

The manuscript entitled "Development of accurate and stable primary standard gas mixtures for global atmospheric acetonitrile monitoring: evaluating adsorption loss and long-term stability" by Tsogt et al. describes two approaches that were followed to develop primary standard gas mixtures (PSM) of acetonitrile at amount of substance fractions relevant for atmospheric monitoring. The lack of stable primary standards – mainly due to surface adsorption losses – is a common problem for many gas compounds (e.g., VOCs such as methanol and acetaldehyde among others), which compromises the comparability of data collected by monitoring networks. Therefore, this work will be an important metrological contribution to the monitoring community.

### General comments

The methods followed to prepare the primary standard gas mixtures are clearly described and the schematic provided increases the clarity of the preparation process. However, the manuscript will benefit from adding some relevant information and details regarding the standards *per se* (e.g., number of standards prepared in each type of cylinder) and the analytical methodology (e.g., GC/FID method followed: oven temperature ramps), as well as a broader discussion of the results found.

1. Are the produced primary standard gas mixtures traceable? If yes, to what? (e.g., traceability to the international system of units (SI), to KRISS). How was traceability achieved? This information is not detailed in the text, although in lines 47–49 the importance of SI-traceability is highlighted.
2. The number of cylinders used in this work should be clearly indicated. In the manuscript it is mentioned that three different types of cylinders were used but for the reader it is not clear if only one cylinder or several cylinders of each type were evaluated. It would be also helpful to provide information about the history of the cylinders: were they new cylinders or were they used previously for other compounds? If the latter, which compounds were present in the cylinders? Did the authors apply any conditioning procedure to the cylinders before the filling?
3. In the section materials and methods, it would be easier for the reader if subsections 2.1 'Materials' (lines 55–77) and 2.2.1 'Preparation of gas mixtures' (lines 78–90) are merged to one. As it is now, it is difficult to understand certain parts of the text, for example, why liquid reagents were selected and evaluated (lines 56-60). Presenting first 2.2.1 and then 2.1 will make the process clearer.
4. A more detail description of the gas mixtures analysis will contribute to the understanding of the results and to their reproducibility and reusability. Was the blank of the system assessed? What was the measurement sequence used? Was the GC/FID calibrated? How? How many replicates were measured of each sample? Were blanks measured within each measurement sequence? What was the GC/FID method used (e.g., oven temperature method: ramps, holding times...)?
5. Information about the way the uncertainty of the standards was estimated (e.g., uncertainty sources, model equations) should be included.
6. To improve the understanding of this work, the authors should consider to add the reasons why some of the tests were not performed on the three types of cylinders (e.g., line 139, line 145).
7. For comparison of the results among cylinders, it will be easier if the plots are presented with the same y-axis scale (e.g., Figure 2 (lines 116–117), Figure 1 (lines 130–131)).
8. In lines 196–199, the authors stated that they can disseminate acetonitrile calibration standards with an expiration period of at least 3 years. As it is described, it seems that the

expiration period applies to both standards (100 nmol mol<sup>-1</sup> and 10 μmol mol<sup>-1</sup>). However, in lines 192–193, it is indicated that the standard at 100 nmol mol<sup>-1</sup> in the Performax cylinder remained stable for 10 months. Some clarification and/or rephrasing might be needed.

9. The conclusions section would be more useful for the metrological and monitoring communities if instead of just summarising the findings of the work, some recommendations for further research to go forward with the gravimetry method for acetonitrile would be also added. For example, do the authors expect a different performance of the cylinders with the same treatment description but different valve material and/or coated valves? Do the authors have recommendations on potential passivation methods? Passivation is mentioned in lines 16, 128 and 168-169 but without giving details on the passivation method.

### Specific comments

1. Line 13: does the value 5 % refer to standard uncertainties or to expanded uncertainties?
2. Lines 35–36: what is special with 'remote marine atmospheres' regarding the incomplete and poorly constrained global budget of acetonitrile?
3. Information about the gas matrix of the PSMs (Line 61) should appear earlier in the text (abstract, Line 51).
4. Line 76–77: it would be good to have more information on the models and manufacturers of the elements of the KRISS gas filling system (or a reference where the system is described).
5. Figure 1 (between lines 88–90): the abbreviation ACN, which is used for the first time in the text, should be introduced in the caption of Figure 1. Adding a frame to the schematic of each method would make the separation between (a) and (b) clearer.
6. Lines 92–97: Missing information on the manufacturer of DB-1 capillary column. How many replicates of each gas mixture was analysed?
7. Equation (1): what was used as reference?
8. Equations (1) and (2): were the peak areas corrected by the system blank?
9. Lines 117-118: the meaning of the different colours (white, grey, black) should be added to the caption of Figure 2, as well as the meaning of 'RF'. Does the second y-axis on the top panel indicate also the normalized RF?
10. A reference or description of the cylinder-to-cylinder division method 29 (lines 120–121) should be added.
11. Line 130: the figure numberings should be revised (currently, there are two Figures 1 and none Figure 3). What is the explanation for the large uncertainty of the black triangle point? For comparison purposes, it would be good to plot also the results of the internal standard (hexane). In this figure, results for cylinders at 200 nmol mol<sup>-1</sup> are shown; it would be good if these cylinders are included in the schematic of Figure 1. Were these cylinders prepared by the conventional or the modified gravimetric method? Why were only the Performax cylinders used for the gas mixtures at 200 nmol mol<sup>-1</sup>? It would be good to add results of the untreated cylinders at 10 μmol mol<sup>-1</sup>.
12. Line 139: what is meant by 'little loss'? Can some figure be given (e.g., < 0.1 %)?
13. What are the x-axis labels of Figures 4–6? It would be good if the authors indicate that they refer to the cylinder number. Adding a table with the cylinder number, the type of treatment and the amount fraction of the cylinder might make the text and figures clearer.

## Technical corrections

Overall: missing space between numbers and '%'

Line 17: The hyphen used in the range (6%-49%) must be replaced by an en dash

Line 28: The character 'x' must be a subscript in  $\text{NO}_x$

Line 30: The digit 3 must be a subscript in the acetonitrile formula ( $\text{CH}_3\text{CN}$ )

Line 52: 'nmol/mol' and ' $\mu\text{mol/mol}$ ' must be written as  $\text{nmol mol}^{-1}$  and  $\mu\text{mol mol}^{-1}$

Line 53: The symbol 'k' must be introduced (coverage factor *k*) and its font style changed to italic.

Line 63: 'nmol/mol' must be written as  $\text{nmol mol}^{-1}$

Line 86: 'nmol/mol' must be written as  $\text{nmol mol}^{-1}$

Line 94: Missing verb in the sentence 'For  $\text{nmol mol}^{-1}$  GC/FID with a cryogenic (liquid nitrogen) pre-concentrator used. '

Lines 120–121: Missing space between 'method' and '29'

Line 121: 'nmol/mol' must be written as  $\text{nmol mol}^{-1}$

Line 143: the digit '-1' must be a superscript ( $\text{nmol mol}^{-1}$ )

Line 149: The font style of *RF* should be changed to normal for consistency.

Line 167: the digit '-1' must be a superscript ( $\text{nmol mol}^{-1}$ )

Figures 1 and 2: 'nmol/mol' and ' $\mu\text{mol/mol}$ ' must be written as  $\text{nmol mol}^{-1}$  and  $\mu\text{mol mol}^{-1}$