Precision and Bias of Precursor Gas Instruments Using Proposed vs. Current CFR Precision and Bias Estimators

Louise H. Camalier
USEPA, Office of Air Quality Planning and Standards

24th Annual National QA Conference
San Diego, CA
April 13, 2005

Precursor Gas Monitoring

Development of the NCore network :

Higher sensitivity in instruments is needed to monitor precursor gases that lead to particle and ozone formation

Precursor gases tested:

Carbon Monoxide (CO)

Sulfur Dioxide (SO_2)

Reactive oxides of nitrogen (NO_y)

Precursor Gas Instrumentation

OAQPS' testing facility
(RTP, NC)

CO and SO_2:

- 2 samplers
  API and Thermo

NO_y:

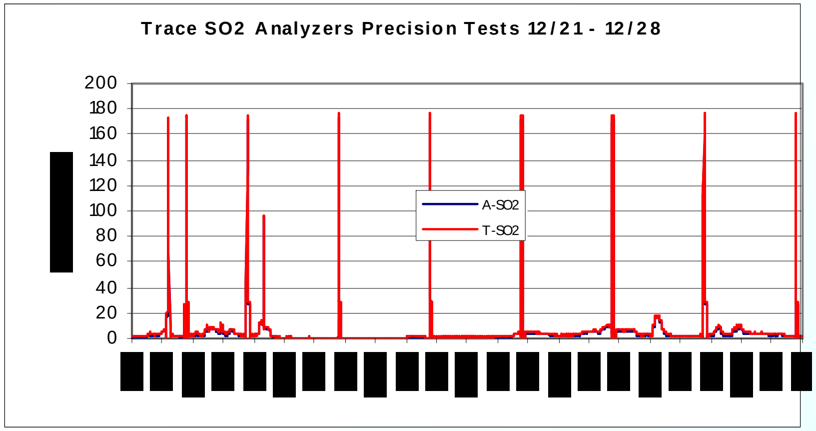
- 1 sampler, 2 channels
  Thermo

Testing Procedures

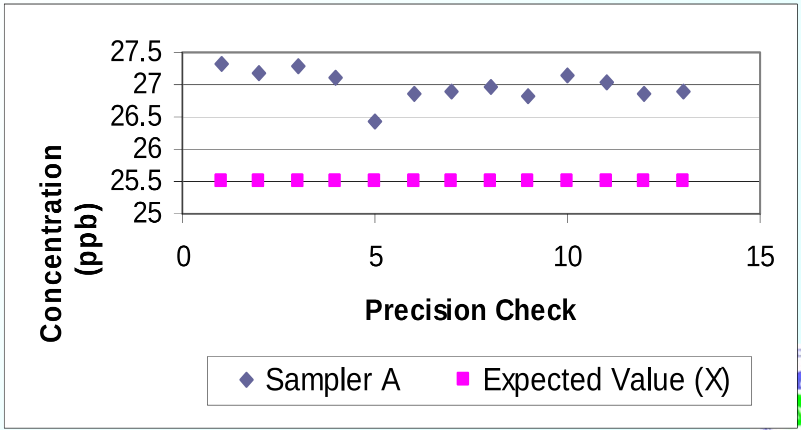
Precision check:

- Run zero air (pre-zero)
- Collect readings using a target concentration
- Average concentration from collected readings
- Run zero air (post-zero)

Precision Check for SO_2



Precision Response for SO_2



After Data Collection

Y_i: Sampler

X : Target concentration

d_i : Relative Percent Difference (individual bias)

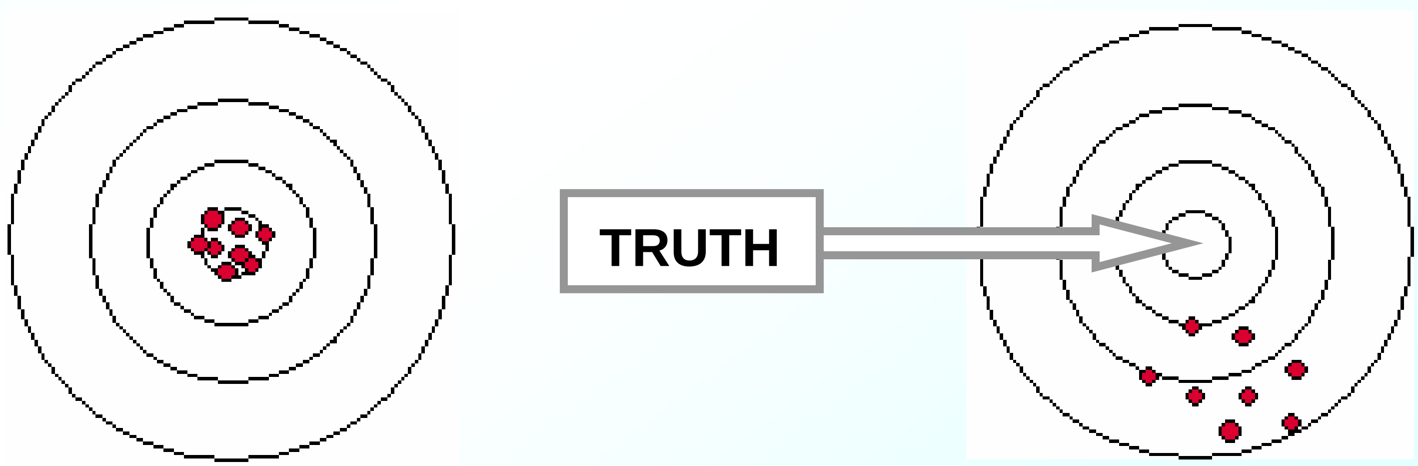
$$d_i = \frac{Y_i - X}{X} \cdot 100$$

Dealing with “Real-World” Data

Target and ambient concentrations serve as…

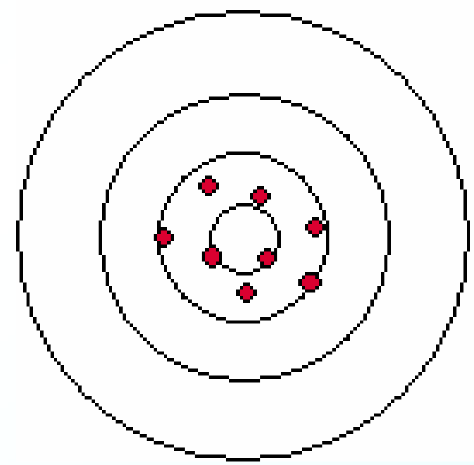
Combinations of bias and precision within measurements result in…

TRUE VALUES **OUR DATA**



Precision

"A measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions"



$$precision\_est = s_{d_i} = \sqrt{\frac{1}{n-1}\left[\sum_{i=1}^{n} d_i^2 - \frac{1}{n}\left(\sum_{i=1}^{n} d_i\right)^2\right]}$$

**** Equation 3 in CFR, precision equation is at the site level***

New Precision

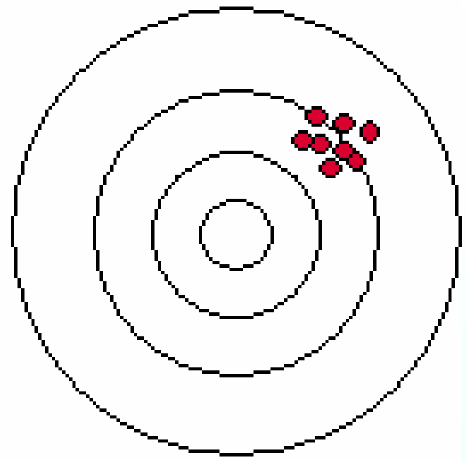
Precision is more conservative when evaluated at the 90% one-sided upper confidence level

$$new\_precision\_est = precision\_est \cdot \sqrt{\frac{n-1}{\chi^2{}_{0.1,(n-1)}}}$$

** Where $\chi^2_{0.10,(n-1)}$ is the 10th percentile of a Chi-Squared Distribution*

Bias

"A systematic or persistent distortion of a measurement process which causes errors in one direction"



$$bias^{*} = \frac{1}{n} \cdot \sum_{i=1}^{n} d_i$$

** Bias estimator is not established in current CFR*

New Bias

Absolute Bias Point Estimate:

$$m_{abs} = \frac{1}{n} \cdot \sum_{i=1}^{n} \left| d_i \right|$$

Absolute Bias Upper Bound (NEW BIAS):

$$new\_bias = m_{abs} + t_{0.95,(n-1)} \cdot \frac{s_{d\_abs}}{\sqrt{n}}$$

Where $t_{0.95,(n-1)}$ is the 95th quantile of a Student's t distribution with n-1 df and s_{d_abs} is the standard deviation of the absolute value of the relative percent differences

Associating a Sign to the Absolute Bias

A sign (+/-) is associated with the absolute bias only if the 25th and 75th percentiles of the relative differences have the ***same sign***

Sampler A | **Sampler B**

P75 = +8.1

Zero

P25 = -12.9

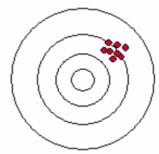
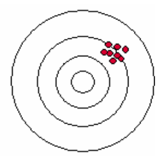
P75 = -13.9

P25 = -28.1

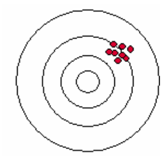
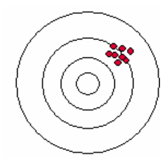
BIAS (%)

CO (Sampler A):	
OLD BIAS	**NEW BIAS**
-0.7	**14.6**
CO (Sampler B):	
OLD BIAS	**NEW BIAS**
-22.9	**-27.7**

Preliminary Results for SO_2

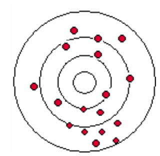
Sampler A			
Prec. (%)		**Bias (%)**	
OLD	**NEW**	**OLD**	**NEW**
0.9	**1.3**	**5.8**	**+6.3**
Sampler B			
Prec. (%)		**Bias (%)**	
OLD	**NEW**	**OLD**	**NEW**
1.0	**1.4**	**10.8**	**+11.3**

Preliminary Results for NO_y

Channel A 			
Prec. (%)		**Bias (%)**	
OLD	**NEW**	**OLD**	**NEW**
1.5	**2.2**	**9.5**	**+10.3**
Channel B 			
Prec. (%)		**Bias (%)**	
OLD	**NEW**	**OLD**	**NEW**
1.6	**2.3**	**10.3**	**+11.1**

Preliminary Results for CO

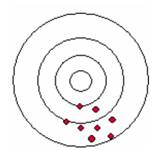
Sampler A



Prec. (%)		Bias (%)	
OLD	NEW	OLD	NEW
15.2	18.1	-0.7	14.6

NO SIGN

Sampler B



Prec. (%)		Bias (%)	
OLD	NEW	OLD	NEW
16.5	20.1	22.9	-27.7

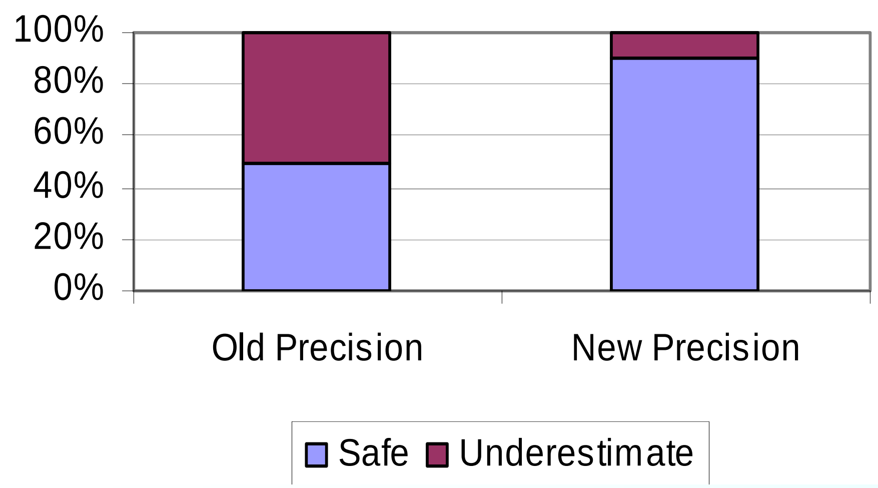
Advantages of Conservative Methods

Provides a more stringent goal that can lead to improved data quality:

- Minimizes probability of making harmful decisions due to unknown risk
- Early detection of calibration problems
- Performance-based system allows state/locals flexibility in QC check frequency

Behind the Theory (A Simple Simulation)

Current CFR technique *risks underestimating measurement uncertainty* ***50% of the time***



New, conservative estimators reduce risk of *underestimating to* ***5-10% of the time***