

Certificate of measurement



4005

Natural Gypsum – Major Oxides and Trace Elements Certified Reference Material LGC2700

Certified Value

Constituent	Certified value ^{1,2} (µg/kg)	Uncertainty ^{2,3} (µg/kg)	Coverage factor ³ (k)	Minimum sample intake ⁴ (g)
Mercury	1.35	0.40	2.31	0.5

Assessed Values

Constituent	Number of laboratories	Assessed value ^{1,2} (g/100 g)	Uncertainty ^{2,3} (g/100 g)	Coverage factor ³ (k)	Minimum sample intake ⁴ (g)
Aluminium (as Al ₂ O ₃)	18	2.872	0.056	2.08	1.25
Calcium (as CaO)	19	26.31	0.36	2.07	1.25
Iron (as Fe ₂ O ₃)	19	1.150	0.062	2.10	1.25
Phosphorus (as P ₂ O ₅)	14	0.0367	0.0052	2.12	1.25
Potassium (as K ₂ O)	19	0.830	0.024	2.07	1.25
Silicon (as SiO ₂)	20	10.93	0.22	2.08	1.25
Sodium (as Na ₂ O)	13	0.183	0.018	2.13	1.25
Sulfur (as SO ₃)	15	34.67	0.60	2.07	1.25
Titanium (as TiO ₂)	19	0.1480	0.0075	2.09	1.25
Loss on Ignition	17	19.78	0.71	2.10	2.0
		Assessed value ^{1,2} (mg/kg)	Uncertainty ^{2,3} (mg/kg)		
Nickel	13	9.5	2.0	2.09	0.5
Vanadium	13	21.3	3.2	2.09	0.5
Zinc	12	19.3	3.8	2.09	0.5

Notes:

1. The mercury result is traceable to the SI through the use of NIST SRM3133. For the remaining constituents, the results are traceable to the SI through the physical and chemical standards used by the inter-laboratory study participant laboratories. The assessed values are reported to the same number of decimal places as the uncertainties (reported to 2 significant figures).
2. Values expressed following conditioning of the samples for at least 24 hours in a drying oven at (40 ± 2) °C at a maximum humidity of 50 %.
3. The quoted uncertainty is the half-width of the expanded uncertainty interval calculated using a coverage factor (k), providing a level of confidence of approximately 95 %.
4. The recommended minimum sample intake is based on the mass taken for homogeneity assessment.

Date of Issue: May 2012

Signed: _____

Gill Holcombe (Mrs)
for the Government Chemist

Indicative Values

The following figures are provided for information purposes and should be regarded as indicative values only.

Constituent	Indicative value ¹ (g/100 g)
Magnesium (as MgO)	3.2
Manganese (as MnO)	0.030
Strontium (as SrO)	0.20
	Indicative value ¹ (mg/kg)
Arsenic	2.4
Barium ²	170
Chromium	15
Cobalt	3.8
Copper	5.0
Lead	4.2
Thallium	0.18

Notes:

1. The indicative value for each constituent was assigned as the robust estimate of location of the accepted laboratory data.
2. Participants were encouraged to report data for other constituents they measure routinely on this type of material. There were sufficient data sets reported for barium to provide an indicative value.

Explanation of Terms

The constituent values have been categorised as certified, assessed or indicative depending on the source and spread of the data obtained.

The data for the **certified values** were obtained via analyses carried out at LGC using ID-ICP-MS (isotope dilution inductively coupled plasma mass spectrometry).

The data for the **assessed values** were obtained from an inter-laboratory study and were not considered to be of the same metrological quality as the certified value.

Values were classified as **indicative** where a) the small number of laboratories or the distribution of the results was considered unsuitable for assigning a sufficiently reliable value, or b) where there was no known value for the QC material which was analysed during the inter-laboratory study.

Acknowledgements

Production of this reference material and certificate was supported by the UK National Measurement System Measurement for Innovators Programme. The 'Joint Industry Project' (which facilitated the production of this material and materials numbered LGC2701, LGC2702 and LGC2703) was initiated by British Gypsum, and aimed to address the lack of high quality trace element reference data available for gypsum based materials.

LGC would like to thank British Gypsum and Bruker AXS for their financial support as well as their in-kind contributions.

Our thanks also go to the British Geological Survey for their guidance during the early stages of this project, and for carrying out the preparation and homogenisation of the powdered materials under contract.

SPECIMEN

Material Preparation

15 kg of natural gypsum, in the form of small chippings, was obtained from British Gypsum (East Leake, Leicestershire, UK). The material was prepared using a jaw crusher fitted with hardened chromium steel jaws to provide a powder, nominally 3 mm maximum diameter. The crushed material was dried at 30 °C in a calibrated drying oven. After drying, the material was milled in a cleaned 250 mL capacity agate milling vessel on a Retsch PM400 ball mill set at 300 rpm. Milling was continued until the powder passed a calibrated 75 µm stainless steel sieve mesh. The milled material was placed directly into a new cleaned 50 L plastic drum fitted with baffles and homogenised by rotating the drum for not less than 14 hours at 22 rpm on a roller blender.

The material was sub-sampled in aliquots of approximately 75 g into screw capped amber glass bottles. An additional seal (Viton rubber) was inserted beneath the cap of each bottle to ensure the closure was air-tight.

192 units of the candidate reference material were produced, and were stored at (20 ± 5) °C.

Homogeneity

The material was tested for homogeneity by analysing randomly selected units. Sub-samples were prepared as fusion beads, and analysed for aluminium, calcium, iron, magnesium, manganese, phosphorus, potassium, silicon, sodium, strontium, sulfur and titanium content, as the oxides, by XRF (X-ray fluorescence spectrometry); for arsenic, chromium, cobalt, copper, lead, manganese, nickel, thallium, vanadium and zinc content by ICP-MS (inductively coupled plasma mass spectrometry) and for mercury content by ID-ICP-MS.

An uncertainty contribution to allow for possible inhomogeneity was calculated for each constituent, as the higher of the between-unit standard deviation (u_{bb}) and s_w/\sqrt{n} , where s_w is the within-group standard deviation, and n is the number of replicate observations per unit. (For mercury, an additional contribution was included to allow for within-unit inhomogeneity.) This was combined with the characterisation uncertainty, and expanded using a coverage factor (k), to give the uncertainty quoted in the table on page 1.

Stability

The nature of the material is such that deterioration is not anticipated over the life of the material stored under appropriate conditions. The uncertainty associated with long-term instability was considered to be negligible compared with the uncertainty contributions from characterisation and possible inhomogeneity, and was therefore assigned a value of zero.

Certification

This material was characterised for mercury content by LGC using ID-ICP-MS. Other constituents were characterised through an inter-laboratory study.

Analytical Methods Used

Mercury

The sample (0.5 g) was spiked with a solution of enriched ^{199}Hg , obtained from ORNL, (Oak Ridge, TN, USA), to give a predicted $^{200}\text{Hg}:^{199}\text{Hg}$ ratio of 1.

The calibrant was NIST SRM3133, (9.954 ± 0.053) mg/g Hg (at 95 % confidence) in aqueous solution, diluted to an appropriate concentration with high purity 7.5 % HNO_3 /2.5 % HCl. In addition, a second standard obtained from Romil (Cambridge, UK) was measured in the same run.

The analysis for mercury was carried out by CV (cold vapour)/ID-ICP-MS using an Agilent 7500ce ICP-MS operating in gas mode, with helium as the cell gas.

Ten units of the material were analysed, in duplicate, on each of two days.

Major Oxides, Loss on Ignition and Trace Metals

This material was characterised via an inter-laboratory study which took place in October 2010. Participating laboratories were allowed to choose suitable methods with which they were familiar. These methods included Fused Bead XRF, Pellet XRF, ICP-MS, ICP-OES (inductively coupled plasma optical emission spectrometry) and AAS (atomic absorption spectrometry). The number of laboratories that used a particular method is shown in tables 1 and 2.

Loss on ignition was determined gravimetrically at temperatures ranging from 1000 °C to 1100 °C, for 1 hour.

The data from the inter-laboratory study were processed using a robust statistical approach, after screening laboratories based on their performance in analysing a separate QC sample. The value for each constituent was assigned as the robust estimate of location of the accepted laboratory data. Uncertainties were based on the robust estimate of dispersion, taking into account the number of laboratories and corrected for the efficiency of the estimator.

Table 1 Methods used by laboratories to determine major oxide content (accepted results only)

Constituent	XRF	ICP-OES	Flame AAS/ Flame Photometry	Other*
Aluminium (as Al ₂ O ₃)	16	1	-	1
Calcium (as CaO)	17	1	-	1
Iron (as Fe ₂ O ₃)	17	1	-	1
Magnesium (as MgO)	18	1	-	1
Manganese (as MnO)	16	-	1	-
Phosphorus (as P ₂ O ₅)	13	-	-	1
Potassium (as K ₂ O)	17	1	1	-
Silicon (as SiO ₂)	18	1	-	1
Sodium (as Na ₂ O)	13	-	-	-
Strontium (as SrO)	16	1	-	-
Sulfur (as SO ₃)	13	-	-	2
Titanium (as TiO ₂)	18	-	-	1

* Including: gravimetry, colorimetry, titrimetry and elemental analyser

Table 2 Methods used by laboratories to determine trace element content (accepted results only)

Constituent	XRF	ICP-MS	ICP or ICP-OES	Flame AAS/Flame Photometry	GF-AAS	HG-AFS/CV AFS	Not specified
Arsenic	2	2	1	-	1	1	-
Barium	-	-	-	-	-	-	3
Chromium	7	2	4	1	-	-	1
Cobalt	5	3	-	-	1	-	-
Copper	5	-	1	1	-	-	-
Lead	4	3	-	1	-	-	1
Nickel	7	1	3	1	-	-	1
Thallium	1	2	-	-	1	-	-
Vanadium	7	2	3	-	-	-	1
Zinc	7	1	4	-	-	-	-

Intended Use

This reference material is intended for use in the validation of new methods, and for monitoring the performance of methods commonly used in laboratories to analyse samples of gypsum for quality control and environmental monitoring purposes.

Information on how to compare an analytical result with the assigned value can be found in ERM Application Note 1; www.erm-crm.org

Instructions for Use

Before analysing this material, samples must be conditioned by drying in an oven at (40 ± 2) °C, and at less than 50 % humidity, for 24 hours.

The mass of material taken for the homogeneity assessment of each constituent is given in the table on page 1, and represents the minimum mass which should be taken for analysis.

Storage and Shelf Life

The material should be stored at (20 ± 5) °C in the original bottle until it is first opened, and then at (20 ± 5) °C in low humidity conditions with the original bottle tightly closed.

If stored under the recommended conditions, the certified and assessed values will remain valid for 12 months from the date of shipment (see page 7 for shipment date).

Participants

The following laboratories participated in the inter-laboratory study:

Arkema Inc.	Pennsylvania, USA
British Geological Survey	Nottingham, UK
British Gypsum	East Leake, UK
CERAM	Stoke-on-Trent, UK
Council for Geoscience	Pretoria, South Africa
FLUXANA GmbH & Co.KG	Bedburg-Hau, Germany
Geological Survey of Estonia	Tallinn, Estonia
Greenwich University	Chatham, UK
Headwaters Resources, Inc.	Georgia, USA
Holcim (Schweiz) AG	Wuerenlingen, Switzerland
London & Scandinavian Metallurgical Ltd	Sheffield, UK
Montanuniversität Leoben	Leoben, Austria
Nordkalk Oy Ab	Pargas, Finland
Owens Corning	Ohio, USA
PANalytical BV	Almelo, Netherlands
PS Analytical	Orpington, UK
Sibelco	Dessel, Belgium
Terrachem GmbH	Mannheim, Germany
Total Petrochemicals Research	Feluy, Belgium
University of Stellenbosch	Stellenbosch, South Africa
University of Twente	Enschede, Netherlands
Universidad Nacional Autonoma de Mexico	Mexico City, Mexico

Unit Number

Date of Shipment

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Production of this reference material and certificate was supported by the UK National Measurement System Measurement for Innovators Programme.

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