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A technical review of the feasibility of producing certified reference materials for the measurement of gaseous pollutants in ambient air

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Abstract

Within the frame of the EU sponsored project 'Cermatair' (Certified Reference Materials for the Measurement of Gaseous Pollutants in Ambient Air, contract G6RD-CT-2001-00517) the feasibility of preparing and certifying reference materials for the measurement of sulphur dioxide, nitrogen dioxide, carbon monoxide and benzene in ambient air was studied. The project focused on measurements at concentration levels corresponding to limit values given in EU Ambient Air Quality Directives and covered reference materials for the reference methods specified in these Directives and for alternative methods based on diffusive sampling. State-of-the-art technologies for the production and certification of the reference materials were identified through literature surveys. Limited batches of reference materials were prepared and, wherever appropriate, tested for homogeneity. The reference materials were subsequently tested in small-scale external verifications, performed by 2–4 laboratories other than the preparation laboratory, aimed at identifying possible discrepancies between concentration values from the preparation processes and experimental values. The results of these verifications revealed possible mechanisms of certification (based on preparation or measurements). The remaining materials were subjected to a one-year stability study.

Keywords: Air quality; Quality assurance/quality control; Traceability; Certified reference materials

1. Introduction

European Union (EU) Ambient Air Quality Directives (Council of the European Union, 1999, 2000) specify limit values and 'reference' methods for the measurement of several gaseous pollutants (see Table 1).

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Table 1
EU Limit Values and reference methods for gaseous pollutants

Compound	EU Limit value ($\mu g\,m^{-3}$ at 293 K and 101.3 kPa)	Reference period	Reference measurement methodology (CEN Standard Method)
Sulphur dioxide	350	1 h	Automated UV-fluorescence spectrometry (CEN, 2004a)
	125	24 h	
	20	1 year	
Nitrogen dioxide	200	1 h	Automated chemi-luminescence spectrometry (CEN, 2004b)
	40	1 year	
	30	1 year	
Carbon monoxide	10,000	8 h	Automated non-dispersive infrared spectrometry (CEN, 2004c)
Benzene	5	1 year	Pumped sampling on a sorbent cartridge + gas chromatography, both automated and manual (CEN, 2004 d–f)

Table 2
Appropriate reference materials for ambient air monitoring

Compound	Form of reference material	Level
Sulphur dioxide	Cylinder	$150\,nmol\,mol^{-1}$
	Diffusive sampler	0.75 μg
Nitrogen dioxide	Cylinder	$100\,nmol\,mol^{-1}$
	Diffusive sampler	1 μg
Carbon monoxide	Cylinder	$10\,nmol\,mol^{-1}$
Benzene	Cylinder	$1.5\,nmol\,mol^{-1}$
	Charcoal pumped sample tube for solvent desorption	5 μg
	Pumped sample tube for thermal desorption	50 ng
	Charcoal diffusive sampler for solvent desorption	1 μg
	Tube-type diffusive sampler for thermal desorption	100 ng

In addition to the reference methods, an EU Member State 'may use any other method which it can demonstrate gives results equivalent to the reference method'. Examples of potentially equivalent methods—although not specified in the Air Quality Directives—are for long-term measurements based on diffusive sampling for sulphur dioxide, nitrogen dioxide and benzene. Further, these directives set requirements for the required measurement uncertainty in order to guide quality-assurance programs. Certified reference materials (CRM) are essential elements of such programs; they may be used for

- ensuring measurement traceability to SI units,
- assessment of measurement uncertainty in relation to the objectives specified in EU directives,
- ongoing quality control to ensure that these objectives are realized in practice, and
- promoting comparability of measurement results between European member states.

Reference materials appropriate to the concentration levels, reference periods and measurement methods mentioned above are given in Table 2. The levels were based on the assumption of concentration measurements at the limit value for a period corresponding to that recommended in the CEN[1] Standard Method. For methods based on diffusive sampling the levels were based on a 2-week sampling period at the limit value. None of these materials was available from major CRM suppliers. Therefore, it was the main objective of the project Cermatair (Certified Reference Materials for the Measurement of Gaseous Pollutants in Ambient Air) to

[1]CEN = European Standardization Committee.