

Supporting Information

Determination of calcium, iron, and selenium in human serum by isotope dilution analysis using nitrogen microwave inductively coupled atmospheric pressure plasma mass spectrometry (MICAP-MS)

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Table S1: Comparison of the certified mass concentrations of the elements in serum samples (bold) with the values determined with external calibration. Unit for Li, Mg, K, Ca, Fe, Cu, and Zn: mg L⁻¹, Unit for Cr, Mn, As, and Se: µg L⁻¹. n.d. for not determined. The uncertainty provided with each value is the expanded uncertainty, which was set to be twice the standard deviation.

	<i>Li</i>	<i>Mg</i>	<i>K</i>	<i>Ca</i>	<i>Fe</i>	<i>Cu</i>	<i>Zn</i>	<i>Cr</i>	<i>Mn</i>	<i>As</i>	<i>Se</i>
<i>BCR 304</i>	5.91 ± 0.174	44.4 ± 0.72	<i>n.d.</i>	88.04 ± 0.75	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
	6.83 ± 0.51	43.4 ± 2.4	226 ± 16	89.02 ± 2.02	1.5 ± 0.8	0.98 ± 0.18	10.6 ± 4	151 ± 16	16.4 ± 2.1	298 ± 18	5341 ± 190
<i>BCR 637</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	1.11 ± 0.22	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	81 ± 7
	0.01 ± 0.02	15.7 ± 3.1	124 ± 14	49.4 ± 5.2	0.56 ± 0.32	0.9 ± 0.16	2.49 ± 0.62	155 ± 16	6.1 ± 1.4	90 ± 20	1232 ± 84
<i>BCR 638</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	1.43 ± 0.21	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	104 ± 7
	0.06 ± 0.02	16 ± 2.4	120 ± 20	69 ± 5	1.1 ± 1	0.66 ± 0.14	2.45 ± 0.48	169 ± 18	8.4 ± 2	90 ± 12	1467 ± 90
<i>BCR 639</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	2.36 ± 0.14	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	133 ± 12
	0.05 ± 0.02	15.6 ± 2.2	115 ± 20	56.2 ± 3.6	0.95 ± 0.12	0.85 ± 0.14	3.67 ± 0.31	88 ± 14	6.2 ± 1.4	110 ± 16	2279 ± 138
<i>NIST 909C</i>	<i>n.d.</i>	21.76 ± 0.16	162.7 ± 2.7	101 ± 1.1	0.903 ± 0.039	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	118.7 ± 3.3
	0.04 ± 0.02	22.14 ± 2.2	167 ± 10	104.2 ± 4.2	0.941 ± 0.08	0.83 ± 0.15	2.64 ± 0.84	65 ± 12	7.2 ± 4	92 ± 11	1552 ± 68
<i>ClinChek 1</i>	3.76 ± 0.57	16 ± 1.6	<i>n.d.</i>	<i>n.d.</i>	0.859 ± 0.13	0.743 ± 0.111	1.22 ± 0.18	1.58 ± 0.4	2.41 ± 0.6	9.48 ± 1.9	57.7 ± 11
	3.24 ± 0.41	15.4 ± 1.82	102 ± 12	98 ± 13	0.89 ± 0.1	0.74 ± 0.11	2.61 ± 0.62	4.6 ± 1.4	1.99 ± 0.33	73 ± 16	897 ± 59
<i>ClinChek 2</i>	7.58 ± 1.14	21.8 ± 2.2	<i>n.d.</i>	<i>n.d.</i>	1.48 ± 0.22	1.4 ± 0.21	1.7 ± 0.25	5.92 ± 1.19	6.24 ± 1.25	19.3 ± 3.9	105 ± 21
	6.74 ± 0.81	19.8 ± 2.2	101 ± 10	79 ± 9	1.44 ± 0.08	1.28 ± 0.2	1.66 ± 0.75	12.7 ± 3.1	4.8 ± 0.84	70 ± 10	1172 ± 72
<i>Seronorm L1</i>	5.06 ± 1.02	19.3 ± 3.9	148 ± 30	97 ± 20	1.4 ± 0.28	1.12 ± 0.23	1.46 ± 0.29	1.5 ± 0.3	9.4 ± 1.8	<i>n.d.</i>	95 ± 19
	5.18 ± 0.62	18.4 ± 2.1	138 ± 12	106 ± 5.2	1.59 ± 0.22	1.08 ± 0.08	2.9 ± 0.6	5.3 ± 1.52	8.12 ± 1.4	170 ± 26	1296 ± 101
<i>Seronorm L2</i>	10.0 ± 2.0	35.7 ± 7.2	235 ± 47	138 ± 28	2.07 ± 0.42	2.18 ± 0.43	2.09 ± 0.42	3.91 ± 0.79	14.2 ± 2.9	<i>n.d.</i>	139 ± 28
	9.32 ± 0.84	33.4 ± 4.2	210 ± 16	136.2 ± 6.1	2.22 ± 0.16	2.17 ± 0.24	3.35 ± 0.7	10.6 ± 3.2	9 ± 3.2	142 ± 28	3560 ± 162

Table S2: Masses and mass concentrations of the Ca, Fe, and Se spike solutions used for each serum sample. Unit: g. n.d. for not determined.

	<i>Ca (529.25 mg L⁻¹)</i>	<i>Fe (11.02 mg L⁻¹)</i>	<i>Se (100.78 µg L⁻¹)</i>
<i>BCR 304</i>	<i>0.072</i>	<i>n.d.</i>	<i>n.d.</i>
<i>BCR 637</i>	<i>n.d.</i>	<i>n.d.</i>	<i>0.3234</i>
<i>BCR 638</i>	<i>n.d.</i>	<i>n.d.</i>	<i>0.4142</i>
<i>BCR 639</i>	<i>n.d.</i>	<i>n.d.</i>	<i>0.5285</i>
<i>NIST 909C</i>	<i>0.0818</i>	<i>0.0553</i>	<i>0.4605</i>
<i>ClinChek 1</i>	<i>n.d.</i>	<i>0.0547</i>	<i>0.4167</i>
<i>ClinChek 2</i>	<i>n.d.</i>	<i>0.0868</i>	<i>4161</i>
<i>Seronorm L1</i>	<i>0.0799</i>	<i>0.0877</i>	<i>0.3773</i>
<i>Seronorm L2</i>	<i>0.1224</i>	<i>0.1328</i>	<i>0.5561</i>

Table S3: Masses and mass concentrations of the single-element solutions used for reverse ID.

	<i>Mass</i>	<i>Mass concentration</i>
<i>Ca</i>	<i>0.0154 g</i>	<i>100.48 mg L⁻¹</i>
<i>Fe</i>	<i>0.1053 g</i>	<i>10.23 mg L⁻¹</i>
<i>Se</i>	<i>0.8110 g</i>	<i>100.90 µg L⁻¹</i>

Table S4: Corresponding IS and the calibration levels used for external calibration.

	<i>Measured m/z</i>	<i>Internal standard</i>	<i>Calibration levels (µg L⁻¹)</i>
<i>Li</i>	<i>7</i>	<i>⁶Li</i>	<i>0.1 - 10</i>
<i>Mg</i>	<i>24</i>	<i>⁴⁵Sc</i>	<i>10 - 500</i>
<i>K</i>	<i>39</i>	<i>⁴⁵Sc</i>	<i>10 - 500</i>
<i>Ca</i>	<i>40, 44</i>	<i>⁴⁵Sc</i>	<i>10 - 500</i>
<i>Fe</i>	<i>56, 57</i>	<i>⁴⁵Sc</i>	<i>0.1 - 10</i>
<i>Cu</i>	<i>63, 65</i>	<i>⁴⁵Sc</i>	<i>0.1 - 10</i>
<i>Zn</i>	<i>64, 66</i>	<i>⁸⁹Y</i>	<i>0.1 - 10</i>
<i>Cr</i>	<i>52, 53</i>	<i>⁸⁹Y</i>	<i>0.1 - 10</i>
<i>Mn</i>	<i>55</i>	<i>⁸⁹Y</i>	<i>0.1 - 10</i>
<i>As</i>	<i>75</i>	<i>⁸⁹Y</i>	<i>0.1 - 10</i>
<i>Se</i>	<i>78, 80, 82</i>	<i>⁸⁹Y</i>	<i>0.2 - 40</i>

Table S5: Densities of samples and spike solutions determined through weighing.

	ρ (g mL ⁻¹)
<i>BCR 304</i>	<i>1.0100 ± 0.0050</i>
<i>BCR 637</i>	<i>1.00833 ± 0.00764</i>
<i>BCR 638</i>	<i>1.01333 ± 0.00578</i>
<i>BCR 639</i>	<i>1.01833 ± 0.00764</i>
<i>NIST 909C</i>	<i>1.02412 ± 0.00009</i>
<i>ClinChek 1</i>	<i>1.02167 ± 0.00577</i>
<i>ClinChek 2</i>	<i>1.02000 ± 0.00500</i>
<i>Seronorm L1</i>	<i>1.02333 ± 0.00289</i>
<i>Seronorm L2</i>	<i>1.02167 ± 0.00289</i>
<i>Ca Spike</i>	<i>1.00333 ± 0.00289</i>
<i>Fe Spike</i>	<i>1.00500 ± 0.00500</i>
<i>Se Spike</i>	<i>1.00167 ± 0.00289</i>

Table S6: LOD and LOQ for matrix-matched external calibration (in 50 mg L⁻¹ NaCl).

	<i>m/z</i>	<i>LOD</i> (µg L ⁻¹)	<i>LOQ</i> (µg L ⁻¹)
<i>Li</i>	<i>7</i>	<i>0.26</i>	<i>0.88</i>
<i>Mg</i>	<i>24</i>	<i>1.1</i>	<i>3.6</i>
<i>K</i>	<i>39</i>	<i>0.36</i>	<i>1.2</i>
<i>Ca</i>	<i>40</i>	<i>2.3</i>	<i>7.8</i>
<i>Fe</i>	<i>56</i>	<i>0.12</i>	<i>0.39</i>
<i>Cu</i>	<i>63</i>	<i>0.24</i>	<i>0.81</i>
<i>Zn</i>	<i>66</i>	<i>0.40</i>	<i>1.4</i>
<i>Cr</i>	<i>52</i>	<i>0.06</i>	<i>0.21</i>
<i>Mn</i>	<i>55</i>	<i>0.0016</i>	<i>0.0053</i>
<i>As</i>	<i>75</i>	<i>0.30</i>	<i>1.0</i>
<i>Se</i>	<i>80</i>	<i>0.70</i>	<i>2.4</i>