Laboratory Evaluation: Smart Citizen Kit – v2.1
Background

Three **Smart Citizen Kit v2.1** sensors (units IDs: 1, 2, 3; hereinafter **SCK v2.1**) 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.

**SCK v2.1 (3 units tested):**
- VOC Sensor – Metal oxide (AMS CCS811, non-FEM)
  - TVOC output range: 0 – 1187 ppb
  - Accuracy: N/A
  - Measurement interval: 1-min
- Each unit measures: tVOC (ppb)
- Unit cost: ~$119
- Units IDs: 1, 2, 3

**Reference Instruments:**
- **Thermo Fisher 55i**
  - Measures: methane (CH₄) 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
    - 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, 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
• Very strong correlations between the Thermo 55i and GC-FID ($R^2 > 0.99$)
• The two reference instruments reported similar VOC concentrations at both the beginning and the end of evaluation
## Phase 1: Transient Plume Detection

<table>
<thead>
<tr>
<th>Testing Phase #1</th>
<th>Method</th>
<th>Parameters Evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transient Plume Detection</td>
<td>5 VOC plume events at various concentrations in randomized order</td>
<td>• Response time</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• % of peak detection</td>
</tr>
</tbody>
</table>
• The SCK v2.1 sensors detected 100% of the VOC peaks generated.
• The SCK v2.1 detected the VOC peaks within 3-4 minutes after the Thermo 55i detected the peaks; there is a slight time delay in plume detection by the SCK v2.1 sensors.
# Phase 2: Initial Concentration Ramping

<table>
<thead>
<tr>
<th>Testing Phase #2</th>
<th>Method</th>
<th>Parameters Evaluated</th>
</tr>
</thead>
</table>
| Initial Concentration Ramping | • Low conc. ramping with VOC blend (0.06 to 1.6 ppm)  
• ‡High conc. ramping with VOC blend (2 to 8 ppm)  
• 'Low conc. ramping with benzene-only (0.015 to 0.4 ppm)  
• ‡ 'High conc. ramping with benzene-only (0.5 to 2 ppm) | • Sensor detection limit, R², Accuracy, Precision, IMV, data recovery |

*Note: Initial concentration ramps with Benzene-only was not performed for the SCK v2.1 sensors. The benzene-only tests were added to the protocol after experiments were done.

‡Note: These tests are not included in this analysis since they are conducted at a tVOC concentration greater than the maximum output range of the SCK v2.1 sensors.
The SCK v2.1 sensors did not track well with the concentration variation as recorded by the reference above ~ 1 ppm.

Overall, the SCK v2.1 sensors greatly underestimated the VOC concentrations.

The SCK v2.1 sensors showed moderate to strong correlations with the reference instruments.
Phase 3: Effect of Temperature and Relative Humidity

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

- None of these tests were analyzed since the protocol requires 4 ppm tVOC and the sensors’ max output is ~ 1ppm.
Phase 4:
Effect of Gaseous Interferents

Testing Phase #4

<table>
<thead>
<tr>
<th>Effect of gaseous interferents</th>
<th>Method</th>
<th>Parameters Evaluated</th>
</tr>
</thead>
</table>
|                                | • Ozone (1 to 400 ppb; 20 °C/40% RH and VOC = 200 ppb)  
   • Carbon Monoxide (background to 8 ppm; 20 °C/40% RH and VOC = 4 ppm)  
   • Carbon Dioxide (background to 8000 ppm; 20 °C/40% RH and VOC = 4 ppm) | • Response to interferents, Accuracy, Precision, IMV, data recovery |

• None of these tests were analyzed since the protocol requires 4 ppm tVOC and the sensors’ max output is ~ 1ppm, except for the ozone interferent experiment.
Ozone interferent test: sensors were subjected to increasing ozone concentration from background level 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.
- The SCK v2.1 sensors showed mostly zeroes after the addition of ozone.
Phase 5: Outdoor Simulation

<table>
<thead>
<tr>
<th>Testing Phase #5</th>
<th>Method</th>
<th>Parameters Evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outdoor Simulation</td>
<td>• 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%)</td>
<td>• Accuracy, Precision, IMV, data recovery, Analysis of Variance (ANOVA)</td>
</tr>
</tbody>
</table>
The SCK v2.1 sensors did not track the VOC concentration variations as measured by Thermo 55i.

The sensors' VOC reading appeared to decrease with increasing temperature and ozone levels.

When VOC, T, AH and ozone are included in the ANOVA statistical test, T explains ~23% of the variance, with about ~74% of the variance not explained by any variables.

The sensors did not seem to be sensitive to VOC variations.
Phase 6: Final Concentration Ramping

<table>
<thead>
<tr>
<th>Testing Phase #6</th>
<th>Method</th>
<th>Parameters Evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final Concentration Ramping</td>
<td>• Low conc. ramping with VOC blend (0.06 to 1.6 ppm)</td>
<td>• Detection limit, R², Accuracy, Precision, IMV, data recovery</td>
</tr>
<tr>
<td></td>
<td>• High conc. ramping with VOC blend (2 to 8 ppm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Low conc. ramping with benzene-only (0.015 to 0.4 ppm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• High conc. ramping with benzene-only (0.5 to 2 ppm)</td>
<td></td>
</tr>
</tbody>
</table>

*Note: These tests are not included in this analysis since they are conducted at a tVOC concentration greater than the maximum output range of the SCK v2.1 sensors.*
SCK v2.1 vs Thermo 55i vs GC-FID

Initial Ramp

Thermo 55i & GC-FID vs SCK v2.1
VOC Conc. (5-min mean, ppm)

**Thermo 55i**
**GC-FID**

\[ y = 85.87x - 1.2952 \]
\[ R^2 = 0.7278 \]

**Thermo 55i**
**GC-FID**

\[ y = 94.344x - 1.4356 \]
\[ R^2 = 0.6856 \]

Final Ramp

Thermo 55i & GC-FID vs SCK v2.1
VOC Conc. (5-min mean, ppm)

**Thermo 55i**
**GC-FID**

\[ y = -1.0455x + 4.6734 \]
\[ R^2 = 0.328 \]

**Thermo 55i**
**GC-FID**

\[ y = -1.0409x + 4.6551 \]
\[ R^2 = 0.3164 \]
## Summary Statistics

### Initial Ramp

<table>
<thead>
<tr>
<th>Nominal VOC Conc., ppm</th>
<th>Sensors</th>
<th>55i</th>
<th>GC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg, ppm</td>
<td>Precision, %</td>
<td>IMV, %</td>
</tr>
<tr>
<td>0.06</td>
<td>0.017</td>
<td>98.9</td>
<td>29.4</td>
</tr>
<tr>
<td>0.2</td>
<td>0.022</td>
<td>98.1</td>
<td>13.1</td>
</tr>
<tr>
<td>0.4</td>
<td>0.024</td>
<td>98.2</td>
<td>23.6</td>
</tr>
<tr>
<td>1.6</td>
<td>0.032</td>
<td>98.2</td>
<td>24.5</td>
</tr>
</tbody>
</table>
## Summary Statistics

### Final Ramp

<table>
<thead>
<tr>
<th>Nominal VOC Conc., ppm</th>
<th>Sensors</th>
<th>55i</th>
<th>GC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg, ppm</td>
<td>Precision, %</td>
<td>IMV, %</td>
</tr>
<tr>
<td>0.06</td>
<td>4.1</td>
<td>99.7</td>
<td>28.6</td>
</tr>
<tr>
<td>0.2</td>
<td>3.8</td>
<td>99.9</td>
<td>29.9</td>
</tr>
<tr>
<td>0.4</td>
<td>3.8</td>
<td>99.9</td>
<td>30.0</td>
</tr>
<tr>
<td>1.6</td>
<td>3.7</td>
<td>99.8</td>
<td>31.0</td>
</tr>
</tbody>
</table>
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 SCK v2.1 sensors showed inconsistency in behavior during initial and final ramps at both concentration ramps. The sensors greatly underestimated the VOC concentrations during the initial low ramp but showed overestimation during the final ramp.
Phase 6: Benzene-Only Results
GC-FID vs Thermo 55i: Benzene-only

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

\[
y = 1.0977x - 0.0238 \\
R^2 = 0.9924
\]
The SCK v2.1 sensors did not track the concentration variation as recorded by the Thermo 55i and GC-FID in the concentration range of 0 – 0.4 ppm.

The SCK v2.1 sensors showed very weak correlations with the reference instruments.
**Benzene-only: Summary**

<table>
<thead>
<tr>
<th>Nominal VOC Conc., ppm</th>
<th>Sensors</th>
<th>55i</th>
<th>GC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg, ppm</td>
<td>Ref avg, ppm</td>
<td>Sensor Bias Error, ppm</td>
</tr>
<tr>
<td><strong>Avg, ppm</strong></td>
<td>Precision, %</td>
<td>IMV, %</td>
<td>SDL, ppm</td>
</tr>
<tr>
<td>0.015</td>
<td>0.034</td>
<td>99.1</td>
<td>42.7</td>
</tr>
<tr>
<td>0.05</td>
<td>0.014</td>
<td>98.5</td>
<td>84.2</td>
</tr>
<tr>
<td>0.1</td>
<td>0.012</td>
<td>96.5</td>
<td>78.0</td>
</tr>
<tr>
<td>0.4</td>
<td>0.022</td>
<td>97.8</td>
<td>49.6</td>
</tr>
</tbody>
</table>

**Note:** Only the final concentration ramping experiment was carried out using benzene-only as the test gas.
Discussion

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

➢ **Data Recovery:** The SCK v2.1 sensors showed 98-100% data recovery for all experiments

➢ **Intra-model variability:** Low to high intra-model variability was observed among the SCK v2.1 sensors for all experiments

➢ **Sensor Detection Limit (SDL):** SDL for the SCK v2.1 units cannot be determined because the $R^2$ for the correlation between sensor and GC-FID was < 0.8

➢ **Phase 1: Transient Plume Detection**
  • The SCK v2.1 detected the VOC peaks within 3-4 minutes after the Thermo 55i detected the peaks; there is a slight time delay in plume detection by the SCK v2.1 sensors.

➢ **Phase 2: Initial Concentration Ramping**
  • **Coefficient of Determination:** The SCK v2.1 sensors showed moderate to strong correlation/linear response with the corresponding reference VOC data ($R^2$ ~0.7).
  • **Accuracy:** The sensors greatly underestimated the corresponding reference instrument VOC measurements, and the sensor accuracy decreased with increasing VOC concentration ramping tests: 20% to ~2% as VOC concentration increased from 0.06 to 1.6 ppm.

➢ **Phase 3: Effect of Temperature and RH**
  • None of these tests were analyzed since the protocol requires 4 ppm tVOC and the sensors’ max output is ~1ppm.
Discussion

➢ Phase 4: Effects of Gaseous Interferents
  • None of these tests were analyzed since the protocol requires 4 ppm TVOC and the sensors’ max output is ~1ppm, except the ozone interferent experiment.

➢ Ozone
  • **Accuracy**: The accuracy of the SCK v2.1 sensors decreased slightly from ~2.7% to ~0.6% as ozone increased from background level to 400 ppb
  • **Precision**: Low to high precision (~32-98%) was observed among the sensors
  • **Responses to Ozone**: The SCK v2.1 sensors reported mostly zero values after the addition of ozone

➢ Phase 5: Outdoor Simulation
  • The sensors did not track with the Thermo 55i when exposed to a combination of T, RH, ozone and VOC concentrations
  • When VOC, T, AH and ozone are included in the ANOVA statistical test; T explains ~23% of the variance, with about ~74% of the variance not explained by any variables.
  • The sensors did not seem to be sensitive to VOC variations
Phase 6: Final Concentration Ramping

- **Coefficient of Determination**: The SCK v2.1 sensors showed weak correlation/linear response with the corresponding reference VOC ($R^2 \approx 0.3$) and very weak correlations with benzene-only data ($R^2 \approx 0.13$-$0.17$).

- **Accuracy (VOC-blend)**: Low accuracy was observed for the VOC conc. Ramping experiments at 20 °C and 40% RH. The SCK v2.1 sensors overestimated VOC conc. as measured by the reference instruments.

- **Accuracy (benzene-only)**: for the low conc. ramping, the SCK v2.1 sensors generally underestimated the benzene concentrations measured by the Thermo 55i and GC-FID and the accuracy of the sensors ranged from -143% at the lowest concentration to 5% at the highest benzene concentrations.

- **Short-term Sensor Response**: The SCK v2.1 sensors showed inconsistency in behavior during initial and final ramps at both concentration ramps. The sensors greatly underestimated the VOC concentrations during the initial low ramp but showed overestimation during the final ramp.