SCAQMD M313-91

VOC by GC/MS/FID

Technical Discussion
September 5th, 2013

Agenda

Method Endpoint & Other Policy Decisions	Following Meetings

Agenda

Introductions

Technical Presentation	30 minutes
Comparative Data	20 minutes
Analytical Concerns (Previous Meeting)	15 minutes
Take Comments	30 minutes

Extend Meeting? Set Next Agenda?

Method Context

M24
Non-Volatiles
Density
Karl-Fischer
Exempts (if necessary)

Method 24 Analysis Completed

Every Sample

M313 Usage

< 150 g/L Sample Concentration

Inconsistent M24 Weighings

District Rules Or Protocols (CAS)

Limited Applicability

Method Procedure

Calibration

Sample Pre-Screening

Sample & QC Preparation

Sample Processing

Calibration

Calibrated Compound	RRF
Ethylene Glycol	0.5
Propylene Glycol	0.7
Texanol	1.4
1-Butanol	1.3

Pre-Calibrate Commonly Seen Compounds

Iterative In Nature

Sample Pre-Screening

Required Due To Pre-Calibration Requirement

Scenario #1

Sample Pre-screened ➡ No New Compounds Detected

Proceed To Sample Analysis

Sample Pre-Screening

Required Due To Pre-Calibration Requirement

Scenario #2

Sample Pre-screened → At Least 1 New Compound Detected

Must Pre-Calibrate New Compounds

Calibration

Calibrated Compound	RRF
Ethylene Glycol	0.5
Propylene Glycol	0.7
Texanol	1.4
1-Butanol	1.3
Decane	**2.0**

Scenario #2

New Compounds Calibrated & Added To Calibration List

Proceed To Sample Analysis

Sample Analysis

Clear Lacquer

~ 30 Grams →

Lacquer Aliquot

Sample Analysis

Lacquer Aliquot

\+ IPA, Heptane, Triglyme, DIIBA →

Spiked Lacquer
Mixed Well

Surrogate Spikes

Compound	Characteristic	Retention	Functional Group
IPA	Small, Polar	Early	Alcohol
Heptane	Small, Non-Polar	Early-Mid	Alkane
Triglyme	Large, Polar	Mid-Late	Poly-ether
DIIBA	Large, Non-Polar	Late	Ester

Sample Analysis

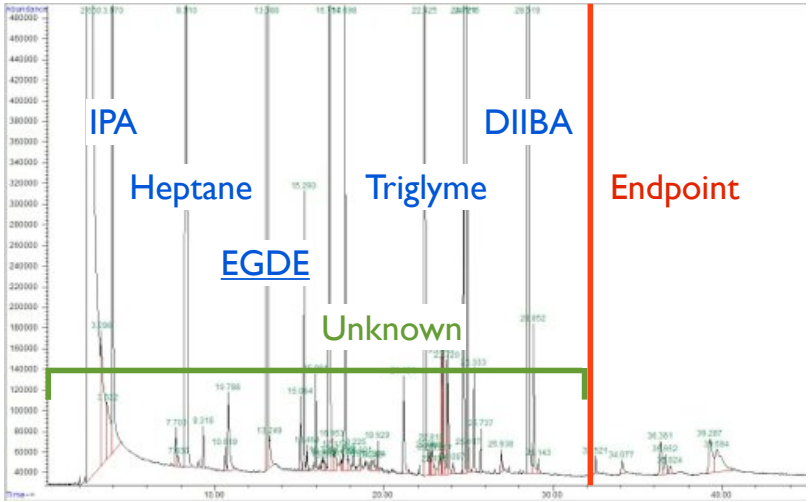
Spiked Lacquer
Mixed Well

➡

2.5 Grams
Of Sample
& EGDE
(Internal Standard)

Diluted Lacquer
To 25 mL
With Solvent

Surrogate Addition



Batch Standards

Run With Every Sample Set

Reagent Blank (RB)

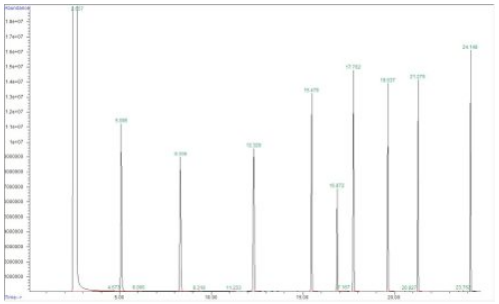
Continuing Spike Verification (CSV)

Target Compound Mix (TCM)

Instrument Optimization Mix (IOM)

Instrument Optimization Mix

Component	Evaluates
C6 - C15	Discrimination
BFB	Fragmentation
Methyl Palmitate	Endpoint
Ethylene Glycol	Resolution
Propylene Glycol	Resolution
Triglyme (0.1 g/L)	LOD



Processing

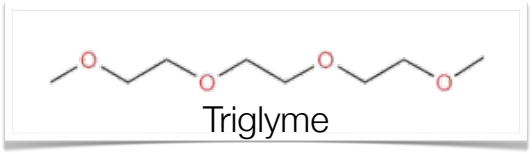
Contaminant Subtraction

Relative Response Factor Assignment

Sum VOC Totals

Triglyme Default Compound

Every Peak First Quantified As



Concentration “As Triglyme”
Dictates Next Step

Surrogate Compound Usage

Concentration As Triglyme

< 0.1 g/L

Action

Ignore Peak

Surrogate Compound Usage

Concentration As Triglyme

0.1 - 1 g/L

Action

Use “As Triglyme” Concentration
For Final VOC Tally

Surrogate Compound Usage

Concentration As Triglyme

1 - 2 g/L

Action

Calculate Using RRF Of Identified Compound
Or A Similar Compound
[Same Functional Groups; 1 Carbon Difference]

Surrogate Compound Usage

Concentration As Triglyme

2+ g/L

Action

Calculate Using RRF Of
Identified Compound Only

QC Recoveries

Surrogate Spikes

Average % Recovery

	D 6886	Intralab
EGDE (IS)	94	92
IPA	101	100
Heptane	94	99
Triglyme	98	99
DIIBA	99	93

M24 Comparative Data

ASTM D6886 Interlab

2010

Sample	M24 (g/L)	M313 (g/L)
#1	-22	6
#2	14	3
#3	-15	13
#4	-34	5
#5	-12	17
#6	-25	5

"Near 0 g/L"

As M24 (Coating)

ASTM D6886
Interlab 2010

Sample	M24 (g/L)	M313 (g/L)
#1	35	70
#2	-6	51
#3	-7	53
#4	-8	55
#5	-7	55

"50 g/L"

As M24 (Coating)

ASTM D6886
Interlab 2010

M24 Comparative Data

Random Samples
2008 - 2012

(g/L)

Sample	M24	M313	Type
#1	5	6	Latex Ceiling Paint
#2	13	**39**	Acrylic Sealer
#3	16	13	Enamel Undercoater
#4	**25**	13	Roof Coating
#5	25	21	Traffic Paint
#6	33	**44**	Acrylic Semi-Gloss
#7	36	36	Matte Finish
#8	42	41	Concrete Coating
#9	47	**83**	Polyurethane Sealer
#10	53	**103**	Flat Varnish

0 - 50 g/L
Samples As
M24 (Material)

Random Samples
2008 - 2012

(g/L)

Sample	M24	M313	Type
#1	**55**	41	Concrete Coating
#2	**59**	46	Exterior Latex
#3	60	**77**	High Gloss Enamel
#4	**63**	43	Wood Watersealer
#5	**72**	57	Traffic Paint
#6	75	74	Penetrating Sealer
#7	**78**	48	Sealer & Finish
#8	**81**	26	Traffic Paint
#9	82	81	Flat Varnish

50 - 100 g/L
Samples As
M24 (Material)

Random Samples
2008 - 2012

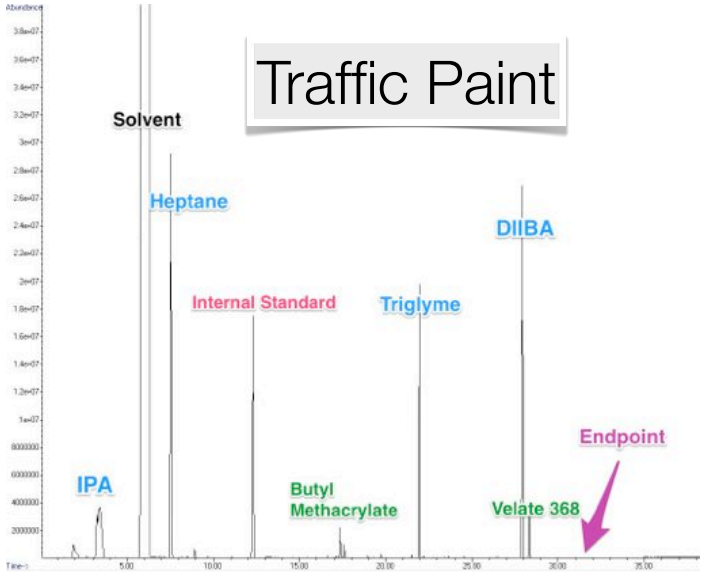
(g/L)

Sample	M24	M313	Type
#1	106	**127**	Concrete Sealer
#2	**110**	90	Exterior House Stain
#3	**125**	80	Flat Varnish
#4	**136**	110	Traffic Paint
#5	**143**	123	Clear Wood Finish

100 - 150 g/L
Samples As
M24 (Material)

Random Samples
2008 - 2012

Traffic Paint



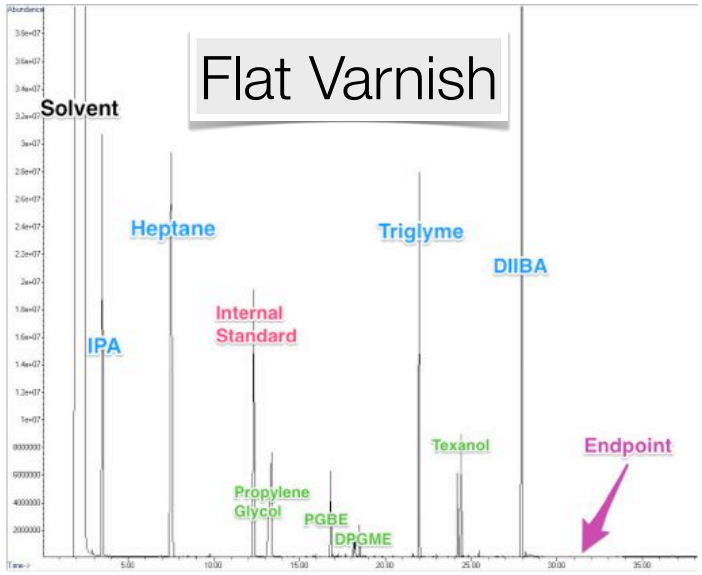
M24

81 g/L

M313

26 g/L

Flat Varnish



M24

53 g/L

M313

103 g/L

Analytical Concerns

Inlet Breakdown

Inlet Cooling With Reference Compound

New Liner Every Sequence

DIIBA Reactivity

Formulation Data

GC/MS Alternative

FID-Only Alternative Method

"Known" Formulations

Reduced QC; IOM mandatory

Will Discuss With EPA

What about D 6886?

Potentially Acceptable Substitute

Endpoint Differences

Use Triglyme Default Compound; IOM Mandatory

Will Discuss With EPA

South Coast AQMD

M313 Test Methodology

Joan Niertit, Principal Chemist
(909) 396-2174
jniertit@aqmd.gov

Brad Parrack, Air Quality Chemist
(909) 396-3071
bparrack@aqmd.gov