Handheld Laser-Induced Breakdown Spectroscopy (LIBS) as a fast and easy method to trace gold

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Supplementary Material (ESI)

Table 1S

Values of the Ag content (wt. %) of the commercial gold alloys

	Reference[1]	EPMA			
		Mean (n=5)	Stdev	RSD (%)	SE (%)
18K2N	16	16.50	0.25	1.51	0.68
18K3N	12.5	12.73	0.14	1.12	0.50
18K4N	9	9.04	0.14	1.58	0.71
18K5N	4.5	4.79	0.09	1.81	0.81
18KPd13	1	0.95	0.04	3.91	1.75
24K	0.01	< LOD			

[1] Value of the Ag content provided by the refiners. LOD corresponds to limit of detection

Table 2S

Analytical values of normalised intensity of the peak at 546.58 nm with their descriptive statistics: mean, relative standard deviation (RSD) and standard error of the mean (SE)

	Normalised intensity (a.u.)	Mean	RSD (%)	SE (%)
24K-shot1	0.07232			
24K-shot2	0.07341			
24K-shot3	0.07363			
24K-shot4	0.07089			
24K-shot5	0.05989			
24K-shot6	0.05779	0.061	15.757	4.751
24K-shot7	0.05859			
24K-shot8	0.05070			
24K-shot9	0.05288			
24K-shot10	0.05596			
24K-shot11	0.05707			
24K-shot12	0.07912			
24K-shot13	0.05665			
24K-shot14	0.05670			
24K-shot15	0.04937			
24K-shot16	0.05035			
18KPd13-shot1	0.32801			
18KPd13-shot2	0.32725			
18KPd13-shot3	0.32806			
18KPd13-shot4	0.31372			
18KPd13-shot5	0.31189			
18KPd13-shot6	0.30387	0.315	8.670	2.614
18KPd13-shot7	0.30324			
18KPd13-shot8	0.29982			
18KPd13-shot9	0.30394			
18KPd13-shot10	0.28117			
18KPd13-shot11	0.26834			
18KPd13-shot12	0.33834			
18KPd13-shot13	0.32300			
18KPd13-shot14	0.31948			
18KPd13-shot15	0.30262			
18KPd13-shot16	0.30112			
18KPd13-shot17	0.39561			
18K5N-shot1	1.49144			
18K5N-shot2	1.47051			
18K5N-shot3	1.49959			
18K5N-shot4	1.38684			
18K5N-shot5	1.40501			
18K5N-shot6	1.36111	1.382	5.232	1.578
18K5N-shot7	1.31230			

18K5N-shot8	1.30107			
18K5N-shot9	1.26729			
18K5N-shot10	1.26579			
18K5N-shot11	1.44854			
18K5N-shot12	1.37668			
18K5N-shot13	1.38613			
18K5N-shot14	1.35711			
18K5N-shot15	1.37295			
18K5N-shot16	1.40498			
18K4N-shot1	2.75475			
18K4N-shot2	2.63509			
18K4N-shot3	2.58304			
18K4N-shot4	2.56556			
18K4N-shot5	2.61189			
18K4N-shot6	2.54293	2.566	7.394	2.229
18K4N-shot7	2.56877			
18K4N-shot8	2.24512			
18K4N-shot9	2.25469			
18K4N-shot10	2.79752			
18K4N-shot11	2.49991			
18K4N-shot12	2.80484			
18K4N-shot13	2.79263			
18K4N-shot14	2.74117			
18K4N-shot15	2.59949			
18K4N-shot16	2.37974			
18K4N-shot17	2.24982			
18K3N-shot1	4.01866			
18K3N-shot2	3.66264			
18K3N-shot3	3.79269			
18K3N-shot4	3.94133			
18K3N-shot5	3.85932			
18K3N-shot6	3.88452	3.745	7.191	2.168
18K3N-shot7	3.90590			
18K3N-shot8	3.31041			
18K3N-shot9	3.23018			
18K3N-shot10	3.72033			
18K3N-shot11	3.60712			
18K3N-shot12	4.02442			
18K3N-shot13	3.62054			
18K3N-shot14	4.03968			
18K3N-shot15	3.97373			
18K3N-shot16	3.23166			
18K3N-shot17	3.84467			
18K2N-shot1	5.32011			
18K2N-shot2	5.18161			
18K2N-shot3	4.99852			
18K2N-shot4	5.00672			
18K2N-shot5	5.18080			

18K2N-shot6	5.12410	4.939	4.808	1.450
18K2N-shot7	4.93599			
18K2N-shot8	4.72360			
18K2N-shot9	4.61360			
18K2N-shot10	4.54820			
18K2N-shot11	4.46399			
18K2N-shot12	5.20204			
18K2N-shot13	5.01905			
18K2N-shot14	4.98887			
18K2N-shot15	5.03402			
18K2N-shot16	4.94525			
18K2N-shot17	4.80710			
18K2N-shot18	4.80318			

Table 3S

EPMA analyses of the Ag content (wt. %) of the gold from the studied French Guiana populations

"Marc" creek					
	Ag (%)		Ag (%)		Ag (%)
A7-1	2.374	B2-1	5.315	X2-1	11.136
A7-2	5.886	B2-2	11.671	X2-2	5.028
A7-3	2.108	B2-3	3.700	X2-3	4.042
A7-4	22.603	B2-4	5.300	X2-4	2.571
A7-5	7.469	B2-5	4.763	X2-5	4.026
A7-6	6.615	B2-6	3.770	X2-6	7.350
A7-7	5.776	B2-7	8.346	X2-7	4.822
A7-8	2.072	B2-8	6.933	X2-8	4.011
A7-9	5.199	B2-9	4.740	X2-9	4.787
A7-10	12.606	B2-10	3.599	X2-10	2.699
A7-11	15.446	B2-11	8.551	X2-11	2.851
A7-12	1.962	B2-12	11.847	X2-12	8.490
A7-13	9.123	B2-13	3.820	X2-13	2.879
A7-14	8.756	B2-14	4.868	X2-14	9.426
A7-15	3.859	B2-15	3.613	X2-15	5.046
		B2-16	6.543	X2-16	2.762
				X2-17	3.972
				X2-18	7.880

"Petit Inini" river					
	Ag (%)		Ag (%)		Ag (%)
33-1	7.659	39-1	6.146	43-1	12.373
33-2	6.915	39-2	6.944	43-2	8.5
33-3	10.194	39-3	6.237	43-3	7.551
33-4	8.684	39-4	7.778	43-4	8.438
33-5	7.091	39-5	7.369	43-5	6.138
33-6	12.096	39-6	7.602	43-6	7.476
33-7	9.55	39-7	6.231	43-7	7.811
33-8	8.103	39-8	6.1	43-8	9.338
33-9	6.269	39-9	11.508	43-9	6.137
33-10	8.244	39-10	4.835	43-10	6.078
33-11	19.05	39-11	7.108	43-11	6.225
33-12	10.388	39-12	8.392	43-12	11.601
33-13	7.446	39-13	2.582	43-13	8.809
33-14	7.115	39-14	9.208	43-14	7.167
33-15	7.87	39-15	6.302	43-15	6.27
33-16	6.712	39-16	12.548	43-16	7.021
33-17	6.913	39-17	8.225	43-17	7.033
33-18	9.629	39-18	7.265	43-18	7.584

33-19	8.845	39-19	7.22	43-19	8.933
33-20	8.807	39-20	10.631		

“Serpent” creek

	Ag (%)		Ag (%)		Ag (%)
30-1	1.407	46-1	1.63	47-1	1.665
30-2	2.116	46-2	2.247	47-2	1.906
30-3	2.082	46-3	1.986	47-3	1.538
30-4	1.763	46-4	1.533	47-4	2.502
30-5	1.349	46-5	2.985	47-5	1.720
30-6	1.102	46-6	1.48	47-6	1.531
30-7	1.583	46-7	1.219	47-7	1.876
30-8	1.773	46-8	1.644	47-8	1.413
30-9	2.101	46-9	1.346	47-9	1.342
30-10	2.065	46-10	1.868	47-10	2.130
30-11	2.374	46-11	2.636	47-11	1.626
30-12	1.293	46-12	2.231	47-12	1.690
30-13	1.742	46-13	2.498	47-13	2.666
30-14	1.988	46-14	6.919	47-14	1.443
30-15	1.566	46-15	1.478	47-15	2.053
30-16	1.448	46-16	1.841	47-16	1.227
30-17	1.384	46-17	1.805	47-17	1.689
30-18	1.575	46-18	1.444	47-18	1.678
		46-19	1.497	47-19	1.661
		46-20	6.661	47-20	1.801
		46-21	2.025	47-21	2.557

“Dimanche” creek

	Ag (%)		Ag (%)		Ag (%)
23-1	4.485	26-1	3.991	29-1	3.848
23-2	1.884	26-2	4.354	29-2	2.091
23-3	4.463	26-3	3.800	29-3	1.023
23-4	2.668	26-4	7.642	29-4	3.446
23-5	2.351	26-5	4.970	29-5	2.807
23-6	1.91	26-6	3.641	29-6	3.531
23-7	1.999	26-7	0.946	29-7	4.172
23-8	2.982	26-8	1.919	29-8	4.188
23-9	6.117	26-9	4.788	29-9	3.302
23-10	4.135	26-10	4.583	29-10	1.989
23-11	4.206	26-11	3.924	29-11	3.261
23-12	6.573	26-12	3.085	29-12	5.112
23-13	2.418	26-13	1.877	29-13	3.575
23-14	3.529	26-14	1.751	29-14	3.484
23-15	2.901	26-15	1.638	29-15	4.836
23-16	2.764	26-16	2.501	29-16	2.291
23-17	3.811	26-17	1.668	29-17	2.320
23-18	2.286	26-18	3.384	29-18	4.948

23-19	2.677	26-19	1.798	29-19	3.642
23-20	5.78	26-20	2.324	29-20	3.510
23-21	2.245	26-21	2.239	29-21	2.485
23-22	2.29	26-22	4.456	29-22	1.850
23-23	3.297			29-23	5.175
23-24	2.157			29-24	7.578
23-25	2.613			29-25	2.371
23-26	8.514			29-26	3.847
				29-27	4.455
				29-28	4.857
				29-29	3.958

“Awa” creek	
	Ag (%)
37-1	16.774
37-2	7.134
37-3	6.577
37-4	5.168
37-5	6.24
37-6	11.019
37-7	5.71
37-8	11.387
37-9	5.672
37-10	6.617
37-11	7.083
37-12	5.884
37-13	5.961
37-14	8.664
37-15	12.311
37-16	6.755
37-17	7.089
37-18	6.633
37-19	6.094
37-20	6.796
37-21	7.315

Table 4S

LIBS analyses of the Ag content (wt. %) of the gold from the studied French Guiana populations

“Marc” creek					
	Ag (%)		Ag (%)		Ag (%)
A7-1	5.40	B2-1	5.82	X2-1	4.12
A7-2	4.57	B2-2	4.97	X2-2	12.72
A7-3	5.02	B2-3	5.04	X2-3	9.63
A7-4	6.32	B2-4	2.57	X2-4	4.61
A7-5	4.93	B2-5	2.54	X2-5	4.11
A7-6	13.09	B2-6	10.87	X2-6	6.54
A7-7	12.58	B2-7	4.48	X2-7	5.55
A7-8	1.08	B2-8	12.78	X2-8	4.38
A7-9	3.27	B2-9	10.78	X2-9	7.22
A7-10	1.31	B2-10	6.39	X2-10	4.31
A7-11	3.51	B2-11	6.18	X2-11	6.76
A7-12	1.42	B2-12	5.96	X2-12	3.34
A7-13	2.26	B2-13	10.42	X2-13	4.91
A7-14	5.83	B2-14	9.40	X2-14	3.76
A7-15	1.66	B2-15	3.11	X2-15	3.92
		B2-16	3.02	X2-16	3.77
		B2-17	6.31	X2-17	8.07
		B2-18	4.22	X2-18	8.22
		B2-19	3.91	X2-19	5.41
		B2-20	7.07	X2-20	5.20
		B2-21	7.35	X2-21	5.19
		B2-22	4.71	X2-22	5.20
		B2-23	2.83	X2-23	6.81
		B2-24	2.75	X2-24	3.48
		B2-25	8.53	X2-25	1.49
		B2-26	7.91	X2-26	1.52
		B2-27	7.64	X2-27	3.93
		B2-28	7.89	X2-28	3.65
		B2-29	10.79	X2-29	3.67
		B2-30	10.35	X2-30	3.59
		B2-31	9.81	X2-31	9.69
		B2-32	2.92	X2-32	8.70
		B2-33	3.01		
		B2-34	4.87		
		B2-35	6.62		
		B2-36	5.50		
		B2-37	3.35		
		B2-38	3.06		
		B2-39	4.86		
		B2-40	4.22		
		B2-41	4.37		

B2-42	2.86
B2-43	2.59
B2-44	2.87
B2-45	5.05
B2-46	2.59
B2-47	6.78
B2-48	5.35
B2-49	2.39
B2-50	2.22
B2-51	5.80
B2-52	5.84
B2-53	10.99
B2-54	11.40
B2-55	5.40
B2-56	11.16

“Petit Inini” river

	Ag (%)		Ag (%)		Ag (%)
33-1	7.41	39-1	6.44	43-1	9.28
33-2	2.46	39-2	7.15	43-2	8.58
33-3	9.13	39-3	7.60	43-3	7.20
33-4	8.83	39-4	11.17	43-4	7.92
33-5	8.43	39-5	5.32	43-5	9.42
33-6	6.98	39-6	9.77	43-6	6.06
33-7	6.11	39-7	7.89	43-7	13.91
33-8	7.52	39-8	7.71	43-8	8.05
33-9	7.16	39-9	6.31	43-9	6.73
33-10	7.13	39-10	6.98	43-10	6.40
33-11	7.45	39-11	6.84	43-11	9.32
33-12	13.33	39-12	6.78	43-12	6.89
33-13	7.60	39-13	5.12	43-13	6.22
33-14	7.32	39-14	5.34	43-14	6.87
33-15	10.88	39-15	8.09	43-15	9.43
33-16	7.70	39-16	8.58	43-16	8.19
33-17	6.41	39-17	6.01	43-17	7.65
33-18	6.46	39-18	12.12	43-18	7.83
33-19	8.75	39-19	7.41	43-19	8.23
33-20	8.85	39-20	2.25	43-20	7.68
33-21	6.66			43-21	8.03
33-22	2.75			43-22	7.71
				43-23	7.26
				43-24	6.67

“Serpent” creek					
	Ag (%)		Ag (%)		Ag (%)
30-1	1.40	46-1	1.29	47-1	1.44
30-2	1.57	46-2	1.32	47-2	1.76
30-3	1.08	46-3	1.74	47-3	1.71
30-4	0.82	46-4	1.48	47-4	1.68
30-5	1.25	46-5	1.23	47-5	1.66
30-6	1.06	46-6	1.01	47-6	2.69
30-7	0.83	46-7	1.31	47-7	1.45
30-8	3.16	46-8	1.07	47-8	1.85
30-9	2.90	46-9	2.87	47-9	2.79
30-10	1.60	46-10	2.79	47-10	2.49
30-11	1.84	46-11	2.72	47-11	1.77
30-12	1.84	46-12	1.30	47-12	1.63
30-13	1.80	46-13	1.82	47-13	1.44
30-14	2.11	46-14	1.40	47-14	1.52
30-15	1.29	46-15	1.33	47-15	1.44
30-16	1.67	46-16	1.34	47-16	1.92
30-17	1.88	46-17	1.29	47-17	1.99
30-18	2.26	46-18	1.68	47-18	1.14
30-19	1.41	46-19	1.56	47-19	1.17
30-20	1.42	46-20	1.41	47-20	1.75
30-21	1.04	46-21	1.91	47-21	1.10
30-22	1.56			47-22	1.13
30-23	1.55			47-23	1.27
30-24	2.71			47-24	1.63
30-25	1.20			47-25	2.55
30-26	0.34			47-26	1.54
				47-27	1.55

“Dimanche” creek					
	Ag (%)		Ag (%)		Ag (%)
23-1	1.41	26-1	3.92	29-1	1.70
23-2	2.69	26-2	3.96	29-2	1.11
23-3	4.68	26-3	3.34	29-3	3.47
23-4	2.50	26-4	7.24	29-4	1.72
23-5	2.23	26-5	7.01	29-5	1.77
23-6	2.80	26-6	3.80	29-6	0.87
23-7	3.65	26-7	3.40	29-7	3.36
23-8	1.83	26-8	1.64	29-8	3.21
23-9	1.88	26-9	2.19	29-9	3.10
23-10	2.00	26-10	1.56	29-10	3.84
23-11	6.36	26-11	3.34	29-11	3.97
23-12	4.69	26-12	3.88	29-12	3.41
23-13	4.58	26-13	4.51	29-13	3.20
23-14	4.30	26-14	4.33	29-14	1.86
23-15	2.00	26-15	0.98	29-15	4.94

23-16	2.51	26-16	0.87	29-16	4.32
23-17	2.45	26-17	0.90	29-17	1.82
23-18	2.36	26-18	4.93	29-18	7.22
23-19	2.54	26-19	4.82	29-19	2.25
23-20	3.04	26-20	1.76	29-20	2.15
23-21	1.56	26-21	2.02	29-21	3.98
23-22	2.32	26-22	1.63	29-22	3.53
23-23	2.34	26-23	1.96		
23-24	5.66	26-24	4.15		
		26-25	3.02		

“Awa” creek	
	Ag (%)
37-1	8.09
37-2	6.41
37-3	5.48
37-4	6.52
37-5	6.06
37-6	6.80
37-7	7.16
37-8	6.55
37-9	6.67
37-10	8.08
37-11	7.38
37-12	5.95
37-13	5.95
37-14	6.75
37-15	5.89
37-16	7.70
37-17	6.61
37-18	4.78
37-19	7.40
37-20	5.88
37-21	7.41

Table 5S

Kolmogorov-Smirnov test for the Ag content between the four "unknown" samples and the French Guiana gold considered in this study

	D	D critical	p-value[1]
sample 43			
“Marc” creek	0.648	0.321	< 0.0001
“Petit Inini” river	0.143	0.348	0.914
“Serpent” creek	1.000	0.340	< 0.0001
“Dimanche” creek	0.939	0.339	< 0.0001
“Awa” creek	0.482	0.406	0.011
sample 46			
“Marc” creek	0.801	0.338	< 0.0001
“Petit Inini” river	0.929	0.363	< 0.0001
“Serpent” creek	0.238	0.356	0.379
“Dimanche” creek	0.633	0.355	< 0.0001
“Awa” creek	1.000	0.420	< 0.0001
sample 29			
“Marc” creek	0.543	0.332	0.0001
“Petit Inini” river	0.883	0.358	< 0.0001
“Serpent” creek	0.570	0.350	0.0001
“Dimanche” creek	0.162	0.349	0.818
“Awa” creek	0.909	0.415	< 0.0001
sample X2			
“Marc” creek	0.233	0.290	0.181
“Petit Inini” river	0.592	0.319	< 0.0001
“Serpent” creek	0.938	0.310	< 0.0001
“Dimanche” creek	0.550	0.309	< 0.0001
“Awa” creek	0.609	0.382	0.0002

[1] the level of significance is $\alpha = 0.05$. Highlighted line corresponds to the population where the unknown sample comes from.