UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Air Quality Assessment Division
Ambient Air Monitoring Group
109 T.W. Alexander Dr., Research Triangle Park, NC 27711

To: Regions, State and Local Agencies

From: Solomon Ricks, EPA – OAQPS Protocol Gas Verification Program Lead SDR 10/25/2017

Bob Wright, EPA – ORD Air and Energy Management Division RSW 10/25/2017

Subject: EPA Protocol Gas NO_2 Standards

The advent and promotion of true NO_2 analyzers to Federal Equivalent Method (FEM) status has led to increased use of these analyzers in ambient monitoring networks. EPA is aware of the air quality community's interest in, and adoption of, practices that use compressed NO_2 gas standards for quality control (QC) checks. The EPA has not issued comprehensive guidance on the use of NO_2 gas standards in quality assurance exercises. However, in the October 2016 edition of the EPA's QA EYE (Issue 20 page 4) it was noted that EPA Office of Research and Development (ORD) experience indicated that NO_2 gas standards could be used to replace iso-propyl nitrate (IPN) and N-propyl nitrate (NPN) for NOy 1-point QC checks. At that time, the Agency expected that commercially available NO_2 standards would follow EPA Protocol Gas requirements[1] specified in 40 CFR Part 58 Appendix A Section 2.6.1. Unfortunately, it appears that in some instances this may not be the case. Therefore, the EPA is raising two important issues that need to be considered by any entity considering the use of the NO_2 gas standards:

1. Do the commercial vendors follow protocol gas requirements, and
2. Are the standards stable?

The Protocol Gas Requirements

In order to produce an EPA Protocol Gas a NIST certified Standard Reference Material (SRM); or a NIST Traceable Reference Material (NTRM); or a Gas Manufacturers Intermediate Standard (GMIS) is required as the analytical reference standard. Unfortunately, at the moment, NIST does not provide an NO_2 SRM. NIST has indicated they are in the process of developing an NO_2 SRM, but there is no timeline in place for when this development will be completed. However, the Netherlands' Van Swinden Laboratory (VSL), has a Declaration of Equivalence[2] with NIST, and they presently produce an NO_2 Primary Reference Material (PRM)[3] that is equivalent to a SRM. This PRM can be used to produce a GMIS to, in turn, produce the NO_2 EPA Protocol Gas. Therefore, if gas producers use VSL PRMs as the NO_2 analytical reference standard and follow the traceability protocol, such NO_2 gas mixtures can be certified as EPA Protocol Gases. Monitoring organizations should check certificates of analysis to ensure that their NO_2

[1] https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards
[2] https://www.vsl.nl/sites/default/files/rtf/DoE%202016-2018%20signed%20by%20NIST%20and%20VSL.pdf
[3] https://www.vsl.nl/sites/default/files/rtf/VSL_primary-gas-standards.pdf

gas producers use the VSL PRMs in production of their NO_2 EPA Protocol Gases. In addition, the EPA plans to send a technical memo to the gas producers participating in the Ambient Air Protocol Gas Verification Program[4] (as well as any others known to the Agency), informing them of our concerns on this issue. The EPA will seek to determine which gas producers are using the VSL PRMs, and make this information available to the air quality monitoring community.

Stability of NO_2 Gas Mixtures

It has also come to the EPA's attention that there are concerns about the cylinders used to store the NO_2 gas mixtures. In standard passivated aluminum cylinders, the NO_2 gas concentration is unstable and degrades over a relatively short period of time. In light of this knowledge, VSL uses SGS™ (superior gas stability) aluminum cylinders from Luxfer[5] for PRM concentrations less than 250 ppm to maintain gas concentration stability. These cylinders have a proprietary interior surface that helps to prevent reactions and concentration degradation. The use of these cylinders have shown a stability of approximately 12 – 18 months. In discussions between the Agency and one specialty gas producer, the producer alluded that there may be certain concentration ranges that may be more stable than others even when using the SGS™ cylinders. The EPA plans to involve appropriate staff from both the Office of Air and Radiation and ORD to engage those specialty gas producers selling NO_2 EPA Protocol Gases to determine appropriate certification periods for the various concentration ranges of NO_2 EPA Protocol Gases they may choose to produce.

Summary

In order to ensure true NO_2 analyzers are properly calibrated and are providing accurate results we suggest the following:

1. All Agencies using true NO_2 analyzers should calibrate their instruments via gas phase titration (GPT) using NO EPA Protocol Gases;
2. After the initial GPT calibration, if the agency has an NO_2 EPA Protocol Gas, that cylinder may be used as a QC check on the instrument if it meets the EPA Protocol Gas requirements described above. Agencies should check these QC concentrations frequently and control chart this data since the cylinder may degrade while the analyzer maintains its calibration.
3. Should an agency notice what might be degradation in the concentration of the gas mixture in the cylinder, that the agency is advised to cease using the cylinder as a QC check and inform the EPA Regional Office. EPA would like to track these results. QC checks following the removal of the unstable NO_2 standard should be completed using GPT or an alternative NO_2 standard.

[4] https://www3.epa.gov/ttn/amtic/aapgvp.html
[5] http://www.luxfercylinders.com/press-releases/690-scientific-technical-gas-sgs-cylinders