Measurement standards for background levels of oxygen-containing volatile organic compounds

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Abstract

A range of oxygenated volatile organic compounds (OVOCs) is present in the atmosphere as a result of direct emissions and as products of atmospheric oxidation. Long-term measurements are important to understand changes to these emission sources and processes. Accurate and stable traceable gas standards are needed to underpin these results.

This work demonstrates equivalence of the primary standards held by the National Physical Laboratory, UK and the Van Swinden Laboratorium, the Netherlands.

Keywords: OVOCs, gas standards, atmospheric measurement, CMCs.

Introduction

The measurement of the amount fraction OVOCs is complicated by the polarity of these components and their ability to form hydrogen bridges. This bilateral comparison explored the feasibility of disseminating metrological traceability by means of gravimetrically prepared reference materials.

The stability of the travelling standard and adsorption losses in the gas standards were studied, and the results were included in the value assignment. VSL used a dynamic primary standard based on diffusion (ISO 6145-8) to study these effects, and the results were compared with the method of Scanlon and Willis used by NPL for the travelling standard.

Scope & Methods

The comparison was performed using a travelling standard at nominally $5\,\mu mol\,mol^{-1}$ for the three OVOCs. The standard was prepared using static gravimetry as described in ISO 6142-1. Both institutes assigned values to the travelling standard, and these results were compared. All pure materials were assessed for purity in accordance with ISO 19229. Prior to and after shipment, the composition of the travelling standard was verified against the primary gas standards of the respective institutes.

The stability of the travelling standard was studied throughout the comparison. A ratio method using a stable component (hexane) and gas chromatography with a flame ionisation detector was used for the assessment. The results of the stability study are shown in figure 3. The timing for the NPL (red dashed box) and VSL measurements (blue dotted box) are also indicated.

Stability assessment

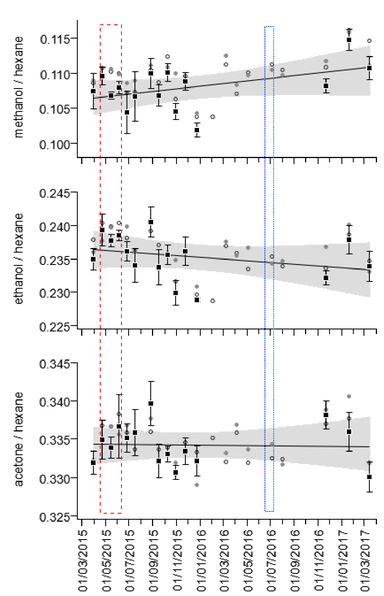

Figure 3: Stability assessment of the gas standard

Results

The results of the determination of the preparative losses are shown in figure 1. The losses decrease from methanol to ethanol to acetone. Both institutes developed a correction to account for these losses. The stability study results are shown in figure 3. The results demonstrate good stability of the used gas standard.

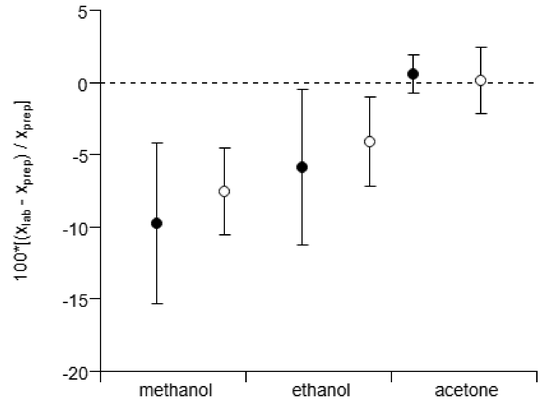

Figure 1: Calculated preparative losses for the amount fractions of methanol, ethanol and acetone (solid points: NPL; open points: VSL)

Figure 2 shows the differences between the results and the associated uncertainties of both institutes. The differences are small in relation to the stated expanded uncertainties. The results indicate that the adsorption effects have been well-recognised and addressed.

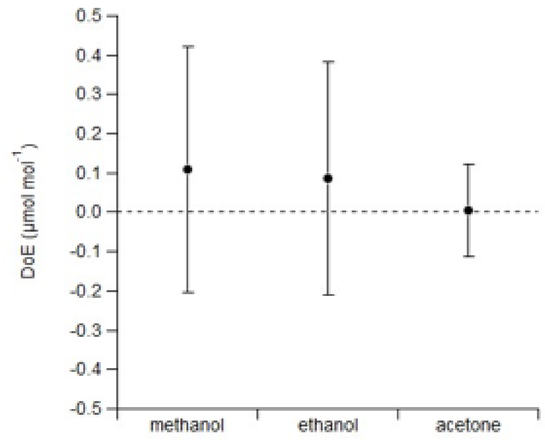

Figure 2: Differences and their expanded uncertainties for the amount fractions of methanol, ethanol and acetone

The expanded uncertainties for the amount fractions range from $0.33\,\mu mol\,mol^{-1}$ to $0.09\,\mu mol\,mol^{-1}$ for NPL and from $0.14\,\mu mol\,mol^{-1}$ to $0.10\,\mu mol\,mol^{-1}$ for VSL. The uncertainties for the amount fractions methanol and ethanol are generally larger, which is due to the fact that these components show the largest adsorption effects.

Conclusion

- The results of this bilateral comparison demonstrate agreement, within the stated expanded uncertainties, between NPL and VSL for methanol, ethanol and acetone.
- Adsorption losses in the cylinders decrease from methanol to ethanol and acetone.
- Recent advances in reducing adsorption losses are promising for realising gas standards at lower amount fraction levels.

References

[1] D. R. Worton, S. Moreno, P. J. Brewer, J. Li, A. Baldan, and A. M. H. van der Veen. Bilateral comparison of primary reference materials (PRMs) containing methanol, ethanol and acetone in nitrogen. *Accreditation and Quality Assurance*, jul 2022.

Future Work

The work presented here is pivotal for the international key comparison CCQM-K174 where similar travelling standards are used, but now with amount fractions in the range $100\,nmol\,mol^{-1}$ to $1000\,nmol\,mol^{-1}$ of methanol, ethanol and acetone in nitrogen.

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