

# Through the Probe Audits for NCORE Trace Gas Monitors

## Low Audit Concentration Levels- Basis for Practical Audit Acceptance Limits

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# Audit Issues: Acceptance Limits at Lower Audit Ranges/Levels; AQS Reporting Gap; & Other TL Audit Issues

- Can we continue using our past audit result acceptance limits?
- Should EPA use the same parameter at lower levels?
- Up to now, EPA has used the same % Difference for all required levels
- Will the Data indicate we have to use PPM or PPB Difference?
- If we do, how should we determine what parameter of PPMs or PPBs (vs % Difference) to use?
- The new audit ranges (40CFR part 58, App.A, Table in Sxn. 3.2.2.2) have both 2 and 3 digits-AQS reporting requires 3, creating reporting gaps



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## Sxn. 3.2.2.2 Says Choose At Least 3 of 5 Concentration Ranges, PPM

Level	O3	SO2	NO2/Y	CO
1	0.02-0.05	.003-.005	0.0002-0.002	0.08-0.10
2	0.06-0.10	0.006-0.10	0.003-0.005	0.50-1.00
3	0.11-0.20	0.02-0.10	0.006-0.10	1.50-4.00
4	0.21-0.30	0.11-0.40	0.11-0.30	5-15
5	0.31-0.90	0.41-0.90	0.31-0.60	20-50



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# Analysis of Gaseous NPAP Audit Data in 2008

- Changed Old Audit Acceptance Limits from 15% to 10%- For Ozone Data confirmed to go ahead, for levels 3,4,&5
- Data was not Sufficient to Change Acceptance Limits for CO, SO<sub>2</sub>, or NO<sub>2</sub>, at the usual (NON-NCORE) Ranges, at Levels 3-5
- Can we Use % Limits Parameter at Levels 1-3
- Initial Analyses for Level 3 indicate % is fine



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# Proposed Non-% Approach for Audit Acceptance Limits for NCORE

- OAQPS-AQAD Statistician Rhonda Thompson reviewed the existing data for 2008, at the new audit level ranges; we 1st looked at Level 3
- Why-Level 3 represents closest surrogate for the NCORE levels, since it is shared at both Std. (3,4,5) and Trace (1,2,3) Levels
- Included Level 1 Ozone\*, and Levels 3&4 for CO & SO2
- Result: Summary of the available data, at the 95% Confidence Limit, in terms of upper and lower Confidence Bounds, in PPM



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# Regions 2,3,7 &10 O3 2008 Data, Level1, in PPM

Ozone Mean	0.000
Standard Deviation	0.003
n	147
Confidence Interval alpha	0.05
Confidence	0.000
Upper Bound	0.000
Lower Bound	-0.001



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# Regions 9,4,5,2,3,7,&10 CO Data, 2008, Levels 3&4,in PPM D,vs %D

CO Mean PPM Diff.*	0.1
Standard Deviation	0.2
n	22
Confidence Interval alpha	0.05
Confidence	0.1
Upper Bound	0.2
Lower Bound	0.0



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# Regions 9,4,5,2,3,7,&10 SO2 Data, 2008, Level 3, in PPM

SO2 Mean	0.000
Standard Deviation	0.003
n	17
Confidence Interval alpha	0.05
Confidence	0.002
Upper Bound	0.001
Lower Bound	-0.002



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# LOW AUDIT CONCENTRATION LEVEL

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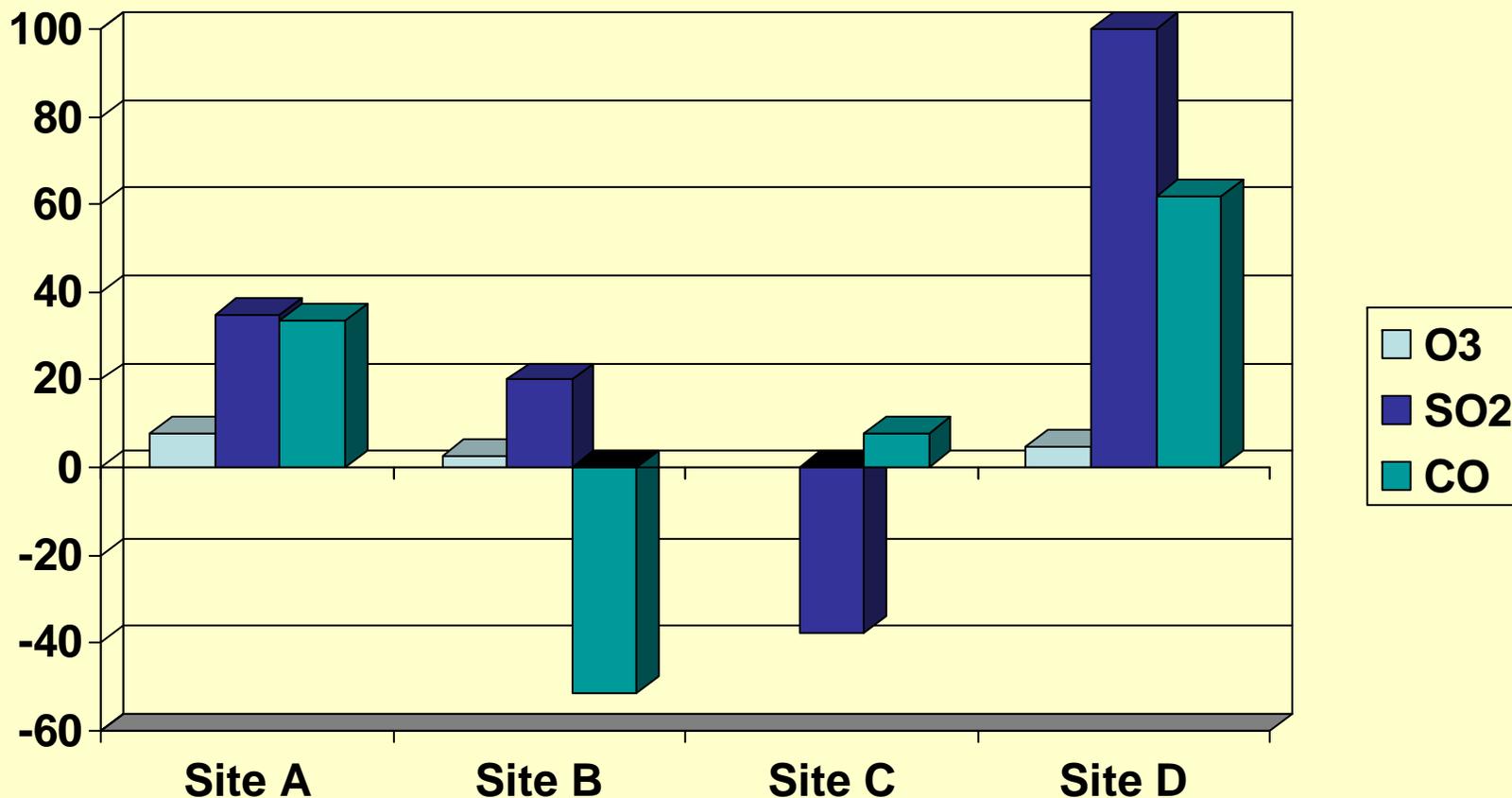


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# Level 1, % Difference Between NPAP & SLT Results



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# Trace Level Audit Data

- Data for 4 Precursor Gas sites; for O<sub>3</sub>, CO and SO<sub>2</sub>; at Levels 1 to 3
- Look at NPAP vs Agency Results in PPM Difference vs % D
- Can we use %D for Levels 1 & 2?



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# Comparison of Actual Difference and Percent Difference

Audit Point	Difference in ppb		% Difference	
	SO2	CO	SO2	CO
Level 3 SO2/CO	-0.006	-0.113	7.9	6.3
Level 2 CO	-0.004	-0.083	10.2	10.0
Level 2 SO2	-0.001	-0.019	28.2	15.8
Level 1 SO2	-0.001	-0.052	34.7	86.7
Level 1 CO	-0.001	-0.037	29.8	33.6

The percent difference of the SO2 audit level 1 comparison was 34.7%, but the actual difference was only 1 ppb.

The question is... Should a comparison that is within 1 ppb but exceeds 15% still considered a failing grade?



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# Summary Regarding PPM or PPB Difference Acceptance Limit

- As EPA accumulates more NCORE Audit Data, we propose applying an upper and lower Bound approach to determine Audit Acceptance limits for the Gases.
- In this way we shall try to answer the question, what #s should be used as TTP Audit Result Difference Acceptance Limits at the Trace Level for CO & SO<sub>2</sub>



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	Audit	Meas	Percent Difference	PPM Difference
SO2	0.003	0.00404	34.7	0.00104
	0.002	0.0024	20	0.0004
	0.004	0.0025	-37.5	-0.0015
	0.002	0.004	100	0.002
	0.01	0.098	880.00	0.088
	0.006	0.007	16.67	0.001
	mean			0.0152
	sd			0.0357
	n			6
	Confidence Interval alpha			0.05
	Confidence			0.029
	Upper Bound			0.044
	Lower Bound			-0.013
CO	0.11	0.147	33.6	0.037
	0.09	0.044	-51.3	-0.046
	0.09	0.097	7.8	0.007
	0.05	0.081	62	0.031
	0.23	0.889	286.52	0.659
	0.14	0.563	302.14	0.423
	mean			0.1852
	sd			0.2870
	n			6
	Confidence Interval alpha			0.05
	Confidence			0.230
	Upper Bound			0.415
	Lower Bound			-0.045

Trace Level  
Acceptance  
Limit Options

Level 1 All Points



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# What Do We See, With All Points Included?

- 1) The Standard Deviation (SD) for CO is much greater than the SD for SO<sub>2</sub>; there is a 10-fold difference
- 2) For both, with all the points included, the Mean and Confidence Interval (CI-Basis for the Bounds) are large



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	Audit	Meas	Percent Difference	PPM Difference
<b>SO2</b>	0.003	0.00404	34.7	0.00104
	0.002	0.0024	20	0.0004
	0.004	0.0025	-37.5	-0.0015
	0.002	0.004	100	0.002
	0.006	0.007	16.67	0.001
<b>mean</b>				0.0006
<b>sd</b>				<b>0.0013</b>
<b>n</b>				5
<b>Confidence Interval alpha</b>				0.05
<b>Confidence</b>				0.001
<b>Upper Bound</b>				0.002
<b>Lower Bound</b>				-0.001

<b>CO</b>	0.11	0.147	33.6	0.037
	0.09	0.044	-51.3	-0.046
	0.09	0.097	7.8	0.007
	0.05	0.081	62	0.031
	<b>mean</b>			
<b>sd</b>				<b>0.0378</b>
<b>n</b>				4
<b>Confidence Interval alpha</b>				0.05
<b>Confidence</b>				0.037
<b>Upper Bound</b>				0.044
<b>Lower Bound</b>				-0.030

Trace Level  
Acceptance  
Limit Options

Level 1 **Points  
Removed**



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## What Do We See, With Some (?Suspect) Points Removed?

- 1) The SD for CO is still greater than the SD for SO<sub>2</sub>; suggests SO<sub>2</sub> analyzer is more stable; this result has been seen in the models from 2 different manufacturers, so the cause may be in the method, not the manufacturer
- 2) The SDs and CIs for both CO and SO<sub>2</sub> are now both much smaller, with the points removed
- 3) Obviously, we need more data



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# Issues with Auditing Trace Level Analyzers

## For Starters...

- What do we use to express audit results to determine pass or fail?
- Lower tank gas concentrations are needed. Lower concentrations may require 6 month recertification, more cost. We will have to check cert. more frequently , at 1<sup>st</sup>, just to prove there is no significant change; if there is change, cks. will be more frequent
- May need lower flow mass flow controllers; some calibrator manufacturers are working on this change
- What audit gas is appropriate for testing the NO<sub>y</sub> converter efficiency and performing the NO<sub>y</sub> audit? Use N- or Iso-Propyl Nitrate, as a safe substitute for HNO<sub>3</sub>, the “NO<sub>3</sub>” of real interest
- Is it reasonable and safe to audit through the probe of NO<sub>y</sub> at the top of a 10m mast? No, but we will have to test to see if there is an effect-maybe after we develop the initial TTP audit SOP



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# Issues with Auditing Trace Level Analyzers

Continued..

- If multi-blend tanks are used, new concentrations will be needed, at more cost. This is because the ratios recommended in EPA's monitoring training do not efficiently accommodate one of the levels in the new Table of Audit Range Levels in 40 CFR Part 58App.A, Sxn 3.2.2.2, for doing the CO and SO<sub>2</sub> TTP audits together (at the same time). This issue will be addressed in our draft TTP Audit SOP Sxn. 6 modification for Trace Level Audits; estimate 1<sup>st</sup> draft will be in AMTIC for review by end of Dec. 09.
- Some SLT agencies say need to heat the NO<sub>y</sub> sampling line to 50°C to keep any HNO<sub>3</sub> in a gaseous state; otherwise it may adsorb on flow path surfaces. The problem with this is that the heat could also effect the other gases. SO<sub>2</sub>, might need 2 parallel sampling flow paths.



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# Data Recording Issues

- Consider More Digits for Levels 1, 2
- Have as many as we need.
- Do not drop any in calculations (in EPA's TTP Workbook; which it seems we were doing for Levels 3-5)
- Consider NOT Rounding off in going from Worksheet to Individual report to Summary Report (doing for 3-5).
- Most Important: CFR uses both 2 and 3 digits for required new audit level ranges, but AQS requires data be reported with 3 digits



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# Proposed “Gapless “ Range Revision

- EPA OAQPS Ambient Air QA Leader and AQS Staff have proposed a “gapless” revision to the promulgated ranges in 40 CFR part 58, Appendix A, Section 3.2.2.2
- Getting the revision into CFR will take time
- The revision has been implemented by AQS; Current AMP 255 did use the revision; stopped since 255 is only for Sxn 3.2.2.2 results, not 2.4; 255 is mainly used for annual SLT data cert.



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PARAMETER	LEVEL	LOWER_LIMIT	UPPER_LIMIT
CO	1	0.08000	0.24999
CO	2	0.25000	1.24999
CO	3	1.25000	4.49999
CO	4	4.50000	17.49999
CO	5	17.50000	50.00000
NO2	1	0.00020	0.00299
NO2	2	0.00300	0.00599
NO2	3	0.00600	0.10999
NO2	4	0.11000	0.30999
NO2	5	0.31000	0.60999
O3	1	0.02000	0.05999
O3	2	0.06000	0.10999
O3	3	0.11000	0.20999
O3	4	0.21000	0.30999
O3	5	0.31000	0.99999
SO2	1	0.00030	0.00599
SO2	2	0.00600	0.01999
SO2	3	0.02000	0.10999
SO2	4	0.11000	0.40999
SO2	5	0.41000	0.90999



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