Electronic Supplementary Information (ESI)

A comparison of calibration strategies for quantitative laser ablation ICP-mass spectrometry (LA-ICP-MS) analysis of fused catalyst samples

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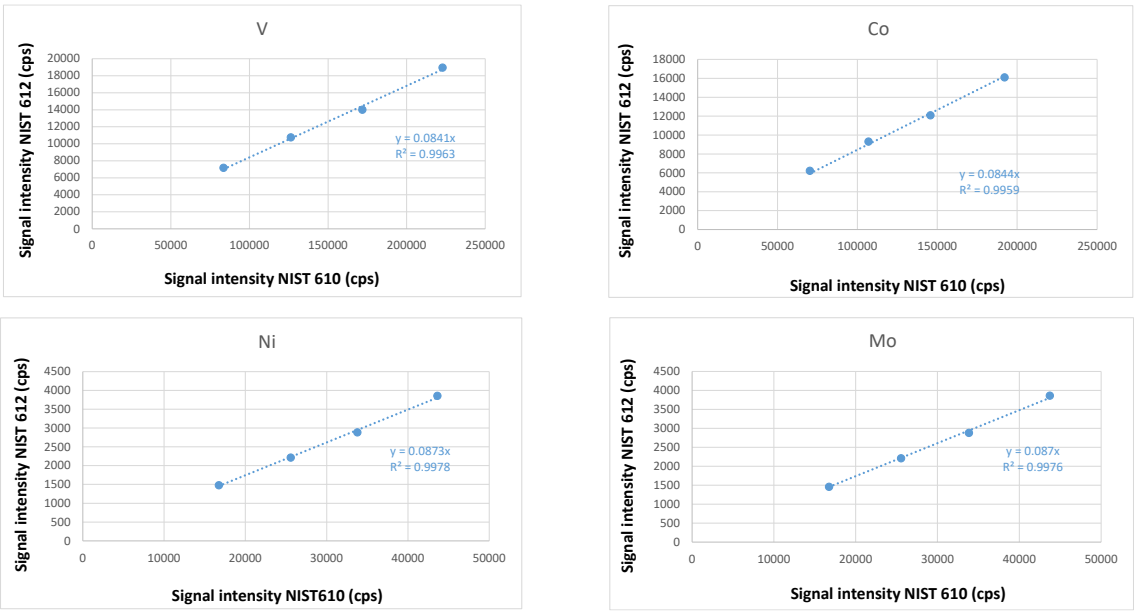
(A) Repetition rate



(B) Beam diameter

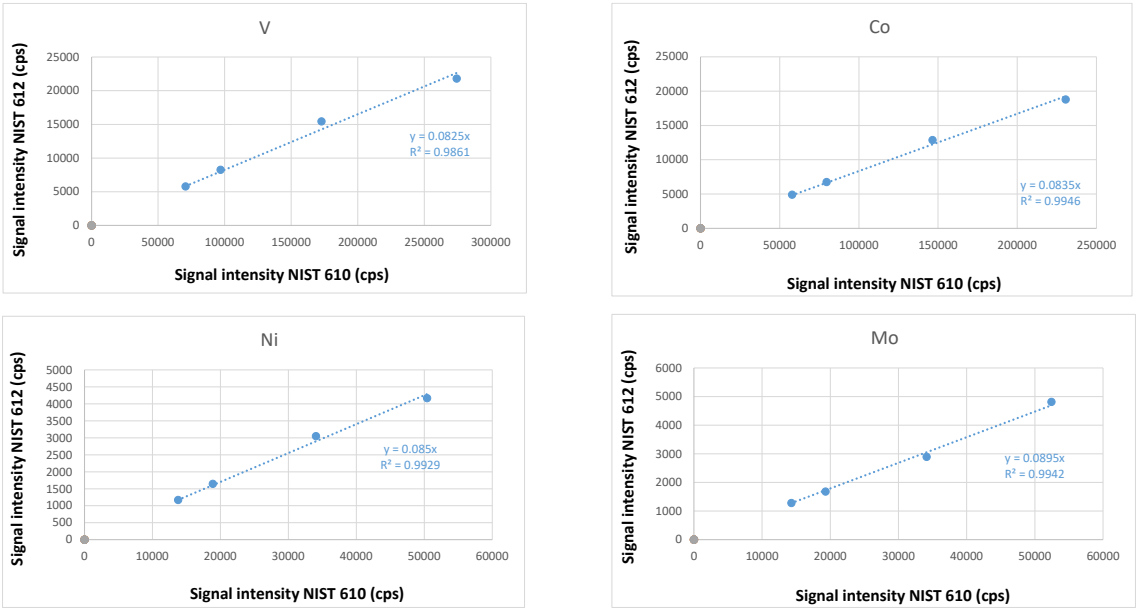
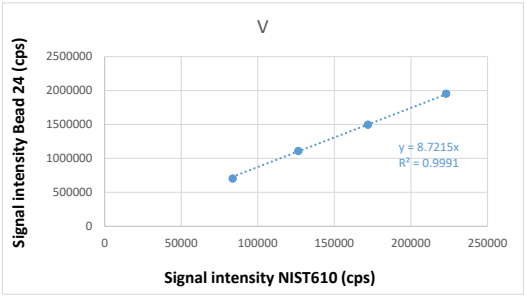
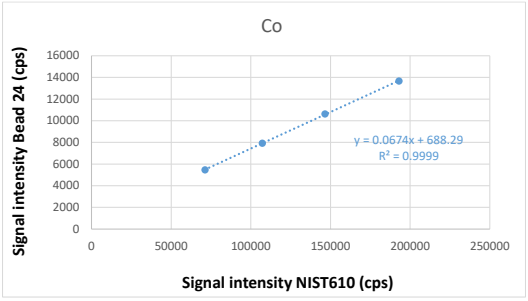
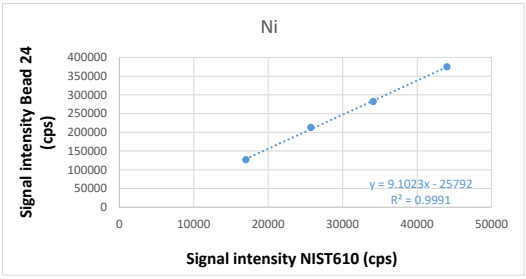


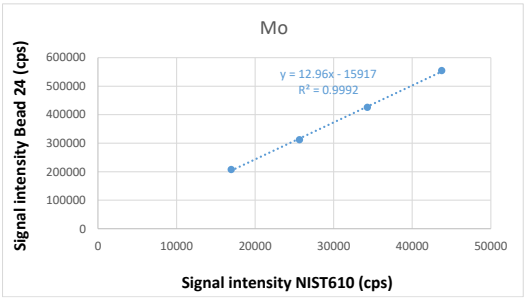
Figure S2. Examples of the correlation lines obtained with the MSC approach when measuring one catalyst sample and using a CRM as standard (Bead 24 vs NIST SRM 610) for all analytes upon modification of the repetition rate (A) and the beam diameter (B).

(A) Repetition rate

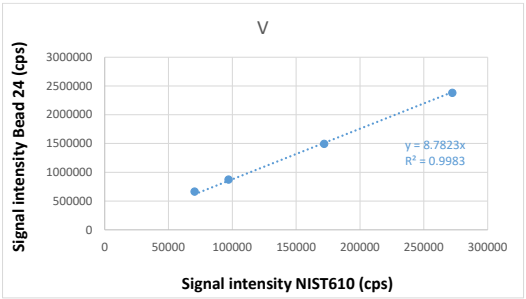


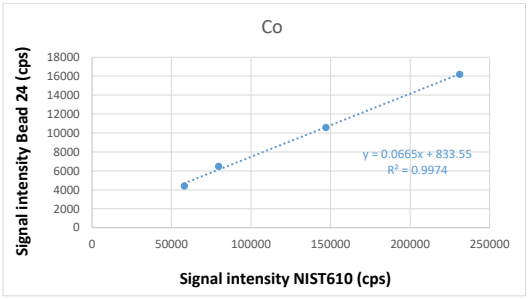


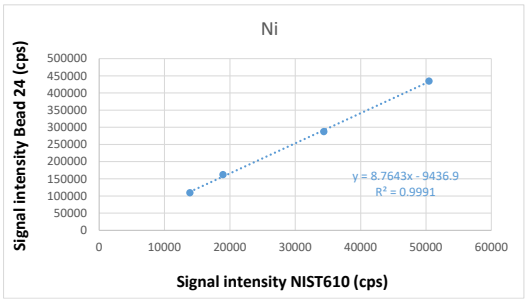




(B) Beam diameter







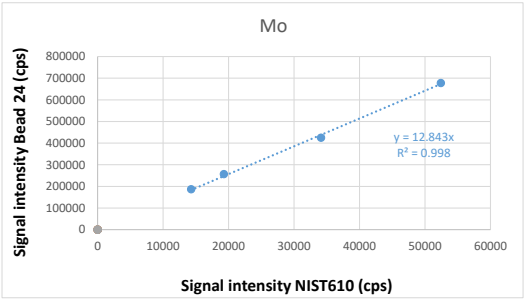
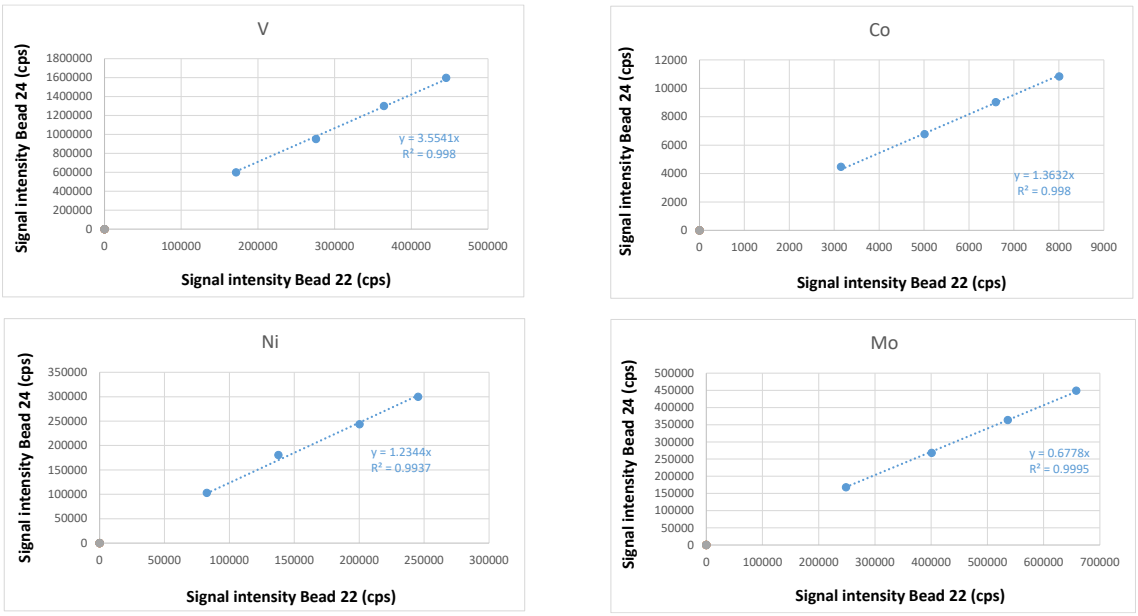


Figure S3. Examples of the correlation lines obtained with the MSC approach when measuring one catalyst as sample and the other catalyst as standard (Bead 24 vs Bead 22) for all analytes upon modification of the repetition rate (A) and the beam diameter (B).

(A) Repetition rate



(B) Beam diameter

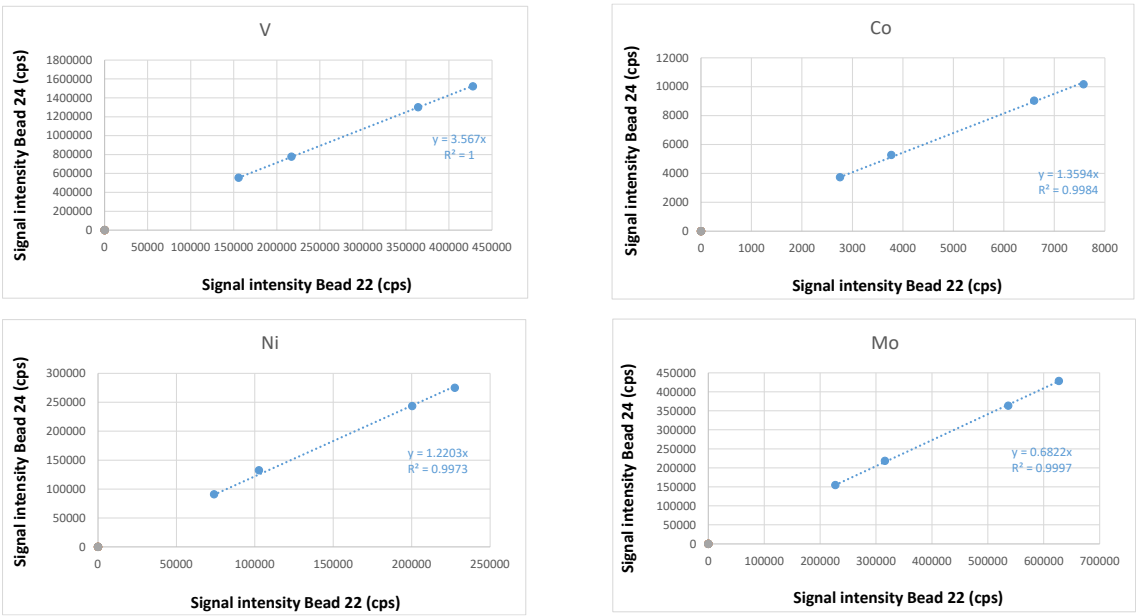
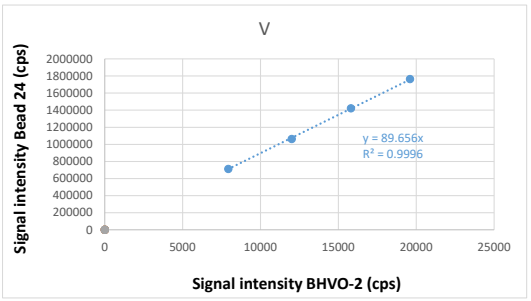
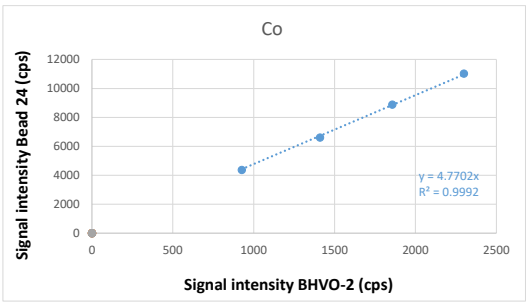
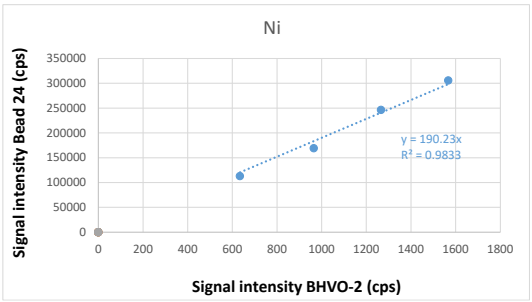


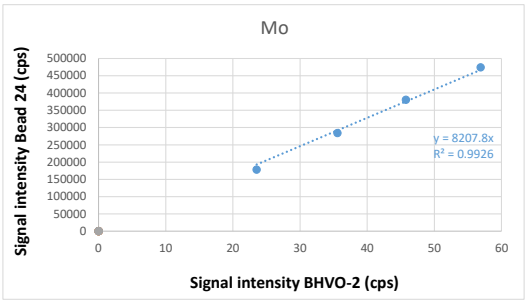
Figure S4. Examples of the correlation lines obtained with the MSC approach when measuring one catalyst sample and using a fused bead obtained from a powdered CRM as standard (Bead 24 vs BHVO-2) for all analytes upon modification of the repetition rate (A) and the beam diameter (B).

(A) Repetition rate

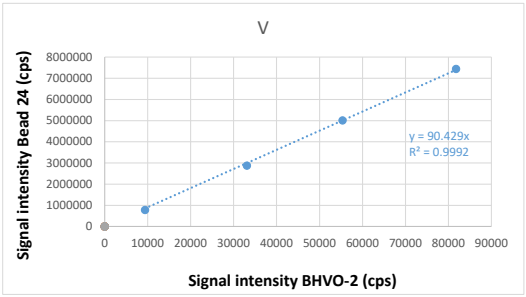


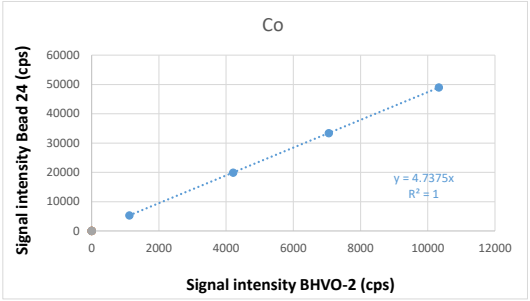


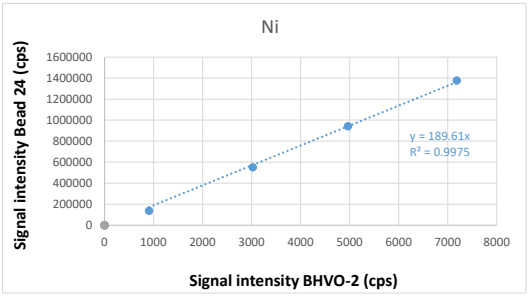




(B) Beam diameter







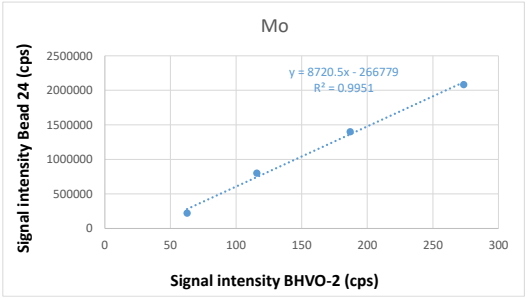


Table S1. Target element concentration data for the two catalyst samples obtained by XRF.

	V (mg kg^{-1})	Co (mg kg^{-1})	Ni (mg kg^{-1})	Mo (mg kg^{-1})
Bead 22	1290 ± 130	27.30 ± 2.73	3370 ± 337	9100 ± 910
Bead 24	4660 ± 470	36.70 ± 3.67	4050 ± 405	5920 ± 592

Table S2. Reference concentration values of Li, V, Co, Ni and Mo for the glass standard reference materials. Uncertainty expressed as 95 % confidence level.[1]

			Concentration (mg kg^{-1})				
			Li	**V**	**Co**	**Ni**	**Mo**
MPI-DING ATHO-G	**Rhyolite glass**	**value**	28.6	3.91	2.13	13	4.8
		uncertainty	1.8	0.34	0.47	5	1
NIST SRM 612	**Synthetic glass**	**value**	40.2	38.8	35.5	38.8	37.4
		uncertainty	1.3	1.2	1	0.2	1.5
USGS GSD-1G	**Basalt glass**	**value**	43	44	40	58	39
		uncertainty	6	2	2	4	3
MPI-DING T1-G	**Diorite glass**	**value**	19.9	190	18.9	10.6	4.2
		uncertainty	0.9	11	0.8	1.3	1.8
USGS BHVO-2G	**Basalt glass**	**value**	4.4	308	44	116	3.8
		uncertainty	0.8	19	2	7	0.2
BIR-1G	**Basalt glass**	**value**	3.0	326	52	178	0.075
		uncertainty	0.7	32	5	18	0.011
USGS BCR-2G	**Basalt glass**	**value**	9	425	38	13	270
		uncertainty	1	18	2	2	30
USGS GSE-1G	**Basalt glass**	**value**	430	440	380	440	390
		uncertainty	60	20	20	30	30
NIST SRM 610	**Synthetic glass**	**value**	468	450	410	458.7	417
		uncertainty	24	9	10	4.0	21
USGS BHVO-2	**Hawaiian basalt**	**value**	4.50	318.2	44.89	119.8	4.07
		uncertainty	0.085	2.3	0.32	1.2	0.16

Table S3. Experimentally determined concentrations (LA-ICP-MS) for the CRMs using external calibration as calibration strategy.

	V (mg kg^{-1})	Co (mg kg^{-1})	Ni (mg kg^{-1})	Mo (mg kg^{-1})
ATHO-G	7.54 ± 8.19	3.12 ± 3.95	12.0 ± 6.4	4.30 ± 8.18
NIST SRM 612	49.3 ± 8.2	40.1 ± 3.9	47.3 ± 6.2	40.1 ± 8.1
GSD-1G	48.2 ± 8.6	39.4 ± 4.1	62.1 ± 7.5	36.3 ± 8.5
T1-G	167 ± 14	18.3 ± 3.9	13.3 ± 6.3	5.50 ± 8.09
BHVO-2G	307 ± 17	42.8 ± 4.1	116 ± 9	4.31 ± 8.08
BIR-1G	274 ± 21	43.8 ± 4.1	145 ± 14	< LoQ
BCR-2G	457 ± 13	42.1 ± 3.9	16.3 ± 6.3	270 ± 12
GSE-1G	405 ± 18	345 ± 7	409 ± 19	352 ± 18
NIST SRM 610	498 ± 9	443 ± 6	500 ± 9	452 ± 10

Table S4. Experimentally determined concentrations (LA-ICP-MS) for the two catalyst samples using external calibration as calibration strategy.

		V (mg kg^{-1})	Co (mg kg^{-1})	Ni (mg kg^{-1})	Mo (mg kg^{-1})
Bead 22	**Without IS**	928 ± 31	21.8 ± 4.0	2550 ± 94	6130 ± 213
	With IS	1220 ± 14	29.1 ± 4.0	3110 ± 22	7690 ± 25
Bead 24	**Without IS**	3930 ± 110	31.7 ± 4.0	3660 ± 112	5000 ± 155
	With IS	4330 ± 50	35.7± 3.9	3760 ± 25	5270 ± 43

Table S5. Experimentally determined (LA-ICP-MS) concentration for the SRMs using the multi-signal calibration strategy (modification of the laser repetition rate or laser beam diameter). NIST SRM 610 was used as the ´reference standard´.

			V (mg kg^{-1})	Co (mg kg^{-1})	Ni (mg kg^{-1})	Mo (mg kg^{-1})
Repetition rate	**Without IS**	**NIST SRM 612**	35.3 ± 0.8	31.0 ± 1.2	37.9 ± 0.4	34.9 ± 1.8
		GSE-1G	404 ± 12	365 ± 10	431 ± 13	366 ± 21
		GSD-1G	38.5 ± 3.3	35.0 ± 2.9	58.2 ± 6.3	36.2 ± 3.7
		BHVO-2G	264 ± 9.4	35.1 ± 2.0	103 ± 4.7	3.38 ± 0.22
	With IS	**NIST SRM 612**	36.7 ± 1.4	32.4 ± 1.0	39.5 ± 1.0	36.3 ± 2.0
		GSE-1G	419 ± 10	380 ± 15	446 ± 4.9	380 ± 19
		GSD-1G	39.9 ± 2.2	36.1 ± 2.2	60.3 ± 1.7	37.5 ± 2.3
		BHVO-2G	313 ± 8	41.6 ± 1.2	121 ± 1.1	3.99 ± 0.20
Spot size	**Without IS**	**NIST SRM 612**	31.8 ± 2.2	27.1 ± 3.2	36.5 ± 2.0	36.1 ± 1.8
		GSE-1G	376 ± 8.6	335 ± 8.2	391 ± 20	352 ± 18
		GSD-1G	39.8 ± 1.2	37.3 ± 1.1	53.8 ± 1.8	35.9 ± 2.1
		BHVO-2G	262 ± 12	40.5 ± 1.0	101 ± 5.6	4.46 ± 1.6
	With IS	**NIST SRM 612**	35.5 ± 2.8	33.1 ± 1.7	37.8 ± 2.1	38.5 ± 2.7
		GSE-1G	452 ± 14	386 ± 10	451 ± 14	395 ± 24
		GSD-1G	42.3 ± 0.9	41.5 ± 1.0	58.5 ± 3.6	38.8 ± 2.9
		BHVO-2G	301 ± 6.1	43.1 ± 1.1	119 ± 4.4	4.17 ± 1.5

Table S6. Experimentally determined (LA-ICP-MS) concentrations for the two catalyst samples obtained using the multi-signal calibration strategy (modification of the laser repetition rate or laser beam diameter) with five reference materials used as reference standards.

	Bead 22		V (mg kg^{-1})	Co (mg kg^{-1})	Ni (mg kg^{-1})	Mo (mg kg^{-1})
Repetition rate	Without IS	NIST SRM 610	884 ± 59	16.3 ± 1.4	2840 ± 185	6350 ± 473
		GSE-1G	962 ± 78	16.9 ± 1.8	2900 ± 250	6750 ± 659
		BHVO-2G	1030 ± 86	20.4 ± 1.5	3210 ± 215	7130 ± 509
		NIST SRM 612	972 ± 64	18.6 ± 1.1	2900 ± 172	6800 ± 437
		GSD-1G	990 ± 146	18.2 ± 3.9	2730 ± 507	667 ± 1096
	With IS	NIST SRM 610	1110 ± 37	20.4 ± 0.8	3540 ± 87	7940 ± 412
		GSE-1G	1160 ± 56	20.5 ± 1.3	3440 ± 245	8100 ± 626
		BHVO-2G	1030 ± 66	20.5 ± 1.0	3130 ± 199	7110 ± 404
		NIST SRM 612	1170 ± 44	22.5 ± 0.7	3500 ± 127	8190 ± 347
		GSD-1G	1230 ± 77	22.8 ± 1.3	3400 ± 263	8330 ± 706
Spot size	Without IS	NIST SRM 610	909 ± 41	17.7 ± 0.6	2880 ± 81	6430 ± 401
		GSE-1G	1030 ± 124	19.7 ± 2.1	3170 ± 223	7280 ± 849
		BHVO-2G	977 ± 79	19.4 ± 1.2	3010 ± 187	7500 ± 1073
		NIST SRM 612	948 ± 39	17.8 ± 0.7	2740 ± 121	6720 ± 573
		GSD-1G	1000 ± 49	19.0 ± 0.9	2900 ± 229	7430 ± 277
	With IS	NIST SRM 610	1430 ± 30	24.0 ± 0.7	4090 ± 91	10300 ± 550
		GSE-1G	1100 ± 142	20.9 ± 2.4	3470 ± 487	8200 ± 1504
		BHVO-2G	1270 ± 90	27.6 ± 1.3	3990 ± 269	9160 ± 1360
		NIST SRM 612	1280 ± 41	24.1 ± 0.7	3700 ± 215	8190 ± 722
		GSD-1G	1230 ± 63	25.8 ± 1.5	3670 ± 325	9530 ± 760

	Bead 24		V (mg kg^{-1})	Co (mg kg^{-1})	Ni (mg kg^{-1})	Mo (mg kg^{-1})
Repetition rate	Without IS	NIST SRM 610	3670 ± 78	24.3 ± 0.8	3820 ± 109	4940 ± 250
		GSE-1G	4000 ± 218	25.3 ± 1.6	3890 ± 331	5250 ± 435
		BHVO-2G	4280 ± 303	30.4 ± 1.8	4290 ± 354	5540 ± 390
		NIST SRM 612	4040 ± 126	27.8 ± 0.8	3910 ± 97	5300 ± 219
		GSD-1G	4140 ± 385	27.4 ± 3.1	3700 ± 529	5250 ± 598
	With IS	NIST SRM 610	4060 ± 99	27.0 ± 0.7	4210 ± 93	5460 ± 289
		GSE-1G	4240 ± 199	27.2 ± 1.7	4090 ± 288	5570 ± 433
		BHVO-2G	3770 ± 240	27.3 ± 1.3	3730 ± 243	4880 ± 285
		NIST SRM 612	4300 ± 152	29.6 ± 1.0	4150 ± 123	5630 ± 231
		GSD-1G	4510 ± 295	30.1 ± 2.0	4050 ± 280	5730 ± 501
Spot size	Without IS	NIST SRM 610	3570 ± 87	25.5 ± 0.6	3790 ± 43	4970 ± 277
		GSE-1G	4620 ± 411	32.5 ± 2.1	4670 ± 543	6490 ± 889
		BHVO-2G	3800 ± 288	29.0 ± 1.2	3900 ± 249	7350 ± 387
		NIST SRM 612	3730 ± 156	26.9 ± 0.7	3600 ± 19.8	4980 ± 261
		GSD-1G	3960 ± 192	28.6 ± 0.9	3810 ± 264	5500 ± 426
	With IS	NIST SRM 610	3810 ± 94	27.5 ± 0.8	4050 ± 61	5300 ± 313
		GSE-1G	3660 ± 412	25.1 ± 2.0	3790 ± 524	5200 ± 967
		BHVO-2G	4590 ± 302	31.8 ± 2.7	4410 ± 389	6940 ± 889
		NIST SRM 612	4790 ± 217	34.2 ± 1.8	4480 ± 211	5210 ± 676
		GSD-1G	4880 ± 247	34.5 ± 1.9	4400 ± 358	5750 ± 663

Table S7. Experimentally determined (LA-ICP-MS) concentrations for one catalyst sample (Bead 22) using the multi-signal calibration strategy (modification of the laser repetition rate or laser beam diameter) with the other catalyst sample (Bead 24) used as reference standard.

			V (mg kg^{-1})	Co (mg kg^{-1})	Ni (mg kg^{-1})	Mo (mg kg^{-1})
Bead 22	**Repetition rate**	**Without IS**	1120 ± 132	24.6 ± 2.9	3010 ± 356	7600 ± 887
		With IS	1270 ± 131	27.8 ± 2.8	3410 ± 374	8610 ± 867
	Spot size	**Without IS**	1180 ± 119	24.3 ± 2.5	3080 ± 339	8000 ± 808
		With IS	1310 ± 132	27.6 ± 2.8	3410 ± 346	8690 ± 872

Table S8. Experimentally determined (LA-ICP-MS) concentrations vs reference (XRF) concentrations for the two catalyst samples using the multi-signal calibration strategy (modification of the laser repetition rate or laser beam diameter) with a fused bead of powdered BHVO-2 reference material (embedded as fused bead) used as reference standard.

			V (mg kg^{-1})	Co (mg kg^{-1})	Ni (mg kg^{-1})	Mo (mg kg^{-1})
Bead 22	**Repetition rate**	**Without IS**	1000 ± 12	20.3 ± 0.4	2560 ± 382	6420 ± 199
		With IS	1290 ± 11	26.9 ± 0.4	3320 ± 190	8400 ± 386
	Spot size	**Without IS**	1110 ± 18	22.5 ± 0.3	2710 ± 43	6740 ± 725
		With IS	1330 ± 16	26.6 ± 0.4	3300 ± 17	8250 ± 731
Bead 24	**Repetition rate**	**Without IS**	3250 ± 60	24.7 ± 0.4	2880 ± 482	4120 ± 95
		With IS	4650 ± 63	35.4 ±- 0.4	4090 ± 223	5870 ± 144
	Spot size	**Without IS**	4280 ± 107	31.0 ± 0.1	3470 ± 38	5160 ± 281
		With IS	4730 ± 115	34.5 ± 0.1	3850 ± 35	5720 ± 314

Table S9. Experimentally determined (LA-ICP-MS) concentrations for the two catalyst samples using the solution-based calibration approach.

	V (mg kg^{-1})	Co (mg kg^{-1})	Ni (mg kg^{-1})	Mo (mg kg^{-1})
Bead 22	1320 ± 87	26.6 ± 4.6	3500 ± 138	9700 ± 398
Bead 24	4540 ± 108	36.2 ± 2.7	4350 ± 100	6370 ± 146

References

1. K. P. Jochum, U. Nohl, K. Herwig, E. Lammel, B. Stoll and A. W. Hofmann, *Geostand. Geoanalytical Res.*, 2005, **29**, 333 – 338.