

A. L. Hagström, ¹ Ph.D.

Trace Amounts of Lead and Bromine in Soot Studied by X-Ray Photoelectron Spectroscopy

Forensic science laboratories are sometimes confronted with the question of whether or not a flammable solvent has been used to initiate a fire. One of the most efficient accelerants is gasoline. Some gasoline for use in motor vehicles contains lead and bromine (tetraethyl lead, tetramethyl lead, and ethylene dibromide) as additives amounting to about 0.4 g/litre. The lead alkyls are added to improve the resistance against knocking, whereas ethylene dibromide is used to expel the lead from the cylinder walls.

The presence of trace amounts of lead and bromine is sometimes taken as an indication of the induction of a fire by gasoline [1,2]. The identification of the accelerant can be made from incompletely burned accelerant found in the debris or from soot created during the fire.

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), involves the measurement of binding energies of electrons ejected by monoenergetic X-rays [3]. The binding energies of the core electrons are characteristic of a given element. The removal of a core electron is accompanied by a substantial reorganization of the valence electrons in response to the effective increase in nuclear charge. Thus, depending on the composition of the surrounding atoms, slightly different binding energies are measured. This chemical shift of the measured binding energies allows, in many cases, a chemical identification of an unknown material to be made.

The present paper describes the application of XPS for determining the chemical states of lead and bromine found in soot obtained from burned gasoline and one type of polyvinyl chloride (PVC) carpet.

Experimental Procedure

The samples studied in this investigation were soot collected on thin foils of aluminum placed about 20 to 30 cm above flames. The soot was obtained from burned gasoline and a PVC carpet (Forshaga Novilon Scandinavia). In the carpet the PVC was used as a backing material. Three samples of each composition were studied in this investigation. Powder samples of lead bromide were also studied as reference.

The ESCA spectra were induced by aluminum $K_{\alpha 1,2}$ radiation (1486.6 eV) in a high vacuum spectrometer ($\leq 1 \cdot 10^{-4}$ Pa). The instrument was operated with a resolution corresponding to a width of about 1.5 eV (full width at half maximum intensity) of the Au $4f_{7/2}$ line. The soot samples had good conductivities, and no charging effects were observed. The Au $4f_{7/2}$ level with a binding energy of 83.8 eV was used as a reference level. The binding energy of the C 1s line from soot varied between 283.8 and 284.4 eV depending on the completeness of combustion of the samples. In the case of lead bromide, the

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¹Project leader, Department of Physics and Measurement Technology, and Forensic Science Center, Linköping University, Linköping, Sweden.

C 1s line from hydrocarbons ($E_B^F = 285.0$ eV, where E_B^F is the binding energy given relative to the fermi level) had to be used as a reference because of charging effects. The binding energies of the Au $4f_{7/2}$ line and the C 1s line resulting from hydrocarbons are in agreement with ± 0.1 eV.

Results

The photoelectrons of lead and bromine studied in this investigation originated from Pb $4f_{5/2,7/2}$, Br $3p_{1/2,3/2}$, and Br $3d_{3/2,5/2}$. The concentration of lead and bromine in the soot varied between different samples but was typically on the order of 1%. Both elements were present in soot from both gasoline and PVC, even though the relative amounts of lead in the PVC samples tended to be smaller than in the gasoline samples.

In Fig. 1 we present the Br $3d_{3/2,5/2}$ spectrum from lead bromide and from soot obtained from gasoline and a PVC carpet. The bromine line appears as a single peak because of an unresolved spin-orbit splitting (Fig. 1, lead bromide). In the case of the gasoline spectrum, however, two peaks appear, indicating the presence of two different bromine compounds. The peak with the lowest binding energy is most probably associated with the formation of lead bromide. The other peak, which is shifted 6.4 eV towards larger binding energy, is more difficult to identify. The peak of the bromine compound formed in soot from the PVC carpet is shifted 7.2 eV relative to the low binding energy peak in the gasoline samples. No traces of a bromine line corresponding to lead bromide were found in the PVC samples. The Br $3p_{1/2,3/2}$ electrons in the PVC samples were not studied because of overlap with the Cl $2p_{1/2,3/2}$ electrons excited by the aluminum $K_{\alpha 3,4}$ radiation.

The binding energy of the spin-orbit split Pb $4f_{5/2,7/2}$ peak was found to be essentially the same within the error limits for the different soot samples. Its binding energy was also

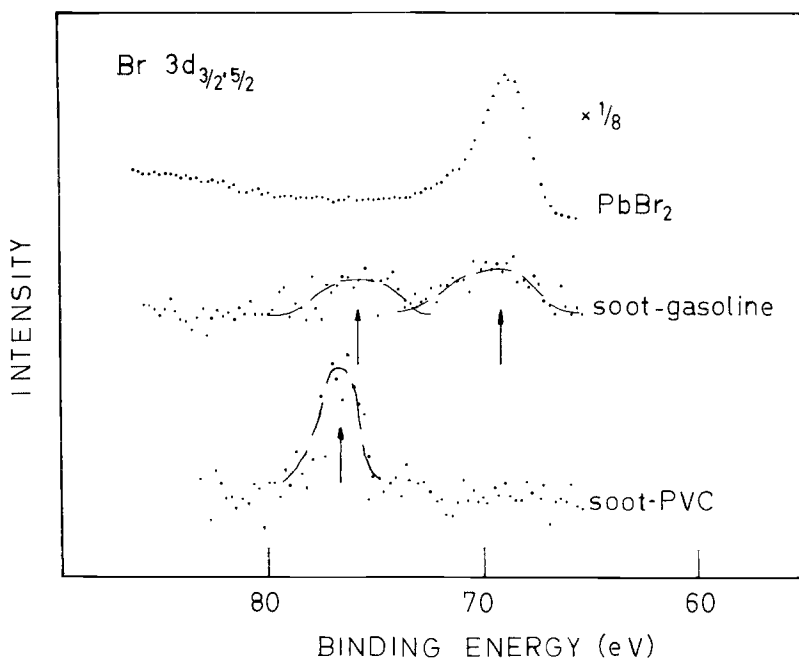


FIG. 1—The Br $3d_{3/2,5/2}$ spectrum in lead bromide and in soot obtained from gasoline and a PVC carpet. The arrows indicate the peak positions for the Br $3d_{3/2,5/2}$ electrons in the soot samples.

found to agree with that in lead bromide and PbO_{th} [4]. The binding energies of the lead and bromine levels studied in this investigation are summarized in Table 1.

Hulett and Carlsson [5] have studied the chemical shifts in the binding energy for the 3d electrons in various bromine salts. They observed a monotonically increasing binding energy for the Br $3d_{3/2,5/2}$ electrons with increasing oxidation number. The bromate (BrO_3^- with oxidation number +5) and perbromate form (BrO_4^- with oxidation number +7) were found to be shifted 5.9 and 7.5 eV, respectively, towards larger binding energy relative to the halide state [5]. Our observed chemical shift of 7.5 eV (relative to the Br $3d_{3/2,5/2}$ peak in lead bromide) in the PVC material is in very good agreement with the value of 7.5 eV given for the perbromate ion [5]. The chemical shift of 6.7 eV in the soot sample from gasoline (relative to Br $3d_{3/2,5/2}$ peak in lead bromide) suggests a mixed state involving both bromate and perbromate.

TABLE 1—Binding energies (eV) of the Pb $4f_{5/2,7/2}$, Br $3p_{1/2,3/2}$, and Br $3d_{3/2,5/2}$ electrons.

| Levels | Soot-Gasoline | Soot-PVC Carpet | Lead Bromide | PbO_{th} [4] |
|----------------|-----------------|-----------------|-----------------|------------------------------|
| Pb- $4f_{5/2}$ | 143.3 ± 0.5 | 143.6 ± 0.5 | 143.5 ± 0.1 | 143.7 |
| Pb- $4f_{7/2}$ | 138.6 ± 0.7 | 138.8 ± 0.5 | 138.7 ± 0.1 | 138.8 |
| Br- $3p_{1/2}$ | 188.1 ± 0.3 | ... | 188.7 ± 0.1 | ... |
| Br- $3p_{3/2}$ | 182.2 ± 0.3 | ... | 182.0 ± 0.1 | ... |
| Br- $3d_{3/2}$ | 69.1 ± 0.3 | 76.3 ± 0.4 | 68.8 ± 0.1 | ... |
| Br- $3d_{5/2}$ | 75.5 ± 0.3 | | | |

Conclusion

We suggest that in the case of a fire accelerated by gasoline, lead and bromine form lead bromide together with states with higher oxidation numbers. On the other hand, no lead bromide is detected in soot obtained from PVC material.

Summary

Soot samples obtained from burned gasoline and a PVC carpet have been studied by ESCA. Special attention was paid to trace amounts of lead and bromine found. Their concentrations were typically on the order of 1%. Strong chemical effects on the binding energy of the Br $3d_{3/2,5/2}$ electrons were observed, indicating the possible formation of different bromine compounds. Identification of the observed structures revealed the formation of lead bromide in soot samples from burned gasoline but not from the burned PVC material. Bromine compounds with higher oxidation numbers were found to be present in both types of soot. These results permit the use of the method in forensic science fire investigations.

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References

- [1] Covey, E. L., "Application of Energy Dispersive X-Ray Spectroscopy in Fire Investigation," *Journal of Forensic Sciences*, Vol. 22, No. 2, April 1977, pp. 325-328.

- [2] Visapää, A. and Heinonen, K., "The Detection of Bromine and Lead Traces in Car Fire Residues," *Criminologist*, Vol. 10, No. 38, 1977, pp. 22-29.
- [3] Hagström, S. B. M. and Fadley, C. S., in *X-Ray Photoelectron Spectroscopy*, L. V. Azaroff, Ed., McGraw-Hill, New York, 1974, pp. 379-444.
- [4] Thomas, J. M. and Tricker, M. J., "Electronic Structure of the Oxides of Lead," *Journal of the Chemical Society, Faraday Transactions, II*, Vol. 71, No. 2, 1975, pp. 329-336.
- [5] Hulett, L. and Carlsson, T. A., "Measurements of Chemical Shifts in the Photoelectron Spectra of Arsenic and Bromine Compounds," *Applied Spectroscopy*, Vol. 25, No. 1, 1971, pp. 33-36.

Address requests for reprints or additional information to
A. L. Hagström
Department of Physics and Measurement Technology
Forensic Science Center
Linköping University
S-581 83 Linköping, Sweden