Development of Mercury Calibration Gases for Mercury CEMS

AIR MONITORING

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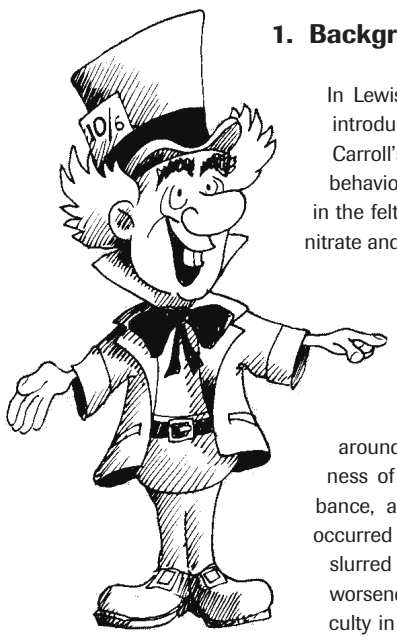


1. Background

In Lewis Carroll's 1865 book Alice's Adventures in Wonderland he introduced us to a character known as the Mad Hatter. Although Carroll's Mad Hatter was fictional, the strange and unpredictable behaviour he displayed was not uncommon among people employed in the felt hat industry in the 1800s. The felting process used mercury nitrate and the constant exposure to the chemical eventually caused the hatters to develop mercury poisoning. The relationship between mercury poisoning and the hatters' behaviour was not understood at the time, but the term "mad as a hatter" was in common usage.

Moving ahead to 1956 (in Southwestern Japan in an area around Minamata Bay), local residents showed symptoms of numbness of the limbs and the area around the mouth, sensory disturbance, and difficulty with everyday hand movements. Also there occurred a lack of coordination, weakness and tremor, slowed and slurred speech, and altered vision and hearing. These symptoms worsened and led to general paralysis, involuntary movements, difficulty in swallowing, convulsions, brain damage, and death. The ailment was at first thought to be genetic in nature and was named Minamata Disease. However, area felines also showed the symptoms, and since the felines were not part of the genetic pool of the area residents, further research found elevated levels of mercury in the bay. These levels were caused by mercury salts being discharged into the bay by a local chemical manufacturing facility. This discovery led to the conclusion that Minamata Disease was, in fact, mercury poisoning.

Mercury, also known as quicksilver, is an element that does not break down. It occurs naturally and is found in very small amounts in oceans, rocks, and soil. It becomes airborne when rocks break down, volcanoes erupt, and soil decomposes. It then circulates and is redistributed throughout the environment.

Large amounts of mercury also become airborne when coal, oil, wood, or natural gas is burned as fuel, or when mercury-containing waste is incinerated. Once in the air, mercury can fall to the ground with rain and snow, landing on soil or in bodies of water, causing contamination. Lakes and rivers are also contaminated when there is a direct discharge of mercury-laden industrial and municipal waste into them. Once in a lake or river, mercury is converted to methylmercury by bacteria and other processes. Fish absorb methylmercury from their food and from water as it passes over their gills. Mercury is tightly bound to proteins in all fish tissue, including muscle. There is no method of cooking or cleaning fish that will reduce the amount of mercury consumed in a meal.

In a U.S. Environmental Protection Agency (EPA) study1 released in February 2003, it was found that about one in every 12 women in the United States have mercury levels in their bodies above the level considered safe by the EPA. About 5 million women—8 percent of those at the childbearing ages of 16 to 49—had at least 5.8 parts per billion of mercury in their blood as of 2000, the report says. In fact, just 3 years ago, the U.S. Research Council estimated that about 60,000 babies born each year in the United States could be at risk of brain damage with possible impacts ranging from learning difficulties to impaired nervous systems. However, based on more recent exposure data published by the U.S. Centers for Disease Control and Prevention, some scientists think the number of at-risk babies could be as high as 300,000. EPA has found that children born to women with blood concentrations of mercury above 5.8 parts per billion are at some risk of adverse health effects, including reduced developmental IQ and problems with motor skills such as eye-hand coordination.

Atmospheric mercury knows no geographic limitations. As stated at the recent United Nations Environment Program (UNEP) meeting in Kenya, "mercury is a substance that can be transported in the atmosphere and in the oceans around the globe traveling hundreds and thousands of miles from where it is emitted." The report went on to state that "the global environmental threat to humans and wildlife has not receded despite reductions in mercury discharges, particularly in developed countries. Indeed it shows that the problems remain and appear, in some situations to be worsening as demand for energy, the largest source of human made mercury emissions, climbs."

The UNEP report states that mercury poisoning of the planet could be best reduced by curbing pollution from power stations. The report, compiled by an international team of experts, says that coal-fired power stations and waste incinerators now account for around 1,500 tons, or 70 percent, of new, quantified manmade mercury emissions to the atmosphere.

In Germany there are restrictions and monitoring requirements for mercury emissions from incinerators. In the United States the Environmental Protection Agency has promulgated mercury cap and trade requirements for coal fired electric utility boilers. This regulation requires the monitoring of mercury on a continuous basis. The use of continuous emissions monitoring systems (CEMS) is well established both in regulation and in practice. Under 40 CFR 60 and 40 CFR 75, electric utilities have utilized CEMS for the monitoring of SO_2, NO_x, CO, CO_2, and O_2 since the 1970s. Under these regulatory requirements, gaseous CEMS "must automatically check the zero (or low level value between 0 and 20 percent of span value) and upscale span (50 to 100 percent of span value) calibration drifts at least once daily." In practice, the daily zero and span checks have been performed by first injecting nitrogen (zero gas) and obtaining a zero reading, and then injecting a span gas of the proper value and obtaining a span reading. For mercury CEMS there is an additional requirement for checking the oxidized mercury converter at least once a week. Mercury CEMS therefore require both Hg^0 and Hg^{+2} traceable standards.

The liquefied natural gas (LNG) industry recognizes that mercury in natural gas, in addition to being a pollutant, also causes problems by fouling compressors. Therefore there is a mercury specification that limits the amount present in the LNG. As is typical in custody transfer situations, both the buyer and the seller monitor the specifications of the product, in this case mercury. This monitoring requires both instrumentation and a traceable standard.

2. Hg^0 Calibration Gas Development

With the potential of mercury CEMS becoming a reality, Spectra Gases Inc. in 1998 initiated a research program to develop a mercury calibration gas that would address the needs of the emerging mercury CEMS requirements. At first, the idea of a mercury calibration gas did not appear to be particularly difficult. However, as the program got under way, it became obvious that there were several potential roadblocks to success. These challenges included (1) the form or forms of mercury that could be utilized (2) the ability to get a known quantity of mercury into a cylinder, (3) having the calibration gas remain stable over an extended period of time, and (4) determination of the concentration of the calibration gas. Spectra Gases' background in producing low (single-digit) ppb level volatile organic compound (VOC) calibration standards provided the required background for resolving the issues.

The form of mercury that could be utilized was readily apparent from the available literature. Only metallic mercury Hg^0 had sufficient vapor pressure to allow any concentration to be incorporated in a high-pressure cylinder. In fact, at Hg^0 concentrations above 30 µg/m3, the pressure in the cylinder has to be reduced in order to prevent possible condensation. Since mercury CEMS measure both the metallic and the oxidized form of mercury, another method would have to be found for calibrating the CEMS for oxidized mercury.

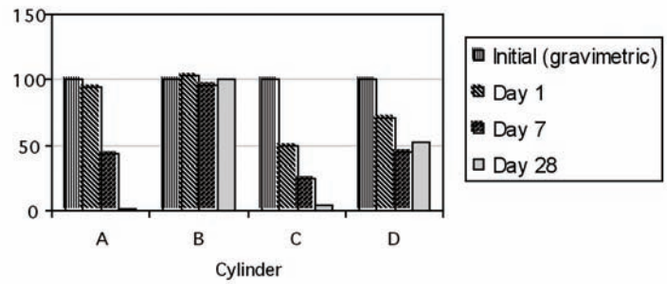
High-quality calibration gases are produced by gravimetric methods. This entails precise weighing of both the minor component or components and the balance gas. To ensure the highest possible accuracy, all measurements are performed on balances and scales that are calibrated on a frequent (at least daily) basis against NIST-traceable standards. Furthermore, external audits of the scales, balances, and standard weights are performed regularly to ensure the accuracy of the measurements. In those instances where the quantity of the minor constituent is so small as to make accurate weighing virtually impossible intermediate standards are produced at a higher concentration. Then a calculated amount of the higher concentration intermediary is weighed into the cylinder, which is then filled to the proper weight with the balance gas. This technique allows us to produce gas standards at ppb levels with excellent repeatability.

Stability is always a consideration in the production and utilization of calibration gases. The U.S. EPA recognizes stability issues by specifying the maximum period of validity for a Protocol calibration standard. This valid period ranges from 6 months up to 36 months, depending upon the minor constituent and its concentration and the composition of the balance gas. It is important to understand the potential for interactions between the components being put into the cylinder. As an example, if one is attempting to produce a nitric oxide (NO) standard, it is most important to eliminate any oxygen (O_2) from the cylinder. At even low levels O_2 will react with NO to form NO_2, and the certification value of the NO concentration will be invalidated. It was determined that mercury vapor and nitrogen (the balance gas) would be stable, thus eliminating a potential problem. The next step in producing a stable calibration standard is to eliminate, or perhaps more correctly to minimize, the interactions between the cylinder and the calibration gas constituents.

High-pressure gas cylinders are constructed from various metals including such materials as carbon steel, stainless steel, and aluminum. Cylinders received from the manufacturer are not immediately usable in calibration gas service, especially if being used for low ppb or ppm standards. The cylinders may still have residues of oils and waxes used in the production of the cylinder. The internal walls of the cylinder may not be "smooth" enough. The cylinder material may be acting similar to a sponge and holding moisture. All of these conditions may adversely impact the stability of a calibration standard. Furthermore there are a number of coating materials that can be applied to the internal surfaces of the cylinder in an attempt to render the surfaces inactive to the constituents that will be placed in, stored in, and dispensed from the cylinder. Among the better-known coating materials there are various Teflon® formulations and silica surface treatments.

To determine (1) if there was a cylinder that could hold a mercury calibration standard, and (2) would the calibration standard be stable over a period of time that would prove acceptable in field use, a test was initiated of multiple cylinder materials, cylinder preparation techniques, and surface treatments. In all, over 100 combinations and permutations were attempted. Figure 1 selects four of

Figure 1



the variations to graphically demonstrate the results of these tests.

The vertical axis is scaled in percent of gravimetric fill; the series represents the analytical readings at days after the fill. As can be seen, some of the tests showed rapid concentration decrease, while others showed slow rates of decrease. However, for a stable calibration gas, the only acceptable condition is no concentration decrease. The combination of cylinder material and cylinder treatment as exhibited by cylinder B showed excellent stability in our short-term tests. This allowed Spectra to move on to long-term studies.

Figure 2

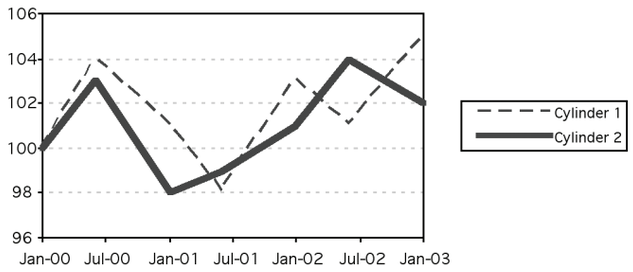


Figure 2 shows the result of the long-term stability study. The vertical axis again is a percentage of the gravimetric fill concen¬tration. As can be seen over the 36-month period the concentrations of both cylinders were extremely stable, varying by less than ±5 percent. This error is attributable to analytical uncertainties.

Analytical uncertainty is a factor in all measurements, whether for analysis of a sample or for the analysis of a standard. Typically when producing gaseous calibration standards, a primary standard is available that has been certified by a recognized metrology source or accepted secondary standards. In the United States this source of primary standards is the National Institute of Standards and Technology (NIST), in the United Kingdom it's the National Physical Laboratory (NPL), and in the Netherlands it is the National Metrology Institute (NMI).

However, since there were no nationally recognized standards for gaseous mercury, Spectra Gases in co-operation with the US EPA and NIST participated in a program whereby NIST analyzed and certified a series of mercury standards which provides Spectra with the ability to provide NIST traceable mercury standards on a commercial basis.

3. Hg^{+2} Calibration Gas Development

Most of the commercially available mercury CEMS analyze elemental mercury (Hg^0), while stack emissions contain elemental, oxidized, and particulate forms of mercury. To analyze total mercury, these analyzers use a converter to convert all of the mercury to the elemental form. This is similar to the measurement of NO_x by chemiluminescence where the analyzer only measures NO and a converter is utilized to convert the NO_x to NO prior to analysis. To confirm the conversion efficiency in a chemiluminescence analyzer, NO_2 is injected prior to the converter and the resulting NO is measured. If all of the NO_2 is converted to NO, then the converter's efficiency is reported as 100 percent.

To solve the need for a traceable oxidized mercury gas standard Spectra Gases developed the MerCal, mercury calibration system.

The MerCal is designed to utilize the traceable elemental mercury standard and react with an oxidizing agent to produce an oxidized mercury standard. To provide traceability, the MerCal incorporates a significantly greater flow of the mercury standard than the oxidizing agent. This yields an oxidized mercury standard gas which has essentially the same concentration as the original elemental mercury standard.

The MerCal provides tremendous flexibility in the field allowing the operator to choose either an elemental or an oxidized mercury standard.

The MerCal is patented in the US and has patents pending throughout the world.

4. Conclusion

Spectra Gases has successfully developed traceable mercury calibration standards for use in both environmentally regulated and process driven applications. The standards have been shown to be stable over long periods of time.

The advantages of compressed gas standards over other available calibration techniques are readily apparent. The MerCal system operates compatibly with existing CEMS, allows full automation of calibration for both elemental and oxidized mercury while eliminating the need for pools of mercury or for highly acidic acid solutions.

References

1. U.S. EPA Press release: EPA ISSUES SECOND REPORT ON TRENDS IN PROTECTING CHILDREN'S HEALTH, 2/24/03.
2. http://www.unep.org/GoverningBodies/GC22/Document/UNEP-GC22-INF3.pdf.