

**COQA Light Sweet Crude
Subcommittee Methods Advisory Panel (MAP)
Meeting - 10/27/21
Sugar Land, TX Meeting**

Next meeting: TBD

Light Sweet Crude Subcommittee Methods Advisory Panel (MAP) discussion and planning meeting.

Highlights:

- Member Attendees
 - 19 present plus 12 online persons in attendance (total 31)
 - Presentation “Light Sweet Crude Subcommittee Methods Advisory Panel (MAP) Frank Hagardorn & Arden Strycker (presenting)” is attached at the end of these minutes

- Meeting Opening
 - Aaron Dillard provided welcome statements to the meeting
 - The focus for the meeting is the MAP work that has been done
 - Due to retirement transition, Frank could not be present in person, but was online for the meeting. Arden in attendance and so presented the slides. Both Arden and Frank worked closely on the material discussed
 - Introductions were made by those attending the meeting.
 - Presentation was turned over to Arden

- Methods Advisory Panel (MAP) Presentation
 - Arden noted that Frank is directing this MAP project. He commented that he assisted similar to some of the other members and will work to represent Frank’s direction in the presentation today. The purpose for this meeting is to bring everyone up to date on activities of the group
 - Status update covers actions items. There were three topics listed from the June meeting that were worked on at the September meeting. Some of the discussion was around High Temp Sim Dis, metals, comparing methods, and H₂S measurement
 - For the H₂S portion, the focus was to go to the CCQTA and discuss what they have done from 2009 until now
 - The notes to these meeting are posted on the COQA web site under this Subcommittee
 - Action items from the June meeting that were carried forward to September
 - Expand companies and methods to those listed previously
 - Look more at ASTM D8252 data and how it compares to D5708
 - Review H₂S in vapor method; this method is not written for crude oil
 - Considerations were made to do a white paper in the future

- Arden led a continuation of the discussion based on action items discussed at the September meeting (starting at the Methods Summary slide in the presentation)
 - Methods that were compared were shown. On the slide, there were also four additional methods where there is nothing listed; various reasons for this, but mostly there are no specification methods. There is a limited amount of data monitored by Argus, but it is not considered a specification
 - Frank did some investigation, and the results are on the table
 - There was particular interest in D7169 appearing sometimes but do not see D7900. There is a similar discussion for H₂S determination
 - With respect the High Temp Sim Dis method, there was no explanation why another method with D7169 would be needed; like why CS₂ is used as a solvent. This is a complicated process; the impact lasts, so to correct, a quenching factor is applied and there was discussion around this at the MAP meeting in September (details on slide). For correction, D7900 was developed with a method to integrate the two peaks. There is thought that D7169 may not capture light ends correctly and that is why D7900 was developed. Arden noted that the reason he mentioned this is that a discussion in the Sept 14 meeting for the advisory panel was that something like this needs to be incorporated and explained as part of our recommendations
- Continued discussion regarding metals determination
 - It was noted that D8252 is a nice method and makes the determination quicker and easier and eliminates many of the sample prep issues. It is new and many in the industry are not aware of the method and discussion around biases and such. Action item is to collect data from anonymous sources; need to be careful because the available data would not be under controlled conditions
 - The method is for Ni and V, but the instrument can do Fe as well, so the MAP is looking into that. There is interest in determination of Fe, yet issue of settling is under discussion and not yet resolved
 - Graphs were shown in the presentation of comparative results with the D8252 to review potential biases. It was noted that ideally the plotted data would follow line on graph. More detailed analysis recommended but can see data does not track the line so there appears to be a potential bias. Another thing to keep in mind is that the level is below the precision limits for D5708, so precision numbers for those methods do not apply here, so cannot ascribe the error bars for reproducibility. At this time, explanations are not presented. A lot of work is being done to compare these kinds of data. The R² (correlation) is not very good. There is interest from the advisory panel, and intention is to collect more data
 - Terry Thompson continued the conversation noting that he thinks there needs to be a couple of goals for establishing bias and assessment. With the data presented here, there is obviously a bias. This procedure demonstrates if the bias is simple or if it will require more tweaks. This discussion depends on what the expectations of this group are. There are issues such as light sweet (crude) can have particles of heavier material that can fall out through the window, and methods need to be thought of like how to treat by adding a heavy higher viscosity oil to hold the material. It is not a simple solution. Do we want to focus on the impact of light sweet and if that is true find someone that is well qualified at looking at statistics to review. Terry noted that he is working with Amy Neacock (sic?) and she can share data as a service. If the

COQA can write a letter, she can provide data. If there is a statistician or someone from the group that can do this, it would be good. There are fudge factors with varying usefulness of how to use bias, and that would be a discussion topic. Big question is do we want to have a generic bias correction from method to method. That is a challenge but for our group seeing additional problems with having enough samples due to time required to do the test, all kinds of variations, and such, do we want to do a method-to-method comparison or focus on the problems of light sweet because of compositions

- Aaron asked the group to consider if we focus on all oils or just stick with light sweet. Decision may be for a later date and maybe the group can get back with Frank on it
- Frank online suggested in order to evaluate D5708, we need to generate data for D5708B. Data generation can be done with this group or we can ask ASTM. Sometimes it takes many hours to get data. Perhaps ASTM can be asked to form a task group to evaluate compare, and contrast
- An attendee suggested that it must be available data that can be used (metals content needs to be within the limits of the test)
- Ranzy Morgan noted that D5708B data was linear line. He asked if the data was smoothed. Frank responded that it was just a linear plot regression and that they are real life results. Dark line on graph is to indicate where the data would be if it was true linear 1:1 and dotted line is the best fit linear correlation for the data on the graph
- Ranzy asked if the data for D8252 and D5708B were from the same samples. Frank responded that it is same samples with both methods
- Frank continued that the group needs to decide how to move forwards. He asked if we want to petition ASTM to generate results
- Satbir Nayar suggested he was not sure if the committee for D5708B would be open to data, but there are quite a few years of data under 10 ppm for D5708 and B and two rounds of D8252
- Frank suggested there may be more data than that. He was under the impression that Satbir presented it about a year ago. His point was that to evaluate methods you need precision and you do not have precision for 5708 to compare. Satbir responded that we do not have that but there is a lot of data perhaps over 5 years; 20-30 data points that could be compared. He suggested that could be looked at and come up with a calculated reproducibility. Frank opened that there is a reason ASTM does not like to do that due to questions on using data that way. Satbir agreed as it is not controlled, and so was not suggesting amending the method with this but was suggesting for the purpose of this group it would be useful. Frank noted then we would just need to get data. Satbir suggest he would provide data or can check with Leslie McHenry if we can get data. He noted he would show some data tomorrow. ‘As we know we have a bias. XOS will always measure total and other ICP method with sample prep will always have lower since there is prep.’
- Terry suggested that also in light sweet crude there is the possibility to have fall out of particulate and problems due to that
- Frank noted D5708B should account for total
- Terry clarified that less viscous light sweet crude is vulnerable to particle fall out so <5um may be ok but larger particulate may have issues with observation. Majority of heavier crude not an issue but light sweet it is. PTP data can be shared if we send a

letter as indicated above. Frank asked Terry his view on best path forward. Terry responded that it would be to find a statistician, write the letter, and evaluate what the results are. Then we can discuss if we want to focus on light sweet and points such as the Fe

- A participant noted that the reason he was in town this week was to meet with participant in HOU futures contract. During the meetings, there have been zero questions on methods of the metals V and Ni. Half the meetings have had questions on measuring for Fe. This was stated to provide context that international buyers would prefer to have the Fe data. Arden noted that there was work that looked at Fe and the data was more predictable, and Frank reminded that D8252 was not written for Fe due to the drop out issues
- Ranzy noted that there is a bit of change with ASTM and Chris (?) was saying that ASTM has a lot of really good data and they would make that accessible. PTP is good real world data so may not be as cut and dry. Frank asked if Ranzy would email him Chris' contact information and Ranzy responded yes
- Continued discussion regarding H₂S determination
 - Arden continued that the H₂S topic came up in the meeting and ideas around it. The method was written for fuel oil and not crude oil and due to that, laboratories modify it to use it with crude oil
 - The MAP approached the CCQTA since they have worked on this since 2009. 'There was a CCQTA Open Forum meeting that we participated in'; as a result some of the members of CCQTA set up a meeting with Frank, Arden, Randy Segato, Dave Murry, and other, summarized the work from 2009 for more than an hour. Arden condensed that into two or so slides. He continued with a discussion from the slides
 - The CCQTA work was started in 2009. The purpose was to design testing framework and standardize the method. There were four methods studied. Arden noted that for those familiar with these methods, they are all different and the results do not compare plus none were made to include crude oil. The CCQTA measured crude oil and did a comparison to start the project. There was interest in the IP method and a bit of focus on that method and comparing the results to the others
 - Conclusion was that UOP163 showed the best precision. Based on the different crudes there were some issues with H₂S release. Every crude is different, so it is not predictable. There were some inconsistencies even in trending. GC method D5623 reports H₂S; it tends to bias significantly low relative to the UOP method. Arden noted that all the methods gave different results
 - Aaron asked which method was favored. Arden suggested that UOP163 was most common, but the method used at most terminals is D5705 which is a vapor component driven by safety. UOP163 gives total H₂S and is good if you want to treat the stream to reduce the H₂S level
 - One of the attendees suggested that there are limitations on D5705 due to time required to do the test, also UOP163 does not necessarily correlate. Arden confirmed that UOP163 is quicker
 - Another one of the attendees noted that working with inline analyzers and calibration, they find that there is sampling issues in the field. Inconsistencies are sampling and how fast they can send the sample to a testing facility. If D5705M is to be done, it is important to try to do get samples in a few hours. Working with D5705, they were

- trying to develop correlation but found it was not a valuable use of time since there is not really a good correlation between the methods
- Arden continued with the point that the CCQTA closed the H₂S method comparison project and started a PVT project. They moved more to equation of state work, and due to a 2013 rail accident in Canada and some in the US, there was increased interest in materials in crude. H₂S is a component so CCQTA wanted to focus more on H₂S in vapor. They developed a prototype test to maintain zero losses in sampling and testing. Pending additional funding. There is an ASTM draft pending final prototype.
 - Frank added that the method is two closed cylinders connected and they have adopted an inert enclosed system. He noted that the options are that we can start our own task force or see if we can support the CCQTA prototype and work with our members already in the CCQTA; there may be additional scope to consider with this Subcommittee in addition to what was addressed by the CCQTA.
 - Continuing to next slide, Arden suggested to also look into misinformation surrounding H₂S and measurements. There is a knowledge gap and it has not really been addressed. Vapor vs liquid measurement is different and that is not really understood by everyone. Whether results are for vapor or liquid determination is rarely ever stated nor understood by everyone, and units of measure are generally not spelled out as mass/mass or mole/mole. These are hugely different. Nor whether the test is evolution versus in-situ, etc.
 - One of the attendees asked for an explanation of the difference between evolution versus in-situ, and Arden responded that it is the difference between what is in liquid and what is in vapor
 - Frank noted that there is interest in standardizing the method. He suggested that we would need to develop a group or have those interested parties get in touch with the CCQTA. That would be a suggested path forward
 - Frank will be setting up another MAP meeting. If there are questions before that, they are to be sent to Frank
 - Meeting conclusion
 - Aaron noted that there was a lot of good discussion today. In addition, there were good comments that Terry provided to consider
 - He stated that we have about 20 people on this advisory panel so we will list who is on it and circulate the meeting minutes
 - Dennis H volunteered to continue as Secretary and will put together the minutes
 - The challenge is to decide where do we go from here. What do we want to do, how do we want to do it, and assign people to take the lead on some things and give others the opportunity to step up. From where we started, we have made progress
 - Aaron thanked all for their attendance and concluded the Light Sweet Crude MAP Subcommittee meeting

Appendices to the Minutes (attached)

- Presentation: Light Sweet Crude Subcommittee Methods Advisory Panel (MAP) Frank Hagardorn & Arden Strycker (presenting) [includes Agenda].

LIGHT SWEET CRUDE SUBCOMMITTEE

METHODS ADVISORY PANEL (MAP)

Frank Hagardorn & Arden Strycker (presenting)

Crude Oil Quality Association

Houston - Sugar Land

October 27, 2021





OUTLINE

- Status (summary, MAP 09.14.2021)
- High Temp Simulated Distillation (ASTM D7169 & D7900)
- Metals, Comparing ASTM D5708 (ICP) & D8252 (X-Ray)
- Measurement of H₂S
 - CCQTA Project Summary



ADVISORY GROUP MEETING, SEPT. 14, 2021

- Notes now posted on COQA website (LSC projects page)
- Review and discuss action items of advisory group meeting, June 9, 2021
 - Expand methods summary to include Argus, Hou Futures, Platts, others
 - Metals, ASTM D8252, assemble data and compare with D5708
 - H₂S in vapor (D5705), method not applicable for crude oil; procedure modified by different labs with limited consistency.
 - H₂S in vapor (D5705), consider reviewing CCQTA publications, other information sources for further steps
 - Consider developing a white paper with MAP recommendations (suggest posting on website)
- Action items, continued (Sept. 14, 2021, discussed here)



METHODS SUMMARY

	CME Method 200	CME Method 201						
Property	DSW	(CME WTI Houston Crude Oil Futures)	MEH WTI Method	Argus AGS ⁴	AGCSBPTFA ⁵	HOU Futures	Platts	Recommendation
Sulfur	ASTM D4294	ASTM D4294	ASTM D4294				ASTM D4294	ASTM D4294
API	ASTM D287	ASTM D287	ASTM D5002				ASTM D5002	ASTM D5002
Viscosity, SFS	ASTM D445, D2161	ASTM D2161	NA					ASTM D445, D2161
TVP (VPCR 4:1, 100F)			D6377				ASTM D6377	VPCR (4:1, 100F) D6377
Reid Vapor Pressure	ASTM D5191	ASTM D5191	D6377 ¹					
Basic Sediment	ASTM D4007, D96	ASTM D4007, D96	ASTM D4007				ASTM D4007	ASTM D4007
Pour Point	ASTM D97	ASTM D97	ASTM D97					ASTM D5853 A
Carbon Residue	ASTM D4530	ASTM D4530	ASTM D4530					ASTM D4530
TAN	ASTM D664	ASTM D664	ASTM D664					ASTM D8045
Nickel	ASTM D5708 B	ASTM D5708 B	ASTM D5708 B				ASTM D5708 B	ASTM D5708 B
Vanadium	ASTM D5708 B	ASTM D5708 B	ASTM D5708 B				ASTM D5708 B	ASTM D5708 B
HTSD	ASTM D7169		ASTM D7169					ASTM D7900, ASTM D7169 with merge
Mercaptans			UOP163				UOP163	UOP163
H2S(D)			UOP163					UOP163
H2S(V)			ASTM D5705M ²					None Available for Crude
Oxygenates			ASTM D7423 ³					None Available for Crude
Organic Chlorides			ASTM D4929 B					ASTM D4929 (A,B,C)
Notes:								
	1	RVPe						
	2	Ambient Temp.						
	3	O/H <400F						
	4	Explanation . . .						
	5	TBD						



HIGH TEMP SIMULATED DISTILLATION, ASTM D7169

- Yield data included in some specifications, ASTM D7169
- MAP current draft recommendation is to add ASTM D7900 with merge algorithm
- Action: Propose adding an explanation for users:
 - Paragraph 1.3, ASTM D7169, a quenching factor is applied for integration of lower BP portion of D7169 to correct the attenuation of CS₂ (solvent). Suggested value given.
 - Quenching value can vary with crude oil
 - An alternate approach is offered in D7169 to merge with D7900 for the C2-C8 region.
 - See ASTM D7169 for a more detailed explanation
- ASTM D7900 not indicated in current specifications (see previous table)

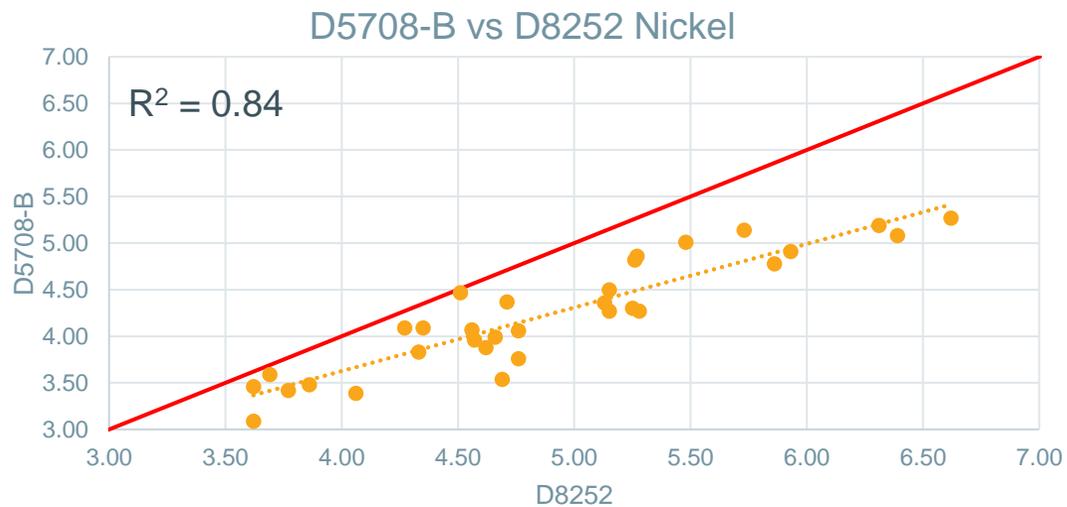
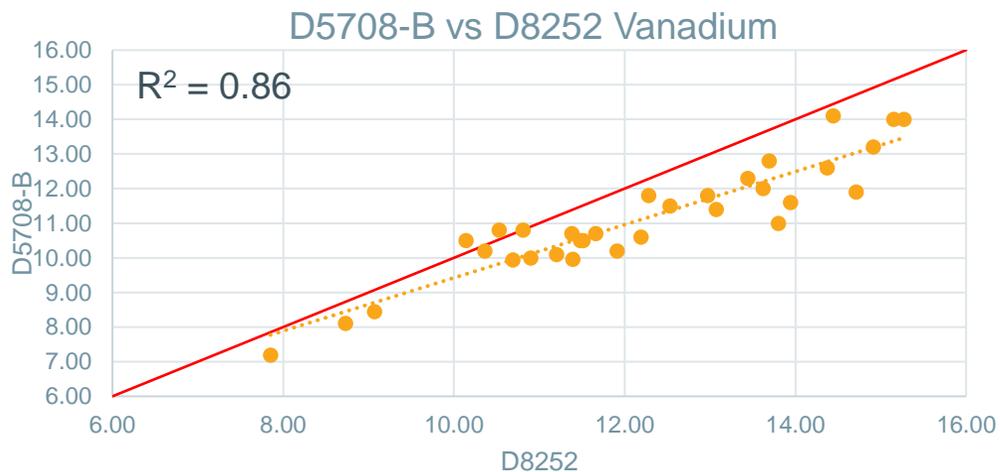


METALS, ASTM D5708 (ICP) & D8252 (X-RAY)

- ASTM D8252 is a newer method; method is easier, quicker, requiring minimal sample preparation
- Action: Collect data, compare and look for potential biases
- V and Ni of greatest interest, Fe also of interest but of somewhat lower priority
- Collected data to date not from a controlled study and has limited statistical significance
- Evidence found that some bias might exist, and MAP suggested putting together a white paper on this topic



BIAS?



Note: More detail data analysis using standard guides should be considered to provide a comprehensive data evaluation



MEASURING H₂S IN VAPOR

Action: Meet with CCQTA and discuss history & progress

- Over a decade of project work; initiated 2009 to design, develop, & promote H₂S testing framework for sampling and analysis in crude oil. **Standardization!**
- Test Method Evaluation Project
 - D5623, D5705, IP570/D7621, UOP163; test methods do not include crude oil
 - Work with Stanhope-Seta (UK) for development of new version IP570/D7621 and testing at Alberta Innovates against 3 other methods with several Canadian and US (WTI, WTS) crudes.
 - Conclusion: UOP163 showed best precision (RSD), IP570/D7621 & D5705 has 'H₂S release' inconsistencies (e.g., '0' vapor with quantifiable data from both liquid analyses)
 - CCQTA recommendation consistent with COQA recommendation of UOP163
 - Worst-case scenario if all H₂S in liquid is evolved
 - **Standardization for objective comparison**
 - HSE risks not addressed in CCQTA recommendation
 - Closed Test Method Comparison Project



MEASURING H₂S IN VAPOR (CONTINUED...)

Action: Meet with CCQTA and discuss history & progress

- H₂S PVT Project – Focus shift to actual risk of H₂S; Must evolve to become risk
 - That is, determine H₂S in vapor from H₂S in liquid, e.g. UOP 163
 - Initial PVT work abandoned for EOS modelling. (Canadian crude oils)
 - Predictive model abandoned – obtaining empirical PVT data not practical on an ongoing basis
- Increased emphasis on H₂S-V due to 2013 incident (Lac Mégantic rail)
- Focus shifted to sampling/testing with ‘zero’ loss. Standardized with range from ppm to % levels with portability. “Sealed D5705”
 - Method development & Proof of Concept; performance testing Summer 2020
- Status:
 - Pending additional funding, early adopters to facilitate further development
 - ASTM Draft pending final prototype



KNOWLEDGE GAPS (H₂S) NOT ADDRESSED

Action: Meet with CCQTA and discuss history & progress

- Mis-information surrounding H₂S
 - Vapor vs liquid results (D5705 vs UOP 163)
 - Units of measure (ppm mol/mol vs ppm mass/mass)
 - Evolved vs in-situ
 - Evolution risk vs volume (1 L vs 100,000 bbl tank)
- Mainline pipelines are not at risk of corrosion due to H₂S
- Refineries are not sensitive to H₂S but are sensitive to H₂S scavengers
- Relationship of risk to laboratory reported results not simple



OPEN DISCUSSION

Action Items with respect to ASTM D8252?

Action items with respect to H₂S?

CCQTA is interested in any feedback and/or interest with respect to H₂S measurements.



WWW.COQA-INC.ORG