* **主量元素分析方法说明**
1. Major element data for whole-rock samples were obtained by X-Ray Fluorescence (XRF) spectrometry on fused glass discs using a PANalytical AXIOS Minerals instrument at the Rock-Mineral Preparation and Analysis Lab, the Institute of Geology and Geophysics (IGG; Beijing),Chinese Academy of Sciences (CAS). The PANalytical AXIOS Minerals equipped with a Rh anode X-ray tube and 4 kW excitation power is a sequential instrument with a single goniometer based measuring channel covering the complete elemental measurement range from F to U in the concentration range from 1.0 ppm to % level, determined in vacuum media [1].
2. Glass discs for WD-XRF analysis were prepared by fusion of 0.6 g of the standard sample with 6.0 g of lithium tetraborate : metaborate (2:1) (Lithium borates 67-33, Claisse, Canada), using Pt-Au crucibles and moulds employing electric fusion equipment (Claisse Fluxy, Corporation Scientific Claisse Inc., Quebec, Canada) [2].
3. Loss on ignition (LOI) was measured as the weight loss of the samples, which was obtained independently by igniting 0.5 g dry sample aliquot in a porcelain crucible for 1.5 h at 1000 °C in a muffle furnace [1].
4. The spectrometer was calibrated after measuring intensities in the following fifty international reference materials: GBW03102, GBW03102, GBW03113, GBW03116, GBW03134, GBW07101, GBW07102, GBW07103, GBW07104, GBW07105, GBW07106, GBW07107, GBW07108, GBW07109, GBW07110, GBW07111, GBW07112, GBW07113, GBW07114, GBW07212, GBW07309, GBW07310, GBW07311, GBW07312, GBW07401, GBW07402, GBW07403, GBW07404, GBW07405, GBW07406, GBW07407, GBW07408 (IGGE, China); AGV-2, BCR-2, BIR-1a, BHVO-2, DNC-1a, DTS-2B (USGS, USA); JGB-2a, JP-1, JH-1a, JG-2, JB-2 (GSJ, Japan); AN-G, BE-N, PM-S, WS-E (GIT-IWG, Groupe International de Travail-International Working Group); DR-N, UB-N (ANRT, Paris); Mica-Fe (CRPG, Centre de Recherches Petrographiques et Geochimiques); The criteria to select these samples were the required interval of concentration [2].
5. GSR-1, GSR-2, and GSR-3 are used to monitor the preparation process and instrument status.
6. Ferrous iron was determined by Xue's titration method. About 0.2 g of sample powder was weighed by determining the difference in the PTFE vessel, and then, the vessel was subjected to a vacuum to remove gases and then refilled with inert gas three times to ensure an inert atmosphere. Next, near-boiling 50% H2SO4 (10 mL) and HF (5 mL) were added to the digestion vessel, then heated under 170 °C for 10 min. Subsequently, saturated boric acid (50 mL) was added. Finally, the resultant mixture was titrated with standard KMnO4 solution. The titration speed was adjusted according to the rate at which the permanganate color disappeared until one drop produced a faint pink color that persisted for 30 s. The final small drops to reach the end-point were flushed from the microburette tip with a wash bottle into the digestion vessels. The microburet was read at the top level of the meniscus. The whole process during sample digestion and titration was carried out under inert atmosphere to prevent oxidation of ferrous material. Blank samples were also prepared, following the same procedure in the absence of the sample. [3] (Dingshuai Xue\*, Hongyue Wang, Yanhong Liu, Liewen Xie, Ping Shen; 2017, Geostandards and Geoanalytical Research,DOI: 2017, Volume 41, Issue 3, Pages 411–425).

The SuperQ software can automatically provide the limit of detection (LOD) for each element. The calculation equation used by the SuperQ software is [1]:

$LOD=\frac{n\sqrt{2}}{s}\sqrt{\frac{R\_{b}}{T\_{b}}}$ (3)

where n is a constant. The default is 2, which corresponds to a significance of 2, with a confidence level of 95%. s is the sensitivity in cps/ppm (cps is counts per second and ppm is μg g-1). Rb is the estimated background intensity in cps at the peak position. Tb is the total measurement time spent on the background.

The limit of detection (LOD) is the lowest concentration level that can be determined to be statistically different from an analyte blank. For quantitative measurements, the limit of quantitation (LOQ) is generally considered to be that value corresponding to 10 standard deviations above the baseline, approximately 3.3 times the LOD.

**Table.** Data for the range of standard sample compositions, limits of detection (LOD) and limits of quantitation (LOQ) of the method.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Number** | **Elements** | **Range of Standard****Sample Composition** | **LOD** **(μg g−1)** | **LOQ****(μg g−1)** |
|  | Major | (m/m% a) |  |  |
| 1 | SiO2 | 0.62–90.36 | 147.90 | 488.07 |
| 2 | TiO2 | 0.004–7.69 | 29.34 | 96.82 |
| 3 | Al2O3 | 0.1–59.20 | 161.83 | 534.04 |
| 4 | TFe2O3 b | 0.075–25.65 | 16.28 | 53.72 |
| 5 | MnO | 0.001–0.43 | 11.09 | 36.60 |
| 6 | MgO | 0.006–49.40 | 85.41 | 281.85 |
| 7 | CaO | 0.04–51.10 | 49.68 | 163.94 |
| 8 | Na2O | 0.008–10.59 | 77.23 | 254.86 |
| 9 | K2O | 0.003–12.81 | 20.37 | 67.22 |
| 10 | P2O5 | 0.002–6.06 | 16.67 | 55.01 |
|  | ***SO3 c*** | ***0.002–0.9238*** | ***28.74*** | ***94.84*** |
|  | Minor | (μg g-1) |  |  |
| 11 | Ba | 6.4–4000 | 52.67 | 173.81 |
| 12 | Co | 0.12–120 | 8.66 | 28.58 |
| 13 | Cr | 1.6–15500 | 11.19 | 36.93 |
| 14 | Cu | 0.82–1230 | 7.13 | 23.53 |
| 15 | Ni | 0.9–3780 | 5.52 | 18.22 |
| 16 | Rb | 0.8–3600 | 5.51 | 18.18 |
| 17 | Sr | 2.3–12000 | 4.04 | 13.33 |
| 18 | V | 0.0022–768 | 13.16 | 43.43 |
| 19 | Zn | 3.5–1300 | 5.74 | 18.94 |
| 20 | Zr | 0.7–1540 | 2.15 | 7.10 |

a m/m % is the mass percentage; b TFe2O3 is the total iron oxide as ferric iron; c This data is for reference purposes only.

References:

[1] Xue, Ding-Shuai; Su, Ben-Xun; Zhang, Dan-Ping; Liu, Yan-Hong; Guo, Ju-Jie; Guo, Qian; Sun, Jie-Fang and Zhang, Shu-Ying. Quantitative verification of 1:100 diluted fused glass beads for X-ray fluorescence analysis of geological specimens. **Journal of Analytical Atomic Spectrometry**, 2020, DOI: 10.1039/D0JA00273A.

[2] Zhang, Dan-Ping; Xue, Ding-Shuai; Liu, Yan-Hong; Wan, Bo; Guo, Qian; Guo, Ju-Jie. Comparative Study of Three Mixing Methods in Fusion Technique for Determining Major and Minor Elements Using Wavelength Dispersive X-ray Fluorescence Spectroscopy. **Sensors,** 2020, 20, no. 18: 5325.

[3] Xue, Ding-Shuai; Wang; Liu, Yan-Hong; Xie, Lie-Wen; Shen, Ping. Liu, Yan-Hong; An Improved Procedure for the Determination of Ferrous Iron Mass Fraction in Silicate Rocks Using a Schlenk Line-Based Digestion Apparatus to Exclude Oxygen, **Geostandards and Geoanalytical Research**, 2017, 41, 411-425.