

Effect of Iron Oxide Interference on Quantitative Quartz Analysis by X-ray Diffraction

K. Kaelin, D. MacDuff, A. Davis, S. Anderson
Galson Laboratories, East Syracuse, NY 13057

Abstract

Quartz, a crystalline silica polymorph, is regulated in the workplace by OSHA. Iron oxides are found in many workplaces along with crystalline silica; and iron oxides can cause interference in quantitative determination of crystalline silica polymorphs by X-ray diffraction (XRD). This arises from the absorption of X-rays by iron content in the sample. The iron fluoresces, which ultimately causes a reduction in the net intensity of crystalline silica. While it is understood that this phenomena occurs and has an effect on the silica data, the extent of that effect is not well understood.

Objective: To explore the effects of iron on quartz quantitation.

Methods: A study was devised where quartz standards (SRM1878A) were fortified with known amounts of iron (III) oxide and analyzed by X-ray diffraction using a PANalytical Cubix XRD equipped with a copper X-ray tube and an X'Celerator detector. Modified methods NIOSH 7500 and OSHA ID-142 were followed. Three scenarios were studied. The first study included equal amounts of iron oxide and quartz in the same specimen. The second study held quartz content constant at 0.100 mg, an amount commonly seen in workplace air samples, while increasing the amount of iron oxide up to 10 fold over the quartz mass. The third study held quartz content constant at the laboratory's reporting level of 0.010 mg, while increasing the iron oxide content 100 fold.

Results: For all three scenarios, as iron content increased, the quartz diffraction response decreased. Using the example of a sample with 0.100 mg of quartz in the presence of 1.00 mg of iron (III) oxide, the amount of quartz determined is approximately 45% underestimated. The relationship was generally linear and could be determined by least-squares regression analysis.

Conclusions: The quartz response varied among the three scenarios depending on the proportion of iron to quartz.

Introduction

Silica, particularly quartz, is commonly found in a wide variety of workplaces. Silicosis, a preventable lung disease, has been linked to inhalation exposure of airborne quartz. Several organizations, including the Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH), and the American Conference of Governmental Industrial Hygienists (ACGIH), established guidelines on workplace exposure to inhalable quartz that should not be exceeded.

Detection and quantification of silica and/or quartz can be achieved by several different methods, which include gravimetry, microscopy, atomic absorption, colorimetry, Fourier Transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD) [1]. Of these methods, XRD is the industry standard for identification and quantification of quartz (and other silica phases).

Some workplace environments, such as mining sites and construction sites, can present sample matrices that make identification and quantification of quartz challenging. One common example is a sample matrix that contains iron oxide. For a typical XRD instrument configured for quartz identification and quantification, the presence of iron oxide in the sample matrix produces fluorescence and absorption of X-rays. Fluorescence has an effect on the method detection limit due to an increase in background noise. X-ray absorption by iron oxide can have two effects. First, it can decrease the quanta of X-rays that are diffracted towards the detector. Second, absorption of X-rays may cause incomplete sample exposure to incident X-rays. Both of these absorption scenarios will lead to quartz quantification that is low.

The current investigation looks at methods that can be employed to correct for the quantitative effects on quartz of sample matrices that contain iron oxide. The first method is to quantify the effect of known amounts of iron oxide in the presence of a known amount of quartz. The second method employed is to remove iron oxide from a known amount of quartz by chemical methods.

Methods

- Iron oxide (Fe_2O_3) calibration curve: 10 – 1000 μg
- Quartz (SiO_2) in the presence of iron oxide
 - 100 μg quartz with 10 – 1000 μg iron oxide
 - 10 μg quartz with 10 – 1000 μg iron oxide
 - Equal mass of quartz and iron oxide (10 – 1000 μg)

•Chemical removal of iron oxide

- Acid Treatment
 - 3 M hydrochloric acid (HCl)
 - Saturated ethylenediaminetetraacetic (EDTA) acid in 3 M HCl
 - 0.4 M oxalic acid in 3 M HCl
 - 15 M phosphoric acid (H_3PO_4)
 - 7.6 M H_2PO_4
 - 1.5 M nitric acid (HNO_3) and 0.5 M HCl
 - 8 M HNO_3 and 6 M HCl
- Alkaline Treatment
 - 1 M sodium hydroxide (NaOH)
 - 0.4 M oxalic acid in 1 M NaOH
- Chemical Reduction
 - 0.2 M sodium sulfite in 0.01 M HCl

- Samples were prepared for XRD analysis based on modified OSHA ID-142 [1] and modified NIOSH 7500 [2] methods. Samples were deposited onto silver membranes.
- A PANalytical Cubix model XRD equipped with a copper anode, long fine focus X-ray tube and X'Celerator detector was used for instrumental analysis.



Quantitative Effect of Iron Oxide on Quartz

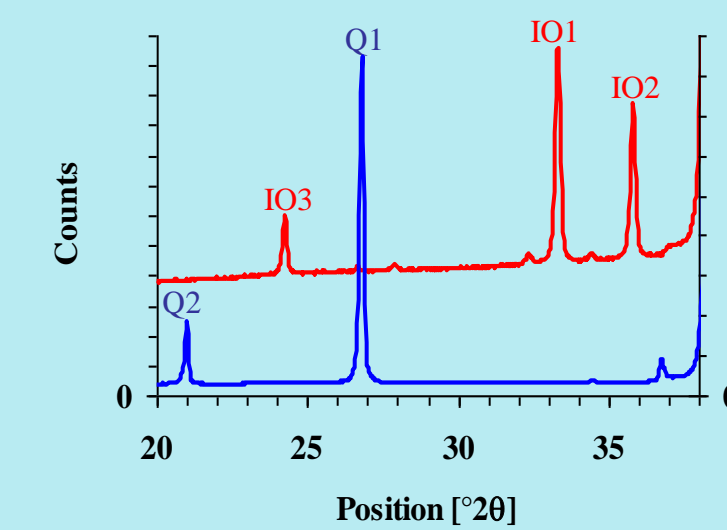


Figure 1. Diffraction pattern for 1000 μg quartz (blue; NIST SRM 1878a) and for 1000 μg iron (III) oxide (red; ACS grade).

	quartz		iron oxide		
	Q1	Q2	IO1	IO2	IO3
Miller Index	[1,0,1]	[1,0,0]	[1,0,4]	[1,1,0]	[0,1,2]
d-spacing (Å)	3.34	4.26	2.69	2.51	3.68
Position ($^{\circ}2\theta$)	26.66	20.85	33.3	35.7	24.2

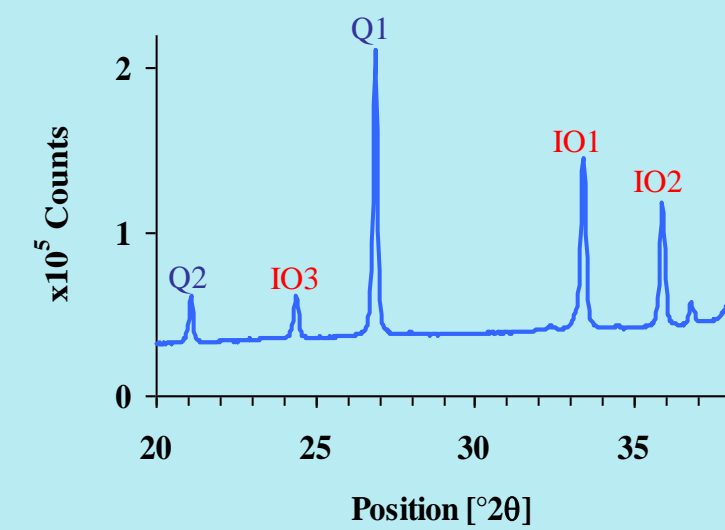


Figure 2. Diffraction pattern for a sample deposit of 1000 μg iron (III) oxide and 1000 μg quartz combined. There are no overlapping diffraction lines between the two analytes.

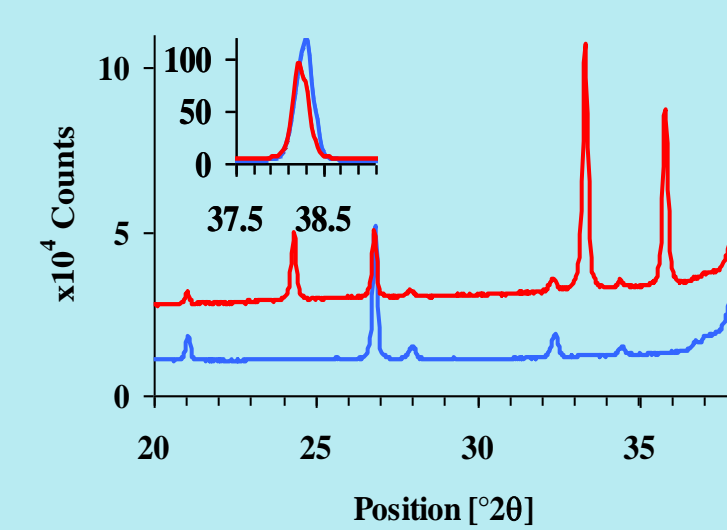


Figure 3. Diffraction pattern for 100 μg quartz in the presence of 10 μg (blue) or 1000 μg (red) iron oxide. Compared to the 10 μg iron oxide sample, the 1000 μg iron oxide sample has an increase in the baseline as a result of iron oxide fluorescence, and has a reduced peak height for equivalent mass of quartz. Absorbance of X-rays by iron oxide leads to reduced peak height for quartz. The inset from (37.5 – 39.1) $^{\circ}2\theta$ is the silver peak from the silver membrane, and the intensity can be used qualitatively as an internal standard. The chlorargyrite coating applied to silver membranes introduces small diffraction lines observed at 27.9 $^{\circ}$ and 32.3 $^{\circ}2\theta$.

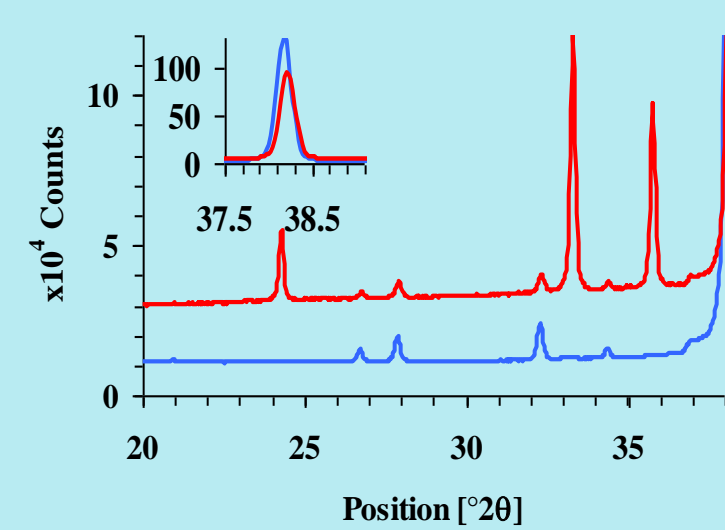


Figure 4. Diffraction pattern for 10 μg quartz in the presence of 10 μg (blue) or 1000 μg (red) iron oxide. Compared to the 10 μg iron oxide sample, the 1000 μg iron oxide sample has an increase in the baseline as a result of iron oxide fluorescence, and has a reduced peak height for equivalent mass of quartz. Absorbance of X-rays by iron oxide leads to reduced peak height for quartz. The inset from (37.5 – 39.1) $^{\circ}2\theta$ is the silver peak from the silver membrane, and the intensity can be used qualitatively as an internal standard. The chlorargyrite coating applied to silver membranes introduces small diffraction lines observed at 27.9 $^{\circ}$ and 32.3 $^{\circ}2\theta$.

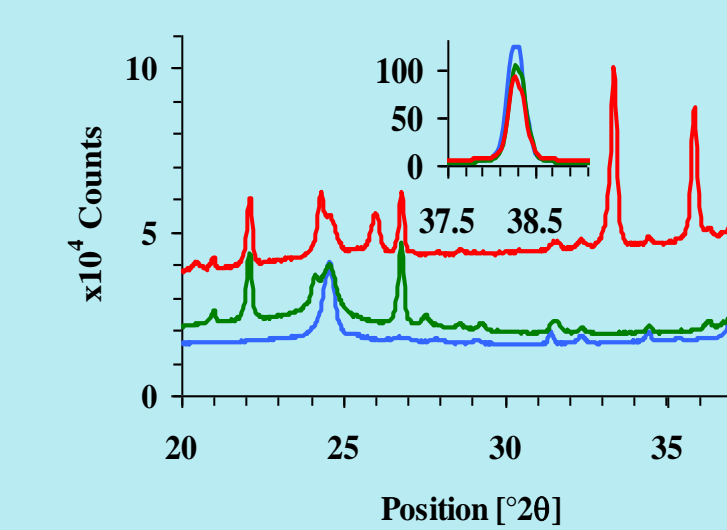


Figure 10. A modified method described by Talvite [3], which uses phosphoric acid for sample clean-up, was used to try to remove iron oxide. A set [(Blank - blue) unfortified, (Control - green) acid treated, fortified with 100 μg quartz, (Iron oxide - red) acid treated, fortified with 100 μg quartz + 1 mg iron oxide] of filters were compared to determine the effect of iron oxide on XRD analysis of quartz. Filters were treated with 25 mL of 7.6 M H_3PO_4 in a Philips beaker covered with a bent-stem funnel. Each beaker was placed on a 240 $^{\circ}C$ preheated hot plate for 8 minutes, occasionally swirling. After cooling, the beaker walls were rinsed with 125 mL of water, followed by 10 mL of fluoroboric acid. These were swirled and allowed to set for 1 hour. Filtration and ashing at 600 $^{\circ}C$ were performed previous to sample deposition for XRD analysis. Diffraction patterns show the presence of an unidentified interference. The iron oxide sample still has iron oxide present. The inset shows the silver peak with a reduced intensity for both the control and iron oxide samples.

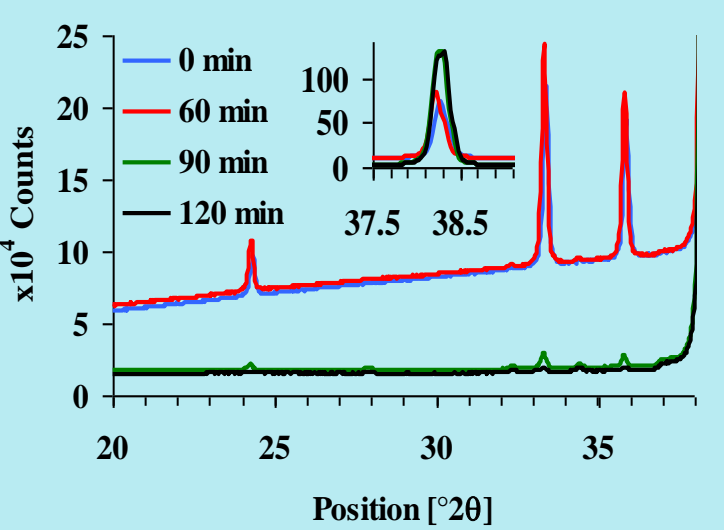


Figure 11. To determine the time required to dissolve iron oxide in a combined aqueous solution of 1.5 M nitric acid + 0.5 M hydrochloric acid, an acid treatment time series of polyvinylchloride (PVC) filters fortified with 1 mg of iron oxide was performed. Fortified filters were placed in ceramic crucibles with 10 mL of acid and then put in a sonicator preheated to 80 $^{\circ}C$. A crucible was removed at 30 minute intervals, followed by preparation for instrumental analysis. Diffraction patterns show the presence (0 min, 60 min) and absence (90 min, 120 min) of iron oxide following acid treatment. Chemical removal by dissolution of iron oxide in the acid solution was achieved after 90 minutes of sonication and heating at 80 $^{\circ}C$. The inset shows the silver peak with a reduced intensity for 0 min and 60 min, and no intensity loss for 90 min and 120 min.

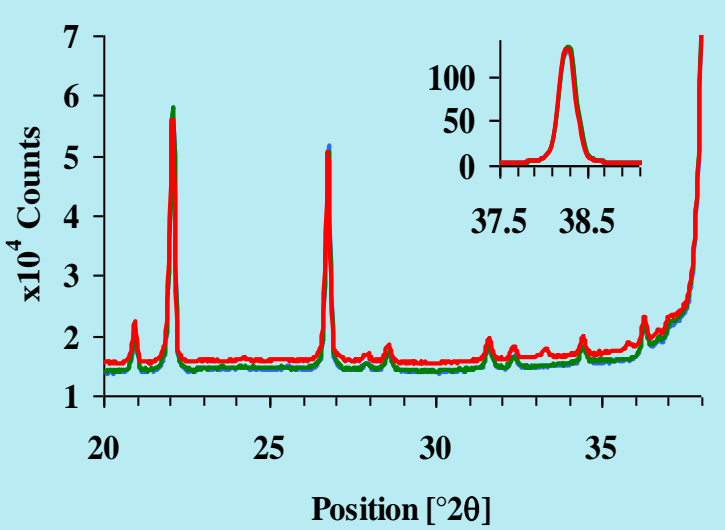
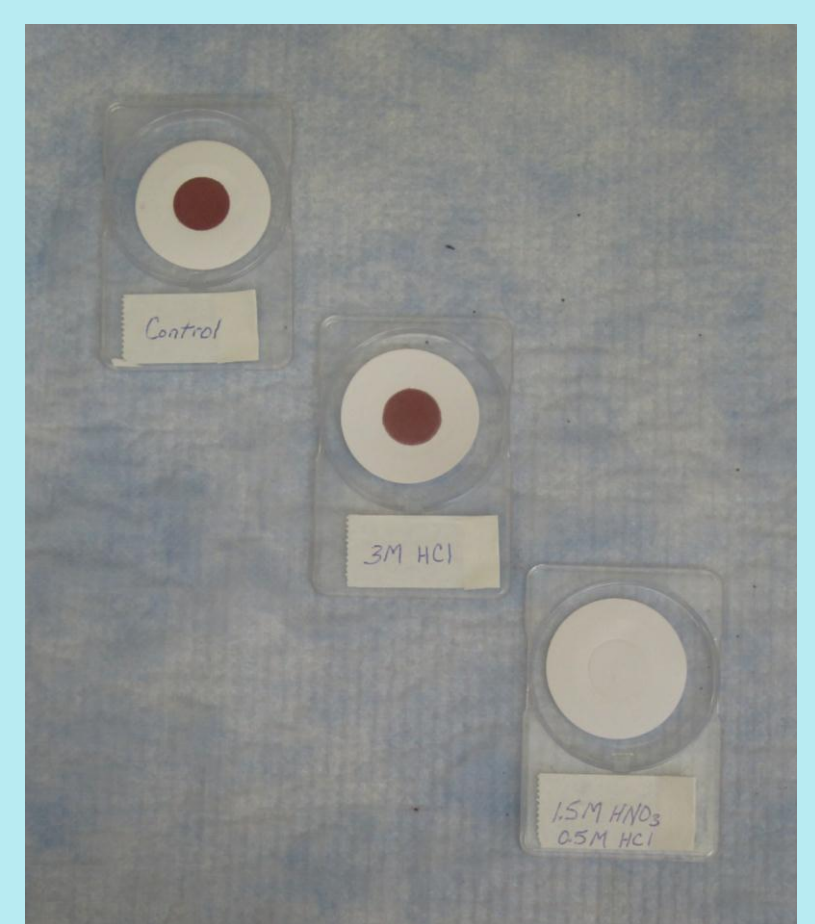


Figure 12. A set [(Control - blue) non-acid treated 100 μg quartz, (Acid Treat - green) acid treated 100 μg quartz, (Iron oxide - red) an acid treated 100 μg quartz + 1 mg iron oxide] of fortified filters were compared to determine the effect of acid treatment and iron oxide on XRD analysis of quartz. The diffraction pattern empirically shows the different treatments have minor effects on quartz. Iron oxide was efficiently removed by acid treatment at 80 $^{\circ}C$ and sonication for 90 minutes.



1.5 M HNO₃ and 0.5 M HCl

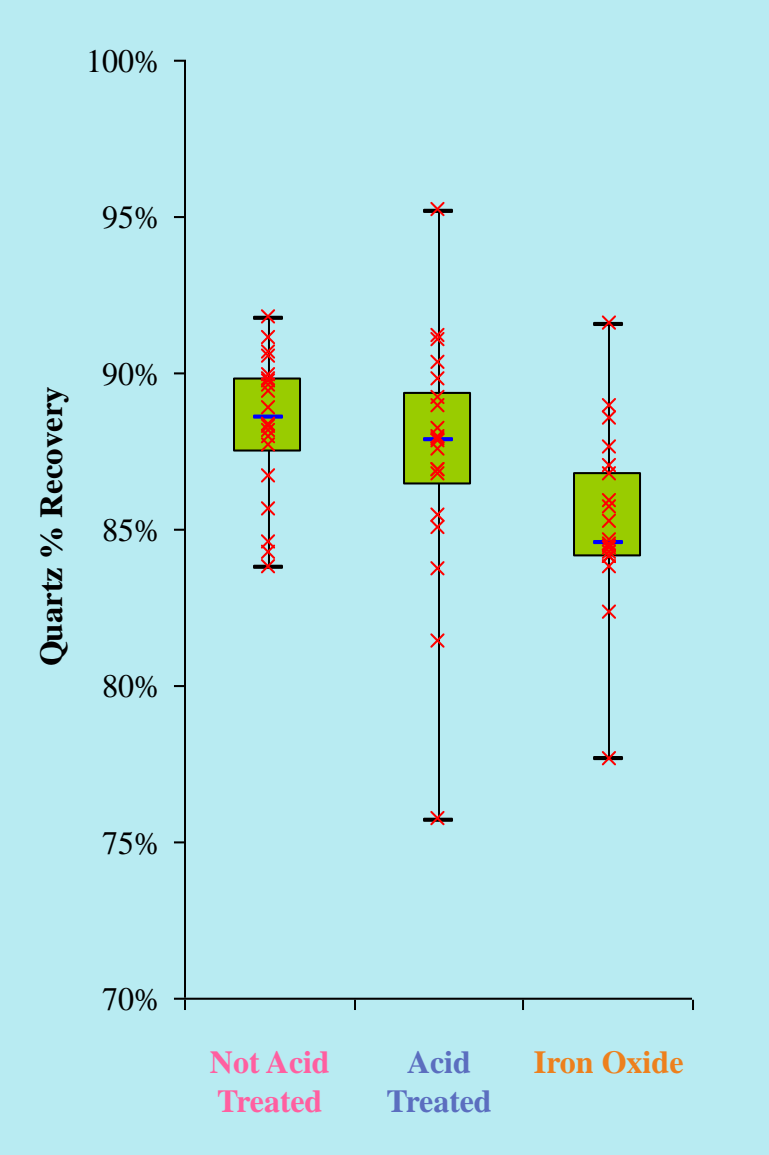


Figure 13. From preliminary chemical removal methods, the combination of nitric and hydrochloric acid was selected for further investigation. The boxplot has results from sets of filters (n=20) that were analyzed by XRD. A set consisted of a non-acid treated 100 μg quartz fortified filter (Not Acid Treated), an acid treated 100 μg quartz fortified filter (Acid Treated), and an acid treated 100 μg quartz + 1 mg iron oxide fortified filter (Iron Oxide). Acid treated samples were sonicated and heated at 80 $^{\circ}C$ for 90 minutes. The blue line is the median, upper and lower lines of the box are the upper (75%) and lower (25%) quartiles, respectively. The top and bottom lines are the maximum (100%) and minimum (0%) of the data set. Individual data points are indicated in red.

The table has statistical data for this experiment. Means from the data sets were compared using a two-sample t-test assuming unequal variances. The P-value for comparing the control to the iron oxide is 0.0006, which suggests there is strong statistical evidence that the means are not equal. The P-value for comparing the acid treated to the iron oxide is 0.069, which suggests there is moderate statistical evidence that the means are not equal. The P-value for comparing the not acid treated to the acid treated is 0.34, which suggests there is weak statistical evidence that the means are not equal.

Chemical Treatment	1.5 M HNO ₃ and 0.5 M HCl		n
	mean	stdev	
Not Acid Treated	88.3%	± 2.3%	20
Acid Treat	87.3%	± 4.0%	20
Iron oxide	85.2%	± 2.8%	20

Iron Oxide Calibration Curves

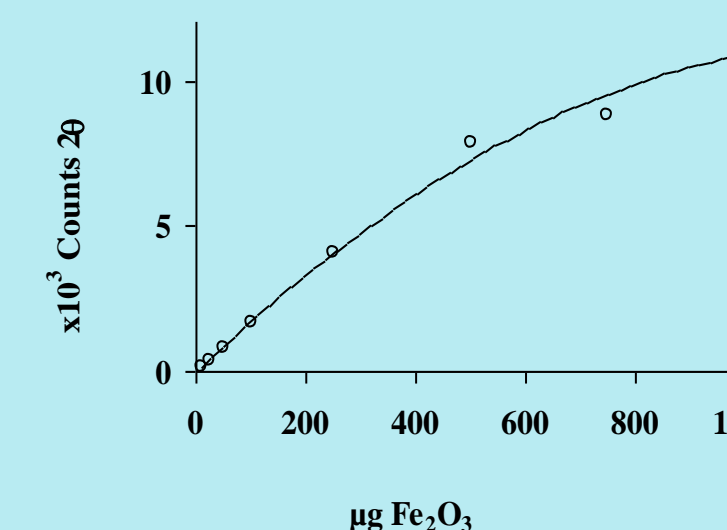


Figure 5. A calibration curve for iron oxide using a polynomial fit of the IO1 diffraction line peak area versus iron oxide mass gives a regression equation of $y = -7.35 \times 10^{-3}x^2 + 18.3x - 47.8$ and a $r^2 = 0.9922$.

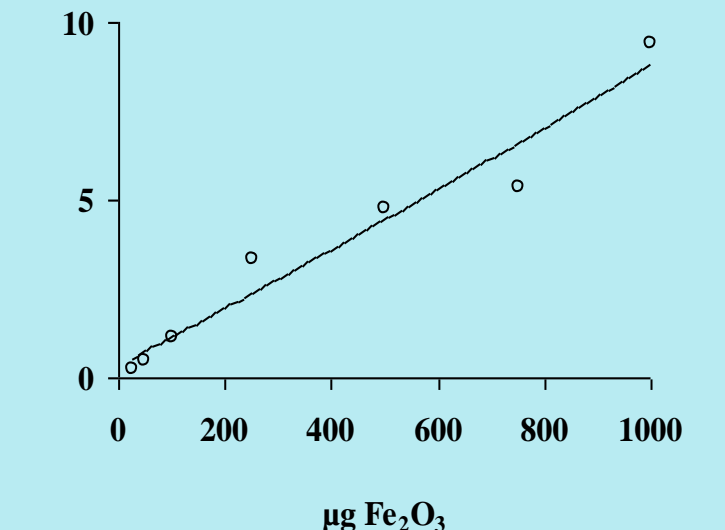


Figure 6. A calibration curve for iron oxide using a polynomial fit of the IO2 diffraction line peak area versus iron oxide mass gives a regression equation of $y = 5.52 \times 10^{-3}x^2 + 7.92x + 353$ and a $r^2 = 0.953$.

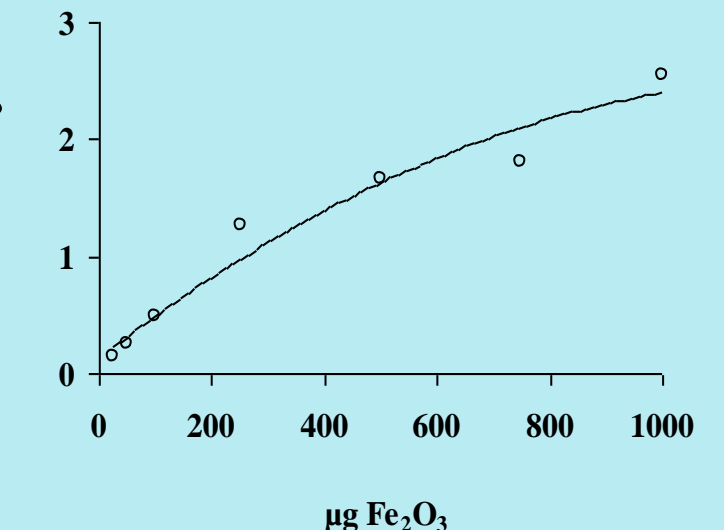


Figure 7. A calibration curve for iron oxide using a polynomial fit of the IO3 diffraction line peak area versus iron oxide mass gives a regression equation of $y = -1.46 \times 10^{-3}x^2 + 3.72x + 136$ and a $r^2 = 0.9586$.



Industry Samples

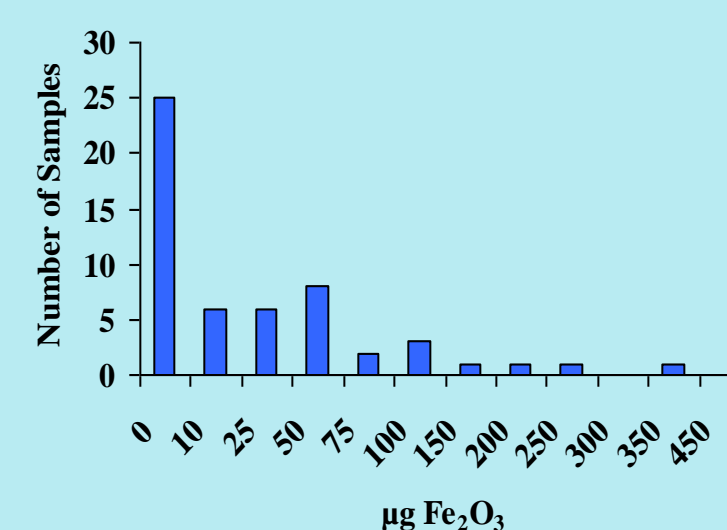


Figure 8. The calibration curve for iron oxide from the IO1 diffraction line was used to determine the amount of iron oxide in industrial hygiene samples (n=54). The bar graph shows the number of samples that are between the μg Fe_2O_3 amounts (e.g. 25 samples between 0 μg and 10 μg).

%Recovery of Quartz with Iron Oxide

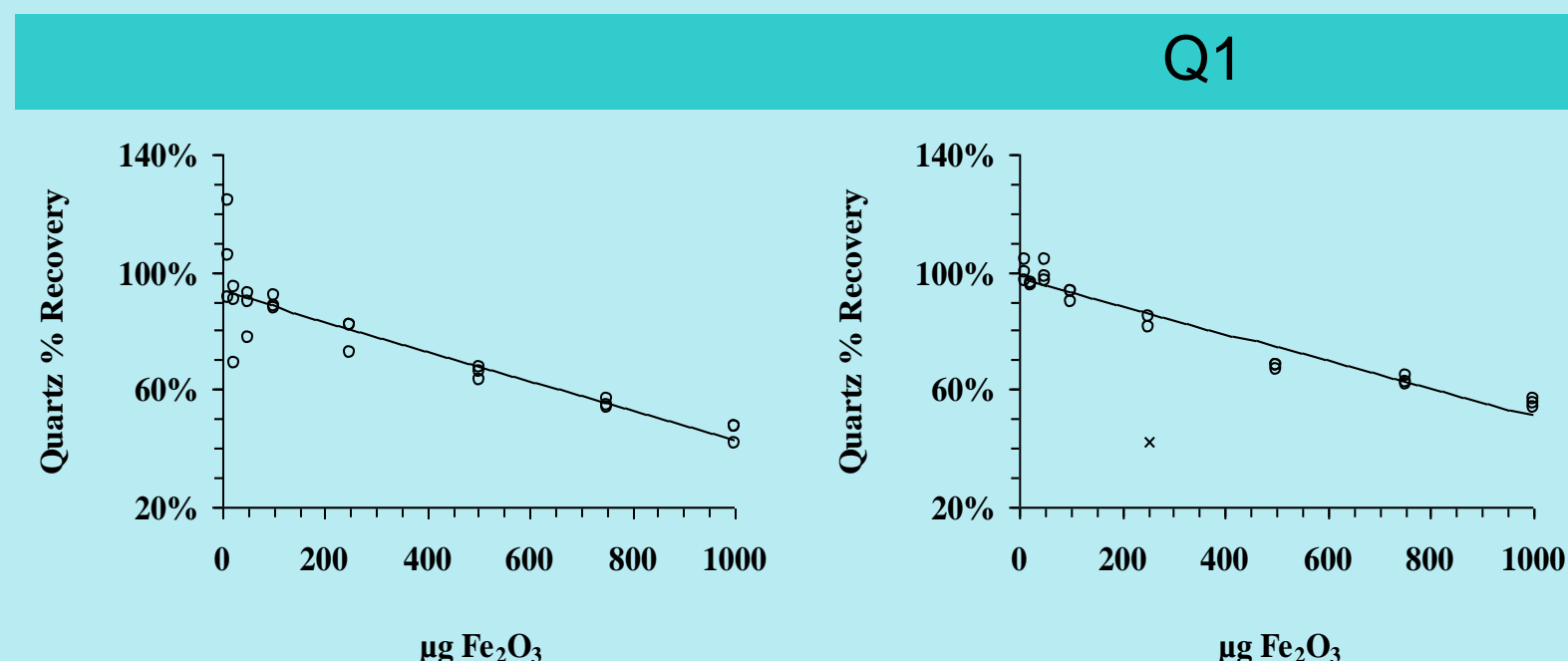


Figure 9. Graphs show the percent recovery of quartz in the presence of a known amount of iron oxide. A series of iron oxide with increasing masses were deposited (from left to right) with equal amounts of quartz, 100 μg of quartz, and (for Q1 only) 10 μg of quartz. In the presence of sufficient iron oxide, a decrease in quartz percent recovery was observed. Correlation coefficients (r), from left to right, are -88.7%, -97.3%, and -80.3% for Q1 and -94.1% and -96.9% for Q2. Data points indicated with an (x) were not included in the correlation analysis. Linear regression analysis indicates, based on regression slopes, a 0.04% - 0.05% reduction in quartz recovery per μg of iron oxide (e.g. 4% - 5% reduced quartz recovery in the presence of 100 μg iron oxide).

Preliminary Iron Oxide Removal Experiments

Chemical	Volume mL	Heat Time min	Sonication Time min	Temperature $^{\circ}C$	Dissolve
15 M H_3PO_4	10	60	-	88 – 103	Y
1.5 M HNO_3 and 0.5 M HCl	10	195 (165)	-	88 – 103	Y
1 M NaOH	10	195	-	88 – 103	N
0.4 M oxalic acid in 1 M NaOH	10	195	-	88 – 103	N
0.2 M sodium sulfite in 0.01 M HCl	10	195	-	88 – 103	N
EDTA in 3 M HCl	10	-	5 & 30	Room Temp	N
0.4 M oxalic acid in 3 M HCl	10	-	5 & 30	Room Temp	N
15 M H_3PO_4	10	-	195	57	Y
1.5 M HNO_3 and 0.5 M HCl	10	-	195	57	Partial
1 M NaOH*	10	-	195	57	N
0.4 M oxalic acid in 1 M NaOH*	10	-	195	57	N
0.2 M sodium sulfite in 0.01 M HCl	10	-	195	57	N

*Crucible crack during sonication

Summary and Conclusions

Iron oxide has a two-fold effect on quantification of quartz during XRD analysis. First, iron oxide fluorescence increases noise seen during analysis. Second, X-ray absorption by iron oxide reduces the diffraction intensity of quartz. Overall, a 0.04% - 0.05% decrease in quartz recovery per μg of iron oxide was observed.

It is possible to remove iron oxide during sample preparation with minimal effect on quartz analysis. The combination of 1.5 M nitric and 0.5 M hydrochloric acids is an effective example from this study.

Acknowledgements

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Future Work

Investigate other phases of silica that are less commonly encountered during sample analysis, such as cristobalite and tridymite, to determine the impact of iron oxide on their analysis.

Develop a regression analysis that accounts for both iron oxide and quartz to calculate a corrected mass of quartz in a sample.

Investigate other chemical combinations that will rapidly dissolve iron oxide without impacting quartz quantification.

Determine the impact of nitric and hydrochloric acid on other mineral interferences to silica analysis by XRD.

References

- [1] OSHA ID-142, Quartz And Cristobalite In Workplace Atmospheres, OSHA 1996.
- [2] NIOSH MAM, 4th ed., Method 7500 Silica, Crystalline by XRD, NIOSH 2003.
- [3] Talvite, N. A. *Determination of Quartz in Presence of Silicates Using Phosphoric Acid Analytical Chemistry* 23(4), 1951, 623-626.