Gas Chromatography: MCERTS Certification for Ambient Air Analysis on Benzene and VOCs

Due to environmental issues, the world of gas analysis is evolving very rapidly. Governments set the rules to limit and control the environmental pollution through legislation. Volatile organic compounds (VOCs), often produced by human activities, are amongst the sources of pollution that need to be identified and quantified for safety reasons. Exposure to high concentrations of certain VOCs is dangerous, even for short times, and the impact of low concentrations of VOCs on people's health and environment has also become a major concern in recent years. The concentration of such compounds can be very different depending on the measurement area and it is a considerable technological challenge to analyse precisely and continuously the VOCs present in air within industrial walls or at the top of a mountain using the same instrument. Presently, only benzene is regulated, but there are moves to measure other VOCs which are known to be ozone precursors.

> *"The NPL, is known worldwide for being at the edge of technology for air quality monitoring and type testing, performed in the laboratory and in the field."*

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Chromatotec and the NPL are members of the European benzene normalization committee

Since 1986, Chromatotec® has been recognised worldwide for their accurate gas analysis, renowned for analysis in the field of ambient air monitoring and natural gas. Gas chromatography (GC) is a common type of chromatography used in analytical chemistry for separating and analysing compounds that can be stable in the vapour state. Chromatotec's products allow the quantification and identification of compounds over a wide range of concentrations (including ppt, ppb, ppm and % levels) using gas chromatography analysers.

In gas chromatography, the mobile phase is a carrier gas, usually an inert gas such as helium, hydrogen or an unreactive gas such as nitrogen or argon. The mobile phase carries the sample to be analysed through a column in order to separate the compounds. The time at which the compounds elute from the column is used to identify the different species whereas the electric intensity measured by the detector allows for quantification. In order to verify the quality of our instruments, Chromatotec® has performed tests and obtained certifications relating to relevant standards, performed by bodies recognised worldwide.

Furthermore, to be compliant with European, Chinese and American performance standards, Chromatotec® has worked and invested in the development and improvement of rapid and accurate analysers.

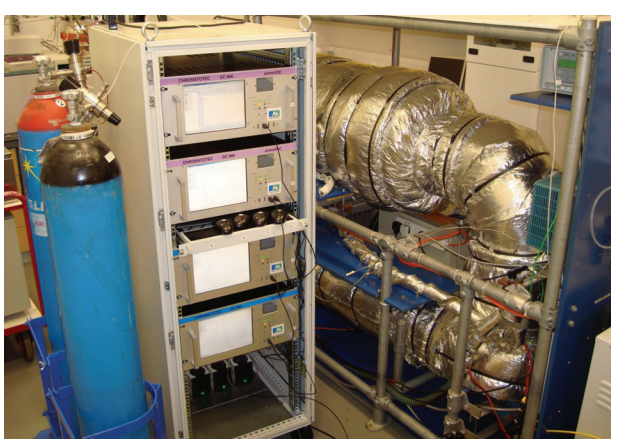
For Continuous Ambient Air Monitoring Systems (CAMS), the Certification Scheme called MCERTS defines tests and performance criteria for the measurement of benzene concentrations and other VOCs using an automated sampling pump with in-situ gas chromatography. There is also a harmonised European standard relating to the measurement of benzene, which is known as EN 14662-3. In the near future, Chromatotec® will be certified ISO 17025 for measurements of benzene and certain other VOCs.

The National Physical Laboratory (NPL -London) is currently one of only a few ISO 17025 accredited European laboratories to perform benzene laboratory and field tests. The NPL in collaboration with airmotec/Chromatotec® proposed a Laboratory and Field Test Programme for approval to Sira Environmental Limited. Sira is the certification body which oversees the MCERTS certification on behalf of the Environment Agency which is an Executive Non-departmental Public Body responsible to the Secretary of State for Environment, Food and Rural Affairs in the UK.

To verify and ensure the accurate performance of Chromatotec's analysers, four CAMS, using two different detector technologies, were simultaneously tested by NPL in their specialised ambient air quality test laboratory in accordance with UKAS-accredited NPL Test Procedure QPAS/B/528a (and later on in the field) and compared against the performance criteria defined in the MCERTS standard for CAMS and EN 14662-3. Both types of CAMS were cyclic automated analysers which sample a known measured volume of air through a sorbent medium for a fixed period of time, and then analyse the amount of the target determinands, trapped using a gas chromatograph. One type of CAM (airmoVOC) employed a Flame Ionisation Detector (FID) to measure the determinands while the second type of CAM (airTOXIC) used a Photo Ionisation Detector (PID).

For the laboratory tests, all four CAMS measured simultaneously from the same gas manifold and sample line. The required determinands were generated from traceable 30 component EU Directive ozone precursor mixtures diluted in nitrogen; a mixture produced by NPL using gravimetry (ISO 17025 for standard production). The parent mixtures were diluted as required in zero nitrogen or scrubbed air. The starting concentration of the determinands in the parent mixtures (before dilution), expressed in units of parts per billion, was nominally the same for all the 30 compounds.

The performance standards were specifically applicable to measurements of ambient benzene vapour in the 0 $\mu g.m^{-3}$ to 50 $\mu g.m^{-3}$ concentration range (standardised at 101.3 kPa and 293 K) but the MCERTS standard could also be applied to other volatile organic compounds (VOCs) with



the agreement of the Certification Committee.

To demonstrate the accuracy of the instruments, Chromatotec® required other VOCs to be tested by carrying out the same procedures defined for benzene. Similar performance characteristics and performance criteria were applied to 12 additional species which are all as critical as benzene for environmental and health issues (Figure 1). 12 peaks are observed, corresponding to 13 components. The determinands m-xylene and p-xylene were analysed as one chromatographic peak and the results were reported as the sum of the two. For example, the certification range for the type-approval tests was 0 µg.m^{-3} to 50 µg.m^{-3} (standardised at 101.3 kPa and 293 K) for benzene, or 0 parts per billion (ppb) to 15.4 ppb where 1 ppb is equivalent to 1 nmol.mol-1. The certification range of the other determinands in the test programme was also defined as 15.4 ppb.

The laboratory test criteria carried out on all compounds were repeatable, short-term drift, dependence on sample gas pressure, lack of fit (linearity), carry over (memory effect), dependence on voltage, dependence on surrounding air temperature, cross interference with ozone, cross interference with water (relative humidity test), and cross interference with organic compounds. The performance criteria were met for benzene covering all the requirements listed above in strict compliance with the current MCERTS and European standard EN 14662-3.

The cross interference with organic compounds, which evaluates the influence of the interference from the sum of possible interfering VOCs at the span concentration value (between 70% and 90% of the certification range) was below 5% for 10 tested interferring compounds for all the four analysers. It is important to highlight that all potential organic cross interferents listed in the EN-14662-3 (methylcyclopentane, 2,2,3-trimethylbutane, 2,4-dimethylpentane, tetrachloromethane, cyclohexane, 2,3-dimethylpentane, 2-methylhexane, 3-ethylpentane, trichloroethylene, n-heptane) were tested.

Among the superior results obtained during laboratory tests, the repeatability at 0.5 µg.m^{-3} for benzene was found to be as low as 0.02 µg.m^{-3} and 0.06 µg.m^{-3} for airTOXIC (PID) and airmoVOC (FID) respectively. To be compliant with the standard method EN 14662-3, the repeatability value must be less than ± 0.3 µg.m^{-3}. Chromatotec's analysers operate continuously in industry and may encounter interference from an unstable surrounding environment. Therefore, the sensitivity coefficients for the influence of voltage and ambient pressure, as well as temperature were tested. These stress tests on the analysers show that they are ideally suited for continuous analysis of industrial ambient air.

In cooperation with airmotec/Chromatotec®, NPL also proposed a Field Test Programme, which was approved by Sira Environmental Limited. The field tests were conducted in accordance with UKAS-accredited NPL Test Procedure QPAS/B/528b, using appropriately calibrated equipment. The tests were performed at the Automatic Urban Rural Network (AURN) monitoring site in Marylebone Road, London W1 (central London). During three months of tests, the maintenance requirements specified by Chromatotec® were followed. The field tests carried out included operational requirements, long term drift, maintenance interval, availability, and reproducibility standard deviation under field conditions.

Long term drift was determined at the span value (between 70% and 90% of certification range) of Benzene, namely 45 µg.m^{-3} (13.9 ppb), over 14 days. All other determinands involved in the test had concentrations of nominally 13.9 ppb. A total of four valid determinand sample injections were employed at the start and end of each drift period, resulting in six sets of data. The CAMS sampled ambient air at all other times when span measurements were not being carried out. The largest value of the drift complied with the requirements: d14d < ± 10 %. Tests on the four different analysers successfully passed or exceeded requirements for benzene and for the additional VOCs species.

Concerning the maintenance interval, Chromatotec® demonstrated the robustness of its analysers by showing that maintenance was not necessary on the instruments, in contrast to the MCERTS scheme which envisaged maintenance every two weeks during the field test period: the performance criteria were met without maintenance. Another parameter tested was the availability, a parameter that weighs the elapsed time of analysis with the ability to give validated results. Results are given in percentage and must be greater than or equal to 90%. For benzene specifically, 99.8% and 100% were obtained with airmoVOC (FID) and airTOXIC (PID) respectively. Once again, these results demonstrate the excellence of Chromatotec® analyser in meeting the performance criteria.

The reproducibility standard deviation test was carried out by comparing the ambient measurement data between pairs of CAMs of the same type throughout the three month trial. It did not include measurements of span gases or down time for maintenance. The values 0.24 µg m^{-3} airmoVOC (FID) and 0.08 µg.m^{-3} airTOXIC (PID) respectively obtained for benzene measurements were in compliance with the required standard: sRF < ± 0.25 µg.m^{-3}. Furthermore, the value of the expanded uncertainty for each CAMS may not exceed the requirements of the Directive 2009/69/EC of the European Parliament and of the Council of 16th November 2000 relating to limit values for benzene and carbon monoxide in ambient air: Abl. Nr. L313, p.12. This standard permits for benzene a maximum value of ±25% for the expanded uncertainty for continuous measurements. The total uncertainty was determined for each CAM using the relevant performance characteristics determined in the laboratory and field tests for the determinand benzene. The results were 12.1% and 15.0% for PID (Model A73022) and FID (Model A21022) respectively, comfortably meeting the requirements of the European Directive.

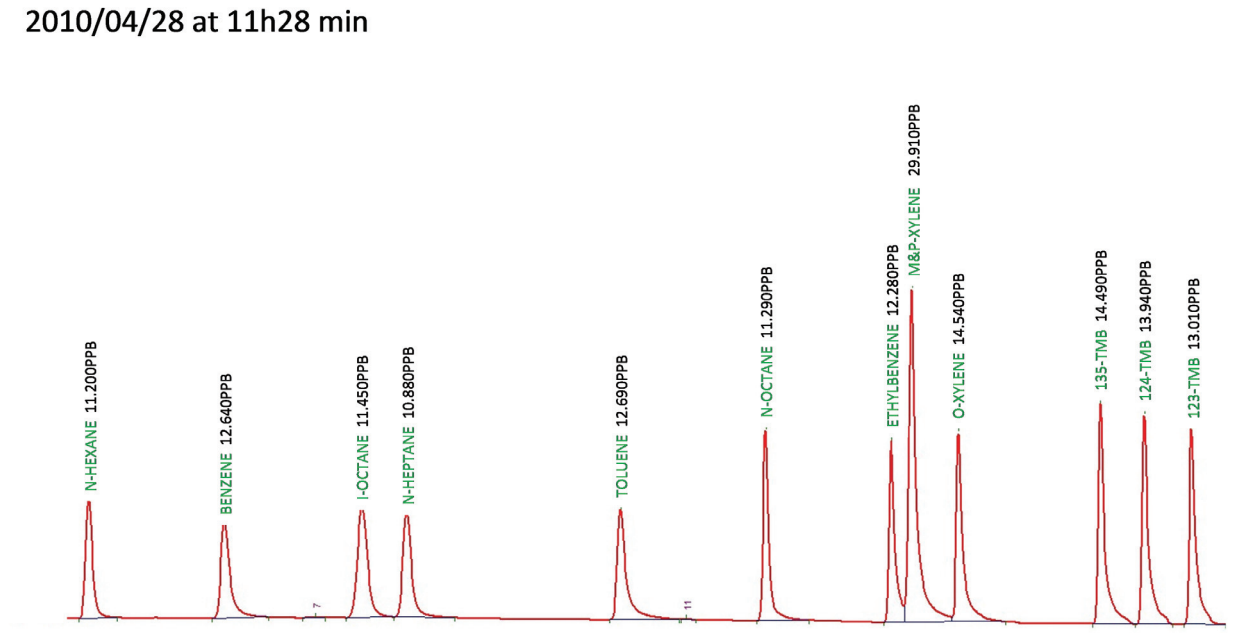


Figure 1: Typical chromatograph obtained during the tests carried out by the NPL. The 13 analyzed compounds are: N-Hexane; Benzene; 2,2,4-Triethyl pentane (i-octane); N-Heptane; Toluene; N-Octane; Ethyl-Benzene; m&p-Xylene; o-Xylene; 1,3,5-Trimethylbenzene; 1,2,4-Trimethylbenzene; 1,2,3-Trimethylbenzene.

Performance characteristic Laboratory tests	Performance criterion	Test result (airmoVOC Serial number 20190309)	Test result (airmoVOC serial number 20730509)	Test result (airTOXIC serial number 20430309)	Test result (airTOXIC serial number 20720509)
Lack of fit, largest residual	< ± 5 %	2.12 %	2.54 %	4.60 %	4.42 %
Repeatability at 0.5 µg m^{-3}	< ± 0.3 µg m^{-3}	0.06 µg m^{-3}	0.20 µg m^{-3}	0.02 µg m^{-3}	0.03 µg m^{-3}
Repeatability at limit value	< ± 5 %	1.84 %	1.42 %	3.74 %	1.34 %
Influence of the interference from ozone	< ± 5 %	1.19 %	1.25 %	0.87 %	1.00 %
Influence of the interference from sum of possible interfering organic compounds at span value	< ± 5 %	3.87 %	4.58 %	1.81 %	2.81 %
Influence of the interference from relative humidity	< ± 4 %	0.001 %	0.001 %	0.78 %	1.16 %
Sensitivity coefficient for the influence of surrounding temperature at span value	< ± 0.2 % K^{-1}	0.03 % K^{-1}	0.08 % K^{-1}	0.16 % K^{-1}	0.10 % K^{-1}
Sensitivity coefficient for the influence of ambient pressure at span value	< ± 1 % kPa^{-1}	0.18 % kPa^{-1}	0.10 % kPa^{-1}	0.26 % kPa^{-1}	0.15 % kPa^{-1}
Sensitivity coefficient for the influence of voltage a span value	< ± 0.2 % V^{-1}	0.022 % V^{-1}	0.010 % V^{-1}	0.031 % V^{-1}	0.027 % V^{-1}
Short term drift (24 hours) at span value	< ± 5 %	1.82 %	0.15 %	0.96 %	0.79 %
Carry over	< 10 % of limit value for second analysis (=0.5µg m^{-3})	0.36 µg m^{-3}	0.41 µg m^{-3}	0.35 µg m^{-3}	0.37 µg m^{-3}

Performance characteristic Field tests	Performance criterion	Test result (airmoVOC Serial number 20190309)	Test result (airmoVOC serial number 20730509)	Test result (airTOXIC serial number 20430309)	Test result (airTOXIC serial number 20720509)
Reproducibility standard deviation	< ± 0.25 µg m^{-3}	0.24 µg m^{-3}	0.24 µg m^{-3}	0.08 µg m^{-3}	0.08 µg m^{-3}
Long term drift at span value (14 days)	< ± 10 %	1.54 %	4.42 %	7.52 %	4.68 %
Maintenance interval	> 14 days	90 days	90 days	90 days	90 days
Availability	> 90 %	96.3 %	99.7 %	100 %	99.9 %

The NPL, is known worldwide for being at the edge of technology for air quality monitoring and type testing, performed in the laboratory and in the field. Their conclusion is that Chromatotec® analysers met the requirements for continuous monitoring of ambient air both indoors and outdoors. The results obtained in the different tests frequently surpassed the limit criteria defined in the standard method EN 14662-3. Chromatotec® analysers are the only instruments on the market which have been tested successfully for 13 VOCs in accordance with MCERTS performance standards and EN 14662-3.

An audit of airmotec/Chromatotec® by Sira was carried out at the end of 2012 in accordance with EN 15267-1 . The company completely fulfilled the requirements of the norm EN 15267-2 relative to air quality: Certification of automated measuring systems Part 2: Initial assessment of the AMS manufacturer's quality management system and post certification surveillance for the manufacturing process.