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Development of benzene, toluene, ethylbenzene and xylenes certified gaseous reference materials

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Abstract. The work describes the production of certified gaseous reference materials of benzene, toluene, ethylbenzene and xylenes (BTEX) in nitrogen from the gravimetric production up to the long term stability tests followed by the certifying step. The uncertainty in the amount fractions of the compounds in these mixtures was approximately 4 % (relative) for the range studied from 2 to 16 µmol/mol. Also the adsorption of the BTEX on the cylinder surface and the tubing were investigated as potential uncertainty source.

1. Introduction

Benzene, toluene, ethylbenzene, m-xylene, p-xylene and orto-xylene (BTEX) compounds can be released to the atmosphere through emissions from motor vehicles, cigarette smoke and oil and gas emissions. BTEX compounds are generated during the processing of petroleum products and also when paints, thinners, adhesives are produced. These compounds can cause damage to the health, since they may lead to lethal diseases such as lung cancer and therefore are classified as carcinogenic. They are monitored in the atmosphere though the World Meteorological Organization, Global Atmospheric Watch Program (WMO-GAW) [1]. These volatile organic compounds (VOCs) components need to be quantified in a high confidence level and the traceability to the International System of Units (SI) has to be assured. Therefore, the use of certified reference material is necessary for this purpose. These certified gaseous reference materials (CRM) are commercialized within various concentrations from some National Metrology Institutes (NMI) and companies with this type of expertise since they are indispensable in the analysis of gaseous media ranges [2,3,4].

BTEX in nitrogen reference materials are usually produced for environmental purposes at ppb range but there is also a demand for higher concentration standards, at levels that can be used in the case of occupational exposure.

The Brazilian NMI, National Institute of Metrology, Quality and Technology (Inmetro), has the knowledge and facilities on producing certified gas mixtures, both binary and multicomponent CRM [5]. However, for BTEX there is no gaseous reference material produced in Inmetro till now and since there is a demand for this CRM this study is very promising and will also help to reduce the importation costs.

These reference materials are usually commercialized in cylinders that have a special surface treatment to minimize wall adsorption. However, recent studies show that depending on the treatment used for the internal cylinder wall this can influence the final concentration of the mixture and has to be taken into account [6].

In the present work the development of a BTEX/N_2 certified reference material is presented and also additional testing to determine the magnitude of the losses due to adsorption.

2. Experimental

Before the gravimetric preparation of the mixture, the cylinder is cleaned by evacuation in a Pfeiffer turbo molecular pumping station followed by filling with high purity nitrogen (N_2) 99.9999 % mol/mol. New 5L aluminium gas cylinders treated with a proprietary process Aculife IV, by Scott Specialty Gases, were used. Before the actual preparation the clean cylinder was evacuated overnight. Afterwards, the empty cylinder is weighed in a mass comparator, Mettler balance, where it is compared against an identical (reference) cylinder. Then the pre-mixture with the BTEX components is transferred via a filling station to the empty cylinder. This process of weighing and filling is repeated for the matrix, N_2. Once the mixture is produced the final composition is calculated by using the added masses of each component that is expressed as mole fraction µmol/mol (ppm) according to ISO 6142 standard [7].

The BTEX in nitrogen mixtures (BTEX/ N_2) were prepared in the range of 2 to 16 µmol/mol from the dilution of a 50 µmol/mol BTEX/ N_2 certified reference material purchased from NPL (National Physical Laboratory). Finally, after the gravimetric concentration of the mixtures produced were determined, the value was validated by comparing it with other primary standards (5,10 and 15 µmol/mol), also purchased from NPL in accordance with the ISO 6143 standard [8]. The analytical method employed was Gas Chromatography by using a Variant GC-SP3800 equipment with a CP Sil-5 CB column, FID, helium carrier and with the following oven program:temperature: 60 ^{o}C, hold 1 min, 10 ^{o}C/min to 140 ^{o}C .

Afterwards, the long term stability studies were performed with five measurements during a period of 15 months after the production of the mixtures. After all the criteria are satisfied the mixtures can be certified. Finally, the certificate value is the gravimetric value and the uncertainty is the contribution of gravimetry, stability and analytical uncertainty.

For the additional tests that evaluate the influence of the cylinder surface treatment on the adsorption of BTEX compounds, a 6 µmol/mol BTEX/ N_2 was transferred to an evacuated cylinder. Gas transferring was performed twice and the mixtures were analyzed the next day, after being homogenized.

3. Results and Discussion

The gravimetric preparation data with the respective uncertainty is obtained by the Gas Metrology software and afterwards the analytical verification takes place to confirm these results.

In order to verify the mixtures produced, a lot of effort was done to optimize the analytical method since ethylbenzene and xylenes are challenging components.

The stability tests were performed with a 5 µmol/mol NPL standard along with the reference material candidates 2,4,6,10 and 16 µmol/mol showed that the difference between the NPL certificate value and the analytical one obtained for the standard is lower for benzene and toluene, while for the other components it was higher than 3% (table 1).

Table 1. The difference between the certificate value and the analytical value for a 5 µmol/mol standard used in the stability tests.

Component	Δ(%)
Benzene	-0.49
Toluene	0.11
Ethylbenzene	3.32
Meta + para - xylene	3.03
Orto-xylene	3.45

The reference material candidates are produced from the dilution of a 50 ± 1.5 µmol/mol standard performed in a filling station, so there could be some adsorption taking place in the line while transferring the gas mixture. In order to minimize this effect the use of extra heating of the line could help, since the pressure involved is high and some condensation could be happening due to the presence of needle valves that are used to reduce the flow, so the exact amount of gas can be introduced precisely into the cylinder. Despite the results observed in table 1, that show that improvement still has to be done, the final results for BTEX/N_2 certified reference materials were satisfactory since the verification and the stability criteria were attended. The final results for the uncertainty are shown on table 2, for gravimetry, verification and stability. Afterwards, the uncertainties are combined and will be presented on the certificate along with the corresponding gravimetric concentration for each component of the mixture. In the case of meta and para xylene, since the peaks cannot be separated with this type of column, they are shown together.

The certificate values of the BTEX/N_2 certified reference material are shown in table 3 and considering that the standard that originated this mixture has a 3% uncertainty the results show that the methodology applied is satisfactory and are in accordance with the gas standards [7,8].

Table 2. Uncertainty values of the BTEX/N_2 certified reference material.

Component	Uncertainty		
	Gravimetry (µmol/mol)	Verification (µmol/mol)	Stability (µmol/mol)
Benzene	0.089	0.065	0.009
Toluene	0.089	0.060	0.013
Ethylbenzene	0.089	0.058	0.007
Meta + para - xylene	0.130	0.158	0.008
Orto-xylene	0.089	0.058	0.008

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Table 3. The certificate value of the BTEX/N_2 certified reference material.

Component	Certificate value	
	Gravimetric concentration (µmol/mol)	Combined uncertainty, *k*=2(µmol/mol)
Benzene	6.01	0.22
Toluene	5.74	0.22
Ethylbenzene	5.80	0.21
Meta + para - xylene	12.21	0.41
Orto-xylene	5.84	0.21
Nitrogen	Balance	

Additional studies were performed to check if the surface treatment of the cylinder could have any influence on the final concentration of the BTEX/N_2 gas mixture. Transferring mixtures from a cylinder to another is a test that is reported by the recent literature especially for low concentrations [6]. The tests performed in this present work show that the BTEX loss averaged 0.4% for all the components after two transferring steps were done in cylinders that have never been used previously (figure 1).

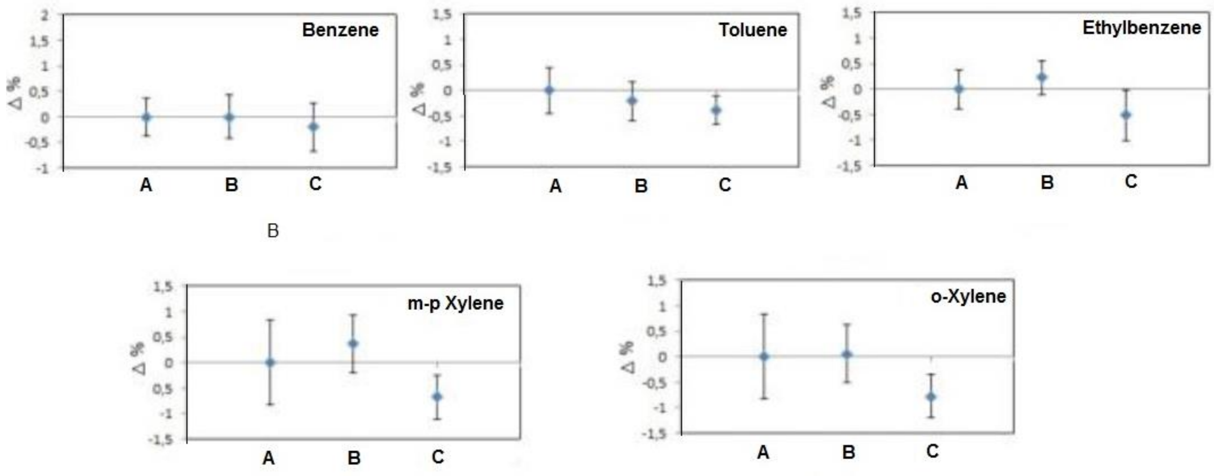

Figure 1.Plot of the delta obtained for the BTEX/N_2, 6 μmol/mol mixture after the transferring steps in the same type of aluminum cylinders, A, B and C (the bars are the relative standard deviation of the analysis).

Since the pressure value of the cylinders are decreasing after each transfer this could influence the results and future tests will be conducted to evaluate this influence before taking into account on the uncertainty budget.

4. Conclusions

The BTEX in nitrogen mixtures were produced and compared to the ones purchased from another NMI. The materials were certified obeying all the requirements.

Preliminary adsorption tests showed a 0.4%. loss of BTEX that can be influenced by the adsorption on the cylinder wall, on the tubing and valves during transferring and by pressure inside the cylinder. Future work is still needed to elucidate this effect and perhaps consider inserting it in the final uncertainty budget. Also studying other sources of loss and testing cylinders from gas vendors are needed.

References

[1] World Meteorological Organization (WMO) GAW Report No. 171: A WMO/GAW Expert Workshop on Global Long-Term Measurements of Volatile Organic Compounds, 2007.

[2] Słomin´ska M, Konieczka P, Namies´nik J 2010 Standard gas mixtures - indispensable reference materials in the analysis of gaseous media Trends in Analytical Chemistry 29 5 419-429.

[3] Grenfell R J P, Milton M J T, Harling A M, Vargha G M Brookes, C Quincey PG and Woods P T 2010 Standard mixtures of ambient volatile organic compounds in synthetic and whole air with stable reference values *Journal of Geophysical Research* **115** 1-16.

[4] Milton M J T, Vargha G M and Brown A S 2011 Gravimetric methods for the preparation of standard gas mixtures *Metrologia* **48** 121-129.

[5] van der Veen A M H *et al.* 2011, Supplementary comparison EURAMET.QM-S4: automotive gas mixtures *Metrologia* **48** Issue 1A, 08016.

[6] Miller W R, Rhoderick G C and Guenther F R 2015 Investigating Adsorption/Desorption of Carbon Dioxide in Aluminum Compressed Gas Cylinders *Anal Chem* **87** 1957-1962.

[7] ISO 6142:2001 - Gas analysis - Preparation of calibration gas mixtures - Gravimetric method,

International Organization for Standardization, Geneva, Switzerland.
[8] ISO 6143:2001 - Gas Analysis - Comparison methods for determination and checking the composition of calibration gas mixture.

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