UPDATE – December 2022: update to the February 2022: ***Concern with Certain Calibration Gas Mixtures Sold as Protocol Gases Not Meeting Long-Term Stability Requirements***

Discussions with the National Institute of Standards and Technology (NIST) concerning the quality of the NIST NO2 standard revealed that this standard contains small but consistent amounts of nitric acid (HNO3). Some converters may not be able to completely convert this HNO3 to nitric oxide (NO) for analysis. There are also concerns about the cost and stability of certified NO2 gas over time. Therefore, we will update the February 2022 memo to be consistent with the language in Section 7.1.4, which states, "*The converter efficiency gas is a manufacturer-certified gas with a concentration sufficient to show NO2 conversion at the concentrations encountered in the source."*

February 2022: ***Concern with Certain Calibration Gas Mixtures Sold as Protocol Gases Not Meeting Long-Term Stability Requirements***

On February 25, 2022, Douglas Jager of EPA-OAQPS and Bob Wright of EPA-ORD sent a memorandum (https://www.epa.gov/amtic/ambient-air-protocol-gas-verification-program) providing notification to specialty gas producers, EPA Regional Offices, 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 Traceability Protocol and thus 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.

We have been asked by several testers and air agencies about the use of NO_2 in N_2 for the NO_X converter efficiency test. As stated in Method 7E Section 7.1.4, "The converter efficiency gas is a manufacturer-certified gas with a concentration sufficient to show NO_2 conversion at the concentrations encountered in the source."

There have also been questions about the use of blended cylinders containing SO_2 and O_2 in a balance of N_2. The maximum O_2 allowed in a SO_2 EPA Protocol Gas is much lower than the mid-range for O_2 used for calibration error (CE) /calibration drift (CD), therefore a blended cylinder can no longer be certified as a protocol gas.

Questions or comments related to this memorandum may be addressed to Kim Garnett, garnett.kim@epa.gov or Walter Lin, lin.walter@epa.gov.

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.