



H₂S Measurement in Crude

COQA Meeting
March 1, 2012
Houston, TX





H₂S Measurement in Crude

- Project Objectives
 - Testing framework for analysis and sampling
 - ◆ Provide most accurate H₂S values
 - ◆ Reduce analytical error, technician variability
 - Educate transportation operators
 - ◆ H₂S potential of crudes in system
 - ◆ Health and safety issues
 - All operators using the same test method and comparing the same data



H₂S Measurement in Crude

- Available Testing Methodologies

- ASTM D5705

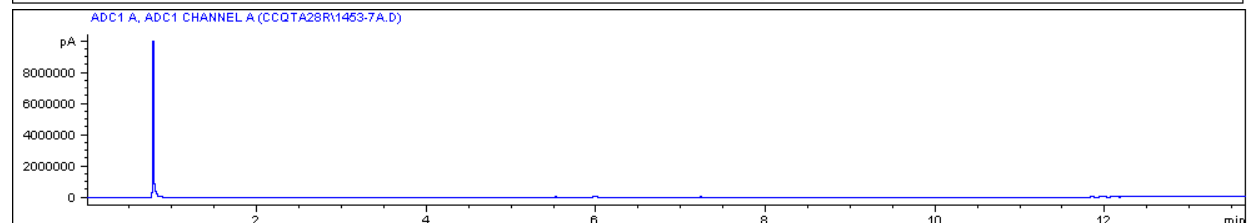
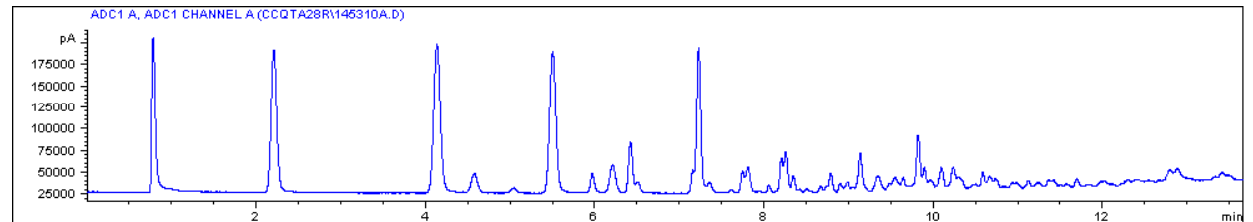
- Easy to perform, low equipment costs
 - Only measures vapor phase H₂S





H₂S Measurement in Crude

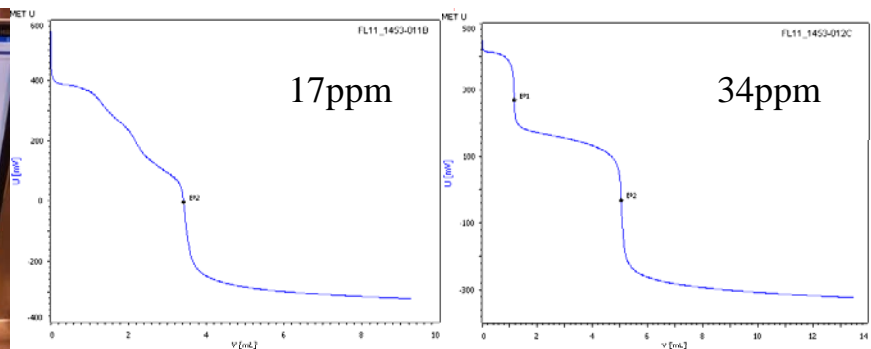
- Available Testing Methodologies, cont.
 - ASTM D5623
 - Provides speciation between (sulfur compounds)
 - High equipment costs (\$80K)
 - Requires experienced technician to operate.
 - Not practical for most terminal operators





H₂S Measurement in Crude

- Available Testing Methodology, cont.
UOP 163
 - Easy to perform, low equipment costs
 - Data interpretation requires skilled technician
 - Only measures liquid phase H₂S





H₂S Measurement in Crude

- Available Testing Methodology, cont.
IP 570
 - Modified for use with Crude Oils
 - Operator independent, little technical training required. NO interpretation required.
 - Measures both liquid and vapor phase H₂S





Method Scope Comparison

- **D5623** – Applicable to distillate, gasoline motor fuels and other petroleum liquids with a FBP <230C. Range 0.1-100mg/kg
- **D5705** – Applicable to residual fuel oil. Applicable to liquids 5.5 @ 40C to 50 and 100C. Range 5-4000ppmv.
- **UOP 163** – Applicable to gasoline, naphtha, light cycle oils, and similar distillates that are liquid at ambient temperature and pressure. Lower quantitation limit is 1.0 mg/kg.
- **IP 570** – Applicable to marine fuels. Range 0-50 mg/kg(Note: Method and instrument has been modified to accommodate for the volatile nature of crude/condensate products to limit the interference from light end components.)



H₂S Measurement in Crude

- Analysis Protocol
 - ◆ As each sample was opened the full set of tests was completed immediately, prior to opening the next sample.
 - ◆ Samples were refrigerated until opened.



Analysis Data

Sample Description	ASTM D445	ASTM D5002	ASTM D5191	UOP 163		ASTM D5705	ASTM D5623	IP 570
	Viscosity@20°C cSt	Density @ 15°C kg/m3	Vapor Pressure DVPE (kPa)	H ₂ S mg/kg	Mercaptan mg/kg	H ₂ S - Vapor ppmv	H ₂ S mg/kg	H ₂ S mg/kg
WTS	19.65	877.6	35.1	36	0	1	24.2	0.54
TK 1106	13.82	856.9	16.7	16	0	0	15.0	0.00
Peace Sour	4.91	816.2	54.9	110	0	>2000	74.9	124.6
Peace Sour				126	0	>2000	67.6	108.2
Peace Sour				127	0	>2000	70.8	126.9
OSA	6.311	865.2	20.6	0	8	0	0.0	0.00
Koch	9.392	839.4	57.3	104	0	>2000	76.7	167.2
Koch				105	0	>2000	61.0	247.0
Koch				104	0	>2000	52.3	204.5
CRL-403	1.345	749.7	85.5	26	237	241	17.2	8.6
CRL-403				27	248	295	19.1	16.4
CRL-403				28	234	268	17.7	6.4
CPM-781	1.279	762.2	72.3	16	40	0.5	14.2	0.02
CPM-781				17	38	1	14.2	0.03
CPM-781				11	56	2	12.2	0.01
CPR-025	1.028	750.3	80.7	34	222	11	17.2	0.09
CPR-025				34	220	12	11.9	0.09
CPR-025				34	225	11	13	0.10



H2S Measurement in Crude

- Potential Interferences
 - Chlorides (halides?)
 - UOP-163 inflection point interpretation
 - ◆ Dave to provide copies of inflection curves to all
 - ◆ Curves were actually very “clean” and relatively easy to interpret
 - Corrosion inhibitors (nitrogen based)
 - Mercaptans? – D5623 segregates the mercaptans and IP570 VPP development was based on removing mercaptan and light hydrocarbon interferences
 - Scavengers – water based cations? (HS- scavengers retaining partial H₂S in “ionic” state)



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Follow Up Discussions

- Agreed that future testing would include SAPA (saturates, aromatics, polars, asphaltenes), C30+ compositional analysis, Karl Fischer titration, and nitrogen testing by D4629
- Agreed that future testing would be done on one only sample from the triplicate sample sets
- Agreed that samples to be tested would be CPR (Peace condensate [Enbridge EP]), CPM (Pembina Drayton Valley condensate [Enbridge EP]), CRL (Plains Midstream Rangeland condensate [Enbridge EP]), PEM (Pembina sweet crude [Kinder Morgan]), and TK1106 [Coffeyville Resources, KS],
- Agreed to proceed with testing matrix ASAP based on Dave Murray's estimate of ~\$5,000 analytical costs and end of February completion estimate



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- Does anyone in COQA audience have any experience/insight that could streamline or focus our efforts??
 - Example: H2S scavengers
 - ◆ Are there naturally occurring varieties??
 - ◆ Would amine based corrosion inhibitors, “bug killers”, or something else be interfering??
- Please contact Bill Lywood
 - ◆ 780-991-9900 or lywood@crudequality.com