

May 25th VOC Working Group Meeting Notes

Attendees:

<u>SCAQMD Staff</u>	<u>Department</u>
Brad Parrack (mod)	AQMD Lab
Ningqing Ran	AQMD Lab
Heather Farr	AQMD Planning
Joan Niertit	AQMD Lab
Hanna Lignell	AQMD Lab
Tereso Banuelos	AQMD Lab

<u>Phone Participants</u>	<u>Representing</u>
David Darling	ACA
Lisa Stone	PPG
Barbara Belmont	American Research and Testing
William Arendt	Emerald Kalama Chemical
Dane Jones	Cal Poly
David Nevison	Valspar
Todd Alexander	Sherwin-Williams
Chris Pollack	Sherwin-Williams
Ray Lukco	Sherwin-Williams
Paul Sutton	Sherwin-Williams
Chris Nardi	Chromaflo
Jerry Powers	Chromaflo
Dan Forestier	Sherwin-Williams
Pat Gieske	Valspar
Dan Knoffe	Rustoleum
Barry Cupp	Sherwin-Williams
Chelsea Ritchie	RCMA
Guy Wilson	Sherwin-Williams
Pawel Rempala	Emerald Kalama Chemical

Joan Niertit began the meeting by reviewing documentation that was provided in April 20th meeting:

- 1) A de-identified spreadsheet printout of the results of an Instrument Optimization Mix (IOM) analysis
- 2) A de-identified page 2 from a typical M313 report, containing surrogate spike recoveries and analytical details
- 3) A de-identified page 3 from a typical M313 report, containing Continuing Calibration Verification (CCV) information for the compounds of interest for that particular analytical sequence
- 4) A working draft of AQMD M313

Joan Niertit reviewed the approach to the Pilot Test that was explained at the previous meeting, and mentioned that some time was spent in the April 20th meeting detailing some of the sample-instrument interactions that occur during sample analysis of paint in a GC.

Joan began responding to comments from the American Coatings Association (ACA) (Comments can be found on the AQMD VOC Working Group website)

In response to ACA Comment 1 (regarding enforcement and reproducibility of M313) Joan indicated that the current repeatability is not assumed to be a flat 10% for samples analyzed by M313 since AQMD has designed M313 to be within 5 g/L VOC Material, as confirmed through both an interlab and an intralab analysis. Joan Niertit indicated that other laboratories are not compliance laboratories, and thus the Pilot Test statistics should not be required to generate reproducibility limits as might be produced in an ASTM style round robin.

David Darling inquired as to what is meant by 5 g/L Material in terms of a VOC Coating error band, and Joan Niertit explained that the VOC Coating results are calculated from a VOC Material value, then recalculated from a VOC Material level 5 g/L below the measured value and 5 g/L above the measured value, thereby giving the VOC Coating error band.

David Darling indicated that he felt that the standard 10% AQMD enforcement policy was not a good fit for this analysis and Joan Niertit reiterated that the standard 10% range is not used for this analysis. Heather Farr indicated that the lower range of the VOC Coating error band is considered before taking action on any samples above the limit and they do not pursue samples with a lower range below the rule limit.

In response to ACA Comment 2 (scope of the M313 Pilot Test), Joan Niertit indicated that it was not prudent to go full-force into a full-round robin with additional samples and duplicate preparations without working out the kinks of the written method first. Joan Niertit read the ASTM guidance on work performed with new methodologies in a round-robin type setting, the gist of which is that a Pilot Test be conducted in at least 2 laboratories using at least 2 samples.

David Darling responded that ACA's concern is related to generating meaningful statistics and that anything generated from this process needs to be significant from a data quality perspective.

Pat Gieske asked about the phrase "working draft" in regards to the method, and wondered if the method itself was still being developed. Joan Niertit responded that the method itself is complete, but the clarity of the written method was the component that is in process and constructive criticism from this process will lead to revisions to improve its clarity.

David Darling expressed concern about bias in the results due to a "pre-qualification" step of labs being required to run an IOM prior to sample analysis. David Darling also expressed concern about some labs not having access to multiple detectors (FID and MS) on the same instrument and asked for clarity on whether discrete instruments and detectors can be used for this Pilot Test.

Joan responded to the issue of bias by responding that all of the qualifications expected of the labs running the method are already in the method and are performed in the AQMD laboratory and that these QC steps are necessary to ensure quality results.

Dane Jones added that he agreed with Joan Niertit and indicated that the "pre-qualification" step is in fact not a pre-qualification step at all, and is merely a step to ensure that the instrument is suitable to use for analysis. Dane Jones added that he felt that the discrimination performance requirements are one of the strongest components of the method.

A phone participant asked about the reason for so much specification as to separation requirements for the mass spec. Joan Niertit responded that the chromatography needs to be resolved as much as possible because it's critical to apply the correct response factors to each constituent and the MS is often your only guide for knowing which response factors to apply to peaks.

Joan Niertit responded to comment 3 (sending out a check standard along with the samples) by indicating that checking the instrument performance before sample analysis was a better path forward than running the samples and the standard at the same time and then being forced to potentially invalidate the results.

A phone participant indicated that they would prefer to run more samples than 3-4 since during this study because they are going to be switching columns and they fear they will lose efficiency by running only a handful of samples at a time. Dane Jones seconded that point, adding that he felt the upfront process of getting the instrument configured and validated with the IOM would be more time consuming than the actual sample analysis. Dane Jones concluded by saying that any time spent on a main instrument running M313 was going to be time spent at the exclusion of samples run by 6886, and that this was going to be an inconvenience for many participating laboratories. Dane asked that the number of samples be increased to allow for a better economy of scale.

Joan Niertit asked about what changes, aside from the column, would be required to re-configure instruments for M313. Dane Jones responded that the column change is the only meaningfully large inconvenience, but that it is still a major inconvenience since participating labs might go through the tedious column swapping process multiple times during the duration of the test.

Joan Niertit suggested that maybe the DB-5 column from 6886 might be allowable for use in this Pilot Test, and Dane Jones indicated that this was a great idea for convenience.

Dane Jones indicated that one large advantage that the DB-5 column has over M313's 624 column is that it has a higher temperature range since the 624 can only go to 260 degrees C. Tereso Banuelos added that the J&W version of the 624 column only goes to 260 degrees, but the Restek version goes up to 320 degrees.

David Darling reiterated that ACA is concerned about the expansion of M313 into other rules and that the Pilot Test should be reflective of the expansion of M313 into other categories.

Joan Niertit concluded her responses to ACA's 3rd comment (use of multiple detectors on the same instrument) and indicated that the only method requirement along those lines is that the analyst know the identity of the peak getting quantified on the FID-side, whether it be by MS or by knowledge of formulation. Separate instruments are acceptable for M313.

David Darling inquired about what would be required from the working group to work towards using the DB-5 column for the duration of the Pilot Test. Joan Niertit indicated concern that the results could later be called into question and each column might need to have its own statistics calculated for it. Joan Niertit added that EPA would need to be OK with it, and Heather Farr added that industry would also need to be accepting of the decision and not hold any Pilot Test statistical deviations against the method since it could be a result of something they were on board with performing. Joan Niertit indicated that this decision would require additional thought.

Pat Gieske added in that the desire of industry is simply to have a method to use to come up with the same numbers no matter who runs it. Pat added that it is widely understood that EPA Method 24 is a poor method for low concentration coatings, but asked if 6886 is going to give meaningfully different results than 313.

Joan Niertit asked if "ballpark" was close enough for industry. Heather Farr added that the purpose of this Pilot Test isn't to compare the results from ASTM D6886 to M313, but to evaluate the error of M313 directly. Pat Gieske mentioned that it was his opinion that the current draft language left too much flexibility and urged AQMD to tie down some of the flexibility, and thus, uncertainty in the method so that it became clear how industry was intended to run the method.

Joan Niertit asked the phone participants if there was any reason to convert an instrument back to a 6886 instrument once the conversion to M313 had been completed. Pat Gieske responded that it is often the case that multiple samples be run in a batch and that 6886 allowed for quicker output.

Joan Niertit asked the phone participants what exactly was quicker about 6886, and Dane Jones responded that there are not nearly as many checks in 6886 as there are in M313, and that the analytical run is shorter. Joan Niertit added that the additional QC was not something that external labs necessarily needed to run if they choose not to, since AQMD will not be utilizing industry's numbers for compliance purposes. Joan Niertit set aside further

discussion on the selection of the column until a follow-up meeting since it might prove to be a lengthier discussion than anticipated.

Joan Niertit transitioned to a next comment (sample types to analyze during the Pilot Test. Joan Niertit presented the following sample types and concentrations as initial options:

50 g/L Flat

50 g/L Semigloss

275 g/L Polyurethane, so long as the VOC Material value is below 150 g/L VOC Material and it is a single-component product

Chelsea Ritchie asked what VOC concentration was meant when discussing “low VOC” for roof coatings, and Joan Niertit clarified that 150 g/L Material is the high concentration cutoff for M313, adding that she was not sure offhand what the regulatory limit was for roof coatings, but that often times round robin style tests are performed at the regulatory limit.

David Darling added that one of the intentions of ACA’s comment letter was to urge the AQMD to look at more problematic coatings during this Pilot Test; biocides, semi-volatiles near Methyl Palmitate’s elution time, and inlet breakdown products.

Heather Farr added that breakdown products do not necessarily need to be subjected to a round-robin style test since they can be demonstrated to be break down and simply not get tallied in the final VOC count.

Joan transitioned to ACA’s 4th comment (Lab visit) and indicated that July would be a good time for a visit, although it would be helpful if Industry could provide a list of things that they would like to see because it would assist AQMD in compiling a work plan for the visit.

Guy Wilson added that Industry originally proposed a visit to the lab because seeing someone perform the method in front of them is much more powerful than simply reading a lengthy method.

Joan Niertit added that there are three components of the method that are a bit discontinuous; sample and standard prep is certainly something that can be performed in front of an audience, but instrument configuration is, for the most part, already complete in the AQMD laboratory and that would be difficult to demonstrate. Joan mentioned that instrument configuration might be better addressed with a good explanation of how AQMD performs the optimization. Lastly, data reduction might be difficult to perform in real time, but AQMD can certainly explain the data reduction process and demonstrate how contaminants are removed during the data workup.

Dane Jones added that the listing of the column in the written method implies use of a standard Agilent 624 column, but the newfound information that AQMD uses a 624 Sil MS column obviates many of his originally had with the 624 column for the Pilot Test; in fact, the higher temperature allowance would allow for the 624 column to be used in the same oven as the DB-5 even when not in active use. Joan Niertit indicated that AQMD would improve the clarity of the written method in regards to column specifications.

Joan Niertit transitioned to responding to Dane Jones’ comments and went straight to comment 2 (allowance of detectors in separate instruments). Joan Niertit indicated that the method has indicated for some time that a single system with 2 detectors is not required for analysis.

Joan Niertit responded to Dane Jones’ second comment (use of THF) and indicated that the method allows for methanol to be used as a solvent, it is just the case that many samples are incompatible with methanol and thus AQMD tends to default to THF.

Joan Nieritit transitioned to Dane Jones 4th comment (sample types for Pilot Test) and indicated that an alkyd would provide interesting results and is a point of interest for AQMD, although she is not sure it's a perfect match for this Pilot Test.

Joan Nieritit added that AQMD considers low VOC samples near 0 g/L to be less interesting for the Pilot Test since "0 is 0" and there just isn't much of an opportunity for labs to deviate from this value.

Dane Jones added that his concern was that one lab could generate a result ~ 0.7 g/L and one lab could generate a result ~7 g/L which would be of interest and that a round robin showing excellent results at the low end of the VOC spectrum could result in an increased interest in running M313 in place of 6886.

Pat Gieske added that his concern with the selected concentration levels was that future regulatory limits should be represented in this study since great agreement at 50 g/L is not a guarantee that there will continue to be great agreement at 15-25 g/L. A phone participant expanded on this point, adding that this was a good reason to include more samples in the study. Dane Jones further added that the high volume of samples sold at the 5 g/L level is cause enough for the pilot test to investigate this level. Dane Jones added that industry is marketing driven at the 5 g/L level and they simply want to know what the precision is at this level so that they can assure customers of what is being sold to them. Guy Wilson added that the zero VOC concept is driven by the Federal Trade Commission and should not be a point of interest for this study.

Joan Nieritit responded that the precision of M313 at 5 g/L is 5 g/L and simply won't change at the low level no matter how many labs run it.

Joan Nieritit responded to Dane Jones' last comment (biocide breakdown; resin decomposition in hot inlet) by responding that labile compounds should be evaluated on a case-by-case basis and indicated that iPBC doesn't break down during calibration, but that there are surely other exemplar labile compounds where a policy decision can be made on a compound-by-compound basis and that these compounds should not be a focus of the Pilot Test.

Brad Parrack transitioned the meeting to the next section of the agenda; the documentation that had been emailed to the group the day before the meeting. Brad indicated that 10 documents had been sent out.

Working from the document titled "AQMD Pilot Test - Phase One", Brad Parrack explained each document's purpose and place in the study. Brad Parrack mentioned that Step One of the Phase One guide was prepared so that participants would know the scope and expectations of the first phase of the Pilot Test and be able to secure necessary instrument components and standards to participate. Brad Parrack asked that interested participants email him by June 1st so that a head count could be collected, but also indicated that this was a provisional agreement since the column allowance had not yet been decided. Brad Parrack indicated that any consumables or other required components, parts, or standards be ordered sooner than later due to the lead time associated with such purchases.

Brad reviewed Step Two of the Phase One Guide and indicated that the Instrument Configuration Guide was written in two sections- section one being a set of recommended instrument parameters as a starting point for labs set to run M313 for the first time, with section two being a suggested set of approaches to configure an instrument if the results of the IOM analysis indicate that further optimization is required.

Brad Parrack continued by indicating that instrument configuration is determined by preparing and analyzing an IOM using the Practical Preparation Guide for Instrument Optimization Mix, with this guide being a step-by-step guide for how to prepare the mix. Brad Parrack asked that the masses which are recorded by the analyst during preparation and the resultant evaluation data of the IOM be entered into the Prep + Discrimination template. Brad Parrack indicated that the masses will be automatically transferred from the prep page into other areas of the template, and that only areas which are colored light blue will require input from participants.

Brad Parrack moved onto Step Three by specifying the injection sequence for the IOM— blank, IOM, blank, IOM on an equilibrated system. Brad Parrack asked that the systems be equilibrated prior to analysis by injecting a number of standards, perhaps 5-7 times, to establish stability of the instrument so that AQMD does not misattribute failing IOMs to poor preparation when it is simply due to a poor baseline after a column switch or some other factor. Brad Parrack asked that integrations be reviewed closely following injections.

Brad Parrack transitioned to Step Four, which is a data entry step for the Prep + Discrimination Template, again stressing that participant input is limited to just the blue section of the sheets. For Step Five, Brad Parrack indicated that the results are evaluated for resolution (ethylene glycol, propylene glycol, EGDE must be resolved) discrimination (85% to 115% % of normalized value for each hydrocarbon) sensitivity (detection of 0.1 g/L triglyme) and retention time drift (< 0.1 min drift for methyl palmitate and EGDE between injections).

Brad Parrack indicated that successful completion of Step Five QC allowed for progression to Step Six where an LOD is study is performed on the 0.1 g/L peak for triglyme by injecting the IOM 5 additional times with or without blanks between injections. 0.02 g/L is the cutoff for LOD sensitivity, and thus any results above that value will require instrument re-optimization back in Step Two.

Brad Parrack indicated that Step Seven was still in process since there was currently no place to upload data upon completion, and that AQMD would also ask for supplemental data such as if the analysis was performed on two separate instruments and which solvent was used.

Lastly, Brad Parrack indicated that there was a contact section at the bottom of the Phase One Guide and that each person who contributed to the documentation be the contact person for their respective portion of the Phase One Guide.

Stephen Foster inquired as to the % purity value that is utilized for the discrimination template, and Brad Parrack responded that Certificate of Analysis values are preferable, but that label purity is acceptable when CofA values are not available.

A phone participant inquired as to why AQMD was asking for lot # information, and Brad Parrack responded that it is so that questions after the fact can be addressed if there is a curious spread of data, and that this is also a good lab practice.

Brad Parrack mentioned that triglyme and other glycols/glycol ethers tend to be hygroscopic and that AQMD's practice is to include molecular sieves in the standard to prevent a loss in response factor when using that standard.

Dane Jones asked if any standards were going to be sent out as part of Phase One, and Brad Parrack responded that nothing will be sent out from AQMD until Phase Two, and even then it was unlikely that a check standard or any component thereof would be included. Dane Jones inquired as to whether or not blanks were required in between the IOM injections and Brad Parrack responded that it was preferable to do so, but probably unnecessary in this instance since there are no difficult compounds that may carry over from injection to injection. Dane Jones asked if an autosampler was required as part of the method, and Brad Parrack responded that auto samplers are not required.

Pawel Rempala asked whether or not the sensitivity requirements need to be met for both FID and MS if using separate instruments for each detector, and Brad Parrack responded that sensitivity requirements must be met for both the MS and FID. Pawel Rempala then inquired about the acceptable load of the column, and indicated that sensitivity could be met on Emerald instrumentation with 50x less sample introduced onto the column, but the column decision had been deferred until later and no guidance was given as to how the 624 and DB-5 columns would relate to each other in terms of sample load. Pawel Rempala concluded by adding that there is additional challenge in working with two detectors in tandem when one is under vacuum and one is at atmospheric pressure, and wondered if there was a procedure in place to check the effective flow rate of the instrument. Brad Parrack

responded that the discrimination profile on the FID is essentially a check that the sample is being delivered to the quantitative detector in a representative fashion without lighter compounds partitioning out selectively towards the MS. Joan Nierit added that the transfer line to the MS, which is a 0.1 ID line, acts as a flow restrictor and assists in delivering the appropriate sample representativeness to the FID.

Brad Parrack concluded the meeting with a promise to finish the column and sample discussion in the near future.