Appendix

Accurate determination of three halogen elements (Cl, Br, and I) in U.S. Geological Survey geochemical reference materials by radiochemical neutron activation analysis and an exhaustive comparison with literature data

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The individual values for three halogens (chlorine, bromine, and iodine) obtained by two to four analyses of 17 U.S. Geological Survey (USGS) geochemical reference materials are tabulated. A required resolution for successful quantification of ^{79}Br using inductively coupled plasma double focusing sector field mass spectrometry (ICP-SFMS) is explained. All the relative standard deviation (RSD) values and each halogen contents for 12 reference materials prepared by Geological Survey of Japan (GSJ), which have been analyzed in our previous work, are tabulated.

1. Individual values of chlorine, bromine and iodine for 17 USGS reference materials

Each sample was repeatedly analyzed two to four times. Individual values of three halogens (chlorine, bromine and iodine) are tabulated in Table S-1. An uncertainty is only due to counting statistics (1σ) in gamma-ray spectrometry. The final value can be obtained from three different measurements: data for the sample to be analyzed; data for reference standards; and data for yield determination by reactivation method. The uncertainty quoted in the table was derived by the propagation of uncertainties from individual gamma-ray measurements.

Table S-1. Individual values for three halogens obtained in this study

Sample	run No.#	Weight (mg)	Cl ($mgkg^{-1}$)	Br ($mgkg^{-1}$)	I ($mgkg^{-1}$)
DTS-2b	13K13-2	154.0	10.4 ± 0.8	0.090 ± 0.014	0.995 ± 0.106
DTS-2b	13K12-4	178.8	10.8 ± 0.6	0.095 ± 0.005	0.650 ± 0.049
DTS-2b	14K14-12	164.9	11.0 ± 0.6	0.094 ± 0.006	0.723 ± 0.052
COQ-1	13K13-9	148.1	28.6 ± 1.7	0.063 ± 0.009	0.381 ± 0.170
COQ-1	13K12-6	150.3	26.4 ± 1.4	0.078 ± 0.008	0.282 ± 0.083
CLB-1	13K13-14	41.8	1160 ± 60	51.2 ± 1.8	630 ± 15
CLB-1	13K12-15	111.8	971 ± 50	48.5 ± 1.8	654 ± 23
CLB-1	14K14-13	53.8	1240 ± 50	45.3 ± 1.3	518 ± 16
CLB-1	14K15-10	101.9	1390 ± 70	63.3 ± 1.8	595 ± 12
SBC-1	13K13-12	39.5	28.2 ± 2.1	0.352 ± 0.033	5.35 ± 0.59
SBC-1	13K12-10	114.1	22.4 ± 1.2	0.362 ± 0.028	4.94 ± 0.23
SBC-1	14K14-6	49.2	24.2 ± 1.9	0.352 ± 0.020	4.94 ± 0.38
DGPM-1	14K14-5	199.5	301 ± 15	0.880 ± 0.054	3.68 ± 0.19
DGPM-1	14K14-11	81.3	329 ± 18	0.806 ± 0.037	3.41 ± 0.20
W-2a	13K13-10	155.8	197 ± 10	0.249 ± 0.023	0.475 ± 0.104
W-2a	13K12-2	126.5	207 ± 8	0.306 ± 0.018	0.286 ± 0.046
W-2a	14K14-4	128.1	219 ± 10	0.320 ± 0.014	0.426 ± 0.071
W-2a	14K15-12	210.9	256 ± 9	0.362 ± 0.015	0.433 ± 0.054
SGR-1b	13K13-6	42.6	22.0 ± 1.6	0.433 ± 0.032	2.15 ± 0.19
SGR-1b	13K12-13	125.1	22.0 ± 1.2	0.384 ± 0.023	2.16 ± 0.23
DNC-1a	13K13-3	200.7	14.5 ± 0.8	0.041 ± 0.005	0.081 ± 0.037
DNC-1a	13K12-9	227.9	16.7 ± 0.9	0.074 ± 0.005	0.132 ± 0.040
DNC-1a	14K14-1	141.0	17.9 ± 1.1	0.067 ± 0.006	0.099 ± 0.045
DNC-1a	14K15-11	201.2	23.3 ± 1.2	0.069 ± 0.003	0.097 ± 0.038
QLO-1a	13K13-4	63.9	222 ± 12	1.07 ± 0.07	0.866 ± 0.141
QLO-1a	13K12-3	143.5	262 ± 12	1.07 ± 0.06	0.677 ± 0.080
QLO-1a	14K14-2	109.7	247 ± 13	0.96 ± 0.05	0.682 ± 0.108
SDC-1	13K13-1	193.0	30.3 ± 1.8	0.105 ± 0.020	0.213 ± 0.044
SDC-1	13K12-8	115.7	29.7 ± 2.1	0.116 ± 0.009	0.161 ± 0.051
GSP-2	13K13-5	197.8	321 ± 16	0.089 ± 0.007	0.074 ± 0.029
GSP-2	13K12-12	114.9	387 ± 17	0.136 ± 0.010	0.097 ± 0.043
GSP-2	14K14-9	135.8	380 ± 18	0.125 ± 0.013	0.054 ± 0.030

Table S-1. (Continued)

Sample	run No.#	Weight (mg)	Cl ($mgkg^{-1}$)	Br ($mgkg^{-1}$)	I ($mgkg^{-1}$)
BHVO-2	13K13-15	105.0	107 ± 6	0.250 ± 0.022	0.314 ± 0.077
BHVO-2	13K12-1	101.7	101 ± 5	0.229 ± 0.014	0.300 ± 0.065
BCR-2	13K13-13	222.4	110 ± 6	0.146 ± 0.012	0.088 ± 0.027
BCR-2	13K12-5	142.7	112 ± 4		0.105 ± 0.051
BCR-2	14K14-3	197.9	113 ± 5	0.143 ± 0.011	0.052 ± 0.033
BIR-1a	13K13-11	280.4	5.06 ± 0.31	0.030 ± 0.002	0.043 ± 0.024
BIR-1a	13K12-11	132.3	5.42 ± 0.34	0.059 ± 0.006	0.045 ± 0.036
BIR-1a	14K14-7	227.3	5.95 ± 0.39	0.027 ± 0.003	0.027 ± 0.019
BIR-1a	14K15-9	333.1	6.14 ± 0.44	0.038 ± 0.002	0.050 ± 0.031
AGV-2	13K13-7	179.5	73.4 ± 3.9	0.108 ± 0.007	0.197 ± 0.052
AGV-2	13K12-14	110.5	72.2 ± 3.8	0.094 ± 0.011	0.197 ± 0.055
Nod-P-1	13K13-16	25.6	1240 ± 60	5.85 ± 0.39	152 ± 5
Nod-P-1	13K12-7	141.2	1230 ± 60	6.01 ± 0.26	175 ± 5
Nod-P-1	14K14-10	43.1	1530 ± 90	4.84 ± 0.26	131 ± 4
Nod-P-1	14K15-13	109.1	1510 ± 80	7.00 ± 0.34	170 ± 7
Nod-A-1	13K13-8	25.4	4520 ± 230	14.7 ± 0.7	365 ± 10
Nod-A-1	13K12-16	29.3	4300 ± 210	14.9 ± 0.6	370 ± 15

2. A required resolution in ICP-SFMS for successful quantification of ^{79}Br

A required resolution in ICP-SFMS can be estimated as follows.

The mass of interest (79) is divided by the difference (δ: 0.00775) between the molecular mass of $^{40}Ar^{39}K$ (78.92609) and that of ^{79}Br (78.91834), and the resolution (m/δm: 10191) required to remove the interference of $(^{40}Ar^{39}K)^+$ from the ^{79}Br signal is obtained.

The mass of interest (79) is divided by the difference (δ: 0.00618) between the molecular mass of $^{63}Cu^{16}O$ (78.92452) and that of ^{79}Br (78.91834), and the resolution (m/δm: 12787) required to remove the interference of $(^{63}Cu^{16}O)^+$ from the ^{79}Br signal is obtained.

The mass of interest (79) is divided by the difference (δ: 0.01460) between the molecular mass of $^{40}Ar^{38}Ar^{1}H$ (78.93294) and that of ^{79}Br (78.91834), and the resolution (m/δm: 5410) required to remove the interference of $(^{40}Ar^{38}Ar^{1}H)^+$ from the ^{79}Br signal is obtained.

3. RSD values and each halogen contents for 12 GSJ materials

In our previous study, the RNAA method was applied to 12 GSJ reference materials[S1]. Each sample was repeatedly analyzed three to four times. Regarding the three halogens in those materials, all the RSD values and their contents are tabulated in Table S-2.

Table S-2. RSD values, means of individual uncertainties, and their ratios for 12 GSJ materials

Sample code	Chlorine		Bromine		Iodine	
	RSD (%)	Contents (mg kg^{-1})	RSD (%)	Contents (mg kg^{-1})	RSD (%)	Contents (μg kg^{-1})
JLk-1	3.0	59.1 ± 1.8	6.8	7.82 ± 0.53	6.9	9050 ± 620
JLs-1	8.5	16.4 ± 1.4	11.4	0.105 ± 0.012	8.8	318 ± 28
JDo-1	13.9	35.9 ± 5.0	8.2	0.622 ± 0.051	4.9	789 ± 39
JSL-1	7.4	13.6 ± 1.0	11.4	0.123 ± 0.014	7.5	107 ± 8
JSL-2	9.9	7.56 ± 0.75	10.0	0.060 ± 0.006	9.3	97 ± 9
JSd-1	10.2	64.0 ± 6.5	5.4	1.84 ± 0.10	8.2	1100 ± 90
JSd-2	6.6	22.7 ± 1.5	3.5	1.13 ± 0.04	9.3	675 ± 63
JSd-3	1.2	25.8 ± 0.3	2.0	3.92 ± 0.08	7.8	4230 ± 330
JCh-1	5.0	4.76 ± 0.24	18.5	0.027 ± 0.005	11.3	115 ± 13
JR-1	7.2	982 ± 71	2.9	2.07 ± 0.06	3.6	84 ± 3
JR-2	4.9	789 ± 39	7.3	1.64 ± 0.12	17.4	86 ± 15
JR-3	9.0	134 ± 12	7.8	0.577 ± 0.045	7.7	482 ± 37

Supplementary references

(S1) Sekimoto, S.; Ebihara, M. *Anal. Chem.* **2013**, *85*, 6336-6341.