



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 7500 and OSHA ID-142.
- Quartz can also be analyzed by an 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 7603 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 be quantitated on the IR at its primary peak at ~798 cm⁻¹ and its secondary peak at ~623 cm⁻¹.
- Quartz, cristobalite, opal, 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

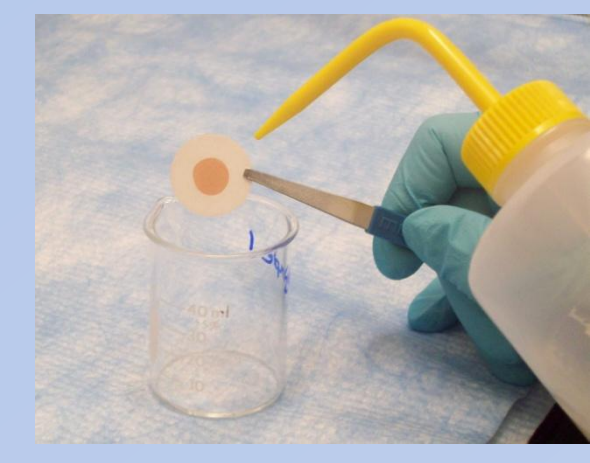
Method	NIOSH 7500	OSHA ID-142	NIOSH 7603	NIOSH 7602
Instrument	XRD	XRD	IR	IR
Silica Polymorph	Quartz	Quartz	Quartz in Coal Mine Dust	Quartz
Quartz Standard	SRM 1878A	SRM 1878A	SRM 1878A	SRM 1878A
Cristobalite Standard	SRM 1879A	SRM 1879A	SRM 1879A	SRM 1879A
Analytical Preparation	Redeposition on silver membrane filter	Redeposition on silver membrane filter	Redeposition on acrylic copolymer filter	Press into KBr pellet

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 Cubix X-ray Diffractometer and Perkin Elmer FTIR 1600.
- Quality control checks redeposited from XRD silver membrane filters to IR copolymer filters were evaluated for both quartz and cristobalite.



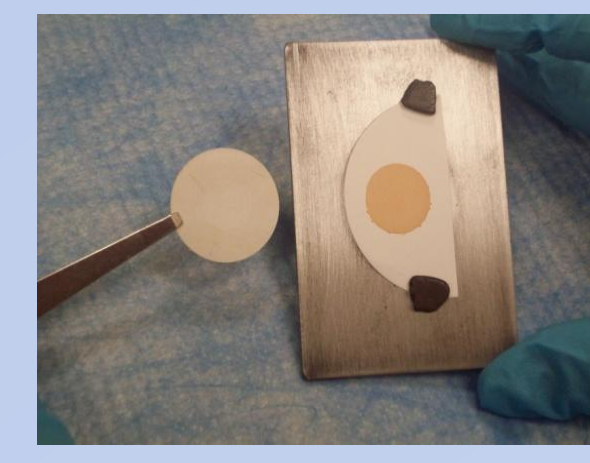
(1) XRD sample needs confirmation by IR.



(2) Rinse in IPA and sonicate.

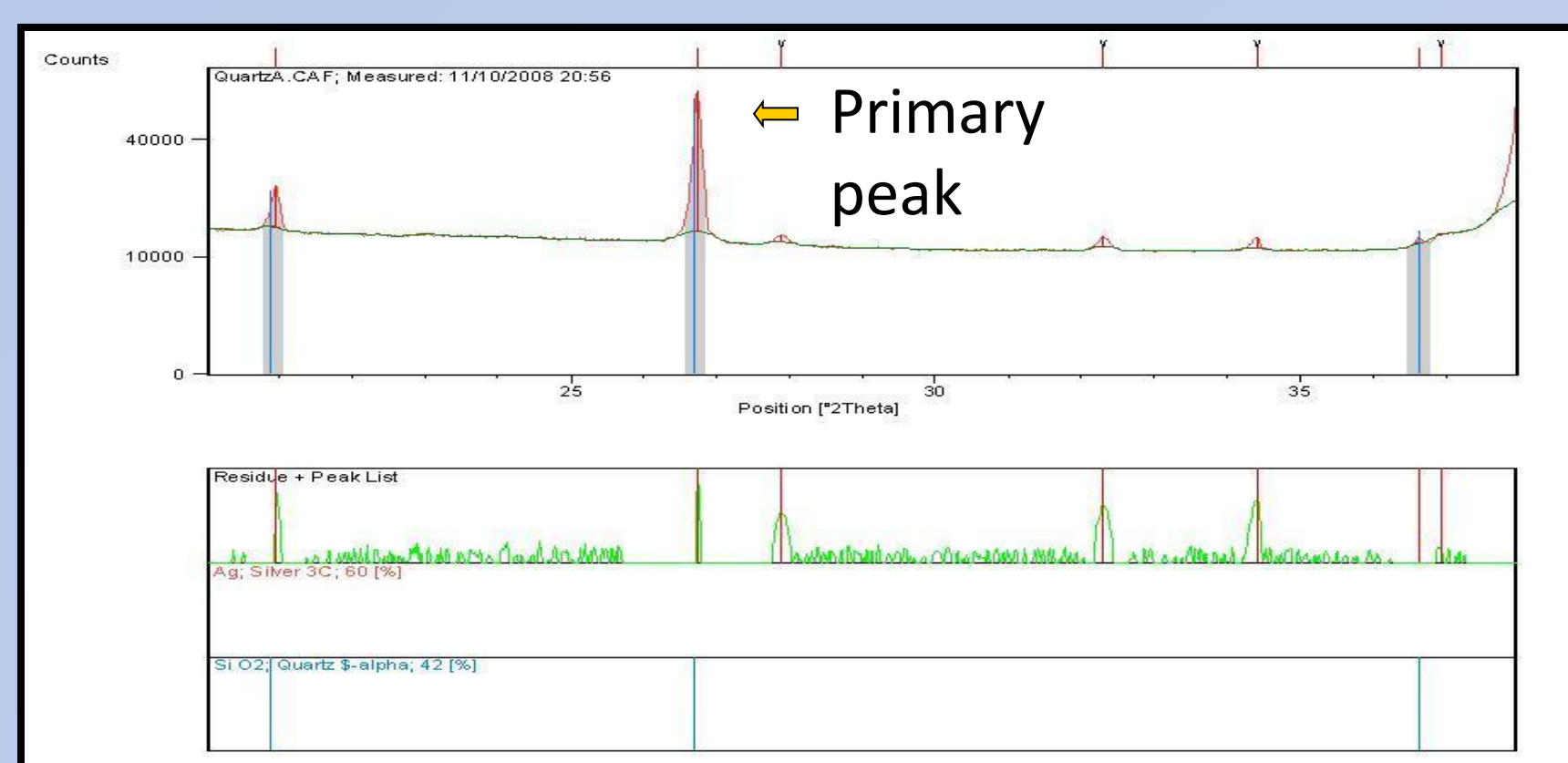


(3) Filtration onto IR filter.

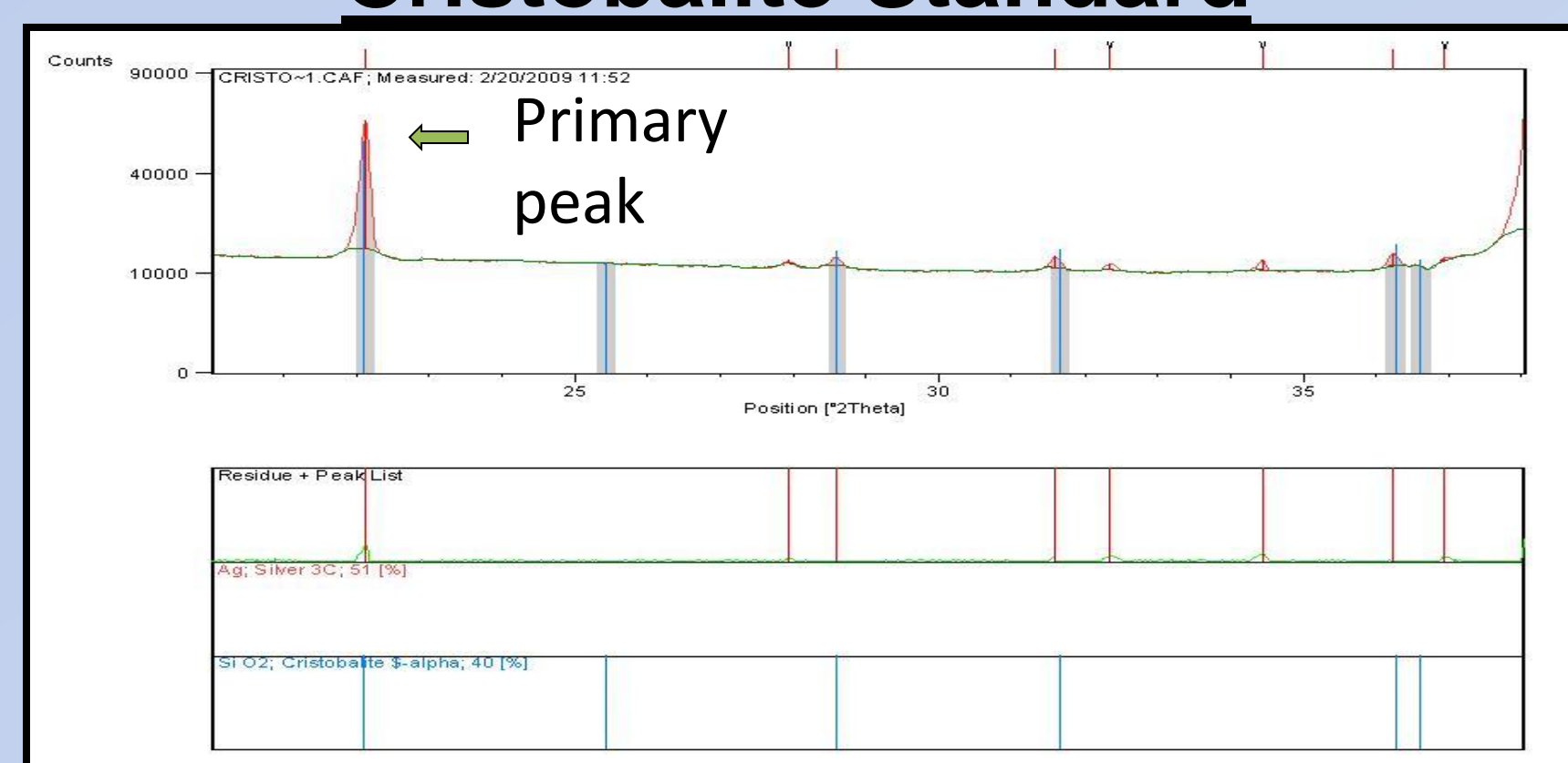


(4) Ready to scan onto IR.

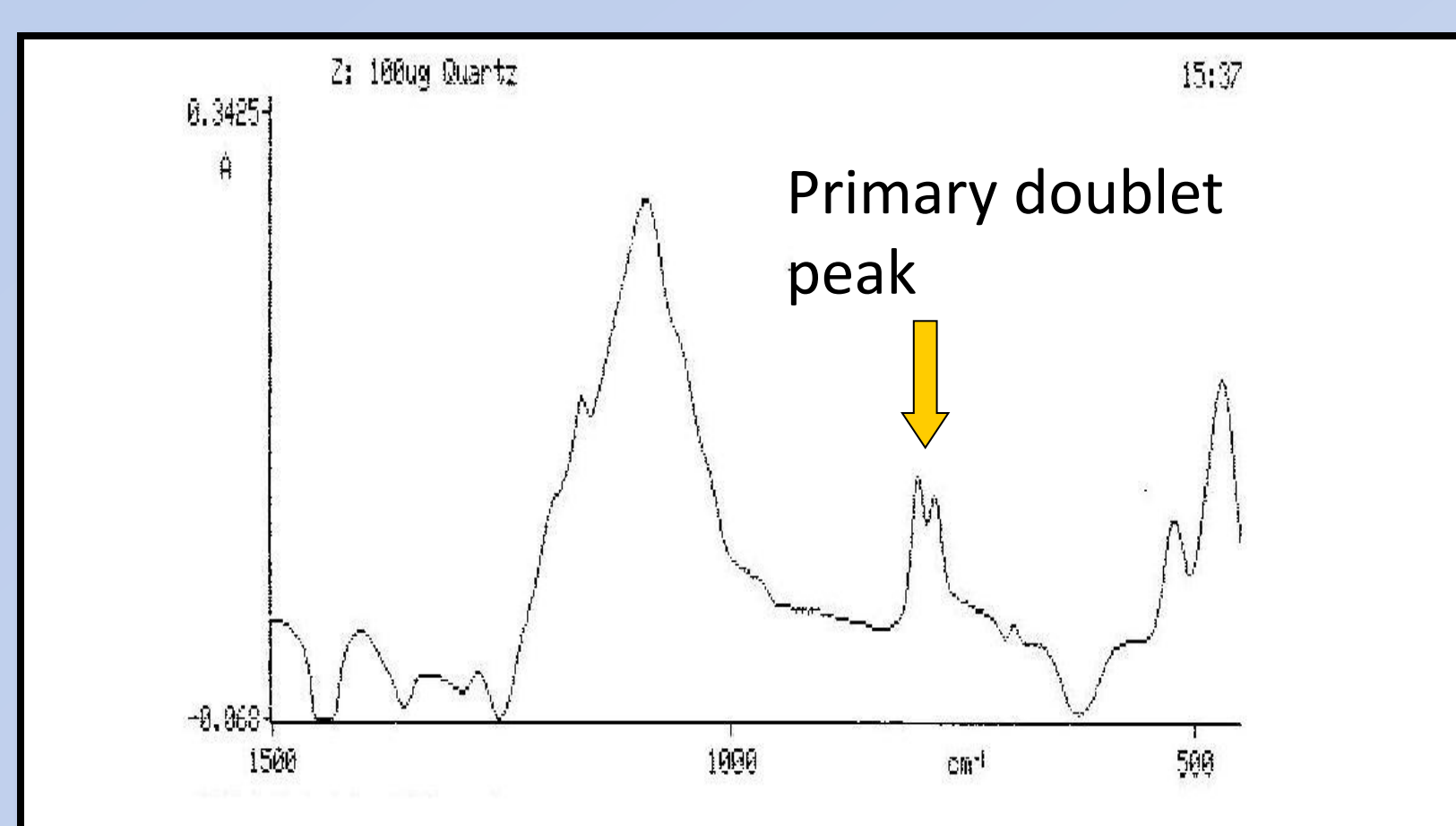
XRD Scan of Quartz Standard



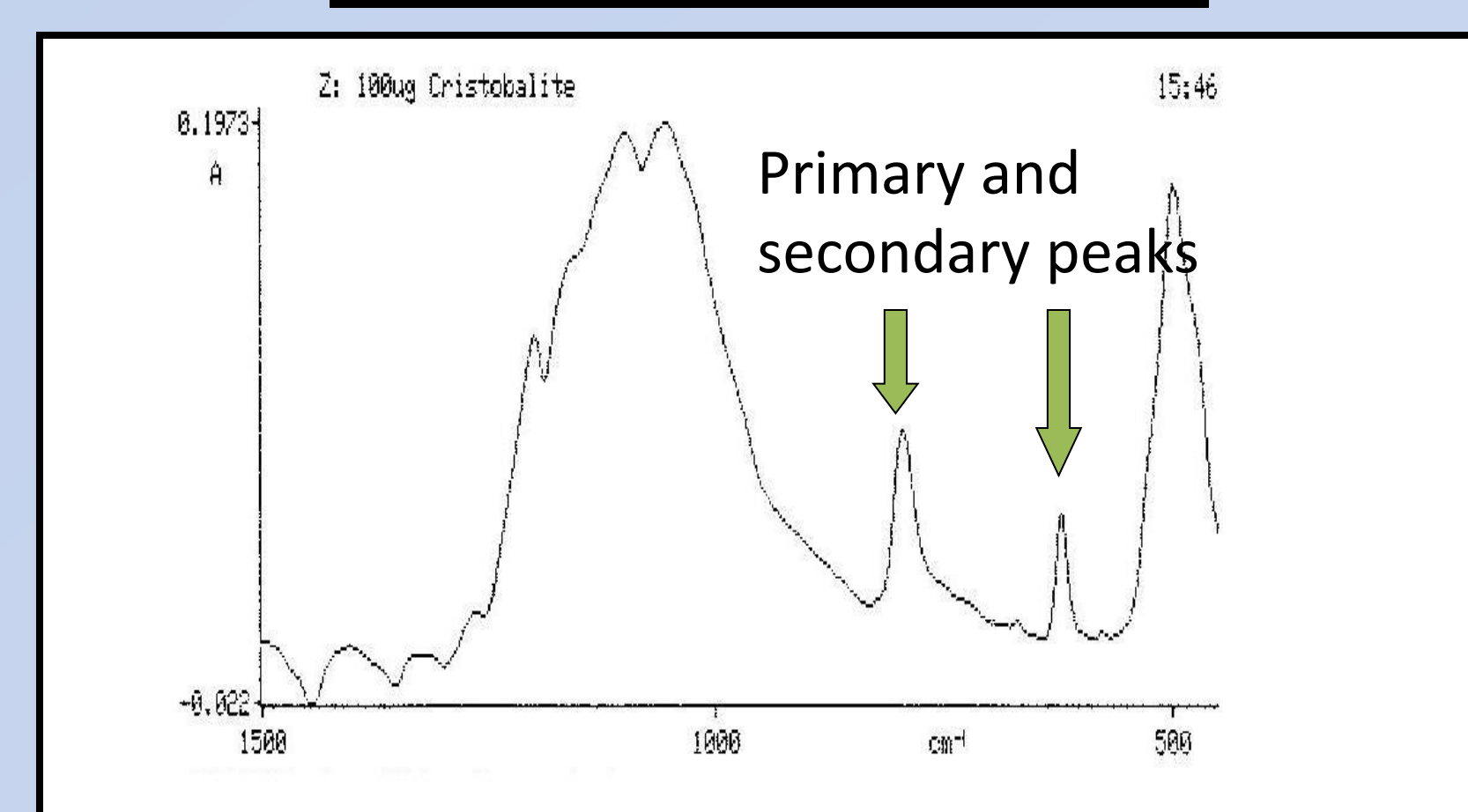
XRD Scan of Cristobalite Standard



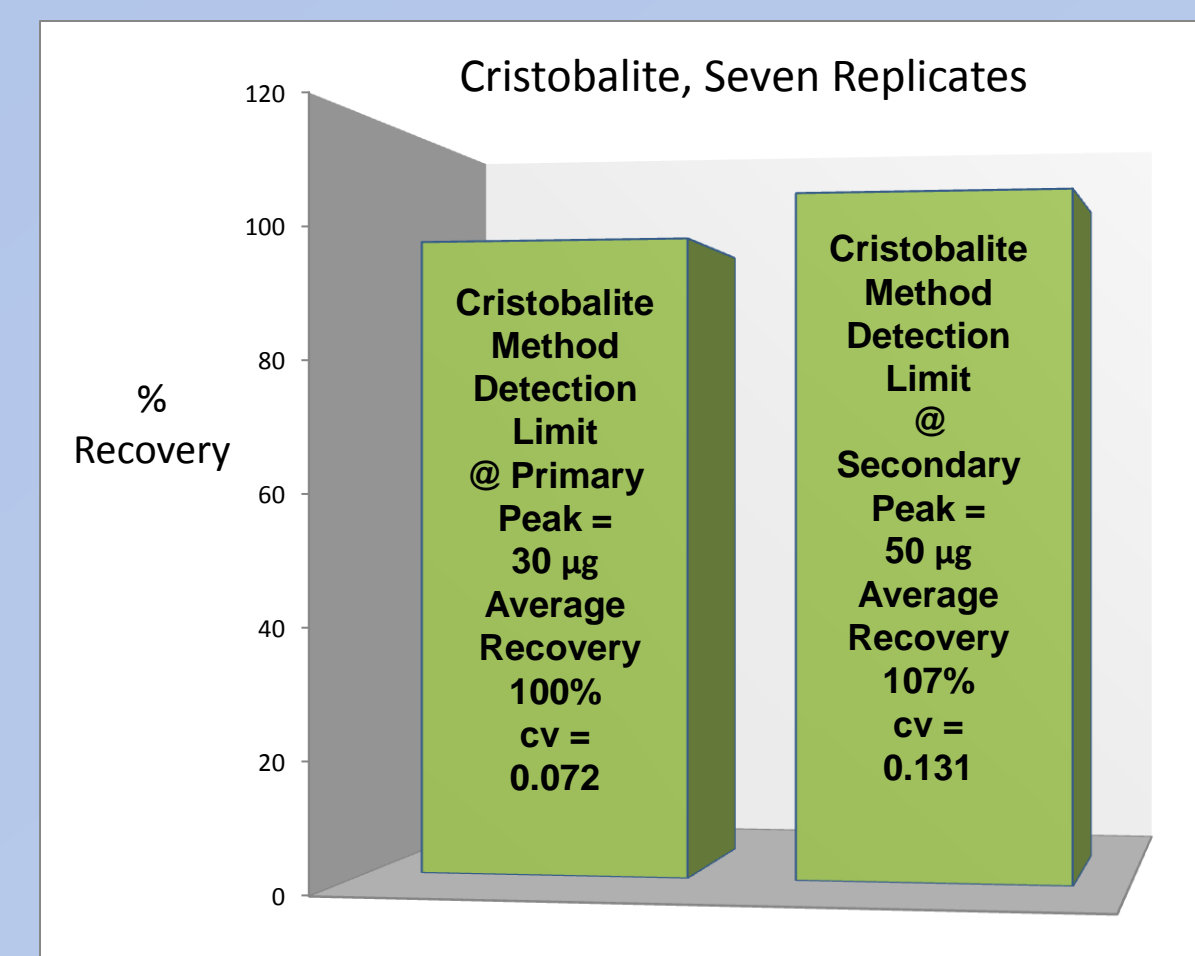
IR Scan of Quartz Standard



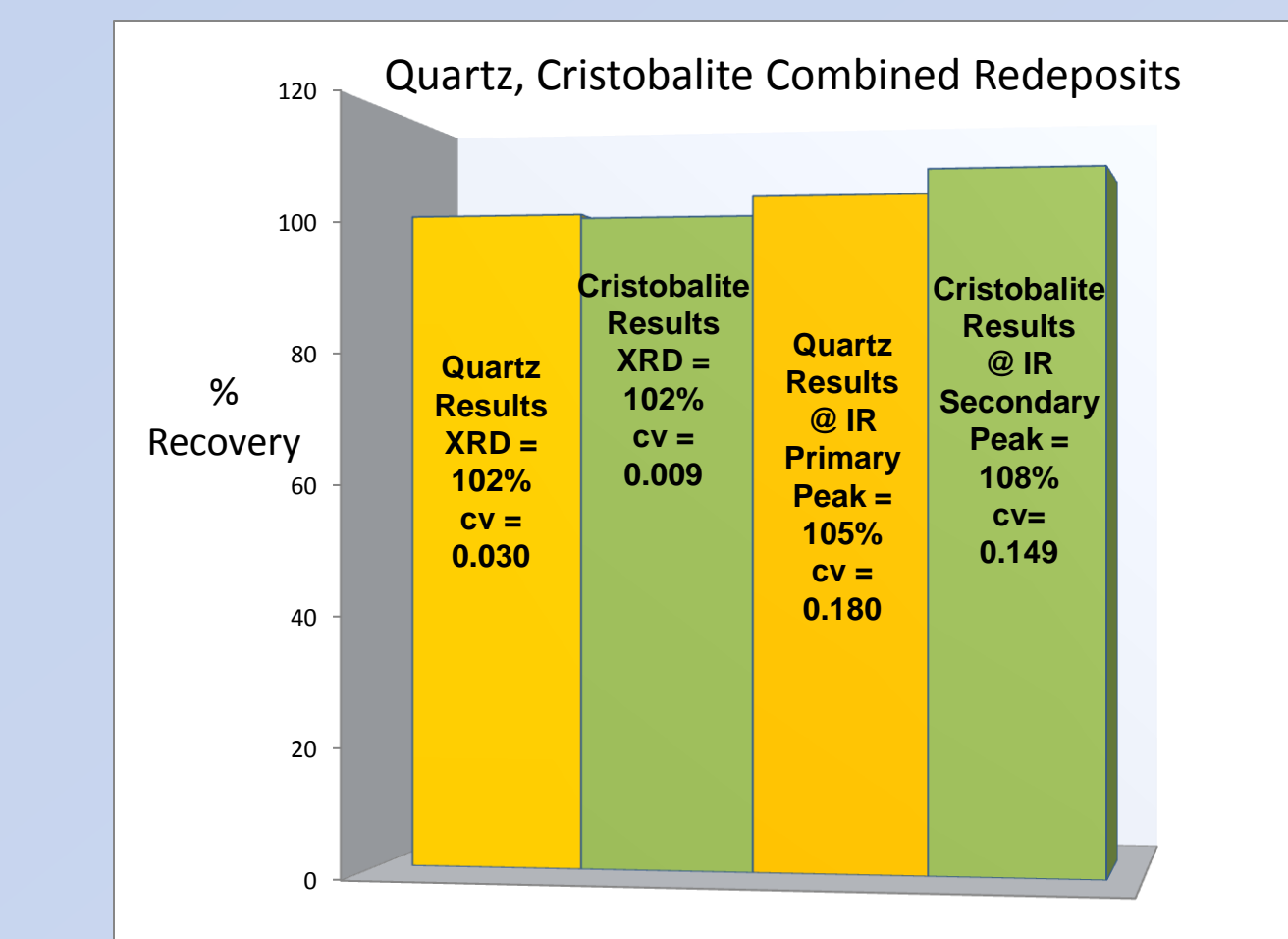
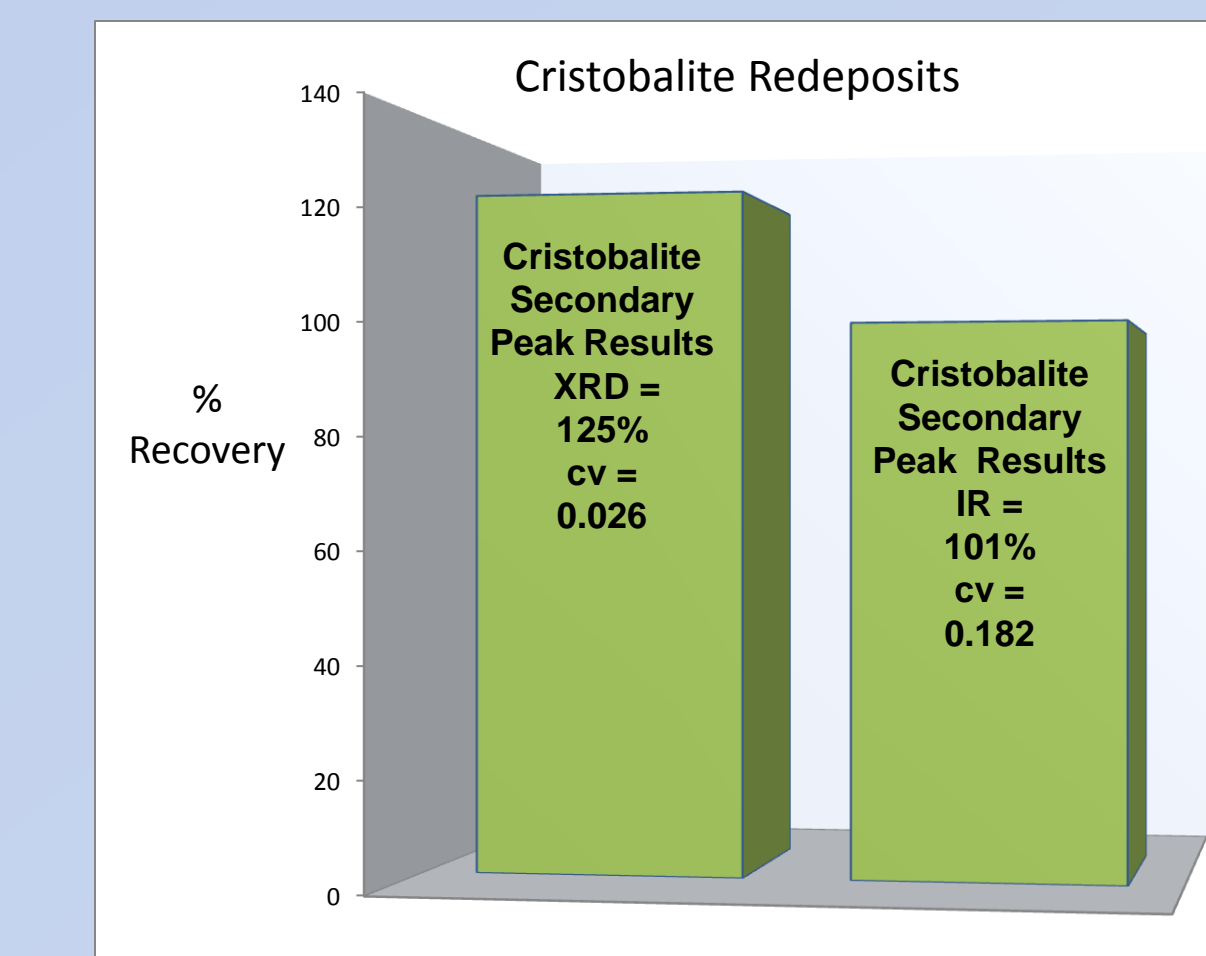
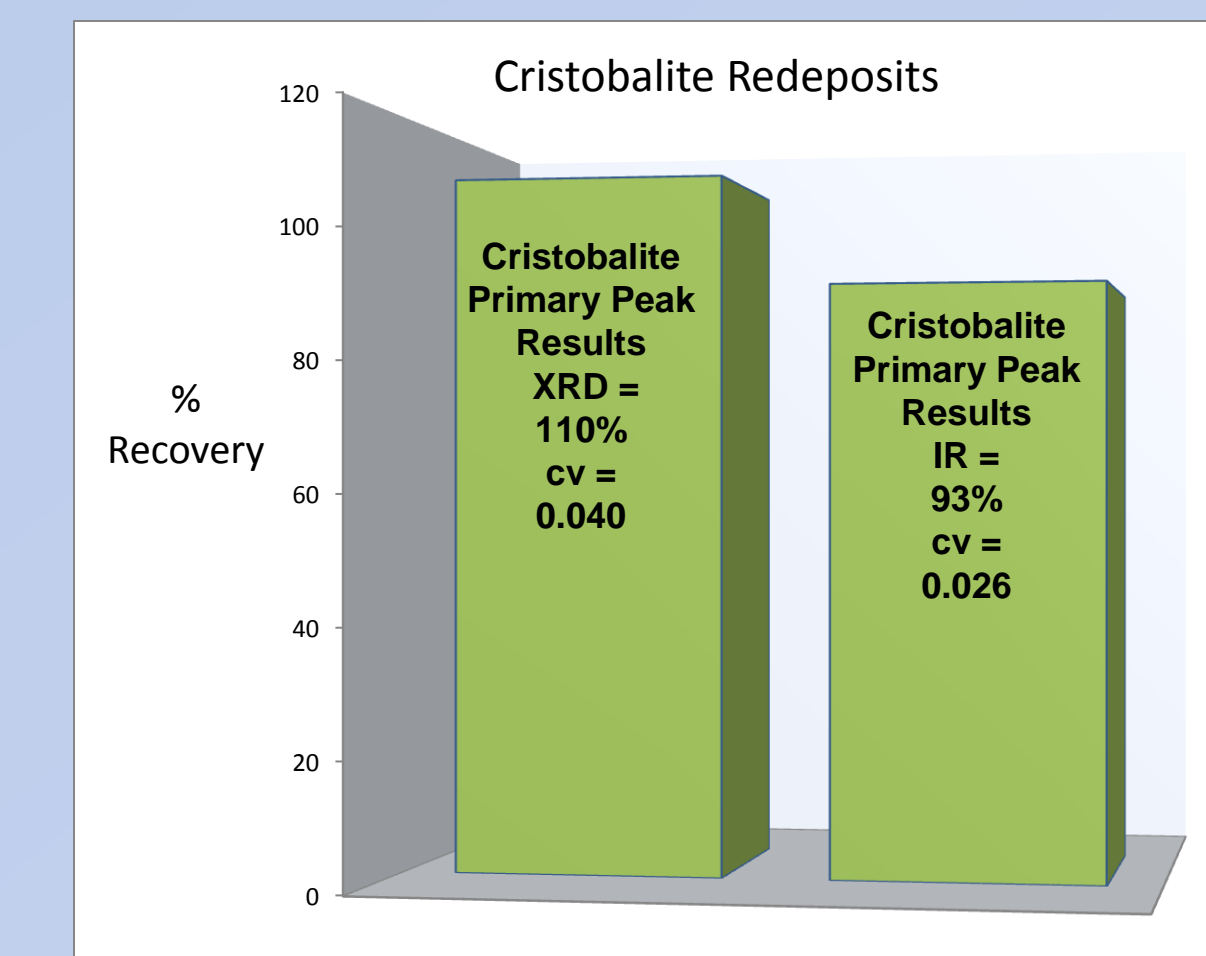
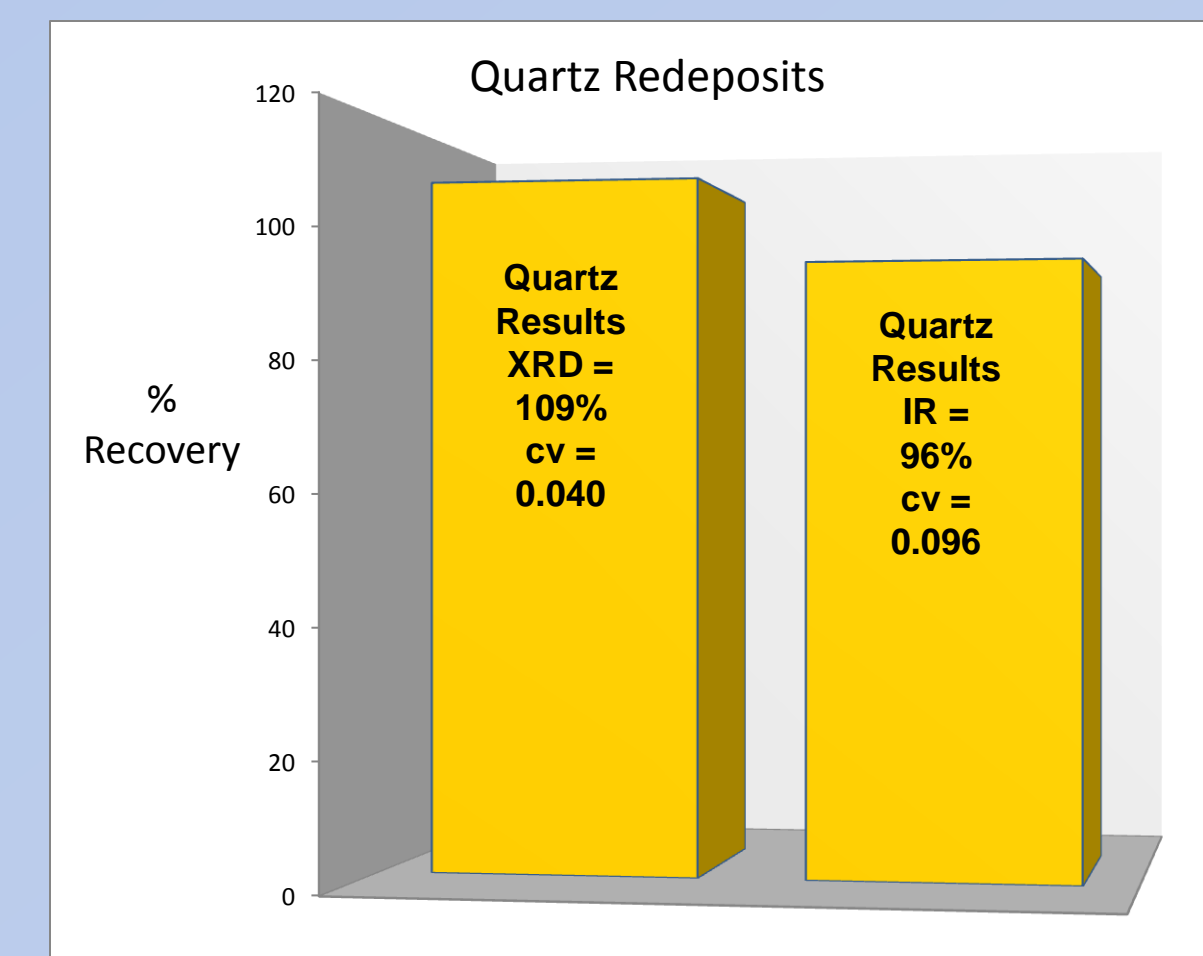
IR Scan of Cristobalite Standard



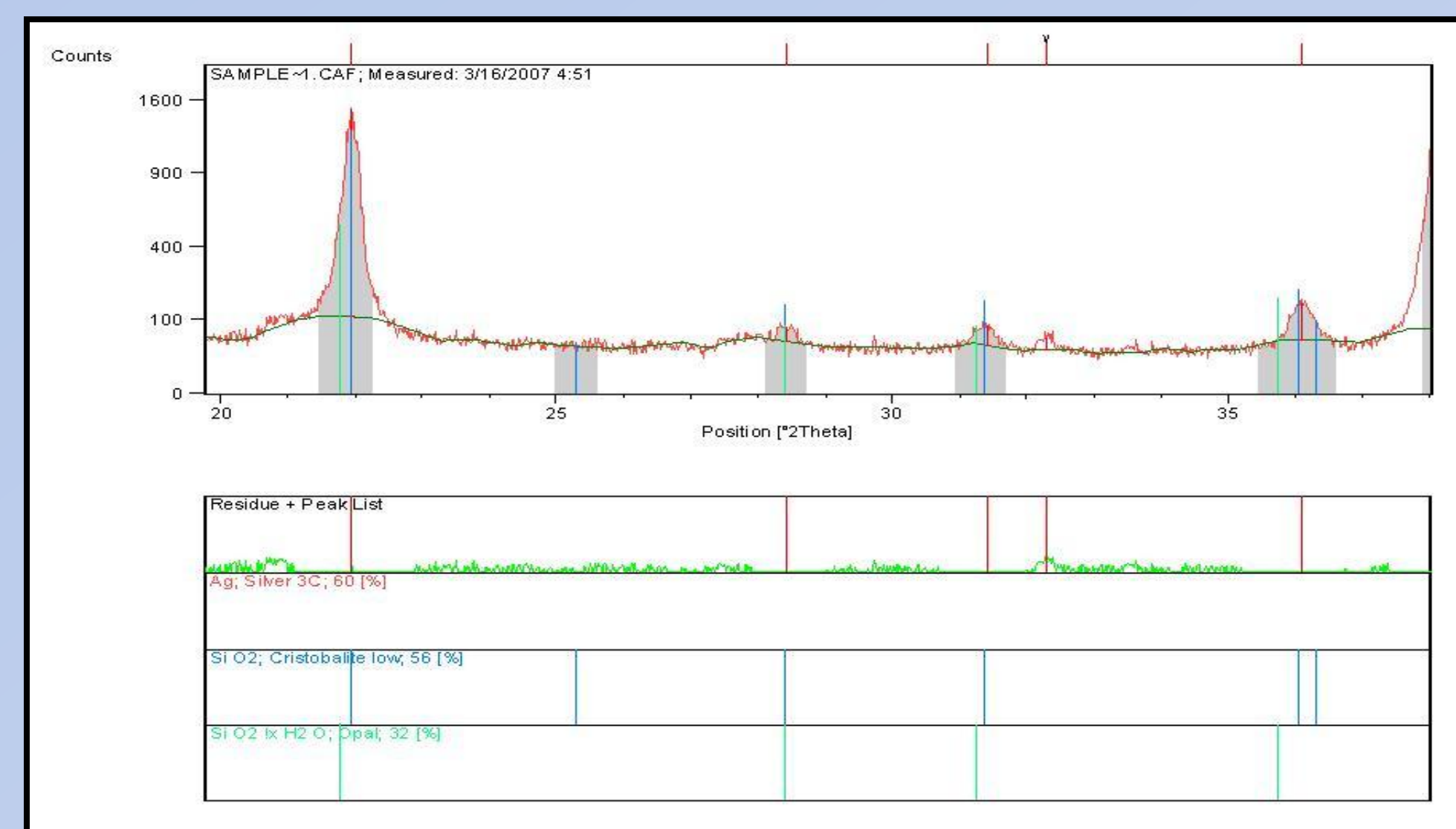
IR Method Detection Limit



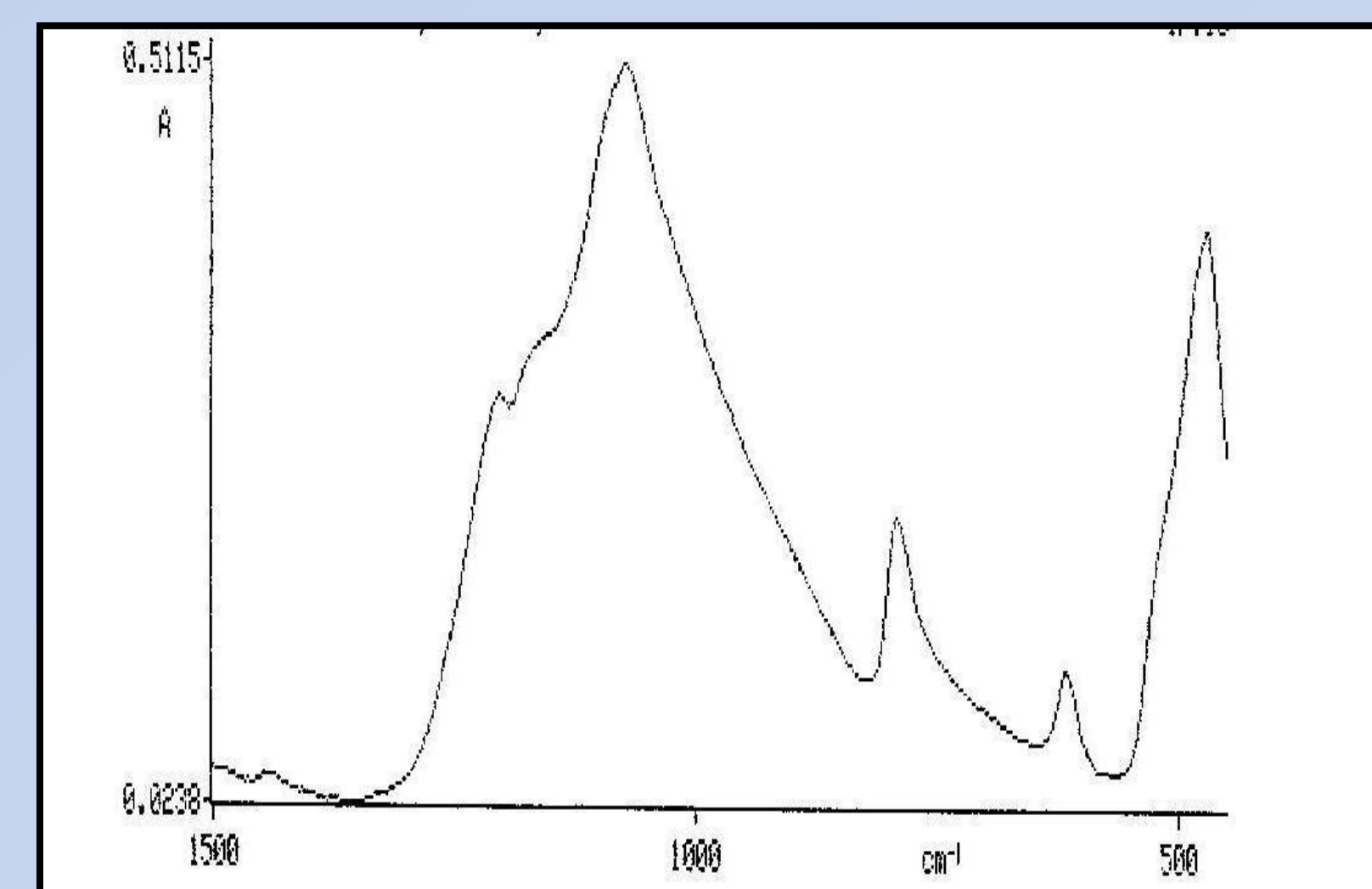
Initial XRD Result Compared to Result after Mineral Transfer to IR Filter, Average % Recovery for Seven Replicates at 100 µg



Sample 1: Workplace Air Sample

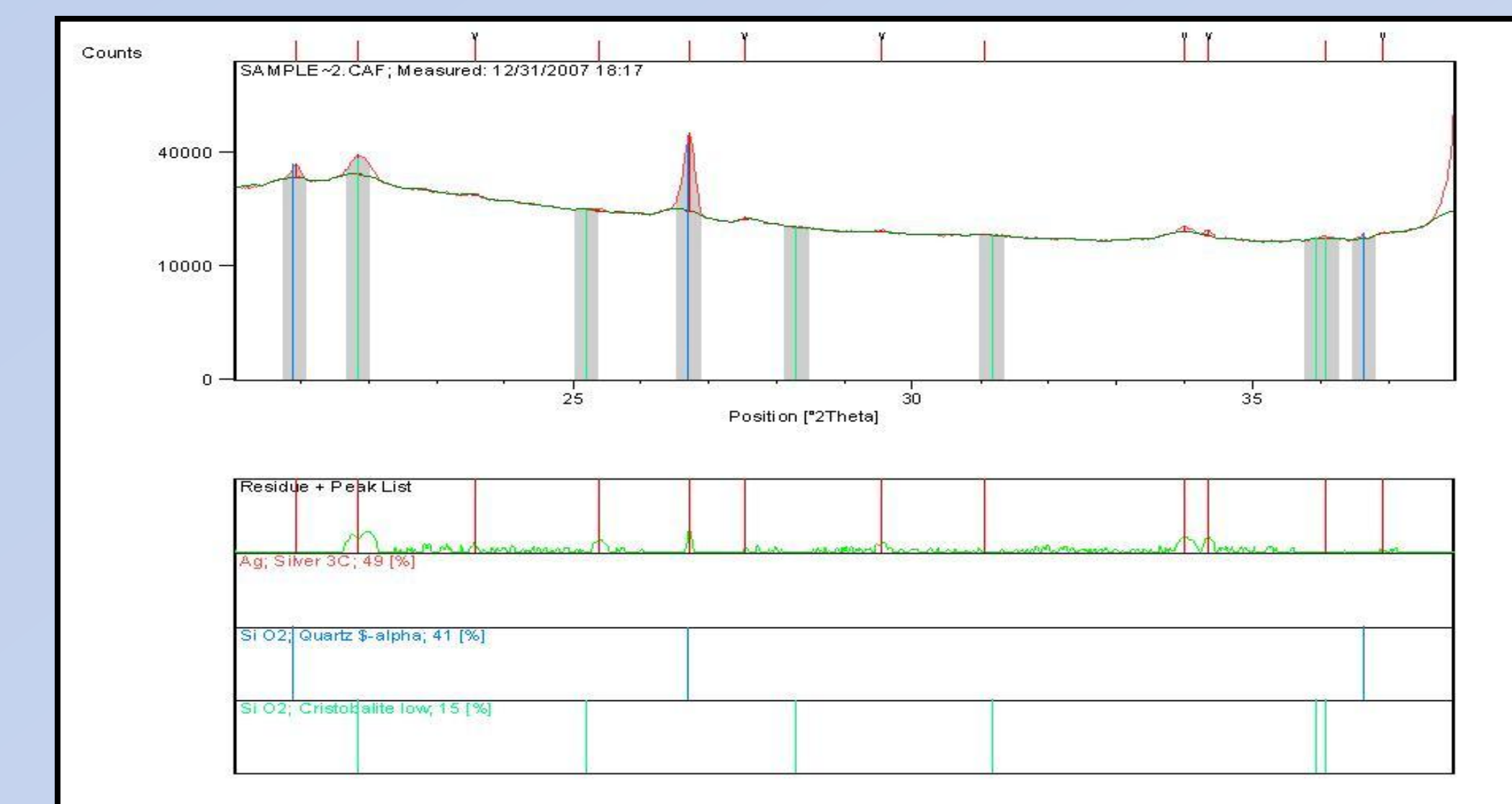


The XRD results were 330 µg at the primary angle, and 231 µg at the secondary angle after a 2x dilution calculation. Cristobalite's peak broadening tendencies can cause angle agreement discrepancies. The library search finds both cristobalite and opal.

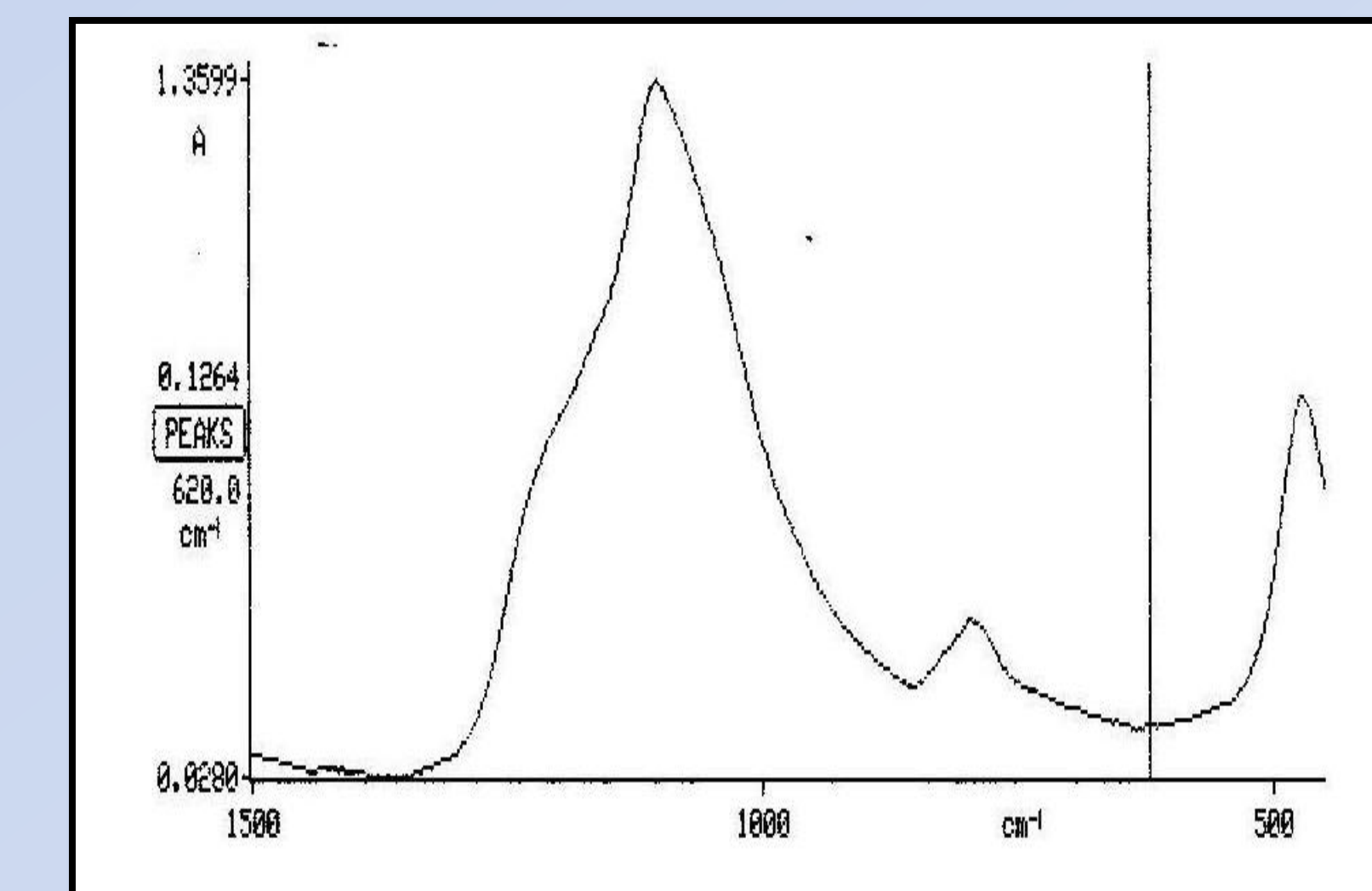


The IR results were 435 µg at the primary peak, and 245 µg at the secondary peak after a 2x dilution calculation. Possibility of amorphous silica interference at the primary peak. IR pattern confirms cristobalite for Sample 1.

Sample 2: Bulk Sample With Quartz

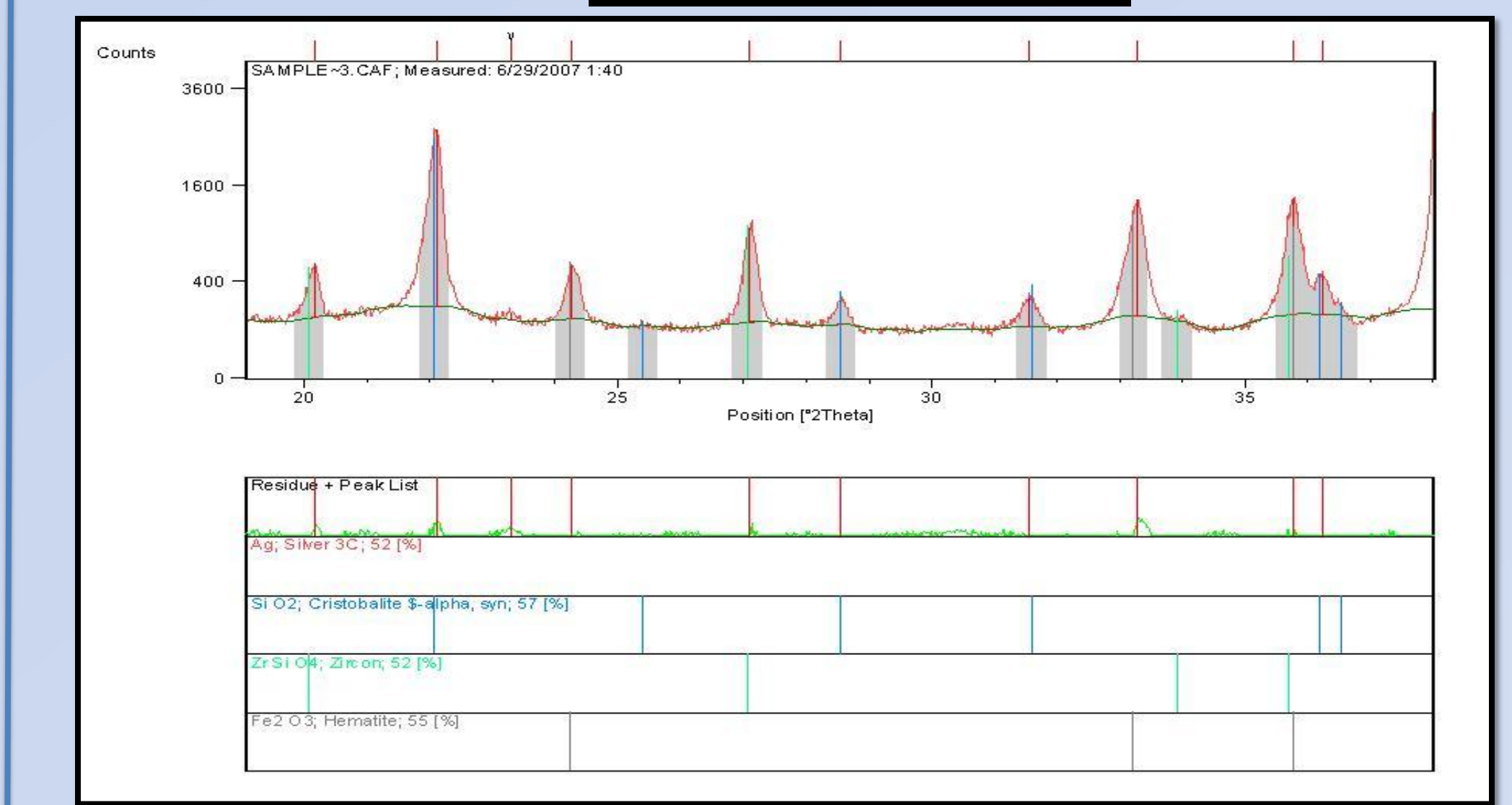


The XRD results were 62 µg at Quartz primary, 42 µg at Cristobalite primary, and the presence of amorphous silica. The cristobalite primary peak is broad. The library search finds only cristobalite, not opal. Particle size discrepancies in bulks can confound quantitation.

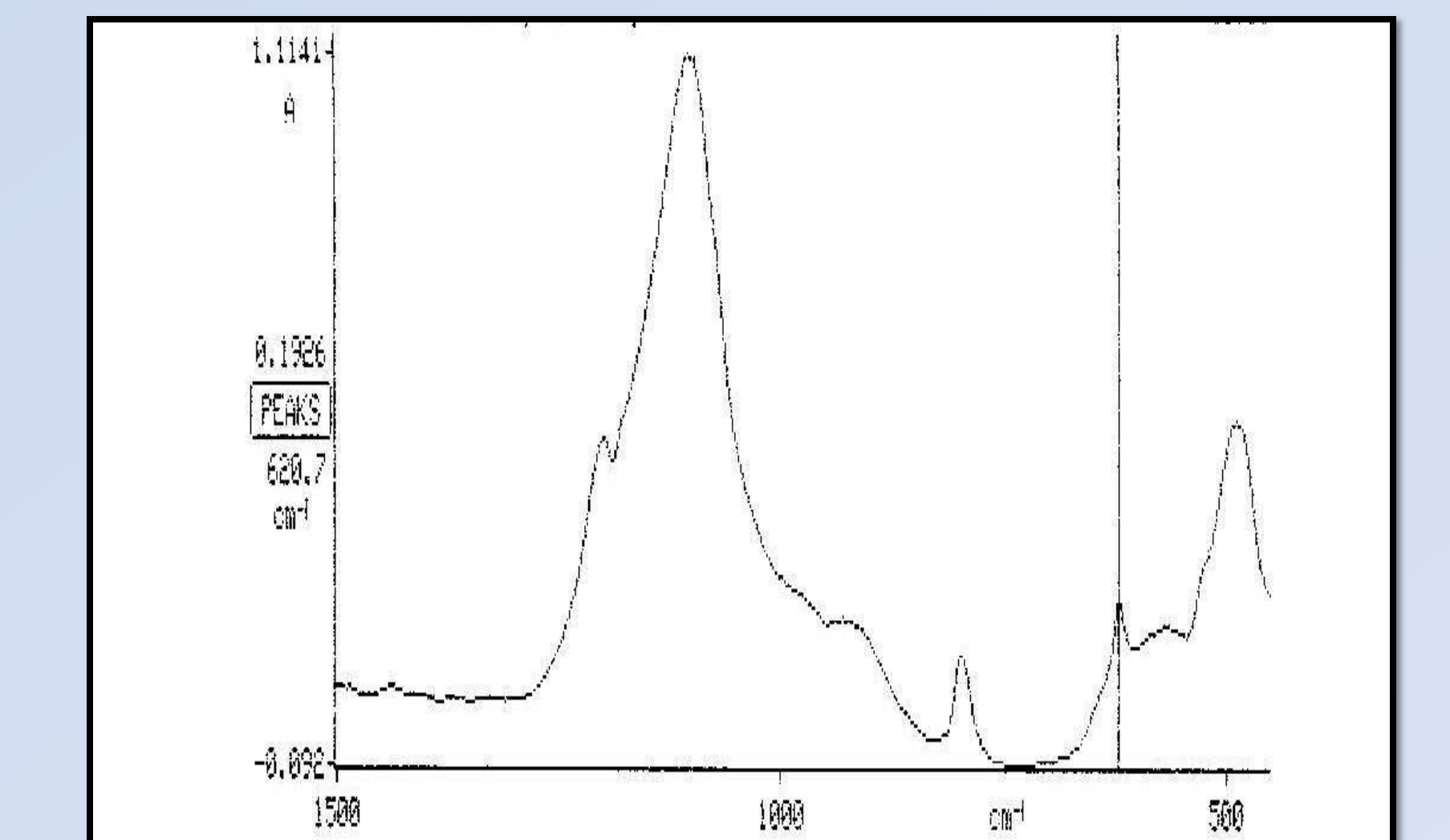


The IR results were 280 µg at Quartz, Cristobalite, and amorphous silica primary; and no absorbance at Cristobalite secondary. IR pattern confirms opal for Sample 2.

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 zircon 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 zircon 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

- (1) NIOSH MAM, 4th ed., Method 7500 Silica, Crystalline by XRD (filter redeposition), NIOSH 2003.
- (2) NIOSH MAM, 4th ed., Method 7603, Quartz in Coal Mine Dust by IR (redeposition), NIOSH 2003.
- (3) NIOSH MAM, 4th ed., Chapter R, NIOSH 2003.
- (4) OSHA ID-142, Quartz and Cristobalite in Workplace Atmospheres, OSHA 1996.

Acknowledgements

Lisa Cole, Florida Institute of Technology; Laura Moran, Galson Laboratories; Tali Baxter, Galson Laboratories