Observations on the use of CEN/TS 17337:2019 on HCl measurements below 10 mg/Nm^3

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HEROES Project

- Focus: Determining new uncertainty requirements for increasingly stringent legislative HCl industrial emission limits
- Background: BAT Conclusions documents are bringing in increasingly stringent HCl emissions limits
  - e.g. 2-6 mg/m^3 for waste incineration, <1-3 mg/m^3 for iron and steel production, 3-12 mg/m^3 for power stations
- One aim in Heroes is to compare the performance of wet chemical SRM-method EN1911 and P-AMS methods (portable automated measuring system)
- Duration 5/2019 – 11/2022, 18NRM04 Heroes
- Funded by Euramet and participants NPL, VTT, CMI, Ineris, EA

Target of this presentation

- Intercomparison measurements performed with continuous P-AMS FTIR and wet chemical method EN1911 in April 2021 in Finland
- In addition, three different filter materials (stainless steel, PTFE and ceramic) were tested as a heated probe filter in FTIR sampling line
  - in order to assess if the filter material has an effect on the measured HCl concentrations
- Focus on the observations related to the use of CEN/TS 17337 Technical Specification document for FTIR and it's quality assurance procedures in the laboratory and field measurements when measuring low HCl concentrations

CEN/TS 17337:2019 (1/2)

- Minimum performance characteristics
  - Zero (≤ 2.0 % of range)
  - Response time (<400 s for NH_3, HCl and HF, < 200 s for other components)
  - Detection limit (≤ 2.0 % of range)
  - Lack of fit (≤ 2.0 % of range)
  - Interferents (total ≤ 4.0 % of range)
- Field procedures
  - Check Gas Approach or Span Approach
  - Validation of sample gas line / losses in line
  - Response time of the measuring system
  - Zero gas check for analyser and entire measurement system (≤ 2.0 % of range)
    - In the beginning and end of the measurement
  - Drift across measurement period (d < 2.0% passed, 2% ≤ d < 5% must be corrected, ≤ 5% failed)

CEN/TS 17337:2019 (2/2)

- Spectral residual test / interference check (interference ≤ 5.0 %)
- Test gas selection guidances
  - Multiple test gases to be used, depending on the system and components
- Guidance to estimate measurement uncertainty

Table 2 Frequency of checks

Checks [a]	Frequency	Action criteria
Cleaning or changing of particulate filters [b]	as required	–
Regular maintenance of the measu-ring system	as required by manufacturer	as required
Response time	at least every year for each measured component and after a change to the sampling system and after measuring system repair	meet performance requirement in 7.2
Lack of fit	at least every year for each measured component and after repair	meet performance requirement in 7.2
Annual calibration or calibration validation [c]	annual if employing Check Gas Approach	(see (a) clause below)

Table 1 Potential test gases ranked in order of reactivity

Rank	Substance
1	HCl
2	NH_3
3	SO_2
4	NO_2
5	CO_2
6	N_2O
7	NO
8	CO

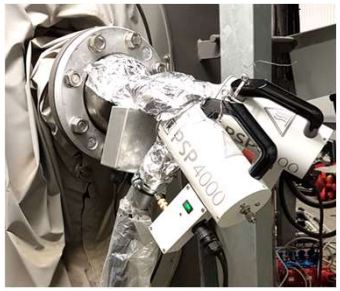
Equipment used

Two independent sampling and analysis equipment

- 2 * Heated sampling probes 1.3 m, 180°C
- 2 * Heated filters (2*M&C PSP4000) 180°C
  - 1st line had all the time stainless steel filter F-3SS
  - 2nd line had alternately filters: Stainless steel F-3SS, Teflon M&C F-2T and ceramic M&C SP-2K
- Heated lines 10 m and 6 m, after pump 1 m lines to analyzers, all 180°C
- 2 * Portable sampling units incl. pump and integrated oxygen measurement
- 2 * FTIR's (Fourier Transform Infrared) Gasmet Dx4000 were used in the measurements

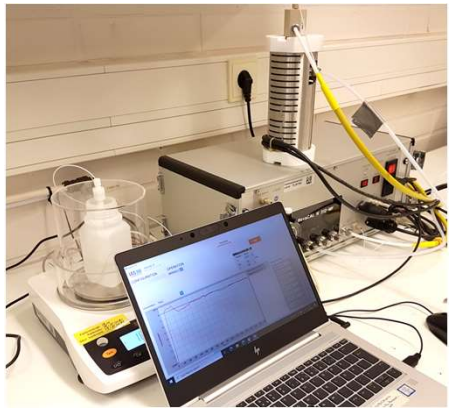
Injecting and vaporizing HCl solution according to wet gas injection approach

- Hovacal vaporization unit with scale, used in laboratory
- Gasmet portable syringe vaporizing unit, on field



HCl Passivation and used test gas

- Test gas was HCl with water moisture
  - HCl 8 mg/m^3 (dry, NTP 0°C) and
  - Water vapour 1.35 vol-% (wet, NTP 0°C)
- HCl was produced in lab from 0.02 mol/l HCl solution using Hovacal, nitrogen flow 9 l/min, total flow splitted to two lines
- And in field, from 0.02 mol/l HCl solution using syringe injection, nitrogen flow 4 l/min
- Line passivation about 1 h was enough with wet HCl gas



Zero cheks in field

- Each day at the start and the end
- All of the measured compounds shall not exceed 2.0 % of respective certification range
- “Certification range” of 10 mg/Nm^3 was used in calculations
- All accepted

		FTIR 1			FTIR 2			Criteria	Notes
		Day 1	Day 2	Day 3	Day 1	Day 2	Day 3		
zero start	HCl mg/Nm^3	0.08	0.11	0.13	0.08	0.02	0.06		
zero end	HCl mg/Nm^3	0.00	0.00	0.07	0.13	0.02	0.00		
zero start	% of range (10)	0.8	1.1	1.3	0.8	0.2	0.6	< 2	accepted
zero end	% of range (10)	0.0	0.0	0.7	1.3	0.2	0.0	< 2	accepted

Check gas approach for testing the FTIR analyser

- At the beginning of the measurement campaign to see that the FTIR analyser is working properly

Check gas approach, test gas of 20 vol-% CO_2				
	FTIR 1	FTIR 2	Criteria	Notes
Difference, CO_2 vol-%	0.6	0.5		
% of range (25)	2.4	2.0	< 5	accepted
HCl mg/Nm^3*	0.04	0.29		
% of range (10)	0.4	2.9	< 5	accepted
* During check gas test. Not clear if this is required by CEN/TS 17337…?				

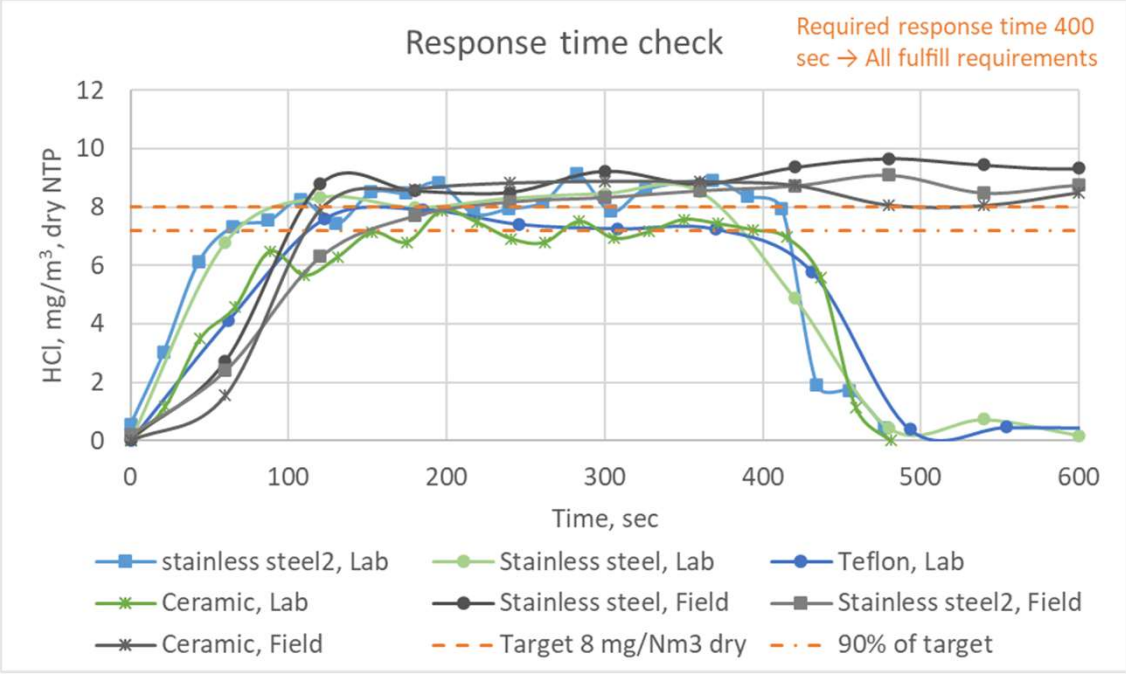
Sample losses in lines

- Fed concentration target 8 mg/Nm^3 dry, ambient temperature 10-16°C
- Differences were < 0.4 mg/Nm^3
  - but used low concentration level caused(?) that criteria was not met
- Day 3 wet gas injection was not stable, ambient temperature

		FTIR 1	FTIR 2				
HCl test gas in field (wet)		Day 1, SS1	Day 1, SS2	Day 2, Ceramic	Day 3, Teflon	Criteria	Notes
line	HCl mg/Nm^3	9.27	8.72	8.65	*		
analyser	HCl mg/Nm^3	9.56	9.10	8.91	*		
	% difference, loss	3.0	4.2	2.9		< 2	All failed
* Wet gas production with syringe injection was not stable. Ambient temperature 6-9°C							

Response time tests in lab and in field

- Lab: Both stainless steel filters had response time about 1 min, Teflon and ceramic filter had a response time between 2 and 3 minutes
- Field: Both stainless steel filters and ceramic filter had response time between 2 and 3 min
  - Teflon filter was not tested due to technical challenges of syringe system caused by low ambient temperature
- All response times < 200 sec (requirement is < 400 sec)



Uncertainty estimations

- For wet HCl 8 mg/Nm^3 test gases (lab and field)
- For sample gas (6 minute period)
- Range of 10 mg/m^3 used in calculations
- In estimations major variations in temperature, pressure, interference, stdev of zero repeatability
- Lowest uncertainty in lab, same level on field and sample

		Test gas in laboratory	Test gas in field	Sample
Average	mg/Nm^3	8.2	9.3	5.3
Stdev	mg/Nm^3	0.44	0.44	0.49
Exp.uncertainty (k=2)	mg/Nm^3	0.7	1.6	1.6
% of measured average		8.6	17	29.9
% of range (10 mg/Nm^3)		7.0	15.8	15.8

Lessons learned

- Quality checks are good, time consumption in field 1-1½h/day
- In the future, we will use wet test gas of HCl e.g. 15 mg/Nm^3 dry + water 0.6 vol-% wet (dp. 0°C)
  - In harsh ambient conditions I probably start to use SO_2 or NH_3 from gas cylinder in field for line validation, drift, sample losses, response time tests
- My conclusion: Wet gas injection systems are not stable enough in field (temperature, vibrations, movements)
  - Daily drift was not measured due to difficulties of syringe injection system
- Line losses exceeded the requirement
  - Due to low level concentration and unstable wet gas injection in field?
- Expanded uncertainty estimation was < 2 mg/Nm^3 in field, in lab < 1 mg/Nm^3

Observations on CEN/TS 17337

- FTIR technique is widely used all over the world and CEN/TS 17337 provides good and important guidance for the users
- Editorially text needs some clarifications, especially for 'test gases' and for requirements
- Preferably, no wet test gases in field conditions
  - Instead, line passivations, response time checks, line losses (for reactive gases) could be done in laboratory conditions
- The sequence of the required procedures is not clear, especially in field
  - Flow chart would be useful
- However, these observations do not diminish the value of CEN/TS 17337

VTT

beyond

the obvious

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