Electronic Supplementary Information (ESI)

In situ ultrasound-assisted synthesis of Fe_3O_4 nanoparticles with simultaneous ion co-precipitation for multielemental analysis of natural waters by total reflection X-ray fluorescence spectrometry

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Table S1. Adjustment of experimental data to Berthelot-Nernst law and Doerner-Hoskins law

	Berthelot-Nernst law		Doerner-Hoskins law	
Analyte	**Equation for linear calibration**	**Correlation coefficient**	**Equation for linear calibration**	**Correlation Coefficient**
Cu	**y = 0. 5991 x - 2E-05**	**0.9312**	**y = 0.5833 x + 0.0135**	**0.9232**
Zn	**y = 2.4713 x - 0.0002**	**0.9975**	**y = 0.6876 x - 0.0138**	**0.9912**
Ge	**y = 35.12 x + 0.0001**	**0.9907**	**y = 0.7769 x - 0.0106**	**0.9824**
As	**y = 2.6019 x + 3E-05**	**0.9913**	**y = 1.058 x - 0.0938**	**0.9863**
Se	**y = 1.709 x - 0.0001**	**0.8326**	**y = 0.7255 x - 0.0271**	**0.9568**
Re	**y = 0.9968 x - 3E-07**	**0.9917**	**y = 1.3417 x + 0.0960**	**0.9574**
Au	**y = 1.7626 x - 0.0002**	**0.9685**	**y = 0.9315 x - 0.0652**	**0.9516**
Hg	**y = 5.3764 x + 2E-05**	**0.9987**	**y = 1.1054 x - 0.0719**	**0.9593**
Tl	**y = 1.0004 x + 3E-05**	**0.9817**	**y = 0.7973 x - 0.0962**	**0.9061**
Bi	**y = 1.1245 x + 3E-05**	**0.9927**	**y = 0.9885 x - 0.0384**	**0.9696**
Pb	**y = 1.0862 x + 9E-05**	**0.9957**	**y = 1.1673 x - 0.0774**	**0.9820**

Table S2. Study of possible interferents in natural waters on the application of the *in situ* UAMS-SIC approach combined with TXRF for multielemental analysis

Interferent	Studied level (mg L^{-1})	Recoveries (%)
NaCl	100	95-104 (except Se, recovery: 65)
	1000	100-107 (except Se, recovery: 68)
	20000	96-107 (except Se, recovery: 62)
	50000	68-76 (except Se, recovery: 34)
Na_2SO_4	100	101-103 (except Se, recovery: 63)
	1000	100-105 (except Se, recovery: 66)
	20000	102-106 (except Se, recovery: 64)
	50000	64-71 (except Se, recovery: 42)
$MgCl_2$	5	98-108 (except Se, recovery: 68)
	20	101-107 (except Se, recovery: 63)
	100	99-107 (except Se, recovery: 61)
	200	51-64 (except Se, recovery: 48)
KH_2PO_4	5	99-108 (except Se, recovery: 65)
	20	100-105 (except Se, recovery: 64)
	100	101-108 (except Se, recovery: 64)
	200	99-105 (except Se, recovery: 68)
$CaSO_4$	50	99-107 (except Se, recovery: 63)
	100	100-108 (except Se, recovery: 64)
	500	100-106 (except Se, recovery: 65)
	2000	100-107 (except Se, recovery: 64)
Na_2CO_3	50	100-103 (except Se, recovery: 64)
	100	97-105 (except Se, recovery: 66)
	500	101-107 (except Se, recovery: 67)
	5000	72-61 (except Se, recovery: 39)
KNO_3	200	95-104 (except Se, recovery: 63)
	5000	100-104 (except Se, recovery: 65)
	12000	100-104 (except Se, recovery: 68)
Humic acid	1	99-108 (except Se, recovery: 64)
	10	99-106 (except Se, recovery: 63)
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*For concentrations of humic acid higher than 10 mg L^{-1}, *in situ* UAMS-SIC can not be performed because Fe_3O_4 NPs are stabilized by the humic acid.

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Table S3. Found values and recoveries obtained by applying the *in situ* UAMS-SIC approach combined with TXRF for different natural water matrices

Sample	Metal added (μg L^{-1})	Metal found (μg L^{-1}) ± standard deviation, N=3 (Recovery (%) ± standard deviation, N=3)										
		Cu	**Ge**	**Zn**	**As**	**Se**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Re**
Drinking water	0	0.8 ± 0.1	< LLD	1.5 ± 0.1	< LLD	< LLD	< LLD	< LLD	1.8 ± 0.1	< LLD	< LLD	< LLD
	10	9 ± 0.1 (89 ± 1)	10 ± 0.2 (103 ± 2)	10 ± 0.2 (100 ± 2)	10 ± 0.1 (99 ± 1)	< LLD	11 ± 0.1 (109 ± 1)	11 ± 0.1 (107 ± 1)	10 ± 0.2 (102 ± 3)	10 ± 0.1 (101 ± 1)	11 ± 0.2 (114 ± 3)	< LLD
	50	50 ± 0.2 (100 ± 1)	51 ± 1 (101 ± 0.3)	50 ± 0.4 (101 ± 1)	50 ± 1 (101 ± 1)	31 ± 1 (63 ± 1)	52 ± 1 (105 ± 2)	48 ± 1 (96 ± 1)	49 ± 1 (98 ± 1)	49 ± 1 (99 ± 2)	50 ± 0.5 (100 ± 1)	51 ± 1 (102 ± 1)
	300	299 ± 1 (100 ± 1)	289 ± 1 (96 ± 1)	302 ± 1 (101 ± 1)	292 ± 2 (97 ± 1)	194 ± 2 (65 ± 1)	303 ± 2 (101 ± 3)	285 ± 1 (95 ± 1)	302 ± 1 (100 ± 1)	300 ± 1 (100 ± 1)	295 ± 2 (98 ± 1)	302 ± 2 (103 ± 1)
Tap water	0	2.5 ± 0.6	< LLD	3.2 ± 0.5	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD
	10	12 ± 1 (95 ± 2)	10 ±0.1 (104 ± 1)	10 ± 0.1 (100 ± 1)	10 ± 0.1 (101 ± 1)	< LLD	10 ± 0.2 (97 ± 3)	11 ± 0.1 (107 ± 2)	10 ± 0.1 (101 ± 1)	10 ± 1 (97 ± 1)	10 ± 0.2 (98 ± 2)	< LLD
	50	49 ± 1 (98 ± 2)	51 ± 1 (102 ± 1)	50 ± 0.1 (100 ± 0.1)	49 ± 0.5 (98 ± 1)	27 ± 1 (54 ± 1)	51 ± 0.4 (102 ± 1)	48 ± 1 (96 ± 2)	50 ± 0.1 (99 ± 0.2)	51 ± 1 (102 ± 1)	47 ± 0.2 (94 ± 0.5)	48 ± 1 (97 ± 1)
	300	310 ± 1 (103 ± 1)	296 ± 1 (99 ± 2)	306 ± 1 (102 ± 1)	303 ± 2 (101 ± 1)	196 ± 1 (65 ± 1)	296 ± 1 (99 ± 0.4)	300 ± 1 (100 ± 1)	295 ± 1 (98 ± 1)	302 ± 1 (101 ± 1)	303 ± 0.1 (101 ± 0.2)	300 ± 1 (100 ± 1.0)
Mineral water	0	0.7 ± 0.1	< LLD	13 ± 1	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD
	10	10 ± 0.1 (100 ± 2)	10 ± 0.1 (101 ± 1)	10 ± 0.3 (100 ± 3)	10 ± 0.2 (100 ± 2)	< LLD	10 ± 0.1 (100 ± 1)	10 ± 0.1 (101 ± 1)	10 ± 0.2 (102 ± 2)	10 ± 0.1 (101 ± 1)	10 ± 0.2 (103 ± 1)	< LLD
	50	50 ± 0.3 (101 ± 1)	50 ± 0.3 (100 ± 1)	51 ± 1 (102 ± 0.1)	50 ± 0.1 (100 ± 0.3)	30 ± 0.4 (60 ±1)	50 ± 0.1 (100 ± 0.3)	50 ± 0.5 (100 ± 0.1)	50 ± 0.2 (100 ± 0.4)	50 ± 0.4 (101 ± 0.1)	50 ± 0.4 (101 ± 0.1)	50 ± 0.4 (101 ± 1)
	300	300 ± 0.4 (100 ± 0.1)	300 ± 0.5 (100 ± 0.2)	300 ± 0.5 (100 ± 1)	301 ± 1 (100 ± 0.2)	191 ± 0.3 (64 ± 1)	301 ± 1 (100 ± 0.2)	300 ± 1 (100 ± 0.3)	300 ± 0.1 (100 ± 0.4)	301 ± 0.2 (100 ± 0.1)	301 ± 0.2 (100 ± 0.1)	300 ± 0.2 (100 ± 0.1)
River water	0	0.30 ± 0.01	< LLD	2.8 ± 0.5	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD
	10	10 ± 0.1 (100 ± 1)	10 ± 0.1 (105 ± 1)	10 ± 1.0 (100 ± 1)	10 ± 0.2 (97 ± 2)	< LLD	10 ± 0.2 (99 ± 2)	10 ± 0.1 (101 ± 1)	10 ± 0.2 (105 ± 3)	10 ± 0.1 (100 ± 1)	10 ± 0.1 (104 ± 1)	< LLD
	50	50 ± 0.2 (100 ± 1)	50 ± 1 (100 ± 2)	49 ± 1 (99 ± 0.4)	50 ± 0.2 (101 ± 0.5)	34 ± 0.2 (68 ± 0.1)	50 ± 1 (100 ± 0.5)	49 ± 0.1 (98 ± 0.3)	50 ± 1 (101 ± 0.5)	51 ± 0.5 (101 ± 1)	50 ± 0.5 (101 ± 1)	50 ± 0.4 (100 ± 1)
	300	301 ± 0.2 (100 ± 1)	301 ± 1 (101 ± 1)	300 ± 0.5 (100 ± 1)	300 ± 0.3 (100 ± 0.1)	192 ± 1 (64 ± 1)	300 ± 1 (100 ± 1)	300 ± 1 (100 ± 1)	300 ± 1 (100 ± 0.3)	300 ± 1 (100 ± 0.4)	301 ± 1 (100 ± 1)	300 ± 0.2 (100 ± 1)
Dam water	0	0.30 ± 0.01	< LLD	0.6 ± 0.1	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD
	10	10 ± 0.2 (101 ± 2)	10 ± 0.1 (105 ± 1)	10 ± 0.1 (104 ± 1)	10 ± 0.1 (100 ± 1)	< LLD	10 ± 0.2 (102 ± 2)	10 ± 0.2 (102 ± 2)	10 ± 0.1 (101 ± 2)	10 ± 0.2 (105 ± 3)	10 ± 0.1 (100 ± 1)	< LLD
	50	50 ± 0.1 (100 ± 0.1)	50 ± 0.1 (101 ± 0.2)	50 ± 0.1 (101 ± 0.1)	50 ± 0.3 (101 ± 1)	38 ± 0.3 (76 ± 1)	50 ± 0.1 (100 ± 0.3)	50 ± 0.1 (100 ± 0.3)	50 ± 0.2 (100 ± 0.4)	50 ± 1 (101 ± 0.1)	50 ± 0.2 (100 ± 0.5)	50 ± 0.2 (100 ± 0.4)
	300	301 ± 0.5 (100 ± 0.2)	300 ± 0.4 (100 ± 0.1)	300 ± 1 (100 ± 0.3)	300 ± 0.2 (100 ± 0.1)	191 ± 1 (64 ± 1)	300 ± 0.5 (100 ± 0.1)	300 ± 0.1 (100 ± 1)	300 ± 0.3 (100 ± 0.1)	301 ± 0.2 (100 ± 1)	300 ± 0.5 (100 ± 0.2)	300 ± 0.1 (100 ± 0.2)
Well water	0	< LLD	< LLD	3.3 ± 0.2	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD	< LLD
	10	11 ± 1 (109 ± 1)	10 ± 0.1 (103 ± 1)	10 ± 0.1 (99 ± 1)	10 ± 0.2 (104 ± 2)	< LLD	10 ± 1 (108 ± 1)	9 ± 0.1 (94 ± 1)	10 ± 0.1 (97 ± 2)	10 ± 0.1 (98 ± 1)	11 ± 0.2 (106 ± 3)	< LLD
	50	51 ± 0.2 (101 ± 0.4)	50 ± 1 (100 ± 1)	51 ± 0.2 (102 ± 0.4)	50 ± 1 (101 ± 1)	39 ± 0.1 (78 ± 1)	51 ± 0.5 (102 ± 2)	50 ± 1 (101 ± 0.3)	49 ± 1 (98 ± 1)	51 ± 1 (102 ± 1)	49 ± 0.4 (98 ± 1)	50 ± 0.3 (101 ± 1)
	300	301 ± 0.3 (100 ± 1)	303 ± 1 (101 ± 3)	302 ± 0.1 (101 ± 0.5)	296 ± 1 (98 ± 0.4)	193 ± 1 (64 ± 0.3)	300 ± 0.4 (100 ± 0.1)	302 ± 1 (101 ± 0.3)	298 ± 0.4 (99 ± 0.5)	300 ± 0.4 (100 ± 1)	300 ± 0.5 (100 ± 1)	301 ± 0.4 (100 ± 1)

LLD: Lowest detection limit