

Metrology for sustainable hydrogen energy applications

**JRP EMPIR 15NRM03
HYDROGEN**

WP2: Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Task 2.2: Methods development

A2.2.2: Validate a speciation method for the measurement of halogenated species in hydrogen

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Summary

Within the hydrogen project analytical methods for most of the impurities listed in ISO standard 14687-2 are being developed. Halogens are among the most challenging impurities to be measured. In VSL measurement methods for two important halogens, hydrogen chloride and hydrogen fluoride were developed. These methods are both based on laser spectroscopy.

In this report, a summary of the methods that have been developed is presented.

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1 Introduction

Within the hydrogen project analytical methods for most of the impurities listed in ISO standard 14687-2 [1] are being developed.

Total halogenated compounds are among the most challenging impurities to be measured. 'Total' measurements are often difficult and hence it is not surprising that currently no analytical method is available that can quantify total halogenated compounds in a traceable and accurate manner. In literature [2] three suggestions have been made to address this issue when the ISO standard is revised, namely:

- replacing 'total halogenated compounds' with a list of key halogenated compounds that can be measured individually
- identifying compounds whose measurement is more routine to act as 'canary species' for hydrogen produced from different sources
- setting different specifications for hydrogen produced from different sources.

Within A2.2.2 VSL developed measurement methods for 2 very challenging halogenates: hydrogen chloride (HCl) and hydrogen fluoride (HF). In particular HCl could be a key halogenated species. A short description of the measurement method for HCl is given including some details on the validation. Work on HF is still ongoing and will be reported later.

2 Development of an analytical method for hydrogen chloride (HCl)

2.1 Measurement system

Figure 1 shows a schematic overview of experimental set-up based on an OPO as light source and CRDS used for the gas detection. The pump laser of the OPO consists of a narrow line width fibre laser (NKT Photonics, output power set at 4.4 mW) which is amplified in a fibre amplifier (IPG Photonics). This combination provides a wide mode-hop free tuning range of 100 GHz and an output power up to 10.5 W at 1064 nm. The output of the amplifier is coupled into the OPO cavity via a collimator (COL), Faraday isolator (FI) and AR-coated focusing lens (L1). The periodically poled crystal (PPLN) from HC-Photonics is contained in an oven and has AR coatings for signal, pump and idler wavelengths. The mirrors are highly transparent for both idler and pump wavelengths and highly reflective for the signal wavelength. The backside of the mirrors is anti-reflective coated for both the pump and idler. Within the PPLN crystal the pump light is converted into the signal and idler with the signal resonating in the OPO cavity.

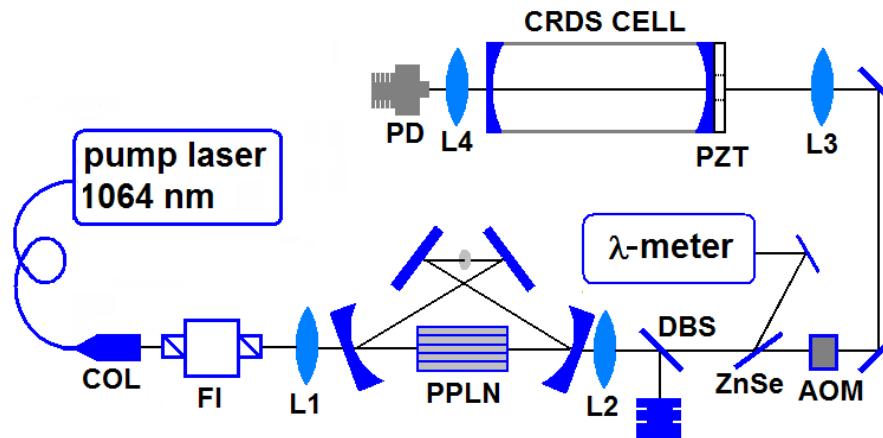


Figure 1 Schematics of the singly resonant cw OPO and CRDS spectrometer. The output of the seed fibre laser is amplified up to maximum 10.5 W and coupled into the OPO cavity. Part of the idler is directed to a wavelength meter and the rest is directed via an Acoustical Optical Modulator (AOM) to the cavity ring down measurement cell.

The output of the OPO is collimated using an uncoated CaF_2 lens (L2). Signal and residual pump are separated from the idler using a dichroic beam splitter (DBS). Part of the idler beam is directed to a wavelength meter (Bristol instruments) using a ZnSe window placed near the Brewster angle. Different PPLN crystals and mirror sets in the OPO cavity are used to cover the entire wavelength range of 2.3-5.1 μm . HCl is analysed most sensitively at the fundamental band in the range of 2700 cm^{-1} to 3050 cm^{-1} .

2.2 Flow system

Initially the system used a SilcoNert 2000 coated measurement cell with polymer tubings and a SilcoNert 2000 coated pressure regulator. For HCl however results by NIST indicate that HCl can be best analyzed using Dursan coated materials [3]. Therefore, later on a Dursan coated CRDS cell was installed. Measurement are typically performed using a flow rate of 30 L/h set by a mass flow controller (coated with SilcoNert 2000). The cell pressure is controlled using a combination of a pressure regulator and a membrane pump and is normally set at atmospheric pressure.

2.3 Validation

Validation of the system was carried out using:

- HCl in H₂ gas standard developed by CEM (46 µmol/mol).
- Commercial HCl in N₂ gas standards (certified by VSL) which are diluted with pure H₂.
- HCl permeation tube in a magnetic suspension balance (this work is still ongoing)
- Comparison with data from spectral databases (Hitran and PNNL database)

LOD

As the current ISO standard only mentions *total halogenates* the requirement for the LoD of a single halogenated species is not obvious except that it must be below the limit value for total halogenates which is 50 nmol/mol. For HCl a LoD below 1 nmol/mol can be obtained by assessing the strongest HCl absorption lines. This is thought to be more than sufficient if HCl needs to be detected.

Selectivity

As many different strong HCl absorption lines are available, the method is very robust and very insensitive to impurities. Only in one case where a hydrogen sample was analyzed with 100's of $\mu\text{mol/mol}$ of a hydrocarbon, interference issues were observed. However, in this case the hydrogen clearly does not fulfill the ISO 14687-2 criteria. In all other practical cases, HCl absorption lines can be selected for which interference is negligible (see the spectral simulations of several impurities in Figure 2). Alternatively, using multi-component analysis the amount fraction can be derived in cases of interferences.

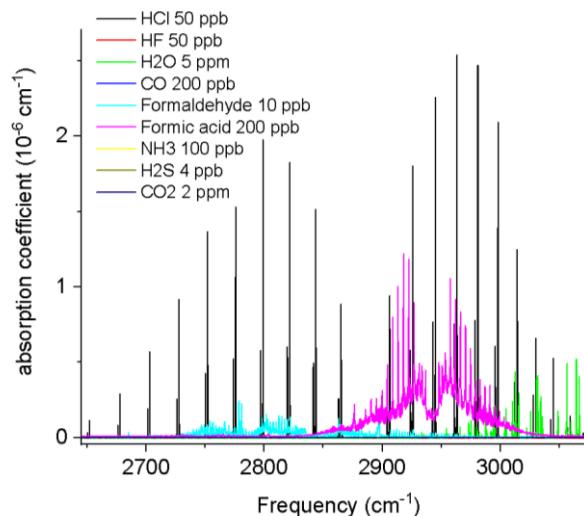


Figure 2 Spectral simulation using PNNL database of the impurities at the limit values according to ISO 14687-2. The black line is HCl at 50 nmol/mol. The absorption signal of 50 nmol/mol HCl is much higher than the detection limit of about $1 \cdot 10^{-8} \text{ cm}^{-1}$. Note the simulation is based on a nitrogen matrix, results in hydrogen will be slightly different (line broadening is affected).

Working range

Many weak, intermediate and strong HCl absorption lines are available that enable the measurement of HCl from the low nmol/mol range up to 100 µmol/mol and more. Too high HCl amount fractions may however damage the CRDS mirror coatings and therefore these have not been tested. The actual range tested with the CRDS spans nearly 4 decades: from 6 nmol/mol up to 46 µmol/mol. Thus, covering the relevant range of ISO 14687-2 and beyond.

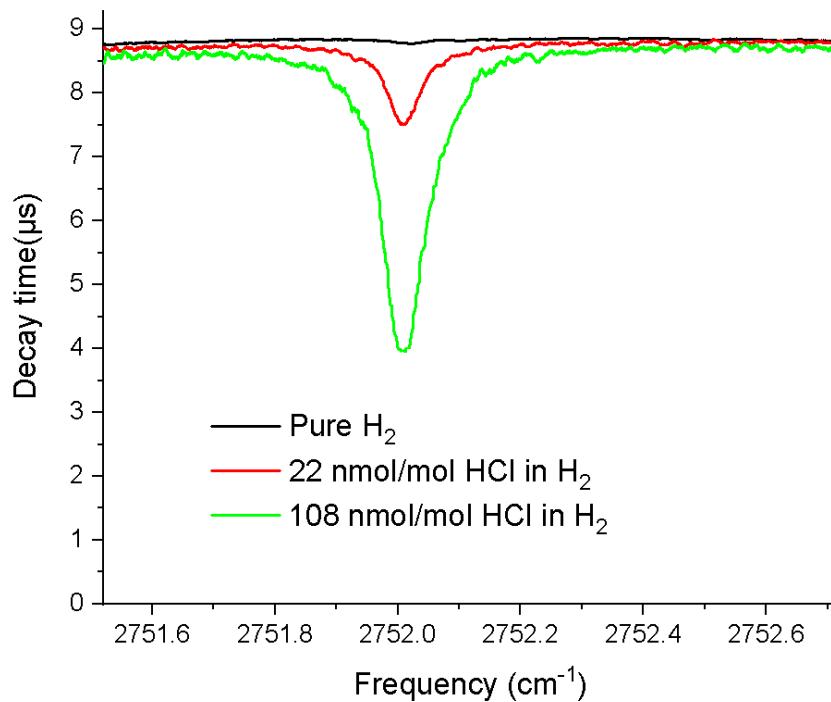


Figure 3 Measurement of a HCl in N_2 standard diluted with pure H_2 (residual N_2 levels 1.2% and 6% for 22 nmol/mol and 108 nmol/mol HCl, respectively). Also shown is a measurement of pure hydrogen (source Air Products).

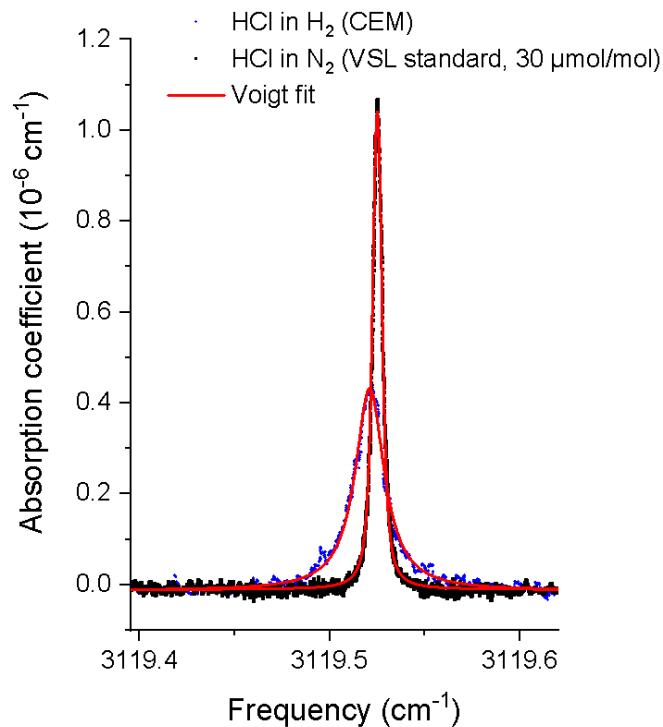


Figure 4 Measurement of high amount fractions of HCl in N_2 and HCl in H_2 (prepared by project partner CEM, nominal 50 $\mu\text{mol/mol}$, certified 45.5 $\mu\text{mol/mol}$). The different broadening of the absorption lines in the two matrices can be clearly seen (in H_2 the lines are relatively much broader). For these measurements of high HCl amount fractions a very weak HCl absorption line was selected.

Time response

Using the Dursan coated cell and a SilcoNert 2000 coated pressure regulator and mass flow controller, measuring HCl amount fractions at low $\mu\text{mol/mol}$ yields a response time in the order of 10 minutes for a system previously flushed with pure hydrogen. For the hydrogen samples analyzed

within this project (WP1) with hitherto unknown HCl amount fractions the samples were first analyzed for formaldehyde and formic acid (less reactive than HCl) and only then for HCl. This way the sample has already flushed for half an hour through the measurement cell.

2.4 Conclusion

A system has been developed and validated for the measurement of HCl in hydrogen. The sensitivity of the system is sufficient to comply with limit set in ISO 14687-2 for total halogenates.

3 References

1. ISO 14687-2 Hydrogen Fuel - Product Specification - Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles, 2012.
2. A.S. Brown, A. Murugan, R.J.C. Brown, Measurement of 'total halogenated compounds' in hydrogen: Is the ISO 14687 specification achievable? Accreditation and Quality Assurance, 2015, Volume 20, Number 3, Page 223
3. C. Goodman, Development of SI-Traceable Certification of Hydrogen Chloride Gas Standards, presentation at Gas Analysis Event, Rotterdam, June 2017