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Review of Quartz Analytical Methodologies: Present and Future Needs

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A review of analytical methods for the qualitative and quantitative determination of crystalline silica is presented. The three prevalent forms of crystalline silica—quartz, cristobalite, and tridymite—are alluded to. Performance and popularity of present quartz analytical methods such as X-ray diffraction (XRD), infrared (IR) spectroscopy, and colorimetry are illustrated using Proficiency Analytical Testing (PAT) Program data. Although substantial improvements in performance have been made since the 1970s, quartz PAT sample results still continue to display high imprecision (>20% coefficient of variation). Past and present analytical methods are detailed in terms of theory and use, and strengths and weaknesses are discussed. Methods include gravimetric, chemical, microscopic, atomic absorption, XRD, IR, and colorimetry. Methods for determining bulk materials such as thermal analysis and nuclear magnetic resonance are briefly discussed. Results of a survey regarding international use of analytical methods for quartz are displayed. Both in the United States and internationally, the most popular methods are XRD and IR. Performance criteria such as detection limits, precision and accuracy, and potential future trends are shown using international data. Future needs for enhancing quartz analysis, such as a comprehensive evaluation of direct-on-filter techniques, an attempt at consensus for tridymite analysis, a consensus for defining analytical performance parameters for quartz in general, and a continued examination of methods for analyzing bulk materials for quartz, are suggested. MADSEN, F.A.; ROSE, M.C.; CEE, R.: REVIEW OF QUARTZ ANALYTICAL METHODOLOGIES: PRESENT AND FUTURE NEEDS. APPL. OCCUP. ENVIRON. HYG. 10(12):991–1002; 1995.

A variety of analytical methods have been used to assess occupational exposures to airborne concentrations of quartz in the workplace and to characterize quartz content in bulk materials. In the United States, the Occupational Safety and Health Administration (OSHA), the Mine Safety and Health Administration (MSHA), and the National Institute for Occupational Safety and Health (NIOSH) have been actively involved in using, evaluating, and advancing analytical methodology for determinations of quartz. Other countries have also progressed in their attempts to assess and categorize a substance that is very prevalent in mining and general industry. The progress of quartz analysis in the United States is reviewed, methods used internationally are presented, and future enhancements are suggested.

History: United States

Approximately 8.2 million American workers (including agricultural workers) are potentially exposed to crystalline silica (primarily quartz) dust each year.[1] Because of the importance of monitoring to the protection of such a large number of workers, numerous analytical methods have been developed for the analysis of crystalline silica by the three governmental entities.[2–11] The high incidence of mine-related illnesses and hazards has historically been the driving force for establishing medical, health, and safety programs in government and industry. To address hazards related to toxic substances and their identification in the western region of the United States, the Occupational Health Field Station (Ft. Douglas, Utah) of the U.S. Public Health Service in the 1940s provided industrial hygiene analytical support. This support function eventually became a part of NIOSH. With the passage of the OSHA Act in 1970, the facility and most of the staff were eventually transferred to OSHA. MSHA, OSHA, and NIOSH continued to aid in the development of exposure assessment techniques for quartz and other toxic substances. Development of assessment techniques followed two tracks:

1. To accomplish its roles of finding health hazards in the workplace and supporting OSHA and MSHA's ability to regulate the work environment, NIOSH searched for sampling and analytical methodology and demonstrated technical feasibility for use in workplace monitoring.
2. To support the enforcement of federal OSHA regulations, the OSHA Salt Lake Analytical Laboratory analyzed samples and provided technical assistance to federal compliance officers. Methods development for quartz and other substances at the laboratory addressed primarily OSHA's analytical needs for enforcing compliance with state-of-the-art equipment. MSHA also provided similar support through their own analytical and regulatory network.

While OSHA and MSHA concentrate on their own needs (i.e., the best scientifically supportable evidence for possible use in the federal courts), NIOSH research is broader in scope and caters to both public and private analytical laboratory settings. NIOSH methods may cover substances not regulated by OSHA and also may contribute to the needs of MSHA. In terms of employee protection, the regulatory jurisdiction of MSHA is mining operations. OSHA covers general industry and construction. For both MSHA and OSHA, compliance air samples are generally obtained from employees with the highest potential exposure, and compliance air samples for quartz are among those samples most often exceeding the OSHA permissible exposure limit (PEL).

What Is Quartz?

In discussing the analysis of crystalline silica, the focus will be on quartz because it is the most abundant surface mineral, amounting to almost 20 percent in the earth's crust. Quartz, specifically the form stable below 573°C, is called alpha quartz. The toxicological response to alpha quartz in occupational settings is particle size dependent, with the health risk most often associated with the respirable size range.

The common names silica, flint, and sand are often applied to quartz. The use of common names should be avoided because they can confuse the issue. For example, the term silica is not synonymous with quartz but corresponds to the chemical silicon dioxide, which includes quartz, cristobalite, tridymite, exotic high pressure forms (e.g., stishovite, coesite), amorphous silica, silica fume, and fumed silica.

Regulated Toxic Forms of Crystalline Silica: Quartz, Cristobalite, and Tridymite

Because alpha quartz is the most abundant toxic form of silica, it is the form most often addressed in industrial hygiene (IH) analytical laboratories around the world. Cristobalite is a high temperature form of silica. It is not thermodynamically stable at room temperature, but can be frozen out as a metastable form by rapid cooling to room temperature. Volcanic explosions can release cristobalite dust into the atmosphere. At ambient temperatures near the earth's surface, quartz is more stable than cristobalite. Accordingly, cristobalite is rare in the environment, but can be produced industrially by treating silica-containing materials with high temperatures (>1470°C). About 4 percent of the nearly 2000 bulks analyzed for silica during the National Occupational Health Survey of Mining by NIOSH have contained greater than 1 percent cristobalite.[12] Primary and secondary standard reference materials (also called certified reference materials) exist for both quartz and cristobalite. Tridymite is another high temperature (>870°C) form of a material that is primarily silica. Tridymite is also metastable at room temperature. Tridymite formation, however, requires the presence of a mineralizer or flux such as sodium oxide. In nature it is found less frequently than cristobalite. It is unclear whether tridymite is a low sodium (low alkali) silicate or an impure silica. The potential for a variable composition makes it difficult to obtain a consensus on the creation of a tridymite standard reference material and consequently the evaluation of its toxicity and laboratory analysis. It is potentially found in industry, but very few data exist on tridymite because of the analytical problems it presents. Occupational exposure to the three substances is regulated by OSHA, with tridymite and cristobalite having lower PELs than alpha quartz.

Quartz Analysis

Relationship to Structure

When a compound can have different crystal structures, they are jointly referred to as crystalline polymorphs of that compound. Quartz, cristobalite, and tridymite are crystalline polymorphs of silica, differing in their respective fixed large-scale periodic patterns. Amorphous silica has a more random large-scale arrangement. At the atomic level, these polymorphs, silica-containing glasses, many silicate minerals, and other common materials have the silicon atom located in the center of a tetrahedron of oxygen atoms. That similarity of chemistry and structure is the major cause of the analytical problems facing the laboratory analyst. The route of analysis often requires exploiting the unique differences in the physics and chemistry of these materials. Analytical laboratories have different resources of equipment, personnel, and time available. Techniques and methods used to analyze IH air samples include gravimetric analysis, chemical analysis, colorimetry, atomic absorption (AA) spectroscopy, microscopy, infrared (IR) spectroscopy, and powder X-ray diffraction (XRD).

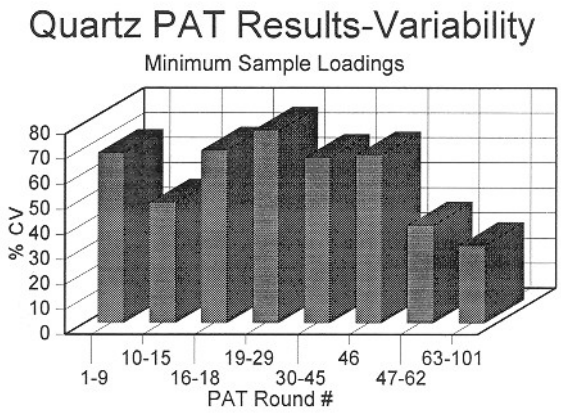

FIGURE 1. PAT results for quartz: variability.

Laboratory Performance

The Proficiency Analytical Testing (PAT) Program was initiated to evaluate and improve performance in IH analytical labs. Quartz is one of the substances used in the PAT Program, and resultant performance of many analytical labs gives an indication of the magnitude of analytical problems associated with quartz. Quartz samples are generated and distributed quarterly to participating labs. Results are compiled for each round and consensus between labs is explored. Rounds 1 through 30 were conducted prior to 1974 (with fewer than 40 labs participating in analyzing quartz) when colorimetry was the dominant method used. Participation in quartz analysis grew from about 40 labs at round 30 to about 125 labs at round 80 before decreasing to the current 93 in round 117. The true values and the control limits for the PAT Program are derived from a smaller set of about 60 reference labs. Figures 1 (derived from Reference 13) and 2 (derived from Reference 14) show overall imprecision data for reference labs participating in the PAT Program analyses for quartz. Overall imprecision includes contributions from both the within-lab imprecision and the variability in overall recovery between labs. Recoveries are dependent on problems associated with instrument calibration and sample losses in handling. Central to instrument calibrations is how well the respirable fraction corresponds to the standard reference material used. Laboratories in the PAT Program have access to the same standard reference material. Figure 1 shows that over time precision has improved. Because the true result is by consensus, accuracy has also improved. Some of the apparent improvement is due to drift in analytical methodology and changes in standard reference materials, matrix, PAT sample preparation, evaluation approach, and laboratory participation.

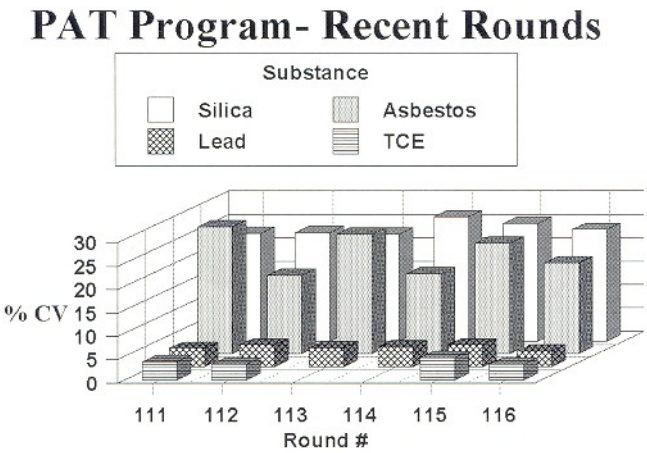

FIGURE 2. PAT results: recent rounds.

Figure 2 compares the percent coefficients of variation (CVs) of recent PAT reference lab results for quartz, asbestos, metals, and the organic solvent trichloroethylene (not included in rounds 113 and 114). Even for the reference labs, the overall imprecision associated with quartz analysis and asbestos is very high compared with other analytes (averaging about 24% for all quartz sample loadings compared with 3 to 6% coefficients of variation for metals and organic compounds). The acceptable range for quartz in PAT results for round 114 even included a negative mass for quartz for the samples with the lowest quartz loading,[15] a physical impossibility resulting from the large spread. The control limits are defined as the mean ± 3 times the standard deviation; therefore, negative control limits will always occur when the relative standard deviation exceeds 33⅓ percent. Large relative standard deviations are more common for quartz analyses at the lower sample loadings. The early data for quartz tended to indicate an asymmetric distribution typical of lognormal distributions, but recently have appeared more symmetric. Starting in round 108 (not shown) the statistical evaluation of quartz results has changed from assuming lognormal to normal distributions. This calculational change has made the lower control limit less stringent.[14] The change to a normal distribution is encouraging; it indicates that the accumulation of sampling and analytical errors is now primarily additive rather than multiplicative. This may be due to the elimination of various sources of systematic error which tend to be multiplicative; however, the large imprecision compared with other analytes in the PAT Program demonstrates there is still room for improvement.

Sources of High Imprecision and Poor Performance

Both sampling and analytical error may contribute to poor performance. The PAT results are not immune to sampling error, and improvements in performance may require changes in sampling. Evidence of problems associated with sampling-related poor performance includes the following:

1. PAT samples for quartz are made from air suspensions deposited on polyvinylchloride filters. Minor variability and error associated with generation and handling are possible. Additional large variations can occur. The PAT Program typically uses light-colored materials that are virtually invisible on the filters. When dark material was included in the NIOSH collaborative tests, occasional leakages to back-up pads were noted.[16] Dust shaken loose from the filters during transit is generally not analyzed. A significant fraction of the dust may occasionally remain in the styrene case used for transport and storage.
2. Analytical problems are generally associated with the high degree of attention still necessary throughout the quartz analysis. Great care is necessary for the preparation of samples and standards from suspensions. Matching of standard and sample particle size is of critical importance. Some interpretation of results is still required, and the application of self-absorption corrections, background corrections, interference stripping, and peak integration is not uniform among participating labs.

Precision and Accuracy: Improvements

The PAT Program does not currently directly test within-lab analytical imprecision. Limited data from sets including samples with similar masses of quartz indicate that average within-lab analytical imprecision amounts to over half of the overall imprecision.[13] If matched samples were routinely provided to participating labs, average within-lab imprecision could be more readily assessed.

The average within-lab precision determined for matched samples in the PAT Program can differ significantly from the within-lab precision for individual labs. When labs receive results back from the PAT program, they should assess their performance and make necessary corrections in methodology. Participating labs may apply the criteria used by Shulman *et al.*[13] for an independent measure of in-house precision when similar loadings are included within or between PAT rounds. Alternately, labs may purchase duplicate sets from the PAT Program for measuring within-lab precision. For quartz analysis, it is strongly recommended that labs monitor analyte recoveries and within-lab imprecision using an in-house quality assurance program.

Lab quality control samples (QCs) for most soluble analytes are prepared from spikes of well-behaved homogeneous solutions of known composition. Preparation of quality control filter samples for quartz in the mass range of 20 to 200 μg is difficult. Laboratory-generated quartz aerosols are not suitable for accurately spiking filters at these low levels, and weighing such low mass spikes introduces unacceptable error in QC preparation. As a result, quartz QCs are normally prepared from liquid suspensions of quartz. Even so, great care is necessary to reduce inhomogeneity in the suspension[16] in order to prepare accurate QCs. With practice, in-house quality control data may show better performance than that indicated by the PAT Program.

Quartz Methods: Historical

Because analytical methods evolve over time to make use of new techniques and technology, the early methods used at government and private laboratories seem primitive by today's standards. Each method has its area of applicability as well as strengths and weaknesses. In the case of crystalline silica, the early methodologies are still used elsewhere to some extent. Others have taken on new roles in the analysis of crystalline silica; for example, the Talvitie cleanup[3,8–11,17] is still com-

mon for removing difficult interferences from bulk and air samples in preparation for colorimetric and X-ray techniques.[18–20] Techniques used to assist in analyzing quartz in the past were somewhat nonspecific. These included gravimetric, chemical, and microscopic techniques. The microscopic or petrographic techniques are less common today. Microscopic analysis for quartz is a powerful technique,[21] but requires well-trained individuals.

Gravimetric Evaluation

The process of weighing dust does not confirm the presence of quartz; all particulate collected (often other minerals) has weight and can be a positive interference. For this reason, gravimetric measurements are useful primarily to monitor unidentified respirable dust exposures (OSHA PEL = 5 mg/m^3) and to screen samples so that the more time-intensive and therefore more expensive analyses are only performed when significant potential exposures are indicated. Weight measurements may also be included as a first step for any of the following methods.

Chemical Methods

Chemical methods are rarely stand-alone methods, but are part of another method. Chemical treatments are used to remove nonsilica contaminants prior to microscopy, colorimetry, etc. Several examples follow.

In a small number of matrices, a simple acid wash can be used to remove easily soluble minerals[22] such as calcium carbonate. A drawback to this cleanup occurs when ionic fluorides are a part of the matrix: the HF formed can also remove the crystalline silicas.

Some materials that are not acid soluble, such as graphite, volatiles, and organic material, can be removed by heating;[5,7] however, simple matrices are not commonly encountered. More vigorous chemical treatments have been developed to make use of slight differences in the chemical reactivity of minerals to remove noncrystalline silica and some minerals.

The Talvitie treatment is a common example of a differential chemical method used to minimize interferences including some silicate minerals. A sequence of reactions including a hot phosphoric acid wash is used to preferentially dissolve everything except the quartz. The technique has to be "tuned" to the specific apparatus used in the analysis. A simple gravimetric weighing of the residue would ideally give the mass of quartz in the sample; however, many substances are as resistant as quartz to the Talvitie treatment. The procedure may be stopped at this point when the Talvitie treatment is used to clean up samples, or additional steps can be used leading up to a colorimetric determination.[3,10,17] The removal of interferences is generally not complete and the analysis can show poor precision due to low recoveries resulting from loss of the smaller particles of quartz and high recoveries resulting from silicate residues.[19]

Another common example is the potassium pyrosulfate fusion.[19] The sample is treated with a molten salt which dissolves a great many metal oxides and leaves the quartz intact. The melt is cooled and the solubilized metals are dissolved in water, leaving the quartz dust which can be analyzed by the methods that follow. Great Britain's Health and Safety Executive uses this approach for some bulk samples.[22]

Microscopy Methods

DUST COUNTING. Dust samples were collected in 95 percent ethanol or isopropanol using an impinger and counted using a microscope.[2] Impingers were cumbersome and limited employee movements, and the use of volatile flammable alcohols presented a fire hazard.

PETROGRAPHIC ANALYSIS. The petrographic microscopy technique is subjective, but it is also extremely sensitive when conducted by a well-trained individual, and in certain cases this method can have excellent results in the analysis of bulk samples.[21] By viewing a well-prepared sample (e.g., after Talvitie treatment) through the microscope one can discern the quartz as blue–yellow particles when viewed between crossed polarizers. The color depends on the orientation of the crystalline fragments in relation to the illuminating polarized light. The optical technique normally requires extensive sample preparation and cleanup. Analysis is done microscopically by the tedious process of counting particles. The method suffers from a difficulty (often inability) in distinguishing silica forms for the small particles involved in air samples; microscopy is useful down to about 0.5 μm. The image of the sample is two-dimensional; the third dimension must be estimated. It is one method in use for the analysis of bulk samples by British Columbia.[23]

Petrographic microscopy has limited applicability and requires particles that are large enough to discern the colors described above and must also consist primarily of single crystallite fragments. Cryptocrystalline and microcrystalline quartz (e.g., tripoli) are materials where the particles consist of tightly bound aggregates of many quartz crystallites in random orientations and cannot be determined by this method.

Atomic Absorption

Analytical methods[9] which used the principle of AA as the end detector for quartz were almost identical to the colorimetric method. Samples were prepared using a hydrofluoric acid/phosphoric acid treatment, and instead of forming a colored complex, samples were then analyzed by AA for total silicon. The amount of quartz potentially present was calculated using a gravimetric factor. The method suffered from interferences and lack of specificity, and was very imprecise at levels below 50 μg quartz.

Quartz Methods: Current

Today in the United States the more accepted methods are colorimetric, XRD, and IR techniques. The MSHA and NIOSH IR methods for quartz in coal dust are very similar;[5,7] subtle differences are noted in the sample preparation. IR and XRD methods are well documented[5,11] and have been thoroughly tested.[16] To examine how popular the three methods are, and how well they perform, PAT Program data were compiled and presented in graphic form.

Figure 3 (derived from Reference 13) shows that the three analytical techniques (colorimetric, XRD, and IR) dominate. Other methods, such as AA,[9] have been used sparingly (shown as "Other" in the figure). The colorimetric procedure predominated for analysis of quartz until about 1974 or round 30 of the PAT Program. Approximately 30 labs consistently used the colorimetric procedure until recently dropping to 15.

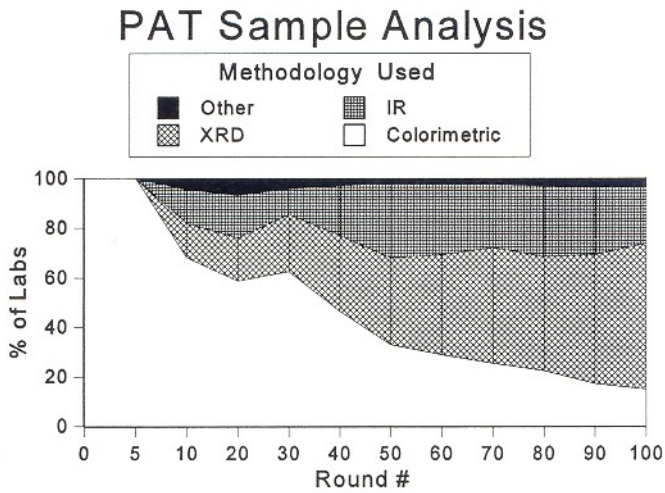

FIGURE 3. PAT Program participation by methodology.

In the United States, XRD is the most popular procedure, with IR coming in second.

Comparing the precision trends indicated in Figure 1 with the methodology trends in Figure 3 demonstrates how well the three techniques compare in terms of overall precision. Figure 1 shows historical data of variability in quartz analysis for minimum sample loading (a worst case scenario). Pooled coefficients of variation showed large imprecision in the beginning when the colorimetric procedure was used extensively. The colorimetric method was used primarily until round 30. As XRD and IR became more popular, the overall precision has gradually improved. This corresponds to technical and procedural improvements in all three analytical techniques and not necessarily the decreased use of the colorimetric procedure over time. For these three methods, appropriate standard reference materials are used for calibrations whenever possible, or secondary standards are substituted which are traceable to standard reference materials.

Powder XRD

The most popular and precise method for quartz analysis is XRD. Because exposure limits (PELs, threshold limit values, recommended exposure limits, etc.) are for specific crystalline forms of silica, a method using the unique three-dimensional crystalline (lattice) structure of each polymorph would have the greatest advantage.

XRD relies on the large-scale crystalline structure of quartz. Because crystalline substances such as quartz have different layering depending upon different perspectives of the crystal, XRD provides several additional analytical peaks. The most sensitive quartz peak is sufficient to distinguish it from cristobalite, tridymite, amorphous silica, and the vast majority of silicate minerals. Three additional quartz diffraction peaks are usually available for analysis and provide quantitative confirmation. These alternate analytical lines are usually sufficient to resolve most interferences, but chemical treatments can be used when needed. In this method, the intensity of diffracted X rays is compared with the intensities observed for known amounts of respirable quartz reference material of comparable particle size distribution.

To illustrate the potential level of involvement for analysis of one sample, Figure 4 is the X-ray data for a sample prepared from settled dust on a hotel patio in Yakima, Washington. The settled dust (particles 90% of which were greater than 150 μm) consisted primarily of material resulting from the eruption of Mt. St. Helens, and subsequent analysis assisted in evaluating the hazard to cleanup and lumber salvage crews. This sample required considerable physical and chemical preparation. The sample was ground and sieved to <45 μm and an aliquot was weighed out and then treated with a customized Talvitie wash procedure optimized to clean up this specific matrix with a minimum loss of cristobalite. It was then deposited on a silver membrane and analyzed for cristobalite and for three different diffraction angles (lines) for quartz. Peak intensities, best determined by peak area, are shown having computer software-selected integration limits, and represent an early stage of data evaluation. The tertiary quartz line (peak on far right of Figure 4) shows how interferences can be compensated for by stripping out an interfering peak. The primary and secondary quartz analytical peaks still have minor interferences that could not be chemically removed. At this stage of the analysis, the sample appears to contain approximately 3 percent quartz and 6 percent cristobalite.

XRD units can have a long, useful life span over which the initial cost can be depreciated. Units in use 20 years after manufacture are common. Compared with other methods in common use, XRD requires the most expensive equipment, approximately $175,000 per unit, which may be offset by offering wide utility for quartz and other crystalline substances. It is also useful for general qualitative analysis of substances found in the workplace. This can be particularly effective in determining the composition of unknown substances encountered in IH inspections, including dry chemical spills discovered on loading docks, materials at construction sites where employees are reporting symptoms indicating exposure to toxic material, and residues remaining after an industrial explosion or fatality. The knowledge gained by use of XRD can assist the IH to assign causes and prevent recurrences.

Sample preparation is normally time intensive to achieve an even thin-layer deposit of the sample for optimum presentation to the X-ray beam. Tetrahydrofuran (THF) is used to dissolve and remove the organic matrix of the filter used to collect the sample and any organic materials collected during sampling. A vacuum filtration system enclosed in an exhaust hood is used to filter out the dust in the THF onto silver membrane filters which are dried on a warm, nonsparking hot plate. (Alternately, a muffle furnace or low temperature asher can also be used in place of the THF treatment.) Calibration standards are prepared in a similar manner using isopropanol suspensions. Partial shielding from the X-ray beam occurs in the case of small quartz particles that fill surface pores in the silver membrane. The net effect of this shadowing is a reduction of analytical sensitivity at low quartz loadings. Nonlinear calibration curves may be necessary to achieve good quantitation at low loadings.

New refinements to XRD sample presentation include a rocking geometry proposed to improve upon the precision and accuracy limitations imposed by the particle statistics.[24] A new approach, direct-on-filter (DOF), which reduces the

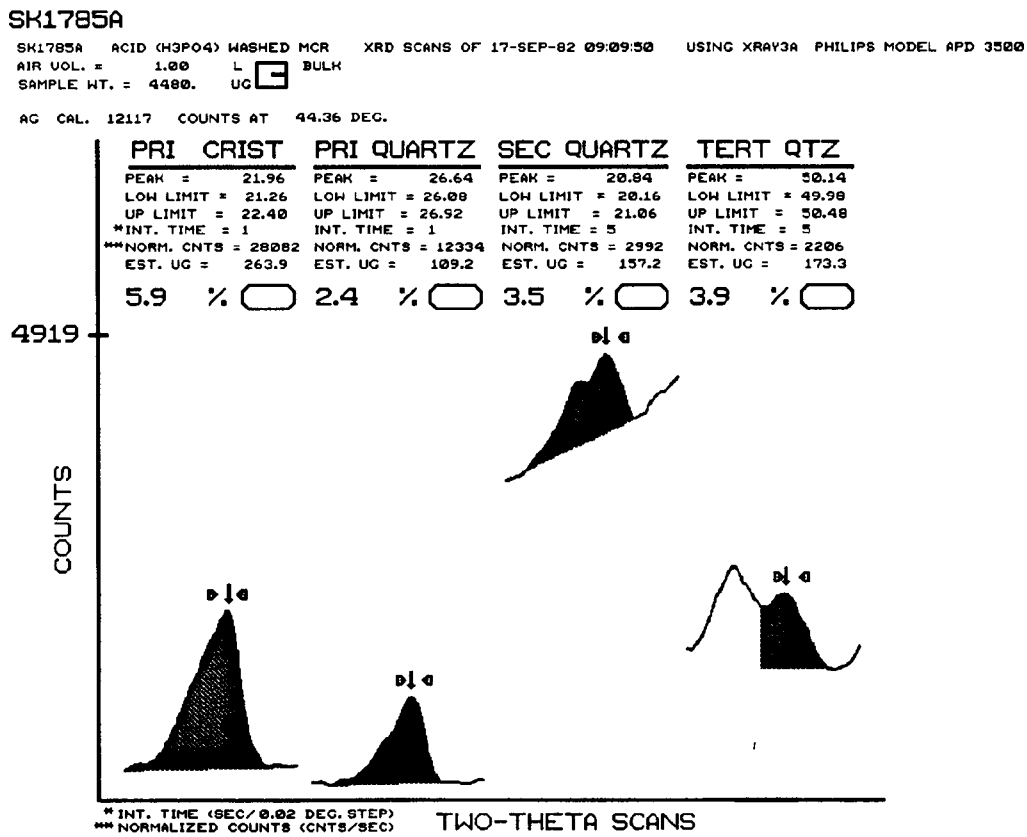

FIGURE 4. XRD scan of Mt. St. Helens sample.

amount of sample preparation, is currently used at some labs. Concepts involving DOF will be discussed below.

In our experience, XRD appears to have more general applicability and is more flexible for quartz analysis than other methods. In addition to quartz and cristobalite, substances such as zinc oxide, vanadium pentoxide, Portland cement, and other crystalline compounds can be confirmed or analyzed.

IR Spectroscopy

IR spectroscopy allows one to distinguish silica (not just quartz) from many other minerals. This method is sensitive to the small-scale structure of quartz because it measures the vibrational energy related to the atomic masses of silicon and oxygen, bond strength, and bonding symmetry. The sample is placed in a beam of IR light, and if any quartz is present the IR light is absorbed at the wavelength corresponding to these specific vibrations. The decrease in the amount of IR light transmitted through the sample at these wavelengths is a measure of the amount of quartz present.

The Lambert–Beer law predicts a linear relationship between the sample absorbance and its concentration. For true linearity, the sample must be a homogeneous solution of uniform thickness (b) and the light must be monochromatic. This law is approximate for quartz analysis because it is not strictly applicable for particulate samples where parts of the IR beam pass through agglomerates and aggregates of the IR-absorbing species, and parts pass between the absorbing particles. Low quartz loadings and sample inhomogeneity can yield lower absorbances than this linear relationship indicates.

Because this method is based on the bonding parameters of quartz, microcrystalline quartz can be analyzed. In theory, no two compounds have the same absorption spectrum. In practice, the IR spectra of different substances with similar bonding can share common absorption bands. This is an advantage for qualitative analysis of new or unknown pure substances because information from the IR spectrum provides clues in making educated guesses of the compound's structure. At the same time, it is a disadvantage for quantitative analysis because it indicates that interferences are possible. These bonding parameters are similar for the crystalline and noncrystalline forms of silicon dioxide because the tetrahedral SiO_4 structure is common to all these substances. Each silicon atom is surrounded by four oxygen atoms located at corners of a tetrahedron, and each oxygen atom joins two silicon atoms. Thus it is difficult to distinguish different crystalline silica forms with IR at the analytical peak at 798 cm^{-1} (12.5 μm). Many silicates also have similar tetrahedral SiO_4 structures which can interfere with the determination of quartz.[25–28] An IR absorption pattern is shown in Figure 5 (after Reference 29) for quartz (Q in Figure 5). Patterns and their close proximity to quartz are also shown—here the amorphous silica (A), cristobalite (C), and kaolinite (K), a significant interference.

Understanding the sample matrix is an important consideration in IR analysis. Certain sample matrices found in the workplace have known interferences. Chemical or heat treatments are the most direct approach used to remove interferences. The IR method is less expensive, but is also less specific

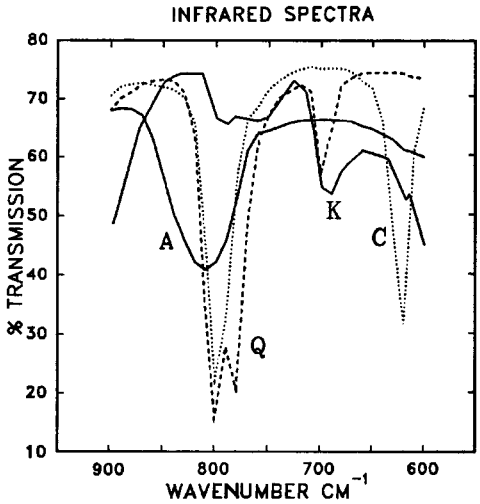

FIGURE 5. IR spectra of quartz (Q), kaolinite (K), cristobalite (C), and amorphous silica (A).

for crystalline silica than is powder XRD. This method is not applicable to all sample matrices, but it can be used to advantage in some well-defined sample matrices.

In a sample containing a mixture of light-absorbing species, the absorbances of different species are additive. This is the source of positive interferences observed in IR. Scattering of the IR beam by particles in the sample can mimic the effect of absorption and can give high backgrounds. If enough measurements can be made of known mixtures of the same substances (at varying concentrations), a multiple linear regression (multivariate analysis) can be performed and the known components in the mixture can all be calculated for samples containing the same ingredients. The positive interference due to each known interferant can be accounted for. Every analysis is subject to analytical error; the analysis of interferants is not immune. Even after all interferants are calibrated, sample inhomogeneity, difficulties in determining baselines, light scattering, differences in particle sizes of standard reference materials and air samples, etc. make undercorrection or overcorrection possible. For the most accurate analysis of quartz, the total absorbance due to interferences must be small in comparison to the quartz absorbance.

The IR analysis of quartz in coal dust is an example of the use of IR on a well-defined sample matrix.[7] The positive interferant kaolinite (a common hydrated aluminum silicate mineral) increases the signal seen on the quartz peak. This interference can be corrected mathematically by estimating the amount of kaolinite present using IR measurements at another wavelength characteristic of kaolinite and subtracting the corresponding predicted amount of interference from the quartz peak. The mathematical correction is most appropriate when the kaolinite is present in small amounts compared to the quartz.

Where the sample matrix permits, the analytical results can be of excellent quality. Some investigators[24,28,29] applied chemometric techniques such as the multiple linear regression approach to use additional analytical data from several key places in the spectrum to resolve known interferences. Results are promising for certain matrices.[28,29]

Two types of IR spectrometers have been used for quartz analyses:

1. The older dispersion IR spectrometers use a slit and a grating (or a prism) to disperse light from an IR source passing through the sample into a spectrum.
2. Recently, the Fourier transform IR (FTIR) has become popular. The FTIR approach has the advantage that it does not disperse the light into a spectrum, does not use a slit, and therefore can make use of more of the IR energy. Because the entire sample can be viewed by the IR beam, greater sensitivity is possible. The sample still needs to be as uniformly dispersed as possible. The main advantage of FTIR is the opportunity to computer process multiple scans of a sample to give signal-to-noise ratios greatly improved over that obtainable from comparable scan times using dispersive IR technology.

Sample preparation for presentation to the IR spectrometer is also time and labor intensive. Samples are processed either by using a low temperature ashing process or by placing them in a muffle furnace to destroy the filter and other organic substances.

Samples can be redeposited on a suitable filter medium in a manner similar to XRD to give a thin-layer presentation of the sample to the IR instrument.[7] Additionally, they can be prepared as a pellet mixed with potassium bromide (KBr). The DOF technique[30] can also be used in IR analysis, bypassing the labor-intensive sample preparation.

It should be emphasized that in the case of both IR and XRD, particle size is an important consideration. Currently, the respirable size fraction is the main focus of analysis. Future emphasis may include analysis of inhalable, thoracic, and respirable fractions.[31] However, these three particle size ranges not only have different sampling efficiencies, but probably all have different analytical sensitivities and would require the preparation and evaluation of different reference materials. An international consensus on the particle-size ranges of these materials and the appropriate sampling devices to achieve those ranges is vital to the advancement of the analytical methodology. Accurate comparisons of exposure data and epidemiological evaluations cannot be done without a consensus in the standard reference material for quartz.

Colorimetric Method (Visible Absorption Spectrophotometry)

The colorimetric method of quartz analysis,[3,10] once the only method used to analyze samples, no longer enjoys a high degree of popularity. The method is still employed, primarily because it is inexpensive, but has many drawbacks.

In the most popular colorimetric method, the residue from the Talvitie treatment is dissolved in hydrofluoric acid, and the dissolved silicon is reacted to form a colored complex that can be analyzed by colorimetric analysis. Colorimetric analysis, like IR spectroscopy, is based on the Lambert–Beer law. This approach is relatively specific to silicon, but cannot differentiate between silica and silicates. Most silicates can interfere, and the results are less precise and accurate than the XRD or IR method. PAT results show that colorimetric recoveries tend to be lower than by IR or XRD.[13] In addition, the colorimetric method cannot distinguish between the different quartz poly-

morphs. Sample preparation is complex, and a very hazardous chemical, hydrofluoric acid, is used in the procedure.

Determination of Quartz Content in Bulk Materials

The methods above are also used to analyze the quartz content in bulk materials. Two additional methodologies have also been recently used when the amount of sample is larger than is normally obtained during personal air sampling. If the sensitivity can be improved, these methods may be included in future analyses of quartz in air samples.

Thermal Analysis

Thermal analysis is a technique that requires a few hundred milligrams of sample, which makes it more amenable to analyzing quartz in commercial products (bulk materials) than for analyzing air samples. Particulate contained in air samples collected using current sampling methodology weighs anywhere from 0 to 15 to 20 mg. At the alpha to beta phase transition temperature near 573°C, the amount of quartz in a sample can be estimated by the change in heat content measured during heating or cooling. As in most other quartz analyses, particle size affects sensitivity. For the most part, bulk sample preparation is relatively simple and few interferences are noted. While it is not appropriate for small amounts of particulate normally found in air samples at this time, thermal analysis can play an important role in determining quartz content in relation to OSHA's Hazard Communication Regulation.[32] A warning of the presence of known or probable carcinogens such as quartz must be communicated to the employee when the concentration exceeds 0.1 percent and potential for exposure exists. This amount represents an analytical level that is difficult to achieve using IR, XRD, or colorimetric techniques. Thermal analysis can also provide relief from potential interferences in bulk materials common to the popular techniques.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (^{29}Si NMR) has been investigated[33] for the analysis of quartz polymorphs for the purpose of meeting the Hazard Communication standard (HAZCOM) requirements for crystalline silica. NMR monitors the electronic environment of the ^{29}Si nucleus, which is extremely sensitive to slight changes in bonding. As a result, peaks of quartz polymorphs occur at different chemical shifts, allowing ^{29}Si NMR to distinguish between silica polymorphs and distinguish silica from silicates. At long enough recycle delay times, peak integrations are directly related to the amount of ^{29}Si present in each electronic environment, simplifying calibration and permitting the quantitative analysis of all polymorphs and many silicates. The analysis is unaffected by particle size as long as the relative amount of surface silica is small. (Surface silica has a different chemical environment than does silica below the surface.) Although the ^{29}Si NMR background is far cleaner than in comparable IR spectroscopy scans, peak overlap of the silica polymorphs also occurs but appears more readily resolvable. Alternate peaks are not available for confirmation. The experimental protocol requires a large amount of sample (200 to 300 mg) and a significant amount of sample preparation to remove paramagnetic contaminants and to transfer the sample to 7-mm single crystal sapphire (Al_2O_3) rotors. The data presented indicate excellent precision and an analytical range extending down to less than 0.1 percent (corresponding to 200 to 300 μg of quartz). NMR instruments are expensive even when compared with XRD instruments. The expense is not offset by sample throughput; the current analytical protocol requires 60 hours to analyze each sample. The method may not be applicable to samples containing paramagnetic species that cannot be chemically removed; for example, some spinels and devitrified mineral wool are very resistant to acid cleanups. One very important potential application, however, would be as an adjunct to the characterization and certification of new crystalline silica standard reference materials.

Summary of Methods Used in the United States

In the United States, IR and XRD predominate for analysis of airborne quartz, with occasional use of the Talvitie-based colorimetric procedure. The colorimetric procedure is the most prone to interference, while the XRD is most resolvable because of the ability to use alternate analytical angles or lines. The XRD method appears to be the most precise, although some IR enthusiasts may disagree; PAT results appear to indicate a slight edge to XRD.[13] The total variability of quartz methods as noted by the PAT Program[13] indicate that imprecision (relative standard deviation, s_r) values have historically been a few percent higher for IR. XRD instrumentation, however, can easily be two to three times more expensive than IR.

Both IR and XRD have advantages over other approaches. Unlike chemical and colorimetric analyses, both IR and XRD are nondestructive analyses; samples and calibration standards can be reanalyzed many times. The different XRD angles associated with the quartz lattice structure allow XRD to be more versatile in identifying and quantitating quartz. One can also simultaneously analyze for other polymorphs such as cristobalite and identify the major crystalline substances present. For quantitative analyses, obtaining standard reference materials is the most important problem facing both IR and XRD.

International Methods: Quartz Analysis

One international industrial hygiene reference[34] indicates that, as of the date of publication (1983), the most common analytical techniques for quartz were XRD and standard chemical methods. There was no mention of dispersive IR or FTIR techniques. To address the current status of the methodology internationally, an informal survey was issued to colleagues practicing IH chemistry in the following countries: Australia, European Union, Japan, Mexico, Norway, Sweden, Taiwan, United Kingdom, and others in the United States (including NIOSH, MSHA, and information from the Chemical Manufacturers Association).

The European Committee for Standardization (CEN) of the European Union is an organization analogous to the American Society for Testing and Materials. The following European countries participate: Austria, Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and United Kingdom. Although these countries are members, not all use XRD, and they do not necessarily adhere exactly to the standard methodology established by the CEN.

TABLE 1. International Use of Three Methods for Quartz Analysis

Nation or Entity	Gravimetric or Similar Use	XRD	IR
Australia[36]	Respirable fraction	Yes	Yes
British Columbia[23,26]	Respirable fraction	Yes	Yes
European Union (formerly EC)[37,38]	Respirable fraction	Yes[A]	Yes[A]
Germany[39]	Respirable fraction[B]	Yes	Yes
Japan[40,41]	Respirable fraction	Yes	No
Mexico[C][42]			
Norway[43]	Respirable fraction	Yes	Yes
Sweden[44]		Yes	No
Taiwan[C][45]			
United Kingdom[22]	Respirable fraction	Yes	Yes
United States[6,11]	Respirable fraction	Yes	Yes

[A]The apparent direction of European Union (formerly European Economic Community) is indicated above. European Union member states may have their own preferred approach.
[B]Germany also uses the beta-irradiation method.
[C]Work is in progress to establish analytical capability on a national level. No method was specified. Blank spaces do not necessarily mean that a method is not used by that country.

The current literature and methodologies from Canada (British Columbia and Ontario) and pre- and post-unification Germany (West Germany is determinative in IH analyses) were reviewed and, if possible, discussed with these participants instead of submission of written survey results.

Participants in the survey were asked to indicate their primary and secondary methods used for quartz analysis and any future changes anticipated, and provide current copies of their methods. Of the primary and secondary methods, participants were asked to select from a list including gravimetric, chemical-colorimetric, AA, optical microscopy, IR, XRD, thermal analysis, or other.

Survey Results: Comparison of Methods

The two major techniques for the analysis of airborne crystalline silica are XRD and IR (see Table 1).

XRD. Countries that use XRD include Australia, Canada, Germany, Japan, Norway, Sweden, the United Kingdom, and the United States. Some of the members of the European Union indicated that a consensus written XRD method is in progress. Therefore, all of the countries surveyed with established methodology use XRD to some extent for quartz analysis.

IR SPECTROSCOPY. Those countries using IR were Australia, Canada, Germany, Norway, United Kingdom, and the United States. A written IR consensus method also appears to be in progress by members of the European Union.

General Comments of Survey Participants

Often in the comments accompanying the surveys there was a tendency to give near equal importance to IR and XRD; each has its advantages. Most countries surveyed indicated that IR was used for samples that were well characterized and that, if interferences were potentially a problem, they would use XRD instead for those samples. Germany uses a beta-irradiation method to measure sample loading; this is a rugged technique used to measure thin films and produces results comparable to the gravimetric method. None selected thermal analysis. New methodology was not indicated by any of the participants.

Mexico and Taiwan have not fully established their own methodology; both are currently putting together national IH labs and will probably use analytical techniques from other countries.

Current Sampling Strategies

Sampling strategies vary internationally. The nylon cyclone, which tends to deposit most in the filter center, is predominately used by OSHA and most of the United States. On the international scene, many other samplers are in use or under evaluation. These may include metal cyclones, similar samplers of local manufacture, or other sampling techniques. The variety of samplers introduces new variables, including different electrostatic properties and different sampling efficiencies at different particle sizes.

Perhaps the most interesting indication of the survey was the apparent widespread acceptance of the DOF technique for either XRD or IR (see Table 2). DOF uses the same filter for both sampling and analyzing the air contaminants. This approach bypasses the intensive sample preparation procedures previously mentioned for XRD and IR. There is a need to test the validity of this procedure at low quartz loadings, particularly those approaching 0.1 × PEL.

DOF advantages include less contamination and sample loss because there is no transfer or redeposition of the sample's dust. There is potentially increased sample analysis output because of reduced sample preparation time.

The main disadvantages to DOF are as follows.

1. It is difficult to adapt the cyclone to a 25-mm sampling cassette. X-ray instruments are normally set up to accept 25-mm diameter filters. Thus a cyclone normally designed to accept a 37-mm cassette is adapted to fit the 25-mm system with varying degrees of success.
2. Most air samples do not present themselves as homogeneous. Employees sampled may be involved in many different operations during the workday. Samples taken on these employees will tend to have different layers of particulates that may not be fully transparent to X rays if they are not redeposited in a thin-layer deposition. Shown in Figure 6 are deposits of mahogany dust on filters using three different particle size selective devices.[35] Nylon cyclone presentation is a continual building dot in the center of the filter. The aluminum cyclone (cut size is approximately 4.6 μm) displays more spread of particulates over the filter. The aluminum cyclone can be readily adapted to 25-mm cassettes. The horizontal elutriator has a very distinct pattern.
3. Aerosol particulates tend to agglomerate into clumps. The standard reference material and air samples may differ in their tendencies to agglomerate. The DOF technique does not break up either of these agglomerates; redeposition commonly uses ultrasonics to break up and disperse the agglomerates to produce the homogeneous presentation needed for accurate XRD and IR analysis.
4. The biggest drawback of DOF is the need to prepare standards using aerosol generation systems to assure stan-

TABLE 2. Detection Limit and Analytical Range for Quartz Analyzed by XRD and IR

Nation or Entity	XRD: Detection Limits or Analytical Range (in Parenthesis)		Infrared: Detection Limits or Analytical Range (in Parenthesis)	
	Redeposited	DOF	Redeposited	DOF
Australia	Yes 10 μg	Yes 20 μg (20–600 μg)	Yes 10 μg	Yes 20 μg (20–600 μg)
British Columbia		Yes	Yes (10–500 μg)	
European Union		Yes[A]		Yes[A]
Germany	Yes		Yes	
Japan	Yes 5 μg	Yes (15–2000 μg/cm²)		
Mexico[B]				
Norway	Yes 10 μg		Yes	
Sweden	Yes 1 μg (1–500 μg)		No	
Taiwan[B]				
United Kingdom		Yes 3,10 μg[C] (10–1000 μg)	Yes 5 μg (5–700 μg)	Yes 10 μg (10–1000 μg)
United States	Yes 10 μg (10–2000 μg)	Yes (200–1200 μg)	Yes 10 μg (10–2000 μg)	Yes (200–1200 μg)

[A]The apparent direction of the European Union is indicated above. Member states may have their own preferred approach.
[B]Work in progress. No particular method was specified.
[C]Lower value is for det. limit of strongest analytical peak; larger value is either of the two next strongest analytical peaks. DOF refers to the direct-on-filter version of the indicated method. Norway intends to look into this approach in the future.

dard/sample matching. Quartz standards are collected using personal sampling devices similar to those used to sample employees. Quality controls should also be generated by this method. Accuracy and analytical range are limited by the weighing error, and generation of DOF standards requires significant amounts of a standard reference material, which are typically expensive and of limited availability.

5. A major problem is presented when there is sample overloading, loose or dislodged dust, samples collected at different sampling rates than that used in standard preparation, interferences requiring chemical treatment, or when bulk samples are submitted (for checking for interferences or HAZCOM compliance). In these cases, one must resort to redeposition.

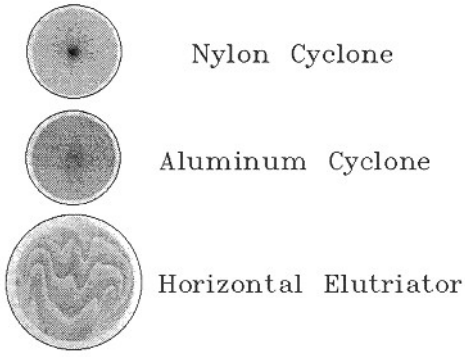

FIGURE 6. Filter sample deposition using different types of aerosol collectors.

Survey Results: Comparison of Method Performance

The various abilities of each method were examined in terms of detection limit, working range, precision, accuracy, etc. These are summarized in Table 2 to determine any significant difference in performance characteristics internationally. Although different values for these variables were discovered, it appears more due to the inconsistency among nations in using a universal method to determine performance (i.e., calculation of detection limits appears to be done in as many different ways as there were responses). Also, many methods did not show detection limits. The DOF version of a method was often indicated as the preferred method.

IR data in Table 2 show a broad range for detection limits and working range. Estimates of precision and accuracy varied widely. The variability seems most likely due to different approaches to calculating and reporting. Values are only for XRD or IR. None of the countries surveyed indicated use of colorimetry or microscopy. It is generally acknowledged in the United States that either XRD or IR is capable of less than 10 percent CV and an overall error (OE) of about ±25 percent. OE also includes potential bias as follows:

$$OE = \pm[|\text{mean bias}| + 2CV] \times 100\%$$

Survey Highlights

Germany uses both IR and XRD. While reflection XRD is the most common XRD technique used to analyze quartz, one of the XRD techniques used in Saarberg, Germany, is sample concentration combined with transmission XRD. X rays are diffracted by quartz but are transmitted through the sample to a detector. Among its advantages, the X rays make only one

pass through the sample and reduce losses due to absorption of X rays in the sample.

Australia indicates that both XRD and IR are used for quartz. A comment enclosed with the survey indicates that cristobalite and tridymite are not analyzed and have been placed in the "too hard" basket.

Norway also uses both XRD and IR. Additionally, on well-defined mixtures an interesting multivariate calibration technique that uses multiple linear regressions claims slightly better precision and accuracy using this technique.[28,29]

Comments from the Swedish National Institute of Occupational Health indicated that they *only* use XRD and *will only* use XRD in the future. The Swedish methodology also claimed to have the best detection limit, 1 μg.

Conclusions and Recommendations

Refinements to XRD and IR techniques will probably dominate in the near future. Entirely new instrumental approaches are not likely in the near term. Analysts are characteristically problem solvers and are innovative in modifying and developing techniques (witness the proliferation of "hyphenated methods" such a gas chromatography—mass spectroscopy, inductively coupled plasma—mass spectroscopy, etc.). Given the huge amount of imagination in the world community, analysts with adequate resources will try anything that suggests improvement. Issues that may be pursued in the future by national and international laboratories include the following:

1. A comprehensive evaluation of DOF.
2. Keeping up with developments in sampling to assure continued analytical capability.
3. A consensus definition of tridymite and a corresponding standard reference material.
4. A consensus on how to report the parameters used to define method performance (agreement on detection limits, etc.).
5. Examination of thermoanalyzers for bulk identification (for HAZCOM)—interference problem in identifying quartz in bulks, especially from 0.1 to 1 percent quartz.
6. A multivariate approach. Norway appears to be having good success with it on specific well-defined matrices. What is the scope of applicability to unforeseen matrices, that is, how rugged is this approach?
7. Support for PAT recommendations. Due to the large spread exhibited in results, more active participation in the PAT Program and establishment of effective quality control programs by all laboratories analyzing quartz are strongly recommended to assure precise and accurate results.
8. More active involvement of institutions of higher education in developing new sampling and analytical techniques to solve practical sampling and analysis problems. For example, higher education is the ideal environment in which to pursue research and development (R&D) and obtain patents with new analytical approaches. Modifying research instrumentation is an avenue of problem solving taken in some forms of graduate research. Analytical labs may not have the time for R&D; they tend to prefer turnkey systems over modified research instrumentation.

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