Application of microwave-induced combustion and isotope dilution strategies for quantification of sulfur in coals via sector-field inductively coupled plasma mass spectrometry

Supplemental Information

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Supplemental Table 1. Quantity descriptions for each variable in the sulfur isotope dilution measurement function.

Quantity Symbol	Quantity Description	Quantity Symbol	Quantity Description	Quantity Symbol	Quantity Description
c_x **(%)**	mass fraction of test portion	c_{blk} **(μmol/g)**	amount content of procedure blank	K_{x1} **(unitless)**	mass bias correction of R_{x1} (32/34) in sample
a_z **(g/mol)**	primary standard molecular mass (SRM 3154)	K_b **(unitless)**	mass bias correction of R_b (34/32)	K_{x2} **(unitless)**	mass bias correction of R_{x2} (33/32) in sample
a_x **(g/mol)**	sulfur molecular mass	K'_b **(unitless)**	mass bias correction of R'_b (34/32)	K_{x3} **(unitless)**	mass bias correction of R_{x3} (32/32) in sample
d_x **(unitless)**	test portion drying correction factor	K_{y1} **(unitless)**	mass bias correction of R_{y1}	K_{x4} **(unitless)**	mass bias correction of R_{x4} (36/32) in sample
m_x **(g)**	mass of test portion in blend	R_{x1} **(unitless)**	ratio sample-measured ratio of enriched isotope to reference isotope (34/32)	K_{z1} **(unitless)**	mass bias correction of R_{z1} (34/32) in primary standard
m'_y **(g)**	mass of spike in spike calibration	R_{x2} **(unitless)**	ratio sample (33/32)	K_{z2} **(unitless)**	mass bias correction of R_{z2} (33/32) in primary standard
R_b **(unitless)**	measured ratio of blend 34/32 spike isotope/reference isotope	R_{x3} **(unitless)**	ratio sample (32/32)	K_{z3} **(unitless)**	mass bias correction of R_{z3} (32/32) in primary standard
R'_b **(unitless)**	measured ratio of spike calibration back blend (34/32) spike isotope/reference isotope	R_{x4} **(unitless)**	ratio sample (36/32)	K_{z4} **(unitless)**	mass bias correction of R_{z4} (36/32) in primary standard
R_{y1} **(unitless)**	measured ratio of 34 spike isotope to 32 reference isotope in the ^{34}S enriched spike material	R_{z1} **(unitless)**	ratio primary standard-measured ratio of enriched isotope to reference isotope (34/32)	C_{Rep} **(unitless)**	Constant = 1 used to incorporate replication uncertainty
m_y **(g)**	mass of enriched spike in blend	R_{z2} **(unitless)**	ratio primary standard (33/32)	C_{dt} **(unitless)**	Constant = 1 used to incorporate detector dead time uncertainty
m_z **(g)**	mass of primary assay standard in spike calibration back blend	R_{z3} **(unitless)**	ratio primary standard (32/32)	C_{bgd} **(unitless)**	Constant = 1 used to incorporate background subtraction uncertainty
c_z **(μmol/g)**	amount content of primary assay standard	R_{z4} **(unitless)**	ratio primary standard (36/32)		

Supplemental Table 2. Example input table for SRM 2682c showing the calculated S mass fraction result c_x, and corresponding metadata used to determine the mean and expanded uncertainty for a single permutation of the ID-MIC-SF-ICPMS measurement function (1 of 32 possible permutations, based on individual sample and spike solution pairs). The metadata are fed into a Kragten spreadsheet to estimate the uncertainty of the ID-MIC-SF-ICPMS method. The data for each quantity are presented in the following pattern: quantity value, reported uncertainty (standard deviation), method of evaluating uncertainty (Type A or Type B), standard uncertainty and degrees of freedom. Reported uncertainties evaluated by Type A methods were normalized to standard uncertainties by division by $\sqrt{n}$. Reported uncertainties with evaluated by Type B methods were modeled as rectangular distributions (normalized to standard uncertainties by division by $\sqrt{3}$), with the exception of published expanded uncertainties, which were normalized to standard uncertainties using the published coverage factor. The S mass fraction data for SRM 2682c described in the text are based on the average of all permutations (0.4902 % ± 0.0068 %).

Quantity Symbol	Quantity Description				Quantity Symbol	Quantity Description				Quantity Symbol	Quantity Description			
c_x (%)	0.4785 % ± 0.0066 % (this permutation)				c_{blk} (µmol/g)	0.028	9.48E-03	A	3.87E-03	5	K_{x1} (unitless)	1.000	1.00E-03	B	5.77E-04	∞
a_z (g/mol)	32.064	3.21E-02	B	1.85E-02	∞	K_b (unitless)	0.915	9.15E-04	B	5.28E-04	∞	K_{x2} (unitless)	1.000	1.00E-03	B	5.77E-04	∞
a_x (g/mol)	32.063	3.21E-02	B	1.85E-02	∞	K'_b (unitless)	0.915	9.15E-04	B	5.28E-04	∞	K_{x3} (unitless)	1.000	1.00E-04	B	5.77E-05	∞
d_x (unitless)	0.882	6.48E-04	A	2.90E-04	4	K_{y1} (unitless)	1.000	1.00E-03	B	5.77E-04	∞	K_{x4} (unitless)	1.000	1.00E-03	B	5.77E-04	∞
m_x (g)	0.105	2.00E-05	B	1.15E-05	∞	R_{x1} (unitless)	0.044	1.09E-04	B	6.31E-05	∞	K_{z1} (unitless)	1.000	1.00E-03	B	5.77E-04	∞
m'_y (g)	0.900	2.00E-05	B	1.15E-05	∞	R_{x2} (unitless)	0.008	1.95E-05	B	1.13E-05	∞	K_{z2} (unitless)	1.000	1.00E-03	B	5.77E-04	∞
R_b (unitless)	0.563	3.38E-03	A	1.51E-03	4	R_{x3} (unitless)	1.000	2.50E-04	B	1.44E-04	∞	K_{z3} (unitless)	1.000	1.00E-04	B	5.77E-05	∞
R'_b (unitless)	0.666	4.00E-03	A	1.79E-03	4	R_{x4} (unitless)	1.55E-04	3.86E-07	B	2.23E-07	∞	K_{z4} (unitless)	1.000	1.00E-03	B	5.77E-04	∞
R_{y1} (unitless)	842.908	1.69E+00	B	9.73E-01	∞	R_{z1} (unitless)	0.044	1.11E-04	B	6.40E-05	∞	C_{Rep} (unitless)	1.000	1.32E-02	A	4.67E-03	7
m_y (g)	0.072	2.00E-05	B	1.15E-05	∞	R_{z2} (unitless)	0.008	1.97E-05	B	1.14E-05	∞	C_{dt} (unitless)	1.000	1.20E-03	B	6.93E-04	∞
m_z (g)	0.909	2.00E-05	B	1.15E-05	∞	R_{z3} (unitless)	1.000	2.50E-04	B	1.44E-04	∞	C_{bgd} (unitless)	1.000	4.18E-03	A	1.58E-03	6
c_z (µmol/g)	158.3	2.31E-01	B	1.15E-01	∞	R_{z4} (unitless)	1.55E-04	3.86E-07	B	2.23E-07	∞						

Supplemental Table 3. Uncertainty descriptions and estimates for each variable in the ID-MIC-SF-ICPMS measurement function. Reported uncertainties evaluated by Type A methods were normalized to standard uncertainties by division by $\sqrt{n}$. Reported uncertainties evaluated by Type B methods were modeled as rectangular distributions (normalized to standard uncertainties by division by $\sqrt{3}$), with the exception of published expanded uncertainties, which were normalized to standard uncertainties using the published coverage factor.

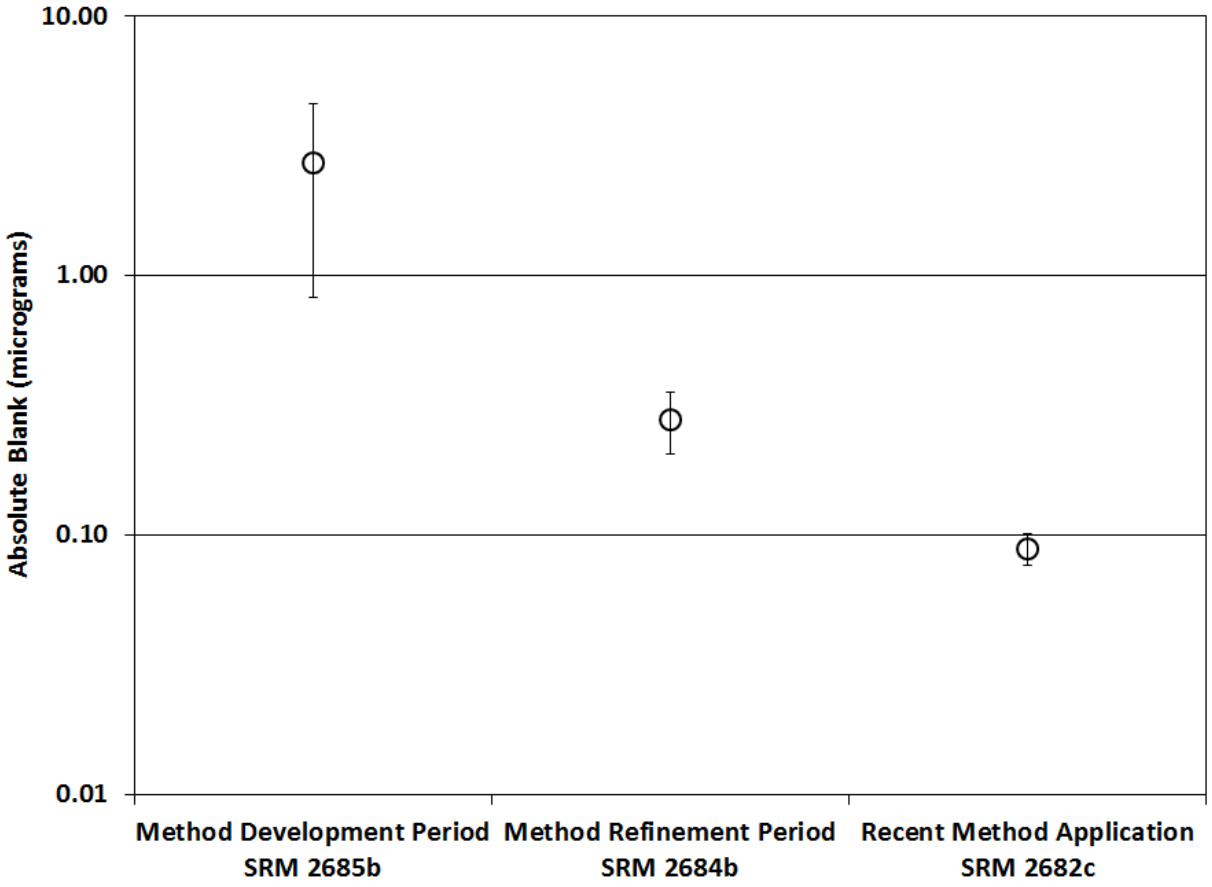
Quantity Symbol	Uncertainty Description	Quantity Symbol	Uncertainty Description	Quantity Symbol	Uncertainty Description
a_z **(g/mol)**	assume 0.1 % of quantity value, based on two times the IUPAC range of possible S atomic weights (range = 32.059 g/mol to 32.076 g/mol)[1]	K_b **(unitless)**	assume 0.1 % of quantity value	K_{x2} **(unitless)**	assume 0.1 % of quantity value
a_x **(g/mol)**	assume 0.1 % of quantity value, based on two times the IUPAC range of possible S atomic weights (range = 32.059 g/mol to 32.076 g/mol)[1]	K'_b **(unitless)**	assume 0.1 % of quantity value	K_{x3} **(unitless)**	assume 0.01 % of quantity value = 1
d_x **(unitless)**	absolute u_i for 5 moisture factor replicates from same bottle	K_{y1} **(unitless)**	assume 0.1 % of quantity value	K_{x4} **(unitless)**	assume 0.1 % of quantity value
m_x **(g)**	two times the 5-place balance readability of 0.00001 g,	R_{x1} **(unitless)**	assume 0.25 % of quantity value, based on usual instrumental measurement precision	K_{z1} **(unitless)**	assume 0.1 % of quantity value
m'_y **(g)**	two times the 5-place balance readability of 0.00001 g	R_{x2} **(unitless)**	assume 0.25 % of quantity value, based on usual instrumental measurement precision	K_{z2} **(unitless)**	assume 0.1 % of quantity value
R_b **(unitless)**	% RSD of 5 replicate isotope ratio measurements across experiment run	R_{x3} **(unitless)**	assume 0.025 % of quantity value = 1	K_{z3} **(unitless)**	assume 0.01 % of quantity value = 1
R'_b **(unitless)**	% RSD of 5 replicate isotope ratio measurements across experiment run	R_{x4} **(unitless)**	assume 0.25 % of quantity value, based on usual instrumental measurement precision	K_{z4} **(unitless)**	assume 0.1 % of quantity value

1. Atomic Weights of the Elements 2011 (IUPAC Technical Report), *Pure Appl. Chem.* **2013**, 85, 5, 1047-1078.

Supplemental Table 3 (continued). Uncertainty descriptions and estimates for each variable in the ID-MIC-SF-ICPMS measurement function. Reported uncertainties evaluated by Type A methods were normalized to standard uncertainties by division by $\sqrt{n}$. Reported uncertainties evaluated by Type B methods were modeled as rectangular distributions (normalized to standard uncertainties by division by $\sqrt{3}$), with the exception of published expanded uncertainties, which were normalized to standard uncertainties using the published coverage factor.

Quantity Symbol	**Uncertainty Description**	**Quantity Symbol**	**Uncertainty Description**	**Quantity Symbol**	**Uncertainty Description**
$\boldsymbol{R_{y1}}$ **(unitless)**	assume 0.2 % of quantity value, based on information on the standard deviation of ^{34}S enrichment, obtained from the spike certificate of analysis	$\boldsymbol{R_{z1}}$ **(unitless)**	assume 0.25 % of quantity value, based on usual instrumental measurement precision	$\boldsymbol{C_{Rep}}$ **(unitless)**	% RSD due to replication for n = 8 processed samples
$\boldsymbol{m_y}$ **(g)**	two times the 5-place balance readability of 0.00001g	$\boldsymbol{R_{z2}}$ **(unitless)**	assume 0.25 % of quantity value, based on usual instrumental measurement precision	$\boldsymbol{C_{dt}}$ **(unitless)**	% RSD of $^{34}S/^{32}S$ isotope ratio, based on using typical experimental count rates for ^{32}S and ^{34}S in a 10K trial Monte Carlo simulation of detector dead time correction calculations, using an experimentally derived instrumental detector dead time setting of 10 ns. An assumption is made that the uncertainty in the assigned dead time is ± 1 ns
$\boldsymbol{m_z}$ **(g)**	two times 5-place balance readability of 0.00001g	$\boldsymbol{R_{z3}}$ **(unitless)**	assume 0.025 % of quantity value = 1	$\boldsymbol{C_{bgd}}$ **(unitless)**	% RSD based on the quotient of standard deviation of ^{32}S signal for an instrumental background solution of 1 % nitric acid mass fraction in water, measured at seven time points and the experimentally measured ^{32}S signal in the analytical sample
$\boldsymbol{c_z}$ **(µmol/g)**	SRM 3154 expanded uncertainty in µmol/g	$\boldsymbol{R_{z4}}$ **(unitless)**	assume 0.25 % of quantity value, based on usual instrumental measurement precision		
c_{blk} (µmol/g)	Standard deviation of blank in µmol/g	K_{x1} (unitless)	assume 0.1 % of quantity value		

Supplemental Figure 1. Absolute ID-MIC-SF-ICPMS procedure blanks in units of micrograms with associated standard uncertainties, showing reduction of average blanks as a function of method development progression. The number of blanks were $n = 5$, for the SRM 2685b project and $n = 6$ for both the SRM 2684b and SRM 2682c projects.



Supplemental Figure 2. Truncated Kragten spreadsheet for SRM 2682c (10 of 34 input columns shown). The most significant sources of uncertainty are readily apparent in the last data column (uncertainties calculated relative to the total variance). The results are based on a single permutation of the ID-MIC-SF-ICPMS measurement function (1 of 32 possible permutations, based on individual sample and spike solution pairs). The S mass fraction data for SRM 2682c described in the text are based on the average of all permutations (0.4902 % ± 0.0068 %).

		u(az)	u(ax)	u(dx)	u(mx)	u(m'y)	u(Rb)	u(R'b)	u(Rep)	u(dt)	u(Bgd)	
		0.019	0.019	0.000	0.000	0.000	0.002	0.002	0.005	0.001	0.002	
	ν_i	99999.000	99999.000	4.000	99999.000	99999.000	4.000	4.000	7.000	99999.000	6.000	
Quantity Name, Symbol	Quantity Value	Quantity Value + u_i										rel $(c_i u_i)^2$
az	32.064	32.083	32.064	32.064	32.064	32.064	32.064	32.064	32.064	32.064	32.064	0.00%
ax	32.063	32.063	32.082	32.063	32.063	32.063	32.063	32.063	32.063	32.063	32.063	0.76%
dx	0.882	0.882	0.882	0.882	0.882	0.882	0.882	0.882	0.882	0.882	0.882	0.25%
mx	0.105	0.105	0.105	0.105	0.105	0.105	0.105	0.105	0.105	0.105	0.105	0.03%
m'y	0.900	0.900	0.900	0.900	0.900	0.900	0.900	0.900	0.900	0.900	0.900	0.00%
Rb	0.563	0.563	0.563	0.563	0.563	0.563	0.564	0.563	0.563	0.563	0.563	19.62%
R'b	0.666	0.666	0.666	0.666	0.666	0.666	0.666	0.668	0.666	0.666	0.666	19.23%
Ry1	842.908	842.908	842.908	842.908	842.908	842.908	842.908	842.908	842.908	842.908	842.908	0.00%
my	0.072	0.072	0.072	0.072	0.072	0.072	0.072	0.072	0.072	0.072	0.072	0.06%
mz	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.00%
cz	158.288	158.288	158.288	158.288	158.288	158.288	158.288	158.288	158.288	158.288	158.288	1.22%
cblk	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.00%
Kb	0.915	0.915	0.915	0.915	0.915	0.915	0.915	0.915	0.915	0.915	0.915	0.91%
k'b	0.915	0.915	0.915	0.915	0.915	0.915	0.915	0.915	0.915	0.915	0.915	0.89%
Ky1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.00%
Rx1	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.09%
Rx2	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.00%
Rx3	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.04%
Rx4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00%
Rz1	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.07%
Rz2	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.00%
Rz3	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.04%
Rz4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00%
Kx1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.01%
Kx2	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.00%
Kx3	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.01%
Kx4	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.00%
Kz1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.01%
Kz2	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.00%
Kz3	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.01%
Kz4	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.00%
Rep	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.005	1.000	1.000	49.93%
dt	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.001	1.000	1.10%
Bgd	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.002	5.72%
MF Value, Y	4785.343	4785.343	4788.107	4783.772	4784.816	4785.282	4771.343	4799.202	4807.676	4788.659	4792.900	100.00%
		-0.001	2.763	-1.571	-0.528	-0.061	-14.000	13.859	22.333	3.315	7.557	$c_i u_i$
Standard Uncertainty, u_c	31.605	0.000	7.636	2.468	0.278	0.004	196.011	192.065	498.751	10.992	57.104	$(c_i u_i)^2$
Degrees of Freedom, ν	18.172	0.00%	0.76%	0.25%	0.03%	0.00%	19.62%	19.23%	49.93%	1.10%	5.72%	rel $(c_i u_i)^2$
Coverage Factor, k	2.101	-0.031	149.279	-5423.971	-45683.649	-5319.927	-9270.188	7750.851	4785.343	4785.343	4785.343	c_i
Expanded Uncertainty, U	66.400										0.014	U_r
← Show/Hide Extra Information												
		Quantity Value - u_i (Results Only)										
MF Value, Y	4785.343	4785.344	4782.580	4786.915	4785.871	4785.405	4799.426	4771.484	4763.010	4782.028	4777.786	
		0.001	-2.763	1.572	0.528	0.061	14.083	-13.859	-22.333	-3.315	-7.557	$c_i u_i$
Standard Uncertainty, u_c	31.642	0.000	7.636	2.471	0.278	0.004	198.323	192.064	498.751	10.992	57.104	$(c_i u_i)^2$
Degrees of Freedom, ν	18.181	0.00%	0.76%	0.25%	0.03%	0.00%	19.81%	19.18%	49.81%	1.10%	5.70%	rel $(c_i u_i)^2$
Coverage Factor, k	2.101	0.031	-149.279	5427.535	45693.721	5320.064	9324.708	-7750.821	-4785.343	-4785.343	-4785.343	c_i
Expanded Uncertainty, U	66.478										0.014	U_r
← Show/Hide Extra Information												
Final Measurement Result												
Measurement Function Value	Standard Uncertainty	Degrees of Freedom	Coverage Factor	Expanded Uncertainty	Relative Expanded Uncertainty		Unit Conversion	S Mass Fraction Value	Expanded Uncertainty U			
Y	u_c	ν	k	U	U_r		mg/kg to %	%	%			
4785.343	31.624	18.167	2.101	66.439	0.014		10000	0.4785	0.0066			
		$u(az)$	$u(ax)$	$u(dx)$	$u(mx)$	$u(m'y)$	$u(Rb)$	$u(R'b)$	$u(Rep)$	$u(Tdt)$	$u(Bgd)$	
No Warning for Zero Sensitivity Coefficients		0.00%	0.76%	0.25%	0.03%	0.00%	19.72%	19.21%	49.87%	1.10%	5.71%	rel $(c_i u_i)^2$
		-0.031	149.279	-5425.753	-45688.685	-5319.995	-9297.448	7750.836	4785.343	4785.343	4785.343	c_i