Supplementary Information

Quantification Capabilities of N2 MICAP-MS with Solution Nebulization and Aerosol Desolvation

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The following supplementary information supports the corresponding paper with additional figures (Figure S1 – S6) and tables (Table S1 – S8).

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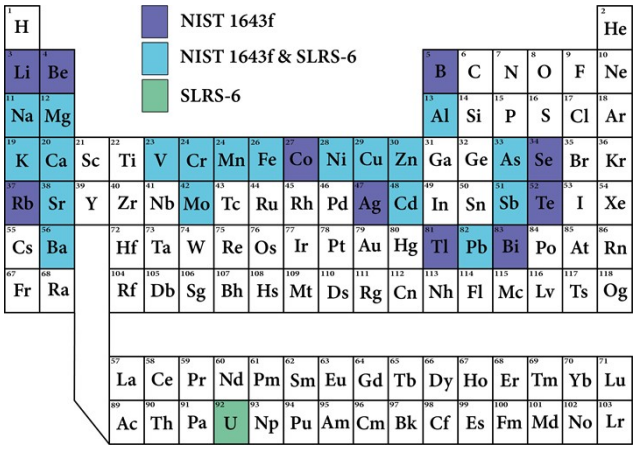

Figure S1: An overview of the certified elements contained in the two water reference materials. The colours in the periodic table indicate which elements were certified for NIST SRM 1643f (dark blue), SLRS-6 (green) or both (light blue).

Table S1: Certified reference mass fraction values for SLRS-6 and NIST 1643f are given with the mass fractions of the multi-element stock solution (MES), which was used to prepare the external calibration by diluting it 4 – 400-fold. The mass fractions in the MES were chosen so that its 20-fold dilution results in similar mass fractions to those of the SLRS-6, NIST 1643f, or the five-fold dilution thereof. For elements that had at least one order of magnitude difference in the mass fractions of the two water reference materials SLRS-6 and NIST 1643f, additional multi-element solutions were prepared that matched the reference samples. All mass fractions are reported in µg kg^{-1}.

Element	SLRS-6			NIST 1643f			MES
Li		-[a]		16.4	±	0.4	336
Be	0.0066[b]	±	0.0022 [b]	13.53	±	0.11	272
B		-[a]		150	±	7	10000
Na	2770	±	220	18640	±	240	64500
Mg	2140	±	60	7380	±	60	35600
Al	33.9	±	2.2	132.5	±	1.2	600
K	650	±	50	1913	±	9	9848
Ca	8770	±	200	29140	±	300	144300
V	0.352	±	0.006	35.71	±	0.27	74.8
Cr	0.252	±	0.012	18.32	±	0.1	39.3
Mn	2.12	±	0.1	36.7	±	0.6	93.7
Fe	85	±	4	92.5	±	0.8	1770
Co	0.053[b]	±	0.012 [b]	25.05	±	0.17	495
Ni	0.617	±	0.022	59.2	±	1.4	119
Cu	24	±	1.8	21.44	±	0.7	451
Zn	1.76	±	0.12	73.7	±	1.7	164
As	0.57	±	0.08	56.8	±	0.4	119
Se		-[a]		11.58	±	0.08	239
Rb		-[a]		12.51	±	0.12	245
Sr	40.7	±	0.3	311	±	18	1020
Mo	0.215	±	0.018	114.2	±	1.7	227
Ag		-[a]		0.960	±	0.008	19.0
Cd	0.0063	±	0.0014	5.83	±	0.13	118
Sb	0.338	±	0.006	54.9	±	0.4	109
Te		-[a]		0.967	±	0.008	18.9
Ba	14.3	±	0.5	513	±	7	1150
Tl		-[a]		6.82	±	0.03	139
Pb	0.17	±	0.026	18.30	±	0.08	39.0
Bi		-[a]		12.50	±	0.10	247
U	0.070	±	0.003		-[a]		1.38

[a] not available; [b] not certified

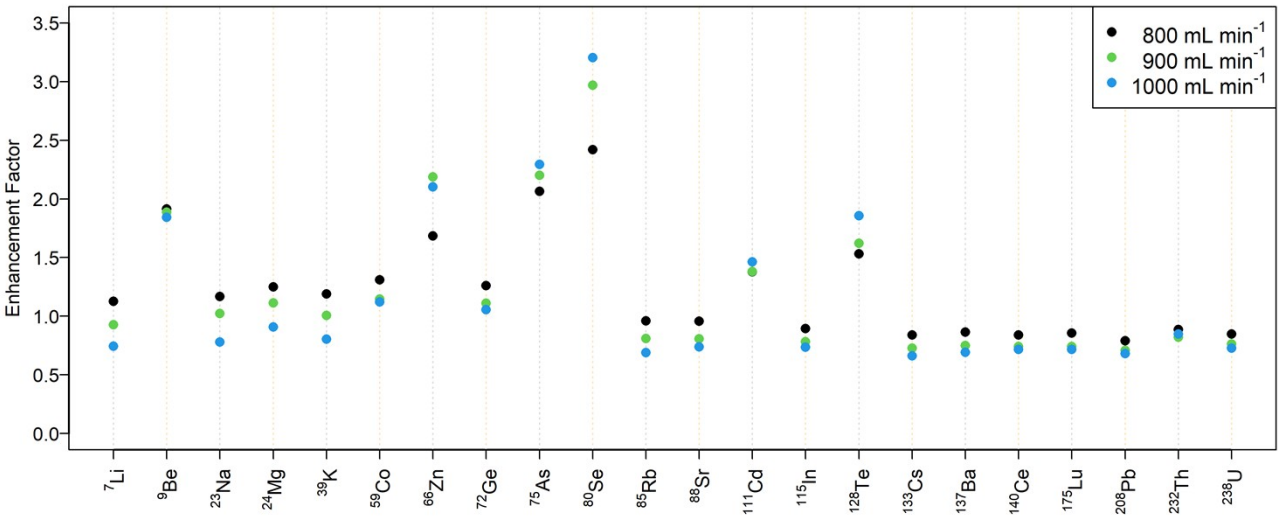

Figure S2: Enhancement and suppression of the desolvated aerosol signal intensity compared to the signal intensity when the desolvator was deactivated. Data is shown for nebulizer gas flow rates of 800 mL min^{-1}, 900 mL min^{-1} and 1000 mL min^{-1}.

Table S2: Enhancement and suppression due to solvent load in dependence on the nebulizer gas flow rate. The ratio of the signal intensities from the setup with the activated to the deactivated desolvator is given for different nebulizer gas flow rates (reported in mL min^{-1}).

Isotope	800	825	850	875	900	925	950	975	1000
$^{7}Li^{+}$	1.13	1.09	0.88	1.04	0.93	0.85	0.71	0.77	0.74
$^{9}Be^{+}$	1.91	1.87	1.76	1.81	1.89	1.90	1.68	1.89	1.84
$^{23}Na^{+}$	1.17	1.00	1.01	1.07	1.02	0.97	0.82	0.83	0.78
$^{24}Mg^{+}$	1.25	1.20	1.15	1.13	1.11	1.08	0.92	0.95	0.91
$^{39}K^{+}$	1.19	1.06	1.04	1.01	1.01	0.96	0.87	0.85	0.80
$^{59}Co^{+}$	1.31	1.21	1.26	1.15	1.15	1.18	1.14	1.14	1.12
$^{66}Zn^{+}$	1.68	1.73	1.77	2.21	2.19	2.39	2.15	2.02	2.10
$^{72}Ge^{+}$	1.26	1.19	1.15	1.14	1.11	1.13	1.16	1.12	1.05
$^{75}As^{+}$	2.06	1.98	2.07	2.15	2.20	2.15	2.36	2.31	2.29
$^{80}Se^{+}$	2.42	2.67	2.90	2.91	2.97	3.07	3.21	3.13	3.20
$^{85}Rb^{+}$	0.96	0.93	0.87	0.83	0.81	0.79	0.75	0.74	0.69
$^{88}Sr^{+}$	0.96	0.94	0.89	0.85	0.81	0.82	0.78	0.78	0.74
$^{111}Cd^{+}$	1.38	1.35	1.34	1.35	1.38	1.39	1.48	1.48	1.46
$^{115}In^{+}$	0.89	0.85	0.85	0.80	0.78	0.78	0.76	0.75	0.74
$^{128}Te^{+}$	1.53	1.53	1.58	1.60	1.62	1.64	1.79	1.76	1.86
$^{133}Cs^{+}$	0.84	0.80	0.79	0.76	0.73	0.73	0.70	0.67	0.66
$^{137}Ba^{+}$	0.86	0.81	0.78	0.76	0.75	0.72	0.72	0.67	0.69
$^{140}Ce^{+}$	0.84	0.83	0.80	0.78	0.74	0.74	0.71	0.72	0.72
$^{175}Li^{+}$	0.86	0.84	0.79	0.76	0.74	0.75	0.73	0.75	0.72
$^{208}Pb^{+}$	0.79	0.78	0.75	0.72	0.71	0.70	0.71	0.67	0.68
$^{232}Th^{+}$	0.89	0.82	0.87	0.79	0.82	0.81	0.83	0.85	0.85
$^{238}U^{+}$	0.85	0.80	0.82	0.75	0.76	0.76	0.77	0.75	0.73
$^{14}N^{16}O^{+}$	0.62	0.66	0.67	0.70	0.72	0.75	0.78	0.79	0.77

Table S3: Calculated plasma temperatures obtained from the pressure reduction method, the Longerich method, and the method from Houk and Praphairaksit (H&P). Temperatures were calculated for solution nebulization (SN) and desolvated (Des) sample introduction for both the N_2 MICAP and the Ar ICP at a nebulizer gas flow rate of 900 mL min^{-1}.

Method	N_2 MICAP		Ar ICP	
	SN	Des	SN	Des.
Pressure reduction	5'220 K	5'400 K	5'780 K	5'850 K
Longerich	12'850 K	16'400 K	13'170 K	12'460 K
H&P LaO^+ / La^+	6'350 K	6'790 K	6'620 K	6'950 K
H&P CeO^+ / Ce^+	5'910 K	6'250 K	6'060 K	6'400 K
H&P PrO^+ / Pr^+	6'200 K	6'580 K	6'080 K	6'390 K

Table S4:Ca matrix tolerance of the N_2 MICAP-MS. The signal suppression of a solution with 100 mg kg^{-1} compared to a solution with 1 mg kg^{-1} is shown for solution nebulization (SN) and desolvated sample introduction (Des). Suppression values are given for raw ion signals and after normalization to ^{115}In as internal standard (w. IS).

Isotope	SN	SN w. IS	Des	Des w. IS
$^{7}Li^+$	- 24 %	- 13 %	- 72 %	- 41 %
$^{9}Be^+$	- 02 %	+ 15 %	- 60 %	- 18 %
$^{11}B^+$	- 07 %	+ 05 %	+ 165 %	+ 436 %
$^{24}Mg^+$	- 21 %	- 11 %	- 64 %	- 27 %
$^{27}Al^+$	- 29 %	- 19 %	- 61 %	- 20 %
$^{51}V^+$	- 13 %	- 02 %	- 57 %	- 12 %
$^{52}Cr^+$	- 18 %	- 07 %	- 59 %	- 16 %
$^{55}Mn^+$	- 20 %	- 10 %	- 60 %	- 20 %
$^{56}Fe^+$	- 14 %	+ 11 %	- 55 %	- 08 %
$^{59}Co^+$	- 10 %	+ 01 %	- 57 %	- 12 %
$^{60}Ni^+$	- 04 %	+ 17 %	- 53 %	- 04 %
$^{63}Cu^+$	- 17 %	- 06 %	- 58 %	- 15 %
$^{66}Zn^+$	- 10 %	+ 02 %	- 52 %	- 01 %
$^{71}Ga^+$	- 18 %	- 08 %	- 56 %	- 10 %
$^{75}As^+$	- 12 %	- 01 %	- 51 %	+ 01 %
$^{80}Se^+$	- 15 %	- 04 %	- 41 %	+ 20 %
$^{85}Rb^+$	- 25 %	- 15 %	- 54 %	- 06 %
$^{98}Mo^+$	- 07 %	+ 05 %	- 51 %	+ 01 %
$^{107}Ag^+$	- 15 %	- 04 %	- 53 %	- 02 %
$^{111}Cd^+$	- 04 %	+ 09 %	- 51 %	+ 02 %
$^{128}Te^+$	- 02 %	+ 12 %	- 46 %	+ 12 %
$^{137}Ba^+$	- 16 %	- 05 %	- 51 %	+ 01 %
$^{208}Pb^+$	- 16 %	- 06 %	- 54 %	- 07 %
$^{209}Bi^+$	- 10 %	+ 01 %	- 53 %	- 04 %
$^{238}U^+$	- 06 %	+ 06 %	- 54 %	- 05 %

Table S5: Abundance normalized sensitivities for selected elements to demonstrate the enhancement observed with aerosol desolvation. Sensitivities are given in cps μg^{-1} kg for two Ca matrix mass fractions to see the decrease in enhancement with higher mass load.

Elements	1 mg kg^{-1} Ca		50 mg kg^{-1} Ca	
	SN	Des	SN	Des
Li^+	830	10'100	630	4'000
Co^+	8'150	80'000	6'730	43'700
As^+	1'370	14'500	1'150	9'100
Pb^+	21'300	160'000	17'600	92'000
U^+	25'500	234'000	22'300	137'000

Table S6: Limits of detection and limits of quantification for elements measured with solution nebulization and desolvation. The LODs and LOQs given in ng kg^{-1} were determined from the slope of the external calibration for the quantification study and the respective blank measurement. The dilution factor has not been considered for the LOQs.

Isotope	LODs		LOQs	
	SN	Des	SN	Des
$^{7}Li^+$	150	17	500	60
$^{9}Be^+$	26	5	90	16
$^{11}B^+$	80	4'000	250	12'000
$^{23}Na^+$	240	400	800	1'400
$^{24}Mg^+$	15	9	50	29
$^{27}Al^+$	24	40	80	140
$^{39}K^+$	9	180	30	600
$^{40}Ca^+$	100	250	300	900
$^{51}V^+$	1.5	0.6	5	1.9
$^{52}Cr^+$	2.3	0.7	8	2.6
$^{55}Mn^+$	1.0	0.3	3	1.1
$^{56}Fe^+$	40	15	130	50
$^{59}Co^+$	4	2.0	14	7
$^{60}Ni^+$	20	3	70	11
$^{63}Cu^+$	12	6	40	21
$^{66}Zn^+$	30	23	100	80
$^{75}As^+$	5	6	16	20
$^{80}Se^+$	11	70	40	230
$^{85}Rb^+$	1.9	0.8	6	2.5
$^{88}Sr^+$	1.1	0.6	4	2.0
$^{98}Mo^+$	2.6	9	9	29
$^{107}Ag^+$	2.7	2.7	9	9
$^{111}Cd^+$	13	3	40	11
$^{121}Sb^+$	1.6	1.0	5	3
$^{128}Te^+$	13	2.3	40	8
$^{137}Ba^+$	6.6	1.8	22	6
$^{205}Tl^+$	1.2	0.9	4	2.9
$^{208}Pb^+$	0.8	1.9	2.6	6
$^{209}Bi^+$	0.7	1.0	2.4	3
$^{238}U^+$	0.3	0.1	1.1	0.4

Table S7: Quantification overview for NIST 1643f with twofold dilution for external calibration and standard addition using solution nebulization (SN) and desolvated sample introduction (Des). All values are reported in µg kg^{-1}.

Quantified	Reference		SN Ext. Cal.		SN Std. Add.		Des Ext. Cal		Des Std. Add.	
Isotope	mean	2SD	mean	2SD	mean	2SD	mean	2SD	mean	2SD
^{7}Li	16.4	0.4	18.0	0.6	16.3	0.8	15.8	0.5	17.3	0.6
^{9}Be	13.53	0.11	13.7	0.8	14.6	1.0	12.0	0.4	13.19	0.22
^{11}B	151	7	162	5	157	5	(284)		(78)	
^{23}Na	18640	240	20700	400	-[b]		17700	500	-[b]	
^{24}Mg	7380	60	8190	150	-[b]		7050	240	-[b]	
^{25}Mg	7380	60	7990	150	-[b]		7070	190	-[b]	
^{27}Al	132.5	1.2	141	3	146	4	126.6	2.6	130	4
^{39}K	1913	9	2010	50	-[b]		1820	50	-[b]	
^{40}Ca	29140	300	30100	600	-[b]		-[c]		-[b]	
^{41}K	1913	9	1919	18	-[b]		1790	60	-[b]	
^{51}V	35.71	0.27	35.7	0.6	38.9	0.6	34.2	0.4	37.8	0.3
^{52}Cr	18.3	0.1	18.4	0.3	17.9	0.6	18.0	0.4	19.40	0.20
^{53}Cr	18.3	0.1	18.0	0.6	18.38	0.22	17.8	0.5	19.2	0.4
^{55}Mn	36.8	0.6	36.0	0.6	36.7	0.8	35.0	1.2	34.0	0.6
^{56}Fe	92.5	0.8	100	3	95.9	1.8	90.1	3.0	87.5	1.2
^{57}Fe	92.5	0.8	185	5	266	5	147	10	155.6	2
^{59}Co	25.05	0.17	25.0	0.5	25.6	0.4	23.7	0.8	25.1	0.3
^{60}Ni	59.2	1.4	58.8	2.0	61.4	1.0	55.9	1.8	66.6	1.2
^{62}Ni	59.2	1.4	56.7	2.2	60.0	1.4	56.4	0.4	65.1	1.0
^{63}Cu	21.4	0.7	19.1	0.4	22.4	0.8	19.8	0.5	22.5	0.5
^{64}Zn	73.7	1.7	85.4	2.8	79.4	1.2	77.6	2.4	86.6	1.4
^{65}Cu	21.4	0.7	19.3	0.4	22.5	0.5	19.5	0.6	22.7	0.4
^{66}Zn	73.7	1.7	85	3	75.6	1.6	76.4	2.6	83.0	1.4
^{75}As	56.9	0.4	56.3	1.2	59.8	0.8	53.8	1.0	54.8	0.5
^{78}Se	11.58	0.08	11.2	0.8	11.6	0.8	11.43	0.24	12.4	0.4
^{80}Se	11.58	0.08	11.27	0.26	11.3	0.6	10.69	0.24	12.0	0.4
^{85}Rb	12.51	0.12	12.33	0.20	13.2	0.3	12.00	0.30	13.3	0.3
^{88}Sr	311	18	329	4	317	5	298	6	288.4	2.4
^{95}Mo	114.2	1.7	110.8	1.8	114.4	2.2	109	3	114.4	1.8
^{98}Mo	114.2	1.7	111.1	2.0	114.8	2.4	110	4	114.0	2.2
^{107}Ag	0.961	0.008	0.96	0.04	0.94	0.04	0.966	0.022	0.905	0.026
^{109}Ag	0.961	0.008	1.03	0.03	1.00	0.06	1.030	0.028	0.982	0.020
^{111}Cd	5.8	0.13	6.12	0.28	5.77	0.24	5.84	0.22	6.09	0.14
^{121}Sb	54.9	0.39	50.0	1.2	54.7	1.0	49.1	1.6	59.3	0.6
^{128}Te	1.0	0.0082	0.89	0.03	0.95	0.05	0.889	0.012	1.046	0.024
^{137}Ba	513	7	510	6	535	6	498	16	512	8
^{138}Ba	513	7	540	14	500	8	490	14	511	16
^{205}Tl	6.82	0.03	6.84	0.22	7.32	0.26	7.0	0.4	7.32	0.18
^{208}Pb	18.30	0.08	17.67	0.20	18.9	0.5	17.7	0.8	18.13	0.22
^{209}Bi	12.50	0.10	12.6	0.3	13.3	0.5	12.3	0.4	13.21	0.18
^{238}U	-[a]		0.0063	0.0013	0.0052	0.0010	0.0055	0.0004	0.0049	0.0006

[a] not available, [b] not determined, [c] detector saturation

Table S8: Quantification overview for NIST 1643f with tenfold dilution for external calibration and standard addition using solution nebulization (SN) and desolvated sample introduction (Des). All values are reported in µg kg^{-1}.

Quantified	Reference		SN Ext. Cal.		SN Std. Add.		Des Ext. Cal		Des Std. Add.	
Isotope	mean	2SD	mean	2SD	mean	2SD	mean	2SD	mean	2SD
^{7}Li	16.4	0.4	15.8	0.8	16.7	0.8	17.4	1.2	15.7	0.6
^{9}Be	13.53	0.11	12.3	2.0	13.0	1.8	12.4	0.8	12.4	0.4
^{11}B	151	7	150	10	141	5	(128)		(124)	
^{23}Na	18640	240	19900	1100	-[c]		18900	1400	-[c]	
^{24}Mg	7380	60	6910	180	-[c]		7390	260	-[c]	
^{25}Mg	7380	60	7740	240	-[c]		7480	200	-[c]	
^{27}Al	132.5	1.2	134	5	144.6	3.0	130	4	124	2.2
^{39}K	1913	9	2040	60	-[c]		1890	70	-[c]	
^{40}Ca	29140	300	29700	800	-[c]		29200	1000	-[c]	
^{41}K	1913	9	1950	50	-[c]		1910	100	-[c]	
^{51}V	35.71	0.27	34.5	1.2	36.27	0.26	36.2	1.0	35.31	0.26
^{52}Cr	18.3	0.1	18.3	0.8	18.7	0.3	18.7	0.4	18.06	0.12
^{53}Cr	18.3	0.1	17.9	0.6	18.3	1.2	18.1	0.3	17.62	0.22
^{55}Mn	36.8	0.6	35.9	1.0	36.23	0.16	35.8	0.8	34.9	0.4
^{56}Fe	92.5	0.8	95.4	2.6	96.6	1.0	92	4	83.5	2.4
^{57}Fe	92.5	0.8	172	8	257.2	6	141	12	151	3
^{59}Co	25.05	0.17	24.4	0.8	25.3	0.4	25.5	1.2	27.0	0.5
^{60}Ni	59.2	1.4	56.8	1.8	60.5	2.0	59.2	2.2	63.1	1.4
^{62}Ni	59.2	1.4	57.1	2.4	58.5	1.4	59.0	2.6	62.4	1.8
^{63}Cu	21.4	0.7	18.6	1.0	21.5	0.4	19.9	0.4	23.17	0.28
^{64}Zn	73.7	1.7	75.8	1.8	75.0	1.4	76.2	2.2	83.2	1.8
^{65}Cu	21.4	0.7	19.0	0.6	22.0	1.0	19.6	0.8	22.2	0.4
^{66}Zn	73.7	1.7	75.6	2.6	72.1	2.0	74.5	3	78.3	2.0
^{75}As	56.9	0.4	55.0	2.2	55.5	1.8	52.4	1.2	55.9	0.5
^{78}Se	11.58	0.08	11.0	1.8	12.3	3.0	12.1	0.8	10.5	0.4
^{80}Se	11.58	0.08	11.1	1.2	11.3	1.4	12.1	0.5	10.1	0.8
^{85}Rb	12.51	0.12	12.7	0.5	12.80	0.18	12.62	0.14	13.39	0.16
^{88}Sr	311	18	291	8	320	6	291	6	293	10
^{95}Mo	114.2	1.7	107.4	2.2	112.0	1.6	109.3	2.0	106.3	1.8
^{98}Mo	114.2	1.7	107.3	3.0	114.0	2.2	109	5	101.9	2.0
^{107}Ag	0.961	0.008	0.97	0.06	0.95	0.10	0.95	0.03	0.88	0.03
^{109}Ag	0.961	0.008	1.02	0.06	1.00	0.10	1.01	0.03	0.935	0.024
^{111}Cd	5.8	0.13	5.9	0.4	6.0	0.5	5.9	0.3	5.9	0.3
^{121}Sb	54.9	0.39	48.3	2.0	54.2	0.4	49.1	1.2	59.1	0.8
^{128}Te	1.0	0.0082	0.85	0.12	0.94	0.08	0.83	0.08	1.05	0.06
^{137}Ba	513	7	510	5	558	5	504	20	468	8
^{138}Ba	513	7	521	16	528	4	479	26	463	16
^{205}Tl	6.82	0.03	6.80	0.22	7.02	0.22	7.4	0.3	7.27	0.22
^{208}Pb	18.30	0.08	17.66	0.22	19.2	0.4	18.6	0.8	18.1	0.6
^{209}Bi	12.50	0.10	12.6	0.4	12.8	0.4	12.4	0.8	13.3	0.6
^{238}U	-[a]		-[b]		-[b]		0.0052	0.0006	0.0067	0.0014

[a] not available, [b] below LOQ, [c] not determined

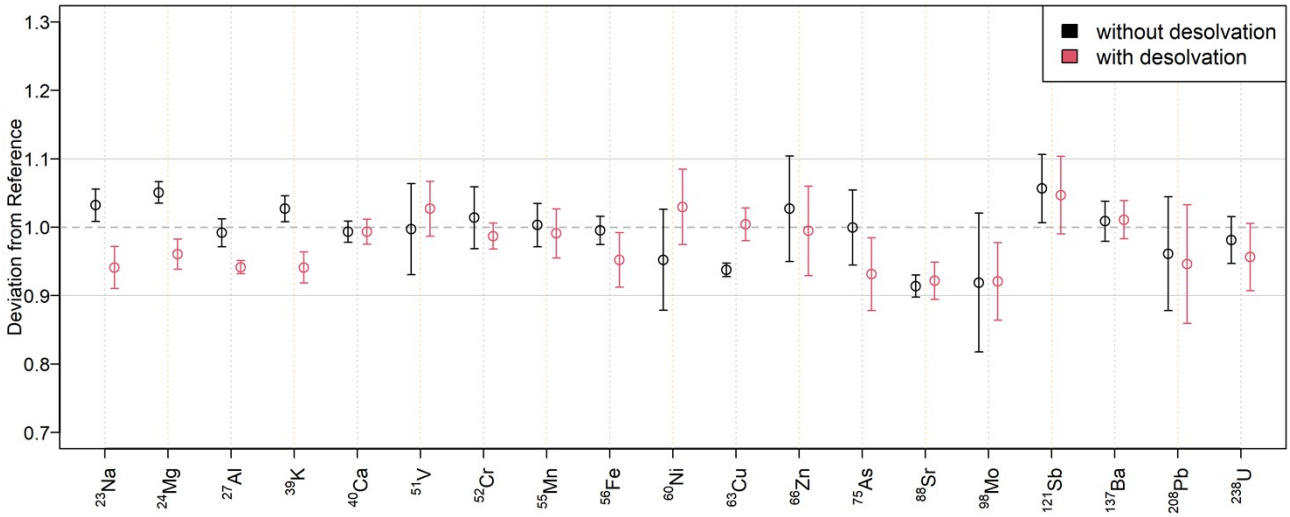

Figure S3: Quantification overview obtained with a twofold dilution of SLRS-6 for solution nebulization (black) and aerosol desolvation (red) using external calibration. For each isotope, the deviation of the obtained mass fractions from the certified reference material is given with error bars representing two times the standard deviation. The grey horizontal lines correspond to a difference of ± 10 % from the certified value.

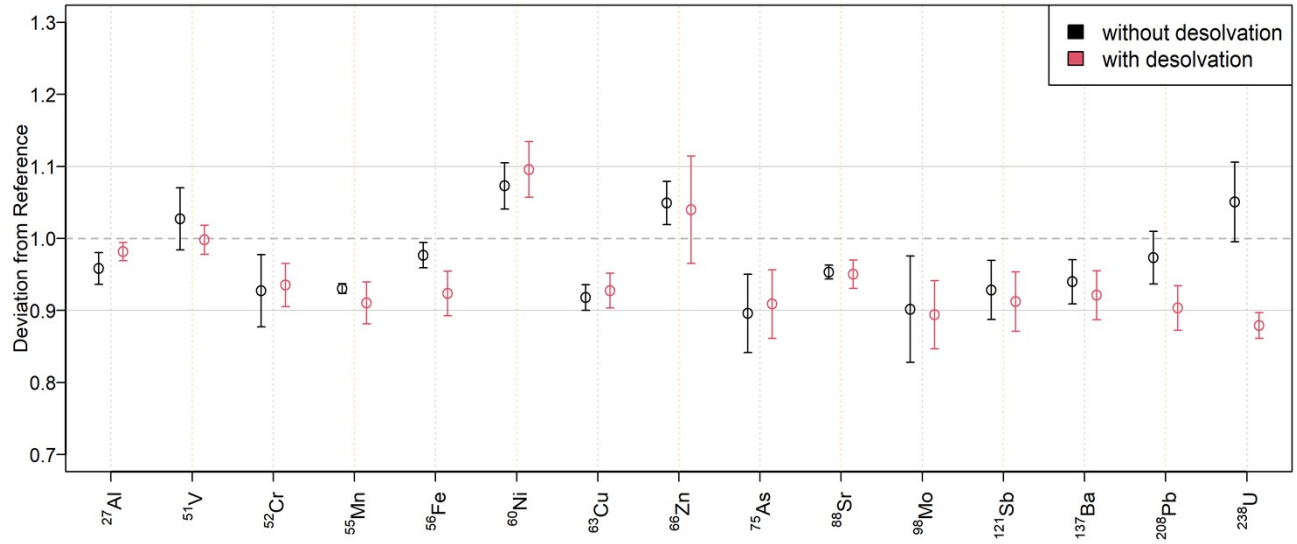

Figure S4: Quantification overview obtained with a twofold dilution of SLRS-6 for solution nebulization (black) and aerosol desolvation (red) using standard addition. For each isotope, the deviation of the obtained mass fractions from the certified reference material is given with error bars representing two times the standard deviation. The grey horizontal lines correspond to a difference of ± 10 % from the certified value.

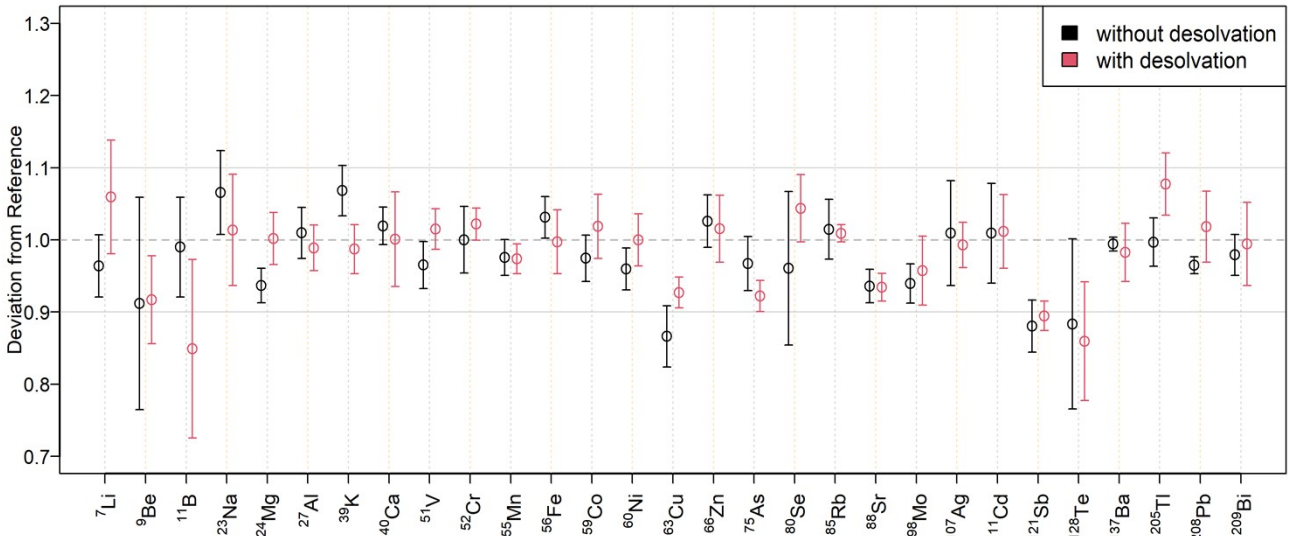

Figure S5: Quantification overview obtained with a tenfold dilution of NIST-1643f for solution nebulization (black) and aerosol desolvation (red) using external calibration. For each isotope, the deviation of the obtained mass fractions from the certified reference material is given with error bars representing two times the standard deviation. The grey horizontal lines correspond to a difference of ± 10 % from the certified value.

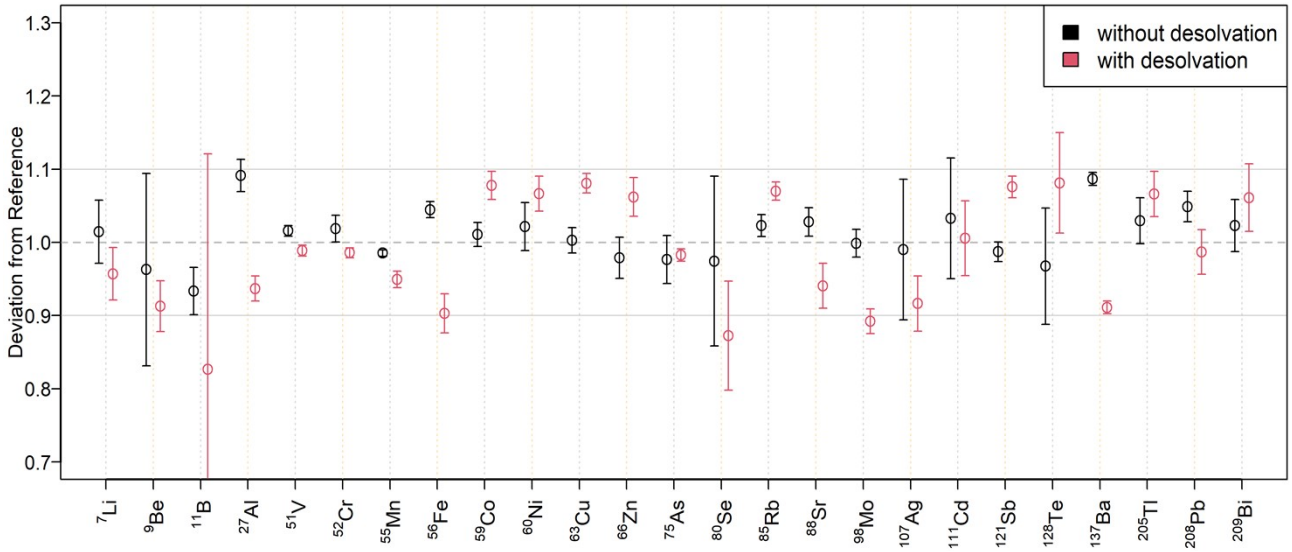

Figure S6: Quantification overview obtained with a tenfold dilution of NIST-1643f for solution nebulization (black) and aerosol desolvation (red) using standard addition. For each isotope, the deviation of the obtained mass fractions from the certified reference material is given with error bars representing two times the standard deviation. The grey horizontal lines correspond to a difference of ± 10 % from the certified value.