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D4 “Good practice guide on the handling and use of static HCl reference materials for end users, including a full uncertainty budget for providing the infrastructure to underpin the measurements of these priority AMCs (HCl, NH_3 and water vapour)”

Organisation name of lead partner for the deliverable

VSL

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Metrology for Airborne Molecular Contaminants II

The metrological community has made significant progress in the development of static reference materials for gases for use in sectors like industry, environment, or energy. For instance, complex natural gas mixtures with state-of-the-art uncertainties have been developed already more than 20 years ago [1]. Several key comparisons have demonstrated next to the preparation skills also the analytical skills of the labs in this area.

In contrast, for the highly reactive compound HCl the gas metrology is still at its infancy while there exists a large need for HCl reference materials, -not only semiconduction industry (HCl is a major airborne molecular contaminant)-, but also for emission monitoring. Within the framework of the MetAMC II project both VSL and NPL have developed static reference materials for HCl at amount fractions of 10 µmol/mol and 1 µmol/mol in a nitrogen matrix. This guide gives guidance on the use of static HCl reference materials as it can take a considerable amount of time (30 minutes or more is typical) before an analyzer provides a stable response when analyzing HCl from a cylinder at such amount fractions.

Contents

1. Introduction

Based on the information collected in A2.1.1 – A2.1.3, this good practice guide gives directions on the handling and use of static hydrogen chloride (HCl) reference materials for end users, including a full uncertainty budget for providing the infrastructure to underpin the measurements of this key airborne molecular contaminant (AMC). It includes information on the types of materials and devices required to sample the reference gas and a range of parameters, such as flow and cylinder pressure, that are required for optimum accuracy.

Information on the HCl gas standards developed by VSL and NPL can be found in section 4. In summary:

- VSL has developed stable HCl mixtures at 10 µmol/mol with a 1 year stability better than 2% within the framework of the MetAMC II project (see subsection 4.1).
- NPL has developed HCl mixtures at 10 µmol/mol with a 1 year stability estimated to be 4% (see subsection 4.2).

While the information given in this guide focuses on HCl, it is also to a large extend applicable to ammonia and in lesser extend to water (for the latter some of the materials like polymers are not suitable).

2. Handling of static HCl reference materials

2.1. Identification of key parameters

Within the framework of the MetAMC II project VSL and NPL have developed static reference materials for HCl at the 10 µmol/mol and 1 µmol/mol in a nitrogen matrix. HCl is a very reactive gas. As a result of this reactivity, it can take a considerable amount of time (30 minutes or more is typical) before an analyzer provides a stable response when analyzing HCl from a cylinder at these amount fractions. Figure 1 shows a typical measurement at VSL of two cylinders analyzed using a Pro-CEAS HCl analyzer from AP2E.

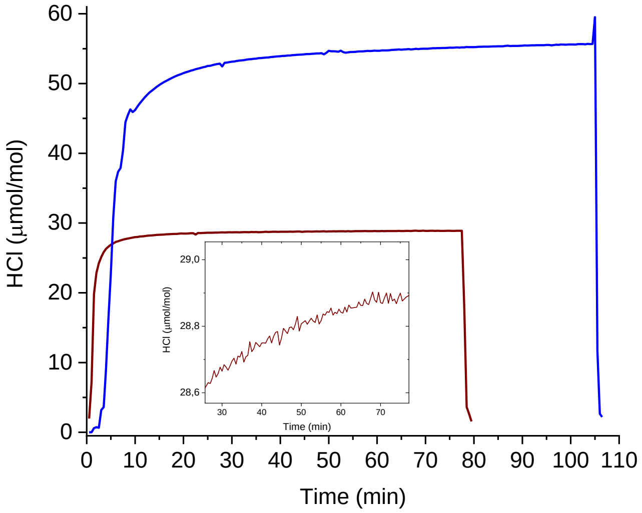

Figure 1 Measurement of 2 cylinders with certified amount fractions of 30.4 ± 0.5 µmol/mol (—) and 56.1 ± 0.5 (—) µmol/mol. The inset show in more detail that the analyzed amount fraction keeps increasing till at least 60 minutes after start of the analysis.

Besides the intrinsic HCl reactivity, several other factors determine the stabilization time. Figure 2 provides a schematic overview of the main factors influencing the response time when analyzing a static HCl gas mixture. The system is split in 3 separate parts: cylinder, sampling system and analyzer (note that the pressure regulator could also be thought of as part of the sampling system).

2.2. Identification of key parameters

Correct choice of materials is one important aspect. This holds for the pressure regulator, sampling system as well as the analyzer itseld. For example in deliverable D1 [1] and in [3] it has been shown that for use as sampling lines, many polymers (e.g., PVDF and PTFE) and certain coated metals (Silconert 2000 coated stainless steel) provide minimal adsorption losses. In contrast, HCl strongly adsorbs on stainless steel and several other metals and such untreated metals are therefore less suitable.

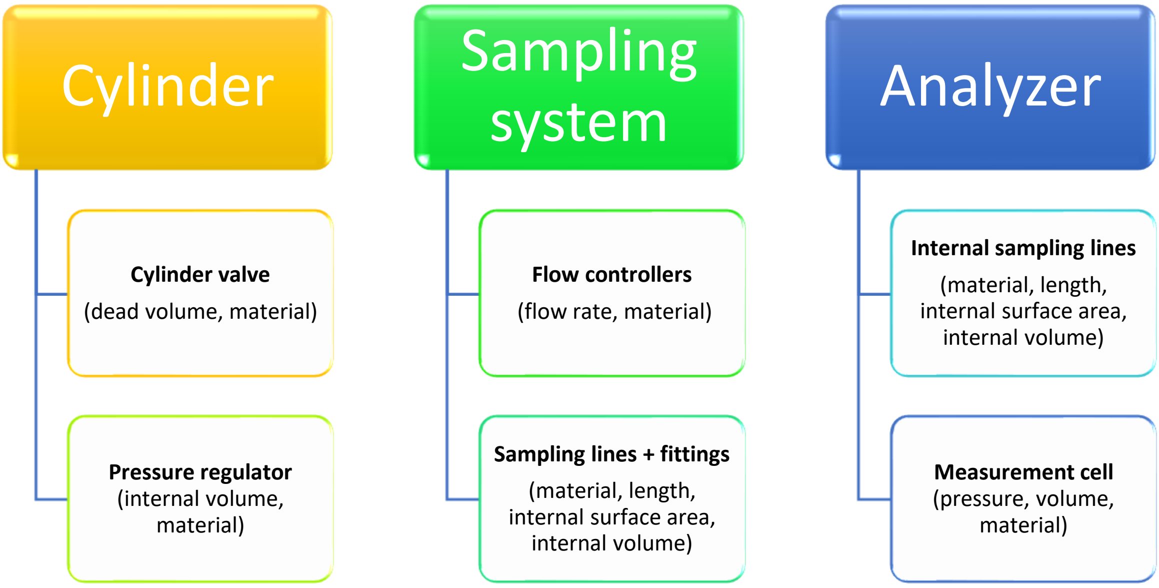

Figure 2 Schematic overview of the main factors influencing the response time when analyzing a static HCl gas mixture.

Even with the use of the best available materials, short sampling lines and sufficiently high flow rates, the response time is long when analyzing low amount fractions of HCl from cylinders. At VSL it was observed that when analyzing HCl at comparably low amount fractions generated by permeation using a magnetic suspension balance, the response time is much shorter, using the same sampling system and HCl analyzer as for the cylinder measurements. This result indicates that the long response time is in this case due to either the cylinder valve (see Figure 3 for a typical example) or pressure regulator. Coated pressure regulators were employed (SilcoNert 2000 treated) and in a separate test it was shown that HCl does not significantly adsorb on or react with the pressure regulator. Therefore, it can be concluded that the cylinder valve is the main factor determining the slow response. Such cylinder valves probably cannot be coated as parts rotate with some friction which would ruin the coating. However, selection of valves with minimal internal volume might help to optimize the response time.

Figure 3 Typical stainless-steel cylinder valve

While the user cannot do something about the valve of the cylinder there are other measures (s)he can take to speed up the response time. One option is to purge the system as described in detail in section 2.3. Further key measures that can be taken are described in section 2.4.

2.3. Removal of residual ambient water vapour: purging

The ambient atmosphere is an omnipresent source of water vapour that can contaminate a measurement system and modify its properties, especially in the case of reactive/hygroscopic compounds such as HCl. Measurements of dry (< 20 nmol/mol H_2O) HCl in nitrogen, performed at NPL, have shown the importance of removing residual water vapour from the measurement system and also preventing the subsequent ingress of water into the system when measuring newly connected samples. Figure 4 shows the stark contrast in rise time between two different measurements of mixtures of the same nominal amount fraction but different sampling procedures. The time series in blue involved repeated purging of the regulator subsystem, via subsequent pressurising and depressurising of the regulator, with the waste bypassing the sampling/measurement system (which was maintained under a flow of compressed air, acting as a “zero” gas), before the sample flow was admitted. For the red time series, the regulator was not purged before the sample was opened to the measurement system meaning that the initial flow of the HCl mixture contained wet atmospheric air, resulting in a tortuously slow increase in HCl signal, which failed to stabilise during a 6 hour measurement period. Indeed, during the same elapsed time of the purged regulator, multiple measurements were made, including a separate sample.

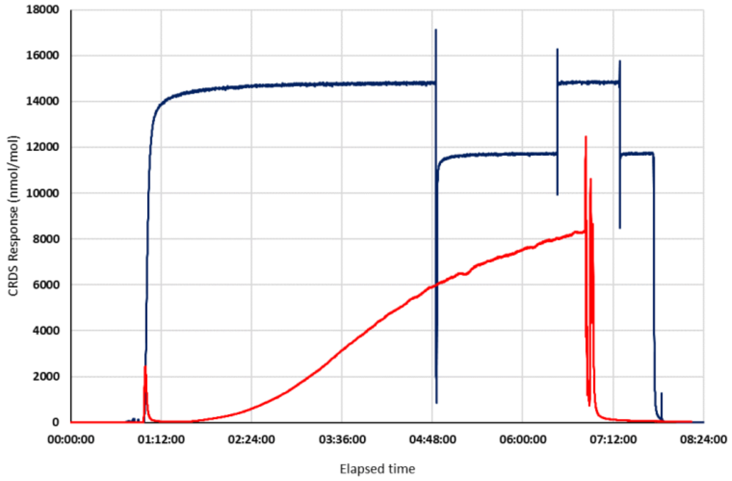

Figure 4 Comparison of rise times using a purging procedure (blue time series) and not using any purging (the red time series). The blue time series clearly shows the advantages of purging ambient air from the regulator before allowing it to pass through the measurement system.

In addition to removing the ambient water vapour, preconditioning of the regulator with HCl is also advised with at least the same nominal amount fraction as the sample mixture or higher. At NPL the drying/preconditioning of the regulator has been performed at the same time using dry HCl mixtures. Once a regulator has been conditioned for measurements of dry HCl mixtures, it is important to keep the regulator conditioned with HCl and prevent ambient moisture from entering when changing over to new sample cylinders, as highlighted in Figure 5 and Figure 6, below.

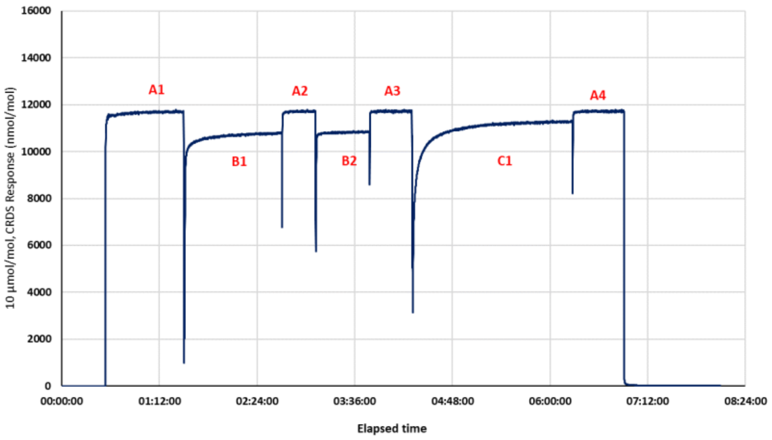

Figure 5 Time series data of HCl measurements of three different mixtures (A, B & C) at ~10 µmol/mol. Measurements A1, B1 and C1 are the initial measurements of each mixture and labels > 1 represent repeat measurements. Please refer to the text for more details.

A1 represents the rise/stabilisation time of the measurement system using a preconditioned/passivated regulator (i.e. the stabilisation time of the sample line and analyser only) and A2-4 are repeat measurements of the same mixture. B1 represents the rise/stabilisation time of a preconditioned regulator that has been purged thoroughly between the cylinder valve and the stem (i.e. the dead volume), through the regulator to waste (bypassing the sample line), and also the sample line itself. B2 is the repeat measurement of mixture B. Finally, C1 is the measurement of mixture C using the same regulator as for mixture B but only the dead volume between the cylinder valve and regulator was purged. It can be seen that the time taken to passivate the sampling line and analyser (A1), is less than the other initial measurements of B and C (B1 and C1 respectively), implying that the stabilisation time is affected most when a new connection has been made to the measurement system, via a cylinder and regulator. This is supported further by the repeat measurements of mixtures A and B, which show considerably shorter stabilisation times. Furthermore, the differences between B1 and C1 show that thorough purging of the entire regulator system has an effect on the stabilisation time, and that purging the dead volume only (as in C1) may not be enough to remove the residual water vapour being purged. However this effect could be due to the regulator being purged less times in total in C1, compared to B1, but demonstrates that the amount of purging between the cylinder valve and sample line (via the regulator) determines the overall stabilisation of the measurement system (and amount of gas required for a measurement).

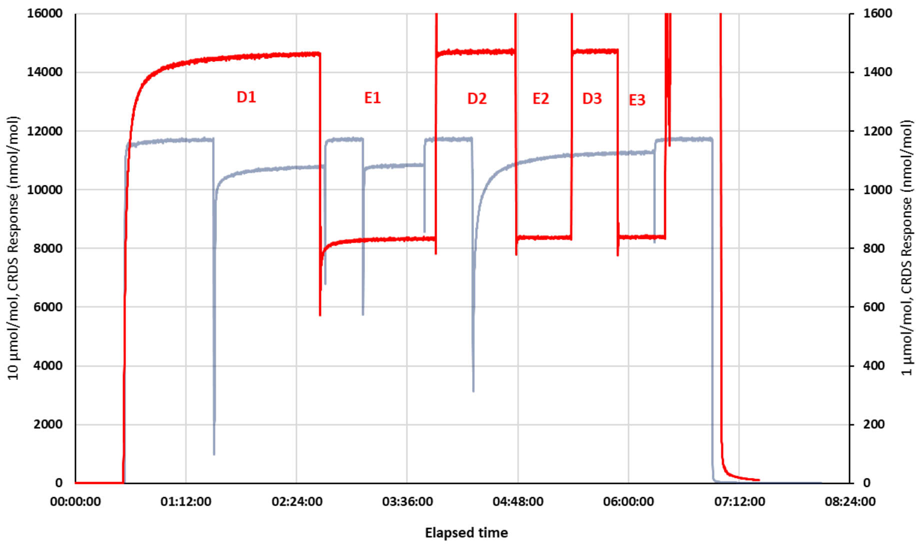

Figure 6 Time series data of HCl measurements of two different mixtures (D & E) at ~1 µmol/mol (red time series, right hand y-axis). Measurements D1 & E1 are the initial measurements of each mixture and labels > 1 represent repeat measurements. The light blue time series (left hand y-axis) is the data from Figure 5, for reference. Please refer to the text for more details.

The time series data shown in the Figure 6 compares the stabilisation times encountered between measurements of nominally 10 µmol/mol (light blue trace, left-hand *y*-axis, same data from Figure 5) and 1 µmol/mol (red trace, right-hand *y*-axis) reference materials. D1 represents the initial HCl stabilisation time of a thoroughly purged regulator and dried (*via* a constant flow of dry nitrogen, H_2O < 20 nmol/mol) critical orifice dilution system, and D2 and D3 are repeat measurements of mixture D. E1 is the initial run of a nominal 1 µmol/mol HCl mixture via a preconditioned and thoroughly purged regulator (similar to B1 in Figure 5), and E2 and E3 are the repeat measurements. The longest stabilisation time is D1 which is attributed to the larger internal volume/wetted surface (which have also yet to be conditioned with HCl) from the dilution system. The figure shows that differences in the initial stabilisation time experienced between mixtures of HCl are similar, over the range 1-10 µmol/mol HCl, when comparing D1 and B1 (Figure 5). This data also show that effective purging can also allow for a greater number of repeat measurements (if the measurement is time limited) since once the initial measurement has stabilised, the repeat measurements are quicker to stabilise, even at 1 µmol/mol.

In summary, measurements at NPL have shown that once suitable materials have been chosen for the sampling/measurement system, purging has been the most significant factor in making repeatable measurement of HCl mixtures between 1-10 µmol/mol. Purging the between the cylinder valve and regulator has been found to greatly reduce the initial stabilisation time (and therefore gas consumption) and reduced the “drift” (*i.e.* slowly increasing signal as the system has not fully stabilised) of subsequent repeat measurements so that both day-today measurements (over a 2 month period) and within-day reproducibility (data from Figure 6) of better than 0.5 % have been obtained. If the measurement period does not allow for stabilisation of the signal i.e. constraints through measurement time and/or gas consumption, the measurement will give a lower limit of the measurement value [6]. Therefore, an uncertainty component that takes into account the stabilisation of the measurement system must be included into the uncertainty budget of the measurement result.

2.4. Measures to optimize the analysis of static HCl gas mixtures

The user can take several measures to speed up the analysis. Faster analysis not only saves on cost of the gas use but also enables to do more analyses per day. Recommended measures for HCl analysis are:

1) Use of only coated materials and polymers. Also flow controlling devices like mass flow controllers should be coated.
2) Use a sampling system with short sampling lines and small internal volume.
3) Use of a gas analyzer with internally coated or polymer materials. The internal cell volume should also be minimal and/or operate at reduced pressure and above ambient temperature.
4) Use a sufficiently high flow rate (order of 0.5 L/min).
5) Before analyzing the cylinder under test, pre-condition the system with a somewhat higher HCl amount fraction than of the cylinder under test.
6) When making a new connection between a cylinder valve and regulator: the regulator must be purged thoroughly (via pressurizing the dead volume and then depressurizing it, multiple times) to remove as much ambient water vapour from the wetted surfaces of the regulator before opening it to the sampling/measurement system. Once a regulator has been sufficiently purged and is leak tight, avoid disconnecting it from the cylinder, unless necessary, to avoid reintroducing water vapour.

Another, somewhat more complex, option might be to add an extra compound to the gas flow that actively passivates the system. This could be something as simple as H_2O (see e.g. [5] for a study done on ammonia but for HCl similar effects have been reported by VTT when using the Hovacal to generate low HCl amount fractions) while other users have successfully applied more exotic compounds like nonafluorobutanesulfonic acid (NFBSA) to speed up the HCl response time [4]). Note that potential interference by the added compound on the analyser/measurement system should be investigated.

Using the 6 recommendations listed here and using a good analyzer, a reproducibility of the measurements in the order of 0.5% can be obtained for analysis of HCl cylinders at 10-100 µmol/mol level.

3. References

1. van der Veen, A. M., Nieuwenkamp, G., Zalewska, E. T., Li, J., de Krom, I., Persijn, S., & Meuzelaar, H. (2020). Advances in metrology for energy-containing gases and emerging demands. *Metrologia*, *58*(1), 012001.
2. MetAMC II deliverable D1: Summary report describing the results of the study into current state-of-the-art spectroscopy methods, materials research for the effects on physical instrumentation in the presence of HCl, and investigations into determining the optimal spectral windows for HCl and water, including the availability of laser sources (window already established for NH_3)
3. http://empir.npl.co.uk/metamcii/wp-content/uploads/sites/43/2019/11/Sampling-lines-for-HCl-measurements.pdf
4. Halfacre, J., Edwards, P., Herndon, S., Roscioli, J., Dyroff, C., Yacovitch, T., ... & Brown, S. (2020, May). A novel spectroscopic approach for detection of chlorine reservoir species: HCl-TILDAS. In *EGU General Assembly Conference Abstracts* (p. 16783).
5. Vaittinen, O., Metsälä, M., Halonen, L., Persijn, S., Leuenberger, D., & Niederhauser, B. (2018). Effect of moisture on the adsorption of ammonia. *Applied Physics B*, *124*(9), 1-8.
6. Flores, E., Viallon, J., Moussay, P., & Wielgosz, R. I. (2013). Accurate Fourier Transform Infrared (FT-IR) Spectroscopy Measurements of Nitrogen Dioxide (NO_2) and Nitric Acid (HNO_3) Calibrated with Synthetic Spectra. *Applied spectroscopy*, *67*(10), 1171-1178.

7. Brewer, P. J., Brown, R. J., Mussell Webber, E. B., van Aswegen, S., Ward, M. K., Hill-Pearce, R. E., & Worton, D. R. (2019). Breakthrough in Negating the Impact of Adsorption in Gas Reference Materials. *Analytical chemistry*, *91*(8), 5310-5315

4. Appendices

4.1. Uncertainty from handling trace HCl reference materials (VSL)

4.1.1. Uncertainty HCl reference materials developed by VSL

Within the framework of the MetAMC II project, at VSL HCl reference materials have been prepared using gravimetric methods at 1 µmol/mol and 10 µmol/mol in a nitrogen matrix. For both amount fractions 2 different cylinder treatments were used (here called treatment 1 and 2) and 4 replicates per concentration and cylinder treatment were used (so in total 16 cylinders). All cylinders had a water volume of 10 L.

Cylinders at 1 µmol/mol proved to be unstable for both cylinder treatments. For the 10 µmol/mol mixtures with treatment 1 (a general-purpose cylinder treatment) half of the mixtures were stable while the other half showed a clear loss in amount fraction (-4% and -6% in 1.5 year).

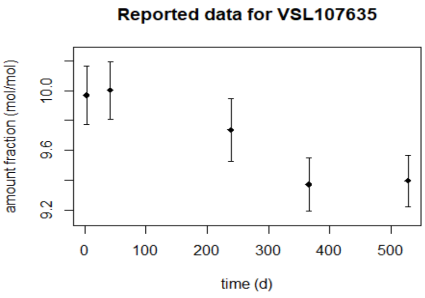

Figure 7 Stability study of HCl mixtures at 10 µmol/mol with cylinder treatment 1.

For the 10 µmol/mol mixtures with treatment 2 (a cylinder treatment specific for HCl) all 4 mixtures proved to be stable for a period of at least 1 year. As an example, Figure 8 shows the measurements for a period of more than 500 days for 2 cylinders showing that this type of cylinder treatment provides excellent stability. Based on the stability data for the cylinders with treatment 2, a 1-year stability of 2% was determined using R programming language and software environment for statistical computing and graphics.

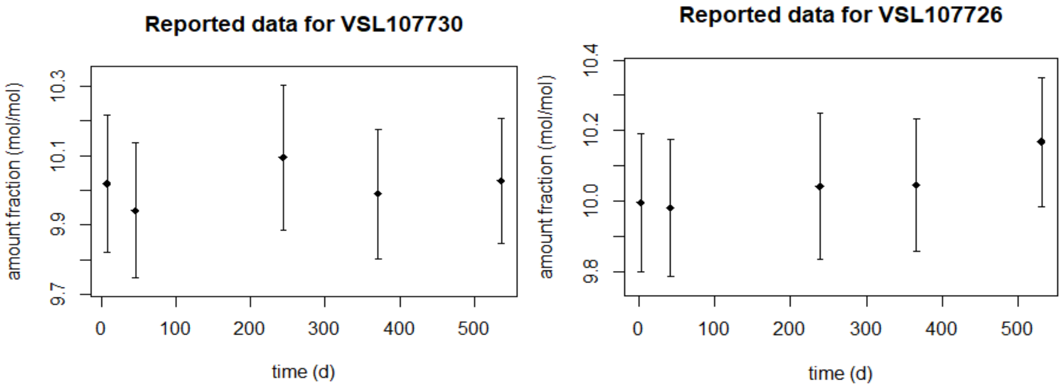

Figure 8 Stability study of two HCl mixtures at 10 µmol/mol with cylinder treatment 2.

4.1.2. Uncertainty from handling trace HCl reference materials (VSL)

In the analysis if sufficient time is allowed to passivate the sampling system beforehand and if the cylinder is analyzed using the guidelines given in subsection 2.4, then a reproducibility of the measurements of 0.5% or better can be achieved. On top of this there is the uncertainty of the gas standard used which is 2% for the 10 µmol/mol mixtures of treatment 2 (see subsection 4.1.1) developed by VSL.

4.2. Uncertainty from handling trace HCl reference materials (NPL)

The main sources of uncertainty in handling static trace reference materials arise from the uncertainty from gravimetric preparation, the value of which is dominated by the measurement uncertainty of the balances used to prepare the mixture (>90 %). Previous work of AMCs including NH_3 and H_2O have shown that there are significant losses of the target component at the trace level when performing binary additions to a mixture via the decant of a parent mixture into a new cylinder. The losses occur onto the wetted surface of the preparation system and measures need to be taken to improve the gravimetric accuracy of the mixture e.g. application of the exchange dilution method [7]. Work in the MetAMCII project has also shown that HCl behaves in a similar fashion with deviations between mixtures prepared via the exchange dilution vs decant methods of 6-10%. Cylinder passivation treatments are also important, in terms of the initial loss of HCl upon preparation (if using a simple decant method) but also the stability of the mixture within a particular cylinder after preparation. Using two different passivation technologies for mixtures at 10 µmol mol^{-1}, the mixture stability is estimated to be within 4 % over a 12-month period. Finally, uncertainties in sampling from the mixture vessel to the analyser can also affect the reproducibility of the measurement of a mixture, especially when using a regulator that has not been previously passivated or has been exposed to ambient air between the switching of samples and then allowing sufficient time for the measurement system to stabilising before switching between samples. If insufficient stabilisation time is allocated for a given sample, deviations of >3 % between repeat measurement of the same sample can be commonly observed, especially between the first and second measurement run.