What Pollutants can be measured and what cannot

If you can’t calibrate for it can you really measure it?

Bob Davis – Airgas Inc.
How do you measure something?

Length = Use a Yard stick
Weight = Use a Scale

Are you certain of the Weight, and Length?

Yes if you can prove the tool you are using for measurement is accurate.
Accurate measurement

• Either you can measure it directly from the very certain tool for measurement (like a yardstick)

• Or you use a scale as a tool that has been calibrated with weights of a known value
Gases are a lot like weight measurement!

- You need a tool to analyze (monitor or analyzer).
- You have to calibrate them with a known gas concentration.
- The outcome will always have some level of uncertainty.
The gas equivalent of a one pound calibration weight

• The NIST organization
  (National Institute of Standards and Testing)

- Verifies gases to be traceable

Standard Reference Materials

OR

NIST Traceable Reference Materials
So, why Are Calibration Gases Important?

• It is the only way to verify accurate readings due to drift for CEMS and other gas analyzers. It is required in the federal register CFR 40 part 60, 63, and 75.

• Without regular calibration the monitors may be reporting incorrectly which could be costly!
Calibration Gas uses

• Measuring for “new” pollutants in ambient tests (method 18 or 25a).
• This could be required in the new method V.
• Not just to protect the people of the community, but the facility itself!
How monitoring a “new” pollutant protect an emitter?

- Some pollutants can interfere with others.
- If my production process is producing “styrene” (Boat Manufacturing), but another plant is producing a pesticide and both do a method 25a or method 18?
How monitoring a “new” pollutant protect an emitter? (cont.)

• If both companies are only required to do a method 25a gaseous organic concentration, or method 18 VOC – GC.

• Unless specified to calibrate and measure for the specific pollutant they would look alike!
So why use a surrogate for the pollutant you are monitoring?

- Some regulations allow it
- Method 25a allows the use of propane to measure for VOCs.
- Method 18 uses Propane

Does it make sense to use surrogates?
Why is the calibration so important?

If you use a surrogate, you could get interference. Or there could be financial issues in some testing (Emissions Credits, State Title V emission fees per ton for VOCs).

Surrogates are NOT allowed where the money is involved for credit trading:

- Some Methods and testing, you have to use EPA protocol gases (Part 75 / Part 60)
- Some Methods you have to use certified Zero Gases (CFR 40 72.2)*
- * (A gas is not a zero gas unless it meets the definition)
What is an EPA Protocol Gas?

You have to use calibration gases that are defined specifically for use in various tests.

These Gases have very specific requirements:
- NIST traceable
- No more than ±2% from tag value
- Pressure requirements of 150psig
Also measuring zero is important.

- Zero gas does not mean zero impurities by definition. Very low level NOx may be off if there is even a tenths of a ppm in the zero.
So there are clear definitions of what a zero is

- The definition is under CFR40 72.2:

- A calibration gas **certified by the vendor** not to contain concentrations of S02, N0x, or total hydrocarbons above 0.1 parts per million (ppm), a concentration of C0 above 1ppm, or a concentration of C02 above 400ppm.

**The auditors are required to check the zeros**

- This has to be on the certification sheet EPA inspectors on site will check (section 5 of the EPA Acid Rain Program CEMS Field Audit Manual).
Why are the calibration gases so important to the regulations?

- Overstating Emissions
- Fines from Understating Emissions
- Paying too much for State Emissions fees
Remember the CEMs are just Billing Meters
Small differences in accuracy cost!

• As prices for allowances climb and new trading programs are added, even relatively small reductions in CEMS over-reporting can net significant savings.
What if you overstate your pollutants to the state?

**Title V or State Fees**

Typically the state will charge a tax per ton for S02 / N0x / VOC’s (each) up to 4000 tons.

**State fees range from $5 ton MS to $81 ton NJ**

*Importance of Accurate measurement*
So what calibration gases are available?

- What are you trying to comply with?
- Part 75 requirements (S02, N0(for N0x))
- Part 60 gets more requirements
Some test methods are very straight forward

- CFR40 part 60 test methods updated 2007:
  - 3A (O2/C02)
  - 6C (S02)
  - 7e (N0x)
  - 10 (C0)
  - 20 (N0x)

- Some methods stayed the same (25,18,etc.)
### Current Gases / Protocol Gases Available / What if one is not available?

<table>
<thead>
<tr>
<th>Component</th>
<th>Can it be a Protocol?</th>
<th>Total Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>Yes</td>
<td>25 ppm - 5000 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>Yes</td>
<td>.5 ppm - 2800 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>Yes</td>
<td>25 ppm - 1000 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>Yes</td>
<td>5 ppm - 8%</td>
</tr>
<tr>
<td>CO₂</td>
<td>Yes</td>
<td>25% - 5000 ppm</td>
</tr>
<tr>
<td>O₂</td>
<td>Yes</td>
<td>.5% - 20%</td>
</tr>
<tr>
<td>Methane</td>
<td>Yes</td>
<td>10 ppm - 1000 ppm</td>
</tr>
<tr>
<td>Propane in Nitrogen</td>
<td>Yes</td>
<td>2% - 5%</td>
</tr>
<tr>
<td>Propane in Air</td>
<td>Yes</td>
<td>3 ppm - 1.1%</td>
</tr>
<tr>
<td>H₂S in Air</td>
<td>Yes</td>
<td>5 ppm – 180 ppm</td>
</tr>
<tr>
<td>HCL*</td>
<td>No (PADER*)</td>
<td>45 ppm - 2800 ppm</td>
</tr>
<tr>
<td>Ammonia</td>
<td>No</td>
<td>2 ppm - 10%</td>
</tr>
<tr>
<td>Mercury</td>
<td>Yes</td>
<td>Elemental only!</td>
</tr>
</tbody>
</table>
Then there is the grey area!

- States will require more monitoring of specific pollutants:
  - HCL
  - Ammonia
  - H2S
With new regulations will come new measurement requirements

- Lead
- S03
- Multi metals
  - Sulfuryl fluoride
  - Lower N0, NH3 ppb levels
  - Mercury Chloride

- They are hard but not impossible
We need to calibrate for the pollutant we are measuring for. This is possible, but there may be some limitations.
If it is determined a pollutant needs to be monitored which ones?

- Typically it goes to:
  - MACT
  - Air Toxics
  - HAPs 188

- Which ones *can* you make a calibration gas for and which ones *cannot* (and *why*)?
What calibration gas can be made for different HAPs?

• Some are easy:
  Acetaldehyde,
  Acetonitrile, Acroleine
  Acrylonitrile, Allyl chloride,
  Benzene, 1,3,Butadiene,
  Carbon disulfide, Carbon
tetrachloride, Carbonyl
sulfide, chlorine, chloroform,
Cresol,
Dichlorobenzene,
  Dichloropropene,
  Dioxane, Ethyl
   Acrylate, Ethyleneoxide,
  Formaldehyde
  Hexane
What calibration gas can be made for different HAPs? (cont)

More easy ones:

- Naphthalene
- Nitrobenzene
- Phenol
- Phosgene
- Quinone
- Styrene
- Tetrachloroethylene
- Toluene
- Trichlorobenzene
- Vinyl Acetate
- Xylenes
Some HAPs have too low vapor pressure to make the gas mixture

- Acetamine, Acrylamide, Biphenyl, Captan,
- Chlorobenzilate, Diazomethane, Dibenzofurans, Dimethyl phthalate
- Dinitrophenol, Hydroquinone, Methyl Isocyanate, Nitrophenol, Pentachlorophenol
- Toxaphene,
Some HAPs polymerize readily, so a gas mixture cannot be made

- Acrylic Acid,
Some HAPs have a boiling point too high to make a gas mixture

- Aminobiphenyl,
- Benzedrine
- Carbaryl
- DinitroCresol
- Ethlene Thiourea
- Nitrobiphely
- Quinone
- Trichlorophenol
Some HAPS are just too toxic or dangerous to handle

- Aniidine
- Diazomethane
- DibromoChlorpropane
- Diethyl Sulfate
- Hydrazine
- Lindane
- Methyl Isocyanate
- Parathion
- Toxaphene
So if you want a pollutant measured and you are not sure if it can be what do you do?

- Determine what the most toxic pollutant is.

- Call a gas vendor and find out if it is possible. Make sure they tell you why not if they can’t.

- Make sure you know the risks of measurement.
What else is important to calibrate for?

- Interferent Gas Mixtures

- Some gases can register false positive readings with others.

- But there are gases specifically for:
  - CFR 40part60 instrumentation test
  - Vapor Interferents, Second Hand Smoke Interferents, Exhaust interferents, etc.
A Case study

In some states Ethanol Plants are starting. Each one poses different pollutants:

There are many Ethanol Related HAPS such as
- Cookers that have Acetaldehyde, Acroline,
- The Fermentation Process produces Formaldehyde, Carbon Dioxide
- The Boiler produces N0x, S02 etc.
Conclusion

• Permits can monitor unique pollutants as long as there is a way to measure them individually!

• Consult your gas companies before you rule out any unique pollutant.