Accuracy and Calibration

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What is the Point of Measurement?

- **A result should equal actual exposure or concentration of the contaminant at the time the sample was taken or the measurement made.**
- **Must correspond to the contaminant of interest -- even if others are present**
- **Must be accurate**

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Selectivity

- **Perkins: The ability of a monitoring method or direct-reading instrument to distinguish among a mixture of contaminants and give a result which reflects the concentration of the particular species of interest (pp 590-591).**

Method/Instrument	Selectivity
gravimetry	
chemical indicator tubes	
gas chromatography	
GC + mass spectrometry	
photoionization detector	
non-dispersive infrared inst.	
x-ray fluorescence spectrometer	

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Accuracy Vs precision

- Common language “accurate”= precise and accurate
- Alternate definition: Accurate if average of many readings close to the true average value
- Precision is the variability of measurements made on an identical sample. Precise if highly repeatable (i.e., consistent)
- Device can be accurate without being precise and vice-versa
- BIAS: The extent to which a method/instrument yields results that are, on the average, generally in one direction from the true value.
- To calibrate, must compare to known levels
  - Primary standard: directly traceable to NIST standard device
  - Secondary standard: calibrated using primary standard

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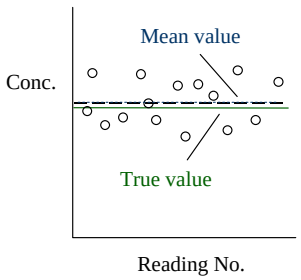
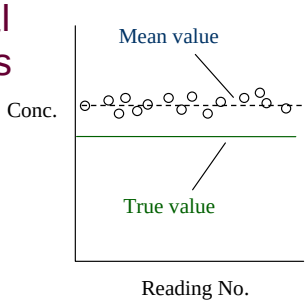
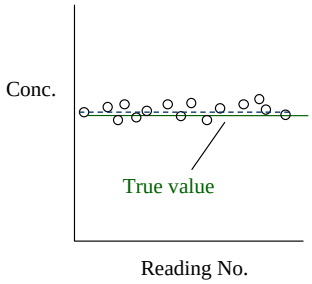
Graphical examples



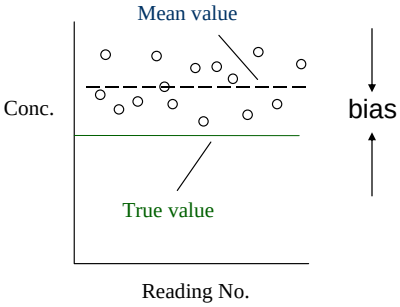
Not precise but accurate



Precise, not accurate



Precise and accurate



Neither precise nor accurate

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Accuracy, Precision & Calibrations

- Accurate, but imprecise devices:
  - Improve precision by averaging many readings
  - Error: $\frac{Error}{True\ Mean} \propto \frac{1}{\sqrt{n}}$
- Precision is more desirable than accuracy — if the inaccuracy is known.
- *Calibrating*: finding the relationship between the true value and the measured value
- Usually used to mean *verification* of calibration

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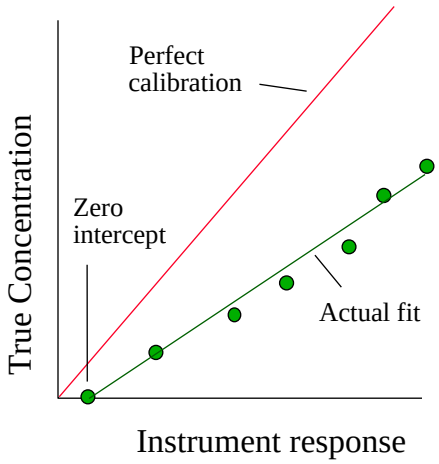
Math of Calibration

- If linear, find slope and intercept
- "Zeroing" sets intercept to zero
- Slope = "gain"
- Perfectly calibrated
  - intercept = 0
  - gain = 1



True= ZeroValue + Gain x InstrumentReading

$C = R_o + m R$

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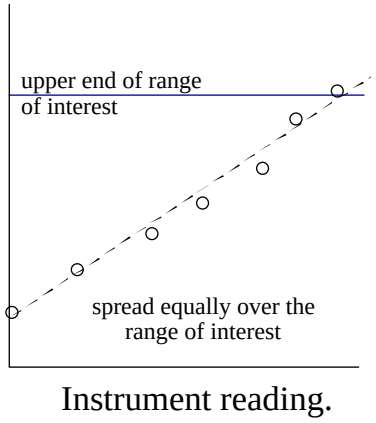
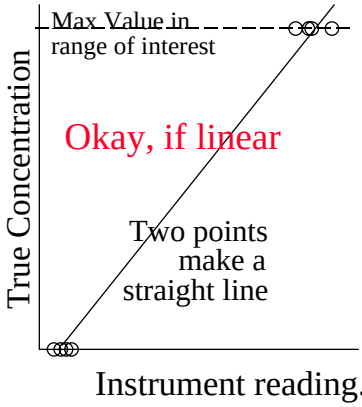
Calibration range

- Be sure to calibrate over range of use
- If not certain of linearity, must be careful in fitting calibration curve that points spread out equally the range of use.





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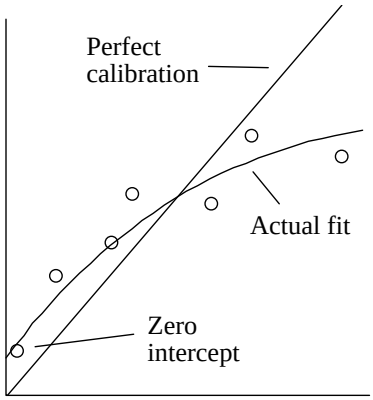
What if non-linear?

- Two point calibration not okay, if non-linear
- Need equal spacing
- Need non-linear curve
  - Exponential
    $y = b\, e^{c\,R}$
  - Polynomial, e.g.
    $y = R_o + c_1 R + c_2 R^2$



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Sensitivity

- **The ability of a method or instrument to give results for contaminant levels which are in the range of interest (pp 587-589).**
- ***EXAMPLES:*** **Does my method have the sensitivity in order to determine the...**
  - **fraction of red marbles in a bag of 100 colored marbles?**
  - **percent of sand in a sugar bowl with approximately a teaspoon of sand?**
  - **parts per million of acetone in the air I breath?**
  - **parts per quadrillion of 2,3,7,8-TCDD in water going into a river?**

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Other Issues

- Stability of instruments
  - instrument drift
  - long-term stability, e.g. internal "calibration"
- Response time
- Difficulty of calibration

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Beware the Black Box Syndrome

- Understand the limitations of your instrument
- Understand the nature of the environment you are monitoring

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In Lab Exercises

- Calibration of volumetric flow devices
  - Secondary standards (e.g., rotatameters)
  - Air sampling pumps
- Calibration of laboratory instruments
- Calibration of field instruments

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Preparation for Calibration Lab

- Set up pump calibration program on your new job
- Should include:
  - Write up of standard method: purpose, apparatus, methods (including how frequently and when should be calibrated), acceptable level of errors, actions to take if unacceptable results (e.g., order new battery if it fails, send back to mfg for repairs if can't produce airflow, etc.)
  - Cumulative log for calibration
    - Date of calibration, Model and serial number of Instrument calibrated, method of calibration, name of person doing calibration, signed initials
  - Record of individual calibrations
    - All of above, plus ….
    - Table of observed values for calibration device and for devices being calibrated

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Questions?

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