

QUALITY CONTROL AND QUALITY ASSURANCE FOR AIR QUALITY SURVEILLANCE NETWORKS

Executive Summary

5TH SEMINAR ON AIR QUALITY IN SPAIN

Santander, October 16, 17 and 18, 2006

1 REFERENCE METHODS IN THE FUTURE DIRECTIVE: STUDY AND COMPARISON OF DIRECTIVES AND SPANISH ROYAL DECREES CURRENTLY IN FORCE ON AIR QUALITY

The draft directive is currently in the process of being drawn up and will replace directive 96/62/EC and its four daughter directives: 1999/30/EC; 2000/69/EC; 2002/3/EC and 2004/107/EC. This directive involves major changes in the reference methods to be used for measuring air quality. For this reason, a study has been undertaken of reference methods in current legislation for each contaminant, and on the methods in the draft directive, placing special emphasis on the most significant differences.

The new UNE-EN methods for determining SO₂, NO₂, CO, O₃ and benzene (automatic), apart from being used to determine these contaminants in ambient air, describe the performance characteristics and specify the relevant minimum requirements for selecting a suitable analyser through type approval tests. They also stipulate the assessment of the suitability of an analyser for use in a fixed location, as well as the requirements for use during sampling, calibration, and quality assurance. They indicate that the type approval tests must be undertaken by a designated body and that this type approval covers assessment of the performance characteristics through tests (at least 2 analysers in the laboratory and 2 analysers in the field). They also stipulate the calculation of expanded uncertainty.

As regards sampling systems, criteria are laid down regarding the effect of losses in average concentrations of the contaminant; conditioning with ambient air, and residence time of the sample from entry into the analyser.

Another important aspect of the new standards is the need to assess the suitability of the analyser under the specific conditions of the measuring location, by studying the following: variations in pressure and temperature of the sample gas; variation in the surrounding air temperature; voltage variation; expanded uncertainty of the calibration gas; frequency of calibration; and a series of interferences which differ for each contaminant.

The new UNE-EN standards also stipulate the minimum content of the type approval reports, field operations reports, and ambient air quality reports. They also indicate the person in charge of undertaking these, in contrast to the standards currently in force, which do not stipulate the content of the reports or only indicate those on ambient air quality.

1.1 SULPHUR DIOXIDE (SO₂)

The reference method currently in force for SO₂ is the UNE-ISO 10498:2006 standard: "Ambient air. Determination of sulphur dioxide. Ultraviolet fluorescence method." In the draft directive the reference method is UNE-EN 14212:2006: "Ambient air quality. Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence."

The most significant specific differences are as follows:

- Calibrations shall be carried out at least every 3 months and after repair. UNE-ISO 10498:2006 stipulates this at the start of the analyser, after maintenance, every six months or annually, and when the analyser shows an excessive drift for zero and span.
- Verification of zero and span shall be carried out at least every 2 weeks, stipulating the acceptance criteria for zero (≤ 5 nmol/mol) and span ($\leq 5.0\%$ of the initial span value) while UNE-ISO 10498:2006 indicates once a week.
- Test gases must be certified at least every 6 months with a rejection criterion for zero (\geq detection limit) and span ($\geq 5.0\%$ of the most recent certified value).
- As regards maintenance, the EN standard indicates a particle filter change at least every 3 months and testing of sampling lines at least every 6 months.

1.2 NITROGEN OXIDES (NO₂ and NO)

The reference method currently in force for NO_x is UNE 77212:1993 "Air Quality. Determination of the mass concentration of nitrogen oxides. Chemiluminescence method". In the draft directive, the reference method is UNE-EN 14211:2006 "Ambient air quality. Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence."

The most significant specific differences are as follows:

- As regards the converter, the EN standard maintains the same converter efficiency ($\geq 95\%$) as UNE 77212:1993, but indicates that the concentration must be corrected when the efficiency of the converter is between 95% and 100%.

- Calibration shall be carried out at least every three months and after repair, whereas UNE 77221:1993 indicates that this will be undertaken as frequently as possible.
- The draft directive stipulates that this shall be carried out with gas cylinders of NO and NO₂, traceable to national standards, whose maximum uncertainty must be $\pm 5\%$, while UNE 77221:1993 standard indicates the use of permeation tubes of NO₂ and NO (after passing through the converter) and dilution of NO₂ with zero air and with a RH of 50%.
- Verification shall be carried out at least every 2 weeks and the verification gases shall be checked using reference gases traceable to national standards, at least every six months, whereas UNE 77221:1993 only indicates that this must be done with zero and 80% of the full scale.
- It stipulates the acceptance criteria for verifying zero gas (\leq LD), and span ($\leq 5\%$ compared with the last certified value).
- It also indicates that lack-of-fit testing must be carried out within one year after installation, as well as after repair, and stipulates the acceptance and frequency criterion.
- The new EN standard indicates the frequency of the study of the converter's efficiency. This shall be at least annually.
- As regards maintenance, it is indicated that the particle filter change should be conditioned with ambient air for 30 min and that the response to the span shall be $> 97\%$.

1.3 CARBON MONOXIDE (CO)

The reference method currently in force for CO is UNE-EN 14626:2006 "Ambient air quality. Standard method for the measurement of the concentration of carbon monoxide by non-dispersive infrared spectroscopy", which is the method which also figures in the draft directive. Before the UNE-EN standard was published, the existing standard was UNE 77252:2003: "Ambient air. Determination of carbon monoxide. Non-dispersive infrared spectrometry method". This was the method normally used.

The most significant specific differences are as follows:

- For zero gas, UNE-EN 14626:2006 stipulates a content of CO $< 0.1 \mu\text{mol/mol}$, whereas in UNE 77252:2003, the CO content is $< 0.09 \mu\text{mol/mol}$.
- Calibration shall be carried out at least every 3 months and after each repair, in contrast to UNE 77252:2003 which stipulates this at the start of the analyser, after maintenance, and when the analyser shows an excessive drift in verifications of zero and span.

- Verification of zero and span shall be carried out at least every 2 weeks, with acceptance criteria for zero ($\leq 0.2 \mu\text{mol/mol}$) and span ($\leq 5.0\%$ of the initial span value), in contrast to UNE 77252:2003 which stipulates verification before and after each sampling period, or daily if the analyser is used continuously and does not stipulate verification acceptance criteria.
- It stipulates certification of test gases; at least every 6 months with a rejection criterion for zero (\geq detection limit) and for span ($\geq 5.0\%$ of the most recent certified value).
- As regards maintenance, the change of particle filter is indicated at least every 3 months and testing of sampling lines at least every 6 months.

1.4 OZONE (O_3)

The reference method currently in force for O_3 is UNE-EN 14625:2005 “Ambient air quality. Standard method for measurement of the concentration of ozone by ultraviolet photometry”. As this has been recently published, the most widely used methodology is the one based on UNE 77221:2000 “Air Quality. Determination of ozone in ambient air. Ultraviolet photometry method”.

The most significant differences between UNE-EN 14625:2005 and UNE 77221:2000 are as follows:

- In the analyser, the EN standard stipulates a number of different tolerances for both the temperature and pressure indicators in the absorption cell.
- Calibration of the analyser shall be carried out at least every three months and after repair, whereas in UNE 77221:2000 this is laid down as every 3 or 4 months.
- Verifications shall be carried out at least every two weeks and recommended every 23 or 25 h, while in UNE 77221:2000 standard this is weekly. Acceptance criteria for verification in the EN standard for zero is $< 5 \text{ nmol/mol}$ and for span $< 5.0\%$ of the initial span value. No criteria are stipulated in UNE 77221:2000
- A lack-of-fit study shall be carried out one year after installation.

1.5 BENZENE

The reference methods currently in force for benzene, as well as in the draft Directive, are the following standards: UNE-EN 14662-1:2006: “Ambient air quality. Standard method for measurement of benzene concentrations. Part 1. Pumped sampling followed by thermal desorption and gas chromatography”; UNE-EN 14662-2:2006: “Ambient air quality. Standard method for

measurement of benzene concentrations. Part 2: Pumped sampling followed by solvents desorption and gas chromatography”, and UNE-EN 14662-3:2006: “Ambient air quality. Standard method for the measurement of benzene concentrations. Part 3: Automated pumped sampling with in situ gas chromatography”. Any of the three may be used.

The first two methods are discontinuous sampling and the third is continuous. The difference between the two discontinuous methods is in the sorbents used, the uncertainty of the flow rate measured, sampling flow rates and systems of desorption used.

The continuous method includes type approval tests similar to those run for the other contaminant gases. The most specific criteria are as follows:

- Two week verification of span and six monthly for zero
- Calibration at least annually and criterion $< \pm 10\%$ of the span value
- Maintenance at least six monthly for the sampling line and filter change every three months
- Determination of the efficiency of collection at least every 3 years, with acceptance criterion ($< 5\%$ of sampling loss)

1.6 PARTICLES

The reference method for determination of PM 10 particles is UNE-EN 12341:1999. The draft directive stipulates the measurement of PM 2.5 particles, as well as their reference method, which is UNE-EN 14907:2006.

The most significant differences between the two standards are:

- While the scope of UNE-EN 12341:1999 is to compare the results of a PM 10 candidate sampler with a PM 10 reference sampler in field tests, and in Annex C the measuring procedure is indicated, the purpose of UNE-EN 14907:2006 is to determine PM 2.5, and only Annex A describes the procedure for the equivalence test.
- Both standards stipulate 2 reference samplers. The low volume sampler at $2.3 \text{ m}^3 / \text{h}$ and filter of 47 mm \varnothing is common to both standards, while the high volume sampler is different. Thus, for PM 10 this is $68 \text{ m}^3 / \text{h}$ with a filter of 203 mm x 254 mm and for PM 2.5 this is $30 \text{ m}^3 / \text{h}$ with a 150 mm \varnothing filter.

- PM 2.5 stipulates that cold surfaces shall be avoided due to condensation, as shall solar heat. The temperature shall be close to ambient temperature ($\leq + 5^{\circ}\text{C}$) directly behind the filter. The filters must be made of glass or quartz in the case of PM 10 and glass, quartz, PTFE or fibre glass covered with PTFE for PM 2.5.
- As regards the efficiency of separation for PM 10, this is stipulated as 99.5% (without specifying particle size) and for PM 2.5 $\geq 99.5\%$ for an aerosol of $0.3\text{ }\mu\text{m}$.
- Conditions in the weighing room are the same for the two standards ($20^{\circ}\text{C} \pm 1^{\circ}\text{C}$; $50\% \pm 5\%$) and the resolution of the balances is $10\text{ }\mu\text{g}$ or lower for PM 10, and PM 2.5: $10\text{ }\mu\text{g}$ or lower for low volume filters, and $100\text{ }\mu\text{g}$ or less for high volume filters.
- PM 2.5 stipulates the need to verify the equipment with weights before weighing and stipulates criteria for low and high volume. It also stipulates the need to do blanks, with their corresponding acceptance criteria. Another feature of the PM 2.5 standard is the need to do 2 weighings for each filter, stipulating an interval between weighings of $\geq 12\text{ h}$ for blank filters and between 24 h and 72 h for loaded filters.
- The PM 2.5 standard indicates the temperature at which the loaded filters shall be transported.
- Regarding collection both standards indicate the need to clean and grease the inlet which, for PM 10, is at least every 20 samples, and in cases where there are high concentrations, up to every 5 samples. For PM 2.5 this stipulation follows the manufacturer's instructions and particle concentrations, the process being undertaken at least every 15 samples.
- The PM 2.5 standard indicates the need to verify flow rate at least every three months and that the temperature and pressure sensors of the sampler shall be calibrated, as shall the balance.
- PM 2.5 also stipulates calculation of uncertainty.

1.7 LEAD (Pb), CADMIUM (Cd), ARSENIC (As) AND NICKEL (Ni)

The reference method for measuring lead in ambient air is UNE 77230:1998. "Ambient air. Determination of the particulate lead content of aerosols collected on filters. Atomic absorption spectrometry method". For Cd, As and Ni, according to Directive 2004/107/EC, the reference method is UNE-EN 14902:2006: "Ambient air quality. Standard method for measurement of Pb, Cd, As and Ni in the PM 10 fraction of suspended particulate material".

The key similarities and differences are:

- UNE-EN 14902:2006 standard undertakes collection of PM 10, according to UNE-EN 12341: 1999, digestion by microwave and analysis by atomic absorption spectrometry with graphite furnace, or mass spectrometry with inductively coupled plasma (quadrupole), while UNE 77230:1998 standard (which is for lead only) does not indicate collection, and undertakes acid digestion and spectrometry analysis by atomic absorption (flame or graphite furnace).
- UNE-EN standard stipulates the method's detection limits based on laboratory filter blanks (\leq 10% of the limit and target value). In the case of using high volume, homogeneity requirements for subsamples are indicated in relation to the content of Pb and the area. UNE 77230 standard does not indicate the detection limit, recoveries, or homogeneity requirements.
- The filters to be used differ: quartz fibre, cellulose nitrate, or cellulose acetate for UNE-EN, and membrane filters or fibre glass in the latter case.
- Digestion of the samples is by microwave in UNE-EN and by condenser + heating plate or furnace or thermoblock in UNE 77230
- Atomic absorption spectrometry in UNE-EN is performed in a graphite furnace, while in UNE 77230 this can be done using a flame or graphite furnace. UNE-EN also allows determination using mass spectrometry with coupled plasma
- Calibration in UNE-EN by GFAAS stipulates a R^2 which shall be ≥ 0.995 . For ICP-MS this is a R^2 which shall be ≥ 0.999 . UNE 77230 standard does not lay down an acceptance criterion for calibration.
- UNE-EN standard indicates estimation of the method's measurement uncertainty.

2 DEMONSTRATION OF THE EQUIVALENCE OF AMBIENT AIR MEASUREMENT METHODS

When a Member State implements the directives, it shall use the reference methods, however as indicated by EU directives and national legislation: "competent authorities may use any other method if they can demonstrate that it produces results which are equivalent to the reference method".

Additionally, for PM 10 it states: "or any method if it can be shown to have a consistent relationship with the reference method. In such cases, the results obtained shall be corrected using a relevant factor, in order to produce equivalent results to those which would have been obtained with the reference method".

From this it is concluded that if the reference methods are not used, equivalence shall be demonstrated.

A method is equivalent to the reference method for measuring a specific air pollutant when it meets the Objectives for Quality of Data (OQD) for the fixed or continuous measurements stipulated in the Air Quality Directives.

Each Member State may propose a method which differs from the reference method and run the equivalence study.

The laboratory which undertakes the equivalence tests shall meet a series of requirements, such as: independence from the manufacturer and ability to demonstrate competence for these tests (UNE-EN ISO/IEC 17025 accreditation for these tests). If the laboratory does not possess the relevant accreditation, this can be replaced, in some cases, by an external audit and aptitude tests.

2.1 TYPES OF EQUIVALENCE TEST

The methods which are candidates for equivalence may differ slightly from the reference method or may be totally different. This is defined as “Variations on a theme” and “Different methodologies”, respectively.

Within “variations on a theme”, are included: use of different converters for nitrogen dioxide; use of different ozone scrubbers; use of different sampling material (adsorbents and filters); use of different analyte recovery procedures; use of calibration procedures, which differ in number and content of analytes in the calibration standards; types of calibration function and frequency; use of different parts of the analysis procedure; use of different storage procedures for PM 10 and PM 2.5 filters, and use of automatic changers for PM 10 and PM 2.5 manual samplers.

“Different methodologies” include, among others: automatic measuring systems for benzene using ultraviolet spectrometry as a detection technique; particle sampling using an inlet of a different size and shape from that specified for PM 10 and PM 2.5 in the reference method; measurement of particles using automatic methods (beta attenuation or oscillating microbalance); use of optical measurement techniques “in situ” for particles; use of different analytical techniques for measuring compounds in sample extracts (liquid chromatography for benzene (ICP-OES for metals); measurement of gases and vapours using diffusive sampling instead of pumped sampling or

automatic methods; automatic measurement of gases based on a different spectrometry technique (FTIR for SO₂); and measurement of gases using sampling by manual aspiration instead of automatic methods.

2.2 PHASES OF THE EQUIVALENCE TEST

The equivalence test consists of 4 phases:

- a) Initial non experimental pre-assessment to check whether the candidate method can potentially comply with the OQDs in the directives, as regards data collection and measurement uncertainty.
- b) Assessment of the uncertainty of the candidate method, based on the principles of ENV 13005 in a series of laboratory tests.
- c) Field tests to confirm the findings of the laboratory tests.
- d) Assessment of uncertainty resulting from comparisons of:
 - Laboratory and OQD uncertainties,
 - Laboratory and field work uncertainties,
 - Field work uncertainty and OQD uncertainty.

2.3 RECOMMENDATIONS TO THE NETWORKS

In the draft directive it is indicated that the Commission may request that Member States prepare and present a report demonstrating equivalence. The Commission will evaluate this in accordance with the as yet unpublished guidelines but which have been presented at the seminar on demonstrating equivalence.

For this reason, if non-reference methods are used, there shall be a report demonstrating equivalence, undertaken by a UNE-EN ISO/IEC 17025 accredited laboratory, at least for the reference method, with which equivalence has been demonstrated.

For the case of PM 10 particles, the equivalent equipment shall have a report following the stipulations of UNE-EN 12341:1999, as well as records which confirm that the tests stipulated in this standard have been undertaken to demonstrate equivalence. This equivalence test shall have

been undertaken by a UNE-EN ISO/IEC 17025 accredited laboratory for UNE-EN 12341:1999 standard, and shall be submitted before acquiring the equipment.

3 TYPE APPROVAL STUDIES FOR CONTINUOUS ANALYSERS

The determination of the concentration of gases (SO₂, NO_x, CO, O₃ and benzene) in ambient air shall meet the requirement for maximum uncertainty of the measured values, prescribed in European legislation. In order to achieve a lower (or equal) uncertainty to the one required, the analysers shall meet the criteria laid down for specific performance characteristics. These performance characteristics shall be assessed through laboratory and field tests. Combining the values of performance characteristics selected with the uncertainty calculation, a verdict can be reached on whether or not the analyser meets the maximum uncertainty criterion prescribed in EU legislation.

Type approval tests shall be carried out by a designated body and type approval must be granted by or on behalf of the competent authority.

It is recommended that the organisation designated for the type approval test is accredited under UNE-EN ISO/IEC 17025 for these tasks.

3.1 LABORATORY TEST

During the laboratory test, different performance characteristics shall be determined, such as: the sensitivity coefficient of sample gas pressure; the sensitivity coefficient of sample gas temperature; the sensitivity coefficient of surrounding air temperature; sensitivity coefficient of electrical voltage; the sample flow to the analyser; the response time; short term drift; repeatability standard deviation; lack-of-fit; interferences; averaging test; differences between the sample/calibration port; memory effect and for NO₂, efficiency test on the converter.

For these fourteen characteristics, the UNE-EN standards lay down the systematic for undertaking the tests, as well as the acceptance criteria which shall be met by the analyser of the approved type.

To determine the performance characteristics for the automatic analysers, gases traceable to national or international standards shall be used. The maximum uncertainty permitted for the gases

used in laboratory tests is $\pm 3\%$. The UNE-EN standards stipulate the purity specifications for the span and for zero in the case of CO, SO₂, NO_x and O₃. Purities for spans and zero are not stipulated for benzene.

3.2 FIELD TESTS

Two analysers shall be tested for a period of 3 months. The analysers shall function in parallel, individually, and at the same sampling point at a measuring station selected with specific ambient air conditions.

The performance characteristics to be evaluated during the field tests are as follows: long-term drift; reproducibility standard deviation in field conditions; period of unattended operation, and period of availability of the analyser.

The systematic and acceptance criteria for these four performance characteristics are stipulated.

3.3 CALCULATION OF EXPANDED UNCERTAINTY FOR TYPE APPROVAL

Type approval of the analyser consists of the following parts:

- The value of each individual characteristic tested in the laboratory and in the field shall meet the stipulated criteria for functioning.
- The expanded uncertainties calculated from standard uncertainties obtained during the laboratory and field tests shall meet the criteria laid down in Directive 2000/69/EC (for benzene and CO); Directive 1999/30/EC (for SO₂, NO and NO₂), and Directive 2002/3/EC (for O₃).

The instrument will be of approved type where the 4 above-mentioned requirements are met.

3.4 RECOMMENDATIONS TO THE NETWORKS

After the draft directive has been approved - and beforehand, if the network manager has decided to change the equipment - it must be ensured that the analyser equipment for SO₂, CO, NO_x, O₃ and benzene are of the approved type.

The draft directive indicates in Annex VI that all new units acquired for applying the Directive shall conform to the reference method or equivalent, at the latest 24 months after the date the directive comes into force.

In addition, all equipment used in fixed measurements shall conform to the reference method or equivalent within five years of the directive coming into force.

4 QUALITY CONTROL AND QUALITY ASSURANCE

The draft directive indicates in Annex 1 that in order to ensure the precision of the measurements and meet the objectives for data quality, the authorities and competent bodies designated under article 3, which include those which assess ambient air quality, shall a) guarantee the traceability of all measurements; b) ensure that the institutions responsible for the functioning of networks and independent stations have an established quality assurance and control system; c) ensure that a process of quality assurance / quality control has been established; d) ensure that the national laboratories which take part in the EU intercomparison exercise are accredited under UNE EN ISO 17025 for 2010, with respect to the reference methods.

The most important elements to be borne in mind in the implementation of a quality system in the network are a) to have written procedures which determine the particular pollutant, as well as procedures on handling equipment, verification and calibration, validation of methods and estimate of uncertainty (both measurement and calibration); b) to identify the equipment and its state of calibration, establishing the frequency of calibration, which may be external (in a laboratory accredited for this purpose) or internal (undertaken by the same network) and the frequency of verification; c) to stipulate acceptance criteria for verifications and calibrations, and d) to undertake internal quality controls and participate in intercomparison exercises.

To evaluate the current status of implementing quality systems in the networks, the Quality Control and Quality Assurance working group drafted a simple survey which it sent through the Spanish Ministry for the Environment to the heads of the different Spanish autonomous communities (self-governing regions) (A.C.s). The survey was divided into two parts, one for gas analysers and the other for particle analysers.

4.1 IMPLEMENTATION OF QUALITY SYSTEMS IN AIR QUALITY NETWORKS IN SPAIN

As has been commented in previous seminars on air quality, the networks should have implemented a quality system specific to that particular network under the UNE EN ISO/IEC 17025 standard, and have required that companies with maintenance contracts comply with this system. In the light of the responses obtained, a summary was drafted on implementing the quality systems and recommendations to the networks.

4.1.1 GAS ANALYSERS

4.1.1.1 QUALITY SYSTEM

Implementation of the quality system under UNE EN ISO/IEC 17025 standard is very deficient, even in networks which indicate that they have implemented it, since a number of inadequate criteria have been stipulated, such as uncertainty of the reference material being equivalent to that of the method, or the fact that the uncertainty of the reference material is given as measurement uncertainty. It should also be pointed out that only four out of fifteen networks indicate uncertainty for the reference material and that only eight have traceability to national or international standards.

As regards the use of validated methods, logically the networks with an implemented quality system use validated methods, although some networks indicate validated methods without indicating measurement uncertainty, or networks without an implemented quality system indicate that they use validated methods, or networks which do not indicate traceability of the reference materials indicate measurement uncertainty. Only two networks indicate measurement uncertainty for ozone. This shows that the programme provided in September 2005 for the A.C.s is not being used.

It is recommended that the networks should:

- a) Implement a quality system which pertains specifically to the network itself and not to the user/maintainer;
- b) Use reference materials for calibration that are traceable to national or international standards (with ENAC, COFRAC, SCS, NPL, NMI, ... certification);
- c) Validate the test methods with the corresponding determination of measure range, quantification limit, accuracy, repeatability, reproducibility,

d) Estimate measurement uncertainty.

4.1.1.2 VERIFICATIONS

The acceptance criteria for verifying the zero for **SO₂** range between 1 ppb and 5 ppb. It is estimated that the value of 1 ppb is very low, due to incongruities with the quantification limit and measurement uncertainty. The future reference method (UNE-EN 14212:2006) stipulates an acceptance criterion for zero as ≤ 5 nmol/mol. (In the information provided by the networks, the term ppb has been maintained but it would be advisable for the networks to use the units of the international system, substituting ppb for nmol/mol.)

As regards the acceptance criterion for span verifications, it is observed that the spans indicated by the different networks range between 200 ppb and 800 ppb. Considering an urban network, it can be established that the span values used are very far from measured concentrations. Acceptance criteria range between 3% and 10%. The 3% criterion is possibly very low and 10% very high. The future reference method establishes an acceptance criterion for span at $\leq 5.0\%$ of the initial value of the span.

The acceptance criteria for zero and range of **NO₂**, and the concentrations of the span are the same as for **SO₂**, for which reason the same comments apply. The future reference method (UNE-EN 14211:2006) establishes an acceptance criterion for zero: \leq LD and for span: $\leq 5\%$ of the most recent certified value.

For **CO**, the acceptance criterion for zero varies between 0.1 ppm and 2 ppm. As regards the span used for verification, this ranges between 7 ppm and 40 ppm. The value of 40 ppm is considered very far from the expected and measured values. Acceptance criteria range between 1% and 10%. Incongruity is also detected between measurement uncertainty and the acceptance criteria for verification of CO in some networks.

The future reference method (UNE-EN 14626:2006) establishes the acceptance criterion for verification as ≤ 0.2 μ mol/mol for zero and $\leq 5.0\%$ of the initial span value for the span.

For **O₃**, the criteria for zero range between 1 ppb and 3 ppb; verification concentrations range between 200 ppb and 400 ppb. These are not generally close to the concentrations to be measured and to acceptance criteria of between 2% and 10%.

The future reference method (UNE-EN 14625:2005) establishes the following criteria: < 5 nmol/mol for zero and $\leq 5.0\%$ of the initial span value for the span.

For benzene, four networks indicate verification, of which one does not reflect the criteria. Out of the other three, two stipulate the criterion for zero as 0.5 ppb and 0.3 ppb, and one does not stipulate a criterion for zero, while span is set at 1%, 5% and 10% of the full scale. The automatic reference method (UNE-EN 14662-3:2006) establishes the acceptance criterion for zero as ≤ 0.5 $\mu\text{g}/\text{m}^3$.

As regards verifications of SO_2 , NO_2 , CO , O_3 and benzene, it would be recommendable that the networks:

- a) do not make adjustments to the verifications;
- b) perform verifications of zero and of a concentration close to the expected concentrations and measurements;
- c) establish the following acceptance criteria for zero:
 - equal or lower than 5 nmol/mol for SO_2 and O_3 ;
 - equal or lower than the detection limit for NO_2 ;
 - equal or lower than 0.2 $\mu\text{mol}/\text{mol}$ for CO ;
 - equal or lower than 0.5 $\mu\text{g}/\text{m}^3$ for benzene.
- d) stipulate span acceptance criteria which are consistent with the quality objectives for the data required by the legislation, bearing in mind that the acceptance criterion for verification shall intervene in the measurement uncertainty, and therefore shall be lower than this. According to the reference methods in the draft directive, this shall be $\leq 5\%$ of the initial range value for SO_2 , CO and O_3 and $\leq 5\%$ of the most recent value certified for NO_2 .

4.1.1.3 CALIBRATIONS

As regards calibration, only three networks indicate acceptance criteria for calibration. These are very different and it also appears that correction on percentage or coefficient of regression is considered but not uncertainty of calibration. This is essential for later determination of measurement uncertainty. One network indicates that it is not applicable to stipulate criteria.

As regards frequencies of verifications and calibrations, these range between every 7 days and monthly for verifications, and between monthly and yearly for calibrations, although one network indicates that it undertakes verifications of zero every 6 months.

The reference methods in the draft directive stipulate frequency of calibrations and verifications. For SO₂, NO₂, CO and O₃ these are: calibration at least every 3 months and after repair, and verification at least every 2 weeks. In the case of ozone, verification is recommended every 23 h or 25 h. For benzene, the automatic reference method establishes at least one calibration annually and verifications at least every fortnight but recommends every 23 h or 25 h.

For this reason the networks are recommended to change the frequency of calibration and verification to what is stipulated in the reference methods.

As regards ozone traceability, all A.C.s except one have traceability to the national ozone standard.

4.1.1.4 QUALITY ASSURANCE INTERCOMPARISONS

All the autonomous community networks (except one) indicate that they participate in intercomparison exercises. Acceptance criteria for intercomparisons in the different networks are very varied, from values for z-score and rate of compatibility (En) to percentages of differences between the network and the Instituto de Salud Carlos III, expanded uncertainty, percentage of the limit value and criteria equal to those of verification.

The document stipulates the assessment criteria (En, z-score and relative error) and their use.

4.1.2 PARTICLE ANALYSERS

4.1.2.1 SYSTEMS USED

Ten networks out of the fifteen who responded to the survey use particle analysers, while five use particle samplers to assess the quality of particles in ambient air. The systems used are very varied: β radiation, oscillating microbalance, and laser, although β radiation is the most widely used technique.

To prevent any condensation in the filter, the tube should be slightly heated, as stipulated by UNE-ISO 10473:2005 (40°C to 50°C). Absence of heating and of available humidity eliminators give rise to positive artefacts, giving particle values which are higher than those really existing. However, heating the tube between the inlet and the analyser, in order to eliminate water vapour, may also eliminate semi-volatile particles. Eight out of the ten networks which use particle analysers indicate that they do not heat the tubes and only two heat at temperatures between 35°C and 50°C.

4.1.2.2 CLEANING AND GREASING

All the networks except one indicate that they clean the inlet, however frequency of cleaning varies between every fortnight and every 4 months. It is estimated that periods over a fortnight are not advisable, in order to maintain similarity with the stipulations in UNE-EN 12341:1999 and UNE-EN 14907:2006. As regards greasing, only two networks out of those who indicate that they clean the inlet, grease it. For reasons of similarity to UNE-EN 12341:1999 and UNE-EN 14907:2006, greasing should be carried out.

Cleaning the connection tube between the inlet and the analyser is carried out with a frequency, between fortnightly and annually. Cleaning at least every six months is necessary and depends on the particle concentration.

From the above, the networks are recommended to:

- a) clean the inlets at least every 15 days and more frequently if the amount of particles is high
- b) note the need to grease the plates
- c) clean the tube between the inlet and analyser at least every six months

4.1.2.3 FLOW RATE CALIBRATION

Out of the ten networks who responded that they used analysers, eight indicate that they carry out flow rate calibration with a frequency which ranges from monthly to annually. As regards the calibration points, some networks do not do calibrate at the point of use.

As a recommendation to the network managers, it can be stipulated that the networks shall:

- a) calibrate the aspiration flow rate of the analysers at the point of use. Calibration may be done externally in a laboratory accredited for flow rate calibration in the range of use, or internally, through an internal calibration procedure, calculating the calibration uncertainty and with flow rate standard with ENAC traceability or equivalent;
- b) undertake calibration with a frequency of at least once a year, and after repair, with intermediate flow rate verifications;
- c) stipulate an acceptance criterion for calibrations which should be $\leq 2\%$.

4.1.2.4 MASS CALIBRATION

Only four networks out of the ten which have reported indicate that they carry out mass calibration. For this reason different procedures are used, such as gauges with a specific value; comparison with high volume sampler and weighted filters. Frequency of calibration ranges is between six monthly and yearly.

The document gives a calibration method defined in UNE ISO 10473:2005.

For all the above reasons, the networks are recommended to carry out mass calibration of the analysers, with respect to gravimetric reference methods, with samplers and gravimetric determination according to UNE-EN 12341:1999 for PM 10 and UNE-EN 14907:2006 for PM 2.5.

4.2 STUDIES ON THE CORRELATION FACTOR BETWEEN PM 10 PARTICLE ANALYSERS AND REFERENCE SAMPLERS (UNE-EN 12341:1999)

As the legislation, in the case of PM 10 particles, permits the use of any method (not reference or equivalent method), if it can be shown that there is a consistent relationship with the reference method, and in view of the fact that the autonomous community networks mainly use automatic analysers, a number of studies have been carried out to calculate the correction factors in different autonomous communities.

The methodology for comparison between automatic analysers and reference samplers stipulates that two campaigns (winter and summer) shall be carried out, with a duration of at least 30 days of valid sampling, each of approximately 24 h.

It is considered that the correlation between the analysers, and to the reference sampler, is valid if the regression coefficient (r^2) is greater or equal to 0.8 and the intercept of the equation of the regression line is lower or equal to $5 \mu\text{g}/\text{m}^3$ in absolute terms. Compliance with these criteria enables us to calculate the Relevant Factor to measurements of PM 10 realized by the automatic systems.

All the analysers studied are β radiation, three different brands, and one of laser. Out of the 18 campaigns carried out in summer and winter, it has only been possible to calculate the factor in four campaigns, as in the others the established criteria were not met.

The possible causes of non-compliance with the criteria, in the light of the quality systems implemented, are as follows:

- a) failure to grease the inlet
- b) inadequate frequency for cleaning the inlet in some cases (monthly, every 4 months)
- c) no flow rate calibration or no evidence of calibration with adequate traceability)
- d) no mass calibration

In addition, and in the light of the results obtained, if there has been no heating (according to the information submitted), the correction factors should be higher than the unit and not lower, as are those obtained. For this reason we once again emphasize the need for adequate maintenance and calibration.

5 DATA VALIDATION OF AIR QUALITY

Validation of the data from the automatic continuous measurement networks is an essential part of the quality assurance and quality control system and is essential as a prior step to their use.

The objective of data validation shall be to identify and eliminate measurements which are not representative of real conditions before these are used for assessment of air quality (calculation of exceedance), validation of modelling results, or for any other exercise which might require interpretation of the data, such as the analysis of the dynamic of pollutants, or the study of episodes of pollution. Elimination will consist of replacing the validation character associated to each datum with a character corresponding to "invalid data" so that the numerical value is not lost and can always be revised.

Within the process of data quality control, it is important to distinguish between automatic filtering carried out in real time at each station, and later validation of data already imported to the data base of the central server. Generally the invalid data which is filtered in the process of validation is due to technical faults which have not been filtered automatically by the system. Data validation, therefore, means the final phase of collecting raw data on concentrations (and meteorological variables) and, at the end of the day, guarantees the quality of data bases on air quality.

Perhaps the most detailed definition of data validation is the one laid down by the EPA: “The purpose of data validation is to detect and then verify any data values that may not represent actual air quality conditions at the sampling station. Effective data validation procedures usually are handled completely independently from the procedures of initial data collection. Moreover, it is advisable that the individuals responsible for data validation not be directly involved with data collection.”

5.1 RECOMMENDATIONS TO THE NETWORKS

- Staff in charge of validation shall be qualified.
- This interpretation requires specific tools (software), consisting fundamentally of programmes for graphic representation in adequate space-time scales, rapidly and flexibly. It is recommendable that the programme for representation itself allows marking and elimination (substitution of the validation character) of the data which requires this.
- The consideration of data as invalid shall always be justified and the reasons for this decision recorded.
- The organisation in charge of data validation shall be different to the body entrusted with maintaining equipment, verification and calibration.
- The staff entrusted with validation shall contrast the interpretation of the data and the technical incidents these suggest with those in charge of maintenance, in order to confirm them.
- It is recommended that automatic tests based on comparison with statistical parameters be used to produce alerts which can facilitate detection of measurements which might be considered as invalid.

- The minimum frequency recommended for data validation is daily. In any case assessment of air quality requires validations monthly and annually. It is also possible to have weekly and seasonal validations.

5.2 OTHER CONSIDERATIONS

In the particular and infrequent case of measurement stations being directly exposed to sporadic emissions in their immediate environment (for example, construction works in the vicinity), high concentrations of contaminants may be obtained. It could therefore be considered that these concentrations are not representative of the air quality in the whole area of the station.

In networks where no validation procedure has been implemented, the quality of the data requires that when equipment verification is carried out and does not meet the specified criteria, the cause of non compliance shall be studied and, if possible, the date when this occurred. This means that all data corresponding to that equipment up to that date shall be cancelled and if the date cannot be determined, up until the previous verification (verifications or checks are internal quality controls for the methods, in order to check the validity of the tests, or they are controls which are carried out on the equipment between calibrations, in order to maintain the confidence in the status of equipment calibrations). Obviously this option involves a major risk of loss of information and may lead to non compliance with the legal requirements as regards minimum time coverage for annual data series.

Method validation and data validation shall be differentiated between each other. Method validation, according to UNE EN ISO/IEC 17025:2005, is the confirmation, through examination and objective evidence, which demonstrates compliance with certain requirements for specific use anticipated for the method. Validation of methods involves determination of the detection limit, quantification limit, selectivity of the method, linearity, limit of repeatability and/or reproducibility, and robustness to external influences and/or cross sensitivity to interference from the sample matrix under test.