Development of accurate and stable primary standard gas mixtures for global atmospheric acetonitrile monitoring: evaluating adsorption loss and long-term stability.

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Abstract. Acetonitrile plays an important role in atmospheric processes and serves as a key tracer of biomass burning, the major emission source of primary carbonaceous particles and trace gases in the global atmosphere. Recognizing its

10   significance, the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) has designated acetonitrile as one of the target volatile organic compounds for global atmospheric monitoring, aiming for data quality better than 20% accuracy and 15% precision. Meeting the objectives of the WMO GAW program requires accurate and stable calibration standards with uncertainties of less than 5%. In this study, we explored the feasibility of gravimetry for developing primary standard gas mixtures (PSMs) in three different types of aluminium cylinders, each with distinct internal surface treatments,

15   at nmol mol^{-1} and µmol mol^{-1} levels with a relative expanded uncertainty of less than 5%. We found that all three types of cylinders were inadequate, without further passivation, for developing acetonitrile PSMs below 10 nmol mol^{-1} due to significant adsorption losses (6% - 49%) onto the cylinder's inner surface. To overcome this challenge, we prepared acetonitrile gas mixtures at 100 nmol mol^{-1} using a modified gravimetric method and at 10 µmol mol^{-1} using a conventional gravimetric method and then evaluated their long-term stability. Results showed that the effect of the adsorption loss at 100 nmol mol^{-1}

20   and 10 µmol mol^{-1} was negated and negligible, respectively. Stability results show that we can disseminate acetonitrile calibration standards at both 100 nmol mol^{-1} and 10 µmol mol^{-1} with a relative expanded uncertainty of 3% and 1%, respectively (with an expiration period of 3 years), meeting the target uncertainty of the WMO GAW program. Further research is still needed to develop accurate and stable acetonitrile calibration standards below 10 nmol mol^{-1} that are closer to atmospheric levels.

1 Introduction

Biomass burning is the largest source of primary fine carbonaceous particles and the second largest source of trace gases in the global troposphere (Akagi, 2011). It also emits a significant amount of short-lived global warming substances, such as volatile organic compounds (VOCs) and NOx, that significantly contribute to ozone formation through photo-chemical reactions (van der Werf, 2017; Chandra, 2020). These photochemical oxidants and fine particles can cause severe regional air

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30   pollution and also contribute to climate change (Ramana, 2010). Acetonitrile (CH3CN), predominantly released from bio-
mass burning, is relatively unreactive, but it plays an important role in atmospheric ion formation through its chemical reaction
with hydroxyl (OH) radicals (Brasseur, 1983; Yuan, 2010). Acetonitrile, with its relatively long atmospheric lifetime ranging
from 3 months to 11 months, has been used as a useful tracer of both controlled and uncontrolled biomass burning in many
research studies (Hamm, 1990; De Gouw, 2003; Singh, 2003; Murphy, 2010). The global budget of acetonitrile is incomplete

35   and poorly constrained due to the limited availability of in-situ measurement data on the atmospheric distribution, even in
remote marine atmospheres (Harrison, 2013). Monitoring its long-term trend is a useful way for analyzing changes in both
natural and anthropogenic acetonitrile emissions in the global atmosphere. Acetonitrile has been measured at various locations
and reported at pmol mol^{-1} levels (Sanhueza, 2001; Warneke, 2001; Sanhueza, 2004), but the measurement uncertainties are
too large to allow comparison between different studies and to gain new insights about its roles in atmospheric chemical and

40   physical processes. The World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) programme has
selected acetonitrile as one of the target VOCs that should be monitored in the atmosphere and set the objective of the data
quality as better than 20% accuracy and 15% precision (WMO, 2006). To achieve this objective, accurate and stable acetonitrile
calibration standards are required with a relative expanded uncertainty of less than 5% (Schultz, 2015). Several types of
calibration standards have been used to measure acetonitrile, including a diluted gas standard from a permeation source with

45   an uncertainty of ±25% (Singh, 2003; Lange, 2002), a standard gas mixture in a cylinder with uncertainties of ±25%
(Sanhueza, 2004) and a liquid solution standard (Zamecnik, 1987). However, the relatively large uncertainties of these
standards do not meet the WMO GAW requirements. Thus, an International System of Units (SI) traceable, accurate, and
stable acetonitrile calibration standard is essential for monitoring its concentrations and temporal and spatial variabilities and
thus understanding its roles in atmospheric processes and climate change. There are several methods, such as static gravimetry

50   (ISO, 2015), dynamic gravimetry (Brewer, 2011), and dynamic dilutions (Kim, 2016), for producing primary standard gas
mixtures (PSMs). This study investigates the feasibility of gravimetry for developing PSMs in three different types (i.e.,
different internal surface treatments) of aluminium cylinders at nmol/mol and μmol/mol levels with a relative expanded
uncertainty of less than 5% (a confidence interval of approximately 95%, k = 2).

2 Materials and methods

2.1 Materials

Both acetonitrile and hexane liquid reagents (Sigma-Aldrich, USA) were analysed to assess their purity using a gas
chromatograph with a flame ionization detector (GC/FID; 7890N, Agilent Technologies, USA) for VOC impurities and a Karl
Fischer coulometer (831 KF, Metrohm, Switzerland) for water impurities. The purity of the acetonitrile reagent was estimated
as 99.9458 cmol mol^{-1} with an expanded uncertainty of 0.0023 cmol mol^{-1} ($k = 2$). The purity of the hexane reagent was

60   calculated as 99.2672 cmol mol^{-1} with an expanded uncertainty of 0.0157 cmol mol^{-1}. No quantifiable acetonitrile was found
in the hexane reagent liquid. High-purity nitrogen gases (Deokyang Co., Ltd, Korea) were used as a diluent and were purified

through a purifier (Micro Torr, SAES Pure Gas, Inc., USA) to remove VOCs to less than 1 nmol mol^{-1}. The acetonitrile content in high-purity nitrogen gases was determined as half its detection limit (0.31 nmol/mol) with an expanded uncertainty of 0.18 nmol mol^{-1}. The acetonitrile and hexane liquid reagents were transferred into the cylinders using gastight syringes with a sample-lock termination fitted with a bevelled-tip stainless steel needle (Hamilton Company, USA). Each syringe was locked by a twist valve on termination, and its needle tip was capped with a septum to minimize the possible evaporation loss of liquid reagents during preparation. To determine the masses of liquid reagents transferred into cylinders, the syringes were weighed on an analytical balance (AT201, Mettler Toledo, Switzerland) with a capacity of 205 g and a resolution of 0.01 mg. To calculate the masses of nitrogen gases introduced into cylinders, the cylinders were weighed before and after gas filling, using a KRISS automatic weighing system equipped with a top-pan balance (XP26003L, Mettler Toledo, Switzerland) with a capacity of 26 kg and a resolution of 1 mg. Gas mixtures were prepared in three different types of 10 L aluminium cylinders (Luxfer, United Kingdom) with different internal surface treatments such as untreated cylinders with nickel chrome plated valves (Hamai, Japan) (here after referred to as Untreated), Experis-treated cylinders (Air Products, Belgium) with stainless steel valves (Rotarex, Luxembourg) (hereafter referred to as Experis), and Performax-treated cylinders (EffecTech, United Kingdom) with stainless steel valves (Rotarex, Luxembourg) (here after referred to as Performax). All gases were introduced into cylinders using a KRISS gas filling system that consisted of a Sulfinert®-treated stainless steel manifold, gate valves, a vacuum pump, and pressure gauges.

2.2 Methods

2.2.1 Preparation of gas mixtures

A set of gas mixtures was prepared using both the conventional gravimetric method (ISO, 2015) and the modified gravimetric method (Brewer, 2011) (Fig. 1.). Hexane, known to be stable in aluminium cylinders (Rhoderick, 2013; Brewer, 2019), was introduced together with acetonitrile to monitor the stability of acetonitrile in cylinders. In the conventional gravimetric method, an aliquot of a parent gas mixture was transferred to another new cylinder and then diluted with pure nitrogen to prepare gas mixtures at lower amount fractions (Fig. 1.a). In the modified gravimetric method, an aliquot remaining in a parent gas mixture after decanting was diluted with pure nitrogen which negates the effect of adsorption loss on the internal surface of cylinders (Brewer, 2019). Gas mixtures at 100 nmol/mol were prepared in both Untreated and Performax cylinders using the modified gravimetric method (Fig. 1.b).
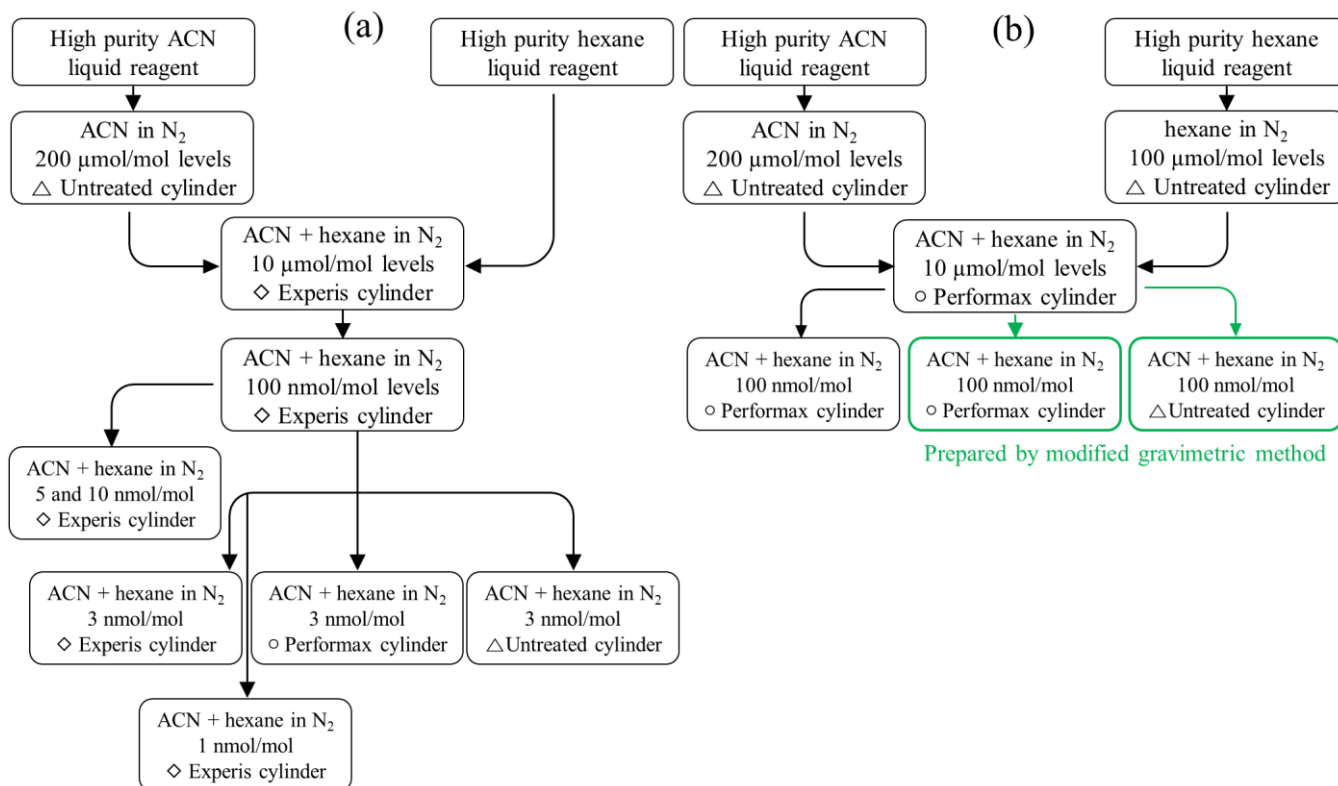
Figure 1. Schematic diagram of the preparation of the acetonitrile gas mixtures with the target amount fractions in specified cylinders, (a) by conventional gravimetric method, (b) by modified gravimetric method.

2.2.2 Analysis of gas mixtures

All gas mixtures at each dilution step were analysed against each other (the first one is typically used as a reference) for verification at μmol mol^{-1} GC/FID with a DB-1 capillary column (60 m length and 0.32 mm diameter with a 1 μm thick film) and 2 μL loop utilized. For nmol mol^{-1} GC/FID with a cryogenic (liquid nitrogen) pre-concentrator used. A sample gas at nmol mol^{-1} was cryogenically concentrated in a Sulfinert®-treated sample loop filled with glass beads. About a volume of 0.5 L sample was trapped in the loop and then injected into the GC/FID under the same conditions as μmol mol^{-1}. The sample inlet to the cryogenic pre-concentrator was described in more detail in a previous study by Kim (2018).

3 Results and discussion

3.1 Evaluation of gas mixtures less than 10 nmol mol^{-1} prepared using conventional gravimetric method

We assessed the consistency of gas mixtures at each dilution step by comparing normalized response factors (RFs) calculated following Eq. (1):

$$\text{Normalized } RF = \frac{RF_{sample}}{RF_{reference}}, \tag{1}$$

and the response factor (RF_i) determined by Eq. (2):

$$RF_i = \frac{GC \ peak \ area_i}{Gravimetric \ amount \ fraction_i}, \tag{2}$$

105   Here, RF_{sample} and $RF_{reference}$ represent the response factor of sample and reference, respectively. The uncertainties of response factors were estimated by combining uncertainties from GC analysis and gravimetric preparation. If gas mixtures are consistent, the normalized response factors should be consistent within their associated uncertainties (i.e., the normalized response factors should not be different from one within their associated uncertainties), considering a wide range of linearity of FID detectors. The normalized RFs of hexane in all cylinders agreed within the uncertainties (less than 0.5%) regardless of

110   cylinder types and amount fractions. However, the normalized RFs of acetonitrile showed inconsistency between cylinders with different treatments and even within cylinders with the same treatment (Fig. 2.). For example, in both Experis and Un-treated cylinders, the normalized RFs of acetonitrile differed by about 10% at the same amount fraction (3 nmol mol^{-1}) while those of hexane remained consistent. These results suggest that the inconsistency of acetonitrile resulted from cylinder characteristics (e.g., adsorption loss) concerning acetonitrile, rather than from the gravimetry preparation itself, as hexane in

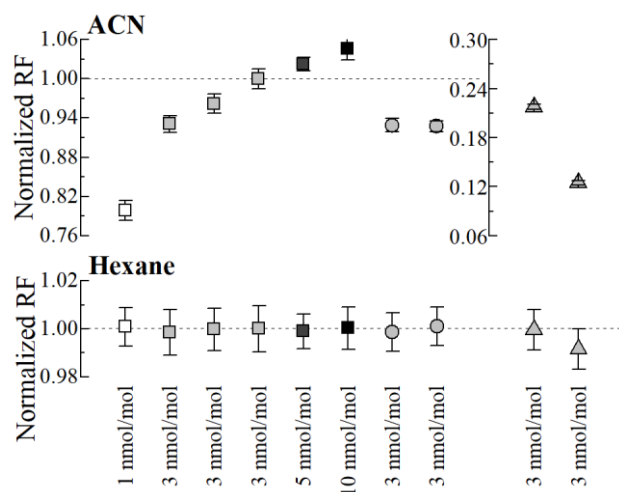115   the same cylinders showed good agreement.

Figure 2. Verification results of acetonitrile and hexane gas mixtures less than 10 nmol mol^{-1}. The error bars show expanded uncertainties (k = 2). The Experis (rectangle), Performax (circle), and Untreated (triangle) cylinders.

3.2 Evaluation of adsorption loss on the internal surface of cylinders

120   To estimate the adsorption loss of acetonitrile on the internal surface of the cylinder, we employed the cylinder-to-cylinder division method29 for 3 nmol/mol gas mixtures prepared in all three types of cylinders. The division method involved

transferring a gas mixture from one cylinder to another new cylinder. Ideally, the peak area ratio of acetonitrile in the two cylinders should be equal to one within analytical uncertainty, indicating little absorption loss. However, while the ratios of hexane remained equal to one for all cylinders, those of acetonitrile were notably lower, showing approximately 12%, 22%, and 98% decreases in peak areas in Experis, Performax, and Untreated cylinders, respectively (Fig. 3.). This suggests about 6%, 11%, and 49% loss of acetonitrile during its gravimetric preparation, primarily attributed to substantial adsorption on the internal surface of the cylinders. This significant loss describes that all three types of cylinders are unsuitable for preparing PSMs less than 10 nmol mol^{-1} without proper passivation of the internal surfaces to minimize adsorption loss.
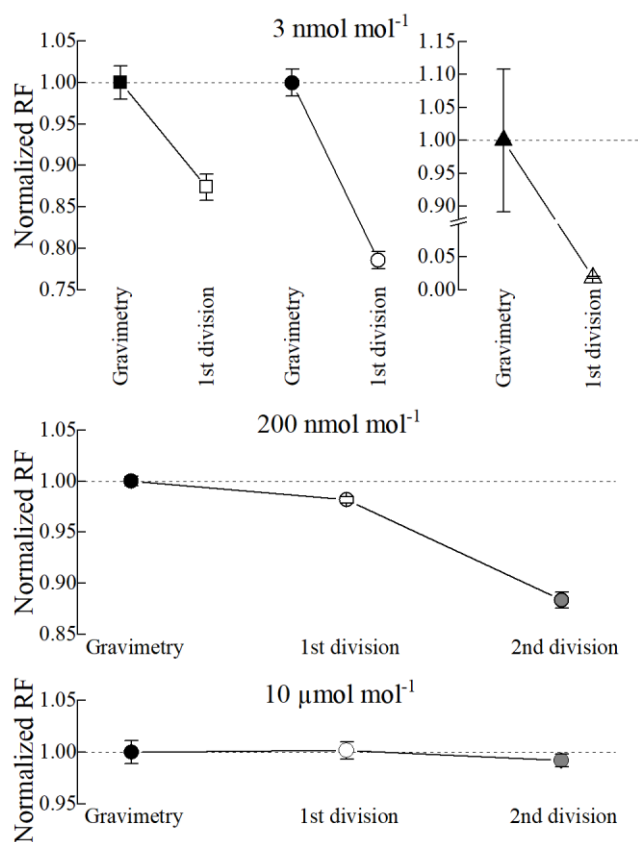
Figure 3. Adsorption loss results of acetonitrile at various amount fractions. The error bars show expanded uncertainties ($k = 2$). The Experis (rectangle), Performax (circle), and Untreated (triangle) cylinders.

Furthermore, we prepared additional gas mixtures exclusively in the Performax cylinders at 200 nmol mol^{-1}, about 70 times higher amount fraction than 3 nmol mol^{-1}, to evaluate whether the adsorption loss was negligible at such a higher amount fraction, given that acetonitrile at 3 nmol mol^{-1} in the cylinders was consistent despite its loss (Fig. 2.). However, we still observed about 0.9% (at first division) and 5% (at second division) adsorption loss of acetonitrile at 200 nmol mol^{-1}. While relative adsorption losses decreased compared with 11% at 3 nmol mol^{-1}, they were still larger than analytical uncertainties.

To further investigate, we conducted addition tests using 10 µmol mol^{-1} (more than 3000 times higher than 3 nmol mol^{-1}) gas mixtures in both Performax and Untreated cylinders. Results showed little loss for both acetonitrile and hexane in the

140   Performax cylinders, whereas approximately 1% to 2% loss of acetonitrile was observed in the Untreated cylinders. The results indicated that while the effect of the adsorption loss at 10 µmol/mol was nullified for acetonitrile in the Performax cylinders, it persisted in the Untreated cylinders.

3.3 Evaluation of gas mixtures at 100 nmol mol-1 prepared using modified gravimetric method

Acetonitrile gas mixtures were prepared at 100 nmol mol^{-1} in Performax cylinders using modified gravimetric method since

145   the effect of the adsorption loss was only nullified in the Performax cylinders at 10 µmol mol^{-1}. For comparison, two additional gas mixtures were prepared in Performax cylinders using the conventional gravimetric method. The consistency of four gas mixtures (i.e., two for each method) was evaluated by comparing the normalized *RF*s. Hexane exhibited consistency across all four cylinders with a relative expanded uncertainty of 0.5% ($k = 2$) regardless of the preparation method. However, acetonitrile showed consistency only within each method (Fig. 4.). Furthermore, the normalized *RF*s of the gas mixtures prepared using

150   the modified method were about 5% higher than those prepared using the conventional method. This discrepancy can be attributed to the fact that the modified method negated the adsorption loss on the internal surface of cylinders, unlike the conventional method. Thus, these results indicate that the modified method could be preferable for preparing acetonitrile PSMs at 100 nmol mol^{-1} rather than the conventional method.
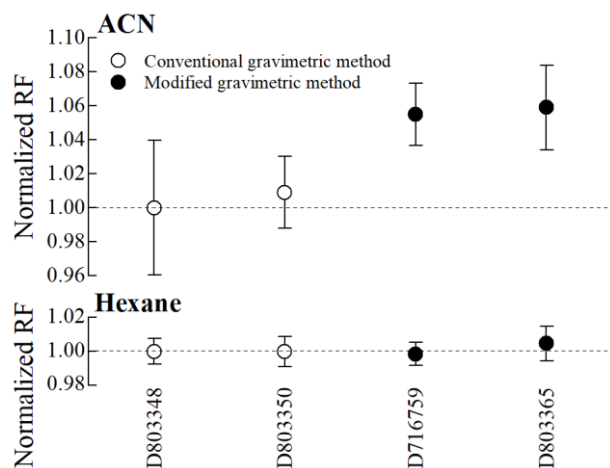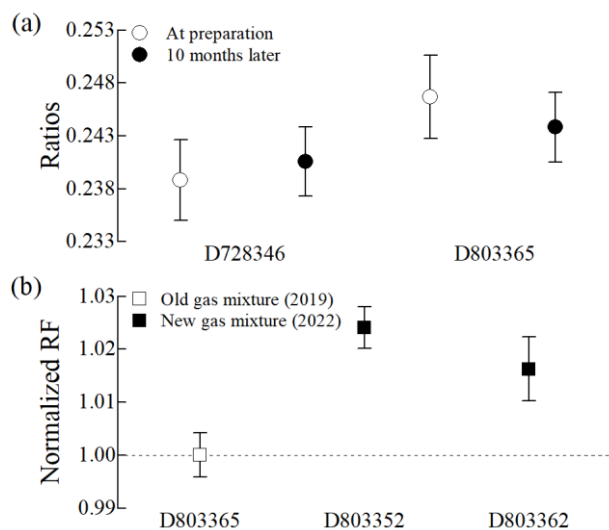

155   **Figure 4. Verification results of the 100 nmol mol^{-1} acetonitrile and hexane in Performax cylinders. Error bars show expanded uncertainties.**

3.4 Long-term stability of acetonitrile PSMs at 100 nmol mol^{-1}

When developing a PSM, ensuring its long-term stability is crucial for disseminating calibration standards and monitoring the long-term trend and the variability of acetonitrile in the atmosphere. Long-term stability was assessed for gas mixtures prepared

160   using the modified method through two approaches: comparing response ratios (i.e., peak area ratios) of acetonitrile to hexane in each cylinder for 10 months (Fig. 5.a) and comparing RFs of new cylinders to those of old cylinders over 3 years (Fig. 5.b). For the 10-month stability assessment, the response ratios of acetonitrile to hexane in each of two cylinders agreed within a relative expanded uncertainty of 2.2% ($k = 2$), indicating stable acetonitrile levels for 10 months (Fig. 5.a). In the case of the 3-year stability, two new gas mixtures prepared in 2022 were compared with an old gas mixture prepared in 2019. The

165   normalized RFs of acetonitrile in both old and new cylinders showed inconsistency within a relative expanded uncertainty of 0.6% ($k = 2$), with a difference of about 2.5%. This difference exceeded the analytical uncertainties, indicating a gradual decrease in acetonitrile levels at 100 nmol mol-1 in Performax cylinders over three years. Although the three-year stability of acetonitrile meets the target uncertainty (5%) of the WMO GAW programme, further studies (e.g., improved passivation methods) are necessary to develop more accurate and stable acetonitrile PSMs at nmol mol^{-1} levels.

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Figure 5. Long-term stability of the 100 nmol mol^{-1} acetonitrile in the Performax cylinders. (a) 10 month-stability (peak area ratios of hexane to acetonitrile); (b) 3 year-stability (RFs are normalized to that of an old gas mixture). Error bars show expanded uncertainties.

3.4 Long-term stability of acetonitrile PSMs at 100 nmol mol^{-1}

175   The results from the previous section indicated that the modified method effectively addressed the issue of adsorption loss on the inner surface of cylinders. However, despite this improvement, there was a gradual decrease in the amount fraction of acetonitrile at 100 nmol mol^{-1} (Fig. 5.b). To further assess the long-term stability, we evaluated the parent gas mixtures (10 µmol mol^{-1}) of 100 nmol mol^{-1} acetonitrile gas mixtures in Performax cylinders (Fig. 1.b) by comparing the RFs of new gas mixtures against an old one (D726463) to assess the three-year stability. The normalized RFs in all four gas mixtures (old and

180   new ones) were consistent within their associated relative expanded uncertainties of 0.90% ($k = 2$) (Fig. 6.). These results indicated that 10 µmol mol^{-1} acetonitrile in Performax cylinders remained stable for about three years.
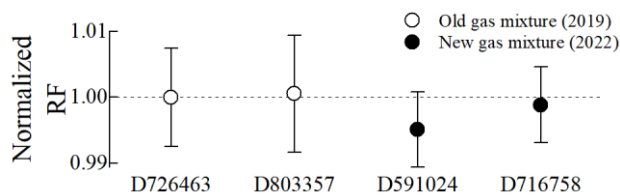
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Figure 6. Long-term stability of the 10 µmol mol^{-1} acetonitrile in the Performax cylinders. Error bars show expanded uncertainties.

4 Conclusions and outlook

185 To support global atmospheric monitoring and enhance our understanding of the atmospheric processes and the roles of acetonitrile in air quality and climate changes, we evaluated the feasibility of three different types of cylinders for preparing gravimetric gas mixtures and then developed acetonitrile primary standard gas mixtures (PSMs). This involved evaluating adsorption loss and long-term stability of acetonitrile in aluminum cylinders with different surface treatments at both nmol mol^{-1} and µmol mol^{-1} levels. Our study revealed that all three types of cylinders tested in this study were unsuitable for

190 developing acetonitrile PSMs below 10 nmol mol^{-1}, due to significant loss (from 6% to 48%) on the inner surface of cylinders during the preparations, unless further surface treatments are developed and applied. However, applying the modified gravimetric method effectively mitigated adsorption loss at 100 nmol mol^{-1}, resulting in good consistency among gas mixtures prepared in Performax cylinders, which remained stable for 10 months. Nevertheless, a subsequent stability study showed a gradual decrease (about 2.5% within less than three years after preparation) in acetonitrile levels with a decrease rate of

195 approximately 0.9% per year. On the other hand, for 10 µmol mol^{-1} acetonitrile gas mixtures in Performax cylinders, we observed little adsorption loss, good consistency, and long-term stability, making them suitable as PSMs. Based on these findings, we can disseminate acetonitrile calibration standards at 100 nmol mol^{-1} with a relative expanded uncertainty of 3% (meeting the target uncertainty of the WMO GAW programme), and at 10 µmol mol^{-1} with a relative expanded uncertainty of 1% with an expiration period of at least 3 years for global atmospheric measurements. However, it is important to note that the

200 amount fractions of acetonitrile calibration standards that can be disseminated are much higher than atmospheric levels, particularly in remote background areas. Therefore, further studies are still needed to evaluate alternative methods such as dynamic dilution, permeation, and dynamic gravimetric methods to generate accurate and stable acetonitrile gas mixtures at levels below 10 nmol mol^{-1}, closer to atmospheric concentrations.

205 ***Author contribution.*** SL and JHK designed the experiments and JHK and BT carried them out. BT prepared the manuscript with contributions from all co-authors.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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