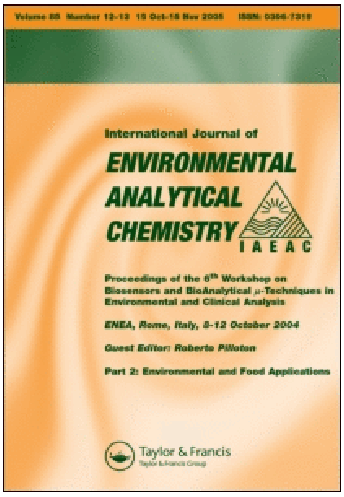

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HARMONISATION OF EC AIR QUALITY DIRECTIVES

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The Environment Institute of the Joint Research Centre in Ispra devotes an important part of its activities to support the Commission of the European Communities in scientific and technical matters. As an example of these activities, a general overview is given of the harmonisation work lead by its Central Laboratory of Air Pollution for the implementation of EC air quality directives in the European Member States. The different stages of a directive's development are reviewed and illustrated with typical examples of harmonisation work recently undertaken.

Preparatory actions for future regulations are illustrated by the recent intercomparison exercise for VOC measurements, realized in view of the coming directive on photo-oxidants.

Quality assurance programmes are developed that are mainly focused on the evaluation of sampling, calibration and measurement techniques in the Member States. Special attention is also paid to the harmonisation of network design. The results of a recent network design campaign realised in Madrid, using passive sampling techniques in combination with mobile measurements, are presented.

An example of the development of scientific and technical progress is given by the intercomparison of primary NO_2 calibration standards, where the reference method of the directive was checked and compared to new standard methods.

KEY WORDS: Air pollution, air quality directive, air pollution monitoring, quality assurance, network design.

INTRODUCTION

The Central Laboratory of Air Pollution is the reference laboratory of the Commission of the European Communities in matter of atmospheric pollution. It provides scientific and technical support to the Commission on EC Air Quality Directives, and is mainly dealing with the harmonisation of air quality measurement methods, the intercomparison of instruments and techniques and the development of measurement techniques and methods. Its main tasks concern:

—preparatory actions for future directives;
—the harmonisation of current directives;
—the development of scientific and technical progress;
—the exchange of technical and scientific information in the Member States.

The role of the Central Laboratory of Air Pollution in the harmonisation process of EC Air Quality Directives is illustrated with typical examples of harmonisation work recently undertaken.

PREPARATORY ACTIONS FOR FUTURE DIRECTIVES

Harmonisation activities are most efficient when they start at an early stage of a directive's development. Preparatory actions for future regulations are therefore conducted in collaboration with the Member States with the scope:

—to assess the state-of-the-art of measuring techniques in the Member States
—to intercompare measurement and calibration techniques
—to test the performances of the instrumentation
—to propose reference methods for measurement and calibration.

Intercomparison of VOC measurements

This activity is illustrated by the recent intercomparison exercise for the measurement of volatile hydrocarbons in ambient air, realised in view of the coming directive on photo-oxidants [1,2]. This new regulation will impose to monitor ambient ozone levels, but will also recommend to measure volatile organic compounds (VOC) in some selected stations of the networks. The Commission is therefore committed to propose a reference method or at least to issue guidelines for harmonised $\frac{\mathrm{VC}}{\mathrm{VOC}}$ measurements in the European air monitoring networks.

The intercomparison was designed with the scope to answer the following questions:

—What is the current state of the art of VOC measurement technology in the European Community?

—What are the performances of the available VOC measurement techniques (sampling, concentration and analysis techniques)?

—What accuracy can be expected presently from routine VOC determinations?

Practical organisation

The exercise took place in September-October 1991 and involved 20 participants selected among leading laboratories in the field of VOC measurements (Table 1). The participation was also extended to scientific organisations outside the EC, currently dealing with VOC measurements in Europe, such as EMEP and TOR.

The intercomparison consisted in the measurement of a dilute mixture of hydrocarbons in nitrogen prepared to simulate an urban atmosphere. This mixture contained 26 individual hydrocarbons (C_2 to C_9), with concentrations ranging from 5 to 100 ppb by volume (Table 2). The list of hydrocarbons largely comprised the compounds relevant for the formation of

Table 1 List of participating laboratories.

Instituut voor Hygiene en Epidemiologie (Belgium)	State General Chemical Laboratory (Greece)
Umweltbundesamt Pilotstation Frankfurt (Germany)	Istituto Inquinamento Atmosferico (Italy)
Institut für Wasser-, Boden- und Lufthygiene (Germany)	Rijksinstituut voor Volksgezondheid en Milieu (The Nederlands)
Instituto de Salud Carlos III (Spain)	University of East Anglia (United Kingdom)
Instituto de Proteccion Radiologica y Medio Ambiente (Spain)	Harwell Laboratory (United Kingdom)
Servicio de Control del Medio Area Metropolitana de Barcelona (Spain)	Imperial College of Science and Technology (United Kingdom)
Institut Universitaire de Technologie GRECA (France)	Fraunhofer Institut für Atmosphärische Umweltforschung (TOR)
Institut National de l'Environnement Industriel et des Risques (France)	Norsk Institutt for Luftforskning (EMEP)
Ecole Nationale Supérieure des Mines de Douai (France)	Joint Research Centre/Ispra (CEC)
EUROPOLL (France)	

photo-oxidants that have been put forward by the working group "VOC Measurement Techniques" of the CEC[3].

The hydrocarbon gas standard was prepared gravimetrically by the National Physical Laboratory in the UK. The hydrocarbon mixtures were contained in passivated aluminium cylinders of 10 litre capacity at a pressure of 7 bar, and were distributed by road and air courier to the participating laboratories. In order to control the stability of the standard mixture, the composition of each individual gas cylinder was measured before and at the end of the exercise.

Discussion

The mean accuracy obtained for the determination of the different hydrocarbons by each laboratory is presented in Figure 1.

Table 2 Composition of the hydrocarbon mixture.

Ethane	1-Butene	Isoprene	Ethyl benzene
Ethylene	trans-2-Butene	n-Hexane	o-Xylene
Acetylene	cis-2-Butene	2-Methyl pentane	m-Xylene
Propane	n-Pentane	3-Methyl pentane	1.2.4-Trimeth. benz.
Propene	i-Pentane	n-Heptane	1.3.5-Trimeth. benz.
n-Butane	trans-2-Pentene	Benzene	
i-Butane	cis-2-Pentene	Toluene	

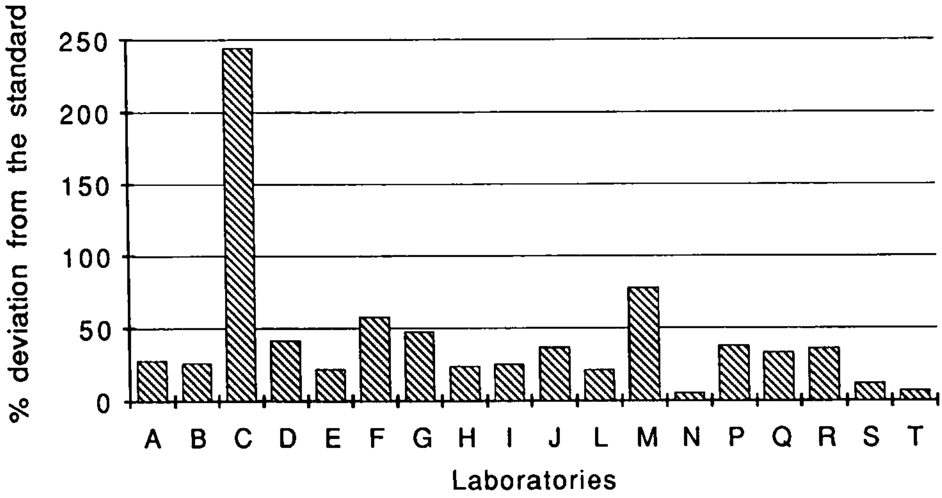

Figure 1 EC intercomparison of VOC measurements – Mean accuracy of the determinations in each laboratory.

Stability of hydrocarbon mixtures The stability of the heavier components (C6 to C9) as well as of acetylene and isoprene has been shown to be poor, questioning the use of gas phase standards for these components. According to the National Physical Laboratory who prepared the gas mixtures, the reason of this instability was attributed to be the poor quality of the implemented cylinders. An earlier intercomparison conducted in 1988 by NPL in the United Kingdom, had shown a good stability with the same cylinders[4]. Recent experiments conducted at NPL with new Scott cylinders seem to be very promising.

Further research is needed about the stability of VOC mixtures in gas cylinders but also in sampling canisters. If the problem of instability for the heavier compounds cannot be solved, it will be necessary to split the sampling and analytical procedures for light and heavier compounds.

Performance of analytical procedures It should be noted that no recommendations were made about the methods to be implemented for sampling, concentrating and analysing the gas sample. Each laboratory was asked to handle the VOC mixture as if it was a routine urban air sample, and to perform all the steps of a routine analysis, using their own analytical techniques.

None of the gas chromatographic techniques used in this exercise proved clearly superior. The systematic errors should be mainly attributed to the variety of sampling and analytical procedures and particularly to the calibration procedures applied in each individual laboratory. However, the best results were obtained in those laboratories which are involved consistently and for longer periods of time in routine VOC measurements and have accumulated a good expertise in this field.

Accuracy of the determinations The overall accuracy of the determinations has been shown to amount 36%, which is rather poor. One may expect that during real routine measurements, this value may even be worse. The repeatability of the successive measurements within each individual laboratory was good (mean RSD of 5%), whereas the reproducibility between the different laboratories was poor (mean RSD of 31%). This suggested that random errors are of lower significance than systematic errors. These were attributed to the variety of sampling and analytical techniques, and particularly to the calibration procedures.

CONCLUSION

The intercomparison has shown that in order to harmonise VOC measurements, with results sufficiently comprehensive and accurate, an improvement in the quality of these measurements is required. An overall accuracy of 15% should be an acceptable target value. It is therefore recommended that:

—the stability of hydrocarbon mixtures in gas cylinders and in sampling canisters should be thoroughly investigated under various conditions;

—the establishment of a protocol for sampling, analytical and calibration procedures, would allow for the minimisation of the systematic errors between laboratories and a better overall performance through the exercise;

—a further intercomparison exercise should be carried out on the basis of the experience gained already from this first exercise.

HARMONISATION OF CURRENT DIRECTIVES

The implementation of EC directives contains a legal implication referring to the following reciprocal commitment:

—on the one hand, the Member States have to demonstrate to the Commission that their methods for sampling, analysis and calibration are equivalent to the reference methods specified in the directive;

—on the other hand, the Commission has to harmonise methods and procedures in order to ensure a reasonable reproducibility of the measurements in the European Member States.

In application of these principles, different actions are undertaken:

—Quality assurance programmes are developed that are mainly focused on the evaluation of the calibration procedures implemented in the Member States and the quality control of the measurements in the networks [5,6,7]. The still on-going quality assurance programme for the NO_2 directive is a good example of this kind of activity;

—Special attention is also paid to the conception of the monitoring networks. After two pilot studies in Paris and Rouen-Le Havre [8,9], a third network design campaign using passive sampling techniques and mobile measurements, was recently realized in Madrid [10].

Assessment of network design—Madrid air quality network

Even if the directives give general guide-lines for network design [11], the correct location of the measurement stations strongly depends on local situations, such as the nature and the distribution of the pollution sources, topography and local meteorological conditions. Correct siting of the monitoring stations, by improving the representativity of measured pollution levels, allows for the reduction of the number of stations and improves the quality of the survey. Considering the very high costs and time consuming work connected with the exploitation of the networks, network design studies are therefore an important cost saving factor.

The Madrid campaign was organised on request of the local authorities in order to control the conformity of the newly installed NO_2 network with the EC recommendations on network design.

Experimental

Passive samplers, as the one developed for NO_2, are an interesting tool for large scale monitoring surveys [12,13,14,15]. They constitute a simple and cheap measurement method, allowing to conduct survey campaigns over large areas within a short period of time. The passive sampler consists in a plastic tube, one end containing a specific absorbent fixing the pollutant gas. The pollutant is collected by molecular diffusion along the tube to the absorbent, where it is retained for subsequent measurement in the laboratory. In the case of nitrogen dioxide, NO_2 is collected on stainless steel mesh discs coated with triethanolamine and is determined spectrophotometrically by a variation of the Griess-Saltzman method. For the Madrid survey, 200 samplers were installed and exposed over two-weekly periods. Complementary to the passive sampler campaigns, mobile measurements were also performed along selected circuits in the urban agglomeration for the pollutants SO_2, NO, NO_2 and CO.

Discussion and conclusion

An example of the NO_2 distribution over the Madrid agglomeration as measured during the summer campaign is represented in Figure 2. Iso-concentration plots with intervals of 15 $\mu g/m^3$ were obtained by interpolation of the measurement data. The iso-concentration plots gave evidence of a higher average concentration in the winter, but peaks over 75 $\mu g/m^3$ were only measured in the summer and were attributed to an increased photochemical activity. The values have been compared to the limit value of the directive, reported to the annual average for the passive measurements and to the 99th percentile for the mobile measurements. The results showed, for a 8/10 days pollution episode, the breach of the 99th percentile Directive's limit value (230 $\mu g/m^3$) at the kerbside of roads carrying heavy traffic. Even if no background site showed an exceeding of the annual limit value (80 $\mu g/m^3$), 11 sites at risk, i.e. between 60 et 80 $\mu g/m^3$, were numbered. The study concluded on the necessity of NO_2 abatement measures and the revision of the siting of some stations.

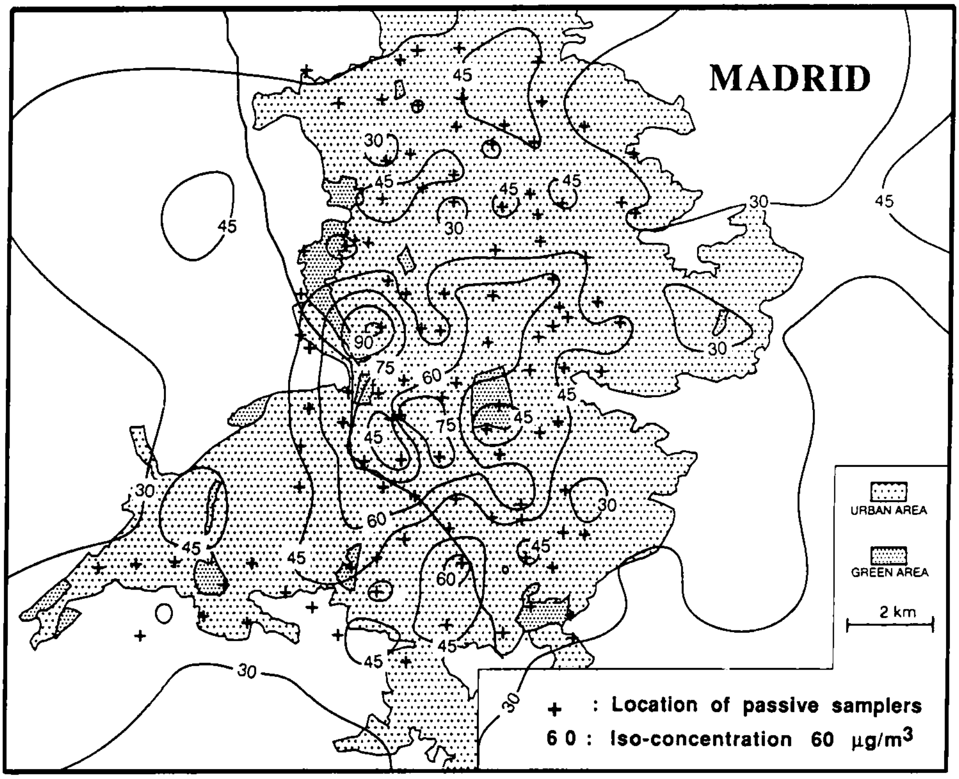

Figure 2 Network design campaing in Madrid–Results of the NO_2 survey during the summer 1990.

DEVELOPMENT OF SCIENTIFIC AND TECHNICAL PROGRESS

Because of fast scientific and technical progress in the field of air quality measurements, up-dating and improving the measuring and calibration methods must be a constant concern and may eventually lead to a revision of the directives. Among the activities in this field, the most important are:

—the development of new monitoring and calibration techniques
—the assessment of new measurement and calibration methods
—the improvement of reference methods

Test of the reliability of NO_2 primary calibration methods

An example of the adaptation of the directives to the scientific and technical progress is given by the intercomparison of primary NO_2 calibration standards, that took place in 1991. Recent investigations on the reliability of the permeation method have shown instability and abnormal reproducibility of the permeation rates of NO_2 tubes, questioning its implementation as calibration reference method of the directive [16,17]. These effects have been attributed to the presence of impurities in the liquid NO_2. On the other hand, new developments in the Saltzman method and the static volumetric method may provide a valuable alternative to the reference calibration method.

An intercomparison study between primary NO_2 calibration standards was therefore designed to answer the following questions:

—how reliable are the NO_2 permeation tubes used in the EC monitoring networks?
—what is the origin of the instability observed in some permeation tubes?
—how well do other primary standards comply with the reference permeation method?

Experimental

A questionnaire sent to national experts on air quality allowed to make a survey of the different permeation tubes used in the EC monitoring networks. A total number of 11 tubes were purchased, covering all the types of commercially available permeation sources in the EC. Some of the tubes were duplicated in order to enhance the representativity of the samples. In a few cases, certified and uncertified tubes of the same type were acquired.

Before the beginning of the stability experiment, the purity of the permeating NO_2 was controlled by FTIR spectrometry. Each tube was left to permeate at a temperature of 40°C over a 24 hour-period in an argon-filled spectroscopic cell before analysis.

A permeation bench was constructed according to ISO standard 6349 allowing the simultaneous operation of 9 permeation sources. The experiment covered a period of 6 months. A thermostated water bath ensured a constant temperature of 40°C within ± 0.1°C. The temperature of the permeation cells was continuously monitored during the experiment. The permeation cells were flushed with a constant flow of dry nitrogen (gas chromatography grade). Fluxes of carrier and dilution gasses were controlled by calibrated mass flow controllers.

The permeation rates of the tubes were controlled gravimetrically on a weekly base. The emission rate of each tube was also determined every week by means of a NO_x analyser calibrated by static volumetric dilution. The static dilution method was used to generate NO mixtures in nitrogen for the calibration of the NO channel. The NO_2 channel of the instrument was subsequently calibrated by gas phase titration.

Using the more stable permeations tubes as NO_2 source, an intercomparison between the following primary calibration standards was also performed:

—static volumetric dilution method (VDI 3490-1985)
—permeation method (ISO 6349-1979)
—Griess-Saltzman wet chemical method (ASTM D 1607-1976)
—Griess-Saltzman wet chemical method (VDI 2453-1990)

The intercomparison was performed at three different concentration levels, from 300 up to 1000 ppb. The wet chemical measurements were repeated 10 times for each determination.

Discussion and conclusion

Impurity analysis From the FTIR determinations, it appeared that the main impurity detected consisted in nitrous oxide, N_2O. In a first analysis, concentrations up to 4.5% were observed for virgin tubes. Certified tubes or already run in tubes in general showed lower concentrations, with levels ranging from 0.2 to 2%. A second analysis (lifetime of the tubes increased by ± 24 hours) showed that these concentrations had dropped to less then 0.5% for all the tubes. This impurity had no noticeable influence on the stability test.

Stability of permeation rates The results of the stability test have demonstrated that the long term stability of the permeation rates was excellent (deviation better than 2%) for all the tubes, provided that they be handled according to ISO norm 6349 (storing in dry atmosphere, temperature control within ± 0.1°C, use of dry primary dilution gas). Unstable permeation rates were observed for two sources which had not been stored in dry atmospheres before the beginning of the test.

Intercomparison of primary calibration standards From the results of the intercomparison, presented in Figure 3, it appeared that permeation and static volumetric dilution method match very closely (within 2%), confirming the validity of the directive's reference calibration method. The VDI and ASTM Saltzman methods when compared to the static volumetric dilution method showed differences up to - 8% and + 23% respectively, in the concentration

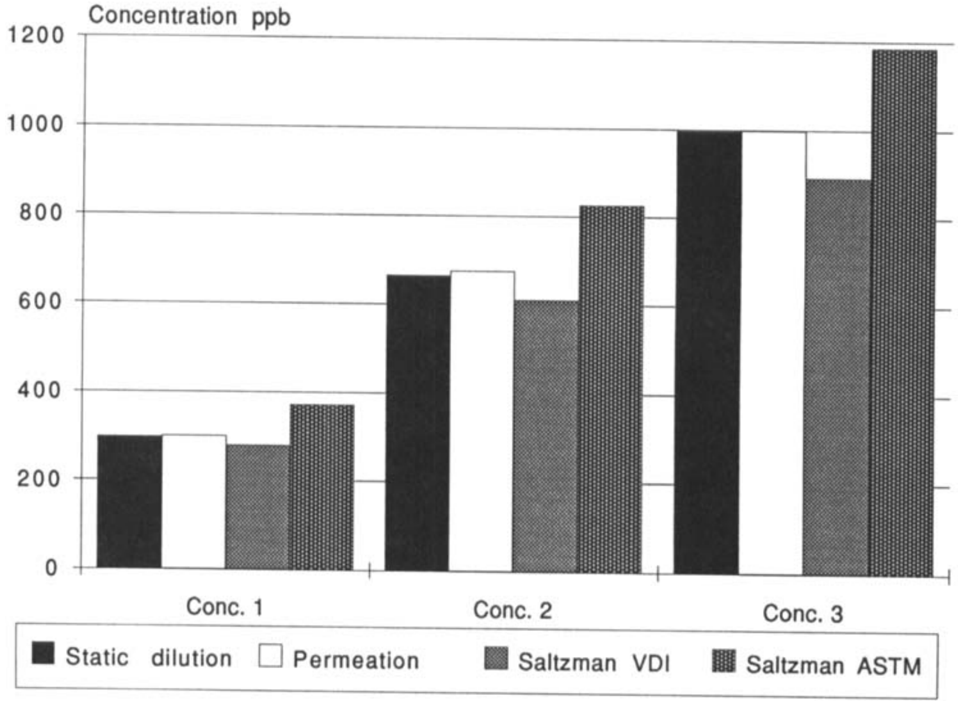

Figure 3 Comparison of primary NO_2 standards.

range 0-1000 ppb. The precision of the determinations for the permeation and static volumetric dilution method was better than 2%, whereas for the VDI and ASTM Saltzman methods mean precisions of respectively 10 and 18% were observed.

EXCHANGE OF TECHNICAL AND SCIENTIFIC INFORMATION

Finally, the exchange of information through the organisation of workshops, the elaboration of guide-lines, the publication of good practice manuals and the organisation of training courses constitute the ultimate tool that will lead to an harmonised implementation of Air Quality directives in the EC. As an example of this activity, instruction manuals for sulphur dioxide and black smoke measurements are about to be published and will be put at the disposal of network managers and technicians [18,19].

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