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Nitrogen Dioxide Calibration Standards for Portable Monitors

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	L	liter
cm ² /min	square centimeter per minute	min	minute
cm ³	cubic centimeter	mL/min	milliliter per minute
g	gram	mm	millimeter
g/cm ³	gram per cubic centimeter	mm Hg	millimeter of mercury
g/hr	gram per hour	ng/min/cm	nanogram per minute per centimeter
g/L	gram per liter	ppm	part per million
gm-mol	gram mole	sec	second
gm-mol/cm ³	gram mol per cubic centimeter	μA	microampere
hr	hour	μg	microgram
K	kelvin	°C	degree Celsius

NITROGEN DIOXIDE CALIBRATION STANDARDS FOR PORTABLE MONITORS

By Joseph E. Chilton,¹ Robert J. Timko,² and Edward J. Chuhta³

ABSTRACT

Mine operators and Mine Safety and Health Administration (MSHA) inspectors use portable gas monitors in underground mines to measure worker exposure to various gases such as methane, carbon monoxide, and nitrogen dioxide (NO₂). Even in relatively small concentrations, NO₂ can produce harmful side effects in underground workers. Mines using equipment powered by diesel engines, carrying out explosive blasting operations, and performing extensive arc welding and/or cutting work will have measurable quantities of NO₂ released by these processes. Workers in these areas often use gas monitors to warn of excessive gas concentrations and to help them determine when to increase ventilation air that will dilute these gases, thus minimizing exposures to this gas. Portable gas monitors, used to measure NO₂ levels, must be calibrated before each use. Calibration is typically performed using a small portable pressurized cylinder containing a certified gas mixture. The certified NO₂ standard mixture, usually 10 ppm NO₂ concentration, is diluted with either air or nitrogen gas.

To determine the stability of commercially available portable gas standards, two different cylinders containing NO₂ in nominal 10-ppm concentrations were examined. One cylinder was diluted in air, the other, in nitrogen. Baseline NO₂ mixtures were generated using a standard liquid NO₂ permeation tube operated at a constant temperature. Final dilutions of the test gas mixtures were made with air or with nitrogen using a mass flow-controlled gas dilution system. This study showed that, when a permeation-type NO₂ generator is used, the electrochemical sensors in portable NO₂ monitors provide identical results for gas mixtures whether they are diluted with air or with nitrogen.

Two different gas monitors, one with a two-electrode sensor and one with a three-electrode sensor, were used to measure gas concentrations in the two commercially available cylinders. One month after the cylinders were delivered, the NO₂-in-nitrogen cylinder, stated to contain 10 ppm NO₂, measured 8.13 ppm. The NO₂-in-air cylinder, also stated to hold 10 ppm NO₂, measured 6.88 ppm. Therefore, before using NO₂ gas cylinders to calibrate monitors, it is recommended that their concentrations be verified either by manufacturer recertification or by comparing the stated cylinder gas concentrations to a laboratory-based permeation tube-generated standard.

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INTRODUCTION

Mine operators and Mine Safety and Health Administration (MSHA) inspectors use portable gas monitors to measure underground worker exposure to nitrogen dioxide (NO₂). Mines that have equipment powered by diesel engines, perform explosive blasting operations, and/or do extensive arc welding or cutting work will have measurable quantities of NO₂ released into the mine air. To dilute high NO₂ concentrations and thus limit worker exposures, mines must aggressively ventilate working sections located downstream of these operations.

The threshold limit value (TLV) time-weighted average (TWA) health limit for NO₂ exposure is 3 ppm for a conventional 8-hr workday and a 40-hr workweek. The allowed ceiling level and the short-term exposure limit (STEL)—a limit determined with instantaneous monitors—are both 5 ppm. The STEL values are taken over a 15-min TWA exposure that cannot be exceeded at any time during the workday even if the 8-hr average TWA is within specifications.⁴ Gas concentrations up to 5 ppm NO₂ in air may cause irritation to the eyes and pulmonary tract. Concentrations between 10 and 20 ppm NO₂ will cause coughing and burning in the throat and induce slowly evolving pulmonary edema. This typically occurs over a 48-hr period. The NO₂ concentration that is immediately dangerous to life or health (IDLH) is 20 ppm for an exposure time up to 30 min. Serious complications, including death, can occur from extended exposures at levels of 100 to 200 ppm [NIOSH 1989, 1994].

MSHA regulations require maintenance of instruments used to obtain NO₂ samples. 30 CFR⁵ 75.320(c) states: "Handheld devices that contain electrical components and that are used for measuring air velocity, carbon monoxide, oxides of nitrogen, and other gases shall be approved and maintained in permissible and proper operating condition." Comments on this rule conclude that "proper operating condition" implies calibration of the instrument. 30 CFR 70, subpart T, addresses the

measurement of exhaust gases from diesel-powered equipment. Under this subpart, 30 CFR 70.1900(b)(2) states that NO₂ shall be "collected and analyzed by appropriate instrumentation which has been maintained and calibrated in accordance with the manufacturer's recommendations." The inference here is that portable NO₂ gas monitors, when used in enforcement work, should be calibrated before each health survey.

Field calibration of working gas monitors involves several steps. Individuals who calibrate monitors use specific concentrations of certified NO₂ mixtures that are contained in portable pressurized cylinders. A flow regulator on the calibration cylinder sets the flow of the certified mixture to 500 mL/min. The gas is then introduced to the monitor through a hose connected to a manufacturer-provided calibration fixture. Once the instrument readout has stabilized, differences between the stated cylinder concentration and the readout are corrected by either adjusting the readout value by software modification or by manually adjusting the gain resistor on the instrument until the readout is equal to the cylinder's stated calibration concentration.

The purpose of this study was to compare calibration gas cylinders having balance gases of nitrogen or air that are commonly used to calibrate portable NO₂ gas monitors. Because even low concentrations of NO₂ can have an extremely adverse effect on individuals working in areas where NO₂ emissions exist, it is imperative that portable NO₂ monitors be accurately calibrated. The importance of this work was noted when a portable calibration gas cylinder, labeled to contain 2 ppm NO₂, was found by using a permeation system-calibrated monitor to contain only 0.9 ppm NO₂. If this calibration cylinder were used to calibrate a field NO₂ monitor, the resulting measurements would be over 100% too high, and a mine could be improperly cited for excessive NO₂ exposure. The accuracy limits for this cylinder over time or the mixture stability were not addressed.

CALIBRATION ANOMALIES

To determine actual NO₂ concentrations in commercially available calibration cylinders, we obtained certified calibration mixtures of NO₂-in-nitrogen and NO₂-in-air from local suppliers. Labels on both calibration cylinders stated that the NO₂ concentration in each was 10 ppm. However, when the monitors calibrated with the NO₂-in-nitrogen mixture were compared to those calibrated with the NO₂-in-air mixture, the

NO₂-in-air mixture results were 20% lower and thus out of compliance. We developed three hypotheses for these observed results:

1. Assuming the two calibration mixtures have equal as-advertised NO₂ concentrations, the sensor response is greater in nitrogen mixtures than in air mixtures.

2. If, as filled initially, the two calibration mixtures had equal NO₂ concentrations, then the oxygen and the NO₂ in the NO₂-in-air mixture may be reacting in the cylinder to reduce the NO₂ concentration in the cylinder over time.

3. The air-diluted cylinder as initially filled had a smaller NO₂ concentration than the nitrogen-diluted cylinder.

⁴The STEL and TWA values cited are those found in the American Conference of Governmental Industrial Hygienists (ACGIH) 1972 TLVs used by MSHA for coal mines and the ACGIH 1973 TLVs used by MSHA for metal and nonmetal mines. Current NIOSH-recommended STEL limits are 1 ppm. Occupational Safety and Health Administration regulations cite 5 ppm as the ceiling value.

⁵*Code of Federal Regulations*. See CFR in references.

METHODS

ELECTROCHEMICAL NO₂ DETECTORS

Direct and continuous measurement of NO₂ concentrations can be made using either color-indicating passive chemical sensors or direct-reading handheld instantaneous monitors that contain electrochemical sensors. The electrochemical sensor is either membrane diffusion-limited or capillary space diffusion-limited and uses electrochemical cells that have two or three independent electrodes. The two-electrode sensor consists of one anode and one cathode. The three-electrode sensor consists of a working electrode, the cathode, a counterelectrode, the anode, and a reference electrode. Both sets of electrodes are held in an electrolyte solution of 2M sulfuric acid in water. Electronic circuitry for the three-electrode cell maintains the ratio of reference to working electrode potential at a fixed voltage and measures the current flowing between the working and counterelectrodes. The two-electrode sensor has an external fixed voltage across the electrodes. The measured cell current is converted to a voltage and amplified. During calibration procedures, the output voltage is adjusted with the zero set potentiometer initially so that the meter display with exposure to pure air is equal to zero. With exposure to calibration gas, the meter display is adjusted with the span set potentiometer to equal the NO₂ concentration stated on the calibration cylinder.

City Technology Ltd., Portsmouth, U.K., produces one example of the three-electrode type of electrochemical NO₂ sensor. The sensitivity of its model 4ND sensor is 0.6 μA/ppm NO₂. This sensor, with an electronic amplifier, has a resolution of 0.1 ppm, a response time of 24 sec for 90% of final signal, and a range of 0 to 20 ppm. Handheld portable gas monitors using these types of electrochemical NO₂ sensors are available from several different manufacturers, including Biosystems, Middletown, CT; Draeger Safety, Inc., Pittsburgh, PA; Industrial Scientific Corp., Oakdale, PA; Mine Safety Appliances Co., Pittsburgh, PA; Crowcon Corp., Milford, OH; and Thermo Electron Corp., Waltham, MA.

CREATING NO₂ STANDARDS USING GAS PERMEATION SYSTEMS

Standard mixtures of gases are obtained typically in one of three ways: from cylinders containing the pressurized standard gas mixture, by mixing pure gases from cylinders with diluent gases using precision gas flow controllers, or from the dilution of gases generated at a fixed rate by a permeation device. The gas permeation system works best for generating mixtures that are reactive with cylinder wall materials or when making low-concentration mixtures with standard gases requiring low total airflows.

To determine the accuracy of an NO₂ monitor in either nitrogen-diluted or air-diluted carrier mixtures, we created known concentrations of NO₂ diluted in air and in nitrogen. The

description that follows also demonstrates that creating accurate gas mixtures using gas permeation systems requires careful procedures and proper consideration of the variables involved. A permeation system produced concentrated NO₂ gas using an NO₂ permeation tube made by VICI Metronics of Poughkeepsie, NY. This permeation tube is a cylindrical FEP⁶ Teflon® plastic tube with a 4.80-mm outside diameter and a 0.80-mm-thick wall. The gas diffusion length is 10 cm; the full permeation tube length including seals is 13.5 cm. The manufacturer states that with two-phase (liquid and gas) equilibrium at a constant temperature, the gas permeation rate will be constant over the life of the tube [VICI Metronics 2004]. At 30 °C, the manufacturer's stated NO₂ permeation rate is 1,715 ± 10 ng/min/cm of tube exposed. Chemical longevity in a standard tube operating at 30 °C with a 75% initial tube fill is calculated as follows:

$$L = \frac{1,400}{p} \times \rho_L, \quad (1)$$

where L = tube lifetime, months;
 p = permeation rate;
 and ρ_L = liquid density, g/cm³.

As an example, assuming a liquid NO₂ density of 1.4 g/cm³ and a stated permeation rate of 1,715 ng/min/cm (at 30 °C), the lifetime of a 10-cm tube would be 1.14 months. Lifetimes can be extended by operating the permeation tubes at 20 °C with an initial measured permeation rate of 4.51 × 10⁻⁴ g/hr, which equals a 759 ng/min/cm loss rate. The calculated permeation tube lifetime then becomes 2.6 months.

The rate of permeation of a gas through the walls of a porous cylindrical tube is written as

$$P_R = (6.283(L \times D)(C_i - C_o)) / \ln(R_1/R_2), \quad (2)$$

where P_R = rate of gas leaving the tube per minute, gm-mol;
 L = tube length, cm;
 D = effective diffusion coefficient through the plastic wall, cm²/min;
 C_i, C_o = inner and outer gas concentrations, gm-mol/cm³;
 and R_1, R_2 = inner and outer cylinder radii, cm.

Since the dry nitrogen flowing over the tube continually ventilates the permeation tube, the outer gas concentration C_o was set to zero. Thus, by Equation 2, the gas evolution rate was constant when the inner concentration was constant. With liquid-vapor equilibrium from both gas and liquid present at a constant temperature, the vapor pressure was also constant. At

⁶Fluorinated ethylene propylene.

constant temperature and pressure, the gas concentration was also constant. The liquid level decreased during the life of the tube, so the inner tube area that was exposed to gas increased as the area exposed to liquid decreased. Since the liquid concentration at the liquid-tube interface was 1,448 g/L (a very high value compared to the gas concentration of 3.4 g/L) and the permeation rate did not change greatly over the life of the tube, the permeation mechanism had to be primarily that of gas permeating through the FEP Teflon® plastic tube.

The NO₂ gas permeation tube was held in a Pyrex® glass U-tube in a constant 20 °C water bath kept at a tolerance of +0.1 °C and -0.1 °C. The inlet side of the U-tube was filled with glass beads to promote temperature stabilization with the dry nitrogen carrier gas. The outlet side of the U-tube held the permeation tube, and Teflon®-lined plastic screw tops sealed the tops of the U-tube. Dry nitrogen carrier gas constantly flowed through the U-tube and over the permeation tube to remove the permeated gas. Stainless steel fittings and tubing connected the U-tube to 6.4-mm inlet and outlet glass tubes. A pressurized nitrogen cylinder contained dry nitrogen carrier gas, which was fed through a molecular sieve-drying column, through a secondary pressure regulator, and through a precision needle valve to maintain the constant dilution gas flow over the permeation tube at 100 mL/min.

Once or twice each week throughout the life of the permeation tube, it was removed from the U-tube holder and weighed on a Mettler-Toledo H51AR semimicro analytical balance having a sensitivity of 10 µg. The tube masses and the measurement times and dates were recorded. From these repeated weight measurements, the rate of NO₂ tube loss was calculated in grams per hour. At the 20 °C bath temperature over a period of several months, the weight loss rate varied from an initial value of 4.5×10^{-4} g/hr to a final value of 3.9×10^{-4} g/hr. Since the weight loss of the tube equaled the gaseous NO₂ delivered to the test device, the NO₂ gas concentration was calculated from the rate of tube weight loss and the measured total gas dilution flow.

CONSTANT PERMEATION RATES

Although VICI Metronics (the manufacturer) states that during the life of the tube at a 30 °C temperature, the permeation rate is relatively constant (within ±2%), this has not been our experience while working at 20 °C. In our tests, the measured permeation rates decreased as the tube aged, almost in proportion to the change in tube liquid level. The boiling point of the liquid in the NO₂ tube is stated to be 21.2 °C. At 20 °C, the liquid was primarily colorless dinitrogen tetroxide (N₂O₄) with a small amount of dissolved brown NO₂. The gas phase was primarily reddish-brown NO₂. In light of the demonstrated nonconstant permeation rate, we measured, at least weekly, the actual NO₂ permeation rate at 20 °C over the life of the tube. This was done to determine the current loss rate that we used for later calculation of the NO₂ concentration at a given time with a given total airflow.

The manufacturer stated that trace water accumulation, during both the tube run and the weighing operations, might explain part of the reduced permeation rate for the NO₂ system. Therefore, to reduce the water content of our nitrogen purge gas, a 22.9-cm-long and 2.5-cm outside diameter molecular sieve water trap from Scott Specialty Gases of Plumsteadville, PA, was placed after the regulator of the pressurized gas cylinder. The generation of standard NO₂ mixtures could conveniently be done if the weight loss of the tube was continually measured over the life of the permeation system. Accuracy of the weight measurement required the use of a semimicrobalance with at least an 8-g capacity. In addition, accurate airflow measurements with a bubble transit time gas flow system, along with reliable temperature and atmospheric pressure instruments, were used to calculate the actual test gas concentrations.

To form a desired concentration for calibration, we mixed the permeated NO₂-in-nitrogen carrier with additional nitrogen or with dilution air. We controlled the quantity of additional nitrogen- or air-dilution mixtures with a control system using model FC-261 mass flow controllers from Tylan Corp. of Carson, CA. This flow system was assembled under a previous research effort by the U.S. Bureau of Mines [Carpenter et al. 1983]. For each specific gas concentration desired, the dilution gas flows were set by adjusting mass flow controller voltage and then measured with a Gilibrator wet-test bubble meter made by Gilian Sensidyne, Clearwater, FL. The total gas flow was the sum of the nitrogen flow over the tube and the diluent gas flow. The equation for the diluted gas concentration is

$$C_F = (w/t) \frac{TG}{FP}, \quad (3)$$

where C_F = diluted gas concentration, ppm;
 w/t = weight loss rate, g/hr;
 T = absolute temperature, K;
 F = total gas flow rate, mL/min;
 P = pressure (usually atmospheric), mm Hg;
 and G = constant containing standard temperature, pressure, and molecular weight values 22.6079×10^6 .

As an example, at a measured permeation loss rate of 4.5×10^{-4} g/hr, a test temperature of 294 K (21 °C), a pressure of 737 mm Hg, and a total gas flow of 1,000 mL/min, the NO₂ concentration was 4.07 ppm. The tube permeation rate at 293 K (20 °C) was sufficient to generate NO₂ concentrations from 1 ppm at a total combined gas flow of 3,600 mL/min to 7 ppm at a total combined gas flow of 500 mL/min.

The final test-gas humidity was adjusted by varying the ratio of two mass-controlled airflows, one dry and one wet, to form the final airflow. Wet air was generated by running the air through a water bubbler. The humidified diluent gas was added to the nitrogen and NO₂ mixture so that the gas phase NO₂ did not contact liquid water. If it had, the gaseous NO₂ would have been lost by dissolution in the liquid water.

RESULTS

INSTRUMENT RESPONSE TO NO₂

Once specific gas mixtures in nitrogen and air carriers were created, the next step was to examine the responses of a commercially available NO₂ monitor in both nitrogen and air carrier gases. In these tests, over 10-min intervals, an Industrial Scientific Corp. TMX412 monitor measured the response to permeation-derived NO₂ in both air-diluted and nitrogen-diluted gas mixtures. Test results are shown in Table 1. The TMX412 monitor included the City Technology 4NT sensor. It gave equal indicated ppm results for NO₂ mixtures whether in air or in nitrogen diluents. The resulting coefficient of determination R² and power regression equations are shown in Figure 1.

These tests were repeated using a two-electrode membrane limited-diffusion NO₂ sensor made by Crowcon Detection Instruments Ltd., Milford, OH. The results of these tests are shown in Table 2. As in the previous tests, the Crowcon sensor indicated that the measured concentrations were essentially the same whether in nitrogen or in air mixtures. The resulting coefficient of determination R² and power regression equations for the Crowcon are shown in Figure 2.

Table 1.—TMX412 NO₂ monitor responses using NO₂-nitrogen and NO₂-air mixtures at selected flow rates

Test	NO ₂ in nitrogen		NO ₂ in air	
	Flow, mL/min	NO ₂ , ppm	Flow, mL/min	NO ₂ , ppm
1	1,851	2.2	1,843	2.2
2	943	4.3	928	4.4
3	630	6.2	618	6.3
4	403	9.4	378	10.0

Table 2.—Crowcon NO₂ monitor responses using NO₂-nitrogen and NO₂-air mixtures at selected flow rates

Test	NO ₂ in nitrogen		NO ₂ in air	
	Flow, mL/min	NO ₂ , ppm	Flow, mL/min	NO ₂ , ppm
1	1,845	1.86	1,845	1.82
2	935	3.59	935	3.57
3	625	5.39	625	5.43
4	402	8.38	402	9.02

The generated diluted NO₂ gas ppm concentration was calculated from the Equation 3 gas flow rate. To simplify, Equation 3 can be rewritten as follows:

$$Q_A \times F = C, \quad (4)$$

where C = constant.

For specific instruments, a calibration factor can be incorporated into the constant of Equation 4 by using the indicated

NO₂ value rather than the value obtained mathematically in Equation 3, as follows:

$$Q_I \times F = C', \quad (5)$$

where Q_I = indicated NO₂ concentration, ppm;
and C' = C multiplied by a calibration factor for the specific instrument being evaluated.

Equation 5 is used to generate the data in Table 3, which shows the TMX412 indicated NO₂. The measured instrument gas flow found in Table 1 was multiplied by the indicated concentration. For these tests the values were almost constant, averaging 3,948 with a standard deviation of 122. It should be emphasized that these permeation tube tests involved all dry-gas mixtures. Test data have been found to change with the moisture content of the atmosphere in which the samples are obtained. The water dependence of the anode reaction indicated that the TMX412 NO₂ sensor is humidity-dependent. The average product value was 4,500 for humidified test mixtures having a room relative humidity of 25%. This value was again obtained by using Equation 5, multiplying the indicated concentration by the airflow. Comparing this higher C' value to dry gas mixtures, an increased sensitivity is indicated.

These tests show that there is no inherent difference in indicated NO₂ values when diluted by equally humidified mixtures of either nitrogen or air, at least for the TMX412 electrochemical NO₂ sensor. Thus, hypothesis 1 that the balance or dilution gas species either nitrogen or air containing oxygen alone caused gas values to differ is proven false.

Table 3.—TMX412 indicated NO₂ concentrations multiplied by flow rates in either nitrogen or air carrier gas

NO ₂ in nitrogen, ppm × mL/min	NO ₂ in air, ppm × mL/min
4,072	4,054
4,055	4,038
3,906	3,893
3,788	3,780

NO₂ CYLINDER TESTS

As previously stated, two cylinders of NO₂ calibration gases were obtained from local distributors. Each cylinder was labeled to contain 10 ppm of NO₂. One was diluted with air; the other, with nitrogen gas. Both cylinders were constructed of aluminum and had an aluminum-alloy, G-35-type on-off control valve, with a C-10 outlet fitting for coupling to a flow control regulator. Pressure in the cylinders was about 33.1 bars. The gas volume at 21 °C and one atmosphere pressure was 73.6 L. Cylinder No. 1, diluted with nitrogen, had an expiration date 1 year after its issue date, whereas cylinder No. 2, diluted with air, had a stated useful life of 6 months.

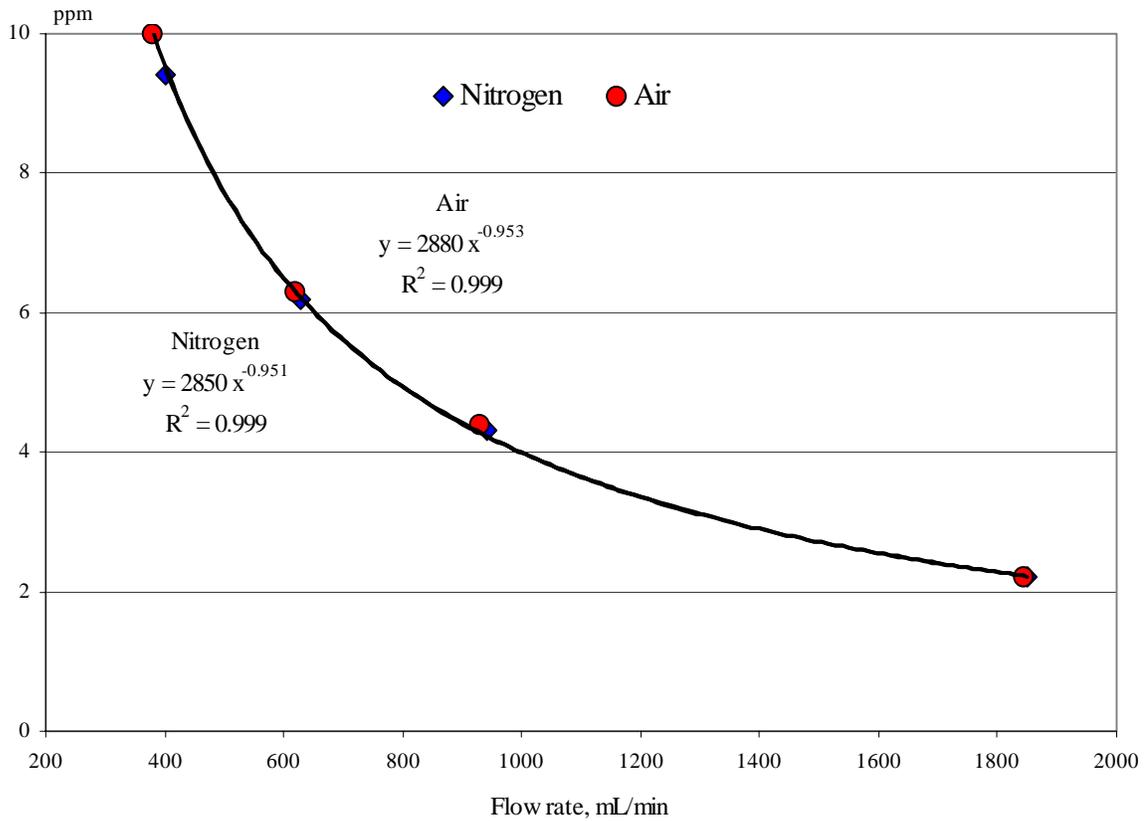


Figure 1.—Graph of TMX412 monitor response to NO₂-nitrogen and NO₂-air mixtures as a function of flow rate with curve-fit results.

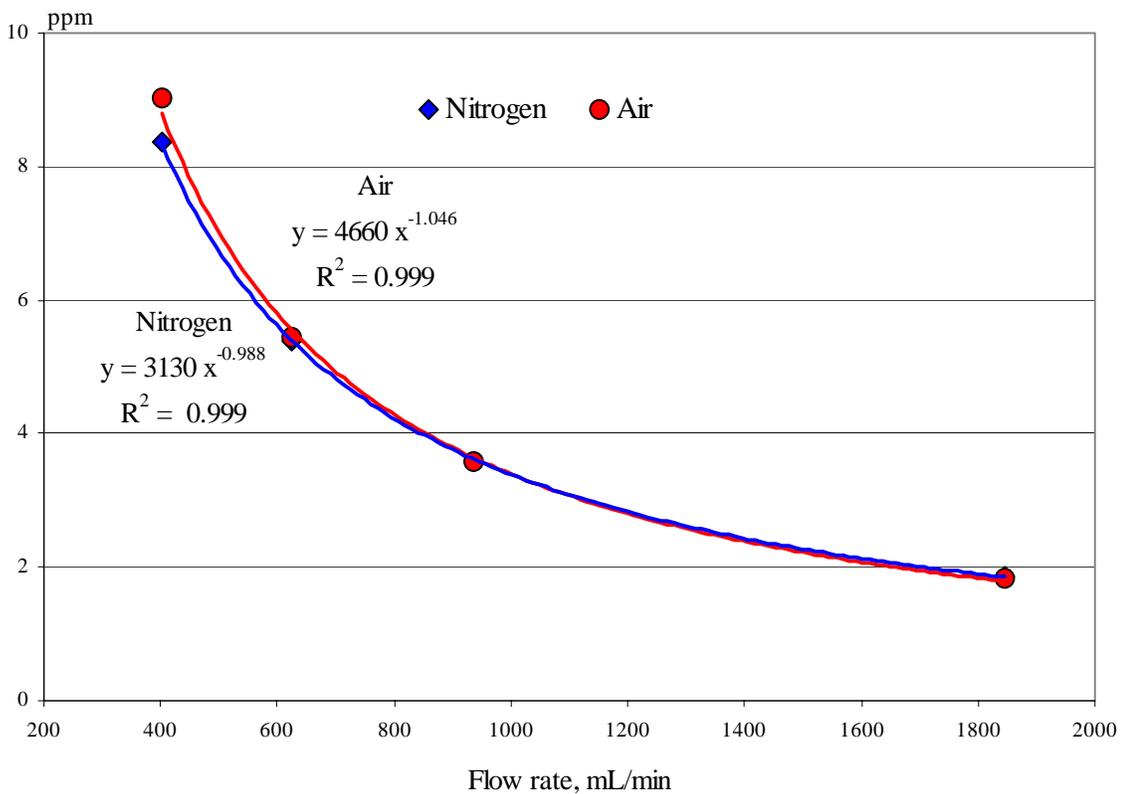


Figure 2.—Crowcon NO₂ monitor graphic results.

A handheld TMX412 monitor and a Crowcon fixed-point monitor were used to measure NO₂ concentrations in the two cylinders. In addition, both monitors measured a concentration of permeation-tube-generated NO₂ mixed with air. The actual cylinder concentrations were based on a calculation of each monitor's measurement. The derived proportion is expressed as

$$C = M_C \times \frac{P}{M_P}, \quad (6)$$

where C = cylinder calculated concentration, ppm;
 M_C = NO₂ monitor cylinder measurement, ppm;
 P = permeation tube calculated concentration, ppm;
 and M_P = NO₂ monitor permeation tube measurement, ppm.

The results are summarized in Table 4.

When the cylinder concentrations were measured in reference to a standard permeation tube-generated gas mixture, the average NO₂ concentrations of both calibration gas cylinders were less than the advertised 10-ppm value. The calculated average NO₂-in-nitrogen mixture value was 8.13 ppm (18% below the labeled value), and the NO₂-in-air mixture value was 6.88 ppm (31% below the labeled value). In comparing the average NO₂-in-nitrogen concentration to the NO₂-in-air concentration, the nitrogen carrier gas was found to be 22% higher. Based on these results, it now seems that hypothesis 2, the mixture is not stable in the air diluent, is correct and that hypothesis 3, initial concentrations were not the same, could be correct.

Table 4.—Parts per million comparisons of permeation tube NO₂ to measured NO₂ for cylinders balanced with nitrogen and air

Monitor	NO ₂ concentration, ppm		
	Cylinder No. 1 10 in nitrogen (label)	Cylinder No. 2 10 in air (label)	Permeation tube 4.20 (calculated)
TMX412 (measured)	9.50	8.10	5.10
TMX calculated cylinder	7.82	6.67	—
Crowcon (measured)	6.97	5.86	3.47
Crowcon calculated cylinder	8.44	7.09	—
Cylinder average	8.13	6.88	—

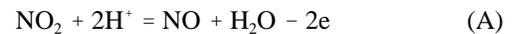
DISCUSSION AND CONCLUSIONS

Portable calibration gas cylinders are normally used to calibrate monitors for in-mine measuring of various gases. If one sets the response of a portable gas monitor to the cylinder stated value, for example 10 ppm, when the actual NO₂ concentration in the cylinder is lower, say, 5 ppm, then the in-mine measurements obtained would be 100% high. Thus, if one used this NO₂ gas cylinder to calibrate a field monitor, a mine site could be improperly cited for a STEL of 6 ppm NO₂ when the true exposure was actually only 3 ppm. To avoid such problems, it is necessary to use calibration gases with known values to calibrate monitors used in mine testing.

The differences in portable monitor responses to NO₂ calibration gases made either in air or in nitrogen were believed to be the result of one or more of three different causes. Hypothesis 1 suggested that there was a difference in response sensitivity of the sensors caused by the presence of either air or nitrogen as the carrier gas. This work found that portable NO₂ monitors with electrochemical sensors are similarly sensitive to equal concentration NO₂ mixtures diluted in either nitrogen or air.

A survey of the chemical reactions that occur within the sensor cell also suggests that the carrier gas either air or nitrogen

should not have a significant effect on NO₂ measurements. The chemical reactions occurring in the sensor cell are shown below. The half-cell reaction at the cathode (the working electrode) of the NO₂ sensor is the reduction of NO₂ to form nitric oxide (NO) and water (H₂O) in the sulfuric acid electrolyte, expressed as follows:



The half-cell reaction at the anode (the counterelectrode) is the oxidation of water (H₂O) to form oxygen (O₂) and hydrogen ions (H⁺):



The net reaction for the total cell is the sum of the two half reactions, the reduction of NO₂, and the production of nitric oxide and oxygen:



The two electrode reactions require only NO₂ and water. Thus, the NO₂ sensor should work equally well in nitrogen or in air calibration gas mixtures since this cell does not use oxygen as a reactant in the total electrode reaction.

Hypothesis 2 suggested that, if the initial gas concentrations were equal in both cylinders, the gas mixture with air decays more rapidly than the gas mixture with nitrogen. This was found to be true for 1-month-old gas cylinders if both mixtures had been originally filled to the same initial gas concentrations. We would suspect that both mixtures were originally designed to be made up to the same concentration since both were labeled as initial 10 ppm. There is no reason to suggest that gas mixtures of NO₂ in air with oxygen should not be stable, for NO₂ does not decompose to NO at room temperatures. Instead, if the air in the cylinder contained water, then the NO₂ could react with the metallic cylinder walls to form N₂, which is a more plausible reason for loss of NO₂ concentration in the aluminum alloy cylinder.

Hypothesis 3 suggested that the initial mixes of the calibration gases were not made to equal concentrations. Since we do not have access to the procedures used by the manufacturer nor specific data on the preparation of cylinders, we cannot prove this hypothesis.

In general, the NO₂-in-air calibration system is preferred for field use since multigas monitors containing in addition an oxygen sensor may be used at worksites together with the NO₂ sensor. If calibration of the NO₂-sensing portion of a multigas instrument is performed in the nitrogen carrier system, the oxygen sensor display will indicate 0%, causing the instrument to alarm with both audible signals and flashing lights. The operation of these alarms requiring battery power during calibration may significantly reduce the charged capacity of the instrument battery and thus limit the subsequent monitor use time.

The measurements reported here are for only one commercial source of cylinder calibration gas. These findings should be confirmed with other calibration gas cylinder sources. Actual cylinder NO₂ concentrations should be calculated by checking the advertised gas concentration against either a primary certified gas mixture, possibly obtained from the National Institute of Standards and Technology or from a permeation tube source maintained at a laboratory site. In addition, we recommend that the actual gas concentration of portable NO₂ calibration cylinders be verified periodically or at least monthly. As previously explained, this pre- and post-calibration requirement becomes crucial prior to using NO₂ monitors for enforcement work.

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