

XRD Opal-C and Crystalline Silica Quantification in DE		Procedure#: LAB WI 700NC
Issue Date: Oct. 20, 2017	Issue#: 001	E-P Reference#: n/a
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1) REVISION HISTORY

Issue Number	Issue Date	Reviewed By	Approved By	Description of Changes
001	Oct. 20, 2017	Corporate Quality Manager Sr. Research Scientist	Corporate Quality Manager Sr. Research Scientist	Non-controlled document for Public access

- 2) **PURPOSE:** This purpose of this procedure is to guide individuals with previous experience in operating the D-5000 x-ray diffractometer in analyzing bulk powder samples for crystalline silica and opal-C content.
- 3) **SCOPE:** This procedure should be used for determination of opaline and crystalline silica phases in diatomaceous and other samples. The quartz intensity ratio (determined using WI 633) shall be used to adjust subsequent peak intensities (by dividing said intensities by the ratio) when quantifying crystalline silica phases. Quantification down to the 0.15% level can be achieved using this test method if interfering phases are not present to a significant extent.
- 4) **RESPONSIBILITY/ OWNER:** Sr. Research Scientist
- 5) **EQUIPMENT AND MATERIALS REQUIRED:**
 - a) Siemens D-5000 X-ray Diffractometer plus associated equipment and controlling software.
 - b) Spex mill or similar.
 - c) Balance, resolution to 0.01g or better
 - d) At least 1 ml of dried, representative split of sample to be tested, milled to a nominal 10 µm top size.
 - e) Corundum spike, alfa alumina powder, 1µm type DX (or similar)
 - f) Respirable cristobalite spike, NIST 1879a
 - g) Respirable quartz spike, NIST 1878a
- 6) **SAFETY/REQUIRED PPE:** Safety glasses must be worn in the lab. Observe radiation safety precautions.
- 7) **ENVIRONMENTAL:** There are no environmental concerns.
- 8) **RECORDS / FORMS:** No set format required. Records must be kept in accordance with each site's ISO 9001 records procedure relating to calibration or verification records. Samples should be logged in Jade sample database with results stored electronically. The sample log in should include the date of testing and sample identifier.
- 9) **PROCEDURE:**
 - a) Energize the diffractometer to 36mA and 50KV.
 - b) Weigh out 0.58 to 1.00g of sample and add 2 to 4% corundum spike.
 - c) Place the sample in a Spex Mill cylinder with one ceramic ball, and blend / mill for 10 minutes.
 - d) Mount the dried, milled sample into the sample holder, taking care to maintain sample homogeneity in all three dimensions. Powder should be placed in the depression and compacted with the edge of a glass slide. Excess should be removed from around the edges of the depression, and the sample again compressed using the edge of the glass slide and excess once again removed. Final compression should be straight down using the flat of the glass slide. The sample level should be exactly even with the top surface of the sample holder, as determined using visual inspection.

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- e) Place the sample holder into the sample spinner, and set the testing parameters (using DataScan 5 or succeeding control software versions) to the following:
 - i) 2-theta range: a minimum to cover both primary and secondary diffraction peaks of quartz and cristobalite, typically 20 to 23° (for cristobalite/opal-C primary and quartz secondary), 25.0 – 27.1° (for quartz primary and corundum secondary), and 30.6 – 32.0° (for cristobalite/opal-C secondary). In some cases, the two theta range will need to be extended to cover tertiary peaks and possible interfering phases.
 - ii) Step-size = 0.02°
 - iii) Step Time = 6.0 seconds per step (for long, qualitative scans to identify interfering phases, the step size can be increased to 0.04° and time reduced to 3 seconds per step).
 - iv) Sample spinner at 15 rpm
- f) Run the sample.
- g) Using Jade software, adjust the 2^θ offset of the pattern so that the corundum peak at 3.480Å is centered at that d-spacing. Inspect the diffraction pattern and determine if quartz and/or cristobalite could be present (check primary and secondary peak locations).
- h) If so, check for possible interfering peaks such as feldspars and micas.
- i) If interfering phases are not present or not significant, then use the software to determine the primary and secondary peak net intensity (CPS), location (centroid d-spacing), and FWHM for quartz and/or cristobalite/Opal-C. Record these values along with the current x-ray tube intensity ratio (see Lab WI 633).
- j) If interfering phases are present, estimate the contributions (in CPS) to net peak intensities, and subtract these amounts from the recorded values.
- k) If the results of calculations (see section 10) indicate that cristobalite and opal-C cannot be differentiated, spike a split of the sample with NIST 1879a respirable cristobalite (10 to 20% spike), mill and blend, and repeat steps 9 and 10.

10) CALCULATIONS:

- a) Enter data in the LH method tab of the Excel Workbook labeled “OSHA and LH bulk XRD”. The spreadsheet calculates whether cristobalite or opal-C is present, and quantifies the opal-C/cristobalite and quartz phases. Alternatively, the following calculations can be used.
- b)
 - (1) **Quartz (%) = (0.0074 *CPS/IR) -0.11** where **CPS** = counts per second (peak net intensity), and **IR** = current x-ray tube net intensity ratio.
 - (a) If the ratio of quartz secondary peak to primary peak net intensity is less than 7%, or the calculated quartz quantity is less than 0.15%, then report quartz as “not detected”. Otherwise, report to the nearest 0.1%.
 - (2) **Cristobalite/Opal-C (%) = (0.0067 *CPS/IR) – 0.27** where **CPS** = counts per second (peak net intensity), and **IR** = current x-ray tube net intensity ratio.
 - (a) If the ratio of secondary to primary peak net intensity is less than 3.3% AND the primary peak d-spacing is greater than 4.065 (between 4.065 and 4.12) AND the sample LOI is at least 0.1%, then the phase present is Opal-C. If the calculated value is less than 0.15%, report as not detected. Otherwise, report results to the nearest 0.1%.
 - (b) If the ratio of secondary to primary peak net intensity is greater than 3.5% AND the primary peak d-spacing is less than 4.062 (between 4.01 and 4.062), then the phase present is cristobalite. If the calculated value is less than 0.15%, report as not detected. Otherwise, report results to the nearest 0.1%.

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- (c) If the conditions of (a) or (b) are not met, then the phase is undetermined and a split of the sample should be spiked with NIST 1879a and re-analyzed. If the second diffraction pattern shows a significant change in primary peak shape (near $22^\circ 2\theta$) and/or secondary peak shape (near $31.5^\circ 2\theta$), then the original phase present should be identified as opal-C. Significant changes in shape include development of two distinct peaks, development of a “shoulder” on the primary or secondary peak at lower D-spacing, or a significant broadening of the peaks (indicating overlapping peaks). If the second diffraction pattern shows no significant change other than in net intensity, then the original phase should be identified as cristobalite.