



Department  
for Environment  
Food & Rural Affairs

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# Quality Assurance and Quality Control (QA/QC) Procedures for UK Air Quality Monitoring under 2008/50/EC and 2004/107/EC

September 2013 (updated September 2016)



Llywodraeth Cymru  
Welsh Government



Department of  
**Agriculture, Environment  
and Rural Affairs**

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Any enquiries regarding this document/publication should be sent to us at:

[agevidence@defra.gsi.gov.uk](mailto:agevidence@defra.gsi.gov.uk)

Department for Environment, Food and Rural Affairs

Nobel House

17 Smith Square

London SW1P 3JR

## Executive Summary

This report has been prepared for the UK Department of Environment, Food and Rural Affairs (Defra) and the Devolved Administrations of Scotland, Wales and Northern Ireland.

Within the UK, air quality monitoring is undertaken to provide information on air pollutant concentrations. The primary function of the monitoring is to provide data for the purpose of assessing the UK's compliance with EU Directives on Air Quality. The data are also used by scientists, policy makers and planners to enable them to make informed decisions on managing and improving air quality for the benefit of health and the natural environment.

The UK's air quality compliance monitoring is divided into several sub-networks for operational and management purposes. The relevant sub-networks are:

- The Automatic Urban and Rural Network (AURN);
- The UK Hydrocarbon Network;
- The UK Urban and Industrial Metals Network;
- The Rural Metals Network; and
- The Polycyclic Aromatic Hydrocarbons (PAH) Network.

To ensure that the data produced are fit for purpose, robust QA/QC procedures are in place for each pollutant. Responsibility for their implementation rests with the relevant management and QA/QC contractors for the sub-network. These ensure the accuracy and precision of the published pollutant concentrations.

This report outlines the EU and UK data quality requirements and describes how these are addressed for all the relevant pollutants monitored. The report covers:

- Measurement methods
- Type-testing and equivalence of analysers
- Data telemetry, and validation of provisional data
- QA/QC including network inter-comparisons and data ratification
- Traceability of the measurements to national and international standards.
- Calculation of uncertainty for comparison with Data Quality Objectives.

Finally, a separate chapter is included, providing additional information on the QA/QC arrangements in place for air quality monitoring in Gibraltar, where these differ from those used in the UK.

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# 1 Introduction

## 1.1 Scope

This document provides information on the quality assurance and quality control (QA/QC) procedures applied to air quality monitoring undertaken within the United Kingdom (UK) to assess compliance with European Union (EU) Directives on air quality.

For operational and management reasons, the UK's air quality compliance monitoring regime is organised into several constituent sub-networks. However, all these networks form part of a single compliance network. The relevant sub-networks are:

- The Automatic Urban and Rural Network (AURN);
- The UK Hydrocarbon Network;
- The UK Urban and Industrial Metals Network;
- The Rural Metals Network; and
- The Polycyclic Aromatic Hydrocarbons (PAH) Network.

This document is not intended as an operational reference manual for day-to-day working purposes. Rather, it is intended to satisfy the requirement for a comprehensive record of the QA/QC procedures used for the UK's various types of compliance monitoring, together in one document.

Section 2 of this document lists the relevant Directives and the pollutants they cover, the reference methods, and the Data Quality Objectives (DQOs). Section 3 then provides an overview of the UK's compliance monitoring - the pollutants measured by each sub-network, techniques used, network operation and quality management procedures.

For each sub-network, this document then describes:

- Type testing and equivalence requirements and procedures (section 4)
- How data are collected from the monitoring sites, how they are handled and how the provisional data are disseminated to the public and other stakeholders (section 5).
- QA/QC: how the instruments are calibrated, the precision and accuracy quantified and monitored, and the processes of data validation and ratification (section 6).

- Details of traceability: in particular, how the requirements of the relevant EU Directives are met, for measurements to be traceable in accordance with ISO/IEC 17025:2005 (section 7).
- Measurement and calculation of uncertainty (section 8).

The final section provides additional information on the QA/QC arrangements in place for air quality monitoring in Gibraltar. The section highlights which aspects differ from those used in the UK and, where differences exist, the procedures used in Gibraltar are outlined.



## 2 EU Requirements

### 2.1 EU Legislation on Ambient Air Quality

EU Directives place a duty on each EU Member State to institute policies to protect and improve its environment and the health of its citizens. The Directives contain Environmental Objectives which set limit and target values for the concentrations of pollutants in ambient air. All Member States must incorporate - or “transpose” - the provisions of EU Directives into their own national law by a specified date.

Directive 2008/50/EC<sup>1</sup> of the European Parliament and of the Council of 21<sup>st</sup> May 2008, on Ambient Air Quality and Cleaner Air for Europe, was adopted in June 2008. This Directive (referred to here as the Air Quality Directive) substantially revised and merged four previous directives and one Decision:

- Directive 1996/62/EC on Ambient Air Quality Assessment and Management (the Framework Directive)<sup>2</sup>, which established a framework under which the EU agreed air quality limit values for pollutants specified in a series of Daughter Directives.
- The First Daughter Directive<sup>3</sup> (1999/30/EC), which set limit values for sulphur dioxide, oxides of nitrogen, particulate matter as PM<sub>10</sub>, and lead (Pb).
- The Second Daughter Directive<sup>4</sup> (2000/69/EC), which set limit values for carbon monoxide (CO) and benzene.
- The Third Daughter Directive<sup>5</sup> (or Ozone Directive, 2002/3/EC), which set target values for the protection of human health and vegetation.
- Council Decision 97/101/EC<sup>6</sup>, which established a reciprocal exchange of air quality monitoring information and data, between the Member States.

The Fourth Daughter Directive (2004/107/EC<sup>7</sup>) covers the four metallic elements cadmium (Cd), arsenic (As), nickel (Ni) and mercury (Hg) together with a group of compounds known as Polycyclic Aromatic Hydrocarbons (PAH). This Directive contains target values for the above metallic elements, also benzo [a] pyrene, used as a “marker” for all PAH species.

The Air Quality Directive retained all the existing air quality standards, and also introduced a framework for assessing PM<sub>2.5</sub> particulate matter. This included limit values, an average exposure indicator, an exposure concentration obligation and a national exposure reduction target.

The provisions of the Air Quality Directive and Fourth Daughter Directive were transposed by the Air Quality Standards Regulations 2010<sup>8</sup> in England, the Air Quality Standards (Scotland) Regulations 2010<sup>9</sup> in Scotland, the Air Quality

Standards (Wales) Regulations 2010 in Wales<sup>10</sup> and the Air Quality Standards Regulations (Northern Ireland) 2010<sup>11</sup>.

As of 12<sup>th</sup> December 2011, Commission Implementing Decision 2011/850/EU<sup>12</sup> introduced new rules for Directives 2004/107/EC and 2008/50/EC as regards the reciprocal exchange of information and reporting on ambient air quality. These rules are commonly known as the air quality e-reporting Implementing Provisions for Reporting.

The Directive provides a common approach to the assessment of ambient air quality for Member States, thus improving comparability of data and benchmarking, through the use of standardised measurement techniques and criteria for monitoring sites and reporting. The QA/QC ensures that these methods and criteria are adhered to in the UK, in order to maximise confidence in the resulting data.

## 2.2 Pollutants Covered

The above Directives require assessment of the following pollutants:

- Sulphur dioxide (SO<sub>2</sub>)
- Nitrogen dioxide (NO<sub>2</sub>) and total oxides of nitrogen (NO<sub>x</sub>)
- Carbon monoxide (CO)
- Benzene
- Particulate matter as PM<sub>10</sub> and PM<sub>2.5</sub>
- Ozone
- Ozone precursor substances (*note – there are no limit or target values, or DQOs, for these.*)
- Lead
- Arsenic
- Cadmium
- Nickel
- Mercury
- Benzo (a) pyrene, as an indicator species for the group of compounds known as PAH.
- Additional recommended PAH species.
- Deposition of PAH and metallic elements in the particulate phase. (*Note – there are no limit or target values for these.*)

The Air Quality Directive also requires the measurement of the following chemical species in the PM<sub>2.5</sub> fraction: sulphate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sodium ion (Na<sup>+</sup>), potassium ion (K<sup>+</sup>), ammonium ion (NH<sub>4</sub><sup>+</sup>), chloride ion (Cl<sup>-</sup>), calcium

ion (Ca<sup>2+</sup>), magnesium ion (Mg<sup>2+</sup>), elemental carbon (EC) and organic carbon (OC). These are to be measured in rural background areas. (Note – there are no limit or target values, or DQOs, for these.)

## 2.3 Data Quality Objectives (DQOs)

DQOs are provided in Annex I (one) of the Air Quality Directive and are summarised in Table 2-1 for the pollutants covered by this report. This table shows the objectives for fixed measurements: objectives are also set for indicative measurements and modelling but are not presented here.

**Table 2-1 DQOs for ambient air quality assessment, fixed measurements**

	SO <sub>2</sub> , NO <sub>2</sub> , NO <sub>x</sub> , CO	Benzene	PM <sub>10</sub> /PM <sub>2.5</sub> & Pb	O <sub>3</sub> and related NO and NO <sub>2</sub>
<b>Fixed measurements</b> <sup>(a)</sup> Uncertainty	15%	25%	25%	15%
Minimum data capture	90%	90%	90%	90% during summer, 75% during winter
Minimum time coverage, urban background and urban traffic	-	35% <sup>(b)</sup>	-	-
Minimum time coverage, industrial sites	-	90%	-	-

(a) The uncertainty (expressed at a 95% confidence level) of the assessment methods will be evaluated in accordance with the principles of the CEN Guide to the Expression of Uncertainty in Measurement (ENV 13005-1999), the methodology of International Organisation for Standardisation ISO 5725:1994 and the guidance provided in the CEN report 'Air Quality – Approach to Uncertainty Estimation for Ambient Air Reference Measurement Methods' (CR 14377:2002E). The percentages for uncertainty in the above table are given for individual measurements averaged over the period considered by the limit value (or target value in the case of ozone), for a 95% confidence interval. The uncertainty for the fixed measurements shall be interpreted as being applicable in the region of the appropriate limit value (or target value in the case of ozone).

(b) Time coverage is distributed over the year to be representative of various conditions for climate and traffic.

Calculation of data coverage and allowance for planned maintenance will be taken into account in determining compliance with the DQOs. In the 4<sup>th</sup> Daughter Directive, DQOs are provided in Annex IV. These are summarised in Table 2-2.

**Table 2-2 Data Quality Objectives of 4<sup>th</sup> Daughter Directive**

	<b>B[a]P</b>	<b>As, Cd and Ni</b>	<b>PAH other than B[a]P, and total gaseous Hg</b>	<b>Total Deposition</b>
Uncertainty				
Fixed and indicative measurements	50%	40%	50%	70%
Modelling	60%	60%	60%	60%
Minimum data capture	90%	90%	90%	90%
Minimum time coverage				
Fixed measurements	30%	50%	-	-
Indicative measurements <sup>a</sup>	14%	14%	14%	33%

<sup>a</sup> Indicative measurements being measurements that are performed at a reduced regularity but fulfil the other data quality objectives

Details of how measurement uncertainty is calculated are provided in section 9. The managers of each sub-network are required to report compliance with the above DQOs on an annual basis. Annual reports from the sub-networks are published online via the “Library” section of the Defra UK Air Information Resource, UK-AIR, under the option for “Monitoring Networks”- see [http://uk-air.defra.gov.uk/library/reports?section\\_id=13](http://uk-air.defra.gov.uk/library/reports?section_id=13) .

## 2.4 Measurement Methods

The EU reference methods of measurement for the various pollutants are specified in Annex VI of the Air Quality Directive. These are the Standard Methods developed

by CEN (the European Committee for Standardisation) and realised in the UK through published British Standards (BS) as follows:

- BS EN14211:2005<sup>13</sup> (NO<sub>x</sub>).
- BS EN14212:2005<sup>14</sup> (SO<sub>2</sub>).
- BS EN14625:2005<sup>15</sup> (O<sub>3</sub>).
- BS EN14626:2005<sup>16</sup> (CO).
- BS EN12341:1999<sup>17</sup> (PM<sub>10</sub>).
- BS EN14907:2005<sup>18</sup> (PM<sub>2.5</sub>).
- BS EN14662-3:2005<sup>19</sup> (benzene, C<sub>6</sub>H<sub>6</sub>).
- BS EN14902:2005<sup>20</sup> (Pb, Cd, As, and Ni in the PM<sub>10</sub> fraction of suspended particulate matter).
- BS EN15853:2010<sup>21</sup>, (Hg deposition).
- BS EN15841:2009<sup>22</sup>, (As, Cd, Pb and Ni in atmospheric deposition).

UK experts work closely with CEN to develop standards describing how analysers should be tested, approved for use, calibrated and have their ongoing performance determined. The standards allow Member States to reliably and consistently quantify the uncertainties associated with their measurements of air pollution. CEN, through the various Working Groups, continue to revise and improve the Standards as new information becomes available. Many of the QA/QC procedures adopted in the UK arise directly from the requirements of the CEN standard methods and are described in later sections of this report.

### 3 Overview of UK Compliance Monitoring

The pollutants measured in the UK air quality compliance monitoring sub-networks are detailed in Table 3-1.

**Table 3-1 The UK's Air Quality Compliance Monitoring in 2012**

Sub-Network	Pollutants
Automatic Urban and Rural Network (AURN)	Ambient concentrations of CO, NO <sub>x</sub> , NO (with NO <sub>2</sub> calculated as NO <sub>x</sub> - NO), SO <sub>2</sub> , O <sub>3</sub> , PM <sub>10</sub> , PM <sub>2.5</sub> .
UK Hydrocarbon Network	Ambient concentrations of Benzene and a range of VOCs
UK Urban and Industrial Metals Network	Ambient concentrations of As, Cd, cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), particulates-bound mercury (Hg[p]), total mercury (Hg[t]), total gaseous mercury (Hg[v]), manganese (Mn), Ni, Pb, platinum (Pt), selenium (Se), vanadium (V), zinc (Zn)
Rural Metals Network	Ambient concentrations, and deposition in the particulate phase, of aluminium (Al), As, barium (Ba), beryllium (Be), Cd, Co, Cr, caesium (Cs), Cu, Fe, mercury (Hg) lithium (Li), Mn, molybdenum (Mo), Ni, Pb, rubidium (Rb), antimony (Sb), scandium (Sc), Se, tin (Sn), strontium (Sr), titanium (Ti), uranium (U), vanadium (V), tungsten (W), Zn
PAH Network	Ambient concentrations, and deposition in the particulate phase, of 40 PAH species including benzo[a]pyrene.
Particle Numbers and Concentrations Network	Elemental Carbon (EC) and Organic Carbon (OC) in PM <sub>2.5</sub> .
UKEAP Network	The following cations and anions in the PM <sub>2.5</sub> fraction, in rural background areas: sulphate (SO <sub>4</sub> <sup>2-</sup> ), nitrate (NO <sub>3</sub> <sup>-</sup> ), sodium ion (Na <sup>+</sup> ), potassium ion (K <sup>+</sup> ), ammonium ion (NH <sub>4</sub> <sup>+</sup> ), chloride ion (Cl <sup>-</sup> ), calcium ion (Ca <sup>2+</sup> ), magnesium ion (Mg <sup>2+</sup> ).

Other air quality research monitoring is undertaken in further sub-networks in the UK but is not detailed here as it is not used for compliance purposes. For information on these other monitoring programmes, please refer to the following page on Defra's online UK Air Information Resource (UK-AIR): <http://uk-air.defra.gov.uk/networks/network-info?view=non-automatic> .

## 3.1 Overview of the AURN

The Automatic Urban and Rural Network (AURN) is the largest automatic monitoring network in the UK and provides the majority of the UK's statutory compliance monitoring evidence base. Data from the AURN are available on Defra's online UK Air Information Resource, UK-AIR at <http://uk-air.defra.gov.uk/>. The AURN aims to:

- Inform the public about air quality in near-real time.
- Provide data for comparison with statutory air quality standards, objectives, target and limit values.
- Assess effects of air pollution on health and the environment
- Inform and support the development of cost-effective planning solutions and identify long-term trends and sources of pollution.
- Inform policy development.
- Provide data for use by the scientific community in research.
- Enhance our understanding of atmospheric chemistry.

### 3.1.1 Pollutants measured in the AURN

The pollutants measured by the AURN are listed in Table 3-1 above.

### 3.1.2 Measurement Techniques Used in the AURN

The AURN consists predominantly of automatic monitoring equipment. Gaseous pollutants are monitored with the defined EU reference methods. For particulate matter the AURN is based on methods which have demonstrated equivalence to the reference method, but which (unlike the reference method) allow continuous on-line monitoring. A small number of sites use Partisol gravimetric samplers providing daily mean results. Details are provided in Table 3-2.

**Table 3-2 AURN Measurement Techniques**

Pollutant	CEN standard/ref method	Details
O <sub>3</sub>	EN 14625:2012 “Ambient air quality – standard method for the measurement of the concentration of ozone by ultraviolet photometry”	<b>UV absorption:</b> ozone absorbs UV light. The absorption of UV by sampled air is used to calculate the ozone concentration.
NO <sub>2</sub> /NO <sub>x</sub>	EN 14211:2012 “Ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide [i.e. nitric oxide] by Chemiluminescence”	<b>Chemiluminescence:</b> this method measures the energy emitted when nitric oxide (NO) is reacted with ozone (O <sub>3</sub> ) in an evacuated chamber to form chemiluminescent nitrogen dioxide (NO <sub>2</sub> ).
SO <sub>2</sub>	EN 14212:2012 “Ambient air quality – Standard method for the measurement of the concentration of sulphur dioxide by UV fluorescence”	<b>UV fluorescence:</b> SO <sub>2</sub> molecules are excited to higher energy states by UV radiation. These excited molecules then release their energy as fluorescent radiation. The intensity of this is used to measure the concentration of SO <sub>2</sub> in sampled air.
CO	EN 14626:2012 “Ambient air quality - Standard method for the measurement of the concentration of carbon monoxide by non-dispersive infra red spectroscopy”	<b>IR absorption:</b> CO strongly absorbs infrared radiation of wavelength 4.5 to 4.9 μm. A reference detection system is used to alternately measure absorption due to CO in the sampled air stream and a high-concentration pure CO signal as a correlated reference. An infrared detector gives a signal proportional to the CO concentration.
PM <sub>10</sub> and PM <sub>2.5</sub>	<p>EN 12341:1999 “Air quality. Determination of the PM<sub>10</sub> fraction of suspended particulate matter. Reference method and field test procedure to demonstrate reference equivalence of measurement methods”</p> <p>EN 14907:2005 “Ambient air quality - Standard gravimetric measurement method for the determination of the PM<sub>2.5</sub> mass fraction of suspended particulate matter”</p>	<p>The AURN uses three methods which are equivalent for one or both parameters:</p> <p>The Filter Dynamic Measurement System (<b>FDMS</b>), which determines particulate concentration by continuously weighing particles deposited on a filter.</p> <p>The <b>Beta-Attenuation Monitor</b> (BAM) which measures the attenuation of beta rays passing through a paper filter on which particulate matter from sampled air has been collected.</p> <p>The <b>Partisol</b> – a gravimetric sampler that collects daily samples onto a filter for subsequent weighing.</p>



Between 2004 and 2006 a series of tests on ambient particulate analysers was undertaken by Bureau Veritas on behalf of Defra and the UK Devolved Administrations (DAs)<sup>23</sup>. The purpose of the test programme was to test the overall performance of a number of 'candidate' particulate matter samplers with that of the EU reference methods for PM<sub>10</sub> and PM<sub>2.5</sub> particulate fractions. The aims of these tests were to assess the achievement of criteria of the DQOs in Annex 1 of the Air Quality Directive, and to provide the required information for the Competent Authority (Defra and the DAs) to decide whether to declare the instruments equivalent to the reference method for use in the UK.

For those particulate matter monitoring instruments that are in the AURN, the previously reported 2006 equivalence trials data (as well as further data collected since) were reprocessed in accordance with the January 2010 version of The Guide to Demonstration of Equivalence (GDE)<sup>24</sup>. This GDE supersedes a version previously published in November 2005. A new document, EN TS16450, will be brought out in the near future and may be incorporated into the Air Quality Directive at a later date.

The 2010 update of the 2006 equivalence trial data showed that for the instruments deployed in the original tests (the Filter Dynamic Measurement System FDMS 8500, Partisol 2025 and PM<sub>10</sub> Unheated Beta Attenuation Monitor BAM 1020), the results and recommendations are still valid<sup>25</sup>. This justifies the UK's continued use of these instruments within the AURN.

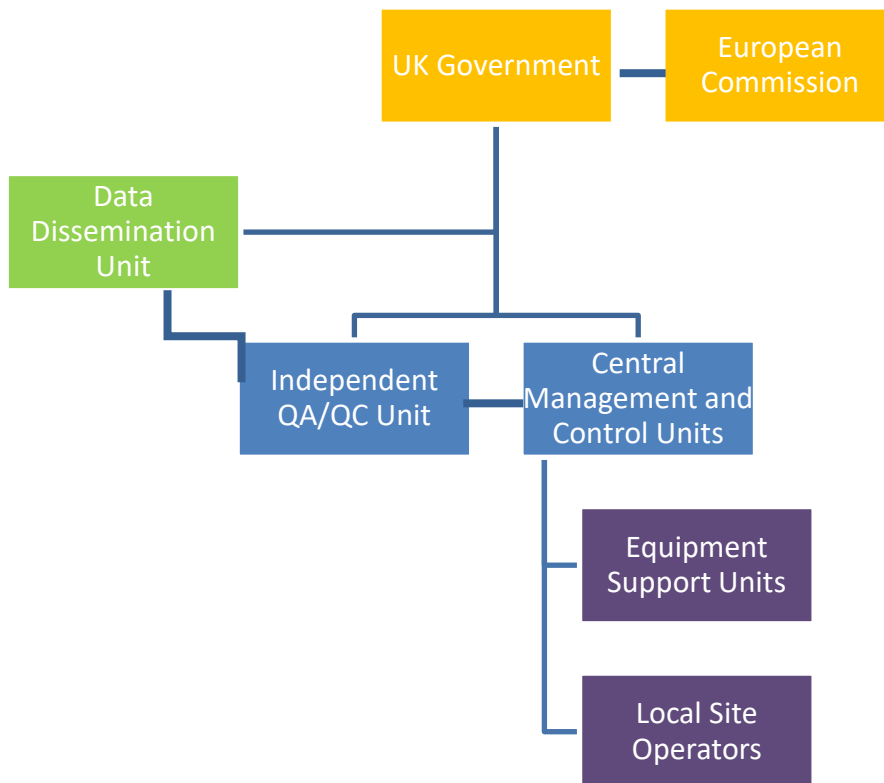
### **3.1.3 AURN Network Operation and Management**

Several organisations are involved in the day-to-day running of the network, under contract to Defra and the DAs. At the time of writing (2013), the role of Central Management and Co-ordination Unit (CMCU) for the AURN is contracted to Bureau Veritas, whilst the Environmental Research Group of King's College London has been appointed as CMCU for a number of AURN monitoring sites in London and the South East. Ricardo-AEA currently undertakes the role of Quality Assurance and Control Unit (QA/QC Unit) for sites within the AURN. The responsibility for operating individual monitoring sites is assigned to local site operators (LSOs) with relevant experience in the field under the direct management of (and under contract to) CMCU. Calibration gases for the network are supplied by Air Liquide UK Ltd and are provided with a United Kingdom Accreditation Service (UKAS) certificate of calibration by Ricardo-AEA. The monitoring equipment is serviced and maintained by a number of Equipment Support Units (ESUs), under contract to the CMCU.

Dissemination of the data from the AURN via the online Air Information Resource (UK-AIR) at <http://uk-air.defra.gov.uk/> and other media such as free telephone services and Twitter is undertaken by the Data Dissemination Unit (under separate

contract). A summary report of the data is also published annually in the “Air Pollution in the UK” series of reports, available online via UK-AIR.

Figure 3-1 summarises the structure of the AURN and the major interactions between the participating organisations.



**Figure 3-1 Structure of the AURN**

Quality control and assurance are managed by the QA/QC Unit, whose primary function is to maintain the data quality and ensure that the EU Directive DQOs are met. In this way this independent unit is able to coordinate the quality efforts of all other AURN stakeholders and approach all QA/QC issues in a focused and structured way.

### 3.1.4 Role of the AURN and QA/QC Unit

The role of the QA/QC Unit is to ensure that data produced by the AURN are robust, reliable and of high quality. These data are reported to the Commission, so should meet the legal obligations and DQOs of the Directives. The QA/QC Unit interacts

closely with the AURN CMCU and Gas Provision contractors to ensure that these network objectives are met.

Compliance with the data capture objectives of the Air Quality Directive, for each pollutant at each site, is currently reported quarterly in the series of reports entitled “QA/QC Data Ratification Report for the Automatic Urban and Rural Network”, available via the Library pages of UK-AIR (see <http://uk-air.defra.gov.uk/library/> ). The quarterly report for the final three months of the year (October to December) contains a summary of data capture for the full calendar year. At the time of writing, the most recent annual report for the AURN is for 2011<sup>26</sup>.

## 3.2 Overview of the Hydrocarbon Network

The Air Quality Directive requires measurement and reporting of benzene (which is covered by the Air Quality Directive as a pollutant in its own right), and ozone precursor substances. The ozone precursor substances include volatile organic compounds (VOCs): Annex X (ten) of the Directive provides a list of 29 species recommended for measurement. The Hydrocarbon Network includes three components: the Automatic Hydrocarbon Network, European monitoring and Evaluation Programme (EMEP) supersites and the Non-Automatic Hydrocarbon Network.

Ozone precursor measurement is carried out by the Automatic Hydrocarbon Network. Automatic hourly measurements of a range of hydrocarbon species (including all the ozone precursor species specified in Annex X of the Directive except formaldehyde and total non-methane hydrocarbons), are made using automated pumped sampling with *in-situ* gas chromatography, at four sites in the UK. The VOCs monitored include benzene. Following advice from the UK Air Quality Expert Group (AQEG) Defra requested additional measurements in response to the potential increase of aldehyde emissions from biofuels. Formaldehyde and acetaldehyde have been measured from August 2012 at five UK sites. These are all co-located with AURN sites.

Two monitoring sites, at Harwell in Oxfordshire and Auchencorth Moss in Lothian, are also part of the European EMEP programme, an international co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe (see <http://pollutantdeposition.defra.gov.uk/emep> for further details).

The four automatic Hydrocarbon Network sites are accompanied by a network of 34 non-automatic sites. These measure ambient concentrations of benzene only, by the CEN standard method<sup>27</sup>, which involves pumping air through an adsorption tube to

trap the compound, which is later analysed in a laboratory. At each site two tubes sample alternately every eight minutes for a fortnightly exposure period. This network monitors compliance with the Air Quality Directive's limit value for benzene. All non-automatic sites in the Hydrocarbon Network are co-located with AURN sites.

### 3.2.1 Pollutants Measured in the Hydrocarbon Network

Table 3-3 shows the compounds measured in the Hydrocarbons network. Only benzene monitoring is required for compliance with the Air Quality Directive.

**Table 3-3 Compounds Measured by the Hydrocarbons Network (including the Automatic Hydrocarbon Network, EMEP supersites and the Non-Automatic Hydrocarbon Network)**

Compounds	
ethane	2-methylpentane
ethene	n-hexane
propane	isoprene
propene	benzene
ethyne	i-octane
i-butane	n-heptane
n-butane	n-octane
trans-2-butene	Toluene
1-butene	ethylbenzene
cis-2-butene	meta- and para-xylene
i-pentane	ortho-xylene
n-pentane	1,3,5-trimethylbenzene
1,3-butadiene	1,2,4-trimethylbenzene
trans-2-pentene	1,2,3-trimethylbenzene
1-pentene	

### 3.2.2 Techniques used in the Hydrocarbon Network

The automatic hydrocarbon network (for ozone precursor compounds and benzene) uses automated pumped sampling with *in-situ* gas chromatography. The sample is drawn from the ambient atmosphere to the analyser in as short a time as possible. This is achieved by use of a high volume sample manifold, where ambient air is drawn through the manifold to a point close to the inlet of the analyser. The rate at which the air is drawn through this high volume inlet is such that the sample remains in the manifold for less than one second. It is then sampled from this point at a low flow rate into the analyser.

The analytical system within the automatic hydrocarbon analyser consists of an automatic trapping/thermal desorption system (using Peltier cooling) connected to a conventional gas chromatograph (GC). The thermal desorber (TD) collects the sample from ambient air. The TD extracts the analytes from the sample onto a Peltier cooled adsorbent trap. The trapped analytes are thermally desorbed and carried through a heated transfer line by carrier gas into the GC. The GC contains two columns and a heartcut device to separate, by volatility, the analytes into two fractions. The more volatile fraction is separated on a PLOT (Porous Layer Open Tubular) column whereas the less volatile fraction is separated on a methyl silicone column. A flame ionization detector monitors the chromatography on each column. The control and data-handling system are run from a computer. The system is supplied with gases from a hydrogen generator, zero air compressor and a helium carrier gas cylinder.

### 3.2.3 Hydrocarbon Network Operation and Management

Several organisations are involved in the day-to-day running of the network, under contract to Defra. At the time of writing (2013), the role of CMCU for the Hydrocarbon Network is contracted to Ricardo-AEA, which also undertakes the role of QA/QC Unit. The responsibility for operating individual monitoring sites is assigned to LSOs with relevant experience in the field under the direct management of (and under contract to) the CMCU. Calibration gases for the network are supplied by the National Physical Laboratory (NPL). The monitoring equipment is serviced and maintained by PerkinElmer, under contract to the CMCU.

Key aspects of the operation and management of this network are as follows:

- Maintenance of the monitoring instruments and associated ancillary equipment in the network.
- Provision of on-site consumables.

- Carrying out preliminary validation of the data, for which proprietary pattern recognition software “MatchFinder” is used along with other computer software.
- Supplying these data to the Data Dissemination Unit.
- Retaining and maintaining the raw and validated air quality data in a separate archive.
- Taking appropriate actions, in consultation with the QA/QC contractor, to ensure that the network achieves the data quality objectives of the Air Quality Directive for benzene.

### 3.2.4 Quality Management in the Hydrocarbon Network

The main aspects of quality management in the hydrocarbon network are:

- Regular visits to network sites (at least once per year) and meetings with the LSOs in order to discuss and review the condition of the site and equipment, data capture and associated issues.
- An annual inter-calibration, with provision of advice, and where necessary, of any service and maintenance requirements arising from the findings.
- Yearly auditing of LSO operations, including the provision of operator training. These audits are timed to coincide with the inter-calibration to ensure cost-efficiency.
- Ratification of validated data provided by the CMCU. The ratified data are transferred to the Defra online air quality information resource (UK-AIR) within three months of receipt of data.
- Quarterly progress reporting to Defra to cover the operation of the network, data capture performance and trend analysis.
- Annual reports are produced to summarise the data collected. These reports describe the data collected and reported for the calendar year.
- Long term data analysis.
- Attendance at the annual network review meeting with the CMCU, Defra, LSOs and other stakeholders.
- Provision of policy advice on hydrocarbon monitoring issues and data interpretation to Defra, LSOs, the Air Quality Expert Group and other review groups as requested.
- Provision of calibration gases for both routine site calibration checks and six-monthly network intercalibrations.
- Provision of annual benzene and ozone precursor measurement data, for reporting to the Commission by 30<sup>th</sup> September of the following year.
- Attendance at any relevant EU intercomparisons and meetings. These are usually held at the EU Joint Research Council, Ispra although in the past

intercomparisons have also consisted of a 'round robin' analysis of travelling gas mixtures.

An annual report is produced covering both the automatic and non-automatic hydrocarbon monitoring. This includes comparison of the Network's performance with the Directive DQOs. The most recent report can be found at [http://uk-air.defra.gov.uk/library/reports?section\\_id=13](http://uk-air.defra.gov.uk/library/reports?section_id=13) <sup>28</sup>.

### 3.3 Overview of the Urban and Industrial Metals Network

The UK Urban and Industrial Metals Monitoring Network measures metal concentrations in PM<sub>10</sub> in urban locations. As of December 2012, this network comprised 25 monitoring sites around the country (15 in England, seven in Wales, two in Scotland and one in Northern Ireland). The Network is also referred to as the UK Heavy Metals Monitoring Network. The contractor responsible for the management of this network is the National Physical Laboratory (NPL).

The Network has the following objectives:

- To achieve compliance with monitoring requirements set out in European legislation.
- To provide data to the UK Government and European Commission (EC) on the UK's performance against the limit values, target values, and DQOs described in the relevant legislation.
- To assess impacts around 'hot spots' of metallic pollution to air, particularly in industrial areas.
- To produce accurate and reliable data for dissemination to the general public and for use by scientific and medical researchers and the air quality community.

The UK Urban and Industrial Metals Monitoring Network is the regulatory air quality monitoring network that fulfils the majority of the UK's obligation under the Air Quality Directives relating to the monitoring of the mass concentrations of lead, nickel, arsenic and cadmium, in the PM<sub>10</sub> phase of ambient air, and total gaseous mercury (referred to as: Hg(v)). The Network forms the basis of the UK's compliance monitoring for:

- The Air Quality Directive (for lead).
- The Fourth Daughter Directive (for arsenic, cadmium, nickel and mercury).

The Urban and Industrial Metals Network does not make any measurements of deposition of metallic elements.

### **3.3.1 Pollutants measured in the Urban and Industrial Metals Network**

The full suite of metals measured by the Network in PM<sub>10</sub> is: arsenic, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead, platinum, selenium, vanadium, zinc and mercury.

### **3.3.2 Measurement Techniques used in the Urban and Industrial Metals Network**

Ambient concentrations of metals are measured by sampling in the PM<sub>10</sub> phase of ambient air, onto filters. This is done using Partisol 2000 instruments (fitted with PM<sub>10</sub> selective inlet heads) operating at a calibrated flow rate, nominally of 1 m<sup>3</sup> h<sup>-1</sup>. This sampling is carried out in accordance with EN 12341:1999. The filters are then returned to the contractor's laboratory where they are analysed to determine the content of various metals in the particulate matter, in order to produce concentration values for these metals in ambient air according to EN 14902:2005.

Total gaseous mercury is additionally sampled onto adsorption tubes at 13 of these Network sites (seven in England, three in Wales, two in Scotland, and one in Northern Ireland). These absorption tubes are then analysed at the contractor's laboratory according to EN 15852:2010<sup>29</sup> to produce concentration values for total gaseous mercury in ambient air.

Weekly concentration data are produced for metals in PM<sub>10</sub> at six locations and for mercury vapour at three locations. All other stations produce data averaged over four-weekly periods. The production of the data is subject to a number of rigorous QA/QC procedures that are detailed in subsequent sections.

### **3.3.3 Analytical Techniques used in the Urban and Industrial Metals Network**

Analysis for particulate-phase metals is carried out by the contractor. This uses PerkinElmer Elan DRC II and Elan 9000 ICP-MS mass spectrometers, following the contractor's procedure, accredited by UKAS to ISO 17025:2005, which is fully compliant with the requirements of EN 14902:2005.

Upon arrival at the contractor's laboratory, the filters are cut accurately in half (for sites where weekly results are produced) and into quarters (where four weekly



results are produced). For the sites producing weekly data each portion is digested at temperatures up to 220°C using an Anton Parr Multiwave 3000 microwave. For the sites producing four-weekly data one quarter of each of the four filters comprising the four week period is digested. The digestion mixtures used are:

- Mercury and platinum: 5 ml of nitric acid and 5 ml hydrochloric acid.
- All other metals: 8 ml of nitric acid and 2 ml hydrogen peroxide.

ICP-MS analysis of the digested solutions is carried out using at least four gravimetrically-prepared calibration solutions. A quality assurance (QA) standard is repeatedly analysed (after every two solutions), and the change in response of the QA standard has been mathematically modelled to correct for the long-term drift of the instrument. The short-term drift of the ICP-MS is corrected for by use of an internal standards mixture (containing elements yttrium (Y), indium (In), bismuth (Bi), scandium (Sc), gallium (Ga) and rhodium (Rh) continuously added to all the samples via a mixing block. Each sample is analysed in triplicate, each analysis comprising five replicates. The amount of each metal in solution (and its uncertainty) is then determined by a method of generalised least squares using software developed by the contractor to construct a calibration curve.

Analysis of total gaseous mercury samples is carried out using a PS Analytical Sir Galahad II analyser with a fluorescence detector, using the contractor's procedure which is accredited by UKAS to ISO 17025:2005, which is in accordance with the published reference method EN 15852:2010. The instrument is calibrated by use of a gas-tight syringe, making multiple injections of known amounts of mercury vapour onto the permanent trap of the analyser. Sampled adsorption tubes are placed in the remote port of the instrument and heated to 900°C, desorbing the mercury onto a permanent trap. Subsequent heating of this trap then desorbs the mercury onto the detector.

### **3.3.4 Urban and Industrial Metals Network Operation and Management**

Operation of the network is currently managed by NPL, using Local Site Operators (LSOs) who are responsible for changing samples using NPL protocols. Samples are sent to NPL's laboratory for analysis. All metal concentrations are analysed by the contractor using strict QA/QC protocols and uploaded to the UK-AIR online data repository. Details of data handling for this network are provided in section 5.4.1.

A service and maintenance contract is in operation, with 6-monthly service rounds and calibrations undertaken by an ESU under subcontract. The ESU is called out as required to deal with any equipment problems that might occur.

The contractor carries out annual site audit visits to all the Network sites. At these visits the site infrastructure, performance and integrity are assessed. The LSOs are also audited and receive extra training where required.

### **3.3.5 Quality Management in the Urban and Industrial Metals Network**

Particulate samples are taken at all sites in the Network using Partisol 2000 instruments (fitted with PM<sub>10</sub> heads) operating at a calibrated flow rate, nominally of 1 m<sup>3</sup> h<sup>-1</sup>, in accordance with EN 12341:1999.

Analysis for particulate-phase metals is carried out by the contractor at its laboratory, using PerkinElmer Elan DRC II and Elan 9000 Inductively Coupled Plasma Mass Spectrometry (ICP-MS), following the contractor's procedure, accredited by UKAS to International Organisation for Standardisation ISO 17025:2005<sup>30</sup>. This is fully compliant with the requirements of EN 14902:2005.

Analysis of total gaseous mercury samples is carried out at the contractor's laboratory using a PS Analytical Sir Galahad II analyser with a fluorescence detector, using NPL's procedure, accredited by UKAS to ISO 17025:2005, which is in accordance with the published reference method EN 15852:2010. A manual variant of EN 15852:2010 used in the Network has been recently shown to be equivalent to the automatic reference method within the uncertainty of the analytical determination.

An annual report is produced, covering both the Urban and Rural Metals Networks. This includes comparison of the Networks' performance with the Directive DQOs. The reports can be found at [http://uk-air.defra.gov.uk/library/reports?section\\_id=13](http://uk-air.defra.gov.uk/library/reports?section_id=13). At the time of writing ( 2013) the most recent report covers calendar year 2011<sup>31</sup>.

## **3.4 Overview of the Rural Metals Network**

The Rural Metals (metals deposition mapping) network measures metal concentrations in PM<sub>10</sub> (at 11 rural sites) and concentrations in rain water (at 14 rural sites). The concentration fields are then combined with the local meteorological data (rainfall etc.) to calculate values for wet deposition (from rain and snow etc.), dry deposition (from dust settling etc.) and cloud deposition (condensation of cloud droplets).

This rural network complements the UK Urban and Industrial Metals Network, which predominantly monitors at industrial and urban locations.

### **3.4.1 Pollutants measured in Rural Metals Network**

A total of 27 different metals are analysed in particulate samples of air (PM<sub>10</sub> fraction) and rainwater collected from 11 sites (with 3 additional rainwater only sites) in rural areas across the UK. The sites were specifically chosen to be representative of background sites, and are as free from local sources of metal emissions as possible, while still being accessible for site operators. The metals analysed are: aluminium (Al), arsenic, antimony, barium, beryllium, cadmium, caesium, chromium, cobalt, copper, iron, lead, lithium, manganese, mercury, molybdenum, nickel, rubidium, scandium, selenium, strontium, tin, titanium, tungsten, uranium, vanadium and zinc. Note that due to quality-control issues, scandium will be removed from the suite of analytes from 2013 onwards. The network also measures continuous mercury concentrations at the two EMEP supersites within the network (Auchencorth Moss and Harwell).

### **3.4.2 Measurement Techniques used in Rural Metals Network**

#### ***3.4.2.1 Particulates***

Aerosol is sampled using Thermo Partisol Plus 2025 sequential PM<sub>10</sub> samplers that are operated at a flow rate of 1 m<sup>3</sup> h<sup>-1</sup> using 47 mm diameter Nitrocellulose filters in FRM-style filter cassettes. The air sampling period is 1 week, with the filter changeover time being set at 06:00 on the morning of the LSO visit. Experience has shown that this approach maximises the chance of detecting and rectifying a sampler fault such as Filter Exchange Error. Filter cassettes are assembled within a laminar flow cabinet in a dedicated clean room (Certified to Class 5 under ISO 14644-1:1999<sup>32</sup>) taking precautions to minimise metal contamination (i.e. using acid washed equipment and clean-room powder-free gloves). Aerosol sampler deployment and changeover of filter cassettes conform to EMEP standards and aim to prevent contamination by providing a rigorous protocol for filter changeover and laboratory preparation prior to analysis.

#### ***3.4.2.2 Heavy Metals in Rainfall***

Bulk collectors, bottle and funnel type, are deployed within the deposition network for the collection of bulk precipitation. The levels of metals found within precipitation are at the µg/l level or lower. It is therefore essential that rigorous protocols are used for cleaning sampling equipment between collector deployments to prevent contamination within the laboratory. Collectors comprising a 5 L polyethylene bottle, 14 cm diameter polyethylene funnel and a debris filter are cleaned by soaking for 24 hours with 0.1 M nitric acid. Bottles, funnels and debris filters are then rinsed with ultra-pure water (> 18 MΩ cm<sup>-1</sup>, Millipore) and finally dried in a filtered air drying

cabinet. Bulk collectors are assembled in a dedicated laboratory, double bagged, and then sent out to field sites in flight cases along with instructions for collector changeover.

### **3.4.2.3 Mercury in rainfall**

An adapted EMEP protocol for sampling mercury in precipitation ([EMEP \(2002\)](#)<sup>33</sup>) is used. The sampling equipment and cleaning protocols are specific for mercury because of this metal's special characteristics i.e. it is present at ng/l levels in precipitation and is prone to background contamination. Briefly, precipitation for the determination of mercury is collected in special precipitation samplers, based on those used within the Swedish National Monitoring Program, the Iverfeldt design. The collector was designed to prevent the diffusion of gaseous mercury ( $Hg_0$ ) into the collection vessel by the use of a 0.5m capillary tube between collection funnel and bottle. Sampling and analysis of bulk precipitation for mercury is particularly prone to contamination and therefore duplicate bulk precipitation samples are collected at each of the 10 network sites at which mercury is monitored.

The precipitation collector was based on the Iverfeldt design with a long tube to reduce mercury diffusion to and from the atmosphere. A number of modifications have been made in order to reduce possible contamination and improve safety of use:

- The funnel and tube are made of Polytetrafluoroethylene (PTFE) as per the Florida Atmospheric Monitoring Survey.
- The debris filter and capillary components are made of PTFE.
- The joints connecting individual components are close fitting and thus designed to reduce contamination from ingress of gaseous  $Hg_0$ .
- To reduce diffusion of gaseous  $Hg_0$  a glass bottle is used for final collection.

Glassware and reagents are rigorously tested in order to identify and reduce sources of contamination. Bottles are cleaned on a monthly basis according to the EMEP protocol by soaking in 1% nitric acid followed by bromate/bromide reagent and a final rinse with ultra pure water.

Mercury samplers are deployed, in duplicate, at the 11 main network sites, pre-acidified with hydrochloric acid as a preservative and changed on a monthly basis. The field protocols are similar to those used for the deployment of bulk precipitation samplers and are designed to prevent sample contamination at the field sites and during transport.

#### **3.4.2.4 Total gaseous mercury**

Mercury in air is sampled using an integrated sampler using the gold amalgamation technique. A small pump pulls air at about 25 ml min<sup>-1</sup> through two sequential traps containing gold coated sand, onto which the mercury adsorbs by amalgamation. This mercury is then released from the traps using thermal desorption during analysis in the laboratory. Two traps are used, the first to capture the bulk of the mercury, the second to catch any breakthrough. During sampling both traps are held at 100°C using an internal heater, to prevent build up of water vapour or organic compounds within the traps, which would impede mercury capture. A dry gas meter is used to give a quantitative concentration of mercury as mass per volume of air sampled. The sampling period is 2 weeks, to ensure a sufficient yield from the first trap, but with the second trap providing backup should the air concentration result in saturation of the first trap and breakthrough on to the second trap.

#### **3.4.3 Analytical Techniques Used in the Rural Metals Network**

With the exception of mercury, all metals are analysed using ICP-MS. Mercury in precipitation is determined by Atomic Fluorescence Spectrometry (AFS) using a PS Analytical Galahad detector employing pre-concentration of mercury on a gold trap to increase instrument sensitivity. Mercury in air is analysed using a PS Analytical Millennium Merlin analyser. The sample traps are thermally desorbed in a flow of argon onto the internal trap of the analyser, which is subsequently desorbed and the mercury content analysed by Cold Vapour Atomic Fluorescence Spectroscopy. Continuous measurements of Total Gaseous Mercury (TGM) are made using Tekran analysers, at two sites - Harwell and at Auchencorth Moss. Harwell monitors TGM only. At Auchencorth Moss additional mercury-speciation units are fitted to the Tekran instrument, allowing it to measure three species, Gaseous Elemental Mercury (GEM), Reactive Gaseous Mercury (RGM) and Particulate Mercury (HgP).

The analytical methods are compatible with:

- BSi British Standards EN 14902:2005, Ambient air quality – Standard method for the measurement of Pb, Cd, As, and Ni in the PM<sub>10</sub> fraction of suspended particulate matter.
- BSi British Standards EN 15853:2010, Ambient air quality – Standard method for the determination of mercury deposition.
- BSi British Standards EN 15841:2009, Ambient air quality – Standard method for the determination of arsenic, cadmium, lead and nickel in atmospheric deposition.

#### **3.4.3.1 Particulate:**

Exposed filters are returned to the analytical laboratory and processed upon arrival: filter identifications and metadata relating to aerosol sampling are entered into a dedicated rural deposition network database (ORACLE and Microsoft Access based) and individual PM<sub>10</sub> filters are assigned codes for processing via a laboratory information management system. Prior to measurement of trace metal contents the PM<sub>10</sub> filters are extracted using the recommended EMEP method for filter dissolution that has been adapted for the specific equipment used by the analyst. Briefly, PM<sub>10</sub> filters are extracted with 10 ml of HNO<sub>3</sub> (Baker, Ultrex II) for 12 minutes at 200°C within sealed Teflon vessels using a microwave digestion system (CEM, MARS Express). The method conforms to the temperature and time requirements for PM<sub>10</sub> filter extraction for trace metals prescribed by EMEP, although differing equipment is used. The concentration of trace metals in PM<sub>10</sub> filter digests is measured using ICPMS operating under standard conditions and employing matrix matched calibration standards and internal standardisation to compensate for instrument drift. Metal concentrations in air (ng m<sup>-3</sup>) are calculated using EMEP methods.

The microwave digestion method used for determining metal contents of PM<sub>10</sub> filters was validated using two standard reference materials (SRMs) A2 and B2, consisting of spiked air filters, from the National Institute of Occupational Health, Norway. Furthermore, although an appropriate and matched SRM was not available for routine ongoing quality control the contract managers decided to certify SRM 1633b (a coal fly ash from the US National Institute of Standards and Technology, NIST) using a microwave digestion method for PM<sub>10</sub> filters. The aim was to provide a material that would be used for monitoring the precision of the PM<sub>10</sub> digestion procedure over time. Note that SRM 1633b has been certified for total metal contents employing hydrofluoric acid and these values are expected to be considerably higher than those obtained using an extraction employing nitric acid only.

The certified filters, A2 and B2, NIST 1633b and a set of unexposed PM<sub>10</sub> filters (to assess background contamination) are extracted using the standard microwave digestion described above. The results for SRM A2 and B2 show that the microwave digestion provides recoveries within ±10% of certified values for the majority of elements for which certified values are available.

#### **3.4.3.2 Mercury in Rainfall:**

On return to the laboratory mercury collector bottles are weighed to estimate rainfall amounts and stored at 4°C prior to analysis. All analysis for mercury is completed within two weeks of the arrival within the laboratory of the first collector from the current deployment cycle. Mercury in precipitation is determined by AFS using a PS

Analytical Galahad detector employing pre-concentration of mercury on a gold trap to increase instrument sensitivity.

#### **3.4.4 Rural Metals Network Operation and Management**

Operation of the network is currently managed by the Centre for Ecology and Hydrology (CEH), using LSOs who are responsible for changing samples using CEH protocols derived from the Chemical Co-ordinating Centre of EMEP. Samples are sent to the CEH laboratories at Lancaster for analysis. The exposed mercury in air cartridges are sent to the CEH laboratory at Edinburgh for analysis. A service and maintenance contract is in operation, with 6 monthly service rounds and calibrations undertaken by Air Monitors Ltd. All data concentrations are analysed by CEH using strict QA/QC protocols and uploaded to the UK-AIR online data repository.

#### **3.4.5 Quality Management in Rural Metals Network**

The project is managed according to the requirements of the Joint Code of Practice for Research, to which both Defra and the current contractor are signatories. In addition, the chemical analysis performed at the contractor's Lancaster laboratory (all analyses with the exception of mercury in air and continuous mercury) are accredited by UKAS to ISO 17025:2005. Methods for the analysis of trace metals in precipitation and air, as well as cation and anion components of precipitation are included within the analyst's accreditation scheme (UKAS Testing Laboratory 2506; specific details can be found at <http://www.ukas.com/>). UKAS accreditation includes an outline of the performance characteristics for the instrumental methods used for the determination of trace metals in precipitation and PM<sub>10</sub> filters as well as mercury in precipitation. The performance characteristics comprise: validation data obtained during the process of laboratory accreditation by UKAS, ongoing quality control and participation in proficiency testing schemes where applicable (eg. LGC Standards Aquacheck: [http://www.lgcpt.com/Default\\_eng.aspx](http://www.lgcpt.com/Default_eng.aspx)).

### **3.5 Overview of the PAH Network**

The PAH Network monitors compliance with the Fourth Daughter Directive, which includes a target value of 1 ng m<sup>-3</sup> for the annual mean concentration of benzo[a]pyrene as a representative PAH, not to be exceeded after 31<sup>st</sup> December 2012. The objective of the PAH Network is therefore to determine the ambient concentrations of PAHs in ambient air in the UK through monitoring and chemical analysis, and deliver the following outputs:

- A UK-wide assessment of current concentrations of PAHs for assessment against the Fourth Daughter Directive and the UK Air Quality Strategy objectives, and provide information for future reviews of the Fourth Daughter Directive and UK Air Quality Strategy.
- Measurements and trends of airborne concentrations of PAHs in representative UK industrial, urban and other areas, and to compare and contrast them with those in rural locations.
- Data and metadata to demonstrate the UK's compliance with the Fourth Daughter Directive, the OSPAR convention and the UNECE Convention on Long Range Transboundary Air Pollutants.
- Data for submission to the UK-AIR Information Resource (<http://uk-air.defra.gov.uk>).
- An improvement in the understanding of PAH source and emission estimates, and to examine their agreement with the National Atmospheric Emissions Inventory ([www.naei.org.uk](http://www.naei.org.uk)). To also input into estimates of atmospheric PAH concentrations, future projections, and the identification of the key areas of uncertainty.

As of January 2013, the Network comprises 31 stations. Twenty of these 31 stations are in England, four in Scotland, four in Wales and three in Northern Ireland.

### **3.5.1 Pollutants measured in PAH Network**

The PAH compounds measured are shown in Table 3-4.



**Table 3-4 Range of PAHs analysed**

<b>PAH number</b>	<b>Compound</b>	<b>PAH number</b>	<b>Compound</b>
1	Naphthalene	21	Benz[a]anthracene
2	2-Methyl naphthalene	22	Cyclopenta[c,d]pyrene
3	1-Methyl naphthalene	23	Chrysene
4	Biphenyl	24	5-Methyl chrysene
5	Acenaphthylene	25	Benzo[b]fluoranthene
6	Acenaphthene	26	Benzo[k]fluoranthene
7	Fluorene	27	Benzo[j]fluoranthene
8	Phenanthrene	28	Benzo[e]pyrene
9	Anthracene	29	Benzo[a]pyrene
10	2-Methyl phenanthrene	30	Perylene
11	2-Methyl anthracene	31	Indeno[1,2,3-cd]pyrene
12	1-Methyl anthracene	32	Dibenz[a,c]anthracene
13	1-Methyl phenanthrene	33	Dibenz[a,h]anthracene
14	4,5-Methylene phenanthrene	34	Benzo[g,h,i]perylene
15	9-Methyl anthracene	35	Anthanthrene
16	Fluoranthene	36	Dibenzo[a,l]pyrene
17	Retene	37	Dibenzo[a,e]pyrene
18	Pyrene	38	Coronene
19	Benzo[b]naph[2,1-d] thiophene	39	Dibenzo[a,i]pyrene
20	Benzo[c]phenanthrene	40	Dibenzo[a,h]pyrene

### 3.5.2 Measurement Techniques used in the PAH Network

All stations utilise the Digitel DHA-80 high volume aerosol sampler. Ambient air is sampled through glass fibre filters and polyurethane foam (PUF) pads, which capture the PAH compounds for later analysis in a laboratory. The Network requires the sampling and analysis of the following types of samples:

***'A' (particulate) samples - samples taken from 'A' (Digitel filter only) stations.*** Samples of the PM<sub>10</sub> fraction of ambient air on a filter. 'A' samples are taken daily at all 31 Network stations using Digitel samplers with automatic filter changers. The duration of the sampling period is 24 hours, with the sample changeover occurring at midnight. The samples are bulked into groups representing calendar months for analysis. Sampling is in accordance with EN 12341:1999.

***'B' (particulate + vapour) samples – samples taken from 'B' (Digitel filter + PUF) stations.*** Samples of the PM<sub>10</sub> fraction of ambient air on a filter, plus the vapour phase of ambient air on a PUF cartridge. 'B' samples are taken for three (non-consecutive) days per week at two Network stations (Auchencorth Moss B & Harwell B) using Digitel samplers with automatic filter and PUF changers. Each sample is collected over 24 hours, and a sample is taken every 72 hours. The samples are bulked into groups representing calendar months for analysis. Sampling is in accordance with EN 12341:1999.

***'C' (deposition) samples - samples taken from 'C' (deposition) stations.*** Deposition samples taken fortnightly at two Network stations (Auchencorth Moss C & Harwell C). Each sample is collected over 14 days, and a sample is taken every 14 days. The samples are bulked into groups representing a four-week time period for analysis. Sampling is in accordance with EN 15980:2011<sup>34</sup>.

Following sampling, all filters, PUFs and deposition gauges are returned to the contractor's laboratory. Analysis takes place according to EN 15549:2008<sup>35</sup> for particulate and vapour phase samples and at an external laboratory for deposition samples according to EN 15980:2011. All analysis is accredited by UKAS to ISO 17025:2005. Analysis takes place for the PAHs listed in Table 3-4.

Analyses of 'A' (particulate) and 'B' (particulate + vapour) samples are carried out in accordance with EN 15549:2008. Samples are bulked into monthly batches (where applicable) and Soxhlet extracted using dichloromethane as the extraction solvent. The extracts are reduced in volume to 10 ml and a 1 ml aliquot of this undergoes a clean-up procedure using silica column chromatography. After clean-up, the sample is again reduced in volume to approximately 1 ml and analysed using gas chromatography – mass spectrometry (GC-MS). The GC-MS is calibrated using a series of calibration standards containing all the PAHs shown in Table 3-4 at a range

of concentrations covering the concentrations expected in the samples. The relative expanded uncertainty in a typical analytical result from a Network sample has been estimated at 20% - well within the DQO of an expanded uncertainty of 50%.

The limits of detection of the GC-MS method are determined by running a series of filter blanks every six months, and a solvent blank with every analytical run.

Analysis of 'C' (deposition) samples is carried out in accordance with EN 15980:2011. In summary, the deposition samples are bulked into four-weekly batches and extracted using liquid-liquid extraction. The resulting extract is dried, reduced to a volume of approximately 1 ml, and analysed using GC-MS as described above.

Final quantification is performed using the contractor's software which provides a generalised least squares best fit for calibration and inverse evaluation data with fully traceable measurement values and uncertainties.

### **3.5.3 PAH Network Operation and Management**

Operation of the network is currently managed by NPL, using LSOs who are responsible for changing samples following NPL protocols. A service and maintenance contract is in operation, with routine servicing undertaken by an ESU under subcontract. The ESU is called out as required to deal with any equipment problems.

The contractor carries out annual site audit visits to all the Network sites. At these visits the site infrastructure, performance and integrity are assessed. The LSOs are also audited and receive extra training where required.

### **3.5.4 Quality Management in the PAH Network**

QA/QC procedures are in place to cover all aspects of the Network management, from sampler operation to chemical analysis and data processing. Details of these can be found in section 6.

An annual report is produced for the PAH Network. This includes details of data capture achieved by the Network over the year. The reports can be found at [http://uk-air.defra.gov.uk/library/reports?section\\_id=13](http://uk-air.defra.gov.uk/library/reports?section_id=13) . At the time of writing ( 2013) the most recent report covers calendar year 2011<sup>36</sup>.

## 3.6 Other Measurements

### 3.6.1 Cations and Anions in Rural PM<sub>2.5</sub>

Measurements of particulate-phase cations and anions in PM<sub>2.5</sub>: sulphate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sodium ion (Na<sup>+</sup>), potassium ion (K<sup>+</sup>), ammonium ion (NH<sub>4</sub><sup>+</sup>), chloride ion (Cl<sup>-</sup>), calcium ion (Ca<sup>2+</sup>), and magnesium ion (Mg<sup>2+</sup>) are measured at two rural background sites. The two monitoring sites used are Harwell in Oxfordshire, and Auchencorth Moss in Lothian. These are both Level II EMEP 'supersites' and provide representative measurements of the atmospheric composition in the north and south of the UK. The monitoring is carried out under the UK Eutrophying and Acidifying atmospheric Pollutants (UKEAP) network contract: the current contractors are the Centre for Ecology and Hydrology (CEH) and Ricardo-AEA, who operate the Auchencorth Moss and Harwell sites respectively.

A Marga 2S is used to sample cations and anions in rural PM<sub>2.5</sub> at both sites. The Marga utilises an automated continuous-flow Wet Rotating Denuder (WRD) coupled to a Steam-Jet Aerosol Collector (SJAC) sampler. It provides hourly measurements of the water-soluble species (listed in the paragraph above) in aerosol PM<sub>2.5</sub> (and PM<sub>10</sub>). It also provides a measure of the concentration of water-soluble trace gases (HCl, HONO, HNO<sub>3</sub>, NH<sub>3</sub>, and SO<sub>2</sub>) in the sampled air. The Marga 2S samples the ambient air through a PM<sub>10</sub> size-selective inlet head at a nominal flow rate of 1 m<sup>3</sup> hr<sup>-1</sup>. The PM<sub>2.5</sub> fraction is separated from the sampled PM<sub>10</sub> by means of a cyclone separator fitted at the inlet to the PM<sub>2.5</sub> WRD. The WRD removes water-soluble gases from the sampled air stream. The sampled particles pass through the denuder unsampled and are activated by steam (generated at 120°C) into droplets in the SJAC and are removed via inertial separation in a cyclone.

The solutions of dissolved gases and aerosol species are analysed on-line, and in near real-time, by ion chromatography (IC). Parallel IC systems are used for the detection of the cationic and anionic species. An internal standard of lithium bromide (LiBr) is used for on-going calibration purposes. Before anion and cation IC analysis, the WRD sample and the internal standard are degassed and mixed. The liquid streams from the WRD and SJAC are collected separately into the syringe pump module which is located in the detector box. The syringe pump module consists of two pairs of syringes (four syringes in total). Two sets of syringes are required to enable tandem analysis and sampling: whilst the solutions in one set of syringes are transported in-turn to the anion and cation columns for analysis the next set are filled with solution from the WRD and SJAC from the PM<sub>2.5</sub> (and PM<sub>10</sub>) sampling box.

The Marga 2S used to measure anions and cation in rural PM<sub>2.5</sub> is a research-grade instrument. Currently there is no proposed or accepted ISO, CEN or equivalent BS

standard method for the determination of the concentration of anionic or cationic species in PM<sub>2.5</sub>. Data handling procedures are given in section 5.6.1 and QA/QC procedures are summarised in section 6.7.1.

### 3.6.2 Elemental Carbon (EC) and Organic Carbon (OC)

Annex IV of the Air Quality Directive requires Member States to measure EC and OC in the PM<sub>2.5</sub> size fraction of particulate matter at rural background locations. This requirement is met by these measurements at Harwell and Auchencorth Moss, made within the research-based Particles Network, which started measurements in late 2011. The parameters EC and OC are effectively defined by the thermo-optical analytical technique used.

Simplistically, the analysis can be considered as having two aspects. Firstly, the measurement of total carbonaceous material (TC) on the filter, by thermal desorption and oxidation followed by carbon detection (usually as methane after the conversion of carbon dioxide and other compounds in a catalytic converter). This aspect can be simply calibrated and quality controlled using calibration solutions on clean filters.

Secondly, the division of TC into EC and OC. This is based on the carbonaceous material that is released during heating in an inert atmosphere being designated as OC, while material that is released after the addition of oxygen to the atmosphere is designated as EC. A correction needs to be made to account for pyrolysis (charring) of organic material during the inert atmosphere phase, based on an optical measurement of the darkening of the filter throughout the process.

The analytical method is currently being standardised by CEN TC 264 WG 35. The document *Ambient air quality – Guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters* (PD CEN/TR 16243:2011<sup>37</sup>) sets out a range of possible analysis protocols, including the two used in the network (termed “NIOSH-like” and “EUSAAR\_ 2”).

Sampling is carried out using reference (Leckel SEQ47/50) PM<sub>2.5</sub> samplers collecting for 7 days onto high purity quartz filters (Pallflex Tissuquartz 2500QAT-UP).

The current contractor at the time of writing (2013) is NPL. This contractor manages the Particles Network, carries out the laboratory analysis, audits the sites and acts as LSO for the Harwell monitoring site. CEH acts as LSO for the Auchencorth Moss monitoring site. Equipment support is currently subcontracted to Enviro Technology Services.

QA/QC consists of checks on the sampling system, such as corrections to the sampled volume after flow calibration, and checks on the laboratory analysis, which

are primarily blank analyses, TC calibrations, and checks with internal reference material. The TC analysis is accredited by UKAS to ISO 17025:2005 – the split into EC and OC will be included in the accreditation when the standard method is decided.

## 4 Type Testing and Equivalence of Analysers

### 4.1 EU Requirements

Annex VI of the Air Quality Directive, 2008/50/EC, defines the reference methods to be used for compliance monitoring. This Annex also sets out the procedure for demonstration of equivalence with the reference methods, which must be followed if any alternative methods are to be utilised. Annex VI part D requires that all new equipment introduced into the network complies with the reference method or has been demonstrated to be equivalent.

For the gaseous analysers, the relevant Standard Methods include a requirement for type testing and approval. The approach used in the UK to conform to this requirement is described in Section 4.2.

For particle monitoring (PM<sub>10</sub> and PM<sub>2.5</sub>) compliance is achieved by ensuring that all analysers used in the network have been demonstrated to be equivalent to the reference methods. The mechanism for demonstrating equivalence for particle monitors in the UK is provided in Section 4.3. Subsequent sections describe the requirements for benzene, metals and PAH compounds.

### 4.2 Type-Approval of Analysers for NO<sub>x</sub>, SO<sub>2</sub>, O<sub>3</sub> and CO

Type-approval tests are used to evaluate a set of performance characteristics for at least two identical analysers in a laboratory and two analysers in the field. The standard specifies a comprehensive and rigorous set of tests and type approval of an analyser is based on conformance of the analyser with all the individual performance criteria. The standards also require the calculation of the overall expanded uncertainty of the measurement result based on the numerical values of all the relevant tested performance characteristics - this is compared with the relevant prescribed maximum uncertainty in the Directive's DQOs (e.g. +/-15% at 95% confidence level for NO<sub>2</sub> at the relevant hourly limit value). The tests and calculations carried out are:

#### Laboratory tests:

- Short-term drift tests at zero and span concentrations (12 hours).

- Response times rising and falling.
- Repeatability at zero concentrations and at the relevant limit or target value (where appropriate).
- Lack of fit (residuals from the linear regression function including the zero value).
- Sensitivity to sample gas pressure and sample temperature.
- Sensitivity to electrical voltage.
- Sensitivity to the temperature surrounding the analyser.
- Effects of interferences from other substances present in the atmospheric samples.
- Effect of fluctuating concentrations (averaging test).
- Converter efficiency where applicable (NO<sub>x</sub>).
- Differences between sample and span inputs, where applicable.

#### **Field tests (3 months):**

- Long-term reproducibility between two analysers during the field measurements.
- Long-term drifts at zero and span levels.
- Period of unattended operation, and fraction of total time the analyser is available for measurements.

#### **Overall uncertainty of measurement results:**

- Determined by combining the type approval results obtained from the relevant tests above, expressed at a 95% confidence level. This process of combining uncertainties is covered by the CEN Standard Methods.

### **4.2.1 Analyser Type Testing in the UK**

For gaseous analysers, the Type Approval testing process is managed in the UK by the Environment Agency under its MCERTS scheme (<http://www.environment-agency.gov.uk/business/regulation/31829.aspx>).

Certification is provided by SIRA, (<http://www.siracertification.com/default.aspx>), the appointed certification body. SIRA is accredited by UKAS to ISO/IEC standard 17065:2012 "Conformity assessment - Requirements for bodies certifying products, processes and services"<sup>38</sup>.

The MCERTS Performance Standards mirror the requirements of the CEN Standard Methods referenced in the Directive, and decisions are made by a certification committee. The relevant performance standard for gases is: Continuous Ambient Air Monitoring Systems (CAMS). UK testing against the standards began in 2005, and a



number of instrument suppliers have successfully had their gaseous analysers type-approved under these schemes. Further details can be found at:

<http://www.siraenvironmental.com/UserDocs/mcerts/MCERTSCertifiedProductsCAM S.pdf>

For measurements in the UK national network, the specific conditions and facilities at each site have been used to calculate measurement uncertainties for individual analysers. These results are published every six months in QA/QC Data Ratification Reports for the Automatic Urban and Rural Network and are available at: [http://uk-air.defra.gov.uk/library/reports?section\\_id=13](http://uk-air.defra.gov.uk/library/reports?section_id=13).

#### **4.2.2 Checks Required on Deployment of Automatic Analysers**

The CEN Standard Methods set a number of operational condition checks that need to be performed for each site and analyser deployed. These are summarised as follows:

- Estimate of the sample gas pressure and temperature variations.
- Estimate of the air temperature and mains voltage variations.
- Estimate of concentrations of a range of potential interferent species (H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, NH<sub>3</sub> and benzene) in the local atmosphere.
- Functional check of the analyser and sampling system.
- Functional check of the data telemetry system.
- Lack of fit (linearity) test.
- Converter efficiency check for NO<sub>x</sub> analysers.
- Determination of the required frequency of filter changes and analyser consumables changes.

These parameters need to be reviewed in order to ensure that all the analysers at all the sites are operating within the operating conditions for which they have been “type approved”, and also to determine the required frequency of certain maintenance actions which may depend on the pollutant concentrations at the particular site, or other factors.

These checks are undertaken during type testing of the instrument, and also as part of the commissioning audit of new monitoring sites.

## 4.3 Equivalence Testing for PM<sub>10</sub> and PM<sub>2.5</sub>

### 4.3.1 Requirements of the Air Quality Directive

The CEN Standard Method for particulate matter (PM) analysers describes both the design of the analyser (the reference method), and the operating methodology. The reference method is a gravimetric technique: however, due to the time required to weigh exposed filters and process the results, data from gravimetric samplers cannot be used for rapid public information purposes. The Directive therefore allows Member States to use alternative techniques where "equivalence" with the reference method can be proven in accordance with specific requirements. A procedure for demonstration of equivalence has been defined by the EC, primarily to ensure measurements with near real-time analysers fulfil the requirements of the DQOs defined in the Air Quality Directive. This procedure is defined in the 2010 GDE, which is available online at <http://ec.europa.eu/environment/air/quality/legislation/pdf/equivalence.pdf> . This is expected to be updated and issued as EN TS16450 in the future.

### 4.3.2 UK Work Programme on Equivalence

The UK has spearheaded an extensive study into the relationships between measurements of a range of automatic analysers and gravimetric samplers with the Reference Method. The results of this initial pioneering test programme can be found in the following reports:

- UK Equivalence Programme for Monitoring of Particulate Matter (available online at [http://uk-air.defra.gov.uk/reports/cat05/0606130952\\_UKPMEquivalence.pdf](http://uk-air.defra.gov.uk/reports/cat05/0606130952_UKPMEquivalence.pdf) )
- Assessment of UK AURN Particulate Matter Monitoring Equipment against the January 2010 GDE (available online at [http://uk-air.defra.gov.uk/reports/cat14/1101140842\\_Assessment\\_of\\_UK\\_AURN\\_PM\\_Equipment\\_against\\_2010\\_GDE.pdf](http://uk-air.defra.gov.uk/reports/cat14/1101140842_Assessment_of_UK_AURN_PM_Equipment_against_2010_GDE.pdf) )

Following this initial study, instrument manufacturers have continued to submit methods for equivalence tests and declaration of suitability. The current status of measurement methods is set out in table form, at the "Certification: MCERTS for UK Particulate Matter" UK-AIR web page at <http://uk-air.defra.gov.uk/networks/monitoring-methods?view=mcerts-scheme> .

### 4.3.3 UK Approval of Equivalence

The responsibility for declaring measurement methods equivalent for use in the UK lies with Defra as the Competent Authority. Many manufacturers have also, but separately, opted to get UK type approval with the “Continuous Ambient Measurement Systems (CAMS)” performance standard (see <http://uk-air.defra.gov.uk/networks/monitoring-methods?view=eu-standards>) through the MCERTS scheme which mirrors the requirements of the 2010 GDE. Defra has developed in partnership with the Environment Agency a new and additional level of certification through the MCERTS scheme which requires the instruments to demonstrate equivalence in a representative particulate matter pollution climate for the UK. This certification is called "MCERTS for Particulate Matter UK" and details are available at <http://uk-air.defra.gov.uk/networks/monitoring-methods?view=mcerts-scheme>.

Other methods have been MCERTS certified for the Performance Standard for Indicative Ambient Particulate Matter. This is entirely different to the CAMS standard. Measurements from *indicative* MCERTS analysers carry a higher measure of uncertainty than reference equivalent analysers. Indicative analysers may not fulfil the requirements of the EU DQOs.

## 4.4 Equivalence and Type Testing of Benzene Measurement Techniques

Automatic hourly measurements for benzene are made using the Ozone Pre-cursor Analyser (OPA) manufactured by Perkin Elmer. This is the best method available for measuring a large suite of VOCs simultaneously. There is no type approved OPA capable of measuring a suite of VOCs. However, many of the key parameters will be available either from literature or from existing test data. There will still be a number of parameters that require additional testing such as non-linearity (“ufit”), reproducibility of the field conditions (“urf”) and uncertainty due to interference with ozone (“uO<sub>3</sub>”). Tests are performed to evaluate these. While these tests would not formally constitute type approval, they will provide a strong indication of fitness for purpose. Once these evaluations are complete, the calculations are updated and provide an assessment of CEN compliant results for every analyser used in the network.

The non-automatic system used for non-automatic monitoring of benzene was developed by NPL. This dual sample tube controlled flow pump unit uses a method described in EN 14662:2005, ‘Ambient air quality – Standard method for

measurement of benzene concentrations'. This method has been validated by NPL and is the reference method for measuring benzene.

## **4.5 Equivalence and Type Testing of Metals Measurement Techniques**

### **4.5.1 Ambient Metals Measurement**

In the Industrial and Urban Metals Network, Gravimetric samplers (Partisol 2000 instruments) are used to sample PM<sub>10</sub> over weekly periods according to EN 12341:1999. The analysis procedure, which is compliant with EN 14902:2005, is accredited to ISO 17025:2005.

Mercury vapour is sampled using a manual sampling set-up compatible with the requirements of EN 15852:2010 and analysed in accordance with EN 15852:2010. The analysis procedure is accredited to ISO 17025:2005.

In 2012, the current contractor assessed the overall equivalence of the reference method EN 15852:2010 to the manual method used on the Network. This is reported in Brown et al. 201239.

In the Rural Metals Network, Partisol 2025 particulate samplers are used. The operational performance of the Partisol 2025 particulate samplers have been verified by the detailed Defra and DAs study test for equivalence in 2004-2006, see [http://uk-air.defra.gov.uk/reports/cat05/0606130952\\_UKPMEEquivalence.pdf](http://uk-air.defra.gov.uk/reports/cat05/0606130952_UKPMEEquivalence.pdf).

The tests carried out were based on the Guidance for the Demonstration of Equivalence of Ambient Air Monitoring Methods issued by an EC Working Group. This Guidance defines an approach to test whether an instrument complies with the DQO for overall uncertainty as defined within the relevant Air Quality Directive which, for PM<sub>10</sub>, is 25%.

The mercury in air and mercury in rain samplers (designed by CEH) have not been through a comparable verification process but were tested against the NPL sampling equipment. The design principles follow the EMEP guidelines for mercury sampling devices and incorporate improvements for data capture.

### **4.5.2 Rural Measurements of Metals Deposition**

As explained in section 3.4, the rainfall samples are collected via passive bulk deposition samplers, using separate bottles for the samples to be analysed for mercury, compared to the samples analysed for other metals. The sample

concentrations are determined by Atomic Fluorescence Spectrometry (AFS; Hg only) and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS; all other metals).

Validation and quality control data for the determination of metals by ICPMS concluded that the instrumental method is suitable for the determination of a wide range trace metals in precipitation. The accuracy and precision for a synthetic rain obtained from Environment Canada are acceptable when compared with certified values. Total uncertainty and limits of detection are also reported. As part of UKAS accreditation, the laboratory is required to carry out an annual audit of method performance by assessing analytical quality control data. An assessment for the period of operation of the rural metal deposition network operation so far (years 2004 to 2012) shows that the determination of trace metals by ICPMS was, and continues to be, fit for purpose. Accuracy is better than  $\pm 5\%$  and precision is, for the majority elements measured, better than  $\pm 5\%$  of the nominal QC value.

The performance of the contractor's laboratory (CEH Lancaster) in the Aquacheck inter-laboratory proficiency testing scheme (group 5b; low level metals) was undertaken using Cu, Cr, Pb, Ni, Zn, Cd and Hg as examples of typical laboratory performance. The performance of the contractor's laboratory in this scheme is acceptable, with the majority of analyses receiving a z score of better than  $\pm 2$ , indicating excellent agreement between the contractor's laboratory and a wide range of UK and worldwide testing laboratories. The performance of all metals determined for the network is tested within Aquacheck or similar schemes.

The contractor also participated in the EMEP "*Analytical intercomparison of heavy metals in precipitation*" between 2006 and 2011. For all metals reported in 2010 (i.e. As, Cd, Cr, Cu, Pb, Ni and Zn) their laboratory met the required data quality objective (DQO) set within the scheme. These are as follows:

- 25% accuracy or better for Pb, Ni, Cr & As concentrations  $< 1\mu\text{g/l}$ , Cd concentrations  $< 0.5\mu\text{g/l}$ , Zn concentrations  $< 10\mu\text{g/l}$  and Cu concentrations  $< 2\mu\text{g/l}$
- 15% accuracy or better for Pb, Ni, Cr & As concentrations  $> 1\mu\text{g/l}$ , Cd concentrations  $> 0.5\mu\text{g/l}$ , Zn concentrations  $> 10\mu\text{g/l}$  and Cu concentrations  $> 2\mu\text{g/l}$ .

Further information about the scheme, including detailed reports relating to laboratory performance, can be found on the EMEP website at

<http://www.nilu.no/projects/ccc/intercomparison.html>

## 4.6 Equivalence and Type Testing of PAH Measurement Techniques

The Digitel DHA-80 samplers now used throughout the Network are considered to be equivalent to the requirements of the European Standard for sampling PM<sub>10</sub> matter (EN 12341:1999). Evidence for this is available in a new version of the standard which is currently being drafted to replace EN 12341:1999. These samplers are therefore considered valid for use with the European Standard method for the measurement of benzo[a]pyrene in ambient air (EN 15549:2008). Samples are taken onto quartz fibre filters for a period of 24 h at a flow rate of 30 m<sup>3</sup> h<sup>-1</sup>.

Deposition sampling is performed as specified in EN 15980:2011, which includes analytical QA/QC. The requirements of EN 12341:1999 do not apply to deposition sampling, only to sampling of PM<sub>10</sub> suspended particulate matter. No reference methods exist for the sampling of PAH vapours.

## 5 Data Telemetry, Validation and Dissemination

In order to provide rapid data on the current air quality situation in the UK, data from the UK's automatic monitoring sites are collected via telemetry from each monitoring site, every hour, and made available on the UK-AIR website. These data are validated, but not fully ratified, and hence are described as provisional data. The process for collecting, validating and disseminating the provisional data is described below. Data handling and validation are also described for pollutants measured by non-automatic techniques, which are not made available on such a short timescale. The full ratification procedures which the data undergo are set out later, in section 6.

### 5.1 Data Handling in the AURN

Data from the UK's automatic monitoring sites are collected via telemetry from each monitoring site, every hour, and made available on UK-AIR. The data are at this stage still provisional, having not yet undergone the ratification process. This section describes the process of collecting, validating and disseminating the provisional data from the AURN.

#### 5.1.1 Collecting the data from AURN sites

The CMCU dials-up via telemetry links (e.g. land-lines, GSM modems and GPRS) to poll data acquired within the hour. Each station is automatically dialled every hour during daytime and alternate hours during the night (1800- 0700). Onboard and external logging systems provide a mechanism of capturing data (either in concentration or raw electronic mV format).

A number of the AURN sites within Greater London are also part of the London Air Quality Network. These sites are also polled hourly, on the same basis as the other AURN sites. Data are collected to two decimal places for CO and to at least one decimal place for other gases and for particles.

#### 5.1.2 Validation of AURN Data

Upon completion of the station poll the fifteen-minute averages (or hourly data in the case of FDMS and BAM particulate monitors) collected from the site operating system are stored in the data management system database. The collected values are referred to as "raw" since they are not scaled and remain in the data

management system “raw” database as a complete record of all values collected from the station. Instrument calibration values derived from site by either LSOs or ESUs are stored in the data management system calibration files and the raw values are automatically scaled by application of the calibration factors present in the system. Automatic screening algorithms (specifically designed macros and a range of tailored scripts for manual data interrogation) are employed to validate the scaled data.

The scaled data are automatically compiled into a prescribed format and emailed to Defra’s Data Dissemination Unit (DDU) by 25 minutes past the hour for upload to the UK-AIR website. Upon completion of any required editing the revised values are automatically re-sent in the next hourly cycle in order to over-write those previously supplied.

### 5.1.3 Dissemination of Provisional AURN Data

Data from the AURN are marked as ‘provisional’ or ‘ratified’ depending on what stage they are at in the process of ratification. When data are first collected from the analyser on site, they are scaled with calibration data from the last calibration. In many cases, this will produce satisfactory data, with problems only arising if the instrument is unstable or drifting rapidly. The data are then automatically screened using computer algorithms to highlight suspect data, but ***no data are deleted at this stage.***

The data sent to UK-AIR are also available – on an hourly basis - on air quality websites operated by the UK Devolved Administrations, Freephone service and Twitter. In addition, daily e-mail bulletins of AURN monitoring data are provided to over 150 media organisations and other network stakeholders - including the BBC and BSkyB, national and regional radio and newspapers and other scientists and journalists.

All of the provisional data, together with all the identified suspect data, undergo full ratification, (as described in section 6.1.8) in 3-month blocks. As part of the ratification process, any suspect data may be reinstated if deemed to be genuine. Following the ratification process, the fully ratified datasets are re-sent to UK-AIR (in 3-monthly blocks, 3 months in arrears) and the provisional data are overwritten with the ratified data.

However, as the data are improved via the ratification process, they are automatically fed through to UK-AIR. This ensures that the provisional data available on UK-AIR always reflect the most up to date, highest quality data available. Initial polled data are maintained by the CMCU through its initial polling software and are maintained as an historical record of the data collection process.



All fully ratified hourly data from the AURN are reported to the Commission annually. Currently provisional measurements for ozone, NO<sub>2</sub>, SO<sub>2</sub> and PM<sub>10</sub> data are supplied on an hourly basis to the EEA air quality website - <http://www.eea.europa.eu/themes/air/air-quality/map>.

From 2014, all provisional AURN data will be made available to the Commission on an “up to date” basis using electronic reporting tools.

#### **5.1.4 Data Handling for Partisol PM Samplers in the AURN**

The AURN includes 17 Partisol 2025 gravimetric samplers, each of which samples either PM<sub>10</sub> or PM<sub>2.5</sub>. The size fraction sampled is determined by a size-selective inlet fitted to the sampler. Sampling is on a daily basis, with automatic filter changeover at midnight. The Partisol sampler holds up to 15 filters. Each batch of filters includes a field blank. The CMCU is responsible for conditioning and weighing the filters before and after exposure. Ambient PM concentrations are calculated from the mass of material collected on the filter (determined by weighing before and after exposure) and the volume of air sampled over the 24 hour period.

Ambient concentrations are calculated by the CMCU and supplied to the QA/QC Unit in spreadsheet format. The QA/QC Unit carries out the ratification process, which checks that:

- The correct day's filter weighing is matched to the correct day's sampling data.
- There were at least 18 hours' valid sampling for each daily sample.
- The sample volume is at least 18m<sup>3</sup>.
- There are no gaps in the dataset.
- There are no values which appear obviously spurious, e.g. unusually low or high, and cannot be accounted for.
- There are no negative values (less than minus the measurement uncertainty).

If both PM<sub>10</sub> and PM<sub>2.5</sub> are monitored using Partisols at the same site, PM<sub>10</sub> should not usually be greater than PM<sub>2.5</sub> (allowance is made for the measurement uncertainty, particularly at rural sites where both PM<sub>10</sub> and PM<sub>2.5</sub> are often low).

Data are ratified three-monthly in arrears. The ratified dataset is sent to the Data Dissemination Unit.

## 5.2 Data Handling for Automatic Hydrocarbon Monitoring

The data management system undertakes preliminary validation of the data using proprietary pattern recognition software, "MatchFinder", which has been specifically modified to compare the chromatograms with 'templates' identifying specific hydrocarbon peaks. This system automatically assigns component labels to peaks within the chromatogram.

The incidence of mis-identification of peaks, and therefore mis-reporting of data, is reduced significantly when compared with use of the peak identification methodology of the instrument system.

This system provides preliminary screening of hydrocarbon monitoring data to identify suspect data. When the fit of data to the MatchFinder templates becomes poor, it can be due to one of a number of reasons; malfunction of the instrument or an early warning of an unusual event such as a pollution episode, are two examples. By means of further manual checking, a decision to delete or retain such data is made by one of the hydrocarbon network data management team. This includes application of approximate site-specific response factors and daily checks of the templates.

All data are manually checked every working day by a trained member of the network management team. During these manual checks a number of parameters are evaluated. System performance is judged on a daily basis and the accuracy of peak integration and identification is monitored, with any necessary actions being taken. The results of the daily checks and any resulting actions are recorded as this will be important information in the data ratification process. The manual checking of the data, rather than basing reliance on the automatic systems, ensures any developing problems are identified quickly and resolved in good time.

Validated data are provided daily to the Data Dissemination Unit for dissemination via UK-AIR.

Before the formal ratification process is started some general 'housekeeping' of the stored data is required. At the sites where speciated measurements are made using the PerkinElmer Ozone Precursor Analyser (PE-OPA) any files not retrieved during the automatic polling of the station data are collected and added to the database.

Data ratification involves a progressive evaluation of chromatograms at three levels; the first level looks particularly in the region of the peaks for benzene and 1,3-butadiene. Further investigations of peaks corresponding to unknown C<sub>8</sub> compounds

are made to ensure the impact of these is minimised in terms of data for known C<sub>8</sub> compounds. Finally, 'merged peaks' are inspected to provide confidence that these have been suitably identified and the correct baselines applied by the integration of the peaks.

The second level of ratification is a ratio analysis of the more volatile compounds, in the C<sub>2</sub>/C<sub>3</sub> region. If a loss of sensitivity is detected, data will be rejected unless it is clear that corrections can be applied.

The final level of the ratification procedure is the application of response factors. This converts the raw peak areas collected from the chromatograms to concentration units. The results of the analyser calibration checks, together with data from the network intercalibrations, are used to produce the response factors. Response factors for the instruments (PE-OPA) generally tend to be very stable.

During the third level of ratification the results of the network intercalibration and instrument audits are evaluated to determine whether any further action is required with respect to data scaling.

This multi-input approach to data ratification is used to provide the necessary level of information to provide the level of confidence needed for the data to be described as "ratified".

On completion of this three-level ratification process the data are sent to UK-AIR, and also stored within the contractor's own QA/QC database.

Formal reporting of data to the EU is undertaken annually by 30<sup>th</sup> September the following year.

## **5.3 Data Handling for Non-Automatic Benzene Monitoring**

The procedures used for non-automatic benzene monitoring are completely different from the automatic monitoring techniques and the data handling procedures reflect these differences.

The project structure requires data to be held and processed by the contractor and by a subcontractor (analytical laboratory).

The primary data handling system (produced by the contractor) is the Sample Registration System (SRS), which has been designed to efficiently and transparently track the progress of a sample (represented by two pumped tubes) throughout the

system. The necessary calculation and quality control routines are also built into the system. The SRS is built using Microsoft Excel.

In principle, each sample exposure has a unique identification made up of two parts; the etched identification mark on the thermal desorption tube (tube ID) and the batch number (each fortnight's set forms a complete batch). As there is a limited number of tubes used (~400 stock tubes which are cleaned, re-filled and re-used), the tube ID will occur more than once during the lifetime of the project. Hence, each sample's identification is a composite of the batch number and tube ID.

This also makes it possible to track the use and performance of individual tubes as they are repeatedly cleaned, re-filled and re-used.

## **5.4 Data Handling for Metals Monitoring**

### **5.4.1 Urban Metals**

Analysis of the Network samples is described in section 3.3.3. This produces individual concentration values for four-weekly or weekly periods. These individual measurement results each have a stated measurement uncertainty, quoted at the 95% confidence level. Annual means at each site are produced by calculating the means of these values, weighted according to the data capture during each period. Network-wide annual means are then produced by averaging annual means from the individual sites, again using appropriate weighting if a site has been monitoring for less than the full year.

A QA/QC circle meeting (the 'quality circle') ratifies ambient concentration data produced by the Network. Personnel performing the ratification procedure are independent of the Network analysis and management process. It is the aim of the ratification procedure to distinguish between changing ambient concentrations (including long terms trends, seasonal variation and single pollution events), and analytical discrepancies within the large amount of Network data. Ratification takes place in accordance with several guidelines, outlined below:

1. Only data where the valid sampling hours are greater or equal to 75% of the total sampling period will be eligible to produce valid concentration data, and count towards the total data capture percentage.

2. Data not meeting the DQOs for uncertainty or time coverage for the relevant air quality Directive are not eligible to produce concentration data and are counted as lost data capture.
3. Data excluded following the ratification procedure will also not be eligible to produce valid concentration data, or count towards the total data capture percentage.
4. Upon production, weekly data for each element at each site are plotted in a time series, or displayed as a continuous list of values which may be easily compared.
5. In the first instance these data are assessed visually for any obvious discrepancies with due regard to long terms trends, short term variability and seasonal variation. Then outlier tests are performed to detect any potentially discrepant data, including the use of powerful chemometric techniques.
6. If valid reasons for obviously discrepant values are found (e.g. incorrect calculation, low exposure time, non-valid exposure volume, analytical error) these values may be either excluded or corrected (depending on the nature of the error).
7. As part of the internal quality and technical auditing procedures, a selection of ambient air concentrations calculated each month are thoroughly audited by a party independent of the analysis procedure. For these samples, the sample number, target analyte, auditor, audit date and status of the data are recorded in a designated spreadsheet after auditing. These audits concentrate most heavily on nickel, arsenic, cadmium, lead and mercury vapour analyses, as these are directly relevant to EC Air Quality Directives.

The data are then transferred to the contractor's secure database and processed ready for submission to UK-AIR. Provisional data are provided quarterly, and updated with the fully ratified annual dataset when this becomes available. The only exception to this is for lead, which the contractor aims to ratify quarterly, as per the requirements of the Directive.

The time resolution of the data provided is weekly at six stations for metals in particulate, weekly at three stations for vapour phase mercury, and four-weekly at all other stations for both particulate-phase metals and vapour phase mercury.

#### **5.4.2 Rural Metals**

The concentrations of metals in the PM<sub>10</sub> digests and precipitation samples generated by the laboratory analysis are uploaded to a database as part of the

reporting requirements of the contractor's UKAS-accredited labs. This database is stored in a central server within CEH, and receives daily back-ups. This database also records all of the relevant metadata on each sample, including the start and end date and time of each exposure period, site operator observations and all of the intermediate data produced during the analytical process.

The data are then filtered via database queries, to produce output tables which normally cover, for example, a single calendar year's worth of data. These output tables are copied into Excel for ease of data. There are separate spreadsheets for the metals. The spreadsheets have been designed to include a separate worksheet for the raw data from each monitoring site. These sheets are linked to pre-programmed sheets which are used to convert the sample acid digest concentrations to concentrations in air data. The spreadsheets have built-in quality assurance checks where appropriate, such as checking there is no overlap in sampling between individual samples etc. The spreadsheets also have in-built formulae to calculate statistics such as the annual mean, data collection rate, etc. The spreadsheet also identifies samples which are below the limit of detection, and greater than the annual mean plus 2x the standard deviation. It also generates the appropriate EMEP flags to accompany the data.

The spreadsheets are all manually checked (on the basis of expert judgement) before the data are prepared for uploading to the UK-AIR portal. This involves copying the data from each site-based worksheet into a single worksheet, where the data are formatted to match the UK-AIR reporting requirements. This final sheet is then saved in Excel format before being saved as a tab delimited text file and uploaded to the UK-AIR portal.

The ratified dataset is uploaded annually to UK-AIR. Provisional data are not supplied.

The time resolution of the concentrations of metals in the particulate phase is weekly (two-weekly for mercury). The time resolution of the measurements of metals in precipitation is also two-weekly.

## **5.5 Data Handling for PAH Monitoring**

Analytical procedures are given in section 3.5.2. A 'quality circle' approach is used to ratify ambient concentration data produced by the UK PAH Network. Personnel performing the ratification procedure are independent of the Network analysis and management process. It is the aim of the ratification procedure to distinguish between changing ambient concentrations (including long terms trends, seasonal

variation and single pollution events), and analytical discrepancies within the large amount of Network data. Ratification takes place in accordance with several guidelines, outlined below:

1. Only data where the valid sampling hours are greater or equal to 75% of the total sampling hours will be eligible to produce valid concentration data, and count towards the total data capture percentage.
2. Data not meeting the DQOs for uncertainty or time coverage for the relevant air quality Directive are not eligible to produce concentration data and are counted as lost data capture.
3. Data excluded following the ratification procedure will also not be eligible to produce valid concentration data, or count towards the total data capture percentage.
4. Upon production, data for each PAH at each site is plotted in a time series, or displayed as a continuous list of values which may be easily compared.
5. In the first instance these data are assessed visually for any obvious discrepancies with due regard to long term trends, short term variability and seasonal variation. Then outlier tests are performed to detect any potentially discrepant data, including the use of powerful chemometric techniques.
6. If valid reasons for obviously discrepant values are found (e.g. incorrect calculation, low exposure time, non-valid exposure volume, analytical error) these values may be either excluded or corrected (depending on the nature of the error).
7. As part of the internal quality and technical auditing procedures, a selection of ambient air concentrations calculated each month are thoroughly audited by a party independent of the analysis procedure. For these samples, the sample number, target analyte, auditor, audit date and status of the data are recorded in a designated spreadsheet after auditing. These audits concentrate most heavily on benzo[a]pyrene (B[a]P) as this is directly relevant to the Fourth Daughter Directive.

The data are then transferred to the contractor's secure database and processed ready for submission to UK-AIR at the appropriate juncture. Data are sent to the Data Dissemination contractor for upload to UK-AIR.

## **5.6 Data Handling for Other Measurements**

### **5.6.1 Cations and Anions in Rural PM<sub>2.5</sub>**

The Marga 2S provides on-line analysis of cations and anions in near real-time by means of IC. The presence and concentration of the cation and anion species in the

sampled in PM<sub>2.5</sub>: (and PM<sub>10</sub>) sulphate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sodium ion (Na<sup>+</sup>), potassium ion (K<sup>+</sup>), ammonium ion (NH<sub>4</sub><sup>+</sup>), chloride ion (Cl<sup>-</sup>), calcium ion (Ca<sup>2+</sup>), and magnesium ion (Mg<sup>2+</sup>) are determined from the resultant chromatograms. Detection of the individual species is based primarily on:

- Peak retention time, and
- Integrated peak area.

From these parameters the concentrations of the species of interest in the sample solution (termed the “liquid concentration”) can be determined. The mass concentrations of the species of interest (termed the “air concentration”) are subsequently determined from the liquid concentration by accounting for the:

- Volume of injected solution (nominally 25 cm<sup>3</sup> of solution and 2.5 cm<sup>3</sup> of internal standard), and
- Sample flow rate (nominally 1 m<sup>3</sup> hr<sup>-1</sup>).

The liquid and air concentrations are written to file to provide an hourly measure of the composition of PM<sub>10</sub> and PM<sub>2.5</sub>.

When commissioned, default retention times of the cations and anions species of interest are entered into the instrument by the instrument manufacturer (Metrohm-Applikon BV, Schiedam, The Netherlands). Over time peak retention times may change due to instrumental factors, e.g. column ageing, as well as environmental factors, such as atmospheric temperature and pressure. In order to account for this, the peak retention times are checked regularly and adjusted accordingly by the LSO. Peaks are identified if they fall within a window of ±5% of the operator defined peak retention time. The Marga 2S system parameters are logged by the instrument and are optimised by the Marga 2S operating software to ensure good resolution of the peaks in the ion chromatographs.

Samples from the WRD or SJAC are injected into the parallel IC columns at 15 minute intervals. The resultant anion and cation chromatograms are written to file for later re-analysis, if required. For a volume of ambient air sampled during hour “H” of the day, the liquid samples from the WRD and SJAC are analysed in the order described in Table 5-1:

**Table 5-1 Marga 2S sampling times, particle size fractions and source**

Time	Size fraction	Source
17 minutes past hour “H+1”	PM <sub>2.5</sub>	WRD (gas-phase)



32 minutes past hour "H+1"	PM <sub>2.5</sub>	SJAC (particle-phase)
47 minutes past hour "H+1"	PM <sub>10</sub>	WRD (gas-phase)
02 minutes past hour "H+2"	PM <sub>10</sub>	SJAC (particle-phase)

The Marga 2S used to measure anions and cations in rural PM<sub>2.5</sub> is a research-grade instrument. Currently there is no proposed or accepted ISO, CEN or equivalent BS standard method for the determination of the concentration of anionic or cationic species in PM<sub>2.5</sub>. QA/QC procedures for the Marga 2S measurements are summarised in section 6.8.1.

### 5.6.2 Elemental Carbon (EC) and Organic Carbon (OC)

No live data are generated at the monitoring site. Two 1.5 cm<sup>2</sup> samples of loaded quartz filter are taken from each filter and analysed separately on a Sunset Laboratories instrument. The separate analyses use two different temperature / time protocols specified in PD CEN/TR 16243:2011, termed NIOSH-like and EUSAAR\_2. The charring correction can be made using either an optical transmittance or reflectance signal; these signals can be generated simultaneously, and both are recorded.

The values of TC, EC and OC obtained by the instrument, in µg (of carbon) per cm<sup>2</sup>, are converted to µg m<sup>-3</sup> using a well-characterised value for the sampled area of the filter, and the sampled volume of air (at ambient conditions), using data downloaded from the samplers by the LSOs, and results from the field flow audit.

Provisional data are ratified, with changes as appropriate, at a quality circle. Ratified data are then released annually via UK-AIR. Currently data from the NIOSH-like protocol only, corrected by both optical transmittance and reflectance (i.e. two sets of data), are disseminated.

## 6 Quality Assurance and Quality Control

In order to produce data that are correct, meaningful and useful, the measurement techniques utilised and data handling must have a sound scientific basis. The data must be both accurate and precise.

**Accuracy** refers to the agreement between a measurement and the true value. It allows us to have confidence that the concentration measured is correct. In turn, this allows us to compare data over time, at different UK locations, or internationally.

**Precision** refers to the repeatability of measurement. A precise instrument will always give the same result if the same measurement is repeated. An imprecise instrument will show some variability in the same situation.

This section describes the QA/QC procedures employed by each network to ensure that the DQOs of the relevant Directives are achieved.

### 6.1 UK National Reference Laboratories

The AQUILA group recognises two UK organisations as National Reference Laboratories (NRLs): Ricardo-AEA and NPL.

The Air Quality Directive outlines the key responsibilities of National Reference Laboratories (NRL) in Annex I (C), summarised below:

- All measurements undertaken in relation to the assessment of ambient air quality are traceable in accordance with the requirements set out in Section 5.6.2.2 of the ISO 17025:2005.
- That institutions operating networks and individual stations have established QA/QC systems.
- That a QA/QC process is established for the process of data collection and reporting.
- That the national laboratories that are taking part in Community-wide intercomparisons are accredited according to ISO 17025:2005, shall be involved in the Community wide QA programmes and shall also coordinate, on the national level, the appropriate realisation of reference methods and the demonstration of equivalence of non-reference methods.

These requirements ensure that there is a clear chain of measurement traceability. The Competent Authorities and their appointed NRLs have a clear responsibility for the quality of data and ongoing commitment to harmonisation and traceability of data throughout Europe.

As further enhancement to these requirements, the NRLs from all Member States participate in biannual meetings of the AQUILA group. This group has a very specific set of roles and responsibilities associated with air pollution measurements<sup>40</sup>.

## 6.2 QA/QC in the AURN

The AURN's QA/QC Unit uses a variety of quality procedures, described in more detail in this section.

The purpose of the QA/QC Unit is to ensure that the AURN data are:

- Genuinely representative of ambient pollutant concentrations in the areas under investigation.
- Comparable and reproducible. Results must be internally consistent and comparable with international or other accepted standards, where these exist.
- Consistent over time. This is particularly important if long-term trend analysis of the data is to be undertaken.
- Representative over the period of measurement; for most purposes, a yearly data capture rate of at least 90% is required for determining compliance with EU limit values.
- Consistent with the DQOs and methodology guidance defined in the EU Directive for relevant pollutants and measurement techniques.

### 6.2.1 Local Site Operator (LSO) calibrations

LSOs are employed in the UK to undertake routine tasks at AURN monitoring stations to ensure that the data output is uninterrupted and of the highest possible quality. The actions of the LSOs therefore affect both data quality and data capture. For this reason LSOs are carefully selected by an evaluation board through a round of competitive tendering undertaken by the CMCU based on their expertise, experience and understanding of the AURN and the importance of data quality. Training, and regular assessment, of the LSOs is carried out at scheduled site audits (by the QA/QC Unit).

The key responsibilities of the LSOs are to:

- Carry out routine operation and calibration procedures for the equipment at the site, in conformance with the LSO manual.
- Identify and report potential problems and changes to the site and surrounding area.
- Identify and report potential safety issues at the site.

- Undertake simple tests and repairs to the site and/or equipment as directed by the CMCU.
  - Attend training (both formal and informal) as requested by the CMCU and/or QA/QC Unit
  - Attend QA/QC site audits as requested.
  - Liaise with other AURN stakeholders as requested by the CMCU.
  - Carry out all activities with regard to relevant health and safety standards.
  - Complete the electronic calibration sheets, checklists and site servicing records in full and email these to the CMCU and QA/QC Unit within 24 hours of each site visit.
  - For sites with gravimetric particulate monitors, return exposed filter magazines to the CMCU within 48 hours of each site visit where appropriate.
  - Undertake other reasonable requests as directed by the CMCU during a pollution episode or other emergency.
  - Attend Annual Review meetings as required.
  - Use their experience of air pollution monitoring to identify and report any faults or potential faults as soon as possible.
  - Provide information on local activities that may affect the pollution climate or site suitability at the monitoring station.
- Change calibration gas cylinders

These responsibilities are carried out during routine visits (every 2 weeks at traffic urban sites, monthly at background urban sites and quarterly at all rural sites) and additional emergency call outs.

### **6.2.2 LSO Manual**

A comprehensive operations manual for the AURN has been produced and disseminated to all site operators. This is a key QA/QC tool, serving to harmonise field procedures and improve the quality of the data produced by the monitoring equipment through accurate calibration and optimised operation. The LSO manual is available electronically via the “AURN Hub” - a website which provides useful information and contact details for LSOs. The most recent update was in July 2012.

Training is also provided to any new LSOs and training updates are available to all LSOs during at the twice-yearly site visits by the QA/QC Unit.

### **6.2.3 LSO Support**

Both the CMCU and QA/QC Unit have a dedicated telephone line and email address which is used by LSOs to access specialist knowledge and advice regarding the AURN sites and equipment.

## **6.2.4 Equipment Support Units (ESU) for Service and Repair**

ESUs are responsible for the routine and emergency maintenance and repair of the monitoring and ancillary equipment at each AURN site. They are directly appointed by the CMCU by competitive tender. The ESUs role is key to achieving the 90% data capture target for all sites and pollutants.

Routine servicing is carried out on a 6-monthly basis and is coordinated with the audit visits of the QA/QC Unit (see Section 6.1.5) to ensure that the necessary instrument parameters and calibrations are recorded to allow full data ratification. Minimum requirements for routine instrument maintenance, testing and calibration are provided to ESUs. All routine service visits are fully documented and completed in accordance with procedures provided by the QA/QC Unit.

In the event of an instrument malfunction, the ESU attends the site to carry out emergency repairs or fit a replacement analyser within 48 hours of notification of the problem as highlighted by the CMCU. Telemetry facilities and automated data checking now also allow for rapid recognition of possible instrument malfunctions and the CMCU typically uses this information to inform the relevant ESU of the likely cause of malfunction.

## **6.2.5 AURN inter-calibration and site audits**

Within the UK, there has been a system of routine site audit and network inter-calibration, involving all network sites, for many years. The primary aims and objectives of the site audit and network inter-comparison exercise can be summarised as follows:

- Check and evaluate a wide range of analyser key functions via a comprehensive set of tests and calibrations - well beyond those that can be checked by routine LSO calibrations.
- Check all on-site calibration standards against common transfer standards that are directly traceable to the gas standards calibration contractor's laboratory (currently Ricardo-AEA) and national metrology standards.

This network inter-calibration is undertaken by the QA/QC Unit at six-monthly intervals and includes every site and every analyser in the network. The inter-calibration therefore provides detailed and quantified information on overall network performance.

Many of the site audit and network inter-calibration procedures used in the UK have now been incorporated into the ongoing QA/QC procedures detailed in the CEN Standard Methods. However, in some cases the CEN methods differ in detail or are

even more exacting than previous requirements. Procedures used in the UK are routinely adapted to be fully compliant with the CEN requirements.

Ozone analysers are audited on a three-monthly basis: because of a requirement to calibrate with a traceable standard every three months, a separate ozone inter-calibration is carried out for this purpose between six-monthly inter-calibrations.

### **6.2.6 AURN inter-calibration procedures**

These exercises provide the following information:

- Evaluation of the concentrations of site calibration cylinders, using a set of certified cylinders (transfer standards) that are taken to all the sites. The concentrations of the site cylinders are used to scale pollution datasets, so it is important to check that the concentration of gases in the cylinders remain stable over time.
- Analyser accuracy and precision, using a series of calibrated gas standards, to ensure reliable datasets from the analysers.
- Calibration of ozone analysers with an ISO17025 certified ozone photometer.
- Instrument linearity, to check that doubling a concentration of gas to the analyser results in a doubling of the analyser signal response. If an analyser is not linear, data cannot be reliably scaled into concentrations.
- Instrument signal noise, to check for a stable analyser response to calibration gases.
- Analyser response time, to check that the analyser responds quickly to a change in gas concentrations.
- Leak and flow checks, to ensure that ambient air reaches the analysers, without being compromised in any way.
- NO<sub>x</sub> analyser converter efficiency, to ensure reliable operation. This is the device that allows the measurement of NO<sub>2</sub> to be undertaken, so it must work correctly.
- Tapered Element Oscillating Microbalance (TEOM) spring constant ( $k_0$ ) evaluation. The analyser uses this factor to calculate mass concentrations, so the value is calculated to determine its accuracy.
- Particulate analyser flow rate checks, to ensure that the flow rates through critical parts of the analyser are within specified limits.
- Zero baseline checks on automatic particulate analysers. Using in-line HEPA filters or equivalent to ensure that the instrument measures zero for particle-free air.
- Site infrastructure and environment checks to ensure that metadata on the station remain accurate and up to date and that any site safety issues are noted for action.

As noted above, these tests performed on site are now undertaken to the exacting requirements of CEN Standard Methods and hence are fully compliant with the Air Quality Directive. The gas calibration contractor is accredited (Calibration Laboratory Number 0401) under ISO 17025:2005 to perform these tests.

Accreditation to ISO 17025:2005 requires:

1. Documented procedures to calibrate analysers
2. Demonstration of competence of operators in performing calibrations
3. Demonstration of traceability of measurements to metrology standards
4. Calculation of uncertainty budgets for measurements reported on Calibration Certificates.

### **6.2.7 Use of Information from the Site Audit and Network Inter-calibration**

The site audit and inter-calibration results provide vital information for the data ratification process. For example if calibration cylinder concentrations or ozone monitor calibration concentrations are identified to have changed at any site then the information from the audit and inter-calibration is used to ensure that the data are correctly rescaled during the ratification process. Also, if faults such as poor converter efficiencies for NO<sub>x</sub> analysers are identified then the data are corrected or deleted in line with the CEN requirements.

### **6.2.8 AURN Data Ratification (Gas Analysers)**

Data validation is followed by more thorough checking at three-month intervals to ensure that the data are reliable and consistent. This latter process is called data “ratification”.

The first step is to go back to the “raw” unvalidated data from the analyser - this allows traceability of all operations on the data within the ratification process to be maintained. The data have already been scaled in near real-time by the CMCU in order to provide the validated provisional data. However, for validation only the latest calibration results are available for data scaling. Re-scaling the data at the start of the ratification process allows any new information gathered over the full 3-month period to be incorporated right at the start of the process.

The “raw” data are scaled into ambient concentrations by removing any baseline zero and multiplying by the scaling factor (sensitivity). This is can be expressed mathematically as follows.

$$c = F \times (V - Z)$$

where:

c = the ambient concentration (ppb)

F = the instrument sensitivity (ppb / mV)

V = the instrument measurement (mV)

Z = the instrument zero baseline (mV)

The instrument sensitivity (F) is calculated during calibrations as follows:

$$F = C / (S - Z)$$

where:

F = the instrument sensitivity (ppb / mV)

C = the concentration of the calibration standard (ppb)

S = the instrument response to the calibration standard (mV)

Z = the instrument response to the calibration zero standard (mV)

Identical formulae are used where the ambient measurements are expressed in ppm units and where the instrument records data in units other than mV: e.g. V or nominal ppb.

These scaling values (Z and F) are derived from a range of instrument calibrations:

- Routine manual LSO calibrations
- Automatic analyser calibrations
- ESU calibrations at services or repair visits
- QA/QC Unit inter-calibrations.

#### **6.2.8.1 Analyser Zero Baseline**

For gas analysers the instrument zero baseline is generally measured every night during the auto-calibration cycle. However, as this auto calibration only checks analyser performance, it is not an absolute calibration. Often, the scrubbing material within the auto-calibration system is spent and hence this estimate becomes



unreliable or, the relevant equipment may not be present on-site. However, this auto-calibration zero is just one estimate of the baseline.

LSOs and ESUs also perform zero baseline measurements and these may also be used to estimate the measurement zero point. However, these can occasionally be unreliable for various reasons. The QA/QC Unit also provides a zero baseline measurement during the inter-calibration.

If necessary a zero baseline can also be estimated from the lowest ambient measurement, since concentration levels are often very low for some pollutants at certain times during a month.

Deciding on the most appropriate zero baseline must account for all these sources of information and is a difficult yet vital task since the choice will affect the reported concentrations. The baseline finally applied to the data is based on the real measurements (auto-calibration, LSO, ESU and QA/QC) and the judgement of the data ratifier using software algorithms developed over many years of experience.

Isolated or occasional negative values are permitted to remain in the dataset so long as they are not less than minus the limit of detection of the method. However, any values less than the negative LoD are rejected.

#### **6.2.8.2 Instrument Sensitivity**

A similar decision is required for the instrument sensitivity. This is estimated from calibrations by certified calibration gas sources such as the SO<sub>2</sub> cylinders used by the LSOs and ESUs. The overnight auto-calibration equipment may produce a sensitivity based on SO<sub>2</sub> permeation tubes or uncertified SO<sub>2</sub> cylinders. There will also be span calibrations made by the QA/QC Unit during the network inter-calibration. Some of these estimates may be unreliable due to equipment failure or the use of non-certified gases. The judgement of the Data Ratifier, aided by the software algorithms, is therefore required to decide what sensitivity should be applied.

#### **6.2.8.3 Instrument Drift**

Besides deciding the best zero baseline and instrument sensitivity, the data ratification must also take account of any analyser drift in either zero or sensitivity. Zero and sensitivity may vary day-by-day but a rapid drift may be the sign of an instrument malfunction. Data ratification must evaluate where data can be accepted, accepted with modification or has to be deleted.

#### **6.2.8.4 Instrument failure**

Instruments may fail for numerous reasons. The equipment is serviced at the regular six-monthly ESU visits but malfunctions can arise between services. Some faults are minor, such as sample flows just below optimum but flow blockages can prevent the instrument from sampling ambient air. Ratification uses all available information: raw measurements, calibrations, alarms, engineer reports etc., to decide if the data can be corrected or needs to be rejected. The commencement of any fault must be determined. This is often a matter of judgement based on experience.

#### **6.2.8.5 NO<sub>x</sub> data processing**

The approach to ratifying NO<sub>x</sub> data is slightly different to that for the other gaseous AURN pollutants.

NO<sub>x</sub> instruments use the chemiluminescent technique to measure NO gas by reaction with an internally generated ozone source. In order to report NO<sub>x</sub>, NO and NO<sub>2</sub> concentrations the instrument has to split the ambient sample into two. NO is measured directly in the first stream. The second stream passes through a catalyst that converts any NO<sub>2</sub> into NO. This stream, known as NO<sub>x</sub>, is then measured. NO<sub>2</sub> is calculated by the difference between the NO<sub>x</sub> from the second stream and the NO from the first.

The efficiency of the converter is crucial to correct determination of NO<sub>2</sub>. The converted efficiency is determined at each inter-calibration visit and where this is less than the required 95%, data are rejected as they are likely to fall below the required DQO. CEN standard 14211:2005 permits scaling at lower efficiencies provided the DQO is still fulfilled.

When the CEN procedures are fully implemented, there will be a requirement to correct data for converters with efficiency between 95% and 98%.

To achieve reliable NO<sub>2</sub> concentrations, the NO and NO<sub>x</sub> channels are ratified separately and then NO<sub>2</sub> calculated by subtraction. This is a more reliable and flexible system than relying on the internal calculation of NO<sub>2</sub> within the analyser.

Calculations must be undertaken in mole fraction units (ppb) and the conversion to mass concentration units (to four decimal places) undertaken separately. This allows NO<sub>x</sub> concentrations to be reported correctly in the units required by the EU Directive ( $\mu\text{g m}^{-3}$  as NO<sub>2</sub>).

Review of the NO<sub>x</sub>/NO<sub>2</sub> ratio over an extended period is a useful tool to assist in data ratification. Seasonal patterns should be reasonably consistent at each monitoring station. Any sudden change in the ratio requires investigation, and unless linked to a

change in the local pollutant emissions around the site it will probably result in rejection of data.

### **6.2.9 AURN Data Ratification (Particle Analysers)**

Ratification of data from particle analysers is generally simpler than for gaseous analysers since there are fewer calibrations and checks which can be carried out in the field.

In most cases day-to-day scaling factors do not need to be adjusted and ratification consists primarily of deciding on the validity (or otherwise) of the measurements. This decision will be based on instrument diagnostics, comparison with co-located measurements and other nearby stations, assessment of prevailing pollution sources, and results of instrument and infrastructure checks carried out at QA/QC audits.

For all types of instruments flow rate and leak checks are carried out during 6-monthly audit visits and services. A ramped correction may be applied to sampled volumes, where flow rates are found to be more than  $\pm 3\%$  out from the flow rate recorded by the instrument. However, if the flow rate differs by more than  $\pm 10\%$  the data are rejected.

For high-resolution 15-minute or hourly measurements it is sometimes apparent that there is a high degree of random instrument instability or “noise” not linked to changes in ambient pollutant concentrations. If this is the case then these data will be rejected.

Further ratification checks for all analysers include:

- That there are no negative values (less than minus the limit of detection).
- That  $PM_{10}$  is greater than  $PM_{2.5}$ , in cases where both parameters are monitored using the same method at the same site (allowing for the measurement uncertainty, particularly at rural sites where both  $PM_{10}$  and  $PM_{2.5}$  are often low).

Additional data ratification considerations for two specific types of AURN particle analysers are discussed in the following sections:

#### **6.2.9.1 TEOM FDMS $PM_{10}$ or $PM_{2.5}$**

The TEOM FDMS instruments introduce two new parameters to ratify: “Base” and “Reference” measurements for particulate matter. The “Base” measurement is essentially a measurement of the non-volatile component of the sampled particulate matter. The “Reference” measurement cycle measures the volatile particulates by

evaporation from the filter and the instrument. Both these parameters are used to calculate the total PM<sub>10</sub> or PM<sub>2.5</sub> (depending on the type of instrument): for example, gravimetric equivalent PM<sub>10</sub> is the sum of the volatile PM<sub>10</sub> and non-volatile PM<sub>10</sub>.

Because the Reference cycle measures the volatile component by evaporation, the Reference measurement is recorded as a *negative* concentration. This is simply a function of the instrument technique; it is necessary to multiply the negative Reference concentration by – 1 to obtain a positive volatile concentration.

Since gravimetric equivalent PM<sub>10</sub> is the sum of the volatile PM<sub>10</sub> and non-volatile PM<sub>10</sub> concentrations, the data processing and reporting of these three parameters are linked. A PM<sub>10</sub> concentration can only be reported if valid Reference and Base measurements were made. Similarly, if the PM<sub>10</sub> is judged to be unreliable (e.g. excessive noise), then both the reference and base concentrations are deleted.

The terms Base and Reference are not used on UK-AIR: the terms “non-volatile” and “volatile” are used instead for better understanding by the public.

For correct operation, the FDMS instruments must operate within certain temperature and humidity tolerances. Hence, the ratification process also closely inspects these data. For example, there must always be at least 4°C separation between the sample and external dew points to prevent condensation on the filter.

Regional volatile PM measurements from the FDMS instruments should be consistent over a large radius (200 km for example). These can therefore be used to assess the validity of measurements from a particular instrument. If there is more than 2 µgm<sup>-3</sup> deviation from the regional mean volatile then further investigation is recommended.

On some instruments a gradual drift in the zero baseline is apparent either in the volatile, non-volatile or both FDMS measurements. The reason for this behaviour is unclear but if the zero baseline offset is measured to be > 2 µgm<sup>-3</sup> at a QA/QC audit visit then further investigation and possible data rejection is required. Replacement of the dryer on the FDMS unit is often found to cure the problem. Zero checks are carried out twice per year: as of 1<sup>st</sup> January 2015, where the zero baseline offset is found to be > 3 µg m<sup>-3</sup> the QAQC contractor may use the result of the zero check to correct for this baseline offset.

#### **6.2.9.2 Non-Automatic Particle Monitors**

Non-automatic PM<sub>10</sub> and PM<sub>2.5</sub> daily mean measurements are collected manually by the CMCU and emailed monthly to QA/QC in spreadsheets.

Instrument alarms and warnings (due to instrument flow outliers for example) are examined by the data ratifier to decide if the daily mean is valid or not. In addition, the QA/QC Unit uses spreadsheets to check that:

- Minimum sampling time (18 hours) and minimum sample volume (18m<sup>3</sup>) are achieved for each daily sample.
- There are no gaps in the dataset which cannot be explained by power or filter exchange failures.
- Any unusually low, high, or otherwise anomalous values are explained, or else rejected as spurious.

A field blank correction, based on an unexposed filter which remains in the filter canister while the other filters in the batch are exposed, is applied to the results. This takes account of any zero baseline artefacts which may occur during the exposure and measurement process. Choice of filter substrate will depend on requirements for any subsequent analysis of the particles collected. However for mass measurements PTFE coated “Emfab” filters are generally preferred to Quartz in order to avoid problems associated with moisture absorption. The issue of field blank correction, and how this process can improve quality control and reduce measurement uncertainty, are set out in a report by Bureau Veritas<sup>41</sup>.

As with other pollutants, account is taken of any measurements at nearby sites or from other instruments at the site in question in order to determine if there are any anomalies with the dataset. Each non-automatic PM sampler is compared with the nearest comparable FDMS (or in some cases, a co-located FDMS).

## **6.2.10 Factors to Consider in Data Ratification**

Data ratification procedures involve a critical review of all available information relating to a particular data set, in order to verify, amend or reject the data. A wide range of inputs need to be considered in the ratification process, as shown in Table 6-1.

The overall aim of the ratification process is to ensure that

- the final ratified dataset contains only valid data
- in the period between site audits, these data remain with the uncertainty level determined at the audit.

The close examination of analyser calibration service history, along with the overview procedures described above ensure that only valid data are retained.

**Table 6-1 Factors to Consider in Data Ratification**

<b>Factor</b>	<b>Relevant Questions</b>
<i>Instrument history and characteristics.</i>	Has the equipment malfunctioned in this way before?
<i>Calibration factors and drift.</i>	Rapid or excessive response drift can make data questionable.
<i>Negative or out-of-range data.</i>	Are the data correctly scaled?
<i>Rapid excursions or “spikes”.</i>	Are such sudden changes in pollution concentrations likely?
<i>Characteristics of the monitoring site.</i>	Is the station near a local pollution sink or source which could give rise to these results?
<i>Effects of meteorology.</i>	Are such measurements likely under these weather conditions?
<i>Time of day and year.</i>	Are such readings likely at this time of day/week/year?
<i>The relationship between different pollutants.</i>	Some pollutant concentrations may be expected to rise and fall together.
<i>Results from other sites in the network.</i>	These may indicate whether observations made at a particular site are exceptional or questionable. Data from other sites in the area can be compared for a given period to determine if measurements from a particular station are consistent with general pollution concentrations.
<i>QA Audit and Service reports</i>	These will highlight any instrumental problems and determine if any correction of the data is necessary for long-term drift etc.

The actual data uncertainty can only be determined at the 6-monthly site audits when all of the required parameters are measured and can be combined with analyser type testing and calibration cylinder uncertainties. The careful application of zero and span calibration data, and careful application of any corrections required as a result of the sites audit (e.g. to account for changing calibration cylinder concentrations) are designed to ensure that the data remain within the uncertainty level determined at the audit.

### **6.2.11 Quality Circle**

The QA/QC Unit uses a Quality Circle approach for final review of the data. The Quality Circle is a meeting involving representation from all disciplines of the QA/QC Unit: quality standards, inter-calibration team and data ratification. The meeting reviews any significant problems and decides on the appropriate actions by consensus. Data issues that are not clear to the ratification team may, for instance, be resolved by the inter-calibration manager's better understanding of the instrument detection principle. The meeting also discusses the results of the QA/QC inter-calibration. The meeting then needs to decide if, and how, any problems observed at the inter-calibration affect the measured data.

The Quality Circle always needs to review data in the light of new information, whether this comes from the inter-calibration exercise or from other sources. Ratified data only rarely need to be revised and re-issued, though this does happen very occasionally. Where a possible fault is suspected but the results of the inter-calibration or other detailed investigations are still awaited then the data may remain as provisional on the Archive until these investigations are completed. Again this only happens infrequently.

A key role of the Quality Circle is to identify where improvements in the overall quality system can be devised. This may be through improved equipment, improved procedures, improved software or software algorithms etc. When such points are identified they are actioned by the QA/QC Unit to ensure continuous improvement in the quality system.

### **6.2.12 UKAS Accreditation (ISO 17025:2005)**

In any monitoring network where traceability of measurements and compliance with DQOs are critical, it is essential that the QA/QC procedures are accredited to recognised, traceable standards. By accrediting key processes in the QA/QC programme, it is possible to demonstrate compliance of the monitoring network to the requirements of the Air Quality Directive. For network inter-calibration procedures, the QA/QC Unit is required to hold UKAS accreditation to ISO

17025:2005 for the on-site calibration of gaseous analysers, determination of TEOM spring constant ( $k_0$ ) and flow measurement of particulate analysers.

Accreditation to ISO 17025:2005 requires an organisation to:

- Document the procedures used to calibrate analysers
- Demonstrate competence of operators in performing calibrations
- Demonstrate traceability of measurements to metrology standards
- Calculate uncertainty budgets for measurements reported on Calibration Certificates.

UKAS is the recognised accreditation body in the UK and performs surveillance visits to the QA/QC Unit annually to assess competence and compliance with all the requirements of ISO 17025:2005.

The Air Quality Directive requires that the measurements are traceable in accordance with ISO 17025:2005. Section 8 of this report describes the traceability of the UK measurements within the AURN, in compliance with this requirement.

In addition, the Directive requires that any laboratory taking part in Community-wide inter-comparisons covering pollutants regulated in the Directive is accredited according to ISO 17025:2005 (by 2010) for the reference methods referred to in Annex VI of the Directive. The accreditation held by the QA/QC unit ensures compliance with this requirement.

The Gas Standards Calibration Laboratory (currently Ricardo-AEA) is also accredited to ISO 17025:2005 (the current contractor is UKAS Calibration Laboratory No 401), and UKAS accreditation conforms to the requirements of ISO 17025:2005 for the certification of gas calibration standards for a range of pollutants within a specified concentration range. This includes the gases and concentrations appropriate to the AURN.

The schedule of UKAS accreditation for the current contractor is available at [http://www.ukas.org/calibration/lab\\_detail.asp?Lab\\_id=896&vMenuOption=3](http://www.ukas.org/calibration/lab_detail.asp?Lab_id=896&vMenuOption=3)

### **6.3 QA/QC of Automatic Hydrocarbon Measurements**

The Air Quality Directive requires benzene data to be reported with an uncertainty of  $\pm 25\%$ . The Directive does not specify a DQO (uncertainty of measurement) for the measurement of the remainder of the hydrocarbon species referred to as ozone precursors.



Type approval, operational methodologies, mechanisms for QA/QC and calculation of measurement uncertainty budgets are clearly prescribed in EN 14662-3:2005. All of these areas need to be completely satisfied before an absolute calculation of measurement uncertainty can be undertaken.

The UK automatic hydrocarbon network is already operated to a high standard and will only need minor adjustment to be fully compliant with section 9 of EN 14662-3:2005. These adjustments centre on annual linearity evaluations, better quantification of calibration measurements and evaluation of site specific variables.

Robust, traceable, documented methodologies are implemented for calibration, data transmission and ratification, providing rigorous QA/QC for the automatic VOC analysers together with regularly undertaken European international intercomparisons at the EC Joint Research Centre (JRC), Ispra and participation in European round-robin exercises.

Routine network operation is carried out as follows:

- Daily checks performed daily by network manager or team member
- LSO visits fortnightly
- Data ratification is carried out quarterly. The ratification process is:
  - Data is reviewed and checked for erroneous data and scaled or removed if necessary
  - Re-assignment of mis-identified peaks
  - The final data is reviewed at a quarterly quality circle meeting with all members of the project team
  - Any outstanding corrections following the quality circle meeting are made by the network manager before dissemination

## **6.4 QA/QC of Non-Automatic Benzene Measurements**

Bi-annual service and maintenance visits are carried out at all measurement sites. Portable appliance Testing (PAT) is performed every other visit (annually). Sampling tubes are sent out to LSOs fortnightly in advance for exposure the following week. Each site receives a travel blank tube at least once per quarter. Samples are analysed at a sub-contractor's laboratory, conditioned and returned to the contractor for re-use.

Data ratification is carried out quarterly. The ratification process is as follows:

- Check blank is <2ng.

- Check audit dates, time and flow rates have been entered correctly.
- Check sampling time is the same for both date/time and counter, investigate erroneous data .
- Check difference between the 2 tubes comprising each sample, investigate suspected erroneous data or mark as not for dissemination.
- Review site operator comments.
- Plot time series for the year to date to identify anomalous data points.
- Compare concentrations with same period in previous year.
- Apply data flags (manually).
- Upload ratified (or provisional if applicable) data to UK-AIR.
- Spot check data on UK-AIR for any inconsistencies.

## 6.5 QA/QC of Urban Metals Measurements

The QA/QC measures employed by the Network to ensure robust sampling are as follows:

- The contractor visits all the Network sites to perform annual site audits.
- At these visits the site infrastructure, performance and integrity are assessed.
- The LSOs are also audited and receive extra training where required.

### 6.5.1 Metals Network Site Audits

During each Network site audit visit the contractor:

- Audits the procedures of the LSO on-site, giving introductory training where necessary, and encouraged LSOs to feed-back into the running of the Network
- Assesses the current condition of all on-site equipment, including the condition of the PM<sub>10</sub> sampling head and impactor plate
- Calibrates the flows of both the particulate (for volumetric and standard flow), and gaseous phase (volumetric flow), monitoring equipment
- Leak tests both the particulate and gaseous phase monitoring equipment
- Calibrates the site rotameter (used by the LSOs for determining the flow rate through the total gaseous mercury sampling line).

### 6.5.2 Metals Network Servicing

The ESU performs preventative maintenance on the samplers twice a year.

The flow rate of the samplers is calibrated at each ESU visit, at the site audit, and once more during the year by the contractor, yielding overall, quarterly flow calibrations.

### **6.5.3 Additional Sampling and Analysis QA/QC Procedures**

A sub-set of the QA/QC procedures employed during Network operation to ensure the quality of the data produced is listed below:

#### **6.5.3.1 Sampling**

- Despatch and analysis of one field-blank filter and one field-blank adsorption tube per site per quarter.
- Thorough checks of the returned filters and adsorption tubes to check for damage during transport. Rejection of damaged filters or tubes.
- Logging of all samples on the contractor's Network database. Rejection of any unidentifiable samples and full investigation of any discrepancies.
- Continued training of, and regular communication with, the LSOs. This includes assessment of performance during site audits.

#### **6.5.3.2 Particulate phase metals (ICP-MS analysis)**

- Optimisation of the ICP-MS prior to each set of analysis. Comparison of the optimised parameters with pre-defined criteria.
- Regular extraction of an appropriate certified reference material (e.g. NIST SRM 1648a or NIES No.8) to check the recovery of the digestion method. Recoveries must be within the limits specified by EN 14902:2005.
- Regular measurement of filter blanks to ensure appropriate blank subtractions are made from measured values.
- Maximum levels for the standard deviation of the five internal standard-corrected measured intensities of each analysis of each sample.
- The maximum absolute weighted residual for all calibration curves (as calculated using the contractor's data processing software) must be less than one.
- Ratification of all data by a Quality Circle of senior scientific experts within the contractor's organisation but independent of the analytical team.

#### **6.5.3.3 Total gaseous mercury (atomic fluorescence analysis)**

- Regular recovery tests carried out by analysing tubes spiked with a known quantity of mercury. Recoveries of between 95% and 105% must be achieved.
- Control limits on changes in instrument sensitivity between analyses.
- Analysis of clean tubes to ensure that blank levels are sufficiently low.
- Novel bracketing calibration procedure for each tube analysed in order to minimise the effect of instrumental drift.

- Ratification of all data by a Quality Circle of recognised senior scientific experts from within the contractor's organisation but independent of the analytical team.

## 6.6 QA/QC of Rural Metals Measurements

Each particulate monitoring site is serviced and audited every 6 months to maintain the site infrastructure, performance and integrity. The operational conditions of the particle samplers are checked daily, and any faults are usually rectified within a few days to maximise the data capture performance.

The analytical processes are subject to the QA/QC requirements of UKAS accreditation for ISO 17025:2005, which includes regular inter-laboratory comparisons of data. The accreditation is held by the contractor's laboratories (CEH Lancaster) for the required analyses. Furthermore, CEH Lancaster participates in the yearly EMEP intercomparison of analytical methods for heavy metals in precipitation run by the Norwegian Institute of Air Analysis (NILU).

The databases are subject to rigorous checks and, in addition, the concentrations in each sample are reviewed by the project manager at least quarterly before being uploaded to UK-AIR. Individual samples which are deemed too high (usually more than 2 x Standard Deviations from that year's annual mean) are flagged as potential outliers that may not be representative of background concentrations.

## 6.7 QA/QC of PAH Measurements

In order to assure robust sampling procedures the following QA/QC measures are undertaken:

- Routine servicing/calibration of the Digitel samplers is carried out at all Network stations once a year by the respective ESU.
- Yearly audits are carried out at all Network stations by the contractor. As part of these visits, the flow is measured using a calibrated and traceable flowmeter (according to EN 12341:1999 and EN 15549:2008), and the LSOs are audited (and, where necessary, retrained). In addition, an updated LSO site operation procedure manual is re-issued when necessary.
- Quarterly measurements of the flow rate of the samplers is performed at all stations (as specified in EN 15549:2008), using calibration kits designed by the contractor.
- Portable appliance testing, periodic (five-year) electrical testing and the updating of risk assessments is also performed at the stations as necessary.

- Analysis of sample blanks and filter blanks is performed.
- Despatch and analysis of field blanks is performed.
- Inspection of all sampling media prior to despatch to stations in accordance with the specifications in EN 15549:2008 and EN 15980:2011. For example, filters are inspected for pinholes, loose material and non-uniformity.
- Inspection of all filters when returned from stations. Samples that are damaged (e.g. torn or wet filters) or returned un-sampled are rejected and the details of these samples are noted in the contractor's Network database.
- Rejection of any unidentifiable samples returned from stations.
- Full investigation of any discrepant or unexpected sampling data (e.g. unexpectedly high or low sample volumes).

In order to ensure the quality of the analytical data, the following QA and QC measures are undertaken:

- Regular assessment of the limit of detection of the GC-MS method.
- Regular extraction and analysis of an appropriate certified reference material (NIST SRM 1649b) in order to check the recovery of the extraction methods. Recoveries must be within the limits specified by EN 15549:2008.
- Use of a range of deuterated PAH analogue species in order to assess (and correct for) the recovery of *each sample*. Following the criterion in EN 15549:2008, if the analytical recovery of d-B[a]P for any sample is determined to be less than 50 %, the result is highlighted as not being valid for inclusion in the calculation of the annual mean concentration.
- The contractor regularly participates in proficiency testing and comparison schemes to benchmark the quality of the analysis provided.
- All analyses are covered by accreditation to ISO 17025:2005.

Deposition sampling is performed as specified in EN 15980:2011. In this case, analytical QA/QC is covered by EN 15980:2011 rather than EN 15549:2008. All other aspects are the same.

## 6.8 QA/QC for Other Measurements

### 6.8.1 Cations and Anions in Rural PM<sub>2.5</sub>

The Marga 2S used to measure anions and cation in rural PM<sub>2.5</sub> is a research-grade instrument. Currently there is no proposed or accepted ISO, CEN or equivalent BS standard method for the determination of the concentration of anionic or cationic species in PM<sub>2.5</sub>.

The Marga 2S uses an internal standard of lithium bromide (LiBr) for on-going calibration purposes. The LiBr solution is manufactured by the LSO. Measurements are rejected if the measured Li<sup>+</sup> and Br<sup>-</sup> ion concentrations deviate by more than ±20% of the known concentration. Currently the concentrations of Li<sup>+</sup> and Br<sup>-</sup> ion in the internal standard are 320 and 3680 µg L<sup>-1</sup>, respectively, in the Marga 2S based at Harwell.

As noted in section 5.6.1, peak retention times may change over time due to instrumental factors, e.g. column ageing, as well as environmental factors, e.g. atmospheric temperature and pressure. In order to account for this, the peak retention times are checked on a regular basis and adjusted accordingly by the LSO. Peaks are identified by the system software if they fall within a window of ±5% of the operator defined peak retention time. Occasionally, measurements may be made where the peak retention time has shifted considerably within a short period of time, e.g. over a period of a couple of hours. This may mean that a peak is missed or misidentified by the system software. In such instances, the resultant anion and cation chromatograms, which are written to file, can be re-analysed and use to verify the presence of species of interest. Once a peak associated with species of interest has been identified the mass concentration of the species can be determined. The retrospective re-analysis of chromatograms is undertaken using proprietary software supplied by the instrument manufacturer (Metrohm-Applikon BV, Schiedam, The Netherlands).

The manufacturer's quoted detection limits for the Marga 2S are given in Table 6-2.

**Table 6-2 Manufacturer's quoted detection limits for the Marga 2S**

<b>Particle-phase species</b>	<b>Detection limit (DL, µg m<sup>-3</sup>)</b>	<b>Gas-phase species</b>	<b>Detection limit (DL, µg m<sup>-3</sup>)</b>
NH <sub>4</sub> <sup>+</sup> ion	0.008	NH <sub>3</sub>	0.008
Na <sup>+</sup> ion	0.008	HCl	0.005

K <sup>+</sup> ion	0.010	HONO	0.008
Ca <sup>+</sup> ion	0.008	HNO <sub>3</sub>	0.005
Mg <sup>+</sup> ion	0.010	SO <sub>2</sub>	0.010
Cl <sup>-</sup> ion	0.005		
NO <sub>3</sub> <sup>-</sup> ion	0.005		
SO <sub>4</sub> <sup>2-</sup> ion	0.008		

Due to the slight changes in peak retention over time, small perturbations in the instrument detection limits have been noted due to changes in the IC columns, which are typically replaced every 2 to 3 months (as shown in Table 6-3). For this reason, the limits of detection (LoDs) of a specific column (either anion or cation) for each species of interest are determined from the Marga 2S measurements, rather than the manufacturer quoted values given in Prior to reporting, the measurements are reviewed. Measurements that fall the below instrument detection limits (including zero values) are replaced with a value of ½ LoD.

A site log book is maintained by the LSO. This is used to record:

- All operational checks undertaken, including instrument checks undertaken, e.g. replacement of instrument components, connective tubing, inlet cleaning
- Problems with the equipment
- Factors which may have a bearing on the PM<sub>2.5</sub> measurements (e.g. pump failure, power cuts, burning or nearby construction work).

The following routine maintenance is undertaken periodically on the Marga 2S based at Harwell:

- Servicing of the Marga 2S sampler is undertaken by the instrument manufacturer.
- The sample flow is measured and calibrated using a traceable flowmeter. The audit sheet is retained by the LSO. This is currently undertaken once a month, but the periodicity maybe reduced to once every 3 months in due course.
- External blank solution checks are performed once a month, typically on the first Friday of each month.
- Daily measurements (chromatograms and instrument parameter log files) from the instrument are backed-up routinely via an FTP connection on a daily

basis (at 02:00) to the contractor's internal server. This is to ensure good data integrity and to limit data loss in the event of the irrevocable failure of the instrument PC.

- System parameters and peak retention times are monitored on a daily basis and adjusted accordingly.
- Instrument working solutions are manufactured according to the manufacturer's guidelines. Working solutions are typically made from stock solutions and replenished on a weekly basis.
- Variations in system parameters and instrument failures are investigated in a timely manner.

The manufacturer's suggested maintenance schedule for the Marga 2S is detailed in Table 6-3.

Measurements from the Marga 2S are compared to other available particulate (PM<sub>2.5</sub>) and gaseous-phase (e.g., SO<sub>2</sub>) measurements made at the site to determine the quality and consistency of the measurements. Provisional measurements that do not agree with measurements from the other instruments are flagged and may be subject to removal from the final, ratified dataset. The ratified measurements are then reported and disseminated via UK-AIR.



**Table 6-3 Suggested maintenance schedule for the Marga 2S**

Maintenance task	1 week	2 weeks	2 months	4 months	6 months
Replace absorbance liquid 20L.	X				
Replace anion and cation eluents.		X			
Replace internal standard solution.			X		
Replace suppressor solution.			X		
Replace sample filter in the WRD.			X		
Replace sample filter in the SJAC.			X		
Replace anion and cation guard columns.			X		
Flush system with cleaning solution.			X		
Replace anion column.			X <sup>(a)</sup>		
Replace cation column.				X <sup>(a)</sup>	
Replace filters (in storage containers) anion, cation, internal standard and H <sub>3</sub> PO <sub>4</sub> .					X
Replace inline filters before pulsation dampeners.					X
Replace inline filters behind suppressor pump.					X
Replace anion and cation sample loops.					X

(a) Replacement frequency depends on the anion eluent and absorbance solution quality. Columns are replaced if exhausted (indicated by the instrument software).

## 6.8.2 Elemental Carbon (EC) and Organic Carbon (OC)

In order to assure robust sampling procedures for EC and OC the following QA/QC measures are undertaken:

- Routine servicing/calibration of the Leckel samplers is carried out at both Network stations once a year by the ESU.
- Yearly audits are carried out at both Network stations by the contractor. As part of these visits, the flow is measured using a calibrated and traceable flowmeter (according to EN 14907:2005), and the LSOs are audited (and, where necessary, retrained). In addition, an updated LSO site operation procedure manual is re-issued when necessary.
- Portable appliance testing, periodic (five-year) electrical testing and the updating of risk assessments is also performed at the stations as necessary.
- Analysis of sample blanks and filter blanks is performed.
- Despatch and analysis of field blanks is performed.
- Inspection of all sampling media prior to despatch to stations. For example, filters are inspected for pinholes, loose material and non-uniformity.
- Inspection of all filters when returned from stations. Samples that are damaged (e.g. torn or wet filters) or returned un-sampled are rejected and the details of these samples are noted in the contractor's Network database.
- Rejection of any unidentifiable samples returned from stations.
- Full investigation of any discrepant or unexpected sampling data (e.g. unexpectedly high or low sample volumes).

In order to ensure the quality of the analytical data, the following QA and QC measures are undertaken:

- Daily machine zero checks and sucrose solution checks. These must be within specified limits.
- Regular analysis of the contractor's internal reference material.
- Regular calibration of the sample temperatures using the recently-available manufacturer's calibration rig.
- TC analysis is covered by accreditation to ISO17025:2005 – the split into EC and OC will be included in the accreditation when the standard method is published.

## 7 Traceability of Measurements

Traceability requires an unbroken chain of measurements all with stated uncertainties - from a primary international or national standard, through the calibration standards used in the network, to the final measurement result.

Calibration standards are a key link in the traceability chain. The methods by which calibration standards are developed and maintained at a national level fall into a number of different categories. These cover calibration standards that are:

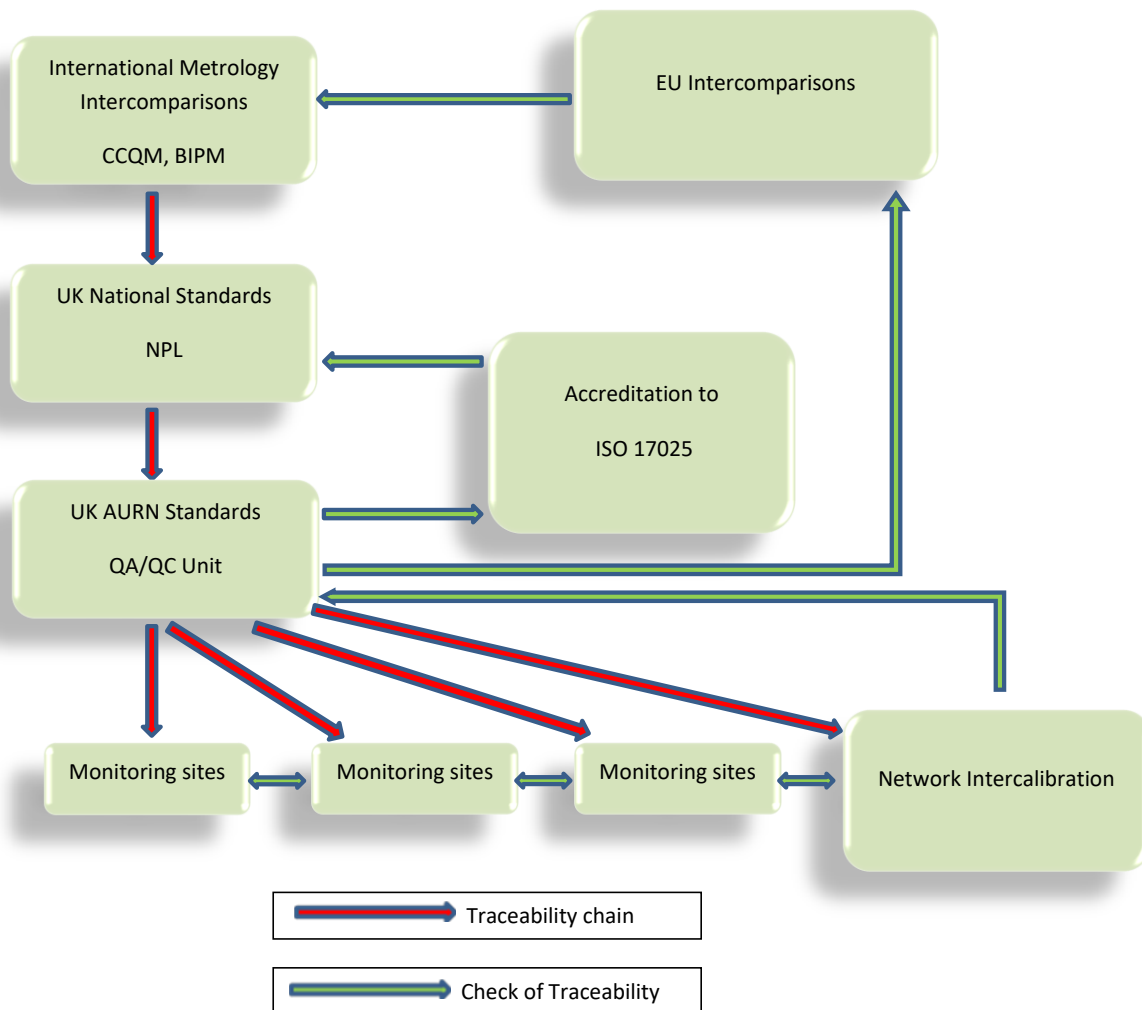
1. Prepared in a manner that is traceable directly to SI units through mass, volume (length), flow (mass and time) etc. These apply to calibration standards for the pollutant gases measured within the AURN ( $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{O}_3$ ), although there are different means of realising and disseminating these, in particular between ozone and the other gases.
2. Not able to be produced in a manner that is directly traceable to SI units but traceability can be achieved by means of the realization of a potentially 'absolute' method such as optical photometry, when implemented under controlled conditions. This method applies for the measurement of metals and PAHs, for example.
3. Not able to be realised in a traceable manner or as a 'primary' or 'absolute' method, but realised instead *by convention or by definition as the reference method*, preferably having the smallest measurement uncertainties achievable using that method. This method applies for  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  measurements.

This section explains how traceability is achieved for gaseous pollutants,  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , benzene, metals and PAH. It does not cover measurement of deposited metals, deposited PAH, rural cations and anions, EC and OC, because the relevant Directives do not contain any DQOs for these parameters.

### 7.1 Traceability for $\text{NO}_x$ , $\text{SO}_2$ , $\text{CO}$ and Zero Air

#### 7.1.1 Overview

The traceability chain for the gaseous pollutants in the AURN is indicated in Figure 7-1. The "chain" is shown in red – from International standards to individual measurement sites. The check procedures adopted in the UK are also highlighted – and shown in green.



**Figure 7-1 Traceability chain and traceability checks for UK AURN gaseous measurements**

### 7.1.2 UK primary gas standards

UK Primary Gaseous Calibration standards are prepared by NPL using gravimetry to weigh specific pollutant gases together with relevant matrix/diluent gases into high-pressure cylinders and then to dilute these gas mixtures to the required low concentrations for ambient air concentration calibrations, as required. This method of preparation of gas standards is directly traceable to the SI mass unit, via a number of accurate weighings (gravimetry). Typical uncertainties of the UK primary gas calibration standards are as follows:

- NO<sub>x</sub> 2%.
- SO<sub>2</sub> 3%.
- CO 2%.

These UK standards are cross-referenced with standards prepared by other national institutes through international inter-calibration exercises coordinated by organisations such as EUROMET.

### **7.1.3 Provision of traceable gas calibration standards to AURN monitoring sites**

All AURN sites have calibration gas cylinders for NO, NO<sub>2</sub>, CO, and SO<sub>2</sub>, as appropriate, which remain at the site. These cylinders are prepared and supplied by the Gas Supplier but prior to delivery to site they are calibrated at the Gas Standards Calibration Laboratory and provided with a UKAS accredited certificate of calibration. The current contractor, Ricardo-AEA, is UKAS Calibration Laboratory No 401; UKAS accreditation conforms to the requirements of ISO 17025:2005.

The Gas Standards Calibration Laboratory has a suite of UK primary gas calibration standards purchased from NPL. The calibration cylinders used at every AURN site are certified against these, and given an ISO 17025:2005 accredited certificate of calibration. Traceability of the calibration gas used at every AURN site is thus linked in an unbroken chain to national and international gas standards. The uncertainty of calibration gas standards provided to the monitoring sites is typically:

- NO 3-3.5%
- SO<sub>2</sub> 3.5%
- CO 2%.

All cylinders used for the AURN network inter-calibration are certified by the Gas Standards Calibration Laboratory. The Gas Standards Calibration Laboratory also undertakes international inter-comparisons at the EU Joint Research Centre to ensure the integrity of the gas standards used in the AURN. As noted in section 6, this is a requirement of both ISO 17025:2005 and the Air Quality Directive in order to demonstrate comparability and traceability.

### **7.1.4 Zero air calibration standards**

As ambient concentrations decrease, the importance of the accuracy of the zero calibration increases. Zero air cylinders are used at most AURN sites. These are traceable to a certified NPL zero air standard with the following specifications:

- NO 0.5 ppb
- SO<sub>2</sub> 0.7 ppb
- CO 20 ppb

These zero gas cylinders are replacing chemical air scrubbers used previously in order to provide a more reliable, consistent and traceable basis for zero calibrations. At a few sites, chemical scrubbers remain in use because reasons such as lack of space prevent the installation of a zero air cylinder.

### **7.1.5 Site calibration and inter-calibration**

The final link in the traceability chain from international gas standards to measurements of air quality at individual measurement sites is provided through the periodic calibration of the analysers with the certified cylinders at each site. At some sites automatic systems provide for daily or 3-daily calibrations. At other sites 2-weekly or monthly manual calibrations are performed.

In order to check the stability of the gas cylinders on site over a period of time, the concentrations of the gases they contain are checked against recently certified cylinders as part of the 6-monthly site inter-calibration exercise. The procedure is analogous to that used in the Gas Standards Calibration Laboratory, but the procedures in this case are not accredited. This is because the conditions for the calibration cannot be reliably controlled at a remote measurement site in the way that they are in the calibration laboratory.

The procedure is therefore to check the site cylinder concentration and if this is shown to have deviated significantly from the certified value the cylinder is removed from the monitoring site for further investigation. If the result shows the cylinder contents have remained stable, the cylinder may be returned to the site for further use. However, if the cylinder concentration has changed significantly, the new concentration value is utilised as part of the process of data ratification for that site whilst immediate replacement of the cylinder is recommended.

## **7.2 Traceability for Ozone**

Unlike stable gases such as CO, NO etc., ozone is too reactive to be prepared in gas cylinders. However, the UV absorption ozone photometer is an absolute method of monitoring, governed by the Beer-Lambert law. Calibration of ozone analysers in the UK are performed using reference ozone photometers, which are themselves calibrated against an ozone standard reference photometer (SRP).

The Bureau International des Poids et Mesures (BIPM) maintains three NIST SRPs in the UK (there are others elsewhere in Europe). These are used as ozone reference standards to underpin its international comparison programme. The BIPM

and NIST are cooperating to transfer the international responsibility for the comparison of national ozone standards to the BIPM.

### **Provision of traceable O<sub>3</sub> calibration standards to all AURN ozone monitoring sites**

Transfer reference photometers are used for calibration of ozone analysers. These are calibrated every 6 months by NPL against their SRP, providing UKAS accredited calibrations in the range 0 to 1 ppm with a  $\pm 3.0\%$  relative uncertainty (at the 95% confidence level).

The QA/QC Unit's transfer reference photometers are commercial photometers certified to UK standard. These photometers are used to calibrate the ozone analysers at all AURN sites every three months. The uncertainty of the calibration of on-site analysers is typically 3-4%. Hence, there is an unbroken chain of traceability to national and international ozone standards.

As an independent check, the QA/QC Unit also participates in EU network inter-calibrations for ozone, organised by the JRC. In addition, the QA/QC Unit also provides UKAS accredited calibrations of photometers used by the network's service engineers, enabling them to provide a traceable ozone analyser calibration as part of their routine service and maintenance.

## **7.3 Traceability for PM<sub>10</sub> and PM<sub>2.5</sub>**

Manual gravimetric methods for particulate monitoring of PM<sub>10</sub> and PM<sub>2.5</sub>, as specified in the European standards EN 12341:1999 and EN 14907:2005 respectively are defined as the European Reference methods for particle monitoring in Air Quality Directive. These two standards specify methods that cannot be considered as traceable to the SI system of units in a rigorous manner. The sampling is by a method defined by convention, and the mass measurement can clearly be defined as traceable to SI units. However, the main problem is that the measurement itself is not well defined, as the particles comprising the material sampled will have different shapes, sizes and compositions.

As noted earlier (section 5.1), UK measurements of PM<sub>10</sub> and PM<sub>2.5</sub> are largely undertaken with automatic measurement techniques, in order to fulfil the rapid dissemination requirements of 2008/50/EC. The manual sampling methods are therefore to be used as references against which other measurement techniques used for monitoring PM<sub>10</sub> and PM<sub>2.5</sub> for EU regulatory purposes, may be compared. As a result of such comparisons, other methods of measurement may be demonstrated to be "equivalent" and accepted for the purposes of reporting results to

the EU. This concept of the demonstration of “equivalence” is specified in a document prepared by the EU and involves comparisons in the field of any other method for monitoring PM<sub>10</sub> or PM<sub>2.5</sub> with the relevant reference method.

The above standards therefore represent reference methods that are specified by definition and with no real traceability to the SI system of units (with the exception of a requirement to determine the mass flow of air through the monitor). This inability to achieve traceability is partially as a result of the complex variable and ill-defined size, shape and composition, of the particulate matter being monitored.

The UK has conducted a detailed and comprehensive equivalence testing programme for PM<sub>10</sub> and PM<sub>2.5</sub>. Latest results can be found on [UK-AIR](#) and the SIRA MCERTS websites.

### **7.3.1 On-site checks**

During the network 6-monthly inter-calibration exercise the flow rates of all network analysers are calibrated by UKAS accredited procedures. For TEOM and TEOM FDMS analysers the spring constant “k<sub>0</sub>” is also checked. This checks the most basic parameters of the measurement – flow and mass – and ensures correct operation of the analysers.

In addition ongoing QA/QC equivalence checks are incorporated into the network via long-term co-located sampling of PM<sub>10</sub> and PM<sub>2.5</sub> with both TEOM FDMS and gravimetric (Partisol) samplers at four sites in the network.

## **7.4 Traceability of Automatic Hydrocarbon Measurements**

The uncertainty of NPL VOC gas standards is stated on the certificate as an expanded uncertainty with a coverage factor of approximately 95% in the units of the gravimetric amount fraction. This uncertainty is a combination of the gravimetric uncertainty in the preparation of the mixtures and an allowance for drift over the two-year period the certificate is valid. NPL carries out continuous stability checks on the VOC standards.



## 7.5 Traceability of Non-Automatic Benzene Measurements

UKAS accredited flow checks are carried out on a six monthly basis at audit/service visits by the contractor. Certificates are provided each audit period. UKAS accredited measurements by GC-MS for benzene from Carbopak X sorbent material is carried out by the subcontractor.

## 7.6 Traceability of Metals Measurements

### 7.6.1 Urban and Industrial

As explained above, metrological traceability ensures that any result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty. Here, a 'reference' can be a definition of a measurement unit through its practical realisation, or a measurement procedure including the measurement unit for a non-ordinal quantity, or a measurement standard. The measurement results obtained by this network are therefore calibrations and fully traceable to national standards and to primary realisations of the relevant SI units.

Each site is flow checked on a quarterly basis with flow calibrators traceable to national standards. Both the ESU and the contractor use the same ISO 17025:2005 accredited calibration service to calibrate their flow meters. Analysis in the laboratory is traceable to the NIST series of mono-elemental standards which realise the mole, and to the definition of the kilogram through the gravimetric preparation of standard solutions.

Where traceability to SI base units is not possible because the measurement is defined by the procedure – here, PM<sub>10</sub> sampling – the relevant documentary standard is followed (EN 12341:1999).

Whilst not ensuring traceability *per se*, analytical results for metals are validated by the regular measurement of relevant certified reference materials: NIST SRM 1648a, ERM-CZ120 or NIES No.8.

## 7.6.2 Rural

Partisol flow calibrations are determined with a Streamline Pro MultiCal System, traceable to NIST Reference Standards sn10961, sn10961, sn10963, and sn913930-M1.

The analytical laboratory used is accredited to ISO 17025: 2005 by UKAS. In compliance with section 5.6 (clauses 5.6.2.1.1 and 5.6.2.2.1 ) of ISO 17025:2005, the laboratory maintains a system whereby all analyses are traceable to SI units by means of an unbroken chain of calibrations and comparisons linking them to relevant primary standards of the SI units of measurement. This applies to both measurement equipment used (e.g. balances) and analytical reference materials.

The Tekran instrument (used for TGM and speciated mercury measurement) is a mercury mass measurement method. It is auto calibrated using an internal permeation source. This source is externally verified / calibrated with a with a primary reference standard of saturated mercury at a known temperature with a volumetric syringe to introduce a known mass of mercury. This is carried out using the Tekran 2505 mercury vapour calibration unit, which meets the requirements of BS EN 15852 . Field trials and inter-comparison between methods for measuring atmospheric mercury found good agreement between sampling methods including the Tekran analyser<sup>42,43</sup>.

## 7.7 Traceability of PAH Measurements

The measurement results obtained by this network are calibrations and fully traceable to national standards and to primary realisations of the relevant SI units.

The sampler flow rate is checked by the LSO on a quarterly basis and during the annual audit by the contractor. The flow meter for the PAH Network is calibrated traceable to national standards using an ISO 17025:2005 accredited service. Analysis in the laboratory is traceable to the NIST series of mono-elemental standards which realise the mole, and to the definition of the kilogram through the gravimetric preparation of standard solutions.

Where traceability to SI base units is not possible because the measurement is defined by the procedure – here, PM<sub>10</sub> sampling – the relevant documentary standard is followed (EN 12341:1999 and EN 15549:2008).

Whilst not ensuring traceability *per se* analytical results are validated by the regular measurement of relevant certified reference materials: NIST SRM 1649b, ERM-CZ100.

The above applies to measurements of both suspended PAH concentration and deposited PAH.

## 8 Uncertainty of the Measurements

This section sets out the uncertainty calculation philosophy and the typical uncertainty values for measurements of ambient concentrations of gaseous pollutants, PM<sub>10</sub>, PM<sub>2.5</sub>, benzene, metals and PAH. It does not cover measurement uncertainty of rural cations and anions, EC and OC, because the relevant Directives do not contain any DQOs for these parameters.

In general, all measurement uncertainties are calculated using very similar methodologies. The first stage of the process is set by the EC which, based on health impact information, specifies a Limit or Target Value for a pollutant, together with a DQO for that Value. By way of an example, the annual mean Limit Value for NO<sub>2</sub> is 40µgm<sup>-3</sup>, with a DQO of ±15% for fixed measurements. Therefore an annual mean measurement reported at 40 µgm<sup>-3</sup> must have an associated uncertainty of no more than ±6µg/m<sup>3</sup>.

The next stage in the process is determined by critical assessment of the performance of the analyser making the measurement. Using principles from the Guide to the Uncertainty of Measurement (GUM)<sup>44</sup>, all of the possible components associated with making a measurement are identified, their effects on the measurement quantified and then combined to provide a total uncertainty for the measurement.

For example, the uncertainty associated with making a fixed measurement of carbon monoxide will be influenced by the uncertainty of a number of factors, for example:

- The concentration of calibration gases (zero and span).
- The noise associated with the analyser signal (to zero and span gases).
- The response of the analyser to any interfering gases.
- The response of the analyser to other interferences (temperature, electricity supply, etc.).
- Any lack of linear response of the analyser.

Once all of the possible contributions are identified and evaluated, the results are combined in a “root-sum-square” calculation to arrive at the total measurement uncertainty at the Limit or Target Value.

For all pollutants regulated by EC Directives, standard methods have been published that describe exactly how to perform the evaluations and calculations, together with minimum requirements for ongoing Quality Control procedures.

Member States are required to use instrumentation that have been tested against these standard methods and fulfil the requirements of the DQO. Ongoing QC

obligations must be fulfilled to ensure that the instruments and associated infrastructure continue to produce data that are compliant with the DQO.

## 8.1 Uncertainty in the AURN

As a result of all of the QA/QC operations undertaken within the AURN and described in this report, the uncertainty of the measurements can be reliably determined using the methodology defined in the CEN Standard Methods. This determination of uncertainty is required to demonstrate compliance of the measurements made within the AURN with the DQOs of Air Quality Directive.

The Directive requires full implementation of the CEN Standard Methods of Measurement throughout the network by June 2013. The UK has complied by the due date.

Analysers used in the AURN have been fully tested against the performance requirements of the CEN standard methods. The results obtained vary not only by pollutant type but also by manufacturer. Following verification of the performance test results, minor variations to the uncertainty calculations are made to account for analyser and specific field operation functions e.g. NO<sub>x</sub> converter efficiency tests and cylinder uncertainties. The results of these calculations are summarised in Table 8-1.

**Table 8-1 Calculated Best Measurement Uncertainty of AURN Data using CEN methodology**

Instrument	NO <sub>x</sub>	CO	SO <sub>2</sub>	O <sub>3</sub>
API A + E series Analysers (at Limit Value)	14%	10%	13%	12%
Horiba 370 series Analysers (at Limit Value)	12%	11%	12%	9%
Thermo I series Analysers (at Limit Value)	10%	10%	13%	11%
ME 9800(UK) series Analysers (at Limit Value)	11%	14%	11%	12%
EU Directive DQO (at Limit or Target Value)	15%	15%	15%	15%

Table 8-1 shows that the data obtained from the analysers tested to date fulfil the requirements of the EU Directive DQOs. The calculations at this stage necessarily

contain a number of assumptions about aspects of analyser field performance that will need to be regularly evaluated on site.

The instruments referred to in the table are NO<sub>x</sub> analysers, but the quoted uncertainties apply to measurements of NO<sub>2</sub>, this being the only one of the NO<sub>x</sub> species for which the CEN standard provides an uncertainty budget calculation.

For PM<sub>10</sub> and PM<sub>2.5</sub>, a similar process is employed, but because performance tests using certified calibration standards is not possible, demonstration of equivalence is conducted using a series of comparison tests against a reference sampling device. The UK equivalence trials have demonstrated that data derived from all analysers that meet the equivalence criteria conform to the EU Directive DQOs for PM<sub>10</sub> and PM<sub>2.5</sub> i.e. 25% at the limit value (Table 8-2).

**Table 8-2 Calculated Best Measurement Uncertainty of AURN PM Data using CEN methodology**

Instrument	PM <sub>10</sub>	PM <sub>2.5</sub>
TEOM 1400AB with 8500 FDMS	9%	16%
BAM 1020	9%	13%
Partisol 2025	8%	11%

## 8.2 Uncertainty of Automatic Hydrocarbon Measurements

A statement of measurement uncertainty is only required for benzene. All other pollutants are excluded from this requirement.

As noted earlier, the PE analyser used in the UK network has not been type approved for the automatic measurement of benzene as specified in EN14662-3:2005. Measurement of the ozone pre-cursor pollutants is not currently regulated by a standard method, and there are no type approved analysers available that measure both benzene and the pre-cursors. From a monitoring perspective, this makes cost-effective automatic monitoring of benzene and ozone pre-cursors challenging.

The EN14662-3:2005 standard is currently undergoing revision to align more closely with the inorganic gas standards followed in the AURN. It is likely that the test

programme will be sufficiently different from the old type approval that the performance of all analysers will need to be re-evaluated.

This likely change in the standard method makes evaluation of measurement uncertainty complex. The UK has a staged approach to fulfilling this requirement:

- The four automatic analysers in the network are calibrated with certified gas mixtures.
- The four automatic analysers have been regularly intercompared against co-located samples collected using the pumped sampler methodology. Results of these comparisons show that the difference between the techniques is less than 10%.
- The UK regularly participates in round robin calibration exercises, where the concentrations of known gas mixtures are evaluated with a calibrated analyser. In the most recent exercise, the maximum deviation of reported benzene concentrations from the reference value was 7.6%.
- The UK also participates in international intercomparison exercises, where test gases are generated and sampled simultaneously by a number of different analysers owned by Member States.

In addition, calculation of the uncertainty of the calibration factor of an analyser is routinely undertaken, using the principles of the GUM to define the inputs into the calculations. These tests demonstrate that the uncertainty of the calibration factors is routinely better than 25%

These approaches provide confidence that the calibration and monitoring methodologies used by the UK are sufficiently robust to fulfil the requirements of the benzene DQO (25%).

## **8.3 Uncertainty of Non-Automatic Benzene Measurements**

Flow checks are carried out on a six monthly basis at audit/service visits. The calculated uncertainty for the Non-Automatic Hydrocarbon sites is typically 15%, expressed at a 95% level of confidence. This includes contributions from the contractor's UKAS accredited low flow measurements, desorption efficiency and analysis uncertainty.

## 8.4 Uncertainty of Metals Measurements

### 8.4.1 Urban

The range of uncertainties covering the majority of analyses of single filters and tubes are shown in Table 8-3 below. All figures are a combination of the analytical and sampling uncertainties and have been derived using full ISO GUM compliant uncertainty budgets developed from measurement equations which describe the entire measurement process. All values are stated to a coverage factor of  $k = 2$ , providing a level of confidence of approximately 95%.

The measurement uncertainties displayed in Table 8-3 are representative of the range of uncertainties covering the majority of individual measurements over a typical sampling period (here, one week), as required by the Air Quality Directives. The vast majority of the measurements used to compile the data above were of ambient concentrations well below the relevant target values. It is calculated that in the region of the appropriate target value – where the Air Quality Directive’s uncertainty DQOs apply (except for Hg(v) where there is no target value) – these relative uncertainties will be significantly lower.

#### **8.4.1.1 Measurement of uncertainty of the annual average**

ISO 11222:2002<sup>45</sup> “Air quality - Determination of the uncertainty of the time average of air quality measurements” is used to determine the uncertainty in the annual mean for each element at each sampling location. This is easily done since the contractor produces a statement of uncertainty with each measurement result.

Data capture across the Network remains high (and any gaps in coverage have generally occurred evenly throughout the year). The uncertainty in the annual mean values are dominated by analytical and sampling uncertainty, with only small uncertainty contributions arising from time coverage below 100%. The effect of these contributions is calculated using the method described in ISO 11222:2002 “Air quality - Determination of the uncertainty of the time average of air quality measurements”. In all cases annual mean uncertainties are compliant with the DQOs for uncertainty in the Air Quality Directives.



**Table 8-3 Expanded Relative Uncertainties over a typical sampling period of 1 week**

<b>Analyte</b>	<b>Expanded Relative Uncertainties</b>	
	<b>Single measurement range<sup>(a)</sup></b>	<b>EC Directive maximum<sup>(b)</sup></b>
As	16 - 26 %	40 %
Cd	13 - 20 %	40 %
Co	18 - 38 %	-
Cr	14 - 32 %	-
Cu	11 - 15 %	-
Fe	12 - 17 %	-
Mn	11 - 15 %	-
Ni	10 - 14 %	40 %
Pb	8 - 13 %	25 %
Pt	40 - 50 % <sup>(c)</sup>	-
Se	20 - 35 %	-
V	11 - 16 %	-
Zn	10 - 14 %	-
Hg(p) <sup>(d)</sup>	20 - 40 %	-
Hg(v) <sup>(d)</sup>	13 - 20 %	50 %

(a) 'Single measurement range' shows the range of uncertainties covering the majority of analyses of single filters and tubes by the current contractor during 2011.

(b) 'EC Directive maximum' shows the maximum permissible uncertainty at the target value allowed by the relevant EU Air Quality Directive.

(c) Many Pt measurements are below the limit of detection, the uncertainty quoted refers to those measurements that are above the detection limit.

(d) Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively.

Expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant Air Quality Directives metals are given in Table 8-4 below. These apply at the relevant limit value or target value.

**Table 8-4 Annual Mean Uncertainties**

<b>Analyte</b>	<b>Relative Expanded Uncertainties<sup>(a)</sup></b>	
	<b>Annual Mean</b>	<b>EC Directive maximum</b>
As	25 %	40 %
Cd	14 %	40 %
Ni	16 %	40 %
Pb	14 %	25 %
Hg(v) <sup>(b)</sup>	20 %	50 %

(a) Relative expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant Daughter Directive metals, averaged across the Network.

(b) Hg(v) refers to total gaseous mercury. For Hg(v) there is no limit or target value stated in the Fourth Daughter Directive at which this maximum allowable uncertainty applies.

## 8.4.2 Rural

For the measurement of trace metals by ICPMS the total expanded uncertainties measured at 5 µg l<sup>-1</sup> shows a coefficient of variation better than 5% for all elements except Li, Be, Zn and Sn. The coefficients of variation for Li, Be, Zn and Sn are 10.5%, 9.3%, 23.4% and 10.3% respectively. The total expanded uncertainty for the determination of mercury by the AFS method is 25% at 10 ng l<sup>-1</sup>.

For the Directive metals, samples are checked for an expanded uncertainty of 10 % (equivalent to 2 times the standard deviation of that year's annual mean). The concentrations are checked against the limit value / target value concentrations, but are always well below these values.

In the case of metals deposition measurements made by the Rural Metals Network, Concentrations in rainwater are also checked for an expanded uncertainty of 10 % (equivalent to 2 times the standard deviation of that year's annual mean).

## 8.5 Uncertainty of PAH Measurements

The range of uncertainties covering the analyses of ambient PAHs by the present contractor is shown in

Table 8-5 below. All figures are a combination of the analytical and sampling uncertainties and have been derived using full ISO GUM compliant uncertainty budgets developed from measurement equations which describe the entire measurement process. All values are stated to a coverage factor of  $k = 2$ , providing a level of confidence of approximately 95%.

These uncertainties only apply to *ambient* PAH measurement. The expanded uncertainties for all species measured in deposition are 60%.

As the measurement method is optimised for the measurement of B[a]P (PAH number 29), the uncertainty requirement is lowest for the PAHs with the retention closest to B[a]P.

Other factors affecting the specified uncertainty requirement include: volatility, typical peak shape, and retention time proximity to the internal standard and the nearest surrogate standard.

### **8.5.1 Measurement uncertainty of the annual average**

ISO 11222:2002 “Air quality - Determination of the uncertainty of the time average of air quality measurements” is used to determine the uncertainty in the annual mean for each element at each sampling location. This is easily done since the contractor produces a statement of uncertainty with each measurement result.

Data capture across the Network remains high (and any gaps in coverage have generally occurred evenly throughout the year). The uncertainty in the annual mean values are dominated by analytical and sampling uncertainty, with only small uncertainty contributions arising from time coverage below 100%. The effect of these contributions is calculated using the method described in ISO 11222:2002.

In all cases annual mean uncertainties are compliant with the DQOs for uncertainty in the Air Quality Directives.

The relative expanded uncertainty in a typical analytical result for B[a]P from a Network sample was estimated to be 20% to 30% - well within the DQO of an expanded uncertainty of 50%. For B[a]P this applies at the target value.

**Table 8-5 Range of PAHs analysed, with the respective uncertainties of measurement.**

PAH number	Compound	Expanded Uncertainty	PAH number	Compound	Expanded Uncertainty
1	Naphthalene	50 %	21	Benz[a]anthracene	35 %
2	2-Methyl naphthalene	50 %	22	Cyclopenta[c,d]pyrene	35 %
3	1-Methyl naphthalene	50 %	23	Chrysene	35 %
4	Biphenyl	50 %	24	5-Methyl chrysene	35 %
5	Acenaphthylene	50 %	25	Benzo[b]fluoranthene	25 %
6	Acenaphthene	50 %	26	Benzo[k]fluoranthene	25 %
7	Fluorene	50 %	27	Benzo[j]fluoranthene	25 %
8	Phenanthrene	50 %	28	Benzo[e]pyrene	25 %
9	Anthracene	50 %	29	Benzo[a]pyrene	25 %
10	2-Methyl phenanthrene	45 %	30	Perylene	25 %
11	2-Methyl anthracene	45 %	31	Indeno[1,2,3-cd]pyrene	25 %
12	1-Methyl anthracene	45 %	32	Dibenz[a,c]anthracene	25 %
13	1-Methyl phenanthrene	45 %	33	Dibenz[a,h]anthracene	25 %
14	4,5-Methylene phenanthrene	45 %	34	Benzo[g,h,i]perylene	25 %
15	9-Methyl anthracene	45 %	35	Anthanthrene	25 %
16	Fluoranthene	45 %	36	Dibenzo[a,l]pyrene	35 %
17	Retene	45 %	37	Dibenzo[a,e]pyrene	35 %
18	Pyrene	45 %	38	Coronene	35 %
19	Benzo[b]naph[2,1-d]thiophene	35 %	39	Dibenzo[a,i]pyrene	35 %
20	Benzo[c]phenanthrene	35 %	40	Dibenzo[a,h]pyrene	35 %

## 9 Gibraltar

The air quality monitoring procedures used in Gibraltar are in most cases the same as in the UK. They are briefly summarised as follows:

1. NO<sub>x</sub>, SO<sub>2</sub>, CO and O<sub>3</sub>: as for the AURN
2. PM<sub>10</sub> and PM<sub>2.5</sub>: as for the AURN using Partisol samplers and an FDMS monitor.
3. Metals: as for the Urban and Industrial Metals Network except that daily rather than weekly samples are bulked for analysis.
4. PAH: as for the PAH Network
5. VOCs (benzene and ozone precursors) - as for the Automatic Hydrocarbon Network.

For more information on air quality monitoring in Gibraltar please refer to the website “Air Quality in Gibraltar” at <http://www.gibraltarairquality.gi/> .

## 10 References

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- <sup>2</sup> Council of the European Union (1996) “*Directive 96/62/EC on Ambient Air Quality Assessment and Management*”. [online]. Available at <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31996L0062:EN:NOT> (Accessed 20 Sep 2013).
- <sup>3</sup> Council of the European Union (1999) “*Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air*”. [online]. Available at <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31999L0030:EN:NOT> (Accessed 20 Sep 2013).
- <sup>4</sup> European Parliament and Council of the European Union (2000) “*Directive 2000/69/EC of the European Parliament and of the Council of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air*”. [online]. Available at <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32000L0069:EN:NOT> (Accessed 20 Sep 2013).
- <sup>5</sup> European Parliament and Council of the European Union (2002) “*Directive 2002/3/EC of the European Parliament and of the Council of 12 February 2002 relating to ozone in ambient air*”. [online]. Available at <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32002L0003:EN:NOT> (Accessed 20 Sep 2013).
- <sup>6</sup> “*Council Decision 97/101/EC*”. [online]. Available at <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31997D0101:EN:NOT> (Accessed 20 Sep 2013).
- <sup>7</sup> European Parliament and Council of the European Union (2004) “*Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air*”. [online]. Available at <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32004L0107:EN:NOT> (Accessed 20 Sep 2013).
- <sup>8</sup> UK Government “*UK Air Quality Standards Regulations 2010*”. [online]. Available at <http://www.legislation.gov.uk/ukxi/2010/1001/contents/made> (Accessed 20 Sep 2013).
- <sup>9</sup> Scottish Government “*The Air Quality Standards (Scotland) Regulations (2010)*”. [online]. Available at <http://www.legislation.gov.uk/ssi/2010/204/made> (Accessed 20 Sep 2013).
- <sup>10</sup> Welsh Government “*The Air Quality Standards (Wales) Regulations 2010*” [online]. Available at <http://www.legislation.gov.uk/wsi/2010/1433/contents/made> (Accessed 20 Sep 2013).

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<sup>11</sup> Department of Environment, Northern Ireland “*The Air Quality Standards Regulations (Northern Ireland) 2010*”. [online]. Available at <http://www.legislation.gov.uk/nisr/2010/188/contents/made>.

<sup>12</sup> “*Council Decision 2011/850/EU*”. [online]. Available at <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:335:0086:0106:EN:PDF> (Accessed 20 Sep 2013).

<sup>13</sup> CEN “*EN 14211:2005 Ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by Chemiluminescence*”. 2005

<sup>14</sup> CEN “*EN 14212:2005 Ambient air quality – Standard method for the measurement of the concentration of sulphur dioxide by UV fluorescence*”. 2005

<sup>15</sup> CEN “*EN 14625:2005 Ambient air quality – standard method for the measurement of the concentration of ozone by ultraviolet photometry*”. 2005

<sup>16</sup> CEN “*EN 14626:2005 Ambient air quality - Standard method for the measurement of the concentration of carbon monoxide by non dispersive infra red spectroscopy*”. 2005

<sup>17</sup> CEN “*EN 12341:1999 Air quality. Determination of the PM<sub>10</sub> fraction of suspended particulate matter. Reference method and field test procedure to demonstrate reference equivalence of measurement methods*”. 1999

<sup>18</sup> CEN “*EN 14907:2005 Ambient air quality - Standard gravimetric measurement method for the determination of the PM<sub>2.5</sub> mass fraction of suspended particulate matter*”. 2005

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