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"ION-TYPES", A USEFUL CONCEPT IN THE INTERPRETATION OF HIGH-RESOLUTION MASS SPECTRA

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The conventional interpretation of mass spectra involves, in general, two principles: First, the recognition of a familiar "pattern" which one has observed previously with substances of known identity and/or, second, the presence of abundant ions of a particular mass or of a mass difference from the molecular weight. An experienced person is quite familiar with these characteristic masses (m/e 74 for methyl esters, m/e 98 for dicarboxylic esters, m/e 149 for dialkylphthalates, m/e 124 for aspidospermine-like alkaloids, etc.) but they may appear as magic to the uninitiated as they do not seem to exhibit any direct relationship to the functional group they indicate.[1]

The advent of high resolution mass spectrometry coupled with sophisticated data acquisition and data processing techniques has added a new dimension to mass spectrometric data, namely the consideration of the elemental composition rather than mass of the ions produced in the spectrometer[2].

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In the course of interpreting such data during the past few years it soon became apparent that the volume and complexity of the data obtained for a single compound make it difficult to digest unless one arranges them in a form that more clearly presents the chemical relationship (rather than the mass relationship) of the molecular ion and fragment-ions, e.g. in the form of an "element map"[3].

As an extension of this principle we have found another concept very useful, namely the presentation of the spectrum, or part thereof, as "ion-types", a form most closely related to the structurally significant aspects of an ion in the terminology of the organic chemist: These aspects are the number of carbon atoms and the number and variety of heteroatoms present in the ion as well as the number of double bonds and/or rings (DB-R). It should be noted that the number of hydrogen atoms is totally irrelevant as we subconsciously always translate it into degree of unsaturation or cyclization. Table I illustrates the relationships between accurate mass, elemental composition and "ion-type" (OF=saturated fragment, 9M=molecule with 9 rings or double bonds).*

Table I

Mass	Elemental Composition	Ion-Type
99.11737	C_7H_{15}	OF
197.08406	$C_{13}H_{11}NO$	9M N=1, O=1

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* Ions resulting from the net-cleavage (bonds broken minus bonds made) of one bond are termed "fragment-ions" (F); all others formally correspond to positively charged molecules, M (either the original one or those formed by fragmentation).

Two aspects of this presentation make it very useful for the interpretation of mass spectra: First, the predominance of a particular ion-type (encompassing a range of carbon numbers) in a spectrum is indicative of a particular structural type. Second, the ion-type of characteristically abundant ions remains unchanged for homologs, whereas their nominal mass often increases by the additional CH_2-unit (e.g. m/e 74 for methyl esters, m/e 88 for ethyl esters or α-methyl methyl esters, etc.).

In the simplest case, namely the spectra of aliphatic, saturated hydrocarbons, C_nH_{2n+1} ions (OF) are the most predominant ones. They will also appear in other compounds having relatively large alkyl substituents, but will play a less important role because of the well known inability of alkyl fragments to compete with other functional groups for the positive charge.

This is illustrated by the results obtained in the case of N-butyloctylamine, for which the two most abundant ion-types read as follows (to preserve space only the first two entries of the ion-type list are shown):

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INT/ C INT/ C INT/ C INT/ C INT/ C INT/ C  S-INT DB-R HET.AT.
 74/ 1 298/ 2  40/ 3  34/ 4 895/ 5  17/ 6
  4/ 8 289/ 9   9/10   8/12   0/ 0   0/ 0   1668   OF  N= 1

102/ 3 166/ 4  80/ 5  19/ 6   0/ 0   0/ 0    367   OF  --
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It is clear that the most abundant ions formed from this compound are alkyl amine fragments, i.e. they contain one nitrogen atom and are completely saturated (no ring or double bond). This is, of course, typical for all alkyl amines. The structural details can be deduced by consideration of the variations of intensity (column heading INT) vs. carbon number (column heading C). The largest carbon number indicates the minimum number of carbon atoms present (12). The predominance (1668 relative intensity units) of alkyl amine ions with nine (INT = 289) and five (INT = 895) carbons reveals the preference for the elimination of a C_3- and a C_7-olefin, respectively, which is indicative of the presence of C_4 and C_8 substituents (derived by cleavage of the C-C bond next to nitrogen). The intensities at other carbon numbers can be used to reveal branching in the chains analogous to conventional interpretation techniques.

The second most abundant ion-type is the alkyl ions (OF, no heteroatom) detectable up to C_6. The less saturated alkyl amine and alkyl ion-types which follow are not shown.

As to be expected, aromatic or heterocyclic systems show ion-types corresponding to a large number of double bonds or rings and heteroatom(s), if any. Thus, many indole alkaloids, for example, exhibit abundant ions of the types 6F, N=1 and 7M, N=1, originating from the indole nucleus. The presence of methoxyl groups on this nucleus changes only the oxygen content but not the number of double bonds and nitrogens.

These few cases suffice to outline the potentialities of the ion-type principle. It is particularly useful in the case of the interpretation of the spectra of compounds about which very little is known, and was applied, for example, in the determination of the structure of a new nucleoside (N_6-isopentenyl-adenosine)^4. When using this or any related approach, one has, of course, to keep in mind that it is the elemental composition of the fragment-ion which is determined. This may not represent the actual distribution in the parent molecule, if rearrangements other than simple hydrogen transfer occur.

The translation of the accurate mass of an ion to its ion-type can be accomplished by conversion of elemental compositions first and from there to ion-type and carbon number. We have found it more convenient, however, to develop a new approach producing ion-types directly, by having the computer calculate the mass of each ion-type to be possibly encountered for a specified set of heteroatoms with C equals 0. To these masses (which may be even negative values) the mass of CH_2 (14.0156) is consecutively added, and the sum compared with the masses found for the compound. In this manner, the ion-types are generated in the most suitable form (increasing carbon number) and have only to be rearranged in terms of decreasing subtotal of intensity (S-INT).

We are presently using the principle outlined in this paper to develop a system for the computer-interpretation of high resolution mass spectra.

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