Comprehensive VOC Analysis of Architectural Coatings

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Overview

- VOC definitions
- Indirect vs. direct methods
- Modifications to ASTM 6886
- New methods development
- Headspace analysis
- California manual for VOC determination
VOC Definitions

- VOLATILE ORGANIC COMPOUND (VOC) is any volatile compound of carbon, excluding methane, carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, ammonium carbonate, and exempt compounds which participates in atmospheric photochemical reactions.
- VOCs are “solvents” which “evaporate” from the coating during and after application, excluding exempt compounds.
- **U.S.** VOCs are what you measure by EPA Method 24 (ASTM Practice D3960).
- **ISO (Europe)** VOCs are compounds with boiling points lower than diethyladipate (polar compounds) or tetradecane (non-polar compounds).

VOC definitions

- Material VOC: grams of VOC per liter of coating
  \[ VOC_{material} = \frac{g_{VOC}}{L_{paint}} \]
- Coating VOC (regulatory VOC): grams of VOC per liter of coating – liters of water – liters of exempts
  \[ VOC_{coating} = \frac{g_{VOC}}{(L_{paint} - L_{water} - L_{exempts})} \]
Traditional VOC Measurement

- Determine density of coating
  - Weight-per-gallon cup
- Determine “solids” of coating
  - Heat at 110°C for 1 hour
  - ASTM 2369
- Determine water in coating
  - GC or Karl-Fisher titration

Weight per gallon and solids

Weight per gallon cup

ASTM 2369:
paint + water, 110°C for one hour
Significance of ASTM D 2369 solids determination

- Actually defines VOC
- Problems:
  - Depends on oven
  - Depends on paint matrix
    - Resin – type
    - Pigments
    - Additives
    - Multicomponent reactive coatings
  - Depends on amount of sample and water or solvent
    - ASTM currently examining for total revision – possibly no solvent
    - Different labs use different amounts of water/solvent

Water determination

- Karl Fisher titration
- Problems:
  - Size of sample
  - Matrix
  - Solvent
  - Uncertainty
- Gas Chromatography
  - Uncertainty
Experimental Data Used to Calculate VOC Values

\[ f_v = \text{weight fraction of total volatile content} \]
\[ (1 - \text{weight fraction solids content}) \]

\[ f_{voc} = \text{weight fraction of VOC content} \]

\[ f_w = \text{weight fraction of water content} \]

\[ D_p = \text{density of paint in g/L} \]

\[ D_w = \text{density of water in g/L} \]

\[ f_{ex} = \text{weight fraction exempt solvent} \]
\[ \text{(must include term for each exempt solvent)} \]

\[ D_{ex} = \text{density of exempt solvent in g/L} \]

VOC Calculations for Method 24 (no exempts)

Equations based on Method 24 (ASTM 3960) for coating and material VOC using indirect method:

\[ VOC_{coating} = \frac{(f_v - f_w)D_p}{1 - [f_w(D_p/D_w)]} \]

\[ VOC_{material} = (f_v - f_w)D_p \]
Direct VOC Measurement

- Determine density of coating
  - Weight-per-gallon cup
- Determine “solids” of coating
  - Heat at 110 C for 1 hour
  - ASTM 2369
- Determine fraction VOC directly
  - Gas chromatography
  - ASTM D 6886

VOC Calculations for Direct Method based on ASTM D-6886 (no exempts)

Equations used for direct method based on fraction of VOC content (ASTM D-6886):

\[
VOC_{coating} = \frac{f_{voc}(D_p)}{1 - [(f_v - f_{voc})(D_p / D_w)]}
\]

\[
VOC_{material} = f_{voc} D_p
\]
• Prepare sample with known amounts of possible analytes and internal standard(s)

• Obtain areas for each peak from GC

• Calculate relative response factors for each analyte

\[ RF = \frac{AA \times MI}{AI \times MA} \]

where AA and AI are areas of analyte and internal standard and MA and MI are masses of analyte and internal standard

• GC of dry fog coating

• Prepare sample of coating with known mass of internal standard

• Obtain areas for each peak from GC

• Calculate fraction analyte for each analyte found

\[ FA = \left( \frac{(AA \times MI)}{(AI \times RF)} \right) / \text{mass coating sample} \]

• Total VOC fraction is sum of all analyte fractions
ASTM D 6886-03

Standard Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography

Assumptions

- For air-dry waterborne architectural coatings with a material VOC level below 5%, the number of different individual solvents will be a small, and
- The probable solvents are likely to be ethylene glycol (EG), propylene glycol (PG), ethylene glycol butyl ether (EB), diethylene glycol butyl ether (DB), and/or Texanol (TX).
Coating Analysis by Direct Injection (with modifications to ASTM D6886)

- Add 0.6 to 0.8 g of coating to a 20 or 40 mL vial containing 3-5 g of ceramic beads and 10mL of THF or acetone or IPA containing 1 mg/mL ethylene glycol diethyl ether (EGDE). Mix the contents by shaking.
- Alternatively, add 0.6-0.8 g of coating to a 20 or 40 mL vial containing ceramic beads and add 10.0mL of THF or acetone or IPA. Add 20 μL EGDE and reweigh. Mix the contents by shaking.
- Inject 1μL of the coating solution/dispersion into a GC with flame ionization detection and calculate the amount of each VOC present in the coating using experimental peak areas and measured response factors.

ASTM D6886 sample preparation

- Teflon lined septum cap
- Ceramic beads (mixing aid)
- Sample + solvent + EGDE
- Paint sample
GC Retention Time Library

VOC methods used by California regulatory agencies

<table>
<thead>
<tr>
<th>agency</th>
<th>method(s)</th>
<th>analysis</th>
<th>type of VOC analysis (indirect or direct)</th>
<th>uncertainties</th>
</tr>
</thead>
<tbody>
<tr>
<td>California Air Resources Board (CARB)</td>
<td>310</td>
<td>VOCs and exempts in consumer products</td>
<td>indirect analysis of total volatile content, direct analysis of exempts using GC/FID</td>
<td>3% for total volatiles, none given for exempts</td>
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<tr>
<td>South Coast Air Quality Management District (SCAQMD)</td>
<td>313, 303</td>
<td>VOCs and exempts</td>
<td>direct analysis of VOC by GC/MS, exempt by GC/TC</td>
<td>none given</td>
</tr>
<tr>
<td>Bay Area Air Quality Management District (BAAQMD)</td>
<td>21, 22, 41, 43</td>
<td>VOCs and exempts in coatings</td>
<td>indirect analysis of total volatile content, exempts by GC/TC and GC/FID</td>
<td>none given</td>
</tr>
</tbody>
</table>
### Precision Values

<table>
<thead>
<tr>
<th></th>
<th>ASTM Method</th>
<th>Reproducibility</th>
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<tbody>
<tr>
<td>Density</td>
<td>1475</td>
<td>1.8%</td>
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<tr>
<td>Volatile</td>
<td>2369</td>
<td>4.7%</td>
</tr>
<tr>
<td>Water (KF)</td>
<td>4017</td>
<td>4.9%</td>
</tr>
<tr>
<td>VOC-Direct</td>
<td>6886</td>
<td>16.2%</td>
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### Water-borne Coatings from the 2001 ARB Coatings Survey

<table>
<thead>
<tr>
<th>coating class</th>
<th>fv</th>
<th>fw</th>
<th>fvoc</th>
<th>Dp</th>
<th>VOCreg (g/L)</th>
<th>inter-laboratory</th>
<th>inter-laboratory</th>
<th>Direct Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete Curing Compounds</td>
<td>0.78</td>
<td>0.74</td>
<td>0.040</td>
<td>1018.3</td>
<td>155</td>
<td>207</td>
<td>102</td>
<td>25</td>
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<tr>
<td>Fire Retardant - Clear</td>
<td>0.55</td>
<td>0.54</td>
<td>0.015</td>
<td>1165.02</td>
<td>33</td>
<td>127</td>
<td>68</td>
<td>5</td>
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<tr>
<td>Fire Retardant - Opaque</td>
<td>0.43</td>
<td>0.40</td>
<td>0.030</td>
<td>1365.72</td>
<td>90</td>
<td>86</td>
<td>43</td>
<td>14</td>
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<tr>
<td>Flat</td>
<td>0.47</td>
<td>0.44</td>
<td>0.030</td>
<td>1365.72</td>
<td>103</td>
<td>106</td>
<td>53</td>
<td>16</td>
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<tr>
<td>Industrial Maintenance</td>
<td>0.45</td>
<td>0.47</td>
<td>0.080</td>
<td>1239.78</td>
<td>298</td>
<td>70</td>
<td>32</td>
<td>28</td>
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<tr>
<td>Lacquers</td>
<td>0.68</td>
<td>0.56</td>
<td>0.120</td>
<td>1030.28</td>
<td>292</td>
<td>95</td>
<td>42</td>
<td>35</td>
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<tr>
<td>Nonflat - High Gloss</td>
<td>0.54</td>
<td>0.46</td>
<td>0.080</td>
<td>1209.98</td>
<td>218</td>
<td>88</td>
<td>41</td>
<td>29</td>
</tr>
<tr>
<td>Nonflat - Low Gloss</td>
<td>0.51</td>
<td>0.47</td>
<td>0.040</td>
<td>1261.86</td>
<td>429</td>
<td>106</td>
<td>52</td>
<td>19</td>
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<tr>
<td>Nonflat - Medium Gloss</td>
<td>0.56</td>
<td>0.50</td>
<td>0.060</td>
<td>1208.68</td>
<td>184</td>
<td>106</td>
<td>51</td>
<td>28</td>
</tr>
<tr>
<td>Recycled</td>
<td>0.51</td>
<td>0.42</td>
<td>0.090</td>
<td>1269.88</td>
<td>245</td>
<td>81</td>
<td>37</td>
<td>31</td>
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<tr>
<td>Roof</td>
<td>0.43</td>
<td>0.41</td>
<td>0.020</td>
<td>1269.88</td>
<td>53</td>
<td>78</td>
<td>40</td>
<td>8</td>
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<tr>
<td>Varnishes - Clear</td>
<td>0.69</td>
<td>0.58</td>
<td>0.110</td>
<td>1042.26</td>
<td>290</td>
<td>105</td>
<td>47</td>
<td>36</td>
</tr>
<tr>
<td>Wood Preservatives</td>
<td>0.96</td>
<td>0.82</td>
<td>0.040</td>
<td>1018.3</td>
<td>247</td>
<td>327</td>
<td>156</td>
<td>40</td>
</tr>
</tbody>
</table>
Problem areas for ASTM 6886

- 2K - analyze separate components or mixture (before or after reaction)?
- UV cure - how do you measure cure volatiles?
- Powder coatings - what, if anything, comes off when powder is cured?
- Semi-volatiles remaining in the paint film? (Texanol, plasticizers, other coalescents)

Summary of new methods developed as part of CARB project

- Standard Test Method for Direct Analysis of the VOC and HAP Content of Multi-Component Coatings by Gas Chromatography (2K Method)
- Standard Test Method for the Direct Analysis of the Common Hazardous Air Pollutants (HAPs) in Solventborne Air-Dry Coatings by Gas Chromatography (HAP Method)
- Standard Test Method for Determination of the VOC Content Remaining in Paint Films After Total Volatile Content Determination by ASTM Method D2369 (Film Extraction Method)
Standard Test Method for the VOC and HAP Content of Multi-Component Coatings by GC

• Use for solventborne and waterborne multi-component coatings curing by chemical reaction and coatings which cure by heating (i.e. melamine-cure coatings and powder coatings)
• Prepare 100 grams of mixed coating, transfer 100 mg to 20mL headspace vial, seal and allow to cure for 24-26 hours at ambient temperature
• Heat sample for 30 minutes at 110°C, cool, add known quantity of acetone containing internal standard, and mix.
• Solution analyzed by gas chromatography using 5% phenyl/95% polydimethylsiloxane (PMPS) capillary column
• May use THF as solvent if sample contains acetone.
• Acetone and isopropyl alcohol may coelute. If either present, confirm using Carbowax™ capillary column. Other possible coeluting compounds are PM acetate/ethylbenzene, 2-butoxyethanol/o-xylene – can adjust heating rate using PDMS column
• Sample cures under application conditions with no added solvent
• Obtain total fraction VOC and fractions of any exempt solvents and HAPs

Standard Test Method for Determination of Common HAPs in Solventborne Air-Dry Coatings by GC

• Determine MIBK, toluene, commercial xylene, cumene, naphthalene if present at 0.01 weight percent or greater
• Known weight of coating dispersed in THF or acetone, internally standardized, analyzed by GC to give speciated composition of VOCs including HAPS
• Solid phase microextraction (SPME) using GC/FID or GC/MS may be used for identification of VOCs present
• Possible co-eluting compounds can be separated using PMPS column by varying heating rate
• Cumene introduced from Aromatic 100
• Naphthalene introduced from Aromatic 150
SPME Sampling Syringe

- Fused-silica fiber tip coated with Carbowax-divinylbenzene (or other adsorbing material) is placed in contact with coating headspace.
- Solvent molecules in headspace are adsorbed and concentrated on fiber.
- Fiber is withdrawn into protective metal sheath and inserted into hot GC injection port where solvent molecules are thermally desorbed onto column.
Standard Test Method for Determination of the Semi-volatile Content Remaining in Paint Films after ASTM Method D2369

- Fundamental difference between EPA Method 24 and ASTM D6886
  - For EPA Method 24, semi-volatiles remaining in the paint film after ASTM D2369 are not counted as VOCs
  - For ASTM D6886 (direct analysis) the total amount of all semi-volatiles in the paint is determined
  - For consistency, the amount of semi-volatiles remaining in the film must be subtracted from the amount obtained using the direct method
- Immediately after a D2369 determination (solids), the aluminum pans are cut up, placed in a 125 mL Erlenmeyer flask, and 20 mL of acetone or MEK are added. Flask is stirred for 12-24 hours, extracting remaining VOCs from film
- 5.0 mL of THF or acetone with internal standard added, and solution analyzed using GC
- VOCs with BP > 250°C and retention times ≥ Texanol® are determined.
- Peaks may appear in chromatogram not seen in original unheated sample due to oxidative degradation
- VOCs obtained from the extracted sample are subtracted from the original VOC amount obtained from the unheated sample

Recommended VOC Analysis Methods

<table>
<thead>
<tr>
<th>Coatings Type</th>
<th>Recommended Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-dry waterborne coatings without exempt solvents, VOC content &lt; 10%</td>
<td>Revised D6886 and Extraction Method</td>
</tr>
<tr>
<td>Air-dry waterborne coatings without exempt solvents, VOC content &gt;10%</td>
<td>Revised D6886 or EPA Method 24</td>
</tr>
<tr>
<td>Air-dry solventborne coatings, without exempt solvents</td>
<td>EPA Method 24; Use Revised D6886 and HAP Method if HAP content is to be measured</td>
</tr>
<tr>
<td>Air-dry solventborne coatings, with exempt solvents</td>
<td>Revised D6886 to determine exempt solvents and speciated VOC content</td>
</tr>
<tr>
<td>Solventborne 2K coatings, solids content &lt; 90%</td>
<td>EPA Method 24 for mass-based VOC content; new 2K method if HAP content or speciated content is desired</td>
</tr>
<tr>
<td>Solventborne 2K coatings, solids content &gt;90%</td>
<td>EPA Method 24 with new High Solids volatile method</td>
</tr>
<tr>
<td>Waterborne 2K coatings</td>
<td>New 2K method</td>
</tr>
<tr>
<td>Coatings containing Silanes, Siloxanes and Silane-Siloxane Blends</td>
<td>ASTM D5095 for total volatile content and new D6886 for speciation</td>
</tr>
<tr>
<td>Coatings containing semi-volatile organic compounds and/or with boiling points greater than 250°C and D 6886 primary capillary column retention time greater than Texanol®</td>
<td>Revised D6886 and Extraction Method</td>
</tr>
</tbody>
</table>
**GC analysis - direct and dynamic headspace**

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**Sample Preparation**

- Add neat coating to 20mL vial containing ceramic media
- Add internal standard and mix
- For waterborne, add 10.0mL internal standard in water and mix
- Transfer 10-20 mg of above to 20mL headspace vial
- Equilibrate for 20 minutes in headspace oven
Headspace GC of a SB melamine-cure automotive primer

1. Methanol
2. IPA
3. MEK
4. iBuOH
5. nBuOH
6. MIBK
7. Toluene
8. BuOAc
9. EtBz
10. Xy, m&p
11. oXy,
12. Aromatics
13. Naphthalene

Headspace GC of a GMA Acrylic Powder Coating

1. MMA
2. AIBN
3. BMA
4. GlyMA
5. Benzoin
Static headspace analysis:
conclusions

- Headspace analysis is useful for analysis of high-boiling volatiles – no need to analyze dried film
- Headspace analysis may be useful for analysis of semi-volatiles
- Headspace analysis allows sample to be tested under actual curing conditions – useful for powder coatings and high-temperature cure coatings
- Headspace cannot provide consistent analyses of highly polar analytes, such as glycols
- More work is needed before static headspace can be included in VOC analysis methods

The future?  VOC defined by boiling point marker

ISO 11890-2, Paints and varnishes – Determination of volatile organic compound (VOC) content – Part 2: Gas-chromatographic method - uses a boiling point limit of 250°C and defined chromatographically by the retention time of diethyl adipate on a 60m poly(6% cyanopropylphenyl/94% dimethylsiloxane) (DB-1301™) capillary column.
First use of BP marker in US: Green Seal GS-11 Standard

VOC: Any organic compound which participates in atmospheric photochemical reactions as defined by the U.S. EPA in 40 CFR 51.100 (s) and has an initial boiling point lower than or equal to 280°C measured at standard conditions of temperature and pressure.

Summary

- A suite of VOC analysis methods has been developed for use in analyzing any architectural coating sold in California
- For high VOC solventborne coatings with no exempt compounds, EPA Method 24 provides an accurate and simple procedure for determining VOC
- These new methods were tested against those used by regulatory agencies and industry and were found to be at least equal in quality and generally superior to other methods.
- A California Manual for Determination of the VOC Content of Architectural Coatings was developed.
VOC Manual

APPENDIX : California Manual for Determination of the VOC Content of Architectural Coatings

This manual is a compilation of new methods developed at California Polytechnic State University and a listing of required existing methods for use in the determination of the VOC content of all architectural coatings sold in California. These new methods are under development and have been presented to ASTM and will be submitted for comment and balloting before the end of the year. This manual is not intended to replace any of the existing district methods manuals but is intended to complement them. This manual will be revised on a regular basis to incorporate new methods and to update changes in existing methods.

Links:

- California Manual for Determination of the VOC Content of Architectural Coatings (and final report for this project)
  - http://www.arb.ca.gov/coatings/arch/testmethod.htm
- Questions, comments, training?
  - djones@calpoly.edu