TELEDYNE INSTRUMENTS
Advanced Pollution Instrumentation
A Teledyne Technologies Company

Understanding Trace-Level Precursor Gas Monitors

Training and guidance information for State and County Personnel

Sponsored and Hosted by:
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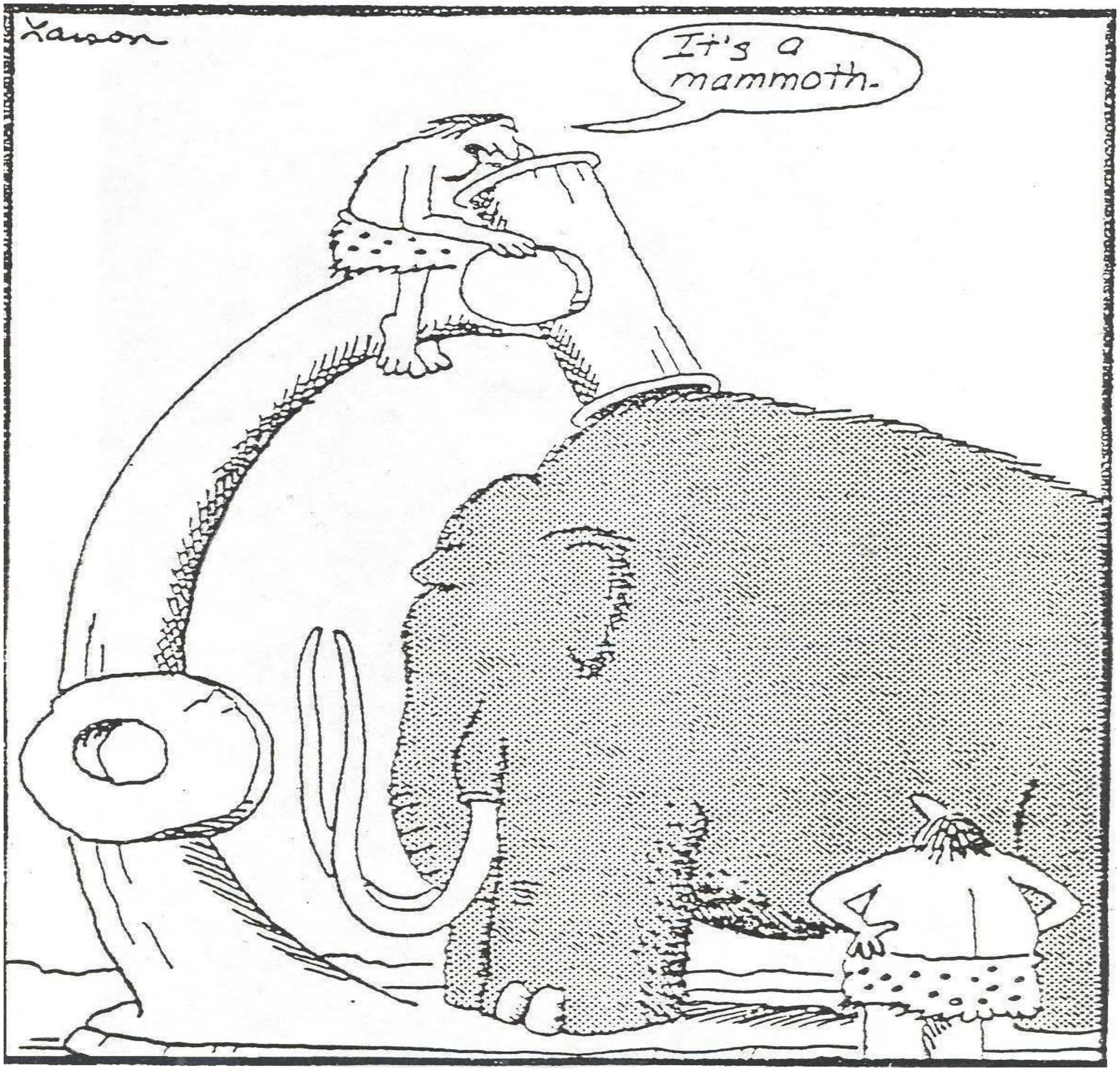
Compiled by:
AirQuality Research & Logistics, LLC

Trace Precursor Gas Program



Words of Wisdom

Reid Matusek, Connecticut DEP

"Similar to" ≠ "Same as"

Trace gas monitors contain many of the same components as “standard” monitors and operate on the same general principles. However, the design/operational differences required to reliably report trace-level concentrations make operation of trace monitors more complex (and in some cases) significantly more complex.

Outline

1. Overview

A) What are "trace" gases?

B) Why monitor "trace" level concentrations?

C) Why monitor "trace" level concentrations now?

D) How do "trace" monitors differ from "standard"?

2. Monitoring Site Infrastructure

A) How can infrastructure impact ambient data?

B) Data acquisition

3. Critical Trace Monitor Subsystems

A) CO "auto-reference" system

B) SO_2 Monitors

C) NOy line/converter losses

Outline *(cont.)*

4. **Quality assurance**

- A) Equipment
- B) Supplies
- C) Safety
- D) Auditing
- E) Performance checks
- F) Multi-point calibrations
- G) Documentation

5. **Data Review**

- A) EPA criteria
- B) Ambient time series
- C) Data auditing

Additional Information Sources

http://www.epa.gov/ttn/amtic/precur.html
Instrument SOP's, EPA training info, tech docs

http://www.epa.gov/ttn/amtic/pretecdoc.html
TAD – V.4

http://epa.gov/ttn/amtic/files/ambient/monitorstrat/precursor/whitpap.pdf
EPA "White paper" on NAAMS trace monitoring

http://www.epa.gov/ttn/amtic/files/ambient/monitorstrat/precursor/qaissues.ppt
qaissues.ppt

http://www.epa.gov/ttn/amtic/files/ambient/monitorstrat/precursor/P+B%20Guidance3_14_07.pdf
Guideline on the Meaning and the Use of Precision Data Required by 40 CFR Part 58 Appendix A

What are EPA’s “trace” gases?

– **CO**	(currently a Criteria Pollutant)
– **SO_2**	(currently a Criteria Pollutant)
– **NO/NOy**	(first cousin to NO/NOx)
– **NH_3**	($PM_{2.5}$ precursor *)
– **HNO_3**	(roles in $PM_{2.5}$ & O_3 formation*)

*Not covered by this workshop.

What are EPA's "trace" gases?

Nitrogen oxides definitions:

NOx = NO + NO_2

NOy = NOx + NOz (Total Reactive Nitrogen)

NOz = HONO+HNO_3+PAN+NO_3+N_2O_5 +HNO_4+Organic Nitrates+Halogenated Nitrogen

- N_2O & Ammonia are NOT included in NOz.

Why Monitor “Trace-gas” concentrations?

1) **Some (SO_2/NOx) are FP precursors (many FP non-attainment areas).**

2) **Some (CO/NOy) participate/characterize O_3 life-cycle(O_3 NA areas).**
[Proposed O_3 NAAQS revision will increase # NA areas & NCore sites]

3) **CO can be a surrogate for urban “plumes”.**

4) **Criteria pollutant concentrations are generally declining.**
5) **[When hourly data falls below MDL result is random numbers – bad data is worse than no data]**

5) **Support/evaluate emission strategies via modeling.**

6) **Support long term health studies re 5-year NAAQS review cycle.**

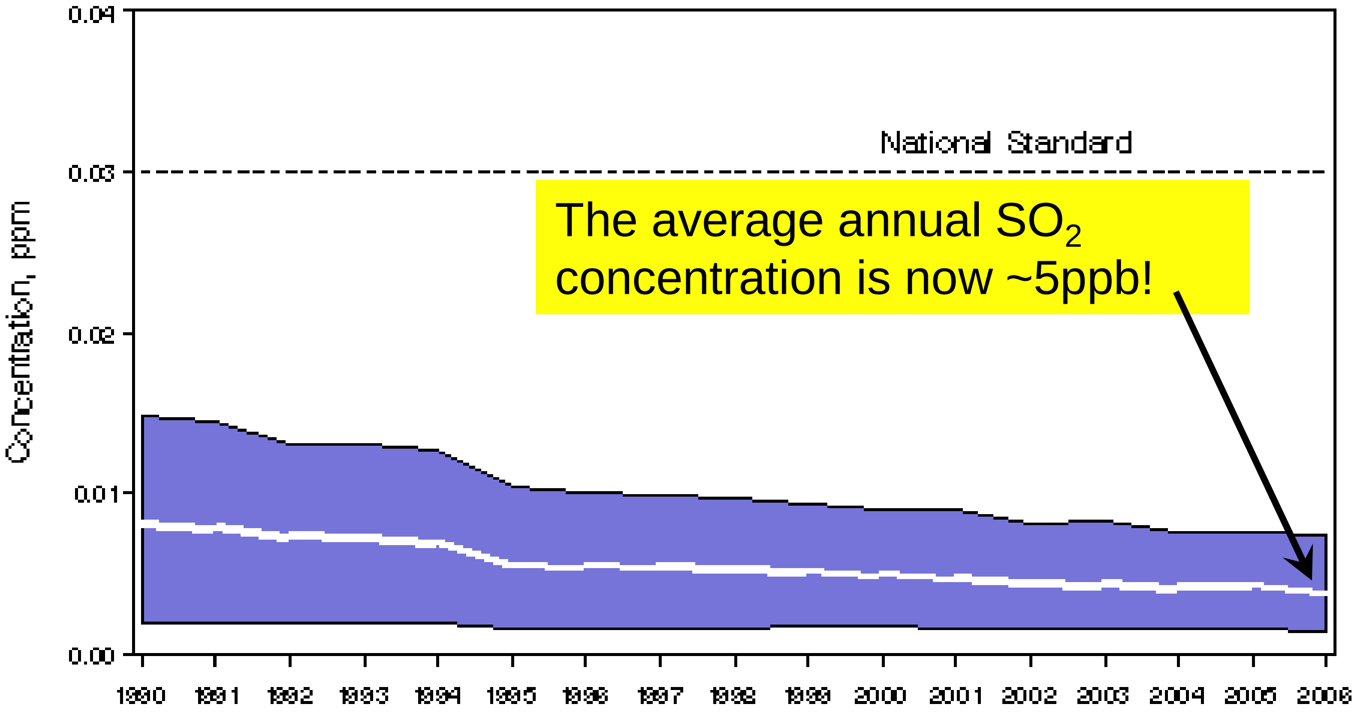
7) **Trace gas data can support other scientific studies.** **[e.g., ecosystem assessments. Also carbon, nitrogen and sulfur (w. H_2 & O_2) are the most abundant inorganics in the Earth-Air-Water system and dominate most combustion processes- understanding their concentrations and distributions helps put other measurements in perspective]**

SO$_2$ National Trend

SO2 Air Quality, 1990 — 2006

(Based on Annual Arithmetic Average)

National Trend based on 295 Sites



The average annual SO$_2$ concentration is now ~5ppb!

1990 to 2006 : 53% decrease in National Average

Last Generation SO_2 Monitor vs Trace-Level Monitor

	TAPI 100E	TAPI 100EU	Thermo 43iTLE
Ranges:	0-50 ppb to 0-20,000 ppb, user selectable. Dual ranges and auto ranging supported	0-5 ppb to 0-20,000 ppb, user selectable. Dual ranges and auto ranging supported	0-10 ppb to 0-1000ppb preset
Units:	ppb, ppm, mg/m^3	ppb, ppm, mg/m^3	ppb, ppm, mg/m^3
Zero noise:	200 ppt (RMS)	25 ppt (RMS)	25 ppt (RMS)
Zero drift:	< 0.5ppb/24 hours	< 0.2 ppb/24 hours	< 0.2 ppb/24 hours
Span drift:	<0.5% of FS/24 hours	< 0.5% of FS/24 hours	+/- 1 % per week
Lower Detectable Limit:	400 ppt	50 ppt	50 ppt
Response time:	<100 seconds to 95 %	< 120 seconds to 95%	80 seconds
Sample flow rate:	650 cc/min ±10%	650 cc/min ±10%	500 cc/min
Linearity:	1% of full scale	1% of full scale	+/- 1% of full scale
Operating Temp. Range:	5 - 40°C	5 - 40°C	5℃ - 40℃
USEPA Equivalancy:	yes	yes	no

Note that the Lower Detection Level for a “standard” SO_2 monitor is only one tenth of the typical annual average SO_2 concentration!

Why monitor "Trace" level concentrations?

Summary

Monitoring trace gases gives us;

1) Information on secondary pollutants,
2) Information on pollutant transport,
3) Support/eval. of control program performance,
4) Support for health effects studies,
5) Support for other scientific studies and
6) Data at significantly lower levels than in past decades.

Why monitor “Trace” level concentrations now?

- As seen in the previous slides, perhaps the most important consideration in migrating toward trace-gas monitoring is the fact that ambient concentrations of many criteria pollutants are at a point where improved technology is required.

- However, there are other considerations.

Why monitor "Trace" level concentrations now?

1) It's an EPA mandate (for details see:

http://www.epa.gov/ttn/amtic/stratmem.html).

2) Key control programs are kicking in that will accelerate the decline in ambient concentrations.

   a) the Clean Air Interstate Rule (CAIR)

   b) NOx SIP "call"

   c) New sulfur-in-fuel regulations

3) Continuation of existing programs will further the decline of ambient concentrations (MS fleet age).

How do "Trace" monitors differ from "Standard" monitors?

- **CO – inlet line dryer, frequent baseline adjustment, more <u>sensitive</u> detector w. better T. control (*allows shorter ARef cycle*).**
- **SO_2 – stronger UV source, better optical filters (*primary excitation, NO interference*), better HC rejection, longer path.**
- ***NOy* – converter moved to front of inlet line *(reduce nitric acid loss)*, higher flows *(red. O_3/NO Rxn)*, use "pre-reactor" to zero out HC/O_3 *chemiluminescence.***
- **specificity vs sensitivity concept and options for network operators.**

This completes the Overview section.

Questions or comments?

Monitoring Site Infrastructure

- Shelter Exterior/Location
- Shelter Interior
- Data Acquisition

Monitoring Site Infrastructure

1) Shelter location/exterior

- i) Meteorology (prevail wind direction, fetch)
- ii) Representativeness (must avoid certain sources @ trace SO_2 sites)
- iii) Manifold (material, design w. cleaning in mind)
- iv) Inlet height
  - a) NOy – 10 meters, 270° unobstructed, min 20 m to trees, opaque line
  - b) CO 3-15 meters, 270° unobstructed, min 20 m to trees
  - c) SO_2 3-15 meters, 270° unobstructed, 20 m min, 1 m v/h separation from support
  - d) Discuss uniform inlet height @ NCore sites (include PM and O_3)

Monitoring Site Infrastructure

1) Shelter location/exterior

i) Meteorology

For "transport-oriented" sites;

no local sources, only minor obstructions in the prevailing wind direction and insure sufficient "fetch",

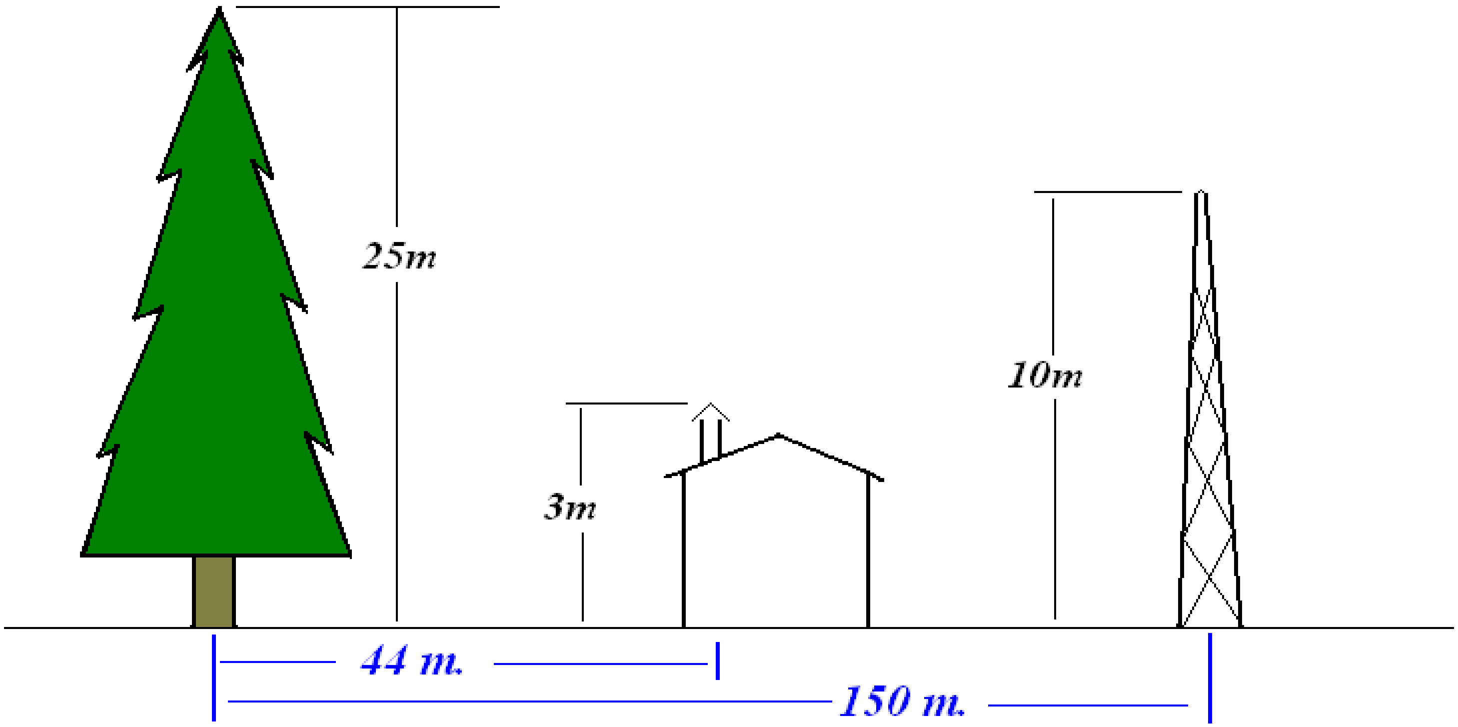
distance to flow obstruction GTE 10x diff in elevation between sensor and height of obstruction for wind data,

GTE 2X for criteria pollutants.

For "urban-scale" sites;

some source impact unavoidable – be selective! Vertical measures are critical – distance from obstruction must be 2X the diff in elevation between inlet and height of obstruction.

Monitoring Site Infrastructure



Monitoring Site Infrastructure

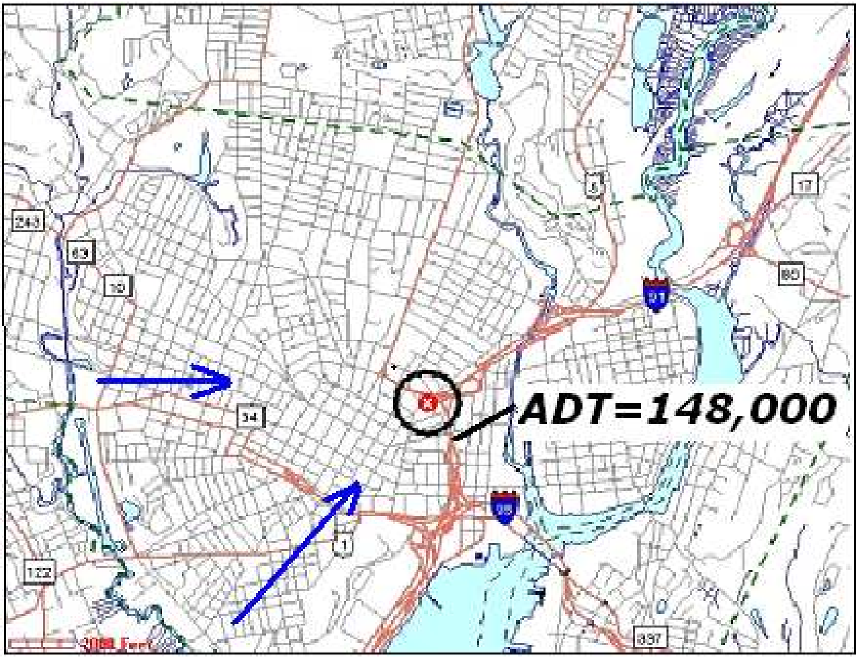
1) Shelter location/exterior

ii) Representativeness

1) Designated (EPA) “scale” sets minimum distance to most nearby sources but be certain to avoid;

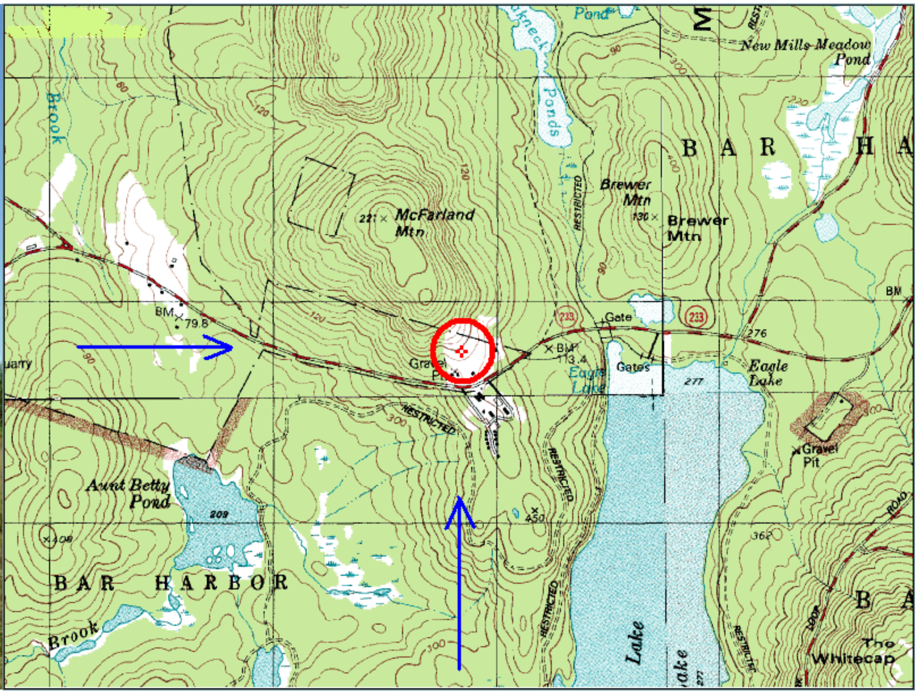
a) NO sources @ trace SO_2 sites,
b) CO_2 sources @ trace CO sites and
c) Ammonia sources @ trace NOy sites!

New Haven, CT – State St.



Prevailing winds at this site (blue arrows) bring emissions from the Central Business District of New Haven to the State St. site but mobile source emissions, from traffic on I-91 to the East typically do not impact the site.

McFarland Hill, ME - RAIN Site



The remote location of this site (an island off the Northern coast of Maine) minimizes the impact of virtually all local sources making it a good "transport" site. Prevailing westerly winds are strongly impacted by the Atlantic Ocean (~2 miles to the South) which creates a strong North/South "sea breeze" effect.

Monitoring Site Infrastructure

1. Shelter location/exterior

iii) Manifold

1) Non-reactive, preferably glass (but opaque).
2) Design for frequent/easy maintenance.
3) Seek uniformity across network.

Monitoring Site Infrastructure

1) Shelter location/exterior

iv) Inlet height

1) Depends (sometimes) on monitoring “scale”.

2) Generally 3 -15 meters agl for gases (but NOy =10m) (PM inlets typically 2-7 m agl).

Monitoring Site Infrastructure

1) Shelter interior

i) Temperature

1) Do not even <u>approach</u> the dew point in lines or manifold !!

2) Keep variations to the absolute minimum (e.g. 1.5° C).

3) Seasonal temperature set-points are desirable
(e.g. 25-30° C. summer/ 20-25° C winter).

4) Shield instruments/lines from AC "breeze".

5) Consider use of back-up AC unit
(interior temps wo AC can approach 50° C !).

Monitoring Site Infrastructure

1) Shelter interior

ii) Manifold

1) Shortest is best (performance and cleaning).

2) Employ minimum flow (but monitor it remotely).

3) Attach only inlet lines (calibrator output is exception).

4) If z-air drawn from manifold use caution in location.

5) Use care in locating calibrator “dump”.

Monitoring Site Infrastructure

Data Acquisition

1) Seek uniformity across network.
2) Digital acquisition is best.
3) Insure “live” zeros.
4) If auto-range employed, calib. each channel.
5) Insure capture of critical diagnostic data.
6) Protect your data.
7) Use 1-min avgs. for strip chart emulation.
8) If analog acq. used, calibrate initially/annually.

Monitoring Site Infrastructure

Data Acquisition

1) Seek uniformity across network (esp w analog acq).

i) channel #'s
ii) ranges
iii) formats
iv) goes for math/synthetic channels too!

Monitoring Site Infrastructure

Data Acquisition

2) Digital acquisition is best.

(less noise, drift)

3) Insure “live” zeros.

(Include slightly negative values in data stream)

4) Analog auto-ranging systems require calibration of each channel.

Monitoring Site Infrastructure

Data Acquisition

5) Insure capture of critical diagnostic data.

i) CO – pressure, flow, box T., detector T. (for cat.).
ii) SO_2 – flow, all lamp info, stray light.
iii) NOy – vacuum, PMT T., ozonator flow, NO/NOx slopes and intercepts.

Monitoring Site Infrastructure

Data Acquisition

6) Protect your data.

(passwords for all systems, 3-levels of backup, off-site storage of backed-up data)

7) Use 1-min averages for strip chart emulation.

(hourly reports can focus on 1-hour averages)

8) If analog acquisition used, calibrate initially/annually.

(another plus for digital acquisition)

This completes the Monitoring Site Infrastructure section.

Questions/comments?

Critical Trace Monitor Subsystems

A) CO "Auto-Reference" cycle

1) What's it for?
   - *i) nulls H_2O and CO_2 interference*
   - *ii) adjusts detector offset (no gain adj.)*

2) How does it work?
   - *i) creates "zero" air ($CO => CO_2$)*
   - *ii) hot cat or non-cat oxidation*
   - *iii) frequent z-air injection (e.g., hourly)*
   - *iv) auto adjust of offset*
   - *v) check function/efficiency monthly*

Critical Trace Monitor Subsystems

A) CO "Auto-Reference" cycle (cont.)

3) Things to watch for
   i) check ARef data daily
   ii) long-term, down drift (e.g., CO<80ppb)
   iii) out-of-range catalyst temps
   iv) timely replacement of catalyst

4) Secondary systems
   i) inlet dryer functionality (look for big "zero value")
   ii) optical bench temperature stability (check often)
   iii) ultra-sensitive detector
      (check with ARef on/off, T. should stay in-spec)

Critical Trace Monitor Subsystems

B) SO_2 Monitors

1) New type HC “kicker” reduces positive interference from aromatics and PNA’s (napthalene).

2) NO rejection ratio (100:1 or greater) verified in situ (NO interference is positive & greater than the HC bias, use caution if cal gas blended with NO!).

3) Beware of stray light (positive bias).

4) Unlikely but negative bias from large or *rapid change in* H_2O *is possible (quenching).*

Critical Trace Monitor Subsystems

C) NOy Monitors

1) HC/O_3 pre-reactor

2) Inlet lines
    i) use PFA Teflon® "gross" filter
    ii) use opaque inlet lines.

3) High flow/low chamber pressure.

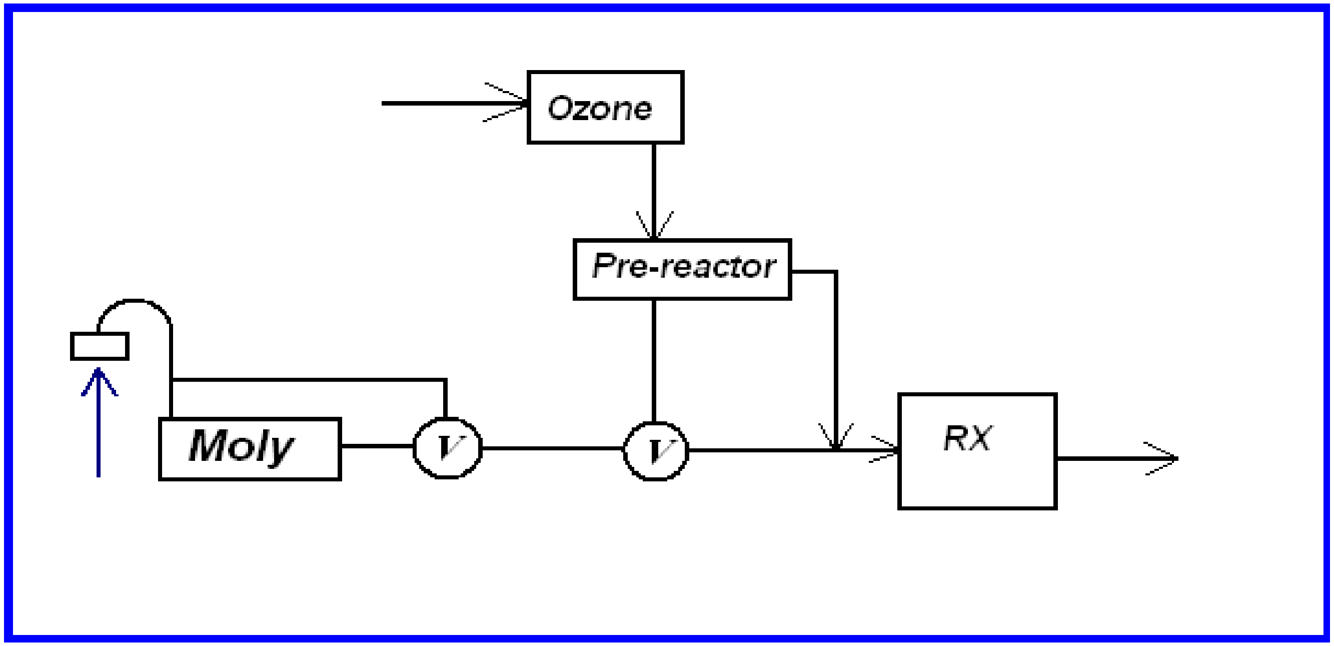
4) Converter
    i) exterior mounting
    ii) set converter temp. to avoid NH_3 conversion
    iii) monthly converter efficiency check
    iv) annual converter challenge.

Critical Trace Monitor Subsystems

C) NOy Monitors

1) HC/O_3 pre-reactor.

(Chemiluminesence from O_3 reaction w. olefins, amines, terpenes is subtracted from NO/O_3 reaction via pre-reactor)



Critical Trace Monitor Subsystems

C) NOy Monitors

2) Inlet lines

i) use PFA Teflon® "gross" filter

(TAD suggests ½ of teflon® filter holder).

ii) use opaque, custom inlet lines

(supplied by manufacturer).

Critical Trace Monitor Subsystems

C) NOy Monitors

3) High flow/low chamber pressure.

(high flow required to minimize NO/O_3 reaction time)

(chamber pressure is critical, hold to ± 0.3 in Hg)

Critical Trace Monitor Subsystems

C) NOy Monitors

4) Converter

- i) exterior mounting to reduce HNO_3 losses
- ii) set converter temp to avoid NH_3 conversion
  (TAD suggests 350°C. but 325° C. is safer).
- iii) monthly converter check
  (use NO_2 and IPN, need 95% efficiency).
- iv) annual converter challenge
  (after complete cal, test converter w. IPN and "possibly" NH_3 perm tube – need <5% NH_3 conversion).

Warranty/Repair Questionnaire Model 100EU

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1. ARE THERE ANY FAILURE MESSAGES? ____

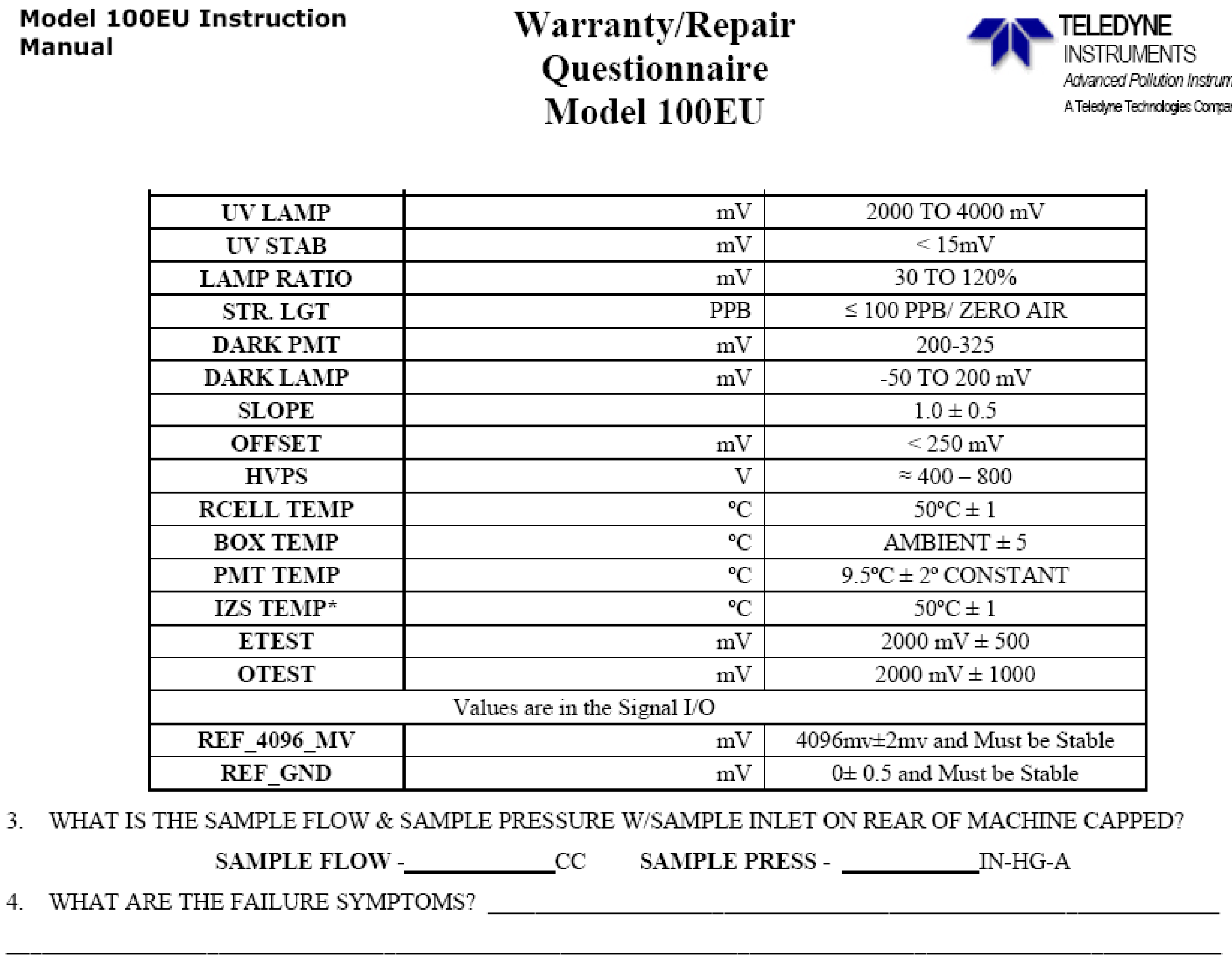
____

____

2. PLEASE COMPLETE THE FOLLOWING TABLE: (**NOTE:** ***DEPENDING ON OPTIONS INSTALLED, NOT ALL TEST PARAMETERS BELOW WILL BE AVAILABLE IN YOUR INSTRUMENT)***

*IF OPTION IS INSTALLED

Parameter	Recorded Value	Acceptable Value
RANGE	PPB/PPM	
STABIL	PPB	≤0.3 PPB WITH ZERO AIR
STABIL2	PPB	<= 1 PPB WITH ZERO AIR
PRESS	IN-HG-A	AMBIENT (- 2) IN-HG-A
SAMPLE FLOW	cm^3/MIN	650 ± 10%
PMT SIGNAL WITH ZERO AIR	mV	-20 TO 150 mV
PMT SIGNAL AT SPAN GAS CONC	mV PPB/PPM	0-5000 mV 0-20000 PPB
NORM PMT AT SPAN GAS CONC	mV PPB/PPM	0-5000 mV 0-20000 PPB



Model 100EU Instruction Manual

Warranty/Repair Questionnaire Model 100EU

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UV LAMP	mV	2000 TO 4000 mV
UV STAB	mV	< 15mV
LAMP RATIO	mV	30 TO 120%
STR. LGT	PPB	≤ 100 PPB/ ZERO AIR
DARK PMT	mV	200-325
DARK LAMP	mV	-50 TO 200 mV
SLOPE		1.0 ± 0.5
OFFSET	mV	< 250 mV
HVPS	V	≈ 400 – 800
RCELL TEMP	°C	50°C ± 1
BOX TEMP	°C	AMBIENT ± 5
PMT TEMP	°C	9.5°C ± 2° CONSTANT
IZS TEMP*	°C	50°C ± 1
ETEST	mV	2000 mV ± 500
OTEST	mV	2000 mV ± 1000
Values are in the Signal I/O		
REF_4096_MV	mV	4096mv±2mv and Must be Stable
REF_GND	mV	0± 0.5 and Must be Stable

3. WHAT IS THE SAMPLE FLOW & SAMPLE PRESSURE W/SAMPLE INLET ON REAR OF MACHINE CAPPED?

SAMPLE FLOW -____________CC SAMPLE PRESS - ___________IN-HG-A

4. WHAT ARE THE FAILURE SYMPTOMS? ____

____

This completes the Critical Trace Subsystems review.

Questions or comments?

Quality Assurance

A) Equipment

1) Regulators

i) use stainless steel (Teflon coated diaphragm), consider low internal volume & LOX cleaning.

ii) dedicate to 1 gas, seal ports when idle, don't "loan" to others, use case for transport.

iii) "dead heading" a regulator may contaminate cylinder (open main valve = gas flow).

Quality Assurance

A) Equipment

1) Regulators

iv) inspect high pressure mating surfaces and gasket before mounting regulator (do not "crack" high pressure valve to purge!).

iv) TAD wants 3 purges (SO_2) before cal. (3-valve regs. are available that can trap cal gas).

v) use SS or Teflon between cylinder & calibrator.

Quality Assurance

A) Equipment

2) flow indicators must be NIST traceable

(bubble meter, frictionless piston, other?).

3) calibrators

i) MFC=NIST trace, ±2%, air=20 lpm, gas 100 ccm.

ii) flows at STP (760 mmHg, 25°C).

iii) equilibration required in extreme weather (T/RH).

Quality Assurance

A) Equipment

4) z-air sources

i) lower the better but must be < instrument LDL

(CO<10ppb, SO_2<0.50ppb, NO<0.50ppb).

ii) activated C_2 performance varies by maker

(see TAD sect. 3, p. 22).

iii) soda lime/sodium carbonate are C_2 alternatives.

iv) carulite/hopcalite for CO removal (MnO_2+CuO).

Quality Assurance

A) Equipment

4) z-air sources

v) use ambient air as z-air source (not room air !).

vi) use compressed ultra z-air for comparison (quarterly basis or trouble shooting).

vii) maintain continual flow through z-air supply (can be at a reduced rate when not actually in use).

Quality Assurance

B) Other Supplies

1) compressed calibration gases

i) NIST traceable, ±2% accuracy.

ii) cylinder interior stabilized.

iii) TAD recommended ranges, CO=200-300ppm, SO_2=10-15ppm, NO=20-25ppm (If cylinder conc. <10ppm, have mfgr. certify 30 day stability).

iv) matrix should be N_2 – not air.

v) H_2O is deadly to trace gases – avoid at all costs!

Quality Assurance

B) Other Supplies

2) some use for perm tubes but TAD does not recommend (except NH_3 NOy converter challenge).

3) tubing/fittings PTFE or stainless (PFA for NOy).

4) bound notebook with numbered pages/indelible pen.

Quality Assurance

C) Safety

1) gases

- *i) MSDS – read, heed, keep available.*
- *ii) transit placards – check with your DOT.*
- *iii) cylinder must always be secured, full/MT, idle/in-use, cradle-to-grave !*
- *iv) always vent calibrator to shelter exterior (caution if dumping into sample manifold).*
- *v) leak check ALL high pressure connections EVERY time (use OSHA approved eye protection).*

Quality Assurance

C) Safety

2) electrical
  i) high voltage present in all monitors/calibrators!
  ii) dry off equipment before plugging in.
  iii) avoid standing water !

3) falls
  i) inspect ladders frequently.
  ii) use OSHA fall protection gear.

Quality Assurance

D) Auditing

1) proficiency testing (TAD ss 5.4.1)

- *i) annual blind 4-pt audit for each monitor (z-chk not specified !?)*
- *ii) % FS 3-8, 15-20, 35-45, 80-90 (but note 10/17/06 CFR pp 61,305-6)*
- *iii) NOy needs zero + 4 NO pts + 4 NO_2 pts + converter efficiency check.*
- *iv) NIST traceable MFC check required.*
- *v) independent personnel & equipment.*

Quality Assurance

D) Auditing

ii) % FS 3-8, 15-20, 35-45, 80-90 (but note App. A, Part 58,10/17/06 CFR pp 61,305-6)

	Concentration Range (ppm)		
Audit Level	***CO***	***NO_2***	***SO_2***
1	**0.08 - 0.10**	**0.0002 - 0.002**	**0.0003 - 0.005**
2	**0.50 - 1.0**	**0.003 - 0.005**	**0.006 - 0.01**
3	**1.50 - 4.0**	**0.006 - 0.10**	**0.02 - 0.10**
4	**5.0 - 15.0**	**0.11 - 0.30**	**0.11 - 0.40**
5	**20.0 - 50.0**	**0.31 - 0.60**	**0.41 - 0.90**

The next topic is determination of an analyzer’s Method Detection Limit (MDL).

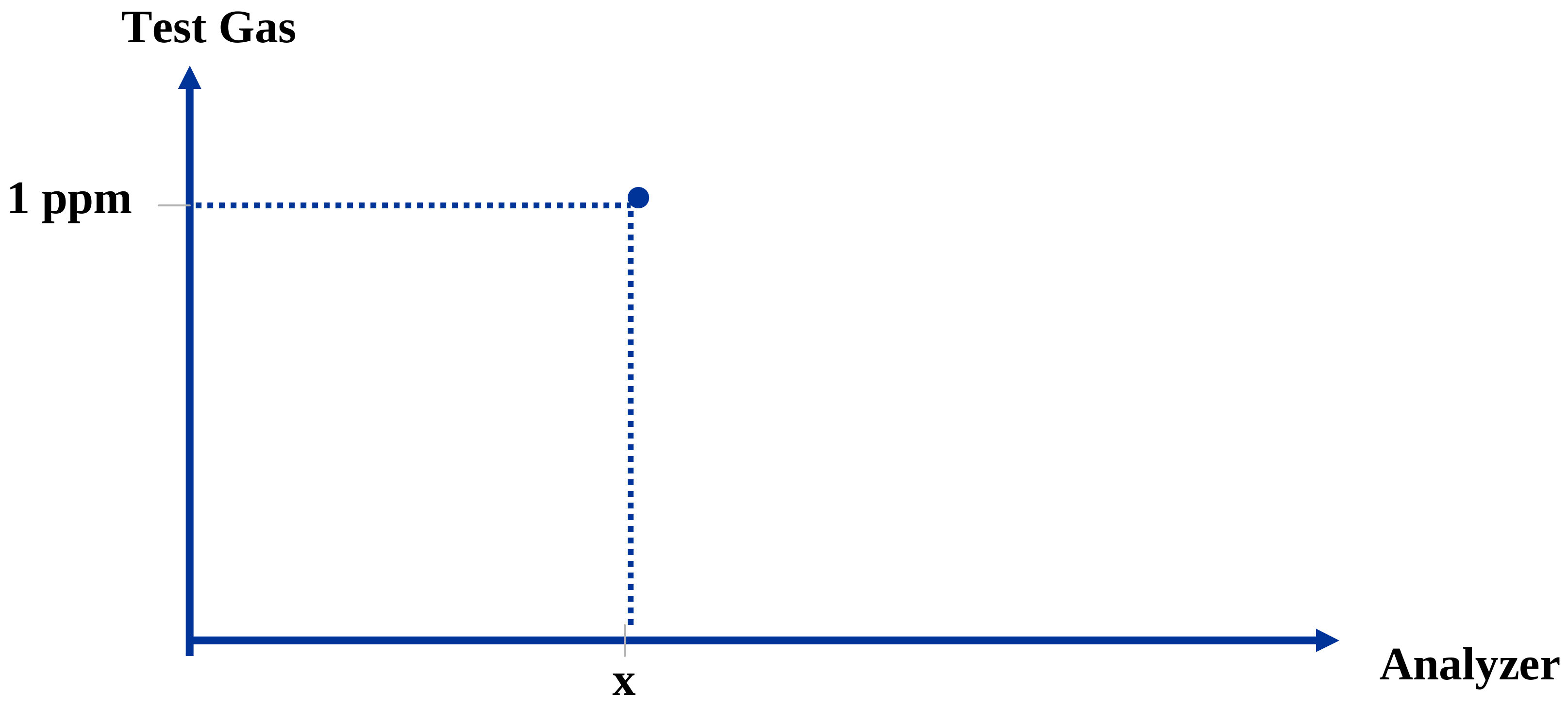
But first let’s take a quick look at how “factory reported” analyzer performance specifications are derived.

Analyzer Specifications

Analyzer Specifications

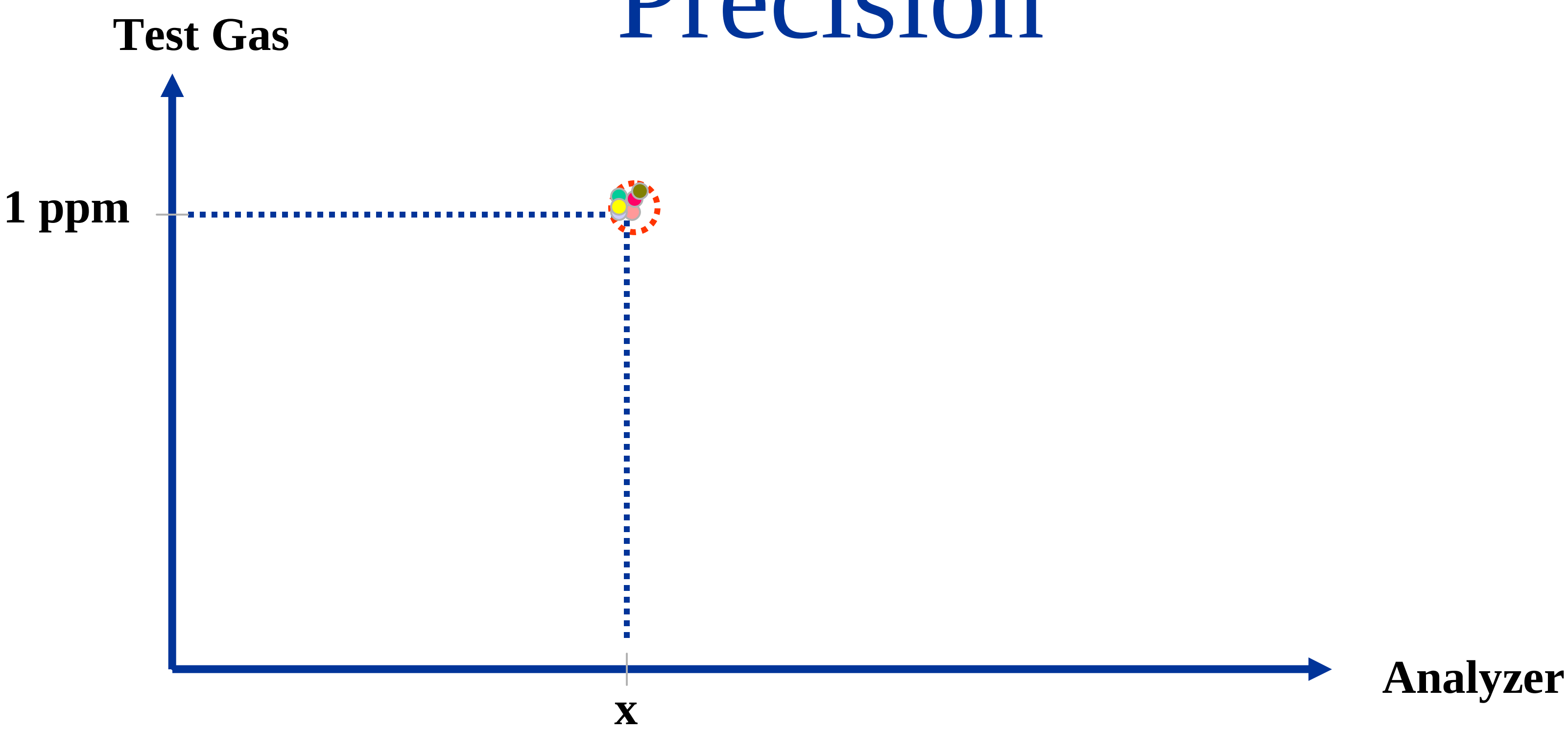
- Analyzer specifications are often misunderstood.
- However, there are precise definitions for the individual specs that are given to us by the USEPA and others.
- These definitions are nearly universal for gas analyzers.
- This presentation demonstrates these definitions.

Precision



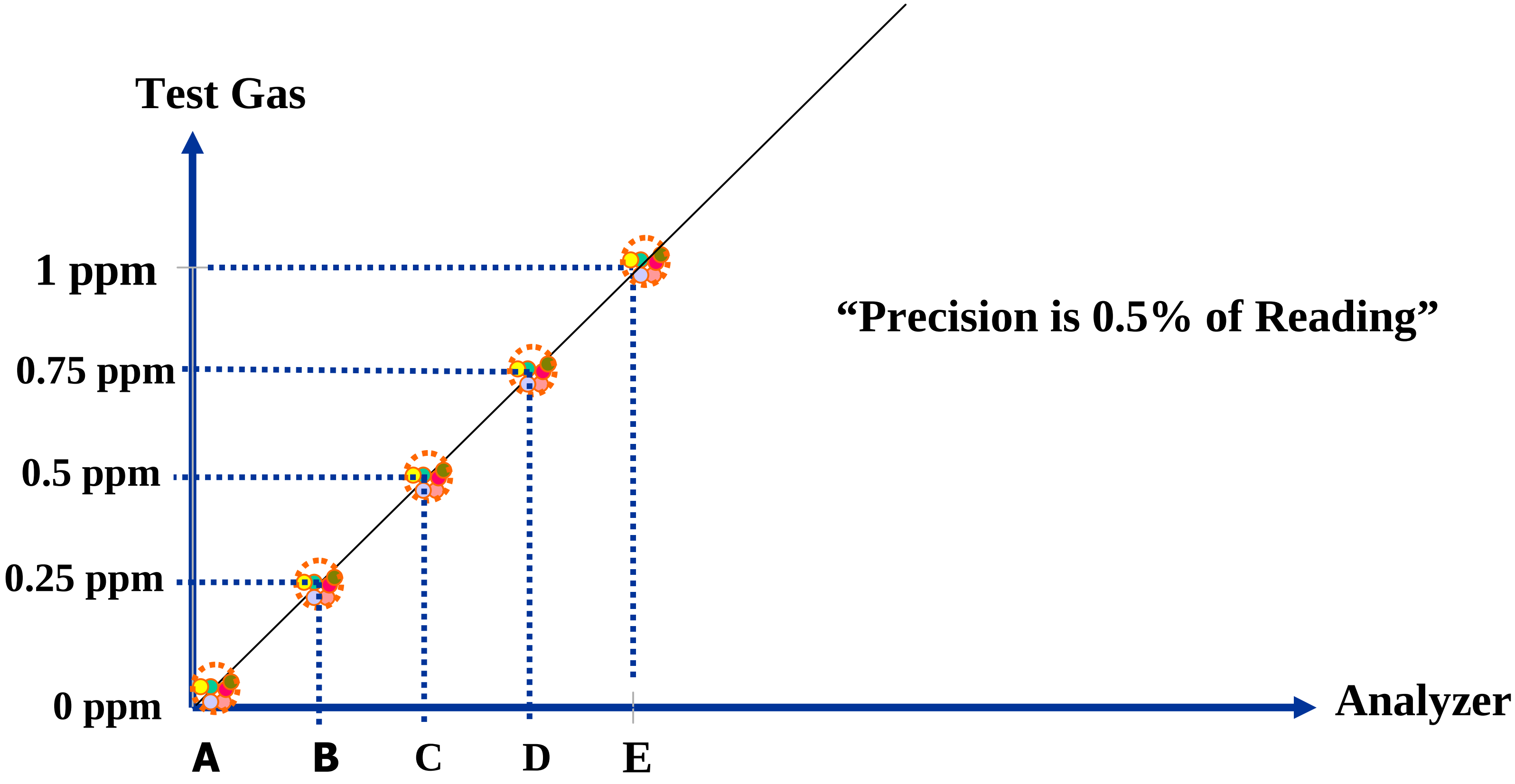
When we challenge an analyzer with a known concentration of test gas, for example, 1 ppm, the analyzer will give some concentration reading, x.

Precision



When we challenge the analyzer repeatedly with the same test gas, say six times, the analyzer will give a number of concentration readings [different colored dots], which are (hopefully) grouped around the point x. The *standard deviation* of these six trials, at that point, is called the *precision* of the analyzer at that point. More will be said about Standard Deviations later.

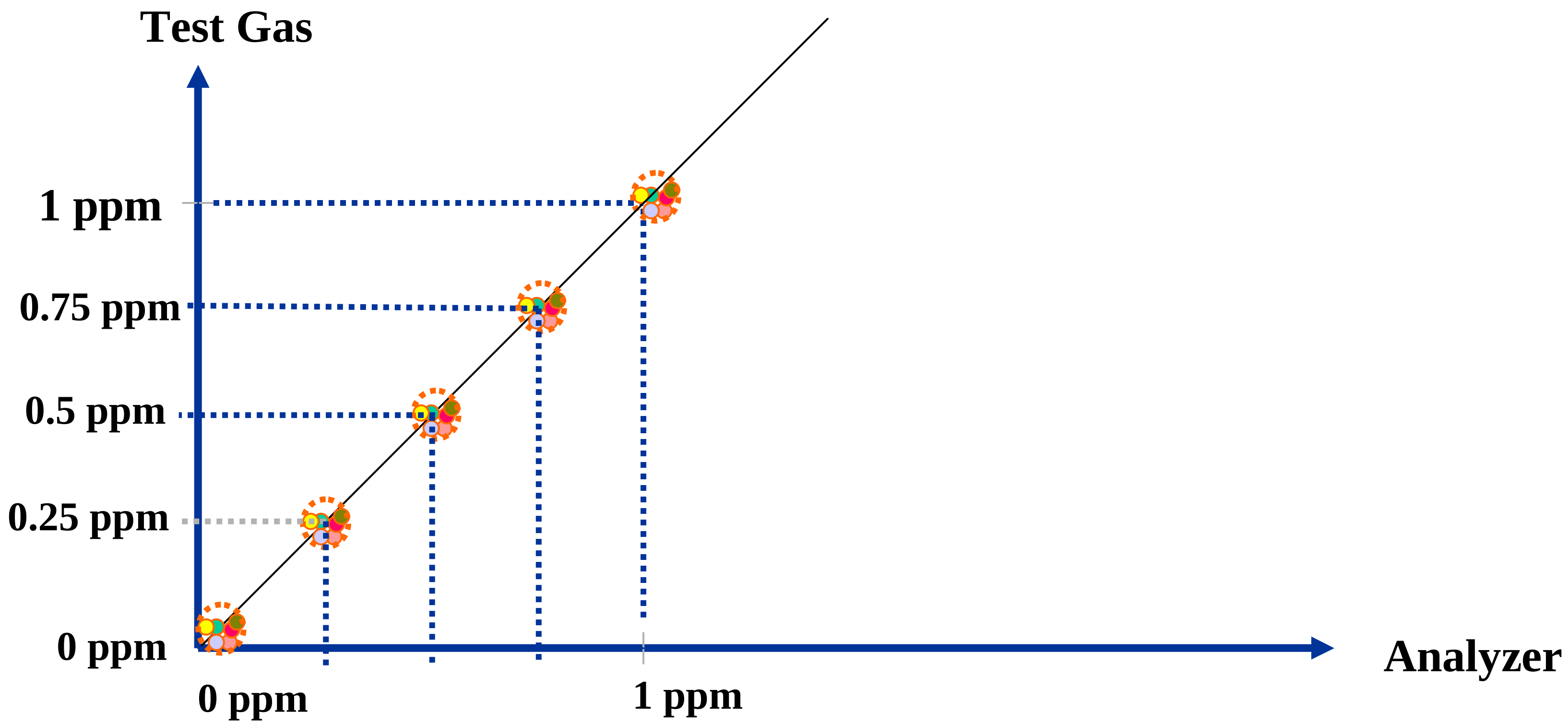
Precision



"Precision is 0.5% of Reading"

If we repeat this experiment at several points along the analyzer's range, we can find the average standard deviation over all of these points. Then we can express precision as a *Percent of Reading*.

Accuracy



When we adjust (*calibrate*) the analyzer to match the calibration gas concentration, we are actually adjusting the accuracy. Accuracy is the actual error of the analyzer in measuring a particular concentration.

Accuracy:
The Archery Analogy

- When an archer shoots a group of arrows and they all hit the same place on the target, that is ***precision*** (***repeatability***).
- When the archer adjusts his aim (***calibrates*** his aim) and hits the bullseye, that is ***accuracy***.

Ultimate Accuracy of an AQM Measurement

- The sources of errors in any measurement are combined as the square root of the sum of the squares of the errors. Consider a “perfect” calibration:
  - Cylinder Concentration Error = 1%
  - Calibrator Mass Flow Controller Error = 1% Each (x2 MFC’s = 2%)
  - Analyzer Precision Error = 0.5%

Ultimate Accuracy

$$= \sqrt[2]{(\text{Cylinder})^2+(\text{MFC})^2+(\text{MFC})^2+(\text{Precision})^2}$$

$$= \sqrt[2]{(0.01)^2+(0.01)^2+(0.01)^2+(0.005)^2}$$

$$= \sqrt[2]{0.000325}$$

$$= 0.01803$$

$$= 1.8\%$$

Linearity

We expect an analyzer to be linear. That is, we expect the analyzer to have a voltage output that is double every time we double the inlet gas concentration.

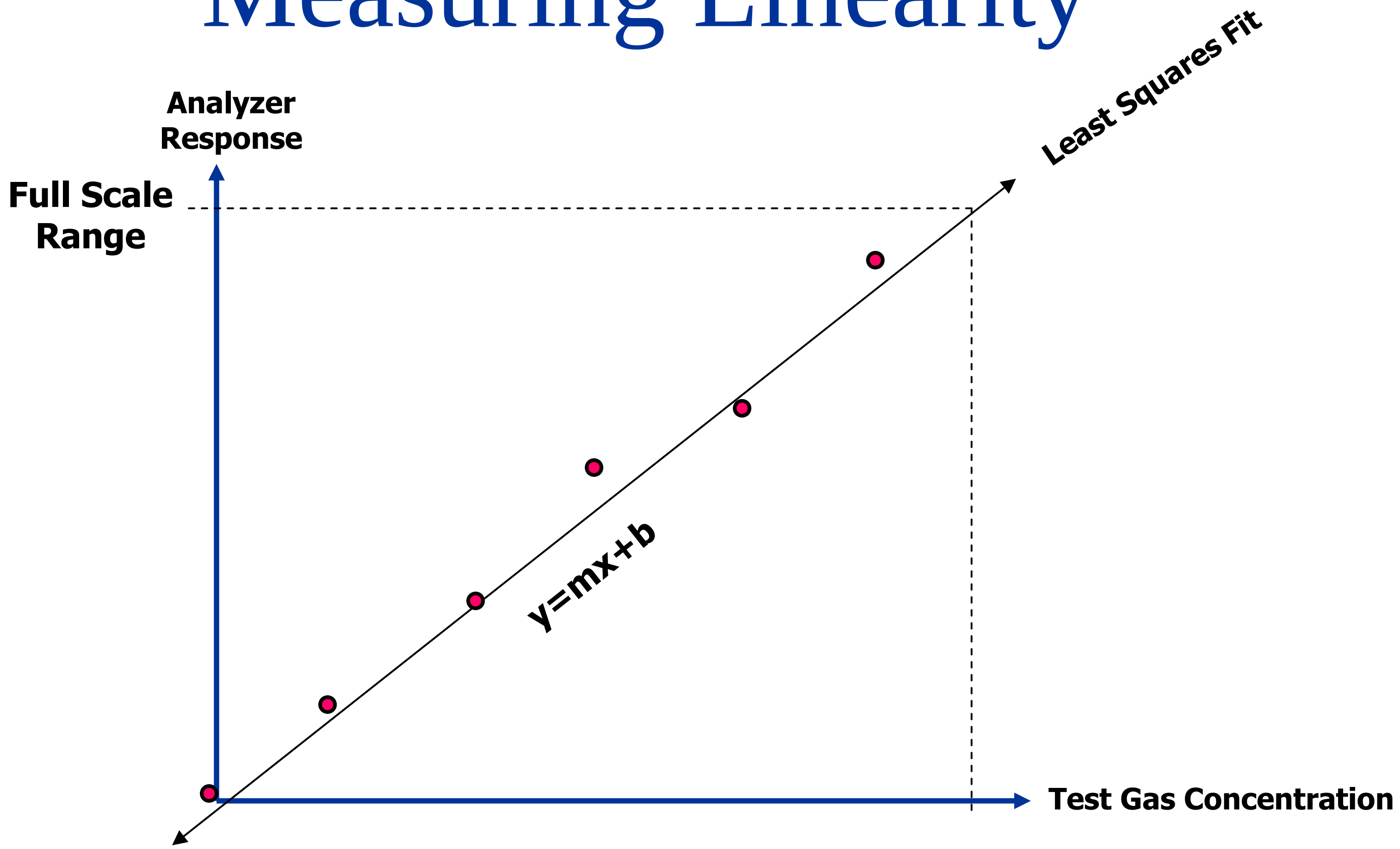
Therefore, the perfect analyzer is described by the following equation…

Linearity

$$y = mx + b$$

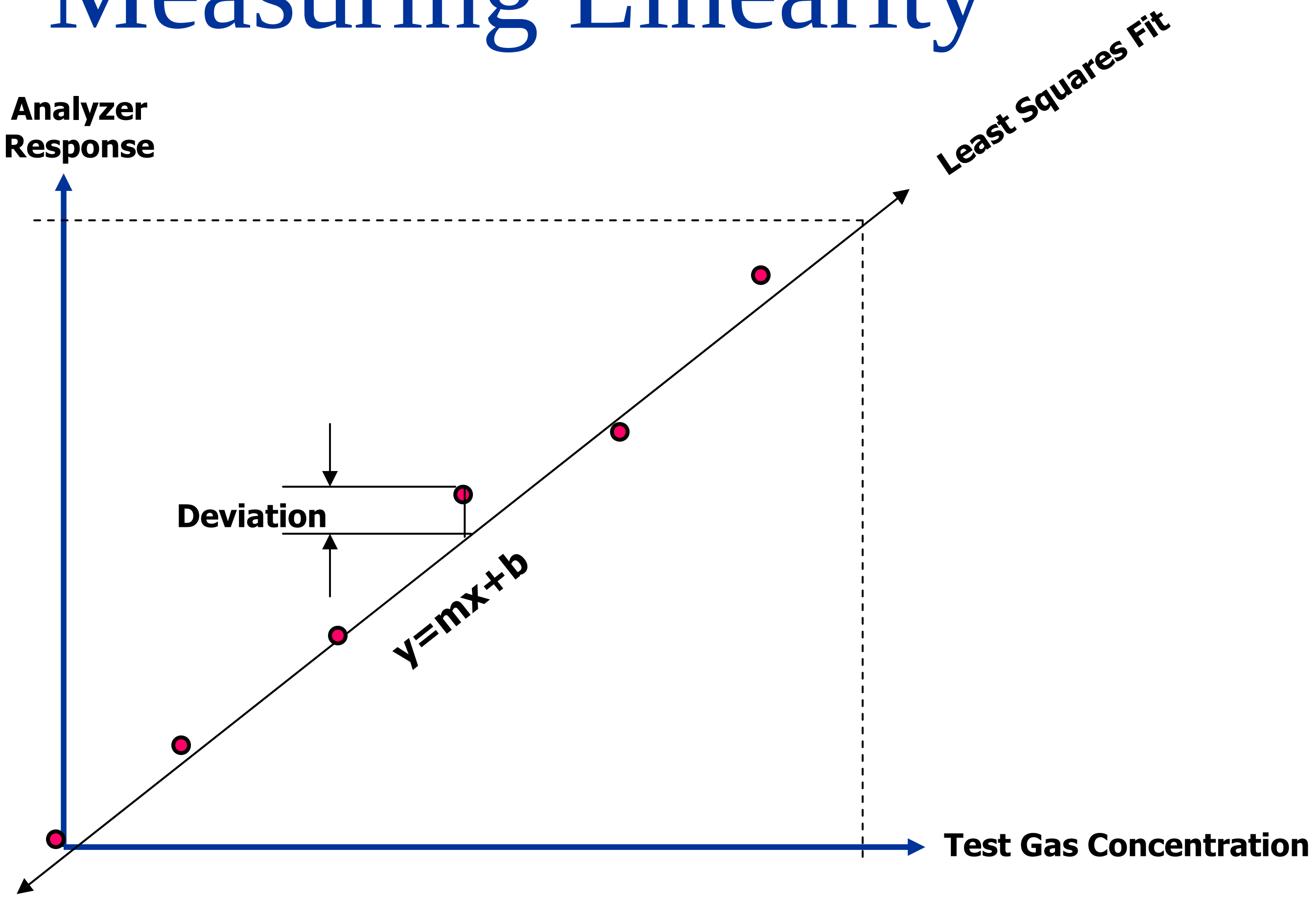
…where x is the gas input concentration, y is the analyzer's output concentration, m is the slope of the equation (perfect analyzer = 1) and b is the zero intercept of the equation (perfect analyzer = 0.0 ppb).

Measuring Linearity



Linearity **is the average maximum deviation from the least squares fit for six trials of six points each. It is expressed as a *Percent of Full Scale (%FS).***

Measuring Linearity

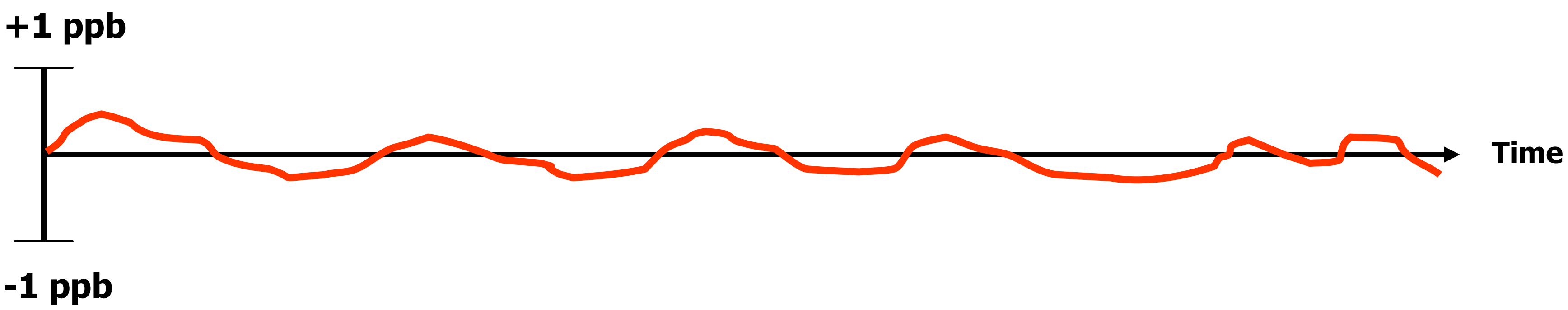


Linearity **is the average maximum deviation from the least squares fit for six trials of six points each. It is expressed as a *Percent of Full Scale (%FS).***

Noise

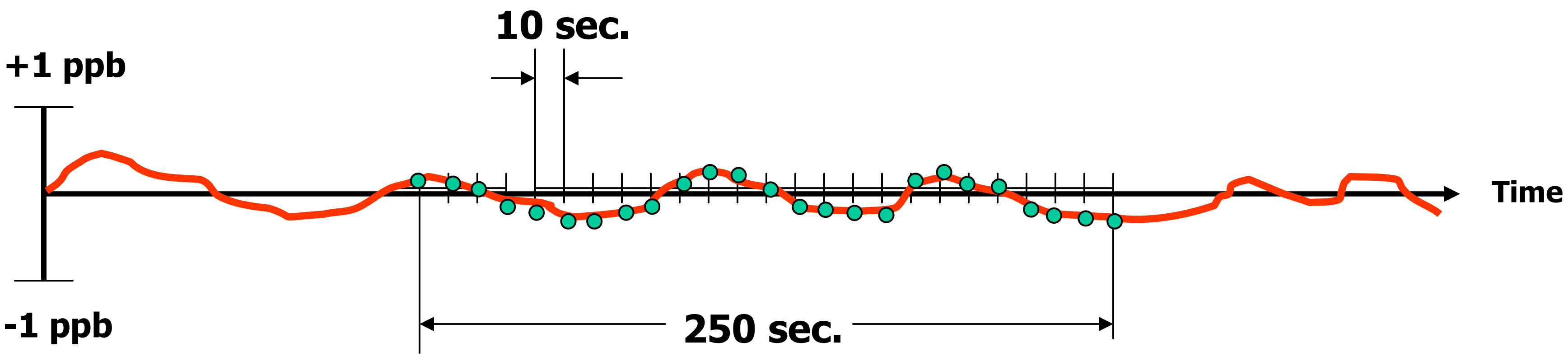
- *Noise* is really small variations around a particular concentration.
- *Span Noise* is the variability of the analyzer while measuring a gas whose concentration is 80% of the analyzer's range (*span gas*).
- *Zero Noise* is the variability of the analyzer's response when you input *zero gas* (gas without any of the target gas in it.)

Zero Noise



In order to measure Zero Noise, we first put zero gas into the analyzer an let it stabilize. The reading will now be very close to zero.

Zero Noise



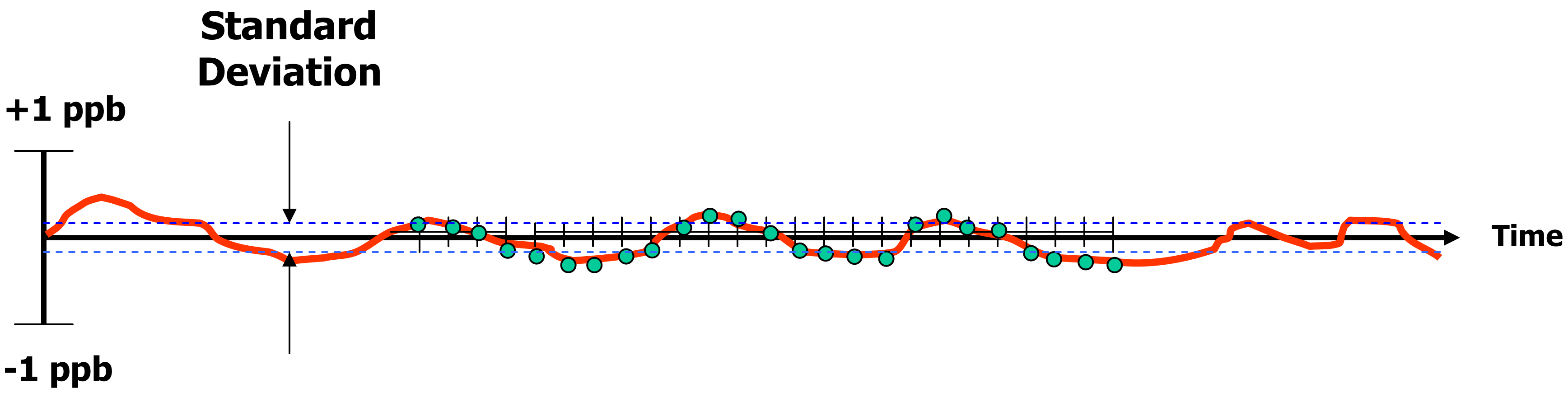
Now we take a representative period of 250 seconds and divide it up into 10-second intervals. Then we sample the output of the analyzer every ten seconds (25 samples) over this period.

Zero Noise

$$\sigma = \sqrt{\frac{\sum_{k=1}^{25}(C_k - a)^2}{24}}$$

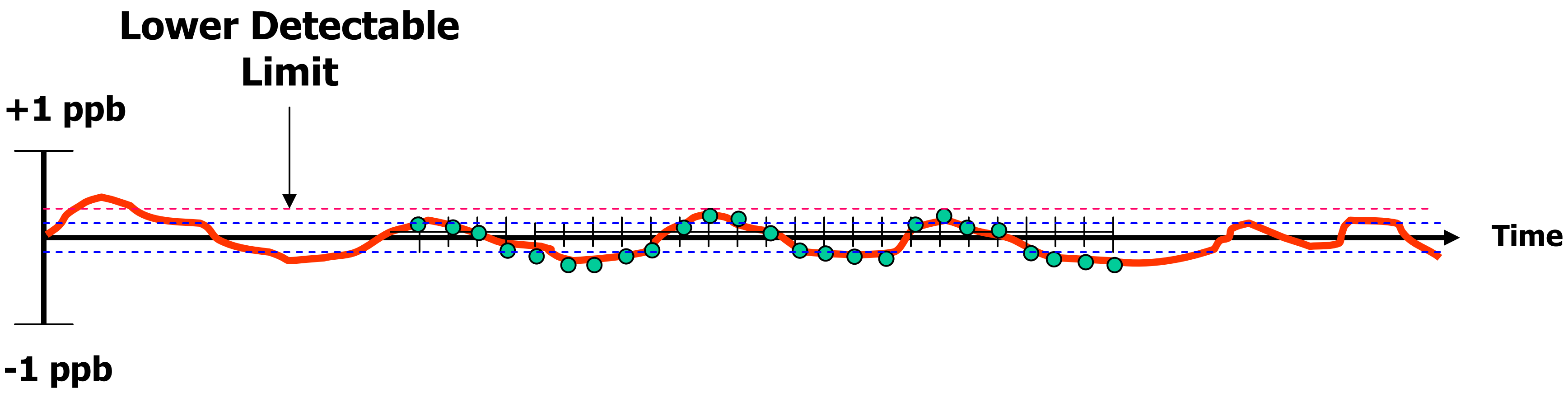
Using the 25 discrete samples, we calculate the *standard deviation* (σ) using the above formula, where C_k is the kth discrete sample concentration, and "a" is the average of all samples.

Zero Noise



The standard deviation is some concentration, expressed in the analyzer's concentration units (ppb, ppm, etc.). This is considered to be the noise.

Lower Detectable Limit



Lower Detectable Limit **(also called *LDL, Detection Limit*, or *Sensitivity*) is defined as twice the noise. This gives a Signal-to-Noise Ratio of 2:1 at the LDL.**

Quality Assurance

E) Performance checks (TAD)

1) Method Detection Level (MDL)

*i) "…the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero…." ******

ii) generally > LDL (as-installed operating perform.).

iii) after site installation & yearly (pending evaluation of historical performance).

iv) MDL = (Avg StDev 7 replicate analyses [near expected MDL]) x Student t-test value for # of test measurements).

Quality Assurance

E) Performance checks (TAD)

1) Method Detection Level (MDL)
   - v) To calculate;
     - a) use a concentration of 2.5 to 5 times the instrument signal/noise ratio* (1-5 times expected MDL**),
     - b) run zero gas through analyzer,
     - c) dilute gas to estimated concentration level and collect readings for 20-25 1-min. observations,
     - d) repeat 7 times over the course of 5 -14 days,
     - e) average the concentrations for the 7 days.

Quality Assurance

E) Performance checks (TAD)

1) Method Detection Level (MDL)

v) To calculate;

f) Use:

$$MDL = t_{.01,(n-1)} \cdot s$$

where $t_{.01,(n-1)}$ represents the 99th quantile of a Student's t distribution with (n-1) degrees of freedom and n represents the number of replicate measurements and *s* is the standard deviation.

Quality Assurance

E) Performance checks (TAD)

- 2) Level 1 Z/S checks
    - *i) need dedicated on-site calibrator (high quality MFC’s and cal gases needed but non-NIST ok).*
    - *ii) daily Z then 70-90% FS*.*
    - *iii) z-drift LTE 0.5% FS*.*
    - *iii) span drift LTE 15% (control charts very helpful).*
    - *iv) if response GT 15%*
        - *a) check z/s with QA calibrator.*
        - *b) if still GT 15% do MPC & recertify on-site calib.*
        - *c) if response ok, check/recertify on-site calib.*

Quality Assurance

E) Performance checks (TAD)

3) bi-weekly precision checks
   - *i) same calibrator as Level 1 Z/S checks.*
   - *ii) z-check not included.*
   - *iii) challenge concentration = ~10% FS*.*
   - *iv) precision results calculated quarterly.*
   - *v) no limits on precision results (Level 1 checks used to keep precision within bounds).*

4) NOy converter efficiency check (initially, MPC's).

Quality Assurance

F) Multi-point Calibrations

1) frequency

   i) initially, after repairs or interruption of > few days or if Level 1 span check is $\geq$ 15% (TAD minimum: CO/NOy=quarterly, SO_2=6 mos.).

2) number/value of cal points

   i) zero plus three upscale concentrations.

   ii) first CO MPC (in lab) might use 4th (3-8% FS) pt.

Quality Assurance

F) Multi-point Calibrations

3) configuration

i) normal sampling path

ii) NOy will be problematic (tower up/down, very long lines, opaque lines, other???).

Quality Assurance

G) Documentation

1) NIST certificates
   - *i) all gases and flow standard(s).*
   - *ii) multiple stds. needed to keep in-house current (6 month, or longer, delay in recertification).*

2) laboratory
   - *i) certifications (transfer NIST authority).*
   - *ii) notes (documents issues and clarifications).*

3) field notes (ID’s problems/solutions).

4) does your paper trail support testimony in court?

5) records retention rules dictate how long to keep docs.

This completes the QA section.

Questions or comments?

Data Review

A) EPA criteria

1) Precision

i) calculated quarterly & submitted to EPA.

ii) TAD equations are correct but text is not clear.

iii) "95% probability" limits are old terminology prior to CV usage.

iv) precision goal perhaps better stated:

> *"The goal is to have upper 90% "confidence limit" for the CV be LT 15% as calculated per Equation 2, p. 8. Sect. 2 et seq…"* *****

v) a better source is "qaissues.ppt" by Mike Papp.

Data Review

A) EPA criteria

1) Precision

vi) where Eq. 1; $d_i = \frac{Y_i - X}{X} \cdot 100$

Yi = reported concentration

X = target concentration and

Eq. 2;

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^{n} d_i^2 - \left(\sum_{i=1}^{n} d_i \right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{X^2_{0.1,n-1}}}$$

where $\chi^2_{0.10,(n-1)}$ is the 10th percentile of Chi-squared distribution.

Data Review

A) EPA criteria

1) Precision example:

Number	***Input (ppb)***	***Response (ppb)***	***d_i [(Res-In)/In]***	***d_i^2***
1	**10.0**	**9.9**	**-1.0%**	**0.01%**
2	**10.0**	**10.8**	**8.0%**	**0.64%**
3	**10.0**	**11.4**	**14.0%**	**1.96%**
4	**9.8**	**10**	**2.0%**	**0.04%**
5	**9.8**	**9.9**	**1.0%**	**0.01%**
6	**9.8**	**10.5**	**7.1%**	**0.51%**
n=6				
sum d_i^2 =				**3.17%**
(sum d_i)^2 =			**9.7%**	

$$CV = \sqrt{(6(3.17) - (9.7))/(6)(5)} \ \mathbf{x} \ \sqrt{5/9.236} = 4.1\%$$

4.1% represents a 90$^{\%}$ upper confidence level on the CV estimate.

Data Review

A) EPA criteria

2) Bias (similar to TAD precision discussion)

i) calculated quarterly & submitted to EPA.

ii) TAD equations are correct but text is not clear.

iii) "95% probability" limits are old terminology prior to CV usage.

iv) bias goal perhaps better stated:

"The goal is to have upper 95% "confidence limit" for the absolute average bias that is 15% or less." Equation 2, p. 8. Sect. 2 et seq…"*

v) better source is "qaissues.ppt" by Mike Papp

Data Review

A) EPA criteria

2) Bias (similar to TAD precision discussion)

vi) calculation of the "sign" (+ or -) of the bias is also better addressed in Mike Papp's presentation.

(involves similarity, or not, of signs in 25th and 75th percentiles).

Bias calculations are somewhat more involved than those for precision – see "*Guideline on the Meaning and the Use of Precision Data Required by 40 CFR Part 58 Appendix A*"

(http://www.epa.gov/ttn/amtic/files/ambient/monitorstrat/precursor/P+B%20Guidance3_14_07.pdf)

Data Review

A) EPA criteria

3) Representativeness
   - *i) subject to monitoring goals.*
   - *ii) insured via site selection and QA activities.*

4) Completeness
   - i) same as NAMS, (75%).
   - ii) track on on-going basis (alert EPA if failing).

5) Comparability
   - *i) sought within and across networks.*
   - *ii) insured via TAD equipment specs & procedures.*

Data Review

A) EPA criteria

6) Method Detection Level

i) crucial meta-data for trace level work.

ii) target MDL for CO = 80 ppb, (5 min. avg.).

iii) target MDL for SO_2 = 0.30 ppb, (5 min. avg.).

iv) target MDL for NOy = 0.20 ppb, (5 min. avg.).

Data Review

A) EPA criteria

7) Lower Detectable Limit (LDL)

i) vendor supplied.

ii) typically lower than MDL.

iii) target for CO = 40 ppb (5 min. avg.).

iv) target for SO_2 *= 0.20 ppb (5 min. avg.).*

v) target for NOy = 0.10 ppb (5 min. avg.).

(LDL = 2 X Zero noise & ZN = StDev of 25 one minute zero values)

Data Review

A) EPA criteria

8) Linear range (TAD)

i) CO = 0.040 ppm to 5 ppm.

ii) SO_2 = 0.20 ppb to 100 ppb.

iii) NOy = 0.10 ppb to 200 ppb.

iv) if higher range needed set monitor to auto-range on multiple logger channels (but you must calibrate each channel).

Data Review

A) EPA criteria

9) Zero/span drift (TAD)

- *i) unadjusted response to z/s gas over 24 hours.*
- *ii) CO = Z < 100 ppb, S < 1% FS (12 & 24 hrs).*
- *iii)* SO_2 *= Z < 0.20 ppb, S < 1% FS (12 & 24 hrs).*
- *iv) NOy = Z < 0.10 ppb, S < 1% FS (12 & 24 hrs).*
- *v) check during acceptance testing and as part of trouble shooting routine.*

Data Review

B) Time series graphs

1) Ambient concentrations

i) is trace too noisy?

ii) is trace too “quiet”?

iii) is zero “live”?

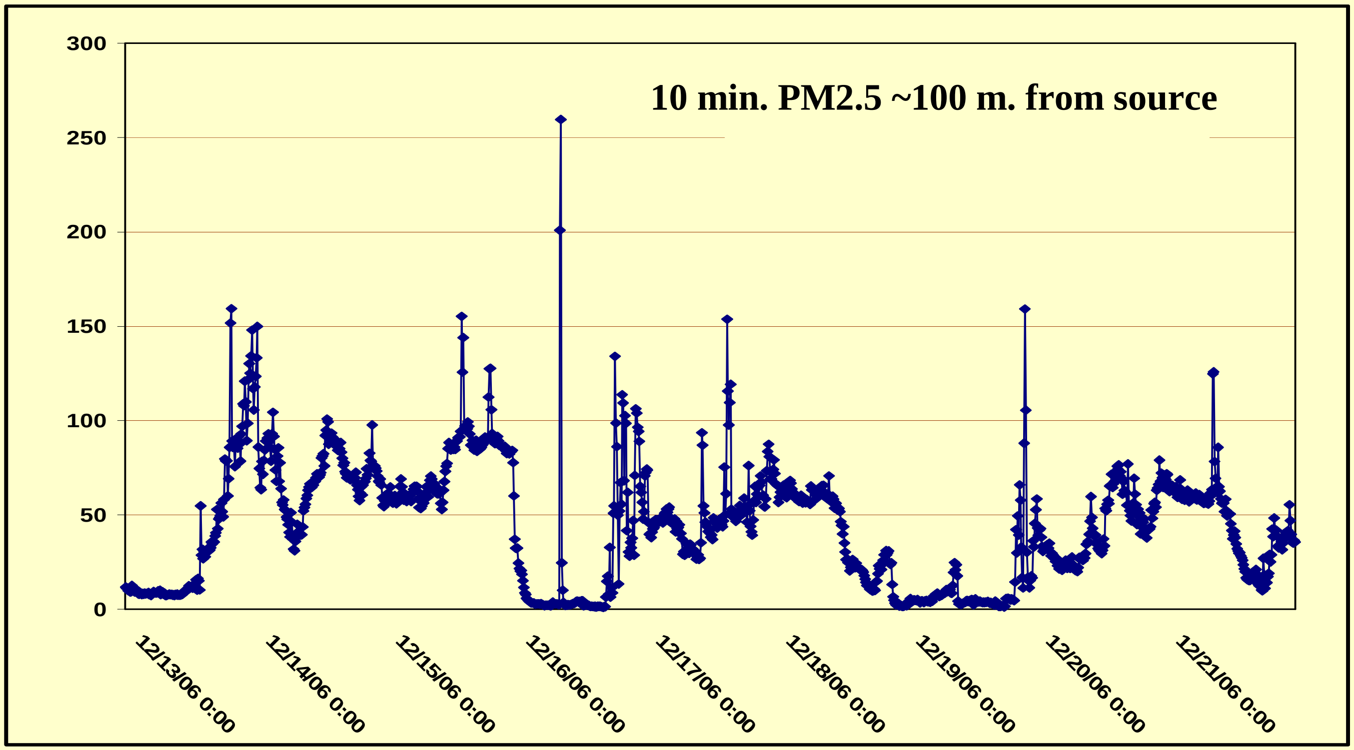
iv) is baseline drift evident?

Data Review

B) Time series graphs

i) is this trace too noisy?

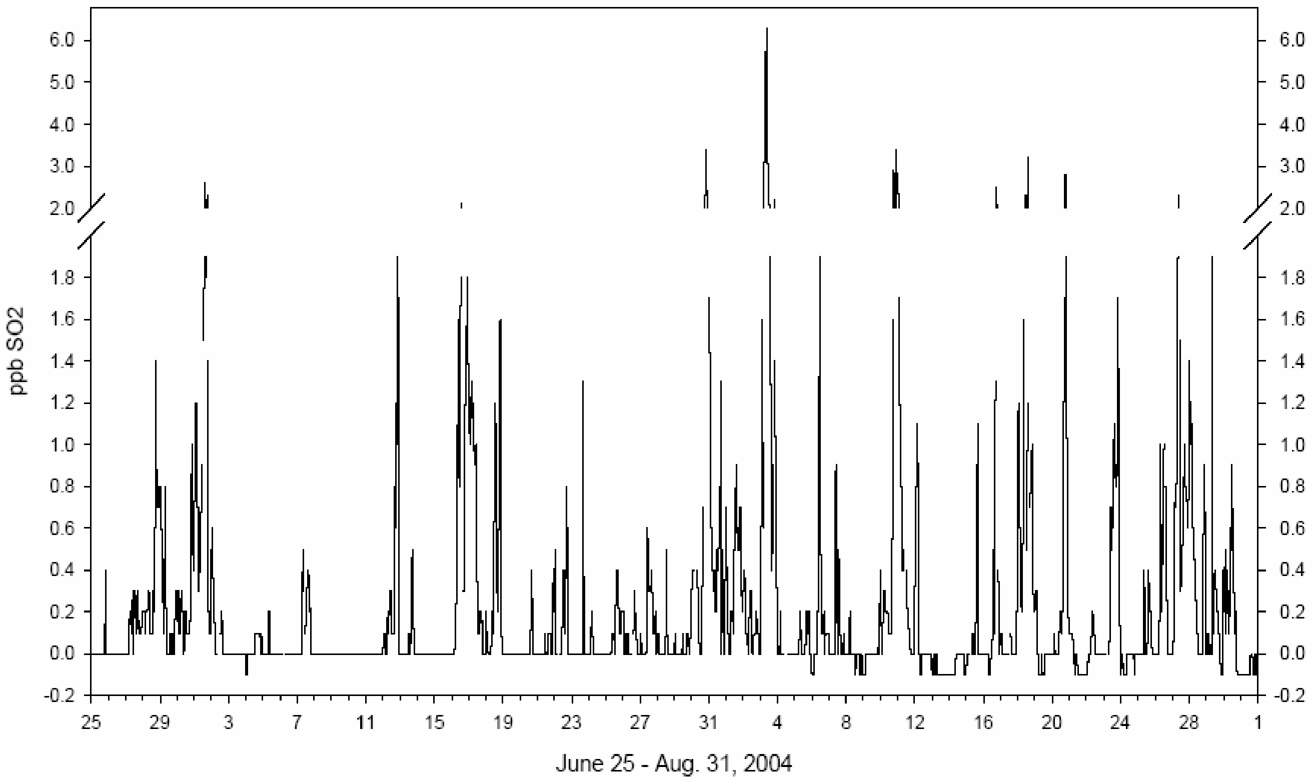
Depends on what is measured & where.



Data Review

B) Time series graphs   iii) is zero “live”?

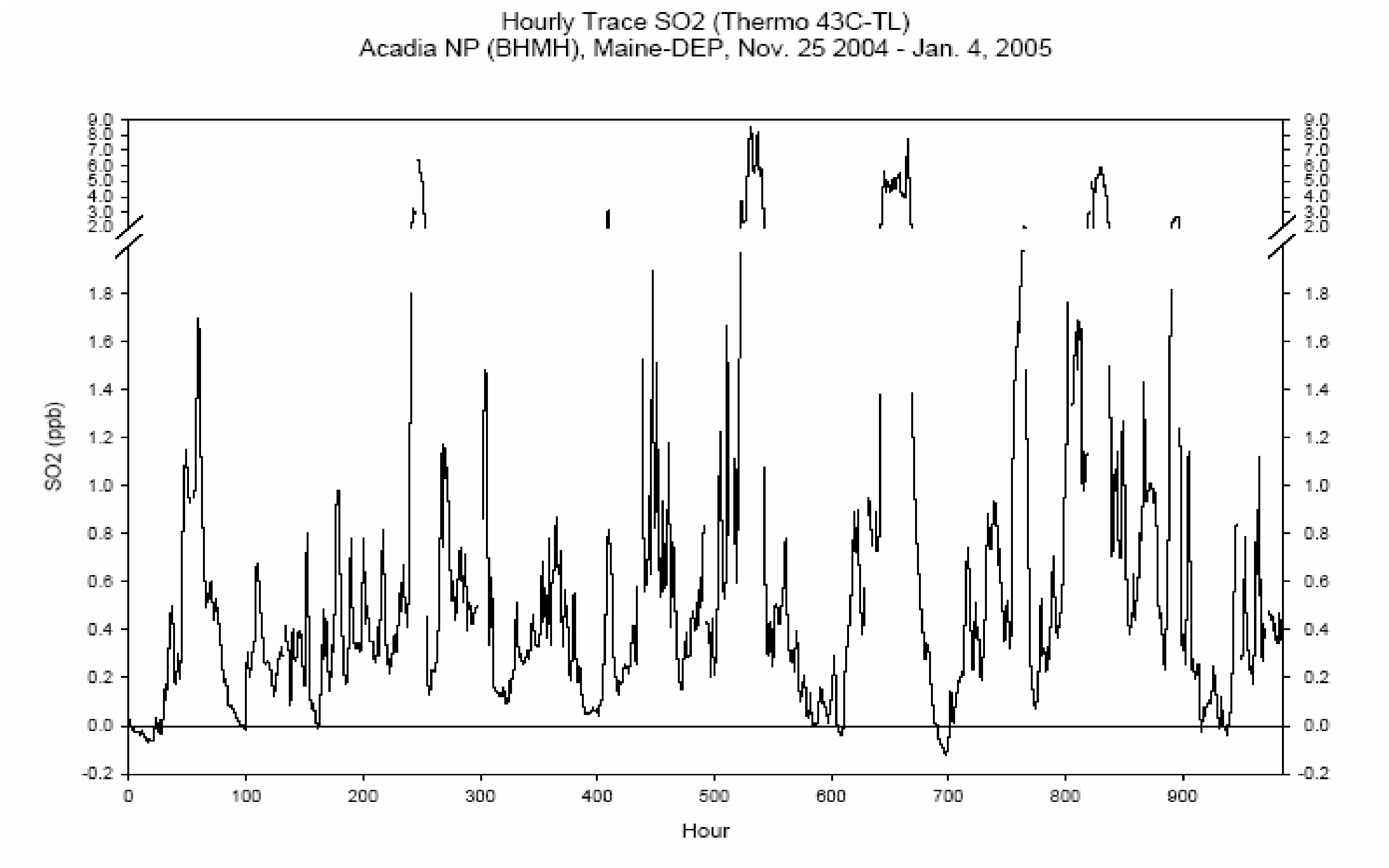
Hourly Trace SO2 (Thermo 43C-TL)
Acadia NP (BHMH), Maine-DEP June-August, 2004



Slide courtesy of George Allen, NESCAUM.

Data Review

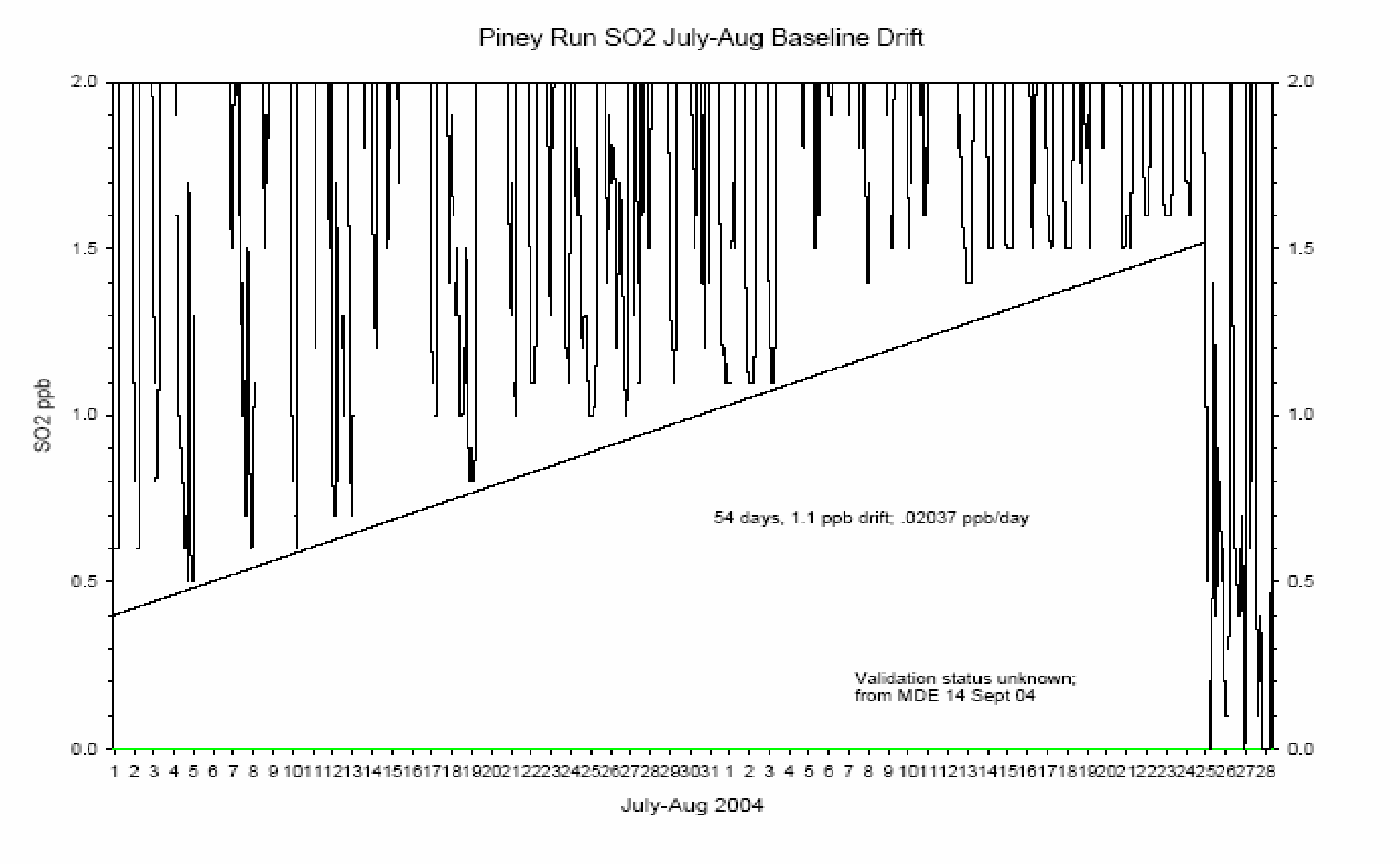
B) Time series graphs iii) is zero "live"?



Slide courtesy of George Allen, NESCAUM.

Data Review

B) Time series graphs iv) is baseline drift evident?


Piney Run SO2 July-Aug Baseline Drift

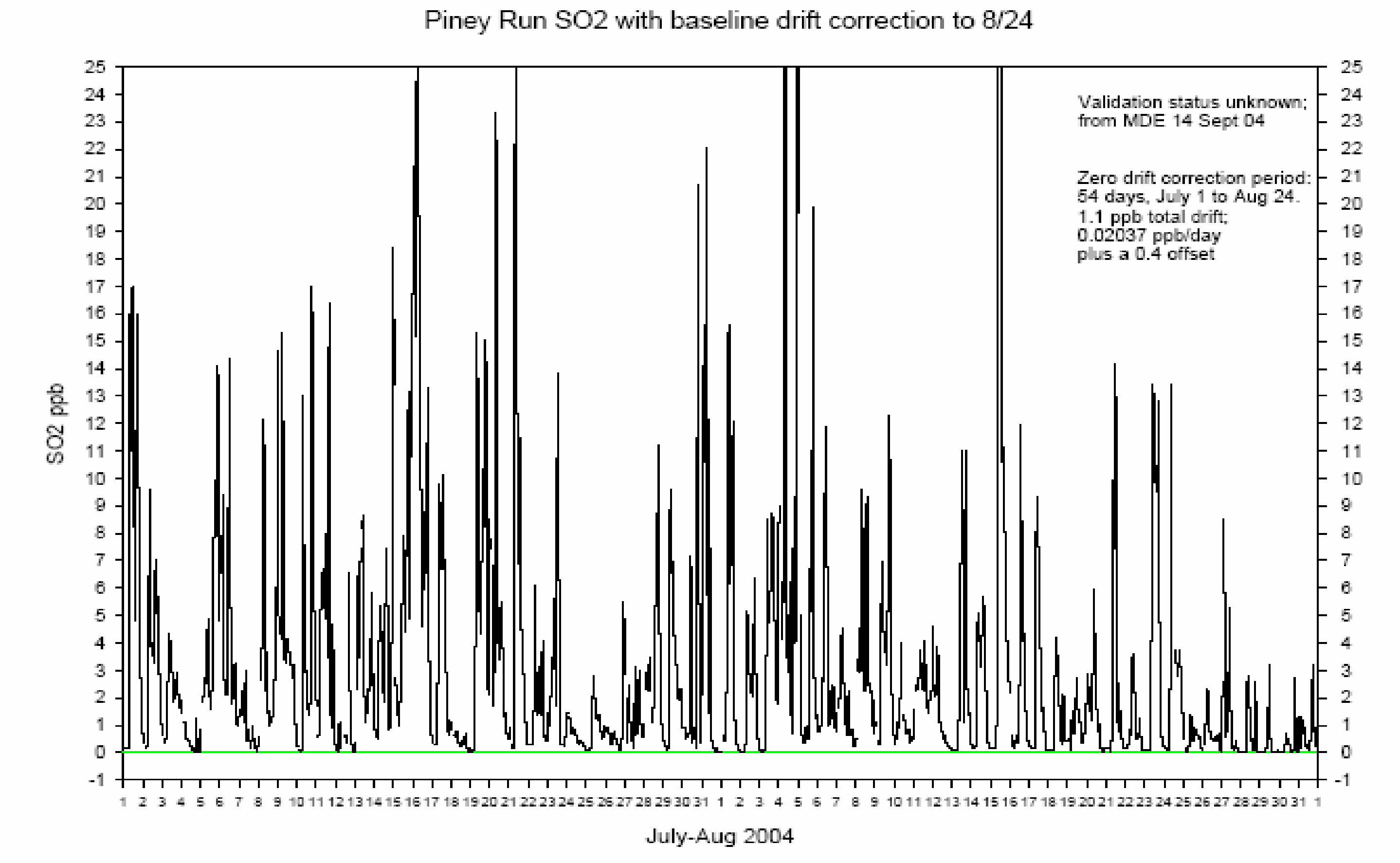
54 days, 1.1 ppb drift; .02037 ppb/day

Validation status unknown;
from MDE 14 Sept 04

Slide courtesy of George Allen, NESCAUM.

Data Review

- **B) Time series graphs** iv) is baseline drift evident?



Piney Run SO2 with baseline drift correction to 8/24

Validation status unknown;
from MDE 14 Sept 04

Zero drift correction period:
54 days, July 1 to Aug 24.
1.1 ppb total drift;
0.02037 ppb/day
plus a 0.4 offset

Slide courtesy of George Allen, NESCAUM.

Data Review

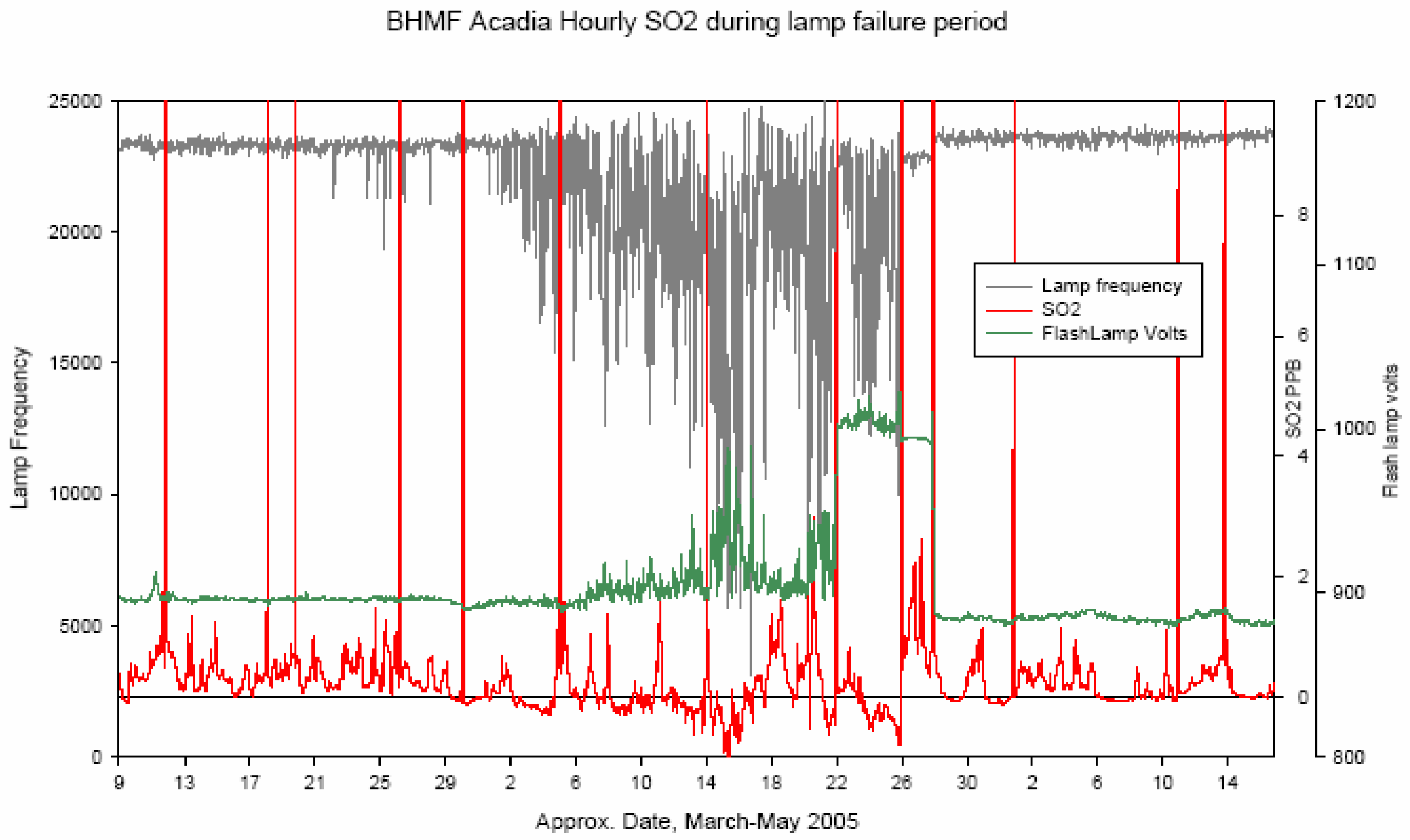
B) Time series graphs

2) Operating parameters (that are not checked daily)

- i) DC power supply voltage (all monitors).
- ii) “stability” during z/s (all monitors).
- iii) CO hourly z-response.
- iv) CO “wheel” values (N_2 & CO).
- v) CO cell pressure (upset may cause non-linearity).
- vi) CO slope and offset values.
- vii) SO_2 all lamp parameters.
- viii) SO_2 stray light.
- ix) NOy pre-reactor zero (high if H_20 in PMT housing).
- x) NOy cell pressure (hold to $\pm$ 0.3 in Hg).

Data Review

- **B) Time series graphs** 2) Operating parameters – Example



Slide courtesy of George Allen, NESCAUM.

Data Review

•C) Data auditing

- 1) Tracing a few data pts from “cradle to grave” can
- uncover hidden problems.
- *i) done routinely for “exceedance” values but should*
- *include low concentrations (e.g., precision pts).*
- *ii) do quarterly before EPA data submittal.*
- *iii) especially important for analog data acquisition !*

In Summary:

- Avoid site-related interferences.
- Switch to digital data acquisition asap.
- Use easy-to-clean manifolds.
- Carefully select Z-air supplies/calibrators.
- Find/develop training material for new folks.
- Capture critical operating data “on the fly”.
- Give early data extra scrutiny.
- Start/maintain a dialog with other monitoring groups on issues and answers.

This completes the Data Review Section.

Questions or comments?

The Six Phases of a Project

1. **Enthusiasm**
2. **Disillusionment**
3. **Panic**
4. **Search for the guilty**
5. **Punishment of the innocent**
6. **Praise and honor for the non-participants**

Jargon

HONO = nitrous acid

HNO_2 = nitric acid

HNO_4 = peroxynitric acid

NO_3 = nitrate

N_2O = nitrous oxide

PAN = peroxyactylnitrate

PNA = poly-nuclear aromatic