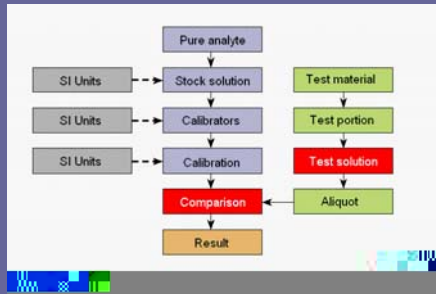


# Matrix Effects and Uncertainty

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A framework for further study

## Where the problems occur in traceability chains



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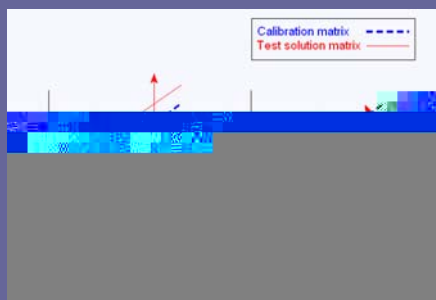
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## Matrix effects--definitions



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## Methods of reducing matrix effects

1. Matrix is effectively constant among test materials of the defined class.  
**-Matrix matching**
2. Matrix varies to a consequential degree between test materials of the defined class.  
**-Matrix modification**  
**-Modelling**  
**-Internal calibration**

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## Uncertainty estimation after matrix correction

- **Systematic methods**  
Derive the uncertainty estimate directly from the calibration model.
- **Random variations**  
Treat the matrix variation as a random variable.
- **Worst case scenarios**  
Study an example with extreme deviation of the matrix from the calibrators.

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## Modelling

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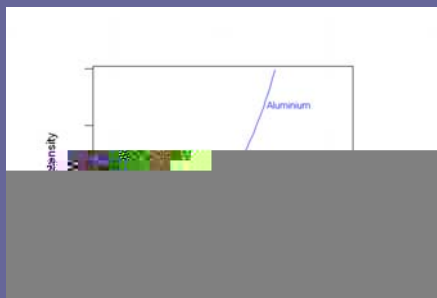
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## An example of modelling (simplified for clarity)



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## Calibration and uncertainty models

- $(S) = (Mo) + k(AI)$

where  $(Mo)$ ,  $(AI)$  are the concentrations of molybdenum and aluminium,  $k$  is a calibration factor and  $(S)$  is the total signal.

- $(Mo) = (S) - k(AI)$

$$u^2(Mo) = u^2(S) + k^2 * u^2(AI)$$

(assuming that  $k$  is invariate).

## Uncertainty terms

- $u^2(S) = v^2(Mo) + w^2(Mo)*(S)^2$

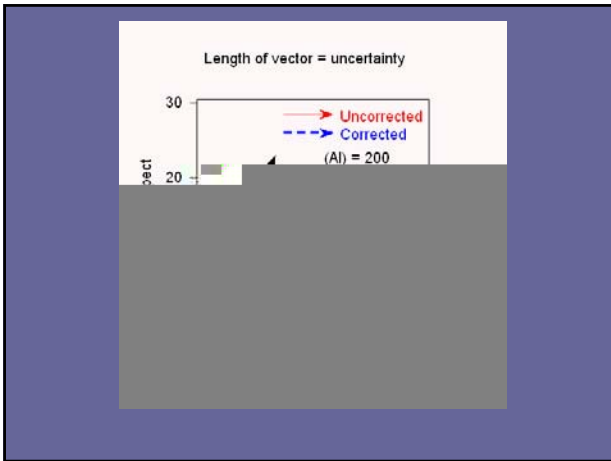
- $u^2(AI) = v^2(AI) + w^2(AI)*(AI)^2$

where  $v(.)$  is a constant uncertainty related to the detection limit and  $w(.)$  provides an uncertainty proportional to the concentration.

## Effect of correction on uncertainty

True molybdenum concentration  $(Mo) = 5$  ppm

$(AI)$	True signal (ppm Mo)	Uncorrected signal (ppm)	Corrected concentration (ppm)
0	5.0	1.0	10.1
50	10.0	1.1	10.1
200	25.0	1.3	10.1




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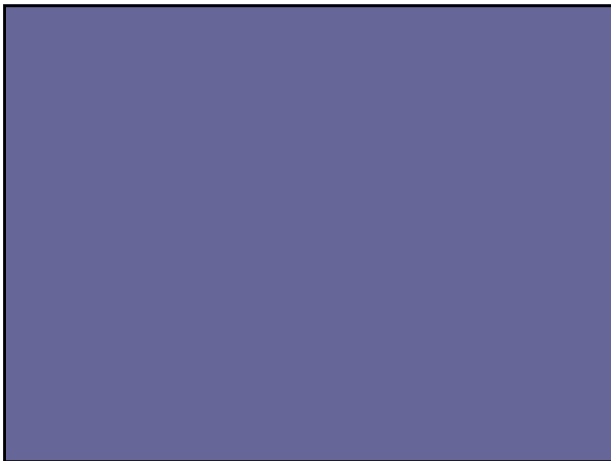
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**Modelling--summary**

- Correction for bias by modelling often increases the precision contribution to uncertainty but (hopefully!) decreases the combined uncertainty.
- In most instances, unnecessary bias correction will *increase* uncertainty.

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## Random studies

## Random studies

This method is appropriate where the causes of the matrix effects are obscure or too complex to model.

- Take a number of representative test materials.
- Measure the apparent concentrations of the analyte (in duplicate).
- Calculate the differences (found minus expected).
- Calculate the between matrix standard deviation by analysis of variance.

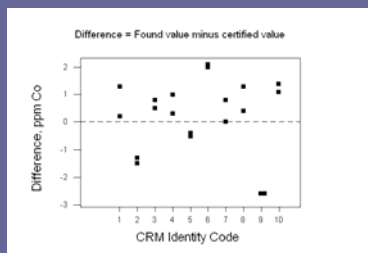
## Analytical “health-warnings”

- Reference materials (i.e., with known true values) are best for this application, but the uncertainties on the reference values are often

### Example: 10 Geological CRMs: Analyte is Co

ID Code	Certified value	Result 1	Result 2	Difference 1	Difference 2
1	10,2	11,5	10,4	1,3	0,2
2	12,9	11,4	11,6	-1,5	-1,3
3	9,8	10,3	10,6	0,5	0,8
4	6,7	7,7	7	1	0,3
5	7,5	7	7,1	-0,5	-0,4
6	6,4	8,5	8,4	2,1	2
7	11,1	11,1	11,9	0	0,8
8	10,1	11,4	10,5	1,3	0,4
9	7,2	4,6	4,6	-2,6	-2,6
10	11,4	12,8	12,5	1,4	1,1

### Results on CRMs



No net bias apparent

ANOVA gives:

$$MSW = 0.17$$

$$MSB = 3.67$$

from which

$$\sigma_0 = 0.4$$

$$\sigma_1 = 1.3$$

“Worst Case” Scenario

## “Worst Case” Scenario

1. Select a material likely to produce an extreme matrix effect, and estimate its effect.
2. This effect can be regarded as the extreme of a range width  $2A$ . The associated standard uncertainty is  $A/3$ .
3. This is a crude expedient, but it is sometimes has the useful outcome of eliminating a suspected matrix effect from further consideration.

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## More Health Warnings

- **Uncertainty is very variable** — it has large relative uncertainty when estimated from few (>20) results. It is seldom useful to report an uncertainty to better than one significant figure.
- **Uncertainty is heteroscedastic** — you may need to take this into account if the expected concentration range is large. This would require a **large** experiment.

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## and finally....

- Matrix effects come in two main forms – translational and rotational, and mixtures of the two. Failure to distinguish between them may give rise to misleading results.
- Many methods of treating rotational effects (*e.g.*, standard additions) rely for their effectiveness on the prior treatment of translational effects (*e.g.*, by background correction).

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