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Bob Davis – Scott Specialty Gases

The Value of Accurate Calibration In Emissions Trading

The trading of emissions began in the United States for SO2 in an effort to decrease the amount of SO2 in the atmosphere in a fair manner. The fair manner refers to the fact that the coal fired plants need to reduce their emissions of S02 but not to "shut down" facilities which cannot comply. The emphasis was on the economic side of emitting gases. The program was directed at the 110 largest producers of Acid Rain in 1995 to reduce S02 compared to the base line 1980 levels. Here is a rough idea of how it works.

Company A:

Permitted Tons of Emissions (S02) Per year 100 tons
Actual Tons of Emissions Emitted In 1999 90 tons
Difference in tons to be sold to Commodity Broker 10 tons@ $230/ton Total return: $2,300.

Company B:

Permitted Tons of Emissions (S02) Per year 100 ton
Actual Tons of Emissions Emitted in 1999 110 tons
Difference in tons to be purchased from Commodity Broker 10 tons@ $230/ton Total cost: $ 2,300.

- **Dollar value to retool the plant $100,000. (est.)**

This plan has contributed significantly to cleaning the air. In some states the 1990 rain fall pH had a level of 4.4 (roughly the pH of some carbonated beverages). The average pH in 1998 rainfall had a level of 4.2 which is a 50% decrease in acidity on the logarithmic scale. As well there has been an estimated increase in the use of electrical power produced from these plants by 5% in some of the states where acid rain is produced, based on the Kilowatt hours produced from these facilities.

A next Phase is N0x:

Based on plans from many states in the Ozone Transport Region of the Northeast United States there were 450 facilities subject to the new rule. The rule has been held back in some states due to EPA court case which is in appeal. However, some states are moving ahead with these emissions trading to reduce N0x by hundreds of thousands of tons. But in this case the average price per ton is between **$3,000. To $18,000**. This is extremely significant for the purchaser and the seller a lot of money can be made or lost in this new arena of trading N0x emissions.

What are the Certification Requirements and Procedures:

Certification testing requirements are noted in the Code of Federal Regulations part 75. Depending on the requirements of reductions of emissions detailed procedures are set forth to determine the span and range settings of the analyzer. In general dual range monitors are required if the full-scale range of the analyzer is too low to measure uncontrolled emission rates. In some circumstances, existing data may be used for an initial certification. After the initial certification testing is completed, a data report that includes all test data, an electronic data report (in most cases) Verification and certification statement must be submitted to the State after testing is completed.

Accuracy:

Due to the extremely sensitive nature of trading credits and recording emissions there is a tight requirement for maintaining a high level of accuracy, there are extensive operational and Quality Assurance requirements of the emissions Monitoring system. Although the Quality Assurance Plan does not need to be submitted to the state, it must be developed and maintained on site. The follow tests must be performed to assure quality to the monitoring system based on a typical N0x emissions trading source for a typical Annual testing:

Component	Daily	Quarterly	Annually	Other Significant Test
1. N0x,C02,02,CEMs	Calibration Check	Linearity Test	RATA	
2. Flow CEMS	Calibration Check Interference Check		RATA	
3. Moisture	Calibration Check	Linearity Test	RATA	
4. Fuel Flow Meters	Calibrate every 2 yr. or			Every 4 operating quarters
5. Alternative Heat Input	Calibration Check	Linearity Test	RATA	

From these tests come the Initial Certification requirements, which will vary, based on the emission source tested:

Certification	Calibrations Error/ Drift Test	Linearity Check	RATA
1. **N0x or S02 Initial Certification**	<2.5% of Span	<5% of Reference or 5ppm	<7.5%* **to**<20% Lb/mmBTU
2. **C02 or 02 CEMS use To determine Heat input (not part of CEMS)**	**<**.5% of Span	<5% of Reference of <.5% of C02 or 02	<10% to <20% or +- 2%C02/02
3. **Stack Flow CEMS**	<3% of Span	<15% or <2fps;	
4. **Moisture System**	<3% of Span	<5% of reference or <.5%O2	<15% or 1% H2O

* For Acid Rain Utilities if this is passed with in 7.5% this test is only required annually within 10% and the test must be performed Semi Annually.

Uncertainty of it all:

Even with all of the accuracy tests and measures and quality assurance it is still all based on the accuracy of the monitors which can a skew the measurement of all the above tests. If a monitor were calibrated with a gas which was off certification by 10% it would create havoc with the accuracy of tons of gas being emitted out of the stack. Millions of dollars are at stake in true value of credits to be traded compounded by the fact that if emissions are misstated the number of tons "permitted" for emissions will be decreased as well.

There for, there are standards set to give as accurate as possible to determine the actual monitor values taking out some of the uncertainty of the tests.

Calibration Gases:

As defined in the Code of Federal Register/ Vol.58, No 6 a Calibration Gas is defined as:

1. A standard Reference Material (SRM)
2. A National Institute of Standards Testing (NIST)/ EPA approved Certified Reference Material (CRM)*
3. A Protocol Gas or
4. Zero Ambient Air material.

- ***Sources used for Reference Standards:***
  -NTRM (Produced by an independent gas vendor and qualified by NIST)
  -SRM (NIST certified but produced under contract with independent gas vendor)

-PRM (Primary Reference Material produced by the Netherlands Nmi and recognized by NIST as equivalent to SRM's)
-GMIS (Gas vendor produced under EPA guidelines and referenced to NTRM's SRM's or PRM's)

EPA Protocol Gas Definition:

EPA has defined the "Protocol gases must be vendor certified to be within 2% of the concentration specified on the cylinder label."

Ways to get closer accuracy:

Even following the prescribed government regulations many emission sources go further to insure accuracy of their monitors in the case of a "surprise" EPA inspection or to insure that passing linearity or a RATA goes smoothly. Some of the questions, which can be asked, are:

1. **What precautions does your calibration gas company take to prevent cross contamination of components in cylinders?**

   Do they use high purity raw materials? How are the cylinders treated?

2. **How can I be sure the contents of the cylinders are not contaminated By previous contents?**

   How well are the cylinders tracked for history of contents and where they have been (customers) previous use.

3. **What is the calibration gas company's track record in supplying Products to your emissions source? What have been their results in blind Audits?**

   You can check on their track history with other references. The EPA has a site on their web page at WWW.EPA.gov*, which is dedicated to results of blind audits of calibration gases.*

4. **Describe the certificates and labels supplied with the calibration gas Company's cylinders. Can the customer verify product accuracy? from the information provided? Does the calibration gas company offer certification on line?**

   Do the labels meet the requirements of the EPA? Does the label provide The data used to calculate the concentrations as well as the

instruments and standards used in the analysis for reproducibility? If the company has access to provide certificates on line it is an advantage for access when required.

1. **What is the gas calibration company's standard lead time for Delivery of gases?**

   Make sure that enough time is allowed for custom concentrations, but not such a long lead-time that it may delay testing or scheduling problems (down time).

2. **What sort of Technical Support is available? How can the customer Access this support?**

   Is there a person readily available to answer technical and logistical questions? Is their availability of Internet support for technical questions?

3. **What is the gas calibration company's manufacturing internal Rejection rate for EPA protocols?**

   This can be very telling if it is 0%, which may raise questions, or if the rate is too high.

4. **What is the best blend tolerance the gas calibration company can achieve for multi-component blends?**

   What is the most accurate multi component blend a company can provide a multi component blended cylinder could replace three cylinders.

5. **Is there a multi plant quality assurance program?**

   This would indicate whether a cylinder made at one facility would be comparable (analysis) with the same cylinder component(s) made at another facility.

6. **How does the gas calibration company provide certified concentrations for N0x in Protocols?**
   This can be define differently depending on the company some may measure N02 some may define it by N0x = N0 + N02 due to the fact that N0x is <u>not</u> one component but a potential of 5 different components.

7. **What manufacturing techniques are used to blend the Protocol mixes?**
   Are they made by a gravametric process or some other customized process?

12. What cylinder quality control procedures are used to control reactive component effects?

Are their safe guards used to make sure that moisture and other contaminates will not effect the contents of the cylinders? What is the composition of the cylinders?

13. Have the gas calibration company describe their raw material quality control practices.

Insure that the incoming raw materials are analyzed for a wide range of contaminants that include typical impurities. The purity of raw material and accuracy of purity should be able to be calculated.

14.What are the qualities of the raw materials used to produce calibration gases?

What are the grades of materials and how do they conform to the gas company's policy? Make sure they are not buying the lowest cost materials (usually).

15. How accurate of a calibration curve is determined by the gas calibration company.

The calibration residuals are the indicator of the curve accuracy.

16. Can the gas calibration company provide a +-1% accuracy cylinder?

In any measurement process, there is some error. Accuracy is calculated to be summing all the possible sources of error in the measurement process. It means that the "true" value lies with in a +-1% interval around the actual measured cylinder. The source of the "true" value comes from the reference standard that was used to name the cylinder in the analytical process. That is why the quality of the reference standard is so important! What is the confidence interval, which is calculated?

17. What parameters are controlled in the gas calibration company's analytical process to achieve +-1% accuracy?

The quality of the reference standard accuracy, the statistical control of the instrument calibration curve, the repeatability of the instrument measurement and the stability of instrument calibration curve, the repeatability of the instrument measurement and the stability of the instrument response both short term (noise) and long term (drift) must be controlled to provide accurate concentration numbers.

18. What types of reference standards does the gas calibration company use to produce Protocol gases?

Do they use different classes of reference gases to produce "true" values to produce different grades of accuracy? (i.e. a NTRM, SRM, PRM, are closer to the base accuracy of the standard for a 1% than a GMIS reference standard which may have too many uncertainties and make it a 2% accuracy)

19. Does the gas calibration company participate in any of the reference gas programs?

Have they ever provided the standards to NIST? Assist the PRM program or NPL program?

20. What is the gas calibration company's inventory of reference standards?

Do they have enough range of standards to make the required blends without too much dilution?

21. What role does the gas calibration company's reference standard play in the overall role of product accuracy?

Realizing that the reference standard is the source of the "true" value it is the largest factor in controlling accuracy. If a gas calibration company provides the accuracy of the reference standard in calculating the accuracy of the calibration gas there is a greater confidence in the contents.

22. What types of instruments are used to analyze the gas calibration company's gases?

This is very important to the ability of the company to insure that their gases are being analyzed accurately according to their use.

23. How frequently does the gas calibration company calibrate their instruments?

This is very essential to consistent results and should be asked.

24. How many reference standard data points does the gas calibration company use to construct a calibration curve?

Obviously, the more the better.

25. What range of concentrations does the gas calibration companies calibration companies cover?

Does the company use all the ranges necessary for your gases?

26. What data quality criteria must calibration curve data meet in order to achieve a +- 1% accuracy?

What is the calibration residual calculated on? What is the R-value for fit on the curve of confidence?