



Uncertainty in Source Monitoring Measurements



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Introduction

This talk will

- Review requirements for reporting uncertainty
- Discuss what uncertainty is
- Look at the issues with regard to source monitoring
- Describe the approaches and advice available
- Act as a taster for the STA TTS on Uncertainty



Why all this fuss over uncertainty ?

- Current and proposed legislation both national and international require that emission data are reported together with an estimate of the uncertainty
- European Directives such as the Hazardous Waste Incineration Directive require data quality objectives to be met.
- These are expressed as uncertainty requirements on the reported values.





Example of EC requirements

➤ The Waste Incineration Directive requires

- CO 10%
- SO₂ 20%
- NO₂ 20%
- Dust 40%
- TOC 30%
- HCl 40%

- Expressed at the limit value, for a single measurement with a level of confidence of 95%



Environment Agency and MCERTS

- The EA's MCERTS scheme requires that monitoring is carried out to recognised methods
- Technical guidance notes (eg M2 and MIDs)
- MCERTS for organisations requires UKAS accreditation to ISO 17025
- The OMA scheme raises the value of monitoring done under ISO17025 to operators



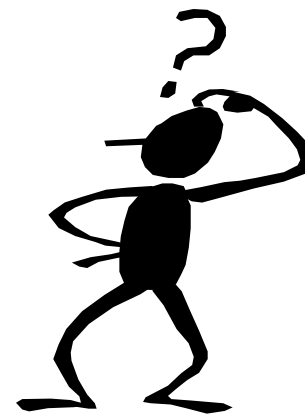
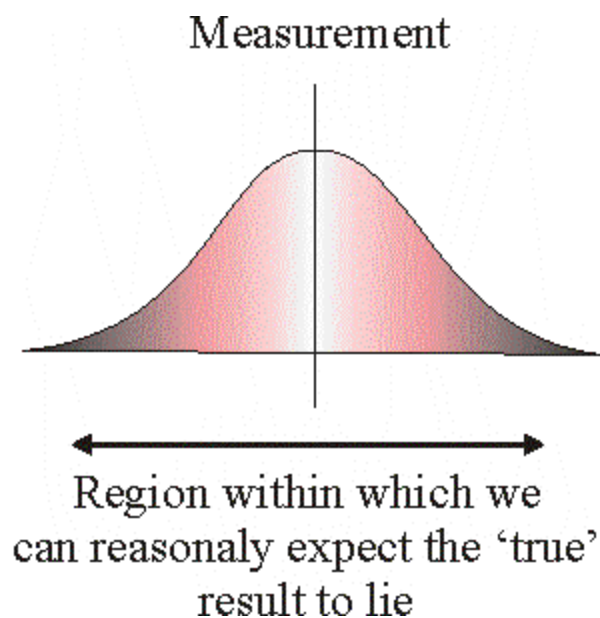
ISO 17025 requirements

- All measurements shall have and apply a procedure for estimating uncertainty
- Where rigorous approach not possible – ‘shall at least attempt to identify all the components of uncertainty and make a reasonable estimation’
- If a well characterised test method exists which specifies limits to the major sources of uncertainty and specifies how to report them, then it may be sufficient to follow the standard
- In many stack monitoring standards this is questionable



What is Uncertainty ?

- It is a quantifiable property of a measurement
- 'A measure of spread about the result of a measurement, within which we can reasonably expect the true result to lie'

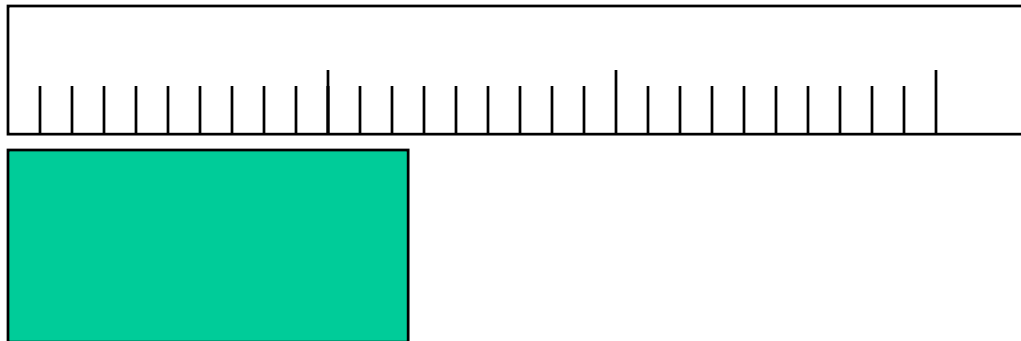


What is not uncertainty

- **Accuracy** - strictly speaking accuracy is not a quantifiable term
- **Error** – this is the difference between the measurement result and the unknown (and unknowable) true result
- **Note** - gross errors or mistakes are not quantified within uncertainty – it is assumed the measurement has been performed correctly



Basic concept of measurement uncertainty



Uncertainty in our ability to read the ruler
Uncertainty in the ruler scale
Change in the ruler due to temperature

Calibrate the ruler
Repeat the measurements
Test the ruler for temperature dependence
~(type approval)
Control the environment



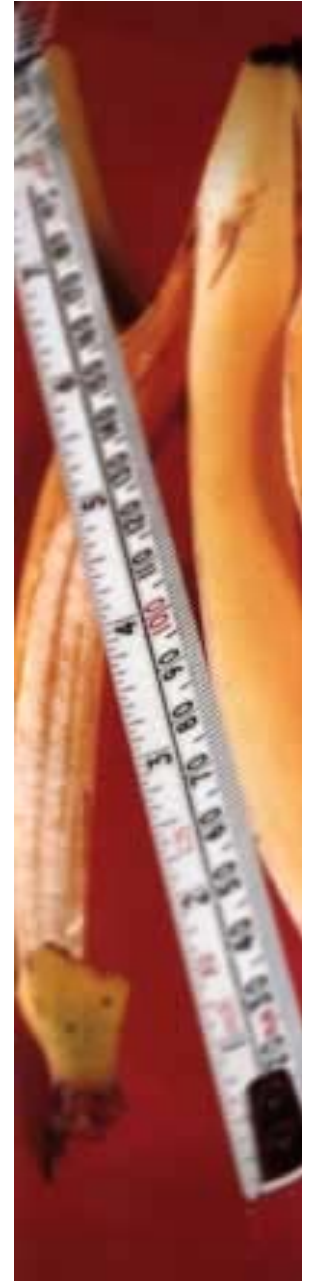
Simple approach

- With our ruler example, we can always measure the block, with different rulers, different people, multiple times
- After all that we can look at the statistics
- Calculate uncertainty from the standard deviation of our results



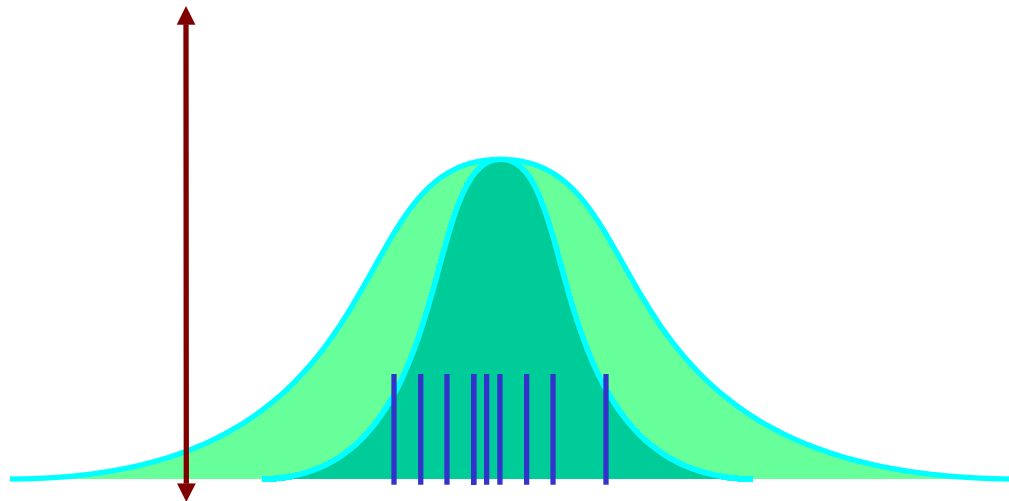
The problem with stack monitoring

- With stack monitoring, we do not have a fixed block to measure
- We probably don't even have a particularly good ruler
- The calibration doesn't cover the whole measurement
- Any variation we see in the results could easily be due to changes in the stack



Repeatability, Bias, and Uncertainty

- Repeatability – variation between successive measurements
- Bias – systematic – constant, difference
- Uncertainty – quantification of all causes of ‘error’



Stating uncertainty

- Reported as an interval with a level of confidence
- how big the uncertainty is and how sure we are about it
- $X \pm U$ with a level of confidence of 95 %
- There are a number of ways of calculating uncertainty



Tools to help

- Measurement Standards, SRM's
 - If followed exactly may be able to quote uncertainty
 - Give performance criteria which can be used
- Guide to Uncertainty in Measurement
- General ISO/CEN standards on uncertainty
- STA's guidance, TTS
- TGN - M2
- Other guides and interpretations
 - Eurochem, NPL guide, training courses



Measurement Uncertainty given in Standard Methods

- Should all include a statement of the uncertainty of the method
 - In general these are not blanket statements for the measurement as a whole
 - Simple example – generally only apply to a single measurement, and won't include corrections for stack conditions
- CEN are adopting a unified approach to uncertainty, currently in ambient standards but will extend to emission standards
- Validated – generally under only a subset of conditions
- Example - EN12619:1999 - TOC(FID)
 - Reports results of trials on hazardous waste incinerator and municipal waste incinerator.
 - Quotes 'likely', and 'approximate' uncertainties for instruments complying with standard



Problems with standards

- Still many older standards, even CEN ones eg EN 1948-Dioxins, EN 1911 HCl which don't provide a statement of the measurement uncertainty
- Give statements of internal repeatability and external repeatability
- These on their own are not a statement of uncertainty



Other Standard Methods

- Older ISO standards rarely give uncertainty information, though they may quote results of limited validations or present some performance characteristics
- EPA Methods rarely give and estimate of the uncertainty. They require audit samples to agree to eg 10%, and may state detection limits and precision/bias.



QA/QC CEMs

- For CEMs EN 14181 provides procedure for the QA/QC of AMS
 - Assessment of a method as being suitable - ‘type approval’ – MCERTS and ISO 14956
 - Determine uncertainty of methods will meet directive requirements
 - Defined QA/QC regime
 - designed to ensure CEM results have uncertainty determined above
 - Includes calibration against SRM, continued control and AST
- SRMs are being drafted which are intended to meet the above requirements. These are both manual and instrumental.



Consistent Approach to uncertainty

- There is a consistent approach for uncertainty calculation
- Guide to the Expression of Uncertainty in Measurement – GUM
- Provides an overarching methodology for calculating uncertainty
- Several more accessible guides based on the GUM have been written
- STA's – Guidance on Assessing Measurement Uncertainty in Stack Emissions Monitoring
 - How to estimate uncertainty due to deviations from a method
- EUROCHEM Guide – second edition



ISO Standards-Uncertainty

- Guidance documents
 - Guide to the expression of Uncertainty in Measurement (GUM)
 - International Vocabulary for Metrology (VIM)
- The ISO standards being produced under TC 146 SC 4 form a set of related methods addressing the uncertainty of air quality measurements
 - ISO 9169
 - ISO 14956
 - ISO 11222
- ISO 5725 Parts 1-6 Accuracy Trueness and Precision of measurement methods and results
- ISO 3534 Parts 1-3 Cover the definitions of statistical terms



ISO standards

- New ISO standard being developed which aims to provide guidance on estimating uncertainty for air quality applications (ambient and emissions)
- Currently working draft (WD 20988)
- Will provide procedures specifically targeted at some of the key issues
- Examples based on typical cases
 - Reference methods
 - Manual sampling
 - CEMS



ISO 5725

- ISO 5725 Parts 1-6 , Accuracy (trueness and precision) of measurement methods and results
- Based on the assessment of a method as enacted by a set of measurement laboratories measuring controlled test samples
- Defines two measures of uncertainty,
 - trueness - the difference of the mean result from the expected result
 - precision - the variability of the results
- No assessment of influences beyond those occurring within the intercomparison measurements.



ISO TC 146 SC 4 Standards

- These standards form a set designed to provide a toolkit of standards to help form the estimation of the uncertainty of an air quality monitoring result
- Conform to the GUM methodology
- Interrelated and consistent
- ISO 14956 is parallel voted as a CEN standard QAL 1



ISO 9169

- ISO 9169 'Air quality - Determination of performance characteristics of measurement methods'
 - currently under revision (new draft to include ISO 6879 - definition of terms)
 - Defines characteristics of a measuring method and provides a toolkit of methods to determine these.
- Defines characteristics such as
 - accuracy test
 - lack of fit (linearity)
 - drift
 - repeatability
 - capability of detection (ISO 11843)
 - response time
 - influence quantities
 - range



ISO 14956

- ISO 14956 Air quality - Evaluation of a measurement method by comparison with a stated measurement uncertainty
 - Provides the tools to enable the overall uncertainty of a measuring method to be determined from the individual performance characteristics.
 - Under revision, new draft in line with the principles of the GUM
 - Allows a measurement method to be compared with a required



Calculating Uncertainty

- Describe two approaches –
- Top down and bottom up
- These are being harmonised
- Look at issues in stack monitoring



Top down or Bottom up?

- Top down – overall uncertainty, from repeated applications of the method
- This is the ISO 5725 approach
- Many manual methods adopt this method
- Get a measure of repeatability and reproducibility
- Try to cover the combined effect of as many causes of uncertainty as possible
- New approach in CEN folds this within the GUM approach



Bottom up

- Define the measurement process
 - In principle we should know the 'measurement equation'
- Identify all potential sources of uncertainty
- Quantify these as standard uncertainties (variances)
 - by repeated measurement - Type A
 - by estimation - Type B
 - Insignificant contributions may be ignored
- Combine these as square root of the sum of the variances
 - for random uncorrelated sources
- Expand the combined uncertainty to give an estimate of the uncertainty with a required level of confidence by multiplying by a coverage factor
- Main drawback is that not all sources of uncertainty may be known or considered, and various assumptions are implicit



Determining Uncertainty Sources

- Repeated measurement (Type A)
 - Gives uncertainty contribution directly as variance
 - Only covers random uncertainty sources which vary during the measurements
- Use of stated uncertainty for a method (Type B)
 - Many standards do not give a full uncertainty statement
 - ISO 5725 style determinations – may overestimate uncertainty of an individual lab
 - Need to follow procedure exactly
 - Stated uncertainty may not apply to application
- Information from other sources (Type B)
 - Certificate for calibration gas
 - MCERTS test report
 - Manufacturers test report
 - result from UKAS analysis laboratory

- It is important not to 'double count' sources of uncertainty



Intrinsic Uncertainty Sources

- Intrinsic – internal sources of uncertainty invariant under operating conditions
 - For an instrumental method could be determined by type approval – MCERTS certificate
 - May be determined as part of method validation
 - May be determined by experiment
 - Can use these in our uncertainty estimation



Extrinsic Uncertainty Sources

- External – influence factors
- May be known, or previously (MCERTS) determined sensitivities – ie a known response to temperature or water vapour
- In this case we can either
 - Control the influence – no uncertainty contribution
 - Measure and correct for the influence-uncertainty contribution due to correction
 - Estimate uncertainty from known range of influence – potentially significant uncertainty
- To determine the standard uncertainty of these sources it is necessary to multiply the influence by the sensitivity



Combining Uncertainty Components

- Each identified component of uncertainty should be determined and expressed as standard uncertainty u_x , in units of the measurement.
- Uncertainties which are determined from repeated measurements we can calculate the standard uncertainty as the standard deviation of the results
- If a Type B uncertainty is quoted with a level of confidence we can obtain the standard uncertainty by dividing by the relevant coverage factor
- For other sources we may have to assume a distribution. Eg rectangular distribution, for which the standard uncertainty is the width/ $\sqrt{3}$
- Should consider relevant averaging for the measurement we are considering
 - Eg Calibration gas uncertainty will not average out



Combined Uncertainty

- Sum as variances

$$u_c^2 = \sum u_x^2$$

- u_x be independent, uncorrelated
- Some correlations can be handled by considering the measurement, for example the case of calibration gas mentioned on the previous slide is in effect a correlated uncertainty



Expanded Uncertainty

- In order to assign a level of confidence to our measurement we need to expand the combined standard uncertainty U
- Multiply by a coverage factor, k
- Usually we require a level of confidence of 95%
- The exact value of k depends the number of degrees of freedom in our measurement and the distribution
- Usually we use $k=2$

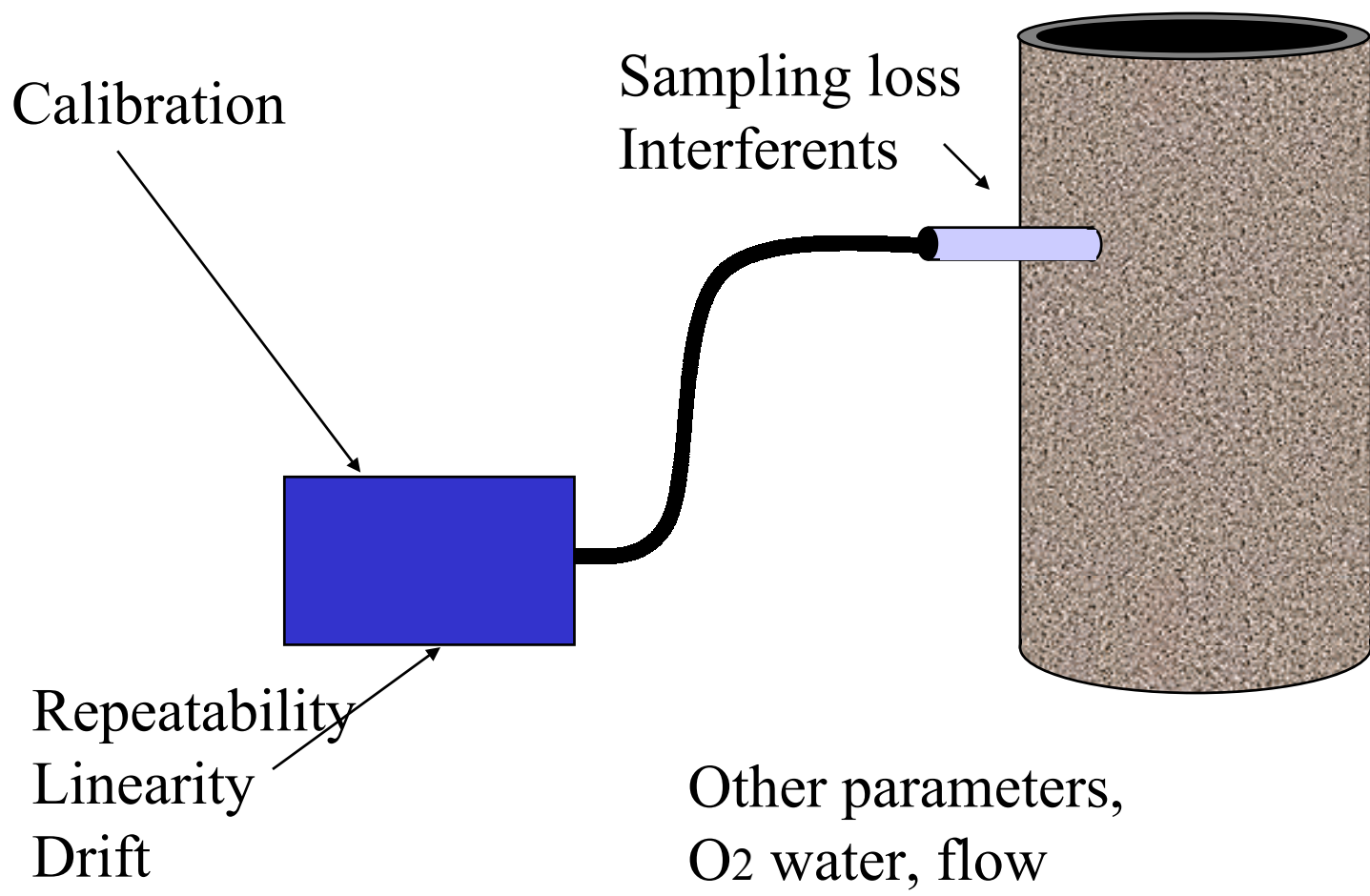


Expression of Uncertainty

- In units of the measurement or as a percentage of the measurement
- With a stated level of confidence – usually at 95% and with a statement of the coverage factor, k , used



Basic model of a stack measurement



Issues in stack monitoring

- Source varies, so cannot easily look at repeated measurements
- Calibration doesn't cover the whole measurement
- Validation in standards doesn't cover whole range of application
- Variations to standard methods often required



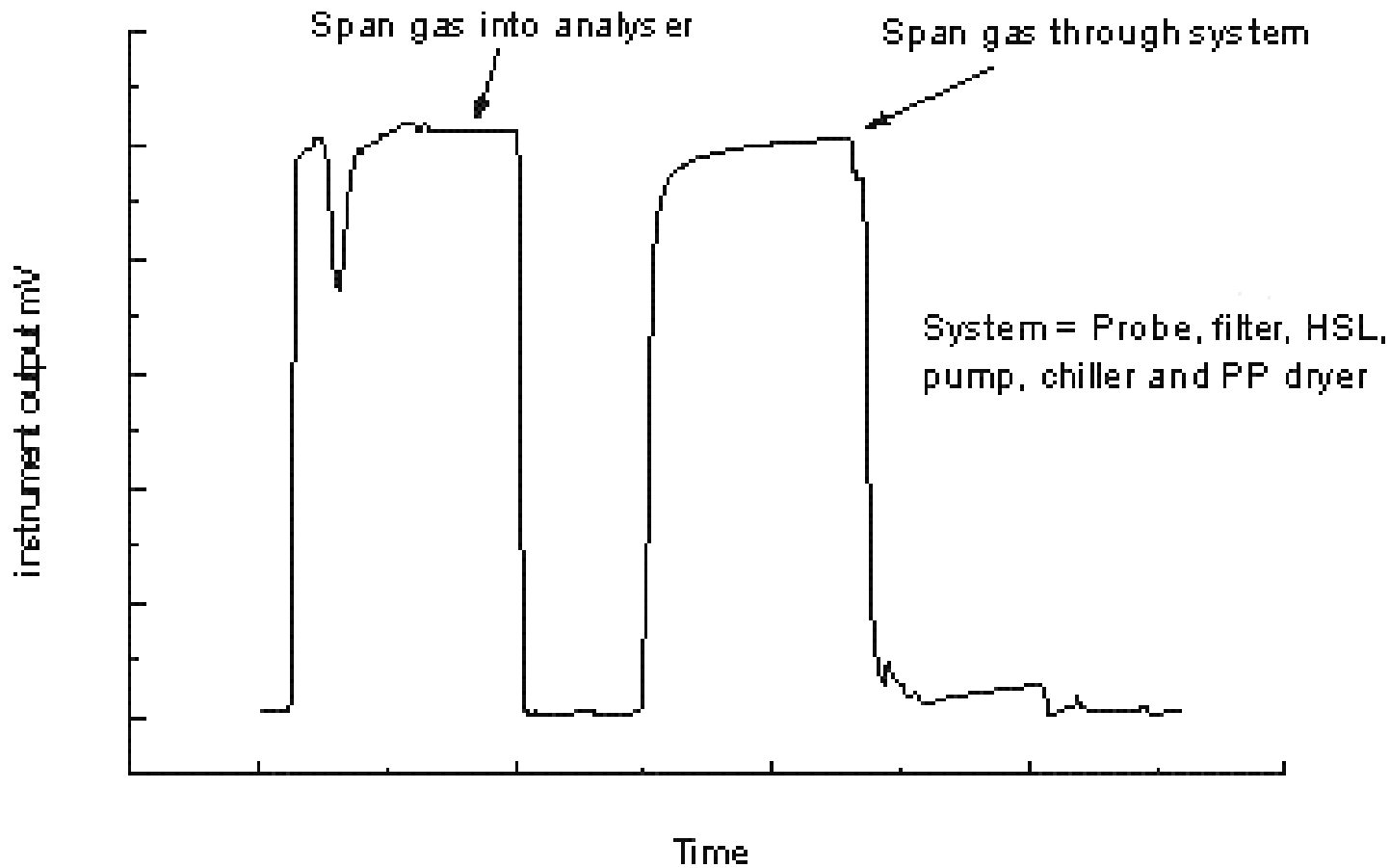
Example of an Uncertainty Calculation

- CO monitor used in a mobile laboratory
- 30 minute measurement
- Full scale 0-200 ppm CO
- Sources
 - Intrinsic instrumental parameters – determined from tests – repeatability, linearity (converter for NO_x), voltage stability
 - Influence factors – Interfering gases
 - Calibration gas – uncertainty of the gas and uncertainty due to instrument repeatability while calibrating
 - Sampling loss check
 - Drift over measurement period
 - Normalisation to standard conditions – uncertainty in determination of O₂, pressure and temperature



Typical System Test

Typical System 'Bias' Test with SO₂



Uncertainty Source	Distribution	u	Period	u	u ²	
		ppm		half hour measurement		
Repeatability Over measurement	Stdv	1	per minute	0.129099	0.02	
Calibration repeatability	Stdv	1	per minute	0.316228	0.10	
Calibration mixture CO ₂ (12%)	2% of value with level of confidence of 95%	1	per calib mixture	1	1.00	
	0.7% FS	1.4	Half hour	1.4	1.96	
Drift	zero	.1% FS per 24hr	0.004167	Half hour	negligible	0
	span	Rectangular	0.001042	Half hour	negligible	0
Flow rate fluctuation	1% FS	0.288675	Half hour	0.288675	0.08	
	Rectangular				0	
Sampling Loss	1% value	0.5	Half hour	0.5	0.25	
Linearity	1% FS	1.154701	Half hour	1.154701	1.33	
Oxygen	2%	1	Half hour	1	1.00	
				Uc	2.40	
				Uc 95%	4.79	

Result = 50 ± 4.8 ppm with a level of confidence of 95%



QA/QC

- As well as just calculating uncertainty
- We can use uncertainty analysis to see how to control uncertainty
- If most of the uncertainty is due to one uncertainty contribution
 - Can control or improve that characteristic
 - Control external influences
- Eg you can have best equipment and procedures in the world, but if you then calibrate with poor gas you've thrown all the hard work out of the window



Uncertainty in the STA

- Working on revised guidance
- Targetted at your issues
- TTS with workshops in the new year
- Looking to produce tools such as spreadsheets to handle common problems



Conclusions

- At some level you will all need to address and calculate uncertainties
- Consistent approaches do exist
- There are a number of guides and tools available
- There are some particular issues with stack monitoring
- STA, NPL and CEN/ISO are producing more tools



Some Questions for You

- Technical Transfer Seminar
Uncertainty
 - What are the main areas you want us to cover ?
 - What resources would you like us to produce ?

- NPL DTI funded programme
 - Valid Analytical Methods – physical programme
 - Next 3 year programme being formulated now
 - What areas do you feel are important

