

# A new certified reference material for benzene measurement in air on a sorbent tube: development and proficiency testing

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**Abstract** A certified matrix reference material (CRM) for the measurement of benzene in ambient air has been developed at Laboratoire National de Métrologie et d'Essais. The production of these CRMs was conducted using a gravimetric method fully traceable to the International System of Units. The CRMs were prepared by sampling an accurate mass of a gaseous primary reference material of benzene, using a high-precision laminar flowmeter and a mass flow controller, with a PerkinElmer sampler filled with CarboPack™ X sorbent. The relative standard deviations obtained for the preparation of a batch of 20 tubes loaded with 500 ng of benzene were below 0.2%. Each CRM is considered independent from the others and with its own certified value and an expanded uncertainty estimated to be within 0.5%, lower than the uncertainties of benzene CRMs already available worldwide. The stability of these materials was also established up to 12 months. These CRMs were implemented during proficiency testing, to evaluate the analytical performances of seven French laboratories involved in benzene air monitoring.

**Keywords** Certified reference material · Air monitoring · Benzene · Proficiency testing

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## Introduction

Monitoring of air quality is one of the major concerns of our society for the environment and health. It must be conducted both in ambient air (industrial emissions, car traffic, etc.) [1, 2] and in indoor air (buildings, equipment, external environment, behaviour of occupants) [3–5]. Poor air quality is suspected of being responsible for the increase of chronic diseases such as asthma [6, 7].

Because of their toxicity, their recurrence and their chemical reactions in the environment, volatile organic compounds (VOCs) are among the air pollutants for which monitoring is particularly important.

In particular, benzene is recognized as carcinogenic to humans, according to the European Classification and the International Center for Research on Cancer (IARC) [8]. To protect human health, the “Daughter” Directive 2000/69/EC [9] establishes the benzene limit at  $5 \mu\text{g}/\text{m}^3$ . Moreover, a set of guideline values for indoor air quality determined according to exposures are already effective in France (e.g.  $10 \mu\text{g}/\text{m}^3$  for an exposure time longer than 1 year) [10]. Benzene compound is also recognized as a marker of traffic pollution (gasoline vehicles). In combination with toluene measurements, benzene measurements are used as an indicator to determine the chemical age of urban air masses [11].

In France, the monitoring of benzene in ambient air is performed by the French Air Quality Monitoring Networks (AASQA), by sampling air on activated carbon cartridges, as recommended by the US EPA. According to Annex VII of European Directive 2000/69/EC of 16 November 2000 [12], the reference method for the sampling of benzene in air is based on “pumped sampling onto sorbent-based tubes”. Then, benzene is removed from the sorbent, by thermal desorption or solvent extraction, and analysed by gas chromatography to determine its concentration [13].

To assess measurement accuracy and trueness of laboratories' analytical methods and to ensure metrological comparability of measurements results, it is necessary to have common references traceable to the International System of Units (SI) [14]. Certified reference materials (CRMs) are defined in the *International vocabulary of metrology* (VIM) as materials, sufficiently homogeneous and stable with reference to specified properties, which have been established to be fit for their intended use in measurement or in examination of nominal properties, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures [15]. Very few CRMs are available for the analysis of benzene in air by thermal desorption [16–19]. To produce this kind of CRM, an accurate quantity of benzene has to be loaded onto a sorbent tube. Two methods are described in the literature: The first one is based on spiking sample tubes with a known mass of benzene by injection of a known mass or volume of a solution of benzene in methanol and subsequent purging of the methanol. This method can be applied with good results [19]. Nevertheless, it will result in materials that have less similarity to real field samples. An alternative traceable preparation method is based on the sampling of accurately known volumes of a generated gas standard mixture. In this case, the accuracy of the generation of gaseous standard mixtures will directly impact the quality of the CRM.

Several techniques have been developed and are used for the generation of gaseous standard mixtures and these are generally classified as dynamic methods, using diffusion and permeation techniques [20–23], or as static methods [24–26]. Moreover, there are other methods based on thermal decomposition of compounds bonded to silica gel or glass surfaces [27–29] and microwave-assisted generation [30].

A typical static method, based on ISO 6142 [31], is the gravimetric preparation of primary standards (i.e. cylinders). Cylinder reference materials for benzene can be prepared by traceable techniques. A known mass of benzene is introduced into a cylinder with a suitably deactivated inner wall and suitable appendices, after which a known mass of balance gas (normally high-purity nitrogen) is added.

Currently, no CRMs for the measurement of benzene by thermal desorption prepared from such gravimetric mixtures are available. Furthermore, although Carbopack X is used by AASQAs to measure benzene in ambient air by pumped sampling because of its suitability for long-term monitoring, and although it is necessary to have CRMs identical to field samples so the same analytical method can be used for both, CRMs are only available on Tenax™ TA [16, 18].

Therefore, Laboratoire National de Métrologie et d'Essais (LNE) has developed a method for the production of a

CRM on Carbopack X containing 500 ng of benzene, corresponding to a 1-week sampling at the limit specified in EU legislation. To provide a reference value directly traceable to the SI, and to minimize uncertainties (0.5%), a gravimetric method was established.

The loading of benzene onto a Carbopack X cartridge was done by sampling an accurate mass of a gravimetric primary reference material (PRM) of benzene with a high-accuracy laminar mass flow controller (MFC) [32].

## Materials and methods

### Reference tubes

Because of analytical issues that could lead to measurement errors [33], it is of primary importance to be able to analyse the CRM with the same analytical procedure as for the real sample. In consequence, the reference tubes have to be similar to real samples. Such materials are composed of three essential components: tube, sorbent material and cap, which define their use, their artefacts and their limits. In this study, stainless steel PerkinElmer tubes ( $90 \pm 6.35$  mm, inner diameter 5.0 mm) supplied by TERA Environnement® were used. These tubes are suitable for thermal-desorption unit systems and, developed by Brown et al. [34], are the most widespread axial sorbent tubes for monitoring of VOCs.

The sorbent material chosen was Carbopack X (40/60 mesh), which is a substance intermediate between graphitized carbon and a molecular sieve, suitable for benzene air monitoring [35]. Moreover, Carbopack X is suitable for long-term sampling owing to its large safe sampling volume [36]. Each tube is filled with 500 mg of sorbent. This quantity was chosen to match with tubes used by laboratories from AASQA, to achieve a maximum duration of sampling [37]. The bed of Carbopack X is retained at one end by a metal gauze, and at the other end by a metal gauze and a spring. To lower the risk of contamination by permeation of compounds onto the sorbent, Swagelok® brass caps with polytetrafluoroethylene (PTFE) ferrules were used to seal the tubes.

### Primary reference material

As already mentioned, CRMs have to be as similar as possible as real samples. This is true for the choice of the tube and the sorbent material, and is also true for the type of interactions that link the target compound and the sorbent. Therefore, in this study, great care was taken to achieve a gas-to-sorbent load. In consequence, a PRM was used. This PRM was prepared gravimetrically by transferring parent gases quantitatively from supply cylinders to a cylinder in which the calibration gas

mixture will be contained as recommended by ISO 6142. These materials, prepared at LNE, are traceable to international measurement standards recognized by signatories to an international agreement and intended to serve worldwide [38]. Worldwide national standards laboratories regularly participate in intercomparison campaigns to demonstrate their accuracy. The uncertainties of mixtures of this kind of are between 0.1 and 0.4%, depending on the concentration of the compounds. These PRMs can be used for different applications, including air quality measurements. During this study, these primary measurement standards were used to load an accurate mass of benzene onto a sorbent tube. Two different PRMs of benzene in nitrogen were independently prepared at LNE. One was used for the preparation of CRMs, the other for the loading of measurement standards, exhibiting benzene concentrations of  $364.34 \pm 0.75 \text{ nmol mol}^{-1}$  (PRM1) and  $372.29 \pm 0.74 \text{ nmol mol}^{-1}$  (PRM2), respectively.

For such mixtures, impurities usually comprise between 20 and 30 ppt of benzene. The stability of a PRM is determined over 3 years under laboratory conditions ( $21 \pm 2 \text{ }^\circ\text{C}$ ). The stability study is conducted by comparison with other primary gas mixtures from a different national metrology institute.

#### Analytical system

The loaded tubes were analysed using a PerkinElmer automatic thermal desorption (ATD) system (TurboMatrix ATD 50) coupled with a gas chromatograph (GC; Autosystems XL) and a flame ionization detector (FID). In ATD, compounds sampled on the sorbent phase are removed by heating and transferred by an inert carrier gas (He) into the GC. The cold trap used to preconcentrate the sample was a PerkinElmer air monitoring trap composed of Carbopack B/Carbosieve SIII. The column was a ValcoBond VB-5 (5% phenyl methylpolysiloxane): 60 m  $\times$  0.25-mm inner diameter  $\times$  0.25  $\mu\text{m}$ .

The analytical method described in this part was optimized and validated for a wide range of VOCs, including benzene, toluene, ethylbenzene and xylene, and other compounds such as trichloroethylene and undecane. This method allowed a quantitative and a repeatable analysis of benzene.

#### Thermal desorption

The desorption of benzene was carried out in two stages. First, the Carbopack X cartridge was heated at  $400 \text{ }^\circ\text{C}$  for 20 min (maximum temperature of the sorbent material) and back-flushed by  $100 \text{ mL min}^{-1}$  of helium (desorb flow plus inlet split flow) to ensure complete desorption of compounds retained on the 500 mg of Carbopack X. A split of  $20 \text{ mL min}^{-1}$  of helium was used to dilute the sample reaching the cold trap. Meanwhile, the temperature of the trap was maintained at  $-30 \text{ }^\circ\text{C}$  to enhance the retention of benzene. Then, the cold trap was heated at  $325 \text{ }^\circ\text{C}$  at a rate of  $40 \text{ }^\circ\text{C s}^{-1}$  while back-flushing with He onto the GC column at a flow rate of about  $40 \text{ mL min}^{-1}$  (column flow plus outlet split flow). The trap was maintained at  $325 \text{ }^\circ\text{C}$  for 20 min for conditioning purposes before the next analysis. An outlet split of  $35 \text{ mL min}^{-1}$  was applied after the trap to avoid signal saturation. The parameters for thermal desorption are listed in Table 1.

#### Gas chromatography

The retention time of benzene for the analysis of Carbopack X cartridges is about 6 min. The temperature programme of the GC oven began at  $40 \text{ }^\circ\text{C}$  and followed the temperature profile of  $40 \text{ }^\circ\text{C}$  for 8 min,  $20 \text{ }^\circ\text{C min}^{-1}$  to  $80 \text{ }^\circ\text{C}$  and  $10 \text{ }^\circ\text{C min}^{-1}$  to  $170 \text{ }^\circ\text{C}$ , for a total GC analysis time of 19 min. This method enables a narrow chromatographic peak at a retention time of 6 min to be obtained. The detection of benzene was carried out by a FID, because of its high sensitivity, large field linearity and stability over time. The parameters for gas chromatography are listed in Table 2.

#### Production of reference materials

##### General description

The traceable preparation method is based on the introduction of an accurately known mass of benzene (500 ng) onto sample tubes (Carbopack X) by injection of a known mass of a gaseous PRM of benzene in nitrogen generated using a gravimetric method (ISO 6142:2001). This part describes the loading

**Table 1** Thermal desorption parameters for the analysis of benzene

Primary desorption		Secondary desorption	
Parameter	Value	Parameter	Value
Desorption time (tube)	20 min	Desorption time (trap)	20 min
Desorption Temperature	$400 \text{ }^\circ\text{C}$	Low trap temperature	$-30 \text{ }^\circ\text{C}$
Cold trap temperature	$-30 \text{ }^\circ\text{C}$	Heating rate	$40 \text{ }^\circ\text{C s}^{-1}$
Desorption flow rate	$80 \text{ mL min}^{-1}$	High trap temperature	$325 \text{ }^\circ\text{C}$
Inlet split	$20 \text{ mL min}^{-1}$	Outlet split	$35 \text{ mL min}^{-1}$

**Table 2** Optimized gas chromatograph (GC)/flame ionization detector (FID) parameters for the determination of benzene

Parameter	Value
Carrier gas	He (purity 99.999%)
Transfer line temperature	220 °C
Column pressure	35 psi
Oven temperature (start)	40 °C over 8.50 min
First ramp	20 °C min <sup>-1</sup> up to 80 °C
Second ramp (end)	10 °C min <sup>-1</sup> up to 170 °C
Detector temperature	250 °C
Hydrogen flow rate (FID)	45 mL min <sup>-1</sup>
Air flow rate (FID)	450 mL min <sup>-1</sup>

procedure developed and the optimization of parameters influencing the adsorption of benzene onto Carboxpack X tubes.

#### Conditioning of sorbent tubes

Prior to the loading, it is necessary to verify that the sorbent tubes are free of the compounds of interest. Then, the tubes must undergo a conditioning treatment to obtain a mass of benzene less than 2 ng [13]. All tubes are conditioned before loading by heating them at 400 °C for 300 min while purging them with 100 mL min<sup>-1</sup> of purified helium. Each tube is then analysed to check the benzene levels. If the quantity is higher than 2 ng, the tubes have to undergo one more conditioning cycle. Afterwards, to prevent the risk of contamination, the tubes are placed at 4 °C in a non-polluted environment, waiting for the loading phase.

#### Gas flow controller

The PRM stream was controlled and measured by an highly accurate Molbloc/Molbox™ flow calibration system supplied by DHI®, also traceable to international measurement

standards. The measurement principle of this laminar flowmeter is based on the theory of laminar flow and on the thermodynamic properties of gases [39]. The mass flow of gas drawn through the laminar path is calculated using the geometric constant of the laminar path determined by gravimetric calibration, the differential of pressure between the gas upstream and downstream of the Molbloc flow element, and using thermodynamic properties of gases. This system covers the flow rate range from less than 1 mL min<sup>-1</sup> to 500 mL min<sup>-1</sup> with accuracy up to ±0.2% for a variety of gases. It corresponds to an uncertainty 2–5 times lower than what is generally found for conventional MFCs. The implementation of this device allows one to determine accurately the mass of gas driven through cartridges and consequently to determine accurately the mass of benzene loaded on CRMs. The the loading time is controlled by a computer-supported unit (Molbox) with uncertainties estimated as about ±0.15 s, which corresponds to an absolute uncertainty of 0.02%.

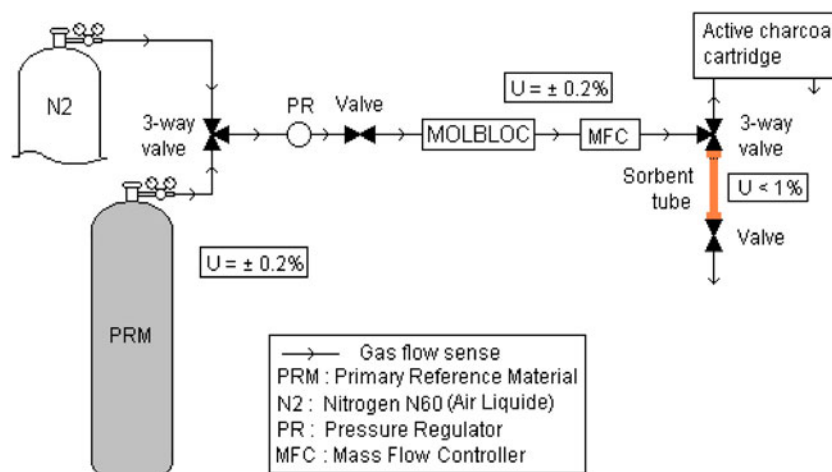
#### Loading method

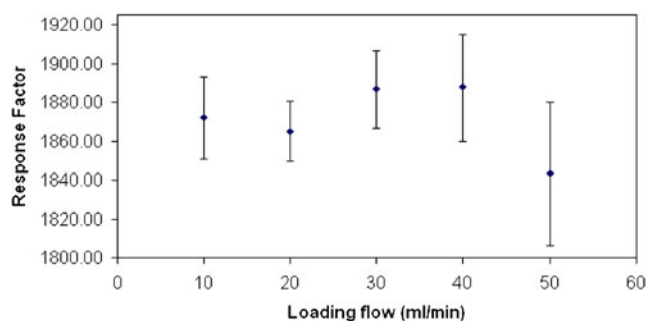
Reference materials are prepared using a gravimetric method developed at LNE, based on the sampling of an accurate mass of a PRM of benzene. This flow is controlled by a high-precision gas flow standard (Molbloc). The mass of benzene loaded on the tube is calculated from the mass and the concentration of the gas drawn through the tube. Figure 1 shows a scheme of the loading system.

Besides the loading phase, the a flow of nitrogen is continuously drawn through the system to condition it. Then, the three-way valve is switched, shutting off the nitrogen flow and allowing the flow of the PRM to go to the system. At the output, the gas is purified using an active charcoal cartridge.

Meanwhile, cleaned Carboxpack X tubes are placed at room temperature (20±2 °C) to maintain the tubes at a

**Fig. 1** The loading system for volatile organic compound certified reference material





**Fig. 2** Influence of the loading flow rate on the efficiency of the benzene sorption on tubes. Measurement was repeated three times for each level. The response factor is the ratio between the chromatographic peak area and the quantity of compound loaded on the tube. Error bars are expanded uncertainties, where  $k=2$

homogeneous temperature. Then, the brass caps are removed and the tube is directly connected to the system to minimize the risk of contamination.

One hour before the loading of Carboxpack X cartridges, the three-way valve switches to the PRM, allowing the standard gas mixture instead of nitrogen to go through the system.

Once a steady flow has been reached, the valves are opened simultaneously on each side of the tube, allowing the flow of the PRM to go through the Carboxpack X tube. During the loading, a constant flow is continuously drawn through the system.

At the end of the sampling, both valves are closed and the cartridge is disconnected from the system, and then closed with the brass caps attached and stored at 4 °C in a refrigerator.

### Optimization

Two parameters control the deposition of benzene onto the sorbent tube: the standard gas flow and the loading time. Therefore, they were evaluated to test their influences on the benzene adsorption efficiency and on the loading repeatability. Each test discussed below was conducted using a primary standard gas mixture of benzene (PRM2) and the MFC with an estimated full scale of measurement of 0.5% (Bronkhorst® Hi-Tec MFCs).

#### Loading flow

Five levels of loading flow rate were evaluated: 10, 20, 30, 40 and 50 mL min<sup>-1</sup>, using a constant loading time (8 min). For each, three replicates were realized. To compare the values obtained, which are proportional to the flow rate, the response factor (RF) was calculated. It corresponds to the ratio between the chromatographic peak area of benzene and the quantity of compound loaded on the tube. Figure 2 shows the RF depending on the loading flow rate. The errors bars displayed in this figure correspond to an

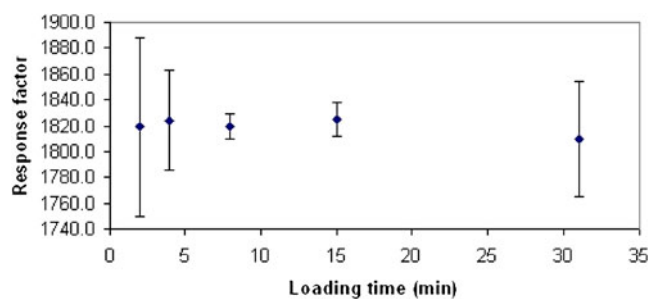
expanded uncertainty ( $k=2$ ) twice the standard deviation of the RF.

There is no statistical difference between 10, 20, 30 and 40 mL min<sup>-1</sup> as all error bars overlap. The standard deviations observed, around 0.5%, are similar. However, a flow rate of 50 mL min<sup>-1</sup> seems to slightly reduce the RF and increases the dispersion of benzene loaded on tubes. If the RF decreases, the mass of benzene sorbed on the tube also decreases. The use of a loading flow rate less than 50 mL min<sup>-1</sup> seems to be necessary to ensure repeatable and efficient benzene sorption on tubes. We chose to fix the value of the loading flow rate at 40 mL min<sup>-1</sup>.

#### Loading time

Five loading times were evaluated—2, 4, 8, 15 and 31 min—using a constant flow of the benzene PRM2. Each point was repeated three times. For the same reason as before, Fig. 3 represents the RF depending on the loading time. The errors bars displayed in this figure correspond to twice the standard deviations.

From these results it can be seen that the loading time is not a critical factor for the preparation of reference materials as long as the mass flow is well defined. Indeed, although all the error bars are quite small (from 0.3% for 8 min to 2.2% for 2 min), they all overlap. There is no significant difference between 2, 4, 8, 15 and 31 min. It appears that the sampling time may affect slightly the repeatability of the loading. Indeed, a short sampling time (2 and 4 min) gave higher standard deviations than those observed for 8 and 15 min. The stabilization of the gas flow passing through the system could explain these observations. Furthermore, a longer sampling time (more than 30 min) also appears to increase the dispersion of the results. For our purpose, a loading time ranging between 5 and 30 min was considered suitable to reduce the dispersion of the mass of benzene loaded on the CRM.



**Fig. 3** Influence of the loading time on the efficiency of the benzene sorption on tubes. Measurement was repeated three times for each level. The response factor is the ratio between the chromatographic peak area and the quantity of compound loaded on the tube. Error bars are expanded uncertainties, where  $k=2$



### Calculation and uncertainties

The optimization was implemented to select the flow rate and loading time allowing maximum repeatability of the method. From these two parameters, a PRM with a concentration of benzene suitable to reach the target mass of benzene (500 ng) loaded on Carboxpack X tubes was prepared at LNE. This mass corresponds to a 7-day sampling at 10 mL min<sup>-1</sup> of an atmosphere at the benzene annual mean limit (5 µg m<sup>-3</sup>) sets by Directive 2000/69/EC. The values of the parameters used for the loading of the CRMs are given in Table 3.

The mass of benzene loaded on CRMs ( $m_{ben}$ ) is calculated according to Eq. 1. This mass is considered as a gravimetric value.

$$m_{ben} = \frac{C_{ben} \times M_{Ben} \times (x + E_x)}{M_{N_2}}, \quad (1)$$

where  $C_{ben}$  refers to the benzene concentration of PRM1 (nmol mol<sup>-1</sup>),  $M_{ben}$  and  $M_{N_2}$  corresponds to the molar mass of benzene and nitrogen (g mol<sup>-1</sup>), respectively,  $x$  corresponds to the mass of the PRM drawn through each tube measured by the Molbloc flowmeter (mg) and  $E_x$ , the correction factor, corresponds to the trueness of the Molbloc flowmeter. The bias related to the presence of air between the valve and the tube is defined in milligrams of the PRM.

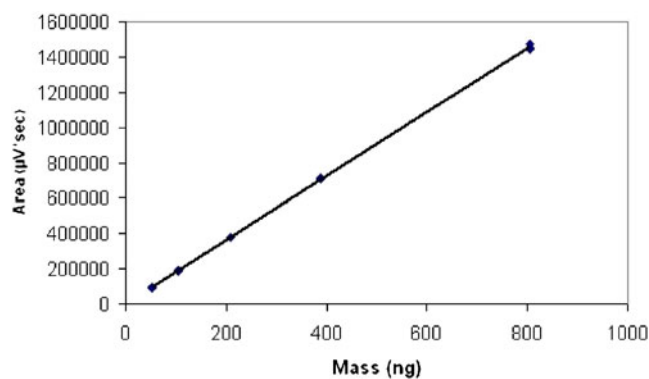
The mass of gas (PRM) drawn through each tube measured by the Molbloc flowmeter ( $x$ ) is calculated from the loading flow rate and the loading time. The uncertainties on the mass of benzene loaded on tubes were calculated using the uncertainty propagation law, from the *Guide to the expression of uncertainty in measurement* (GUM) [40] (Eq. 2):

$$u_{m_{ben}}^2 = \sum_{i=1}^N \left( \frac{\partial m_{ben}}{\partial x_i} \right)^2 \times u^2(x_i) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left( \frac{\partial m_{ben}}{\partial x_i} \right) \left( \frac{\partial m_{ben}}{\partial x_j} \right) u(x_i, x_j) \quad (2)$$

where  $u_{m_{ben}}$  is the standard uncertainty on the loaded benzene mass,  $m_{ben}$  is the mass of benzene contained on the reference tube (ng),  $x_i$  are the variables ( $C$ ,  $M_{ben}$ ,  $M_{N_2}$ ,  $x$ ,  $E_x$ ),  $u(x_i)$  is standard uncertainty associated with variables and  $u(x_i, x_j)$  is the covariance between the variables.

**Table 3** Loading parameters

Parameters	Value
Flow rate (mL min <sup>-1</sup> )	40±0.14
Time (min)	9.75±0.05
Benzene concentration of PRM1 (nmol mol <sup>-1</sup> )	364.34±0.73



**Fig. 4** Linear regression ( $y=1809.3x+2151.9$ ;  $R^2=0.9998$  determination coefficient) modelling the relationship between the mass of benzene loaded on tubes and the analytical response. Measurement was repeated three times for each level

The error related to the flowmeter is directly integrated into the mass calculation of benzene loaded on the tube. The expanded uncertainty ( $k=2$ ), corresponding to a 95% confidence level) obtained from the target mass of benzene deposited on tube is estimated to be within ±0.5%.

### Calibration

To carry out the quantitative analysis of benzene loaded on reference materials, the thermal desorption/GC system was calibrated. This calibration was performed using measurement standards prepared independently by sampling from the gas mixture (PRM2) onto conditioned Carboxpack X sample tubes: nine calibration standards (3×3 levels), spanning from 415 to 623 ng, to cover the target mass of CRMs.

For GC/FID analysis, the uncertainty on the analysed benzene mass is calculated according to the French technical specifications FD X 43-070-5 [41], derived from the GUM. The linear regression, the repeatability, the drift and the analytical standards are taken into account to evaluate the measurement uncertainty. Their contributions to the standard uncertainty are, respectively, 5.2, 31.5, 5.3 and 58.1%. Thus, analytical standards represent the major contribution to the standard uncertainty. The expanded measurement uncertainty ( $k=2$ ) was estimated as 3.6%.

### Results

Having developed and optimized the benzene loading procedure, we extensively tested the method to validate and to certify the gravimetric value of the reference material. In consequence, key parameters such as adsorption efficiency, linearity and measurement trueness were evaluated. Moreover, the homogeneity and the stability of a test batch of CRMs were also tested. Then, the CRM

**Table 4** Variance analysis

Source of variation	Square deviations	Degrees of freedom	Mean square	$F_{\text{observed}}$	$F_{(5\%)}$	$F_{(1\%)}$
Explained	$3.63671 \times 10^{12}$	1	$3.637 \times 10^{12}$	53560	4.96	10.04
Nonlinearity	$1.14361 \times 10^8$	3	$3.812 \times 10^7$	0.562	3.71	6.55
Residual	$6.78615 \times 10^8$	10	$6.786 \times 10^7$			
Total	$3.63750 \times 10^{12}$	14				

developed was used during proficiency testing conducted by seven French laboratories to verify its usability by various analytical laboratories.

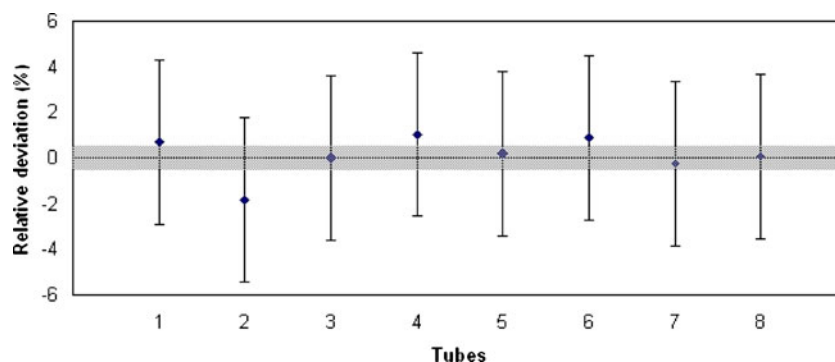
#### Adsorption efficiency

To evaluate the sorbent tube efficiency (to control if benzene was totally trapped onto the tube), two tubes connected in series were charged. Then, all tubes were analysed separately. These experiments were realized in triplicate. The quantities of benzene adsorbed on the first tubes in the series are in good agreement with the target value. Furthermore, the quantity of benzene analysed on the second tube placed just after the first tube was always below the quantification limit. So, we can state that benzene was quantitatively trapped on the first tube. Considering the sorbent and the flow rate chosen, this result was not a surprise, but this confirmation is key for the robustness of the method.

#### Linearity

As the objective of this work was to demonstrate the ability of this method to load tubes with a well-defined target value of benzene on tubes, the linearity of the loading method had to be checked. Fifteen measurement standards were loaded ( $3 \times 5$  levels) spanning from 52 to 805 ng to include the target mass (500 ng) of the CRM. The results obtained for the linearity testing are shown in Fig. 4.

**Fig. 5** Relative deviations calculated, from a batch of eight loaded tubes, between the mass of benzene adsorbed on each tube and the analysed ones. The grey area shows the uncertainty of the gravimetric value and error bars display analytical uncertainties



A statistical test of linearity, comparing explained and nonlinear variances to the residual variance (repeatability) was carried out. This comprises two steps:

- Validation of the linear regression (linear regression is validated if  $F_{\text{explained}} > F_{(1\%)}$ )
- Verification of the linearity of the response over the considered range (linear response is verified if  $F_{\text{nlm}} < F_{(1\%)}$ )

$F_{\text{critical}}$  values are obtained from the Fisher–Snedecor table risk  $\alpha=1\%$  (or 5%) and the degrees of freedom  $df_1$  and  $df_2$ . The variance analysis is given in Table 4.

According to the analysis of variance, the model is acceptable ( $F_{\text{explained}} > F_{(1\%)}$ ) and the response is linear over the range considered ( $F_{\text{nlm}} < F_{(1\%)}$ ). We can, hence, conclude that there is a linear relation between the measured area of the benzene peak and the target loaded mass. Indeed, the measured quantities of benzene are proportional to the value of benzene fixed on the tubes.

#### Measurement trueness

Ensuring the measurement trueness of analysis is a crucial step before large-scale production of any reference material. To do so, two primary standard gas mixtures of benzene were prepared independently (PRM1 and PRM2). Eight tubes with PRM1 and the PRM2 was used in the thermal desorption/GC-FID calibration.

As the masses of benzene loaded on the tubes are not always exactly the same, relative deviations were calculated. The relative deviation corresponds to the difference

**Table 5** Gravimetric value and analysed value obtained for eight loaded tubes

Tube	Gravimetric value	$U$ ( $k=2$ )	Analysed value	$U$ ( $k=2$ )
1	501.0	2.5	504.4	18
2	500.4	2.5	491.1	18
3	500.3	2.5	500.3	18
4	500.8	2.5	506.0	18
5	500.0	2.5	500.8	18
6	500.7	2.5	505.0	18
7	500.2	2.5	498.8	18
8	500.4	2.5	500.6	18
RSD (%)	0.1	–	0.9	–

RSD relative standard deviation

between the gravimetric value and the analysed value (AV), multiplied by 100 and divided by the gravimetric value (Eq. 3):

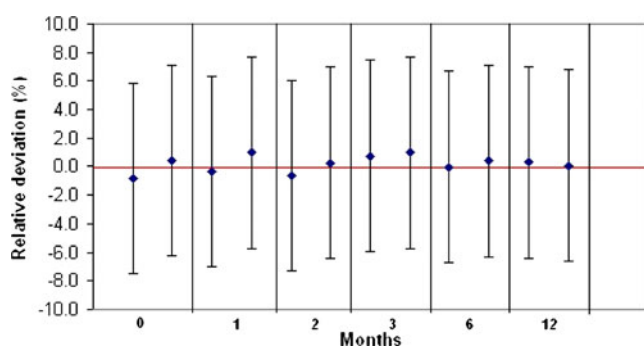
$$RD = \frac{(AV - GV)}{GV} \times 100, \quad (3)$$

where RD is the relative deviation, AV is the analysed value and GV is the gravimetric value. The closeness of agreement between the mass of benzene drawn through the tube, considered as the reference gravimetric value, and the analysed value was evaluated (Fig. 5).

All error bars overlap and include the  $x$ -axis, which corresponds to agreement between the gravimetric and the analysed values. For each loaded tube, the gravimetric value is not significantly different from the analysed value. As the loading and the analytical steps were performed with two independent PRM, the measurement trueness is established.

#### Batch homogeneity testing

Homogeneity testing of a production lot is of the highest importance for the certification of a reference material. Indeed, it should demonstrate the validity of the certified values and their uncertainties in the analysis of individual units. The aim of this test is to verify, on a reasonable



**Fig. 6** Relative deviation between the theoretical and analysed masses obtained during a stability study of 12 months

number of units, that all units of the CRM batch may be considered “identical” [42].

To evaluate the homogeneity of a test batch, eight Carbopack X tubes were loaded using the system described previously and analysed by the same protocol. They were prepared with a short time delay to realize as far as possible batch production.

The gravimetric value and the analysed value obtained for each loaded tube and their associated uncertainties for each tube as well as the relative standard deviations are given the Table 5.

For the gravimetric value, the standard deviation is less than 0.2%, which is lower than the estimated uncertainty (0.5%). And the analytical value, with an uncertainty of about 3.6%, has a standard deviation less than 1%. According to the estimated uncertainties, there is no

**Table 6** Analytical system and calibration method used by laboratories during the proficiency testing

Laboratory	Analytical system	Calibration method	Range
1	ATD/GC/ FID	Loaded tubes: liquid spiking	43–860 ng (5 levels)
2	ATD/GC/ FID	Loaded tubes: sampling from gas mixture	NS
3	ATD/GC/ FID	Loaded tubes: sampling from gas mixture	415–622 ng (3 levels)
4	ATD/GC/ MS	Loaded tubes: liquid spiking	220–660 ng (3 levels)
5	ATD/GC/ FID	Loaded tubes: liquid spiking (internal calibration)	NS
6	ATD/GC/ FID	Loaded tubes: sampling from gas mixture	49–687 ng
7	ATD/GC/ MS	Loaded tubes: sampling from gas mixture	50–750 ng (4 levels)

ATD automatic thermal desorption, MS mass spectrometer, NS none specified



**Table 7** Thermal desorption parameters used by participating laboratories for the analysis of benzene

Thermal desorption parameters		Laboratory 1	Laboratory 2	Laboratory 3	Laboratory 4	Laboratory 5	Laboratory 6	Laboratory 7
Primary desorption	Time (min)	25	15	20	20	10	15	10
	Tube temperature (°C)	400	400	400	375	280	400	400
	Trap temperature (°C)	-30	NS	-30	NS	-30	10	10
	Desorb flow rate (mL min <sup>-1</sup> )	50	NS	100	NS	NS	35	30
	Inlet split (mL min <sup>-1</sup> )	0	NS	19	NS	NS	0	0
Secondary desorption	Time (min)	NS	NS	20	NS	5	10	10
	Trap temperature (°C)	350	NS	325	NS	280	350	350
	Temperature gradient (°C s <sup>-1</sup> )	40	NS	40	NS	40	40	40
	Outlet split (mL min <sup>-1</sup> )	40	NS	37	NS	NS	10	5
Carrier gas		NS	NS	He	NS	NS	NS	He
Trap type		NS	NS	Carbopack B	NS	Tenax TA	Carbopack B	Carbopack B
Column pressure (psi)		32	NS	34	NS	NS	30.5	NS

statistical difference between the gravimetric and the measured values. These observations indicate that no inhomogeneity has been detected. The loading method allows the preparation of a homogeneous batch of reference material.

#### CRM stability testing

A stability study was conducted to ensure the stability of these materials over time, and especially to establish the dispatch conditions for these materials. For this purpose, 18 tubes of Carbopack X were prepared according to the protocol previously developed. Of those 18 tubes, six were used as blank samples and 12 tubes were loaded on the same day with a PRM of benzene ( $1.028 \pm 0.058 \mu\text{mol mol}^{-1}$ ). Then, after the loading phase described before, the tubes were hermetically closed with brass caps and PTFE ferrules, and stored at 4 °C.

According to previous studies, between 0 and 40 °C, the mass of compound adsorbed on tubes is not significantly influenced by the storage temperature [43]. Nevertheless, it was decided to store them at 4 °C to reduce the risk of pollution by other volatile organic contaminants.

Two loaded tubes and one blank tube, randomly chosen, were analysed on different dates during a period of 12 months. These three tubes were analysed in the same laboratory on the same day. All tubes were prepared and analysed at LNE to allow the study over a long time scale.

Calibrations were performed the day of the analysis by loading tubes at three different concentrations (358.2, 501.5 and 644.9 ng) repeated three times (nine tubes).

The results of the stability testing are represented by the relative deviations of different tubes according to time (Fig. 6).

No instability of the benzene reference material was detected after 12 months of storage. This study is still in progress.

#### Proficiency testing

##### Organization

Proficiency testing [44] aiming at the determination of the performance of seven individual laboratories for specific tests or measurements was recently conducted in France. During this campaign, the reference materials developed in this work were used to ensure that participating laboratories could make reliable measurements of benzene on Carbopack X cartridges. This large blind testing operation was also very useful to test the external consistency of the CRM and its conservation during the phase of its use (transport, storage, etc.). This study required the preparation of 49 Carbopack X tubes, following the protocol described earlier. Of those 49 tubes, seven were used as blank samples and 42 tubes were loaded with PSGM1 prepared gravimetrically at LNE. The target mass of benzene was around 500 ng. The tubes were sent at a temperature less than 4 °C. Each participating laboratory received a set of six loaded tubes and one unopened blank tube. Of these six loaded tubes, five were analysed by the participating laboratory and the last one was returned to the organizing laboratory (LNE). This tube allows the evaluation of the influence of transport on the tubes (benzene stability, locking system, transport temperature, etc.).

Seven laboratories (ATMO Picardie, Amiens, France; Ecole des Mines de Douai, Douai, France; Institut National de l'Environnement et des RISques, Verneuil-en-Halatte, France; Laboratoire Interrégional de Chimie, Schiltigheim, France;

**Table 8** GC parameters used by participating laboratories for the determination of benzene

GC parameters	Laboratory 1	Laboratory 2	Laboratory 3	Laboratory 4	Laboratory 5	Laboratory 6	Laboratory 7
Transfer line temperature (°C)	225	NS	220	NS	NS	250	250
Column type	NS	NS	VB-5 (methylpolysiloxane) (60 m × 0.25 mm × 0.25 µm)	NS	Rtx-1 (polydimethylsiloxane) (60m × 0.22mm × 0.2µm)	CP-Sil 5 CB	NS
Carrier gas (mL min <sup>-1</sup> )	NS	NS	He	NS	NS	NS	He
Temperature method	NS	NS	40 °C (8.5 min) 20 °C min <sup>-1</sup> → 80 °C (0 min)	NS	NS	35 °C (10 min) 5 °C min <sup>-1</sup> → 140 °C (0 min)	45 °C (10 min) 5 °C min <sup>-1</sup> → 140 °C (1 min) 15 °C
Detector parameters							
FID	NS	NS	250		NS	250 °C (3 min)	15 °C min <sup>-1</sup> → C min <sup>-1</sup> → 250 °C (3 min)
Temperature (°C)	NS	NS	250		NS	250	
H <sub>2</sub> flow rate (mL min <sup>-1</sup> )	NS	NS	45		NS	35	
Air flow rate (mL min <sup>-1</sup> )	NS	NS	450		NS	350	
MS				NS			NS

LNE, Paris, France; TERA Environnement, Crolles, France; and Université de Corse, Corte, France) participated in the proficiency testing.

Each participant had to specify in the report the analytical system, the calibration method, the analytical protocol used, the analysed values for each tube and the detailed calculation of uncertainties. Table 6 gives the analytical system and the calibration method used during the proficiency testing by participating laboratories.

All analytical systems were based on the same principle: gas chromatography. Only two of the seven participants used a mass spectrometer for benzene detection, and the others adopted a FID.

Different calibration methods were used by participating laboratories to analyse benzene reference materials. The method most often used was the loading of sorbent tubes with a standard gaseous mixture (laboratories 2, 3, 6 and 7). The other laboratories implemented liquid standard solutions to calibrate their analytical system, either by vaporizing the solution onto sorbent tubes (laboratory 1) or by vaporizing the liquid solution directly in the benzene reference material as an internal standard (laboratory 5).

Tables 7 and 8 give the thermal desorption and gas chromatography parameters used by participating laboratories. Unfortunately, all laboratories did not provide all the analytical parameters used.

## Results

No noticeable influence of transport on the mass of benzene loaded on sealed Carpack X tubes was observed. Indeed, no differences between gravimetric values and analysed values were found (Fig. 7).

There is no significant influence of transport on the mass of benzene trapped on the reference materials, except for the loaded tube of laboratory 1, and the analytical results obtained by this laboratory were statistically identical to the gravimetric value. Several

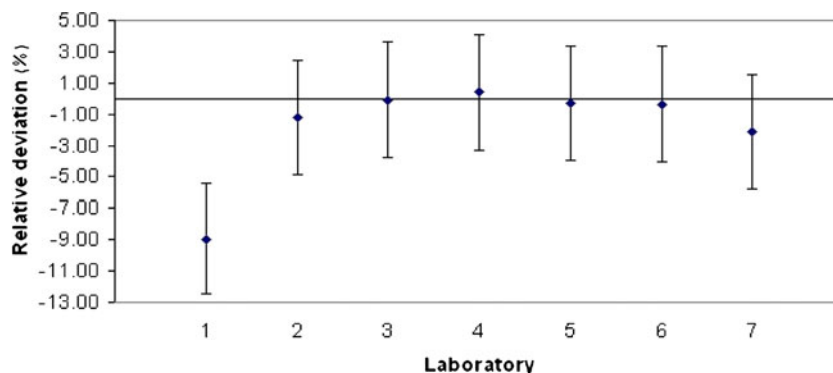
issues can explain this problem: no controlled-storage conditions, ill-conditioned tubes, etc.

The results obtained by the participating laboratories were then compared with the target value of benzene loaded on each tube. The mean mass of benzene was not calculated for each laboratory; each tube sent was considered independent, with a different mass of benzene. The relative deviation obtained by each laboratory for each reference tube is graphically represented in Figs. 8 and 9.

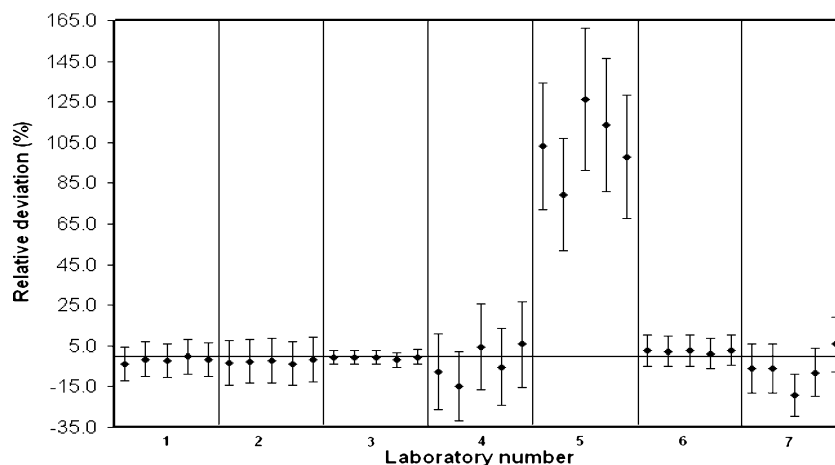
The error bars (confidence interval) displayed in Fig. 9 correspond to the expanded uncertainty calculated by each participant. For all laboratories, taking into account uncertainties, the analysed masses are equivalent to the gravimetric values, confirming the efficiency of the loading method developed. Only the laboratory 5 obtained important relative deviations up to 100%, in comparison with results obtained by other participants that are between 0.3 and 19%. An inappropriate calibration method (internal calibration), and a lower desorption temperature (280 °C) could explain the dispersion and the importance of the difference between the target value and the analysed value for laboratory 5. Furthermore, a dilution problem was revealed by this laboratory to explain the aberrant results obtained. To enhance the visualization of the results, the data for laboratory 5 are not shown in Fig. 9.

All uncertainty bars partly cover the *x*-axis (0% of relative deviation), which corresponds to agreement between the gravimetric value and the analysed value. Thus, the masses of benzene analysed by six of seven laboratories are statistically equal to the target values. Only laboratory 7 had an outlier result. The results obtained by laboratory 4 (maximum relative deviation 15%) and laboratory 7 (maximum relative deviation 19%) appear relatively scattered. An explanation could come from the detection method used by these laboratories. Indeed, they both used a mass spectrometry system for the quantification of benzene, whereas the other laboratories used FID devices. The signal dispersion of the mass spectrometer signal is higher than that of FID signals. So this may be the reason why the results of laboratories 4 and 7 are more scattered

**Fig. 7** Relative deviation between gravimetric values and analysed values for “transport tubes” during the proficiency testing



**Fig. 8** Relative deviation between gravimetric and analysed values obtained during the proficiency testing



than the results obtained by FID. Indeed, the FID appears to be suitable for this kind of analysis.

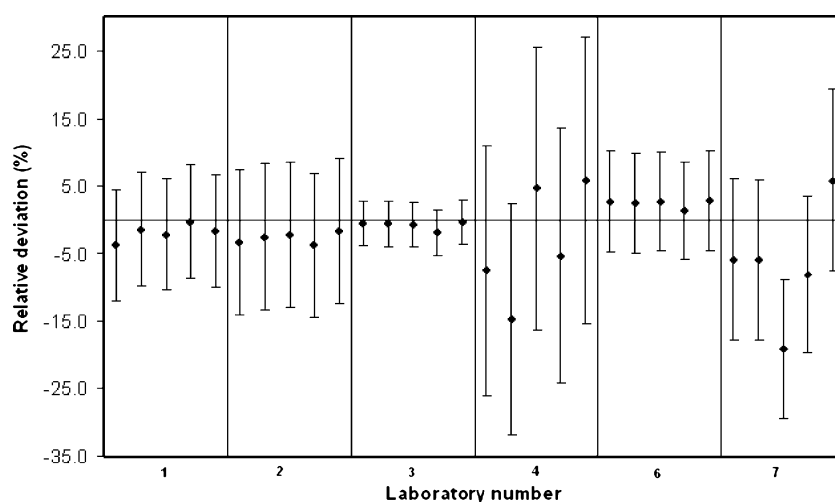
To estimate uncertainties on the analysed mass of benzene, the laboratories used the technical specification FD X 43-070-5 [31]. The sources of uncertainty identified by all participants include linear regression, repeatability, analytical drift and the desorption efficiency. Only laboratory 3 did not consider the efficiency of desorption as a source of uncertainty related to the mass of benzene analysed, because it was considered to have already been included in the linear regression. The handling of the tubes (losses of sorbent, losses of vapour or contamination) and the calibration are the major sources of error.

## Conclusion and perspectives

A whole gravimetric method has been developed to produce a CRM for the monitoring of benzene in air. The results

presented in this study demonstrate that a batch of Carbopack X tubes loaded with 500 ng of benzene can be prepared and analysed with a relative standard deviation lower than 1%, which is less than for other published methods for the production of reference materials of benzene commercially available. No instability was detected after 6 months of storage. These matrix reference materials were tested during proficiency testing, for which six of seven laboratories found good agreement between the gravimetric values of benzene loaded by the organizing laboratory and the masses of benzene analysed by the participating laboratories. These results confirmed the efficiency of the loading method developed. The results included the criteria of homogeneity, stability and accuracy, as required for a reference material. Besides, a European interlaboratory test will be performed to validate the outcomes obtained during this initial work. A reference material containing different VOCs monitored in ambient and indoor air is still under development for quality control

**Fig. 9** Relative deviation between gravimetric and analysed values obtained during the proficiency testing, except for laboratory 5



and for calibration of measurements. Some other projects are currently under way: feasibility studies of reference materials for aldehydes (formaldehyde) and NO<sub>2</sub>.

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