Supplementary Materials:

Characterizing the Urban Mine—Challenges of Simplified Chemical Analysis of Anthropogenic Mineral Residues

Paul Martin Mählitz [1,*], Amund N. Løvik [2], Renato Figi [3], Claudia Schreiner [3], Claudia Kuntz [1], Nathalie Korf [1], Matthias Rösslein [4], Patrick Wäger [2], and Vera Susanne Rotter [1,*]

[1] Chair of Circular Economy and Recycling Technology, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany; claudia.kuntz@tu-berlin.de (C.K.); nathalie.korf@tu-berlin.de (N.K.)
[2] Technology and Society Laboratory, Swiss Federal Laboratories for Materials Science and Technology, Empa, CH-9014 St. Gallen, Switzerland; amund.loevik@empa.ch (A.N.L.); patrick.waeger@empa.ch (P.W.)
[3] Advanced Analytical Technologies, Swiss Federal Laboratories for Materials Science and Technology, Empa, CH-8600 Dübendorf, Switzerland; renato.figi@empa.ch (R.F.); claudia.schreiner@empa.ch (C.S.)
[4] Particles-Biology Interactions Laboratory, Swiss Federal Laboratories for Materials Science and Technology, Empa, CH-9014 St. Gallen, Switzerland; matthias.roesslein@empa.ch
* Correspondence: p.maehlitz@tu-berlin.de (P.M.M.); vera.rotter@tu-berlin.de (V.S.R.); Tel.: +49-30-3142-2619 (V.S.R.)

This supplement contains:
11 Pages
3 Figures
8 Tables

Contents

Figures

Tables

1. Method description and validation

1.1. Method description of halogen analysis in BATT sample

A sample mass of 0.1-0.2 g (n = 5) was weighed in, and 5 ml 1M NaOH (MERCK p.a.) was used as an absorption reagent. The digestate was filled up to a final volume of 50 ml (Polypropylene volumetric flask) and prepared using an IC-H+-ion exchanger with a dilution of 1:10 followed by membrane filtration at 0.2 µm. Ion chromatography was applied for direct detection of F and Cl. The measurement setup comprised a Methrom IC 882 Compact Plus with Methrom ASUPP 475 Guard as precolumn and Methrom A-Supp 5-150 as a separation column. A mixture of 3.2 mM Na_2CO_3 p.a. and 1.0 mM $NaHCO_3$ p.a. (MERCK p.a.) were used as eluent combined with an injection volume of 20 mL and flux of 0.7 ml/min.

Table S1. Parameters of the validated method for the determination of total halogens F and Cl.

Materials and methods	Specification of the validated method
Digestion method	PARR® Oxygen digestion bomb (IKA)
Pressure	30 bar
Number of digestions	n=5
Weight of the sample taken	0.1 – 0.2 Gramm
Absorption reagents	5 mL 1M NaOH p.a.
Final volume	50 mL
Quality of acids	MERCK p.a.
Measurement method	Ion chromatography (IC), direct detection
Sample preparation	IC-H^+-ion exchanger, dilution of samples: 1:10 dilution and membrane filtration (0.2 µm)
Device type	Methrom IC 882 Compact Plus
Precolumn	Metrohm ASUPP 4/5 Guard
Separation column	Metrohm A-Supp 5-150
Eluent	3.2 mM Na_2CO_3 p.a. + 1.0 mM $NaHCO_3$ p.a.
Injection volume	20 µL
Flux	0.7 mL/min
Validation	Element spikes, added before digestion

1.2. Arsenic mass fraction and element recovery

Figure S1 shows the results of the arsenic determination testing various digestion acids. The digestion with HNO_3-H_2O_2 performed badly in comparison to aqua regia and H_2SO_4-HNO_3 when comparing the recovery rates in the sample (RRS).

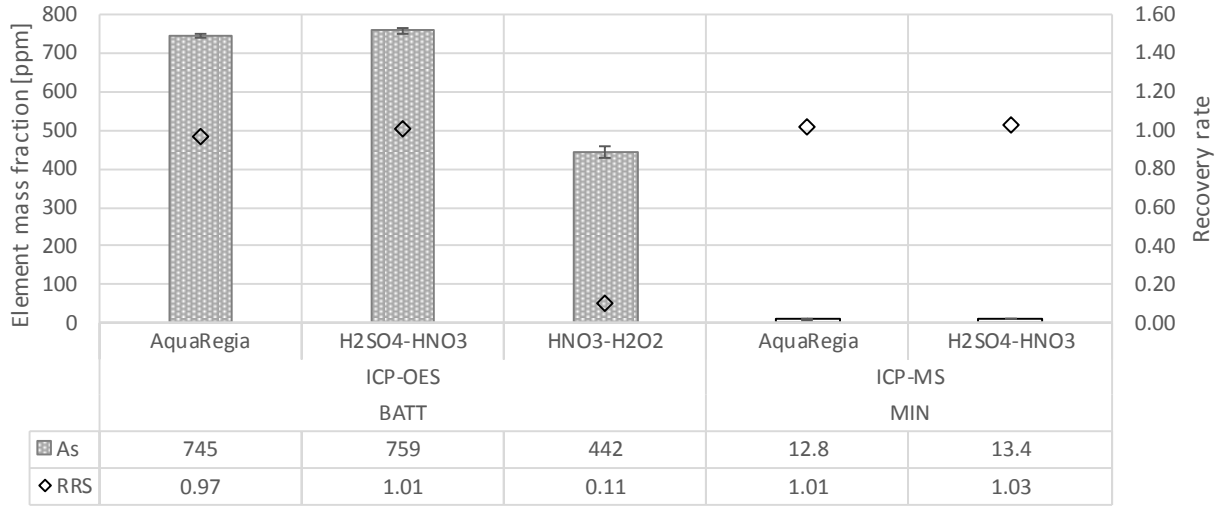

Figure S1. Mass fraction and recovery of arsenic in BATT and MIN sample.

1.3. Recovery rate of liquid standards (RRL) for the in-house method

Table S2 shows the recovery rates in liquid standards (RRL) in HNO_3 measured with ICP-OES by laboratory 2 (L2).

Table S2. Recovery rates measured in liquid standard samples.

Recovery rate (RRL)	Element concentration in HNO_3 acid [mg/L]				
Element	**0**	**0.25**	**2**	**10**	**80**
Ag	n.d.	1.00	1.00	-	-
Al	n.d.	-	-	-	1.00
As	n.d.	1.01	1.04	-	-
Ba	n.d.	1.02	-	-	-
Cd	n.d.	1.00	-	-	-
Co	n.d.	-	1.01	-	0.99
Cr	n.d.	-	-	1.01	-
Cu	n.d.	-	-	-	1.00
Fe	n.d.	-	-	-	1.00
Li	n.d.	-	1.00	-	-
Mg	n.d.	-	1.01	-	-
Mn	n.d.	-	-	-	1.01
Mo	n.d.	-	1.03	-	-
Na	n.d.	-	0.99	-	-
Ni	n.d.	-	-	-	1.00
Pb	n.d.	-	1.05	-	1.00
Sb	n.d.	-	1.02	1.01	-
Sr	n.d.	-	1.00	-	-
Ti	n.d.	1.00	-	-	-
V	n.d.	0.99	-	-	-
Zn	n.d.	-	-	1.01	0.99

n.d.: not determined.

1.4. Sample homogeneity

Sample homogeneity was tested with an ANOVA *F* test using the ED-XRF results of laboratory L2.

Table S3. Homogeneity test results for BATT and MIN sample.

Element		**Ag**	**Al**	**As**	**Au**	**Ba**	**Bi**	**Br**	**Ca**	**Cd**	**Ce**	**Cl**	**Co**	**Cr**	**Cu**	**Fe**
BATT	*F* (α=0.01)	0.89	0.6	0.74	n.d.	0.6	n.d.	0.61	0.88	1.54	n.d.	0.64	n.d.	1.33	0.59	0.79
	f = 3.53	h.	h.	h.	n.d.	h.	n.d.	h.	h.	h.	n.d.	h.	n.d.	h.	h.	h.
MIN	*F* (α=0.01)	n.d.	7.63	n.d.	n.d.	2.3	n.d.	n.d.	1.33	n.d.	0.85	1.45	2.92	n.d.	n.d.	4.05
	f = 4.03	n.d.	n. h.	n.d.	n.d.	h.	n.d.	n.d.	h.	n.d.	h.	h.	h.	n.d.	n.d.	*n.h.*
Element		**Ga**	**Ge**	**In**	**K**	**La**	**Mg**	**Mn**	**Mo**	**Nb**	**Nd**	**Ni**	**P**	**Pb**	**Pd**	**Pr**
BATT	*F* (α=0.01)	n.d.	n.d.	n.d.	0.88	n.d.	n.d.	0.72	1.55	0.4	0.27	0.54	0.82	1.35	n.d.	0.39
	f = 3.53	n.d.	n.d.	n.d.	h.	n.d.	n.d.	h.	h.	h.	h.	h.	h.	h.	n.d.	h.
MIN	F (α=0.01)	0.62	n.d.	n.d.	16.59	0.77	4.2	n.d.	n.d.	1.1	1.7	n.d.	0.22	n.d.	n.d.	1.0
	f = 4.03	h.	n.d.	n.d.	*n.h.*	h.	*n.h.*	n.d.	n.d.	h.	h.	n.d.	h.	n.d.	n.d.	h.
Element		**Pt**	**Rb**	**S**	**Sb**	**Si**	**Sn**	**Sr**	**Th**	**Ti**	**U**	**V**	**W**	**Y**	**Zn**	**Zr**
BATT	*F* (α=0.01)	n.d.	n.d.	0.81	0.58	0.6	0.7	0.84	n.d.	0.13	n.d.	n.d.	n.d.	n.d.	0.81	0.89
	f = 3.53	n.d.	n.d.	h.	h.	h.	h.	h.	n.d.	h.	n.d.	n.d.	n.d.	n.d.	h.	h.
MIN	*F* (α=0.01)	n.d.	4.64	n.d.	n.d.	13.99	1.0	5.93	n.d.	n.d.	n.d.	n.d.	2.88	1.71	2.83	0.22
	f = 4.03	n.d.	n. h.	n.d.	n.d.	n. h.	h.	*n.h.*	n.d.	n.d.	n.d.	n.d.	h.	h.	h.	h.

n.d.: not determined due to invalid or too few measurement results with ED-XRF, n.h.: not homogeneous, h.: homogeneous.

2. Chemical analysis results of validated and in-house method

2.1. Results of the validated method

Table S4 shows the elemental composition of both battery and mining sample with the respective (relative) standard deviation (R)SD, recovery rates in the sample (RRS), and method specifications, such as measurement device, isotope/measurement line, gas mode, and digestion acid.

Table S4. Element composition of BATT and MIN sample determined with the validated method.

Element	Detector	ICP-OES [nm]	Gas	Acid	BATT					MIN				
		ICP-MS	mode		Mean	SD	RSD	RRS	n	Mean	SD	RSD	RRS	n
		[isotope]			[ppm]	[ppm]	[%]	[%]		[ppm]	[ppm]	[%]	[%]	
Al	ICP-OES	396.2	-	HNO_3-H_2O_2	70,600	1,030	1	108	5	-	-	-	-	-
Al	WD-XRF	-	-	-	-	-	-	-	-	30,700	432	1	-	5
As	ICP-MS	75As	He	Aqua regia	-	-	-	-	-	13	1	8	101	4
As		75As	He	H_2SO_4-HNO_3	-	-	-	-	-	13	-	-	103	4
As	ICP-OES	189.0	-	H_2SO_4-HNO_3	759	7	1	101	5	-	-	-	-	-
Au	ICP-MS	197 -> 197Au	O_2	Aqua regia	3	1	33	98	4	-	-	-	-	-
Ba	ICP-MS	138 -> 138Ba	O_2	HNO_3-HCl-HF	-	-	-	-	-	82	2	2	93	3
C	LECO	-	-	-	9,000	-	-	-	-	500	-	-	-	-
Ca	WD-XRF	-	-	-	-	-	-	-	-	22,100	217	1	-	5
Cd	ICP-MS	111Cd	He	HNO_3-H_2O_2	46	2	4	104	5	-	-	-	-	-
Ce	ICP-MS	140 -> 156Ce	O_2	Aqua regia	27	2	7	100	5	-	-	-	-	-
Ce	ICP-OES	418.7	-	Aqua regia	-	-	-	-	-	646	15	2	96	4
Cl*	O2IC	-	-	-	5,690	395	7	-	-	-	-	-	-	-
Co	ICP-MS	59 -> 75Co	O_2	HNO_3-HCl-HF	-	-	-	-	-	16	1	6	83	3
Co	ICP-OES	238.9	-	HNO_3-H_2O_2	6,520	61	1	100	5	-	-	-	-	-
Cr	ICP-MS	52Cr	He	HNO_3-HCl-HF	-	-	-	-	-	28	2		100	3
Cu	ICP-OES	324.8	-	HNO_3-H_2O_2	39,100	892	2	101	5	-	-	-	-	-
Dy	ICP-MS	163 -> 179Dy	O_2	Aqua regia	-	-	-	-	-	12	1	8	92	3
F*	O2IC	-	-	-	21,300	6,070	28	-	-	-	-	-	-	-
Fe	ICP-OES	238.2	-	HNO_3-H_2O_2	78,500	712	1	97	5	-	-	-	-	-
Fe	WD-XRF	-	-	-	-	-	-	-	-	362,000	2,340	1	-	-
Ga	ICP-MS	69 -> 69Ga	O_2	HNO_3-HCl-HF	-	-	-	-	-	16	0	0	97	3
Gd	ICP-MS	157 -> 173Gd	O_2	Aqua regia	-	-	-	-	-	19	1	6	94	3
K	WD-XRF	-	-	-	-	-	-	-	-	13,700	305	2	-	5
La	ICP-MS	139 -> 155La	O_2	Aqua regia	46	3	7	97	5	-	-	-	-	-
La	ICP-OES	408.7	-	Aqua regia	-	-	-	-	-	354	9	3	98	4
Li	ICP-MS	7	He	Aqua regia	-	-	-	-	-	33	1	3	83	3
Li	ICP-OES	610.4	-	HNO_3-H_2O_2	26,800	459	2	102	5	-	-	-	-	-
Mg	WD-XRF	-	-	-	-	-	-	-	-	29,400	409	1	-	5
Mn	ICP-OES	257.6	-	HNO_3-H_2O_2	167,000	2,470	1	101	5	-	-	-	-	-
Mn	WD-XRF	-	-	-	-	-	-	-	-	740	89	12	-	5
Na	WD-XRF	-	-	-	-	-	-	-	-	10,400	363	3	-	-
Nb	ICP-MS	93 -> 109Nb	O_2	HNO_3-HCl-HF	-	-	-	-	-	19	2	11	102	3
Nd	ICP-MS	146Nd	He	Aqua regia	-	-	-	-	-	216	5	2	99	3
Ni	ICP-MS	60Ni	He	HNO_3-HCl-HF	-	-	-	-	-	27	1	4	100	3
Ni	ICP-OES	231.6	-	HNO_3-H_2O_2	21,800	556	3	97	5	-	-	-	-	-
P	ICP-OES	213.6	-	Aqua regia	4,100	52		98	5	-	-	-	-	-
P	WD-XRF	-	-	-	-	-	-	-	-	2,820	84	3	-	5
Pb	ICP-OES	220.4	-	HNO_3-H_2O_2	642	21	3	100	5	-	-	-	-	-
Pd	ICP-MS	108Pd	He	HNO_3-H_2O_2	1	0	0	108	5	-	-	-	-	-
Pr	ICP-MS	141 -> 157Pr	O_2	Aqua regia	-	-	-	-	-	57	1	2	92	3
Rb	WD-XRF	-	-	-	-	-	-	-	-	300	0	0	-	4

Element	Detector	ICP-OES [nm] ICP-MS [isotope]	Gas mode	Acid	BATT					MIN				
					Mean [ppm]	SD [ppm]	RSD [%]	RRS [%]	n	Mean [ppm]	SD [ppm]	RSD [%]	RRS [%]	n
Sb	ICP-OES	206.8	-	Aqua regia	937	10	1	96	5	-	-	-	-	-
Si	WD-XRF	-	-	-	-	-	-	-	-	139,000	709	1	-	5
Sm	ICP-MS	147Sm	He	Aqua regia	-	-	-	-	-	27	1	4	90	3
Sn	ICP-MS	118Sn	He	HNO_3-HCl-HF	-	-	-	-	-	113	1	1	100	3
Sr	ICP-MS	88 -> 88Sr	O_2	HNO_3-HCl-HF	-	-	-	-	-	26	2	8	107	3
Th	ICP-MS	232 -> 248Th	O_2	Aqua regia	-	-	-	-	-	11	1		88	-
Ti	ICP-OES	334.1	-	Aqua regia	8,890	338	4	96	5	-	-	-	-	-
Ti	WD-XRF	-	-	-	-	-	-	-	-	2,440	114		-	5
V	ICP-MS	51 -> 67 V	O_2	HNO_3-H_2O_2	65	2	3	98	5	-	-	-	-	-
V	WD-XRF	-	-	-	-	-	-	-	-	840	55	7	-	5
W	ICP-MS	182W	He	HNO_3-HCl-HF	-	-	-	-	-	56	1	2	98	3
Y	WD-XRF	-	-	-	-	-	-	-	-	100	16	16	-	4
Yb	ICP-MS	172Yb	He	Aqua regia	-	-	-	-	-	6	1	17	86	3
Zn	ICP-OES	206.2	-	HNO_3-H_2O_2	15,000	162	1	103	5	-	-	-	-	-
Zn	WD-XRF	-	-	-	-	-	-	-	-	95	17	18	-	4
Zr	ICP-MS	90Zr	He	HNO_3-HCl-HF	-	-	-	-	-	47	2	4	102	3

SD: standard deviation, RSD: relative standard deviation, RRS: recovery rate sample, n: number of measurements, O2IC: oxygen digestion bomb with ion chromatography, bold font: exceedance of deviation +/- 20%.

2.2. Results of the wet-chemical in-house method

The method specification and results of the wet-chemical in-house analysis is shown in **Table S5**. All results are given with (relative) standard deviation (R)SD and recovery rates (RRB, RRS). Data are compared to the results of the validated method and are expressed as an absolute difference to the mean (mean diff. abs.), the relative difference to the mean (mean diff. rel.) and significant difference between both methods (signif. diff. (*t*-test)).

Table S5. Chemical analysis results of the wet-chemical in-house method.

Element	Procedure in-house method				In-house method						Comparison		
	det	OES [nm] MS [isotope]	prep	sample	Mean [ppm]	SD [ppm]	RSD [%]	RRB [%]	RRS [%]	n	mean diff. abs. [ppm]	mean diff. rel. [%]	Signif. diff. (*t*-test)
Al	OES	396.2	HNO3-H2O2	BATT	55,900	4,980	9	93	85	6	-14,700	-21	Yes
As	MS	75As	Aqua regia	BATT	635	32	5	100	83	6	-124	-16	Yes
As	OES	189.0	Aqua regia	BATT	624	29	5	96	88	6	-135	-18	Yes
As	OES	189.0	Aqua regia	MIN	17	1	6	99	86	3	+4	+31	No
Au	MS	197Au	Aqua regia	BATT	2	1	5	110	91	6	-1	-33	No
Ba	OES	455.4	Aqua regia	MIN	40	6	15	108	101	3	-42	-51	Yes
Cd	MS	111Cd	HNO3-H2O2	BATT	12	1	8	113	245	6	-34	-74	Yes
Cd	OES	214.4	HNO3-H2O2	BATT	36	2	6	89	86	6	-10	-22	Yes
Ce	MS	140Ce	Aqua regia	BATT	13	1	8	100	142	6	-14	-52	Yes
Ce	OES	404.0	Aqua regia	MIN	379	26	7	102	103	3	-267	-41	Yes
Co	OES	238.8	HNO3-H2O2	BATT	4,970	441	9	96	98	2	-1,560	-24	No
Co	OES	228.6	Aqua regia	MIN	19	0	0	99	88	3	+3	+19	No
Cr	OES	267.7	Aqua regia	MIN	18	2	11	99	86	3	-9	-33	Yes
Cu	OES	324.8	HNO3-H2O2	BATT	35,600	2,330	7	93	92	6	-3,480	-9	No
Dy	OES	353.1	Aqua regia	MIN	8	0	0	97	121	3	-4	-33	No
Fe	OES	238.2	HNO3-H2O2	BATT	71,800	4,790	7	90	85	6	-6,620	-8	No
Ga	OES	294.3	Aqua regia	MIN	49	4	8	108	120	3	+33	+206	Yes
Gd	OES	336.2	Aqua regia	MIN	28	1	4	102	98	3	+10	+56	Yes
La	MS	139La	Aqua regia	BATT	16	2	12	101	160	6	-30	-65	Yes

Element	Procedure in-house method				In-house method						Comparison		
	det	OES [nm] MS [isotope]	prep	sample	Mean [ppm]	SD [ppm]	RSD [%]	RRB [%]	RRS [%]	n	mean diff. abs. [ppm]	mean diff. rel. [%]	Signif. diff. (*t*-test)
La	OES	333.7	Aqua regia	MIN	305	7	2	103	95	3	-49	-14	Yes
Li	OES	670.7	Aqua regia	MIN	53	2	4	101	97	3	+20	+61	Yes
Mn	OES	257.6	HNO3-H2O2	BATT	151,000	10,300	7	97	88	6	-16,600	-1	Yes
Nb	OES	390.4	Aqua regia	MIN	103	1	1	103	104	3	+84	+442	Yes
Nd	OES	430.3	Aqua regia	MIN	199	15	8	95	88	3	-17	8	No
Ni	OES	231.6	HNO3-H2O2	BATT	18,000	2,220	12	98	97	2	-3,710	-17	No
Ni	OES	231.6	Aqua regia	MIN	25	1	4	113	96	3	-2	-7	No
P	MS	31P	Aqua regia	BATT	3,020	152	5	96	88	6	-1,070	-26	Yes
P	OES	213.6	Aqua regia	BATT	3,200	69	2	92	88	6	-899	-22	Yes
Pb	MS	208Pb	HNO3-H2O2	BATT	432	28	6	83	92	6	-210	-33	Yes
Pb	OES	220.4	HNO3-H2O2	BATT	510	31	6	92	103	6	-132	-21	Yes
Pd	MS	108Pd	HNO3-H2O2	BATT	1	0	0	90	103	6	0	0	No
Pr	OES	417.9	Aqua regia	MIN	71	5	7	97	85	3	+14	+25	No
Sb	MS	121Sb	Aqua regia	BATT	877	56	6	101	95	6	-60	-6	No
Sb	OES	206.8	Aqua regia	BATT	820	51	6	94	91	6	-117	-12	Yes
Sm	OES	359.2	Aqua regia	MIN	47	2	4	NA	NA	3	+20	+74	Yes
Sn	OES	189.9	Aqua regia	MIN	109	4	4	111	94	3	-4	-4	No
Sr	OES	421.5	Aqua regia	MIN	10	0	0	102	92	3	-16	-62	Yes
V	MS	51V	HNO3-H2O2	BATT	29	2	7	NA	NA	6	-36	-55	Yes
V	OES	292.4	Aqua regia	MIN	871	1	0	94	91	3	+31	+4	No
Y	OES	360.0	Aqua regia	MIN	64	3	5	101	93	3	-36	-36	No
Yb	OES	328.9	Aqua regia	MIN	13	0	0	97	91	3	+7	+117	Yes
Zn	MS	66Zn	HNO3-H2O2	BATT	18,200	1,440	8	77	71	6	+3,150	+21	Yes
Zn	OES	206.2	HNO3-H2O2	BATT	12,700	658	5	90	101	6	-2,370	-16	Yes
Zn	OES	206.2	Aqua regia	MIN	65	12	18	113	86	3	-30	-32	No
Zr	OES	339.1	Aqua regia	MIN	257	17	7	93	92	3	+210	+447	Yes

Mean: arithmetic mean, SD: standard deviation, RSD: relative SD, RRB: recovery rate blind, RRS: recovery rate sample, n: number of measurements (n), mean diff.: absolute difference between the means, mean diff. rel.: relative differences, signif. diff.: Welch's *t*-test results of significant differences between the means, det: determination method, OES: ICP-OES, MS: ICP-MS, prep: preparation method (acid mixture), BATT: battery sample, MIN: mining waste sample, bold font: an exceedance of deviation +/- 20%.

2.3. Results of in-house ED-XRF measurement

Table S6. Chemical analysis results of the XRF in-house method.

Element	Procedure in-house method			in-house method				comparison		
	det	prep	sample	mean [ppm]	SD [ppm]	RSD [%]	n	mean diff. abs. [ppm]	mean diff. rel. [%]	Signif. diff. (*t*-test)
Al	ED-XRF	-	BATT	84,700	12,800	15	36	+14,100	+20	Yes
Al~	ED-XRF	-	MIN	39,200	3,060	8	24	+8,490	+28	Yes
As	ED-XRF	-	BATT	735	130	18	36	-24	-3	No
As	ED-XRF	-	MIN	24	6	25	16	+11	+85	Yes
Ba	ED-XRF	-	MIN	214	42	2	24	+132	+161	Yes
Ca	ED-XRF	-	MIN	21,600	1,060	5	24	-457	-2	No
Cd	ED-XRF	-	BATT	51	7	14	36	+5	+11	Yes
Ce	ED-XRF	-	BATT	206	18	9	4	+179	+663	Yes
Ce	ED-XRF	-	MIN	689	67	1	24	+43	+7	No
Co	ED-XRF	-	BATT	505	132	26	7	-6,020	-92	Yes
Co	ED-XRF	-	MIN	1,490	286	19	24	+1,470	+9,210	Yes
Cu	ED-XRF	-	BATT	35,700	5,790	16	36	-3,420	-9	Yes
Fe	ED-XRF	-	BATT	81,600	10,400	13	36	+3,180	+4	No

Element	Procedure in-house method			in-house method				comparison		
	det	prep	sample	mean [ppm]	SD [ppm]	RSD [%]	n	mean diff. abs. [ppm]	mean diff. rel. [%]	Signif. diff. (*t*-test)
Fe~	ED-XRF	-	MIN	314,000	21,300	7	24	-48,200	-13	Yes
Ga	ED-XRF	-	MIN	33	11	33	24	+17	+106	Yes
K~	ED-XRF	-	MIN	21,900	2,660	12	24	+8,170	+59	Yes
La	ED-XRF	-	BATT	186	40	22	32	+140	+304	Yes
La	ED-XRF	-	MIN	440	43	1	24	+86	+24	Yes
Mg~	ED-XRF	-	MIN	49,000	7,370	15	24	+19,600	+67	Yes
Mn	ED-XRF	-	BATT	165,000	20,300	12	36	-2,540	-2	No
Mn	ED-XRF	-	MIN	1,120	42	4	3	+384	+52	Yes
Nb	ED-XRF	-	MIN	20	2	1	24	+1	+5	No
Nd	ED-XRF	-	MIN	1,140	132	12	24	+923	+427	Yes
Ni	ED-XRF	-	BATT	19,500	3,370	17	36	-2,210	-10	Yes
P	ED-XRF	-	BATT	3,120	320	1	36	-977	-24	Yes
P	ED-XRF	-	MIN	2,540	223	9	24	-279	-10	Yes
Pb	ED-XRF	-	BATT	541	100	18	36	-101	-16	Yes
Pr	ED-XRF	-	MIN	518	61	12	24	+461	+809	Yes
Rb~	ED-XRF	-	MIN	322	33	1	24	+22	+7	Yes
Sb	ED-XRF	-	BATT	1,980	350	18	36	+1,050	+112	Yes
Si~	ED-XRF	-	MIN	160,000	10,200	6	24	+21,100	+15	Yes
Sn	ED-XRF	-	MIN	536	60	11	24	+423	+374	Yes
Sr~	ED-XRF	-	MIN	43	4	9	24	+17	+65	Yes
Ti	ED-XRF	-	BATT	12,300	1,730	14	36	+3,410	+38	Yes
W	ED-XRF	-	MIN	154	32	21	24	+98	+175	Yes
Y	ED-XRF	-	MIN	111	43	39	24	+11	+11	No
Zn	ED-XRF	-	BATT	18,800	3,150	17	36	+3,780	+25	Yes
Zn	ED-XRF	-	MIN	159	18	11	24	+64	+67	Yes
Zr	ED-XRF	-	MIN	72	13	18	24	+25	+53	Yes

Mean: arithmetic mean, SD: standard deviation, RSD: relative SD, n: number of measurements (n), mean diff. abs.: absolute difference between the means, mean diff. rel.: relative differences, signif. diff.: Welch's *t*-test results of significant differences between the means, det: determination method, prep: preparation method (acid mixture), BATT: battery sample, MIN: mining waste sample, bold font: an exceedance of deviation +/- 20%, ~: inhomogeneous distribution in a sample according to ANOVA *F* test.

3. Applicability of simplified in-house methods

Table S7 and **Table S8** show the applicability of simplified in-house methods for MIN and BATT, respectively. The elemental compositions determined with the validated method are compared to the simplified method expressed as the relative difference (mean diff. rel.) and significance test results of the t-test and the specific element recovery in the blind sample (RRB) and the sample matrix (RRS) as a dimensionless factor.

Table S7. Overview of applicability of in-house methods for MIN sample.

Sample		MIN								
Preparation					-		Aqua Regia			
Detection		validated methods		Homogeneity	ED-XRF (L2)		OES			
Element group	Element	mean [ppm]	SD [ppm]	ANOVA F	mean diff. rel. [%]	Signif. diff. (*t*-test)	mean diff. rel. [%]	Signif. diff. (*t*-test)	RRS	RRB
Ferrous metals	Cr	27	2	n.d.	<LOD	-	-0.33	Yes	0.86	0.99
	Fe	362,000	2,340	**n.h.**	-0.13	Yes	-	-	-	-
	Mn	740	89	n.d.	0.52	Yes	-	-	-	-
	Nb	19	2	h	0.05	No	4.42	Yes	1.04	1.03
	Ni	27	1	n.d.	<LOD	-	-0.07	No	0.96	1.13
	V	840	55	n.d.	<LOD	-	0.04	No	0.91	0.94
Non-ferrous metals	Al	30,700	432	**n.h.**	0.28	Yes	-	-	-	-
	Co	16	1	h	92.12	Yes	0.19	No	0.88	0.99
	Mg	29,400	409	**n.h.**	0.67	Yes	-	-	-	-
	Sn	113	1	h	3.74	Yes	-0.04	No	0.94	1.11
	Zn	95	17	h	0.67	Yes	-0.32	No	0.86	1.13
Others	Ca	22,100	217	h	-0.02	No	-	-	-	-
	K	13,700	305	**n.h.**	0.59	Yes	-	-	-	-
	P	2,820	84	h	-0.10	Yes	-	-	-	-
	Rb	300	-	**n.h.**	0.07	Yes	-	-	-	-
	Si	139,000	709	**n.h.**	0.15	Yes	-	-	-	-
Specialty metals	As	13	1	n.d.	0.85	Yes	0.31	No	0.86	0.99
	Ba	82	2	h	1.61	Yes	-0.51	Yes	1.01	1.08
	Ga	16	-	h	1.06	Yes	2.06	Yes	1.20	1.08
	Li	33	1	n.d.	n.d.	-	0.61	Yes	0.97	1.01
	Sr	26	2	**n.h.**	0.65	Yes	-0.62	Yes	0.92	1.02
	W	56	1	h	1.75	Yes	-	-	-	-
	Zr	47	2	h	0.53	Yes	4.47	Yes	0.92	0.93
Specialty metals (REE)	Ce	646	15	h	0.07	No	-0.41	Yes	1.03	1.02
	Dy	12	1	n.d.	n.d.	-	-0.33	No	1.21	0.97
	Gd	18	1	n.d.	n.d.	-	0.56	Yes	0.98	1.02
	La	354	9	h	0.24	Yes	-0.14	Yes	0.95	1.03
	Nd	216	5	h	4.27	Yes	-0.08	No	0.88	0.95
	Pr	57	1	h	8.09	Yes	0.25	No	0.85	0.97
	Sm	27	1	n.d.	n.d.	-	0.74	Yes	-	-
	Y	100	16	h	0.11	No	-0.36	No	0.93	1.01
	Yb	6	1	n.d.	n.d.	-	1.17	Yes	0.91	0.97

n.d.: not determined due to invalid or too few measurement results with ED-XRF, n.h.: not homogeneous, h.: homogeneous, green: values are within the acceptance range of 100 % +/- 20 %, red: values exceed the acceptance range of deviation 100 % +/- 20 %.

Table S8. Overview of applicability of in-house methods for BATT sample.

Sample		BATT																			
Preparation		validated methods		Homo-			Aqua Regia								HNO_3-H_2O_2							
Detection				geneity	ED-XRF (L2)		MS				OES				MS				OES			
Element group	Element	mean [ppm]	SD [ppm]	ANOVA F	mean diff. rel. [%]	Signif. diff. (*t*-test)	mean diff. rel. [%].	Signif. diff. (*t*-test)	RRS	RRB	mean diff. rel. [%]	Signif. diff. (*t*-test)	RRS	RRB	mean diff. rel. [%]	Signif. diff. (*t*-test)	RRS	RRB	mean diff. rel. [%]	Signif. diff. (*t*-test)	RRS	RRB
Ferrous	Fe	78,500	712	h	0.04	No	-	-	-	-	-	-	-	-	>LOQ	-	-	-	-0.08	No	0.85	0.90
metals	Mn	167,000	2,470	h	-0.02	No	-	-	-	-	-	-	-	-	>LOQ	-	-	-	-0.10	Yes	0.88	0.97
	Ni	21,800	556	h	-0.10	Yes	-	-	-	-	-	-	-	-	>LOQ	-	-	-	-0.17	No	0.97	0.98
	V	65	2	n.d.	<LOD	-	-	-	-	-	-	-	-	-	-0.55	Yes	-	-	<LOQ	-	NA	NA
Non-ferrous	Al	70,600	1,030	h	0.20	Yes	-	-	-	-	-	-	-	-	>LOQ	-	-	-	-0.21	Yes	0.85	0.93
metals	Co	6,520	61	n.d.	-0.92	Yes	-	-	-	-	-	-	-	-	>LOQ	-	-	-	-0.24	No	0.98	0.96
	Cu	39,100	892	h	-0.09	Yes	-	-	-	-	-	-	-	-	>LOQ	-	-	-	-0.09	No	0.92	0.93
	Pb	642	20	h	-0.16	Yes	-	-	-	-	-	-	-	-	-0.33	Yes	0.92	0.83	-0.21	Yes	1.03	0.92
	Ti	8,890	338	h	0.38	Yes	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Zn	15,000	162	h	0.25	Yes	-	-	-	-	-	-	-	-	0.21	Yes	0.71	0.77	-0.16	Yes	1.01	0.90
Others	Cl	5,690	395	h	-0.21	Yes	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	P	4,100	52	h	-0.24	Yes	-0.26	Yes	0.88	0.96	-0.22	Yes	0.88	0.92	-	-	-	-	-	-	-	-
Precious	Au	3	1	n.d.	<LOD	-	-0.33	No	0.91	1.10	<LOQ	-	-	1.05	-	-	-	-	-	-	-	-
metals	Pd	1	-	n.d.	<LOD	-	-	-	-	-	-	-	-	-	0.00	No	1.03	0.90	<LOQ	-	-	-
Specialty	As	759	7	h	-0.03	No	-0.16	Yes	0.83	1.00	-0.18	Yes	0.88	0.96	-	-	-	-	-	-	-	-
metals	Cd	46	2	h	0.11	Yes	-	-	-	-	-	-	-	-	-0.74	Yes	2.45	1.13	-0.22	Yes	0.86	0.89
	Sb	937	10	h	1.12	Yes	-0.06	No	0.95	1.01	-0.12	Yes	0.91	0.94	-	-	-	-	-	-	-	-
Specialty	Ce	27	2	n.d.	6.63	Yes	-0.52	Yes	1.42	1.00	<LOQ	-	-	0.97	-	-	-	-	-	-	-	-
metals (REE)	La	46	3	n.d.	3.04	Yes	-0.65	Yes	1.60	1.01	<LOQ	-	-	0.99	-	-	-	-	-	-	-	-

n.d.: not determined due to invalid or too few measurement results with ED-XRF, n.h.: not homogeneous, h.: homogeneous, green: values are within the acceptance range of 100 % +/- 20 %, red: values exceed the acceptance range of deviation 100 % +/- 20 %, </> LOD: below or above limit of detection, </> LOQ: below or above limit of quantification.

4. Matrix interferences in ED-XRF measurement

Overlapping of spectra causes false readings and over-/underestimations, as shown below for Co and La in the BATT sample. **Figure S2** shows how Fe and Ni partially overlap the spectra of cobalt (Co-Kα and Co-Kβ). **Figure S3** shows the spectra of lanthanum (La-Lα and La-Lβ), which are partially overlapped by Ti and Cr.

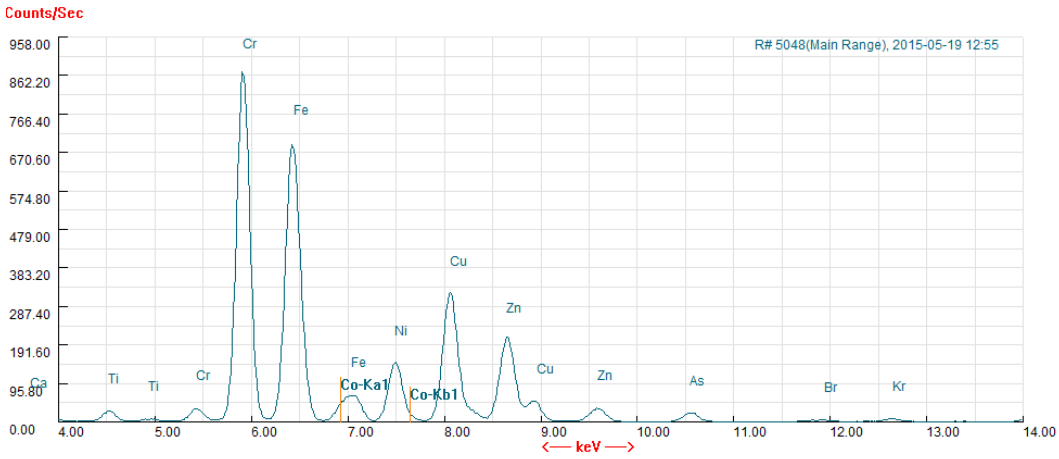

Figure S2. The ED-XRF energy spectrum (4–14 keV) of the BATT measurement.

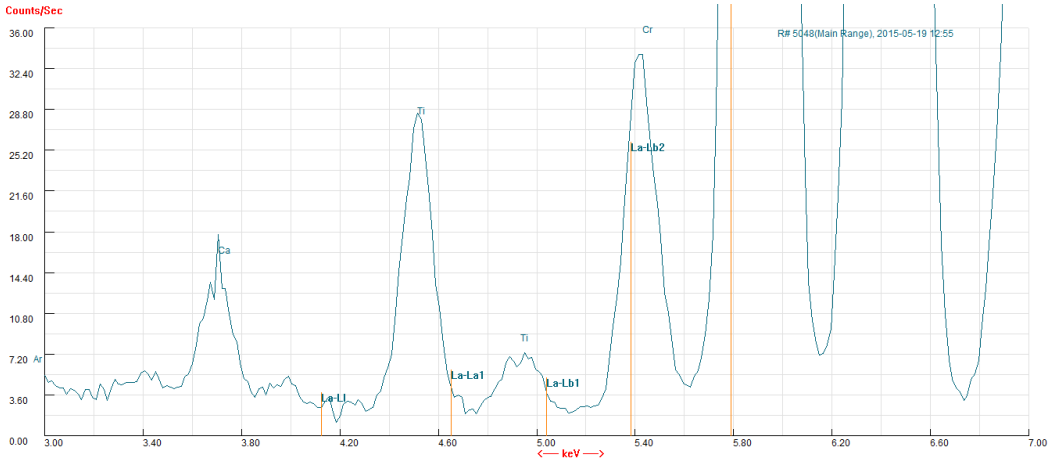

Figure S3. The ED-XRF energy spectrum (3–7 keV) of the BATT measurement.