Site Audits

Air Quality Measurement Seminar

Monday 9th July 2007

David Butterfield, NPL
Contents

Why perform an audit?

Audit results
- Gaseous measurements
- Particulate measurements
- Sample system collection efficiency
Why Perform An Audit?

Regular audits are required by legislation if data is to be reported to the EC (to be explained further in Paul Quincey’s talk)

They provide evidence needed to:

- ratify individual datasets (to be covered in the next 2 talks)
- ensure comparability of data between sites in the Network
- ensure comparability of data year on year
- allow proper comparison with data from elsewhere, eg by assessing the measurement uncertainty
- discover malfunctions, problems and human errors that would otherwise be missed, eg cylinder drifts, leaks, sample line losses …
Site Audits

NPL is UKAS Accredited to ISO17025 for Site Audits

Tasks performed: Uncertainty, 95% k=2

- Analyser Calibration 4%
- Determination of on site standard concentration 4%
- NO₂ molybdenum converter efficiency test 1.5%
- Analyser span noise test 2 ppb
- Analyser zero noise test 1 ppb
- Particulate analyser calibration 1.5%
- Particulate analyser flow rate test 2%
- Sample system collection efficiency test 5%
Site Audits

Equipment needed:

• Gas Standards - recently certified, e.g. NO, NO₂, SO₂ and CO
• Ozone photometer – recently certified against NIST Standard Reference Photometer
• Flow Standard – recently certified
• Gas dilution system with gas phase titration facility
• TEOM filters of known mass
Audit Results
Obvious Faults Found

<table>
<thead>
<tr>
<th>Fault</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaking analyser</td>
<td>10</td>
</tr>
<tr>
<td>PM head excessively soiled</td>
<td>10</td>
</tr>
<tr>
<td>Leaking switching valve in NOx analyser</td>
<td>4</td>
</tr>
<tr>
<td>Analyser non-linearity &gt; 10%</td>
<td>3</td>
</tr>
<tr>
<td>Inaccessible TEOM head</td>
<td>3</td>
</tr>
<tr>
<td>High noise levels on either span or zero</td>
<td>2</td>
</tr>
<tr>
<td>Logger Problem</td>
<td>1</td>
</tr>
<tr>
<td>TEOM flow fault</td>
<td>1</td>
</tr>
<tr>
<td>Manifold fault</td>
<td>1</td>
</tr>
</tbody>
</table>

Most leaks fixed by NPL before progressing with audit
SO$_2$ Analysers

CMCU Factor / Measured Factor

Ratio >1 Over Reporting Levels in Real Time

Sites = 23

Ratio

Number of Sites

Sites = 23

NPL
National Physical Laboratory
CO Analysers

CMCU Factor / Measured Factor

Ratio >1 Over Reporting Levels in Real Time

Sites = 7

Number of Sites

Ratio

Sites = 7
O$_3$ Analysers

CMCU Factor / Measured Factor

 Sites = 27

Ratio >1 Over Reporting Levels in Real Time
NO Cylinder Degradation

<table>
<thead>
<tr>
<th>Site</th>
<th>% NO_2 of NO_x</th>
<th>Site</th>
<th>% NO_2 of NO_x</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Herts 3</td>
<td>17</td>
<td>Redbridge 4</td>
<td>11</td>
</tr>
<tr>
<td>Greenwich 7</td>
<td>3</td>
<td>Tower Hamlets 4</td>
<td>11</td>
</tr>
<tr>
<td>Islington 2</td>
<td>6</td>
<td>Hackney 6</td>
<td>6</td>
</tr>
<tr>
<td>Hackney 6</td>
<td>6</td>
<td>Hillingdon 2</td>
<td>4</td>
</tr>
<tr>
<td>Greenwich 12</td>
<td>4</td>
<td>Richmond Mobile</td>
<td>4</td>
</tr>
<tr>
<td>East Herts 2</td>
<td>4</td>
<td>Redbridge 3</td>
<td>3</td>
</tr>
<tr>
<td>Greenwich 9</td>
<td>4</td>
<td>Hillingdon 1</td>
<td>3</td>
</tr>
<tr>
<td>Redbridge 1</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NO → NO_2 in the cylinder

Possibility of NO_2 being reported low due to incorrect NO factor
NO$_2$ molybdenum converter inefficiency test

- **Failed**

Percentage Inefficiency

Number of sites

- **Failure caused by unstable analyser**
# Particulate analyser calibration

<table>
<thead>
<tr>
<th>Site</th>
<th>Mass equivalent of noise on $F_0$ $\mu g$</th>
<th>Site</th>
<th>Mass equivalent of noise on $F_0$ $\mu g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Croydon 3</td>
<td>19</td>
<td>Hounslow 4</td>
<td>31</td>
</tr>
<tr>
<td>Lewisham 2</td>
<td>12</td>
<td>Thames Rd South PM2.5</td>
<td>12</td>
</tr>
</tbody>
</table>
Particulate analyser flow rate - Sensor Flow

Under reported PM$_{10}$ concentrations

Target
3.0

Sites = 61
Particulate analyser flow rate - Total Flow

Target 16.67
Sites = 58

>PM$_{10}$ sampled

Number of Sites

Total Flow, litres per minute
Sample System Collection Efficiency Test
Overview – Phase 1

High Concentration Cylinder
10 ppm NO₂ and SO₂
1000 ppm CO

Zero Air Cylinder

MFC → MFC

O₃ generator

Test Manifold

Analysers

Concentrations ~ EU Limit Values
Overview – Phase 2

High Concentration Cylinder
10 ppm NO₂ and SO₂
1000 ppm CO

Zero Air Cylinder

MFC

O₃ generator

Inlet Manifold

Analysers

Concentrations ~ EU Limit Values
Sample System Collection Efficiency Results

Nitrogen Dioxide

Sites tested = 21

Collection Efficiency, %

Sites = 21
Sample System Collection Efficiency Results

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Collection Efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>Sulphur Dioxide</td>
<td></td>
</tr>
<tr>
<td>Sites = 6</td>
<td>96</td>
</tr>
<tr>
<td>Ozone</td>
<td></td>
</tr>
<tr>
<td>Sites = 4</td>
<td>90</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td></td>
</tr>
<tr>
<td>Sites = 2</td>
<td>96</td>
</tr>
</tbody>
</table>

Traced to a very long sample line
Summary

Site audits provide a vital element of external quality assurance, significantly increasing the accuracy of some of the data produced and confidence in all of it.