Approved by General Administration of Quality Supervision,
Inspection and Quarantine of the People's Republic of China
GBW10010—GBW10019

# Certificate of Certified Reference Material

# Biological Sample



Date of Certification

Date of Expiration



Institute of Geophysical and Geochemical Exploration

(Langfang China)

**Certified values and uncertainties for GBW10010-GBW10019**

| Element | GBW10010 Rice | GBW10011 Wheat | GBW10012 Com | GBW10013 Soybean | GBW10014 Cabbage |
|---|---|---|---|---|---|
| Al ($10^{-2}$) | 0.039±0.004 | 0.0104±0.0010 | 0.032±0.003 | (0.043) | 0.0166±0.0022 |
| As ($10^{-6}$) | 0.102±0.008 | 0.031±0.005 | 0.028±0.006 | 0.035±0.012 | 0.062±0.014 |
| B($10^{-6}$) | 0.92±0.14 | (0.55) | 0.86±0.11 | 15.8±1.5 | 19.6±1.7 |
| Ba($10^{-6}$) | 0.40±0.09 | 2.4±0.3 | 0.45±0.16 | 3.3±0.4 | 12±2 |
| Be($10^{-9}$) | 1.8±0.4 | (0.85) | 1.7±0.4 | 3.5±0.6 | (1.8) |
| Bi($10^{-9}$) | (2.0) | (2.5) | 2.8±0.9 | (2) | 2.8±0.7 |
| Br($10^{-6}$) | 0.56±0.13 | (0.33) | 0.46±0.09 | (0.6) | 6.0±1.3 |
| Ca($10^{-2}$) | 0.011±0.001 | 0.034±0.002 | 0.0055±0.0008 | 0.153±0.008 | 0.70±0.02 |
| Cd ($10^{-9}$) | 87±5 | 18±4 | 4.1±1.6 | (11) | 35±6 |
| Ce($10^{-6}$) | 0.011±0.002 | 0.009±0.002 | 0.12±0.02 | 0.040±0.006 | 0.044±0.004 |
| Cl($10^{-2}$) | 0.040±0.004 | 0.086±0.003 | 0.050±0.006 | 0.008±0.002 | 0.64±0.07 |
| Co ($10^{-6}$) | (0.010) | (0.008) | (0.012) | 0.125±0.012 | 0.089±0.014 |
| Cr(l$0^{-6}$) | (0.09) | 0.096±0.014 | (0.11) | 0.28±0.04 | 1.8±0.3 |
| Cs(l$0^{-6}$) | 0.014±0.005 | (0.010) | 0.010±0.004 | 0.043±0.006 | 0.082±0.012 |
| Cu($10^{-6}$) | 4.9±0.3 | 2.7±0.2 | 0.66±0.08 | 10.2±0.5 | 2.7±0.2 |
| Dy($10^{-9}$) | (0.8) | (0.8) | 3.2±0.8 | 2.4±0.6 | 2.6±0.7 |
| Er($10^{-9}$) | (0.32) | (0.31) | 1.7±0.4 | 1.0±0.2 | (1.4) |
| Eu($10^{-9}$) | (0.3) | (0.8) | (0.6) | 1.3±0.5 | (3.6) |
| Fe($10^{-6}$) | 7.6±1.9 | 18.5±3.1 | 13.3±1.5 | 139±4 | 98±10 |
| Gd($10^{-9}$) | (0.75) | (0.91) | 4.3±0.9 | 3.3±0.9 | 3.1±0.5 |
| Ge($10^{-9}$) | (5) | (2) | (1) | (2.5) | (4) |
| Hf($10^{-6}$) | (0.12) | (0.03) | | | |
| Hg($10^{-9}$) | 5.3±0.5 | (1.6) | (1.6) | (1.5) | 10.9±1.6 |
| Ho($10^{-9}$) | (0.12) | (0.12) | 0.66±0.15 | (0.5) | (0.5) |
| I($10^{-6}$) | (0.09) | (0.06) | (0.06) | (0.05) | 0.24±0.03 |
| K($10^{-2}$) | 0.138±0.007 | 0.140±0.006 | 0.129±0.007 | 1.86±0.09 | 1.55±0.06 |
| La($10^{-6}$) | 0.008±0.003 | 0.006±0.002 | 0.057±0.006 | 0.023±0.004 | 0.024±0.003 |
| Li($10^{-6}$) | 0.044±0.007 | 0.024±0.005 | 0.038±0.006 | 0.062±0.014 | 0.54±0.08 |
| Lu($10^{-9}$) | (0.04) | (0.04) | (0.21) | (0.13) | (0.16) |
| Mg($10^{-2}$) | 0.041±0.006 | 0.045±0.007 | 0.018±0.002 | 0.230±0.014 | 0.241±0.015 |
| Mn($10^{-6}$) | 17±1 | 5.4±0.3 | 1.55±0.08 | 28±1 | 18.7±0.8 |
| Mo ($10^{-6}$) | 0.53±0.05 | 0.48±0.05 | 0.045±0.009 | 0.71±0.04 | 0.71±0.07 |
| N($10^{-2}$) | 1.61±0.04 | 2.40±0.06 | 1.40±0.07 | 6.7±0.3 | 2.8±0.2 |
| Na(l$0^{-6}$) | 25±8 | 17±5 | (10) | (15) | 1.09±0.06(%) |
| Nb($10^{-6}$) | | (0.008) | (0.009) | (0.011) | (0.014) |
| Nd($10^{-6}$) | (0.004) | 0.0046±0.0014 | 0.022±0.004 | 0.016±0.003 | 0.015±0.002 |
| Ni($10^{-6}$) | 0.27±0.02 | 0.06±0.02 | 0.097±0.014 | 4.0±0.3 | 0.93±0.10 |
| P($10^{-2}$) | 0.136±0.006 | 0.154±0.007 | 0.061±0.003 | 0.66±0.03 | 0.46±0.03 |
| Pb($10^{-6}$) | 0.08±0.03 | 0.065±0.024 | 0.07±0.02 | 0.07±0.02 | 0.19±0.03 |
| Pr($10^{-9}$) | 1.1±0.3 | 1.1±0.4 | 7±1 | 4.5±0.5 | 4.0±0.6 |
| Rb(l$0^{-6}$) | 3.9±0.3 | 2.6±0.2 | 2.1±0.2 | 14.2±0.7 | 19.6±1.0 |
| S($10^{-2}$) | 0.147±0.024 | 0.178±0.017 | 0.123±0.016 | 0.364±0.027 | 0.72±0.05 |
| Sb(l$0^{-6}$) | (0.004) | (0.006) | (0.008) | (0.005) | (0.012) |
| Sc($10^{-9}$) | (2.5) | (3) | 3.5±0.9 | (6.6) | (7) |
| Se($10^{-6}$) | 0.061±0.015 | 0.053±0.007 | 0.021±0.008 | (0.022) | 0.20±0.03 |
| Si($10^{-2}$) | 0.025±0.003 | (0.008) | 0.008±0.001 | (0.013) | 0.024±0.005 |
| Sm($10^{-9}$) | (0.9) | 0.95±0.28 | 3.2±0.5 | 3.1±0.3 | 3.2±0.7 |
| Sr($10^{-6}$) | 0.30±0.05 | 2.5±0.3 | 0.19±0.05 | 9.9±0.6 | 48±3 |
| Tb($10^{-9}$) | (0.10) | (0.10) | 0.73±0.24 | (0.42) | (0.5) |
| Th($10^{-9}$) | (4) | (2) | 4.6±1.5 | 6.8±1.4 | 9±3 |
| Ti($10^{-6}$) | (2) | (2) | 1.6±0.5 | | (9) |
| Tl($10^{-9}$) | (0.7) | (0.5) | (0.4) | (2.3) | (6.3) |
| Tm($10^{-9}$) | (0.05) | (0.04) | (0.27) | (0.2) | (0.23) |
| U($10^{-9}$) | (1.2) | (1.6) | (2.3) | (2.5) | 20±3 |
| V($10^{-6}$) | (0.03) | 0.034±0.012 | 0.30±0.11 | (0.08) | (0.11) |
| Y($10^{-6}$) | 0.052±0.009 | 0.023±0.005 | 0.021±0.004 | 0.022±0.004 | 0.015±0.002 |
| Yb(l$0^{-9}$) | (0.3) | (0.34) | 1.6±0.2 | 1.2±0.4 | 1.4±0.4 |
| Zn($10^{-6}$) | 23±2 | 11.6±0.7 | 2.9±0.3 | 38±2 | 26±2 |

**Certified values and uncertainties for GBW10010-GBW10019(continued)**

| Element | GBW10015 Spinach | GBW10016 Tea | GBW10017 Milk powder | GBW10018 Chicken | GBW10019 Apple |
|---|---|---|---|---|---|
| Al($10^{-2}$) | 0.061±0.006 | 0.094±0.009 | (0.003) | 0.016±0.003 | 0.007±0.001 |
| As($10^{-6}$) | 0.23±0.03 | 0.09±0.01 | 0.031±0.007 | 0.109±0.013 | 0.020±0.004 |
| B($10^{-6}$) | 25±2 | 14±1 | 1.56±0.22 | 0.76±0.13 | 19±3 |
| Ba($10^{-6}$) | 9.0±0.8 | 9.6±0.5 | 1.0±0.3 | 1.5±0.4 | 2.5±0.3 |
| Be($10^{-9}$) | 17±2 | 10±2 | | (1.3) | (1.0) |
| Bi ($10^{-9}$) | 13.5±1.0 | 18±2 | (1.2) | 1.3±0.4 | (2.5) |
| Br($10^{-6}$) | 10±2 | 2.7±0.5 | 5.7±1.4 | 1.6±0.4 | (0.2) |
| Ca($10^{-2}$) | 0.66±0.03 | 0.326±0.008 | 0.94±0.03 | 0.022±0.002 | 0.049±0.001 |
| Cd($10^{-9}$) | 150±25 | 62±4 | | (5) | 5.8±1.2 |
| Ce($10^{-6}$) | 0.66±0.05 | 0.39±0.05 | (0.004) | 0.06±0.01 | 0.025±0.005 |
| Cl($10^{-2}$) | 1.08±0.07 | 0.044±0.003 | 0.81±0.09 | 0.153±0.015 | (0.008) |
| Co($10^{-6}$) | 0.22±0.03 | 0.22±0.02 | 0.030±0.007 | (0.010) | 0.026±0.006 |
| Cr($10^{-6}$) | 1.4±0.2 | 0.45±0.10 | 0.39±0.04 | 0.59±0.11 | 0.30±0.06 |
| Cs($l0^{-6}$) | 0.13±0.02 | 0.32±0.06 | 0.034±0.005 | 0.070±0.013 | (0.02) |
| Cu($10^{-6}$) | 8.9±0.4 | 18.6±0.7 | 0.51±0.13 | 1.46±0.12 | 2.5±0.2 |
| Dy($10^{-9}$) | 41±8 | 25±6 | (0.45) | 1.1±0.4 | (1.1) |
| Er($10^{-9}$) | 17±3 | 14±4 | (0.16) | (0.8) | (0.65) |
| Eu($10^{-9}$) | 11.1±1.4 | 6.7±1.4 | (0.4) | (0.7) | (0.7) |
| F($10^{-6}$) | (14) | 57±15 | | | |
| Fe($10^{-6}$) | 540±20 | 242±18 | 7.8±1.3 | 31±3 | 16±2 |
| Gd($10^{-9}$) | 54±7 | 31±5 | | (1.4) | 0.95±0.11 |
| Ge ($10^{-9}$) | (20) | (8) | | (2) | |
| Hf($10^{-6}$) | (0.04) | (0.17) | | | |
| Hg($10^{-9}$) | 20±3 | 3.8±0.8 | (2.2) | 3.6±1.5 | (2) |
| Ho($10^{-9}$) | 8.1±1.7 | 5.4±1.2 | (0.07) | (0.26) | (0.25) |
| I($10^{-6}$) | 0.36±0.12 | (0.13) | 1.12±0.23 | (0.08) | 0.12±0.04 |
| K($10^{-2}$) | 2.49±0.11 | 1.63±0.07 | 1.25±0.05 | 1.46±0.07 | 0.77±0.04 |
| La($10^{-6}$) | 0.35±0.04 | 0.25±0.02 | (0.0025) | 0.024±0.004 | 0.014±0.004 |
| Li($10^{-6}$) | 1.46±0.23 | 0.14±0.02 | (0.04) | 0.034±0.007 | 0.115±0.009 |
| Lu($10^{-9}$) | 3.0±0.9 | 3.0±0.8 | | (0.10) | |
| Mg($10^{-2}$) | 0.552±0.015 | 0.186±0.011 | 0.096±0.007 | 0.128±0.010 | 0.039±0.006 |
| Mn($10^{-6}$) | 41±3 | 500±20 | 0.51±0.17 | 1.65±0.07 | 2.7±0.2 |
| Mo($10^{-6}$) | 0.47±0.04 | 0.040±0.012 | 0.28±0.03 | 0.11±0.01 | 0.08±0.02 |
| N($10^{-2}$) | 3.4±0.2 | 5.1±0.3 | 3.8±0.2 | 14.8±0.5 | 0.31±0.03 |
| Na($10^{-2}$) | 1.50±0.06 | 0.009±0.001 | 0.47±0.03 | 0.144±0.009 | 0.116±0.009 |
| Nb($10^{-6}$) | (0.06) | (0.025) | (0.008) | (0.006) | |
| Nd($10^{-6}$) | 0.28±0.03 | 0.15±0.02 | (0.002) | 0.0095±0.0035 | (0.006) |
| Ni($10^{-6}$) | 0.92±0.12 | 3.4±0.3 | (0.18) | 0.15±0.03 | 0.14±0.05 |
| P($10^{-2}$) | 0.36±0.02 | 0.45±0.03 | 0.76±0.03 | 0.96±0.08 | 0.066±0.004 |
| Pb($10^{-6}$) | 11.1±0.9 | 1.5±0.2 | 0.07±0.02 | 0.11±0.02 | 0.084±0.032 |
| Pr($10^{-9}$) | 75±5 | 42±4 | (0.7) | 2.8±0.6 | 1.8±0.3 |
| Rb($10^{-6}$) | 30±2 | 117±5 | 11.6±0.7 | 33±2 | 5.0±0.6 |
| S($10^{-2}$) | 0.45±0.04 | 0.30±0.03 | 0.25±0.02 | 0.86±0.05 | 0.063±0.004 |
| Sb($10^{-6}$) | 0.043±0.014 | 0.022±0.006 | (0.006) | | (0.006) |
| Sc($10^{-9}$) | (93) | (23) | (2.8) | (4.5) | |
| Se($l0^{-6}$) | 0.092±0.024 | 0.098±0.008 | 0.11±0.03 | 0.49±0.06 | (0.018) |
| Si($10^{-2}$) | 0.212±0.024 | 0.099±0.008 | | (0.013) | 0.0050±0.0013 |
| Sm($10^{-9}$) | 56±5 | 29±3 | (0.5) | 1.3±0.5 | 1.5±0.5 |
| Sr($10^{-6}$) | 87±5 | 9.1±1.2 | 5.3±0.6 | 0.64±0.08 | 6.9±0.5 |
| Tb($10^{-9}$) | 7.2±0.7 | 4.5±0.7 | (0.7) | (0.23) | |
| Th($10^{-9}$) | 114±19 | 38±12 | (2.8) | (4.5) | 4.0±0.3 |
| Ti($10^{-6}$) | (28) | (14) | | | |
| Tl($10^{-9}$) | (49) | (50) | (0.9) | (14) | (1.8) |
| Tm($10^{-9}$) | 3.1±0.9 | 2.6±1.0 | | (0.11) | (0.12) |
| U($10^{-9}$) | 89±11 | 10±2 | (3) | (3) | 8.2±1.8 |
| V($10^{-6}$) | 0.87±0.23 | 0.17±0.03 | (0.06) | (0.06) | (0.028) |
| Y($10^{-6}$) | 0.20±0.04 | 0.23±0.03 | 0.008±0.003 | 0.007±0.002 | 0.008±0.002 |
| Yb($10^{-9}$) | 19±4 | 18±4 | | (0.7) | (0.66) |
| Zn($10^{-6}$) | 35.3±1.5 | 51±2 | 34±2 | 26±1 | 2.1±0.4 |

Data following "±"are uncertainties.Data enclosed in brackets are proposed values.

The series of ten biological CRMs is mainly used in biogeochemical investigation and evaluation for agricultural environment, and hygienical inspection of food for carrying out chemical analysis as calibration samples and for monitoring the quality of measurements.

**1. Sample collection and preparation**

The samples were collected from representative producing areas. After selected material, cleaned and dried by airing, the grains were dried at 60°C and then ground by a high-alumina ball mill or crushed by a pulverizer. Following the lyophilisation vegetables, chicken and apple were ground by a high-alumina ball mill. After ground, the samples were passed through a 80 mesh sieve (the samples containing much fat or sugar were passed through a 60 mesh sieve).The samples from minus sieve were mixed until they were homogeneous. The samples were packed into 60ml high density polyethylene bottles for distribution, then irradiated with $^{60}Co$ to kill the bacteria. The bottles were later sealed in the outer bags which were made up of double lightproof compound films. Chicken, milk powder and soybean are preserved at -10℃.The others are kept in a shady and dry place at temperatures below 26 °C. The weight prepared for each sample w as 60-100kg.

**2. Test of homogeneity and stability**

Twenty-four subsamples were selected at random from each sample for homogeneity testing. About eight elements with different chemical properties and concentrations were analysed by powder XRF in duplicate. Under the good analytical precision, the calculated F values obtained by analysis of variance (ANOYA) indicated that all elements tested can be considered to be distributed homogeneously. The stability test of the samples was evaluated by determining various elements with different chemical properties and concentrations four times in one year. No significant statistical variations were observed, therefore the samples can be considered to be stable. Periodical stability tests will carry on in future.

**3. Sample analysis**

A multi-laboratory collaborative analysis scheme was adopted in the certification procedure. Fourteen institutes, and laboratories with high analytical level in China analysed these samples. More than ten reliable analytical methods based on different principles of measurement were employed in sample certification, such as ICP-MS, ICP-AES, INAA, XRF, AFS, AAS, GFAAS, VOL, POL, COL, IC, IES and AES.

**4. Certified values and uncertainties**

The certified values should meet the following requirements. Tire number of data sets taking part in the statistical analysis was not less than six sets. Two or more reliable analytical methods without obvious bias on different principles were used. The analytical data were obtained from laboratories mat could provide good precision. Any values that did not satisfy the above conditions were assigned proposed values, indicated with parentheses, provided not less than three laboratory method average data sets were available.The uncertainty of certified values was estimated using the formula $U=t_{0.05}\cdot\sqrt{u_a^2+u_b^2}=t_{0.05}\cdot\sqrt{(s/\sqrt{n})^2+[R/(2\sqrt{3m})]^2}$, where $u_a$ and $u_b$ are Type A and Type B of standard uncertainty respectively, $t_{0.05}$ is the listed values of t-distribution at the 95% confidence level where degree of freedom is n-1,s the standard deviation, n the number of data sets used, R the extremum difference of the method average data (the methods with two or more than two data sets took part in the estimation and the methods with only one data set could be merged into one) and m the number of analytical methods. When a single analytical method was used in the certification analysis, the standard deviation was taken as the estimating uncertainty of certified value.

**5. Package and storage**

The least sample package is 35g/bottle.The minimum sampling weight for analysis is 0.2g.It is necessary to keep bottle tightly closed after used and store samples in a desiccator at a shady and dry place, the temperature of which should be below 26 °C. If the sample is mold, stop using it immediately.