Determination of the amount fo lead in water using double isotope dilution and inductively coupled plasma mass spectrometry

This is the example A7 of the EURACHEM / CITAC Guide "Quantifying Uncertainty in Analytical Measurement", Second Edition.

The amount content of lead in water is measured using Isotope Dilution Mass Spectrometry (IDMS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

In this case a 'double' isotope dilution is applied. It uses a well characterised (ideally certified) material of natural isotopic composition as a primary assay standard. Two blends are then prepared: blend b, which is a blend between known masses of the sample and the enriched spike, and blend b', which is the blend between the enriched spike and the primary assay standard. The isotope ratios of the primary assay standard, the spike, the sample and the two blends are measured using ICP-MS. Together with the weighing data of the blends, the amount content of lead in the sample can be calculated.

Model Equation:

{equation for the double isotope dilution}

$c_x = (c_z * m_{y1} / m_x * m_z / m_{y2} * (K_{y1} * R_{y1} - K_{b1} * R_{b1}) / (K_{b1} * R_{b1} - K_{x1} * R_{x1}) * (K_{b2} * R_{b2} - K_{z1} * R_{z1}) / (K_{y1} * R_{y1} - K_{b2} * R_{b2}) / (\Sigma K_{zi} R_{zi}) * (\Sigma K_{xi} R_{xi})) - c_{blank}$;

$\Sigma K_{xi} R_{xi} = K_{x1} * R_{x1} + K_{x2} * R_{x2} + K_{x3} * R_{x3} + K_{x4} * R_{x4}$;

$\Sigma K_{zi} R_{zi} = K_{z1} * R_{z1} + K_{z2} * R_{z2} + K_{z3} * R_{z3} + K_{z4} * R_{z4}$;

{calculation of the molar mass of the lead of the primary assay standard 1}

$M_{Pb\ Assay1} = (K_{z1} * R_{z1} * M_{z1} + K_{z2} * R_{z2} * M_{z2} + K_{z3} * R_{z3} * M_{z3} + K_{z4} * R_{z4} * M_{z4}) / (\Sigma K_{zi} R_{zi})$;

{concentration of the primary assay standard z which is used for the double IDMS}

$c_z = m_2 / d_2 * m_1 * w / d_1 / M_{Pb\ Assay1} * k_{mol}$;

{calculation of the K-factors for the various isotope ratios measured}

$K_{b1} = K_{0\_b1} + K_{bias\_b1}$;

$K_{b2} = K_{0\_b2} + K_{bias\_b2}$;

$K_{x1} = K_{0\_x1} + K_{bias\_x1}$;

$K_{x2} = K_{0\_x2} + K_{bias\_x2}$;

$K_{x3} = K_{0\_x3} + K_{bias\_x3}$;

$K_{x4} = K_{0\_x4} + K_{bias\_x4}$;

$K_{y1} = K_{0\_y1} + K_{bias\_y1}$;

$K_{z1} = K_{0\_z1} + K_{bias\_z1}$;

$K_{z2} = K_{0\_z2} + K_{bias\_z2}$;

$K_{z3} = K_{0\_z3} + K_{bias\_z3}$;

$K_{z4} = K_{0\_z4} + K_{bias\_z4}$;

List of Quantities:

Quantity	Unit	Definition
c_x	µmol/g	amount content of the sample x
c_z	µmol/g	amount content of the primary assay standard z
m_{y1}	g	mass of enriched spike in blend b
m_x	g	mass of sample in blend b
m_z	g	mass of primary assay standard in blend b'
m_{y2}	g	mass of enriched spike in blend b'
K_{y1}		mass bias correction of R_{y1}
R_{y1}		measured ratio of enriched isotope to reference isotope in the enriched spike, $n(^{208}Pb)/n(^{206}Pb)$
K_{b1}		mass bias correction of R_{b1}
R_{b1}		measured ratio of blend b, $n(^{208}Pb)/n(^{206}Pb)$
K_{x1}		mass bias correction of R_{x1}
R_{x1}		measured ratio of enriched isotope to reference isotope in the sample x, $n(^{208}Pb)/n(^{206}Pb)$
K_{b2}		mass bias correction of R_{b2}
R_{b2}		measured ratio of blend b', $n(^{208}Pb)/n(^{206}Pb)$
K_{z1}		mass bias correction of R_{z1}
R_{z1}		measured ratio of enriched isotope to reference isotope in the primary assay standard z, $n(^{208}Pb)/n(^{206}Pb)$
$\Sigma K_{zi}R_{zi}$		sum of all mass bias corrected ratios of the primary assay standard
$\Sigma K_{xi}R_{xi}$		sum of all mass bias corrected ratios of the sample
c_{blank}	µmol/g	observed amount content in procedure blank
K_{x2}		mass bias correction of R_{x2}
R_{x2}		measured ratio of sample, $n(^{206}Pb)/n(^{206}Pb)$
K_{x3}		mass bias correction of R_{x3}
R_{x3}		measured ratio of sample, $n(^{207}Pb)/n(^{206}Pb)$
K_{x4}		mass bias correction of R_{x4}
R_{x4}		measured ratio of sample, $n(^{204}Pb)/n(^{206}Pb)$
K_{z2}		mass bias correction of R_{z2}
R_{z2}		measured ratio of sample, $n(^{206}Pb)/n(^{206}Pb)$
K_{z3}		mass bias correction of R_{z3}
R_{z3}		measured ratio of sample, $n(^{207}Pb)/n(^{206}Pb)$
K_{z4}		mass bias correction of R_{z4}
R_{z4}		measured ratio of sample, $n(^{204}Pb)/n(^{206}Pb)$
$M_{Pb\ Assay1}$	g/mol	molar mass of the primary assay standard
M_{z1}	g/mol	nuclidic mass of ^{208}Pb
M_{z2}	g/mol	nuclidic mass of ^{206}Pb
M_{z3}	g/mol	nuclidic mass of ^{207}Pb

Quantity	Unit	Definition
M_{z4}	g/mol	nuclidic mass of ^{204}Pb
m_2	g	aliquot of the first dilution of the primary assay standard
d_2	g	total mass of the second dilution of the primary assay standard
m_1	g	mass of the lead piece for primary assay standard
w	g/g	purity of the metallic lead piece, expressed as mass fraction
d_1	g	total mass of first dilution of the primary assay standard
k_{mol}	µmol/mol	conversion factor 10^6 µmol = 1 mol
K_{0_b1}		mass bias correction of R_{b1} as determined at time 0
K_{bias_b1}		other contributions to the mass bias of R_{b1}
K_{0_b2}		mass bias correction of R_{b2} as determined at time 0
K_{bias_b2}		other contributions to the mass bias of R_{b2}
K_{0_x1}		mass bias correction of R_{x1} as determined at time 0
K_{bias_x1}		other contributions to the mass bias of R_{x1}
K_{0_x2}		mass bias correction of R_{x2} as determined at time 0
K_{bias_x2}		other contributions to the mass bias of R_{x2}
K_{0_x3}		mass bias correction of R_{x3} as determined at time 0
K_{bias_x3}		other contributions to the mass bias of R_{x3}
K_{0_x4}		mass bias correction of R_{x4} as determined at time 0
K_{bias_x4}		other contributions to the mass bias of R_{x4}
K_{0_y1}		mass bias correction of R_{y1} as determined at time 0
K_{bias_y1}		other contributions to the mass bias of R_{y1}
K_{0_z1}		mass bias correction of R_{z1} as determined at time 0
K_{bias_z1}		other contributions to the mass bias of R_{z1}
K_{0_z2}		mass bias correction of R_{z2} as determined at time 0
K_{bias_z2}		other contributions to the mass bias of R_{z2}
K_{0_z3}		mass bias correction of R_{z3} as determined at time 0
K_{bias_z3}		other contributions to the mass bias of R_{z3}
K_{0_z4}		mass bias correction of R_{z4} as determined at time 0
K_{bias_z4}		other contributions to the mass bias of R_{z4}

m_{y1}: Type B normal distribution
Value: 1.1360 g
Expanded Uncertainty: 0.0002 g
Coverage Factor: 1

Weighings are performed by a dedicated mass metrology lab. The procedure applied was a bracketing technique using calibrated weights and a comparator. The bracketing technique was repeated at least six times for every sample mass determination. Buoyancy correction was applied. The uncertainties from the weighing certificates were treated as standard uncertainties, Type B.

m_x: Type B normal distribution
Value: 1.0440 g
Expanded Uncertainty: 0.0002 g
Coverage Factor: 1

Weighings are performed by a dedicated mass metrology lab. The procedure applied was a bracketing technique using calibrated weights and a comparator. The bracketing technique was repeated at least six times for every sample mass determination. Buoyancy correction was applied. The uncertainties from the weighing certificates were treated as standard uncertainties, Type B.

m_z: Type B normal distribution
Value: 1.1029 g
Expanded Uncertainty: 0.0002 g
Coverage Factor: 1

Weighings are performed by a dedicated mass metrology lab. The procedure applied was a bracketing technique using calibrated weights and a comparator. The bracketing technique was repeated at least six times for every sample mass determination. Buoyancy correction was applied. The uncertainties from the weighing certificates were treated as standard uncertainties, Type B.

m_{y2}: Type B normal distribution
Value: 1.0654 g
Expanded Uncertainty: 0.0002 g
Coverage Factor: 1

Weighings are performed by a dedicated mass metrology lab. The procedure applied was a bracketing technique using calibrated weights and a comparator. The bracketing technique was repeated at least six times for every sample mass determination. Buoyancy correction was applied. The uncertainties from the weighing certificates were treated as standard uncertainties, Type B.

R_{y1}: Type A summarized
Mean: 0.00064
Standard Uncertainty: =0.00004/sqrt(8)
Degrees of Freedom: 7

Each ratio has been measured 8 times. The experimental uncertainty is therefore divided by sqrt(8).

R_{b1}: Type A summarized
Mean: 0.29360
Standard Uncertainty: =0.00073/sqrt(8)
Degrees of Freedom: 7

Each ratio has been measured 8 times. The experimental uncertainty is therefore divided by sqrt(8).

R_{x1}: Type A summarized
Mean: 2.1402
Standard Uncertainty: =0.0054/sqrt(8)
Degrees of Freedom: 7

Each ratio has been measured 8 times. The experimental uncertainty is therefore divided by sqrt(8).

R_{b2}: Type A summarized
Mean: 0.5050
Standard Uncertainty: =0.0013/sqrt(8)
Degrees of Freedom: 7

Each ratio has been measured 8 times. The experimental uncertainty is therefore divided by sqrt(8).

R_{z1}: Type A summarized
Mean: 2.1429
Standard Uncertainty: =0.0054/sqrt(8)
Degrees of Freedom: 7

Each ratio has been measured 8 times. The experimental uncertainty is therefore divided by sqrt(8).

c_{blank}: Type A summarized
Mean: $4.5 \cdot 10^{-7}$ µmol/g
Standard Uncertainty: =4.0e-7/sqrt(4)
Degrees of Freedom: 3

The procedure blank was measured using external calibration. The procedure blank was measured four times. The experimental standard deviation is divided by sqrt(4) to obtain the standard uncertainty.

R_{x2}: Constant
Value: 1

This is the ratio of n(^{206}Pb)/n(^{206}Pb), which is by definition equal to 1.

R_{x3}: Type A summarized
Mean: 0.9142
Standard Uncertainty: =0.0032/sqrt(8)
Degrees of Freedom: 7

Each ratio has been measured 8 times. The experimental uncertainty is therefore divided by sqrt(8).

R_{x4}: Type A summarized
Mean: 0.05901
Standard Uncertainty: =0.00035/sqrt(8)
Degrees of Freedom: 7

Each ratio has been measured 8 times. The experimental uncertainty is therefore divided by sqrt(8).

R_{z2}: Constant
Value: 1

This is the ratio of n(^{206}Pb)/n(^{206}Pb), which is by definition equal to 1.

R_{z3}: Type A summarized
Mean: 0.9147
Standard Uncertainty: =0.0032/sqrt(8)
Degrees of Freedom: 7

Each ratio has been measured 8 times. The experimental uncertainty is therefore divided by sqrt(8).

R_{z4}: Type A summarized
Mean: 0.05870
Standard Uncertainty: =0.00035/sqrt(8)
Degrees of Freedom: 7

Each ratio has been measured 8 times. The experimental uncertainty is therefore divided by sqrt(8).

M_{z1}: Type B normal distribution
Value: 207.976636 g/mol
Expanded Uncertainty: 0.000003 g/mol
Coverage Factor: 1

The nuclidic masses and their respective uncertainties are taken from literature. G. Audi and A. H. Wapstra, Nuclear Physics, A565 (1993).

M_{z2}: Type B normal distribution
Value: 205.974449 g/mol
Expanded Uncertainty: 0.000003 g/mol
Coverage Factor: 1

The nuclidic masses and their respective uncertainties are taken from literature. G. Audi and A. H. Wapstra, Nuclear Physics, A565 (1993).

M_{z3}: Type B normal distribution
Value: 206.975880 g/mol
Expanded Uncertainty: 0.000003 g/mol
Coverage Factor: 1

The nuclidic masses and their respective uncertainties are taken from literature. G. Audi and A. H. Wapstra, Nuclear Physics, A565 (1993).

M_{z4}: Type B normal distribution
Value: 203.973028 g/mol
Expanded Uncertainty: 0.000003 g/mol
Coverage Factor: 1

The nuclidic masses and their respective uncertainties are taken from literature. G. Audi and A. H. Wapstra, Nuclear Physics, A565 (1993).

m_2: Type B normal distribution
Value: 1.0292 g
Expanded Uncertainty: 0.0002 g
Coverage Factor: 1

Weighings are performed by a dedicated mass metrology lab. The procedure applied was a bracketing technique using calibrated weights and a comparator. The bracketing technique was repeated at least six times for every sample mass determination. Buoyancy correction was applied. The uncertainties from the weighing certificates were treated as standard uncertainties, Type B.

d_2: Type B normal distribution
Value: 99.931 g
Expanded Uncertainty: 0.01 g
Coverage Factor: 1

Weighings are performed by a dedicated mass metrology lab. The procedure applied was a bracketing technique using calibrated weights and a comparator. The bracketing technique was repeated at least six times for every sample mass determination. Buoyancy correction was applied. The uncertainties from the weighing certificates were treated as standard uncertainties, Type B.

m_1: Type B normal distribution
Value: 0.36544 g
Expanded Uncertainty: 0.00005 g
Coverage Factor: 1

Weighings are performed by a dedicated mass metrology lab. The procedure applied was a bracketing technique using calibrated weights and a comparator. The bracketing technique was repeated at least six times for every sample mass determination. Buoyancy correction was applied. The uncertainties from the weighing certificates were treated as standard uncertainties, Type B.

w: Type B normal distribution
Value: 0.99999 g/g
Expanded Uncertainty: 0.000005 g/g
Coverage Factor: 1

The purity of the metalic lead can be obtained through analysis or a supplier's certificate.

d_1: Type B normal distribution
Value: 196.14 g
Expanded Uncertainty: 0.03 g
Coverage Factor: 1

Weighings are performed by a dedicated mass metrology lab. The procedure applied was a bracketing technique using calibrated weights and a comparator. The bracketing technique was repeated at least six times for every sample mass determination. Buoyancy correction was applied. The uncertainties from the weighing certificates were treated as standard uncertainties, Type B.

k_{mol}: Constant
Value: $1{\cdot}10^6$ µmol/mol

K_{0_b1}: Type A summarized
Mean: 0.9987
Standard Uncertainty: =0.0025/sqrt(8)
Degrees of Freedom: 7

The K_0's are measured using a certfied isotopic reference material, and they are calculated according to the following equation:

$K_0 = R_{certified}/R_{observed}$

When looking at the uncertainty contributions of $R_{certified}$ and $R_{observed,}$ it is clear that the contribution of $R_{certified}$ can be neglected for this example. Henceforth, the uncertainties on the measured ratios, $R_{observed}$, are used for the uncertainties on $K_{0.}$

The original measurement data for the determination of K_0 is not shown in this example.

K_{bias_b1}: Type B normal distribution
Value: 0
Expanded Uncertainty: 0.001
Coverage Factor: 1

This bias factor is introduced to account for possible deviations in the value of the mass discrimination factor (these could be variations over time, as well as other sources of bias, such as multiplier dead time correction, matrix effects etc.). The values of these biases are not known in this case, but they are assumed to be around 0, therefore a value of 0 is applied. An uncertainty is associated to this bias, which is estimated from experience. In this case a standard uncertainty of 0.001 is considered to be sufficient to cover all effects.

K_{0_b2}: Type A summarized
Mean: 0.9983
Standard Uncertainty: =0.0025/sqrt(8)
Degrees of Freedom: 7

The K_0's are measured using a certfied isotopic reference material, and they are calculated according to the following equation:

$K_0 = R_{certified}/R_{observed}$

When looking at the uncertainty contributions of $R_{certified}$ and $R_{observed,}$ it is clear that the contribution of $R_{certified}$ can be neglected for this example. Henceforth, the uncertainties on the measured ratios, $R_{observed}$, are used for the uncertainties on $K_{0.}$

The original measurement data for the determination of K_0 is not shown in this example.

K_{bias_b2}: Type B normal distribution
Value: 0
Expanded Uncertainty: 0.001
Coverage Factor: 1

This bias factor is introduced to account for possible deviations in the value of the mass discrimination factor (these could be variations over time, as well as other sources of bias, such as multiplier dead time correction, matrix effects etc.). The values of these biases are not known in this case, but they are assumed to be around 0, therefore a value of 0 is applied. An uncertainty is associated to this bias, which is estimated from experience. In this case a standard uncertainty of 0.001 is considered to be sufficient to cover all effects.

K_{0_x1}: Type A summarized
Mean: 0.9992
Standard Uncertainty: =0.0025/sqrt(8)
Degrees of Freedom: 7

The K_0's are measured using a certfied isotopic reference material, and they are calculated according to the following equation:

$K_0 = R_{certified}/R_{observed}$

When looking at the uncertainty contributions of $R_{certified}$ and $R_{observed,}$ it is clear that the contribution of $R_{certified}$ can be neglected for this example. Henceforth, the uncertainties on the measured ratios, $R_{observed}$, are used for the uncertainties on $K_{0.}$

The original measurement data for the determination of K_0 is not shown in this example.

K_{bias_x1}: Type B normal distribution
Value: 0
Expanded Uncertainty: 0.001
Coverage Factor: 1

This bias factor is introduced to account for possible deviations in the value of the mass discrimination factor (these could be variations over time, as well as other sources of bias, such as multiplier dead time correction, matrix effects etc.). The values of these biases are not known in this case, but they are assumed to be around 0, therefore a value of 0 is applied. An uncertainty is associated to this bias, which is estimated from experience. In this case a standard uncertainty of 0.001 is considered to be sufficient to cover all effects.

K_{0_x2}: Constant
Value: 1

This mass bias correction refers to the ratio of $n(^{206}Pb)/n(^{206}Pb)$, which is by definition equal to 1 and not measured. Therefore no mass bias correction is needed, the factor is equal to 1.

K_{bias_x2}: Constant
Value: 0

This mass bias correction refers to the ratio of $n(^{206}Pb)/n(^{206}Pb)$, which is by definition equal to 1 and not measured. Therefore no mass bias correction is needed, this factor is equal to 0.

K_{0_x3}: Type A summarized
Mean: 1.0004
Standard Uncertainty: =0.0035/sqrt(8)
Degrees of Freedom: 7

The K_0's are measured using a certfied isotopic reference material, and they are calculated according to the following equation:

$K_0 = R_{certified}/R_{observed}$

When looking at the uncertainty contributions of $R_{certified}$ and $R_{observed,}$ it is clear that the contribution of $R_{certified}$ can be neglected for this example. Henceforth, the uncertainties on the measured ratios, $R_{observed}$, are used for the uncertainties on $K_{0.}$

The original measurement data for the determination of K_0 is not shown in this example.

K_{bias_x3}: Type B normal distribution
Value: 0
Expanded Uncertainty: 0.001
Coverage Factor: 1

This bias factor is introduced to account for possible deviations in the value of the mass discrimination factor (these could be variations over time, as well as other sources of bias, such as multiplier dead time correction, matrix effects etc.). The values of these biases are not known in this case, but they are assumed to be around 0, therefore a value of 0 is applied. An uncertainty is associated to this bias, which is estimated from experience. In this case a standard uncertainty of 0.001 is considered to be sufficient to cover all effects.

K_{0_x4}: Type A summarized
Mean: 1.001
Standard Uncertainty: =0.006/sqrt(8)
Degrees of Freedom: 7

The K_0's are measured using a certfied isotopic reference material, and they are calculated according to the following equation:

$K_0 = R_{certified}/R_{observed}$

When looking at the uncertainty contributions of $R_{certified}$ and $R_{observed,}$ it is clear that the contribution of $R_{certified}$ can be neglected for this example. Henceforth, the uncertainties on the measured ratios, $R_{observed}$, are used for the uncertainties on $K_{0.}$

The original measurement data for the determination of K_0 is not shown in this example.

K_{bias_x4}: Type B normal distribution
Value: 0
Expanded Uncertainty: 0.001
Coverage Factor: 1

This bias factor is introduced to account for possible deviations in the value of the mass discrimination factor (these could be variations over time, as well as other sources of bias, such as multiplier dead time correction, matrix effects etc.). The values of these biases are not known in this case, but they are assumed to be around 0, therefore a value of 0 is applied. An uncertainty is associated to this bias, which is estimated from experience. In this case a standard uncertainty of 0.001 is considered to be sufficient to cover all effects.

K_{0_y1}: Type A summarized
Mean: 0.9999
Standard Uncertainty: =0.0025/sqrt(8)
Degrees of Freedom: 7

The K_0's are measured using a certfied isotopic reference material, and they are calculated according to the following equation:

$K_0 = R_{certified}/R_{observed}$

When looking at the uncertainty contributions of $R_{certified}$ and $R_{observed,}$ it is clear that the contribution of $R_{certified}$ can be neglected for this example. Henceforth, the uncertainties on the measured ratios, $R_{observed}$, are used for the uncertainties on $K_{0.}$

The original measurement data for the determination of K_0 is not shown in this example.

K_{bias_y1}: Type B normal distribution
Value: 0
Expanded Uncertainty: 0.001
Coverage Factor: 1

This bias factor is introduced to account for possible deviations in the value of the mass discrimination factor (these could be variations over time, as well as other sources of bias, such as multiplier dead time correction, matrix effects etc.). The values of these biases are not known in this case, but they are assumed to be around 0, therefore a value of 0 is applied. An uncertainty is associated to this bias, which is estimated from experience. In this case a standard uncertainty of 0.001 is considered to be sufficient to cover all effects.

K_{0_z1}: Type A summarized
Mean: 0.9989
Standard Uncertainty: =0.0025/sqrt(8)
Degrees of Freedom: 7

The K_0's are measured using a certfied isotopic reference material, and they are calculated according to the following equation:

$K_0 = R_{certified}/R_{observed}$

When looking at the uncertainty contributions of $R_{certified}$ and $R_{observed,}$ it is clear that the contribution of $R_{certified}$ can be neglected for this example. Henceforth, the uncertainties on the measured ratios, $R_{observed}$, are used for the uncertainties on $K_{0.}$

The original measurement data for the determination of K_0 is not shown in this example.

K_{bias_z1}: Type B normal distribution
Value: 0
Expanded Uncertainty: 0.001
Coverage Factor: 1

This bias factor is introduced to account for possible deviations in the value of the mass discrimination factor (these could be variations over time, as well as other sources of bias, such as multiplier dead time correction, matrix effects etc.). The values of these biases are not known in this case, but they are assumed to be around 0, therefore a value of 0 is applied. An uncertainty is associated to this bias, which is estimated from experience. In this case a standard uncertainty of 0.001 is considered to be sufficient to cover all effects.

K_{0_z2}: Constant
Value: 1

This mass bias correction refers to the ratio of $n(^{206}Pb)/n(^{206}Pb)$, which is by definition equal to 1 and not measured. Therefore no mass bias correction is needed, the factor is equal to 1.

K_{bias_z2}: Constant
Value: 0

This mass bias correction refers to the ratio of $n(^{206}Pb)/n(^{206}Pb)$, which is by definition equal to 1 and not measured. Therefore no mass bias correction is needed, this factor is equal to 0.

K_{0_z3}: Type A summarized
Mean: 0.9993
Standard Uncertainty: =0.0035/sqrt(8)
Degrees of Freedom: 7

The K_0's are measured using a certfied isotopic reference material, and they are calculated according to the following equation:

$K_0 = R_{certified}/R_{observed}$

When looking at the uncertainty contributions of $R_{certified}$ and $R_{observed,}$ it is clear that the contribution of $R_{certified}$ can be neglected for this example. Henceforth, the uncertainties on the measured ratios, $R_{observed}$, are used for the uncertainties on $K_{0.}$

The original measurement data for the determination of K_0 is not shown in this example.

K_{bias_z3}: Type B normal distribution
Value: 0
Expanded Uncertainty: 0.001
Coverage Factor: 1

This bias factor is introduced to account for possible deviations in the value of the mass discrimination factor (these could be variations over time, as well as other sources of bias, such as multiplier dead time correction, matrix effects etc.). The values of these biases are not known in this case, but they are assumed to be around 0, therefore a value of 0 is applied. An uncertainty is associated to this bias, which is estimated from experience. In this case a standard uncertainty of 0.001 is considered to be sufficient to cover all effects.

K_{0_z4}: Type A summarized
Mean: 1.0002
Standard Uncertainty: =0.006/sqrt(8)
Degrees of Freedom: 7

The K_0's are measured using a certfied isotopic reference material, and they are calculated according to the following equation:

$K_0 = R_{certified}/R_{observed}$

When looking at the uncertainty contributions of $R_{certified}$ and $R_{observed,}$ it is clear that the contribution of $R_{certified}$ can be neglected for this example. Henceforth, the uncertainties on the measured ratios, $R_{observed}$, are used for the uncertainties on $K_{0.}$

The original measurement data for the determination of K_0 is not shown in this example.

K_{bias_z4}: Type B normal distribution
Value: 0
Expanded Uncertainty: 0.001
Coverage Factor: 1

This bias factor is introduced to account for possible deviations in the value of the mass discrimination factor (these could be variations over time, as well as other sources of bias, such as multiplier dead time correction, matrix effects etc.). The values of these biases are not known in this case, but they are assumed to be around 0, therefore a value of 0 is applied. An uncertainty is associated to this bias, which is estimated from experience. In this case a standard uncertainty of 0.001 is considered to be sufficient to cover all effects.

Interim Results:

Quantity	Value	Standard Uncertainty
c_z	0.09260484 µmol/g	$27.77 \cdot 10^{-6}$ µmol/g
K_{y1}	0.999900	$1.335 \cdot 10^{-3}$
K_{b1}	0.998700	$1.335 \cdot 10^{-3}$
K_{x1}	0.999200	$1.335 \cdot 10^{-3}$
K_{b2}	0.998300	$1.335 \cdot 10^{-3}$
K_{z1}	0.998900	$1.335 \cdot 10^{-3}$
$\Sigma K_{zi} R_{zi}$	4.113314	$3.905 \cdot 10^{-3}$
$\Sigma K_{xi} R_{xi}$	4.112123	$3.902 \cdot 10^{-3}$
K_{x3}	1.000400	$1.591 \cdot 10^{-3}$
K_{x4}	1.001000	$2.345 \cdot 10^{-3}$
K_{z3}	0.999300	$1.591 \cdot 10^{-3}$
K_{z4}	1.000200	$2.345 \cdot 10^{-3}$
$M_{Pb\ Assay1}$	207.2103448 g/mol	$665.1 \cdot 10^{-6}$ g/mol

Uncertainty Budgets:

c_x: **amount content of the sample x**

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
c_z	0.09260484 µmol/g	$27.77 \cdot 10^{-6}$ µmol/g				
m_{y1}	1.1360000 g	$200.0 \cdot 10^{-6}$ g	normal	0.047	$9.5 \cdot 10^{-6}$ µmol/g	0.3 %
m_x	1.0440000 g	$200.0 \cdot 10^{-6}$ g	normal	-0.051	$-10 \cdot 10^{-6}$ µmol/g	0.3 %
m_z	1.1029000 g	$200.0 \cdot 10^{-6}$ g	normal	0.049	$9.7 \cdot 10^{-6}$ µmol/g	0.3 %
m_{y2}	1.0654000 g	$200.0 \cdot 10^{-6}$ g	normal	-0.050	$-10 \cdot 10^{-6}$ µmol/g	0.3 %
K_{y1}	0.999900	$1.335 \cdot 10^{-3}$				
R_{y1}	$640.00 \cdot 10^{-6}$	$14.14 \cdot 10^{-6}$	normal	-0.077	$-1.1 \cdot 10^{-6}$ µmol/g	0.0 %
K_{b1}	0.998700	$1.335 \cdot 10^{-3}$				
R_{b1}	0.2936000	$258.1 \cdot 10^{-6}$	normal	0.21	$55 \cdot 10^{-6}$ µmol/g	9.3 %
K_{x1}	0.999200	$1.335 \cdot 10^{-3}$				
R_{x1}	2.140200	$1.909 \cdot 10^{-3}$	normal	-0.016	$-31 \cdot 10^{-6}$ µmol/g	2.9 %
K_{b2}	0.998300	$1.335 \cdot 10^{-3}$				
R_{b2}	0.5050000	$459.6 \cdot 10^{-6}$	normal	-0.14	$-64 \cdot 10^{-6}$ µmol/g	12.7 %
K_{z1}	0.998900	$1.335 \cdot 10^{-3}$				
R_{z1}	2.142900	$1.909 \cdot 10^{-3}$	normal	0.020	$38 \cdot 10^{-6}$ µmol/g	4.4 %
$\Sigma K_{zi}R_{zi}$	4.113314	$3.905 \cdot 10^{-3}$				
$\Sigma K_{xi}R_{xi}$	4.112123	$3.902 \cdot 10^{-3}$				
c_{blank}	$450.0 \cdot 10^{-9}$ µmol/g	$200.0 \cdot 10^{-9}$ µmol/g	normal	-1.0	$-200 \cdot 10^{-9}$ µmol/g	0.0 %
K_{x2}	1.0	0.0				
R_{x2}	1.0					
K_{x3}	1.000400	$1.591 \cdot 10^{-3}$				
R_{x3}	0.914200	$1.131 \cdot 10^{-3}$	normal	0.013	$15 \cdot 10^{-6}$ µmol/g	0.7 %
K_{x4}	1.001000	$2.345 \cdot 10^{-3}$				
R_{x4}	0.0590100	$123.7 \cdot 10^{-6}$	normal	0.013	$1.6 \cdot 10^{-6}$ µmol/g	0.0 %
K_{z2}	1.0	0.0				
R_{z2}	1.0					
K_{z3}	0.999300	$1.591 \cdot 10^{-3}$				
R_{z3}	0.914700	$1.131 \cdot 10^{-3}$	normal	-0.013	$-15 \cdot 10^{-6}$ µmol/g	0.7 %
K_{z4}	1.000200	$2.345 \cdot 10^{-3}$				
R_{z4}	0.0587000	$123.7 \cdot 10^{-6}$	normal	-0.013	$-1.6 \cdot 10^{-6}$ µmol/g	0.0 %
$M_{Pb\ Assay1}$	207.2103448 g/mol	$665.1 \cdot 10^{-6}$ g/mol				
M_{z1}	207.976636000 g/mol	$3.000 \cdot 10^{-6}$ g/mol	normal	$-130 \cdot 10^{-6}$	$-400 \cdot 10^{-12}$ µmol/g	0.0 %

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
M_{z2}	205.974449000 g/mol	$3.000 \cdot 10^{-6}$ g/mol	normal	$-63 \cdot 10^{-6}$	$-190 \cdot 10^{-12}$ µmol/g	0.0 %
M_{z3}	206.975880000 g/mol	$3.000 \cdot 10^{-6}$ g/mol	normal	$-58 \cdot 10^{-6}$	$-170 \cdot 10^{-12}$ µmol/g	0.0 %
M_{z4}	203.973028000 g/mol	$3.000 \cdot 10^{-6}$ g/mol	normal	$-3.7 \cdot 10^{-6}$	$-11 \cdot 10^{-12}$ µmol/g	0.0 %
m_2	1.0292000 g	$200.0 \cdot 10^{-6}$ g	normal	0.052	$10 \cdot 10^{-6}$ µmol/g	0.3 %
d_2	99.93100 g	0.01000 g	normal	$-540 \cdot 10^{-6}$	$-5.4 \cdot 10^{-6}$ µmol/g	0.0 %
m_1	0.36544000 g	$50.00 \cdot 10^{-6}$ g	normal	0.15	$7.4 \cdot 10^{-6}$ µmol/g	0.2 %
w	0.999990000 g/g	$5.000 \cdot 10^{-6}$ g/g	normal	0.054	$270 \cdot 10^{-9}$ µmol/g	0.0 %
d_1	196.14000 g	0.03000 g	normal	$-270 \cdot 10^{-6}$	$-8.2 \cdot 10^{-6}$ µmol/g	0.2 %
k_{mol}	$1.0 \cdot 10^{6}$ µmol/mol					
K_{0_b1}	0.9987000	$883.9 \cdot 10^{-6}$	normal	0.062	$55 \cdot 10^{-6}$ µmol/g	9.4 %
K_{bias_b1}	0.0	$1.000 \cdot 10^{-3}$	normal	0.062	$62 \cdot 10^{-6}$ µmol/g	12.1 %
K_{0_b2}	0.9983000	$883.9 \cdot 10^{-6}$	normal	-0.070	$-62 \cdot 10^{-6}$ µmol/g	12.0 %
K_{bias_b2}	0.0	$1.000 \cdot 10^{-3}$	normal	-0.070	$-70 \cdot 10^{-6}$ µmol/g	15.3 %
K_{0_x1}	0.9992000	$883.9 \cdot 10^{-6}$	normal	-0.034	$-30 \cdot 10^{-6}$ µmol/g	2.8 %
K_{bias_x1}	0.0	$1.000 \cdot 10^{-3}$	normal	-0.034	$-34 \cdot 10^{-6}$ µmol/g	3.6 %
K_{0_x2}	1.0					
K_{bias_x2}	0.0					
K_{0_x3}	1.000400	$1.237 \cdot 10^{-3}$	normal	0.012	$15 \cdot 10^{-6}$ µmol/g	0.7 %
K_{bias_x3}	0.0	$1.000 \cdot 10^{-3}$	normal	0.012	$12 \cdot 10^{-6}$ µmol/g	0.4 %
K_{0_x4}	1.001000	$2.121 \cdot 10^{-3}$	normal	$770 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$ µmol/g	0.0 %
K_{bias_x4}	0.0	$1.000 \cdot 10^{-3}$	normal	$770 \cdot 10^{-6}$	$770 \cdot 10^{-9}$ µmol/g	0.0 %
K_{0_y1}	0.9999000	$883.9 \cdot 10^{-6}$	normal	$-49 \cdot 10^{-6}$	$-44 \cdot 10^{-9}$ µmol/g	0.0 %
K_{bias_y1}	0.0	$1.000 \cdot 10^{-3}$	normal	$-49 \cdot 10^{-6}$	$-49 \cdot 10^{-9}$ µmol/g	0.0 %
K_{0_z1}	0.9989000	$883.9 \cdot 10^{-6}$	normal	0.042	$37 \cdot 10^{-6}$ µmol/g	4.3 %
K_{bias_z1}	0.0	$1.000 \cdot 10^{-3}$	normal	0.042	$42 \cdot 10^{-6}$ µmol/g	5.5 %
K_{0_z2}	1.0					
K_{bias_z2}	0.0					
K_{0_z3}	0.999300	$1.237 \cdot 10^{-3}$	normal	-0.012	$-15 \cdot 10^{-6}$ µmol/g	0.7 %
K_{bias_z3}	0.0	$1.000 \cdot 10^{-3}$	normal	-0.012	$-12 \cdot 10^{-6}$ µmol/g	0.4 %
K_{0_z4}	1.000200	$2.121 \cdot 10^{-3}$	normal	$-750 \cdot 10^{-6}$	$-1.6 \cdot 10^{-6}$ µmol/g	0.0 %
K_{bias_z4}	0.0	$1.000 \cdot 10^{-3}$	normal	$-750 \cdot 10^{-6}$	$-750 \cdot 10^{-9}$ µmol/g	0.0 %
c_x	0.0537374 µmol/g	$179.9 \cdot 10^{-6}$ µmol/g				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
c_x	0.05374 µmol/g	$180 \cdot 10^{-6}$ µmol/g	1.00	manual