

## **CANADIAN CERTIFIED REFERENCE MATERIALS**

### *Certificate of Analysis*

**FOUR NORTH-AMERICAN NATURAL GYPSUM ROCK SAMPLES TYPE:  
CALCIUM SULFATE DIHYDRATE  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$**

#### **GYP-A, GYP-B, GYP-C and GYP-D**

Prepared and issued by the Analytical Group of Domtar Inc. Research Center in Senneville, (Montreal), Quebec, Canada in cooperation with Domtar Inc. Gypsum Products Laboratory in Caledonia, Ontario, Canada. Analyses of the samples were kindly provided by the participating laboratories. The received round-robin results were statistically evaluated and processed at the Research Center in Senneville (Montreal).

#### **SELECTION AND PREPARATION OF THE SAMPLES**

The four natural gypsum rocks were specially selected with respect to the present impurities from three localities in Canada and one in the United States. The objective was to prepare four homogenous bulk samples ranging from a relatively pure gypsum to a quite impure one. Variation of the impurities in the samples should assist the analyst in setting-up calibration procedures within the covered ranges and allow for the analysis of variety of industrial gypsum.

Each of the four samples was chosen from a large dried and pulverized (-100 mesh) gypsum rock sample, weighing several tons. Each sample was thoroughly mixed, homogenized in a mechanical blender, quartered and mixed again. The homogeneity of each sample was verified by X-ray fluorescence spectrometry (XRF).

#### **STABILITY AND INSTRUCTIONS FOR DRYING AND STORAGE**

The long term stability of the samples has not been rigorously tested. The results of the thermal analysis scans (DTA-TGA) carried out on freshly prepared samples and then repeated several years later showed no significant differences in the combined water and carbon dioxide content.

**ATTENTION – VERY IMPORTANT :** The portion of the sample used for analysis should be dried before use for a minimum of 1 hour at  $40^\circ\text{C} \pm 3^\circ\text{C}$ . In no circumstances should the temperature of drying exceed  $45^\circ\text{C}$ . Sufficient drying is completed in 2-3 hours at the recommended temperature. Use of excessive temperatures will cause dehydration of calcium sulfate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  to calcium sulfate hemihydrate,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , resulting in partial decomposition of the sample.. Therefore, the samples should be stored at room temperature ( $15$  to  $25^\circ\text{C}$ ), away from direct sunlight or other sources of heat. It is recommended that bottles be tightly closed after each use.

#### **QUANTITY AND PACKAGING**

The samples are packaged for laboratory use in  $100\text{g} \pm 0.5\text{g}$  quantities. Wide mouthed, air-tight polyethylene bottles, provided with a polypropylene lid were chosen for packaging and easy transportation.

#### **LOSS ON IGNITION**

Loss on ignition was determined by several laboratories on the dried  $40^\circ\text{C}$  sample, heated for 1 hour at  $1000^\circ\text{C}$ . The loss on ignition values will be important for laboratories using borate fusion as a sample preparation method (1, 2 and 3). Studies carried out by thermal analysis (DTA-TGA) in an atmosphere of air, confirmed that except for the losses of combined water and carbon dioxide from the gypsum and the impurities, the main ignition product, calcium sulfate,  $\text{CaSO}_4$  (anhydrite), remains stable up to  $1200^\circ\text{C}$ .

## NATURAL IMPURITIES

The initial study of the samples by thermal analysis (DTA-TGA) and by X-ray diffraction (XRD), pointed mainly to the presence of calcite, dolomite and quartz as impurities. Ramik and Wicks from the Mineralogy Department of Royal Ontario Museum in Toronto, carried out a thorough study of the impurities, using a high resolution Guinier camera. Later, in 2005 the quantification of the impurities was carried out using the separation method of Kocman (7) and Quantitative X-Ray Rietveld Analysis. The approximate concentrations of impurities in weight percent are listed below.

| <u>GYP-A</u>   | <u>GYP-B</u>  | <u>GYP-C</u>     | <u>GYP-D</u>                   |
|----------------|---------------|------------------|--------------------------------|
| anhydrite (2)  | anhydrite (2) | anhydrite (1.5)  | dolomite (9)                   |
| dolomite (0.2) | dolomite (8)  | dolomite (25)    | quartz (8)                     |
| quartz (0.4)   | calcite (2.4) | quartz (1.6)     | microcline (2)                 |
|                | quartz (0.5)  | microcline (1.5) | Fe-K-illite, kaolinite (trace) |

## ANALYTICAL METHODS USED

The values reported for the major elements were determined by a variety of analytical methods such as gravimetry, atomic absorption spectrophotometry (AA), plasma emission (ICP), X-ray fluorescence) spectrometry (XRF), thermogravimetry, coulometry, selective ion electrode, neutron activation analysis (INAA) and gas evolution techniques. Determinations of trace elements were dominated mainly by spectroscopy (ICP, AA) and neutron activation analysis (INAA). Full details of the study were published in Geostandards Newsletter (4)

## STATISTICAL EVALUATION OF THE ROUND-ROBIN RESULTS

The round-robin results received from the individual laboratories were processed by a computer program originally written by Dybczynski (5) and later expanded and modified by Rousseau (6). The Dybczynski-Rousseau computer program uses four statistical criteria for the rejection of 'outliers'. These are Dixon's and Grubb's criteria, followed by tests for skewness and kurtosis of the data sets. The last two tests check for the distortions caused by non-Gaussian distribution of the data.

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Senneville, Quebec, Issued : February 1986

Senneville, Quebec, August, 1991 (revision of trace element values)

Montreal. Quebec, March, 2001 (linguistic revisions, Certificate of Analysis reprinted )

Montreal. Quebec, March, 2005 (quantification of impurities, consensus values unchanged)

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**CONSENSUS VALUES**

(all values are based on a sample dried at 40°C)

**MAJOR ELEMENTS IN WEIGHT PERCENT**

(Std. Deviations in Parentheses)

|                                    | GYP-A         | GYP-B         | GYP-C         | GYP-D         |
|------------------------------------|---------------|---------------|---------------|---------------|
| CaO                                | 32.9 (0.2)    | 32.8 (0.4)    | 30.4 (0.7)    | 28.2 (0.6)    |
| SO <sub>3</sub>                    | 46.2 (0.5)    | 41.0 (0.6)    | 33.0 (0.4)    | 36.7 (0.4)    |
| MgO                                | 0.18 (0.04)   | 1.80 (0.1)    | 5.35 (0.3)    | 1.73 (0.1)    |
| Al <sub>2</sub> O <sub>3</sub>     | 0.10 (0.04)   | 0.17 (0.04)   | 0.79 (0.06)   | 2.03 (0.1)    |
| Fe <sub>2</sub> O <sub>3</sub> T * | 0.05 (0.01)   | 0.07 (0.01)   | 0.40 (0.04)   | 1.08 (0.06)   |
| P <sub>2</sub> O <sub>5</sub>      | 0.011 (0.004) | 0.010 (0.003) | 0.018 (0.007) | 0.025 (0.008) |
| SiO <sub>2</sub>                   | 0.45 (0.13)   | 1.05 (0.12)   | 3.5 (0.2)     | 8.7 (0.3)     |
| K <sub>2</sub> O                   | 0.021 (0.008) | 0.05 (0.01)   | 0.36 (0.06)   | 0.54 (0.07)   |
| Na <sub>2</sub> O                  | 0.009 (0.003) | 0.021 (0.005) | 0.022 (0.005) | 0.07 (0.03)   |
| SrO                                | 0.11 (0.01)   | 0.14 (0.02)   | 0.35 (0.03)   | 0.18 (0.02)   |
| H <sub>2</sub> O + G               | 19.4 (0.1)    | 17.80 (0.08)  | 14.37 (0.05)  | 16.39 (0.07)  |
| H <sub>2</sub> O + Clay            | -             | -             | -             | 0.37 (0.02)   |
| CO <sub>2</sub>                    | 0.47 (0.06)   | 5.0 (0.2)     | 11.2 (0.2)    | 3.6 (0.3)     |
| % Total:                           | 99.90         | 99.91         | 99.76         | 99.62         |
| % L.O.I. **                        | 20.06 (0.08)  | 22.85 (0.03)  | 25.93 (0.04)  | 20.82 (0.02)  |

\* Total iron calculated as Fe<sub>2</sub>O<sub>3</sub>

\*\* Loss on ignition at 1000°C (1hr)

H<sub>2</sub>O+ G Combined water determined at 250°CH<sub>2</sub>O+ Clay Water released from clay (kaolinite) between 450-550°C (TGA)**TRACE ELEMENTS IN ALPHABETICAL ORDER**

Mean concentrations in micrograms/gram ( µg/g)

| Element | GYP-A         | GYP-B         | GYP-C       | GYP-D       |
|---------|---------------|---------------|-------------|-------------|
| As      | 0.21 (0.04)   | 0.28 (0.06)   | 2.5 (0.6)   | 3.1 (0.9)   |
| Ba      | 28 ?          | 22 (8)        | 52 (9)      | 107 (15)    |
| Br      | 0.2 (0.07)    | 0.4 ?         | 1.7 (0.2)   | 1.3 (0.4)   |
| Cd      | 0.5 (0.04)    | -             | -           | -           |
| Ce      | 0.7 (0.2)     | 1.18 (0.22)   | 5 (0.8)     | 9 (1)       |
| Cl      | 12 (3)        | 31 (4)        | 142 (25)    | 225 (30)    |
| Co      | 0.4 (0.1)     | 0.3 (0.1)     | 1.3 ?       | 2.4 (0.5)   |
| Cr      | 0.7 (0.2)     | 1.3 (0.4)     | 4 (1)       | 11 (2)      |
| Cs      | 0.1 ?         | 0.15 ?        | 0.37 (0.10) | 1.3 (0.3)   |
| Cu      | -             | -             | -           | 10 ?        |
| Dy      | -             | 0.06 ?        | 0.4 ?       | 0.7 (0.1)   |
| Eu      | 0.03 ?        | 0.04 ?        | 0.13 ?      | 0.18 (0.03) |
| Hf      | 0.03 ?        | 0.10 ?        | 0.23 (0.05) | 0.41 (0.07) |
| Hg      | 0.003 ?       | <0.002?       | -           | <0.002 ?    |
| La      | 0.24 (0.07)   | 0.54 (0.08)   | 2.9 (0.3)   | 4.6 (0.5)   |
| Lu      | 0.006 ?       | 0.007 ?       | 0.03 (0.01) | 0.06 (0.01) |
| Mn      | 19 (5)        | 10 (2.5)      | 65 (5)      | 200 (30)    |
| Mo      | 0.7 ?         | 0.4 ?         | 3.3 ?       | 1 ?         |
| Nd      | -             | -             | 4 ?         | -           |
| Rb      | 1.00 (0.45)   | 1.5 (0.5)     | 8 (1)       | 24 (3)      |
| Sb      | 0.04 ?        | 0.026 (0.006) | 0.18 (0.03) | 0.27 (0.05) |
| Sc      | 0.08 (0.03)   | 0.17 (0.05)   | 0.73 (0.15) | 2.0 (0.5)   |
| Sm      | 0.040 (0.009) | 0.08 (0.02)   | 0.47 (0.06) | 0.84 (0.12) |
| Ta      | -             | 0.02 ?        | 0.03 ?      | 0.13 (0.05) |
| Th      | 0.10 (0.03)   | 0.14 (0.04)   | 0.52 (0.07) | 1.4 (0.2)   |
| Ti      | -             | 65 (20)       | 225 (25)    | 505 (70)    |
| U       | 0.10 (0.02)   | 0.23 (0.05)   | 0.72 (0.07) | 0.65 (0.1)  |
| V       | 1.0 (0.4)     | 1.33 (0.04)   | 5 (2)       | 15 (3)      |
| Yb      | 0.020 (0.004) | 0.03 (0.01)   | 0.16 (0.04) | 0.4 (0.1)   |
| Zn      | 5 ?           | 5 ?           | 17 (5)      | 18 (4)      |
| Zr      | 9 ?           | -             | 27 (3)      | 27 ?        |

? Provisional value only, less than 5 results available, or std. deviation too high

- Value not available

## **PARTICIPANTS OF THE ROUND-ROBIN ANALYSES**

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