UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

February 25, 2022

MEMORANDUM

SUBJECT: EPA Protocol Gas Long-Term Stability Requirements

FROM: Douglas Jager, EPA-OAQPS, Ambient Air Monitoring Group
Bob Wright, EPA-ORD, Air Methods and Characterization Division

TO: EPA Regional Offices,
Regulatory Agencies Performing Ambient Air Monitoring,
and Specialty Gas Producers

This memorandum provides notification to specialty gas producers and to State, Local, and Tribal (SLT) ambient air monitoring programs that gaseous calibration standards used for the calibration and the QA/QC of monitors intended to demonstrate compliance with the National Ambient Air Quality Standards (NAAQS) must be EPA Protocol Gases. The *EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards* defines the assay requirements that must be followed for a candidate standard to be certified as an EPA Protocol Gas, including a seven-day stability test for reactive gas mixtures. Candidate standards that pass the stability test are assumed to be stable throughout the maximum certification periods that are listed in Table 2-3 of the protocol (see attached). These periods are based on the certification periods for the corresponding Standard Reference Materials (SRMs) from the National Institute of Standards and Technology (NIST), which has evaluated SRM stability over multiple years. Gas mixtures that are not listed in Table 2-3 have not been demonstrated to have long-term stability and cannot be certified as EPA Protocol Gases.

EPA is aware that, in some cases, SO_2-in-air and NO_2-in-N_2 standards may have been certified by specialty gas producers as EPA Protocol Gases. These standards are not listed in Table 2-3 of the protocol and are not EPA Protocol Gases. EPA is working with the producers to notify them to cease certifying or otherwise indicating that these standards are EPA Protocol Gases until their long-term stability has been demonstrated to EPA and the protocol has been revised to include them in Table 2-3.

Some proprietary interior surface coatings for cylinders are available (e.g., Luxfer Superior Gas Stability (SGS™) cylinders and Catalina Mirror Finish™ cylinders) that are designed to increase the stability of reactive gas mixtures such as NO_2-in-N_2. Some national metrology institutes (NMIs), e.g., the Netherlands' NMI, the Van Swinden Laboratory (VSL), use these cylinders for storing their NO_2-in-N_2 Primary Reference Materials (PRMs). To date however, EPA has not received adequate long-term stability data for the commercially prepared NO_2-in-N_2 standards in these cylinders to determine the appropriate maximum certification period for NO_2-in-N_2 as an EPA Protocol Gas.

EPA is recommending that SLT ambient air monitoring programs review the certificates of analysis for their gaseous calibration standards to ensure they are listed in Table 2-3 of the protocol. SLTs should focus their review to ensure that:

- no SO_2 standards with an air balance are used for regulatory monitoring. These standards are not EPA Protocol Gases and as such do not meet the regulatory QA requirements found in Section 2.6.1 of 40 CFR Part 58, Appendix A. Additionally, Section 4.1.6 of 40 CFR Part 50, Appendix A-1 requires that the SO_2 standards be balanced with N_2, not with air; and
- no NO_2-in-N_2 standards are used for regulatory monitoring. These standards are not EPA Protocol Gases and as such do not meet the regulatory QA requirements found in Section 2.6.1 of 40 CFR Part 58, Appendix A. Additionally, direct dilution of NO_2 cylinder standards is not an approved method in 40 CFR Part 50, Appendix F for the generation of test atmospheres for NO_2 analyzers.

Request for specialty gas producer data demonstrating long-term stability of SO_2-in-air and NO_2-in-N_2 standards- Currently EPA is aware of long-term stability concerns for SO_2-in-air and NO_2-in-N_2 standards that are stored in standard passivated aluminum cylinders. It is EPA's understanding that some producers feel that they can reliably produce stable SO_2-in-air and NO_2-in-N_2 standards. EPA encourages those producers to submit long-term stability data and supporting documentation to EPA by contacting Bob Wright at wright.bob@epa.gov. Stability results submitted to EPA-ORD by specialty gas producers will be treated as confidential business information (CBI). If the standards can be shown to EPA's satisfaction to be stable, Table 2-3 will be revised to include these standards

EPA Regional offices should begin incorporating a review of the certificates of analyses for these SO_2-in-air and NO_2-in-N_2 standards during scheduled Technical Systems Audits. SLT ambient air monitoring programs identifying suspect SO_2-in-air and NO_2-in-N_2 standards used for calibration or QA/QC of their regulatory ambient air monitoring network should notify their EPA Regional Office. This communication will facilitate EPA expediting the notification of specialty gas producers and will allow EPA to provide timely guidance with any data validation questions pertaining to the use of suspect calibration standards. EPA Regional Office Quality Assurance Coordinators should contact Doug Jager at jager.doug@epa.gov if they find SO_2-in-air and NO_2-in-N_2 standards that are certified as EPA Protocol Gases.

cc: EPA Regional Office Air Monitoring Coordinators
EPA Regional Office Quality Assurance Coordinators
Protocol Gas Verification Program participants during Calendar Year 2022
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TABLE 2-3. Maximum Certification Periods[a] for Calibration Standards in Passivated Aluminum Cylinders

Components	Balance gas	Concentration range	Period (years)
Ammonia	Nitrogen	5 to 50 ppm	1
Carbon dioxide	Air[b]	360 to 420 ppm	8
Carbon dioxide	Nitrogen	5 ppm to 20%	8
Carbon monoxide	Air	40 to 500 ppb	TBD
Carbon monoxide	Air	500 ppb to 10%	8
Carbon monoxide	Nitrogen	1 ppm to 15%	8
Formaldehyde	Nitrogen	0.5 to 10 ppm	1
Hydrogen chloride[c]	Nitrogen	10 to 5000 ppm	2
Hydrogen sulfide	Nitrogen	1 to 1000 ppm	3
Methane	Air	1 to 1000 ppm	8
Methane	Nitrogen	500 ppb to 10%	8
Methanol or ethanol	Nitrogen or Air	75 to 500 ppm	4
Natural gas components[d]	Natural gas	Contact NIST	4
Nitric oxide	O_2-free nitrogen[e]	0.5 to 50 ppm	3
Nitric oxide	O_2-free nitrogen[e]	50 ppm to 1%	8
Nitrous oxide	Air	300 ppb to 5%	8
Oxides of nitrogen[f]	Air	3 ppm to 1%	3
Oxygen	Nitrogen	10 ppm to 25%	8
Propane	Air	0.1 to 500 ppm	8
Propane	Nitrogen	5 ppb to 2%	8
Sulfur dioxide	Nitrogen	1 to 50 ppm	4
Sulfur dioxide	Nitrogen	50 ppm to 1%-	8
Volatile organics	Nitrogen	1 ppb to 1 ppm	4
Zero air material[g]	Air	Not applicable	Unlimited
Multicomponent mixtures	—	—	See text
Mixtures with lower concentrations	—	—	See text

[a] Specialty gas producers may elect to certify candidate standards for less than the maximum certification period. Each producer has discretion in this matter. See text.
[b] "Air" is defined as a mixture of oxygen and nitrogen where the minimum concentration of oxygen is 10 percent and the concentration of nitrogen is greater than 60 percent.
[c] Hydrogen chloride may be contained in passivated aluminum or nickel-coated steel cylinders.
[d] Natural gas components are methane, ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane, helium, nitrogen, and carbon dioxide.
[e] O_2-free nitrogen contains ≤ 100 ppb of oxygen.
[f] NIST defines its total NO_X standards as containing nitrogen dioxide plus contaminant nitric acid.
[g] Concentrations of SO_2, NO_X, and THC are not >0.1 ppm; concentration of CO is not >1 ppm; and concentration of CO_2 is not >400 ppm as per 40 CFR Part 72.2. Zero air material may be contained in steel cylinders.