QUANTITATIVE ANALYSIS OF QUARTZ IN PERLITE BY X-RAY DIFFRACTION

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INTRODUCTION

Quartz has been of interest in occupational health for several years, because it can cause silicosis. New regulations, OSHA (1989) list perlite as a nuisance dust, and this is of particular interest in New Mexico, because 85 % of the perlite produced in the United States is mined in this state. In order to better assure the well being of the public using New Mexico products, the New Mexico Bureau of Mines and Mineral Resources has begun a program to improve the sensitivity and accuracy of low level quartz determinations in perlite.

The new OSHA regulations conclude that perlite is nontoxic when airborne total particulate concentrations are 15 mg/m^3 or below and when crystalline silica concentration is less than 1 weight %. The agency has established an 8-hour permissable exposure level (PEL) of 15 mg/m^3 time weighted average (TWA) for total perlite dust containing less than 1 % quartz, and has established a 5 mg/m^3 TWA PEL for respirable perlite. These limits will protect workers from significant risk of eye, skin, or other physical irritation. This regulation is based on a Group 2A classification as a probable carcinogen in humans, at the 0.1 % crystalline silica level, by the International Agency for Research Cancer (IARC). IARC (1987a,b) found sufficient evidence for carcinogenicity of crystalline silica in animals and limited evidence in humans. Perlite is not listed as a carcinogen by OSHA or the National Toxicology Program.

Free silica commonly occurs in perlite in trace amounts. Crystalline silica can occur as several polymorphs. The most common polymorphs are quartz, cristobalite, and tridymite. Quartz is the only common form of crystalline silica in perlite, so initial research concentrated on the quartz content of perlite (Hamilton and Peletis, 1988).

Early attempts to analyze rocks for free quartz included the potassium pyrosulfate digestion method (Trostel and Wynne, 1940 and Gysin and Reelf, 1951 and 1952). Other methods include optical microscopy and heavy liquid separation (Hamilton and Peletis, 1988). All these methods are time consuming and lack the required precision and accuracy to meet both OSHA and IARC thresholds.

Traditional XRD analysis of quartz in industrial dusts uses well-established procedures (Klug and Alexander, 1974) that are sensitive to quartz at the 1 % level. With the new regulations, sensitivity is required at the 0.1 % level. As existing analytical methods could not adequately determine quartz at this new level, Mansville Sales Corporation initiated the development of an XRD method to determine quartz in perlite at the 0.1 % concentration (Hamilton and Peletis, 1988 and 1989). Work at the New Mexico Bureau of Mines and Mineral Resources (NMBMMR) confirmed the work of Hamilton and Peletis (Barker and Mckee, 1989). The present report will discuss continuing research at the NMBMMR on the determination of low levels of quartz in perlite.

SAMPLE PREPARATION

Sample preparation is important in XRD analysis, especially for quantitative work. Unknowns must be representative of the bulk perlite and must be ground very fine. Standards and unknowns must be presented to the x-ray beam in a reproducible and uniform manner.

Industrial Standards

Manville Sales Corporation provided us with seven of their in-house natural perlite standards (Table 1). The standards were supplied in powder to granular form and ranged in weight from 40 to 75 grams. Five to ten grams of standard were ground for three minutes in a tungsten carbide ring puck mill as instructed by Manville (Hamilton and Peletis, 1988).

Table 1. Industrial standards (Manville Sales Corp.)

STANDARD	REPORTED QUARTZ CONCENTRATION*
PA130 #1	ND
PA130 #2	0.2
PA130 #3	ND
PA130 #4	0.2
PA116 #5	0.4
PA610 #6	0.1
PA4000 #7	0.2

*values are from Hamilton (1989, written communication)

Laboratory Standards

Laboratory standards were prepared by blending ground window glass and standard Ottawa Sand (SOS) quartz sold by Fisher Scientific. The compositions of these are shown in Table 2. Window glass was chosen for the standards because it was convenient and because it contains elements (Ca, Na, Fe, Mg) that make it possible to determine the quartz concentration in the standards by chemical analysis.

Ten to fifteen gram batches of glass were ground for 30 minutes in a model 8000 Spex Mixer/Mill equipped with a tungsten carbide grinding set. Using a Microjet 5 high speed grinder with a 20 ml. agate mortar and pestle, ten gram batches of SOS were ground. Both the glass and SOS were homogenized before mixing.

A practical range of quartz concentrations was prepared by repeatedly re-diluting an initial 1:1 mixture of SOS + glass with glass in 1:1 increments. Prior to each dilution, the mixtures were blended for 12 minutes in the Spex Mixer/Mill then split into 10 gm aliquots. The resulting progression of concentrations is shown in Table 2. It departs from ideality, because it is not necessary to precisely mix in a 1:1 ratio.

Grinding

Reproducibility in XRD analyses is dependent on uniform, fine grain size. Also, small grain size will decrease the effects of extinction and microabsorption (Klug and Alexander, 1974). Proper grinding using uniform weights and identical grinding time improves reproducibility.

Table 2. Artificial standards prepared from quartz and common glass.

STANDARD	QUARTZ CONCENTRATION AS MIXED
APS50Q	50.754
APS25Q	25.879
APS12Q	12.377
APS6Q	6.157
APS3Q	3.064
APS1.5Q	1.510
APS.78Q	0.751
APS.39Q	0.370
APS.20Q	0.187
APS.10Q	0.0953
APS.05Q	0.0477

Several grinding strategies were tried. At first, an alumina mortar and pestle was used. Dry grinding in acetone, and grinding in liquid nitrogen were both investigated, but powders produced from each of these methods were too coarse for XRD analysis. While the Microjet 5 grinder can produce a fine-grained powder in a short time, the agate grinding set may contaminate the perlite with quartz, so the Microjet 5 was not used.

The Spex Mixer/Mill was the last grinder tested. Unknowns were ground for thirty minutes using the tungsten carbide grinding set. The Mixer/Mill produces a fine powder, does not contaminate the samples, and can be dedicated to perlite analysis alone.

Brindley and Brown's (1980) maximum size criterion of $1/100\mu$, where μ is the mean linear absorption coefficient of the particles gives approximately 2.5 μm as the maximum allowable particle size for quantitative clay analysis. Our samples are not clays, and their particle size is something less than 20 μm; however, we feel that our observed intensity errors are acceptable in view of the increased grinding time that would be required to decrease particle size by a factor of 10.

Briquetting

The purpose of briquetting samples is to achieve reproducible presentation of the powder sample to the x-ray beam. Because preferred orientation does not seem to be a problem with analysis of quartz in perlite, the use of this method has two advantages: 1) sample preparation is rapid, and 2) the XRD sample can be analyzed by x-ray fluorescence spectroscopy without a further sample preparation step.

The briquetting die used was designed by Volborth (1963). We modified the die by inlaying a polished disk of silicon carbide in its anvil. It produces a briquette with an analytical surface 30 mm in diameter.

Standards were split, and 1.0 gram of each weighed out. The powder was introduced into the briquetting die and backed with boric acid. The sample was then compressed under a five-ton load and the die disassembled. One to three drops of deionized water were placed on the analytical surface of the pellet and allowed to soak in. The water helps drive out entrained air and improve intergranular adhesion of grains. The die was reassembled and the sample was compressed under a twenty ton load. Figure 1 graphically shows the reproducibility of duplicate standard briquettes containing 0.2 % quartz.

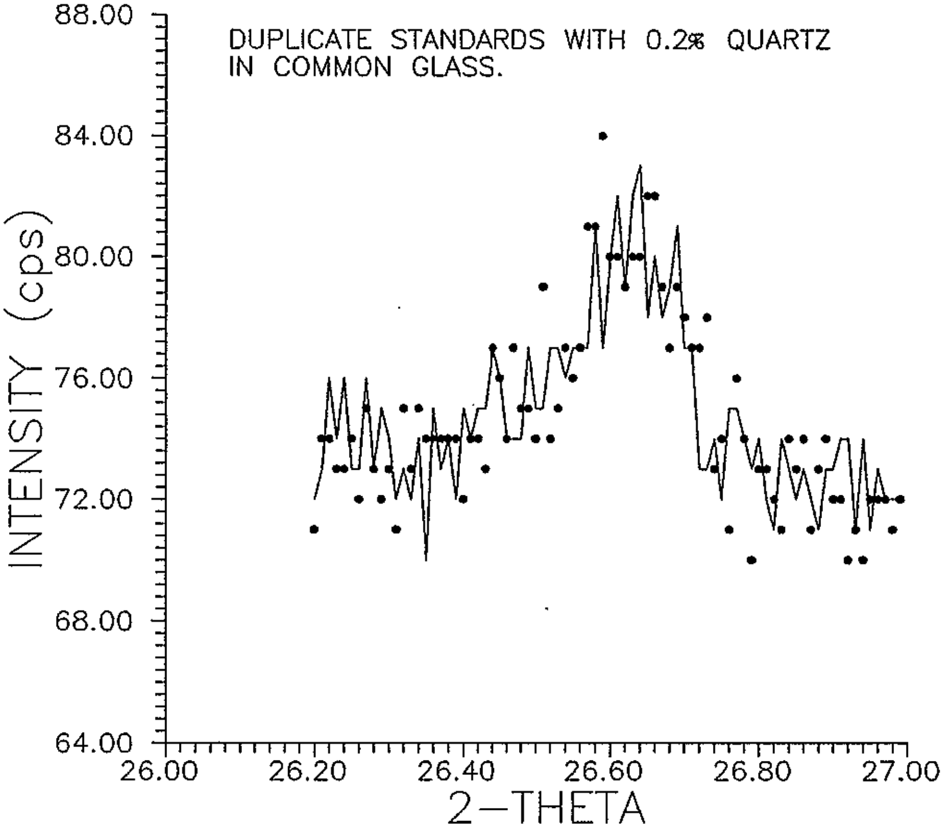

Figure 1. Reproducibility of duplicate briquettes

SAMPLE ANALYSIS

Samples were analyzed on a Rigaku D/MAX diffractometer controlled by a DEC PDP 11/23 computer using the manufacturer's software. The diffractometer is equipped with a long, fine focus, Cu X-ray tube, graphite monochromator, and a scintillation counter. Machine and slit settings are shown in Table 3.

Pellets were mounted in the sample spinner designed by Renault (1984). At the beginning of each run of several standards, a pure SOS pellet was run to correct for drift and to serve as an instrumental standard. Figure 1 graphically shows the reproducibility of 0.20% quartz in duplicate pellets.

The instrumental conditions are given in Table 3. The diffractometer was set-up to step scan over the (101) quartz peak at 26.66 degrees two-theta (Cu radiation). Considerations of convenience and counting statistics led us to adopt the machine settings given in Table 3 which allow one analysis per hour of machine time. Under these conditions, the peak intensity of quartz at 0.2 % is about 500 counts and reproducible at the 4 % level.

Table 3. Instrumental conditions.

MACHINE SETTINGS	SLITS
40 Kv	1° DS
25 mA	1° SS
0.01° Step Width	0.30 mm RS
40 Sec./Step	0.30 mm MS
26.2°-27.0° Scan Range	

Feldspar, mica, clays, and other common minerals in perlite have peaks that overlap with the (101) peak of quartz. To check for possible peak overlap, a scan from three degrees to sixty degrees two-theta is run on unknowns. Peak overlap is evaluated on an individual basis.

Raw binary data used by the PDP computer were converted to ASCII form. Files are then transferred to an IBM PC 5-1/4 inch diskette using the communications software, SOFTCOM, developed by The Software Store of Marquette, IL.

The data files were edited on a personal computer to remove text and then reduced by the deconvolution program of Wiedman, et al. (1987). This program precisely establishes background and enhances peak resolution without changing the integrated intensity. Good peak resolution is important in the analysis of unknowns in order to reveal the presence of interferences. The program of Weidman, et al. (1987) improves resolution by revoving instrumental broadening and minimizing the effects of random counting error on deconvolution. Figure 2 shows the deconvolution and background correction as applied to a laboratory standard with 0.20 % quartz.

The profile of the pure quartz standard, SOS, serves as an instrumental standard. Peak areas are integrated because differences in crystallinity require analysis of peak area, not peak height.

After peak integration, the counts are normalized to the SOS integrated counts. Calibration curves are constructed using the normalized integrated counts versus quartz concentrations.

Both straight line (Figure 3) and second order (Figure 4) calibration curves fit the data reasonably well. The first is fit over the whole range of possible quartz concentrations and the second over a short range of low concentrations.

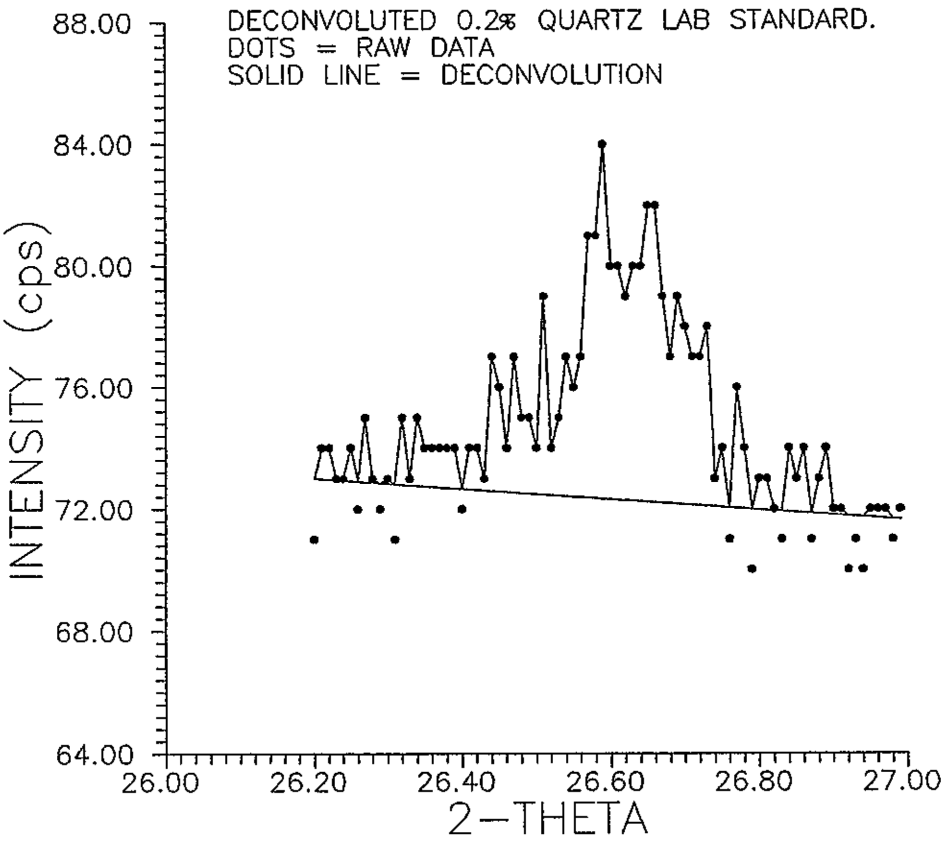

Figure 2. Deconvolution and background correction for a laboratory standard with 0.20% quartz.

The second order curve is shown in Figure 4. It is preferred for several reasons. It has a lower root mean square (RMS) of residuals (Table 4); its intercept is closer to zero than the straight line curve; and it has more practical application to the quartz concentrations of interest in industrial perlite.

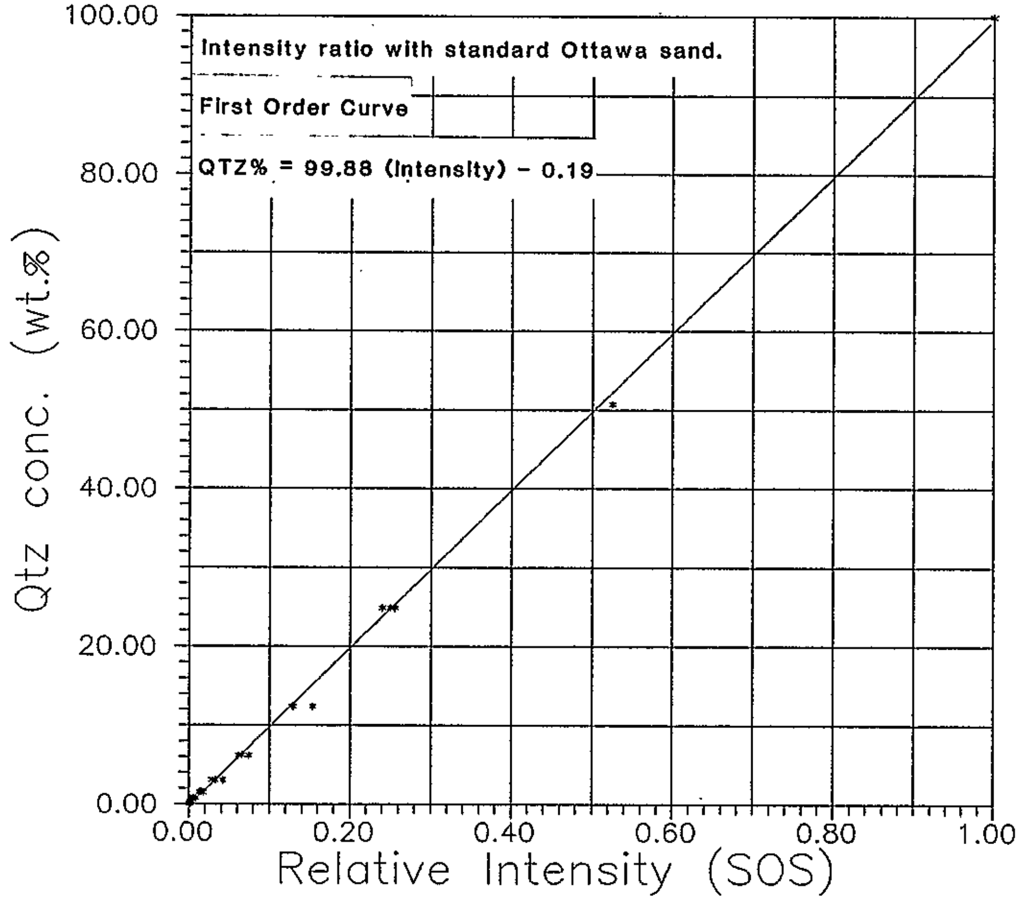

Figure 3. Straight line calibration curve of quartz in laboratory standards.

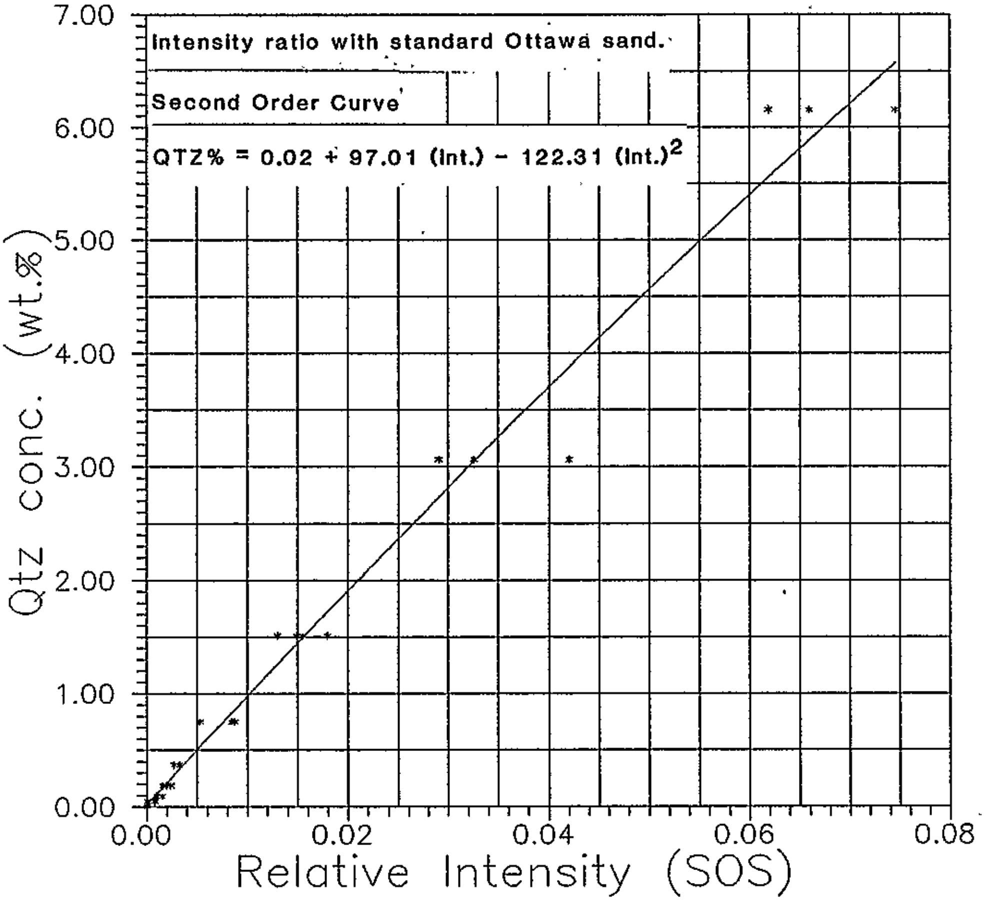

Figure 4. Second order calibration curve for low concentrations of quartz in laboratory standards.

Under ideal conditions, the standards should form a first order linear curve with a zero intercept. This is expected when the mass absorption coefficient (MAC) of the matrix equals the MAC of the analyte (Alexander and Klug, 1948). The shape of the second order curve suggests that the MAC of quartz is greater than the MAC of the glass (Alexander and Klug, 1948), but in fact, the glass contains components that make its MAC greater than quartz.

No doubt the shape of the calibration curve is an artifact of sample preparation. At higher quartz concentrations, the standards have greater spread on figures 3 and 4. And far exceed the error due to counting statistics. This variation is probably due to inadequate mixing of the higher quartz standards. As sample preparation progresses from 50% quartz to less than 0.05%, the blending and grinding time of the quartz increases. Consequently, mixing is better for the lower concentrations than for the higher. We suspect that random error introduced by inhomogeneity has biased the countrates of intermediate concentrations upward and that the mean error introduced at the 50 % quartz level is propagated to lower concentrations.

Table 4. STATISTICS FOR THE CALIBRATION CURVES

	First Order	Second Order
RMS	60.6 %	25.1 %
Precision	32.1 %	16.9 %
LLD	0.20 %	0.05 %

RMS = Root mean square of residuals
Precision at 0.1 %level.
LLD calculated at 3σ.

Precision at the 0.1 % level is 16.9 % (table 4). The lower limit of determination at three sigma is 0.05 % (table 4). Accuracy can not be determined until a set of well-characterized standards are available.

SUMMARY

The method presented in this paper has good precision, is as rapid as can be expected with ordinary X-ray tube power, and can detect quartz in perlite at the 0.1 % level. The samples can be prepared and presented to the x-ray beam in a reproducible manner.

Future research will include the study of the effect of variation in mass absorption coefficients and how they affect the calculation of quartz content. A second area of interest will be to reformulate the laboratory standards to reduce the analytical variation at high quartz concentration. Also, a larger set of standards will be produced.

It would be of help to have a set of natural perlite standards that have been analyzed by a number of different laboratories and techniques. Improvement in sensitivity is expected to occur at higher x-ray tube power, but expensive equipment is required for that.

The method presented here could also be used for cristobalite and tridymite if the proper standards are used. This method is also applicable to other materials in addition to perlite.

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