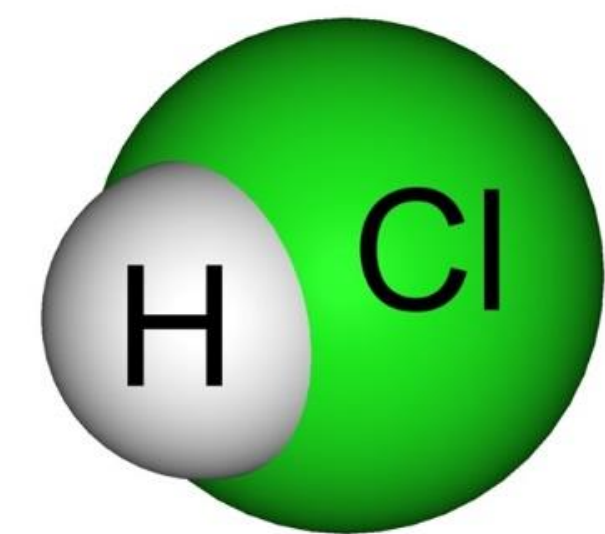
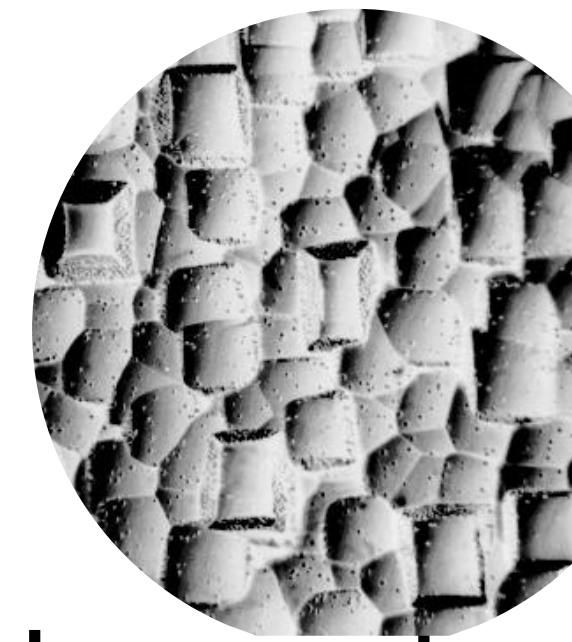


Novel techniques for generation of trace levels HCl gas reference standards

Yoana R. Hristova, Michael K. M. Ward, David R. Worton email:yoana.hristova@npl.co.uk

Introduction:

- Hydrogen chloride (HCl) is a corrosive and harmful airborne molecular contaminant (AMC)
- AMCs are closely monitored in advanced manufacturing due to their chemical contamination of products and processes



- As a result, there is an ever-increasing demand for on-line monitoring of AMCs at trace level
- In order to monitor AMCs such as HCl there is a need for accurate gas reference materials to provide confidence in measurement
- Due to the reactive nature of HCl e.g. rapid reaction with water vapour present in air, there are currently no commercially available traceable standards providing unbroken chain of international comparisons and primary reference materials (PRMs) at $\mu\text{mol mol}^{-1}$ level

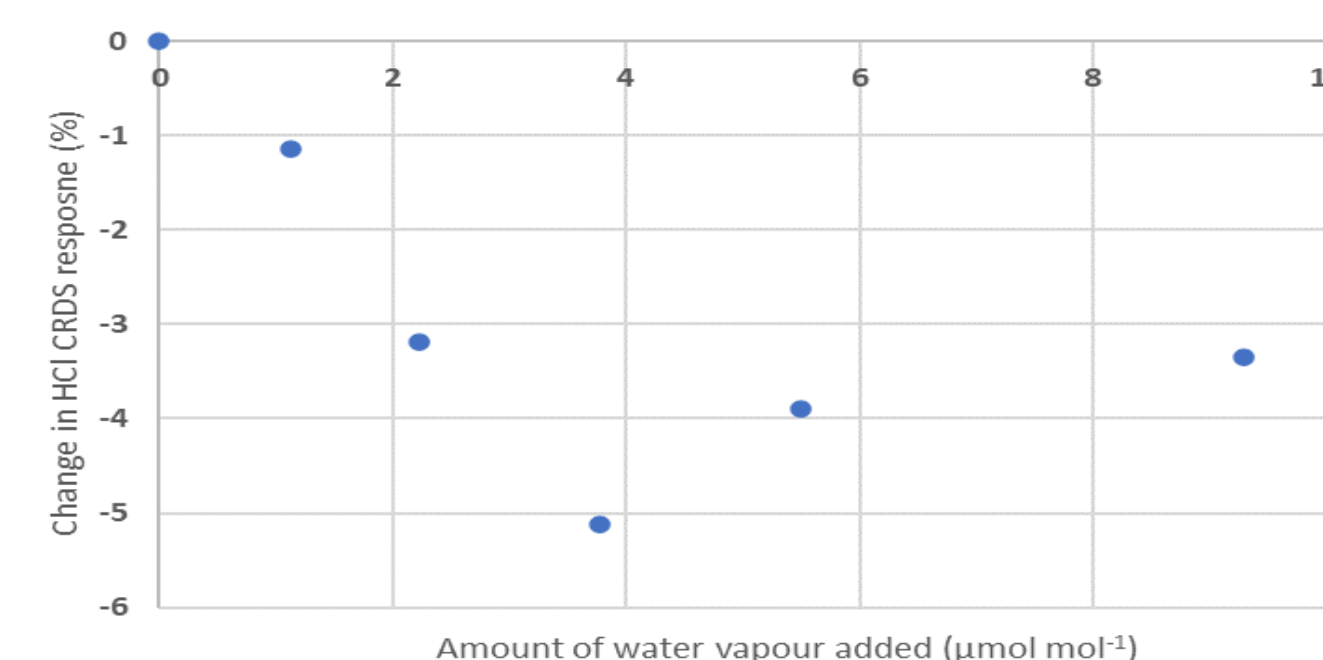


Figure 1: A decrease in HCl CRDS response as a function of water vapour added to the HCl mixture in N_2 , generated at 10 nmol mol^{-1} .

- Here we demonstrate the development of novel methods for producing traceable standards

Exchange dilution – NPL innovation method to limit preparation losses due to HCl reactive nature

- Dilution from pure substance
- Initial decant and dilution
- Consequent dilution performed in **the same cylinder**:

- Small aliquot released
- Remaining mass measured and diluted further

Brewer et al. Anal. Chem. 2019, 91, 5310–5315

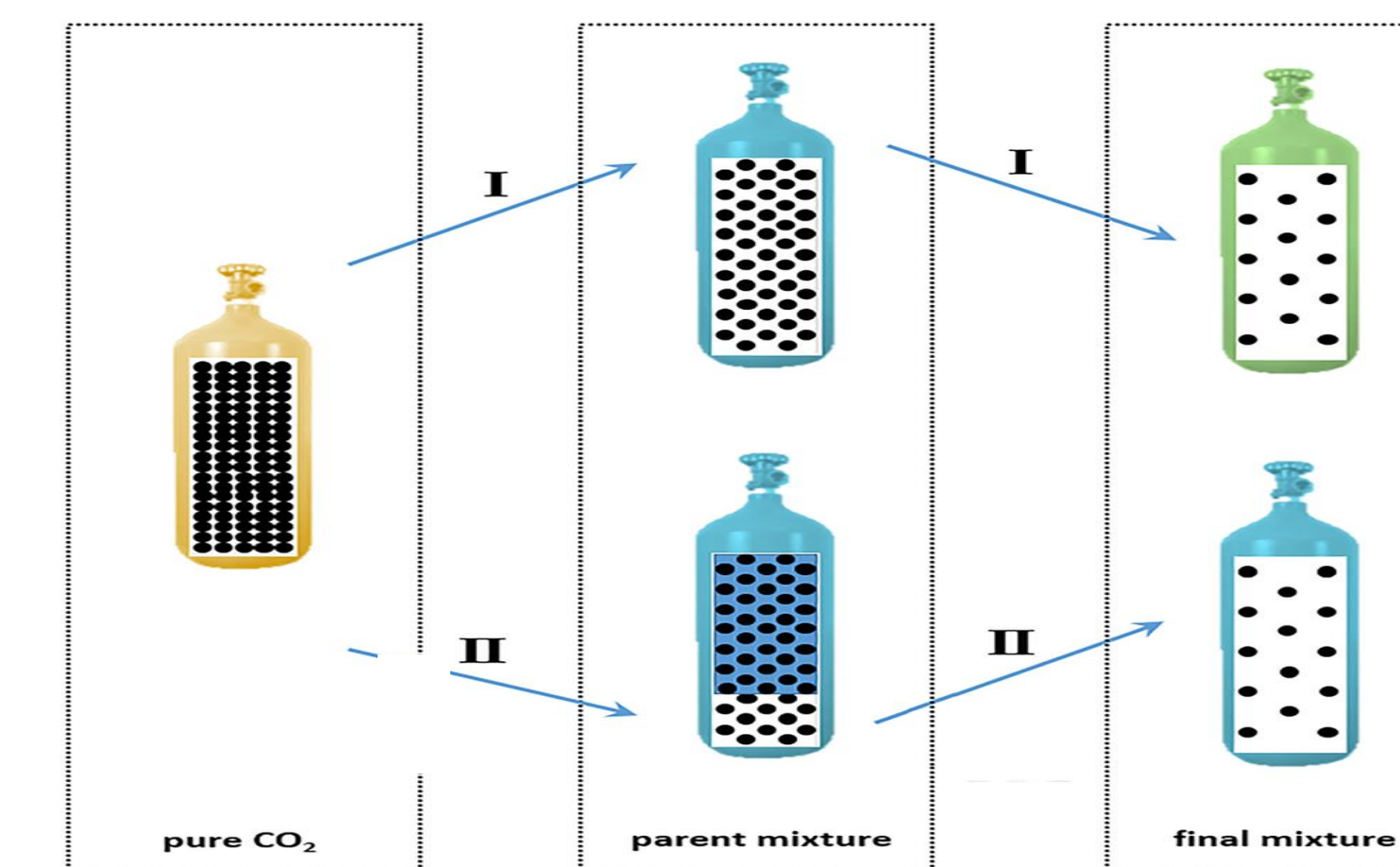


Figure 2: Gas mixture preparation via exchange dilution method.

Development of High Accuracy Dilution Device

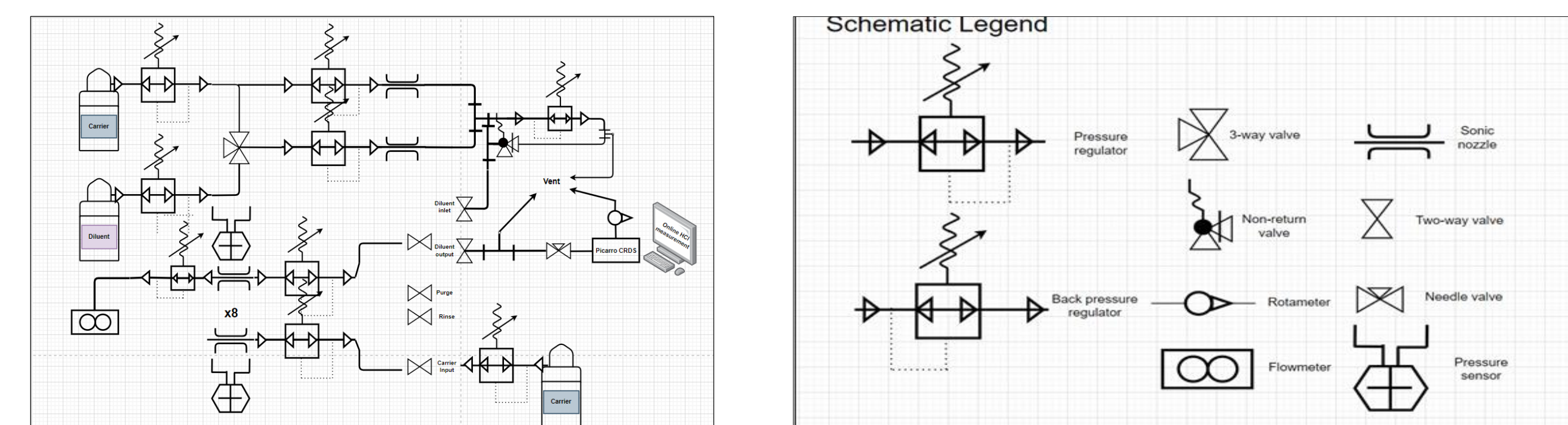


Figure 3: Dynamic dilution device developed at NPL coupled with Sonimix 2106.

- Another way to negate absorption
- Dynamic device offers dilution range of 1:1000 of state-of-the-art HCl in N_2 PRM to sub nmol mol^{-1} required for AMCs industrial monitoring
- Coupled with bespoke Cavity ring-down spectroscopy (CRDS) analyser for real-time measurements

Generation of the dynamic reference mixtures (1-15) nmol mol^{-1} range

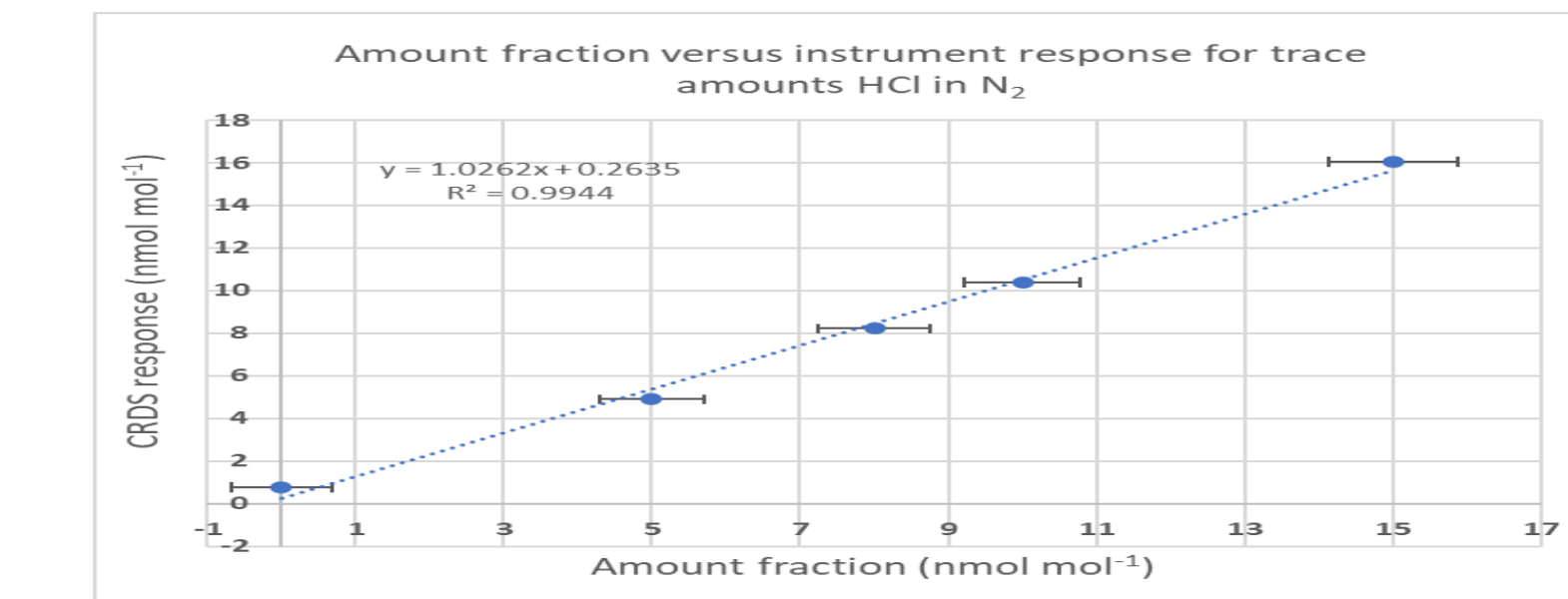


Figure 4: A plot of dynamic generated amount fraction of HCl vs CRDS response.

- Linear behaviour in the low nmol mol^{-1} range indicative of accurate detection and interpretation of the results
- Repeatable results when diluting standards at different amount fractions demonstrating consistency of measurements

Summary

- A two-stage dynamic dilution device was developed allowing generation of stable trace HCl in the (1-15) nmol mol^{-1} region
- The diluted standards were prepared by novel exchange dilution method to negate absorption losses during preparation
- The effect of water vapour was examined which demonstrated decreased HCl response
- Future work will include evaluating the stability of the static PRMs used for dilution over 6 to 12 months period for potential decay due to reactivity

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