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M4R PROJECT – CONSULTANCY FOR ELEMENT MATERIALS TECHNOLOGY: SUMMARY OF CONSULTATION REGARDING IMPLEMENTATION OF MEASUREMENT METHODS CEN/TS 17337:2019 AND PREN 16429 FOR THE MONITORING OF POLLUTANTS FROM INDUSTRIAL PROCESSES REGULATED UNDER THE INDUSTRIAL EMISSIONS DIRECTIVE

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M4R Project – Consultancy for Element Materials Technology: Summary of Consultation Regarding Implementation of Measurement Methods CEN/TS 17337:2019 and prEN 16429 for the Monitoring of Pollutants from Industrial Processes Regulated under the Industrial Emissions Directive

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1 INTRODUCTION

This report provides a transcript of a Q & A consultation carried out for Element Materials Technology under the Measurement4Recovery (M4R) programme. The Environment Agency for England with agreement from Element Materials Technology were also party to the consultation as a relevant stakeholder. The consultancy concerned the measurement of 'reactive' gases from industrial processes regulated under the Industrial Emissions Directive (2010/75/EU) in accordance with CEN/TS 17337:2019 'Stationary source emissions - Determination of mass concentration of multiple gaseous species - Fourier transform infrared spectroscopy' and prEN 16429 'Stationary source emissions — Reference method for the determination of the concentration of gaseous hydrogen chloride (HCl) in waste gases emitted by industrial installations into the atmosphere' addressing various measurement issues. The consultancy was led by Marc Coleman who is convenor of CEN/TC 264/WG 36 'Emissions – FTIR Measurement' who elaborated CEN/TS 17337 and who is UK expert to CEN/TC 264/WG 3 'Emissions – HCl and HF' and therefore possesses knowledge of the discussions and rational with respect to the elaboration of the two methods. Issues are discussed including: considerations if applying for flexible scope; alignment of CEN/TS 17337 and prEN 16429 with respect to response time and sampling system validation; differences in CEN/TS 17337 and TGN M22 pass-fail criteria for sampling system validation and the merits of allowing a deviation for the former; consideration of sampling system validation using analyte spiking.

2 CONSULTANCY ON THE IMPLEMENTATION OF CEN/TS 17337 AND PREN 16429

2.1 SUMMARY OF QUESTIONS AND ANSWERS

2.1.1 (Q1) Re the calibration of all possible components – would this still fit with flexible scope, i.e. we can add components on then if we want to do them again we'd need to validate?

One thing to consider here is that UKAS will most likely expect to see the flexible part of the procedure carried out with reasonable frequency. If additional components are not being frequently added during routine monitoring work, then to demonstrate the procedure and competence of the user UKAS would most likely require 'dummy' work to be carried out. It's likely this would only be internal, and a component could in principle be added with minimal laboratory work and no need for any field work. However, if components are not likely to be added with a reasonably frequency an approach of a fixed scope with infrequent applications to extend the scope may be more cost effective then maintaining a flexible scope.

Assuming the question of "…the calibration of all possible components…" is with reference to Clause 9.3 on 'annual calibration or calibration validation' then there are the following considerations. Whether the scope is flexible, or the user has a fixed scope and is applying for an extension to the fixed scope the requirements are the same. If the component being added is covered by an SRM (see Clause 7.1) then the portable automated measuring system (P-AMS) is required to have been type approved in accordance with EN 15267-4. If so, there is no need to demonstrate equivalence (EN 14793) since this is now embedded within EN 15267-4 and will have been demonstrated as part of the type approval, i.e. if equivalence to the applicable SRM is not successfully achieved the type approval is failed. However, currently there is a period of grace as P-AMS type approved under EN 15267-4 are not readily available. Hence, use of P-AMS type approved under testing from EN 15267-3 remains permitted (and most likely will do for some time). Elsewhere in Europe this would mean that for the SRM covered component it would be necessary to demonstrate equivalence to the SRM in accordance with EN 14793, which would often be prohibitively expensive. However, the EA stipulate in Annex B of 'Performance standard for organisations carrying out manual stack emission monitoring', version 8, that it is only necessary to demonstrate equivalence of a P-AMS (or T-CEM as it's known in the UK) if the P-AMS does NOT have an MCERTS certificate. To add a

component NOT covered by an SRM (see Clause 7.2) the user needs to carry out five tests: zero, response time, detection limit, lack of fit; interferents. The last of these tests may be carried out computationally (see Annex B of CEN/TS 17337).

Ongoing QA/QC requirements are then the same for the added component as all others, i.e. annual response time and lack of fit tests. The lack of fit test can 'double up' in that the exact same data used to demonstrate lack of fit can be used to demonstrate that the calibration remains valid under Clause 9.3.3, which is also an annual requirement.

2.1.2 (Q2) If a parameter is not associated with a limit that we test I can see clients just accepting non accredited tests with FTIR which I assume would be ok if this was previously flexible scope and the cost is prohibitive for us if the client won't cover that

Certainly, for a measurement that is outside of a given scope then as long as it is stated as such it can still be claimed that CEN/TS 17337 is being followed.

2.1.3 (Q3) the 400s for reactive gases proves a problem then I can see us reverting to extractive tests which would be more time and cost we would have to pass on

All CEN P-AMS based methods (EN 15058, EN 14789, EN 14792, EN 16429, CEN/TS 17021) now require the P-AMS to have been type approved in accordance with EN 15267-4. To fit into the overall CEN framework CEN/TS 17337 requires the same. On the one hand questioning the validity of a response time test result leads down a dangerous path as if that test result can't be relied upon, what's to say any of the test results can be relied upon? Without trust in the TUV/MCERTS certificates P-AMS based monitoring becomes unviable. However, on the other hand, it is generally recognised that users have undeniably had issues in reproducing response time test results for the reactive gases (HF, NH_3, HCl).

TGN M22 dealt with this by removing the test requirement for HF, NH_3 and HCl. As a non-CEN document and only having domestic applicability this was possible, however, as mentioned above this wasn't a viable option for CEN/TS 17337 and would not have been supported by TC 264 'Air Quality'.

In terms of a practical 'work around' there are one or two options. With respect to a response time test in the field then after setting up the measurement system one option is to place the probe and sample stack gas to passivate the apparatus (15 min can be sufficient depending on flow rate). If the system has been allowed to fully passivate then the response time test requirement should be routinely met. Furthermore, from a QAL2 perspective it is the response time of a fully stack gas passivated P-AMS that is the parameter that needs to be known. i.e. the difference between the response time of an un-passivated P-AMS and a passivated AMS will not show to what degree one lags behind the other when both measuring stack gas over a 3-day period.

With respect to the annual response time test in the laboratory the above is generally not possible as there is no such source to sample from. However, dry passivation - although taking significantly longer to achieve then wet passivation - will then allow the response time test requirement to be met. An example is shown below of a real annual response time test using ~16 $mg.m^{-3}$ of HCl. After a significant period of dry passivation of the measuring system the HCl/N_2 is switched out and pure N_2 switched in, once stable zero readings (<2% of range) are achieved the rise response time test is initiated and this achieves a time of <400s, as equally does the fall time test, hence, both serving

(along with other annual tests) to confirm the P-AMS system is in normal working order post manufacturer annual servicing.

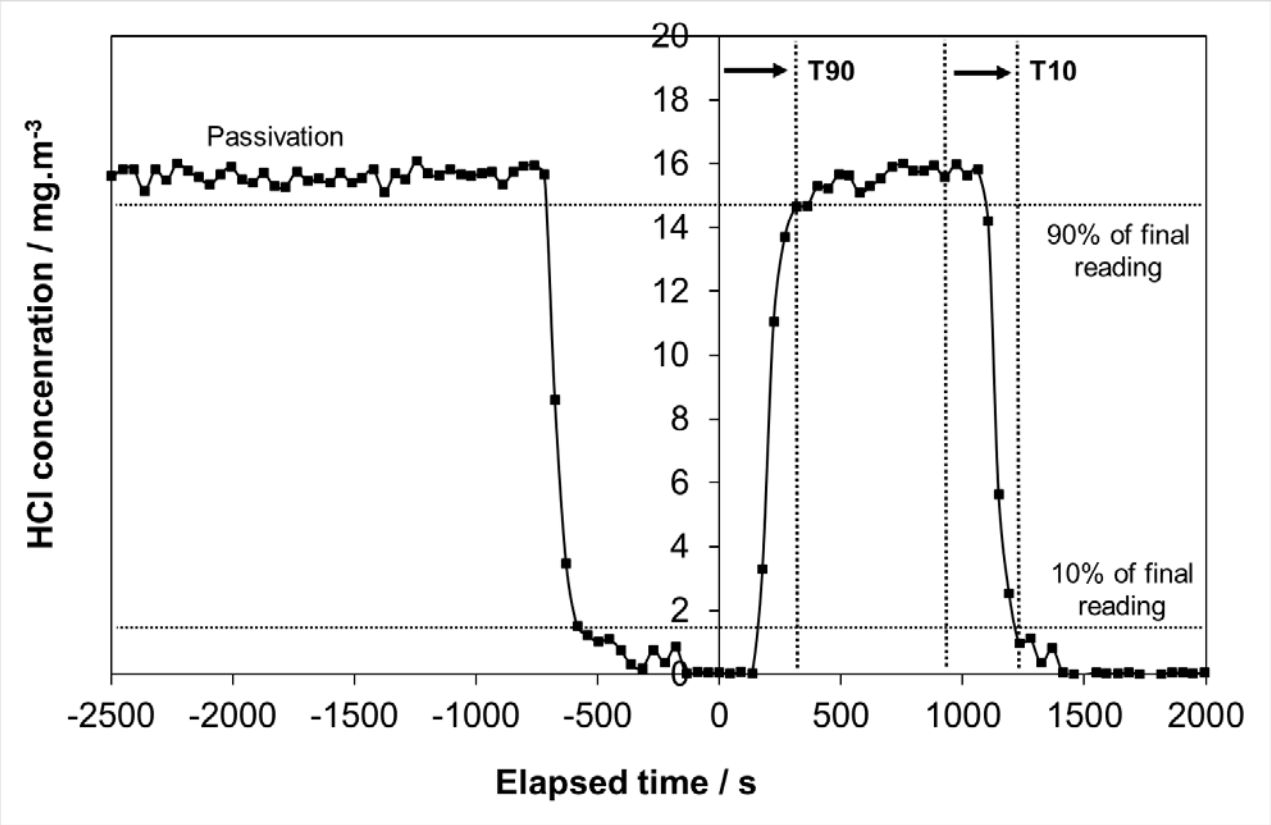

Figure 1: Real example of annual rise and fall response time testing switching between pure N_2 and ~16 mg.m^{-3} HCl/N_2 after dry passivation (with ~16 mg.m^{-3} HCl/N_2) of the measuring system.

Publication of SRM EN 16429, HCl by P-AMS

EN 16429 is a document higher in the CEN hierarchy than CEN/TS 17337 and is the defacto recognised SRM for HCl by P-AMS. EN 16429 was requested by EC Mandate and has been through formal validation similar to the other SRMs (except without a round robin laboratory component as this is not a 'wet chemistry' method). The rationale behind the EC Mandate was that EN 1911 is now defined as a method for 'total chlorides' and therefore the community needs an SRM that measures only HCl. EN 16429 is species specific (HCl) and any optical technique that meets the requirements of EN 15267-4 is permitted, however, if the technique selected is an FTIR then EN 16429 refers to the additional QA/QC provided in CEN/TS 17337. EN 16429 doesn't as such require a field response time to be determined, but importantly it does **require WET zero and span goes to be applied directly into the analyser and then down the entire system (i.e. HovaCAL type approach)**. **The difference between the wet HCl readings direct into the analyser and then down the entire system must agree to 2% or better**. CEN/TS 17337 aligns with this test requirement from the SRM. (As part of the sample line validation the user could determine the response time if there is a need, but it is not mandatory in EN 16429).

Across Europe nations who so far have rejected a P-AMS based approach to HCl monitoring and preferred to stay with wet chemistry methods (e.g. Germany) are unlikely to change their approach and so will mandate the use of EN 1911 and most likely only allow the use of EN 16429 + CEN/TS 17337 for non-regulatory / investigative purposes. How those nations that have embraced P-AMS monitoring will respond is as yet unclear. From a recent survey under the EMPIR Heroes project it appeared as though there was more use of domestic approaches based on TGN M22 (the forerunner to

CEN/TS 17337) than CEN/TS 16429 (the forerunner to EN 16429 prior to EC Mandate and validation). However, now 16429 has been validated to EN level and is the defacto SRM for HCl by P-AMS we may see this change.

2.1.4 (Q4) Is it true the response time in the field was not in the standard at final draft stage and only got entered back in by mistake due to an editorial comment?

It is not correct that the response time test was not in the final draft stage of the document. However, what is correct is that an earlier draft of CEN/TS 17337 had a different approach with respect to sample line validation. In this earlier draft there was a proposed approach where a user could differentiate between a sample line in the field that was “unaltered” from that in the annual testing and one that was “altered”. If the sampling system was different in some way (length / material / flow rate / etc.) from that used in the annual tests, then the user would have to do what is in the current published version of CEN/TS 17337 – i.e. pass the most reactive gas (most likely HCl) into the analyser, then down the sampling system and demonstrate the 2 values agree to <=2%, and also demonstrate a response time of <400s. However, in this earlier draft of CEN/TS 17337 if the user could show the sampling system was the same as that used in the annual testing the user could then pick ANY gas to validate the sampling system as long as it was one that had been used in the annual testing. So, if for example this was CO, in the field the user would pass CO directly into the analyser and then down the sample line and demonstrate the two values agree to <=2%, and also determine the response time. This response time would have to agree with that obtained in the annual testing (allowing some tolerance).

The argument against the “unaltered” sample line approach was that something like CO is not a sufficiently robust test. If, for example, there is a build-up of dirt a user could very easily loose reactive gases from the stack. This would be shown up by dry HCl but not dry CO.

2.1.5 (Q5) Do you know why a response time was not included in EN 16429 but is included for HCl in TS 17337? Also, I’m not sure if EN 16429 and TS 17337 should be linked together. I think it would be simpler to have accreditation to either EN 16429 (“traditional” analyser approach) or to TS 17337 (this would be an AM to EN 16429 and EN 1911, using the FTIR’s multi gas analyser approach).

It's not clear why there isn’t a specific in-field response time test in EN 16429 (for further discussion on this see next question). However, it is noted that there are tests to validate the sampling system in-field. EN 16429 - in common with the pre-2017 versions of EN 15058 and EN 14792 – requires the user at the start of the measurement period to pass test gas of the measurand (so HCl in this case) into the analyser and then down the sample line and agree to <= 2%. Then at the end of the measurement period the user must pass HCl through the complete measuring system once more to determine drift. It had been a requirement to do this with dry HCl. However, during the EC Mandated validation it was shown that better / quicker / more reliable results could be achieved with a wet gas injection approach compared to dry. Hence, post validation, EN 16429 was changed to require in-field testing to be done with wet zero and wet span gas and NOT allow the use of dry gas.

So, in terms of sample line validation EN 16429 and CEN/TS 17337 are aligned if injecting wet gas. The difference is that CEN/TS 17337 also allows sample line validation with dry gas or even analyte spiking, i.e. 3 approaches are permitted.

It is worth noting that for some time sample line validation with wet gas injection has been discussed at CEN (since clearly it’s far more representative of measuring a stack than dry gas, and also will pick

up cold spots) but it wasn't until the validation of EN 16429 that the membership had the confidence to require it in a standard.

2.1.6 (Q6) In terms of response time checks on site, the other CEN SRMs for gas sampling do not require them. They include a statement about minimising line length and being aware of what the response time is when calibrating CEMS. I wonder if we can argue that because the response time is tested as part of EN 15267-4 (using equipment that is not practical for routine monitoring work) and will be checked annually at the base location it does not need to be repeated on site. I think it is also ok to agree that there is no need to do an analyser check followed by a system check. Just doing a system check only should be ok. The pass criteria in M22 of 5% could be used (this is the same as the analyser check criteria, so meeting it through the entire system is a more challenging test anyway).

This proposal has merit. In addition, EN 14181 itself does deal with relative response times of the P-AMS and AMS, and so users should already be considering this in their procedures for the implementation of this standard. Hence, it's not unreasonable to relax the response time testing in CEN/TS 17337 on this basis. To do so would present little risk to quality. The more important test really is the validation of the sampling system. In CEN/TS 17337 the requirement for this test was relaxed compared to TGN M22. Under CEN/TS 17337 HCl is passed into the analyser and must agree with the certified value to <=5%, it is then passed down the sampling system and this reading must agree with the analyser reading to <=2%. So currently there could be up to 7% difference to the certified value and the test would still comply. Putting HCl ONLY down the entire measuring system and being required to agree with the certified value to <=5% is indeed more stringent. Hence again, there seems little risk to quality if the sample line was validated under the more stringent requirement as in TGN M22. (This assumes all users are using the Check Gas approach rather than the Zero and Span approach, which is now an option under the TS).

2.1.7 (Q7) One of the other items raised was to do with analyte spiking and the 70% recovery. How would that then be applied to recovery corrections, for example if 70% was achieved then is that just 70% recovery for all or does 70% equate to 100%? Although, this approach is unlikely to be used in Europe.

The analyte spiking in CEN/TS 17337 and TGN M22 was based on the approach used in USA standards (see USEPA 320 and ASTM D-6348-12). Neither of the American standards give any instruction of what a user should do with the recovery result from an uncertainty budget perspective, hence, neither do CEN/TS 17337 or TGN M22. An omission, but in reality, it's very difficult to know what should be done with the result. If, for example, the recovery was as low as 70% (which would be a pass, just) and losses of 30% were included in the uncertainty budget then compliance with the required uncertainty for most species would probably be as issue. Alternatively, the assumption might be made that any recovery from 70% to 100% means the losses in the sampling system are zero. However, this is a significant assumption to make. Some further reading has revealed that USEPA 321 places some further recommendations on the application of analyte spiking. The standard states that if the concentration of HCl in the stack varies by more than 5% that analyte spiking 'should' not be used. However, importantly the standard goes on to state that correcting data to the recovery is carried out subject to approval by the Administrator. If data are corrected there is then some justification for not including sample line losses in the uncertainty budget, as this source of bias is being corrected for potentially only leaving a residual error. Whilst this is a better approach to analyte spiking than is in

USEPA 320 and ASTM D6348-12, it does require more work by the user in terms of demonstrating the concentration in the stack doesn’t vary by more than 5%.