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Methods of testing cement — Report of a test programme — Chemical analysis by x-ray fluorescence

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

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ISO/TR 12389 was prepared by Technical Committee ISO/TC 74, *Cement and lime*.

Introduction

This Technical Report summarizes the results of inter-laboratory testing of the chemical analysis of cement by x-ray fluorescence undertaken by laboratories in Japan, in Asian countries and in Europe. This testing programme was planned and conducted by the Committee on Cement Chemistry, Japan Cement Association and extended to the members of ISO in Asia and members of CEN/TC 51/WG 15 (Revision of methods of testing cement) in Europe. A total of 42 laboratories participated.

The wet method is a longstanding technique used for chemical analysis of cement. However, since this manner of analysis is extremely time-consuming, more rapid methods have been investigated, leading to the development of chemical analysis of cement by x-ray fluorescence (XRF method). As a result, Japanese Industrial Standard JIS R 5204 was established in July 2002.

JIS R 5204 established a scheme to confirm the validity of calibration equations when the concentrations of a pair of validation beads made from certified reference materials satisfy the criteria for both the repeatability limits and accuracy limits specified in JIS R 5204. Use of this validation system improves the repeatability and accuracy of results obtained by the JIS R 5204 method.

Since an International Standard for this analysis method had not yet been established, the Japanese National Committee for ISO/TC 74 (J/TC 74) proposed the “Development of chemical analysis of cement by x-ray fluorescence” to ISO/TC 74 in June 2004. The English version of JIS R 5204 was included as the first working draft at that time.

In order to introduce JIS R 5204 to Asian members of ISO/TC 74 and to promote technical exchange among them, an inter-laboratory testing programme was organized. This inter-laboratory testing was carried out with the participation of 16 laboratories in Japan and 14 outside Japan, mostly Asian members of ISO/TC 74.

As this first part of the round-robin testing was taking place, work was in progress within CEN committee TC 51/WG 15 to produce a standard method for the chemical analysis of cement by x-ray fluorescence. The Japanese Industrial Standard JIS R 5204 was accepted by this committee and, working jointly with the Japanese co-opted member, was incorporated into the draft for ISO 29581-2. At the invitation of the Japanese Cement Association, members of CEN/TC 51/WG 15 were invited to join in the Japanese/Asian round robin and in 2005 twelve European laboratories participated. The results of their testing are included in this report.

Those laboratories that obtained analyses of JCA-CRM-1 and/or JCA-CRM-2 satisfying the criteria for both the repeatability limits and accuracy limits for all components were defined as “Q-laboratories”. A comparison of the results for “Q-laboratories” with those obtained from other inter-laboratory testing for all constituents other than CaO indicates that the variation was equal to or smaller than that of wet analysis. The variation in results for CaO in “Q-laboratories” was slightly larger than that by wet analysis. Therefore, this inter-laboratory testing demonstrates that the accuracy of results obtained by the JIS R 5204/ISO 29581-2 method is generally the same as that for the wet method.

Methods of testing cement — Report of a test programme — Chemical analysis by x-ray fluorescence

1 Scope

This Technical Report describes the results of the inter-laboratory testing of the chemical analysis of cement by x-ray fluorescence. In the first instance, the inter-laboratory testing was carried out in Japan and in Asian countries in accordance with JIS R 5204:2002. A total of 30 laboratories, 16 in Japan and 14 outside Japan, participated in the original testing programme. A further 12 European laboratories participated in tests with the same materials in 2005 in accordance with EN 196-2, a development by CEN/TC 51/WG 15/TG 1 of JIS R 5204. The latest version, developed as ISO 29581-2, is, as of the date of publication of this Technical Report, in the process of being circulated for technical enquiry.

The test samples used were Portland cement conforming to CEM I of EN 197-1 and a mixture of Portland cement and blast furnace slag. The mixture corresponded to the composition of Portland blast furnace slag cement, class B, specified in JIS R 5211 and CEM III/A of EN 197-1. Cement reference materials for x-ray fluorescence analysis (No. 601A) are used for the calibration standards, and certified reference materials JCA-CRM-1 and JCA-CRM-2 are used as the validation materials.

Constituents analysed include SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, K_2O, TiO_2, P_2O_5, MnO and SrO. The loss on ignition is also determined.

The ISO round robin is a method-performance study conducted under close to optimum conditions with clear calibration and measurement guidelines. This is conducive to producing “best practice” values representative of the ideal situation. However, ISO 29581-2 is intended for use under everyday conditions in laboratories that operate to “good practice”. Annex D sets out the results of some international round robins carried out by a large number of laboratories demonstrating the suitability of ISO 29581-2 as a means for comparing the everyday performance of laboratories.

2 Test methods

2.1 General arrangements

The outline of the inter-laboratory testing is shown in Table 1.

Table 1 — Outline of the inter-laboratory testing

Test method	First part – JIS R 5204:2002 Second part – ISO 29581-1
Test samples	JCA #1 Portland cement JCA #2 Cement made by mixing Portland cement with blast furnace slag (composition corresponding to Portland blast furnace slag cement Class B specified in JIS R 5211 and CEM III/A of EN 197-1)
Calibration standards	Cement reference materials for x-ray fluorescence analysis, JCA No. 601A
Validation materials	JCA-CRM-1 Ordinary Portland cement JCA-CRM-2 Portland blast furnace slag cement
Constituents determined	SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, K_2O, TiO_2, P_2O_5, MnO, SrO, loss on ignition (LOI)

2.2 Test method and constituents to be determined

The first phase of this inter-laboratory testing was based on JIS R 5204. The second phase of this inter-laboratory testing was based on ISO 29581-2. There were no substantial differences between the two methods. For the remainder of this report they will be referred to as “the XRF method”.

Twelve constituents: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, K_2O, TiO_2, P_2O_5, MnO, and SrO, determined by XRF method using glass beads, and loss on ignition were to be evaluated. Although SO_3 for Portland blast furnace slag cement was outside the scope of JIS R 5204, it was an option for Sample #2 in this testing.

3 Samples

3.1 Test samples

Two test samples were used: Portland cement (Sample #1) conforming to EN 197-1 CEM I, and a cement mixture of Portland cement and blast furnace slag (Sample #2). Sample #2 corresponded to the B-type Portland blast furnace slag cement specified in JIS R 5211 and CEM III/A of EN 197-1. Approximately 30 g of each sample was distributed.

3.2 Calibration standards

Cement reference materials for x-ray fluorescence analysis (see NOTE), provided by the Japan Cement Association, were used for the calibration standards.

Approximately 12 g of each standard of JCA No. 601A was distributed to the foreign laboratories. The only requirement was that seven or more calibration standards be used when making calibration equations in accordance with the XRF method.

NOTE JCA No. 601A is a set of 15 cement reference materials consisting of nine Portland cements and six Portland blast furnace slag cements.

3.3 Validation materials

Validation of calibration equations was specified in the XRF method. Certified reference materials JCA-CRM-1 and JCA-CRM-2, provided by the Japan Cement Association, were used as the validation materials.

Approximately 30 g of each CRM was distributed to the laboratories.

3.4 Participating laboratories

3.4.1 Japan

An announcement of the inter-laboratory testing was sent out to members of the Japan Cement Association. In response to the announcement, 16 laboratories registered as participants in this testing programme. A list of participating laboratories is shown in Annex A.

3.4.2 Asia

An announcement of the inter-laboratory testing was sent out to Asian members registered as P-members or O-members in ISO/TC 74 (See NOTE). Sixteen laboratories responded to the announcement and expressed their desire to participate, and 14 laboratories registered for the programme. A list of participating laboratories is shown in the Annex A.

NOTE The announcement was sent out to member bodies registered in ISO/TC74, and to Cement Associations of the members; see Reference [10].

3.4.3 Europe

Invitations were issued to the members of European Standards Organization Technical Committee TC 51, *Cement and building limes*, Working Group 15, *Methods of testing cement*, Task Group 1, *Analysis by x-ray fluorescence*, to nominate participating laboratories. Twelve laboratories undertook to participate. A list of participating laboratories is shown in Annex A.

4 Method for analysis of results

4.1 Statistics

Symbols and definitions of statistical terms used in this report are shown in Table 2.

Table 2 — Definitions of the statistical terms

Statistical term	Abbreviation/symbol	Definition of the statistical term [a]
Average	Av./ $\bar{x}$	$\bar{x} = \frac{\sum_{i=1}^{i=n} x_i}{n}$
Maximum value	Max.	Maximum value in the data
Minimum value	Min.	Minimum value in the data
Range	—	Range is equal to max. minus min.
Standard deviation	S.D./σ	$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$
Coefficient of variation	C.V./C_V	$C_V = \frac{\sigma \times 100}{\bar{x}}$, expressed as a percentage

[a] n is the number of laboratories; x is the mean value of a pair of results from each laboratory.

4.2 Definition of Q-laboratories

4.2.1 General

In this inter-laboratory testing, a Q-laboratory is one where the concentration of a pair of validation beads made from certified reference materials satisfies the criteria for both the repeatability limits and accuracy limits set out in the XRF method.

4.2.2 Validation procedure

4.2.2.1 Determination of the concentration of a pair of validation beads made from at least one certified reference material for all analysis constituents.

4.2.2.2 Check that the difference in the concentration, rounded off to three decimal places, of a pair of validation beads is within the repeatability limits obtained from Equation (1):

$$\log(y) = 0{,}48 \log(x) - 1{,}499 \qquad (1)$$

where

y is the repeatability limit, as a percentage;

x is the mean value of the concentration of a pair of validation beads, as a percentage.

When x is less than 0,5 %, a limit for y of 0,020 % is applied to all values.

NOTE Equation (1) is specified in JIS R 5204.

4.2.2.3 Check that the difference between the mean values, rounded off to two decimal places, of the concentration of a pair of validation beads and the "certified values" of the certified reference materials are within the accuracy limits specified according to the level of concentration in Table 3 for each analysed constituent.

Both JCA-CRM-1 and JCA-CRM-2 are used for the validation materials in this inter-laboratory testing. However, in the XRF method, the use of just one certified reference material is permitted. Therefore, for the purpose of this inter-laboratory test, the validations are considered as satisfied if the analysis of either JCA-CRM-1 or JCA-CRM-2 meets the validation criteria. Laboratories that obtained concentrations of JCA-CRM-1 and/or JCA-CRM-2 satisfying the criteria for both the repeatability limits and accuracy limits for all constituents, were defined as "Q-laboratories" in this inter-laboratory testing. In ISO 29581-2, these are referred to as "expert" laboratories.

Table 3 — Accuracy limits for analysis validation

Level of the certified value (% absolute)	Accuracy limits for analysis validation (% absolute)
0,00 to 0,49	0,02
0,50 to 0,99	0,03
1,00 to 6,99	0,08
7,00 to 14,99	0,12
15,00 to 29,99	0,15
30,00 to 49,99	0,20
50,00 to 79,99	0,25
80,00 to 100,00	0,30

5 Results and considerations

5.1 Laboratory number

Validation results for all laboratories and results of determination for Q-laboratories are shown in Tables B.1 to B.8. Laboratories No. 1 to No. 16 represent laboratories in Japan; Laboratories No. 101 to No. 113 represent ISO member laboratories outside Japan. Although there were 14 participating laboratories outside Japan, the report submitted by Laboratory No. 114 is mentioned only in Tables B.2, B.4, B.6 and B.8, because the laboratory carried out XRF analysis by the pellet method. Laboratories No. E1 to E12 represent laboratories participating in the European stage.

5.2 Validation results for all laboratories

The difference in concentration for each pair of JCA-CRM-1 is shown in Table 4, and that for JCA-CRM-2 is shown in Table 5. The difference between the mean values of concentration for each pair of JCA-CRM-1 and the certified values is shown in Table 6, and that for JCA-CRM-2 is shown in Table 7.

Data in the shaded cells of Table 4 and Table 5 denote results that did not satisfy the required criteria for repeatability. Data in the shaded cells of Table 6 and Table 7 represent results that did not satisfy the required criteria for accuracy limits. “-” in each table indicates that there is no report from the laboratory for that constituent.

The presence of data in the shaded cells indicates that some validation results did not satisfy the required criteria for repeatability or accuracy limits. Therefore, in determining the Q-laboratories according to the definition described in 4.2, 27 laboratories were judged as Q-laboratories.

Table 4 — Difference in concentrations for each pair of validation beads
(All laboratories — Validation material: JCA-CRM-1)

Laboratory ref.	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %	Na_2O %	K_2O %	TiO_2 %	P_2O_5 %	MnO %	SrO %
1	0,039	0,028	0,009	0,180	0,006	0,010	0,015	0,007	0,000	0,001	0,000	-
2	0,034	0,004	0,001	0,072	0,005	0,032	0,001	0,003	0,007	0,001	0,001	0,000
3	0,012	0,005	0,017	0,018	0,012	0,028	0,013	0,002	0,003	0,001	0,000	-
4	0,080	0,010	0,013	0,020	0,001	0,009	0,002	0,004	0,004	0,002	0,000	0,000
5	0,032	0,012	0,003	0,004	0,003	0,009	0,001	0,003	0,002	0,001	0,000	0,000
6	0,024	0,027	0,002	0,083	0,039	0,012	0,011	0,007	0,008	0,002	0,002	0,000
7	0,014	0,013	0,003	0,046	0,005	0,006	0,002	0,002	0,005	0,000	0,001	0,000
8	0,040	0,006	0,004	0,115	0,010	0,008	0,007	0,001	0,008	0,001	0,000	0,000
9	0,011	0,017	0,004	0,041	0,003	0,006	0,001	0,001	0,002	0,001	0,000	0,000
10	0,028	0,035	0,003	0,012	0,017	0,017	0,007	0,001	0,003	0,000	0,000	-
11	0,012	0,006	0,008	0,061	0,014	0,018	0,012	0,010	0,004	0,005	0,001	-
12	0,011	0,006	0,006	0,073	0,005	0,024	0,007	0,002	0,011	0,000	0,003	0,001
13	0,018	0,004	0,003	0,042	0,009	0,005	0,002	0,000	0,004	0,000	0,001	0,000
14	0,080	0,029	0,006	0,112	0,006	0,001	0,002	0,018	0,013	0,010	0,001	0,000
15	0,090	0,008	0,004	0,038	0,003	0,015	0,002	0,001	0,006	0,000	0,001	0,001
16	0,007	0,011	0,004	0,014	0,003	0,008	0,008	0,001	0,005	0,002	0,000	0,000
101	0,005	0,005	0,007	0,006	0,012	0,130	0,006	0,004	0,003	0,003	-	-
102	0,017	0,058	0,004	0,005	0,007	0,001	-	0,000	-	-	-	-
103	0,020	0,020	0,010	0,060	0,170	0,020	0,010	0,010	-	-	-	-
104	0,016	0,020	0,009	0,193	0,011	0,035	0,010	0,016	0,002	0,004	0,001	0,000
105	0,084	0,052	0,008	0,024	0,001	0,006	0,003	0,001	0,011	0,003	0,000	0,001
106	0,118	0,014	0,002	0,090	0,002	0,014	0,017	0,003	-	-	-	-
107	0,006	0,211	0,008	0,045	0,033	0,032	0,005	0,006	-	0,011	0,001	-
108	0,010	0,010	0,010	0,020	0,010	0,010	0,030	0,000	-	0,000	-	-
109	0,032	0,009	0,014	0,116	0,003	0,015	-	0,002	-	-	-	-
110	0,122	0,099	0,059	0,041	0,261	0,136	0,082	0,161	-	0,022	-	-
111	0,040	0,030	0,010	0,010	0,020	0,000	0,010	0,000	0,010	0,010	0,000	0,000
112	0,110	0,010	0,000	0,020	0,090	0,010	0,000	0,000	-	-	-	-
113	0,030	0,030	0,010	0,150	0,090	0,030	0,010	0,000	0,000	0,010	0,000	0,000
E1	0,112	0,045	0,013	0,039	0,007	0,025	0,009	0,002	0,006	0,000	0,000	0,000
E2	0,001	0,053	0,008	0,016	0,019	0,021	0,002	0,005	0,002	0,003	0,000	-
E3	0,020	0,050	0,040	0,030	0,000	0,060	0,000	0,000	0,000	0,010	0,000	0,000
E4	0,034	0,012	0,009	0,038	0,008	0,003	0,005	0,002	0,000	0,003	0,001	0,000
E5	0,020	0,010	0,020	0,050	0,010	0,010	0,010	0,010	0,010	0,030	0,000	0,000
E6	0,036	0,039	0,003	0,093	0,003	0,042	0,004	0,004	0,001	0,010	0,001	-
E7	0,208	0,051	0,003	0,204	0,051	0,006	0,008	0,006	0,010	0,005	0,001	0,001
E8	0,085	0,036	0,002	0,014	0,004	0,007	0,011	0,001	0,004	0,000	0,001	0,000
E9	0,038	0,039	0,008	0,169	0,028	-	0,009	0,001	0,011	-	-	-
E10	0,010	0,010	0,020	0,050	0,020	0,000	0,000	0,000	-	-	-	-
E11	0,003	0,005	0,007	0,010	0,021	0,002	0,000	0,002	0,001	0,000	0,001	0,000
E12	0,240	0,014	0,022	0,700	0,001	0,017	0,020	0,011	0,007	0,007	0,001	0,000
Average	0,048	0,028	0,010	0,076	0,025	0,021	0,009	0,008	0,005	0,005	0,001	0,000
Max.	0,240	0,211	0,059	0,700	0,261	0,136	0,082	0,161	0,013	0,030	0,003	0,001
Min.	0,001	0,004	0,000	0,004	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Range	0,239	0,207	0,059	0,696	0,261	0,136	0,082	0,161	0,013	0,030	0,003	0,001
Certified analysis	20,99	5,260	2,670	65,210	2,130	2,050	0,260	0,560	0,350	0,280	0,060	0,050
Limit value	0,150	0,080	0,080	0,250	0,080	0,080	0,020	0,030	0,020	0,020	0,020	0,020

NOTE Data in shaded cells represent results that did not satisfy the required criteria for repeatability specified for “expert” laboratories for the XRF method.

Table 5 — Difference in concentrations for each pair of validation beads
(All laboratories — Validation material: JCA-CRM-2)

Laboratory ref.	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 [a] %	Na_2O %	K_2O %	TiO_2 %	P_2O_5 %	MnO %	SrO %
1	0,001	0,001	0,003	0,002	0,002	0,00	0,005	0,006	0,001	0,000	0,000	-
2	0,051	0,010	0,001	0,020	0,018	0,03	0,003	0,002	0,014	0,002	0,000	0,000
3	0,032	0,010	0,013	0,013	0,009	-	0,009	0,001	0,000	0,000	0,001	-
4	0,008	0,016	0,006	0,047	0,010	0,02	0,003	0,003	0,000	0,001	0,003	0,000
5	0,038	0,019	0,001	0,012	0,009	0,02	0,001	0,001	0,002	0,000	0,000	0,000
6	0,113	0,044	0,018	0,105	0,025	0,03	0,012	0,007	0,007	0,002	0,000	0,000
7	0,009	0,003	0,001	0,038	0,026	0,00	0,000	0,001	0,002	0,001	0,000	0,000
8	0,005	0,016	0,003	0,040	0,003	0,00	0,000	0,000	0,007	0,001	0,001	0,000
9	0,094	0,016	0,001	0,101	0,012	-	0,002	0,002	0,004	0,000	0,001	0,000
10	0,035	0,091	0,015	0,183	0,040	-	0,011	0,002	0,003	0,000	0,001	-
11	0,020	0,030	0,002	0,100	0,047	0,00	0,016	0,000	0,014	0,001	0,001	-
12	0,006	0,052	0,020	0,022	0,004	-	0,014	0,004	0,006	0,000	0,001	0,001
13	0,010	0,008	0,003	0,058	0,008	0,01	0,002	0,000	0,005	0,000	0,000	0,000
14	0,071	0,052	0,006	0,156	0,009	0,01	0,008	0,004	0,014	0,015	0,003	0,001
15	0,052	0,006	0,005	0,021	0,001	0,01	0,006	0,002	0,003	0,001	0,000	0,000
16	0,054	0,046	0,006	0,019	0,011	0,03	0,005	0,002	0,003	0,000	0,001	0,001
101	0,005	0,039	0,011	0,060	0,013	-	0,017	0,001	0,001	0,000	-	-
102	0,022	0,011	0,004	0,029	0,008	0,00	-	0,001	-	-	-	-
103	0,020	0,070	0,010	0,000	0,140	0,03	0,010	0,000	-	-	-	-
104	0,034	0,039	0,010	0,188	0,009	0,02	0,007	0,017	0,003	0,001	0,003	0,000
105	0,043	0,019	0,002	0,010	0,020	0,00	0,004	0,004	0,010	0,005	0,006	0,000
106	0,057	0,045	0,043	0,107	0,015	-	0,002	0,001	-	-	-	-
107	0,121	0,014	0,048	0,012	0,015	-	0,009	0,005	-	0,002	0,003	-
108	0,250	0,060	0,000	0,250	0,020	0,03	0,070	0,000	-	0,010	-	-
109	0,054	0,023	0,013	0,057	0,002	0,02	-	0,010	-	-	-	-
110	0,022	0,119	0,018	0,138	0,037	0,02	0,021	0,019	-	0,008	-	-
111	0,060	0,050	0,010	0,070	0,030	0,02	0,000	0,000	0,010	0,020	0,000	0,000
112	-	-	-	-	-	-	-	-	-	-	-	-
113	0,050	0,050	0,020	0,050	0,030	-	0,010	0,010	0,010	0,000	0,000	0,000
E1	0,045	0,063	0,025	0,121	0,002	0,179	0,008	0,005	0,007	0,007	0,001	0,001
E2	0,003	0,003	0,008	0,017	0,002	0,025	0,005	0,005	0,001	0,006	0,002	-
E3	0,010	0,010	0,010	0,030	0,030	0,020	0,000	0,000	0,000	0,010	0,000	0,000
E4	0,062	0,054	0,001	0,111	0,026	0,047	0,013	0,001	0,001	0,002	0,004	0,002
E5	0,040	0,030	0,010	0,120	0,100	0,030	0,015	0,000	0,003	0,010	0,001	0,002
E6	0,002	0,019	0,008	0,041	0,033	-	0,000	0,003	0,000	0,007	0,002	-
E7	0,118	0,052	0,001	0,179	0,008	0,013	0,003	0,002	0,003	0,005	0,001	0,001
E8	0,049	0,003	0,014	0,070	0,038	0,005	0,008	0,002	0,000	0,004	0,000	0,000
E9	0,063	0,025	0,006	0,082	0,008	-	-	0,001	0,016	-	-	-
E10	0,010	0,010	0,010	0,040	0,000	0,000	0,000	0,000	-	-	-	-
E11	0,086	0,030	0,006	0,052	0,009	0,003	0,008	0,001	0,000	0,001	0,000	0,001
E12	0,260	0,193	0,023	0,430	0,005	-	0,016	0,003	0,003	0,009	0,000	-
Average	0,052	0,036	0,010	0,080	0,021	0,022	0,009	0,003	0,005	0,004	0,001	0,000
Max.	0,260	0,193	0,048	0,430	0,140	0,179	0,070	0,019	0,016	0,020	0,006	0,002
Min.	0,001	0,001	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Range	0,259	0,192	0,048	0,430	0,140	0,179	0,070	0,019	0,016	0,020	0,006	0,002
Certified analysis	25,66	8,940	2,080	56,330	3,050	-	0,240	0,310	0,500	0,070	0,150	0,070
Limit value	0,150	0,120	0,080	0,250	0,080	-	0,020	0,020	0,030	0,020	0,020	0,020

NOTE Data in shaded cells represent results that did not satisfy the required criteria for repeatability specified for "expert" laboratories for the XRF method.

[a] SO_3 for JCA-CRM-2 is outside the scope of JIS R 5204.

Table 6 — Differences between the mean value of the concentrations of a pair of validation beads and the certified value
(All laboratories — Validation material: JCA-CRM-1)

Laboratory ref.	SiO_2 %		Al_2O_3 %		Fe_2O_3 %		CaO %		MgO %		SO_3 %	
	Mean value [a]	Diff. [b]	Mean value [a]	Diff. [b]	Mean value [a]	Diff. [b]	Mean value [a]	Diff. [b]	Mean value [a]	Diff. [b]	Mean value [a]	Diff. [b]
1	20,96	-0,03	5,27	0,01	2,61	-0,06	65,29	0,08	2,11	-0,02	2,08	0,03
2	20,92	-0,07	5,26	0,00	2,65	-0,02	65,33	0,12	2,13	0,00	2,02	-0,03
3	20,94	-0,05	5,25	-0,01	2,68	0,01	65,11	-0,10	2,14	0,01	2,08	0,03
4	20,97	-0,02	5,26	0,00	2,68	0,01	65,20	-0,01	2,14	0,01	2,08	0,03
5	20,93	-0,06	5,26	0,00	2,67	0,00	65,24	0,03	2,13	0,00	2,09	0,04
6	20,93	-0,06	5,24	-0,02	2,61	-0,06	65,17	-0,04	2,12	-0,01	2,07	0,02
7	21,00	0,01	5,27	0,01	2,66	-0,01	65,20	-0,01	2,17	0,04	2,06	0,01
8	20,92	-0,07	5,27	0,01	2,68	0,01	65,05	-0,16	2,16	0,03	2,06	0,01
9	20,91	-0,08	5,26	0,00	2,61	-0,06	65,21	0,00	2,12	-0,01	2,07	0,02
10	20,96	-0,03	5,24	-0,02	2,63	-0,04	65,32	0,11	2,11	-0,02	2,08	0,03
11	21,02	0,03	5,28	0,02	2,67	0,00	65,21	0,00	2,12	-0,01	2,07	0,02
12	20,98	-0,01	5,27	0,01	2,68	0,01	65,27	0,06	2,14	0,01	2,09	0,04
13	21,03	0,04	5,27	0,01	2,68	0,01	64,98	-0,23	2,14	0,01	2,05	0,00
14	21,00	0,01	5,28	0,02	2,72	0,05	65,40	0,19	2,15	0,02	2,07	0,02
15	21,04	0,05	5,26	0,00	2,67	0,00	65,21	0,00	2,11	-0,02	1,98	-0,07
16	21,01	0,02	5,29	0,03	2,67	0,00	65,18	-0,03	2,15	0,02	2,09	0,04
101	21,05	0,06	5,29	0,03	2,62	-0,05	65,34	0,13	2,12	-0,01	2,03	-0,02
102	21,17	0,18	5,21	-0,05	2,64	-0,03	66,29	1,08	2,13	0,00	2,43	0,38
103	20,98	-0,01	5,21	-0,05	2,64	-0,03	65,25	0,04	2,14	0,01	2,08	0,03
104	20,98	-0,01	5,24	-0,02	2,63	-0,04	64,96	-0,25	2,10	-0,03	2,08	0,03
105	21,02	0,03	5,27	0,01	2,64	-0,03	65,38	0,17	2,18	0,05	2,06	0,01
106	20,95	-0,04	5,26	0,00	2,67	0,00	65,13	-0,08	2,12	-0,01	2,06	0,01
107	21,06	0,07	5,42	0,16	2,69	0,02	64,47	-0,74	2,15	0,02	2,04	-0,01
108	20,90	-0,09	5,26	0,00	2,62	-0,05	65,17	-0,04	2,10	-0,03	2,06	0,01
109	20,98	-0,01	5,26	0,00	2,63	-0,04	65,50	0,29	2,11	-0,02	1,95	-0,10
110	20,91	-0,08	5,25	-0,01	2,61	-0,06	65,13	-0,08	2,17	0,04	1,99	-0,06
111	20,92	-0,07	4,98	-0,28	2,62	-0,05	64,68	-0,53	2,38	0,25	2,00	-0,05
112	21,00	0,01	5,86	0,60	2,58	-0,09	64,77	-0,44	2,06	-0,07	1,80	-0,25
113	22,98	1,99	5,24	-0,02	2,64	-0,03	65,28	0,07	2,02	-0,11	2,06	0,01
E1	20,91	-0,08	5,26	0,00	2,66	-0,01	65,16	-0,05	2,14	0,01	2,20	0,15
E2	20,80	-0,19	5,30	0,04	2,61	-0,06	65,00	-0,21	2,11	-0,02	2,07	0,02
E3	20,79	-0,20	5,17	-0,09	2,71	0,04	65,17	-0,04	2,27	0,14	1,98	-0,07
E4	20,93	-0,06	5,28	0,02	2,65	-0,02	65,01	-0,20	2,17	0,04	2,04	-0,01
E5	21,01	0,02	5,25	-0,01	2,65	-0,02	65,33	0,12	2,14	0,01	2,07	0,02
E6	20,95	-0,04	5,23	-0,03	2,68	0,01	65,16	-0,05	2,15	0,02	2,13	0,08
E7	21,00	0,01	5,27	0,01	2,69	0,02	65,34	0,13	2,15	0,02	2,07	0,02
E8	20,89	-0,10	5,27	0,01	2,58	-0,09	65,13	-0,08	2,14	0,01	2,07	0,02
E9	20,99	0,00	5,22	-0,04	2,68	0,01	65,21	0,00	2,15	0,02	-	-
E10	21,09	0,10	5,16	-0,10	2,61	-0,06	65,14	-0,07	2,11	-0,02	2,01	-0,04
E11	20,75	-0,24	5,27	0,01	2,67	0,00	65,52	0,31	2,17	0,04	1,99	-0,06
E12	20,88	-0,11	5,29	0,03	2,67	0,00	64,91	-0,30	2,15	0,02	2,05	0,00
Average	21,01		5,27		2,65		65,19		2,14		2,06	
Max.	22,98		5,86		2,72		66,29		2,38		2,43	
Min.	20,75		4,98		2,58		64,47		2,02		1,80	
Range	2,23		0,88		0,14		1,82		0,36		0,63	
S.D.	0,325		0,111		0,033		0,268		0,053		0,085	
C.V.	1,5		2,1		1,3		0,4		2,5		4,1	
Certified value	20,99		5,26		2,67		65,21		2,13		2,05	

Table 6 (*continued*)

Laboratory ref.	Na_2O %		K_2O %		TiO_2 %		P_2O_5 %		MnO %		SrO %	
	Mean value [a]	**Diff.** [b]	**Mean value** [a]	**Diff.** [b]	**Mean value** [a]	**Diff.** [b]	**Mean value** [a]	**Diff.** [b]	**Mean value** [a]	**Diff.** [b]	**Mean value** [a]	**Diff.** [b]
1	0,26	0,00	0,54	-0,02	0,34	-0,01	0,29	0,01	0,07	0,01	-	-
2	0,26	0,00	0,53	-0,03	0,35	0,00	0,28	0,00	0,07	0,01	0,04	-0,01
3	0,26	0,00	0,57	0,01	0,36	0,01	0,28	0,00	0,06	0,00	-	-
4	0,26	0,00	0,56	0,00	0,36	0,01	0,29	0,01	0,06	0,00	0,04	-0,01
5	0,26	0,00	0,56	0,00	0,36	0,01	0,28	0,00	0,06	0,00	0,04	-0,01
6	0,27	0,01	0,58	0,02	0,34	-0,01	0,29	0,01	0,06	0,00	0,04	-0,01
7	0,25	-0,01	0,56	0,00	0,36	0,01	0,28	0,00	0,06	0,00	0,04	-0,01
8	0,25	-0,01	0,56	0,00	0,35	0,00	0,28	0,00	0,06	0,00	0,04	-0,01
9	0,26	0,00	0,57	0,01	0,35	0,00	0,29	0,01	0,07	0,01	0,04	-0,01
10	0,24	-0,02	0,57	0,01	0,35	0,00	0,28	0,00	0,07	0,01	-	-
11	0,25	-0,01	0,53	-0,03	0,36	0,01	0,29	0,01	0,06	0,00	-	-
12	0,27	0,01	0,57	0,01	0,35	0,00	0,28	0,00	0,06	0,00	0,04	-0,01
13	0,26	0,00	0,56	0,00	0,36	0,01	0,29	0,01	0,06	0,00	0,04	-0,01
14	0,27	0,01	0,58	0,02	0,33	-0,02	0,30	0,02	0,06	0,00	0,04	-0,01
15	0,27	0,01	0,56	0,00	0,35	0,00	0,29	0,01	0,06	0,00	0,04	-0,01
16	0,26	0,00	0,58	0,02	0,35	0,00	0,28	0,00	0,06	0,00	0,04	-0,01
101	0,23	-0,03	0,57	0,01	0,35	0,00	0,29	0,01	-	-	-	-
102	-	-	0,60	0,04	-	-	-	-	-	-	-	-
103	0,28	0,02	0,58	0,02	-	-	-	-	-	-	-	-
104	0,24	-0,02	0,56	0,00	0,34	-0,01	0,27	-0,01	0,07	0,01	0,04	-0,01
105	0,25	-0,01	0,60	0,04	0,35	0,00	0,29	0,01	0,07	0,01	0,04	-0,01
106	0,27	0,01	0,57	0,01	-	-	-	-	-	-	-	-
107	0,25	-0,01	0,56	0,00	-	-	0,28	0,00	0,06	0,00	-	-
108	0,26	0,00	0,59	0,03	-	-	0,28	0,00	-	-	-	-
109	-	-	0,57	0,01	-	-	-	-	-	-	-	-
110	0,28	0,02	0,58	0,02	-	-	0,29	0,01	-	-	-	-
111	0,28	0,02	0,57	0,01	0,38	0,03	0,36	0,08	0,07	0,01	0,04	-0,01
112	0,19	-0,07	0,58	0,02	-	-	-	-	-	-	-	-
113	0,26	0,00	0,58	0,02	0,35	0,00	0,28	0,00	0,07	0,01	0,04	-0,01
E1	0,26	0,00	0,56	0,00	0,35	0,00	0,29	0,01	0,06	0,00	0,04	-0,01
E2	0,27	0,01	0,57	0,01	0,34	-0,01	0,29	0,01	0,07	0,01	-	-
E3	0,26	0,00	0,55	-0,01	0,35	0,00	0,30	0,02	0,07	0,01	0,05	0,00
E4	0,27	0,01	0,57	0,01	0,34	-0,01	0,29	0,01	0,07	0,01	0,04	-0,01
E5	0,27	0,01	0,58	0,02	0,35	0,00	0,28	0,00	0,07	0,01	0,04	-0,01
E6	0,13	-0,13	0,56	0,00	0,35	0,00	0,31	0,03	0,06	0,00	-	-
E7	0,27	0,01	0,56	0,00	0,36	0,01	0,28	0,00	0,06	0,00	0,05	0,00
E8	0,27	0,01	0,57	0,01	0,34	-0,01	0,28	0,00	0,07	0,01	0,04	-0,01
E9	0,26	0,00	0,56	0,00	0,34	-0,01	-	-	-	-	-	-
E10	0,29	0,03	0,57	0,01	-	-	-	-	-	-	-	-
E11	0,25	-0,01	0,57	0,01	0,34	-0,01	0,28	0,00	0,06	0,00	0,05	0,00
E12	0,25	-0,01	0,57	0,01	0,35	0,00	0,29	0,01	0,07	0,01	-	-
Average	0,26		0,57		0,35		0,29		0,06		0,04	
Max.	0,29		0,60		0,38		0,36		0,07		0,05	
Min.	0,13		0,53		0,33		0,27		0,06		0,04	
Range	0,16		0,07		0,05		0,09		0,01		0,01	
S.D.	0,027		0,015		0,010		0,015		0,005		0,003	
C.V.	10,2		2,6		2,7		5,3		8,4		6,9	
Certified value	0,26		0,56		0,35		0,28		0,06		0,05	

NOTE Data in shaded cells represent concentrations that did not satisfy the required criteria for accuracy limits for "expert" laboratories specified for the XRF method.

[a] "Mean value" is the mean value of the concentrations of a pair of validated beads.

[b] "Diff." is the difference between the mean value of the concentrations of a pair of validated beads and the certified value for the validation material.