Quality control for geological sample analysis

Hubei Geological Research Laboratory Caihua Xiong



1. Classification of geological samples

2. Test quality control method of geological samples

3. Classification and usage of reference substances

4. Test quality control of regional geochemical sample



Classification of geological samples

1 Classification of geological samples

According to the characteristics of geological samples

Rock, sediment, soil, ore, water (groundwater, surface water, mineral water, sea water, irrigating water, engineering water), coal, petroleum, organisms, atmospheric bulk deposition

For different kind of samples, required sample preparation, digestion and analysis method with different quality control method are different.

According to the purpose Of geological work

Geochemistry investigation samples, regional geological investigation samples, mineral and geology exploration samples, Hydrogeology, engineering Geology and environmental geology samples, petroleum geological samples

For different analysis objects, different analysis elements and contents, required analysis error is different.



Test quality control method of geological samples



Quality control during sample preparation

Preparation of pollution-free samples





Minimum sample size and representativeness

During the preparation of representative samples, it is necessary to crush and divide samples many times. The dividing follows Qeqott formula:



Q—Minimum reliable quality of the sample , kg d—Maximum particle diameter of the sample , mm K—dividing coefficient determined according to the characteristics of rock and ore samples Test quality control method of geological samples

Quality control during sample preparation

Minimum sample size and representativeness

Classification of rock and mineral	К
Fe, Mn (Contact metasomatism 、deposition、metamorphism) Cu, Mo, W Ni, Co (sulfide) Ni(silicate), monohydrallite (uniform) monohydrallite (non-uniform, such as pyritization monohydrallite.	0.1 ~ 0.2 0.1 ~ 0.5 0.2 ~ 0.5 0.1~0.3 0 3 ~ 0 5
calcareous alumine breccia et al.) Cr Pb, Zn, Sn Sb, Hg magnesite, limestone, dolomite Nb, Ta, Zr, Hf, Li, Rb, Cs, Sc and rare earth element P, S, quartzite, kaoline, clay, silicate, fluorspar, talcum, ophiolite, graphite , Salt alumstone, feldspar, gypsum, arsenic, boron rock barite(fluorite barite, sulfide barite, iron barite, clay barite)	0.3 ~ 0.3 0.2 0.1 ~ 0.2 0.05 ~ 0.1 0.1 ~ 0.5 0.1 ~ 0.2 0.02 0.2 ~ 0.5

Note1 : For samples of gold and platinum family, the standard of "Preparation of samples of gold and platinum family" is adopted.

Note 2: Rock and mineral unlisted in the table, K=0.2 is adopted without expriment.

Dividing coefficient of main rock and mineral (K)

Test quality control method of geological samples

Quality control during sample preparation

Preparation of common rock and mineral samples



Preparation scheme of common rock and mineral samples

Test quality control method

of geological samples

02

Quality control during sample preparation

Drying temperature and analysis particle size requirement of various rock and mineral samples

Classification of various rock	Particle size after	Drying temperature/°C	note
and mineral samples	crushing/mm		
Silicate, such as granite	0.097~0.074	105	
Limestone, dolomite, and alunite	0.097	105	
Quartzite	0.074	105	
Kaolin, clay	0.097~0.074	Samples without drying, water content corrected	
Apatite	0.125	105~110	GB/T 1868-1995
Pyrite	0.149	100~105°C or samples without drying, water content corrected	GB/T 2460-1996
Boron rock	0.097	60	
Gypsum	0.125	55	
Mirabilite	0.250~0.177	Samples without drving, water content corrected	
Iron ore	0.097~0.074	105~110	GB/T 1361-1978
Manganese ore	0.097	Samples without drving, water content corrected	
Chromite, ilmenite	0.074	105	
Copper ore, lead zinc ore	0.097	60~80	
Monohydrallite	0.097~0.074	105	
Tungsten ore, tin ore	0.097~0.074	105	
Bismuth ore, antimony ore,			
molybdenum ore andarsenic ore	0.097	60~80	
Nickel ore, navajoite and cobalt ore	0.097	105	
Mercury ore	0.149	Samples without drving,	
Gold, silver and platinum family	0.074	60~80 (Samples of Au and Pt family without drying)	
Uranium ore	0.097~0.074	105	
Kerogen shale	0.250~0.177	Samples without drying	
Geochemistry sample	0.097-0.074	60a	
Phase analysis, ferrous measure	0.149	Samples without drying	
Rare element ore	0.097	105	
Rutile	0.097	105	
Serpentinite, steatite and pyrophyllite	0.097	105	
Celestite, barite and fluorite	0.097	105	
Rock salt sample	0.149	Samples without drying, water content corrected	
Monomineral sample	0.074	105	
Macker	0.097	105	
Batt	0.125	105	

a: exceeding this temperature is not permitted.



Quality Test of samples preparation

▲ Requirement of scrap rate:

scrap rate = $\frac{\text{weight of orginal sample or final dividing reserved sample(g)}}{\text{weight or orginal sample or final dividing reserved sample(g)}} \times 100$

▲ Requirement of samples mass difference during preparation:

dividing mass difference = $\frac{\text{weight of reserved sample}(g) - \text{weight of discarded sample}}{\text{weight of sample before being divided }(g)} \times 100$

▲ Internal quality examination of samples preparation and quality sieving examination of samples:

sieving rate (%) = $\frac{\text{weight of sample seived from specified sieve number}}{\text{total weight of sample before being seived (g)}} \times 100$



Principles:



To meet client requirement



To meet the requirement of relevant laws and regulations, standards or norms



04

05

Detection limit, degree of accuracy and degree of precision are suitable for geological samples

Staff, equipment capacity and environmental condition

Safe, cost and without delay



▲ According to components to be measured and analysis purpose





Determination of standard method





▲ Non-standard methods should be affirmed with the methods below.





Monitoring with reference substance or control samples

1-2 and 2-3 reference substance control samples should be included with analysis samples less than 10 and more than 10 respectively in a batch. Monitoring samples could be added for special samples or samples with high requirements. For regional geological investigation, different control samples should be chosen.

▲ Methods added for standard substance: distributed randomly or evenly in the location of samples in a batch .



Monitoring with reference substance or control samples

- ▲Accuracy control: single test result of reference substance should be in the permission limit.
- Accuracy control index for rock and mineral analysis

Relative error permission limit of standard substance(or some certain component) (Y_B) is:

$$Y_B = \frac{1}{\sqrt{2}} Y_C = \frac{1}{\sqrt{2}} C \times (14.37 X_0^{-0.1263} - 7.659)$$

 Y_c —relative error permission limit of some certain component of duplicate sample , % ; X_0 —standard value of standard substance (of some certain component); C—relative error permission limit coefficient of component duplicate sample of some mineral



Recovery experiment of added standard reference

▲ Accuracy control index of recovery of added standard reference during rock and mineral analysis

permission mint of recovery						
Component content	10 ⁻⁶ -10 ⁻⁴	>10-4				
Adding standard recovery (%)	90~110	95-105				

permission limit of recovery



Number of analysis duplicate samples should be based on general requirement of clients or relative standards. For rock and mineral analysis:



Analysis duplicate samples is 20~30% of total samples in each batch with random sampling method.



Analysis duplicate samples is 100% when analysis samples of each batch is less than 5.



Random sampling duplicates is 5~10% of total samples in each batch for semi-quantitative spectrometric analysis



Random sampling duplicates increases for special samples or samples with high requirement until reaches 100%



▲ Relative duplicates error permission limit of rock and mineral samples

Mathematic model of relative duplicates error permission limit

$$Y_{C} = C \times (14.37 X_{ave}^{-0.1263} - 7.659)$$

 Y_c ——Relative duplicates error permission limit of some certain component , 100% ; X_{\pm} —average mass fraction of the component , % ;

C——Relative duplicates error permission limit coefficient of some certain component (see DZ/T 0130.3-20)



Mathematic model of relative duplicates error permission limit for precious metal component:

$$Y_{G} = 14.43 C X_{G ave}^{-0.3012}$$

where:

Y_G—Relative duplicates error permission limit of some certain component for precious metal mineral, %;

XG——Duplicate samples mass fraction of some certain component some time for precious metal mineral, 10⁻⁶;

C—Duplicates error permission limit coefficient for precious metal mineral, see appendix A in DZT 0130.3.

Application scope of the mathematic model:

For Au, 0.2~100) X10⁻⁶; More than 10X10^{-6,} 4.33% executed; less than 0.2X10⁻⁶, 33.4 executed.

■ For Ag, 5~100) X10⁻⁶; more than 10X10⁻⁶,7.21% executed; less than 5 X10⁻⁶, 33.4% executed.

■ For Pt, Pd, Os, Ir, Rh and Ru, (0.2 ~5) X10⁻⁶; more than 5X10⁻⁶, 12.4% executed; less tan 0.2 X 10⁻⁶, 33.4% executed.



▲ Relative duplicates error permission limit of rock and mineral samples

C=1, calculation of permission limit (YC), see appendix C in DZ/T130.3-2006

When Y_c calculated more than 30%, 30% executed.

When content of main mineral elements is less than cutoff grade, error is not considered. If the clients have special requirement, determined based on consultation each other.



05

01

02

03

Permission limit coefficient of trace non-ferrous metals, rare and scattered elements is 1. Less than 5×10^{-6} , 5×10^{-6} executed.

Permission limit for semi-quantitative spectrometric analysis is or less than 30%.



For phase analysis except iron, permission limit can adopt 50%



▲With repeatability limit(r) or reproducibility limit (R) of standard method as determining criteria of duplicate analysis.

With repeatability limit(r) or reproducibility limit (R) of standard method as permission limit of precision degree (Y_{cr} or Y_{CR}); Absolute value of repeatability limit(r) or reproducibility limit is less than or equals precision degree (Y_{cr} or Y_{CR}), qualified; otherwise unqualified.



Interlaboratory test comparison and proficiency testing

Interlaboratory test comparison results is based on GB/T 15483 with reproducibility limit of interlaboratory proficiency testing or other corresponding methods as control indicator.

Different results relevance of analysis samples

Relevance of various components of different mineral

For different geological samples, content of various elements or components should be in some certain range correlatively, or in reasonable proportion, which can be used as a method for test quality examination.



Relevance of various components of analysis samples

Content sum test



For soil speciation analysis, sum test could be adopted.



Other effective test methods

Blank experiment: at least 2 blank samples should be analyzed with samples simultaneously for each batch of geological samples test. If necessary, rectified.

Test results could be monitored with statistics method to find and prevent the generation of system error.



01

02

Statistic analysis should be carried out for standard substance or monitoring samples added in the batch to produce real time monitoring diagram.



Content distribution statistics should be carried out for batch sample analysis results to find abnormal value.



Three-level laboratory quality review with particular emphasis.



Classification and usage of standard substances

03 Classification and usage of standard substances



Geochemistry materials

rock (granite, basalt, andesite, shale, quartzite, limestone, ultrabasic rock); soil (various soil in China, soil effective state component, soil speciation component); sediment (stream sediment, lake sediment, seabed sediment, coast and shoal sediment); biological sample (rice, wheat, maize, soybean, Chinese cabbage, garlic, spinach, tea, apple, chicken, prawn, pork liver, scallop, milk powder, citrus, green bean, carrot, celery, green Chinese onion, nori, pollen, spirulina)



Metallic ores

nonferrous metals ore, ferrous metal mineral, rare resources, rare earth and rarely scattered resources, precious metal ores, including raw ore, ore concentrate, tailings, slag.



Non-metal ores and construction materials

Silicate, clay, feldspar, steatite, kaoline, gypsum, graphite, cement et al.

03 Classification and usage of standard substances

▲ selection principle of standard substances

Content level of standard substances is in accordance with expected level Matrix of standard level is close to that of samples to be measured as far as possible

Uncertainty of standard substances should meet quality expectation of client Selection of standard substances

The same speciation should be adopted for standard substances and samples to be measured

Standard substances should be in validity period under required storage condition.

Numbers of standard substances should be enough for the total experiment plan.



Geochemical mapping in low density region, 1 : 1,000,000

1:200,000 is for regional geochemical exploration, 1:500,000 is for rare region, 1:200,000 is adopted currently.

1:50,000, 1:10,000, and 1:5000 is for general geochemical investigation.

1:250,000 for multipurpose regional geochemical investigation

1:250,000 and 1:50,000 is for regional geochemical assessment to serve multipurpose regional geochemical investigation

1:50,000 is for land quality geochemical assessment mainly, 1:250,000, 1:10,000 and 1:5,000 is adopted.

Regional geochemical investigation

Current management standard of analysis test quality

 DZ/T 0258-2014 Specification of Multi-Purpose Regional Geochemical Survey (1:250000)

DZ/T 0167-1995 Specification of Regional Geochemical Survey (1:200000)

 DZ/T 0011-2015 Specification of Semi-detailed Geochemical Survey (1:50000)

 DZ/T 0289-2015 Specification of Regional Ecosystem Geochemistry Assessment

DZ/T 0145-2017 Specification of Soil Geochemistry Survey

DZ/T 0295-2016 Specification of Land Quality Geochemistry Assessment

- DZ/T0248-2014 Technical Regulation of Geochemical Rock Survey
- Specification of Regional Geochemical Exploration (1:250000)(draft for deliberation) 2010



Selection of analysis method

▲ Requirement of method detection limit

Requirement of method detection limit for various indicator unit: µg/g

	Detection limit (DL)				Detection limit (DL)		
element	Multi-Purpose	Geochemical exploration	1:50,000 Semi-detailed Geochemical Survey	element	Multi-Purpose	Geochemical exploration	1:50,000 Semi-detailed Geochemical Survey
Ag	0.02	0.02	0.03	F	100	100	100
As	1	1	1	Ga	2	2	
Au	0.0003	0.0003	0.0003	Ge	0.1	0.1	
В	1	5	5	Hg	0.0005	0.0005	0.0005
Ва	10	50	50	Ι	0.5	0.5	
Ве	0.5	0.5	1	La	5	30	40
Bi	0.05	0.1	0.1	Li	1	5	10
Br	1.0	1.0		Mn	10	30	30
Cd	0.03	0.05	0.1	Мо	0.3	0.4	0.5
Ce	1	1		Ν	20	20	
Cl	20	20		Nb	2	5	5
Co	1	1	1	Ni	2	2	3
Cr	5	15	15	Р	10	100	100
Cu	1	1	1.5	Pb	2	2	5



Technique requirement and quality control of total element analysis

Selection of analysis method

▲ Requirement of method detection limit

Requirement of method detection limit for various indicator(continued) unit: µg/g

Detection limit		etection limit (D	L)		Detection limit (DL)		
element	Multi-Purpose	Geochemical exploration	1:50,000 Semi-detailed Geochemical Survey	element	Multi-Purpose	Geochemical exploration	1:50,000 Semi-detailed Geochemical Survey
Rb	10	10		Zn	4	10	15
S	30	50		Zr	2	10	10
Sb	0.05	0.1	0.2	SiO ₂	0.1*	0.1*	
Sc	1	1		Al ₂ O ₃	0.05*	0.05*	
Se	0.01	0.01		TFe ₂ O ₃	0.05*	0.05*	Fe 1000
Sn	1	1	1	MgO	0.05*	0.05*	
Sr	5	5	10	CaO	0.05*	0.05*	
Th	2	4	5	Na ₂ O	0.05*	0.05*	
Ti	10	100	100	K ₂ O	0.05*	0.05*	
TI	0.1	0.1		TC	0.1*		
U	0.1	0.5	1	Corg.	0.1*		
V	5	20	20	рН	0.10**		
W	0.4	0.5	0.5	Pd		0.0001	
Y	1	5	7	Pt		0.0002	



Technique requirement and quality control of total element analysis

Selection of analysis method

Requirement of method accuracy degree

	A	Accuracy degree↔			I	¢	
Element≓ content₽	$\overline{\Delta \lg C} \; (\text{GBW}) = \lg \overline{C_i} \; - \lg C_s ^{\omega}$		Element≓ content₽	nte ^j nte ^j RSD%(GBW)= $\frac{\sqrt{\sum_{i=1}^{i} (C_i - C_s)^2}}{\frac{n-1}{C_s}} \times$		×100₽	
	Multi-Purpose	Geochemical- exploration+	1:50,000- Semi-detailed-		Multi-Purpose₽	Geochemical exploration#	1:50,000- Semi-detailed-
≤3D _L · ₽	⊴0.10₽	≤0.10₽	⊴0.13₽	ą	≤17₽	≤17₽	≤15%₽
≥3D _L ,	≤0.05₽	≤0.05₽	≤0.11₽	ą	≤10₽	≤10₽	≤10%+²
≥1%⊷	⊴0.04₽	⊴0.04₽	≤0.07₽	ą	≤8₽	≤8₽	≤7%≁
≥5%⊷	¢₽	≤0.02₽	C.	ą	C*	S₽	¢,

Requirement of method accuracy degree and precision degree

Note: average of 12 measured values of each GBW standard substance. Cs is average of standard value of each GBW standard substance. n is measured times for GBW standard substance. Ci is single measured value of each GBW standard substance.

Technique requirement and quality control of total element analysis

Internal quality control in chemical analysis laboratory

▲ accuracy degree control

Accuracy degree control is carried out with primary standard substance. For multi-purpose geochemical survey, 12 soil standard substances are added as code sample every 500 samples. For 1:250,000 regional geochemical exploration, 12 stream sediment standard substances are added 9 times each map sheet. For 1:50,000 semi-detailed geochemical survey, 2 primary standard substances or provincial monitoring samples developed are added every 50 samples.

Calculation method:

Logarithmic difference (ΔlgC) between measured value and standard value is calculated separately for each element each analysis.

Technique requirement and quality control of total element analysis

Internal quality control in chemical analysis laboratory

▲ accuracy degree control

02

Requirement of method accuracy degree and precision degree for routine analysis

	Accuracy degree↔			Precision degree+ ²		
	∆ lgC(GBW)·=· lgC _i -lgC _s ·or₊ ^j			$\lambda = \sqrt{\frac{\sum_{n=1}^{i} (\lg C_i - \lg C_s)^2}{4 - 1}} $		
Element≓ content₽	$\overline{\Delta \lg C} = \frac{\sum_{i=1}^{4} \left (\lg C_{Ri} - \lg C_{RS}) \right }{4}$					
	Multi-Purpose+	Geochemical exploration₽	1:50,000- Semi-detailed-	Multi-Purpose#	Geochemical exploration₽	1:50,000- Semi-detailed-
≤3D _L . •	≤0.12₽	≤0.15₽	≤0.17₽	≤0.17₽	≤0.20₽	≤0.20₽
≥3D _{L⁴2}	≤0.10₽	≦0.10₽	≤0.15₽	≪0. 15₽	≤0.17₽	≤0.17₽
1%-5%	≤0.07₽	≤0.07₽	≤0.10₽	≤0.10₽	≤0.12₽	≤0.15₽
> 5%+	≤0.05₽	≤0.05₽	≤0.07₽	≪0. 08₽	≤0.08₽	≤0.07₽

Technique requirement and quality control of total element analysis

Internal quality control in chemical analysis laboratory

▲ accuracy degree control

Allowable relative deviation or Au standard substances and samples

Content range (ng/g).	relative deviation= $\frac{ A_1 - A_2 }{\frac{1}{2}(A_1 + A_2)} \times 100\%^{3}$
0.3~1*	≤100⊷
1~30+	≤66.6₽
>.30,0	≤50¢

Note: A1, fundamental analysis results; A2, examined analysis results.

◆ For multi-purpose geochemical survey, primary standard substances are required to be added. For each element, qualification rate of analysis accuracy degree is \geq 98%. For Au, it is \geq 96%.

 ◆ For 1:250,000 geochemical exploration and 1:50,000 semi-detailed geochemical survey, primary standard substances are required to be added. .For each element, qualification rate of analysis accuracy degree is ≥98%.
For Au, it is ≥90%.

Technique requirement and quality control of total element analysis

Internal quality control in chemical analysis laboratory

▲ precision degree control



Technique requirement and quality control of total element analysis

Internal quality control in chemical analysis laboratory

▲percent of report

◆ For multi-purpose geochemical survey, required percent of report for each element is >95% and total percent of report is ≥99%.

◆ For 1:250,000 geochemical exploration, required percent of report for each element is >95%.

For 1:50,000 semi-detailed geochemical survey required percent of report for each element is >90%.

Technique requirement and quality control of total element analysis

Internal quality control in chemical analysis laboratory

Repetitive verification

Range of content	Relative duplicate difference= $\frac{ A_1 - A_2 }{\frac{1}{2}(A_1 + A_2)} \times 100$			
Range of content	Multi-purpose	geochemical exploration	1:50,000 semi-detailed geochemical survey	
Less than 3 times detection limit	≤30%	40%	≤50%	
More than 3 times detection limit	≤25%	40%	≤50%	
Map sheet sampling rate	5%	3%-5%	3%-5%	
Original qualification rate of single element	90%	90%	90%	
Outlier sampling rate	No requirement	3%	3%	
Qualification rate of outlier sampling rate	85%	90%	85%	

Note: A1, fundamental analysis results; A2, examined analysis results.

▲ Repetitive verification

For standard substance or monitoring samples in routine analysis, monitoring diagram and parameter table of quality parameters are prepared to determine whether system deviation exists.

External quality control in chemical analysis laboratory

▲ standard control sample



02

03

Preparation of standard control sample: multiple group of standard control samples are prepared with primary standard substances having corresponding characteristics according to various ratio to obtain standard control sample with various concentration and matrix. 150 samples in each group.

Standard value determination of various elements in standard control samples. In principle, it is determined base on standard value of various element content in original standard substance, and proportion of prepared control samples participated. After calculation, it becomes trial value of various element is standard control sample.



▲ standard control sample added

Prepared standard control samples are added in each batch (about 50 numbers). 4 samples are added in each batch (for 1:50,000 semi-detailed geochemical survey, 2 samples are required.) Vacant number is reserved by sampling institute in advance. Code samples are required to be analyzed with samples at the same time.

*External quality control in chemical analysis laboratory

▲ quality parameter of standard control sample

Accuracy degree of standard control sample

With 150 standard control samples as a statistic unit. Logarithmic difference between measurement value and standard value of standard control samples is analyzed statistically based on single control unit and single element. Permission limit should be in accordance with internal quality control of "Requirement of daily analysis accuracy degree and precision degree with single element qualification rate of more than 90%.

Precision degree of standard control sample

Logarithm standard deviation λ of single element control sample is analyzed statistically according to batch, 1:50,000 map sheet,1:100,000 map sheet or entire map sheet element. Permission limit should be in accordance with internal quality control of "Requirement of routine analysis accuracy degree and precision degree with single element qualification rate of more than 90%.

Correlation between measurement value and standard value of standard control samples

With 150 standard control samples as a statistic unit. Correlation coefficient R between standard control sample measurement value of single element and standard trial value is analyzed statically, besides, parameters such as Xmin, Xmax and median are considered. For R of single element, R≥0.900 is required.

Equal precision test between measurement value and standard value of standard control samples



With 150 standard control samples as a statistic unit. Variance between measurement value and standard value is analyzed statically. Variance test (F test) of two samples is compared. F test value is required less than F critical value.

Technique requirement and quality control of total element analysis

Ottilization quality feedback of test data

▲ Control of suppositional similar figure

Suppositional figure of standard control sample



Based on trial value of various element in added control samples, ranking bitmap is drawn with ranking 1 : 50000 map sheet. With SUFFER, suppositional contour geochemical diagram of various element in 150 standard control samples are drawn as suppositional standard geochemical diagram for similarity comparison.

Precision degree of standard control sample



Based on analysis report data provided by the lab, 150 standard control sample data are rejected, based on which, suppositional geochemical diagrams of various element are drawn according the method above.

Correlation between measurement value and standard value of standard control samples



Similarity discrimination of analysis quality is carried out for total data provided by the lab with visual comparison method combined with parameters such as accuracy degree and precision degree of control samples analyzed statically.



Technique requirement and quality control of total element analysis

Otilization quality feedback of test data

▲ Element geochemical diagram control

Based on sample analysis data provided by the lab, according to corresponding requirement, various element geochemical diagram is drawn. Based on the conformity between background (and abnormal condition) and geological condition, sample analysis data quality is assessed in general.

MANY THANKS