



## **X-ray absorption of 3M activated carbon samples**

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## Report Review

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## 1. Background

Three samples consisting of different form of activated carbon, were presented by 3M for analysis at the Canadian Light source synchrotron facility. The samples were labeled BAM 108, BAM 109 and activated carbon, as the standard. The BAM samples consisted of shiny black spheres, whereas the activated carbon samples was a coarse powder.

Two types of experiment were conducted on the sample, namely X-ray absorption spectroscopy and X-ray photoemission spectroscopy.

X-ray absorption spectroscopy (XAS) is a technique wherein the absorption characteristics of a particular core level of an element of interest is probed using tunable synchrotron light, thereby generating an outgoing photoelectron and the interaction of the resulting photoelectric wave with neighboring atoms. The resulting absorption spectrum is due to a dipole transition which is proportional to the unoccupied density of states (K-edge XANES probes states with p-type character and L-edge XANES probes states with s- or d-type characters) and is a reflection of the local environment around the atom of interest. The structure observed in the XAS spectra is very sensitive to the formal oxidation state of an element and reflects marked differences in the local geometry between species with the same formal oxidation state. X-ray absorption spectroscopy can be performed at different edges within an atom, such as probing the K and L edge of elements like Iron and Carbon, giving both complimentary and additional information about the element of interest.

In order to collect the XANES spectra, we collected the data in the Total electron yield (TEY) mode. In the TEY technique, the current from the sample generated by the ejection of photo-, Auger and secondary electrons is directly measured. Due to the shallow escape depth of secondary electrons, this technique gives spectra from species in the first few nanometers of material. To collect XANES spectra, the incident photon energy is scanned across the maximum in the 1s and 2p absorption cross sections giving increased elemental sensitivity over other traditional surface science techniques.

Synchrotron X-ray Photoemission (SR-XPS) also gives knowledge about the chemical components and the chemical environment they are in. Photoemission data can be used as a complement to XAS data. In particular, a photoemission survey scans is a useful tool to determine the surface composition of materials. Photoemission is intrinsically surface-sensitive since the electron escape depth is typically less than 5nm. There are three main advantages to using synchrotron radiation for photoelectron spectroscopy's, in place of laboratory based X-ray sources; resolution, intensity and tunability. The intensity of the incoming synchrotron light means that smaller features are more easily visible, and gives a resolution of about 25meV. The ability to change the incident energy, allows us to perform depth profiling experiments without changing the surface of the sample, by mechanical means such as sputtering. Sputtering a sample



may preferentially remove one material vs another thereby changing the sample surface composition.

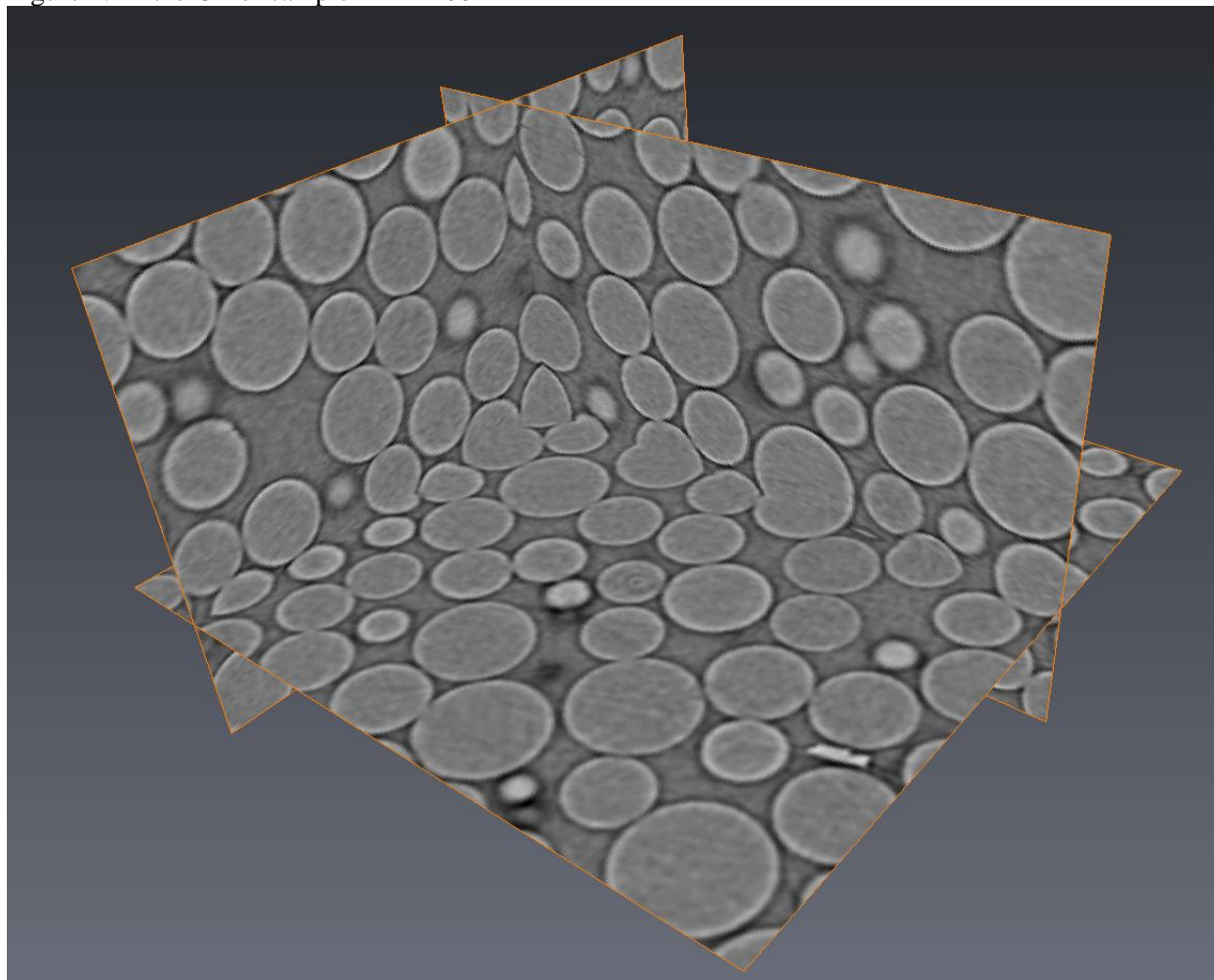
## 2. Sample Preparation for X-ray absorption.

It was noted during sample handling that the samples were very electrostatic, in particular the spherical samples from BAM 108 and Bam 109, were repulsed by the spatula, and various metal substrates. Therefore the samples were prepared in two different ways.

In the first experiment, the samples were placed on conductive carbon tape, in the second experiment they were placed onto conductive copper tape. The samples were used as is, in the case of BAM 108 and 109, whereas as the activated carbon standard was ground up a little to ensure complete coverage of the tape.

Figure 1 shows a micro computed tomography of sample 108 in a plastic test tube. It can be seen that the electrostatic balls are actively repulsing each other.

Figure 1. Micro CT of sample BAM 108

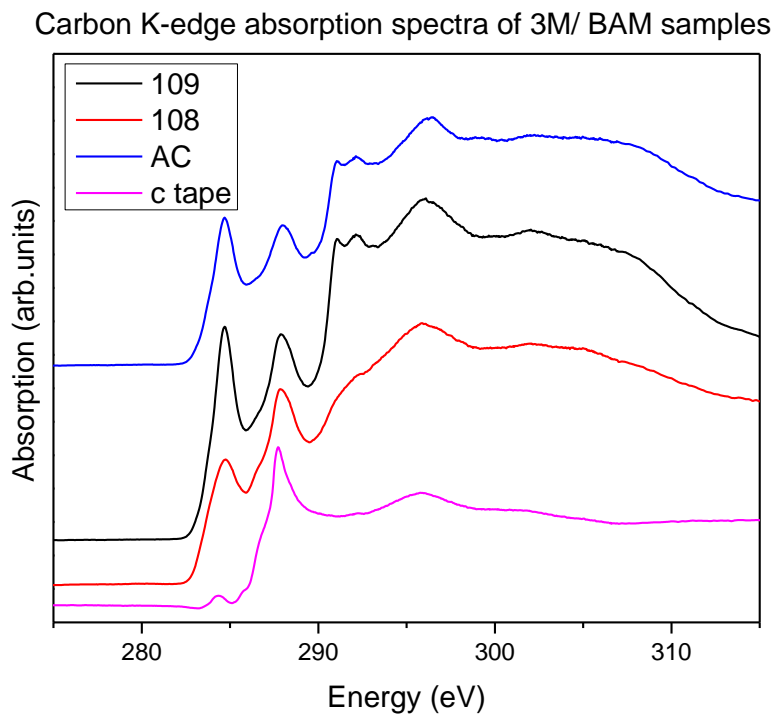




### 3. X-ray absorption results

Figure 2 shows the X-ray absorption of the three supplied samples on carbon tape, along with a spectrum taken from carbon tape as a reference.

Figure 2.

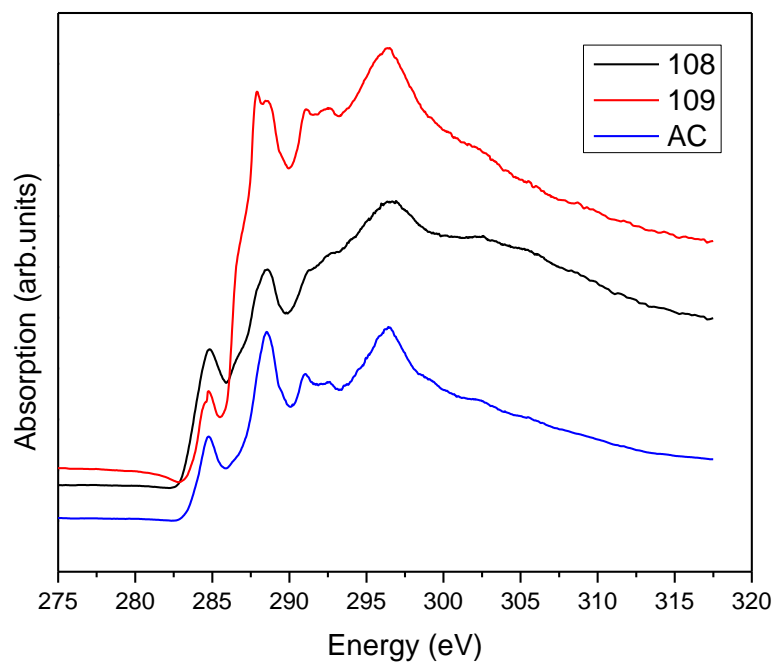


In order to rule out large contribution from the carbon tape, the absorption spectra were repeated using conductive copper tape as the substrate. The data is shown in figure 3. It can be seen that the data does resemble the data shown in Figure 2, however due to the time difference in taking these spectra there could well be sample degradation occurring. However the overall shape gives confidence in the data on carbon tape.



Figure 3.

Carbon K-edge absorption spectra of 3M/ BAM samples on Cu tape





#### 4. Energy calibration and normalisation procedure

All the absorption spectra were normalised by scanning over the carbon edge on a clean piece of gold, and the resulting flux dips in the spectra due to adventitious carbon on the optics of the beamline were calibrated as described in reference 1 by A. Scholl et al [1]. The second dip in the spectrum taken off gold was calibrated to 290.5, giving an energy difference of 2.5eV. Subsequently all spectra are normalised to the correct energy calibration. Figure 4, shows a Carbon K-edge absorption spectrum taken of a clean gold reference.

Figure 4.

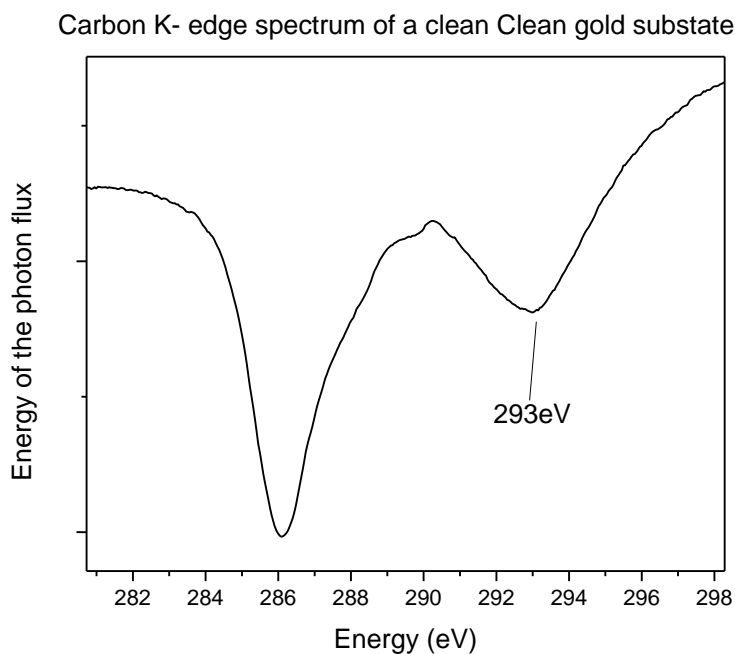






Figure 5. shows the dips in the flux curve over the carbon K edge on a clean piece of gold on an energy calibrated beamline.

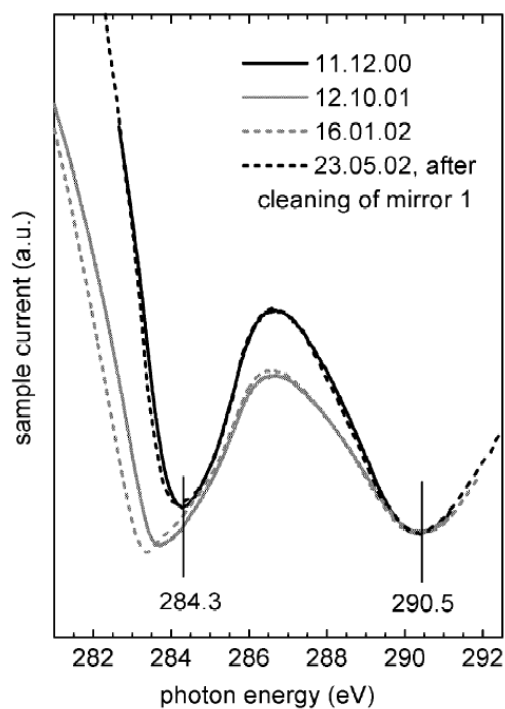


Fig. 2. Comparison of flux curves using the current from a clean Ag sample (total electron yield) recorded at the U49/1-PGM (three older data) and the UE52/PGM (latest spectrum), respectively. The energy scales were recalibrated, and the intensities were adjusted at the second dip in the flux curve.

Subsequently, all energy scales in X-ray absorption were normalised to the second gold peak at 290.5, an energy difference of 2.5 eV.

X-ray absorption was attempted at the Oxygen and Nitrogen K edges, however no signal was observed.



## 5. Photoemission results

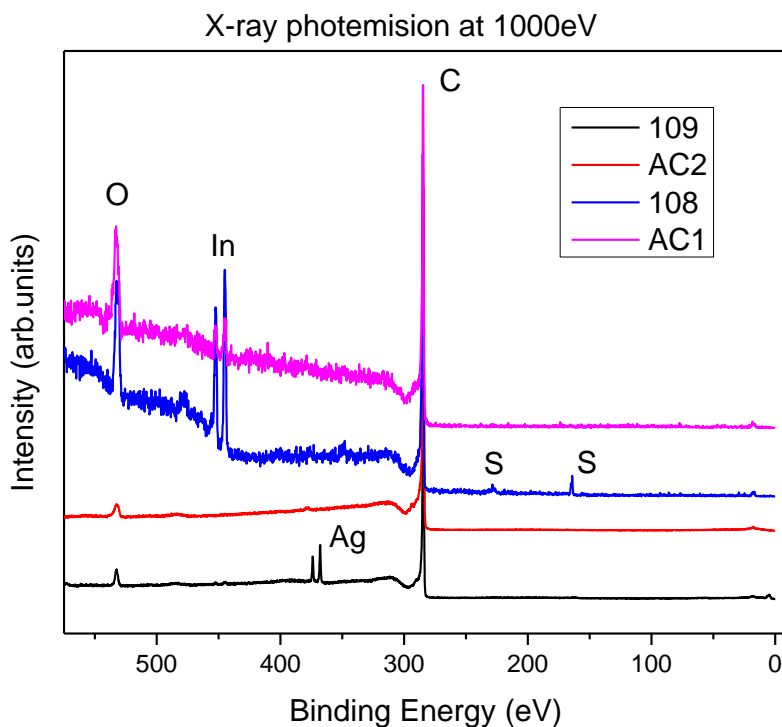
Different sample preparation methods were attempted on these samples, due to fears about charging effects, and contamination effects.

BAM 108 and Activated Carbon 1(AC1), were placed on scraped on indium foil, whilst Bam 109 was placed on silver conductive past, and Activated Carbon 2 (AC2) was placed on Conductive copper foil.

A broad scan at 1000 eV of all 4 samples is shown in figure 6.

The samples are very clean and consist of carbon, oxygen and peaks from the substrate. However on close examination it can be seen that for sample 108, there are some small S peaks 230 and 160 eV. It was not possible to fit the carbon data for these samples as the data was not consistent from one scan to another, suggesting either sample charging or that the samples were being destroyed by the beam. It was noticed that there were sample changes if more than two absorption scans were taken at the same spot.

Figure 6.



Figures 7, 8 and 9, show Photoemission scans of BAM 109, Activated carbon, and BAM 108 at an excitation energy of 500 eV.



Figure 7.

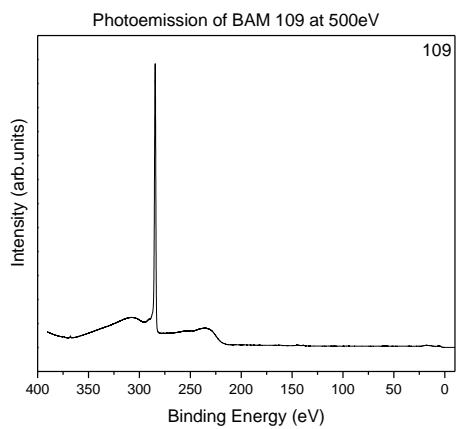


Figure 8.

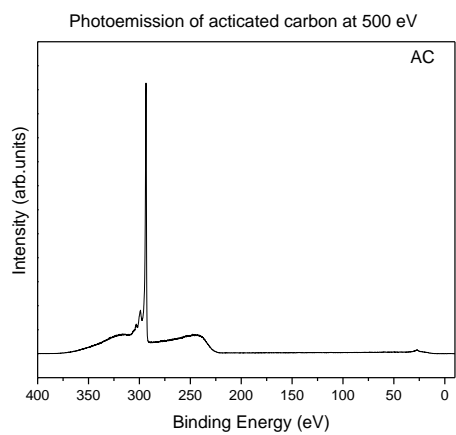
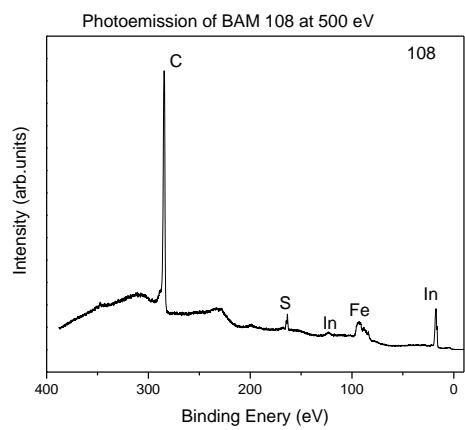


Figure 9.



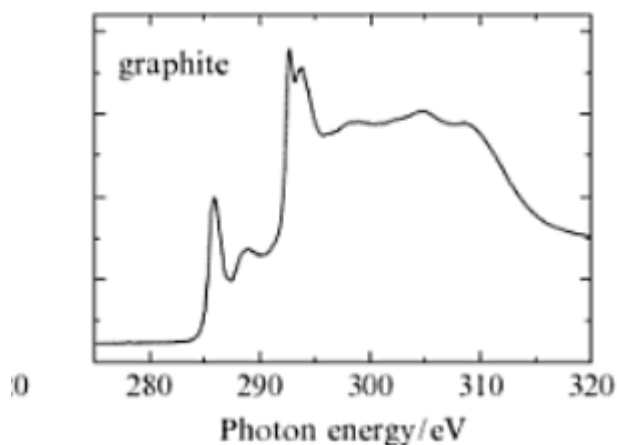


## 6. Discussion and Conclusions

The photoemission results demonstrate that the samples mainly consist of carbon. However sample BAM 108 did show the presence of Sulphur at both 1000 eV and 500 eV. No Sulphur was observed from BAM 109 and the activated carbon standard. At present the carbon data cannot be fitted with accuracy, due to sample degradation in the presence of the excitation beam. This can be mitigated, however that will be discussed in section 7.

The X-ray absorption results clearly show two things, one that the spectra for activated carbon and BAM 109 are identical, and greatly resemble the spectrum of graphite shown in Figure 10[2].

Figure 10.



Whereas the overall shape of BAM 108 is similar, however it lacks the double peak at 291, and 292 eV observed in the other two samples. The peak positions are tabulated below in Table 1. It can be seen that the underlying spectrum of the carbon tape substrate has little effect on the spectra, with the caveat that it may be contributing to the shoulder on the near side of the second peak at 288 eV.

Table 1.

	Peak 1 (eV)	Peak 2 (eV)	Peak 3 (eV)	Peak 4 (eV)	Peak 5 (eV)
BAM 108	284.7	288	-	292.1	295.9
BAM 109	284.7	288	291	292.1	295.9
Activated carbon	284.7	288	291	292.1	296.3



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There are three diagnostic absorption features of graphite [3], a peak centered at 284.7 that correspond to a  $\pi^*$  transitions, a sharp peak located at 291 eV, that has been attributed to a  $\sigma^*$  exciton, and a second broader  $\sigma^*$  transition at 292eV.

Note an energy difference of 0.5 eV, from the reference paper, which we attribute to the difficulty in calibrating carbon when adventitious carbon is always present. However as our spectra were calibrated to clean gold we are confident in these values. Significantly the sharp excitonic peak at 291 is missing in BAM 108. As graphite is known to be sp<sup>2</sup> hybridized with 1 dangling carbon bond, it is proposed that, in BAM 108, there is another bond being formed with the Carbon, beyond that formed in the graphite layer. As was observed in the photoemission data, this could well be a carbon Sulphur bond. In fact when the image obtained from the micro CT is analyzed, it is clear that there is a shell surrounding the sphere, which could contain most of the Sulphur. Unfortunately the micro CT was not performed on the BAM 109 sample. In addition the first  $\pi^*$  peak is broadened in BAM 108 compared to the BAM 109 and activated carbon, suggestion some further  $\pi$  bonding is present.

In reference [4] where graphite is bonded to Fluorine, it is observed that the Excitonic peak also disappears.

Interestingly, no signal from Oxygen or Nitrogen was observed at their respective K edges.

## 7. Future directions

In order to fit the photoemission carbon peak, it would be necessary to repeat the photoemission experiment, firstly with a laboratory source, and ensure that a different area of the sample was illuminated after 20/ 30 minutes, to avoid beam damage. In addition hard X-ray photoemission could be performed to determine whether the Sulphur on BAM 108 was also below the surface. Sulphur X-ray absorption could also be performed on the Sulphur K or L edges, alongside some Sulphur carbon reference compounds to determine what form of Sulphur could be present.

Microtomography could be performed on BAM 109 to determine, whether that materials also has a shell like structure.

In-situ or real world experiments could be performed, by dosing the samples with gases whilst taking the absorption spectra before and throughout and after out the dosing.

## 8. References

- [1] A. Scholl et al. Journal of Electron Spectroscopy and Related Phenomena 129(2003) 1-8.
- [2] Astrophysics and Space Science Proceedings, Protection of Materials and Structures from the space environment. Edited by J. Kleinman et al.
- [3] J. A Brandes et al. Carbon 46 (2008) 1424-1434.
- [4] Y. Ahmad et al. The Journal of Physical Chemistry 117 (2013) 13564-13572.