Annex 2

A. Comparison of the quantities of trace elements extracted from sludges with aqua regia (EN 13346) and with hydrofluoric and perchloric acids (AFNOR NF X 31-147)
Information provided by Henri Ciesielski, INRA - Laboratoire d'Analyses des Sols, France

This document gives the relationships observed for trace elements extracted from sludges according to a CEN standard and a French standard. The following results (graphs 1 to 6) were presented during a TC 308 WG1/TG1 meeting. Comparisons for nutrients are also available.

Methods
EN 13346: Determination of trace elements and phosphorous – Aqua regia extraction methods (method A)

AFNOR NF X 31-147: Soils, sediments - Total solubilizing by acid attack. This method was subsequently standardised in ISO TC 190 under the reference ISO 14869-1.

Samples and results
100 samples collected in various urban wastewater treatment plants of France. The study was carried out in the Soil Analysis Laboratory of Arras belonging to the French National Institute of Agronomic Research.

For any element considered, results are well correlated ($R2 > 0.98$).
Except for Cr, differences between the calculated slopes do not exceed ± 3%.
HF extracts higher quantities of Cr than aqua regia.

Figure 1 : Comparison Cd (HCl/HNO3) and Cd (HF)

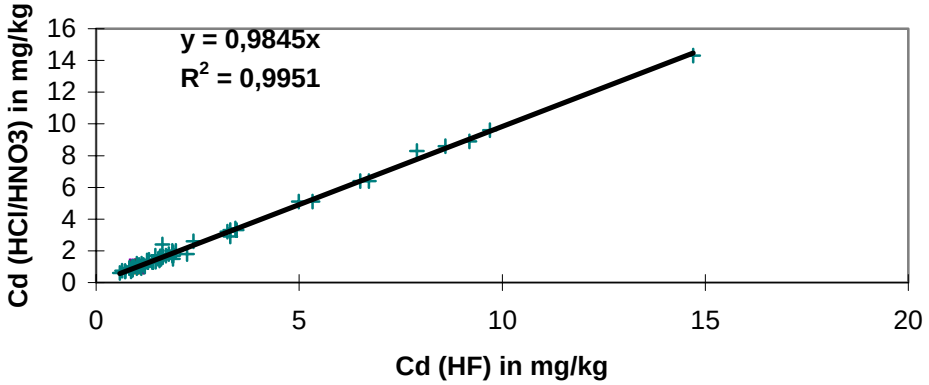


Figure 2 : Comparison Cr (HCl/HNO3) and Cr (HF)

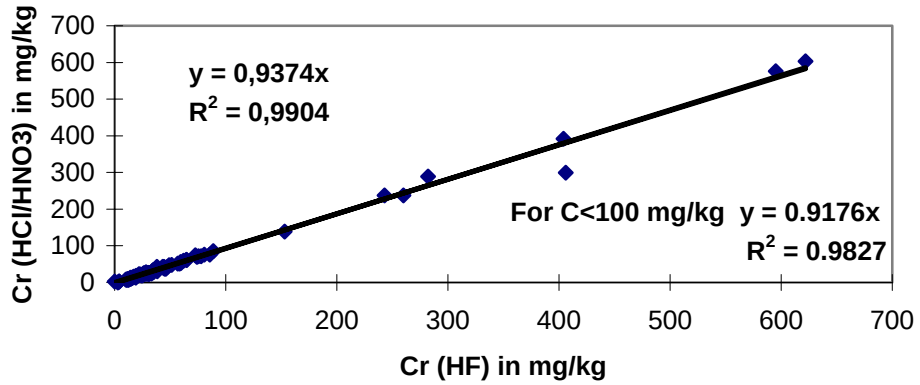


Figure 3 : Comparison Cu (HCl/HNO3) and Cu (HF)

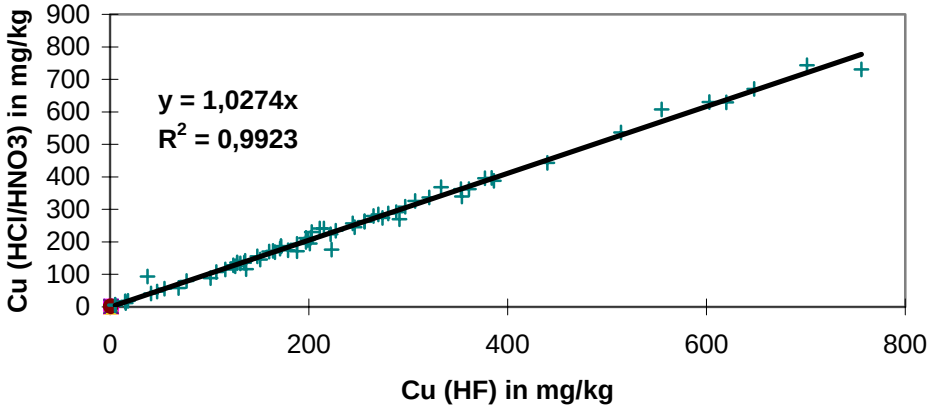


Figure 4 : Comparison Ni (HCl/HNO3) and Ni (HF)

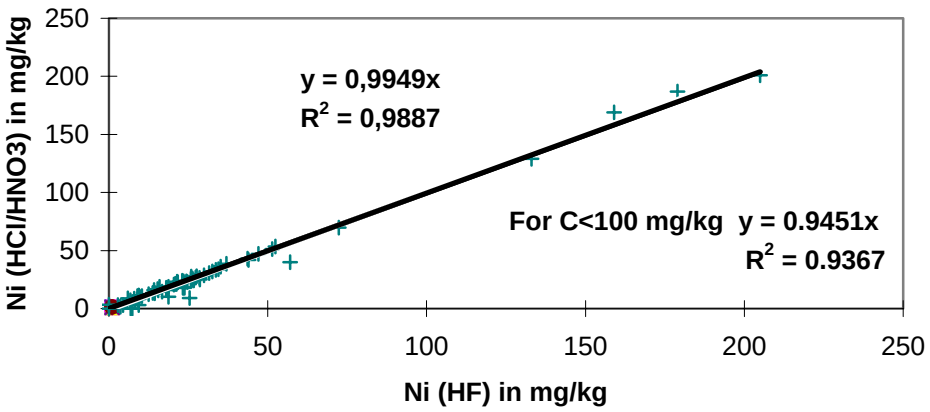


Figure 5 : Comparison Pb (HF) and Pb (HCl/HNO3)

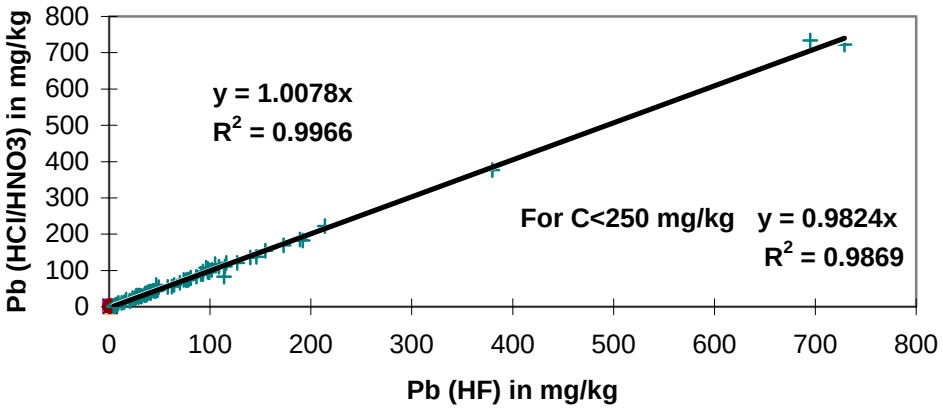
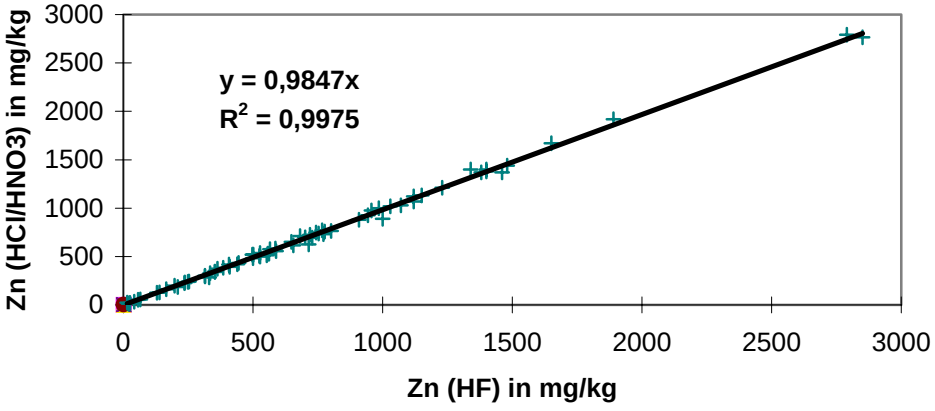


Figure 6 : Comparison Zn (HCl/HNO3) and Zn (HF)



B. Comparison of the quantities of trace elements extracted from soils with aqua regia (ISO 11466) and with hydrofluoric and perchloric acids (ISO 14869-1)
Information provided by Henri Ciesielski, INRA - Laboratoire d'Analyses des Sols, France

This document gives some relationships (graphs 1 to 6) observed between the quantities of trace elements extracted from soils according to 2 ISO standards.

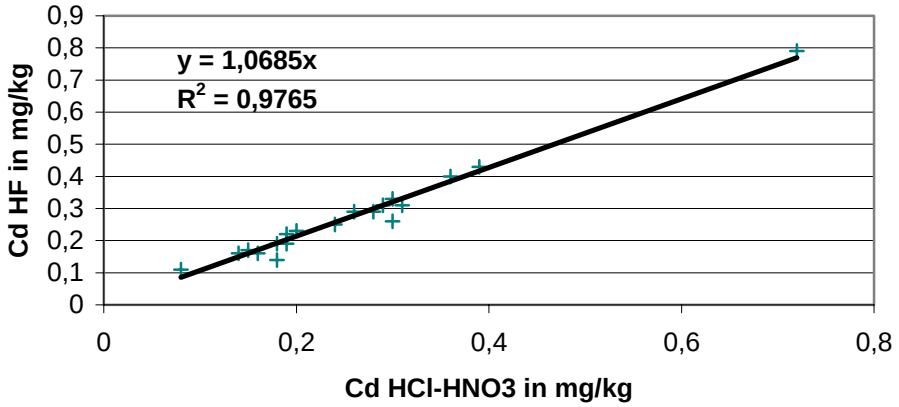
Methods
ISO 11466: Extraction of trace elements soluble in aqua regia

ISO 14869-1: Dissolution for the determination of total element content
Part I: Dissolution with hydrofluoric and perchloric acids

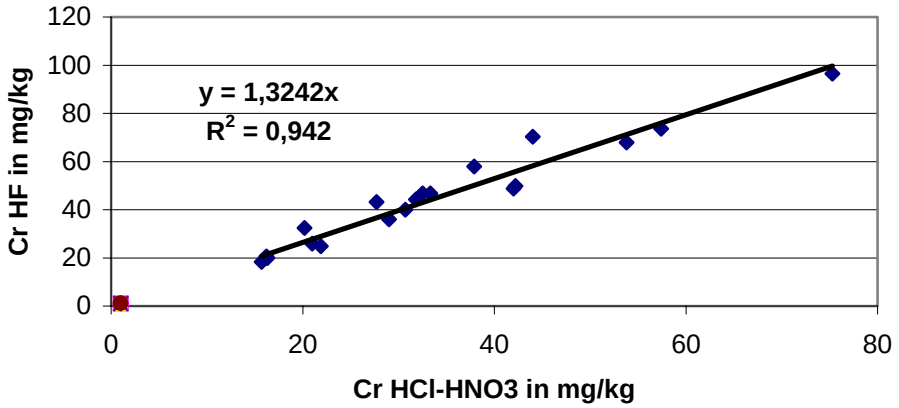
Samples and results
20 acid and calcareous soil samples collected in various regions of France. Results were obtained within interlaboratory trials organised by BIPEA (French organisation for the development of analytical methods) involving about 15 laboratories for each method.

Except for Pb the results are well correlated ($R^2 > 0.94$).
HF, compared to aqua regia, extracts more than 30% of Cr. For the other elements, HF always gives higher results but the differences in the calculated slopes do not exceed 11%.

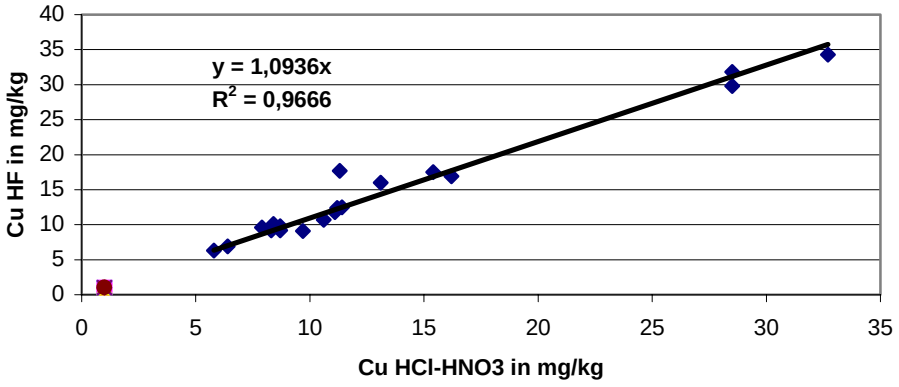
COMPARISON Cd HCl-HNO3 / Cd HF



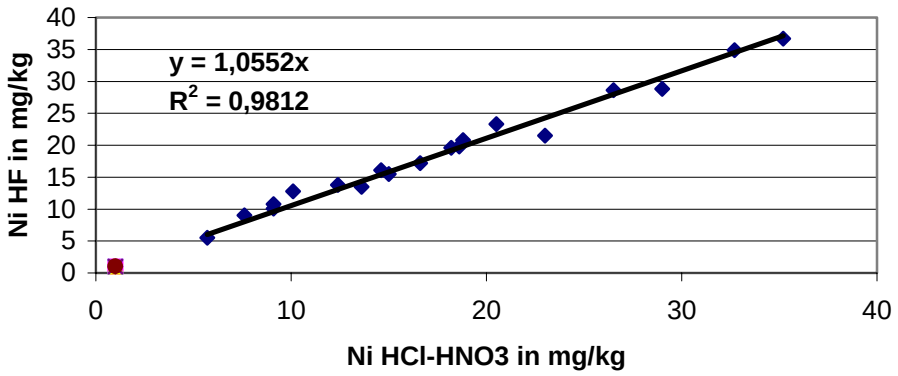
COMPARISON Cr HCl-HNO3 / Cr HF



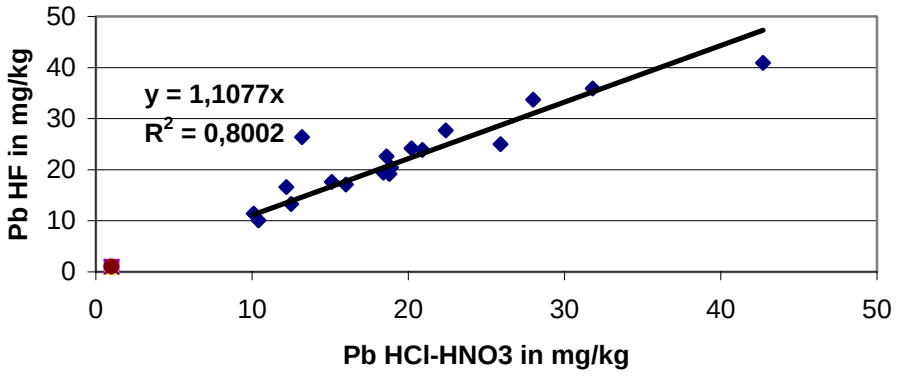
COMPARISON Cu HCl-HNO3 / Cu HF



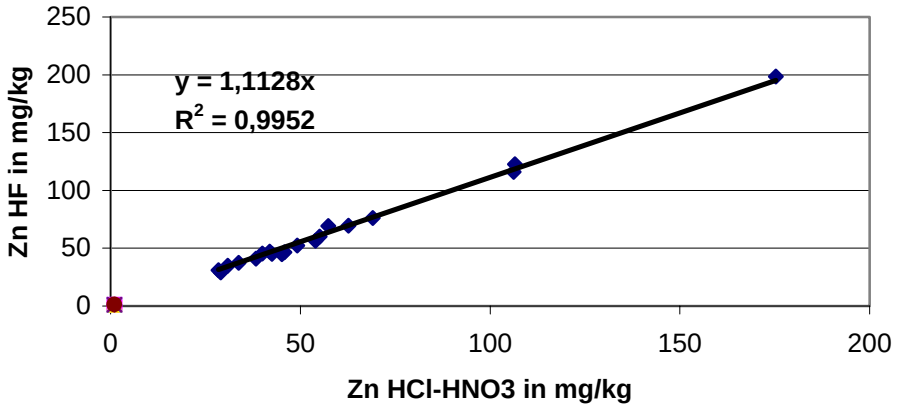
COMPARISON Ni HCl-HNO3 / Ni HF



COMPARISON Pb HCl-HNO3 / Pb HF



COMPARISON Zn HCl-HNO3 / Zn HF



C. Influence of sample particle size on aqua regia digestion method
Results of the robustness study for EN 13656 and EN 13657

Table 1 Influence of sample particle size on aqua regia digestion method (Giove 2000)
Matrix: coal bottom ash, analytical results in mg/kg

	mg	µm	Al	StdDev	Ba	StdDev	Be	StdDev	Mg	StdDev
Aqua regia	100	90	108614	7001	1400	89	6.7	0.4	615.5	34.0
	300	90	100263	4301	1162	22	5.7	0.2	560.0	18.6
	500	90	100365	4642	1137	65	5.6	0.2	545.8	21.7
	300	560	81163	8667	949	77	4.5	0.4	420.1	42.9
Total	100	90	162888	3983	2088	101	8.9	0.3	876.2	43.0
	300	90	152504	3781	1798	109	8.4	0.2	734.1	44.6
	400	90	160125	4122	1875	69	8.2	0.1	799.3	32.6
	500	90	159060	11191	1817	17	7.9	0.4	755.2	15.9
	300	560	119963	18421	1577	153	9.0	0.2	600.7	127.2

	mg	µm	Co	StdDev	Cr	StdDev	Cu	StdDev	Fe	StdDev
Aqua regia	100	90	30.9	2.2	40.7	2.1	26.5	0.9	24873	1946
	300	90	25.2	1.0	34.5	1.3	22.6	1.0	22021	690
	500	90	24.3	0.8	34.3	1.4	22.9	0.5	20751	745
	300	560	18.3	2.3	24.7	3.5	18.3	1.4	15725	1948
Total	100	90	47.5	2.3	131.1	5.8	40.3	1.1	35766	2572
	300	90	43.9	1.0	122.1	1.4	38.1	0.8	34535	1311
	400	90	42.2	0.6	116.1	2.2	37.4	0.7	30883	1397
	500	90	41.2	2.0	112.8	6.7	36.9	2.4	31749	2446
	300	560	44.9	0.8	122.6	1.8	38.2	1.0	34025	1308

	mg	µm	Mn	StdDev	Mo	StdDev	Ni	StdDev	Pb	StdDev
Aqua regia	100	90	339	13	2.6	0.4	122	5	22.5	1.2
	300	90	287	13	2.3	0.2	108	7	20.4	0.8
	500	90	279	13	2.0	0.1	116	8	18.2	0.6
	300	560	224	24	1.9	0.5	91	9	15.3	2.8
Total	100	90	431	16	3.0	0.8	152	17	28.6	2.6
	300	90	413	6	2.5	0.4	148	5	29.4	4.6
	400	90	404	8	2.1	0.2	135	8	29.4	1.2
	500	90	389	18	2.2	0.3	133	9	25.9	1.8
	300	560	426	7	2.1	0.3	151	8	25.4	1.7

	mg	µm	Sn	StdDev	Ti	StdDev	V	StdDev	Zn	StdDev
Aqua regia	100	90	5.5	1.8	5020	423	249	6	38.7	1.6
	300	90	3.7	1.1	3749	116	223	6	25.7	1.1
	500	90	3.6	1.0	3481	74	226	9	24.8	1.5
	300	560	3.4	2.6	2689	437	196	15	28.7	4.1
Total	100	90	13.7	1.5	8459	230	293	14	47.7	3.7
	300	90	8.9	1.1	8299	268	279	3	41.7	4.0
	400	90	7.5	0.3	8237	184	277	7	35.6	0.4
	500	90	6.6	0.8	8346	505	267	13	34.5	2.5
	300	560	9.1	1.6	8589	219	281	8	44.0	3.4

Most selected elements (Al, Ba, Be, Co, Cr, Cu, Fe, Mg, Mn, Mo, Pb, Ni, Ti, V) show almost the same behavior: as the particle size of sample increases, recovery gets lower.

D. Validation data for Sewage Sludge of EN 13657

Table 2 Results of the round robin test for validation of EN 13567

SAMPLE CEN9/99 "SEWAGE SLUDGE SL11 POWDER"																								
	Method A: Microwave assisted with aqua regia in closed vessel								*Method - B: Microwave assisted, with aqua regia in semi-open vessel*								*Method C: Thermal heating, with aqua regia in reflux systems*							
	N	L	NA	XREF	Mean	% Recov	% Reprod	% Repeat	N	L	NA	XREF	Mean	% Recov	% Reprod	% Repeat	N	L	NA	XREF	Mean	% Recov	% Reprod	% Repeat
Al	67	16	5		81847.8		6.7	2.5	21	6	1		77367.8		16.7	1.7	29	7	0		79678.5		24.6	6.4
Sb	44	11	0		9.77		151.1	30.8	8	3	0		3.24		56.5	1.8	22	5	0		2.99		64.1	10.6
As	39	10	4		4.67		78.3	14.6	10	3	0		4.42		32.1	8.3	28	7	0		2.41		73.4	20.1
B	33	8	2		279.94		15.6	3.4	12	3	1		282.57		14.1	0.9	19	4	0		328.05		28.4	16.6
Ba	51	12	8		76.52		8.6	2.7	22	6	4		75.52		4.5	1.2	27	6	0		61.8		18.9	7.9
Be	26	6	6		0.45		48.9	11.3	6	2	0		3		74.5	0	14	3	0		1.13		55.5	13.7
Cd	78	19	11		0.68		99.6	12	23	6	0		1.02		112.4	20.8	30	7	9		0.26		67.6	36.3
Ca	60	14	0		57231.7		11	5.9	19	5	5		58796.6		4	5.8	21	5	0		58521		17.2	2.6
Cr	97	24	5		78.02		10.9	4	27	7	0		73.22		10.8	3.1	44	10	0		80.18		19.6	5.4
Co	57	15	0		3.99		57.3	8.6	12	4	0		5.43		48.1	52.5	30	7	0		3.41		49.5	10.7
Cu	100	24	1		96479.8		12.9	3.5	31	8	0		93526.1		6.3	1.4	40	10	5		94191.3		9.5	2
Fe	85	21	3		4449.03		10.8	3.5	26	7	0		4437.73		4.2	2.3	47	11	0		4125.21		13.8	6.9
Pb	100	24	3		9339.37		10.9	2.8	31	8	0		9323.84		3.5	1.2	42	10	5		9739.83		10.2	3.3
Mg	60	14	0		2309.07		14.2	4.2	21	6	4		2177.29		5	2.9	21	5	0		1992.14		19	5.6
Mn	96	24	1		591.06		12	3.2	31	8	0		583.76		3.6	1.4	50	12	1		590.52		8.8	3
Hg	43	11	0		0.33		121.4	27	16	4	0		0.36		32.9	6.2	23	5	0		0.15		66	11.3
Mo	26	7	6		4.31		10.2	6.4	20	5	0		4.91		49.9	9.5	15	4	0		3.65		12	6.9
Ni	104	26	1		1727.32		10.4	3.2	26	7	5		1719.96		5.5	1.7	49	11	0		1710.41		25.1	5.8
P	18	4	10		4724.51		3.8	6.3	22	5	0		5834.64		33.9	5.6	13	3	0		4012.85		24.7	6.7
K	48	12	4		629.48		39.1	6.8	11	3	0		436.27		31.7	5.5	21	5	0		467.76		58.6	3.8
Se	26	6	0		5.52		99	16.5	2	1	0		10		0	0	9	2	0		2.78		81	0
Ag	28	7	0		10.53		14.7	13.1	18	4	0		7.73		20.5	11.8	18	4	0		9.68		21	7
S	26	6	0		61982.3		8.8	1.7	7	2	0		60495.7		2.6	2.5	10	2	0		59697.9		12.8	1.8
Na	64	15	0		11040.6		22.7	6	7	2	0		12595.7		7.7	1.3	28	6	1		11805.5		10.8	4.3
Sr	41	10	10		200.79		5.6	2.4	15	4	0		197.3		3.3	2.2	18	4	0		195.16		9.5	2.2
Sn	35	8	5		19154.7		5.2	6.6	15	4	0		16768.4		15.1	5.1	14	3	0		17840		18.2	1.8
Te	9	2	0		7.78		36.2	0	9	2	0		1.44		38.9	0	10	2	0		7.5		35.1	0
Tl	11	3	7		1.81		9.8	11.1	11	3	0		3		173.2	0	9	2	0		7.22		38.9	0
Ti	21	5	3		29.78		28.2	8.9	8	3	9		26.34		10.1	0.5	12	3	0		24.64		35.7	3
V	31	8	23		5.75		12.3	2.2	22	6	0		6.09		89.4	31.7	22	5	5		8.32		70.4	24.1
Zn	103	25	0		230.12		34.2	5.5	31	8	0		323.33		44.6	7	52	12	1		209.32		34.1	22.2

N = Number of results, L = Number of laboratories, NA = Number of outliers, XREF = Conventional true value (where applicable)

SAMPLE CEN10/99 "SEWAGE SLUDGE" (BCR 146R)																								
	Method A: Microwave assisted with aqua regia in closed vessel								*Method - B: Microwave assisted, with aqua regia in semi-open vessel*								*Method C: Thermal heating, with aqua regia in reflux systems*							
						%	%	%						%	%	%						%	%	%
	N	**L**	**NA**	**XREF**	**Mean**	**Recov**	**Reprod**	**Repeat**	**N**	**L**	**NA**	**XREF**	**Mean**	**Recov**	**Reprod**	**Repeat**	**N**	**L**	**NA**	**XREF**	**Mean**	**Recov**	**Reprod**	**Repeat**
Al	79	20	0	25130	20690.2	82.3	19.1	6	20	6	1	25130	18942.7	75.4	13.7	2.1	37	9	0	25130	21230.3	84.5	25.4	5.4
Sb	32	8	4	16.25	9.23	56.8	21.1	7.4	17	5	0	16.25	9.1	56	57.4	5.6	19	5	0	16.25	7.24	44.6	55.8	4.8
As	56	14	0	6.3	6.33	100.4	50.9	15.8	15	4	0	6.3	8.61	136.6	33.4	11.6	33	8	0	6.3	6.32	100.2	49.9	37.9
B	23	6	0		38.18		36.8	15.4	11	3	0		30.87		33.8	6	15	4	0		21.9		15	16.8
Ba	63	15	0	735	572.84	77.9	20	4.6	19	5	1	735	391.83	53.3	16.9	7.7	23	5	0	735	479.31	65.2	13.9	13.7
Be	31	7	2		0.79		10.5	5.5	18	4	0		1.1		53.3	4.2	18	4	0		1.05		31.4	7.2
Cd	86	21	14	18.76	17.16	91.5	8.6	4.5	22	6	4	18.76	15.75	84	13	2.3	49	12	0	18.76	16.51	88	14.9	9.1
Ca	60	14	0	154600	140455	90.9	8.7	3.7	18	5	5	154600	145312	94	7.3	1.4	27	6	1	154600	154356	99.8	17	4.4
Cr	107	26	0	196	164.91	84.1	13.4	3.4	27	8	4	196	157.48	80.3	12.3	4.4	49	11	4	196	165.94	84.7	14	3.3
Co	66	17	0	7.39	6.05	81.8	19.2	5.7	22	7	0	7.39	7.59	102.8	37.4	22.5	41	10	0	7.39	6.13	82.9	33.7	7.7
Cu	116	28	0	837.9	804.93	96.1	13.1	7.2	35	10	5	837.9	798.91	95.3	9.4	2.3	34	8	9	837.9	771.47	92.1	3.7	2.8
Fe	93	23	0	16100	13906.8	86.4	11.4	3.6	21	6	5	16100	13922.4	86.5	6.8	1.9	38	9	5	16100	13508.3	83.9	11.6	4.8
Pb	102	25	0	608.7	534.3	87.8	13.4	3.4	31	8	0	608.7	562.93	92.5	7.6	1.7	46	11	5	608.7	541.77	89	10.8	3.8
Mg	64	15	0	10460	9031.16	86.3	9.3	3.3	21	6	5	10460	8449.24	80.8	8.1	1.9	30	7	1	10460	9446.1	90.3	17.8	8.5
Mn	96	24	0	323.5	274.45	84.8	10.6	2.8	37	9	0	323.5	281.41	87	8.6	1.6	47	11	0	323.5	265.87	82.2	14.1	3.1
Hg	45	11	0	8.62	7.44	86.3	23.9	10.3	18	5	0	8.62	8.73	101.3	16.8	6.9	35	8	0	8.62	7.21	83.6	26	11.4
Mo	32	8	4		7.95		8.1	5.2	17	5	0		8.09		29.6	5.7	16	4	0		8.67		13.2	2.9
Ni	105	26	4	69.7	61.25	87.9	18.7	4.6	31	8	0	69.7	59.17	84.9	15.3	2.7	53	12	0	69.7	58.4	83.8	17.3	5.4
P	31	7	1	25600	27626	107.9	2.4	2.9	24	6	0	25600	30286.2	118.3	17.5	5	18	4	0		6068.72		8.1	4.3
K	56	14	0	5240	2025.58	38.7	34.7	17.3	16	5	1	5240	1306.19	24.9	24.8	9.4	30	7	5	5240	1313.79	25.1	33.7	5.3
Se	26	6	0		5.46		62.4	10.3	11	3	0		3.48		141.7	4.6	6	2	0		4.22		41.1	0
Ag	38	9	0		190.91		23.1	1.9	24	6	0		205.89		6.6	5.2	18	4	1		198.75		4.4	1.1
S	26	6	0	10620	9188.44	86.5	17.7	2.4	2	1	0		9180		0	0	10	2	0	10620	9021.6	84.9	15.4	8.7
Na	44	11	6	1804	777	43.1	28.1	4.3	6	2	0		481.82		5.9	10.1	41	9	0	1804	701.27	38.9	55.2	18.3
Sr	46	11	5	1179	1027.18	87.1	4.9	2	11	3	1	1179	975.11	82.7	4.4	2.4	19	4	0	1179	1019.59	86.5	10.6	1.3
Sn	30	7	3	95.8	59.79	62.4	32.5	6.3	15	4	0	95.8	61.15	63.8	33	3.8	14	3	0	95.8	63.94	66.7	28.6	4.6
Te	9	2	0		7.78		36.2	0	9	2	0		1.44		38.9	0	9	2	0		7.78		36.2	0
Tl	29	7	0	2771	302.74	10.9	58	21.7	21	6	0	2771	182.77	6.6	59.4	19	14	3	0	2771	183.56	6.6	34.1	7.2
Ti	22	5	0		3.54		44.6	4.3	15	4	0		1.68		127.5	2	9	2	0		3		84.5	0.8
V	50	12	8	42.7	34.08	79.8	8.4	3.5	14	4	8	42.7	27.76	65	3.4	2.8	31	7	0	42.7	41.21	96.5	56.3	4.9
Zn	105	26	7	3061	2858.47	93.4	8.9	4.1	31	8	0	3061	2761.77	90.2	7.1	3.1	47	11	6	3061	2819.79	92.1	11.6	6.4

N = Number of results, L = Number of laboratories, NA = Number of outliers, XREF = Conventional true value (where applicable)

E. Reproducibility % values of "cleaned data sets" Inter-laboratory validation of EN 13656 and EN 13657

Table 3 Comparison of reproducibility for all the samples used in the round robin test for validation of EN 13567

	Clean metals solution (analysis only)	Pre-digested fly ash (CW6) (analysis only)	Powder fly ash (CW6) (digestion + analysis)	Pre-digested ash (CW4) (analysis only)	Powder ash (CW4) (digestion + analysis)	Pre-digested ink sludge (CW12) (analysis only)	Powder ink sludge (CW12) (digestion + analysis)	Pre-digested sludge (SL11) (analysis only)	Powder sludge (SL11) (digestion + analysis)
Al	9.3	10.5	25.4	13.9	17.7	18.1	22.4	10.4	6.7
Sb	11.4	25.1	24.4	22.6	20	62.1	89.8	21.5	103.9
As	13.2	29.8	30.6	28.8	27.6	25.5	52.5	25.9	78.1
B	36.2	9.1	16.2	8.8	9.4	72.5	68.7	13.1	15.6
Ba	6.5	41.1	36.8	31.7	108.8	9.8	18.9	65.9	8.6
Be	11.3	50.8	11.7	19.9	17.4	109.5	116.9	22.6	147.8
Cd	10.1	11.3	14.1	11.8	12.7	13.5	112	20.5	32.1
Ca	9.5	11.8	14.2	13.3	12.9	10.2	7.9	6	11
Cr	6.3	14.7	12.1	13.7	17.6	13.8	11.4	15	10.2
Co	9.3	28.6	27.9	18.9	22.6	29.9	22.5	18.7	24.9
Cu	9.5	10	20.3	7.5	13	7.8	10.3	12.4	13.2
Fe	9.1	14.2	12.6	9.8	11	9.5	11.8	15.1	11
Pb	7.9	13.3	11.5	8.7	10.8	7.7	8.6	25	11.2
Mg	9.3	7.7	8.8	8.6	12.6	12.1	25.9	5.2	14.2
Mn	7.8	13.9	12.7	13.2	12	11.7	11.9	20.5	12.2
Hg	11.7	28.4	37.4	15.8	17.2	11.1	48.9	45.2	52.7
Mo	4.5	19.3	9.6	14.7	9.8	17.2	70.4	31.6	11.1
Ni	7.3	16.2	13	13.3	19.2	19	31.8	10	10.6
P	16.9	20.4	5.8	6	2.3	10	3.2	24.5	3.8
K	63.6	13.2	9.5	23.3	12.2	18.9	47.9	44.9	39.1
Se	10.7	10.8	8.9	15.1	12.1	37.2	206.7	19.9	110.2
Ag	99.4	27.8	17.3	42.8	24.9	22.3	73.6	24.2	14.7
S	9.5	11.7	10.3	6.9	24.2	9.6	9.4	2.9	8.8
Na	29.9	12	12.5	14.4	20.1	14.7	22.4	16.8	22.7
Sr	7	13.9	11.5	14.2	13.5	15	14.5	11.1	5.6
Sn	10.2	54.9	7.9	11.7	10.6	40.1	147	63.3	5.2
Te	61.9	77.5		8.4		0		4.3	
Tl	9.7	109	82.8	104.5	103.8	36.1	75.8	23.2	203
Ti	5.9	35.7	14.2	22.9	23.8	34.5	4.2	50.2	28.2
V	13	38.9	14.9	21.3	13.1	30.6	34.2	21.7	17.6
Zn	12	12.1	9.9	13.4	12.1	9.9	11.5	23.7	34.9
Average	17.4	25.6	18.2	18.7	21.5	23.9	46.4	23.1	35.6