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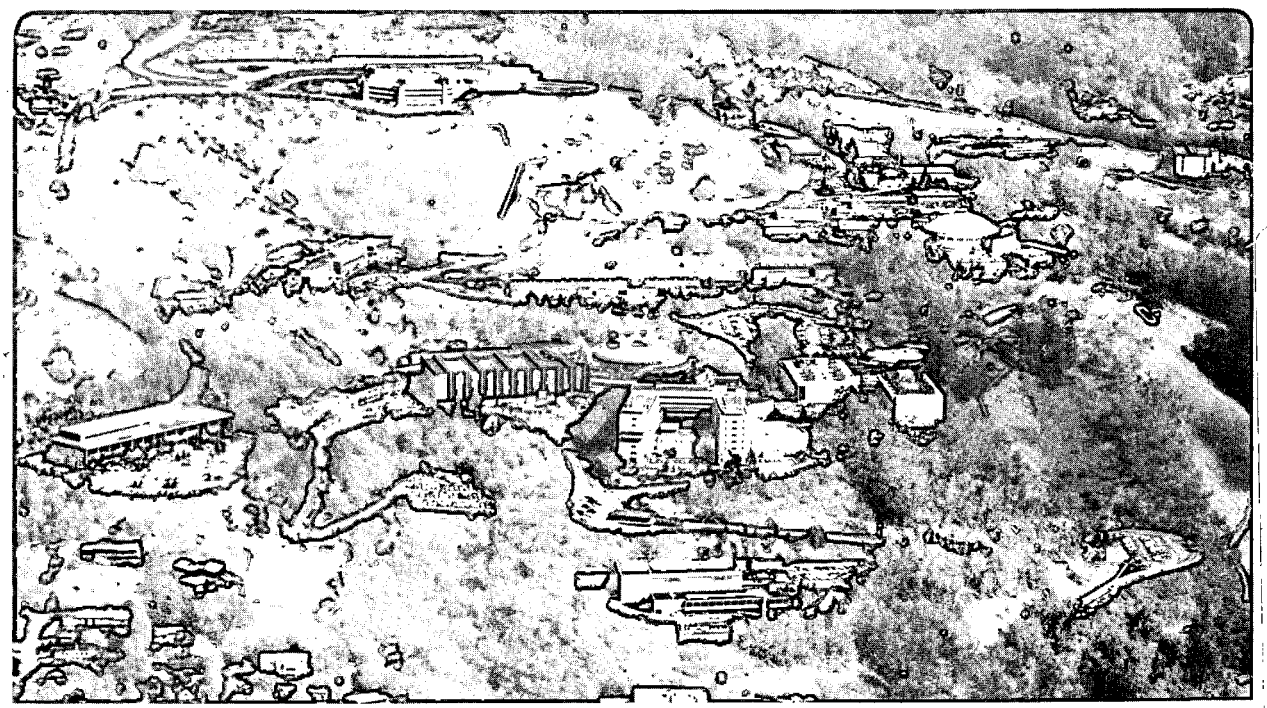

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DEVELOPMENT OF A CALIBRATION METHOD FOR QUANTITATIVE X-RAY POWDER DIFFRACTION OF SIZE-SEGREGATED AEROSOLS

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INTRODUCTION

X-ray powder diffraction (XPD) is an important tool for the chemical characterization of atmospheric aerosol samples particularly when combined with elemental analysis obtained from X-ray fluorescence (XRF) measurements of the same specimen. Aerosol samples obtained in typical monitoring studies consist of thin, uniform deposits of particles corresponding to a known size distribution with aerodynamic equivalent diameters of less than 10 microns.[1] This is an ideal form for X-ray fluorescence analysis since absorption and matrix enhancement effects are minimized. However, the ability to perform quantitative X-ray powder diffraction without the use of internal standards is restricted by several factors which affect the linearity of response between diffracted intensity and sample concentration. In addition to the normal photoelectric absorption due to passage of the X-rays through the sample, XPD intensities can be affected by primary and secondary extinction due to diffraction of the incident beam[2], particle size effects[3-7] and preferred orientation of particles.[8] Although no satisfactory, analytical solution to this class of problems has been devised, several approaches have been adopted for performing quantitative XPD for the case of relatively thick samples.[9-11]

Cline and Snyder have reported that X-ray powder diffraction intensities are strongly influenced by the crystallite sizes of the phases present.[3-5] These same authors have described the effects of extinction on X-ray powder diffraction intensities for smaller particles, particularly for the 5 μm to 10 μm particle size range. Nakamura has reported the quantitative determination of calcium sulfate and calcium carbonate in airborne dusts.[6] To reduce errors due to crystallite size, the standards were ground until the half-width of the diffraction line employed for the determination was identical to that of the dust samples. Kohyama has suggested that, to minimize the effects of the difference of crystallite size between the standard and the

sample, X-ray powder diffraction intensity must be measured by peak area rather than peak height.[7]

The present study focuses on evaluating potential problems associated with XPD analysis of thin layers of particles collected on membrane filters such as would be the case for atmospheric aerosol samples and certain other classes of environmental and geological samples. These samples differ from those previously investigated in quantitative XPD in that absorption effects are minimized but particle size and preferential alignment artifacts may be more significant. The current U.S. Environmental Protection Agency (EPA) aerosol monitoring programs emphasize the use of sampling devices which collect size-segregated aerosols of aerodynamic equivalent diameter less than 10 μm.[1] The approach used in the present experiments is to prepare thin deposits of size-segregated particles and compare the results obtained by both XRF and XPD in order to determine the extent to which conventional thin film XRF calibration methods can be applied to quantitative XPD analysis.

PREPARATION OF STANDARDS

The preparation of standards with known particle size distribution can achieved by utilizing the size dependence of particle sedimentation in viscous liquid or gaseous media. Smith et al. have described a spray drying process used to prepare spherical particles that minimize preferred orientation in powders.[8] Initially, the materials are prepared for spray drying by grinding and then either Stokes Law settling or sieving is employed. Particles between 1 μm and 10 μm are desired. Three to four grams of the fine powder are required. An organic binder is used in the suspension medium. Hard spherical particles in the 40 μm - 50 μm size range are produced and are used to obtain XPD patterns.

The present investigation employed a similar approach in which calculated particle settling velocities were used to establish the parameters for obtaining solutions which contained a known particle diameter range of specific minerals. To achieve these ends we required a fluid of relatively low density and viscosity. Since the eventual thin deposits were to be prepared by filtration, it was also desirable that the fluid would not wet the particles and yet evaporate relatively slowly so that thin deposits would not easily flake. For these experiments, isopropyl alcohol was selected as the fluid medium.

Theoretical

The mass, m (g), of spherical particles of diameter, d (cm), may be expressed as:

$$m = \frac{1}{6}\pi\rho_1 d^3 \qquad (1)$$

where ρ_1 is the density of the mineral particle (g/cm^3).

For a fluid of density ρ_2 and with a coefficient of viscosity η (g/sec*cm), the particle settling velocity V (cm/sec) may be expressed as:

$$V = \frac{1}{18} \frac{(\rho_2 - \rho_1)\, d^2 G}{\eta} (1 - \exp(-18\eta t/\rho_1 d^2)) \qquad (2)$$

where G is the acceleration of gravity (980 cm/sec^2) and t is time (sec).

Under most practical cases, the particle settling velocity is the terminal settling velocity attained after acceleration for a short period of time. Thus, the period of time required for all particles greater than a specific size to fall any given distance can be easily calculated.

Experimental

A three step approach was utilized to obtain solutions that contained suspended particles within a specific size range. In the first step, particles that were larger than the size range desired were removed via a settling process. During the second and the third steps, the vast majority of the particles that were smaller than the size range desired were drawn off, leaving particles that were theoretically within the specific size range.

Table 1.

Mineral	Density g/cm^3	Aerosol Diameter Size Range µm	Step 1 min.	Step 2 min.	Step 3 min.
Calcite	2.71	2 - 5	425	3150	3150
		7 - 10	105	260	260
		15 - 20	27	56	56
		25 - 30	12	20	20
Gypsum	2.32	2 - 5	480	3570	3570
		7 - 10	120	290	290
Quartz	2.62	2 - 5	435	3240	3240
		7 - 10	110	265	265
Alumina	3.97	2 - 5	330	2460	2460
		7 - 10	83	200	200

For the experiments undertaken, approximately 500 mg quantities of finely pulverized mineral matter were placed in 100 ml graduated glass cylinders 19 cm long. The cylinders were filled with 99 ml of isopropyl alcohol and thoroughly agitated by vigorous shaking. The walls of the cylinders were washed down with 1 ml of alcohol. Table 1 lists the settling intervals used to achieve segregation for specific particle size ranges for four minerals. After the settling interval shown in step 1, the top

80 ml (15.2 cm) of the solutions were carefully aliquoted and transferred to additional cylinders. This yielded solutions containing particles of sizes less than the listed maximum aerosol diameters. Additional 19 ml quantities of alcohol were added, and the solutions were vigorously agitated. Again, the walls of the cylinders were washed down with 1 ml of alcohol. After the settling intervals shown in step 2, the top 95 ml (17.3 cm) of the solutions were carefully aliquoted. The remaining 5 ml of the solutions were made up to 99 ml and the above process repeated to ensure a more thorough removal of the smaller particles. After an equivalent period of time the top 95 ml of the solutions were carefully aliquoted. The particles that were within the listed size ranges were either on the bottoms of the cylinders or in the remaining 5 ml of the solutions. A small fraction of particles less than the desired size range remained in the sample. Theoretically, the vast mass of the particles accumulated should fall within the listed size range.

Solutions with particles < 2 μm were obtained by combining the aliquots drawn off in steps 2 and 3 for the 2 μm - 5 μm case.

Table 2.

Mineral	Aerosol Diameter Size Range μm	Calculated Physical Cross Sections μm^2	Measured Mean Cross Sections μm^2
Quartz	< 2	< 1.7	3 ± 2
	2 - 5	2 - 10	7 ± 3
	7 - 10	20 - 41	21 ± 15
Calcite	< 2	< 1.6	0.9 ± 0.4
	2 - 5	2 - 10	5 ± 2
	7 - 10	20 - 40	24 ± 13
	15 - 20	90 - 160	91 ± 36
	25 - 30	250 - 360	246 ± 108

Scanning electron microscope (SEM) photographs were taken of deposits prepared from solutions of suspended particles for both quartz and calcite. Table 2 lists the aerosol diameters that our experiments were designed to realize during the particle size segregation separations. The associated physical cross sections were calculated assuming spherical particles of appropriate density. SEM photographs of deposits prepared from solutions containing suspended particles of calcite for five different size ranges are shown in Figure 1. The particles were not spherical but irregular in shape. The measured mean cross sections shown in Table 2 were calculated from data obtained from the figures using the fraction of particles corresponding to more than 90% of total mass. The shapes of the particles suggest that the true mass of the particles could easily be greater than one would calculate for spherical particles of equivalent cross sections. Nevertheless, the mean cross sections determined with the SEM are within reason of the calculated physical cross sections. These data clearly substantiate that we

obtained size segregated particles that were close to the size range for which the experiments were designed.

Standard samples were prepared by filtering the individual solutions on a volumetric basis to achieve a range of deposit loadings. Polytetrafluoroethylene (PTFE) filters were chosen as the substrata to be used to collect the size segregated particulate deposits. PTFE filters are superior to other membrane or fiber filters for quantitative XPD.[9-10] PTFE filters are of relatively low mass thickness and yield less scattered background than other filter media for XRF and XPD. Particles are collected on the surface and they yield good particle retention qualities for most filter loadings encountered. For our experiments, 37 mm PTFE filters (2 μm pore size) with a plastic support ring were used.

Dilute solutions of suspended particles were prepared for both quartz and gypsum from the initial solutions prepared. This allowed us to volumetrically measure smaller quantities of suspended particles. Thus, deposits could easily be prepared for a wider range of mass loadings. A glass fritted filtration apparatus that yielded a 2.4 cm diameter deposit was employed. Aliquots of suspended particle solutions were made up to 25 ml with isopropyl alcohol. A 2 cm high column of pure alcohol was poured in the filtration system followed by the 25 ml solution containing the suspended particles. The initial column of alcohol served to ensure uniform sample distribution. With slight vacuum, the particles were slowly filtered over a period of approximately 5 minutes. The deposits were mounted in plastic holders using metal support rings.

RESULTS AND DISCUSSION

The actual sample mass loadings realized were ascertained by using energy dispersive XRF.[11] Ti K radiation provided by a secondary target was used to excite X-rays from the sample. The intensity, I_j, of a characteristic X-ray line from an element j of concentration, m_j (g/cm^2), in a thin uniform deposit may be expressed:

$$I_j = K_j \, m_j \, Ab_j \tag{3}$$

where K_j is the excitation-detection efficiency of the X-ray system for the X-ray line from element j, and Ab_j is the absorption correction. The absorption correction factor for a homogeneous uniform deposit integrated over a mass thickness, m (g/cm^2), is expressed:

$$Ab_j = \frac{\mu m}{1\text{-}e^{-\mu m}} \tag{4}$$

The mass absorption coefficient term, μ(cm^2/g), is calculated by summing the contribution of each element and is correctly expressed:

$$\mu = \sum_{i=1}^{n} (\mu_e^i \csc \vartheta_1 + \mu_f^i \csc \vartheta_2)\, w_i \qquad (5)$$

where μ_e and μ_f are the total mass absorption coefficients of element i for the exciting and the fluorescent radiation, respectively; w_i is the weight fraction of element i; and ϑ_1 and ϑ_2 are the angles formed by the exciting and the fluorescent radiation with the surface of the sample. For very thin mass loadings, the absorption correction factor has a value of unity.

X-ray Fluorescence Results

We wanted to substantiate that the solutions could be used to prepare deposits of known mass loadings. XRF determinations were carried out in a helium atmosphere. Initial mass loading values were determined for each mineral deposit. Then, through an iterative process using equation 3 and X-ray mass absorption coefficient data from McMasters et al.[12], final values with absorption corrections were calculated. Shown in Table 3 are the results ascertained for deposits of quartz for the different particle size ranges. In order to minimize pipetting errors for the lighter loadings, a 10 ml volume of the original solution of suspended particles was diluted to 100 ml and used for all volumes listed that are less than 5.00 ml.

Table 3.

Aerosol Diam. Size Range µm	Volume of Orig. Sol. ml	Initial XRF Mass Loading µg/cm^2	Iterated Absorption Correction	Final XRF Mass Loading Determined µg/cm^2	Mass Load./ Volume (µg/cm^2)/ ml
< 2	5.00	49.7	1.024	50.9	10.2
	10.00	101.5	1.051	106.7	10.7
	20.00	182.9	1.098	200.9	10.4
	40.00	345.9	1.212	419.2	10.5
2 - 5	0.30	22.7	1.011	22.9	76.3
	0.60	45.0	1.022	46.0	76.7
	1.20	85.4	1.043	89.1	74.3
	2.50	175.1	1.094	191.6	76.6
	5.00	311.7	1.185	369.4	73.9
	10.00	527.8	1.387	732.1	73.2
	20.00	770.0	1.794	1381.4	69.0
7 - 10	0.30	14.4	1.007	14.5	48.3
	0.60	29.3	1.014	29.7	49.5
	1.20	57.2	1.028	58.8	49.0
	2.50	117.7	1.060	124.8	49.9
	5.00	216.5	1.119	242.3	48.5
	10.00	412.3	1.268	522.8	52.3
	20.00	653.2	1.560	1019.0	51.0

The relatively small deviations realized in the mass loadings per ml of original solution is fortuitous for the two

larger particle size ranges. If one assumed that the particles were spheres, simple calculations would show that a complete monolayer of coverage would not have been realized for most mass loadings determined. The SEM photographs suggest that the particles are oblong. Thus, complete monolayer coverage could be realized with lighter mass loadings than calculated for spheres. The samples used in the analysis were also inspected by optical microscopy to determine if coverage were less than a monolayer for the large particle, low mass loading case. Although quantitative measurements were difficult, the particle size and fractional coverage were consistent with the predicted particle size distribution. The excellent internal consistency of the XRF results indicates that the thin-layer absorption corrections constitute an excellent approximation for the intermediate particle size case which applies here.

Minor corrections to the S determinations were made for enhancement effects caused by Ca K X-rays for gypsum deposits of mass loadings greater than 200 $\mu g/cm^2$. Two gypsum mass loading values were calculated for each deposit using both the Ca and the S results. A standard deviation of only 2% was realized between the paired mass loading values.

Table 4 lists the range of mass loadings prepared for quartz, gypsum and alumina deposits. Also shown are the mean values and standard deviations ascertained for the mass loadings (ug/cm^2) realized per ml of solution. The small deviations realized, typically 3%, verify that solutions with suspended particles can be quantitatively aliquoted to prepare deposits across a wide dynamic range of known mass loadings. Results are not shown in Table 4 for calcite, as calcite deposits were prepared for samples collected from five sites throughout three countries.

Table 4.

Mineral	No. of Deposits	Particle Size Range µm	Range of Loadings $\mu g/cm^2$	Deposit Loadings ($\mu g/cm^2$)/ ml
Quartz	4	< 2	50 - 400	10.3 ± 0.3
	7	2 - 5	20 - 1400	74.3 ± 2.7
	7	7 - 10	15 - 1000	49.8 ± 1.5
Gypsum	3	< 2	15 - 70	1.63 ± 0.05
	8	2 - 5	15 - 2000	50.9 ± 0.9
	7	7 - 10	10 - 750	18.4 ± 0.4
Alumina	3	< 2	14 - 28	1.41 ± 0.02
	4	2 - 5	40 - 160	8.02 ± 0.29
	4	7 - 10	65 - 250	12.7 ± 0.3

A series of thin deposits for a single mineral such as these could easily be used to determine the excitation-detection efficiency factor, K_j, of an X-ray fluorescence spectrometer system for a mineral element. If one were to use an incorrect value

for K_j, the determined deposit loadings per ml of solution would not be constant. This is due to the fact that as the deposit mass loading values increase, the absorption corrections calculated by equation 4 correspondingly have an increased effect on the final mass loadings determined.

To further test the capability of quantitatively using solutions with suspended particles, quadruplicate mixed mineral deposits that contained alumina, quartz, and gypsum were prepared for two particle size ranges. The results ascertained are listed in Table 5. The XRF determined values include corrections for matrix absorption which varied from 2 to 10%. The true values listed are the values calculated from the volumes of the solutions aliquoted for the individual minerals. These results clearly illustrate that mixed mineral standard deposits can easily be prepared.

Table 5.

Particle Size Range µm		Alumina µg/cm^2	Silica µg/cm^2	SO3 µg/cm^2	CaO µg/cm^2
2-5	XRF	6.3 ± 0.4	73.4 ± 1.0	23.8 ± 0.4	16.4 ± 0.2
	True	8.0 ± 0.3	74.3 ± 2.7	23.7 ± 0.6	16.6 ± 0.4
7-10	XRF	13.3 ± 1.1	48.5 ± 1.0	8.0 ± 0.2	5.6 ± 0.1
	True	12.7 ± 0.3	49.8 ± 1.5	8.6 ± 0.2	6.0 ± 0.1

X-ray Diffraction Results

The realization of quantitative XPD analysis requires that a known relationship be established between the measured intensity of selected diffraction line(s) in the diffractogram and the amount of material in a thin, uniform sample deposit. For most analytical methods, such relationships are achieved either by reducing the magnitude of processes affecting the linearity of response or by applying mathematical corrections during data analysis. In the case of XRF analysis of thin films, absorption effects are reduced and simple absorption calculations can be used to achieve quantitative analysis without internal standards. In the case of XPD, similar methods can be used to correct for photoelectric absorption.

There exists other mechanisms inherent in the XPD process which affect linearity of response and which are less amenable to solution. These include primary and secondary extinction of the primary beam due to diffraction which occurs for crystallites which are aligned at a critical angle with respect to the incident beam. Primary extinction refers to the reduction in penetration depth of X-rays into a particular single crystal for those X-rays in the beam which satisfy the Bragg condition. The effective penetration depth of these X-rays can be reduced by several orders of magnitude with respect to conventional photoelectric penetration depths. The thin depth of penetration associated with this absorption process, and the difficulty in

constructing satisfactory models with which to apply corrections, contribute substantially to the difficulty of performing quantitative XPD.

Secondary extinction describes the effective shielding of particles within the sample which are shielded by diffracting crystallites nearer the surface. This effect is reduced for thin samples with coverages of a few monolayers. On the other hand, the uniformity of XPD response requires an isotropic ensemble of particle orientations in the sample and a sufficient population of particles at any particular angle to give a statistically significant diffracted intensity. Lightly loaded samples acquired from large-particle size distributions can be prone to nonlinearities arising from failure to satisfy either of these criteria.

In order to determine the limitation which these effects impose on realistic sample loadings, we have used the deposits previously described that were calibrated by quantitative XRF. The X-ray diffraction patterns were acquired for all mineral deposits using a diffractometer designed by Thompson et al.[13] This system employed a multielement position sensitive detector which had the advantage not only of increasing the system sensitivity for thin samples, but also reduced the adverse effect of insufficient particle statistics by observing each Bragg reflection at a series of sample orientations. Cu K-alpha radiation (λ = 1.542 Å) was employed. Through the use of programmed vertical slits, a constant beam spot size of 15 mm x 10 mm was maintained for the scan across a 2-theta range of 20 to 50 degrees. The Bragg equation is:

$$n\lambda = 2d \sin \vartheta \tag{6}$$

where d(Å) is the spacing between the Bragg reflecting atomic planes and ϑ is the angle which the incidence radiation makes with the planes. Measurements were carried out on all of the deposits listed in Table 4. Reflections from a d-spacing range of 4.4 Å to 1.8 Å were observed. Table 6 lists the integrated intensities determined for the most intense diffraction lines measured for quartz, gypsum, and alumina. The diffraction intensities measured have been adjusted for X-ray absorption using equation 7:

$$I_c = I_m \frac{2\mu m \csc \vartheta}{1-e^{-2\mu m \csc \vartheta}} \tag{7}$$

where I_c and I_m are the corrected and the measured X-ray diffraction intensities, respectively, and μ (cm^2/g) is the mass absorption coefficient of the mineral for Cu K-alpha radiation, and m (g/cm^2) is the mass loading determined by XRF.

The results in Table 6 clearly illustrate that the X-ray powder intensities are strongly influenced by the size of the crystalline mineral particles for the size range of < 2 µm to 10 µm. Thus, it is imperative that particle size be taken into consideration when one makes quantitative XPD determinations for aerosols collected on thin filters. The data in Table 6 also

shows that the diffraction intensities per $\mu g/cm^2$ of loading were relatively constant for any given mineral particle size range. Thus, it can be assumed that preferred orientation was not of major consideration for the above deposits. If preferred orientation prevailed, the effects would have been observed in the diffracted intensities measured for the lighter sample loadings for the largest particle size range. In such a case, a random orientation distribution of the crystalline particles would not have existed.

Table 6.

Mineral	Particle Size Range µm	hkl	d Å	Intensity/ ($\mu g/cm^2$)
Quartz	< 2	101	3.34	2.47 ± .07
	2 - 5			2.87 ± .17
	7 - 10			3.71 ± .40
Gypsum	< 2	141	3.06	0.85 ± .06
	2 - 5			0.90 ± .03
	7 - 10			1.14 ± .07
Alumina	< 2	113	2.09	0.66 ± .01
	2 - 5			0.82 ± .04
	7 - 10			1.09 ± .05

Similar determinations were carried out for calcite samples collected from five sites within three countries. Three deposits of varying mass loadings were prepared for each of the individual particle size ranges studied for the different sources. The mass loadings prepared were determined as described above by XRF. Initially, we planned to use the X-ray powder diffraction intensities for the most intense reflection (hkl = 104). However, preferred orientation effects were observed, particularly for the larger particle size fractions examined. The effects were most pronounced for the lighter sample loadings. Consequently, we chose a less intense reflection (hkl = 202) with a d spacing of 2.095 Å for which preferred orientation was not of serious consideration. The results determined are shown in Table 7.

As shown, the XPD intensities determined were not constant for calcite samples collected from the different sites. The deposits prepared from calcite samples collected at Joplin Co., Missouri and Poona, India had the largest relative intensity deviations from the mean values for all five sites. The mean cross sections measured for size segregated samples of calcite collected from Joplin Co., Missouri are listed in Table 2. Corresponding values were determined with the SEM for the three smaller particle size ranges prepared for calcite from Poona, India. The values determined (μm^2) were 2.4 ± 0.6, 3.5 ± 1.6, and 33 ± 12, respectively. These results reflect that XPD intensities realized for the same particle size range of any

given mineral collected from different geographical regions can vary at least 10%.

Table 7.

Particle Size Range (μm)	< 2	2 - 5	7 - 10	15 - 20	25 - 30
Source	XPD Intensity "202" / (μg/cm^2)				
Crestmore, California	0.28 ± 0.01	0.31 ± 0.02	0.34 ± 0.01		
Joplin Co., Missouri	0.31 ± 0.02	0.34 ± 0.01	0.37 ± 0.02	0.39 ± 0.02	0.43 ± 0.02
Calaveras Co., California	0.27 ± 0.04	0.32 ± 0.01	0.36 ± 0.01		
Guanajuato, Mexico	0.27 ± 0.02	0.33 ± 0.03	0.34 ± 0.05		
Poona, India	0.23 ± 0.01	0.27 ± 0.01	0.31 ± 0.01		
Mean Value	0.27 ± 0.03	0.31 ± 0.03	0.34 ± 0.02		

DISCUSSION

Our results demonstrate that calculated particle settling velocities can be used as a tool in the preparation of thin deposits of size-segregated particulate standards. The correspondence between calculated and experimental size distributions of prepared standards has been verified using both scanning electron microscopy and optical microscopy. Energy dispersive X-ray fluorescence analysis has established the quantitative relationship between volumetric measurements and deposited mass of the particle standards for both single and multiple mineral standards prepared from several independently calibrated solutions.

Standards of selected minerals were used in an experimental study directed toward understanding the limitations of quantitative chemical analysis of thin deposits using X-ray powder diffraction. Our results clearly indicate that measured diffraction intensities are strongly influenced by the size distribution of the crystalline particles and to some degree by the source of the mineral particles. For the particle size ranges studied, the discrepancy between measured and predicted intensities increased with increasing particle size. This is opposite to the effect previously observed using thicker standards and may be attributed to the difference in relative magnitude of primary and secondary extinction experienced in the two types of samples.

Nevertheless, the results indicate that quantitative XPD analysis of thin particle deposits can be achieved within reasonable limits of precision using our method of standardization provided the particle size distribution is known. For most current aerosol analysis programs, the aerodynamic size distribution of the collected particles is known, with a maximum cutoff diameter of 10 μm. For particle distributions peaked below this cutoff, the corrections due to primary and secondary extinction are reduced and systematic errors of 10% or less can be achieved. This is more than adequate to measure the relative contributions of individual chemical species to the total sample composition.

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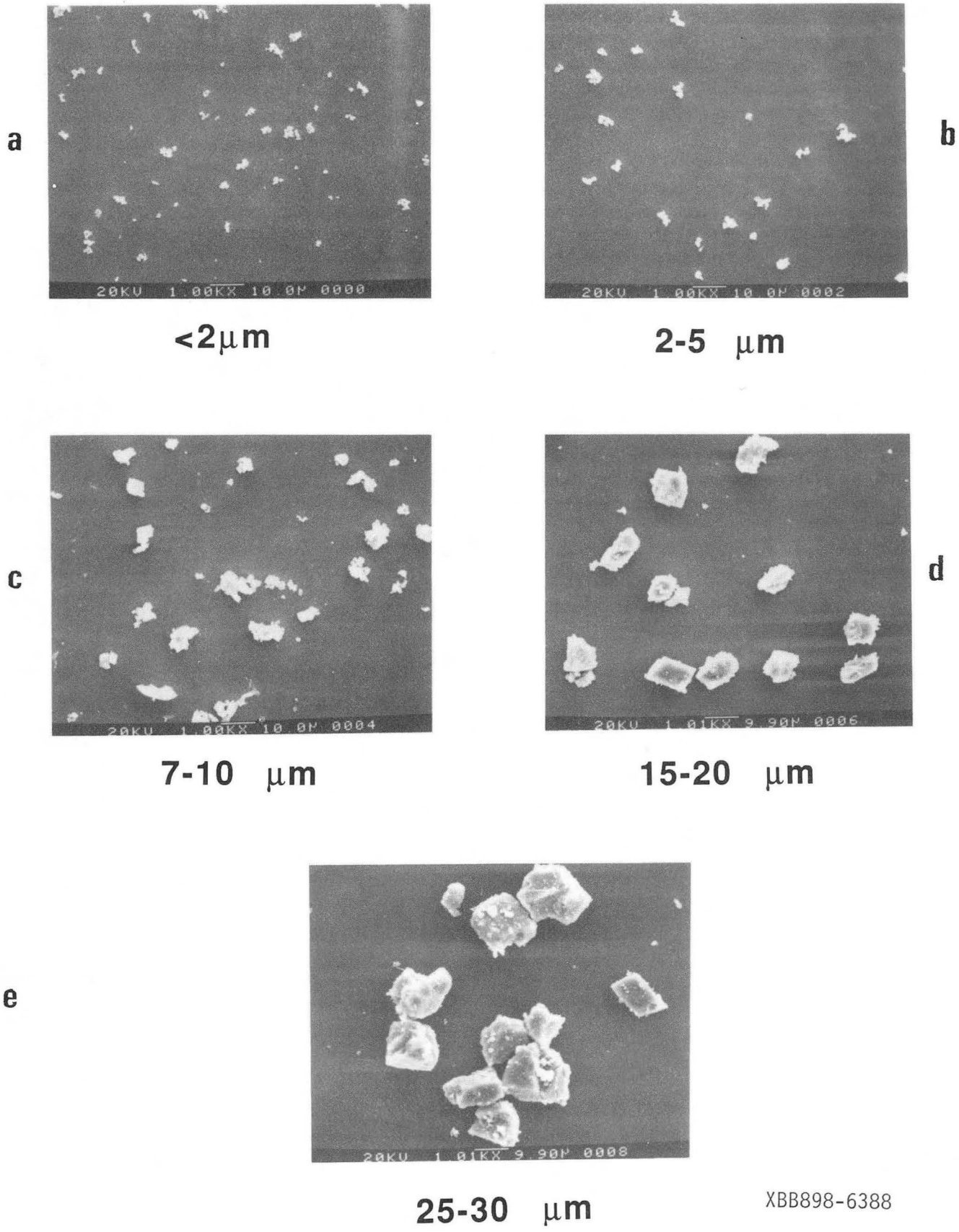

Fig. 1 SEM photograph of calcite particles for five different size ranges; a) < 2 µm, b) 2 µm - 5 µm, c) 7 µm - 10 µm, d) 15 µm - 20 µm, e) 25 µm - 30 µm.

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