Determination of As in particulate matter using Se as an internal standard by multi-element electrothermal atomic absorption spectrometry.

Supplementary Material

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Quantity	***Units***	***Definition***
alpha	μL/ (uL °C)	Thermal expansion coefficient
reps		Replicates
temperature	°C	Temperature
Vpipet	μL	Volume of the bulk solution pipetted for preparing the stock solution
Vpipet2	μL	Volume of the stock solution pipetted for preparing the first dilution solution
Vfirstdil	μL	Volume of the first dilution solution pipetted for preparing the second dilution solution
Vsecdil	μL	Volume of the second dilution pipetted for preparing the working solution
Vsampling	μL	Sampling volume
Vafterdigest	mL	Final volume of the sample after digestion
Fsample		Dilution factor of the sample
Cbulk	μg/L	Arsenic concentration of the bulk solution
Cstock	μg/L	Arsenic concentration of the stock solution
Cworksolution	μg/L	Arsenic concentration of the working solution
Cstd	μg/L	Mean concentration of all calibration standards
Aij	AU	Integrated absorbance of the j measurement of the calibration standard i
Astd	AU	Mean absorbance of all calibration standards
β1	AU/ (μg/L)	Calculated best fit slope (gradient) of the calibration curve
β0	AU	Calculated best fit intercept of the calibration curve
ARij	AU	Integrated absorbance of the j measurement of the i fortification level solution
Cobsi	μg/L	Mean arsenic concentration of the i fortification level solution
dbiasi		Bias component of the uncertainty of Cobsi
drepi		Reproducibility component of the uncertainty of Cobsi
Ci	μg/L	Final arsenic concentration of the i fortification level solution (all components of uncertainty included)

Suppl. Table 1: Terms and definitions of the Mathematical code used in MCM when Se was not used as internal standard.

Mathematica program code used for the uncertainty estimation based on MCM without the use of an internal standard

```
reps=1000000;

alpha=0.00021;

meansN={meanVpipet,meanVpipet2,meanVfirstdil,meanVsecdil,meanVsampling};

sdN={sdVpipet,sdVpipet2,sdVfirstdil,sdVsecdil,sdVsampling};

meanU={meanVafterdigest,meanT ,meanCbulk};

sdU={sdVafterdigest,sdT ,sdCbulk};

Temperature=22;

meanA1={A11,A12,A13};

meanA2={A21,A22,A23};

meanA3={A31,A32,A33};

meanA4={A41,A42,A43};

meanA5={A51,A52,A53};

meanAR1={AR11,AR12,AR13};

meanAR2={AR21,AR22,AR23};

meanAR3={AR31,AR32,AR33};

meanAR4={AR41,AR42,AR43};

sdAi=0.001897;

a=(2meanU-sdU Sqrt[12])/2;

b=(2meanU+sdU Sqrt[12])/2;

Vpipet=Table[RandomReal[NormalDistribution[meansN[[1]],sdN[[1]]]],{reps}];

Vpipet2=Table[RandomReal[NormalDistribution[meansN[[2]],sdN[[2]]]],{reps}];

Vfirstdil=Table[RandomReal[NormalDistribution[meansN[[3]],sdN[[3]]]],{reps}];

Vsecdil=Table[RandomReal[NormalDistribution[meansN[[4]],sdN[[4]]]],{reps}];

Vsampling=Table[RandomReal[NormalDistribution[meansN[[5]],sdN[[5]]]],{reps}];
```

```
Vafterdigest=Table[RandomReal[{a[[1]],b[[1]]}],{reps}];

T=Table[RandomReal[{a[[2]],b[[2]]}],{reps}];

Cbulk=Table[RandomReal[{a[[3]],b[[3]]}],{reps}];

Vpipet=Vpipet(1+alpha(T-Temperature));

Vpipet2=Vpipet2(1+alpha(T-Temperature));

Vfirstdil=Vfirstdil(1+alpha(T-Temperature));

Vsecdil=Vsecdil(1+alpha(T-Temperature));

Vsampling=Vsampling(1+alpha(T-Temperature));

Vafterdigest=Vafterdigest(1+alpha(T-Temperature));

Fsample=Vafterdigest/Vsampling;

Cstock=(Cbulk*Vpipet)/Vfirstdil;

Cworksolution=(Cstock*Vpipet2)/Vsecdil;

Cstd=(6Cworksolution)/25;


aA1=(2meanA1-sdAi Sqrt[12])/2;bA1=(2meanA1+sdAi Sqrt[12])/2;aA2=(2meanA2-sdAi Sqrt[12])/2;bA2=(2meanA2+sdAi Sqrt[12])/2;

aA3=(2meanA3-sdAi Sqrt[12])/2;bA3=(2meanA3+sdAi Sqrt[12])/2;aA4=(2meanA4-sdAi Sqrt[12])/2;bA4=(2meanA4+sdAi Sqrt[12])/2;

aA5=(2meanA5-sdAi Sqrt[12])/2;bA5=(2meanA5+sdAi Sqrt[12])/2;

A11=RandomReal[{aA1[[1]],bA1[[1]]},reps];A12=RandomReal[{aA1[[2]],bA1[[2]]},reps];

A13=RandomReal[{aA1[[3]],bA1[[3]]},reps];A21=RandomReal[{aA2[[1]],bA2[[1]]},reps];

A22=RandomReal[{aA2[[2]],bA2[[2]]},reps];A23=RandomReal[{aA2[[3]],bA2[[3]]},reps];

A31=RandomReal[{aA3[[1]],bA3[[1]]},reps];A32=RandomReal[{aA3[[2]],bA3[[2]]},reps];

A33=RandomReal[{aA3[[3]],bA3[[3]]},reps];A41=RandomReal[{aA4[[1]],bA4[[1]]},reps];
```

```
A42=RandomReal[{aA4[[2]],bA4[[2]]},reps];A43=RandomReal[{aA4[[3]],bA4[[3]]},reps];

A51=RandomReal[{aA5[[1]],bA5[[1]]},reps];A52=RandomReal[{aA5[[2]],bA5[[2]]},reps];

A53=RandomReal[{aA5[[3]],bA5[[3]]},reps];

Astd1=A11+A12+A13;

Astd2=A21+A22+A23;

Astd3=A31+A32+A33;

Astd4=A41+A42+A43;

Astd5=A51+A52+A53;

Astd=(Astd1+Astd2+Astd3+Astd4+Astd5)/15;


\[Beta]1=(5Total[Astd*Cstd]-Total[Cstd]*Total[Astd])/(5Total[Cstd^2]-Total[Cstd]^2);

\[Beta]0=Mean[Astd]-\[Beta]1*Mean[Cstd];


aAR1=(2meanAR1-sdAi Sqrt[12])/2;bAR1=(2meanAR1+sdAi Sqrt[12])/2;

aAR2=(2meanAR2-sdAi Sqrt[12])/2;bAR2=(2meanAR2+sdAi Sqrt[12])/2;

aAR3=(2meanAR3-sdAi Sqrt[12])/2;bAR3=(2meanAR3+sdAi Sqrt[12])/2;

aAR4=(2meanAR4-sdAi Sqrt[12])/2;bAR4=(2meanAR4+sdAi Sqrt[12])/2;

AR11=RandomReal[{aAR1[[1]],bAR1[[1]]},reps];AR12=RandomReal[{aAR1[[2]],bAR1[[2]]},reps];

AR13=RandomReal[{aAR1[[3]],bAR1[[3]]},reps];AR21=RandomReal[{aAR2[[1]],bAR2[[1]]},reps];

AR22=RandomReal[{aAR2[[2]],bAR2[[2]]},reps];AR23=RandomReal[{aAR2[[3]],bAR2[[3]]},reps];

AR31=RandomReal[{aAR3[[1]],bAR3[[1]]},reps];AR32=RandomReal[{aAR3[[2]],bAR3[[2]]},reps];

AR33=RandomReal[{aAR3[[3]],bAR3[[3]]},reps];AR41=RandomReal[{aAR4[[1]],bAR4[[1]]},reps];
```

```
AR42=RandomReal[{aAR4[[2]],bAR4[[2]]},reps];AR43=RandomReal[{aAR4[[3]],bAR4[[3]]},reps];

AR1mean=(AR11+AR12+AR13)/3;AR2mean=(AR21+AR22+AR23)/3;AR3mean=(AR31+AR32+AR33)/3;AR4mean=(AR41+AR42+AR43)/3;

Cobs1=(AR1mean-\[Beta]0)/\[Beta]1;Cobs2=(AR2mean-\[Beta]0)/\[Beta]1;Cobs3=(AR3mean-\[Beta]0)/\[Beta]1;Cobs4=(AR4mean-\[Beta]0)/\[Beta]1;


dbias1=Table[RandomReal[NormalDistribution[0,0.094]],{reps}];

dbias2=Table[RandomReal[NormalDistribution[0,0.081]],{reps}];

dbias3=Table[RandomReal[NormalDistribution[0,0.029]],{reps}];

dbias4=Table[RandomReal[NormalDistribution[0,0.018]],{reps}];

drep1=Table[RandomReal[NormalDistribution[0,2.41]],{reps}];

drep2=Table[RandomReal[NormalDistribution[0,14.7]],{reps}];

drep3=Table[RandomReal[NormalDistribution[0,10.5]],{reps}];

drep4=Table[RandomReal[NormalDistribution[0,7.69]],{reps}];

C1=Cobs1*Fsample+dbias1+drep1;C2=Cobs2*Fsample+dbias2+drep2;

C3=Cobs3*Fsample+dbias3+drep3;C4=Cobs4*Fsample+dbias4+drep4;

Mean[C1]

Mean[C2]

Mean[C3]

Mean[C4]
```

Suppl. Table 2: Terms and definitions of the Mathematica code used in MCM when Se was used as internal standard.

Quantity	***Units***	***Definition***
alpha	μL/ (uL ^{o}C)	Thermal expansion coefficient
reps		Replicates
temperature	^{o}C	Temperature
Vpipet	μL	Volume of the bulk arsenic solution pipetted for preparing the stock solution
Vpipet2	μL	Volume of the stock arsenic solution pipetted for preparing the first dilution solution
Vfirstdil	μL	Volume of the first dilution of the arsenic solution pipetted for preparing the second dilution solution
Vsecdil	μL	Volume of the second dilution of the arsenic solution pipetted for preparing the working solution
Vsampling	μL	Sampling volume
Vafterdigest	mL	Final volume of the sample after digestion
Fsample		Dilution factor of the sample
Cbulk	μg/L	Arsenic concentration of the bulk solution
Cstock	μg/L	Arsenic concentration of the stock solution
Cworksolution	μg/L	Arsenic concentration of the working solution
Cstd	μg/L	Mean concentration of all calibration standards
Aij	AU	Integrated absorbance of the j measurement of the calibration standard i
Astd	AU	Mean absorbance of all calibration standards
β1	AU/ (μg/L)	Calculated best fit slope (gradient) of the calibration curve
β0	AU	Calculated best fit intercept of the calibration curve
ARij	AU	Integrated absorbance of the j measurement of the i fortification level solution
Cobsi	μg/L	Mean arsenic concentration of the i fortification level solution
dbiasi		Bias component of the uncertainty of Cobsi
drepi		Reproducibility component of the uncertainty of Cobsi
Ci	μg/L	Final arsenic concentration of the i fortification level solution (all components of uncertainty included)

VpipetSe	µL	Volume of the bulk selenium solution pippeted for preparing the stock solution
VpipetSe2	µL	Volume of the stock selenium solution pipetted for preparing the first dilution solution
VfirstdilSe	µL	Volume of the first dilution of the selinium solution pipetted for preparing the second dilution solution
VsecdilSe	µL	Volume of the second dilution of the selenium solution pipetted for preparing the working solution
CbulkSe	µg/L	Selenium concentration of the bulk solution
CstockSe	µg/L	Selenium concentration of the stock solution
CworksolutionSe	µg/L	Selenium concentration of the work solution solution
ARISij	AU	Integrated absorbance of the j measurement of the fortification level solution of the analyte to internal standard
AntoISij	AU	Integrated absorbance of the j measurement of the calibration standard i (arsenic to internal standard selenium)

Mathematica code used for the uncertainty estimation based on MCM when Se was used as an internal standard

```
alpha=0.00021;
reps=1000000;
meansN={meanVpipet,meanVpipet2,meanVfirstdil,meanVsecdil,meanVsampling,meanVpipetSe,meanVpipetSe2,meanVfirstdilSe,meanVsecdilSe};
sdN={sdVpipet,sdVpipet2,sdVfirstdil,sdVsecdil,sdVsampling,sdVpipetSe,sdVpipetSe2,sdVfirstdilSe,sdVsecdilSe};
meanU={meanVafterdigest,meanT ,meanCbulk,meanCbulkSe};
sdU={sdVafterdigest,sdT ,sdCbulk,sdCbulkSe};
Temperature=22;
meanAntoIS1={AntoIS11,AntoIS12,AntoIS13};
meanAntoIS2={AntoIS21,AntoIS22,AntoIS23};
meanAntoIS3={AntoIS31,AntoIS32,AntoIS33};
meanAntoIS4={AntoIS41,AntoIS42,AntoIS43};
meanAntoIS5={AntoIS51,AntoIS52,AntoIS53};
meanARIS1={ARIS11,ARIS12,ARIS13};
meanARIS2={ARIS21,ARIS22,ARIS23};
meanARIS3={ARIS31,ARIS32,ARIS33};
meanARIS4={ARIS41,ARIS42,ARIS43};
sdAi=0.63797521;
a=(2meanU-sdU Sqrt[12])/2;
b=(2meanU+sdU Sqrt[12])/2;
Vpipet=Table[RandomReal[NormalDistribution[meansN[[1]],sdN[[1]]]],{reps}];
Vpipet2=Table[RandomReal[NormalDistribution[meansN[[2]],sdN[[2]]]],{reps}];
VpipetSe=Table[RandomReal[NormalDistribution[meansN[[6]],sdN[[6]]]],{reps}];
VpipetSe2=Table[RandomReal[NormalDistribution[meansN[[7]],sdN[[7]]]],{reps}];
Vfirstdil=Table[RandomReal[NormalDistribution[meansN[[3]],sdN[[3]]]],{reps}];
Vsecdil=Table[RandomReal[NormalDistribution[meansN[[4]],sdN[[4]]]],{reps}];
VfirstdilSe=Table[RandomReal[NormalDistribution[meansN[[3]],sdN[[3]]]],{reps}];
VsecdilSe=Table[RandomReal[NormalDistribution[meansN[[8]],sdN[[8]]]],{reps}];
Vsampling=Table[RandomReal[NormalDistribution[meansN[[9]],sdN[[9]]]],{reps}];
Vafterdigest=Table[RandomReal[{a[[1]],b[[1]]}],{reps}];
T=Table[RandomReal[{a[[2]],b[[2]]}],{reps}];
Cbulk=Table[RandomReal[{a[[3]],b[[3]]}],{reps}];
CbulkSe=Table[RandomReal[{a[[4]],b[[4]]}],{reps}];
Vpipet=Vpipet(1+alpha(T-Temperature));
Vpipet2=Vpipet2(1+alpha(T-Temperature));
VpipetSe=VpipetSe(1+alpha(T-Temperature));
VpipetSe2=VpipetSe2(1+alpha(T-Temperature));
```

```
Vfirstdil=Vfirstdil(1+alpha(T-Temperature));
Vsecdil=Vsecdil(1+alpha(T-Temperature));
Vsampling=Vsampling(1+alpha(T-Temperature));
Vafterdigest=Vafterdigest(1+alpha(T-Temperature));
Fsample=Vafterdigest/Vsampling;
Cstock=(Cbulk*Vpipet)/Vfirstdil;
CstockSe=(CbulkSe*VpipetSe)/VfirstdilSe;
Cworksolution=(Cstock*Vpipet2)/Vsecdil;
CworksolutionSe=(CstockSe*VpipetSe2)/VsecdilSe;
Cstd=(6Cworksolution)/25;

aAntoIS1=(2meanAntoIS1-sdAi Sqrt[12])/2;bAntoIS1=(2meanAntoIS1+sdAi
Sqrt[12])/2;aAntoIS2=(2meanAntoIS2-sdAi
Sqrt[12])/2;bAntoIS2=(2meanAntoIS2+sdAi Sqrt[12])/2;
aAntoIS3=(2meanAntoIS3-sdAi Sqrt[12])/2;bAntoIS3=(2meanAntoIS3+sdAi
Sqrt[12])/2;aAntoIS4=(2meanAntoIS4-sdAi
Sqrt[12])/2;bAntoIS4=(2meanAntoIS4+sdAi Sqrt[12])/2;
aAntoIS5=(2meanAntoIS5-sdAi Sqrt[12])/2;bAntoIS5=(2meanAntoIS5+sdAi
Sqrt[12])/2;
AntoIS11=RandomReal[{aAntoIS1[[1]],bAntoIS1[[1]]},reps];AntoIS12=RandomRea
l[{aAntoIS1[[2]],bAntoIS1[[2]]},reps];
AntoIS13=RandomReal[{aAntoIS1[[3]],bAntoIS1[[3]]},reps];AntoIS21=RandomRea
l[{aAntoIS2[[1]],bAntoIS2[[1]]},reps];
AntoIS22=RandomReal[{aAntoIS2[[2]],bAntoIS2[[2]]},reps];AntoIS23=RandomRea
l[{aAntoIS2[[3]],bAntoIS2[[3]]},reps];
AntoIS31=RandomReal[{aAntoIS3[[1]],bAntoIS3[[1]]},reps];AntoIS32=RandomRea
l[{aAntoIS3[[2]],bAntoIS3[[2]]},reps];
AntoIS33=RandomReal[{aAntoIS3[[3]],bAntoIS3[[3]]},reps];AntoIS41=RandomRea
l[{aAntoIS4[[1]],bAntoIS4[[1]]},reps];
AntoIS42=RandomReal[{aAntoIS4[[2]],bAntoIS4[[2]]},reps];AntoIS43=RandomRea
l[{aAntoIS4[[3]],bAntoIS4[[3]]},reps];
AntoIS51=RandomReal[{aAntoIS5[[1]],bAntoIS5[[1]]},reps];AntoIS52=RandomRea
l[{aAntoIS5[[2]],bAntoIS5[[2]]},reps];
AntoIS53=RandomReal[{aAntoIS5[[3]],bAntoIS5[[3]]},reps];
AntoISstd1=AntoIS11+AntoIS12+AntoIS13;
AntoISstd2=AntoIS21+AntoIS22+AntoIS23;
AntoISstd3=AntoIS31+AntoIS32+AntoIS33;
AntoISstd4=AntoIS41+AntoIS42+AntoIS43;
AntoISstd5=AntoIS51+AntoIS52+AntoIS53;
AntoISstd=(AntoISstd1+AntoISstd2+AntoISstd3+AntoISstd4+AntoISstd5)/15;

\[Beta]1=(5Total[AntoISstd*Cstd]-Total[Cstd]*Total[AntoISstd])/(5Total[Cstd^2]-
Total[Cstd]^2);
\[Beta]0=Mean[AntoISstd]-\[Beta]1*Mean[Cstd];
```

```
aARIS1=(2meanARIS1-sdAi Sqrt[12])/2;bARIS1=(2meanARIS1+sdAi Sqrt[12])/2;
aARIS2=(2meanARIS2-sdAi Sqrt[12])/2;bARIS2=(2meanARIS2+sdAi Sqrt[12])/2;
aARIS3=(2meanARIS3-sdAi Sqrt[12])/2;bARIS3=(2meanARIS3+sdAi Sqrt[12])/2;
aARIS4=(2meanARIS4-sdAi Sqrt[12])/2;bARIS4=(2meanARIS4+sdAi Sqrt[12])/2;
ARIS11=RandomReal[{aARIS1[[1]],bARIS1[[1]]},reps];ARIS12=RandomReal[{aARIS1[[2]],bARIS1[[2]]},reps];
ARIS13=RandomReal[{aARIS1[[3]],bARIS1[[3]]},reps];ARIS21=RandomReal[{aARIS2[[1]],bARIS2[[1]]},reps];
ARIS22=RandomReal[{aARIS2[[2]],bARIS2[[2]]},reps];ARIS23=RandomReal[{aARIS2[[3]],bARIS2[[3]]},reps];
ARIS31=RandomReal[{aARIS3[[1]],bARIS3[[1]]},reps];ARIS32=RandomReal[{aARIS3[[2]],bARIS3[[2]]},reps];
ARIS33=RandomReal[{aARIS3[[3]],bARIS3[[3]]},reps];ARIS41=RandomReal[{aARIS4[[1]],bARIS4[[1]]},reps];
ARIS42=RandomReal[{aARIS4[[2]],bARIS4[[2]]},reps];ARIS43=RandomReal[{aARIS4[[3]],bARIS4[[3]]},reps];
ARIS1mean=(ARIS11+ARIS12+ARIS13)/3;ARIS2mean=(ARIS21+ARIS22+ARIS23)/3;ARIS3mean=(ARIS31+ARIS32+ARIS33)/3;ARIS4mean=(ARIS41+ARIS42+ARIS43)/3;
Cobs1=(ARIS1mean-\[Beta]0)/\[Beta]1;Cobs2=(ARIS2mean-\[Beta]0)/\[Beta]1;Cobs3=(ARIS3mean-\[Beta]0)/\[Beta]1;Cobs4=(ARIS4mean-\[Beta]0)/\[Beta]1;

dbias1=Table[RandomReal[NormalDistribution[0,0.048]],{reps}];
dbias2=Table[RandomReal[NormalDistribution[0,0.063]],{reps}];
dbias3=Table[RandomReal[NormalDistribution[0,0.017]],{reps}];
dbias4=Table[RandomReal[NormalDistribution[0,0.008]],{reps}];
drep1=Table[RandomReal[NormalDistribution[0,0.042]],{reps}];
drep2=Table[RandomReal[NormalDistribution[0,0.048]],{reps}];
drep3=Table[RandomReal[NormalDistribution[0,0.015]],{reps}];
drep4=Table[RandomReal[NormalDistribution[0,0.083]],{reps}];
C1=Cobs1*Fsample+dbias1+drep1;C2=Cobs2*Fsample+dbias2+drep2;
C3=Cobs3*Fsample+dbias3+drep3;C4=Cobs4*Fsample+dbias4+drep4;
Mean[C1]
Mean[C2]
Mean[C3]
Mean[C4]
```