Occupational Health Analytical Chemistry

Quantitation Using X-Ray Powder Diffraction

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Particulate contaminants are of extreme importance in occupational health because of their effect on the respiratory system. Such contaminants may be grouped into several physiological categories depending on their overall effect (1). Three categories are of importance to this discussion: (1) inert, (2) minimal pulmonary fibrosis producing, and (3) extensive pulmonary fibrosis producing. Dust aerosols which produce no known injuries when inhaled but may cause discomfort and minor irritation to the lung, are classed as nuisance and/or inert. Examples of such dusts include particulate clay, limestone, gypsum or aluminum oxide. If a dust contaminant is known to produce nodulation (discrete deposits of particulate) and diffuse fibrosis (growth of nonelastic tissue) in the lung, the material is classed as minimal pulmonary fibrosis producing. Dusts in this category include barium sulfate, iron oxide and tin oxide. The third category, extensive pulmonary fibrosis producing, includes dusts such as silica and asbestos. These dusts are known to produce a significant degree of nodulation and fibrosis in the lung.

Exposure to inorganic chemicals in the workplace has been traditionally evaluated using elemental analysis. However, in recent years some attention has been given to the toxic effects of specific compounds rather than elements, e.g., chromic acid (2), nickel subsulfide (3), zinc oxide (4), and sodium hydroxide (5). It is therefore important that the occupational health chemist develop the capability to identify and quantitate chemical compounds. To this end, X-ray powder diffraction (XRD) is a unique tool for

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crystalline particulate analysis. Every species has a unique powder diffraction pattern; thus, it is possible to identify each species in a sample by either a manual or computerized search (6) of crystalline standards. Upon identification of the compounds present in the sample, each may be quantitated since the diffracted intensity for a given profile or peak of the diffraction pattern is proportional to the amount present in the sample. Furthermore, the non-destructive nature of XRD permits additional analyses by other techniques should this be necessary.

Recognizing the applicability of XRD to occupational health chemistry, Lennox and Leroux (7) suggested a number of chemical species which would be suitable for XRD analysis: arsenic trioxide, beryllium oxide, mica, vanadium oxides, calcium fluoride in ceramic materials, as well as a number of organics such as DDT, lindane and chlordane. Unfortunately, the general application of XRD to the quantitation of industrial hygiene samples has not been realized and the majority of these analyses are restricted to free silica and to a lesser extent asbestos and talc.

Table I lists several XRD analytical methods recently developed in the NIOSH laboratories. For each analyte, the analytical range, detection limit and analytical precision are listed. The method numbers refer to the NIOSH Manual of Analytical Methods (8). As indicated in the table, there are several NIOSH methods available for free silica analysis. Method No. P&CAM 109 incorporates the internal standard approach as developed by Bumsted (9). The other two methods S-315 and P&CAM 259 are based on the substrate standard method. The major difference between the two is the direct sampling on silver membrane filters (S-315). This paper will address the various methods of quantitation, sample collection and procedures for matrix absorption corrections that have been used in this laboratory for the analysis of crystalline particulate contaminants in the workplace.

Methods of Quantitation

Because X-ray powder diffraction deals with solid samples, the analytical variables are different from those associated with the analysis of liquid or solution samples. Principle among these are particle size effects, uniform sample surface, crystallinity and X-ray absorption. Although particle size and a non-uniform sample surface are serious problems, their

TABLE I

Permissible Exposure Levels And XRD Analytical Methods

Analyte	Standard mg/M^3	Analytical Range, mg/M^3	Relative Std.Dev.	NIOSH Method
Zinc oxide	5.0 (a)	0.03-2.4	0.10	P&CAM 222
Zirconium oxide	5.0 (b)	0.03-1.5	0.08	P&CAM 250
Chrysotile	0.15 (c)	0.025-0.25	0.07	P&CAM 309
Fibrous tremolite		0.012-0.25	0.14	
Quartz	0.05 (a)	0.030-1.3		P&CAM 109
		0.025-0.4	0.07	S 315
		0.025-2.4	0.10	P&CAM 259

(a) NIOSH recommended standard
(b) American Conference of Governmental Industrial Hygienists
(c) West German mass standard; c.f. ref. 30.

effects can be reduced or eliminated through careful sample preparation. Field sample crystallinity is, perhaps, the most uncontrollable variable which effects quantitative XRD analysis. Often the analyte is generated in the workplace under adverse conditions; conditions significantly different from those used in the laboratory for the preparation of standards. Thus, to lessen the effect of the variation in degree of crystallinity between standards and samples, the diffraction peak area rather than peak height must be measured.

Both historically and currently, X-ray absorption by the sample has had a major impact on the development of analytical methodology. While the theory of X-ray absorption is complex, the observed effect is straight forward. As X-rays pass through a material they are absorbed; the extent of the absorption depends upon the thickness and nature of the absorbing medium. Diagramatically the specific factors influencing X-ray absorption are pictured in Fig. I. The sample thickness (t) and the diffraction angle (θ) determine the path length of the X-rays through the absorbing material, while the chemical composition of the matrix determines the degree of absorption per unit length. By knowing the thickness (or area, mass and density) of the sample and its exact chemical composition it is possible to calculate the absorption effect and thereby make corrections. However, for an actual filter sample collected in the workplace environment these parameters are rarely known and often impossible to determine. Therefore, to account for the X-ray absorption effect on quantitative analysis, two experimental procedures have been utilized in the X-ray laboratory: the internal standard procedure and the substrate standard procedure.

Internal Standard Procedure. The first of these absorption correction methods was developed by Alexander and Klug (10) and involves the addition of a known amount of an internal standard to the sample. If the analyte and the internal standard have diffraction profiles at approximately the same angle, their intensities will be equivalently influenced by matrix absorption. Thus, the intensity ratio of the internal standard to that of the analyte can be used as a quantitative measure of the amount of analyte present. To effectively use the internal standard procedure, a number of requirements must be met. First, the standard should have a strong diffraction peak near that of the analyte, but not so close as to interfere. Secondly, the density, particle size and mass absorption coefficient of the analyte and standard should be similar. Thirdly, the analyte, standard and any matrix must be chemically inert relative to each other and finally, a homogeneous mixture of sample and standard must be generated.

The major drawbacks to this method as a general quantitative procedure include the rather stringent requirements for the internal standard, the preparation of a homogeneous mixture of standard and sample, and the additional time required for the measurement of the two phases. Furthermore, since it is not always possible to know in advance whether the matrix contains strongly absorbing materials, the internal standard must be added to every sample as a precautionary measure.

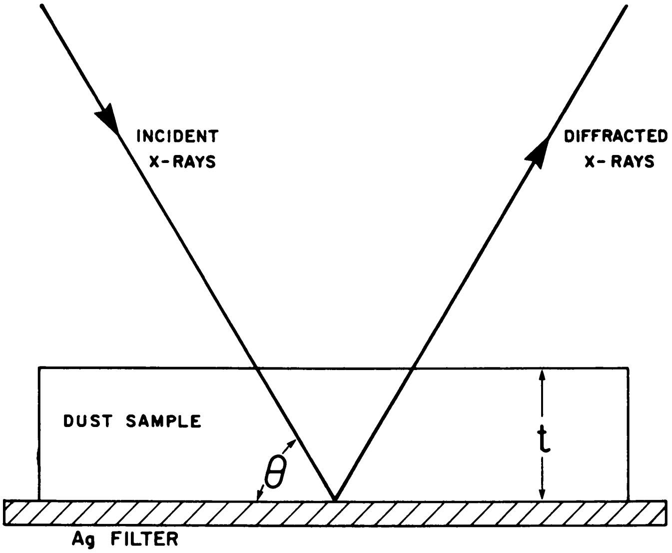

Figure 1. Geometric factors that affect the degree of x-ray absorption

Bumstead (9) chose native fluorite as an internal standard for the analysis of quartz in coal dust. His procedure consisted of mixing 0.20 mg fluorite into each water suspension of standard and sample and depositing on silver membrane filters for a calibration curve (fluorite/quartz intensity ratio vs. mg quartz). The application of this method to coal dust samples containing less than 1% quartz produced acceptable results; relative standard deviation (RSD) was 18.2% (9).

Substrate Standard Procedure. The second method, also known as the external standard procedure, depends on the measurement of a diffraction peak from the substrate supporting the sample. This method is based on the work of two independent groups. Leroux, Lennox and Kay (11) developed a procedure for calculating an absorption correction based on the diffracted and transmitted intensities from a bulk sample. Williams (12) simplified this process by mounting the sample on a fine grained copper metal foil and measuring the intensity of the diffracted radiation from this foil with and without the sample in place. A correction factor can then be calculated from the observed attenuation of the copper diffraction peak. Leroux and co-workers (13,14) extended the Williams technique by replacing the copper foil with a silver membrane filter and applied the method to the analysis of quartz.

To calculate the absorption correction, Γ, the following equation is employed:

$$\Gamma = \frac{-R \ln T}{1 - T^R}$$

where:

R = sin θ substrate / sin θ analyte

$T = I_{Ag}/I^{o}_{Ag}$

I_{Ag} = diffracted intensity for the substrate with sample deposition

I^{o}_{Ag} = diffracted intensity for the substrate without sample deposition

The observed intensity or weight of analyte is then multiplied by Γ to give the corrected intensity or weight. The substrate standard method requires that the substrate be crystalline (such as a silver membrane filter) and assumes a uniform sample distribution. The major drawback to this approach is the possibility of overlap of the analyte profile with that of the substrate profile.

Sample Collection and Preparation

For occupational health investigations, personal sampling is done in the breathing zone of the exposed worker. To accomplish this, a portable sampling pump must be attached to the worker and a collection device positioned near the breathing zone, usually attached to the shirt collar. This device consists of a plastic holder (filter cassette) containing the membrane filter. Typical filters used for the collection of particulates include Mine Safety Appliance's (MSA) FWSB (polyvinylchloride) and Gelman Sciences DM-5000 (polyacrylonitrile-polyvinylchloride). Flow rates for personal sampling usually range from 1.0 - 2.0 L/min with 1.7 L/min being the recommended sampling rate.

When the working environment is suspected of containing dusts formed by comminution (quartz, asbestos, talc), a size selecting device (cyclone) is added to the sampling train to insure the collection of only respirable particles. The addition of the cyclone is a distinct advantage for XRD analysis since this produces a sample in which the particle size is known and a standard can be selected to match. A sampling setup with a cyclone and a closed face filter cassette is shown in Figure 2. Dust laden air entering the side of the cyclone must make an abrupt change in direction to be pulled through the filter. Larger particles impact on the sides of the cyclone and do not reach the filter.

Sampling procedures are often dependent on the method of sample preparation as well as the physical and chemical properties of the analyte. For most analytes that are collected by the above method the usual procedure is to ash the filter in either a low temperature plasma asher or a muffle furnace, disperse the residue in a suitable liquid such as isopropanol using ultrasonic agitation, and filter the suspension through a silver membrane filter. In addition, if the internal standard method is used, the chosen standard must be added to the residue suspension prior to filtration.

Regardless of the analytical procedure chosen for the analysis, several advantages are derived from the ashing/re-deposition process. These advantages include

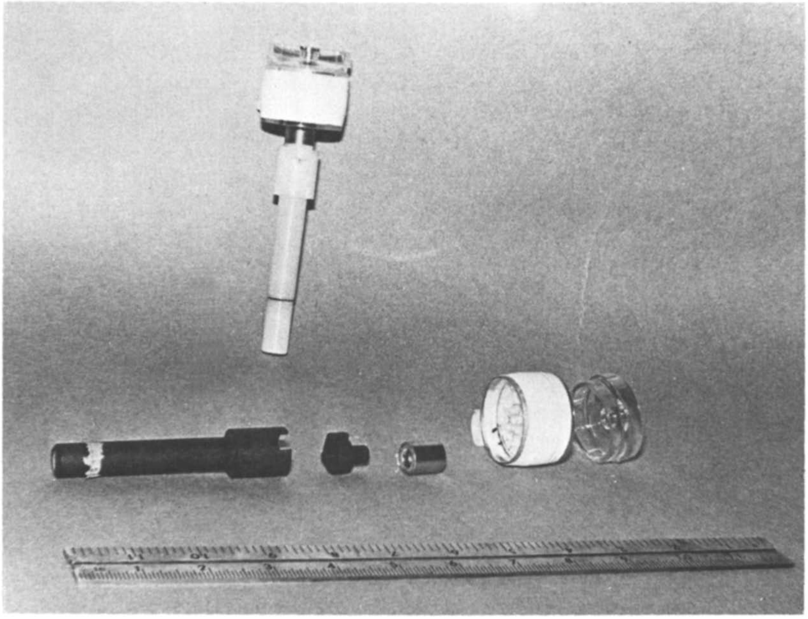

Figure 2. Personal sampling device consisting of a filter cassette and a 10-mm nylon cyclone

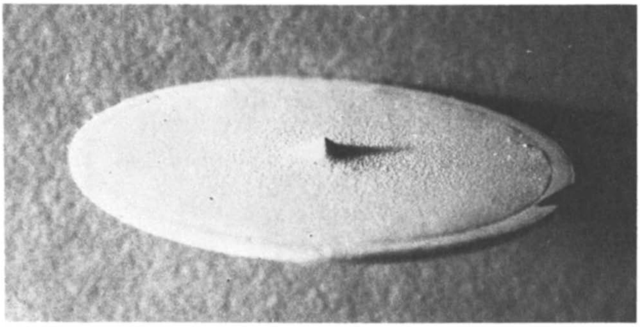

Figure 3. Illustration of a dust sample collected with a closed face cassette showing dust deposition in the center of the filter

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the elimination of most organic interferants, the formation of a uniform dust distribution on the filter, the low flat X-ray background of the silver filter (9,15) and the potential for making absorption corrections. However, if the analyte is sensitive to this preparative technique, e.g., chemically reactive during ashing, then an alternate sample collection method must be employed. Since a uniformily thick dust layer must be presented to the X-ray beam, the standard closed face filter cassette and cyclone cannot be used because of the tendency to accumulate a greater quantity of dust in the center than at the edge of the filter. Figure 3 is a good example of this problem. Although experimental evidence is lacking, the open face cassette tends to collect the required uniform dust layer. However, this collection device is more prone to abuse by the worker, is difficult to transport back to the laboratory without disturbing the uniform dust layer, and does not collect the respirable fraction.

When samples are collected with an open face filter cassette and analyzed directly, the internal standard method is not amenable to the analysis. Henslee and Guerra (16) developed a procedure for direct analysis of quartz on polyvinyl chloride filters; however, the procedure did not allow for absorption corrections. Allen, Samimi, Ziskind and Weil (17) also analyzed for quartz directly on organic membrane filters. Their method of determining matrix absorption corrections is based on the percent attentuation of the sample background compared to the background of the standards. Altree-Williams (18) modified the substrate standard method to accommodate samples collected directly on Nuclepore filters. Matrix absorption was accounted for by mounting a clean silver membrane filter beneath the Nuclepore filter. The absorption correction was then determined as described previously. In agreement with Altree-Williams, preliminary experiments in this laboratory suggested that this procedure is viable for the measurement of samples which cannot be treated by the standard preparative techniques, e.g., organic solids.

Standards Preparation

There are two basic laboratory methods for the preparation of filter standards--dust generation and the liquid suspension technique. Dust generation has a distinct advantage because of the ability to produce atmospheres similar to the workplace which can then be sampled using standard techniques. Equipment for dust generation can be as simple as the apparatus described by Leroux (19) or as sophisticated as that shown in Figure 4. This apparatus consists of a Wright Dust Feeder (20), a charge neutralizer and a dust chamber fitted with an exhaust manifold. The attachment of sampling devices to the manifold permits the collection of the generated dust on the membrane filters. A set of filter standards are prepared by varying the sampling times and the concentration of the dust in the chamber. Although dust generation may appear relatively straight forward, the technique requires considerable expertise and does not exactly match the treatment of field samples; hence, this procedure is not generally applicable in a routine analytical laboratory.

For the liquid suspension technique, a weighed quantity of the standard (particle size < 10 μm) is dispersed in a suitable liquid such as isopropanol. For most applications, suspensions in the range 10-50 mg/L are adequate. Filter calibration standards are easily prepared by pipetting aliquots of the suspension and filtering through a 0.45 μm silver membrane filter; however, classical analytical techniques must be modified when dealing with suspensions. During the pipetting operation, the aliquot must be brought up to the mark. If the suspension is treated as a solution, it is possible, due to settling within the pipette, that a highly concentrated drop of suspension will be lost when the pipette is adjusted to the mark from above. To facilitate the preparation of a uniform dust layer, a small volume of the suspending liquid (isopropanol) is added to the filtration apparatus prior to the addition of the aliquot. Vacuum is not applied until the aliquot has been added and all washings of the filtration apparatus have been accomplished.

In order to obtain a uniform suspension, the standard must be ground to a particle size < 10 μm. This can be achieved using a liquid nitrogen "freezer" mill and sieving the ground material using either dry or wet sieving. For compounds which tend to agglomerate during dry sieving, the wet sieving technique of Kupel (21) is preferable. To insure complete dispersal of the solid throughout the suspending liquid, an ultrasonic bath or probe is essential.

There has been considerable concern among XRD researchers on the errors which may result from pipeting aliquots from a suspension, errors which could

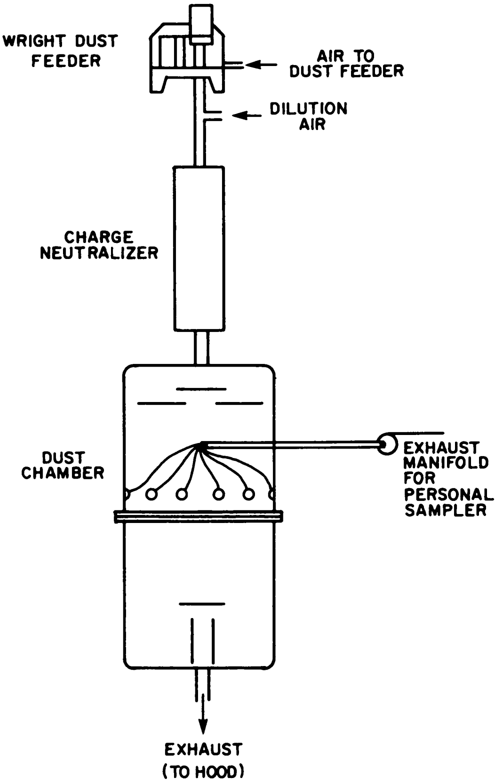

Figure 4. Dust generation system: the Wright dust feeder introduces dust into the air stream at a constant rate to produce test atmospheres.

significantly affect the overall precision and accuracy of the method. Henslee and Guerra (16) weighed their filters before and after deposition of the standard. Of 30 filters, 84% agreed with dilution data to within ± 12 µg. Furthermore, calibration curves based on weight data did not show any better precision than those based on liquid suspension data. These authors concluded that it would be advantageous to invest time in multiple determinations based solely on the liquid suspension data.

A similar comparison has been conducted in this laboratory. We have been specifically concerned that the capillary tip of the pipette might generate poor precision by promoting the formation of agglomerates. To test for effects on the accuracy and precision, three different techniques were used for placing pure talc on three sets of silver filters. In the first technique samples of talc were weighed, suspended in isopropanol, and the entire suspension filtered through the silver filters. In the second and third techniques, a transfer pipette and a transfer pipette with the capillary tip removed were used to draw aliquots from a suspension containing 1000 µg/mL of talc. The average talc peak intensities and associated standard deviations were used to assess and compare the precision and accuracy of the three methods. Statistical tests showed that the precision and accuracy attained with either pipette is the same as that found with the weighed samples, demonstrating that pipettes can be used to remove aliquots from suspensions with concentrations as high as 1000 µg/mL (22).

Haartz, Bolyard and Abell (23) used atomic absorption spectrophotometry to check filter standards prepared by the suspension technique. Zinc oxide was "spiked" on DM-800 filters and quantitated by AAS and XRD. Results from these measurements are shown in Table II. An average deviation of 2.1% was found between the two techniques. Although this data does give a considerable degree of confidence to the use of the suspension procedure for standards preparation, additional data for other analytes is needed for conclusive proof.

Measurement and Data Analysis

There are two methods for experimentally measuring the diffracted intensity: peak height and peak area. Klug and Alexander (24) have noted that peak heights can only be used when they are known to

TABLE II

Comparison of XRD and AAS Results
For Zinc Oxide on Filters

Nominal Value μg	AAS Results μg (a)	XRD Results μg (a)	Percent Diff.
250	250.7	249.3	0.5
400	383.0	367.7	4.0
475	473.3	467.7	1.3
700	689.0	683.3	0.8
925	928.0	891.3	4.0

(a) Values reported are the average of three samples.

be proportional to the corresponding integrated intensities. Furthermore, peak width and consequently peak height are a function of crystallite size and lattice imperfection. Thus, for samples generated in the workplace where these effects could be significant, it is essential that integrated intensities be measured.

Regardless of which quantitative procedure is chosen, i.e., internal standard or substrate standard, the measurement of the analyte profile is identical. Typically, filter samples contain light dust loadings, generally a maximum of two mg total dust, and the expected analyte weight may typically be less than 500 μg. To precisely measure the integrated intensity at this level, considerably longer counting times are required than might ordinarily be employed in XRD analysis. Experimentally, intensity measurements are usually made in one of two ways. The usual approach utilizes a scaler/timer to accumulate the diffracted radiation as the profile is continuously scanned. Alternatively, using a computer controlled diffractometer, integrated intensities are easily obtained by step scanning through the analyte profile. A counting rate of 10 sec per 0.02° 2θ step (0.12°/min) is typical. With the exception of chrysotile, which has a very broad primary peak, the typical analyte requires step scanning through a 2θ range of $1.0-1.5^\circ$ which requires approximately 15-20 minutes of analysis time. For chrysotile, which has a rather broad primary profile (22), the analysis time increases to approximately one hour. While it is possible to reduce the analysis time somewhat, there will be a consequent loss in sensitivity.

To account for absorption effects, an additional measurement is required. With the internal standard method, the profile for the internal standard must be measured for both calibration standards and samples. The rather small quantity of analyte present in the sample requires the addition of a similar quantity of internal standard (∿ 200 μg) necessitating the measurement of the standards profile under essentially the same conditions as that of the analyte. Consequently, the internal standard method requires an additional measurement time approximately equal to that of the analyte. Under conditions noted above, this would amount to approximately thirty minutes total analysis time per sample.

In the substrate standard method the absorption effect is determined using the transmittance ratio ($T = I_{Ag}/I^{o}_{Ag}$). The determination of the transmittance involves additional measurements, i.e., step scanning over the silver profile, to obtain I_{Ag} and I^{o}_{Ag}. I_{Ag} is measured for each filter sample and I^{o}_{Ag} can be obtained several ways as discussed below. These additional measurements can be performed very quickly compared to the more lengthy measurements of the internal standard because the silver peak is quite intense. A step scan of the silver diffraction profile plus background counting time can be accomplished in about two minutes with better than 1% precision.

Abell, et.al. (<u>25</u>) considered several procedures for determining I^{o}_{Ag}. The simplest, an averaging method, involves one additional measurement for each sample and standard. Samples and standards are prepared using filters from the same box; I^{o}_{Ag} is determined for each filter by step scanning through the silver 100 line after the diffraction profile of the analyte is measured. Standards having less than 200 μg of material are essentially "clean" silver filters for absorption purposes; therefore, the diffracted intensities determined for these standards are essentially I^{o}_{Ag} values. The average of the individual I^{o}_{Ag} values is an estimate of I^{o}_{Ag} for an individual filter within a given box. An RSD of approximately 4% was found when this procedure was used to determine T (<u>25</u>).

There are two "single filter" methods for determining T. One involves measuring I^{o}_{Ag} on a clean filter before depositing the sample and measuring I_{Ag} and analyte intensities. The other involves measuring the analyte and silver (I_{Ag}) intensities on a dust laden filter and then measuring I^o_{Ag} on the reverse side. The latter approach was first proposed by Leroux (14). Thatcher (26) found a large difference in silver intensity from the two sides of clean filters and adopted the former method. Altree-Williams (27) also adopted the former method after finding a 7% RSD in intensities from different filters. The large differences found by these researchers disagree with that found for the smallest pore size (0.45 μm) silver filters by Abell *et al.* (25). They also found the front reverse method to have slightly better precision than the averaging method.

The following example illustrates a typical application of an absorption correction calculation. A dust sample containing 135 μg chrysotile asbestos and 4365 μg talc was deposited on a silver membrane filter. The net diffracted intensity for chrysotile when compared to an established calibration curve indicated only 88 μg present. Comparison of the sample's silver diffracted intensity (I_{Ag} = 42454 counts) to the established average value (I^o_{Ag} = 59379 counts) indicated that an absorption effect was present. From this intensity data the transmittance, ($T = I_{Ag}/I^o_{Ag}$), was determined to be 0.713. T can then be determined either by solving Eq. 1 or from a table of correction factors which can be prepared before hand either manually or by computer. In this case, T was 1.6. Thus, the corrected weight of chrysotile was 138 μg in excellent agreement with the amount "spiked" on the filter.

Proponents of the internal standard procedure have questioned the validity of the substrate standard method to adequately correct for matrix absorption. Leroux and coworkers (11,13,14) have presented data which support the method; in addition, several measurements were performed in this laboratory to verify the validity of the method (22). Mixtures of chrysotile in talc (1-7%) were prepared and various quantities "spiked" on silver filters. Table III illustrates the results obtained after correcting for matrix absorption as compared with the uncorrected data. Overall, there is excellent agreement between the corrected weight and the "spiked" weight.

As is the case for any quantitative analysis scheme, the precision and accuracy of the results depends significantly on the calibration standards. Because the quantities of dust to be measured correspond with the lower end of the instrumental range, long counting times, as previously noted, are

TABLE III

QUANTITATIVE MEASUREMENT OF CHRYSOTILE USING CORRECTED & UNCORRECTED INTENSITIES

Percent Chrysotile in Talc	Uncorrected Weight	Actual Weight	Corrected Weight
7	151	175	188
7	118	140	139
7	93	105	106
5	93	125	119
7	67	70	74
7	60	63	62
7	46	49	49
7	28	28	28
5	93	125	119
5	75	100	99
5	60	75	77
5	35	50	44
5	33	40	39
5	26	30	31
3	113	180	191
3	88	135	138
3	63	90	87
3	56	72	71
3	45	54	55
3	37	45	44
3	31	36	36
1	61	150	168
1	49	100	102
1	42	70	78
1	34	50	52
1	23	30	27
7	93	105	106

necessary to compensate to some extent for the increased degree of imprecision. Thus, several filter calibration standards at each level must be prepared to obtain the best calibration curve. A linear regression analysis of the net intensity vs weight of standard data helps to insure the best precision.

Of the several parameters associated with an analytical method, detection limit is a very important but often a little understood parameter. In X-ray powder diffraction the detection limit is defined as the amount of material which will produce a net intensity that is equal to three times the standard deviation of the background as measured over a time period equal to that used in measuring the corresponding peak (28). It cannot be emphasized too strongly that the detection limit is useful only in ascertaining an analyte's presence with a reasonable degree of confidence. Quantitation is generally impossible at this level. In addition, the range of the calibration curve between the detection limit and the lowest measured standard is a "gray area". Measurements made in this region are based essentially on extrapolation of the calibration curve so that results must be considered as unreliable.

Matrix Interferences

Quantitative analysis of field samples must, of course, be performed under identical conditions to those used in analyzing the standards. Prior to the actual analysis, a powder pattern of a bulk sample such as rafter dust, an area sample, or a heavily loaded filter is obtained to determine information about the matrix. This information may necessitate some modification to the analytical method, such as quantitatively measuring the secondary peak because of a matrix interference with the primary peak. Such a modification usually results in poorer sensitivity because of the reduced intensity of the secondary peak.

The number of compounds with profiles that overlap the primary analyte profile are potentially very large, but the number of compounds which are potential interferences in occupational health usually depends on the industry in which the analyte is collected. Altree-Williams (18) collected samples at several industries where quartz and kaolinite or feldspar/mica

TABLE IV

Matrix Interferences

Analyte	Interference
Quartz	Mica, biotite, potash, feldspars, silimanite, zircon, graphite, iron carbide, lead sulfate
Zinc Oxide	α-iron oxide, $(NH_4)_3ZnCl_5$, $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$, Zn
Chrysotile	Chlorite, antigorite, lizardite, anthophyllite

were present. He did not find these substances to present an interference to the quartz XRD analysis. Freedman, et. al. (29) analyzed coal dusts which contained clay minerals using infrared absorption and XRD. They noted good agreement between the two techniques particularly when the samples were ashed prior to analysis. Some potential interferences are listed in Table IV for the quartz, chrysotile and zinc oxide primary peaks. If organic interferences are present, they can usually be eliminated in the ashing step. For the case where there is significant overlap, little can be done unless the analyte has a secondary line of sufficient intensity for quantitation. For example, 20 μg of quartz can be quantitated using the primary peak; with the secondary peak, only 100 μg can be quantitated.

If the secondary or other less intense peaks are not usable and the degree of overlap is not too severe, two other approaches are possible. The simpler approach is to use longer wavelength radiation. Changing from the widely used copper radiation (1.54A) to chromium radiation (2.29A) allows a slight improvement in resolution. Figure 5 illustrates the improved resolution of zircon interference with quartz. This approach would only be practical for the situation where samples with a similar interference were regularly received. The second, and more complex, approach to the problem is the use of deconvolution or peak stripping techniques. This approach is being actively pursued by a number of researchers and shows promise as a viable solution to the interference

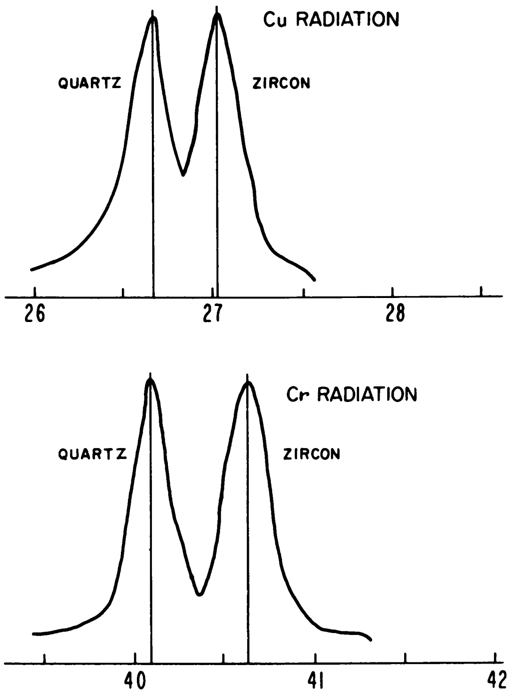

Figure 5. Effect of radiation wavelength on quartz and zircon profiles. The two profiles are better resolved with a chromium target tube ($\lambda = 0.229$ nm) than with a copper tube ($\lambda = 0.154$ nm).

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problem. Thus, a combination of radiation type, a deconvolution computer program and a judicious choice of X-ray optics may solve many of the interference problems.

Conclusion

The trend in industrial hygiene work is to identify the particular species responsible for an occupational health problem, although assessment of exposures to inorganic materials previously has most often been based on elemental analysis. When a solid inorganic compound is to be identified and quantified, X-ray diffraction should be among the approaches considered. This paper has outlined the use of X-ray powder diffraction as a tool for the identification and quantitation of crystalline particulates. It has been shown that the substrate standard method is the preferred quantitative procedure for several reasons: (1) easy adaptability to most analytes; (2) fast analysis time (as compared to the internal standard procedure); and (3) accurate determination of matrix absorption effects. While there are a number of reasons why a given compound may not be amenable to this technique, it is likely that the list of analytes will be added to in the future.

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Disclaimer

Abstract

X-Ray powder diffraction (XRD) has assumed increasing importance as an analytical technique for the identification and quantitation of contaminants in the workplace environment. Traditionally, the major use of this technique has been for the analysis of free silica, talc and asbestos; however, because of the increasing need for the quantitation of chemical

compounds as opposed to elements, the importance of XRD in the analytical laboratory has grown considerably. This paper will reveiw the application of XRD to the analysis of dust contaminants collected on membrane filters. The advantages and disadvantages of the internal and substrate (external) standard procedures are also discussed. The latter method, currently in use at NIOSH, is discussed in detail emphasizing the use of the silver membrane filter for re-deposition of the dust sample and for the correction of matrix absorption. This analytical procedure has been applied to the analysis of free silica, zinc oxide, zirconium oxide and chrysotile.

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