New VOC Analytical Methodologies and Potential Effects on Formulations

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Science Simplified

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Topics:

- Brief History of VOC Methods
- Comparison of EPA Method 24 vs ASTM D6886
- Results of Low-VOC and Zero-VOC Paints
- Results of Humectants & Surfactants
- Results of Conventional and Low-VOC Colorants
- Results of Low-VOC Coalescents and Additives
- Comparison of Zero-VOC Paints
- How Does This Data Relate to Formulations?
- What to Ask Your Suppliers?

Changing VOC Analytical Methods

- Historically based on EPA Method 24
- EPA 24 remains the “Official Certified Standard”
- Newer GC Methods gaining preference
  - ASTM D6886, SCAQMD M313
- New methods improve accuracy of very low VOC products
- However, new problems may be introduced
- Formulators, regulatory managers, manufacturers must understand how this may affect products
- Need to ask the right questions of your suppliers

EPA Method 24 vs ASTM D6886

- **EPA Method 24:**
- Approved ~1984
- Accuracy for VOC >100 g/l = Good
- Accuracy for VOC <100 g/l = High Variability
- VOC Measurement = Indirect

- **ASTM D6886:**
- Approved 2003
- Accuracy for VOC >100 g/l = Good
- Accuracy for VOC <100 g/l = Good
- VOC Measurement = Direct

EPA Method 24 for VOC

- EPA 24 requires 4 pieces of data:
  - %NVM (1 hr @ 110 deg C), ASTM D-2369
  - Density (lbs/gal), ASTM D-1475
  - % Water (by KF titration), ASTM D-4017
  - % Exempt Solvent (if any, by GC), ASTM D-4457

- EPA dictates exact methods to be used
- At VOC <50 g/l (high water content) EPA 24 has high variability due to poor water accuracy
- Small errors can have large effect on VOC
- Most in Industry would agree

ASTM D6886 for Solvents/VOCs

- Gas Chromatograph Method
- 1st approved by ASTM in 2003
- Reapproved in 2012 with some minor changes:
  - 500 ppm limit -> 50 ppm limit per compound
  - Good for Low-VOC paints
  - Directly measures solvents/volatiles
  - Same calculation for VOC as EPA 24
  - Determines water by difference
    - (% Volatile - % Solvent by GC = %H_2O)
  - Method is becoming the Industry standard

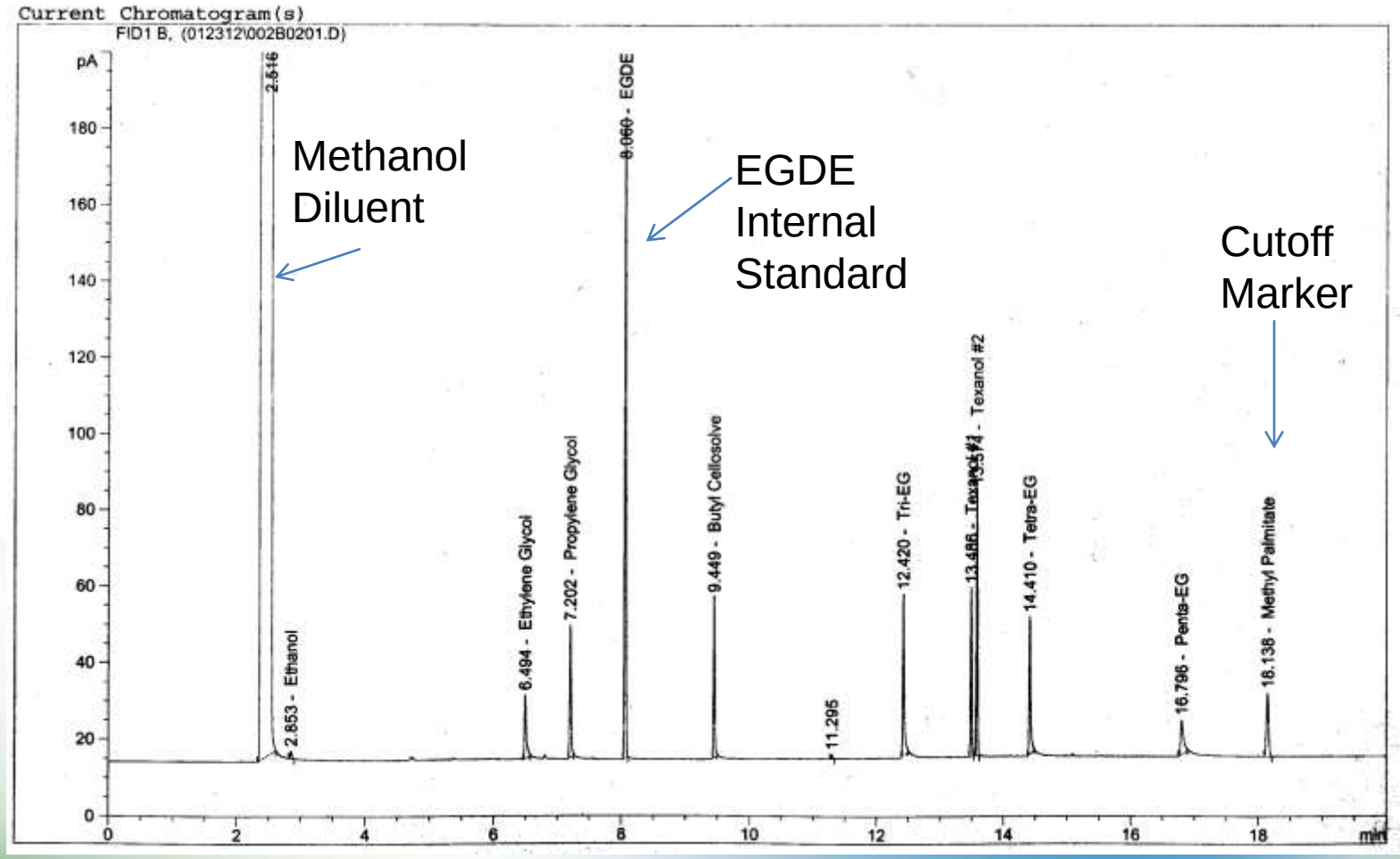
ASTM D6886 Analytical Procedure

- 0.7g paint sample + 10 ml Methanol (in duplicate)
- Add 10 ul EGDE Internal Standard
- Mix, sonicate, settle-out pigment or centrifuge
- Analyze by GC-FID (+ GCMS for positive ID)
- Specific instrumental conditions defined
- Quantify the volatiles/solvents detected that elute before Methyl Palmitate marker (~18.5 minutes)
- Methyl Palmitate chosen by SCAQMD based on BP, volatility, vapor pressure, etc.

GC Chromatograms:

- Low-VOC paint (<50 g/l)
- Humectants/Surfactants
- Low-VOC Coalescents
- Consumer Paint Comparisons
- Various Additives
- “Zero-VOC” paint
- Colorants (Conv/Low-VOC)
- Common Solvents/Co-Solvents

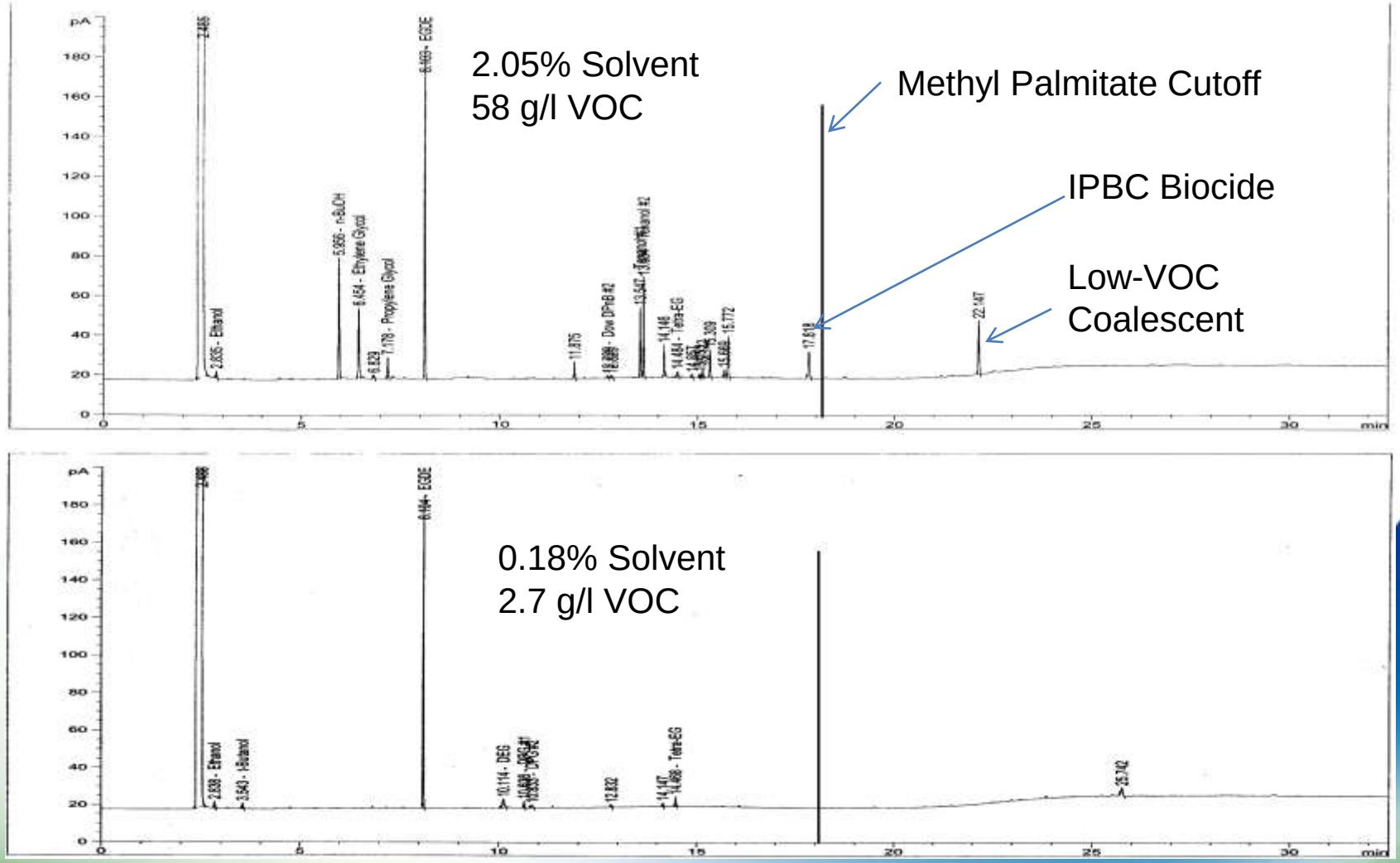
Chromatogram of Common Solvents



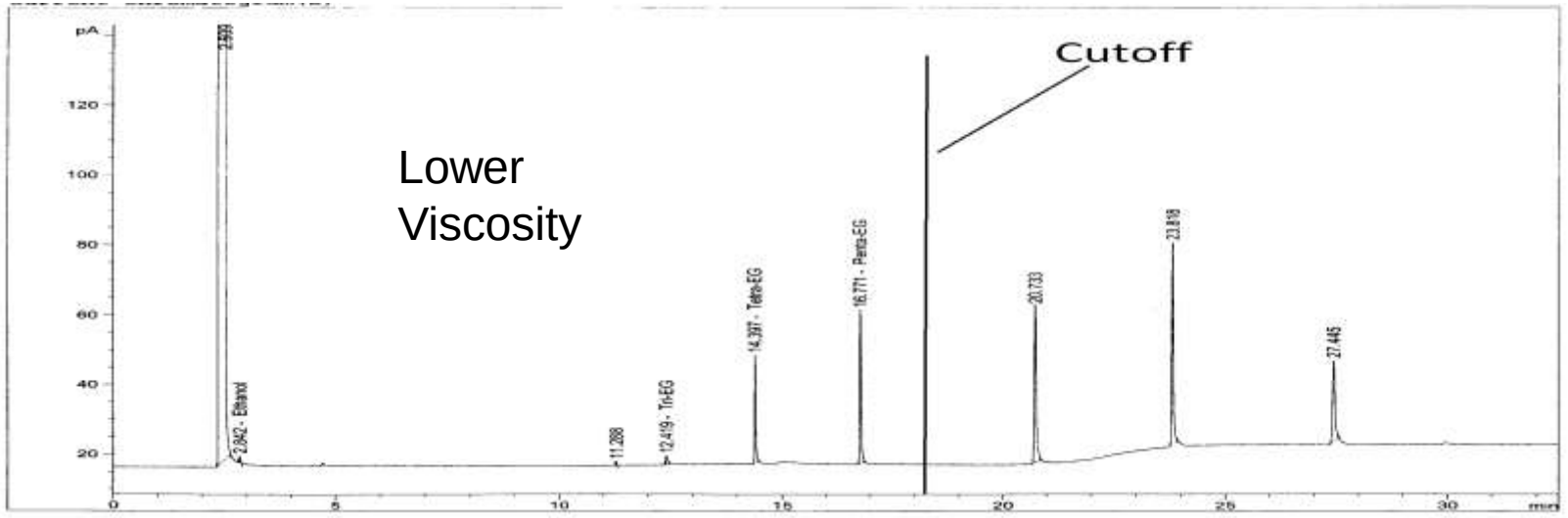
Retention Times for Common Compounds

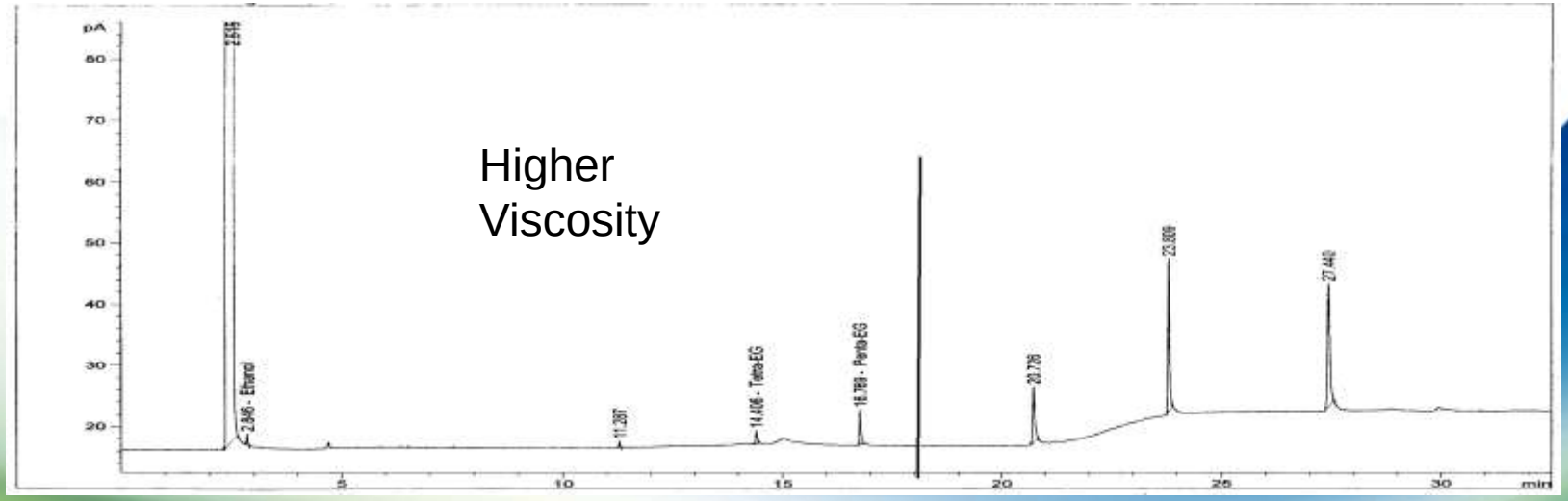
Ret Time	Name
3.02	Ethanol
3.40	IPA
3.76	t-Butanol
6.15	n-Butanol
6.38	Dowanol PM
6.64	EG
7.35	PG
7.65	AMP-95
9.34	n-Butyl Ether
9.66	Butyl Cellosolve
10.23	DEG
10.86	2-Ethylhexanol
12.26	Butyl Carbitol
12.60	Tri-EG
13.35	Vantex-T
13.68	Texanol #1
13.76	Texanol #2
14.62	Tetra-EG
15.83	IPBC
17.11	Penta-EG
18.54	Methyl Palmitate

Paints: Low-VOC vs "Zero-VOC"

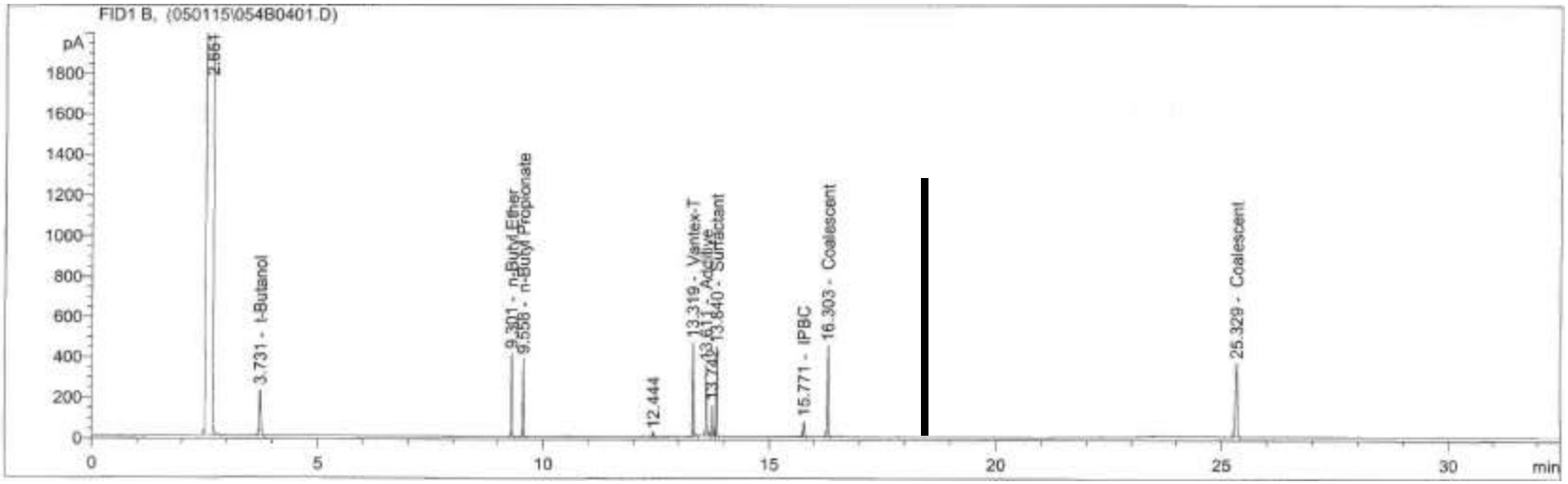


Humectants

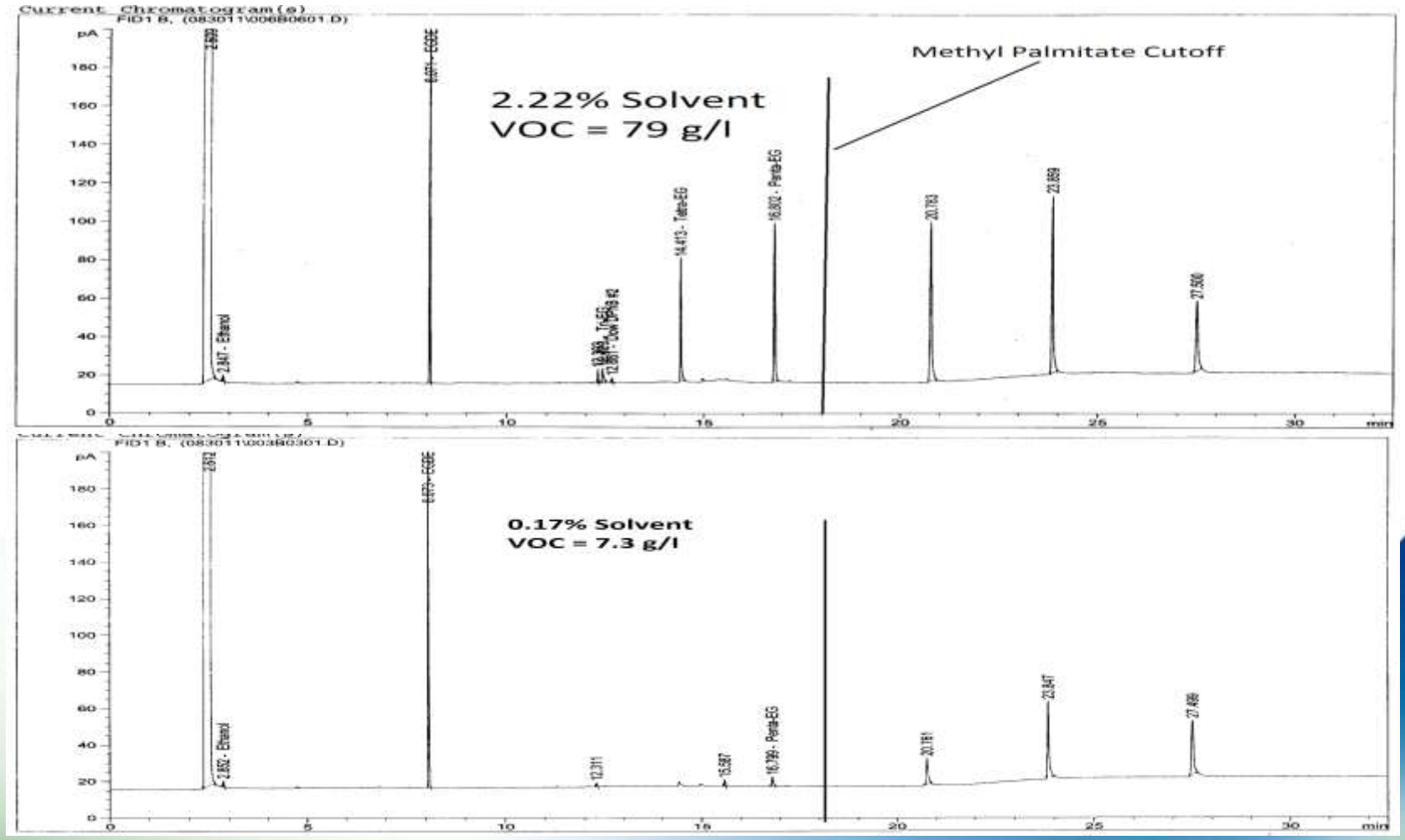

Cutoff
Lower
Viscosity
pA
2.939
2.942 - Ethanol
11.288
12.419 - TriEG
14.397 - Tetra-EG
16.771 - Penta-EG
20.733
23.818
27.445
min


Higher
Viscosity
pA
2.946 - Ethanol
11.287
14.406 - Tetra-EG
16.789 - Penta-EG
20.726
23.809
27.449
min

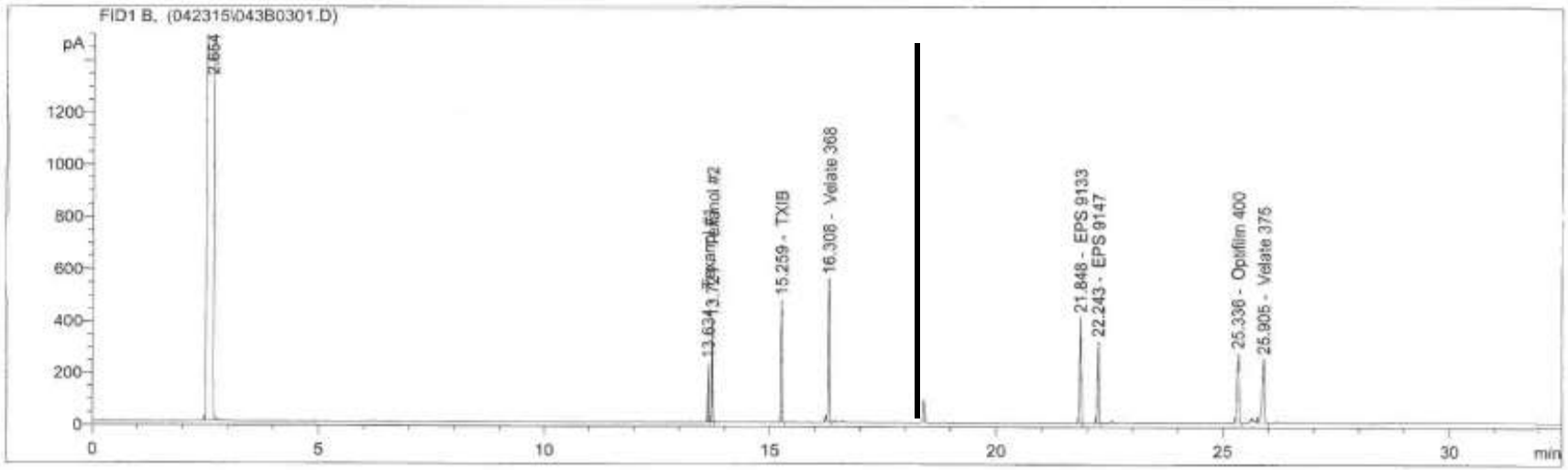
Resin + Surfactant +Additives

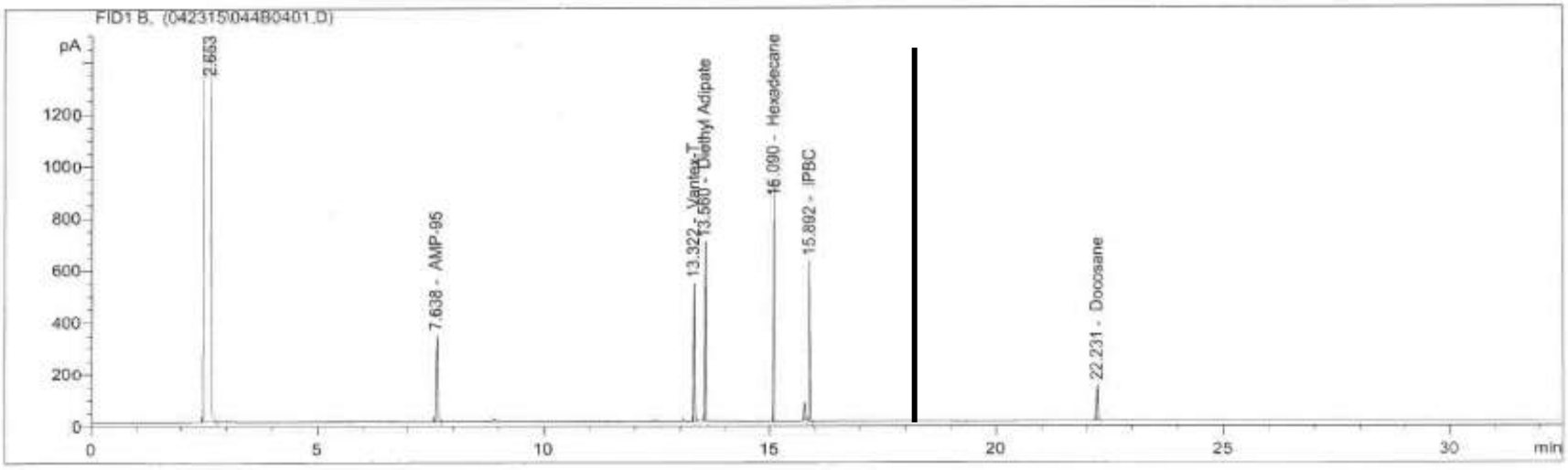


Colorants: Traditional vs Low-VOC



Coalescents, Additives, BP Markers



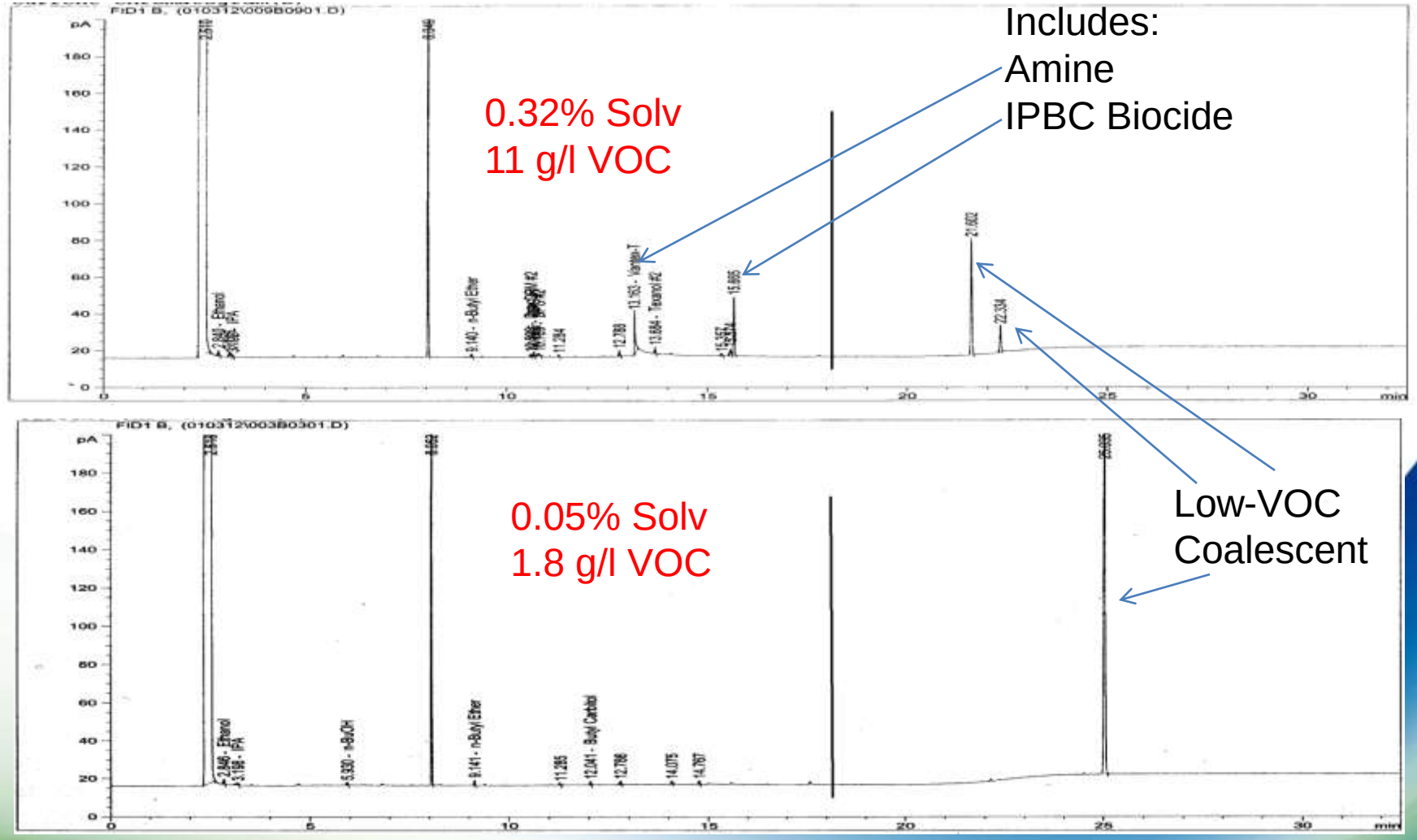


Low-VOC Coalescents

- Texanol
- Paraplex WP-1
- Velate 368
- Dapro FX-514
- Methyl Palmitate
- EPS 9133
- EPS 9147
- Santicizer 160
- Loxanol EFC 100
- Optifilm 400

- 13.8 min = VOC
- 13, 15, 19, 23 = Partial VOC
- 16.5 = VOC
- 17.8 = VOC
- 18.4 = Cut-off for VOC
- 21.3 = Not VOC
- 22.4 = Not VOC
- 24.5 = Not VOC
- 25.1 = Not VOC
- 25.5 = Not VOC

Zero-VOC Paint Comparisons



Example VOC Calculation

- % NVM = 50.00%
- % Volatile = 50.00%
- % Solvent = 0.15%
- % Water = 49.85% by difference
- Wt/Gal = 10.40 lbs
- VOC (lb/gal) = 0.04 lb/gal
- VOC (g/l) = 5.0 g/l

Remember:

- GC-based methods are but one of many methods used for VOC worldwide
  - EPA 24
  - SCAQMD M313
  - ISO-11890
  - ISO-17895
  - Emission Chamber Testing

Summary:

- GC methods such as ASTM D6886 and M313 are a direct measurement of volatiles.
- Caution: GC methods give false positives
- Some common biocides, additives, and low-VOC coalescents give positive results using this method
- Especially critical with zero-VOC paints
- If concerned, run these GC methods
- The analysis of raw materials and additives is a must before the development of new paints
- Formulators/Regulators: Ask suppliers very specific questions about their products:
    - What is the VOC of your product?
    - According to what method?

Thank You

- Contact:

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