

# XPS analysis of frozen 1,4-dibromobenzene

## Keywords

large area XPS,  
sample cooling

## Application Note MO443(A)

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## Introduction

The molecule 1,4-dibromobenzene is of interest as a precursor for the synthesis of conjugated polymers with applications in nanoelectronic and electronic devices. Whilst the synthesis of such conjugated polymers in solution is well-established, these reactions result in disordered structures. This problem can be mitigated by using atomically flat single crystal substrates. The most successful approach is the metal surface catalysed coupling of halogenated hydrocarbons, which is the subject of extensive research <sup>[1,2]</sup>.

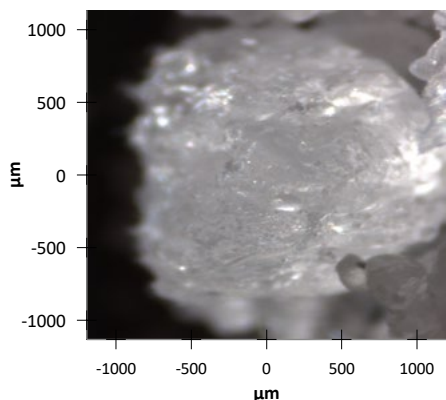
1,4-dibromobenzene has a vapour pressure of 0.0575 mmHg at 25°C <sup>[3]</sup> such that it will volatilise in vacuum at room temperature. To achieve XPS characterisation this organic material requires cooling to <100°C before pumping and introduction to the analysis chamber.

## Experimental

As received 1,4-dibromobenzene <sup>[4]</sup> was pressed into a powder well mounting accessory on the heat/cool sample holder and placed on the appropriate position on the sample magazine. The sample entry chamber (SEC) was then sealed and backfilled with dry nitrogen. The chamber was purged for 10 minutes before the liquid nitrogen Dewar was filled to commence sample cooling whilst continuing to purge the chamber. Once a sample temperature of ca. -50°C was achieved the sample entry chamber was pumped to a base pressure in the 10<sup>-7</sup> torr. This was achieved within 10 minutes. It should be noted that the rate of cooling significantly increased once the chamber was evacuated, reaching below -100°C within 20 minutes.

In parallel to cooling the sample in the SEC the sample stage in the analysis sample was pre-cooled. Once the sample temperature below -100°C was achieved the automated sample transfer was started which transferred the sample from the sample magazine to sample stage in the analysis chamber. During the sample transfer there is no active cooling however the thermal mass of the sample holder is such that the sample remains below -100°C throughout the transfer process and active cooling is resumed as soon as the sample holder is gripped in the analysis chamber.

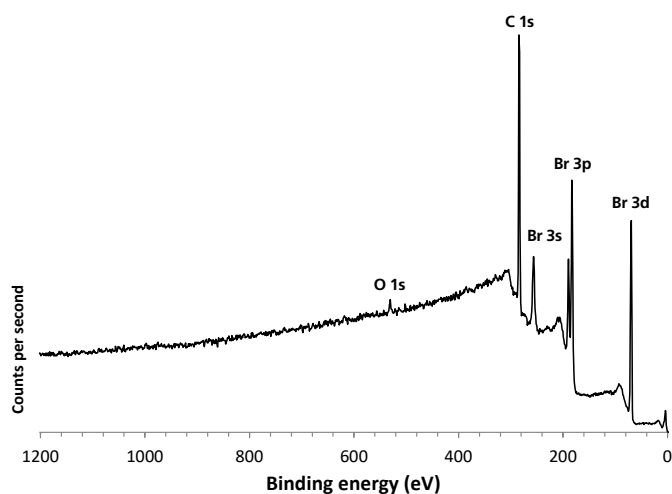
At this point XP spectra were acquired. Photoelectrons were excited using monochromatic Al K $\alpha$  X-rays (1486.6eV). Sample charging was prevented by use of the low-energy electron-only charge neutralisation system. The base pressure of the analysis chamber was maintained below 5x10<sup>-8</sup> torr range during the experiment.



**Figure 1:** 1,4-dibromobenzene in the XPS analysis position.

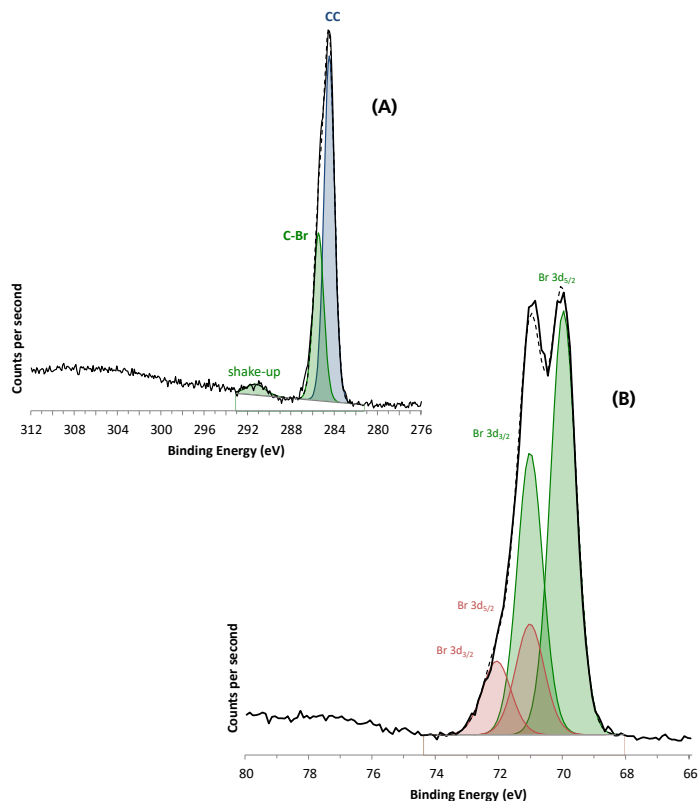
## Results

The cooling of the 1,4-dibromobenzene ensured that it remained in solid form throughout the measurements as shown in figure 1. The survey spectrum shows that in addition to bromine and carbon there is <1.5 atomic % contribution from oxygen.



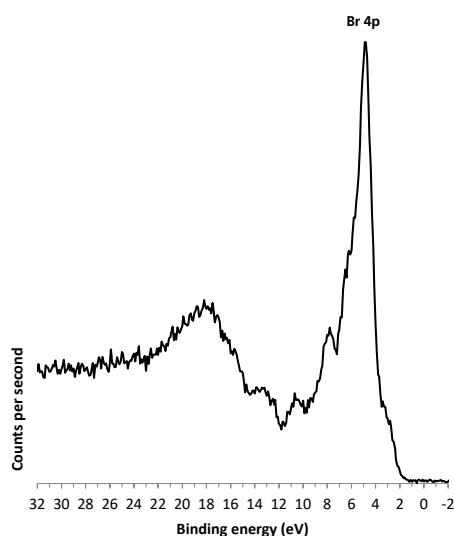
**Figure 2:** large area (300  $\mu\text{m}$  x 700  $\mu\text{m}$ ) survey spectrum from the 1,4-dibromobenzene.

The high resolution spectra for C 1s and Br 3d were acquired allowing the chemistry of the material to be investigated. Figure 3a and 3b show the C 1s and Br 3d high resolution spectra respectively. The peak for carbon bonded to bromine occurs at 285.8 eV, with the aromatic C–C at 284.8 eV. It is noted that the model of best fit has Shake-up structure associated with the aromatic benzene ring fitted with a single component at 291.6eV.



**Figure 3A:** C 1s high resolution spectrum, charge-corrected for the C aromatic at 284.8eV.

The Br 3d spectrum comprises of a pair of doublets, shown in figure 3b, with 1.05 eV separation between the Br 3d<sub>5/2</sub> and 3d<sub>3/2</sub> components. The sample analysed is made up of molecular crystals which are likely stacked via  $\pi - \pi$  interactions of the aromatic rings as well as halogen bonding of the end groups, analogous to hydrogen bonding. At the solid–vacuum interface it is probable that one of the two bromine atoms is closer to the surface and is under-coordinated or even removed. It is proposed that the higher binding energy Br 3d doublet (Br 3d<sub>5/2</sub> at 71.4 eV) arises from the bulk ‘intact’ molecules in the crystalline bulk, whilst the lower binding energy doublet (Br 3d<sub>5/2</sub> at 70.3 eV) arises from the under coordinated bromine at the solid–vacuum interface.



**Figure 4:** X-ray excited valence band spectrum of 1,4-dibromobenzene.

The valence band spectrum is often of interest as it is sensitive to the molecular structure of the material and can reflect the changes in the valence electron distribution. This means that the valence band is sensitive to X-ray induced damage during the analysis. Both valence band and core level spectra were acquired using the spectrometer in large area analysis mode where a combination of magnetic immersion and electrostatic lenses efficiently transfer the photoelectrons to the 165 mm mean radius hemispherical analyser so that spectra were collected in a matter of minutes. It is noted that no changes were observed in sequential valence band spectral acquisitions. This is an important observation as halogenated hydrocarbons are known to be easily damaged by X-ray exposure [5].

## Conclusion

It has been demonstrated that a sample of 1,4-dibromobenzene can be analysed using the AXIS Supra. The sample was frozen to -100°C prior to pumping in the sample entry chamber (SEC). The sample was transferred to the analysis chamber, analysed by XPS and removed to the SEC all with a sample temperature below -100°C to ensure that the sample didn't sublime under UHV conditions. Analysis of the sample was achieved without X-ray degradation as spectra were collected in large-area, high-sensitivity mode limiting the total X-ray exposure of the sample to 15 minutes. The Br 3d spectrum indicated that there were 2 chemical states associated with the bromine.

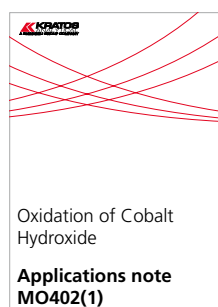
## Acknowledgements

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