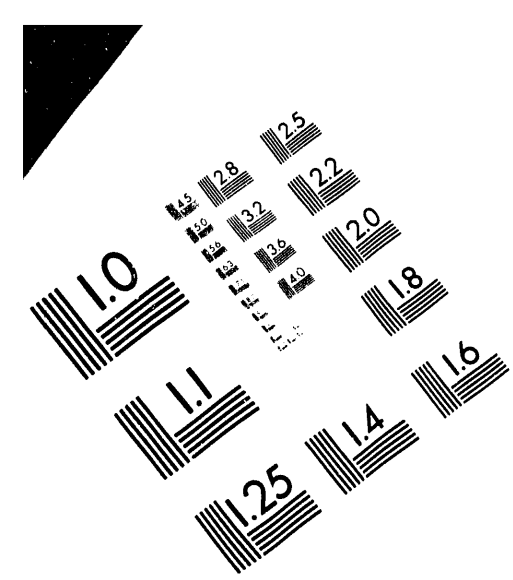

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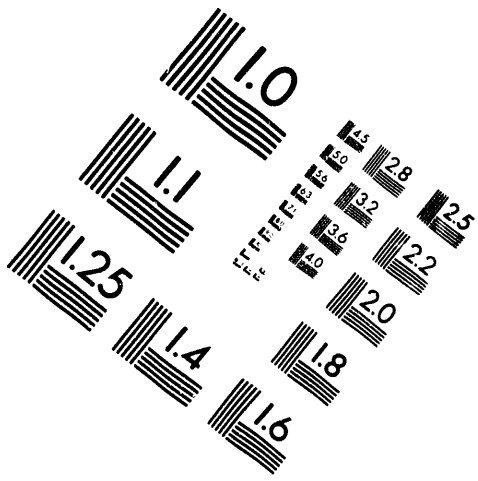

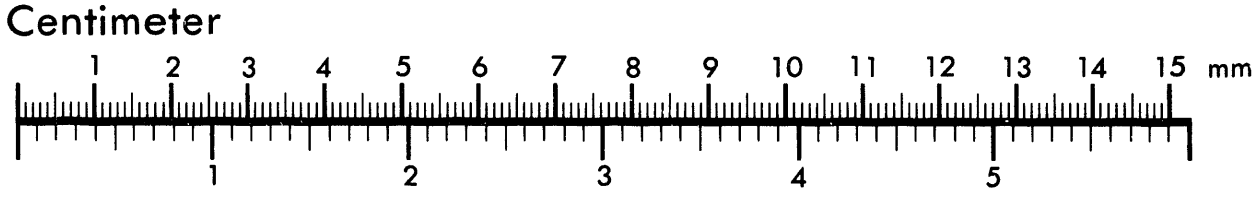

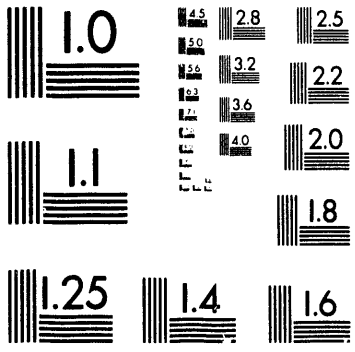

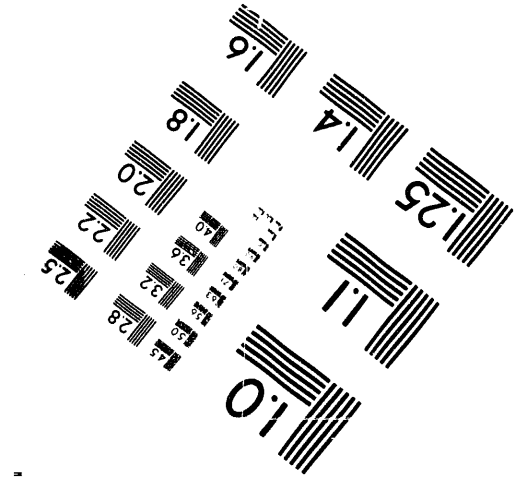

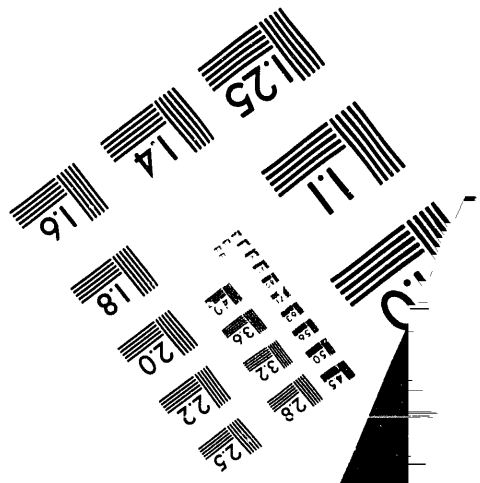

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Quarter report #7, 4/1/93-6/31/93
Advanced NMR-Based Techniques for Pore Structure Analysis of Coal

DE-FG22-91PC91296

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Background

One of the main problems in coal utilization is the inability to properly characterize its complex pore structure. Coals typically have micro/ultra-micro pores but they also exhibit meso and macroporosity. Conventional pore size techniques (adsorption/condensation, mercury porosimetry) are limited because of this broad pore size range, microporosity, reactive nature of coal, samples must be completely dried, and network/percolation effects. Small angle scattering is limited because it probes both open and closed pores. Although one would not expect any single technique to provide a satisfactory description of a coal's structure, it is apparent that better techniques are necessary. Small angle scattering could be improved by combining scattering and adsorption measurements. Also, the measurement of NMR parameters of various gas phase and adsorbed phase NMR active probes can provide pore structure information. We will investigate the dependence of the common NMR parameters such as chemical shifts and relaxation times of several different nuclei and compounds on the pore structure of model microporous solids, carbons, and coals. In particular, we will study the interaction between several small molecules (^{129}Xe, ^{3}He, $^{2}H_2$, $^{14}N_2$, $^{14}NH_3$, $^{15}N_2$, $^{13}CH_4$, $^{13}CO_2$) and the pore surfaces in coals. The project combines expertise at the UNM (pore structure, NMR), Los Alamos National Laboratory (NMR), and Air Products (porous materials).

Work completed during the last quarter

Our current work may be divided into three areas: small-angle X-ray scattering (SAXS), adsorption, and NMR.

1. SAXS.

From our previous report, we had concluded that dibromomethane, chlorodibromomethane and 1,2-dibromoethane were the solvents that exhibited the best contrast match to silica and carbon. We conducted further studies saturating CPG 75 with these solvents. From the results shown in Fig. 1, we concluded that dibromomethane is indeed the best contrast matching solvent. To further confirm this, we vapor loaded CPG 75 with chlorodibromomethane (Fig. 2) to full saturation pressure and found that the match is not as good as that of the dibromomethane. We did this to eliminate the fact that the scattering in the liquid loaded sample might have been suppressed by the liquid around the sample particles. We also studied SAXS data of gels (Fig. 3) prepared in our laboratories from Ludox. The above experiments confirmed that dibromomethane is indeed the best contrast matching solvent.

We conducted SAXS studies on the Amoco super carbon. In the last report, we discussed the liquid loaded samples of Amoco super carbon. We saturated the samples with dibromomethane vapor for the normal 24 hours and for 36 hours. We found that both of them showed a complete match. The bending at large q disappeared completely (Fig. 4) indicating that all the small pores get filled. So the small amount of scattering is from the large pores or the particle surfaces. The Amoco super carbon was not found as suitable for adsorption studies due to the wide range of pore size and also because the super carbon is chemically modified. So we used carbon # 7461-071.03 (also from Air Products Inc.) for preparing the adsorbed samples (see Fig. 5). The liquid loaded sample blocks all the scattering showing a very effective contrast match. Even the sample loaded to a $P/P_o = 0.60$ also exhibits very little scattering. The samples loaded to lower P/P_os show that the small size range i.e. the high q values completely disappears. We notice that the porod region becomes steeper with increasing P/P_o. Also the point where the curve flattens out goes to lower q value with increasing P/P_o. The lowest P/P_o value we have acheived is 0.13. Even at this loading, we find that the small pore size does vanish. We have to load the samples to lower P/P_o. It is not possible to go below these levels of P/P_o with the present equipment. So we are using a pulsing method whereby we expose the sample to vapor for limited amount of time. Thus, we can load samples to lower than P/P_o.

In the third quarterly report, we mentioned that increasing the q range to larger values would help us get a better idea of the pore and surface structure of the carbons. We have since analyzed these samples at Brookhaven National Laboratories and the data shows very promising results. Scattering curves for the Brookhaven and UNM experiments are shown in Figures 6 and 7. A preliminary examination of the data shows a similar trend in the pore size. The results are tabulated below:

Sample ID	% CCl_4	Pore Size (Å)	
		UNM data	BNL data
7461-071.03	30	6.0	6.3
7461-071.18	113	6.8	7.1
7461-071.19	81	6.2	7.2
7461-071.20	60	6.1	6.7
7461-071.21	102	6.6	7.4

There is a marked similarity in the trend of pore size versus % CCl_4 in the data sets. There are a few discrepancies, however. The deviation in pore sizes for the different loadings is not proportional. A closer look needs to be taken and further detailed analysis of the data will help us determine the reasons for the deviations. The data refinement procedure and the different X-ray set-ups could contribute to these discrepancies.a

2. ADSORPTION.

As reported in the previous quarter, detailed adsorption experiments are being carried out in order to assess the pore structure of the activated carbons supplied by our industrial partners, Air Products. Till the last quarter, experiments

involving the adsorption of nitrogen at 77 K, CO_2 at 274 K, and methane at 298 K had been carried out, and a detailed analysis of the data obtained by low pressure as well as high pressure experiments had provided valuable information about the pore structure of the carbons. However, among the concerns that arose during characterization, was whether it is always feasible to carry out high pressure measurements of the type we carried out. Measurements of this type are expensive and cumbersome. It is therefore of interest to see whether it is possible to obtain similar results by using only low-pressure measurements, but carried out at several temperatures; particularly, at temperatures low enough so that the entire range of relative pressures can be covered without having to exceed the capabilities of commercially available adsorption systems. Thus we aim to later replicate the results from our high-pressure measurements by carrying out ambient pressure measurements, but at a lower temperature.

CO_2 adsorption experiments were carried out on one of the carbons (7461-071.21) at 193.2 K, which is close to the sublimation point of CO_2 (195 K). The experiment was carried out up to ambient pressures. This is within the capabilities of commercial systems such as the Micromeritics ASAP 2000, which is the low pressure instrument used for this study. We will attempt to correlate the 193 K isotherm to our earlier low and high pressure measurements at 274 K.

According to Dubinin and coworkers, any isotherm on a microporous solid can be reduced to a single temperature-invariant characteristic curve; that is, in transformed coordinates, the adsorption isotherms obtained at different temperatures, for a particular adsorbent-adsorbate system, will fall on the same characteristic curve. The derivation of this curve involves plotting the adsorbed volume, V, against RT (log P_o/P). Here, P_o is the saturation vapor pressure of the adsorbate at the temperature studied, and V is the volume of the adsorbed phase at a particular relative pressure, thus being equal to the volume of the pores filled at that particular relative pressure.

So far, as mentioned above, only one of the carbons in the series has been studied in this way, and we are trying to resolve some uncertainties, such as assumption of the density of the adsorbed phase, calculation of the vapor pressure, and the possibility that at the low temperatures of the study, restricted diffusion effects might arise due to the low mobility of CO_2 molecules under such conditions. After these difficulties are resolved, we shall proceed with low-temperature CO_2 adsorption experiments on all the carbons in the series, and attempt to compare these results with those obtained earlier. Complete results will be reported in the

next quarter after the difficulties have been resolved and a comparison with the previous results has been established.

3. NMR Techniques.

During the quarter, we continue to perform NMR experiments using ^{129}Xe and $^{15}N_2$ as a function of temperature. The main thrust of this work was two-fold. First, imogolite tubular aluminosilicates were studied as a function of outgassing temperature. We were interested in seeing if the two distinct pore types associated with the inner diameters of the tubes (0.8 nm) and the pores associated with the region between three tubes which are in a close-packed array (~0.3 nm). The second part of our NMR effort is directed at understanding the change in freezing point of fluids in microporous solids as a means of determining pore size. To date, we have not had conclusive results and experiments are continuing.

Work planned for next quarter

1. Measure adsorption isotherm of contrast-matched adsorbates such as dibromomethane on CPG-75, CPG-350, Cabot L-90, and Alltech silica gel. Relate the change in scattering curves versus the thickness of adsorbed film to pore structure parameters such as pore surface roughness, pore geometry, and pore size distribution.
2. Continue ^{129}Xe, $^{14}N_2$, $^{14}CH_4$ and $^{15}N_2$ NMR experiments of fluids adsorbed in porous solids.
3. Perform additional contrast matching-SAXS measurements on carbons.

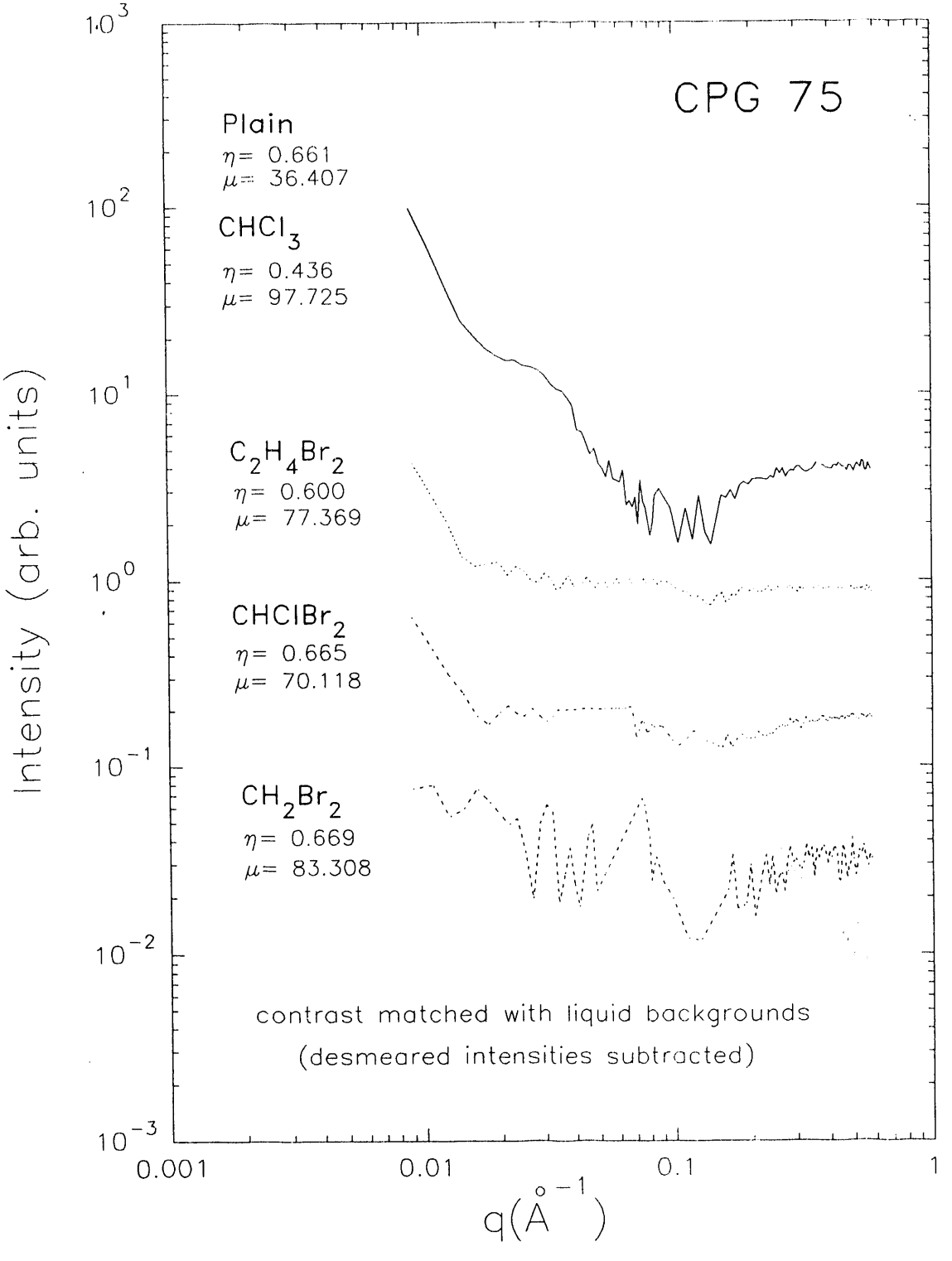

Fig. 1. Liquid saturated CPG 75 using solvents of different electron densities.

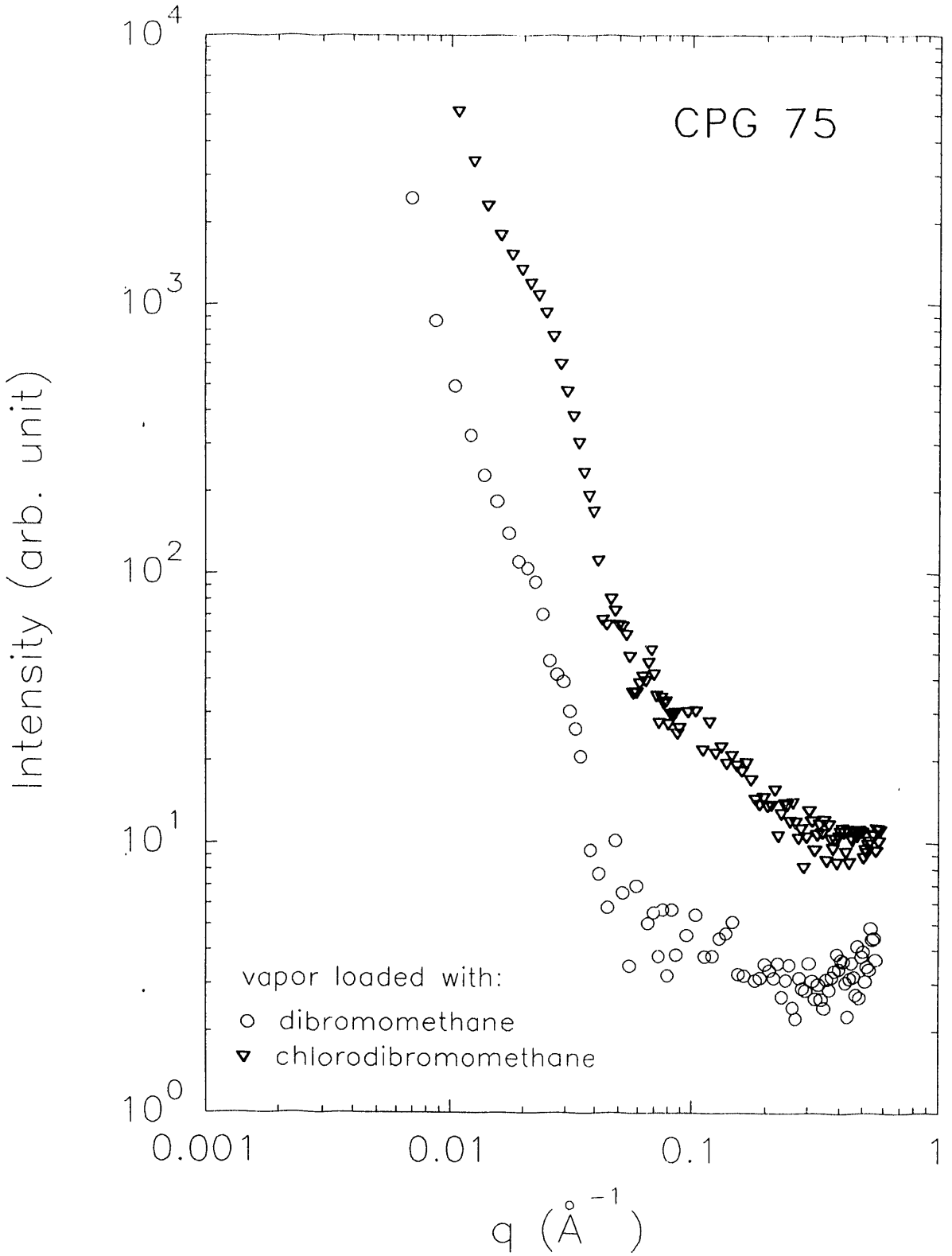

Fig. 2. CPG 75 fully loaded with different vapors

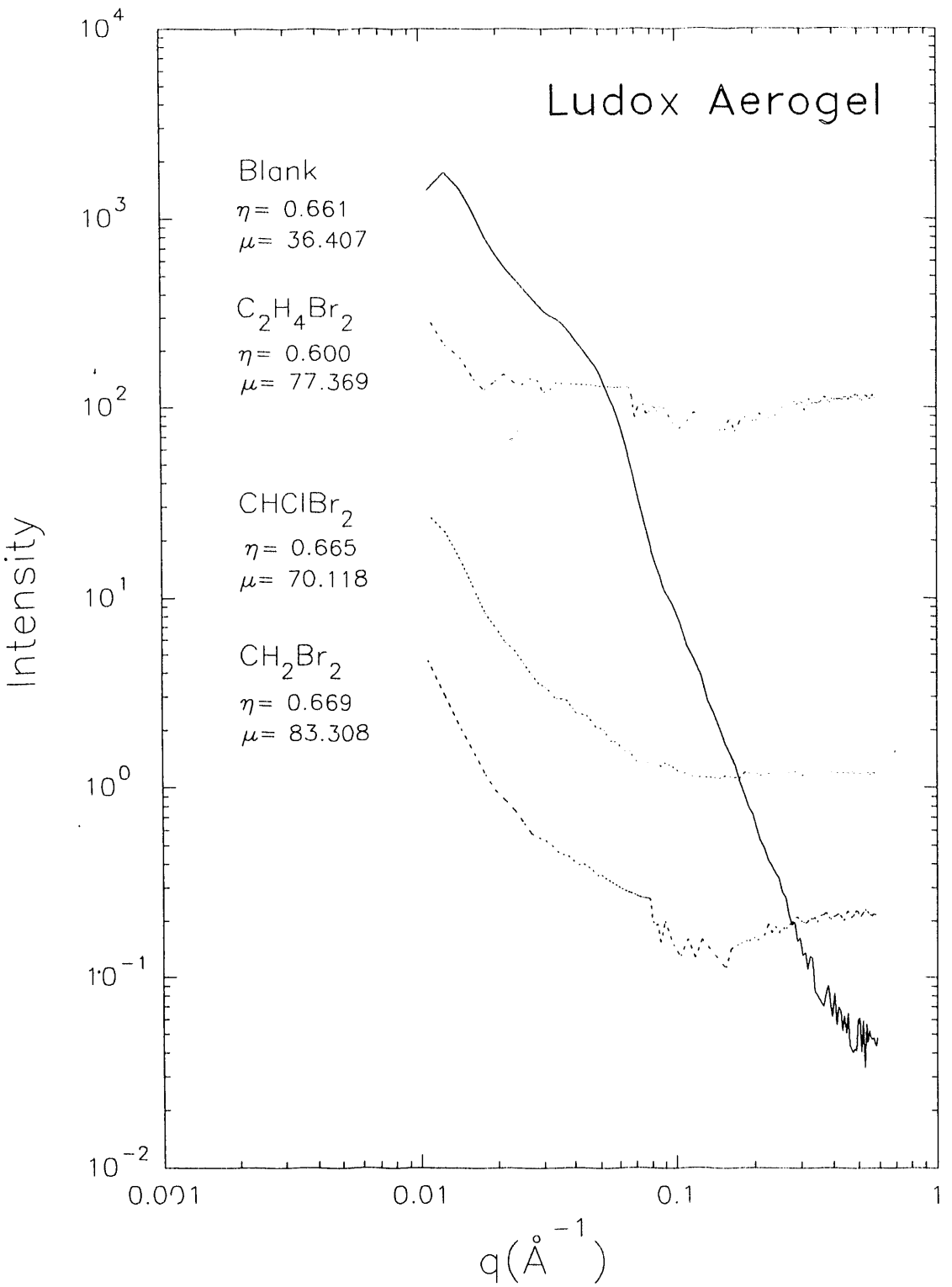

Fig. 3. Ludox aerogel saturated with solvents of different electron densities.

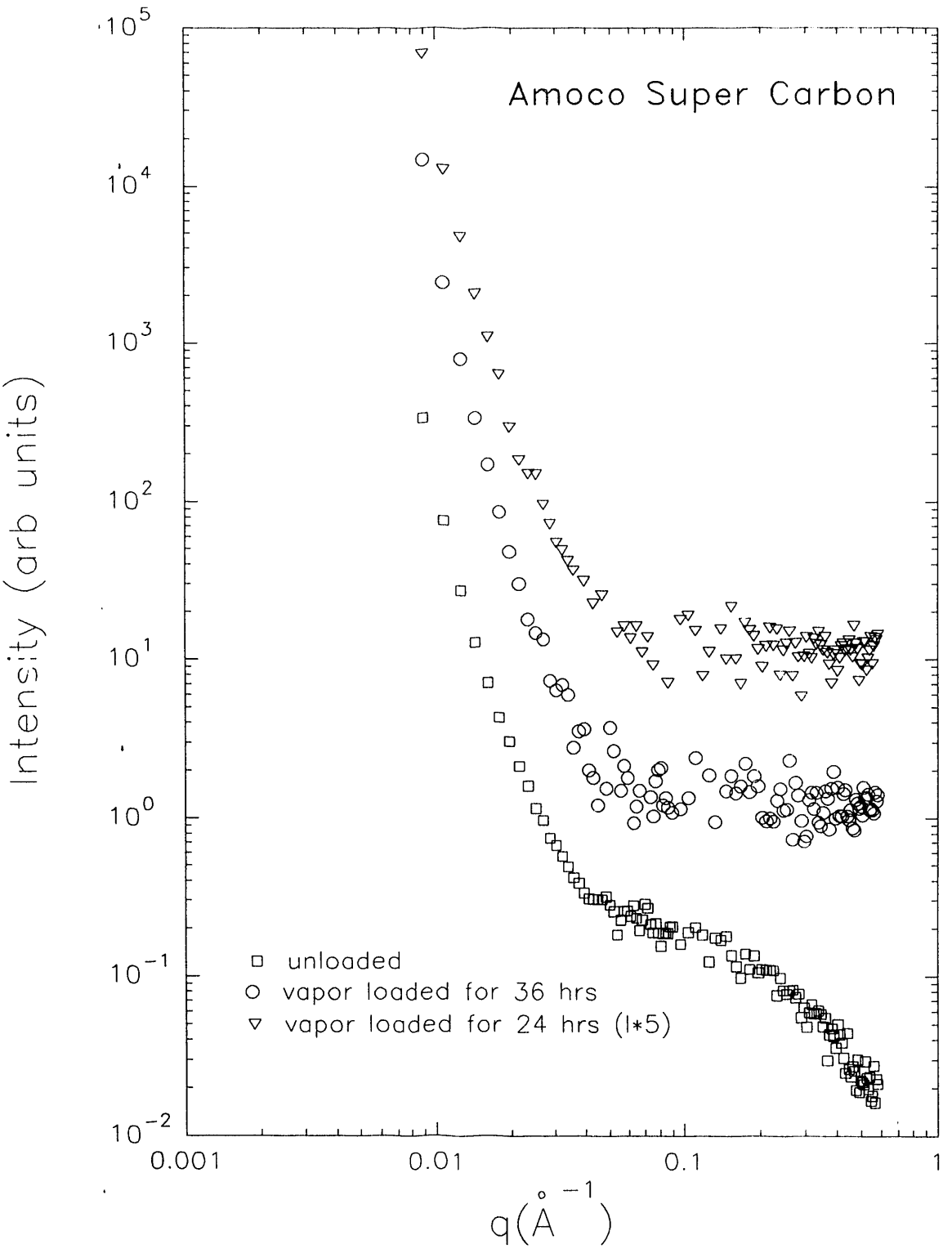

Fig. 4. Amoco Super Carbon saturated with dibromomethane vapor for different time periods.

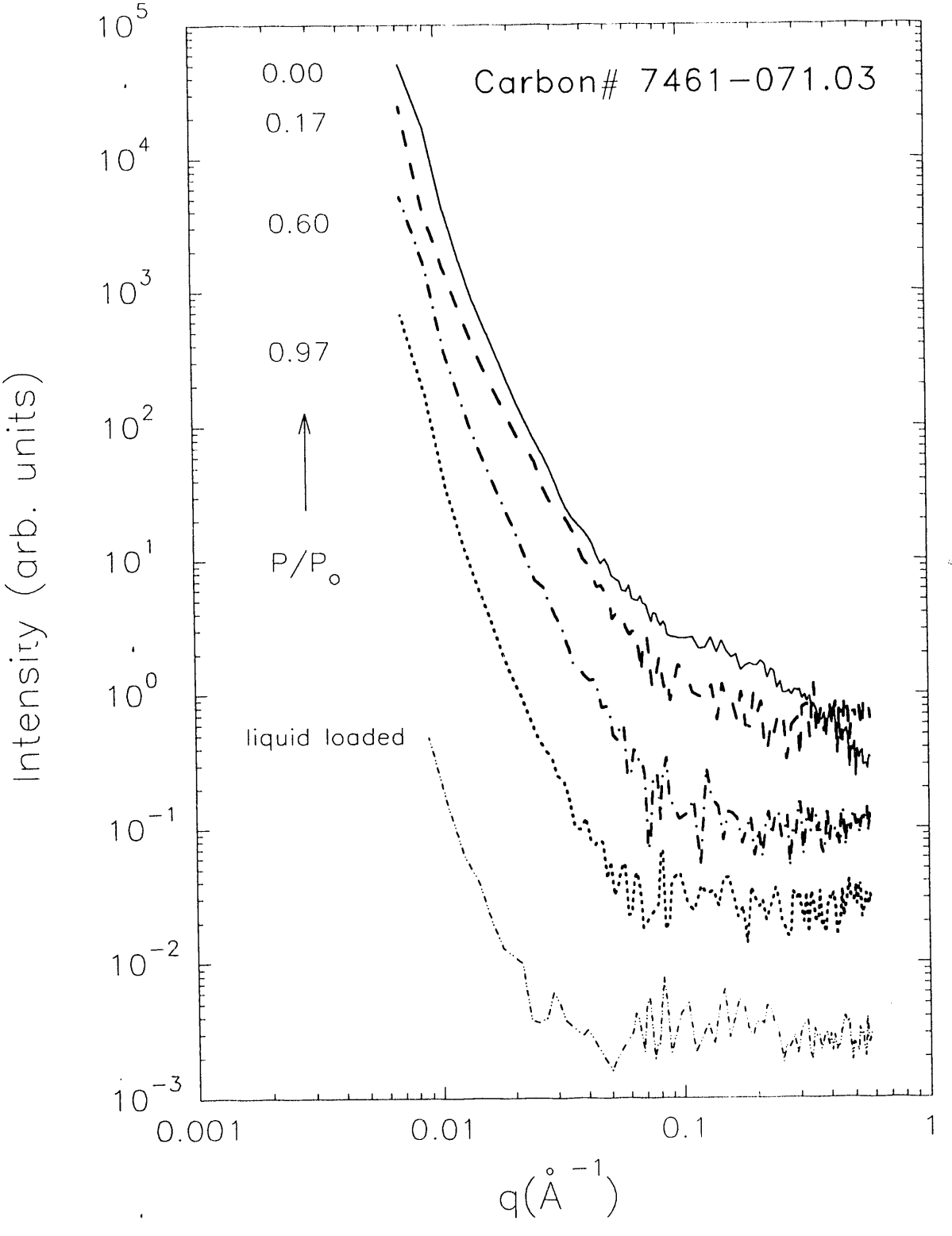

Fig. 5. Carbon adsorbent # 7461−071.03 saturated with liquid and vapor at different P/P$_o$s of dibromomethane

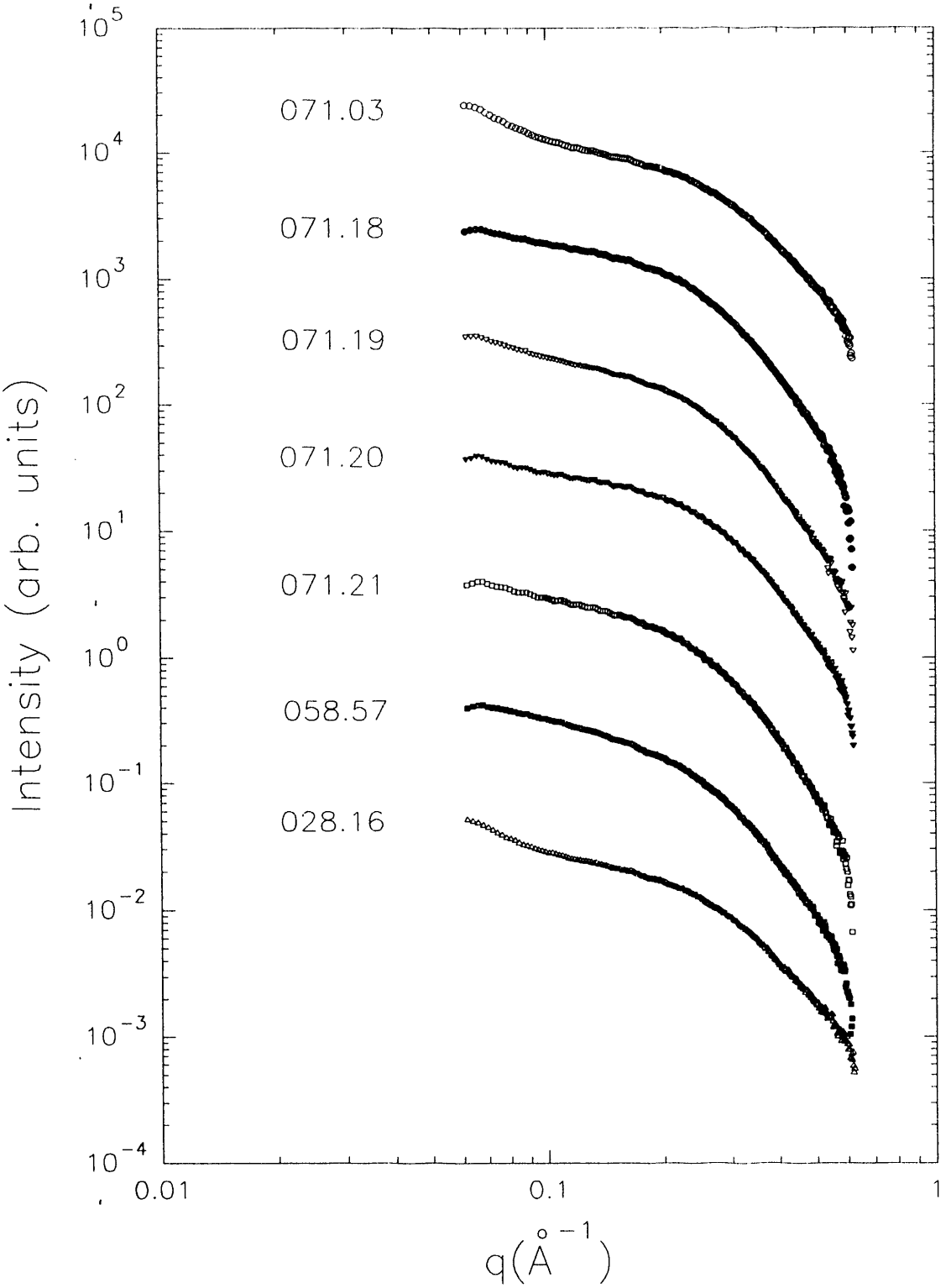

Fig. 6. Scattering data of the carbons from the 7461 series analyzed at Brookhaven National Laboratories.

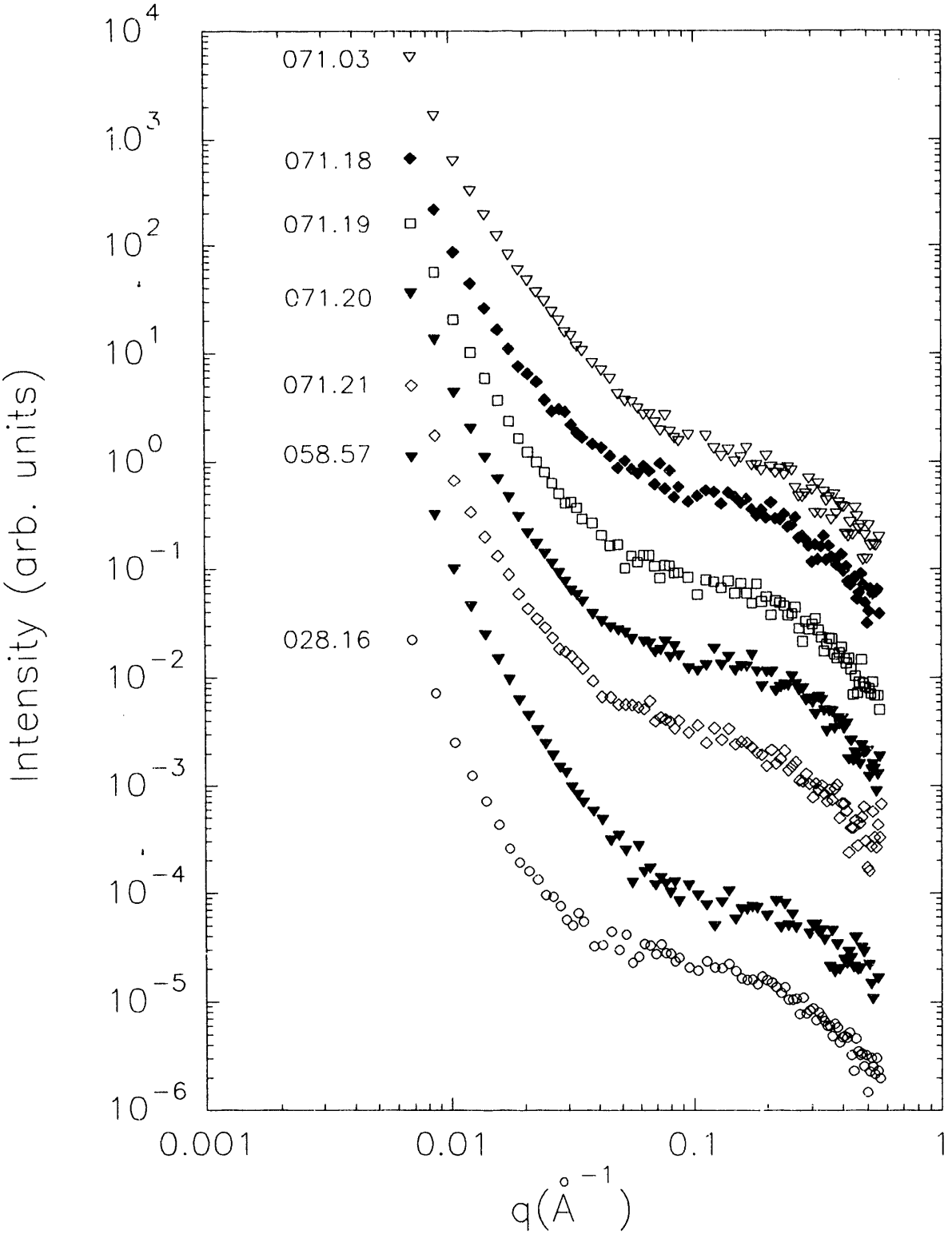

Fig. 7. SAXS data of the carbons from the 7461 series analyzed at UNM.

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