

Sensitive Determination of Biologically Important Transition Metals by ICP-QMS Using Micro-ultrasonic Single Droplet Nebulization

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Table of Contents

Fig S1. Effect of different sample matrices on the recoveries and the correction results of matrix effects by Ge internal standard. A and B correspond to the recoveries for the high dissolved

solids and organic matter without Ge internal standard correction, respectively. C and D show the results after Ge internal standardization correction. The error bars indicate the standard deviation for 11 measurement replicates. The dashed red lines indicate the bias tolerance of $\pm 15\%$.

Fig S2. Calibration graphs of the elements of Mn(A), Co(B), Ni(C), Cu(D), Zn(E) with Ge as internal standard. Comparison of the detection sensitivity between MUSDN-ICP-QMS and PN-ICP-QMS at an introduced mass of 1pg(F). The right axis indicates the corresponding sensitivity enhancement factors of MUSDN relative to PN.

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Tab S2. Measurement results of elements in digested serum CRMs.

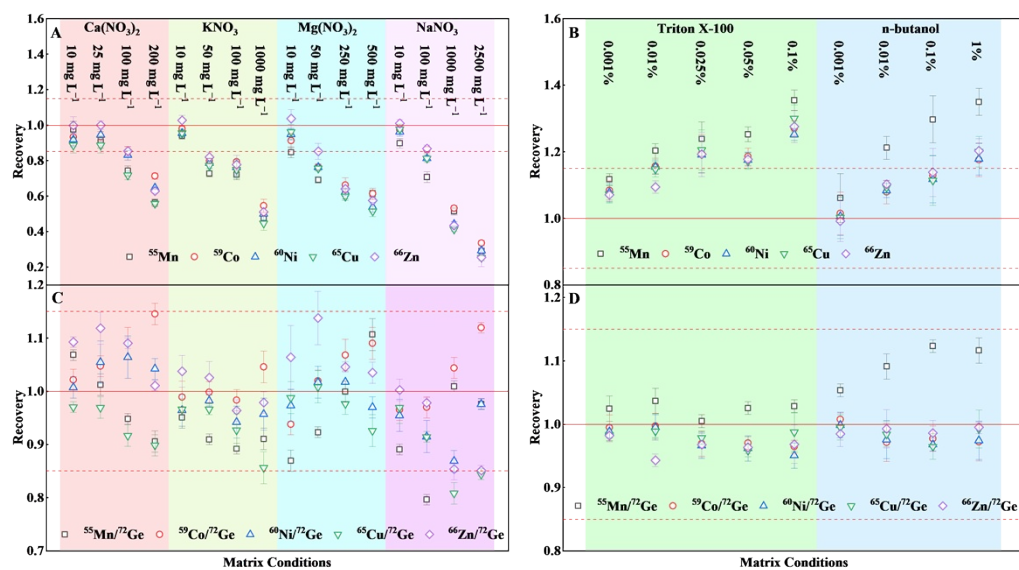


Fig S1. Effect of different sample matrices on the recovery of target analytes before and after correction with Ge internal standard. (A) High dissolved solids matrices (Ca, K, Mg, Na) without internal standard correction; (B) Organic matrices (Triton X-100, n-butanol) without internal standard correction; (C) High dissolved solids matrices with Ge internal standard correction; (D) Organic matrices with Ge internal standard correction. The dashed red lines indicate the bias tolerance of $\pm 15\%$. Error bars represent the standard deviation ($n = 6$). Detailed numerical data (including raw and corrected recoveries with standard deviations) are provided in Tab S2.

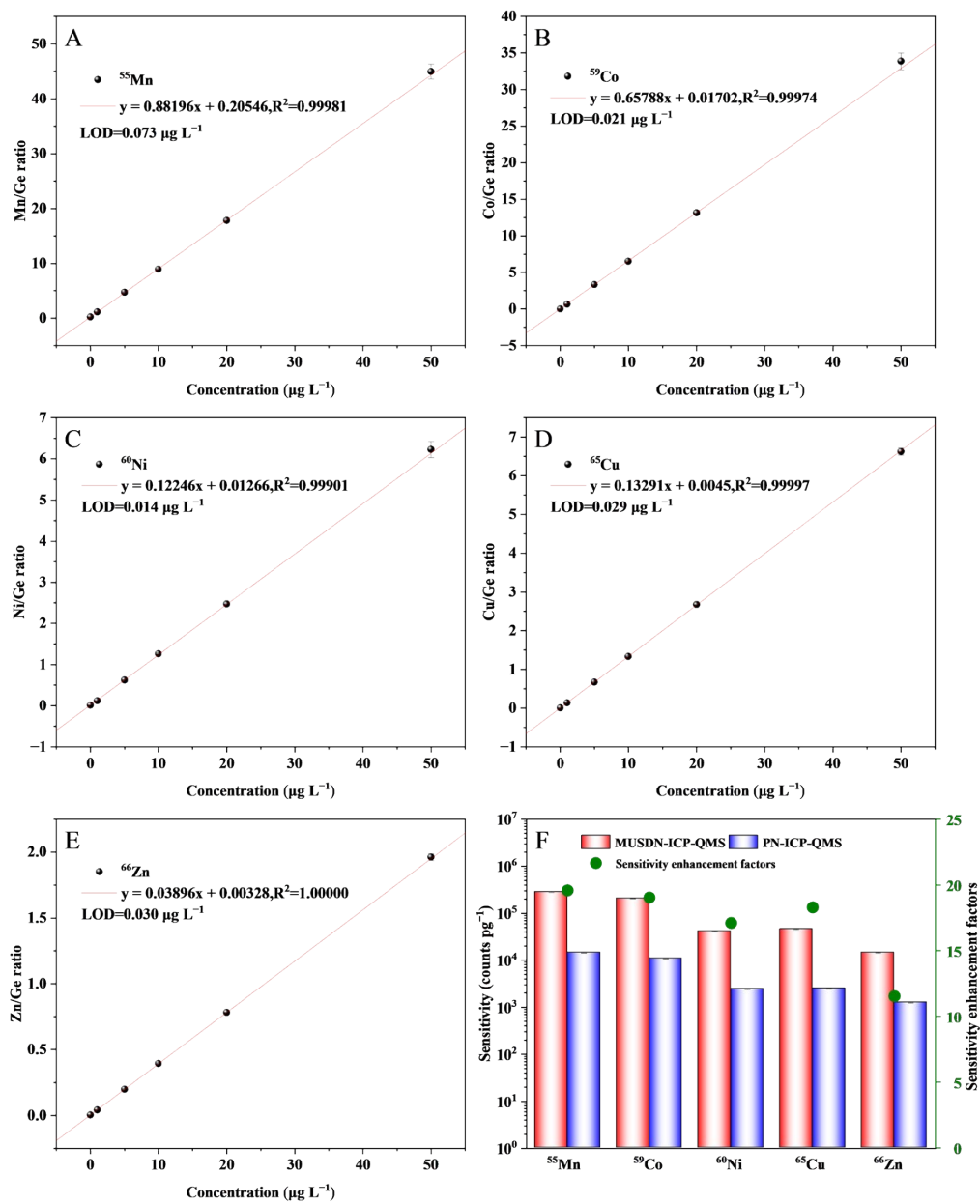


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Tab S1. Effect of different sample matrices on the recoveries and the correction results of matrix effects by Ge internal standard.

Matrices	Conc.	Mn		Co		Ni		Cu		Zn	
		Raw	Corr.	Raw	Corr.	Raw	Corr.	Raw	Corr.	Raw	Corr.
2% HNO_3	n/a	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$\text{Ca}(\text{NO}_3)_2$	10 mg L^{-1}	0.98±0.04	1.07±0.01	0.93±0.05	1.02±0.02	0.92±0.04	1.01±0.02	0.89±0.04	0.97±0.01	1.00±0.05	1.10±0.01
	25 mg L^{-1}	0.90±0.03	1.01±0.02	0.94±0.03	1.05±0.02	0.94±0.03	1.05±0.04	0.89±0.04	0.97±0.02	1.00±0.02	1.12±0.03
	100 mg L^{-1}	0.74±0.03	0.95±0.01	0.85±0.02	1.09±0.03	0.83±0.03	1.06±0.04	0.72±0.02	0.92±0.02	0.85±0.03	1.10±0.01
	200 mg L^{-1}	0.56±0.02	0.91±0.02	0.71±0.02	1.14±0.02	0.65±0.01	1.04±0.02	0.56±0.01	0.90±0.02	0.63±0.01	1.01±0.01
KNO_3	10 mg L^{-1}	0.94±0.02	0.95±0.02	0.98±0.01	0.99±0.03	0.95±0.02	0.96±0.03	0.96±0.02	0.97±0.02	1.03±0.03	1.04±0.03
	50 mg L^{-1}	0.73±0.02	0.91±0.01	0.80±0.01	1.00±0.02	0.78±0.03	0.98±0.01	0.77±0.03	0.97±0.01	0.82±0.03	1.03±0.03
	100 mg L^{-1}	0.72±0.03	0.90±0.01	0.79±0.04	0.98±0.02	0.76±0.04	0.94±0.03	0.75±0.05	0.93±0.03	0.78±0.05	0.96±0.02
	1000 mg L^{-1}	0.48±0.01	0.91±0.02	0.54±0.04	1.04±0.03	0.50±0.04	0.96±0.03	0.45±0.04	0.86±0.03	0.51±0.02	0.98±0.02
$\text{Mg}(\text{NO}_3)_2$	10 mg L^{-1}	0.85±0.03	0.87±0.02	0.91±0.04	0.94±0.02	0.94±0.03	0.97±0.03	0.96±0.04	0.99±0.03	1.04±0.05	1.06±0.06
	50 mg L^{-1}	0.70±0.02	0.92±0.01	0.76±0.02	1.02±0.02	0.76±0.01	1.02±0.03	0.76±0.02	1.01±0.03	0.85±0.04	1.14±0.05
	250 mg L^{-1}	0.61±0.03	1.00±0.02	0.66±0.04	1.07±0.03	0.62±0.02	1.02±0.00	0.60±0.02	0.98±0.02	0.64±0.02	1.04±0.01
	500 mg L^{-1}	0.61±0.02	1.11±0.03	0.61±0.03	1.09±0.03	0.54±0.03	0.97±0.02	0.51±0.03	0.92±0.03	0.57±0.02	1.03±0.02
NaNO_3	10 mg L^{-1}	0.90±0.02	0.90±0.01	0.97±0.02	0.96±0.02	0.96±0.02	0.95±0.03	0.98±0.03	0.97±0.03	1.01±0.02	1.00±0.02

Tab S1 (Continued).

Matrices	Conc.	Mn		Co		Ni		Cu		Zn	
		Raw	Corr.	Raw	Corr.	Raw	Corr.	Raw	Corr.	Raw	Corr.
NaNO ₃	100 mg L ⁻¹	0.71±0.03	0.80±0.01	0.86±0.02	0.97±0.02	0.81±0.01	0.91±0.03	0.81±0.02	0.91±0.01	0.87±0.02	0.98±0.01
	1000 mg L ⁻¹	0.51±0.02	1.01±0.01	0.53±0.02	1.04±0.02	0.44±0.01	0.87±0.02	0.41±0.01	0.81±0.02	0.44±0.01	0.85±0.02
	2500 mg L ⁻¹	0.29±0.03	0.98±0.01	0.33±0.02	1.12±0.01	0.29±0.02	0.98±0.01	0.25±0.02	0.84±0.01	0.25±0.05	0.85±0.01
Triton X-100	0.001%	1.12±0.02	1.02±0.02	1.08±0.03	0.99±0.02	1.07±0.03	0.99±0.01	1.07±0.02	0.98±0.01	1.07±0.02	0.98±0.01
	0.01%	1.20±0.02	1.04±0.02	1.16±0.02	1.00±0.02	1.15±0.02	0.99±0.02	1.15±0.02	0.99±0.01	1.09±0.02	0.94±0.01
	0.025%	1.24±0.05	1.00±0.01	1.19±0.06	0.97±0.02	1.19±0.05	0.97±0.02	1.20±0.06	0.98±0.01	1.19±0.07	0.96±0.02
	0.05%	1.25±0.02	1.02±0.01	1.18±0.03	0.97±0.01	1.17±0.02	0.96±0.02	1.17±0.02	0.96±0.01	1.18±0.02	0.97±0.01
	0.1%	1.35±0.03	1.03±0.01	1.27±0.02	0.96±0.01	1.25±0.02	0.95±0.02	1.30±0.04	0.99±0.03	1.28±0.05	0.96±0.03
n-butanol	0.001%	1.06±0.07	1.05±0.01	1.01±0.06	1.01±0.01	1.01±0.06	1.00±0.02	1.00±0.06	1.00±0.02	0.99±0.06	0.98±0.02
	0.01%	1.21±0.03	1.09±0.02	1.07±0.04	0.97±0.03	1.08±0.02	0.98±0.03	1.10±0.02	0.98±0.02	1.10±0.01	0.99±0.03
	0.1%	1.30±0.07	1.12±0.01	1.13±0.08	0.98±0.02	1.12±0.07	0.97±0.01	1.11±0.07	0.96±0.02	1.14±0.07	0.98±0.02
	1%	1.35±0.04	1.12±0.02	1.18±0.05	0.97±0.03	1.18±0.05	0.97±0.03	1.20±0.04	0.99±0.03	1.20±0.04	1.00±0.01

Note: Values are presented as mean ± SD (n = 6). Raw recovery = (analyte signal in sample matrix / analyte signal in 2%HNO₃). Corrected recovery = [(analyte / Ge) signal in sample matrix] / [(analyte / Ge) signal in 2%HNO₃]. n/a: not applicable (reference matrix). Conc.: concentration.

Tab S2. Measurement results of elements in digested serum CRMs.

Sample name	Parameter	Mn	Co	Ni	Cu	Zn
Seronorm™ trace-element	Reference	10.1 ±	1.04 ±	5.28 ±	1050	1390
Serum L-1 (n = 3)	value (µg L ⁻¹)	2.0	0.21	1.06	± 211	± 280
	Measured	9.30 ±	1.09 ±	5.51 ±	988 ±	1230
	value (µg L ⁻¹)	0.09	0.03	0.16	22	± 29
Seronorm™ trace-element	Reference	14.8 ±	3.03 ±	9.7 ±	1961	1940
Serum L-2 (n = 3)	value (µg L ⁻¹)	2.4	0.43	1.4	± 239	± 270
	Measured	13.5 ±	3.32 ±	10.3 ±	1840	1920
	value (µg L ⁻¹)	0.2	0.07	0.7	± 17	± 127