MAIN EDITION

BUREAU OF ANALYSED SAMPLES LTD

BRITISH CHEMICAL STANDARD CERTIFIED REFERENCE MATERIAL

CERTIFICATE OF ANALYSIS

BCS-CRM No. 392

FLUORSPAR

Prepared under rigorous laboratory conditions and, AFTER CERTIFICATION ANALYSIS IN GREAT BRITAIN, issued by the Bureau of Analysed Samples Ltd.

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ANALYSES

Mean of 4 values - mass content in %.

All results relate to the dried (110°C) sample.

Analyst No.	SiO_2	CaF_2	CaO	BaO	S	CO_2	Pb
1	0.71	97.2	0.49	0.35	0.13	0.49	0.16
2	0.62	97.4	0.52	0.40	0.12	0.46	0.19
3	0.70	97.3	0.52	0.38	0.12	0.46	0.19
4	0.70	97.0	0.51	0.40	0.11	0.48	0.15
5	0.68	97.0	0.52	0.30	0.10	0.49	0.18
6	0.66	96.8	0.51	0.42	0.12	0.45	0.15
7	0.65	97.6	0.54	0.32	0.12	0.51	0.18
8	0.64	97.4	0.57	0.39	0.11	0.51	0.21
M_M	**0.67**	**97.2**	**0.52**	**0.37**	**0.12**	**0.48**	**0.18**
s_M	0.04	0.3	0.03	0.05	0.01	0.03	0.03

The above figures are those which each Analyst has decided upon after careful verification.

M_M: Mean of the intralaboratory means. s_M: standard deviation of the intralaboratory means.

CERTIFIED VALUES (Cv)

mass content in %

	SiO_2	CaF_2	CaO	BaO	S	CO_2	Pb
Cv	**0.67**	**97.2**	**0.52**	**0.37**	**0.12**	**0.48**	**0.18**
C(95%)	0.03	0.3	0.02	0.04	0.01	0.02	0.02

The half width confidence interval **C**(95%) = $\frac{t \times s_M}{\sqrt{n}}$ where "t" is the appropriate two sided Student's t value at the 95% confidence level for "n" acceptable mean values.

For further information regarding the confidence interval for the certified value see ISO Guide 35:2006 sections 6.1 and 10.5.2.

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NOTES ON METHODS USED

SILICA

Analysts Nos. 1, 2, 6 and 7 determined silica gravimetrically by hydrofluoric acid treatment of the insoluble residue from the acetic acid/bromine attack (see under Calcium Fluoride). Nos. 3, 4 and 8 fused with sodium hydroxide and determined the silica photometrically. After acidifying the extract the silica was determined as silicomolybdate yellow (No. 4) or molybdenum blue (Nos. 3 and 8). No. 5 used X-ray fluorescence spectroscopy.*

CALCIUM FLUORIDE

Analysts Nos. 1, 6 and 7 digested the sample with acetic acid/bromine, followed by potassium bromide/bromine and finally with ammonium acetate solution; calcium fluoride remains insoluble whilst calcium carbonate and sulphate are dissolved.[1] After filtration and treatment of the silica with hydrofluoric acid the residue was treated with perchloric acid (Nos. 1 and 6) or sulphuric acid (No. 7) and the calcium was titrated with EGTA (Nos. 1 and 7) or separated as the oxalate and titrated with permanganate (No. 6). No. 2 fused the sample with fusion mixture/boric acid, extracted with hydrochloric acid and titrated with EDTA. No. 3 separated fluorine by pyrohydrolysis using vanadium pentoxide as an accelerator. The hydrogen fluoride evolved was collected in sodium hydroxide solution and titrated with cerous nitrate/EDTA. No. 4 fused with sodium carbonate and sodium pyroborate to separate calcium from fluoride. The carbonate precipitate was dissolved in acid and calcium precipitated as oxalate and determined gravimetrically after ignition to calcium oxide. No. 5 carried out a direct perchloric acid treatment to remove fluorine and titrated the calcium with EDTA. Nos. 2, 4 and 5 made a correction for acid-soluble calcium oxide. In addition Nos. 1, 2, 4, 5, 6 and 7 made a correction for the small amount of acid-soluble calcium fluoride. No. 8 separated the fluoride as fluosilicic acid by distillation according to the method of Willard and Winter[2] and titrated potentiometrically.

Analyst No. 4 also determined the calcium by separation as oxalate and titration with permanganate[1] and found 96.8%. No. 5 also used a pyrohydrolysis method and found 97.1%.

CALCIUM OXIDE

All Analysts except Nos. 6 and 7 carried out a selective extraction of soluble calcium compounds by digestion in 10% acetic acid. Nos. 1 and 2 determined the dissolved calcium by titration with EDTA in the presence of triethanolamine. No. 4 determined it by flame photometry. No. 5 determined it by loss in weight as carbon dioxide and conversion to calcium oxide. Nos. 3 and 8 used atomic absorption spectroscopy. Nos. 6 and 7 determined calcium oxide in the filtrate from the acetic acid/bromine attack (see under Calcium Fluoride). No. 6 separated the lead as molybdate and the soluble calcium was then precipitated as the oxalate and determined gravimetrically after ignition to calcium oxide. No. 7 titrated with EGTA. All Analysts made a correction for the small amount of acid-soluble calcium fluoride.[3]

BARIUM OXIDE

All Analysts except No. 5 determined barium oxide gravimetrically as barium sulphate. Nos. 1, 2 and 7 determined it in the insoluble residue from the acetic acid/bromine attack (see under Calcium Fluoride). No. 4 after double fuming with perchloric acid. No. 6 fused the sample with sodium carbonate and potassium nitrate, extracted in water and filtered; the filtrate was treated with dilute sulphuric acid to precipitate the barium. No. 8 used the Bidtel procedure.[4] No. 5 used X-ray fluorescence spectroscopy.*

SULPHUR

All Analysts except Nos. 3 and 8 determined sulphur gravimetrically. No. 1 fused with potassium carbonate/potassium nitrate, extracted in water and filtered; the resulting solution was then evaporated with hydrochloric acid to remove fluoride and the sulphate was precipitated as barium sulphate. No. 2 fused with sodium carbonate/boric acid, extracted in dilute hydrochloric acid then separated sulphur chromatographically on an alumina column.[5] Nos. 4, 5 and 7 decomposed the sample with perchloric acid. No. 6 fused with sodium carbonate/potassium nitrate, extracted in water and filtered; sulphur was determined in the filtrate. Nos. 3 and 8 used a combustion method and completed by iodimetric titration.

CARBON DIOXIDE

Analysts Nos. 1 and 3 treated the sample by boiling with hydrochloric acid, No. 2 with 10% acetic acid, No. 4 with a mixture of 50% hydrochloric acid and 1% boric acid; these Analysts all absorbed in soda-asbestos and completed gravimetrically. No. 5 determined total carbon by a combustion procedure. No. 6 determined carbon dioxide by loss in weight after treatment with hydrochloric acid in a Schrötter apparatus. No. 7 used an infrared gas analyser. No. 8 evolved carbon dioxide with hydrochloric acid, absorbed in barium hydroxide and titrated the barium carbonate with acid.

LEAD

Analysts Nos. 1, 2, 3, 7 and 8 determined lead by atomic absorption spectroscopy. Nos. 4 and 6 determined lead gravimetrically as the molybdate. No. 5 dissolved the sample in perchloric acid and determined lead by square-wave polarography.

REFERENCES

1. "Standard Methods of Analysis" of the United Steel Companies Ltd., 5th Edition 1961.
2. Willard and Winter, Ind. Eng. Chem. Anal., 1933, **5**, 7.
3. Scott, "Standard Methods of Chemical Analysis" Fifth Edition, 1939, Vol. 1.
4. Bidtel, J. Ind. Eng. Chem., 1912, **4**, 201; 1914, **6**, 265.
5. Nydahl, Anal. Chem., 1954, **26**, 580.

* Fused cast bead technique, calibration with synthetic standards.

DESCRIPTION OF SAMPLE

Bottles of 100g powder graded <150µm (100 mesh) for chemical analysis.

INTENDED USE & STABILITY

The sample is intended for the verification of analytical methods, such as those used by the participating laboratories, for the calibration of analytical instruments in cases where the calibration with primary substances (pure metals or stoichiometric compounds) is not possible and for establishing values for secondary reference materials.

It will remain stable provided that the bottle remains sealed and is stored in a cool, dry atmosphere. When the bottle has been opened the lid should be secured immediately after use. If the contents should become discoloured (e.g. oxidised) by atmospheric contamination they should be discarded.

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For BUREAU OF ANALYSED SAMPLES LTD,

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