### Laboratory Evaluation: Aeroqual S500-PID





### Background

Three Aeroqual S500-PID sensors (units IDs: 1, 2, 3) were evaluated in the South Coast AQMD Chemistry Laboratory under controlled Volatile Organic Compound (VOC) and interferent gas concentrations, temperature, and relative humidity. The sensor measurements were compared with two reference instruments (Thermo Fisher Scientific, Model 55i; hereinafter Thermo 55i and Agilent gas chromatograph with flame ionization detection, Model 6890N Network; hereinafter GC-FID) measuring the same pollutant.

#### Aeroqual S500-PID (3 units tested):

- VOC Sensor PID (Aeroqual, non-FEM)
  - > TVOC output range: 0-30 ppm
  - Accuracy of Factory Calibration: < ±0.02 ppm</p>
    - +10%
  - > Measurement interval: 1-min
- Each unit measures: VOC (ppb)
- Unit cost: ~\$3120
- ➤ Units IDs: 1, 2, 3



Aeroqual S500-PID



#### **Reference Instruments:**

Thermo Fisher 55i  $\succ$  Measures: methane (CH<sub>4</sub>) and non-methane hydrocarbon (NMHC) ➢Unit cost: ~\$27,000 Specifications: ➤Measurement ranges: 0-50 ppm Limit of Detection (LOD): 50 ppb Analysis time: ~70 seconds  $\triangleright$  Accuracy: ±1% of range Repeatability: ±2% of measured value or 50 ppb (whichever is larger) Drift: ±2% of span over 24 hours Ambient operating temperature: 15-35 °C Sample temperature: ambient to 35 °C **Agilent Gas Chromatograph** Flame Ionization Detection ➤Time Resolution: 22-min ➤Unit cost: ~ \$100,000 Limit of Detection (LOD): dependent on the species, GC-FID typically <1 ppb

### Outline

- 1. Reference instruments comparison
- 2. VOC blend results (Phase 1 through Phase 6)
- 3. Benzene-only results (Phase 6)
- 4. Discussion

# **VOC Blend Results**

# GC-FID vs Thermo 55i: VOC Blend

#### **Beginning of Evaluation**

**End of Evaluation** 



- Very strong correlations between the Thermo 55i and GC-FID (R<sup>2</sup> > 0.98)
- The two reference instruments reported similar VOC concentrations at both the beginning and the end of evaluation

# Phase 1: Transient Plume Detection

Testing Phase #1	Method	Parameters Evaluated
Transient Plume Detection	5 VOC plume events at various concentrations in randomized order	<ul><li> Response time</li><li> % of peak detection</li></ul>

#### Aeroqual S500-PID vs Thermo 55i



- The Aeroqual S500-PID sensors detected 100% of the VOC peaks generated.
- Unit 1 reported lower VOC values compared to Units 2 and 3 throughout the test
- The Aeroqual detected the VOC peaks as fast as the Thermo 55i detected the peaks; there is effectively no measurable time delay in plume detection by the Aeroqual S500-FID sensors (and that any apparent delay of the reference instrument is due to different sampling times of the sensors vs. the reference).

# Phase 2: Initial Concentration Ramping

Testing Phase #2	Method	Parameters Evaluated
Initial Concentration Ramping	<ul> <li>Low conc. ramping with VOC blend (0.06 to 1.6 ppm)</li> <li>High conc. ramping with VOC blend (2 to 8 ppm)</li> <li>*Low conc. ramping with benzene-only (0.015 to 0.4 ppm)</li> <li>* High conc. ramping with benzene-only (0.5 to 2 ppm)</li> </ul>	<ul> <li>Sensor detection limit, R<sup>2</sup>, Accuracy, Precision, IMV, data recovery</li> </ul>

\*Note: Initial concentration ramp with Benzene-only was not performed for the Aeroqual S500-PID sensors. The test was added to the protocol after experiments were done.

#### Aeroqual S500-PID vs Thermo 55i vs GC-FID



- The Aeroqual S500-PID sensors tracked well with the concentration variation as recorded by the reference instruments in the concentration range of 0 - 8 ppm.
- Overall, the Aeroqual S500-PID sensors underestimated the VOC concentrations < 6 ppm and overestimated the VOC concentrations at 8 ppm as measured by the Thermo 55i
- The Aeroqual S500-PID sensors showed very strong correlations with the reference instruments. (R<sup>2</sup> > 0.97).
- Unit 1 reported lower
   VOC values compared to
   Units 2 and 3 throughout
   the test

# Phase 3: Effect of Temperature and Relative Humidity

Testing Phase #3	Method	Parameters Evaluated
Effect of Temperature and RH	<ul> <li>*Extreme Conditions: hot/humid; cold/dry and VOC = 4ppm</li> <li>RH interference: 15% to 80% RH; T = 20°C and VOC = 4 ppm</li> <li>T interference: 20°C to 10°C to 30°C to 20°C; RH = 40% and VOC = 4 ppm</li> <li>*T interference: 20°C to 10°C to 30°C to 20°C; AH = constant and VOC = 4 ppm</li> </ul>	<ul> <li>Climate susceptibility, Accuracy, Precision, IMV, data recovery</li> </ul>

\*Note: Extreme conditions and temperature interference test at constant absolute humidity (AH) were not performed for the Aeroqual S500-PID sensors. These tests were added to the protocol after experiments were done.

### **RH** interference



- RH had minimal effect on the VOC concentrations measured by the Thermo 55i as RH increased from 25% to 80%, with temperature held constant at 20°C
- The Aeroqual S500-PID sensors showed a decrease in concentration as RH increased from 20% to 80%
- Unit 1 reported lower VOC values compared to Units 2 and 3 throughout the test

#### Temperature interference



- The Temperature interference test was conducted at constant RH of 40%. A temperature interference test conducted at constant absolute humidity (AH) may show a different apparent response to temperature changes. However, a temperature interferent test at constant AH was added to the protocol after conclusion of this testing
- T had minimal effect on the VOC concentrations measured by the Thermo 55i
- Unit 1 reported lower VOC values compared to Units 2 and 3 throughout the test
- A temperature change appears to cause sensor response to go toward the opposite direction, especially when temperature increases.
- On average, the VOC concentration measured by the Aeroqual S500-PID sensors increased by ~0.45 ppm as T decreased from 20°C to 10°C; then decreased by 0.74 ppm as T increased from 10°C to 30°C and finally increased by 0.54 ppm as T decreased from 30°C to 20°C

# Phase 4: Effect of Gaseous Interferents

Testing Phase #4	Method	Parameters Evaluated		
Effect of gaseous interferents	<ul> <li>Ozone (1 to 400 ppb; 20 °C/40% RH and VOC = 200 ppb)</li> <li>Carbon Monoxide (background to 8 ppm; 20 °C/40% RH and VOC = 4 ppm)</li> <li>Carbon Dioxide (background to 8000 ppm; 20 °C/40% RH and VOC = 4 ppm)</li> </ul>	<ul> <li>Response to interferents, Accuracy, Precision, IMV, data recovery</li> </ul>		

#### **Ozone Interferent**



- Ozone interferent test: sensors were subjected to increasing ozone concentration from background level of ~18 ppb to 400 ppb while holding VOC concentration constant at 0.2 ppm
- Ozone had minimal effect on the VOC concentrations measured by the Thermo 55i
- Unit 1 reported lower VOC values compared to Units 2 and 3 throughout the test
- The Aeroqual S500-PID sensors responses did not vary as ozone concentration varied

### **CO** Interferent



- CO interferent test: sensors were subjected to increasing CO concentration from background level to 8ppm while holding VOC concentration constant at ~4 ppm
- CO had minimal effect on the VOC concentrations measured by the Thermo 55i
- Unit 1 reported lower VOC values compared to Units 2 and 3 throughout the test
- The Aeroqual S500-PID sensors showed a slight increase (6.5%) in concentration as CO increased from a background value of ~0.6 ppm to ~8 ppm

### CO<sub>2</sub> Interferent



- CO<sub>2</sub> interferent test: sensors were subjected to increasing CO<sub>2</sub> concentration from background level to 8ppm while holding VOC concentration constant at ~4 ppm
- CO<sub>2</sub> had minimal effect on the VOC concentrations measured by the Thermo 55i
- Unit 1 reported lower VOC values compared to Units 2 and 3 throughout the test
- The Aeroqual sensors showed a slight increase (5.2%) in concentration as CO<sub>2</sub> increased from a background value of ~366 ppm to ~9000 ppm

# Phase 5: Outdoor Simulation

Testing Phase #5	Method	Parameters Evaluated
Outdoor Simulation	<ul> <li>Various combination of Ozone (0 to 100 ppb) and VOC (200 to 400 ppb) concentrations, T (10 to 30 °C) and RH (10 to 80%)</li> </ul>	<ul> <li>Accuracy, Precision, IMV, data recovery, Analysis of Variance (ANOVA)</li> </ul>

### **Outdoor Simulation: ANOVA Analysis**



Percent of Variance in Sensor Signal Explained

# Phase 6: Final Concentration Ramping

Testing Phase #6	Method	Parameters Evaluated
Final Concentration Ramping	<ul> <li>Low conc. ramping with VOC blend (0.06 to 1.6 ppm)</li> <li>High conc. ramping with VOC blend (2 to 8 ppm)</li> <li>Low conc. ramping with benzene-only (0.015 to 0.4 ppm)</li> <li>High conc. ramping with benzene-only (0.5 to 2 ppm)</li> </ul>	<ul> <li>Sensor detection limit, R<sup>2</sup>, Accuracy, Precision, IMV, data recovery</li> </ul>

#### Aeroqual S500-PID vs Thermo 55i vs GC-FID

**Initial Ramp** 



Final Ramp

#### Aeroqual S500-PID vs Thermo 55i vs GC-FID

#### **Initial Ramp** Thermo 55i and GC-FID vs Aeroqual S500-PID VOC Conc. (5-min mean, ppm) Thermo 55i GC-FID 2.5 y = 1.5584x + 0.1821Thermo 55i & GC-FID $R^2 = 0.9795$ 2.0 1.5 1.0 .5449x+0.1211 $R^2 = 0.9825$ 0.5 1:1 line 0.0 1.5 2.0 2.5 0.0 0.5 1.0 Average of 3 Aeroqual S500-PID Units



**Final Ramp** 





Low Ramp

High Ramp

### **Summary Statistics**

#### **Initial Ramp**

Sensors				55i			GC			
Nominal VOC Conc., ppm	Avg, ppm	Precision, %	IMV, %	SDL, ppm	Ref avg, ppm	Sensor Bias Error, ppm	Sensor Accuracy, %	Ref avg, ppm	Sensor Bias Error, ppm	Sensor Accuracy, %
0.06	0.00	N/A	N/A	Unit 1: 0.06 –	0.11	-0.11	0.0	0.06	-0.06	0.0
0.2	0.03	97.8	164.1	0.08 Unit 2: 0.03 -	0.28	-0.25	10.2	0.20	-0.17	12.8
0.4	0.12	99.8	131.3	0.08 Unit 3: 0.04 –	0.50	-0.38	24.8	0.40	-0.28	30.3
1.6	0.99	99.8	43.6	0.09	1.66	-0.67	59.4	1.55	-0.59	62.2
2	1.3	99.7	38.1		2.1	-0.9	59.5			
4	3.3	99.8	30.2		4.1	-0.8	81.1			
6	5.8	99.7	27.0		6.1	-0.3	95.5			
8	8.6	99.6	25.0		8.2	0.4	94.7			

### **Summary Statistics**

#### **Final Ramp**

Sensors					55i			GC		
Nominal VOC Conc., ppm	Avg, ppm	Precision, %	IMV, %	SDL, ppm	Ref avg, ppm	Sensor Bias Error, ppm	Sensor Accuracy, %	Ref avg, ppm	Sensor Bias Error, ppm	Sensor Accuracy, %
0.06	0.11	100.0	100.0	Unit 1: 0.04-	0.06	0.05	28.6	0.06	0.05	8.5
0.2	0.18	99.9	91.0	0.12 Unit 2: 0.02-	0.18	0.00	98.1	0.18	0.00	98.4
0.4	0.31	99.9	80.5	0.07 Unit 3: 0.03-	0.36	-0.05	85.2	0.38	-0.07	81.4
1.6	1.17	99.8	60.1	0.09	1.37	-0.19	85.8	1.46	-0.29	79.9
2	1.5	99.7	57.5		1.8	-0.2	87.7			
4	3.5	99.8	45.5		3.5	0.1	98.0			
6	5.9	99.8	39.6		5.2	0.7	87.2			
8	8.5	99.9	35.6		7.1	1.4	80.0			

### **Short-Term Sensor Response Change**

• Short-term sensor response change is characterized as the change in reference-sensor regression between the initial and final concentration ramping experiments



 The final concentration ramping regression slope decreased, suggesting that the Aeroqual S500-PID sensors on average became more sensitive to unit changes in VOC concentrations compared to the initial concentration ramping. The final concentration ramping regression intercept decreased, suggesting that the Aeroqual S500-PID sensors on average reported a higher baseline compared to the initial concentration ramping.

# Phase 6: Benzene-Only Results

### GC-FID vs Thermo 55i, benzene-only



• Very strong correlations between the Thermo 55i and GC-FID ( $R^2 > 0.99$ )

### Aeroqual S500-PID vs Thermo 55i vs GC-FID







1

2

3

4

- The Aerogual S500-PID ٠ sensors tracked well with the concentration variation as recorded by the reference instruments in the concentration range of 0 - 2 ppm.
- Overall, the Units 2 and ٠ 3 overestimated the Benzene-only concentrations while Unit 1 underestimated as measured by the reference instruments.
- The Aeroqual S500-PID ٠ sensors showed very strong correlations with the reference instruments. ( $R^2 > 0.99$ ).
- Unit 1 reported lower ٠ VOC values compared to Units 2 and 3 throughout the tests.

### **Benzene-only: Summary**

Sensors				55i			GC			
Nominal VOC Conc., ppm	Avg, ppm	Precision, %	IMV, %	SDL, ppm	Ref avg, ppm	Sensor Bias Error, ppm	Sensor Accuracy, %	Ref avg, ppm	Sensor Bias Error, ppm	Sensor Accuracy, %
0.015	0.09	99.7	172.3	Unit 1: 0.01-	0.03	0.05	-59.9	0.02	0.07	-325.8
0.05	0.11	99.7	157.4	0.04 Unit 2: 0.01-	0.07	0.03	54.3	0.05	0.05	-2.6
0.1	0.15	99.5	145.6	0.02 Unit 3: 0.01-	0.14	0.01	96.2	0.11	0.04	60.5
0.4	0.42	99.8	108.1	0.03	0.52	-0.10	81.5	0.41	0.01	97.8
0.5	0.54	99.8	90.9		0.67	-0.13	80.3			
1	1.16	99.8	76.9		1.25	-0.10	92.3			
1.5	1.94	99.8	68.0		1.92	0.02	99.1			
2	2.81	99.9	62.1		2.58	0.23	91.1			

Note: only one concentration ramping experiment was carried out using benzene-only as the test gas.

 The following slides provide results and discussion to all testing phases, including results from VOC blend and Benzene-only tests

- > Data Recovery: The Aeroqual S500-PID sensors showed 100% data recovery for all experiments
- Intra-model variability: Moderate to high intra-model variability was observed among the Aeroqual S500-PID sensors for all experiments
- Sensor Detection Limit (SDL): The SDL of the Aeroqual S500-PID sensors ranged from 0.03 to 0.09 ppm in the initial VOC ramp and 0.02 to 0.12 ppm in the final VOC ramp; The SDL of the sensors ranged from 0.01 to 0.04 ppm in the Benzene-only ramp.

#### > Phase 1: Transient Plume Detection

 The sensors showed 100% plume detection recovery and detected the VOC peaks as fast as the Thermo 55i detected the peaks; there is effectively no measurable time delay in plume detection by the Aeroqual S500-PID sensors

#### Phase 2: Initial Concentration Ramping

- Coefficient of Determination: The Aeroqual S500-PID sensors showed very strong correlation/linear response with the corresponding reference VOC data (R<sup>2</sup> > 0.97 for low VOC conc. ramping and R<sup>2</sup> > 0.99 for high VOC conc. ramping).
- Accuracy: The sensors underestimated the corresponding reference instrument VOC measurements, and the sensor accuracy increases with VOC concentration for the respective VOC conc. ramping tests: 0% to ~60% as VOC concentration increased from 0.06 to 1.6 ppm and ~60% to ~95% as VOC concentration increased from 2 to 8 ppm.

- > Phase 3: Effect of Temperature and RH
  - Accuracy: The accuracy of the sensors decreased from 96% to 74% as RH increased from 20% to 80% RH and accuracies appear to recover as the temperature returns to 20 °C and stabilizes
  - Precision: The precision of the Aeroqual S500-PID sensors were ~100% for temperature and RH interference testing
  - *Climate susceptibility:* The Aeroqual S500-PID sensors showed a decrease in concentration as RH increased from 20% to 80%. A temperature change appears to cause sensor response to go toward the opposite direction of temperature change, especially when temperature increases.

#### Phase 4: Effects of Gaseous Interferents

- > Ozone
  - Accuracy: The accuracy of the Aeroqual S500-PID sensors increased slightly from ~22% to ~28% as ozone increased from background level of ~18 ppb to 400 ppb
  - **Precision:** High precision (~99-100%) was observed among the sensors
  - Responses to Ozone: The Aeroqual S500-PID sensors responses did not vary as ozone concentration varied
- > CO
  - Accuracy: The accuracy of the Aeroqual S500-PID sensors stayed fairly constant (97%-99%) as CO increased from background level of ~0.6 ppm to 8 ppm
  - **Precision:** High precision (~100%) was observed among the sensors
  - Responses to CO: The Aeroqual S500-PID sensors showed a slight increase in concentration as CO increased from a background value of ~0.6 ppm to ~8 ppm



- Phase 4 Effects of Gaseous Interferents (Continued):
  - ▷ CO<sub>2</sub>
    - Accuracy: The accuracy of the Aeroqual S500-PID sensors stayed fairly constant (97%-100%) as CO<sub>2</sub> increased from background level of ~366 ppm to ~9000 ppm
    - **Precision:** High precision (~100%) was observed among the sensors
    - Responses to CO<sub>2</sub>: The Aeroqual S500-PID sensors showed a slight increase in concentration as CO<sub>2</sub> increased from a background value of ~366 ppm to ~9000 ppm

#### Phase 5: Outdoor Simulation

- The sensors tracked well with the Thermo 55i when exposed to a combination of T, RH, ozone and VOC concentrations
- Thermo 55i VOC accounts for ~92% of the variance when all variables (T, AH and ozone and VOC concentrations) are included in the ANOVA statistical test; and temperature and AH explain a small percent (<4%) of the variance, at least for expected ambient conditions</li>
- The predictive power is highest for VOC for all sensors. This suggests the sensors mainly respond to the VOC concentrations and do not seem to be affected much by environmental factors in the range of expected ambient conditions

- Phase 6: Final Concentration Ramping
  - Coefficient of Determination: The Aeroqual S500-PID sensors showed very strong correlation/linear response with the corresponding reference VOC and benzene-only data (R<sup>2</sup> > 0.99)
  - Accuracy (VOC-blend): For the low VOC conc. ramping, the Aeroqual S500-PID sensors generally underestimated the VOC concentrations measured by the Thermo 55i and GC-FID. For the high VOC conc. ramping, the Aeroqual S500-PID sensors generally overestimated Thermo 55i VOC concentration at 20 °C and 40% RH. The accuracy of the Aeroqual S500-PID sensors increased initially then decreased as VOC concentration increased for both low and high VOC conc. ramping experiments.
  - Accuracy (benzene-only): For the low conc. ramping, the Aeroqual PID sensors generally
    overestimated the benzene concentrations measured by the Thermo 55i and GC-FID and the accuracy
    of the sensors ranged from -326% at the lowest concentration to 98% at the highest benzene
    concentrations. For the high conc. ramping, the Aeroqual PID sensors generally underestimated
    benzene concentration < 1.5 ppm and overestimated the benzene concentrations > 1.5 ppm as
    measured by the Thermo 55i. The accuracy of the Aeroqual S500-PID is higher at higher benzene
    concentrations.
- **Short-term Sensor Response:** The final concentration ramping regression slope decreased, suggesting that the Aeroqual S500-PID sensors on average became more sensitive to unit changes in VOC concentrations compared to the initial concentration ramping. The final concentration ramping regression intercept decreased, suggesting that the Aeroqual S500-PID sensors on average reported a higher baseline compared to the initial concentration ramping.