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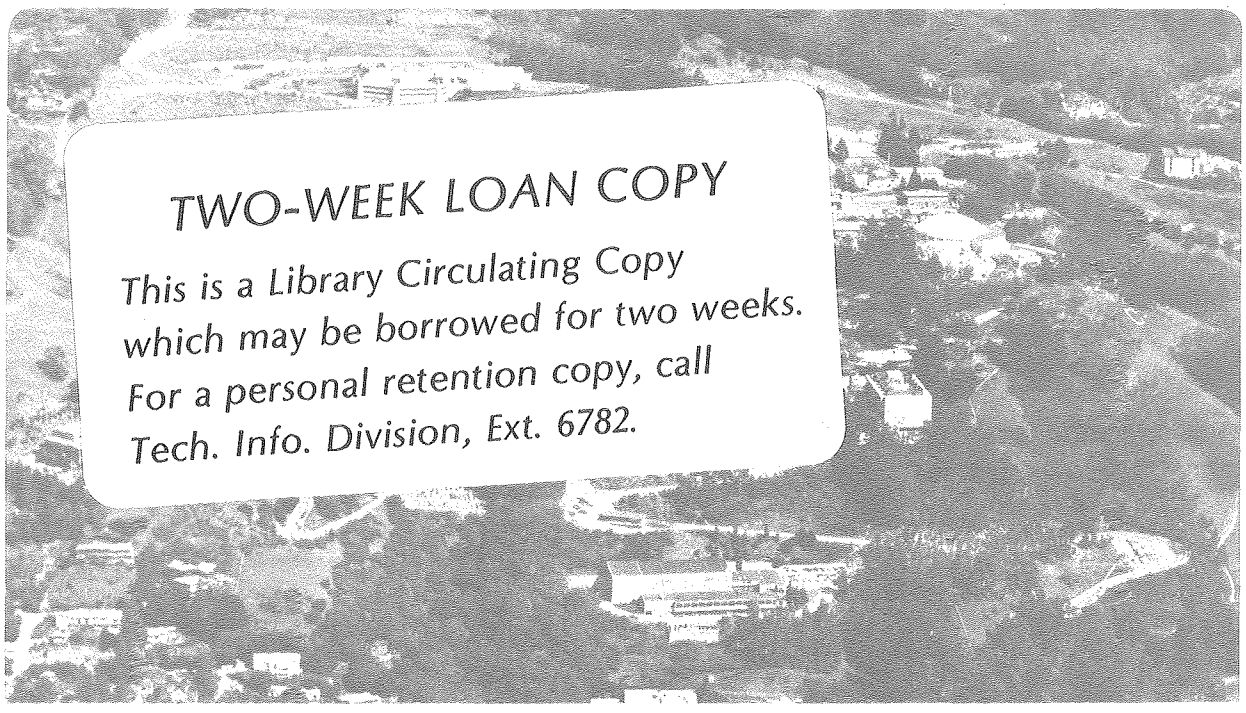


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# Line Broadening Effects In X-Ray Powder Diffraction Analysis Of Air Particulates*

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**On leave from Department of Physics, Western Australian Institute of Technology, Bentley, Western Australia.

# Line Broadening Effects In X-Ray Powder Diffraction Analysis of Air Particulates*

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## ABSTRACT

Measurements of the FWHM profile widths for the <200> x-ray powder diffraction line of synthetic $(NH_4)_2SO_4$ samples of specific particle size has shown that the FWHM contribution due to particle size is dominated by instrumental factors for the size range considered, 5.0μm down to 0.1μm. Given the size distributions typically observed in urban aerosol, particle size effects should not cause troublesome smearing of the x-ray powder diffraction lines unless the particles are formed from component single crystal domains of size substantially below 0.1μm.

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## INTRODUCTION

X-ray powder diffraction (XPD) analysis of air particulates is a technique with considerable potential for routinely identifying and subsequently estimating the levels of crystalline compounds in filtered air samples. Recent XPD studies of ambient air samples (Brosset et al, 1975; Biggins and Harrison, 1979a-c; O'Connor and Jaklevic, 1979a) have clearly shown the presence of compounds of anthropogenic and natural origins. Davis et al (1977,78) have investigated various aspects of XPD quantitative analysis. In view of the success achieved in qualitative studies, it appears likely that quantitative results will be obtained routinely in the near future. It is therefore important to critically examine XPD analytical procedures to determine the general validity of results obtained. Various sources of systematic error (e.g., preferred orientation, presence of amorphous material, line broadening, absorption effects) require detailed study before the results of both qualitative and quantitative studies can be fully accepted. In this paper we examine the line broadening effects which may occur with small particles.

Line broadening in powder diffraction, the theory of which is outlined in the following section, refers to the inverse relationship between particle size and diffraction line width which results in progressive smearing of the pattern lines at sub-micron levels. As the limit of zero particle size is approached, the diffraction lines will progressively merge into the pattern background.

We pay particular attention to samples deposited on membrane filter pairs by dichotomous air sampling and subsequently analysed by the x-ray powder diffractometry (XPDFT) technique. XPDFT is being developed as one of a growing list of routine procedures (β-ray attenuation, x-ray fluorescence analysis, extended fine structure absorption spectroscopy) which can be performed on the same filter (Goulding et al, 1976; Jaklevic et al, 1976;1979; Loo et al, 1979). The dichotomous samples divides the collected material into fine (<2.4μm) and coarse (2.4μm - 20μm) fractions which deposit on twin membrane filters. The 2.4μm cut-point mainly divides the material into the smaller particles coming from anthropogenic sources and the larger category from natural sources. Therefore in the context of this study, we have considered typical particle size distributions of anthropogenic particles in ambient air as providing circumstances in which line broadening is most likely to be encountered. The particulate material selected for analysis was $(NH_4)_2SO_4$ in the mineral form mascagnite.

It is well known that the typical urban aerosol consists of a bimodal distribution with the anthropogenic materials in the accummulation mode with mass median diameter at approximately 0.3μm, and that the course particle mode has a median diameter of 3μm, the minimum between the two modes occurring at about 2.5μm (Whitby, 1978). Data on anthropogenic particle size distributions for particular crystalline species is virtually non-existent. However it is possible to infer data from other measurements on sized samples, for example using mass and elemental data. Wagman et al (1967), in a study of urban sulphate aerosol in four cities found geometric mass mean diameters (GMMD) in the range of 0.4 - 0.5μm with small but significant portions extending below 0.1μm. In

similar analyses of the chemically related ammonium ion concentration, Lee and Patterson (1969) obtained similar distributions with GMMD's ranging 0.3 - 0.4μm. Lee et al (1972) in an extensive survey of size distributions for trace metal components obtained similar data for Pb, the most significant metal in urban air, and for other elements. Generalising on the basis of these data , we can conclude that the particle distributions have a GMMD in the range 0.1 - 1μm and that a minor fraction of the material is in the sub-0.1μm category.

In order to assess the significance, if at all, of line broadening arising from the various portions of the size distribution, synthetic samples of $(NH_4)_2SO_4$ have been prepared with aerosol generation equipment which provides highly precise control over particle size. The synthetic samples and several air-filtered samples known to be rich in $(NH_4)_2SO_4$ were examined by XPDFT.

## DIFFRACTION LINE BROADENING

The theory of diffraction line widths has been reviewed by Klug and Alexander (1974). There are three preferred means of representing diffraction line width, the full width at half maximum (FWHM), the integral breadth (IB), and the peak variance. The FWHM approach is usually employed to specify the widths of observed peaks, and the other procedures provide more mathematically tractable estimates. The IB estimate is closely related to FWHM being the width of an equivalent rectangle which has the same area and peak height as the observed profile. The component of IB due to small particle broadening can be represented by the Scherrer formula,

$$\beta = \frac{K\lambda}{L \cos \theta} \text{ radians}$$

where $\lambda$ is the radiation wavelength, L the mean dimension of the crystallites in the sample, $\theta$ the Bragg angle of the line, and K a constant approximately equal to unity and related to the crystallite shape and to the way in which $\beta$ and L are defined.

In practical terms, the significance of small particle broadening depends on the relative contributions of $\beta$ and the instrumental broadening factors as the latter normally dominate the diffraction line width. The $\beta$ values obtained from the Scherrer formula for various particle sizes are given in Table 1 for typical values of $\lambda$ (1.54 Å) and $\theta$ ($5^\circ$ - $25^\circ$). Also included in the tables for purposes of comparison are values of FWHM derived from diffraction patterns of St. Louis, fine-particle, sulphate aerosol samples (O'Connor and Jaklevic, 1979a). If we set $\beta = 0.05^\circ$ as a nominal level above which small particle broadening becomes noticeable, the formula predicts that this limit is approached as L nears 0.1μm and that for 0.01μm particles the lines may become severely smeared.

Some caution must be exercised in applying the Scherrer formula to air particulates as the quantity L is not necessarily synonynous with the concept of particle size as used in atmospheric science. The formula applies to single crystal (i.e., crystallographically ordered) particles whereas discrete air particulates may comprise an aggregrate of single crystals. Therefore the Scherner formula provides a lower limit for the small particle broadening contributions to the total profile, and accordingly the estimates in Table 1 could be lower limits. As the broadening effect may well be more pronounced than is indicated by

theory, the importance of experimental measurement of diffraction line widths is clearly underlined.

## EXPERIMENTAL

Synthetic samples were prepared by condensing $(NH_4)_2SO_4$ droplets of known particle size and concentration onto tetrafluorethylene membrane filters (unbacked TEFLON,* nominal 1μm pore size, mass/area ≃ 1 mg/cm$^2$). A Berglund-Liu monodisperse liquid droplet generator was used to generate sample sets of particle size 1 μm and 5 μm, the values being computed from the instrumental settings and subsequently verified by scanning electron microscopy of several samples. As the monodisperse generator cannot be readily used to prepare sub-micron samples, a second aerosol generation instrument was used to generate smaller particles. A Model 3076 Constant Output Atomiser (Thermosystems, Inc.) was adjusted to generate polydisperse $(NH_4)_2SO_4$ droplets of mean size 2.0 μm which produced solid particles of mean size 0.1 μm. It was not feasible to produce substantially smaller particles. For each of the three sample size categories, a set of samples was prepared covering the concentration range 5 - 50 μg/cm$^2$.

Diffraction data were generated with a Norelco powder diffractometer as detailed by O'Connor and Jaklevic (1979b), the principal details being as

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follows. The x-ray source was a Cu-anode x-ray tube of focal spot dimensions 0.1 x 1.0 $cm^2$, with a take-off angle of 3°, and driven at 40kV and 20 mA with a full-wave power supply. The diffracted beam was filtered with a 7.4 μm Ni foil and measured with a Xe proportional chamber and associated 0.15 mm receiving slit. The peak chosen for profile analysis, that for the <200> diffraction line, was selected on the basis that it is the most intense of the well-resolved lines for $(NH_4)_2SO_4$. All samples were scanned by counting for 500s at each of 20 detector positions at intervals of 0.04° across the peak.

In preparing the diffraction data for profile analysis, plots of $(NH_4)_2SO_4$ diffraction peak integrated intensity versus sulfur concentration (the latter being measured by energy dispersive x-ray spectrometry) were generated to verify that the solid particles deposited on the filters were essentially $(NH_4)_2SO_4$. The linearity of the plots pointed to the conclusion that other compounds, which might interfere with the $(NH_4)_2SO_4$ diffraction lines, were not produced in observable amounts. As a further check on possible interferences, the complete diffraction patterns for several patterns were carefully examined for evidence of other compounds.

The FWHM values of the recorded profiles were computed by iterative least squares with a Gaussian model and an associated linear background of variable slope. The estimated standard deviations associated with the FHNM set were derived in the conventional manner from the inverse of the normal equations.

## RESULTS AND DISCUSSION

The FWHM values, the estimated standard deviations, and the means for each size are given in Table 2. The results clearly show that only marginal broadening effects were observed in the experiment and that the effects were not as pronounced as had been indicated by the Scherrer formula.

The 0.1μm mean FWHM, 0.18°, is 0.020° greater than the value for the 1.0 μm samples (the difference representing 2.9 standard deviations) and 0.023° in excess of the value for 5.0 μm samples (3.3 standard deviations). On this basis it appears that the profiles for all three sizes are dominated by instrumental factors and that there may be some broadening at 1.0 μm. However it should be emphasized that the broadening is trivial in practical terms. According to the Scherrer formula the line should broaden by 0.01° as the particle size is reduced from 5.0 to 1.0 μm and by a further 0.08° as the size is further reduced to 0.1μm. The observed profiles for 0.1 μm particle therefore indicate that the Scherrer formula overestimates the line broadening due to particle size. For this reason the predicted value of 0.89° for $10^{-2}$μm particles may substantially exceed that observed in practice.

Although the results suggest that particle-size induced line broadening should not assume any importance in the powder diffraction analysis of air particulates, it should be appreciated that particles comprising an assembly of single crystal domains will show pronounced line broadening if the domains are smaller than, say, 0.01 μm. Thus it is possible that a compound which occurs as polycrystalline particulates can be undetected

by XPD although present in significant amounts. This underlines the importance of performing research on the morphology of air particulates.

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## REFERENCES

Biggins P.D.E. and Harrison R.M. (1979a) Atmospheric chemistry of automotive lead Environ. Sci. Tech. 13, 558-565.

Biggins P.D.E. and Harrison R.M. (1979b) Characterization and classification of atmospheric sulfates J. Air Poll. Control Assoc. 29, 838-840.

Biggins P.D.E. and Harrison R.M. (1976c) The identification of specific chemical compounds in size-fractionated atmospheric particulates collected at roadside sites Atmos. Env. 13, 1213-1216.

Brosset C., Andreasson K., and Ferm M. (1975) The nature and possible origin of acid particles observed at the Swedish west coast, Atmos. Env. 9, 631-642.

Davis B.L. and Cho N. (1977). Theory and application of x-ray diffraction compund analysis to high-volume filter samples. Atmos. Env. 11, 73-85.

Davis B.L. (1978) Additional suggestions for x-ray quantitative analysis of high-volume filter samples. Atmos. Env. 12, 2403-2406.

Goulding F.S., Jaklevic J.M. and Loo B.W. (1978). Aerosol anlysis for regional air pollution study. U.S. Environmental Protection Agency Report No. EPA-600/4-78-034.

Jaklevic J.M., Landis D.A. and Goulding F.S. (1976). Energy dispersive x-ray fluorescence spectrometry used pulsed x-ray excitation. Adv. in X-ray Analysis 19, 253-265.

Klug H.P. and Alexander L.E. (1974) X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. Chapter 9. Wiley Interscience (2nd ed.).

Lee R.E., Goranson S.S., Enrione R.E. and Morgan G.B. (1972) The NASN cascade impactor network. Part II. Size distribution measurements of trace-metal components Environ. Sci. Tech. 6, 1025-1030.

Lee R.E. and Patterson R.K. (1969) Size determination of atmospheric phosphate, nitrate, chloride, and ammonium particulate in several urban areas. Atmos. Env. 3, 249-253.

Loo B.W., French W.R., Gatti R.C., Goulding F.S., Jaklevic J.M., Llacer J. and Thompson A.C. (1978). Large scale measurement of airborne particulate sulfur. Atmos. Env. 12, 759-771.

O.Connor B.H. and Jaklevic J.M. (1979a) Chemical analysis of ambient aerosol samples by x-ray powder diffractometry. Lawrence Berkeley Laboratory Report, LBL-9496.

O'Connor B.H. and Jaklevic J.M. (1979b) X-ray diffractometry of airborne particulates deposited on membrane filters. Lawrence Berkeley Laboratory Report, LBL-9041.

Wagman J. Lee, R.E. and Axt C.J. (1967) Influence of some atmospheric variables on the concentration and particle size distributions of sulphate in urban air Atmos Env. 1, 479-489.

Whitby K.T. (1978) The physical characteristics of sulfur aerosols. Atmos. Env. 12, 135-159.

Table 1. Integral line breadths according to the Scherrer formula and typical observed FWHM values for air samples.

| | β | | |
|---|---|---|---|
| L* | $\theta = 5^\circ$ | $\theta = 15^\circ$ | $\theta = 25^\circ$ |
| 10 μm | $0.89 \times 10^{-3}(^\circ)$ | $0.93 \times 10^{-3}(^\circ)$ | $0.97 \times 10^{-3}(^\circ)$ |
| 1 | $0.89 \times 10^{-2}$ | | |
| $10^{-1}$ | $0.89 \times 10^{-1}$ | | |
| $10^{-2}$ | 0.89 | | |
| FWHM** | $0.14^\circ$ | $0.16^\circ$ | $0.18^\circ$ |

*From Scherrer formula,

$$\beta = \frac{1.54 \times 10^{-4}}{L(\mu m) \times \cos\theta} \times 57.3^\circ$$

**Measured values from fine particle, sulphate, aerosol samples (O'Connor and Jaklevic, 1979a).

Table 2 FWHM values of profiles measured with $(NH_4)_2SO_4$ samples of known particle size.

| Particle Size | Loading | FWHM* | Mean FWHM* |
|---|---|---|---|
| 0.1 μm | 6.2μg | 0.171 (0.006)° | |
| | 7.4 | 0.181 (0.008) | |
| | 9.7 | 0.193 (0.009) | |
| | 49.1 | 0.173 (0.009) | 0.180 (0.004)° |
| 1.0 μm | 8.3 | 0.160 (0.006)° | |
| | 12.1 | 0.162 (0.008) | |
| | 13.7 | 0.154 (0.007) | |
| | 39.4 | 0.165 (0.006) | 0.160 (0.004)° |
| 5.0μm | 8.9 | 0.147 (0.009)° | |
| | 15.5 | 0.157 (0.005) | |
| | 25.2 | 0.162 (0.008) | |
| | 36.5 | 0.161 (0.008) | 0.157 (0.004)° |
| St. Louis air filter sample (fine fraction) | | | 0.164 (0.008)° |

*Standard deviations in parentheses.