified in section 3.3.

## 3.3 Initial Testing of Non-Aerosol Products and the Non-Propellant Portion of Aerosol Products

The non-aerosol product or non-propellant portion of an aerosol product is analyzed to determine the total volatile material present in the sample and to determine the presence of any exempt or prohibited compounds. This analysis is conducted by performing the following tests:<sup>1</sup>

Simple Concept:  
separate liquid from propellant and analyze separately

\*Not suitable for expanding foam products without special consideration\*

# Liquid Fraction - USEPA Method 24

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## Analysis List

Solids

Water by Karl-Fischer

Density

Default VOC determination method for ambient/moisture cure products

Induction time - 24 hour default for reactive materials

Analyzed in tandem with SCAQMD M303 for exempts

# USEPA Method 24 – Solids Test

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Notes: 24 hour induction time; 110 °C, 60 minutes in oven

# USEPA Method 24 – Water & Density



Left: KF Water Titration  
Right: Density in Garner Cup



# Liquid Fraction - SCAQMD M303

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Determination of Exempt  
Compounds

Performed on a GC-MS-FID

Exempts quantified and  
discounted from VOC tally



# AQMD Rule 102 Exempt Compounds

EXEMPT Compounds are any of the following compounds

(A) Group I

1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee)  
1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC 225cb)  
3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC 225ca)  
acetone  
ethane  
chlorodifluoromethane (HCFC-22)  
trifluoromethane (HFC-23)  
2,2-dichloro-1,1,1-trifluoroethane (HCFC-123)  
2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124)  
pentafluoroethane (HFC-125)  
1,1,2,2-tetrafluoroethane (HFC-134)  
1,1,1,2-tetrafluoroethane (HFC-134a)  
1,1-dichloro-1-fluoroethane (HCFC-141b)  
1-chloro-1,1-difluoroethane (HCFC-142b)  
1,1,1-trifluoroethane (HFC-143a)  
1,1-difluoroethane (HFC-152a)  
cyclic, branched, or linear, completely fluorinated alkanes

cyclic, branched, or linear, completely fluorinated ethers with no unsaturations  
cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations  
sulfur-containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.  
difluoromethane (HFC-32)  
1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane (C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>)  
2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane [(CF<sub>3</sub>)<sub>2</sub>CF<sub>2</sub>OCH<sub>3</sub>]  
1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub>)  
2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane [(CF<sub>3</sub>)<sub>2</sub>CF<sub>2</sub>OC<sub>2</sub>H<sub>5</sub>]  
parachlorobenzotrifluoride (PCBTF)  
methyl acetate  
methyl formate  
propylene carbonate  
1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea)  
trans-1,3,3,3-tetrafluoropropene (HFO-1234ze)  
trans-1-chloro-3,3,3-trifluoropropene (HFO-1233zd)

Source:

# Other Methods

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## **AQMD Method 313 – Determination of Volatile Organic Compounds (VOC) by Gas Chromatography/ Mass Spectrometry/ Flame Ionization Detection (GC/MS/FID)**

- “Dilute and Shoot”
- Not intended for polymerizing materials

## **ASTM D8142-17 - Determining Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation using Micro-Scale Environmental Test Chambers**

- The measurement of emissions during spray application and within the first hour following application is outside of the scope of this test method
- Potential VOC adsorption on chamber walls
- Adsorption/Desorption efficiency for VOC on adsorption tubes

## **ASTM WK40292 - Determination of Vapor-Phase Organic Compounds Emitted from Spray Polyurethane Foam (SPF) Using Sorbent Tubes Analyzed by Thermal Desorption Gas Chromatography and Mass Spectrometry**

- We would like to know more!

# Method Development Attempts

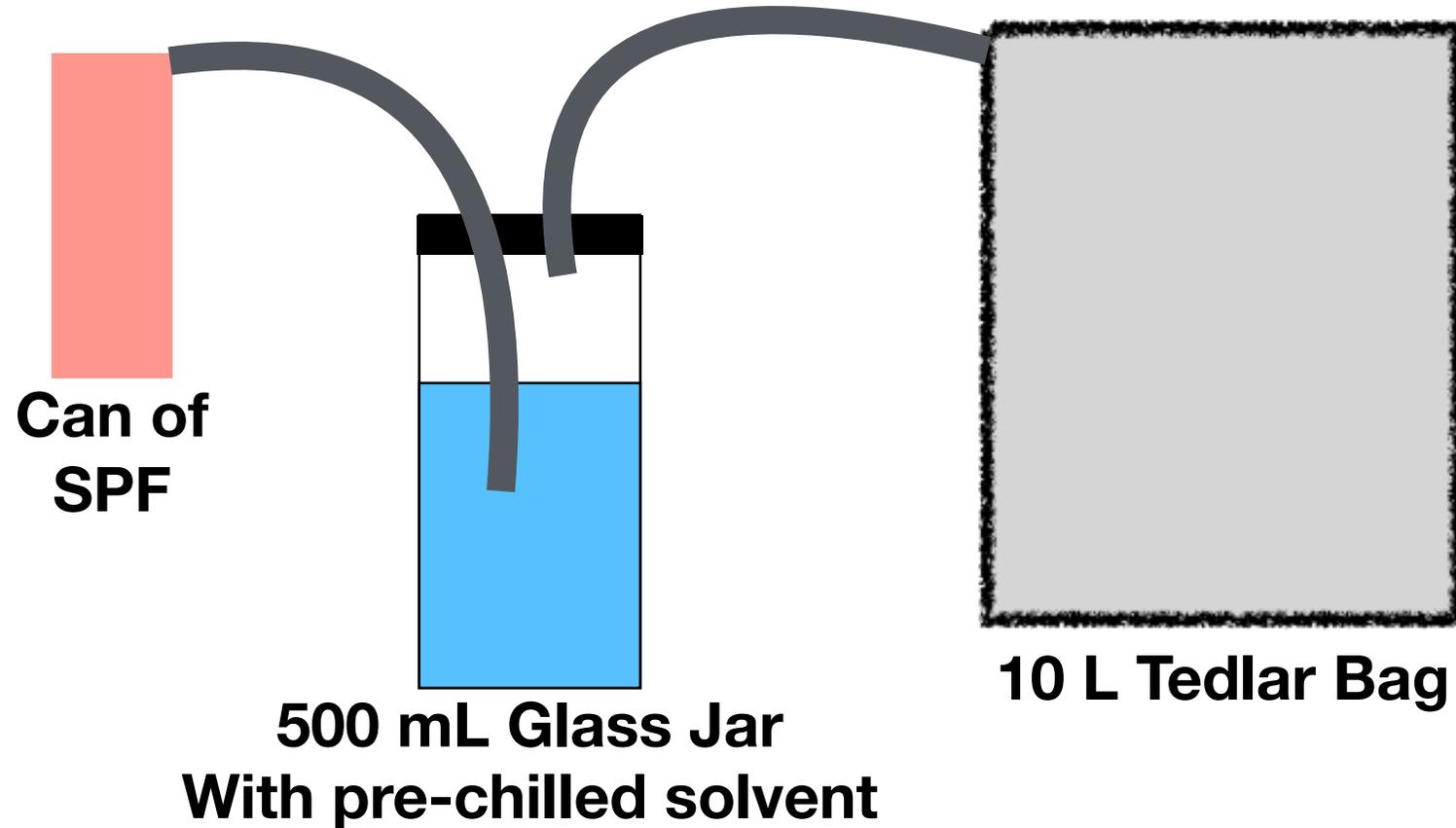
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Two different approaches attempted to date:

1. “Solvent Trapping”
2. “Temperature Trapping”

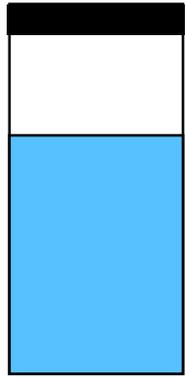
# Solvent Trapping Method

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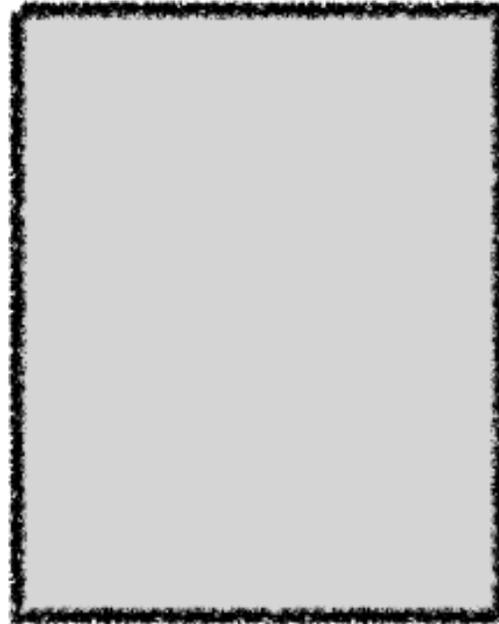


# Solvent Trapping – Post Collection

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**500 mL glass jar  
M24 following drying**

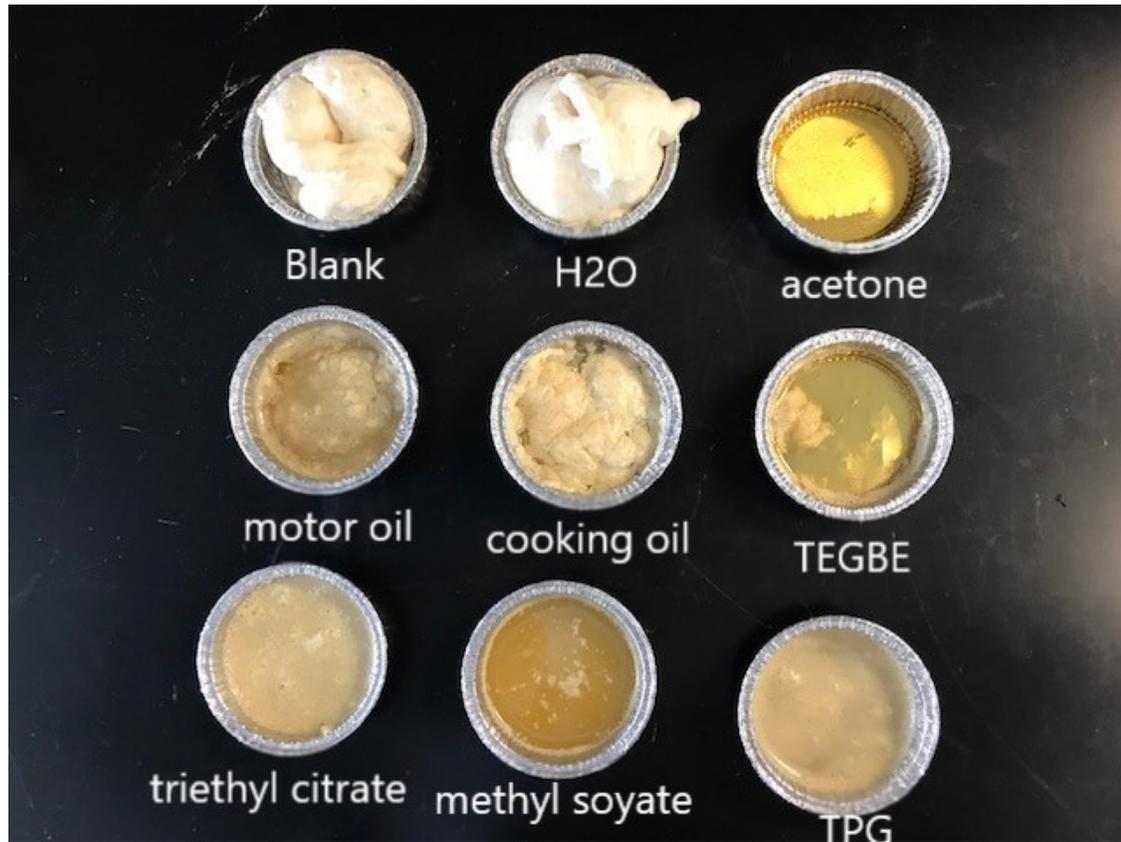


**10 L Tedlar bag  
GC-MS/TCD**

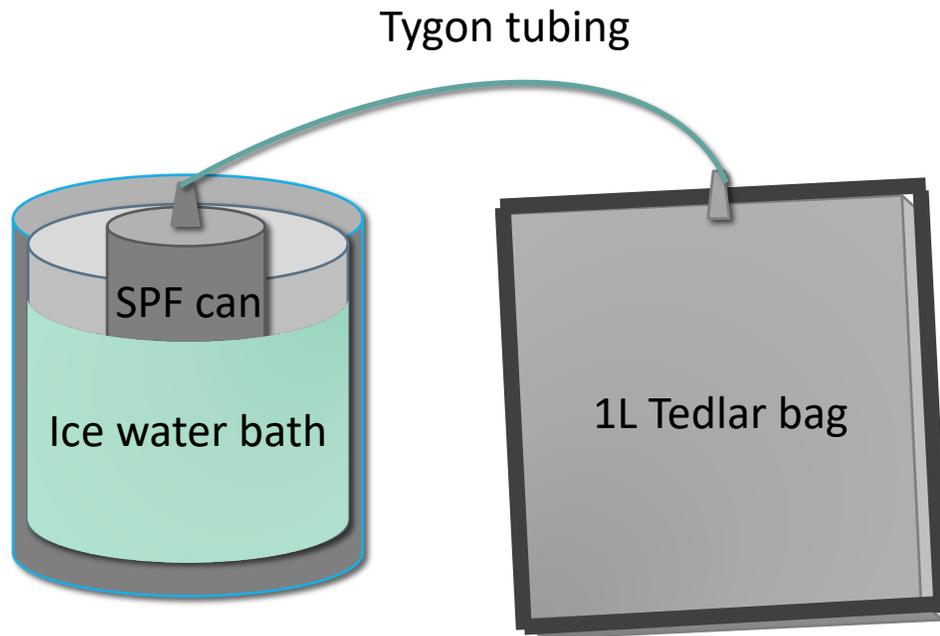
## Challenges

1. Solvent choice?
2. Solvent blow-through?
3. NV Solvent Correction?
4. Tedlar bag permeation?
5. “Dirty” transfer line?
6. Mass Balance?

# Solvent Performance



# Temperature Trapping Method



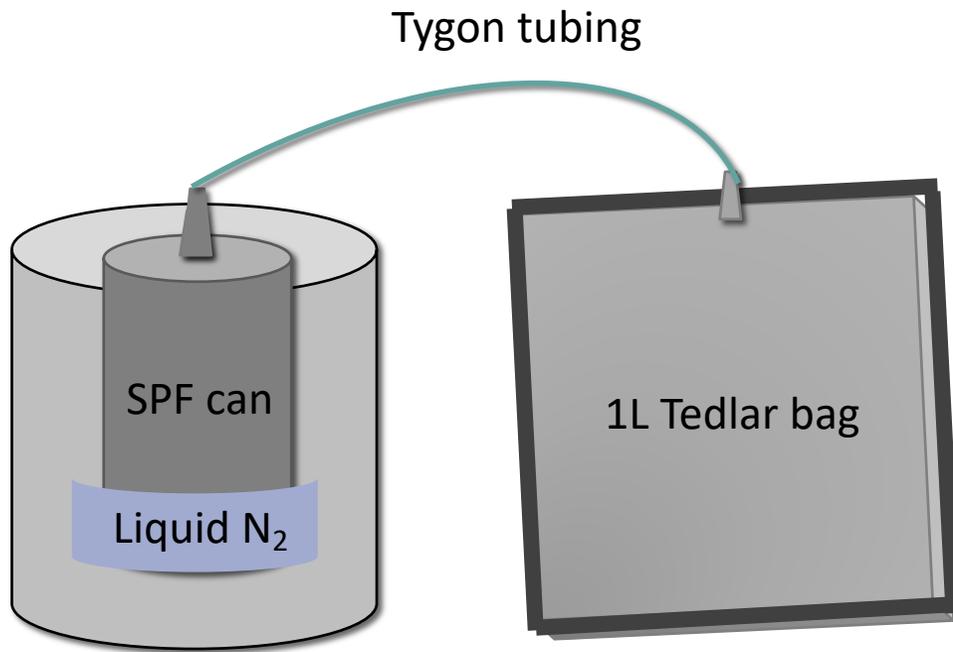
Attempt to trap  
condensable liquid at  
bottom of can

Chill can in ice water for 1  
hour (0°C/32°F)

Bubbling observed at  
product valve during  
propellant collection



# Temperature Trapping – 2<sup>nd</sup> Attempt



Successfully traps condensables

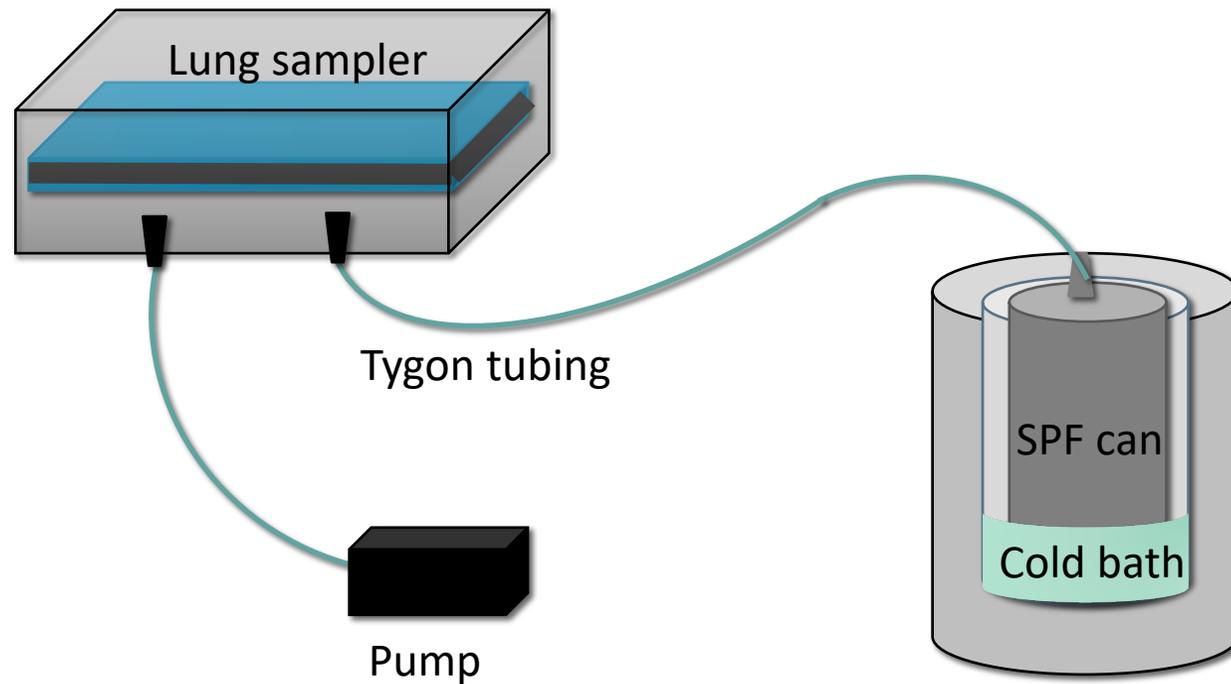
Successfully collects propellant following removal from bath

Liquid N<sub>2</sub> = -196°C/-321°F;  
Overkill?



# Potential Temperature Trapping Modifications

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Optimal bath temperature?

- Dry ice/acetone =  $-78^{\circ}\text{C}/-108^{\circ}\text{F}$
- Liquid  $\text{N}_2$ /acetone =  $-94^{\circ}\text{C}/-137^{\circ}\text{F}$

Lung sampler to meter and measure gas collection and provide more "draw" of propellant from chilled canister

# Post-Collection Analysis

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$$\text{VOC g/L Coating} = \frac{\text{Mass of all VOC (L + G, excludes exempts)}}{\text{Volume of all non-water, non-exempt matter (L+ G)}}$$

Liquid Fraction (L)	
Approach	Purpose
EPA M24	% NV, % Water, Density
SCAQMD M303	% Exempts

Gaseous Fraction (G)	
Approach	Purpose
GC-FID	Hydrocarbon Speciation
GC-ECD or TCD	% Exempts (HFC/HFOs)

# Pathway to an approved method

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Written method completed with stakeholder contribution

Submittal to EPA and CARB for approval

- Requires statistical method validation
- Must meet quality control expectations

Approving bodies may or may not require round robin testing

Rule language will not require amendment with South Coast AQMD  
Executive Officer approval

# Request for Information

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1. How are canisters filled by MFG? How are the materials delivered and pressurized?
2. What is the rough volume and mass of propellant and sealant?
3. Are all canisters the same between manufacturers?
  - No dip tube?
  - Similar valving?
  - Similar fill heights?
4. How are VOC values listed on canisters currently determined?
5. Any obvious modifications to method for major improvements?

# Request for Information - Additional Questions

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6. Both approaches utilize tedlar bags- is this problematic for certain propellant blends?
7. How are products changing to meet new rule limits? Will this method “keep up”?
8. Can you put us in contact with anyone who participated in ASTM WK40292?
9. Are there any other methods currently in development that share goals with ours?
10. Do you recommend any specialty equipment?

# Next Steps

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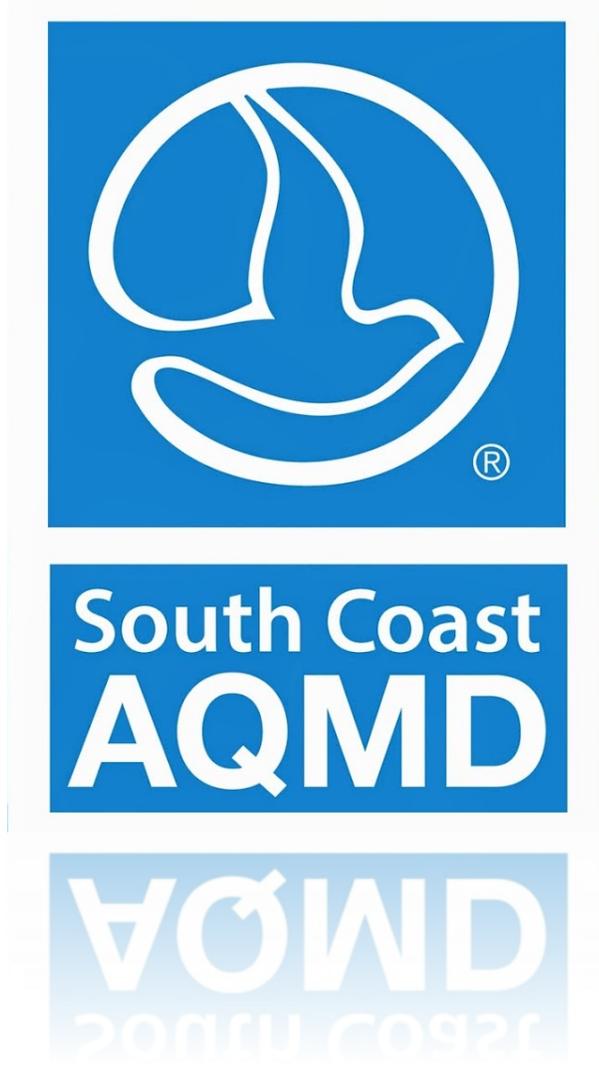
This presentation posted to AQMD website and linked through email newsletter

Receive feedback from stakeholders over next 2 weeks ([bparrack@aqmd.gov](mailto:bparrack@aqmd.gov))

- Information can be submitted as CBI (Confidential Business Information)
- Staff available to meet with individual stakeholders

Continued development based on feedback and new information

Future meeting to update stakeholders on progress



Questions?