Measurement uncertainty – implications for the enforcement of emission limits

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INTRODUCTION

The second generation EC Directives such as the Waste Incineration Directive (WID), Large Combustion Plant Directive (LCPD), Solvents Directive (SD) and the Pollution Prevention and Control Directive (IPPC) impose not only emission limits on individual pollutants but also specify the measurement uncertainty that has to be achieved by automated monitoring systems and incorporated in the process of regulation. This approach creates a link between the Directives and a variety of auxiliary standards describing the monitoring techniques, calibration methods and measurement quality assurance and management.
Despite the fact that measurement uncertainty requirements are clearly stated in the Directives it is difficult for regulatory authorities across Europe to ensure that they have resolved this issue in a comparable and consistent manner and have effective implementation procedures. One of the problems encountered by the regulatory authorities is that the measurement uncertainty assessment methodologies established for air emissions do not translate well into other media such as water and land where the custom and practice are substantially different. Another problem has been continuing adherence to the methodological principle of reliance on manual standard reference methods (SRMs) that have been left behind by rapidly advancing technology, no longer reflect best available techniques, and may not be best suited to act as a basis for measurement quality management.
The objective of this paper is to examine the way in which the measurement uncertainty is estimated and to find the best way of using uncertainty information in the regulatory process. The philosophy of compliance assessment is also reviewed in order to establish the best practice allowing for technically sound and legally robust approach where a measure of non-compliance severity is defined leading to different follow-up actions.

ESTIMATION OF MEASUREMENT METHOD UNCERTAINTY

Whenever decisions are made on the basis of analytical results, it is important to have some indication of the suitability of the results for the purpose at hand. The principle of analysing the measurement results in such a way that the uncertainty is always interpreted in favour of the process operator forms a basis of the regulatory approach in many countries. Measurement uncertainty and its interpretation in the process of compliance assessment has also become an important feature of the current generation of industrial process directives. The measurement uncertainty is also specified in the Air Quality Directives. All these directives impose a limit on the measurement uncertainty as a condition of the suitability of results for regulatory purposes. It is therefore very important that the compliance assessment process takes the measurement uncertainty into account in a consistent way across all the industrial processes and determinants for which the emission limits have been prescribed.
The term uncertainty usually describes the range of values that the true value can be expected to fall within at the user specified level of probability. The uncertainty of a measurement delivered by an analyser or a measuring procedure can be attributed to a number of component uncertainties that must be identified and quantified. The overall uncertainty (or combined uncertainty) results from both systematic and random effects and can be represented by a single value. The measurement uncertainty can be assessed in the following ways:

- Repeatibility analysis by one laboratory using standard reference materials. This is a good and convenient way of assessment as the information produced includes the combined effect of many sources of uncertainty;

- Inter-laboratory comparisons (reproducibility analysis). A collaborative study carried out e.g. to validate a published method may be a good source of data to support an uncertainty estimate. This approach often includes paired comparisons and Round Robin tests;
- Estimates based on instrument specification, calibration results, proficiency test data and the results of fundamental research on the principle of the method;
- Estimations based on considered judgement. This approach is the least defensible and may contain a large degree of subjectivity.

The final stage of the uncertainty estimation process is the combination of component uncertainties to determine the combined expanded uncertainty to be used in the compliance assessment. There are a number of statistical approaches available but the most commonly used is the one described in the ISO Guide to Uncertainty in Measurement (GUM). The combination involves calculation of a square root of the sum of squares of the component uncertainties on the assumption that the errors are additive or subtractive.

QUANTIFICATION OF MEASUREMENT METHOD UNCERTAINTY IN STACK EMISSION MONITORING STANDARDS

Currently available standard methods, whatever their origin, are not transparent in their approach to measurement uncertainty. The availability of information on uncertainty can be summerised as follows:

- Old standards do not mention uncertainty;
- In older particulate matter standards the term “accuracy” is used but measurement uncertainty is probably implied without specifying the confidence limit;
- New standards are not consistent in quantifying the measurement uncertainty – internal and external variability, repeatability and reproducibility, external uncertainty etc have been variously derived from method validation studies;
- Most methods require revisiting the issue of uncertainty and may require conducting additional validation tests to be able to form a view on their uncertainty at limit value.

The first generation of EC Directives on incineration and combustion did not address the issue of uncertainty in their approach to emission limit values. The simple way of looking at permits and their requirements relied on comparing absolute measurement results with the limit value and assuming that any value above the limit constitutes a breach. This approach is illustrated in Fig 1. However, regulatory experience has demonstrated on numerous occasions that such a practice can be easily challenged in courts and is not sufficiently robust and defensible.

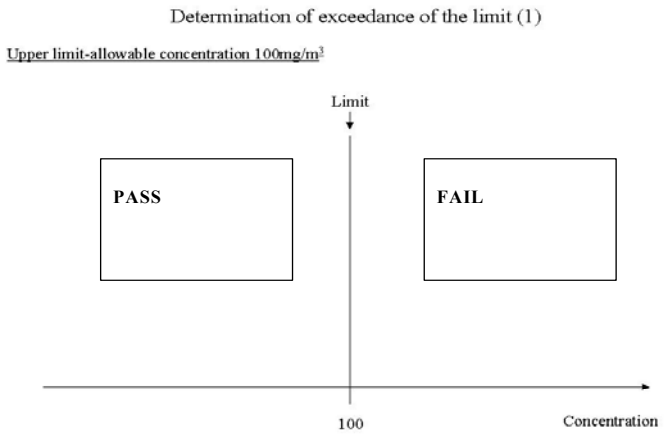

Fig.1 Approach to assessment of compliance with regulatory limit based on absolute value

Measurement uncertainty is specified as a regulatory requirement in the second generation EC Directives and the equipment used to for the measurements of stack emissions must be capable of delivering measurement uncertainty (95% confidence intervals) equal to or better than the values given in Table 1.

Table 1 Measurement uncertainties specified in WID and LCPD

Pollutant	95% confidence interval
Total dust	30%
TOC	30%
HCl	40%
SO_2	20%
NO_x	20%
CO	10%

Examples of measurement uncertainty estimates for different species based on monitoring experience are given in Appendix1.
WID and LCPD require that measurement uncertainty is always subtracted from the result leading to the regulatory situation illustrated in Fig. 2. When the measurement result is below the limit and the limit value is outside the confidence interval the process is in clear compliance of the emission standard. Even when the measured value exceeds the limit but is still within the confidence interval the process is still compliant. A clear case of non-compliance occurs when the measurement result exceeds the limit by a margin greater than half of the confidence interval.

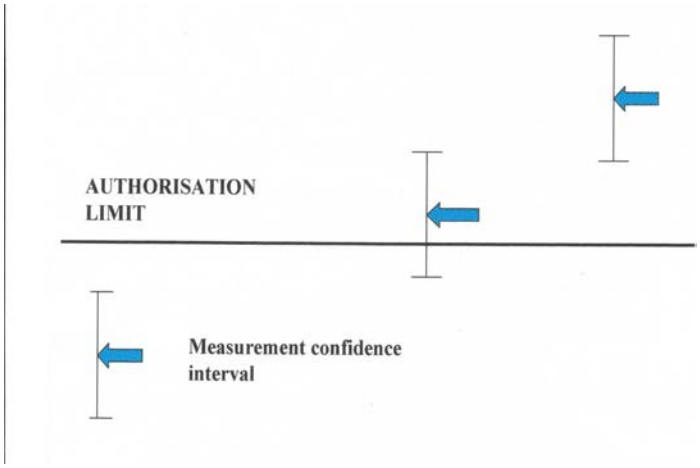

Fig. 2 Incorporation of measurement uncertainty into compliance assessment process in the requirements of WID and LCPD

Fig. 3 illustrates the concept of allowable measurement uncertainty and the 95% confidence interval constituting a safe zone within which the measurements may be grouped without triggering a response from the regulatory authorities. This becomes critical if an industrial process operates close to the emission limit value but is of lesser importance much below or above the limit.

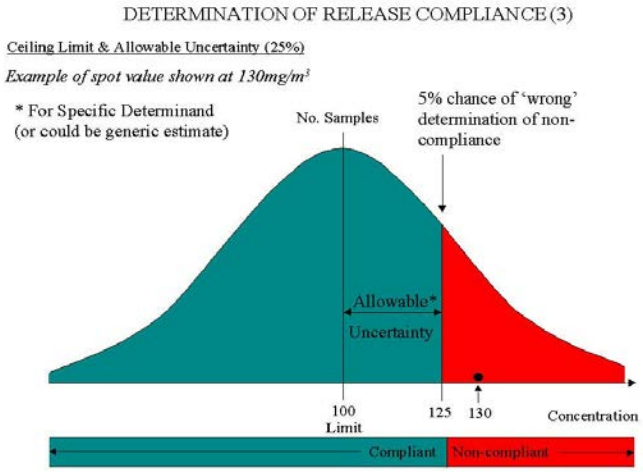

Fig.3 Approach to assessment of compliance with regulatory limit incorporating the concept of measurement uncertainty

It is clear that the degree of non-compliance may be judged from how much the measurement result is above the limit value and what is the associated estimate of the probability of wrong determination. It is possible to devise a scheme where the severity of non-compliance is categorised in terms of the probability of incorrect determination leading marginal non-compliance, substantial non-compliance and gross non-compliance. Such an analysis enables a risk-management based approach to enforcement. Each scenario may require different regulatory response from increased surveillance to direct intervention and process closure.

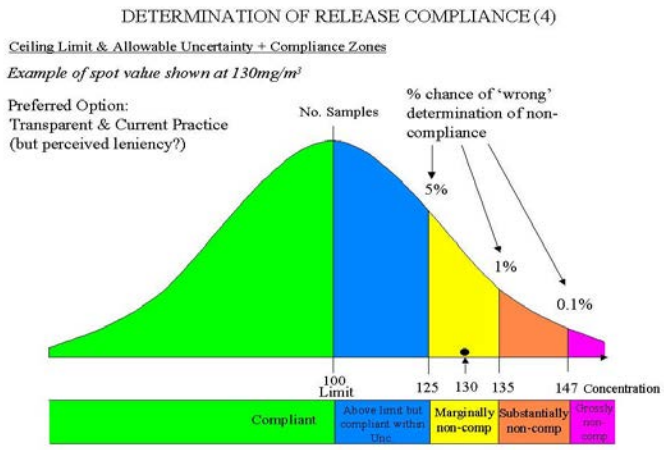

Fig. 4 Severity of non-compliance with regulatory limit

CONTROVERSIAL ASPECTS OF THE SUBTRACTION OF UNCERTAINTY

The administrative principle of subtracting a reasonable proportion of the possible measurement uncertainty from a single measurement value close to the regulatory limit gives a “benefit of the doubt” to the process operator. Stringent adherence to the principle of automatic subtraction of measurement uncertainty during the whole of the data processing and assessment process is less defensible and reduces the technical and scientific utility of the measurement process. This is clearly illustrated by the following examples:

- Subtraction of the uncertainty from low instrument readings may lead to negative values and ignores the fact that the measurement uncertainty depends on the magnitude of measured quantities, being best defined at limit value;
- It may be not correct to calculate percentile values from the corrected instantaneous results;
- Calculation of annual averages using values corrected for uncertainty introduces a bias that does not exist in real life and will have an impact on, for example, emission inventories;
- The value of process emission measurements for policy development work and public information is reduced.

The increased availability of automated measurement methods offers policy makers improved information and the regulator opportunities for better control mechanisms. Under ideal circumstances the mean of a large set of measurements, such as that from an automated measurement system (AMS), approaches the true population mean. A greater confidence in the estimate of the mean, together with the known method uncertainty, better enables the observer to judge the level an emission limit is likely to be exceeded by. The measurement, however, is usually made on a process waste stream that has its own variability and so the observed result is a combination of both the measurement and process variance. There is a case, based on risk-management principles, to instigate more regular testing where there is a danger of breach of emission limits – the higher the probability of a breach (see Fig 3) the more frequently inspections (independent measurements) might be made. If the time series data thus derived demonstrates a continuing pattern of exceedence the probability increases that an operator is consistently and repeatedly breaching the spirit of the regulation. In such circumstances there is a justification for the benefit of the doubt to be progressively removed.

CONCLUSIONS

- The knowledge of measurement uncertainty is a fundamental requirement in the process of regulatory compliance assessment;
- Currently the compliance assessment process has to give full “benefit of the doubt” to the site operator but it is desirable to devise a harmonised EU scheme whereby the regulatory response would be in proportion to the severity of potential non-compliance;
- There is still insufficient information on the uncertainty of measurements using manual sampling trains and continuous analysers;
- Instrument certification schemes provide comprehensive information on measurement uncertainty and their use should be encouraged;
- Regulatory Authorities across EU should aim to develop a common compliance assessment approach to meet the requirements of the relevant Directives and be consistent and fair in regulation.

ACKNOWLEDGMENTS

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Appendix 1 Examples of uncertainty estimates for compliance assessment of measured stack releases to air

DETERMINAND	SAMPLING METHOD	METHOD DESCRIPTION	AVERAGING TIME	UNCERTAINTY ESTIMATE
ACIDIC SPECIES				
Total acidity as SO_2 equivalent	BS6069	Wet chemistry	Half an hour to several hours	25 %
HF	US EPA Method 26	Wet chemistry	Half an hour to several hours	25%
HCl	US EPA Method 26	Wet chemistry	Half an hour to several hours	25%
HCl	EN 1911	Wet chemistry	Half an hour to several hours	20-50%
HCl	Gas filter correlation analyser	Automatic analyser	User definable	18%
H_2S	In-situ NDIR analyser	Automatic analyser	User definable	15%
SO_2	US EPA Method 6	Wet chemistry	Half an hour to several hours	20%
SO_2	BS 6069 Section 4.1	Wet chemistry	Half an hour to several hours	20%
SO_2	In-situ NDIR analyser	Automatic analyser	User definable	15%
SO_2	Electroche -mical cell analyser	Automatic analyser	User definable	15%
NO_x	In-situ NDIR analyser	Automatic analyser	Use definable	15%
NO_x	Chemilumi -nescent analyser	Automatic analyser	User definable	12%
NO_x	Electroche -mical cell analyser	Automatic analyser	User definable	20%
METALLIC SPECIES				
Total metals	US EPA method 29	Wet chemistry	Half an hour to several hours	50-200%
INORGANIC SPECIES				
Ammonia	In-situ NDIR analyser	Automatic analyser	User definable	15%
Ammonia	Chemilumi -nescence	Automatic analyser	User definable	15%

Phosphorus as P_2O_5	US EPA Method 29	Wet chemistry	Half an hour to several hours	50-200%
Tar fumes	US EPA Method 23	Wet chemistry	Half an hour to several hours	50-200%
ORGANIC SPECIES				
VOC speciated	Adsorption - thermal desorption	Manual sampling method	Half an hour to several hours	25%
Dioxins TEQ	US EPA Method 23	Wet chemistry	Six to eight hours	50 - 100%
Dioxins TEQ	BS 1948-1 Filter method Dilution method Cooled probe method	Wet chemistry	Six to eight hours	50 - 100%
Amines	Absorption on silica gel	Wet chemistry	Half an hour to several hours	25%
Organic sulphur compounds	Adsorption onto resin	Manual sampling method	Half an hour to several hours	25%
Benzene	Adsorption thermal desorption	Manual sampling method	Half an hour to several hours	25%
Polynuclear aromatic hydrocarbons (PAH)	Adsorption onto resin	Manual sampling method	1 hour to several hours	50-100%
MISCELLANEOUS				
Particulates	ISO/DIS 12141 Dust at low concentra-tion	Manual sampling method	Half an hour to several hours	8%
Particulates	Extractive Beta ray absorption	Automatic analyser	User definable	20%
Particulates	In-situ light scattering analyser	Automatic analyser	User definable	20%
PM_{10}	US EPA Method 102 and 201A	Manual sampling method	User definable	50%

Oxygen	Para-magnetic analyser	Automatic analyser	User definable	10%
Oxygen	Zirconia probe analyser	Automatic analyser	User definable	5%
Water vapour	Infrared analyser	Automatic analyser	User definable	10%
Water vapour	Gravi-metric	Manual method	Half an hour to several hours	25%
CO	Extractive NDIR analyser	Automatic analyser	User definable	12%
Gas velocity	Tribo-electric	Automatic analyser	User definable	5%
Gas velocity	Ultrasonic	Automatic analyser	User definable	5%

Note: The uncertainties quoted in this table have been determined at 95% confidence level i.e by multiplying the repeatability standard deviation by a coefficient equal to 1.96.