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New good practices for emission measurements and relevance of the SRM with respect to these requirements/practice

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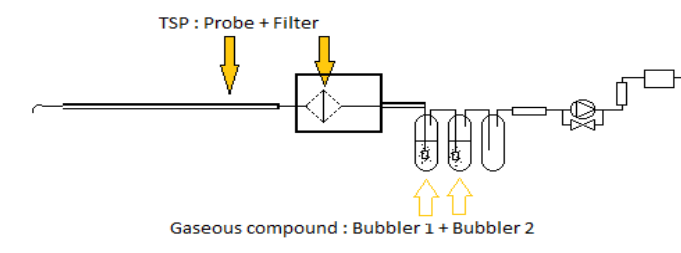
1. New good practices for emission measurements

The French accreditation body (Cofrac) has recently improved its reference document “LAB REF 22” dedicated to emission measurements by fixing enhanced measurement practices and new requirements to implement SRMs and to determine measurement results. The French regulation is also moving forward with Cofrac to fix new requirements to be in line with this new document.

- **Rule for summation of the results when some are lower than the LoQ**

Background

The rules to sum up the concentrations of a compound captured on different compartments of the sampling line (filter, rinsing of the probe, different impingers or bubblers or cartridge, rinsing...)



or to sum up different congeners (PCDD/PCDF; PCB, PAH) or different compounds of the same family (e.g. Heavy metals) differ from one laboratory to another. Then, the comparison of results from different sources can become problematic.

Sometimes, the rule of summation may be very conservative and some plant like the large combustion plants, with a very high emission flow, may arise in the national inventory among the most emitting installation. Such a situation is very unlikely but may occur when a laboratory facing the summation of compartments associated to results below LoQ chooses to consider them as equal to LoQ. The same situation may occur when one sum up a list of compounds of the same family.

We can avoid this situation by requiring :

- a sensible rule for summation of concentrations
- and an adaptation of the implementation of the SRMs to reach a LoQ adapted to the measurement task.

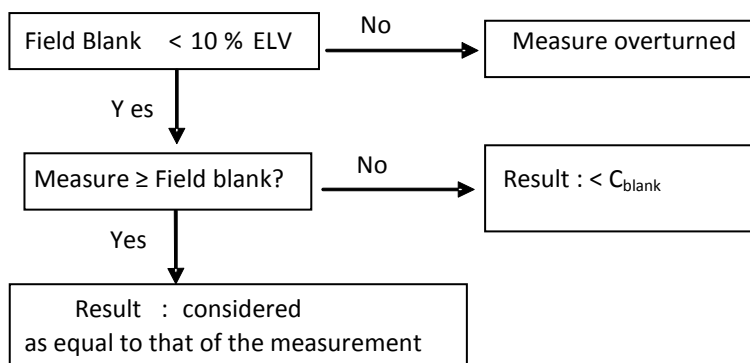
Rule of summation of concentrations

For results lower than $LoQ/3$: the compound will be considered as not detected ; a zero value will be considered for the summation.

For results between $LoQ/3$ and LoQ : the compound will be considered as detected ; a $LoQ/2$ value will be considered for the summation

Comparison of concentrations with the field blank

LAB REF 22 recalls the rules :



To compare the measurement result with the field blank value, the rule of calculation stated above in the case of analyses lower than the LoQ must be observed, whenever the results of the measurement are from the analysis of several compartments or only one (see example in the table hereafter).

Examples of application for an ELV equal to 70 mg/m₀³

Measure (M), in mg/m ₀ ³		Field Blank (C _{blank}), in mg/m ₀ ³		Conformity C _{blank}	Comparison M / C _{blank}	Result
Compartment 1	Compartment 2	Compartment 1	Compartment 2			
< 3 (LoQ)	< 1 (LoQ/3)	< 1 (LoQ/3)	< 1 (LoQ/3)	C	1,5+0 > 0+0 M > C _{blank}	= 1,5
< 3 (LoQ)	< 1 (LoQ/3)	< 3 (LoQ)	-	C	1,5+0 = 1,5 M = C _{blank}	= 1,5
< 3 (LoQ)	< 1 (LoQ/3)	3,5	< 1 (LoQ/3)	C	1,5+0 < 3,5 M < C _{blank}	< 3,5
3,2		3,8	-	C	3,2 < 3,8 M < C _{blank}	< 3,8
< 3 (LoQ)		< 1 (LoQ/3)			1,5 > 0 M > C _{blank}	= 1,5
3,2	< 3 (LoQ)	3,8	-	C	3,2+1,5 > 3,8 M > C _{blank}	= 4,7
3,2	< 1 (LoQ/3)	3,4	-	C	3,2+0 < 3,4 M < C _{blank}	< 3,4
4	< 1,2 (LoQ/3)	< 3,6 (LoQ)	< 3,6 (LoQ)	3,6 + 3,6 > 7 NC		
3,2	< 3 (LoQ)	4,1	< 3 (LoQ)	4,1+3 > 7 NC		

Checking of conformity of absorption efficiency

For a calculation of an absorption efficiency which requires summing up concentrations, it is necessary to consider: a null concentration for the compartment where the concentration is lower than $LoQ/3$ and a concentration equal to $LoQ/2$ if the measured value lies between $LoQ/3$ and LoQ .

To have a common approach for all “manual methods” it is allowed, when the measured concentration is low and when the first efficiency criterion cannot be reached, that a second criterion applies: the concentration in the last washing-bottle has to be lower than the LoQ .

These contractual arrangements will have clearly to be indicated in the test report.

- **An implementation of the SRM adapted to the measurement task**

The French regulation and LAB REF 22 require that the control laboratory adapts the duration of its sampling and/or use an analytical technique making it possible to reach a limit of quantification (LoQ) lower than 10 % of the ELV for the measurand aimed by the ELV (for an individual compound or a sum of compounds).

The laboratory must show that it made the provisions to implement this requirement by providing the values of LQ expressed in the same units as the VLE in his test report (on dry gas at O_2 ref concentration).

LAB REF 22 specifies the way to calculate the limit of quantification for the automatic and manual methods:

- in the case of the automatic methods, the LoQ is given EN 15267-3:

$$LoQ = 4 \times S_{r0} \text{ for automated methods}$$

- for « manual methods », an approximate of the LoQ of the method is calculated starting from the LoQ of the analytical step divided by the volume of sample gas, expressed under the conditions of the ELV, and the rule which applies is:

$$LoQ = 10 \times S_{r0} + C_{\text{average,blank}} \text{ for « manual methods »}$$

Then, the laboratory has to check if the uncertainty at this LoQ is less than 60 %. If it is not the case, the LoQ has to be raised. The LoQ is determined according to § 5.2.3 of the standard NF T 90-210.

$$U_{LoQ} \leq 60 \% \quad \text{for manual method}$$

2. Relevance of SRMs

AFNOR has studied the relevance of the current SRM with respect to the requirements:

1. The expanded uncertainty at the daily ELV must fulfill the requirement of the SRM and when there is none, it should not exceed 50 % of that of the AMS fixed by the IED
2. $LoQ < 10 \% ELV$

The table given hereafter studies the situation for incineration plants.

Summary of uncertainties at the level of daily ELV

Expanded uncertainties are estimated from the reproducibility confidence intervals obtained during intercomparison measurement campaigns with a sampling duration of 1 hour.

Parameter	ELV	U in %	Comments
Dust	5 mg/m ³	≈ 70	Rinsing of the probe is the main source of uncertainty Criterion : U < 0,5 U _{max} (15%) is not fulfilled
	10 mg/m ³	≈ 60	
SO ₂ (sulfur dioxide)	5 mg/m ³	≈ 120	Criterion : U < 0,5 U _{max} (10%) is not fulfilled → extension of sampling duration is not realistic → change the SRM ?
NO _x (nitrogen oxides)	50 mg/m ³	≈ 13	We are close to 0,5 U _{max} (10%) Criterion can be reached for higher ELV
COT (total organic carbon)	10 mg/m ³	≈ 40%	Criterion : U < 0,5 U _{max} (15%) is not fulfilled
CO (carbon monoxide)	50 mg/m ³	≈ 17%	Criterion : U < 0,5 U _{max} (5%) is fulfilled for concentrations > 120 mg/m ³
HCl (chlorhydric acid)	10 mg/m ³	≈ 80%	Criterion : U < 0,5 U _{max} (20%) is not fulfilled → Extend duration to 4h00 or change the method?
HF (fluorhydric acid)	1 mg/m ³	No data	Criterion U < 0,5 U _{max} (20%) is not fulfilled → change the method
Cd+Tl (cadmium and tellurium)	0,05 mg/m ³	>100 %	No Criterion
Hg (mercury)	0,05 mg/m ³	≈ 50 %	Criterion not fulfilled → Extend the sampling duration ?
Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V (antimony, arsenic, lead, chromium, cobalt, copper, manganese, nickel, vanadium)	0,5 mg/m ³	>100 %	No Criterion
PCDD/PCDF (dioxins / furans)	0,1 ng/m ³	Probably > 50%	No criterion Sampling duration is already > 6 h
PAH (polycyclic aromatic hydrocarbons)	0,01 mg/ m ³		No criterion

Conclusion: Among compounds which are used for continuous monitoring and for which IED has defined a maximum uncertainty U_{max} (CO, NO_x, SO₂, TVOC, Dust, HCl, HF, NH₃) for incineration plants, none of them fulfills the requirement of an uncertainty better than ½ of U_{max} defined for AMS, at the daily ELV defined. The target is almost reached for NO_x.

For manual SRMs a better uncertainty could be reached by carrying out much longer sampling, but this could be not sufficient and economically demanding.

For automatic SRMs, the level of uncertainty is generally better (CO, tVOC) but the sensitivity to interfering compounds does not allow reaching a sufficiently low level of uncertainty. A better technic with higher selectivity seems to be necessary in the future.

Summary of LoQ of SRMs

For manual methods a sampling duration of 1 h has been considered

Parameter	ELV	LoQ	comments
Dust	5 mg/m ₀ ³ 10 mg/m ₀ ³	2-3 mg/m ₀ ³	Criterion LoQ < 1/10 ELV not fulfilled ⇒ sample higher volumes or longer ⇒ use instack filtration
SO ₂ (sulfur dioxide)	5 mg/m ₀ ³	≈ 0,15 mg/m ₀ ³	Criterion LoQ < 1/10 ELV fulfilled LoQ of automatic methods is generally worse but some certified instruments can fulfill the criterion
NOx (nitrogen oxides)	50 mg/m ₀ ³	≈ 2 mg/m ₀ ³	Criterion LoQ < 1/10 ELV fulfilled
COT (total organic carbone)	10 mgC/m ₀ ³	≈ 0,15 mgC/m ₀ ³	Criterion LoQ < 1/10 ELV fulfilled
CO (carbon monoxide)	50 mg/m ₀ ³	0,3 - 1,3 mg/m ₀ ³	Criterion LoQ < 1/10 ELV fulfilled LoQ of certified analysers may be worse
HCl (chlorhydric acid)	10 mg/m ₀ ³	0,3 mg/m ₀ ³ Ion Chromat. 0,03 mg/m ₀ ³ Spectroscopy	Criterion LoQ < 1/10 ELV fulfilled
HF (fluorhydric acid)	1 mg/m ₀ ³	≈ 0,5 mg/m ₀ ³	Criterion LoQ < 1/10 ELV fulfilled for ELV ≥ 5 mg/m ₀ ³
Cd+Tl (cadmium and tellurium)	0,05 mg/m ₀ ³	Close to 2 µg/m ₀ ³ for each compound	Criterion LoQ < 1/20 ELV fulfilled
Hg (mercury)	0,05 mg/m ₀ ³	Close to 2 µg/m ₀ ³	Criterion LoQ < 1/10 ELV fulfilled
Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V	0,5 mg/m ₀ ³	Close to 2 µg/m ₀ ³ for each compound	Criterion LoQ < 1/90 ELV fulfilled
PCDD/PCDF (dioxins / furans)	0,1 ng/m ₀ ³	0,3 to 10 pgITEQ/m ³ (3 m ³ sampled) ICP mass	LoQ ≤ 1/100 ELV for each compound
PAH (polycyclic aromatic hydrocarbons)	0,01 mg/ m ₀ ³	Close to 0,3 µg/m ₀ ³ for each compound	

Conclusion: Among compounds which are used for continuous monitoring and for which IED has defined a maximum uncertainty U_{max} (CO, NO_x, SO₂, TVOC, Dust, HCl, HF, NH₃) for incineration plants, most of them fulfill the criterion $LoQ < 1/10$ ELV except for dust and HF.

3. General Conclusion

The French accreditation body (Cofrac) has recently fixed new measurement practices and new requirements to implement SRMs and to determine measurement results :

- a sensible rule for summation of concentrations when some of them are below LoQ,
- the adaptation of the implementation of the SRMs to reach a LoQ adapted to the measurement task.

These good practices allow :

- to standardize the practices for all the fields (water, air) for the choice of LoQ with a maximum level of uncertainty,
- to be able to compare the results from one lab to another and from one site to another,
- to get inventories more representative of the actual situation

The SRMs have been reviewed, for the field application of incineration, to check consistency with these new good quality requirements.

It appears that :

- the LoQ of the SRMs are adapted except for dust and HF
- the actual uncertainty of SRMs at the level of ELV is often much higher than what is necessary for the control the conformity of the ELV or to implement the calibration of AMS according QAL2.