



# Improving the Quality of Stationary Source Measurements

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# Agenda

- Introduction to the SSAS Table
- The Importance of Concentration Ranges and Acceptance Limits
- Case Study: Method 25
- The Chicken-and-Egg Dilemma
- Latest Developments





# Introduction to the SSAS Table

The SSAS Table...

- Is analogous to Fields of Proficiency Testing (FoPT) Tables used by the TNI PT Program
- Defines the concentration ranges and acceptance limits for TNI-approved analytes for the SSAS Program
- Specifies methods to be used for each analyte
- Provides footnotes regarding audit sample preparation

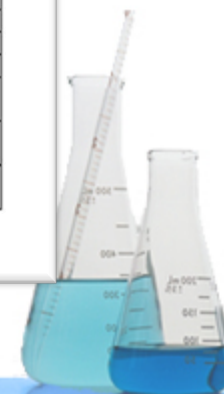


# Introduction to the SSAS Table

EPA Clean Air Act Performance Audit Samples  
Stationary Source Audit Sample (SSAS) Table <sup>18, 19</sup>  
Revision 5, Effective April 15, 2014

Matrix	NELAC Analyte Code	Analyte <sup>1</sup>	Concentration Range	Acceptance Criteria <sup>2</sup>	ASRL <sup>3</sup>
		<b>Inorganics in Impinger Solution</b>			
		<b>EPA Method 6 and 8<sup>4,5</sup></b>	mg/dscm		mg/dscm
Air & Emissions	4010	Sulfur Dioxide	50-2000	± 15% at < 150 ± 10% ≥ 150 fixed acceptance limit	42
		<b>EPA Method 8<sup>4,5</sup></b>	mg/dscm		mg/dscm
Air & Emissions	4020	Sulfuric Acid mist	5.0-150	± 15% at < 20 ± 10% ≥ 20 fixed acceptance limit	4.2
		<b>EPA Method 7<sup>4,6</sup></b>	mg/dscm		mg/dscm
Air & Emissions	3885	Oxides of Nitrogen	100-2000	± 15% fixed acceptance limit	85
		<b>EPA Method 13A and 13B<sup>4,7</sup></b>	mg/dscm		mg/dscm
Air & Emissions	1730	Fluoride	1.0-50	± 15% fixed acceptance limit	0.85
		<b>EPA Method 26 and 26A<sup>8</sup></b>	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
		<b>Metals on Glass/Quartz Fiber Filters<sup>9</sup></b>			
		<b>EPA Method 29</b>	µg/filter		µg/filter
Air & Emissions	1005	Antimony	25-250	± 25% fixed acceptance limit	19
Air & Emissions	1010	Arsenic	20-250	± 25% fixed acceptance limit	15
Air & Emissions	1015	Barium	20-250	± 25% fixed acceptance limit	15
Air & Emissions	1020	Beryllium	10-250	± 25% fixed acceptance limit	7.5
Air & Emissions	1030	Cadmium	10-250	± 20% fixed acceptance limit	8.0
Air & Emissions	1040	Chromium	15-250	± 20% fixed acceptance limit	12
Air & Emissions	1050	Cobalt	10-250	± 25% fixed acceptance limit	7.5
Air & Emissions	1055	Copper	10-250	± 25% fixed acceptance limit	7.5
Air & Emissions	1075	Lead	20-350	± 20% fixed acceptance limit	16
Air & Emissions	1090	Manganese	10-250	± 30% at < 20 ± 20% ≥ 20 fixed acceptance limit	7.0
Air & Emissions	1105	Nickel	20-250	± 30% at < 30 ± 20% ≥ 30 fixed acceptance limit	14
Air & Emissions	1140	Selenium	20-250	± 30% at < 40 ± 25% ≥ 40 fixed acceptance limit	14

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# Introduction to the SSAS Table

The SSAS Table does not...

- Define technology to be used

- e.g. Method 29 can be run by multiple technologies; lab chooses which to run

- Define which audit samples are commercially available

- e.g., Methods 23 and 25 are listed in the SSAS Table, but audits for those methods are not commercially available as of Aug 2014





# Introduction to the SSAS Table

The SSAS Table also does not...

- Define which methods/analytes require audits
  - EPA defines required methods/analytes
  - EPA's List of Required Audit Samples published on the web at <http://www.epa.gov/ttn/emc/email.html>





# Introduction to the SSAS Table

How were methods/analytes chosen to be added to the SSAS Table?

- Audit samples provided by the EPA audit program





# Importance of Concentration Ranges and Acceptance Limits

- ❑ Regulations set limits on emissions from stationary sources
- ❑ Audit samples are used to assure the quality of the measurements of these emissions
- ❑ Audit samples are as similar to real-world samples as reasonably possible
- ❑ Concentration ranges of audit samples should therefore include the concentrations of interest in samples







# Importance of Concentration Ranges and Acceptance Limits

- EPA Final Rule requires that acceptance limits are set so 90% of qualified Laboratories produce results within limits for 95% of future audits
- For many methods and analytes, accuracy of results varies with concentration
- It is important to have historical data upon which to base acceptance limits





# Importance of Concentration Ranges and Acceptance Limits

How were concentration ranges and acceptance limits defined in the SSAS Table?

- Historical data from the EPA audit program was evaluated by TNI SSAS Expert Committee
- EPA Final Rule (and TNI SSAS Standard) require biennial review of acceptance limits by TNI to determine whether changes are needed





# Importance of Concentration Ranges and Acceptance Limits

- Some methods required more in-depth evaluation to reach a consensus on the concentration range and acceptance limits
- Method 25 (Non-Methane Organic Compounds) demanded the most effort, by far, of all methods in the SSAS Table



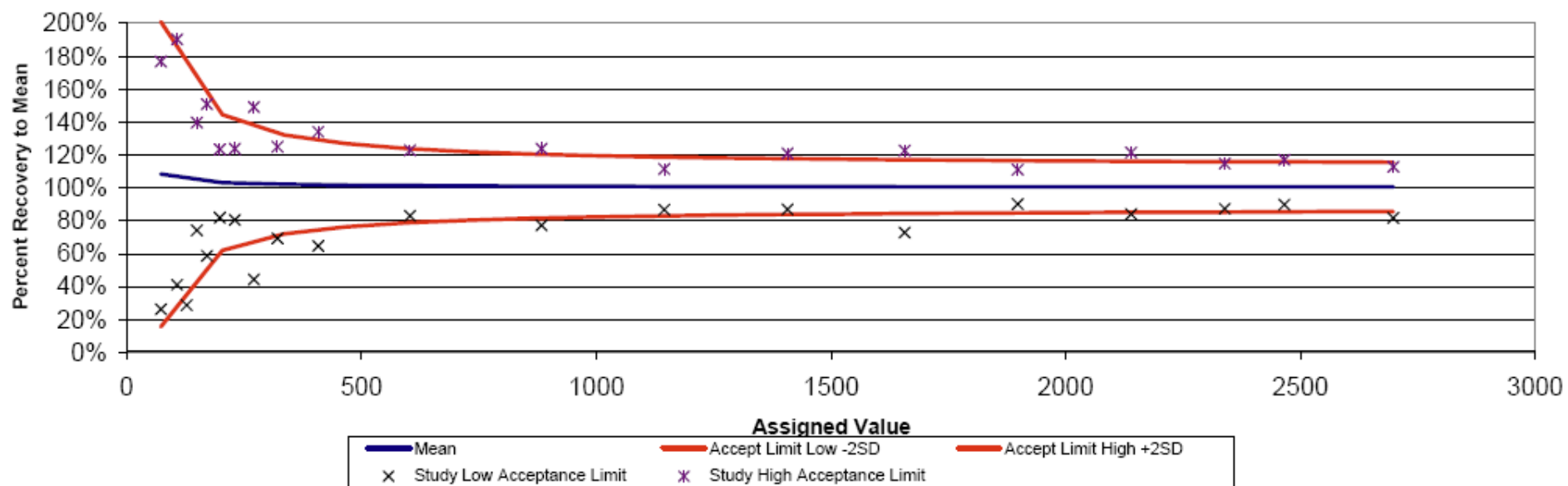
## Case Study: Method 25

- Current concentration range 150-2500 ppmC
- Current acceptance limits fixed at  $\pm 50\%$  assigned value
- Some members of the SSAS Expert Committee wanted the lower end of the concentration range changed to 50 ppmC
- Limited historical data below 150 ppmC
- Available data suggested performance degrading at low concentrations



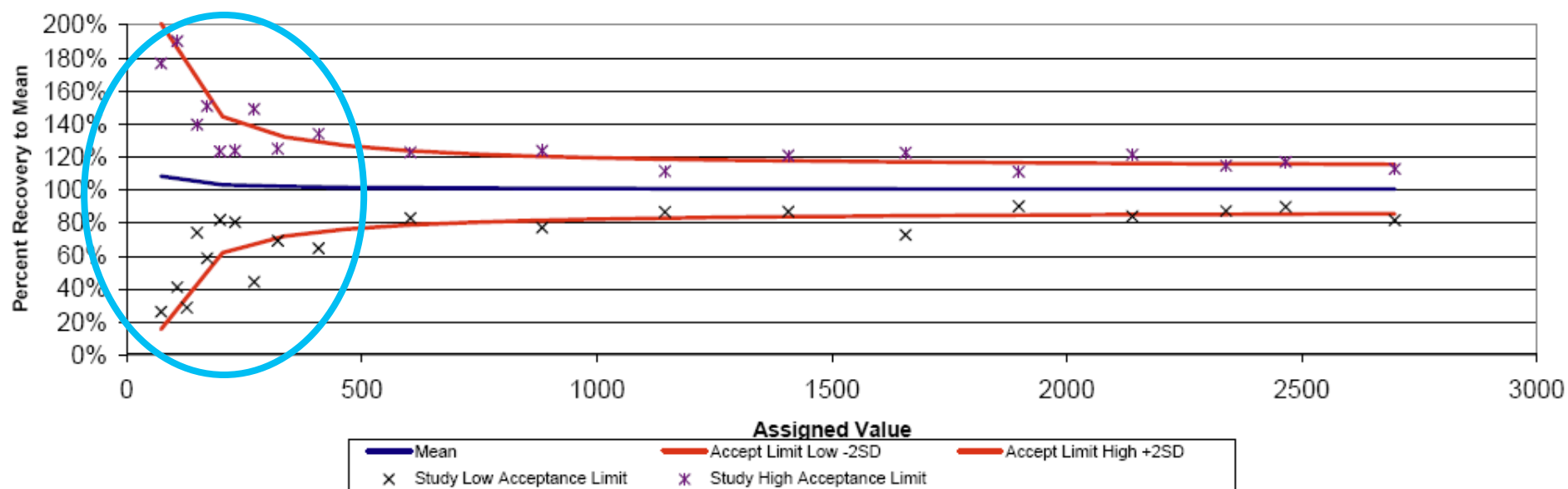
# Case Study: Method 25

Proposed NELAC Linear Regression Equation  $\pm 2$  stdev



# Case Study: Method 25

Proposed NELAC Linear Regression Equation  $\pm 2$  stdev



## Case Study: Method 25

- Considerations:
  - Blank subtraction
  - Interferences
  - Use of tracer gases
  - Difficulty of acquiring more data at low levels
  - Different techniques used by Stationary Source Testers
  - Limited number of laboratories performing the method
  - Nature of the method (testing the Tester, not just the Lab)





## Case Study: Method 25

- Industry experts were consulted
- VOC Reporting, Inc. and Triangle Environmental Services, Inc. teamed with Liquid Technologies Corp. to conduct a self-funded study of Method 25 performance under field and lab conditions







## Case Study: Method 25

- SSAS Table Subcommittee thoroughly examined all available data and recommended retaining the 150-2500 ppmC concentration range, but changing the acceptance limits to a regression equation to adjust for the degraded performance at lower levels
- Motion FAILED!





## Method 25 Actions Taken

- If consensus cannot be reached on new acceptance limits for Method, what about improving Method 25 itself?
- Method 25 Subcommittee formed to look into ways to improve Method 25 performance
- Alternate Method 25Z prepared and submitted to EPA
- Instructions drafted to standardize field procedures





## Method 25 Lessons Learned

- Formal procedures needed by SSAS Expert Committee for updates to the SSAS Table
- Used FoPT Table Management SOP from PT Program as the basis for new SSAS SOP
- SOP defines how requests for changes to the SSAS Table are processed by the SSAS Expert Committee
- Approved August 2012







## The Chicken-and-Egg Dilemma

1. To expand concentration range, historical data is needed to establish acceptance limits
2. To collect historical data, audit samples must be ordered
3. To order audit samples, the audit sample must be required by EPA
4. To be required by EPA, the audit sample must have acceptance limits established by TNI (Go back to Step 1!)





# The Chicken-and-Egg Dilemma

- Discussions held with EPA to resolve the dilemma
- EPA Suggested Approach #1:  
Extrapolate from the existing data what labs could achieve at lower levels. Add a safety margin to this and set temporary acceptance limits. Once enough data is then collected, re-establish the acceptance criteria based on this new historical data.





# The Chicken-and-Egg Dilemma

- EPA Suggested Approach #2:  
Base temporary limits on the repeatability of the Providers (RSD of  $<1/6$  acceptance limits). Labs should be able to meet 6x the Providers repeatability for temporary acceptance limits. Maybe expand this to 10x for a safety margin to start. Once enough data is then collected, re-establish the acceptance criteria based on this new historical data.





# Latest Developments

- July 2014: SSAS Table Management SOP updated with EPA's suggested approaches for setting initial acceptance limits
- SOP updated with new section explicitly defining procedures for making changes to concentration ranges or acceptance limits for existing methods/analytes
- Audit samples required by EPA as of 6-16-2013; first biennial review of SSAS Table acceptance limits due **June 2015**

