Supplementary Information (SI) for Journal of Analytical Atomic Spectrometry.

Supplementary Material to

Determination of Ultralow Iridium Concentration in Small Geological Samples: Isotope Dilution Coupled with Multiple Ion Counting Inductively Coupled Plasma Mass Spectrometry

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Table S1 Analytical methods used for determining iridium concentrations in previous studies.

Ref.	Analysis technique	Pre-processing method	Sample size	Method detection limit	Procedural blank [a]	RSD [b]	Experiment period
Ebihara et al. (2022)[1]	INAA		0.1 g	1 pg g $^{-1}$	NA	<6%	> one month
	(Q)ICP-MS	NiS fire-assay, acid dissolution	5 g	10 pg g $^{-1}$	NA	<6%	
Tyutyunnik et al. (2020)[2]	(SF)ICP-MS	Acid and alkaline digestion	1 g	3 pg g $^{-1}$	NA	1-4%	
Ni et al. (2019)[3]	(Q)ICP-MS	NiS fire-assay and acid digestion	10-20 g	12 pg g $^{-1}$	70 pg	4.5%-17.5%	
Chu et al. (2015)[4]	ID-MC-ICP-MS	Carius tube	2-4 g	NA	2 pg	0.9%-21%	
Ishikawa et al. (2014)[5]	ID-(Q)ICP-MS	Carius tube or HPA-S	1-2 g	NA	0.4-26 pg	5%-29%	
Li et al. (2014)[6]	ID-(Q)ICP-MS	Carius tube	1-2 g	NA	3.5 pg	6%-16%	
Wang and Becker (2014)[7]	ID-(SF)ICP-MS	HPA-S	0.5-1 g	1.5 pg g $^{-1}$	0.7 pg	8%-32%	
Amossé (2007)[8]	(Q)ICP-MS	Alkaline digestion	1-20 g	40 pg g $^{-1}$	40 pg	<8%	
Qi et al. (2004)[9]	ID-(Q)ICP-MS	Acid and alkaline digestion, Te coprecipitation	10 g	30 pg g $^{-1}$	500 pg	7.6%-20%	
Meisel and Moser (2004)[10, 11]	ID-(Q)ICP-MS	HPA-S	1-2 g	NA	2 pg	1.5%-39%	

Table S1 (continued).

Analytical methods used for determining iridium concentrations in previous studies.

Ref.	Analysis technique	Pre-processing method	Sample size	Method detection limit	Procedural blank [a]	RSD [b]	Experiment period
Jensen et al. (2003)[12]	ID-MC-ICP-MS	Carius tube	0.2-1 g	NA	<10 pg	3-18%	
Pretorius et al. (2003)[13]	(SF)ICP-MS	Carius tube	~1 g	3 pg g^{-1} [c]	<9 pg	~25%	
Meisel et al. (2001)[14]	ID-(Q)ICP-MS	HPA-S	2 g	120 pg g^{-1}	48 pg	4-27%	
Jin and Zhu (2000)[15]	(SF)ICP-MS	Alkaline digestion, Te coprecipitation	1-20 g	1.4 pg g^{-1}	70 pg	3-55%	
Pearson and Woodland (2000)[16]	ID-(Q)ICP-MS	Carius tube	1-5 g	3 pg g^{-1}	<10 pg	2%-27%	
Morcelli and Figueiredo (2000)[17]	RNAA	Alkaline and acid digestion Te-coprecipitation	0.5 g	4 pg g^{-1}	NA	14-36%	>20 days
Dai et al. (2000)[18]	INAA	Alkaline digestion	0.2-1 g	NA	<70 pg	1%-15%	>one month
Oguri et al. (1999)[19]	(Q)ICP-MS	NiS fire-assay, Te-coprecipitation	20 g	2 pg g^{-1}	80 pg	<8%	

Table S1 (continued).

Analytical methods used for determining iridium concentrations in previous studies.

Ref.	Analysis technique	Pre-processing method	Sample size	Method detection limit	Procedural blank [a]	RSD [b]	Experiment period
Yi and Masuda (1996)[20]	ID-(Q)ICP-MS	Acid dissolution and alkali fusion	~1 g	50 pg g^{-1}	NA	<6.5%	
Colodner et al. (1993)[21]	ID-(Q)ICP-MS	Acid dissolution	~1 g	6 pg g^{-1}	NA	~20%	
Jackson et al. (1990)[22]	(Q)ICP-MS	NiS fire -assay and Te coprecipitation	15 g	100 pg g^{-1}	300 pg	4-14%	
Hoffman et al. (1978)[23]	INAA	NiS fire-assay	30-50 g	100 pg g^{-1}	NA	<6%	

[a] The data are relative to the respective sample size.

[b] RSD: relative standard deviation. Calculated from reported sample data (ppb level) in the literatures.

[c] Instrumental detection limit

NA: Not reported in the literature

ID-(Q)ICP-MS: Isotope dilution quadrupole ICP-MS

(SF)ICP-MS: sector field ICP-MS

Table S2 Data for 191Ir and 193Ir intensities, as well as193/191 Ir ratios against varied Ir concentrations.

Ir conc (pg g^{-1})	191 Intensity (cps)	2SD	193 Intensity (cps)	2SD	193/191 Ir	2SD
0.87	570	12	989	8	1.68555	0.0253
8.77	5943	46	10331	48	1.6873	0.0048
86.42	59707	376	103724	614	1.6866	0.0014
430.94	294167	2834	510908	5676	1.68677	0.0015
860.62	590839	5891	1026296	12909	1.68749	0.0015
1057.49	716316	7549	1244888	16212	1.68671	0.0014

Note: The iridium solution was prepared through gradient dilution using a balance, starting from a 1000 ppm standard solution. The intensity and isotope ratio presented are the averages of three measurements.

Table S3 Comparison of calculated concentrations obtained via the ID method at optimal isotope ratios against actual concentrations for a range of pure iridium solutions with established concentrations.

Actual Ir conc (pg g^{-1})	2SD	Calculated Ir conc (pg g^{-1})	2SD
4.72	0.09	4.54	0.19
8.27	0.15	8.32	0.08
20.02	0.37	20.27	0.11
40.00	2.89	40.33	0.02
80.90	1.50	80.78	0.06
160.80	2.99	162.38	0.20
201.89	3.73	203.10	0.30
244.49	4.54	244.24	0.09

Note: The actual Ir concentrations were determined based on the masses measured using a balance, with the 2SD of the actual concentrations calculated through error propagation. The calculated Ir concentrations represent the averages of three measurements.

Table S4: Data for Ir isotope offsets resulting from variations in the concentrations of matrix elements, including Ca, Mg, Na, K, and Fe.

Element	X/Ir	193Intensity/191Intensity	2SD	N
Na	10000	1.6878	0.0034	3
	5000	1.6876	0.0031	3
	1000	1.6875	0.0028	3
	500	1.6869	0.0016	3
	100	1.6868	0.0012	3
	10	1.6886	0.0014	3
Mg	10000	1.6888	0.0015	3
	5000	1.6853	0.0011	3
	1000	1.6881	0.0020	3
	500	1.6865	0.0036	3
	100	1.6867	0.0008	3
	10	1.6884	0.0014	3
Fe	10000	1.6881	0.0039	3
	5000	1.6873	0.0024	3
	1000	1.6890	0.0034	3
	500	1.6885	0.0008	3
	100	1.6867	0.0039	3
	10	1.6866	0.0043	3
Ca	10000	1.6870	0.0005	3
	5000	1.6843	0.0017	3
	1000	1.6869	0.0015	3
	500	1.6873	0.0019	3
	100	1.6865	0.0051	3
	10	1.6851	0.0012	3
K	10000	1.6871	0.0032	3
	5000	1.6876	0.0005	3
	1000	1.68845	0.0012	3
	500	1.6876	0.0013	3
	100	1.6886	0.0032	3
	10	1.6860	0.0048	3

Table S5 Data for Ir isotope offsets resulting from variations in the concentrations of matrix elements and element-based interferences, including Hf, Lu, Eu, Pt and Os.

Element	[X]/Ir	^{193}Intensity/^{191}Intensity	2SD
Hf	0.01	1.6861	0.0003
	0.1	1.6862	0.0001
	1	1.6861	0.0002
	10	1.6864	0.0003
	50	1.6876	0.0001
	100	1.6889	0.0001
	500	1.6981	0.0005
	1000	1.7091	0.0004
	10000	1.8232	0.0043
Lu	0.01	1.6865	0.0001
	0.1	1.6866	0.00006
	1	1.6862	0.0003
	10	1.6862	0.0003
	50	1.6843	0.0002
	100	1.6826	0.00004
	500	1.6700	0.0002
	1000	1.6542	0.0018
	10000	1.5166	0.0136
Eu	0.01	1.6864	0.00002
	0.1	1.6864	0.0004
	1	1.6862	0.0004
	10	1.6857	0.0003
	50	1.6860	0.0002
	100	1.6861	0.0006
	500	1.6853	0.0003
	1000	1.6844	0.0008
	10000	1.6715	0.00001
Pt	0.01	1.6863	0.0003
	0.1	1.6865	0.00008
	1	1.6864	0.00004
	10	1.6863	0.00009
	50	1.6866	0.0003
	100	1.6867	0.0002
	500	1.6869	0.0007
	1000	1.6868	0.0007
	10000	1.6904	0.0070
Os	0.01	1.6867	0.00002
	0.1	1.6866	0.0001
	1	1.6866	0.0003
	10	1.6865	0.0004
	50	1.6866	0.000003

Table S5 (Continued)

Data for Ir isotope offsets resulting from variations in the concentrations of matrix elements and element-based interferences, including Hf, Lu, Eu, Pt and Os.

Element	[X]/Ir	^{193}Intensity/^{191}Intensity	2SD
	100	1.6867	0.00004
	500	1.6858	0.0030
	1000	1.6858	0.0007
	10000	1.6791	0.0063

Note: The natural isotopic ratio of Ir is 1.6866 [24].

Table S6 Data for Ir isotope offsets resulting from variations in the concentrations of matrix elements, including Hf, Lu, Eu, Pt and Os, through reaction collision cell.

Element	[X]/Ir	^{193}Intensity/^{191}Intensity
Hf	0.01	1.7547
	0.1	1.7556
	1	1.7637
	10	1.8447
	50	1.9534
	100	2.1149
	500	3.1787
	1000	4.5056
	10000	10.3976
Lu	0.01	1.7554
	0.1	1.7531
	1	1.7297
	10	1.4996
	50	0.9717
	100	0.7097
	500	0.2662
	1000	0.1713
	10000	0.0694
Eu	0.01	1.7490
	0.1	1.7496
	1	1.7501
	10	1.7455
	50	1.7323
	100	1.7152
	500	1.6095
	1000	1.5037
	10000	0.9397

Table S7 Data for calculated interference ion yields on Ir for elements Hf, Lu, Eu, Pt and Os, with and without the use of collision reaction cell.

Element	[X]/Ir	Ion yield (CCT)	Ion yield (without CCT)
Hf	50	8.8e-3	3.0e-5
	100	8.5e-3	3.7e-5
	500	7.7e-3	3.9e-5
	1000	7.5e-3	4.0e-5
	10000	4.7e-3	3.9e-5
Lu	50	4.3e-3	5.1e-6
	100	4.2e-3	4.7e-6
	500	4.1e-3	4.7e-6
	1000	4.0e-3	4.8e-6
	10000	3.9e-3	4.7e-6
Eu	50	2.6e-6	3.7e-6
	100	6.0e-5	1.2e-6
	500	1.1e-4	1.1e-6
	1000	1.1e-4	6.8e-7
	10000	1.1e-4	1.2e-6

Note: the ion yields equal to HfO/Hf, LuO/Lu and EuAr/Eu.

Table S8 Determined Ir concentrations by the method established in this study of 11 geo-standard materials, including sample weight and raw isotope ratios measured for each sample.

Sample	Weight (g)	191/193Ir	Calculated concentrations (pg g^{-1})
DTS-2-1	0.137	8.7197	2880
DTS-2-2	0.146	7.8154	3220
Average±2SD			2983±455
W-2-1	0.764	2.1273	374
W-2-2	0.750	2.1894	392
Average±2SD			383±26
GSP-2-1	0.797	3.6505	17
GSP-2-2	0.801	3.3214	19
GSP-2-3	0.805	3.0359	16
GSP-2-4	0.791	3.4556	18
Average±2SD			18±3
QLO-1-1	0.793	7.3790	7
QLO-1-2	0.804	6.3747	8
QLO-1-3	0.780	7.9443	6
QLO-1-4	0.801	6.8706	6
QLO-1-5	0.798	7.5124	6
Average±2SD			6±2
GSR-1-1	0.798	11.1920	4
GSR-1-2	0.796	11.4256	4
Average±2SD			4±0
JG-2-1	0.806	16.9415	5
JG-2-2	0.802	17.4921	5
Average±2SD			5±0
JR-2-1	0.792	3.6296	8
JR-2-2	0.804	2.7845	11
JR-2-3	0.799	3.2299	10
JR-2-4	0.785	4.1116	8
Average±2SD			9±3
SBC-1-1	0.444	1.2521	116
SBC-1-2	0.432	1.8762	94
Average±2SD			105±30
Nod-A-1-1	0.063	3.2525	8315
Nod-A-1-2	0.049	3.7458	9007
Average±2SD			8661 ±980
SDC-1-1	0.796	7.8154	24
SDC-1-2	0.797	8.7197	20
Average±2SD			22±6
COQ-1-1	0.795	15.6778	26
COQ-1-2	0.793	19.1301	18
Average±2SD			22±6

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