

HYDROGEN CHLORIDE EMISSIONS MONITORING: EUROPEAN SURVEY OF PRACTICES, ISSUES AND OPINIONS



This paper assesses the results from a survey on how hydrogen chloride (HCl) in stack gas emissions from industrial processes is measured by organisations based in Europe that do periodic short-term measurements. The survey was done by asking organisations to complete a questionnaire.

The questions focused on the use of different monitoring techniques and the implementation of associated European monitoring methods (that is Committee of European Normalisation (CEN) standards).

The results of the survey showed that there are a variety of different approaches used throughout Europe for the measurement of HCl. The preference remains for the use of a wet chemistry method, as opposed to automated systems. However, the survey has shown that the approach to determining the uncertainty of the wet chemistry method varies between test laboratories with some using an uncertainty provided by the analysis laboratory and others using a fixed uncertainty provided in the CEN standard.

This work was part of a European Metrology Programme for Innovation and Research (EMPIR) project on "Determining new uncertainty requirements for increasingly stringent legislative HCl industrial emission limits" (18NRM04).

Introduction

Hydrochloric acid (HCl) is acutely toxic to all forms of life, erodes buildings and other infrastructure, and contributes to the formation of photochemical smog. The latter of these leading to health effects causing a range of respiratory problems, from respiratory irritation to reduced lung function. With the acidification of ecosystems remaining a significant issue [1] – particularly given that the acidification risk has been previously underestimated [2] – and with 77.1% of the total amount of HCl pollution emitted by installations covered by the European Pollutant Release and Transfer Register (E-PRTR) coming from thermal power stations and other combustion processes [3], the motivation for legislating with increasingly stringent emission limits is clear.

The Industrial Emissions Directive (IED [4]) regulates emissions from large scale industrial sites. It set an emission limit for HCl of 10 mg/m³, which national regulators are required to stipulate in permits that allow the operation of industrial installations. At the request of the European Commission (EC) the Committee of European Normalisation (CEN) Technical Committee 264 'Air quality' developed and published EN 1911 'Stationary source emissions – Determination of mass concentration of gaseous chlorides expressed as HCl – Standard reference method' in 2010 [5] to support the enforcement of the legislative emission limits. It should be noted that EN 1911 actually pre-dated 2013's IED and was produced to support previous legislation that has been replaced by the IED.

The role of EN 1911 is twofold: (a) 'compliance monitoring', periodic (often annual) measurements to demonstrate compliance of a process with stipulated emission limits; (b) annual calibration / calibration check of the in-situ process plant operator analyser (referred to as an automated measuring system – AMS) in accordance with EN 14181 [6]. Given calibration under EN 14181 is performed via parallel measurement of the same stack gas by the AMS and SRM (standard reference method), then the quality (uncertainty) of both compliance and AMS emissions data is dependent on the uncertainty of the SRM. The method described in EN 1911 involves extracting gas out of the stack and bubbling it through a series of glass absorbers filled with deionised water. After each sample is taken (the sample time is typically 30 minutes) solutions are decanted and sent to an analytical laboratory for quantification of chlorides.

Within EN 1911 there is a mandatory uncertainty requirement of 30% ($k = 2$) of the emission limit. Consequently, as emission limits become increasingly stringent so do the absolute uncertainty requirements. Under the IED many processes have been regulated at an emission limit of 10 mg/m³.

However, best available technique (BAT) conclusions documents, which support the IED for sector specific industries, have specified increasingly stringent limits. For example, HCl limits of 2 – 6 mg/m³ for waste incineration [7], 3 – 12 mg/m³ for large combustion plants [8], and ≤1.5 mg/m³ for non-ferrous metals industries [9]. With increasingly stringent uncertainty requirements, questions have arisen over the effectiveness of EN 1911 to demonstrate compliance with such limits. This has been recognised by CEN/TC 264 'Air Quality' [10], the technical committee who produced EN 1911. Evidence from proficiency testing schemes has indicated that stack testing organisations have struggled to comply with the uncertainty requirements at emission limits of 10 mg/m³ [11]. This means complying with the uncertainty requirements at increasingly stringent limits will be even more of a challenge.

The European Metrology Programme for Innovation and Research project HEROES [12] has characterised the performance of EN 1911 at low levels of HCl using stack simulator facilities [13,14,15,11] to provide the evidence base needed for national regulators to set realistic uncertainty requirements at low limit values. The project has also characterised portable optical technologies so data are available for ongoing discussions on the viability of these techniques and suggesting revisions to EN 1911, so that it meets future measurement needs.

The HEROES project has carried out a stakeholder survey to understand current opinions on EN 1911 and optical techniques in order to gauge perceived advantages, disadvantages, and preferences. Here we report and discuss the results from that survey.

Survey Demographic

The survey was conducted via a well-established on-line survey provider. As shown in Figure 1, of the 32 respondents the greatest proportion was from the UK (28%), followed by Finland (16%) and Germany (13%). The respondents comprised of organisations reporting employee numbers ranging from 10's to 1000's. As shown in Figure 2, 67% of the respondents defined themselves as solely an independent test house, 8% defined themselves as a proficiency testing provider and 11% as a research institute. Of the 8% defining themselves as other, this included a ministerial department, an independent state institution, and a system integrator. Overall the returned data encompassed a broad range of organisations in terms of size and business interests, but with a clear weighting (as intended) towards the end users, whose main business interest is carrying out emission measurement services based on EN 1911 and portable optical techniques.

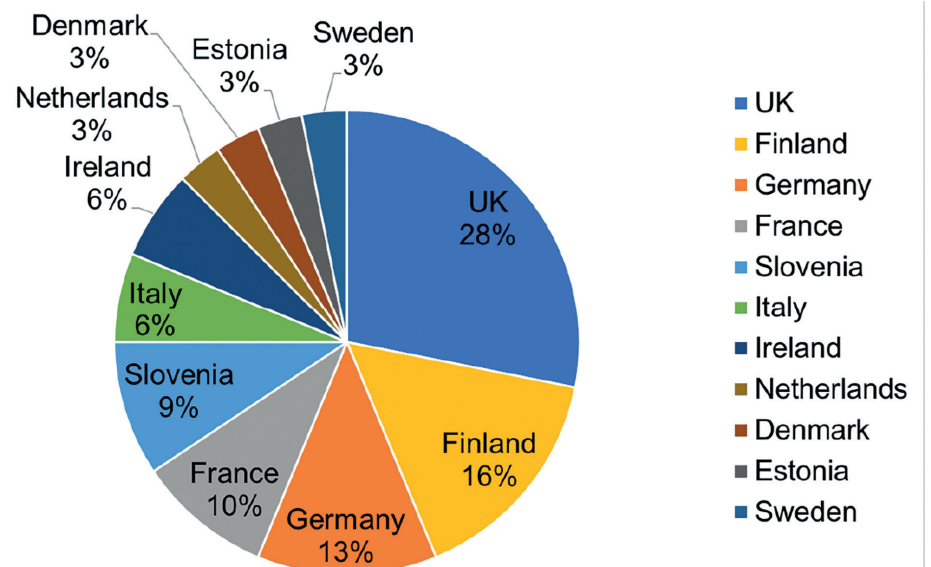


Figure 1: Survey participation by country.

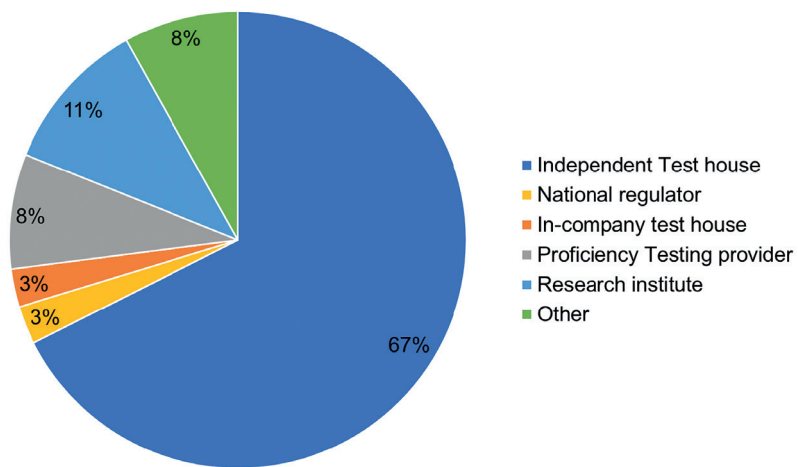


Figure 2: Survey participation by organisation type

Survey Trends

Of the respondents providing measurement services it was found that 52% offered EN 1911 only, 6% a portable optical technique only and 42% both (Figure 3).

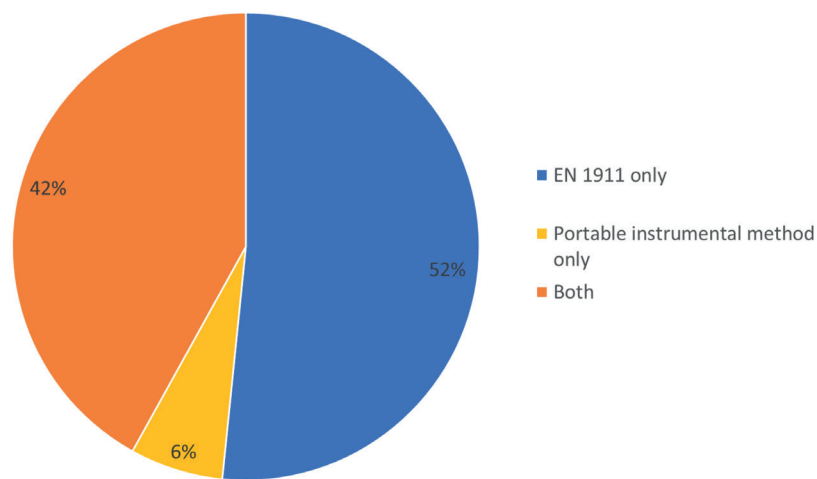


Figure 3: Monitoring methods offered as measurement services

From Figure 4 it was found that 76% of respondents employed ion chromatography to measure chloride samples collected from the stack, with 3% silver titration and 6% mercuric-thiocyanate spectrophotometry. 3% of respondents stated that they use a different analytical technique (which they did not specify).

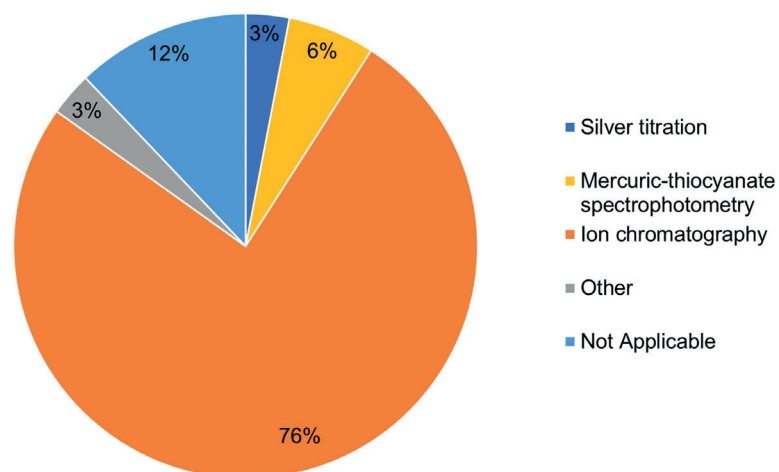


Figure 4: Analytical quantification technique used under EN 1911

In the first version of EN 1911 (the current revision being published in 2010) it was mandatory to passivate the sampling system to minimise losses of HCl to the internal walls of the sampling equipment. A lack of passivation risking bias in terms of under-reading the first sample taken from the stack; no effect on subsequent samples would be expected as passivation should have occurred during the first sample. In the 2010 revision passivation was changed to a recommendation. In the survey it was found that more than half (53%, Figure 5) of respondents no longer passivated their sampling systems. Regarding QAL2 calibration (where the process operator's instrument is calibrated against the applicable CEN SRM) under EN 14181 at least 15 samples are required, so there may be negligible impact on the calibration function if there is some bias in the first sample. Regarding compliance monitoring a minimum of 3 samples are taken and an average calculated, so here there potentially could be a greater impact. However, without further study it's not possible to state if this change is leading to a significant bias.

One of the questions posed in the survey was "how test houses estimated the analytical quantification uncertainty". Participants were asked if, for the quantification step, they used the full analytical laboratory uncertainty or if they only considered the laboratory's standard deviation of repeatability. Some test houses use a value specified in EN 1911 (that is 2.5%) for the analytical laboratory uncertainty, rather than using one determined by the analytical laboratory. In EN 1911 there is an overall uncertainty requirement of 30% ($k = 2$) of the emission limit, but under this there are uncertainty sub-requirements (EN 1911, Table 1). For example, volume of absorbance solution

($\leq 1.0\%$); volume of gas extracted from the stack ($\leq 2.0\%$); sample line leaks ($\leq 2.0\%$). However, there are no such sub-requirements with respect to the quantification step, instead in EN 1911, Table 2, there is a requirement that the analytical laboratory demonstrates the repeatability of $\leq 2.5\%$. Using a fixed value does not take account of bias sources of uncertainty that should be estimated by the analytical laboratory. To achieve ISO/IEC 17025 accreditation an analytical laboratory will have assessed their uncertainties (precision and bias sources), so, these values should be included in the uncertainty assessment. Only 50% of respondents stated that they used the full uncertainty from the analytical laboratory. This result may go some way to explaining why performance in proficiency testing schemes [11] is often poorer than the uncertainties test house's claim, that is, uncertainties from the quantification step are underestimated. EN 1911 should be revised to provide sub-uncertainty requirements for the analytical step, so it is clear how the uncertainty calculation is determined.

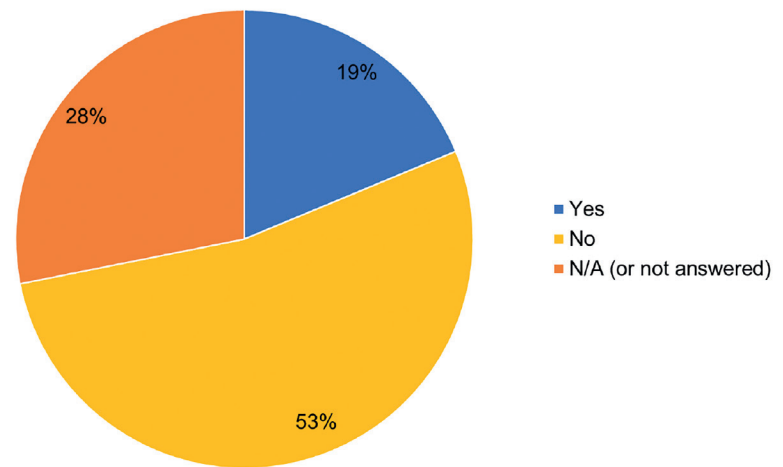
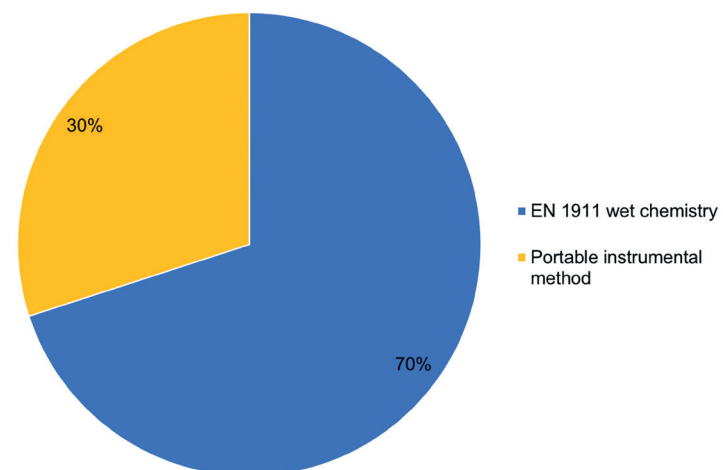


Figure 5: Sample line passivation as part of EN 1911 test.

One question asked which approach respondents would prefer to use? Here, 70% of respondents stated that they would prefer to use EN 1911 (Figure 6). The fact that 70% would prefer EN 1911 implies a proportion of those routinely using portable optical techniques would prefer to use EN 1911. In addition, they were also asked to justify their answer, 52% of the organisations that chose EN 1911 stated that they chose this method because of its reliability. It was also seen to be simpler



than the portable method.

Figure 6: Preferred approach to be used for HCl monitoring.

The survey asked participants to describe any issues they associated with each approach. With respect to EN 1911, 54% either provided no response or responded that they considered the method had no issues. Of the remaining 46%, issues were raised including: variation of quantitative results between different analytical laboratories; loss of HCl in sample lines; EN 1911 should mandate sample line passivation; it's not suitable to use when other inorganic chlorides are present; interference issues when ammonia is present. The presence of ammonia is most likely referring to the formation of ammonium chloride. If it forms upstream of the filter, then it could get caught on the filter and therefore the bound chloride would be missing from the deionised water giving a negative bias. However, formation downstream of the filter is likely to reach the deionised water and be readily dissolved, that is there would be no impact on the measurement. However, in theory this should be a greater issue with portable analysers as after the filter the ammonium chloride will deposit on internal walls and mirrors. Causing both a negative bias in the measurement result and possibly also a poorer signal to noise ratio of the instrument, which will potentially have an impact on performance.

With respect to issues with portable optical techniques 58% of participants provided no response. The remaining participants raised issues including: the length of time it took for systems to warm up and be ready for use; sampling system conditioning times; cross-interference; ammonium chloride formation. With respect to warm up times this is probably referring to the fact that whilst portable systems will warm up and be ready to use in an hour or two, to obtain reliable data a longer time is generally needed (several respondents recommended leaving overnight when possible). With respect to long times to condition the sampling system, this no doubt refers to the passivation of the measuring system using dry HCl as part of testing the integrity of the sampling system. Depending on the materials used for the sampling apparatus and analyser measuring cell it can sometimes take hours to obtain stable readings for the on-site QA/QC test. However, it is worth

noting that EN 16429 (a standard providing method for measuring HCl emissions by portable instruments [16] – this method is species specific (HCl) but not technique specific, whereas CEN/TS 17337 is technique specific (FTIR) but not species specific (i.e. can be followed for emission species other than HCl)) has made a significant change in how measuring systems are validated on-site; it mandates validation using wet gas injection (that is dry HCl is not permitted). Up until recently CEN were not confident enough in the reliability of wet gas injection to standardise it. However, equipment and knowledge have improved to the point where this could be done. In the EC Mandated validation of EN 16429 it was shown that measuring systems could be validated not only significantly more quickly but also with less variance than dry gas. Also, although dry gas would show if HCl was being lost because filters have not been cleaned, it would not show if there were cold spots leading to condensation losses. Injection of a wet gas would test for both. The comment on cross-interference may in part be referring to the need to make sure of a high-quality water vapour calibration, as water vapour is a key spectroscopic cross-interference with HCl (for example some FTIR manufacturers recommend recording new water vapour reference spectra every 6 months).

Conclusions

Completed questionnaires were received from 32 organisations. Responses were received from 11 European countries. Around two thirds of the respondents were independent test laboratories.

52% of organisations used a classical wet chemistry method, 42% used optical portable analysers and 6% used both. However, 70% of respondents stated they would rather use wet chemistry than an automated technique.

Of the respondents offering wet chemistry, around three quarters used ion chromatography to measure chloride samples. This shows that ion chromatography is the most popular analysis method.

Half of the respondents did not passivate their sampling equipment when using a wet chemistry method to measure HCl. In the first version of the CEN standard for HCl this was a mandatory requirement but in the subsequent revision it became an optional requirement. Some respondents raised concerns about this because they believed the passivation test should be done.

The survey highlighted that half of the respondents that use a wet chemistry method did not use a measurement uncertainty determined by an analytical laboratory.

The survey asked participants to describe any issues they associated with each approach. About half of the respondents did not raise any issues. The following issues were raised about the wet chemistry method: variations in laboratory analysis; losses in sample lines; passivation of sample lines; interferences, such as from ammonia. The following issues were raised about automated methods: length of time for the system to be ready to use; cross interference; effects of ammonium chloride.

The fact that an automated technique takes more time to set up may explain why most respondents preferred to use a wet chemistry method.

The results from this survey have provided information that has been useful to other areas of work related to the project on "Determining new uncertainty requirements for increasingly stringent legislative HCl industrial emission limits". Further information on this project is available from: <https://empir.npl.co.uk/heroes/>.

Acknowledgements

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