

Real time detection of nitrogen dioxide: Issues, concerns, setting alarms and interpreting data

Bob Henderson

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Robert E. Henderson

- Speaker Biography

Bob Henderson is the President of GfG Instrumentation, Inc., a leading supplier of portable and fixed gas detection products. GfG's instruments are used in atmospheric monitoring applications all over the world.

Robert has over 38 years of experience in the design, marketing and manufacture of gas detection instruments. Robert is a past Chairman, and in-coming Chair of the AIHA Real Time Detection Systems Technical Committee. He is also a past Chairman and current member of the AIHA Confined Spaces Committee. He is also a past Chair of the Instrument Products Group of the ISEA. Robert has a BS in biological science and an MBA from Rensselaer Polytechnic Institute.

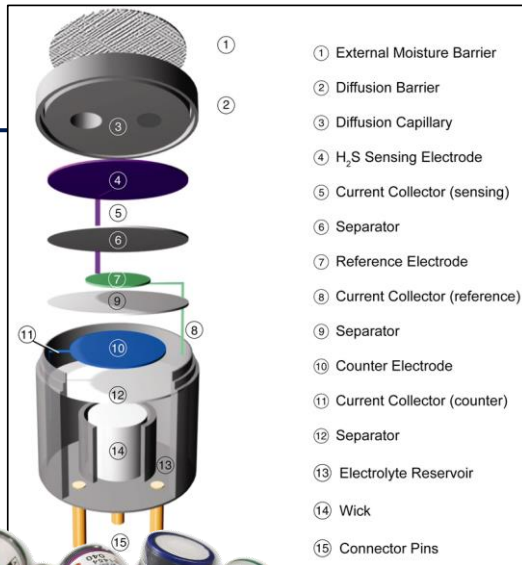
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Substance-specific electrochemical sensors

- Gas diffusing into sensor reacts at surface of the sensing electrode
- Sensing electrode made to catalyze a specific reaction
- Use of selective external filters further limits cross sensitivity



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Typical Electrochemical Detection Mechanism

H₂S Sensor:

Hydrogen sulfide is oxidized at the sensing electrode:

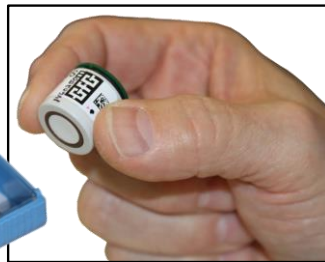
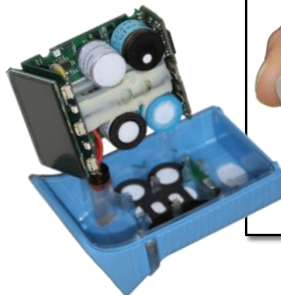


The counter electrode acts to balance out the reaction at the sensing electrode by reducing oxygen present in the air to water:



And the overall reaction is: $\text{H}_2\text{S} + 2\text{O}_2 \longrightarrow \text{H}_2\text{SO}_4$

City Technology 4HS Signal Output: 0.7 μA / ppm H₂S

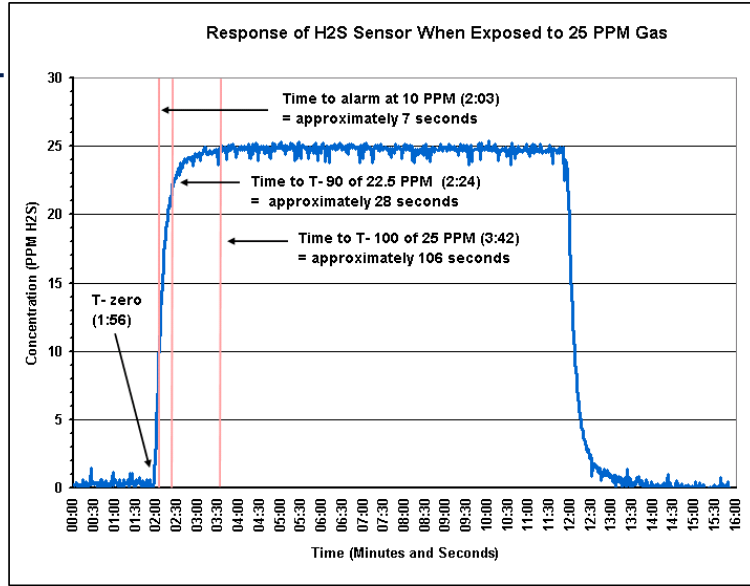


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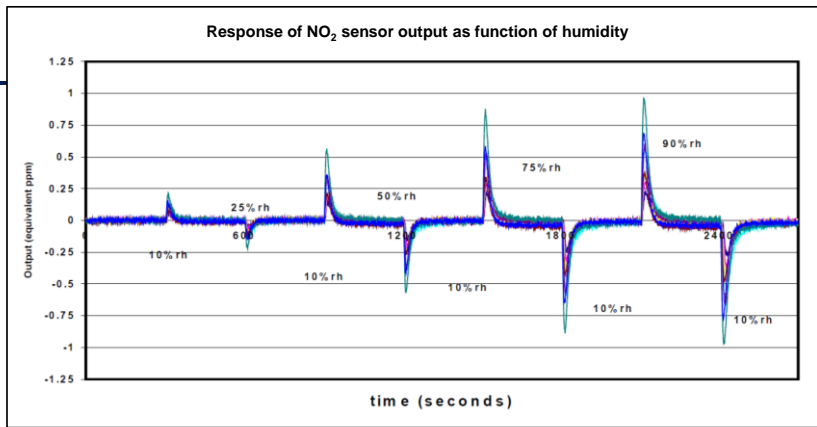
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Electrochemical Sensor Performance



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Effects of humidity on EC sensors

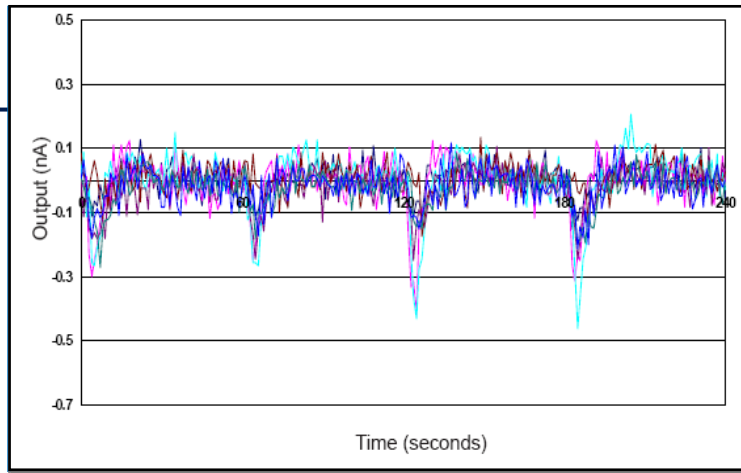


- Sudden changes in humidity can cause "transients" in readings
- Sensor generally stabilizes rapidly
- Avoid breathing into sensor or touching with sweaty hand

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Signal to noise ratio of EC sensors

- Electrochemical amperometric gas sensors have a background current in addition to the current from the oxidation or reduction of the gas to be detected
- This background current is commonly referred to as zero current or "noise"
- Noise is random (stochastic) fluctuation of the electrical signal around a central value
- Noise is measured by the Root-Mean-Square (RMS) value of the fluctuations over time.
- The SNR is defined as the average over time of the peak signal divided by the RMS noise.
- When significant, can interfere with measurements at low gas concentrations.



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Different sensors can have different performance characteristics

- Sources for zero current "noise" include:
 - Anodizing or cathodic reduction of the working electrode
 - Electrochemical oxidation or reduction of the sensor electrolyte
 - Electrolyte contamination by the working electrode
 - Reduction of oxygen in the ambient air
- Typical amperometric toxic gas sensor is three electrode design
 - The auxiliary (reference) electrode has the same catalyst structure as the working electrode but is not in contact with the measuring gas
 - By subtracting the current of the auxiliary electrode from the total current of the working electrode, noise is removed from the measurement signal
- Usability of sensor at low concentrations defined by RMS noise value
 - Some NO₂ sensors limited to 0.1 ppm
 - Some NO₂ sensors offer better resolution down to 0.05ppm or 0.02 ppm
 - More limited measurement range is often tradeoff for better resolution

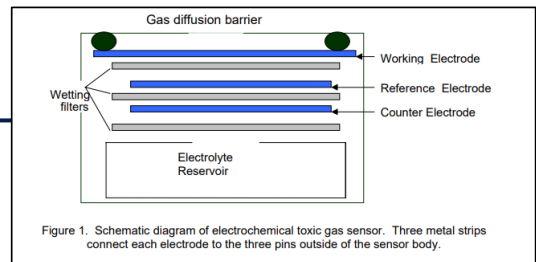


Figure 1. Schematic diagram of electrochemical toxic gas sensor. Three metal strips connect each electrode to the three pins outside of the sensor body.

Courtesy Alphasense

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Oxidizing vs. reducing gases

- Sensors for reducing gases:
 - Detection reaction generates current at working electrode; overall reaction consumes O_2
 - H_2S
 - CO
 - SO_2
 - PH_3
- Sensors for oxidizing gases:
 - Detection reaction consumes power at working electrode; overall reaction generates O_2
 - Cl_2
 - NO_2
 - O_3
 - HCl
 - HF
 - ClO_2



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Oxidizing gas sensor detection reaction

- Chlorine sensor detection reaction:
 - Sensing electrode:

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$
 - Counter electrode:

$$\frac{1}{2} O_2 + 2H^+ + 2e^- \longrightarrow H_2O$$
 - Overall:

$$Cl_2 + H_2O \longrightarrow 2Cl^- + \frac{1}{2}O_2 + 2H^+$$
- Nitrogen dioxide detection reaction:
 - Sensing electrode:

$$NO_2 + 2H^+ + 2e^- \longrightarrow NO + H_2O$$
 - Counter electrode:

$$\frac{1}{2} O_2 + 2H^+ + 2e^- \longrightarrow H_2O$$
 - Overall:

$$NO_2 \longrightarrow NO + \frac{1}{2} O_2$$



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**Select performance characteristics typical
electrochemical SO₂ sensor at 20°C**

Signal: 0.5 ± 0.1 µA/ppm

Linear signal over wide range:

0.1 µA = 0.2 ppm

1.0 µA = 2.0 ppm

4.0 µA = 8.0 ppm

Measurement range: 0-20 ppm SO₂

Resolution (electronics dependent): 0.1 ppm

Response Time (T₉₀): < 25 seconds

**Relative responses of City Technology 4S – Rev. 2 sulfur
dioxide (SO₂) sensor at 20°C**

Gas	Concentration used (ppm)	Reading (ppm SO ₂)
Carbon monoxide (CO)	300	< 1
Nitric oxide (NO)	50	0 to 5.0
Nitrogen dioxide (NO ₂)	6	< -10
Hydrogen sulfide (H ₂ S)	25	< 0.1
Chlorine (Cl ₂)	5	< -2
Ammonia (NH ₃)	20	0
Hydrogen (H ₂)	400	< 1
Hydrogen cyanide (HCN)	10	< 5
Acetylene (C ₂ H ₂)	10	< 30
Ethene (C ₂ H ₄)	50	< 45

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**Select performance characteristics typical
electrochemical NO₂ sensor at 20°C**

Sensoric 4ND Citicel is three electrode design

Linear signal: 0.60 ± 0.15 mA/ppm

Measurement range: 0-20 ppm NO₂

Resolution (electronics dependent): 0.1 ppm

0.012 µA = 0.02 ppm

0.03 µA = 0.05 ppm

0.06 µA = 0.1 ppm

Response Time (T₉₀): < 25 seconds

What about ozone?

Not listed on sensor data sheet

But interferes strongly (about 1.2)

Equivalent concentration O₃ produces higher reading than NO₂

Relative responses of Sensoric 4ND CiTiceL NO₂

Gas	Concentration used	Reading (ppm NO ₂)
Alcohols	1000	0
Carbon dioxide	5000	0
Chlorine	1	1
Nitric oxide (NO)	100	0.4
Sulfur dioxide (SO ₂)	20	-5
Hydrogen	3000	0

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Be aware of potential cross sensitivity issues!



- Incompatibility issues may make calibration difficult or impossible
- Sometimes better to install incompatible sensors in different instruments

G460 instrument #3, readings from coal seam vent, SO₂ and NO₂

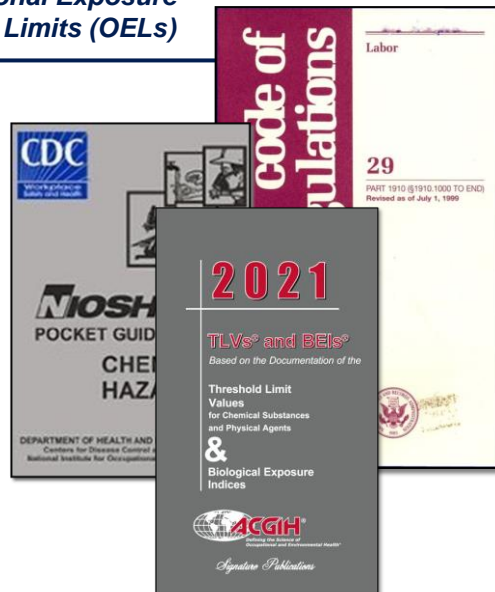


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Occupational Exposure Limits (OELs)

- Depend on jurisdiction and activity
- Sets limits for unprotected worker exposure to a listed toxic substance
- Limits for gases and vapors given in "Parts-per-Million" (ppm) concentrations
- Do not provide direct guidance for how to set instrument alarms!



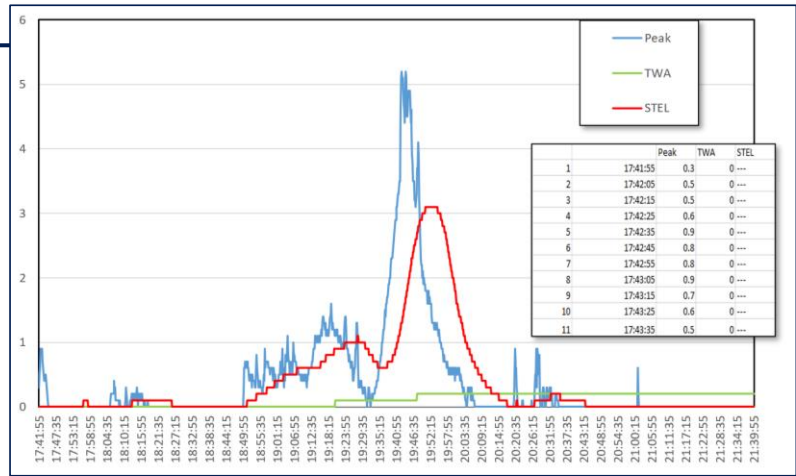
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Typical alarms in personal and multi-sensor gas detectors

- Gas alarms settable by user:
 - Peak (instantaneous) Low
 - Peak (instantaneous) High
 - STEL (15 minute)
 - TWA (8 hour)
- Non-user settable alarms:
 - Over limit concentration
 - Negative alarm
- Sometimes settable by user:
 - Measuring range
 - Resolution



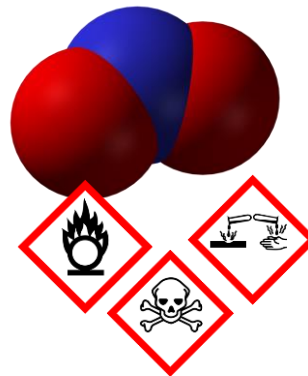
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Exposure limits for NO₂

- US OSHA PEL:
 - Ceiling = 5 ppm
- US NIOSH REL:
 - 15 min. STEL = 1.0 ppm
- Old TLV:
 - 8 hr. TWA = 3.0 ppm
 - 5 min. STEL = 5.0 ppm
- New 2012 TLV
 - 8 hr. TWA = 0.2 ppm



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ACGIH Guidance

For many substances with a TLV–TWA, there is no TLV–STEL.

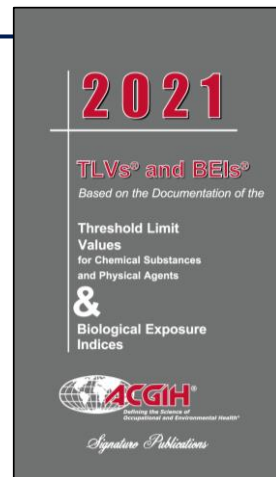
Never-the-less, short-term peak exposures above the TLV–TWA should be controlled, even where the 8-hour TLV–TWA is within recommended limits.

The following default short-term exposure limits apply to those TLV–TWAs that do not have a TLV–STEL:

Transient increases in workers' exposure levels may exceed 3 times the value of the TLV–TWA level for no more than 15 minutes at a time, on no more than 4 occasions spaced 1 Hour apart during a workday, and under no circumstances should they exceed 5 times the value of the TLV–TWA level when measured as a 15-min TWA.

In addition, the 8-hour TWA is not to be exceeded for an 8-hour work period.

This guidance on limiting peak exposures above the value of the TLV–TWA is analogous to that for the TLV–STEL, and both represent 15-minute exposure limits.



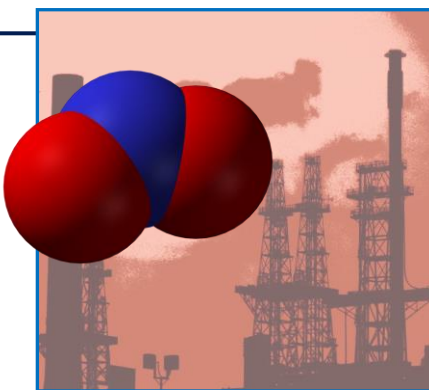
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Suggested alarm settings for NO₂

- Suggested alarms:
 - OSHA PEL or NIOSH REL:
 - Low: 3.0 ppm
 - High: 5.0 ppm
 - STEL: 1.0 ppm
 - TWA: 1.0 ppm
 - TLV®:
 - Low: 0.6 ppm
 - High: 1.0 ppm
 - STEL: 0.6 ppm
 - TWA: 0.2 ppm



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What should you do for extended work shifts?

- Most industrial hygienists use Brief and Scala model
 - Corrects for increased exposure time and decreased recovery time
 - Simple to use
 - Very conservative
- Adjusted TLV =

$$= \text{TLV} \times \frac{(8)}{h} \times \frac{(24 - h)}{16}$$

Where h = # of hours worked per day

- Model used for chemicals where the TLV® is based on acute or chronic toxicity and not for chemicals that have a TLV® based on irritation (i.e. Ammonia)
- For 12 hour shift according to this model the TWA TLV® limit should be reduced to one-half the 8-hour value

Datalogging parameters

- Number of stored intervals in internal memory – set by manufacturer
- Datalogging interval (generally 1 sec. to 1 hr.)
- Logged values per interval (typically):
 - User choice:
 - Peak
 - Average
 - Representative
 - STEL
 - TWA
- How are the time history alarm calculations affected by the choice of data-logging interval?
 - They're not!
 - PEL calculations are continuously updated by the instrument
 - The datalogging interval simply specifies how often the instrument stores a "snap-shot" of the current readings for the purposes of generating a printed report or database file of test results

	Peak	TWA	STEL						
1	17:41:55	0.3	0	---	60	17:51:45	0	0	---
2	17:42:05	0.5	0	---	61	17:51:55	0	0	---
3	17:42:15	0.5	0	---	62	17:52:05	0	0	---
4	17:42:25	0.6	0	---	63	17:52:15	0	0	---
5	17:42:35	0.9	0	---	64	17:52:25	0	0	---
6	17:42:45	0.8	0	---	65	17:52:35	0	0	---
7	17:42:55	0.8	0	---	66	17:52:45	0	0	---
8	17:43:05	0.9	0	---	67	17:52:55	0	0	---
9	17:43:15	0.7	0	---	68	17:53:05	0	0	---
10	17:43:25	0.6	0	---	69	17:53:15	0	0	---
11	17:43:35	0.5	0	---	70	17:53:25	0	0	---
12	17:43:45	0.4	0	---	71	17:53:35	0	0	---
13	17:43:55	0.5	0	---	72	17:53:45	0	0	---
14	17:44:05	0.4	0	---	73	17:53:55	0	0	---
15	17:44:15	0.5	0	---	74	17:54:05	0	0	---
16	17:44:25	0.4	0	---	75	17:54:15	0	0	---
17	17:44:35	0.3	0	---	76	17:54:25	0	0	---
18	17:44:45	0.2	0	---	77	17:54:35	0	0	---
19	17:44:55	0.1	0	---	78	17:54:45	0	0	---
20	17:45:05	0	0	---	79	17:54:55	0	0	---
21	17:45:15	0	0	---	80	17:55:05	0	0	---
22	17:45:25	0	0	---	81	17:55:15	0	0	---
23	17:45:35	0	0	---	82	17:55:25	0	0	---
24	17:45:45	0	0	---	83	17:55:35	0	0	---
25	17:45:55	0	0	---	84	17:55:45	0	0	---
26	17:46:05	0	0	---	85	17:55:55	0	0	---
27	17:46:15	0	0	---	86	17:56:05	0	0	---
28	17:46:25	0	0	---	87	17:56:15	0	0	---
29	17:46:35	0	0	---	88	17:56:25	0	0	---
30	17:46:45	0	0	---	89	17:56:35	0	0	---
31	17:46:55	0	0	---	90	17:56:45	0	0	0.1
32	17:47:05	0	0	---	91	17:56:55	0	0	0.1
33	17:47:15	0	0	---	92	17:57:05	0	0	0.1
34	17:47:25	0	0	---	93	17:57:15	0	0	0.1
35	17:47:35	0	0	---	94	17:57:25	0	0	0.1
36	17:47:45	0	0	---	95	17:57:35	0	0	0.1
37	17:47:55	0	0	---					
38	17:48:05	0	0	---					
39	17:48:15	0	0	---					
40	17:48:25	0	0	---					

So how accurate are the readings?

- Instrument manufacturers frequently state accuracy of +/- 5% of readings
- NO₂ sensor measurement range is typically 0 – 20 ppm
- If the instrument is set to display readings in ± 0.1 ppm increments:
 - From 0 – 2.0 ppm the accuracy is +/- 0.1 ppm, from 2.0 to 20 ppm the accuracy is +/- 5% of reading
- If the instrument is set to display readings in ± 0.02 ppm increments:
 - From 0 – 0.4 ppm the accuracy is +/- 0.02 ppm, from 0.4 to 20 ppm the accuracy is +/- 5% of reading
- What about designs that digitally filter readings near zero?
 - Some instruments have a “dead band” or digital filtering to reduce fluctuation in readings near zero
 - Affects visible readings but not the time history calculations or logged Peak values
 - Some designs introduce digital stickiness near zero, which decreases as measurement values rise, other designs use a dead-band that shows a reading of zero throughout the band
 - For instance, if the instrument resolution is 0.1 ppm and has a dead-band of +/-0.2 ppm, (two steps away from zero) visible readings will show 0 ppm whenever the signal is within this band, and the first visible reading above zero would be 0.3 ppm



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How does the accuracy of the cal gas affect the accuracy of the readings?

- Standard NO₂ cal gas with 10 ppm NO₂ is available with $\pm 3\%$ accuracy, 12-months shelf-life dating
- Using $\pm 3\%$ accuracy gas, when the resolution of the NO₂ sensor is 0.1 ppm, the new accuracy statement for the combined instrument and cal gas system becomes 0.1 ppm or $\pm 8\%$ of reading, whichever is greater
 - So from 0 – 1.25 ppm the accuracy is ± 0.1 ppm
 - From 1.25 – 20.0 ppm the accuracy is $\pm 8\%$ of reading
- When the resolution of the NO₂ sensor is 0.02 ppm
 - From 0 – 0.25 ppm the accuracy is ± 0.02 ppm
 - From 0.25 – 20.0 ppm the accuracy is $\pm 8\%$ of reading

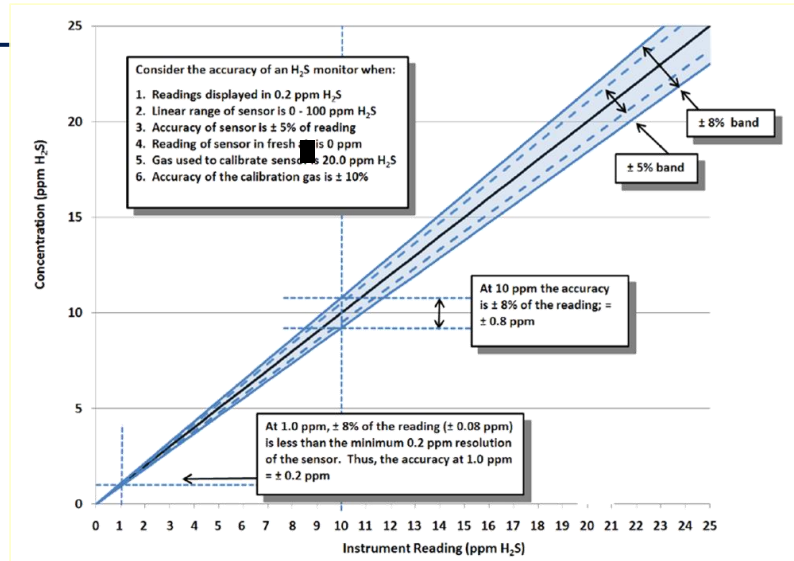


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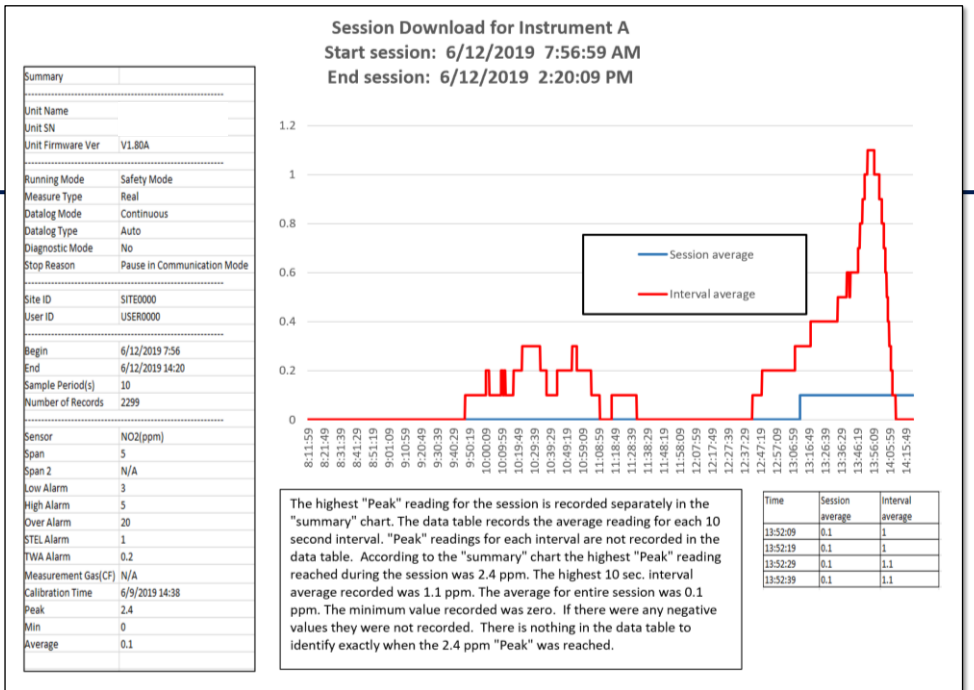
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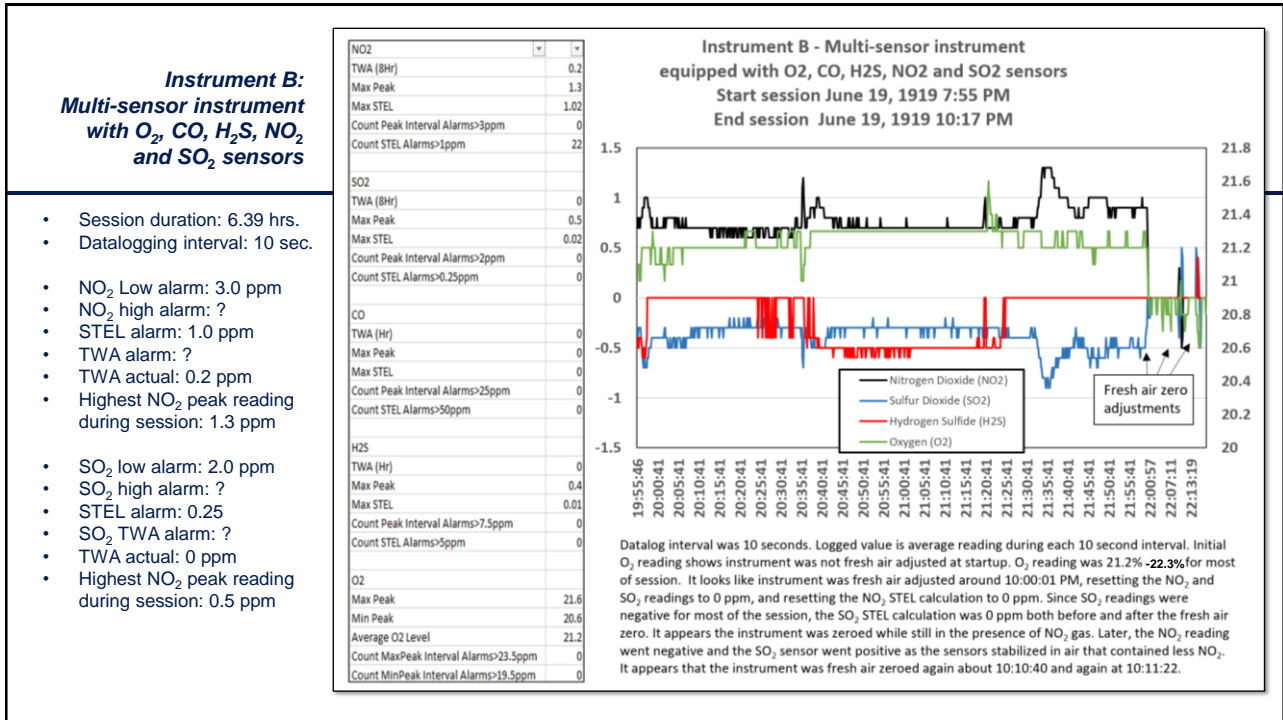
Combined effects of sensor and calibration gas accuracy



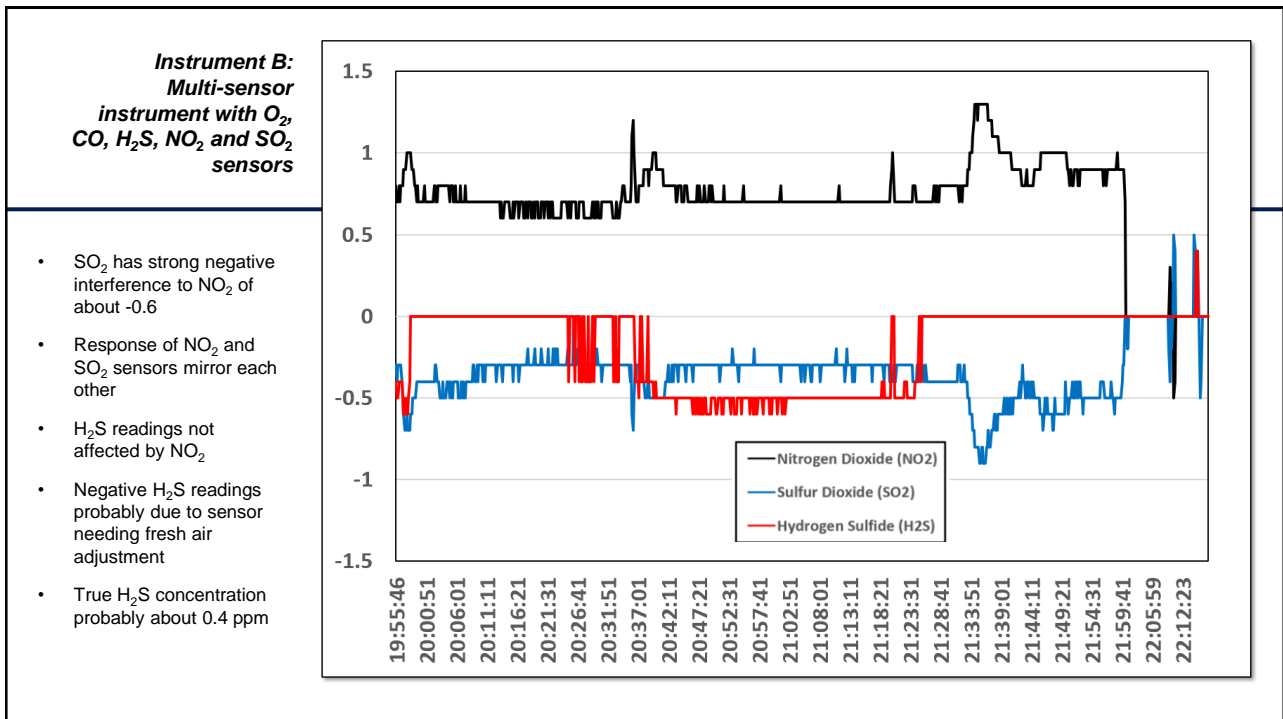
Instrument A: Single-sensor personal NO₂ datalogger

- Session duration: ~ 6.4 hr.
- Low alarm: 3.0 ppm
- High alarm: 5.0 ppm
- STEL: 1.0 ppm
- TWA: 0.2 ppm
- Peak reading during session: 2.4 ppm
- Session duration: 6.39 hrs.
- Datalogging interval: 10 sec.
- Session average (TWA): 0.1 ppm





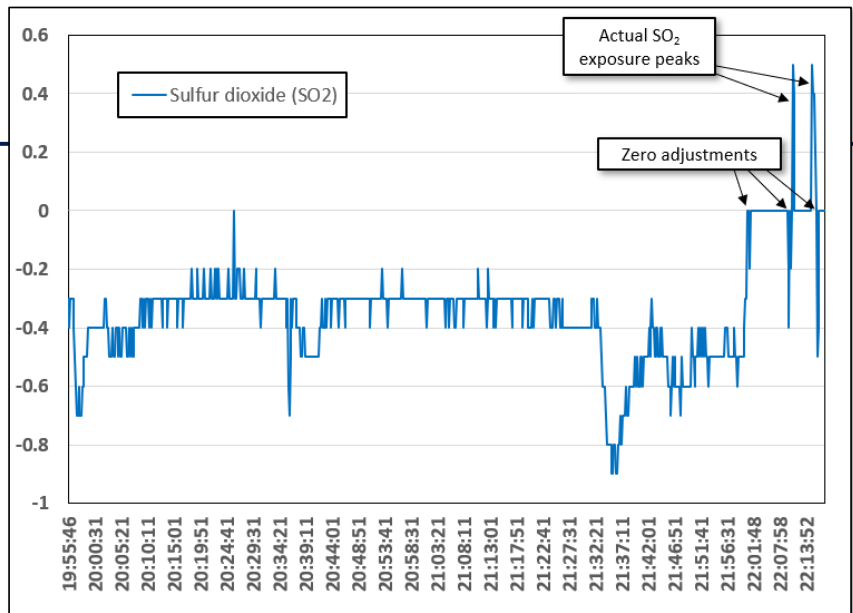
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Instrument B:
Multi-sensor instrument
with O₂, CO, H₂S, NO₂
and SO₂ sensors

- Chart shows results for SO₂ only
- SO₂ readings were negative for most of session because of presence of NO₂ gas
- The SO₂ sensor (along with the other sensors) was zero adjusted three times at 22:00, 22:09 and 22:17 in the probable presence of about 0.5 ppm SO₂ gas.

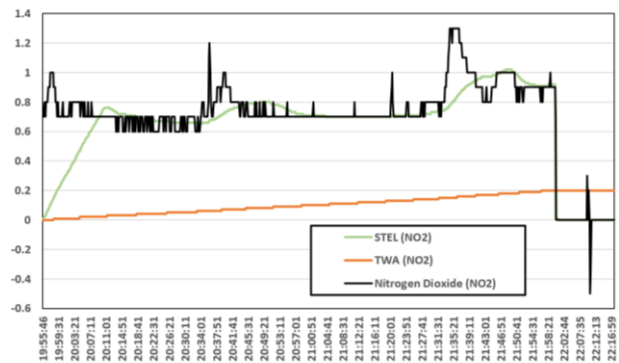


Instrument B:
Multi-sensor instrument
with O₂, CO, H₂S, NO₂
and SO₂ sensors

- NO₂ results (actual logged, STEL and TWA)
- Low alarm: 3.0 ppm
- High alarm: ?
- STEL alarm: 1.0 ppm
- TWA alarm: ?
- TWA (projected): 0.2 ppm
- Peak reading during session: 2.4 ppm
- Session duration: 6.39 hrs.
- Session average: 0.1 ppm

NO2	
TWA (BH)	0.2
Max Peak	1.3
Max STEL	1.02
Count Peak Interval Alarms>3ppm	0
Count STEL Alarms>1ppm	22
SO2	
TWA (BH)	0
Max Peak	0.5
Max STEL	0.02
Count Peak Interval Alarms>2ppm	0
Count STEL Alarms>0.25ppm	0
CO	
TWA (Hr)	0
Max Peak	0
Max STEL	0
Count Peak Interval Alarms>25ppm	0
Count STEL Alarms>50ppm	0
H2S	
TWA (Hr)	0
Max Peak	0.4
Max STEL	0.01
Count Peak Interval Alarms>7.5ppm	0
Count STEL Alarms>5ppm	0
O2	
Max Peak	21.6
Min Peak	20.6
Average O2 Level	21.2
Count MaxPeak Interval Alarms>23.5ppm	0
Count MinPeak Interval Alarms>19.5ppm	0

Instrument B - Multi-sensor instrument
equipped with O₂, CO, H₂S, NO₂ and SO₂ sensors
Start session June 19, 1919 7:55 PM
End session June 19, 1919 10:17 PM



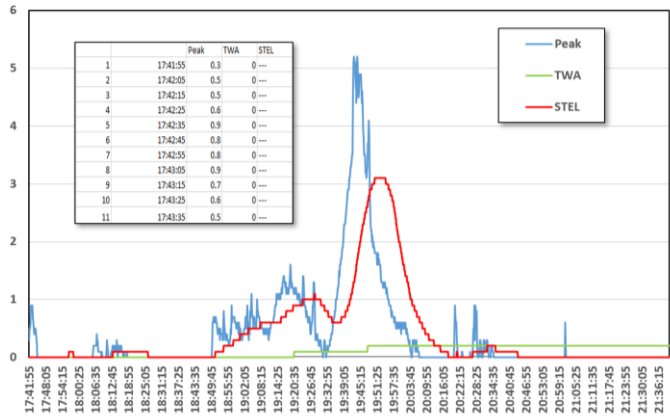
Summary table shows results for all installed sensors. Chart shows results for NO₂ only. Datalog interval was 10 seconds. Logged NO₂ value was the average reading during each 10 second interval. The "MAX PEAK" value of 1.3 ppm in the summary table is logged and retained separately. There is a discontinuity in the logged STEL values around 10:00:01 PM. It looks like the instrument was zeroed at that time, resetting the NO₂ reading to 0 ppm, and resetting the STEL calculation to 0 ppm. The TWA calculation was not reset. It appears the instrument was zeroed while still in the presence of NO₂ gas. Later, the NO₂ reading went negative as the sensor stabilized in air that contained less NO₂. It appears that the instrument was fresh air zeroed again about 10:10:50. The SO₂, H₂S and O₂ readings (which for simplicity are not shown on the chart) were affected by these fresh air

**Instrument C:
Single-sensor personal
NO₂ datalogger**

- Session duration: 4 hours
- Datalogging interval: 10 sec.
- Low alarm: 5.0 ppm
- High alarm: 6.0 ppm
- STEL alarm: 1.0 ppm
- TWA alarm: 0.4 ppm
- Peak reading during session: 5.2 ppm
- Session duration: ~4 hrs.
- Session average (TWA): 0.2 ppm

Summary	
Unit Name	Instrument C
Unit SN	
Unit Firmware Ver	V1.82
Running Mode	Safety Mode
Measure Type	Real
Datalog Mode	Continuous
Datalog Type	Auto
Diagnostic Mode	No
Stop Reason	Pause in Com
Site ID	SITE0000
User ID	USER0000
Begin	43705.73733
End	43705.90289
Sample Period(s)	10
Number of Records	1430
Sensor	NO ₂ (ppm)
Span	5
Span 2	N/A
Low Alarm	5
High Alarm	6
Over Alarm	20
STEL Alarm	1
TWA Alarm	0.4
Measurement Gas	N/A
Calibration Time	43701.30694
Peak	5.2
Min	0
Average	0.4

Session Download for - Instrument C
Single sensor personal NO₂
Start session: 8/28/2019 5:41:55 PM
End session: 8/28/2019 9:39:55 PM



The instrument was not warmed up and zeroed immediately prior to use, and counted down over the first 3 minutes of operation. The highest "Peak" reading reached during the session was 5.2 ppm. The session average was 0.4 ppm. The alarms were set differently (higher) than the alarms in other instruments at the site. The datalog shows 7 intervals (70 seconds) above the low alarm of 5.0 ppm, and 181 intervals (over 30 minutes) above the STEL alarm of 1.0 ppm.

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Important problem: Instrument NO₂ alarms inconsistent!

	Resolution	Low	High	STEL	TWA
Instrument A	0.1 ppm	3.0 ppm	5.0 ppm	1.0 ppm	0.2 ppm
Instrument B	0.1 ppm	3.0 ppm	?	1.0 ppm	?
Instrument C	0.1 ppm	5.0 ppm	6.0 ppm	1.0 ppm	0.4 ppm

- When you have more than one type of instrument in service:
 - Make sure alarms match
 - Make sure datalogger settings match
 - Make sure you understand differences in the way the instruments record information and calculate alarms

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Conclusions

- Define the objectives behind the use of your real time instruments
 - Instrument capabilities need to match requirements
 - Instrument settings need to match objectives
 - Make sure you have sufficient resolution and accuracy
 - Make sure you understand interfering analytes and the effects of ambient conditions on readings
- Datalogging record needs to support objectives
 - Study the manual!
 - Download results and determine whether you understand how the instrument records information, and calculates alarms
- Make sure users are trained
 - Fresh air adjust before each day's use
 - Test and calibrate according to statutory and manufacturer requirements
 - Surveil to make sure settings are correct and that users follow proper procedures
 - Document!

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Thank You!

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