June 2nd VOC Working Group Meeting Notes

Attendees:

### SCAQMD Staff
- Brad Parrack (mod)
- Ningqing Ran
- Heather Farr
- Joan Niertit
- Hanna Lignell
- Tereso Banuelos

### Phone Participants
- Representing
  - David Darling
  - Lisa Stone
  - Barbara Belmont
  - Stan Tong
  - Dane Jones
  - David Nevison
  - Todd Alexander
  - Chris Pollack
  - Ray Lukco
  - Paul Sutton
  - Chris Nardi
  - Dan Forestier
  - Pat Gieske
  - Matt Plate
  - Dan Knoffe
  - Barry Cupp
  - Stephen Foster
  - Barry Marcks
  - Barry Lee
  - Bill Orange
  - Pat Lutz

Brad Parrack opened the meeting by reminding the working group of the key discussion points from the May 25th, 2016 Working Group meeting:

1) Comment Response to ACA and Dane Jones
2) Discussion of the documentation and templates distributed to the working group on May 24th, 2016

Brad Parrack indicated that there were two loose threads which needed to be addressed prior to progressing through Phase One of the SCAQMD Pilot Test.

**Issue 1) Uncertainty regarding the use of the DB-5 column from ASTM 6886.**

Brad Parrack detailed comments that SCAQMD had received regarding the difficulty in using the 624 column in a production setting, and mentioned that SCAQMD appreciated the additional effort that would be required for a lab to switch back and forth between the two columns for production and research. Brad Parrack indicated that after further discussion internally and with EPA officials, it was decided that the DB-624 column would be a requirement for the Pilot Test, as it was a variable in the resultant data that we would be able to control. Brad Parrack indicated
that the Pilot Test was initially proposed as an evaluation of M313 proper, and significant deviations from the written method would call into question the Pilot Test’s ability to meaningfully evaluate method performance.

David Darling inquired as to the number of labs that had provisionally signed up to participate in the Pilot Test. Brad Parrack indicated that 7 labs had signed up, barring any dropouts as a result of the column decision. David asked those on the phone who had provisionally signed up if this decision would impact their participation, and 3 labs confirmed that they would not drop out. Brad Parrack asked that labs which did not provide an indication one way or the other over the phone should send him an email with any updates to their participation status.

Dane Jones emphasized that the model number and part number for the Restek column that SCAQMD uses in their laboratory should be sent out to the working group so that everyone could use the same column since it has an advantageous temperature limit compared to 624 columns manufactured by other companies. Joan Niertit added that such a specification would also require the written method to include a statement indicating that any 624 column with similar temperature limits could be used, and that any recommendation should not be taken as an endorsement by AQMD.

Matt Plate added that the appropriate convention for listing a column without giving an endorsement is to specify its USP phase composition, which in this case would be USPG43. Adding that manufacturer choice is up to each user so long as the phase is the identical and the column can meet the temperature requirements as listed in the method. Brad Parrack indicated that such a change would be added to the written method and posted to the website upon completion.

A phone participant asked for clarification of the column dimensions, and Tereso Banuelos responded that the column had a 0.32 mm ID, a 1.8 um thickness, and 30 m length.

**Issue 2) Finalizing the number of samples to be sent out during the Pilot Test, the sample types to be used, and the VOC concentrations for each sample.**

Brad Parrack stressed AQMD’s commitment to having representative concentrations and sample types, but indicated that there were also logistical and cost concerns that would prevent AQMD from sending out more than 4 samples for this test.

Brad Parrack submitted the following samples and concentrations to the working group as a starting point for discussion:

- 50 g/L Coating Flat
- 50 g/L Coating Semigloss
- ~200 g/L Coating Polyurethane
- ~5-15 g/L Coating Alkyd

David Darling asked AQMD staff if this process was set to be iterative and if AQMD intended to pursue other sample types in the future, since M313 might be written into additional rules. Joan Niertit indicated that there were no objections from AQMD to envision future efforts along those lines. David Darling added that it might be prudent to include a 25 g/L sample to the Pilot Test since AQMD had previously expressed interest in adopting a 25 g/L limit in the future.

Pat Lutz asked that AQMD consider adding a colorant to the Pilot Test. Brad Parrack reiterated the AQMD’s commitment to limiting the number of samples to 4, and asked the group if there was a sample that they would prefer to see dropped if a colorant were to be added.

Dane Jones responded and said that a colorant would be much preferable to either the flat or the semigloss at any concentration, and added that he gets as many requests to analyze colorants as he does paints. Dane added that colorants present an interesting challenge for analysis since they are comprised of so many glycols with varying response factors.
Pat Gieske from Valspar suggested that a super-compliant 10 g/L VOC coating semigloss be added in place of either the 50 g/L flat or 50 g/L semigloss. Pay Gieske added that the semigloss coating would likely present more analytical challenge than a flat due to the presence of additional resin and would be preferable to include in the Pilot Test if choosing between the flat and the semigloss.

The following general concentrations and sample types were ultimately decided upon as a provisional set of samples:

- 5-15 g/L Semigloss latex
- 200 g/L Polyurethane
- 50 g/L Alkyd
- 50 g/L Colorant

Stan Tong indicated that EPA preferred that one of the coatings be at the regulatory level of 50 g/L, and Brad Parrack asked to take the discussion with EPA offline to discuss the difficulties in adding a 5th sample or converting one of the other samples to a concentration near the regulatory limit.

Brad Parrack transitioned to discussing the documents that were distributed prior to the previous meeting on May 25th and asked for any input, suggestions or mistakes that were noticed by the working group.

Brad Parrack reviewed some of the comments that had been received to this point and indicated that the low end of the mass spec scan range was set to be changed from 5 to 18 amu to improve the baseline noise. Brad Parrack added that the 18 amu level was important to monitor since AQMD monitors water levels during air and water checks and likes to use the same instrument parameters for all components in an analytical sequence.

Brad Parrack addressed concerns about the potential to overload the column with a splitless injection and a 1 uL injection volume. Brad Parrack reminded the working group that although the instrument is recommended to be configured in splitless mode, AQMD only runs the inlet in splitless mode for 0.1 to 0.5 min before opening the split vent. Brad Parrack added that the short splitless hold time is less about putting a lot of sample on the column and more about providing more equilibration time in the inlet, allowing for additional discrimination profile repeatability.

Brad Parrack indicated that AQMD had tried split modes in the past, but found them less useful than a splitless injection with a short hold time. Brad Parrack indicated that the Pilot Test participants are welcome to attempt a split injection, but urged that the participants be open to using a splitless injection with a short hold time since it may prove easier to meet all IOM requirements if configured in this manner.

Lastly, Brad Parrack discussed the challenge of using a post-column split with one detector at atmospheric pressure and one detector under vacuum. Since the FID is used for quantitation, it is important that the sample make it to the detector in a representative fashion and that the lower molecular weight compounds not be selectively pulled towards the mass spec side of the split. Brad Parrack indicated that the written test method will be updated to include more discussion as to the impact that transfer line length adds to molecular weight discrimination.

Brad Parrack reiterated that the method is written to allow for samples peaks to be identified on one instrument (MS) and be quantified on another instrument (FID).

Brad Parrack moved on to the last portion of the agenda, which was to schedule an in-person tour of the M313 process. Brad Parrack indicated that the phase one process would likely take 2 months to complete, and that an early July tour and meeting would provide a good opportunity to follow up on group progress and also give visitors enough time to apply lessons learned from the visit to the work that they were doing well in advance of the mid-August deadline. David Darling indicated that the 7th was a reasonable date, but he would check in with the ACA constituents and determine a date that worked best for the most people.
Brad Parrack reiterated that phase one of the Pilot Test is for participating labs to configure their instrument for the method, prepare an IOM, and use the IOM to evaluate the setup of the instrument. Brad Parrack added that although there is no current form to submit data to the AQMD, one would be created sometime around the July meeting date.

Barry Marcks asked about the amount and kind of data that AQMD expected to receive at the end of Phase One, and Brad Parrack responded that AQMD wants not only the completed discrimination templates back from each lab, but also the supporting chromatograms.

Stephen Foster asked for confirmation on the due date for all Phase One data, and Brad Parrack responded that a hard deadline will not be set until the July meeting, but is currently expected to be early August.

Barry Marcks asked if a relative response factor calibration template will be sent out to the working group, and Brad Parrack responded that such a template for RRF determination and VOC g/L calculation will be sent out during Phase Two since Phase One does not require that any calibrations be performed.