DEPARTMENT OF LABOR
MINE SAFETY AND HEALTH ADMINISTRATION
PITTSBURGH SAFETY AND HEALTH TECHNOLOGY CENTER

X -RAY DIFFRACTION DETERMINATION OF QUARTZ AND CRISTOBALITE IN RESPIRABLE MINE DUST

ANALYTES:	Crystalline silica	METHOD NO:	P-2
MATRIX:	Respirable Mine Dust	RANGE:	20 - 500 ug (quartz) 20 - 500 ug (cristobalite)
PROCEDURE:	X-ray Diffraction	$PRECISION_{Total}$:	7-10%
DATE ISSUED:	August 3, 1989	ACCURACY:	± 20% (SAE)

1.0 TECHNICAL OVERVIEW

1.1 INTRODUCTION/PRINCIPLE OF METHOD

This method provides procedures for the determination of airborne respirable quartz and/or cristobalite in the workplace atmosphere by X-ray diffraction (XRD). Samples are collected on a polyvinyl chloride (PVC) filter, low-temperature ashed and resuspended in isopropanol (IPA) and sonicated. The suspended particulate is deposited onto a silver membrane filter. The filter is scanned by XRD at defined angles and the quartz and cristobalite are quantified.

1.2 SAFETY

1.2.1 Laboratory coats, gloves and safety glasses (when working with acids) and gloves and safety glasses (when working with isopropanol) should be worn when performing this procedure.

1.2.2 Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable. Every individual performing this procedure should be familiar with the Material Safety Data Sheets (MSDS) for every reagent used. MSDS are located in MSDS station.

1.2.3 Isopropanol is flammable and must be used in a fume hood.

1.2.4 Concentrated acids are toxic and extremely irritating to skin and mucous membranes; therefore, acids must be handled under the hood. NOTE: Always add acid to water, never add water to concentrated acids, when preparing dilute acid solutions.

1.2.5 Avoid inhaling silica dust. Crystalline silica (respirable) is labeled as a potential carcinogen by NIOSH and is listed as reasonably anticipated to be a human carcinogen in the Eighth Report on Carcinogens.

1.2.6 Radiation badges are worn to detect exposure to low-level radiation. Radiation badges

are also placed on each instrument. Badges are collected monthly to determine exposure.

1.3 SPECIMEN REQUIREMENTS AND PRESERVATION

1.3.1 Air samples are collected on polyvinyl chloride (PVC) filters (5 um pore size), 37 mm cassettes. Samples are collected at approximately 1.7 L/min flow rates. At least one field blank (control) sample should be submitted with each set of air samples. The control must be of the same lot (i.e. same preweight date) as the samples.

If a sample weighs more than 3.5 mg, the sample will be split into increments, and analyzed in its entirety. When splitting samples into increments, each increment must be <3.5 mg. Samples with oversized particles and a filter loading greater than 10 mg are voided with a metal non-metal void code "MNV" and are not analyzed. MNV is noted on the Request for Lab Analysis (RLA) form.

1.4 GLASSWARE

All reusable lab ware (beakers, etc.) is cleaned prior to use by washing with detergent, followed by rinsing with tap water. Glassware may be air-dried or oven dried at 90°C ± 10°C.

1.5 RANGE AND DETECTION

1.5.1 The calibration range is 20 to 500 µg for silica and 20 to 500 µg for cristobalite. Dust samples with weights of at least 0.100 mg are analyzed for quartz; a 0.05 mg minimum sample weight is required for cristobalite analysis.

1.5.2 The method detection limit (MDL) is approximately 5 µg for silica and 10 µg for cristobalite. The method detection limit is defined as "the minimum concentration that can be measured and reported with 99% confidence that the value is above zero".

1.5.3 The working range of silica masses are bracketed by the calibration standards.

1.6 INTERFERENCES

1.6.1 Interference due to mineral dusts other than crystalline silica may be encountered.

1.6.1.1 Samples that exceed the Threshold Limit Value (TLV) calculated from the primary angle silica analysis are subject to analysis at the secondary and tertiary angles. A quaternary angle analysis is performed to confirm the presence of quartz. Results that do not agree within 15% RPD are an indication that interferences are present.

1.6.1.2 Visual inspection is performed by the analyst to determine whether the peak center is shifted, whether there are multiple peaks or shoulders in the integration range, or whether there is any unusual broadening of the peak.

Interferences can be minimized by using multiple diffraction angles for analysis, computer assisted methods of integration, or acid washing of the sample. If an interference is encountered and can not be resolved by software approach for peak area integration or the use of an alternate angle, chemical treatment of the sample should be performed.

1.7 REAGENTS

1.7.1 Isopropanol (IPA), reagent and technical grade.

1.7.2 Quartz standard reference material (SRM), NIST 1878a (current lot), Respirable Alpha Quartz.

1.7.3 Cristobalite SRM NIST 1879 (current lot), Respirable Cristobalite.

1.7.4 Reference sample (mica, Novaculite, quartz or other stable standard) used for data normalization.

1.7.5 1.5% parlodian (paroxylin) in amyl acetate. Used for fixing sample onto the silver membrane filter. Either commercially prepared or prepared by adding 1.5 g of parlodian and diluting to 100 mL with amyl acetate.

1.7.6 Distilled water, Type I or Type II.

1.7.7 If acid washing is necessary, the following concentrated reagents are required:

1.7.7.1 Nitric Acid (69-71%), reagent grade

1.7.7.2 Phosphoric Acid (85%), reagent grade

1.7.7.3 Fluoroboric Acid (48-50%), reagent grade

1.7.7.4 Ammonium Hydroxide (30% aqueous ammonia)

1.8 EQUIPMENT AND SUPPLIES

1.8.1 X-ray powder diffractometer; Philips PW1800, Bruker D4 endeavor or equivalent

1.8.2 Long Fine-Focus copper target x-ray tube

1.8.3 Curved graphite crystal monochromator

1.8.4 Sample holders and sample spinner

1.8.5 Low-temperature radio frequency (RF) asher and vacuum pump; Anatech Model RFX-600 or equivalent

1.8.6 Oxygen tank and two-stage regulator for low-temperature asher, second stage of regulator capable of being set at 2 to 10 psi

1.8.7 Microbalance, capable of weighing to 0.001 milligrams; Mettler MT-5, MT-X or equivalent

1.8.8 Filtration apparatus consisting of: 6-place manifold, fritted support bases and clamps, rubber stoppers, vacuum tubing and 4,000 milliliter (mL) side-arm filtering flask

1.8.9 Aluminum filtering funnels (These are specially fabricated funnels, similar to the Millipore No. XX10-025-40). All funnels used for calibration and analysis must have the same bore diameter.

1.8.10 Aluminum ring specially fabricated to fit the fritted support base

1.8.11 Vacuum source (water aspirator or vacuum pump) with trap (2,000 mL side-arm flask)

1.8.12 Small stainless steel forceps for opening filter cassettes and for handling filters

1.8.13 Petri slides for 47 mm diameter filters; Millipore No.PD15-047-00 or equivalent

1.8.14 Ultrasonic bath, 200 watt input

1.8.15 Wash bottles, polyethylene, 500 mL

1.8.16 Beakers, Pyrex, 50 mL, one per sample to be analyzed

1.8.17 Engraver (used to mark numbers on beakers which are numbered in sequence and grouped in lettered sets to prevent mixing of samples, i.e., A1, A2,...; B1, B2,...;etc.)

1.8.18 Desiccator for storing the silica standard materials

1.8.19 Slide warmer (for drying filters after filtering)

1.8.20 Volumetric pipettes, Class A, Pyrex-type or borosilicate glass, in the following sizes: 2, 4, 6, 10, 20, 30, and 50 mL (for preparing calibration standards)

1.8.21 Pipette bulb, rubber or neoprene

1.8.22 Flasks, volumetric, Pyrex-type with stoppers, 500 mL and 1000 mL

1.8.23 Spatula, micro stainless steel (for weighing out silica standard materials)

1.8.24 Weighing boats

1.8.25 Latex gloves

1.8.26 5.0 μm pore size, 37 mm diameter polyvinylchloride (PVC) filters; Pall Gelman GLA-5000

1.8.27 Drying oven for drying standard reference materials

1.8.28 0.5 um,25 mm PVC filters, Omega P- 052550 or 0.45 mm DM-450,vinyl acrylic copolymer VWR 28149-408

1.8.29 Glass filtration apparatus consisting of a 30 mm diameter fritted glass base. These funnels are used for acid washing and preparing standards on PVC filters.

1.9 STANDARDS

Quartz (NIST SRM current lot of 1878), Cristobalite (NIST SRM current lot of 1879). NOTE: Correct for purity of SRM.

1.9.1 STANDARD PREPARATION

XRDs are recalibrated when the Continuing Calibration Verification (CCV) values differ by more than 10% from the true value. Calibration is also performed when tubes or detectors are replaced, and may be warranted following maintenance to the x-ray generator, goniometer, or sample spinner. CCV standards are used to verify instrument

calibration with each use. Stock standard shelf life is 6 months from preparation date.

1.9.1.1 Preparation of separate quartz or cristobalite stock standards:

1.9.1.1.1 Dry the standards for approximately 2 hours at 110°C in oven. Store in a desiccator.

1.9.1.1.2 Weigh 10.00 ± 0.01 mg of the dried standard and quantitatively transfer to a 1000 mL. volumetric flask (This is a 10 µg/mL stock standard).

1.9.1.1.3 Dilute to volume with isopropyl alcohol (IPA)

1.9.1.1.4 Disperse the analyte in the IPA by sonicating in an ultrasonic bath for approximately 20 to 30 minutes.

1.9.1.1.5 Cool the flask in a cold-water bath until the temperature of the suspension is approximately 20°C.

1.9.1.1.6 Mix thoroughly by inverting the flask numerous times.

1.9.1.2 Preparation of quartz or cristobalite working standards:

1.9.1.2.1 Prepare the filtering apparatus using a 25mm 0.5um PVC filter as the filtration media.

1.9.1.2.2 A series of working standards is prepared by pipetting aliquots of the stock suspension. Prepare working standards in triplicate.

EXAMPLE:

Quartz	Aliquot (mL)	Std. Concentration (µg)
10 µg/mL Std	2,4,6,10,20,30,50	20, 40,60,100,200,300,500

Cristobalite	Aliquot (mL)	Std. Concentration (µg)
10 µg/mL Std	2,4,6,10,30,50	20,40,60,100,300,500

1.9.1.2.3 Invert the flask containing the suspension several times, withdraw the appropriate aliquot and dispense into funnel. Apply vacuum and filter, rinsing the filtration funnel twice with approximately 10 mLs isopropyl alcohol. When all the alcohol has passed through the funnel, remove the filter using forceps, placing the filter deposit on the slide warmer to evaporate any remaining alcohol.

1.9.1.2.4 When all standards have been deposited onto PVC filters, they are placed deposit side down into beakers and then placed into a low temperature asher and ashed for approximately 90 minutes at ~400W forward power and ~135 mL/min oxygen flow. After the ashing cycle is complete, carefully add approximately 10 mL isopropyl alcohol to each beaker, using a squeeze bottle. Deposit the standards onto silver filters using the procedure described in Section 2.4.11-2.4.19.

1.9.1.2.5 Analyze according to Section 3.1.2. Record the silica peak areas and corrected peak locations, and the silver peak areas and locations.

1.9.1.2.6 Silica masses are corrected on the basis of the NIST certified values by factors inserted into the regression template. Perform a regression

analysis of peak area vs. µg of silica for each diffraction angle used for the polymorph of interest using the template located on K:\XRD.lab\Calibration\Blank Calibrationrev1.xls. Do not save over this file. After opening, immediately click on SAVE AS and name the "new file" in the same format as all previous calibration files in the folder (Instrument name and date)

1.9.1.2.7 Check that the coefficient of correlation is at least 0.995. Analyze a series of Initial Calibration Verification (ICV) standards to verify the accuracy of the regression factors. The mean values of the series of ICV standards must be within 5% of the known value for all diffraction angles used for enforcement analysis.

1.10 QUALITY ASSURANCE/QUALITY CONTROL

1.10.1 **Method or Matrix Blank.** A filter (37 mm PVC) that is processed in the same manner as customer samples, e.g. it contains all the reagents in the same volume as used in the processing of samples. Analyze at a rate of one per each analytical batch (maximum of 20 samples). The method or matrix blank must be less than the method detection limit (MDL).

1.10.2 **Field Blank.** A filter submitted with air samples used to verify that contamination of the filter has not occurred in the field during sampling. The field blank should be less than the method detection limit. A field blank is analyzed with each batch of samples.

1.10.3 **Initial Calibration Verification (ICV).** The ICV is a NIST SRM 2679a or separately prepared standard solution. The ICV is a sample that is independent of the standards used to prepare the calibration. The ICV is used to verify the accuracy of the calibration curve. The measured ICV values must be within the NIST SRM acceptance range or, in the case of separately prepared standard within ± 5% of the true value.

1.10.4 **Reference sample.** The reference (monitor) sample is a Novaculite quartz standard used for data normalization. It is analyzed four times with intensities recorded at the beginning of each day of instrument use. The average intensity is calculated. The reference sample monitors the degradation of the X-ray tube. The four values are recorded and the average is used for calculation of final result. This compensates for long-term drift in X-ray tube intensity.

1.10.5 **Continuing Calibration Verification (CCV).** The CCV is a fixed filter standard used for calibration. The CCV does not go through the sample procedure. The CCV is used to re-verify the accuracy of the calibration curve. The measured CCV values must be within 10% of the true values. The CCV is analyzed at the end of each analytical batch for each diffraction angle used for sample analysis to verify calibration.

1.10.6 **Matrix Spikes/QC's.** Three aliquots of NIST 1878a between 75 to 125 micrograms are weighed onto PVC filters and taken through the entire sample preparation procedure, and then analyzed at the primary silica angle. The mean recovery of the set is used to evaluate accuracy, and the standard deviation of the percent recovery of the spikes is used to evaluate precision.

1.10.7 **Media Blank.** Silver membrane filters (25 mm with 0.45-micron pore size) which are of the same lot as those used for sample preparation. The average silver value obtained is used to calculate sample self-absorption.

1.10.8 **Reporting Limit Verification Sample.** A standard prepared at a silica mass equivalent to the method reporting limit (20 ug). It is analyzed once per sample batch for each diffraction angle used for sample analysis. Also known as a Low CCV sample, it is

analyzed at the beginning of each run. The value of the Low CCV must be +/- 20% of the true value.

1.10.9 **Corrective Action By Analysts:**

If the results of control samples exceed the acceptance criteria for an analytical procedure, the system may be "Out-of-Control" causing analytical results generated by that system to be suspect. Laboratory personnel should immediately cease operations and take action to identify and resolve the problem bringing the analytical system back into "Control". These corrective actions shall be documented in the Laboratory Information Management System (LIMS). Corrective action includes the checking of results for calculation and/or transcription errors, preparation/use of new standards, recalibration of instrument, reanalysis of all samples with new controls or reagents. The corrective action taken in an "Out-of-Control" situation shall be documented by placing the corrective action/problem report form in the data packet for the specific run. The laboratory supervisor or Quality Manager is to be notified if the problem cannot be identified and resolved.

1.10.10 **Quality Control Charts**

Control charts are used to determine if the measurement system process is "In Control" and whether the results generated by the measurement system are acceptable. The control chart provides the tool for distinguishing the pattern of indeterminate (random) variation from the determinate (assignable cause) variation. The data from a series of analytical tests are plotted with the vertical scale in units appropriate for the quality characteristic being measured, and the horizontal scale in units of time or sample batch. The control chart is actually a graphical presentation of QC efficiency. If the procedure is "In Control", the results will almost always be within established control limits. Further, the chart will disclose trends and cycles from assignable causes, which are corrected promptly. See Appendix B for control charts. Control charts are located on K:\Xrd.lab\QA\xrdQAyyyy.

1.10.11 The turn around time goal for this analysis is seven working days from the day of receipt.

1.11 PROCEDURE

1.11.1 Preliminary treatment of filters and bulk samples is always necessary prior to analysis.

1.11.2 Refer to Section 2.0 for the preparation and low temperature ashing procedure for filters and bulks.

1.11.3 Follow instrument work instructions in Section 3.0.

1.11.4 After all function verification/preventive maintenance (FV/PM) checks have been completed and recorded (See Appendix C for FV/PM log), the run may be started. The entire run with instrument checks should be set up in accordance with the run sequence outlined in Appendix D.

1.11.5 If any sample is below the MDL established (See 1.5.2); the data will be reported as Non-Detectable (ND).

1.11.6 If the sample is greater than the MDL but less than the reporting limit the result is reported as <0.020mg.

1.11.7 If any sample result exceeds the highest calibration standard the sample is reported as >500 mg.

1.12 CALCULATIONS AND REPORTING

1.12.1 **Filters** (Reporting of quartz in mg)

$$C/1000 = \frac{\hat{I}_x \times f(t) - b}{m}$$

Where:
C = mass in µg

$\hat{I}_x$ = Normalized area for sample peak = $I_x/I_r \times N$
I_x = area of sample
I_r = area of reference specimen
N = area of reference specimen at current calibration

b = intercept of calibration graph (=0)
m =slope of calibration graph, area counts/µg

$f(t) = -R \times \ln T/1 - T^R$ = absorption correction factor
$R = \sin(\theta_{Ag})/\sin(\theta_x)$
$T = \hat{I}_{Ag}/\hat{I}^0_{Ag}$ = transmittance of sample
$\hat{I}_{ag}$= normalized silver peak area from sample
$\hat{I}^0_{Ag}$=normalized silver peak area from media blanks
θ_x = angle of analyte

EXAMPLE:
m= 22.93 Blank Silver Area = 5936.1
Reference specimen at calibration =9339 Current reference specimen=9127
Sample area = 571.93 Sample silver area = 5238.7

R = sin 22.14/sin 13.33 = 0.37687/0.230559 = 1.63459
T = 5238.7/5936.1 = 0.88

$\hat{I}_x = 571.93 \times 9339/9127 = 585.21$

$f(t) = -1.635 \times -0.1273/1 - 0.8114 = 1.108$

$585.21 \times 1.108 = 643.73/22.93 = 28.3$ µg

C/1000 = 28.3/1000 = 0.028 mg

1.12.1.1 To calculate % quartz:

[Mass silica, µg/ (sample mass, mg×1000)] ×100 = %

EXAMPLE: [28.3 µg/ (0.200 mg × 1000)] × 100 = 14.2%

1.12.1.2 To calculate SWA in mg/m^3:

$$SWA = \frac{\text{sample mass, mg} \times 1000 L/m^3}{1.7 \text{ L/min} \times \text{sampling time, min}}$$

EXAMPLE:

$$SWA = \frac{0.200 \times 1000}{1.7 \times 480 \text{ min}}$$

$= 0.245 \text{ mg/m}^3$

1.12.1.3 To calculate TLV in mg/m^3:

TLV for Quartz = 10/ (2 + % quartz)

TLV for Cristobalite = 5/ (2 + % cristobalite)

EXAMPLE: TLV for quartz =

$10/ (2 + 14.2\%) = 0.617 \text{ mg/m}^3$

1.12.2 **Bulks** (Report as approximate %)

$$\text{Approximate \% Analyte} = \frac{\text{weight of analyte found (µg)} \times 100}{\text{total sample weight (µg)}}$$

1.13 DISPOSAL

1.13.1 IPA will be disposed of as liquid organic waste. All acids will be disposed of as inorganic waste.

1.13.2 All filters, standards and quality control samples are considered "Hazardous Waste", and must be disposed of accordingly.

1.14 REFERENCES

1.14.1 OSHA Method ID-142, "Quartz and Cristobalite in Workplace Atmospheres", Revised December 1996.

1.14.2 NIOSH 7500, "Silica, Crystalline, by XRD", Revised 15 January 1998.

2.0 SAMPLE PREPARATION PROCEDURE

2.1 INTRODUCTION/PRINCIPLE OF METHOD

This method can determine the amount of silica and cristobalite particulates in the workplace atmosphere. The airborne particulates are collected on polyvinyl chloride (PVC) filters using calibrated sampling pumps. This method provides for a sample preparation using a low temperature ashing procedure. Ashed samples are subsequently suspended in isopropanol, filtered, deposited onto a silver membrane filter, and analyzed by X-ray diffraction (XRD).

2.2 SAFETY

2.2.1 Gloves and safety glasses must be worn during entire sample preparation process.

2.2.2 Isopropanol is flammable and must be used in a hood.

2.2.3 Concentrated acids are toxic and extremely irritating to skin and mucous membranes; therefore, handle acids under the hood. Laboratory coats, gloves and safety glasses must be worn when working with acids. **ALWAYS ADD ACID TO WATER; never add water to concentrated acids.**

2.2.4 All sample preparation will be performed under a suitable hood.

2.2.5 Avoid inhaling silica dust. Crystalline silica (respirable) is labeled as a potential occupational carcinogen by NIOSH and is listed as reasonably anticipated to be a human carcinogen in the Eighth Report on Carcinogens.

2.3 REAGENTS

2.3.1 Isopropanol, reagent and technical grade.

2.3.2 If acid washing is necessary, the following concentrated reagents are required:

2.3.2.1 Nitric Acid, reagent grade

2.3.2.2 Phosphoric Acid (1:1), reagent grade. Mix equal volumes of deionized water and concentrated phosphoric acid.

2.3.2.3 Fluoroboric Acid (48-50%), reagent grade

2.3.2.4 Dilute Ammoium Hydroxide (5%) – Dilute 25 mL concentrated ammonium hydroxide to 500 mLs with deionized water.

2.4 PROCEDURES

BULKS

2.4.1 Wet sieve with a 10 um sieve, isopropanol and an ultrasonic bath, followed by evaporation of excess alcohol, dry in an oven at 120° C or place on top of a hotplate or slide warmer for approximately two hours and overnight storage in a desiccator.

2.4.2 Weigh approximately 2 mg of sieved dust onto a PVC filter, transfer to a 50-mL beaker and ash in the Low Temperature Asher. Add approximately10 mL isopropanol,and sonicate approximately 3 minutes. Deposit onto a silver membrane filter using the filtration apparatus in the same manner as an air sample.

FILTERS

2.4.3 Samples are received in the x-ray laboratory from the weighing laboratory. Filters having a net weight gain of 0.100 mg or more get analyzed for quartz. If cristobalite is requested, a weight gain of 0.05 mg or more gets analyzed. Samples with <0.100 mg are not analyzed and reported as Analysis Not Performed "ANP". Samples with a weight gain >3.5 mg are split into increments and analyzed.

2.4.4 Generate a work list. Batch samples (19 samples or less plus 1 field blank). Include a lab blank with each batch of samples. Place a blank PVC filter into a beaker labeled for the blank. Batching instructions are found on K:\Xrdlab\Batching.

2.4.5 Using forceps open each filter capsule and remove the filter. Visually inspect and note any abnormalities, i.e. large particles or uneven deposit.

2.4.6 Place the filter into the bottom of the appropriately numbered 50-mL beaker, dust side down.

2.4.7 Repeat steps 2.4.5. - 2.4.6. until all of the samples are placed in 50 mL beakers.

2.4.8 Place three QCS samples as described in 1.10.6 with each batch of samples (19 or less).

2.4.9 Place the beakers in the low temperature asher. Ash for ~90 minutes up to ~400-Watts forward power and an oxygen flow rate of ~135 mL/min. After ashing, carefully add ~10 mL of isopropanol to each beaker making sure no dust is lost.

2.4.10 Place the beakers in an ultrasonic bath and sonicate approximately 3 minutes.

2.4.11 While the samples are sonicating, prepare the filtration apparatus.

2.4.11.1 Using forceps on outer edge of filter, place a silver membrane filter, concave side up, inside the centering ring which is placed on the fritted glass base of the filtration apparatus.

2.4.11.2 Carefully place the aluminum funnel on top of the silver filter, positioning it inside the centering ring. Make sure the funnel is seated completely onto the filter and clamp the funnel into place.

2.4.11.3 Dispense isopropanol in each funnel as a solvent rinse. This also serves as a leak-check on the filtration setup. Drain by applying vacuum. If the alcohol does not pass through the silver membrane filter, determine the cause of the obstruction (Leave slight vacuum with filter in funnel).

2.4.12 Remove sample beaker from ultrasonic bath and check that the dust particles are dispersed.

2.4.13 Pour the sample suspension into the funnel, and rinse the inverted beaker with a stream of isopropanol from the squeeze bottle so that the rinse drains directly into the funnel. Apply maximum suction, and rinse the beaker twice more with ~10-mL aliquots of isopropanol. When most of the isopropanol has drained, apply a final rinse to the funnel walls directly from the squeeze bottle.

2.4.14 Maintain the suction after the isopropanol has drained to partially dry the sample.

2.4.15 Six samples can be processed consecutively on the filtering manifold

2.4.16 Turn off the vacuum, remove the filter funnel, and carefully remove the filter from the fritted base with forceps by holding on the edge. Place filter on slide warmer to completely dry, and then label it using a pen.

2.4.17 Process the remaining filters according to 2.4.12 through 2.4.16.

2.4.18 Place dried labeled filters into corresponding petri dish. Examine filters for evidence of leakage occurring during filtration, i.e. deposit area beyond 13 mm. Note on the work list and RLA form that leakage occurred. If significant leakage occurs, the filter will not be submitted for analysis. In such cases the sample result will be reported as Analysis Not Performed" (ANP) –lab error".

2.4.19 Rinse all funnels with isopropanol before setting up the filtration apparatus for the next set of samples.

ACID WASH PROCEDURE FOR REMOVAL OF INTERFERENCES:

2.4.20 Place silver membrane filter deposit side down into a 50 mL Pyrex beaker. Each set of acid washed samples will include a blank and three QC samples that have been previously analyzed by x-ray diffraction and up to 20 enforcement samples. Add ~10mL of deionized water using a squeeze bottle, and then add 1.5 mL concentrated nitric acid using a pipette. Place on a hotplate to approximately 60°C for ~15 minutes, swirling occasionally until all of the silver membrane has dissolved. Cool to room temperature.

2.4.21 Recover the insoluble residue using 0.5u 25mm PVC filters and all glass filtration apparatus described in 1.8.30. PVC filters are wetted with approximately15 mLs deionized water to overcome their hydrophobic properties; they must then not be permitted to go dry until all aqueous solutions have been filtered. Once the filters have been wetted, pour the nitric acid sample solution into the funnel. When only a few mLs of solution remains in the funnel, rinse the beaker with ~15 mLs deionized water, directing the rinse into the funnel. Repeat this process two more times, then add ~10 mLs dilute ammonium hydroxide directly to the funnel using a squeeze bottle. When only a few mLs of ammonium hydroxide solution remain in the funnel rinse the funnel once more with ~15 mLs deionized water. When the water rinse has passed through the funnel, rinse the beaker with ~15 mLs isopropyl alcohol, directing the rinse into the funnel. Rinse the funnel three more times with ~15 mLs of deionized water, followed by a final rinse with ~15 mLs of isopropyl alcohol. Maintain the vacuum after the alcohol has drained to partially dry the filter.

2.4.22 Remove the filter from the funnel using forceps and place it deposit side down, in the original beaker. Place the beaker on a slide warmer or hot plate set at ~60°C to dry the filter. Ash the samples in a low temperature asher at ~400W forward power and ~135 mL/min oxygen flow, extending the ash time to 180 minutes. For certain nitric acid soluble matrices, such as barites, tronas, halites, gypsums, and dolomites, further acid washing is often unnecessary, and the samples can be deposited onto silver membrane filters as in 2.4.9 through 2.4.14.

2.4.23 If phosphoric acid treatment is needed carefully add ~10 mL of 1:1 phosphoric acid to each beaker immediately after ashing, using a squeeze bottle. Preheat the hotplate to ~300°C for one hour. Process acid wash samples six at a time to minimize variations in temperature and length of heating. Place six beakers containing 1:1 phosphoric acid solution on the hotplate. Cover the beakers with 55 mm diameter watch glasses and heat for ~10 minutes, swirling frequently. Remove the watch glasses and heat an additional 10 minutes, again with frequent swirling. Remove beakers from the hot plate and allow the acid to cool for ~5 minutes, then add ~15mLs hot (85°C) water, followed by 2 mLs fluoroboric acid. Swirl the solution, then let stand approximately one hour. Repeat this

process in batches of six samples or less until the entire set has been acid washed.

2.4.24 Filter the samples as in 2.4.21, omitting the ammonium hydroxide rinse. Dry the filters and ash as in 2.4.22, then proceed to deposit the acid wash residue onto the silver filters for analysis as described in 2.4.9 through 2.4.14.

2.5 DISPOSAL

All reagents used in this procedure will be considered as "Hazardous Waste" and will be disposed of as-organic (isopropanol) or inorganic (acids) waste. All silver membrane filters are considered "Hazardous Waste" and must also be properly disposed.

2.6 REFERENCES

2.6.1 OSHA Method ID-142, "Quartz and Cristobalite in Workplace Atmospheres", Revised December 1996.

2.6.2 NIOSH Method 7500, "Silica, crystalline, by XRD", Revised 15 January 1998.

3.0 INSTRUMENT WORK INSTRUCTIONS

3.1 PROCEDURE

3.1.1 **Instrument Check and Quality Control**

3.1.1.1 The power to the XRD is continually on and, therefore, requires no warm up period. If instrument has been off, follow the start up procedure located on K:\Quality Assurance\X-ray start-up.doc. The XRD operates at 50 kilovolts and 35 milliamperes. The reference sample is run by the "monitor program" four times at the beginning of each day of each instrument use. The four values are recorded and the average is used for calculation of final result. This compensates for long-term drift in X-ray tube intensity.

3.1.1.2 Complete function verification and preventative maintenance (FV/PM) chart for other checks. (See Appendix C).

3.1.1.3 Place the QCS filters and lab blank for the batch to be analyzed in sample holders and place in the sample changer. Place changer in the instrument and measure at the primary silica/silver peak.

3.1.1.4 Analyze the Reporting Limit Standard (Low CCV) at the beginning of the run. If samples require multiple angle analysis, the Reporting Limit Standard will be analyzed at each angle used for sample analysis.

3.1.1.5 The CCV (a fixed filter standard) is analyzed to verify the calibration curve at the end of the run. The primary angle should be checked with each analytical batch. If multiple angles are to be used for sample analysis, the CCV will be analyzed at each angle used for the samples. The calculated CCV value should be ±10% of the true value. If it does not meet acceptance criteria, check the standard for wear and replace if necessary. If not the case the instrument may need recalibrated.

3.1.2 **Measurement**

3.1.2.1 Turn on the computer monitor. Computer hard drive and printer is left on.

3.1.2.2 Load the batch of sample filters (20) into the sample holders and place in the sample changer. Load into instrument and then open the gate.

3.1.2.3 Measure the diffraction peak area for each silica polymorph using the following analytical parameters. Peak locations are listed in degrees two-theta, and can vary slightly. The results of the primary angle analysis will determine if multiple angle analysis is warranted.

Quartz	Scanning Range	Peak Location	Peak Range	Counting Time
Primary	25.96-27.36	~26.66	±0.05	10
Secondary	20.16-21.48	~20.85	±0.05	60
Tertiary	49.48-50.80	~50.16	±0.05	60
Quaternary	59.38-60.70	~59.95	±0.05	60
Cristobalite				
Primary	21.18-22.50	~21.93	±0.10	10
Secondary	35.50-36.82	~36.11	±0.10	60
Tertiary	30.74-32.06	~31.46	±0.10	60

Tridymite				
Primary	21.18-22.50	21.62	±0.05	10
Secondary	TBD	20.50	±0.05	60
Tertiary	TBD	23.28	±0.05	60

NOTE: Step size is 0.04 degrees two theta.

If tridymite is requested, perform a qualitative XRD scan on the primary line. If a peak is present within 0.10 degree two theta, perform qualitative scans at the secondary and tertiary peak locations. If peaks are present within 0.10 degrees two theta of all three tridymite angles, report tridymite as "Present".

3.1.2.4 For each sample, measure the diffraction peak area for silver at the secondary line of 44.28, counting time 1 second per step.

3.1.2.5 To perform the measurements:

3.1.2.5.1 Select the appropriate batch program.

3.1.2.5.2 Enter sample identification data for the run. Sample data files are named based on the last six digits of the LIMS sample number, plus a suffix designating the diffraction peak. The suffix's are as follows:

Analysis	Code
Quartz, primary	A
Quartz, secondary	B
Quartz, tertiary	C
Quartz, quaternary	D
Cristobalite, primary	F
Cristobalite, secondary	G
Cristobalite, tertiary	H
Silver	S

NOTE: Each sample has two entries, one for the silica polymorph and one for silver.

3.1.2.5.3 Run the batch program.

3.1.2.5.4 When the measurements are completed, evaluate and integrate the peak of the analyte of interest for each sample.

3.1.2.5.4.1 From the main menu select (P)attern treatment, then (F)it profile.

3.1.2.5.4.2 Type in the data file name or select the data file through 'show names'. Press enter. The scan is displayed.

3.1.2.5.4.3 Select F1 (continue), then select F8 (graphics), a cross hair cursor appears on the graph. Using the mouse, place the cursor on the peak. Visually inspect the scan to see whether the peak center shifted from that of the analytical line, whether there are multiple peaks or shoulders occur in the integration range, and whether there is any unusual broadening that would indicate possible interference. If present, use the mouse to place

the cursor on the possible interference and perform the integration.

3.1.2.5.4.4 Press F1 (fit) to perform the fit profile. Note the Chi square value. If the Chi square is greater than one and there is evidence of the presence of other peaks, press F1 one to two more times to obtain a better fit. Stop when the Chi square is one or less or when it does not change significantly in the first digit.

3.1.2.5.5 Press F9 (List and Save). Press F9 again to print.

3.1.2.5.6 Escape and press F1. Escape until Main Menu. Select Graphics. Press F1. Press F9 for hard copy. Press enter to print the hard copy of the analyte.

3.1.2.5.7 Escape to get out of Graphics screen. Press escape again to return to main menu and change the data file name for next determination, repeat steps 3.1.2.5 to 3.1.2.5.6.

3.1.2.5.8 When all samples have been integrated and the scans printed, escape back to Main Menu.

3.1.3 **Evaluation**

3.1.3.1 Enter the data, area count for sample and silver, into the XRD spreadsheet located on K:XRD.Lab\Macros. There is a separate spreadsheet for each instrument. Check all cells for correct information for instrument used.

3.1.3.2 Examine the scans. Check the peak locations, proportionate shift of silver angle and analyte angle, etc. Compare the corrected sample peak locations to the corrected silica peak locations at calibration. If analyte peak location is not within ± 0.05°, the analyte of interest is either not present or is masked by a strong interference. The Branch Supervisor or Quality Manager is to be consulted about reporting the data from this sample. If there is a large shift in the silver peak (> 0.3°), repeat the analysis of the sample after resetting the filter in the sample holder

3.1.3.3 The analytical determination can end after scanning only the primary line when the Swift Weighted Average (SWA) is less than the TLV.

3.1.3.4 If the above criterion is not met, i.e. SWA is greater than the TLV, the secondary, and tertiary lines must be analyzed to confirm the presence of quartz. The quaternary line may also be used as an additional check.

3.1.3.5 When the secondary, tertiary and quaternary peak locations are within acceptable limits, and the results of the multiple angle scans are in good agreement, the lowest value obtained from scans at the first three angles is reported. The quartenary peak is only used for confirmation and is not used for enforcement purposes.

3.1.3.6 If major, unresolvable interferences are present at more than two angles or where they may result in an erroneously low value, the acid wash procedure should be performed on the sample filter and the sample should be reanalyzed. See Section 2.5.20-2.5.24 for instructions.

3.1.3.7 If cristobalite is >MDL, the secondary and tertiary lines should be analyzed to confirm the presence of cristobalite and to examine for quantitative evidence of interference.

3.1.3.8 In cases where samples are split into aliquots, the results from each split are summed prior to calculating the percentage of silica. Reporting limit requirements apply to each aliquot (a numerical value for silica cannot be used for an aliquot unless it exceeds the reporting limit).

3.1.3.9 When samples are taken consecutively on the same person, the result of each sample is cumulative, and if necessary, analyze Q2 through Q4 on all.

3.2 REFERENCES

3.2.1 OSHA Method ID-142, "Quartz and Cristobalite in Workplace Atmospheres", Revised December 1996.

3.2.2 NIOSH Method 7500, "Silica, crystalline, by XRD", Revised 15 January 1998.

3.2.3 PW Automatic Powder Diffractometer Operation Manual, 3rd Edition.

3.2.4 Users Guide PC-APD, November 1993.

4.0 APPROVAL AND REVIEW

4.1 APPROVAL

PREPARED BY:

Signature _____ Date _____

REVIEWED AND APPROVED BY:

Signature _____ Date _____

Signature _____ Date _____

Signature _____ Date _____

4.2 ANNUAL REVIEW

NAME _____ DATE_____CHANGES

NAME _____ DATE _____CHANGES

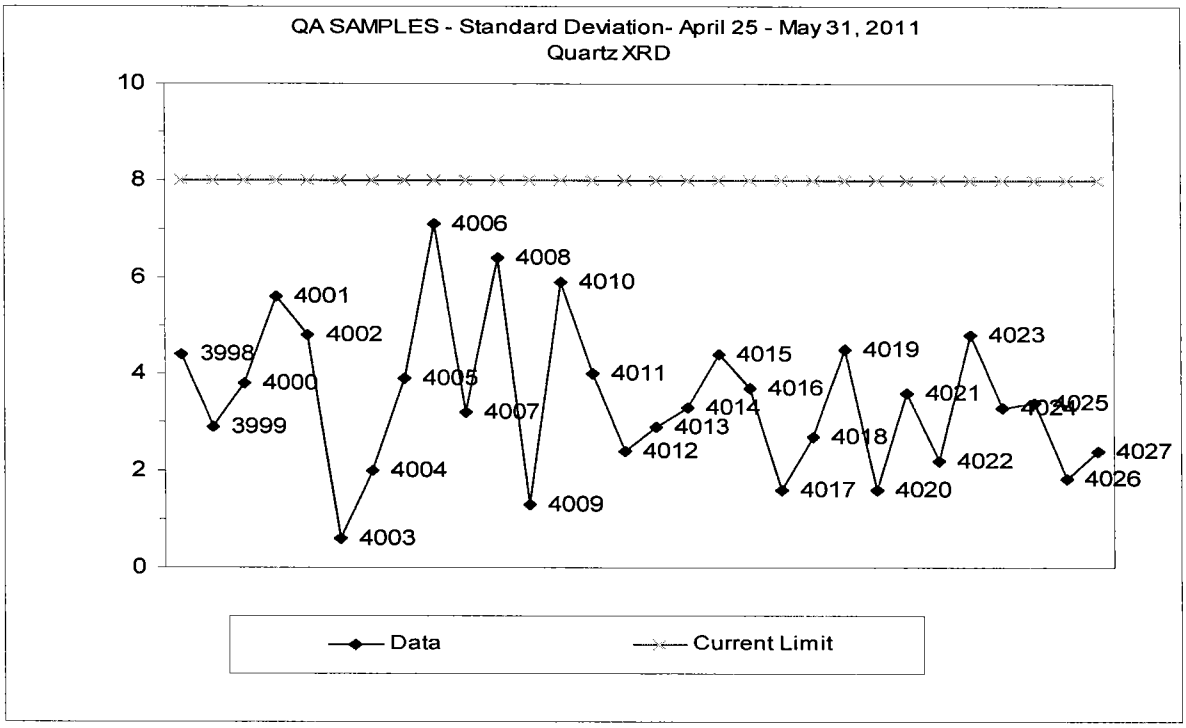
NAME _____ DATE_____CHANGES

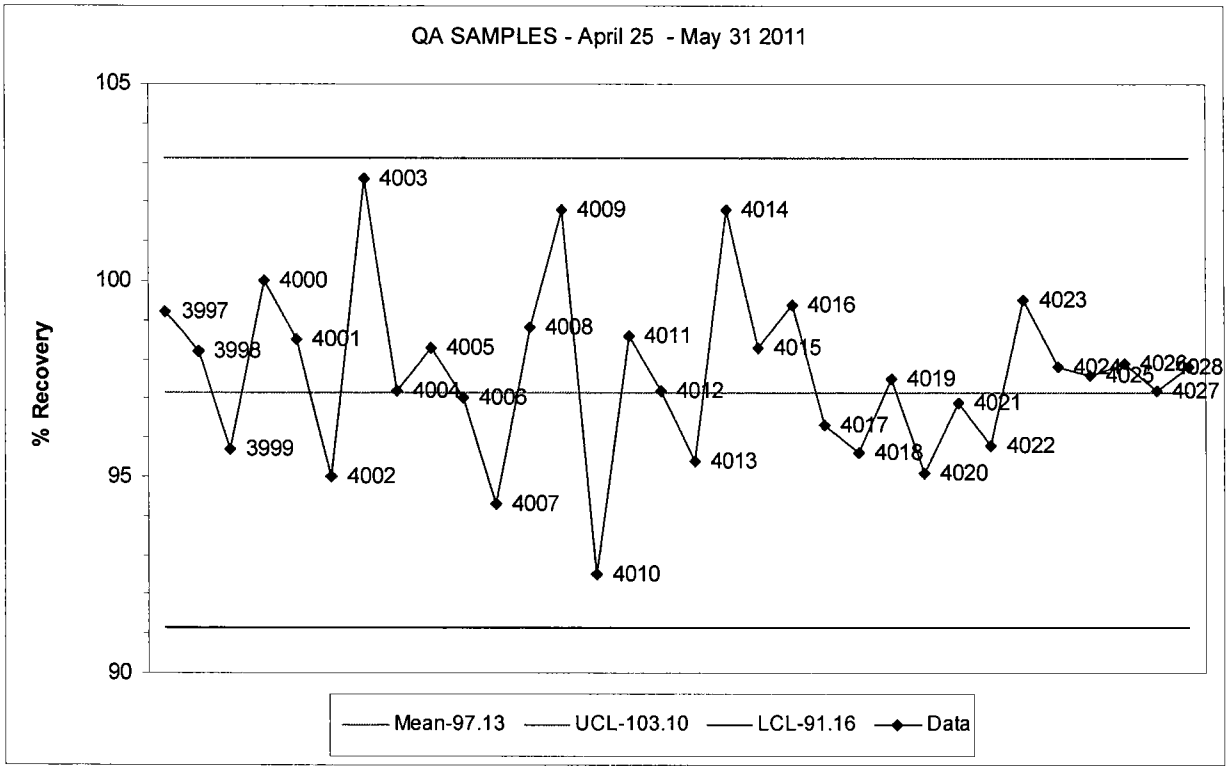
NAME _____ DATE_____CHANGES

NAME _____ DATE _____CHANGES

NAME _____ DATE_____CHANGES

Appendix B. Quality Control Charts. (Updated on K:\XRDLAB\QA)





Appendix C. FV/PM Chart. This chart is located on the K:Quality Assurance\FVPM\

MINE SAFETY AND HEALTH ADMINISTRATION
FUNCTION VERIFICATION/PREVENTIVE MAINTENANCE

INSTRUMENT XRD MSHA# SOP# BEGIN DATE END DATE

PROCEDURE	FREQ	Date											
1. LIGHTS ON & POWERS UP	AU												
2. SCAN REFERENCE SAMPLE 4X BEFORE RUN	AU												
3. RUN CHECK STANDARD (CCV)	AU												
4. CHECK OFFSET	AN												
TECH INITIALS													

CODE: AU = AS USED

AN= AS NEEDED

WK=WEEKLY

MO=MONTHLY

Appendix D. XRD Spreadsheet and Run Sequence (example)

2/12/02		Run# Matrix		XRD Filters		Analyte Peak(Q1A)		Quartz 26.66	
		Instrument		PW1800B		Q2 Q3 Q4		20.85 50.16 59.95	

QA Set			Area	WT. PREP.	WT. ANAL	QC Results %REC	
Number	3838	Q1	1364	80	77	97	ok
Silver	5144	Q2					
		Q3					
Number	3839	Q1	2048	123	116	95	ok
Silver	5161	Q2					
		Q3					
Number	3840	Q1	1525	84	89	105	ok
Silver	4985	Q2					
		Q3					

Quartz Calibration	Ag Corrected Peak Location		Monitor
Q1	26.642	18.5884	14835
Q2	20.852	21.1077	14762
Q3	50.131	13.0198	14815
Q4	59.951	9.4652	14818

	Digestion		Analysis
Method	IPA		XRD
Analyst			
Date performed	03/04/2002		

Monitor Reading		Ag Lot Avg	5130.10	
1	15633	Min. Air Vol.	816	L
2	15654	Blanks MDL	0.005	mg
3	15625	Blank Silver	5810	counts
4	15659	Monitor	14064	counts

Holder Position	Sample ID	ANGLE	Total Area	Silver Intensity	Sample weight (mg)	Result ug	% Quartz	TWA mg/m3	TLV mg/m3	Sample ID	Reported Mass (mg)	Determination of additional peaks
0	Blank	Q1	0	5140	0.000	0				Blank	<0.005	ok
0	Low CCV-20	Q1	325	5493	0.02	18				Low CCV	0.018	ok
0	Low CCV-20	Q2			0.02	17						
0	Low CCV-20	Q3			0.02	20						
0	Low CCv-20	Q4			0.02	18						
3	2001025934	Q1	10830	5335	1.190	603.3	50.70	1.458	0.190	2001025934	0.603	analyze additional peaks
3	2001025934	Q2	12119	5335	1.190	595.5	50.04	1.458	0.192	2001025934	0.596	analyze additional peaks
3	2001025934	Q3	7988	5335	1.190	562.7	47.29	1.458	0.203	2001025934	0.563	TWA >TLV
3	2001025934	Q4	6001	5335	1.190	608.1	51.10	1.458	0.188	2001025934	0.608	TWA >TLV
4	2001025946	Q1	913	5842	0.234	47.5	20.30	0.287	0.448	2001025946	0.048	ok
4	2001025946	Q2			0.234	#NUM!	#NUM!	0.287	#NUM!	2001025946	#NUM!	#NUM!
4	2001025946	Q3			0.234	#NUM!	#NUM!	0.287	#NUM!	2001025946	#NUM!	#NUM!
4	2001025946	Q4			0.234	#NUM!	#NUM!	0.287	#NUM!	2001025946	#NUM!	#NUM!
5	2001025951	Q1	196	5525	0.584	10.6	1.82	0.716	2.621	2001025951	0.011	ok
5	2001025951	Q2			0.584	#NUM!	#NUM!	0.716	#NUM!	2001025951	#NUM!	#NUM!
5	2001025951	Q3			0.584	#NUM!	#NUM!	0.716	#NUM!	2001025951	#NUM!	#NUM!
5	2001025951	Q4			0.584	#NUM!	#NUM!	0.716	#NUM!	2001025951	#NUM!	#NUM!
6	2001025953	Q1	210	5740	0.141	11	7.80	0.173	1.020	2001025953	0.011	ok
6	2001025953	Q2			0.141	#NUM!	#NUM!	0.173	#NUM!	2001025953	#NUM!	#NUM!
6	2001025953	Q3			0.141	#NUM!	#NUM!	0.173	#NUM!	2001025953	#NUM!	#NUM!
6	2001025953	Q4			0.141	#NUM!	#NUM!	0.173	#NUM!	2001025953	#NUM!	#NUM!
7	2001025971	Q1	263	6030	0.135	13.7	10.15	0.165	0.823	2001025971	0.014	ok
7	2001025971	Q2			0.135	#NUM!	#NUM!	0.165	#NUM!	2001025971	#NUM!	#NUM!
7	2001025971	Q3			0.135	#NUM!	#NUM!	0.165	#NUM!	2001025971	#NUM!	#NUM!
7	2001025971	Q4			0.135	#NUM!	#NUM!	0.165	#NUM!	2001025971	#NUM!	#NUM!
8	2001025975	Q1	37	5801	0.466	1.9	0.41	0.571	4.153	2001025975	<0.005	ok
8	2001025975	Q2			0.466	#NUM!	#NUM!	0.571	#NUM!	2001025975	#NUM!	#NUM!
8	2001025975	Q3			0.466	#NUM!	#NUM!	0.571	#NUM!	2001025975	#NUM!	#NUM!
8	2001025975	Q4			0.466	#NUM!	#NUM!	0.571	#NUM!	2001025975	#NUM!	#NUM!
9	2001025976	Q1	1027	5808	0.348	53.4	15.34	0.426	0.577	2001025976	0.053	ok
9	2001025976	Q2			0.348	#NUM!	#NUM!	0.426	#NUM!	2001025976	#NUM!	#NUM!
9	2001025976	Q3			0.348	#NUM!	#NUM!	0.426	#NUM!	2001025976	#NUM!	#NUM!
9	2001025976	Q4			0.348	#NUM!	#NUM!	0.426	#NUM!	2001025976	#NUM!	#NUM!
10	2001025977	Q1	635	5782	0.388	33.2	8.56	0.475	0.947	2001025977	0.033	ok
10	2001025977	Q2			0.388	#NUM!	#NUM!	0.475	#NUM!	2001025977	#NUM!	#NUM!
10	2001025977	Q3			0.388	#NUM!	#NUM!	0.475	#NUM!	2001025977	#NUM!	#NUM!
10	2001025977	Q4			0.388	#NUM!	#NUM!	0.475	#NUM!	2001025977	#NUM!	#NUM!
11	2001025983	Q1	216	6127	0.201	11.2	5.57	0.246	1.321	2001025983	0.011	ok
12	2001025984	Q1	162	5884	0.164	8.4	5.12	0.201	1.404	2001025984	0.008	ok
13	2001025985	Q1	1580	5107	1.161	91.1	7.85	1.423	1.016	2001025985	0.091	analyze additional peaks
13	2001025985	Q2	1654	5107	1.161	84.9	7.31	1.423	1.074	2001025985	0.085	analyze additional peaks
13	2001025985	Q3	1208	5107	1.161	86.7	7.47	1.423	1.056	2001025985	0.087	TWA >TLV
13	2001025985	Q4			1.161	#NUM!	#NUM!	1.423	#NUM!	2001025985	#NUM!	#NUM!
14	2001025986	Q1	346	5918	0.179	18	10.06	0.219	0.829	2001025986	0.018	ok
15	2001025987	Q1	631	5620	0.327	33.7	10.31	0.401	0.813	2001025987	0.034	ok
16	2001026140	Q1	628	5849	0.436	32.6	7.48	0.534	1.055	2001026140	0.033	ok
17	2001026141	Q1	402	5921	0.161	20.9	12.98	0.197	0.667	2001026141	0.021	ok
18	2001026142	Q1	1743	5516	0.690	94.5	13.70	0.846	0.637	2001026142	0.095	analyze additional peaks
18	2001026142	Q2	2027	5516	0.690	96.3	13.96	0.846	0.627	2001026142	0.096	analyze additional peaks
18	2001026142	Q3	1478	5516	0.690	102.6	14.87	0.846	0.593	2001026142	0.103	TWA >TLV
18	2001026142	Q4	1059	5516	0.690	106	15.36	0.846	0.576	2001026142	0.106	TWA >TLV
19	2001026147	Q1	553	5721	0.338	29.1	8.61	0.414	0.943	2001026143	0.029	ok
20	2001026143	Q1			0.000	#NUM!	0.00	0.000	5.000		#NUM!	ok
20	2001026143	Q2			0.000	#NUM!	0.00	0.000	5.000		#NUM!	ok
20	2001026143	Q3			0.000	#NUM!	0.00	0.000	5.000		#NUM!	ok
21	CCV-300ug	Q1	5395	5438	.300	295.1				300ug	0.295	ok
21	CCV-300ug	Q2			.300	297.8						
21	CCv-300ug	Q3			.300	302.4						
21	CCV-300ug	Q4			.300	300.6						

Analyst_____ Supervisor_____