Cristobalite or Opal?  
A Confirmation of XRD Determination using FTIR

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Introduction

- Cristobalite and quartz, both crystalline silica polymorphs and Group 1 human carcinogens, are regulated in the workplace by OSHA.
- Crystalline silica, SiO₂, in workplace air can be analyzed by X-ray diffraction (XRD) methods, NIOSH 7600 and OSHA ID-142.
- Quartz can also be analyzed by infrared spectroscopy (IR) method, NIOSH 7603.
- Cristobalite can be challenging to determine due to its tendency for peak broadening and the similarity of its diffraction pattern to opal.
- Opal is not classified as a carcinogen.

NIOSH 7600 was modified to include analysis of cristobalite by IR to confirm XRD results. Mineral dust from the XRD filter is redeposited on the IR filter and analyzed by IR.

Cristobalite may quantitated on the IR at its primary peak at ~798 cm⁻¹ and its secondary peak at ~623 cm⁻¹.

- Quartz, cristobalite, and amorphous silica all share the same primary peak on the IR. Cristobalite may be determined by its secondary peak in the presence of those interferences.

Crystalline Silica Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>NIOSH 7500</th>
<th>OSHA ID-142</th>
<th>NIOSH 7603</th>
<th>NIOSH 7602</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument</td>
<td>XRD</td>
<td>XRD</td>
<td>IR</td>
<td>IR</td>
</tr>
<tr>
<td>Silica Polymorph</td>
<td>Quartz</td>
<td>Quartz</td>
<td>Quartz in Coal Mine Dust</td>
<td>Quartz</td>
</tr>
<tr>
<td>Quartz Standard</td>
<td>SRM 1878A</td>
<td>SRM 1878A</td>
<td>SRM 1878A</td>
<td>SRM 1878A</td>
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<tr>
<td>Cristobalite Standard</td>
<td>SRM 1878A</td>
<td>SRM 1878A</td>
<td>SRM 1878A</td>
<td>SRM 1878A</td>
</tr>
<tr>
<td>Analytical Preparation</td>
<td>Deposited on silver membrane filter</td>
<td>Deposited on silver membrane filter</td>
<td>Deposited on acrylic copolymer filter</td>
<td>Press into KBr pellet</td>
</tr>
</tbody>
</table>

Methodology

- The calibration curves for the primary and secondary cristobalite peaks were plotted following NIOSH 7603 for Quartz.
- Method detection limits were established at both peaks with standards prepared using the same preparation process as workplace air samples.
- The instruments used were Philips Cubic X-ray Diffractometer and Perkin Elmer FTIR 1600.
- Quality control checks redeposited from XRD silver membrane filter to IR copolymer filters were evaluated for both quartz and cristobalite.

Results

Initial XRD Result Compared to Result after Mineral Transfer to IR Filter, Average % Recovery for Seven Replicates at 100 μg

Sample 1: Workplace Air Sample

The XRD results were 330 μg at the primary angle, and 231 μg at the secondary angle after a 2x dilution calculation. Cristobalite’s peak broadening tendencies can cause angle agreement discrepancies. The library search finds both cristobalite and opal.

The IR results were 435 μg at the primary peak, and 245 μg at the secondary peak after a 2x dilution calculation. Possibility of amorphous silica interference at the primary peak IR pattern confirms cristobalite for Sample 1.

Sample 2: Bulk Sample With Quartz

The XRD results were 62 μg at Quartz primary, 42 μg at Cristobalite primary, and the presence of amorphous silica. The cristobalite primary peak is broad. The library search finds only cristobalite, not opal. Particle size discrepancies in bulks can confound quantitation.

The IR results were 280 μg at Quartz, Cristobalite, and amorphous silica primary; and no absorbance at Cristobalite secondary. IR pattern confirms cristobalite for Sample 2.

Sample 3: Workplace Air Sample

The XRD results were 400 μg at the primary angle, and 434 μg at the secondary angle after 2x dilution calculation. Possible zinc and hematite interferences are present. The library search finds only cristobalite, not opal.

The IR results were 622 μg at primary, and 737 μg at secondary, with possible zinc and hematite interferences, after 4x dilution calculation. IR pattern confirms cristobalite for Sample 3.

Summary and Conclusions

- Some interfering minerals, such as aluminum silicates, obscure crystalline silica peaks on the IR, making confirmation difficult.
- More study is needed on cristobalite’s peak broadening and peak shift tendencies.
- More study is needed on the different types of opal. The availability of a standard reference material would be helpful.

References


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