

Trihalomethane Uncertainty Evaluation





Trihalomethane Uncertainty

We demand guaranteed rigidly defined areas of doubt and uncertainty

Douglas Adams



Trihalomethane Uncertainty

A Long Journey



Thanks for this work go to the team at Johannesburg Water Cydna Laboratories, especially Ms. Ewa Mrozek



Trihalomethane Uncertainty



Purpose of Trihalomethane analysis:

- Johannesburg Water is responsible for the supply and monitoring of drinking water supplied to the greater Johannesburg area as well as for waste water treatment.
- Drinking water is regularly monitored for compliance to SANS 241
- Part of the monitoring concerns THM's, a chlorination by product
- Levels are defined by SANS 241 drinking water standard
- Maximum level is set at 200 ppb



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Analytical methodology:

- Samples, from various points, are taken in glass bottles and preserved with ascorbic acid
- Aliquot is transferred to a vial
- Certified internal standard is added with a syringe
- Calibration curves are generated using standards prepared from certified stock solutions
- Sample is then analysed using a purge and trap sampler coupled to a GC-MS system
- Final result is calculated and reported



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Multi step method of evaluation of the analytical measurement

- **Step 1: Specification and modeling**
- Step 2: Identify the uncertainty sources
- Step 3: Quantify the uncertainty sources
- Step 4: Expand and, if needed, combine standard uncertainties of data sources
- Step 5: Combine the expanded uncertainties
- Step 6: Reporting the uncertainty



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Specification and modelling:

- Full description of the method – prompts one to consider the sources of uncertainty
- Flow diagram assists in this process



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Full Description

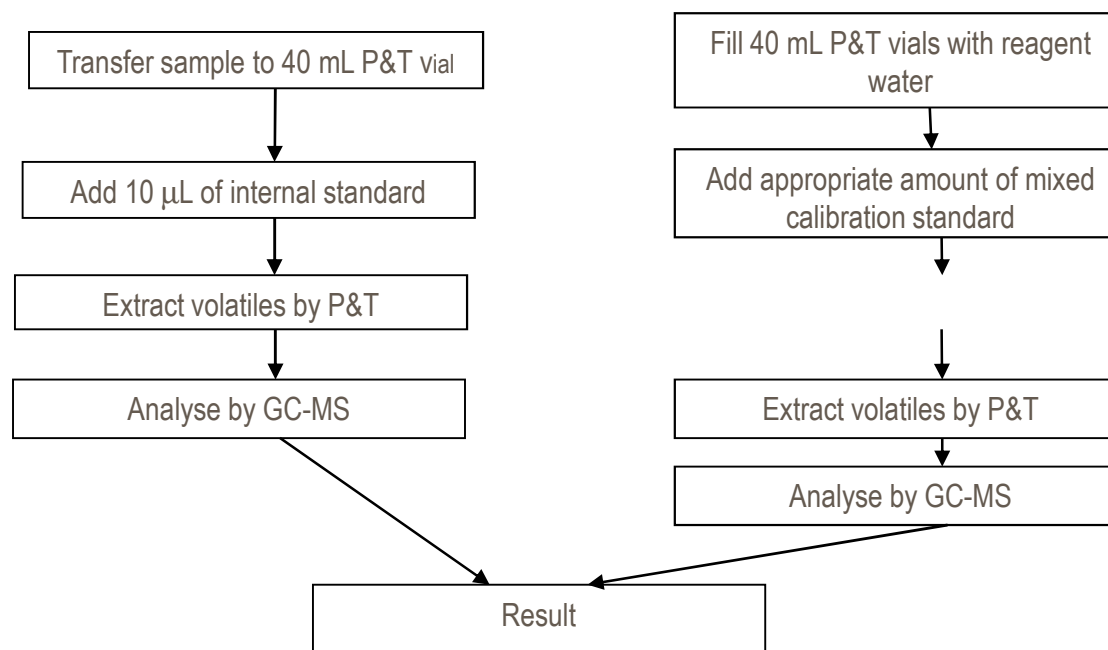
The determination of THM (measurand) in drinking water (matrix), using an internal standard method with purge and trap GC-MS (method). The method range is 1-100 ug/L.



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- Flow diagram





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MODEL

$$: \quad C_{\text{analyte}} = D \cdot I_{\text{analyte}} \cdot C_{\text{int.std.}} / A \cdot I_{\text{int.std.}}$$

Where:

- C_{analyte} = the concentration of the analyte (an individual trihalomethane)
- D = the dilution factor
- I_{analyte} = the peak area of the analyte
- $C_{\text{int.std.}}$ = the concentration of the internal standard
- A = the slope of the calibration curve
- $I_{\text{int.std.}}$ = the peak area of the internal standard



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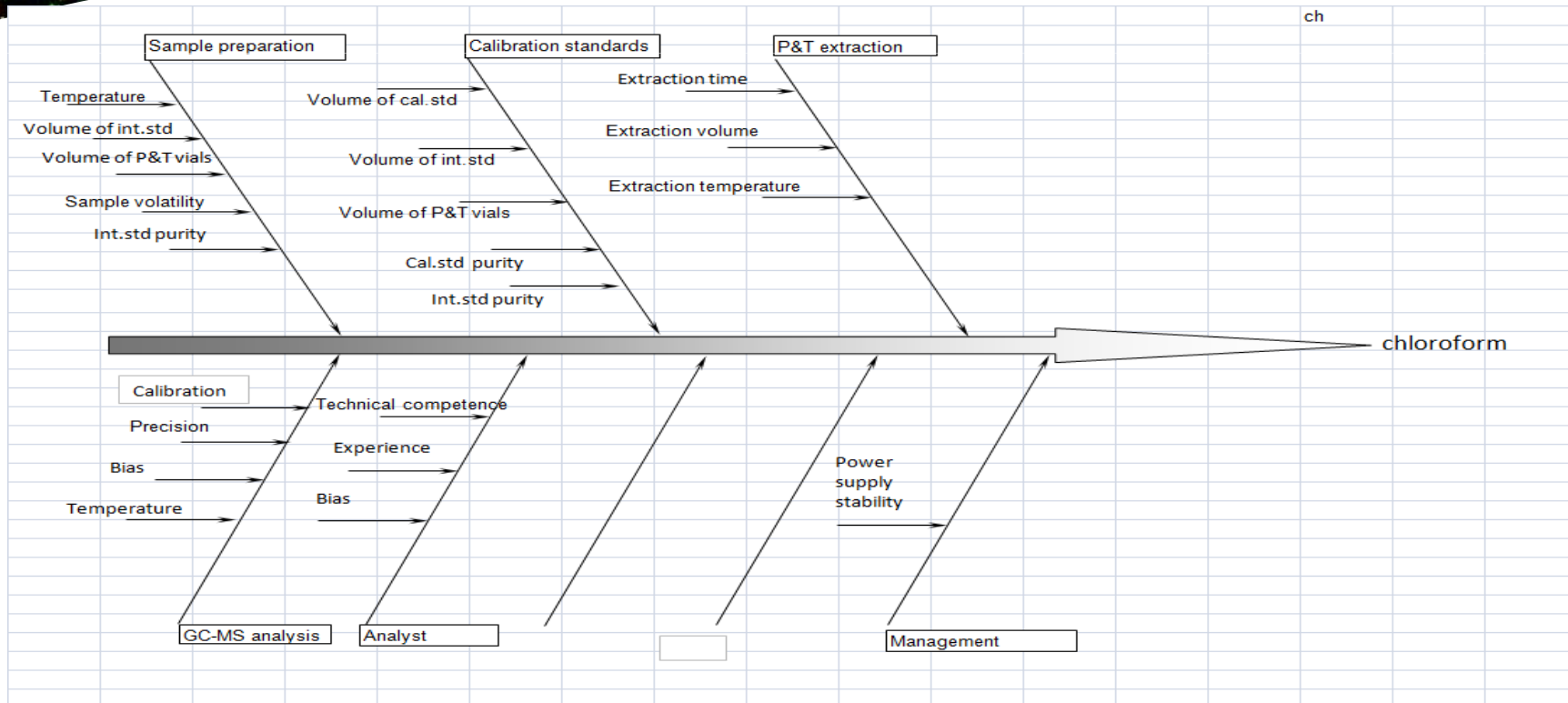
Step 2

Identifying the sources of uncertainty.

- In this step the Ishikawa, popularly known as the fishbone, diagram is used.
- The fishbone is a two stage process. In stage one all possible sources are added to the fishbone, as indicated in the following slide



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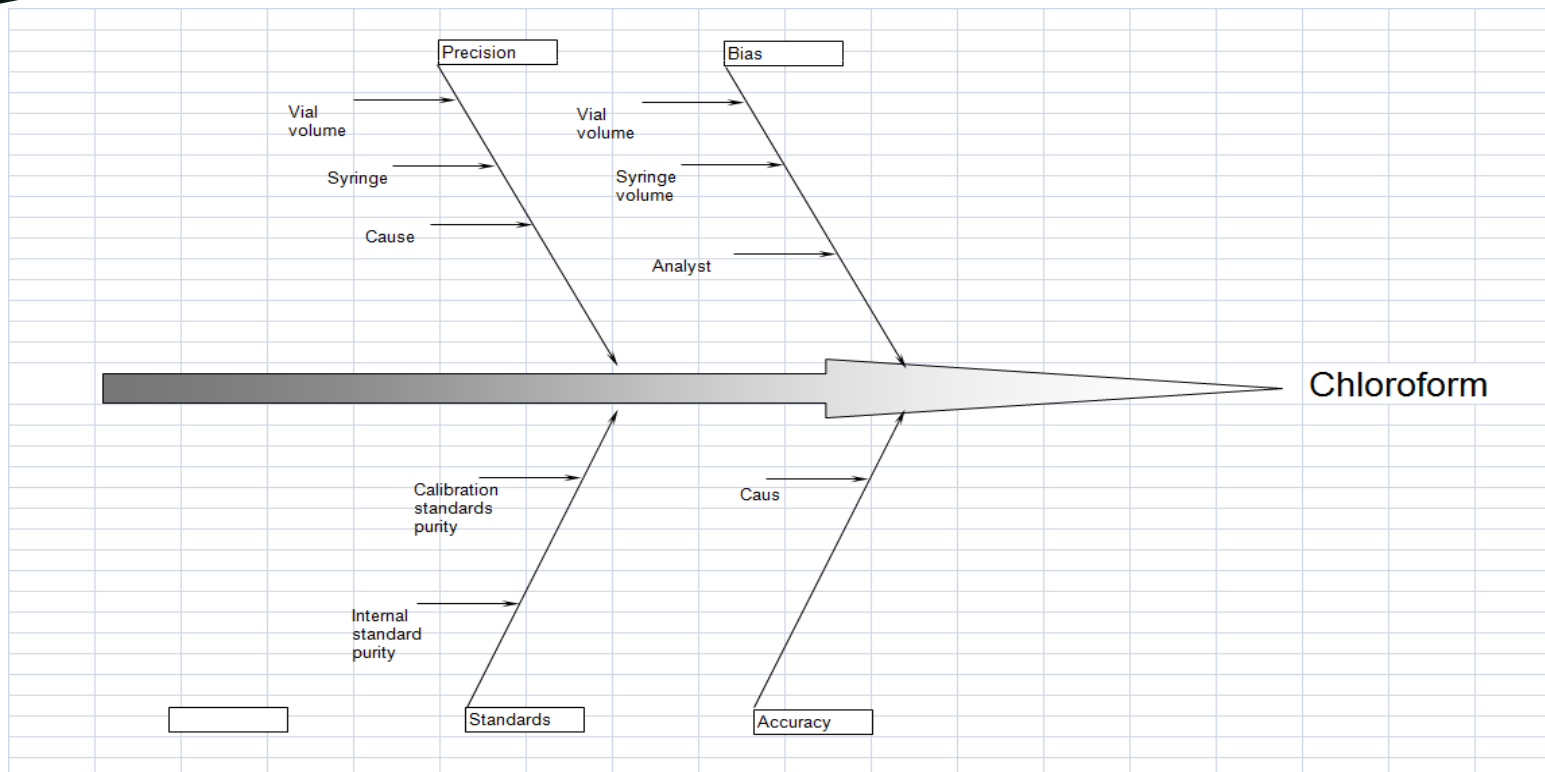
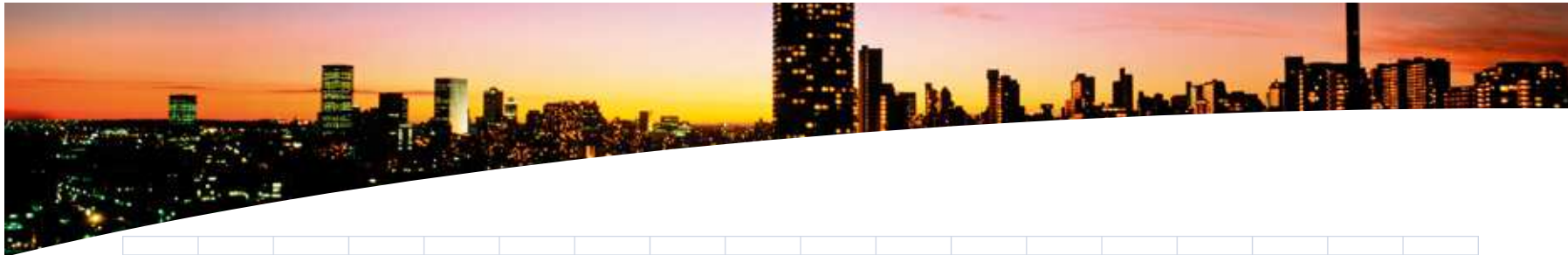


In stage 2 we simplify the fishbone as shown on the next slide. The reasons for the simplifications are:

1. All instrument related parameters would be included in either the calibration or precision bone.
2. All glassware related parameters would be included in the precision bone except vial and syringe
3. The purge and trap extraction procedure is the same for standards, quality controls (QA) and samples and will be included in the precision data as is any analyst variation.



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The resultant fishbone indicated four major sources of uncertainty:

- (i) method precision including reproducibility and repeatability
- (ii) method bias
- (iii) accuracy
- (iv) Calibration standards.



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Step 3

Calculating the expanded uncertainties of the parameters identified

- Vial Example:
The vial volumes were determined by statistical observation. Fifteen replicates were used and the standard uncertainty was calculated as the standard deviation divided by $\sqrt{15}$.
- Syringe Example
The standard uncertainty of the syringe was calculated from the manufactures data assuming a rectangular distribution and thus dividing the standard deviation by $\sqrt{3}$



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- Precision
Replicates of the method QA data were obtained from historical records. A best estimate and a standard deviation were calculated
- Reproducibility
The data obtained from the duplicate sample that was analysed during each run was utilised as a data source for method reproducibility.



- Accuracy – Regression
Calibration data from the previous 36 calibrations was obtained. A best estimate and standard deviation was calculated for the slope of the calibration curve.
- Calibration and Internal Standards
A best estimate and standard deviation was obtained from the certificates supplied.
- Method Bias
The data of 15 spikes, from the method validation document, was used



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Step 4

combine the standard uncertainty of each data source for each bone on the diagram

For this we calculated sensitivity co-efficients using method of approximation as shown in the next slide

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The sensitivity coefficient calculation for one THM component (chloroform) is shown below

MODEL	$C_{\text{analyte}} = D \cdot I_{\text{analyte}} \cdot C_{\text{int.std.}} / A \cdot I_{\text{int.std.}}$				power	%change
					1	1
	$C_{\text{analyte}} =$			25.96	2	0.1
					-1	0.1
CHLOROFORM					-2	0.01

Parameter	best est.	%		Δ	Y	Y'	$\Delta Y = Y' - Y$	C_j
I_{analyte}	10442485	1	0.01	104424.9	25.96126740	26.22088008	0.25961267	2.48612E-06
$C_{\text{int.std.}}$	25	1	0.01	0.25	25.96126740	26.22088008	0.25961267	1.038450696
A	2.834953	0.1	0.001	0.002835	25.96126740	25.93533207	-0.02593533	-9.148416947
$I_{\text{int.std}}$	3326815	0.1	0.001	3326.815	25.96126740	25.93533207	-0.02593533	-7.79584E-06
D	0.9379	1	0.01	0.009379	25.96126740	26.22088008	0.25961267	27.68020834

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For The Model:

CHLOROFORM

$$C_{\text{analyte}} = D \cdot I_{\text{analyte}} \cdot C_{\text{int.std.}} / A \cdot I_{\text{int.std.}} = 25.96$$

Parameter	Units	Best estimate	Half-range	Probability distribution	Divisor	Standard uncertainty, u_i	Sensitivity coefficient, c_i	expanded uncertainty, $(c_i \cdot u_i)$	Uncertainty contribution, $(c_i \cdot u_i)^2$
I_{analyte}									
injection volume (P&T)	mL	25	0.25	rectangular	1.732050808	0.144337567	2.48612E-06	3.5884E-07	1.28766E-13
detector response	counts	10442485	3290470	normal	5.916079783	556190.9441	2.48612E-06	1.382757249	1.912017608
$C_{\text{int.std.}}$									
certificate, $\mu\text{g}/\mu\text{L}$	$\text{ng}/\mu\text{L}$	100	5	rectangular	1.732050808	2.886751346	1.038450696	2.997748945	8.986498734
syringe volume, μL	μL	10	0.1	rectangular	1.732050808	0.057735027	1.038450696	0.059954979	0.003594599
P&T vial volume, mL	mL	42.6	0.2347	normal	3.872983346	0.060599279	1.038450696	0.062929364	0.003960105
D									
	-	0.9379	0.0051585	normal	3.872983346	0.001331906	27.68020834	0.036867437	0.001359208
A									
	-	2.834953	0.412902	normal	6	0.068817	-9.148416947	-0.629566609	0.396354115
$I_{\text{int.std}}$									
injection volume, mL	mL	25	0.25	rectangular	1.732050808	0.144337567	-7.79584E-06	-1.12523E-06	1.26615E-12
detector response	counts	3326815	270022	normal	5.916079783	45642.04843	-7.79584E-06	-0.355818307	0.126606668

Root of sum of squares $u_c(y) = \sqrt{\sum (c_i \cdot u_i)^2}$ 3.380886132



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Combine all the Expanded Uncertainties using root sum of squares.

Analyte	best estimate	Uncertainty Model	Uncertainty Bias	Uncertainty Precision Repeatability	Uncertainty Precision Reproducibility	combined Uncertainty
CHCl ₃	25.96	3.3808861	1.53019	0.340807	0.531721	3.764406



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- Determine the coverage factor (k) at a level of confidence of 95% with Infinite DOF
- This has a value of 1.96 which is rounded up to 2
- Multiply the combined expanded uncertainties by the coverage factor to give method uncertainty

Analyte	best estimate	Uncertainty Model	Uncertainty Bias	Uncertainty Precision Repeatability	Uncertainty Precision Reproducibility	combined Uncertainty	Method Uncertainty
CHCl ₃	25.96	3.3808861	1.53019	0.340807	0.531721	3.764406	7.52881109



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Multi step method of evaluation for the analytical measurement

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- **Step 6: Reporting the uncertainty**

-



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Final Step:

Round and report the data as per the example below.

26 ug/L chloroform +/- 7.6 ug/L at a 95% LOC with a coverage factor of k=2

This is a value of approx. 30%

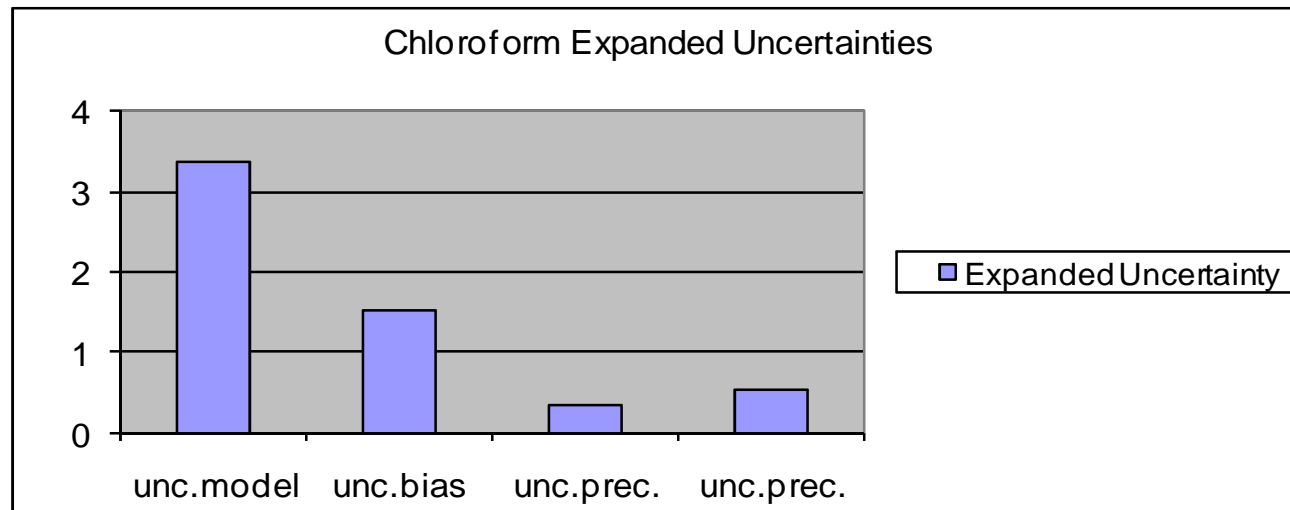


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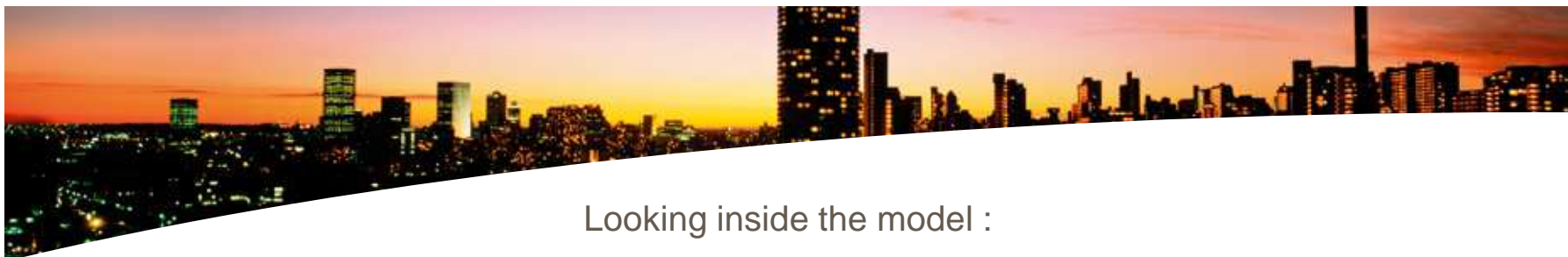
Discussion

What did we learn? Are we satisfied with approx. 30%??

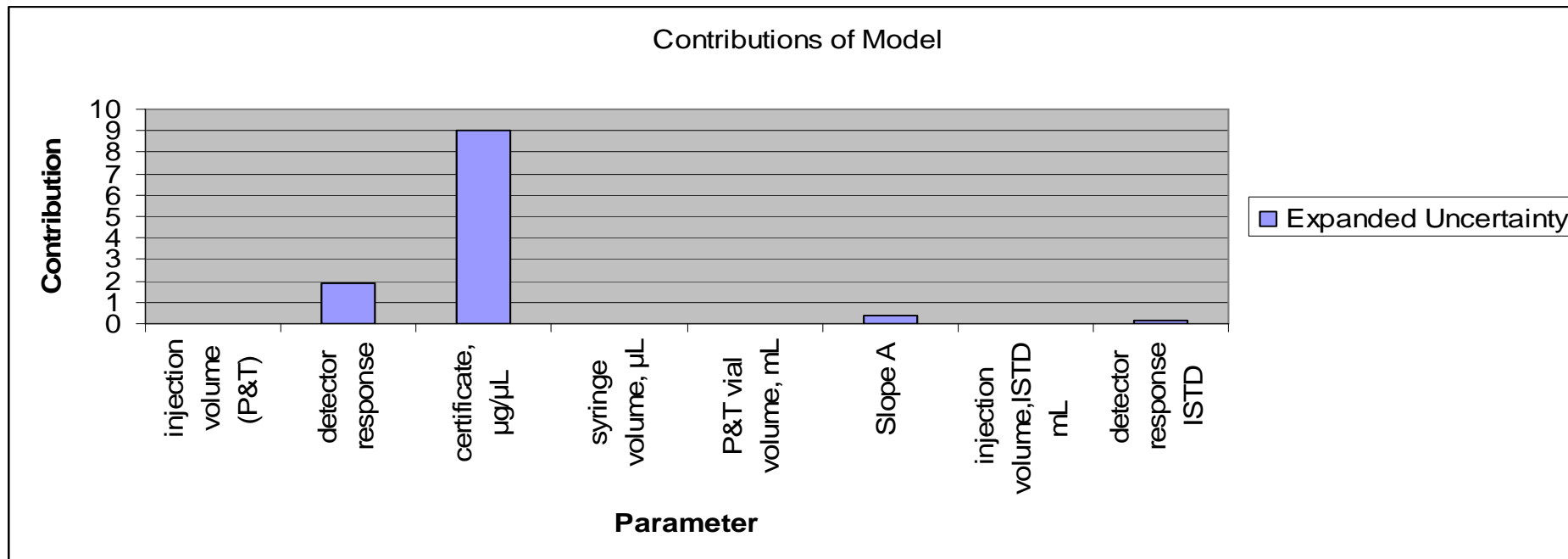




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Looking inside the model :





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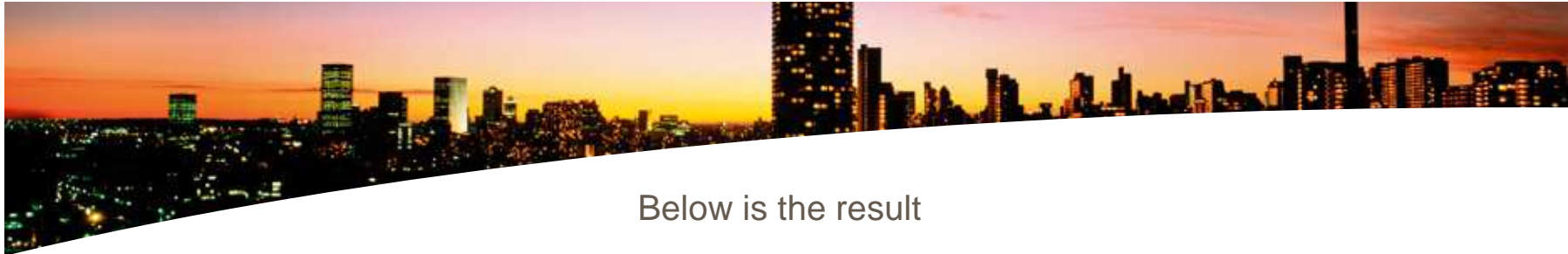
Calibration standards identified as major contributor

Standards had a half range of +/- 5

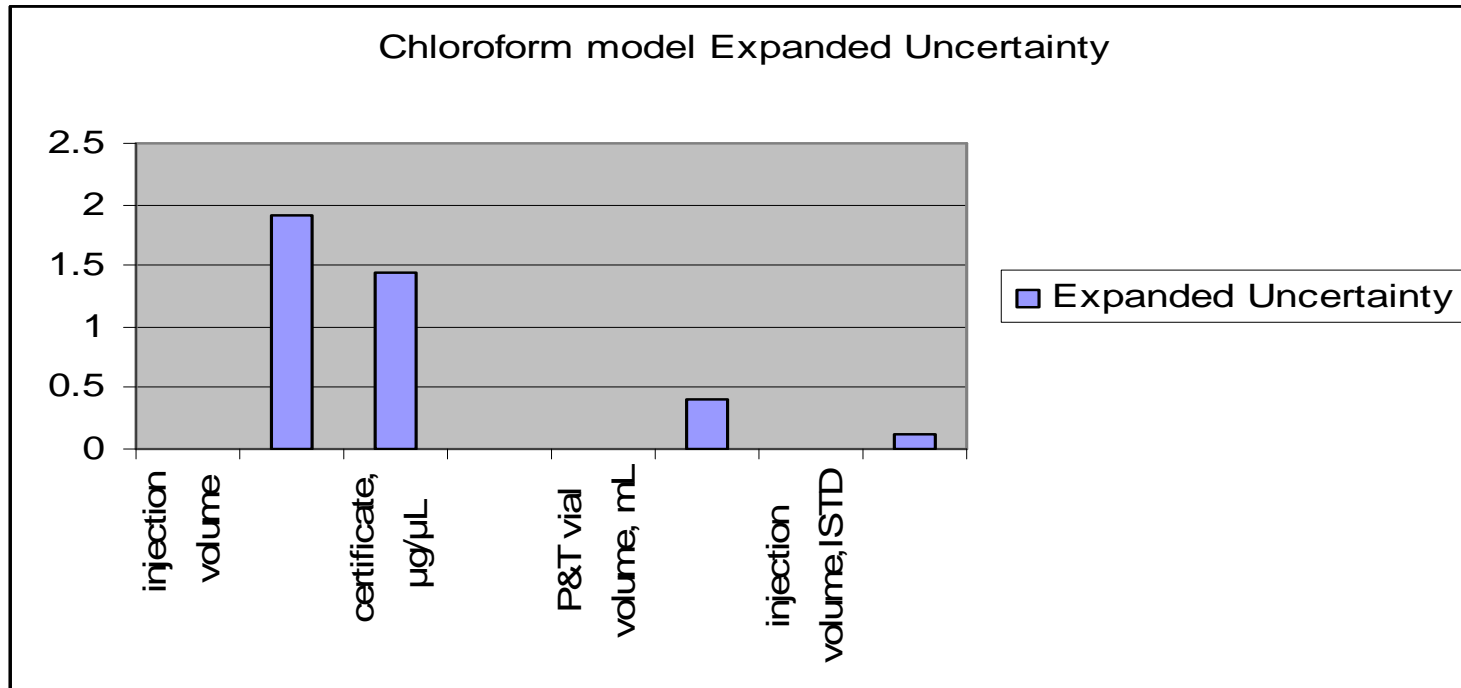
We changed to a standard with a half range of +/- 2



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Below is the result





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Final Step:

Round and report the data as per the example below.

26 ug/L chloroform +/- 5.0 ug/L at a 95% LOC with a coverage factor of k=2

This is a value of approx. **19%**



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Conclusions

- This approach to uncertainty determination had an immediate benefit to the THM method in that we were able to improve method uncertainty by a simple change in the quality of standards purchased.
- The laboratory has acquired an additional level of confidence in results generated.



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- In other methods we have found that 5 litre and even 2 litre volumetric flasks were an issue
Change to 1 litre or 500ml was made with a consequent reduction in method uncertainty
- Reagent purity is also an issue



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- Observation – future research??

The expanded uncertainty for the model = 1.87

The sum of expanded uncertainties of Bias and both precisions (repeatability and reproducibility) = 1.66

Can one deduce that the model contains the other 3?



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“Uncertainty is the only certainty there is, and knowing how to live with insecurity is the only security.”

John Allen Paulos professor of mathematics (probability studies)



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**THANK
YOU**