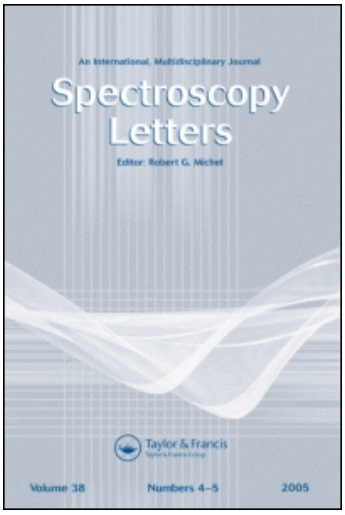

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Study of fragmentation of nucleic acids using metastable mapping. BH^+ ion origin.

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Abstract

The origin of $[BH]^+$ ions from DNA pyrolysis-electron impact spectrum is discussed using metastable mapping and linked scanning tehcniques.

One of the newer additions to computerised techniques used in mass spectrometry is metastable mapping[1,9].

The essential advantage of this technique compared to the traditional metastable ion analysis or the manual linked scanning study is that all metastable ions are recorded and stored on a two dimensional map and can be selected and called one by one by users. The map is usually presented as an x,y graph having on the ordinate and abscissa masses of parent and daughter ions respectively, the latter being proportional to the ESA voltage.

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Three pieces of information can be extracted from the map:

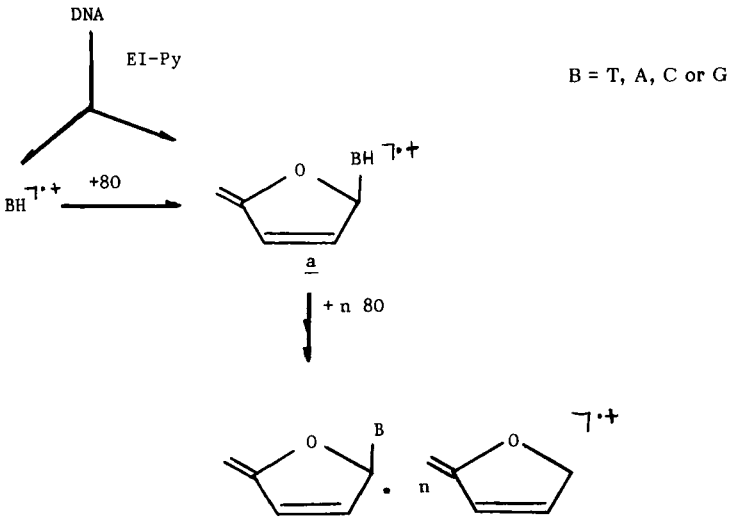
1) daughter ion where the B/E ratio [B-magnetic, E-electrostatic analysers] is maintained constant
2) parent ion spectrum with B^2/E being constant
3) constant neutral loss spectrum - ifnoramtion about the daughter ion resulting from the loss of any neutral fragment.

All this information is a valuable tool for confirmation of the fragmentation route proposed, using time saving 2-dimensional experiment.

The fragmentation pattern of nucleic acids under electron impact-pyrolytical (EI-Py) conditions has been proposed by Loo[2] and Wiebers[3,8] (with some minor improvements resulting from the exact mass results and different pyroprobe use[4,5]) and could be summarised as in Scheme 1. The cleavage of the phosphate bond of nucleic acid produces the nucleoside-like fragment a which gives base + H [BH] ions for all bases (T-thymine, A-adenine, G-guanine and C-cytosine) according to the bases present and their abundance[6]. The ion a could ordinate one (or two) 2-methylfurane residues producing a + 80 (or a + 160) ions.

We are interested in a verification of this fragmentation process. In particular the cleavage of the DNA bonds should produce $[BH]^+$ ions directly or via the nucleoside-like fragment a. If such a consecutive rather than direct formation takes place this fragmentation should come with the corresponding metastable ions. We have applied metastable peak mapping in order to investigate this mechanism and at the same time follow the fate of the deocmposition of $[BH]^+$ ions. Finally we have cross-checked these results with linked scanning experiments.

Scheme 1



The positive ion EI-Py spectrum of DNA from Salmon Sperm is presented in Figure 1. The BH ions are present at m/z 126(T), 135(A), 111(C) and 151(G), the latter being of lower intensity. The ions a for corresponding bases are at 206(T) (weak), 215(A), 191(C) and 231(G). The transitions which have been looked for are then at 206 - 126, 215 - 135, 191 - 111 and 231 - 151.

As can be seen from the map (Fig. 2) these transitions are all absent. The individual plotting of B/E spectra from ions a also does not show corresponding BH ions and Wiebers results (MIKE)[8] show that the ion a is a result of ion-molecule reaction rather than direct pyrolysis. The equivalent B^2/E spectra have been produced for m/z values 111, 126, 135 and 151 as a second and confirmations method. Finally the B/E scan for m/z 126(T) shows as expected m/z 83 only.

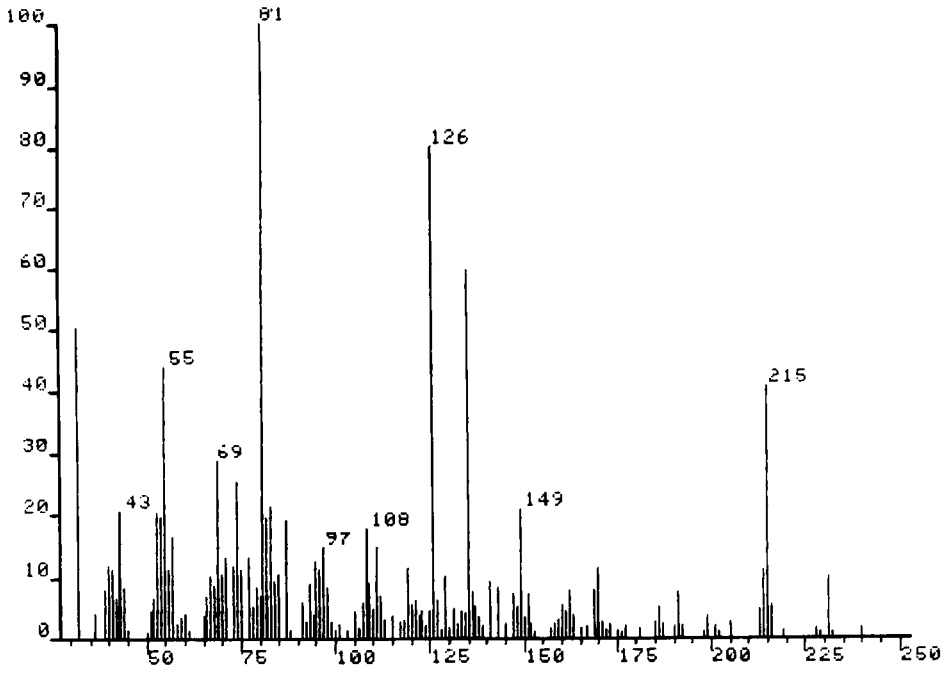


Fig. 1 Pyrolysis electron impact positive ion spectrum of DNA.

In order to clear-up this issue two linked scanning experiments have been performed:

1) parent ion recording from BH ions (B^2/E linked scanning experiment and

11) daughter ion study from the a ions (B + 80, B/E linked scanning experiment).

Both experiments were negative. The setting of a parent search in the first case at e.g. 5.987 kV for m/z 135(A) does not show any ion at 3.759 kV for expected m/z 215. In a similar way in a second case the setting of 5.987 kV at m/z 215 does not generate the expected ion at m/z 135.

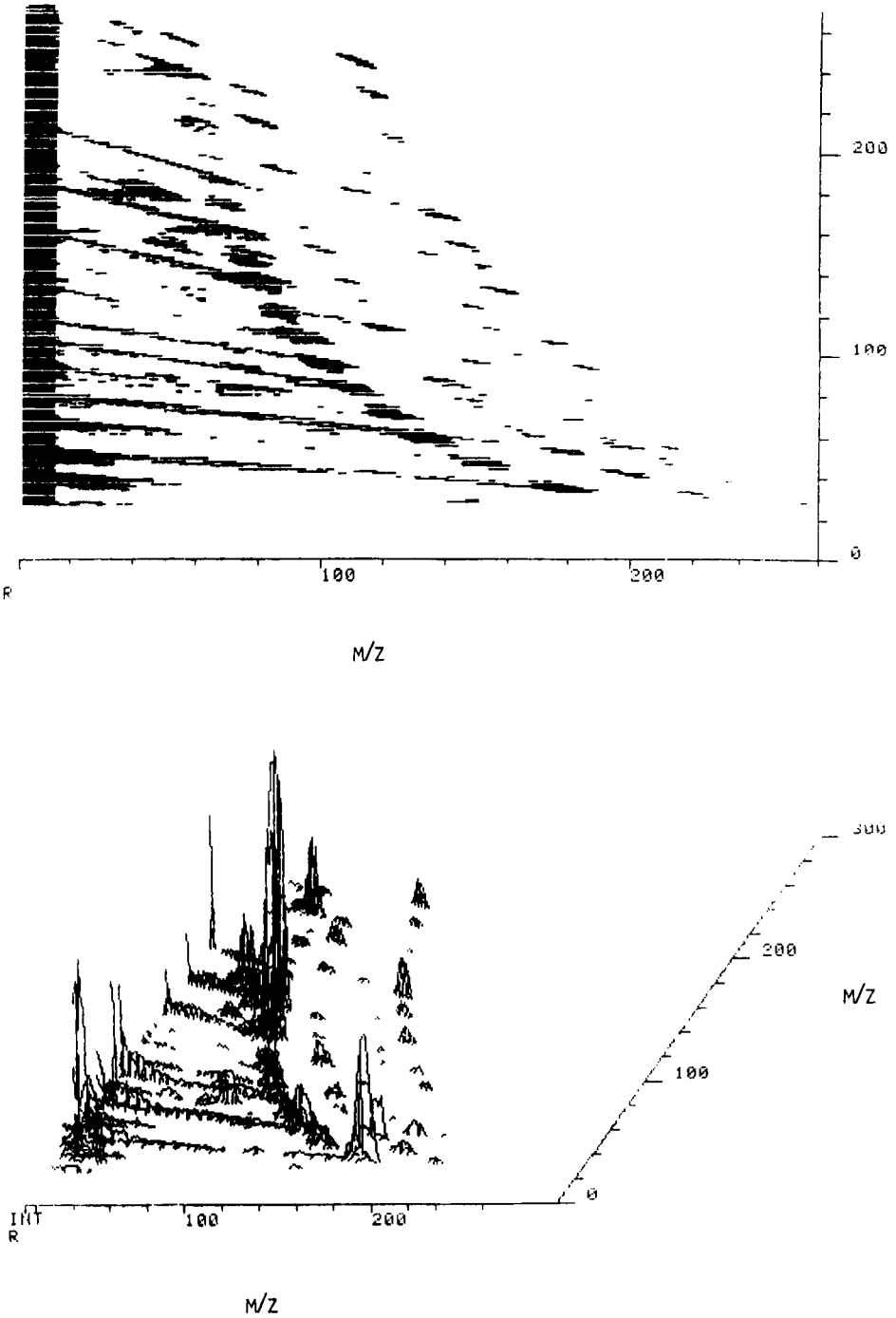


Fig. 2 B/E map for the unimolecular decomposition of ions for DNA (MS 80 - DS 55).

This double checking reveals, contrary to earlier papers[2,3,6], that BH ions may not result from the nucleoside-like ion a. It seems that these ions are directly produced from the pyrolysis of DNA. If such a one-step fragmentation (precursor ion-daughter ion) takes place it is a rapid reaction. Both ions, BH and a, remain a valuable indication of the presence of any given base of DNA.

The spectra of simple nucleosides and nucleotides reveal the presence of intense BH ions[7] which are usually formed via shift of 5'-hydrogen on the heterocyclic acceptor and a cleavage of the glycosidic bond.

Experimental

The electron impact pyrolysis positive ion mass spectrum of DNA (Salmon Sperm, Koch-Light Laboratories) has been performed on a Kratos-MS-80 apparatus at 250^{O} as previously described[3-5] using 1.5 - 2 A 260 (OD) unit. The metastable mapping has been performed using standard software of this instrument. The linked scanning experiments have been performed on a VG - 70 - 35 apparatus on the same quantity of DNA and under similar conditions.

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