HONEYWELL BWTM FLEX 4 SERIES

A Guide to NO/NO₂ Gas Sensing



NITRIC OXIDE & NITROGEN DIOXIDE GAS SENSING

Nitrogen oxide (NOx) can be found in applications ranging from tunneling, power generation, and manufacturing chemicals to the development of rocket fuels. Inhalation incidents are on the rise as these types of applications increase: the National Occupational Exposure Survey (NOES) estimates that more than one million U.S. workers are likely at risk for pulmonary irritants each year. While not explosive by itself, NO₂ can accelerate the burning of combustible materials, resulting in explosions caused by other chemicals or materials. Detection is key to minimizing accidents that can result in asset destruction to say nothing of impacting organization reputation and worker safety.

GAS OVERVIEW

While they are two different gases based on their elemental structure, nitric oxide (NO) and nitrogen dioxide (NO₂) are usually referred to together using the term "nitrogen oxides." Nitric oxide is a colorless, odorless gas; nitrogen dioxide is a reddish-brown gas with a sharp, sweetish, pungent odor.

Confusing? The explanation is simple but there is a difference. "O" is elemental oxygen while " O_2 " is a molecular form of oxygen, often called dioxygen, that occurs when two atoms of oxygen chemically bind together to form an oxygen molecule. Both elemental oxygen and dioxygen have different chemical and physical properties: Nitrogen dioxide is formed when nitric oxide reacts with ozone. So, NO can exist by itself only in environments that do not include ozone, and NO + ozone = NO_2 . NOx is often used as shorthand for both types of gases.

NO is a deadly air pollutant generated by fossil fuel-powered engines in any number of markets and applications as well as by power plants. When a mixture of air and hydrocarbon fuel is burned in an internal-combustion engine or a power plant, the ordinarily inert nitrogen in the air combines with oxygen at very high temperatures – or when exposed to electric sparks – to form nitric oxide. More readily, NO can result from the interaction of diluted nitric acid with copper or mercury.



The nitric oxide and hydrocarbon vapors that are then emitted undergo complex photochemical reactions in the lower atmosphere to form various secondary pollutants called photochemical oxidants, which make up photochemical smog. Nitric oxide combines with water vapor in the upper atmosphere to form nitric acid, one of the components of acid rain (rain occurs when air rises into the upper atmosphere and cools, causing water vapor to condense into water droplets that fall from clouds as rain when the air becomes saturated).

Heightened levels of atmospheric nitric oxide resulting from transportation and industrial activity have also been shown to be one of the causes of gradual depletion of the ozone layer in the upper atmosphere. Sunlight causes nitric oxide to react chemically with ozone (O_3), thereby converting the ozone to molecular oxygen (O_2) and creating NO₂⁻¹.

Occupational hazards can be elevated in indoor spaces and as NO_2 exists in gaseous form both indoors and outdoors, inhalation is generally the primary route of exposure. Direct contact may occur in industrial settings with high gaseous NO_2 concentrations, which can lead to direct eye contact and irritation².

Interestingly, NO occurs naturally in humans and acts a "chemical messenger" that can help assist in internal bodily functions such as neurotransmission (information sharing between neurons), which is important in nervous system functions like digestion and memory. It may also encourage the release of hormones, including growth hormones and insulin. It can act as vasodilator in medical applications, where it is commonly used with a ventilator, often to treat newborn babies with respiratory failure caused by pulmonary hypertension. When inhaled, NO works by relaxing the smooth muscles to widen the blood vessels in the lungs³.

1. https://www.britannica.com/ science/nitric-oxide

2. https://www.ncbi.nlm.nih.gov/ books/NBK138707/

3.www.mayoclinic.org



WHY DEDICATED NO, SENSORS ARE IMPORTANT

Because it is present both indoors and outdoors and its sources are not always readily apparent, NO_2 exposure can be a problem even in industries such as construction and agriculture where many operations are performed out in the open air. It can be widely present even in everyday air and its odor is not always immediately detected, making it easy to encounter and inhale. So dedicated sensors to alert humans in the vicinity to its presence are very important.

 $\rm NO_2$ is toxic at varying levels, depending on the health and age of the person breathing it into their lungs. Inhalation may cause lung injury, asphyxiation, or chronic systemic effects. Once in the body, it can damage internal organs as well as unborn fetuses because it reacts with blood to form methemoglobin, which cannot bind to oxygen and results in a lack of oxygen to tissues and organs.

Low levels can cause a slight cough, mild fatigue, and nausea and eye, nose, and throat irritation are also common. At high concentrations, NO_2 can cause coughing, choking, headaches, abdominal pain, and shortness of breath. Workers may be unaware of ongoing exposures and longer exposures allow a higher concentration of nitrogen oxides to reach the lower airways, leading to delayed lower respiratory tract injury. These types of symptoms may linger for varying lengths of time after exposure, especially if the concentration was high, but even when exposure was relatively limited. This makes it necessary to measure not only the presence of NO_2 but its concentration levels as well⁴.

TABLE 1. NO2 REGULATION LIMITS			
Limit/Level	Туре	Organization	
0.5 ppm	AEGL-1 (8 hrs)	EPA	
6.7 ppm	AEGL-2 (8 hrs)	EPA	
11 ppm	AEGL-3 (8 hrs)	EPA	
5 ppm	С	OSHA	
1 ppm	Short term	NIOSH	

Source: EPA, NIOSH, and OSHA AEGL: Acute Exposure Level Guideline

Personal protective equipment (PPE) requirements by the U.S. Occupational Safety and Health Administration (OSHA) for exposure to NO and NO₂ are Level C, which means that on-site contaminants are unlikely to contact and/or affect the skin. However, as described earlier these are dangerous gases and therefore the requirements for respiratory protection against these chemicals are still quite rigorous; while optional, a two-way communication system and escape-hardened self-contained breathing apparatus (SCBA) are recommended:

TABLE 2. PPE RECOMMENDATIONS ⁵			
Category	Potential Risk		
Respiratory Protection	Positive-pressure, full-face piece self-contained breathing apparatus (SCBA) or Positive pressure supplied air respira- tor (SAR) with SCBA-type auxiliary escape respirator		
Clothing	Totally encapsulating chemical- and vapor-protective suit		
	Chemical-resistant inner suit (e.g., Tyvek coveralls)		
	Long underwear		
	Hard hat (worn under suit)		
Gloves	Inner and outer chemical-resistant gloves		
Boots	Chemical-resistant boots, with steel toe and shank		

4.https://www.ncbi.nlm.nih.gov/ books/NBK554539/

5. https://remm.hhs.gov/osha_epa_ppe.htm

The legal airborne permissible exposure limit (PEL) is 5 ppm as defined by OSHA, not to be exceeded at any time. NIOSH's recommended airborne exposure limit is 1 ppm, also not to be exceeded at any time.

The ACGIH (American Conference of Governmental Industrial Hygienists) recommends a TWA (time-weighted average) of 3 ppm for nitrogen dioxide and 5 ppm STEL (short-term exposure limit). NIOSH (National Institute for Occupational Safety and Health) recommends a PEL (permissible exposure limit) of 5 ppm.

The U.S. Environmental Protection Agency (EPA) maintains a national ambient air quality standard (NAAQS) for nitrogen oxides of 1-hour maximum daily concentration of 100 ppb and an annual standard at a level of 53 ppb⁶.

TABLE 3. NO REGULATION LIMITS			
Limit/Level	Туре	Organization	
1.0 ppm	AEGL-1 (8 hrs)	EPA	
2.5 ppm	AEGL-2 (8 hrs)	EPA	
6.6 ppm	AEGL-3 (8 hrs)	EPA	
10 ppm	TWA (8 hrs)	OSHA	
4.7 ppm	ST	NIOSH	

Source: EPA, NIOSH, and OSHA AEGL: Acute Exposure Level Guideline

As it relates to worker safety, it cannot be overemphasized that while not combustible itself, NO_2 can enable and accelerate the ignition of materials – including other airborne gases or particles – that are flammable, leading to serious fires, especially in oxygen-rich environments.

6.https://www.ncbi.nlm.nih.gov/ books/NBK554539/





APPLICATION OVERVIEW

While NO and NO_2 can be present in a wide variety of industrial applications, we'll take a look at a few specific ones as examples, and then present a summary of the many other industries where effective detection of these gases is important to worker safety and asset protection.

TUNNELING AND UNDERGROUND CONSTRUCTION

OSHA has issued a number of regulations related to the construction of underground tunnels, shafts, chambers, and passageways. As technologies advance, so do both the opportunities for improvement and the overall number of potentially dangerous situations to arise. Working under reduced light conditions, difficult or limited access and egress, and with the constant potential for exposure to air contaminants and the hazards of fire and explosion, underground construction workers face many dangers⁷.

A 2023 study on the presence and impact of nitrogen monoxide (NO) and nitrogen dioxide (NO₂) levels in mining and tunneling operations discussed concerns about compliance. The study focused on the use of a tunnel-boring machine (TBM) and Tier 3 emission locomotives in a recent tunneling project. (Tier 3 is an emissions standard recently developed by the US Environmental Protection Agency [EPA]; it establishes more stringent standards that require covered locomotives to have essentially zero fuel vapor emissions, new test procedures, and a new fuel/ evaporative system leak emission standard over a useful life of 150,000 miles or 15 years, whichever occurs first⁸.

As explained earlier, nitric oxide (NO) is inherently unstable in the air and can spontaneously oxidize to NO_2 . In tunnels, it originates primarily from diesel engines burning fuel that react with airborne water vapor. TBMs are also equipped with emergency that are only used in power supply failures or for high voltage (HV) cable extensions, both of which are potentially hazardous situations when NO_2 is present.

TBMs are used in mining operations for many minerals, including tungsten, magnesium, dolomite, iron, and others, and they are also important when constructing underground tunnels for transportation purposes. They are preferred because their implementation does not require explosives, which are a major source of NO₂ emissions in tunneling construction activities.

A TBM's cutting wheel excavates the soil while also serving as support for the tunnel face to prevent settlement. Additives are then used to condition the excavated material for conveyance above ground. As the TBM advances – up to 50 feet per day – it places concrete segments that fit together to form a tunnel ring that will form the wall of the tunnel. The TBM also uses the rings it builds as traction to keep moving forward, pulling with it all essential equipment including a control room, grout, ventilation equipment, and other tools. At any given time, there are 8-10 people in the TBM to keep it operational.

Gas levels are indicated on the operator control cabin display and a horn signal is given when a limit value is exceeded to warn all personnel working with the TBM. Gas monitoring systems include electrochemical sensors for NO_2 gas detection with specific linearity, range, and resolution information. The TBM stores the average gas concentration during the excavation cycle, and every time the TBM operator presses the ring-built button, the average gas concentration per ring is recorded.



NO2

^{7.}https://www.osha.gov/sites/default/ files/publications/osha3115.pdf

^{8.} https://dieselnet.com/ standards/us/loco.php

As with any industrial operation, continuous productivity improvements are important in underground construction and tunneling operations. It's no surprise, then, that a clear relationship can be observed between the TBM's production and an increase in NO_2 levels. As production increases, the number of locomotives required for transporting rings, grout, and other materials increases, leading to higher NO_2 emissions. Additionally, the study showed a correlation between the planned tunnel length and NO_2 levels. As the tunnel length increases, the TBM's performance improves, but this improvement is accompanied in NO_2 levels. A decrease in air flow rate further contributes to safety challenges.

All told, the study provided new data on the complexity of NO₂ emissions in tunnel construction projects and proved important in emphasizing the necessity for the meticulous management of TBM production, locomotive usage, and ventilation to mitigate the impact on air quality and safeguard worker health, preferably prior to the time that the length of the tunnel begins to change any requirements for updated standards. When emission standards from TBM equipment and locomotives is not optimal, there are repercussions of a significant decrease in occupational exposure limit (OELV) levels, especially concerning NO₂ concentrations.

With growing populations and the need for efficient transportation solutions, cities are increasingly turning to TBMs to expedite the construction of subway tunnels for urban metro systems. Notable examples include the London Crossrail project and the New York City Second Avenue Subway, both of which have utilized TBMs for construction.

TBMs have also been instrumental in the development of hydropower projects and complex underground energy storage facilities for the efficient generation and storage of renewable energy. For instance, TBMs have been employed in the construction of hydropower tunnels in China's Three Gorges Dam project, the world's largest hydropower plant.





As innovations for new TBMs and types of locomotives (Tier 4 and 5) become more prevalent, tunnels will be able to be constructed bigger, better, and longer. They already have improved worker safety through automating and speeding up many of the process steps in creating a tunnel and are also "greener" due to fewer emissions overall as well as not necessitating as much traffic re-routing above ground, which can lead to more emissions from vehicles on roads.

Autonomous TBDs and robotic equipment may result in even greater improvements but the necessity for effective measurement of NO_2 will still exist as long as NO_2 does, which is to say, for the foreseeable future of tunneling and mining⁹.

And always remember...oxygen!

It takes just 30 seconds of oxygen withdrawal for an individual to lose consciousness and at atmospheric levels as low as 5% to 15% methane becomes highly combustible and even explosive. In addition, carbon monoxide levels as low as 0.1% can be fatal after only a few minutes of exposure.

So while monitoring NO_2 is obviously very important in tunneling operations, oxygen is its twin in terms of protecting assets and workers. As oxygen decreases, the potential for increased concentrations of noxious gases and other contaminants such as dust or flying debris also increases the potential for hazardous conditions.

Continuous air quality monitoring can never cease in order to alert workers of increased toxic conditions, be those from more noxious fumes from increased production or leaks or less oxygen – or both. Workers should have access to personal protective equipment (PPE) including not only hard hats and safety goggles but self-contained breathing apparatus (SCBA) as conditions warrant.

Effective ventilation is necessary to ensure a safe and healthy work environment underground. Proper airflow helps control dust, fumes, and other harmful particles. Dust control measures such as water sprays or dust collection systems can minimize respiratory problems and enhance worker safety as well as helping to reduce flammable conditions since even though not combustible on its own, NO₂ can exacerbate combustion of flammable materials such as methane that are often found in underground applications^{10,11}.

POWER GENERATION

The presence and concentration of toxic gases both within power plants and their emissions from those plants are important to the power generation industry.

Inside power plants, their complex operations include high-voltage equipment, flammable materials, and hazardous chemicals. Even a split-second lapse in safety protocols or equipment failure can have catastrophic consequences, resulting in environmental damage, significant infrastructure damage, worker injuries, and even fatalities.

No one understands the significance of power plant safety better than those doing the job and reporting on their challenges: according to the Bureau of Labor and Statistics, the power generation industry had 18 fatalities and more than 5,000 reportable injuries and illnesses between 2019 and 2021. Additionally, OSHA reports that power generation, transmission, and distribution workers face a fatality rate almost three times higher than the national average for all industries.

Most injuries occur as the result of fires, electrical accidents, exposure to hazardous materials, or falls. Highly flammable materials and the potential for electrical sparks create conditions for fires, and coal dust, hydrogen gas, and other materials pose high explosion risks. The high-voltage electrical systems in power 9.https://utilitiesone.com/advancesin-tunnel-boring-machines-forefficient-underground-construction

- 10. https://utilitiesone.com/essentialsafety-guidelines-for-workers-inunderground-construction-tunnels
- 11. https://www.mining-technology. com/sponsored/the-importance-ofatmospheric-monitoring-in-tunnels/

NO NO2

plants not only contribute to igniting fires but also electrical shocks and power outages and their associated hazards if circuits are disrupted. Fuels, lubricants, and chemicals must be labeled, stored, handled, and disposed properly to avoid gas leaks. In short, power plants are inherently dangerous workplaces that benefit substantially from proper use and placement of sensors that monitor and provide alerts when conditions escalate¹².

Outdoors, as power plants emit waste products from their operations into the environment, their interactions with those environments is also important to monitor and improve.

As previously noted, nitrogen dioxide (NO₂) is one of the common toxic air pollutants. The LC50 (Lethal Concentration for 50 % of those exposed) for one hour of NO₂ exposure for humans has been estimated as 174 ppm. The most common air pollutant, sulphur dioxide (SO₂), is mostly found as a mixture of sulfur oxides (SO_x). It is an invisible gas with an unpleasant, sharp smell and the maximum concentration for SO₂ exposures of 30 min to an hour has been estimated as 50 to 100 ppm. The main sources of SO₂ include burning of fossil fuels in power stations, oil refineries, other large industrial plants, motor vehicles and domestic boilers although it is also produced from natural sources like active volcanoes and forest fires.

As with NO₂, when SO₂ is released into the atmosphere it can cause harm to eyes, lungs and throats. It is also toxic to some plants, inducing visible injury and reducing yields. When combined with moisture in the air, SO₂ causes gradual damage to some building materials, such as limestone. SO₂ can readily dissolve in the water droplets in clouds, causing acid rain that affects the natural balance of rivers, lakes and soils, resulting in damage to wildlife and vegetation¹³.

While that may seem like a lot of hazards, clear paths to improvement have been demonstrated. The COVID pandemic, for example, presented a lot of challenges but at the same time, some remarkable opportunities. For example, relevant to NO_2 , take a look at the impact of reduced NO_2 gas concentrations as a direct result of less vehicle emissions...

Improvements continue to be made. From 2022-2023, emission rates at coal facilities for sulfur dioxide (SO₂) and nitrogen oxides improved by 7 % and 3 %, respectively. Roughly half of this improvement resulted from units more effectively operating their existing controls and half resulted from increased utilization of more highly controlled units.

12.https://hsi.com/blog/power-plant-safety 13.https://www.mdpi.com/1424-8220/19/4/905)



NO NO2 Compared to 2022, the 2023 data show a 15 % decrease in NOx emissions, a 24 % decrease in SO₂ emissions, a 7 % decrease in carbon dioxide (CO₂) emissions, and a 17 % decrease in mercury emissions. Additionally, ozone season (May 1 to September 30) NOx emissions decreased by 9 % nationwide and 18 % for the ten states implementing the Good Neighbor Plan¹⁴.

Between 1990 and 2023, annual emissions of SO₂ from power plants fell by 96 % and annual emissions of NOx from power plants fell by 90 %. In 2023, sources in both the Cross-State Air Pollution Rule annual program and the Acid Rain Program together emitted 0.65 million tons of SO₂, a reduction of 11.2 million tons from 1995 levels. Additionally, in 2023, sources in these programs together emitted 0.64 million tons of NOx, a 5.2-million-ton reduction from 1995 levels. While complying with programs to reduce SO₂, NOx, and mercury, power plants reduced their CO₂ emissions by 28 % between 1995 and 2023¹⁵.

In order for scrubbers and other mitigating equipment to maximize their cleaning potential before emissions are released into the environment, power plant emissions have to work as effectively as possible. In comparison to gas detection techniques like optical, acoustic, and gas chromatographic methods, electrochemical sensing is the most popular technique for ambient toxic gas monitoring. The key advantages of electrochemical detection are having low energy linear output with high resolution, good selectivity and repeatability, ppm level detection with high accuracy, and being more inexpensive than other techniques. In the past, electrochemical sensors have been overly sensitive to temperature fluctuations but that problem has essentially been minimized in advanced sensing materials being used in more recent devices.

The future development of toxic gas detection methods is expected to be a vital technology for the emerging Internet of Things (IoT) era, where gas sensors will need to be ultra-low power, low cost, long lifetime, integrable into electronic circuits, mini-sized and often wireless gas sensors for remote air quality monitoring and enhanced automated systems¹⁶.



^{14.}https://www.epa.gov/newsreleases/epaannounces-final-good-neighbor-plan-cutharmful-smog-protecting-health-millions

^{16.} https://www.mdpi.com/1424-8220/19/4/905



^{15.} https://www.epa.gov/newsreleases/epareleases-2023-power-plant-emissions-data

OTHER APPLICATIONS

NO₂ is used in many other markets and applications in addition to those reviewed here. A classic example of nitrogen dioxide toxicity is found in agriculture and is known as "silo filler's disease." Silo filler's disease occurs when the nitrogen dioxide that forms during the decomposition of agricultural organic matter silage (typically corn or other grains) is inhaled. The most significant risk of overexposure occurs within the first month after the silos are filled. Oxides of nitrogen are heavier than air and gather on top of the silage so exposure occurs when a worker enters a silo or opens the hatch without proper respiratory protection. This can result in shortness of breath, cough, or even symptoms consistent with acute respiratory distress syndrome (ARDS).

In a more unusual example, NO_2 can be produced by ice-resurfacing machines (so-called "Zamboni machines") in their emissions as they combust propane. In enclosed spaces without enough ventilation, such as indoor ice-skating rinks, this can be dangerous. This happened in 1987 when 116 people attending an ice hockey game in Minnesota reported various symptoms from cough to coughing up blood due to significant nitrogen dioxide exposure. So, hockey arenas can be added to a list of NO_2 sensor applications¹⁷.

NO and $\mathrm{NO}_{\rm 2}$, as well as $\mathrm{SO}_{\rm 2}$, are used in many other ways beyond those outlined here, including:

- Underground mining
- Agriculture
- Fertilizer production
- Underground parking garages
- Construction and demolition sites that use diesel or gasoline fueled trucks, excavators, loaders, bulldozers, mobile cranes, off-road machinery, and static engines such as pumps and electricity generators
- Wastewater treatment plants
- Electroplating
- Electric arc welding
- Engraving,
- Petroleum production and refining
- Pulp and paper processing
- Distilleries
- Where used as a nitrating agent for organic compounds, oxidizing agents, rocket fuel, and flour bleaching agents
- Indoor kerosene or gas space heaters and gas stoves

17.https://www.ncbi.nlm.nih.gov/ books/NBK554539/



NO NO2

OUR SOLUTION HONEYWELL BWTM FLEX 4 SERIES

With a choice of 12 different sensor types, the Honeywell BW[™] Flex protects workers from multiple gas hazards, in a small, rugged, and easy to use device. BW[™] Flex keeps specialists operating in confined spaces, or general workers on a plant, safe from gas hazards while making safety compliance for the business easy.

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- **Reliable** The Honeywell BW[™] Flex can be used in potentiality explosive atmospheres. Indoor, outdoor, onshore or offshore
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For the detection of the most common gas hazards including: Flammable gas (LEL), oxygen (O_2), carbon monoxide (CO), hydrogen sulphide (H_2 S), carbon dioxide (CO_2), sulphur dioxide (SO_2), chlorine (Cl_2), nitric oxide (NO), nitrogen dioxide (NO_2), and hydrogen cyanide (HCN)



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