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Author

O'Connor, B.H.

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DEPOSITED ON MEMBRANE FILTERS*

B. H. O'Connor and J. M. Jaklevic**

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 U.S.A.

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*Prepared for the U. S. Department of Energy
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**To whom all correspondence should be addressed.

X-RAY DIFFRACTOMETRY OF AIRBORNE PARTICULATES DEPOSITED ON MEMBRANE FILTERS**

B. H. O'Connor and J. M. Jaklevic*

ABSTRACT

Methods are considered for optimizing a conventional Bragg-Brentano x-ray powder diffractometer for the identification of crystalline phases in airborne particulates deposited on membrane filters. The instrumental parameters investigated include detector stepping increment and scan range, K_{β} filtration, and the incident beam divergence slit width. Sample-related factors such as substrate material (cellulose ester, polycarbonate and polytetrafluorethylene), off-axis displacement of the sample, and x-ray induced specimen degradation were also studied. Scan times for sample deposits of several hundred $\mu\text{g}/\text{cm}^2$ are in the vicinity of 24 hours with a 800W tube. These times may be reduced substantially by one or more of the following modifications: rotating anode or synchrotron radiation source, energy dispersive diffractometry, and Bragg-Brentano diffractometry with a position sensitive gas detector.

INTRODUCTION

The technology for the analysis of airborne particulates has progressed considerably in recent years through the use of dichotomous air samplers combined with energy dispersive x-ray fluorescence (XRF) and

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

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β -ray attenuation techniques for the measurement of elemental and mass loadings, respectively.¹⁻³ X-ray powder diffraction (XPD), although a potentially useful complementary tool for crystalline phase analysis of air particulates, has received relatively little attention due to the low sensitivity of conventional XPD procedures when applied to dilute specimens such as the thin, lightly loaded membranes acquired with modern air samplers. Notwithstanding the intensity problem, we emphasize in this report that conventional XPD can be used to provide useful chemical information for air particulates if the instrumental parameters are carefully optimized.

The most notable application of XPD for identifying crystalline phases in aerosol particulate samples is that of Brosset et al.⁴, in which the Guinier photographic method was used to analyze material scraped from air filters which had been loaded with particulate material at a Swedish air sampling station. The patterns revealed the presence of various sulphate compounds. In a similar unpublished study, we have found that Debye-Scherrer photography can also record diffraction patterns with particulates removed from a filter and mounted in a capillary. Although such photographic XPD analyses yield useful information, they suffer from the disadvantage that the filter medium is disturbed, and therefore the methods are in effect destructive. Further, the need for time-consuming sample preparation and subsequent film measurement.

[†]Reference to a company name or product name does not imply approval or recommendation of the product by the University of California or the United States Department of Energy to the exclusion of others that may be suitable.

makes photographic methods prohibitively labor intensive for the analysis of large numbers of samples.

In view of the deficiencies of photographic XPD, the direct measurement of air filters by x-ray powder diffractometry (XPDT) is a preferable strategy. The XPDT methods that have been used for this purpose involve two classes of filter media--1) relatively thick fiberglass or cellulose fiber filters in which a substantial portion of the particulate loading is deeply embedded in the body of the filter^{5,6}, and 2) membrane filter types (e.g., cellulose ester) in which the filter serves as a substrate. The main difficulty with thick filter analysis is the attenuation of radiation by the filter medium. For example, if the analyte is deposited uniformly throughout a cellulose air filter, $\text{CuK}\alpha$ radiation will be attenuated by about 40%. Therefore, the observed signal is weaker than in the corresponding thin film case. The reduction in signal to noise which arises in this way is further diminished by the more intense backgrounds observed with thick filters. This means that sample loadings must be employed at levels in excess of those for membrane filters.

Following the success enjoyed by XRF in thin filter analysis, it would appear that, with sufficiently long diffractometer analysis times, phases can be identified and their concentration estimated by conventional thin film calibration techniques.^{7,8} Currently the only routine application of XPD for airborne particulate analysis is that for α -quartz from mining and quarrying operations. Using a conventional diffractometer to analyze the most intense quartz diffraction line $\langle 111 \rangle$, it is possible to obtain a detection limit of several $\mu\text{g}/\text{cm}^2$ for a measurement time in the vicinity of five minutes.⁹

The motivation for the present study was to evaluate the potential of conventional Bragg-Brentano diffractometry with particular reference to the analysis of thin filter samples such as are obtained from modern dichotomous air samplers. Most of the samples used in the present study were acquired during the St. Louis Regional Air Pollution Study (RAPS) and have been analyzed by XRF for elemental composition. These filters are typically loaded with $100 \mu\text{g}/\text{cm}^2$ of material. The purpose of the following was to demonstrate the feasibility of performing qualitative phase analysis with particular emphasis on the following:

- (i) the optimization of instrumental parameters, and
- (ii) the relative merits of various membrane filter media.

SAMPLE FORMAT

The field samples examined in the study were selected from air samples collected during the period of 1975 to 1977 using automated dichotomous air samplers¹ operating continuously at $50 \ell \cdot \text{min}^{-1}$ over periods of 6 or 12 hours. The fine ($< 2.4 \mu\text{m}$ particle size) and coarse ($2.4\text{--}20 \mu\text{m}$) particles were deposited separately on twin $1.2 \mu\text{m}$ pore size cellulose ester (CE) membrane filters (Millipore type RAWP) of effective diameter 37 mm and mass/area $\approx 4 \text{ mg}/\text{cm}^2$. The filters are individually mounted in $50 \times 50 \times 2.5 \text{ mm}$ plastic holders which are designed to be carried in a standard 36-slide projector cartridge. Prior to XPD examination, the samples had been analyzed for mass and elemental loadings by β -ray attenuation and XRF, respectively.

The mass and elemental loadings provide an assessment of the importance of matrix absorption. If the samples comply with a suitable thinness criterion relation for x-ray absorption, then the diffraction line intensities can be related linearly to the concentration of the

appropriate crystalline phase. For the linearity to hold within 5%, the criterion can be given as $5 \times 10^{-2} \sin \theta / \mu$, where θ is the line Bragg angle and μ the mass attenuation coefficient ($\text{cm}^2 \cdot \text{g}^{-1}$) of the phase. If we assume for purposes of estimation that the fine and coarse fractions are predominantly $(\text{NH}_4)_2\text{SO}_4$ and SiO_2 , respectively, the corresponding limits for $\text{CuK}\alpha$ are 90 and 120 $\mu\text{g}/\text{cm}^2$ for the minimum Bragg angle utilized in the study (5°), and 430 and 570 $\mu\text{g}/\text{cm}^2$ for the maximum value (25°). On this basis, we may set 90 $\mu\text{g}/\text{cm}^2$ as the limit of infinite thinness for matrix-free quantitative analysis with peaks near the lower end of the scanning range, rising to 400 $\mu\text{g}/\text{cm}^2$ at the upper end. The attenuation due to matrix effects within the filter substrate were assumed negligible as the 4 mg/cm^2 cellulose ester substrate would attenuate $\text{CuK}\alpha$ radiation by 10% at maximum. The principal effect of the filter substrate on the measured intensity arises from the degradation in signal to noise ratio from coherent and incoherent scattering from the substrate. This limits the sensitivity of the method such that the choice of filter substrate is an important consideration.

Other membrane filter types considered in the study as alternatives to CE were polycarbonate (PC) and polytetrafluorethylene (PTFE). All three types are used extensively for air sampling in this laboratory and elsewhere. The technical specifications of the filters are listed in Table 1.

DIFFRACTOMETER SETTINGS

The measurements were performed with a Norelco powder diffractometer, and a Cu anode x-ray tube operated at 40 kV and 20mA with a half-wave generator. The tube had focal spot dimensions $0.1 \times 1.0 \text{ cm}^2$, a

take-off angle of 3° , and was fitted with a Ni filter to discriminate against the β -component of the spectrum. The quantum detector was a sealed Xe side-window proportional chamber operating at 1500V, and with a counting efficiency of 50% and resolution of 15% for CuK_α radiation. Pulses were processed with a conventional pre-amplifier/amplifier/SCA chain. The diffractogram was accumulated in a 1024 memory MCA operated in multi-scaling mode. The detector arm was driven by a stepping motor synchronized to the multi-scale advance.

Figure 1 shows the scans acquired over 80×1024 seconds (22.8 hours) for typical fine and course fraction samples collected in six hours at a St. Louis urban sampling site (Station 105). The data were measured with a detector stepping increment = 0.04° , a 1° divergence slit and matching anti-scatter slit, and a 0.15 mm receiving slit ($\Delta_{2\theta} = 0.05^\circ$). Note that the signal to noise ratio is far less than is usually the case in XPDT. However, these data were obtained after the instrument had been carefully aligned and following the optimization of various instrumental parameters as described in the following paragraphs. The problems of analyzing such thin samples are apparent and the necessity for improvements upon conventional technique is clearly illustrated.

Stepping Increment and Scan Range

It has generally been the practice in XPDT to closely match the stepping increment with the setting precision of the detector arm. On this basis, one of the stepping increments, 0.005, 0.01 or 0.02° , is often employed. While this practice tends to maximize the precision of Bragg angle determinations, it is not necessarily an efficient strategy as the uncertainty in peak position $\Delta_{2\theta}$ is dominated by the aperture of the divergence slit W according to $\Delta_{2\theta} = W/R$, where R is the radius of

the goniometer circle (170 mm for Norelco diffractometer). Ayers et al.¹⁰, in discussing the requirements of high speed pattern generation, proposed the extension of stepping increment beyond commonly used values. It was claimed that the step can be as large as 0.01° less than f.w.h.m. and still provide acceptable data if profile fitting procedures are used to sharpen the lines.

In this study we have adopted a slightly different approach by fixing the total measurement time and expanding the stepping increment to minimize the number of data points stored in the MCA while retaining adequate pattern resolution. This is an important consideration in mass survey studies such as the St. Louis RAPS where data storage rapidly becomes a major problem. We demonstrate here that a 1K MCA can be adequate for data acquisition. Fig. 2 shows the influence of stepping increment on the diffractogram with an 0.15 mm receiving slit for the prominent quartet of lines for $(\text{NH}_4)_2\text{SO}_4$, one of the principal compounds in sulfur-enriched urban aerosol. The lines ($\langle 202 \rangle$, $d = 3.14\text{\AA}$; $\langle 211 \rangle$, $d = 3.12$; $\langle 013 \rangle$, $d = 3.06$; and $\langle 020 \rangle$, $d = 2.998$) can be seen in Fig. 1 (fine fraction), in the vicinity of $2\theta = 29^\circ$, with the 3.14 and 3.12 $\text{\AA}$ lines only partially resolved. Note that pattern quality is maintained up to a stepping increment of 0.04° , and does not deteriorate markedly until the increment approaches 0.16° . We have chosen to use 0.04° in generating data for search/match identification procedures and have found this to be acceptable.

The point made above regarding the need to obtain only adequate resolution is especially relevant for survey studies such as the St. Louis RAPS. This is because in such studies the number of possible compounds is limited and therefore there is less need for d-spacing precision than is the case with general XPD work.

Clearly from Fig. 1 the peak intensities decrease to or near background level for $2\theta = 50^\circ$. This is also the case for 50 other patterns examined. On this basis, 50° is recommended as an effective upper limit ($d_{\min} = 1.82 \text{ \AA}$ for $\text{CuK}\alpha$) for work of this nature. The corresponding lower limit for an 0.04° increment and a 1K analyzer $\approx 10^\circ$ ($d_{\max} = 8.85 \text{ \AA}$). In the event that phases are anticipated with longer d-spacings (e.g., clay compounds), we would recommend a 0.05° increment and $2\theta_{\min} \approx 0^\circ$. The minimum d-spacing of $1.82 \text{ \AA}$ requires the exercise of considerable caution in phase identification work, although the potential hazards are very much reduced by the availability of elemental concentrations for the search/match operation. Generally we have found sufficient lines in the range $8.85 > d > 1.82 \text{ \AA}$ for the unambiguous identification of the compounds of interest. For example, there were 7 lines for SiO_2 (α -quartz), 9 for CaCO_3 (calcite), 7 for Fe_2O_3 (hematite), and 30 for $(\text{NH}_4)_2\text{SO}_4$ (mascagnite).

K_β -Filtration

The conventional practice in diffractometry with a Cu tube is to employ a $17 \mu\text{m}$ Ni filter to reduce the K_β -line 60-fold, corresponding to which there is a x2 reduction in the K_α pattern.¹¹ In view of the need to enhance pattern intensity, we have substantially reduced the thickness of the filter while keeping the β peaks barely below the limit of detection. If we denote (i) the unattenuated and attenuated K_α line intensities in total counts as I_α° and I_α , respectively, (ii) the unattenuated background as B_α° and (iii) the mass attenuation coefficients for K_α and K_β radiation as μ_α and μ_β , respectively, then at the limit of detection for the filtered K_β line according to the 3σ criterion,

$$\frac{I_\alpha}{I_\alpha^\circ} \approx \left(\frac{1}{12\sqrt{2}} \cdot \frac{I_\alpha^\circ}{\sqrt{B_\alpha^\circ}} \right)^{\frac{2\mu_\alpha}{\mu_\alpha - 2\mu_\beta}}$$

For the most intense line of $(\text{NH}_4)_2\text{SO}_4$ (see Fig 1), $I_\alpha^0 = 14900$ and $B_\alpha^0 = 27000$ for a point counting time of 80s. The formula above gives $I_\alpha/I_\alpha^0 = 0.74$ which requires $t = 7.4 \mu\text{m}$. This represents a gain of 48% in intensity relative to normal conditions.

An alternative to filtration is to use a pyrolytic graphite monochromator in the diffracted beam. The main purpose of this approach is to improve the signal to noise ratio by discriminating against fluorescent radiation emanating from the sample, and the elimination of the K_β component is an added bonus. Monochromatization is not an effective approach for material deposited on membrane filters as the graphite crystal has insufficient resolution to substantially reduce the main contributors to the background--those due to the filter material (see section below on sample-related factors). Only the component of the background due to the particulate sample can be reduced with graphite, and then only if the component is due to fluorescence, e.g., from Fe in the sample. If the background is reduced by factor k_B and a coherent peak by k_I , the index $\alpha(I)/I$ for the coherent intensity will increase when a monochromator is used unless

$$k_B < \frac{k_I^2(I+2B) - k_I I}{2B}$$

Considering the graphite monochromators currently in use, we may take $k_I = 0.5$ as a representative value. Then, in this case,

$$k_B < 0.25 - 0.125I/B$$

In the present study, the signal: noise ratio I/B lies in the range 0-1. Accordingly, we require that the maximum value of k_B should be in the range 0.125-0.25. This cannot be achieved with infinitely thin samples deposited on the membrane filter substrates such as considered in this study.

A further alternative would be to dispense with filtration and to use a Si(Li) detector in place of the gas counter. The energy resolution of present day Si(Li) detectors is more than adequate for K_B elimination.

Another strategy would be to use an iterative procedure to eliminate the β component numerically. This would require only a knowledge of the variation in peak profile with Bragg angle. The correction would be applied to the peaks in descending intensity order until the computed K_B corrections are negligible with respect to counting statistics.

Divergence Slit

The length L of specimen irradiated for a divergence angle α radians at Bragg angle θ is $\alpha R / \sin \theta$, where R is the radius of the goniometer circle. This results in a progressive reduction in sample coverage with Bragg angle when α is fixed. For $\alpha = 1^\circ$, the value employed for the Fig. 1 scans, the computed L reduces from 34 to 7 mm over the scan range $2\theta = 10-50^\circ$. Thus the 1° slit results in the loss of 66% of the available intensity at $2\theta = 30^\circ$ and 79% at $2\theta = 50^\circ$. The marked loss of intensity with increase in Bragg angle is especially undesirable as this is accompanied by an angularly-dependent loss in coherent signal intensity due to thermal motion effects. Accordingly, a fully optimized XPDT for thin film work should incorporate a continuously variable divergence slit, or a series of fixed slits, to provide broad sample coverage over

the entire scan. This is demonstrated in Fig. 3 which shows the effect of using a continuously variable slit.

SAMPLE RELATED FACTORS

Choice of Sample Substrate--Pattern Background

Fig. 4 compares the background profiles for three membrane filter types which were considered in the study--PTFE, PC and CE. All were run under identical conditions and equal counting times. Both CE and PC have an intense diffuse peak in the vicinity of $2\theta = 18^\circ$ which is also present in the PTFE pattern but as a relatively minor feature. The PTFE background is dominated by a set of sharp peaks which clearly show that its fabric has pronounced crystallinity. Other than these features, the background slopes are similar for the three cases and the count rates are in close agreement when normalized to unit mass/area.

For general survey studies of completely unknown samples, PTFE is the least suitable of the three filters due to the multiplicity of peaks extending over the entire range of measurement. However, this disadvantage may be largely overcome by applying background subtraction. Further, in cases where the number of crystalline phases is limited to a discrete list of compounds, identification will be possible even if background subtraction is not employed. Thus, with $(\text{NH}_4)_2\text{SO}_4$ deposited on PTFE, 14 of the 16 observed peaks are free from background interference. The diffuse peak for PC has such steep shoulders that it will seriously mask diffraction data in the range $4.7 < d < 5.7 \text{ \AA}$ unless background subtraction is performed. However, as in the case of PTFE, the interfering diffuse peak should not be of concern unless entirely

unknown samples are being analyzed. CE is the most suitable of the three for exploratory studies as its diffuse peak does not swamp diffraction lines (see Fig. 1). However, a serious disadvantage of CE is its increase in general background arising from its proportionately greater thickness.

Summarizing the preceding comments, the PTFE and PC filters considered are superior to CE in view of their lower mass/area values which results in proportionately lower background levels. Also, considering that the phases of interest in a given study are mainly predictable, the peaks in the background profiles for PTFE and PC filters are unlikely to interfere substantially with the diffraction peaks. The suitability of PTFE for diffraction analysis is an important finding as PTFE has become the preferred material for elemental and mass analysis of air particulates.

It is instructive to consider the factors responsible for the background features with a view to improving pattern definition. Basically, there are three mechanisms responsible for the observed features: Compton scatter, diffuse scatter due to short-range ordering of the membrane molecules, and diffraction lines caused by long-range ordering. As the Compton: coherent scattering cross-sections are in the ratio 1:2, both Compton and coherent scatter are important in terms of background formation.

Table 2 gives the shift in energy of the $\text{CuK}\alpha$ photons when Compton scattered through angle $2\theta = 10^\circ$ to 50° . Clearly, the Compton component cannot be eliminated by pulse height analysis with state-of-the-art detectors (approx. 150 eV resolution for Si(Li) detectors). Also, filtration cannot be used as the absorption edge discriminates against energies above the edge. The third possibility is crystal

monochromatization. If we take 20 eV as the target resolution value at the center of the scan ($2\theta=30^\circ$), we have from the expression $\Delta E/\Delta\lambda = 12.399 \cot\theta/\lambda$ (ΔE in keV, λ in Å) that the mosaic spread of the analyzing crystal should approximate to $2\theta = 0.04^\circ$. This is substantially below the range of mosaicities found in analyzing crystals (0.1-0.6°). In particular we note that the pyrolytic graphite crystals which are employed frequently in XPDT have a mosaic spread $\sim 0.6^\circ$ which does not permit removal of the Compton component.

The diffuse scatter peaks observed in all three patterns comprise coherent radiation from short-range ordering of the membrane molecules. Accordingly, it is impossible to eliminate this component by energy discrimination. This also applies to the series of sharply defined peaks associated with the PTFE background.

Specimen Displacement

In the ideal Bragg-Brentano case, the sample curvature should match the radius of the focusing circle given by $R/2 \sin\theta$. As the filters are mounted in rigid frames, it is virtually impossible to achieve this condition, and therefore the diffraction peaks broaden progressively with increase in Bragg angle. Given this circumstance, slight deviations in the surface of the filter from its assumed planarity are unlikely to cause a significant increase in the broadening.

The most serious source of error is that due to the displacement of the specimen plane from the goniometer axis. Displacement of the specimen plane by amount Δ_R results in a bias of the pattern $\Delta_{2\theta} = (2\Delta_R/R)\cos\theta$. This source of error can assume serious proportions with transparency slides of the type used in the present study. Variation in the thickness caused by molding irregularities on the

surface of the holder resulted in a mean value in $\Delta_R = 0.10$ mm for 25 samples, ranging from 2.30 to 2.50 mm; and a mean $\Delta_{2\theta} = 0.06^\circ$ for the range 10 to 50° . Systematic errors of this magnitude may invalidate the search/match procedure by moving the pattern beyond the error window normally assumed in searching. For example, in our investigation of particulate crystalline phases using the instrumental parameters for Fig. 1 of this study, the error window for $2\theta = 0.04^\circ$. Accordingly, the systematic error in 2θ caused by sample displacement had to be eliminated. This was accomplished by internally calibrating the 2θ -scale according to the positions of the intense lines from readily identifiable phases such as $(\text{NH}_4)_2\text{SO}_4$ in the fine fraction and SiO_2 in the coarse. However, we stress that this is a contingency measure, and that it will be more acceptable in the future to work with sample frames for which the variation in thickness is < 0.01 mm.

Specimen Degradation

A study by O'Connor et al.¹² of the degradation of urban air particulates during wavelength dispersive XRF (WDXRF) analysis established that the tendency of lead halide particles to break down spontaneously is enhanced by x-ray exposure. In that study, which was confined to the monitoring of Pb and Br levels, it was found that the level of Br in a sample typically reduces by 30% per 30 minutes of exposure (Siemens SRS1 spectrometer, Mo tube at 60kV and 40 mA). Therefore, it might be anticipated that significant compound breakdown might also occur over the long exposures reported in this study (~ 24 hours).

In checking for losses which occur during the course of the scan, we have performed an energy dispersive XRF (EDXRF) quantitative analysis prior to and after various XRD scans. In this regard, it should be

stressed that it has been found in this laboratory that the EDXRF gives negligible degradation relative to the losses reported for WDXRF, presumably because the radiation exposure is relatively small in EDXRF.

The only elements for which substantial and consistent losses were observed during 22 hour XPDFT scans were Br and Cl. For 12 fine fraction air samples, the Br losses ranged between 5 and 30%, and the Cl losses between 10 and 75%.

The effects found underline the need for caution when using XRD procedures to study the chemistry of lead halide compounds in the atmosphere. This point has not been made in the literature describing various XRD investigations of vehicular lead chemistry.

Clearly, the nature and extent of these Br and Cl losses should be investigated in more detail. Additionally, it would be desirable to employ more efficient XRD techniques so that sample irradiation can be substantially reduced (see following section).

IMPROVING DATA ACQUISITION RATES

While it has been demonstrated in this paper that useful diffraction patterns can be obtained by conventional Bragg-Brentano diffractometry with scans in the vicinity of 24 hours, data should be recorded at much faster rates in large scale studies. Various strategies might be adopted, including the use of a more intense x-ray source and/or a more efficient detection system.

The scanning times could be reduced to 5-10 hours using a 1800W x-ray tube in place of the 800W tube used to generate the patterns, and a further order of magnitude gain could be achieved with a rotating anode x-ray tube. The count rates would be in the vicinity of 5000 cps which is within the operational range of scintillation, gas proportional, and

semiconductor detectors. The much higher flux available with synchrotron radiation could virtually eliminate the data acquisition problem.

The detection efficiency could be improved by adopting an energy dispersive (ED) approach. ED diffractometry with tube generated radiation has been discussed frequently in the literature (e.g., refs. 13-15), but the technique has not been extensively used because the resolution limitations of ED detectors gives poorly resolved diffraction patterns. Typically the relative d-spacing uncertainties exceed the values in conventional diffractometry (CXRD) by a factor of two or so. This loss can assume major proportions when studying samples comprising multiple crystalline phases.

A second, and probably more attractive option is the use of a position sensitive gas detector. Recently, Gobel¹⁶ described a Bragg Brentano instrument in which data is obtained about x100 faster than in CXRD by scanning with a high pressure xenon-methane counter which can simultaneously measure 100 channels of information with the angular resolution matching that of CXRD.

CONCLUSION

It has been shown that x-ray diffraction patterns can be generated with airborne particulates deposited on membrane air filters using a conventional Bragg-Brentano diffractometer. Typically, after careful optimization of various instrumental factors, patterns can be generated with a 800W diffraction tube in about 24 hours if the sample concentration is in the vicinity of several hundred $\mu\text{g}/\text{cm}^2$. Data can be generated at much faster rates by various instrumental refinements, the most promising approach appearing to be the use of a position sensitive gas detector which offers a x100 greater improvement in data acquisition rate.

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	Cellulose Ester (CE)	Polycarbonate (PC)	Polytetrafluoroethylene (PTFE)
TYPE	Millipore (RAWP)	Nuclepore	Teflon (without backing)
PORE SIZE	1.2 μm (nominal)	0.1 μm (physical)	1 μm (nominal)
MASS/AREA	4-5 mg/cm^2	1 mg/cm^2	1 mg/cm^2
SUPPLIER	Millipore	Ghia Corporation Pleasanton, CA	Ghia Corporation Pleasanton, CA

TABLE 1. TECHNICAL DETAILS FOR MEMBRANE FILTERS

2θ	ΔE
10°	2 eV
20°	8
30°	17
40°	30
50°	45

TABLE 2. COMPTON ENERGY SHIFTS (ΔE) VERSUS SCATTERING ANGLE (2θ)

FIGURE CAPTIONS

- Fig. 1 Diffractograms recorded for typical heavily loaded St. Louis RAPS samples. Course and fine fraction samples loaded at 232 and 336 $\mu\text{g}/\text{cm}^2$, respectively, on CE filters (see Table 1). $\text{CuK}\alpha$ tube radiation generated at 40kV and 20 mA with half-wave generator; tube focal spot = $0.1 \times 1.0 \text{ cm}^2$, take-off angle = 3° , 8.4 μm Ni filter; 1° divergence slit and 0.15 mm receiving slit; step increment = 0.04° , 1024 steps with 80s counting time per step.
- Fig. 2 Influence of step size on pattern. Conditions, except step size and count per step, as for Fig. 1. Sample is the fine fraction of Fig. 1. Counting time per degree = 2000 seconds.
- Fig. 3 Results of simulation exercise to show enhancement of pattern with use of variable divergence slit to keep sample exposure independent of angle. Fixed slit scan as for fine fraction in Fig. 1. Counts for variable slit case obtained from fixed slit counts with scaling factor $\text{cosec}\theta$ where θ is the Bragg angle.
- Fig. 4 Background comparison for membrane filter types. Diffractometer settings as for Fig. 1. See Table 1 for filter details.

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TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720