Method 8 Audit Sample Issues

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SSAS Program

- Stationary Sources (“Stacks”) are routinely sampled and tested to ensure that emissions from these sources do not exceed defined MCLs in support of the Clean Air Act (CAA).
- Test samples are collected from these sources and sent to a laboratory for testing per an approved air testing method.
- To ensure the laboratory is providing accurate test results, an “Audit” sample is sent along with the test samples for evaluation.
- The audit sample is an emulation of the test sample matrix, but with a known value of the analyte of concern.
- The lab must test the audit sample at the same time, using the same personnel, and the same methods as the test samples.

SSAS Program

- The audit sample results are reported for evaluation based on a pre determined set of criteria.
- Results of the audit sample are used by regulatory agencies to help determine acceptability of test sample results.
- The audit sample program was historically administered by the USEPA.
- As with Proficiency Testing (PT) programs in the past, the EPA decided to privatize the audit sample program.

SSAS Program

- The privatization of the Stationary Source Audit Sample (SSAS) program began in June of 2013.
- In order for an audit sample to be included in the program, at least two “Providers” must be accredited to provide samples.
- There are currently 9 Impinger solutions and 3 Filters available in the program.
- Audit sample designs, methods, concentration ranges, and acceptance limits can be found on the SSAS Table, Revision 5, Effective April 15, 2014.

SSAS Program

- The SSAS program has established an Expert Committee comprised of stakeholders from the government, stack tester, laboratory, and provider communities.
- One responsibility of the Expert Committee is to monitor and trend the results of the audit samples.

Audit Program Statistics - Filter

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Method	# Data Points	Pass	Fail	Pass Rate
12 Lead	101	100	1	99.0%
29 Metals	1725	1692	33	98.1%
29 Mercury	163	157	6	96.3%

Audit Program Statistics - Impinger

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Method	# Data Points	Pass	Fail	Pass Rate
29 Metals	1447	1433	14	99.0%
12 Lead	98	96	2	99.0%
29 Mercury	269	263	6	97.8%
8 Sulfur Dioxide	86	82	4	95.3%
26/26A HCl	534	503	31	94.2%
6 Sulfur Dioxide	90	83	6	92.2%
26/26A HF	136	120	16	88.2%
13A/B Fluoride	171	148	20	86.5%
8 Sulfuric Acid	177	142	35	80.2%

THE SULFURIC ACID MIST IN IMPINGER AUDIT SAMPLE IS

SHOWING A FAILURE RATE MUCH GREATER THAN THE FAILURE

RATES OF OTHER AUDIT SAMPLES

Statistics Breakdown – Sulfuric Acid ERA Audit Samples

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Conc.	# Data Points	Pass	Fail	Pass Rate
Total	171	141	30	82.5%
< 20 mg/dscm	41	31	10	75.6%
< 30 mg/dscm	83	59	24	71.1%
> 50 mg/dscm	47	43	4	91.5%
> 75 mg/dscm	17	16	1	94.1%
>100 mg/dscm	13	12	1	92.3%

Statistics Breakdown – Sulfuric Acid ERA Air and Emission PT Samples

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Conc.	# Data Points	Pass	Fail	Pass Rate
Total	210	171	39	81.4%
< 20 mg/dscm	15	12	3	80.0%
< 30 mg/dscm	75	61	14	81.3%
> 50 mg/dscm	93	83	10	89.2%
> 75 mg/dscm	77	70	7	90.9%
>100 mg/dscm	45	43	2	95.6%

Statistics Breakdown – Sulfuric Acid

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- 28 Labs have reported sulfuric acid data.
- 112 out of 171 (65%) of the sulfuric acid audit samples were analyzed by 6 labs.
- The remaining 59 audits (35%) were analyzed by the other 22 labs.
- The 6 major labs passed 102 out of the 112 audits (91.1%).
- The other 22 labs passed 39 out of the 59 audits (66.1%).

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WHAT CAN BE CAUSING THE HIGH FAILURE RATE

FOR SULFURIC ACID IN IMPINGER IN EPA METHOD 8

Method 8 SSAS Table

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EPA Clean Air Act Performance Audit Samples
Stationary Source Audit Sample (SSAS) Table [18, 19]
Revision 5, Effective April 15, 2014

Matrix	NELAC Analyte Code	Analyte[1]	Concentration Range	Acceptance Criteria[2]	ASRL[3]
		Inorganics in Impinger Solution			
		EPA Method 6 and 8[4, 5]	mg/dscm		mg/dscm
Air & Emissions	4010	Sulfur Dioxide	50-2000	± 15% at < 150 ± 10% ≥ 150 fixed acceptance limit	42
		EPA Method 8[4,5]	mg/dscm		mg/dscm
Air & Emissions	4020	Sulfuric Acid mist	5.0-150	± 15% at < 20 ± 10% ≥ 20 fixed acceptance limit	4.2
		EPA Method 7[4,6]	mg/dscm		mg/dscm
Air & Emissions	3885	Oxides of Nitrogen	100-2000	± 15% fixed acceptance limit	85
		EPA Method 13A and 13B[4,7]	mg/dscm		mg/dscm
Air & Emissions	1730	Fluoride	1.0-50	± 15% fixed acceptance limit	0.85
		EPA Method 26 and 26A[8]	mg/L		mg/L
Air & Emissions	1770	Hydrogen Chloride	5.0-500	± 10% fixed acceptance limit	4.5
Air & Emissions	1775	Hydrogen Fluoride	5.0-500	± 10% fixed acceptance limit	4.5

[4] mg/dscm = milligrams per dry standard cubic meter. Dry gas sample volume for audit sample is equal to 1 dscm

[5] Prepared from Sulfuric Acid in HPLC-grade water.

Method 8 Sampling Train

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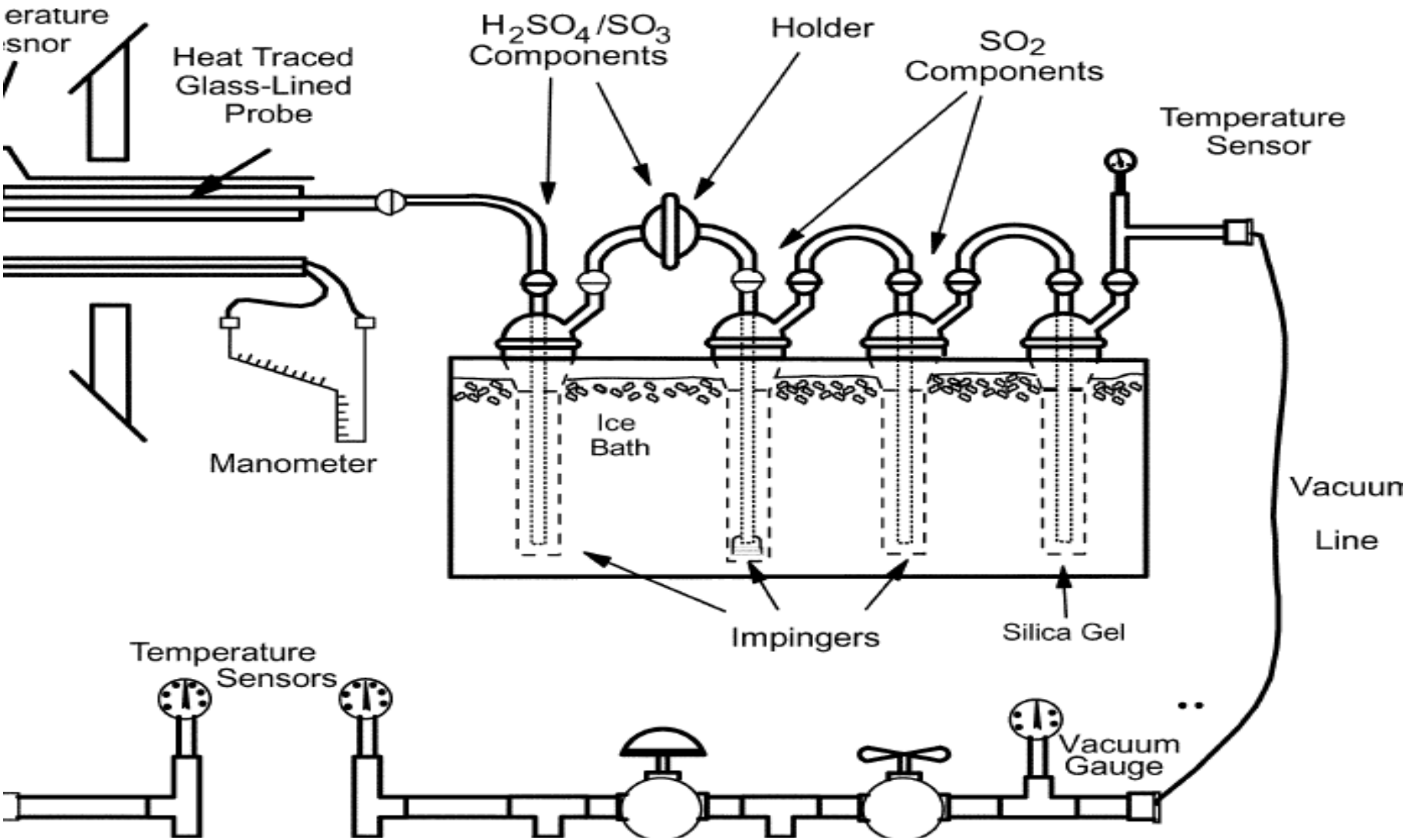

Method 8 for Sulfuric Acid

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EPA Method 8

Determination of Sulfuric Acid and Sulfur Dioxide Emissions from Stationary Sources

Sulfuric Acid Analytical Summary

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- Sulfuric Acid is analyzed from the contents of Impinger #1.
- Impinger #1 is an 80% Isopropanol solution.
- The impinger contains approximately 250 mL of sample.
- 100 mL of this solution is placed into a 250 mL Ehrlenmeyer Flask.
- 2-4 drops of a thorin indicator is added to the flask.
- The sample is titrated using a 0.0100 N barium standard solution to a pink endpoint.

Sulfuric Acid Analytical Summary – What Could Be The Issues

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- The analytical procedure in method 8 details analysis by titration.
- Some laboratories are reporting the titration technique. Some laboratories are reporting Ion Chromatography (IC).
- The statistics are showing that the failure rate increases as the concentration of the audit sample decreases.
- Wrong lighting affects titrant quality.
- Blank subtraction an issue.

Sulfuric Acid Analytical Summary – Analytical Research

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Several participating laboratories were queried about Method 8 analysis.

Sulfuric Acid Analytical Summary – Analytical Research

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Question: Do you ever analyze test samples by IC, and if so, what problems does the 80% IPA present?

- Yes we do.
  - The IPA matrix is not good for the IC columns.
  - The samples need to be diluted a minimum of 5x due to problems with the IC column

Sulfuric Acid Analytical Summary – Analytical Research

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Question: What triggers your decision to run by IC or titration?

- Client Request
- When the endpoint for titration cannot be achieved due to sample matrix

Sulfuric Acid Analytical Summary – Analytical Research

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Question: What problems, if any, does the 80% IPA matrix cause for titration?

- The IPA does not cause problems for titration. It is actually necessary for the chemistry to work correctly. The problem for titration is matrix interferences (i.e. ammonia) which inhibits the salmon pink color change

Sulfuric Acid Analytical Summary – Analytical Research

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Question: What problems would a 3% hydrogen peroxide solution have on analysis by titration?

- The matrix should be 80% IPA for proper color change
- No problems. We matrix match the audit samples to be same as the test samples

Sulfuric Acid Analytical Summary – Analytical Research

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Question: What problems would a 3% hydrogen peroxide solution have on analysis by IC?

- No problems. We matrix match the audit samples to be same as the test samples

Sulfuric Acid Analytical Summary – Analytical Research

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Question: Do you notice any more difficulty analyzing samples at the low end of the SSAS Range (say 5-30 mg/dscm) as opposed to the higher end of the range (50-150 mg/dscm)?

- Absolutely. The color change on the lower audits is very hard to see. The audits at higher concentrations allow for more titrant to be used, leaving more wiggle room for seeing the endpoint.
- In our opinion Method 8 was not written for the lower level ranges.

Sulfuric Acid Analytical Summary – Analytical Research

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Question: The Audit samples come with dilution and analysis instructions. What problems do these instructions cause?

- Method 8 requires analysis in 80% IPA. Some instructions do not include any IPA in the dilution of the audit sample.
- Some instructions include dilution in 3% hydrogen peroxide. Since this is only necessary for sulfur dioxide it is confusing why this should be done for sulfuric acid.
- Some dilution instructions are inconsistent with Method 8 requirements.

Sulfuric Acid Analytical Summary – Analytical Research

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Question: If the dilutions instructions indicated diluting the sample in DI water, what problems would that cause?

- This would be inconsistent with the method.
- None. We would just matrix match with the test samples.
- Some dilution instructions are inconsistent with Method 8 requirements.

Sulfuric Acid Analytical Summary – Analytical Research

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Question: Method 8 requires 250 mL of sample in the impinger. Does a higher final volume (say 1000 mL) in the audit sample cause a problem for calculations?

- No. We often receive test samples with a beginning volume greater than 250 mL.
- The actual volume of sample received does not matter. The calculations are performed using the aliquot of sample taken for the test and not the volume of sample received.

Questions

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- Is the failure rate a result of labs not qualified to do the testing?
- Are the acceptance limits not appropriate at all concentrations in the current concentration range?
- Is the current audit sample concentration range not appropriate for the levels detected in the test samples?
- Is the method not appropriate for the concentrations analyzed (detection limits)?
- Is there a technique bias (IC vs Titration)?
- Should the acceptance limits be split per technique?
- Are the audit samples being provided by the Providers not appropriate for the testing?

Conclusion

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- As we can see, there are multitude of possible causes for the problems with Method 8 sulfuric acid audit samples.
- The Research will continue by the SSAS Expert Committee until cause, if possible, can be determined so the correct adjustment can be made to bring the pass/fail rates to a consistent level with other audit samples/method.

- Stay tuned……..

QUESTIONS???

INPUT???

THANK YOU