7.10 Sulfur-Containing Functional Groups [1]

7.10.1 Aliphatic Thiols [2]

Fragmentation: Elimination of H_2S (Δm 34; or SH, Δm 33, from secondary thiols) followed by loss of alkenes; consecutive losses of ethylene from unbranched thiols. Cleavage of the α,β-C–C bond (next to the SH group) leads to CH_2SH^+ (m/z 47). Note that this fragment also occurs in secondary and tertiary thiols. The S atom is poorer than N, but better than O, at stabilizing such a fragment. Cleavage at the next C–C bonds leads to signals at m/z 61, 75, and 89. In secondary and tertiary thiols, prominent fragments are formed by loss of the largest α-alkyl group.

Ion series: Dominant consecutive alkenyl fragments (C_nH_{2n-1}, m/z 41, 55, 69,...) and smaller aliphatic fragments (C_nH_{2n+1}, m/z 43, 57, 71,...). Sulfur-containing aliphatic fragments: $C_nH_{2n+1}S$ (m/z 47, 61, 75, 89,...). Often significant sulfur-indicating fragments: HS^+, $H_2S^{+\cdot}$, H_3S^+, and CHS^+ (m/z 33, 34, 35, and 45).

Intensities: More intensive peaks in the lower mass range; mostly of the alkene type. Characteristic local maxima from S-containing fragments, $C_nH_{2n+1}S$ (m/z 47, 61, 75, 89,...). In *n*-alkyl thiols, the intensity of m/z 61 is roughly half that of m/z 47; the signal at m/z 89 is more intense than that at m/z 75, presumably because it is stabilized by cyclization.

Molecular ion: Relatively strong except for higher tertiary thiols. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.2 Aromatic Thiols [2]

S

Fragmentation: CS elimination from $M^{+\cdot}$ and $[M-1]^+$, yielding $[M-44]^{+\cdot}$ and $[M-45]^+$. SH elimination from $M^{+\cdot}$ to give $[M-33]^+$.

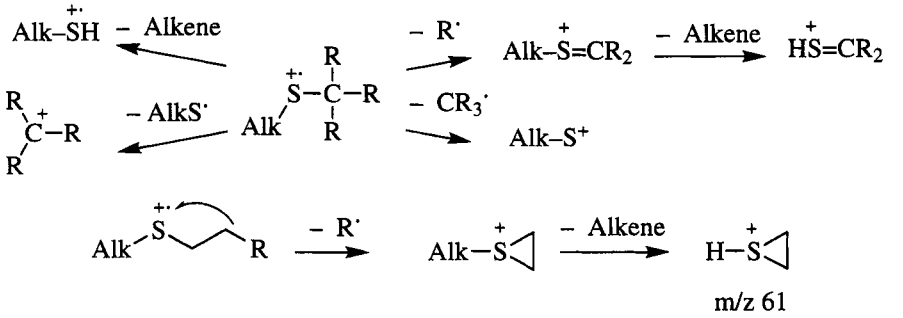
Ion series: HCS^+ (m/z 45) is characteristic besides the aromatic fragments, C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks in the higher mass range.

Molecular ion: Usually dominating; base peak in thiophenol. $[M-1]^+$ is usually strong. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.3 Aliphatic Sulfides [1]

Fragmentation: Loss of alkyl radicals by cleavage of the C–C bond next to S (the largest group being lost preferably) and of the C–S bond, followed by alkene and H_2S elimination. Alkene elimination from $M^{+\cdot}$ to form the corresponding thiol ions. In contrast to thiols and cyclic sulfides, no H_2S or $HS^{\cdot}$ elimination from $M^{+\cdot}$.



In general, the H rearrangements are non-specific. Secondary H transfer predominates over primary H transfer.

Ion series: Sulfur-containing aliphatic fragments, $C_nH_{2n+1}S$ (m/z 47, 61, 75, 89,...). The hydrocarbon fragments may dominate in long-chain sulfides.

Intensities: Intensive peaks in the lower mass range. Characteristic local maxima from S-containing fragments, $C_nH_{2n+1}S$ (m/z 47, 61, 75, 89,...).

Molecular ion: Usually strong. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.4 Alkyl Vinyl Sulfides

S

Fragmentation: Loss of alkyl radicals (Δm 15, 29, 43,...). Elimination of thioethanol (Δm 62) after triple H rearrangement. Dominant m/z 60 ($CH_3CH{=}S^{+\cdot}$) accompanied by m/z 61 ($CH_3CH_2S^+$).

Ion series: Sulfur-containing unsaturated aliphatic fragments, $C_nH_{2n-1}S$ (m/z 45, 59, 73,...). Unsaturated hydrocarbon ions, C_nH_{2n} (m/z 42, 56, 70,...) and C_nH_{2n-2} (m/z 40, 54, 68,...)

Intensities: Intensive peaks evenly distributed over the whole mass range.

Molecular ion: Of medium intensity. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.5 Cyclic Sulfides [3]

Fragmentation: Primary cleavage of the C–C bond next to S, followed by rearrangements and elimination of $CH_3^{\cdot}$ (base peak for tetrahydrothiapyrane) and $C_2H_5^{\cdot}$. In tetrahydrothiophene, $[M\text{-}1]^+$ is also significant. $HS^{\cdot}$, H_2S, and C_2H_4 elimination from $M^{+\cdot}$.

Ion series: Sulfur-containing aliphatic fragments with one degree of unsaturation, $C_nH_{2n-1}S$ (m/z 45, 59, 73, 87, 101,...), m/z 87 being of special dominance.

Intensities: Overall distribution of peaks maximizing in the low mass range due to S-containing fragments, $C_nH_{2n-1}S$ (m/z 45, 59, 73, 87,...).

Molecular ion: Very strong. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.6 Aromatic Sulfides [2]

Fragmentation: Loss of CS (Δm 44) and of HS (Δm 33) from $M^{+\cdot}$.

Ion series: HCS^+ (m/z 45) is characteristic besides the aromatic fragments, C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks mainly in the higher mass range.

Molecular ion: Strong. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.7 Disulfides

Fragmentation: Loss of $RSS^{\cdot}$ leading to alkyl cations and alkene elimination to give $RSSH^{+\cdot}$. Cleavage of the S–S bond with or without H rearrangements, leading to RS^+, $[RS\text{-}H]^{+\cdot}$, and $[RS\text{-}2H]^+$. Loss of one or two S with or without H atoms is a common process in cyclic, unsaturated, and aromatic disulfides.

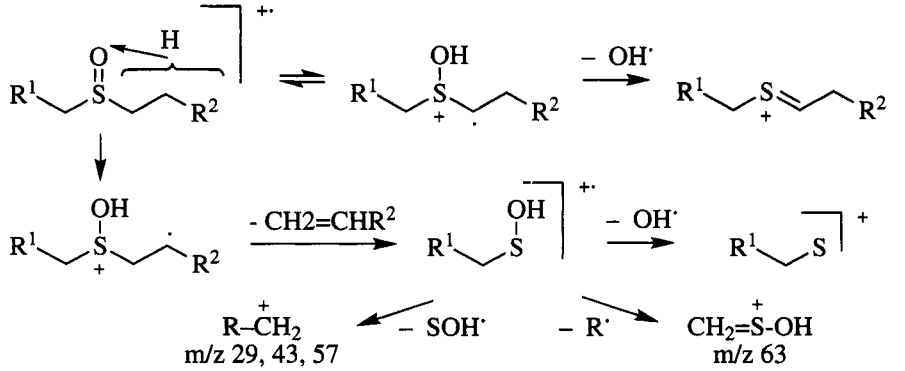
Ion series: In saturated aliphatic disulfides, H_2S_2 and its alkyl homologues are characteristic (m/z 66, 80, 94,...).

Intensities: Variable.

Molecular ion: Usually strong. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.8 Aliphatic Sulfoxides [4,5]

Fragmentation: Most fragments are produced after rearrangement with non-specific H transfer to the O atom and subsequent $OH^{\cdot}$ elimination to yield $[M-17]^+$ or alkene elimination to $[M\text{-alkene}]^{+\cdot}$, followed by $OH^{\cdot}$, $SOH^{\cdot}$ (giving alk^+ ions), or $alk^{\cdot}$ elimination (yielding $CH_2{=}S{-}OH^+$, m/z 63).



Ion series: Characteristic ion at m/z 63 ($CH_2{=}S{-}OH^+$) as well as alkyl and alkenyl fragments, C_nH_{2n+1} (29, 43, 57, 71,...) and C_nH_{2n-1}(27, 41, 55, 69,...).

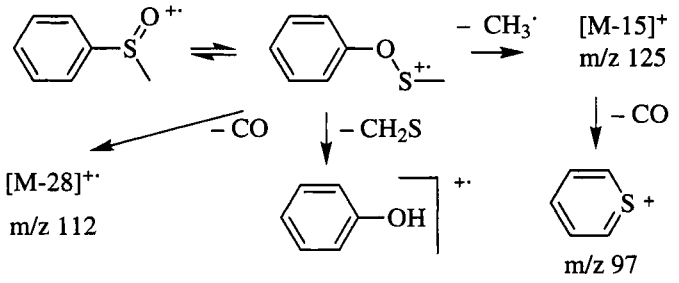
Intensities: Intensive peaks evenly distributed over the whole mass range.

Molecular ion: Of medium intensity. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.9 Alkyl Aryl and Diaryl Sulfoxides [4,5]

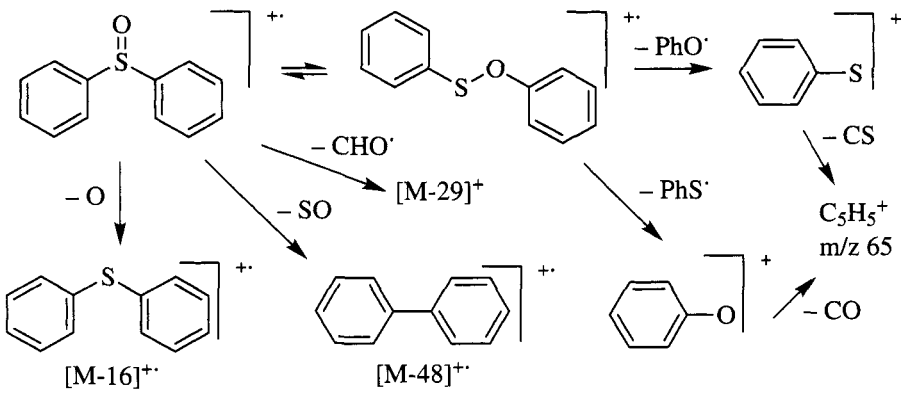
S

Fragmentation: Most fragments of methyl aryl sulfoxides are produced, after rearrangement to $CH_3S{-}O{-}ar^{+\cdot}$, by elimination of CH_2S (yielding $[M-46]^{+\cdot}$, a phenol), of CO (to $[M-28]^{+\cdot}$), and of $CH_3^{\cdot}$ (to $[M-15]^+$). The latter ion loses CO to give the thiapyranyl cation (m/z 97 if ar is phenyl).



The skeletal rearrangement is not relevant for the fragmentation of higher alkyl aryl sulfoxides. Here, direct cleavage of the C–S bonds and McLafferty rearrangements dominate.

For diaryl sulfoxides, elimination of SO (to give $[M-48]^{+\cdot}$) as well as of O, OH$^{\cdot}$, and COH$^{\cdot}$ (yielding $[M-16]^{+\cdot}$, $[M-17]^{+}$, and $[M-29]^{+}$). After rearrangement to sulfenates, fragmentation of the S–O bond to produce ar–S^{+} and ar–O^{+} ions, which further lose CS and CO, respectively, to give $C_5H_5^{+}$ (m/z 65).



Ion series: Besides the ions described under *Fragmentation*, mainly fragments of the aromatic type, i.e., C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...), as well as O- and S-containing ions.

Intensities: Intensive peaks mainly in the high mass range.

Molecular ion: Very strong. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^{+}$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.10 Aliphatic Sulfones [4,5]

S

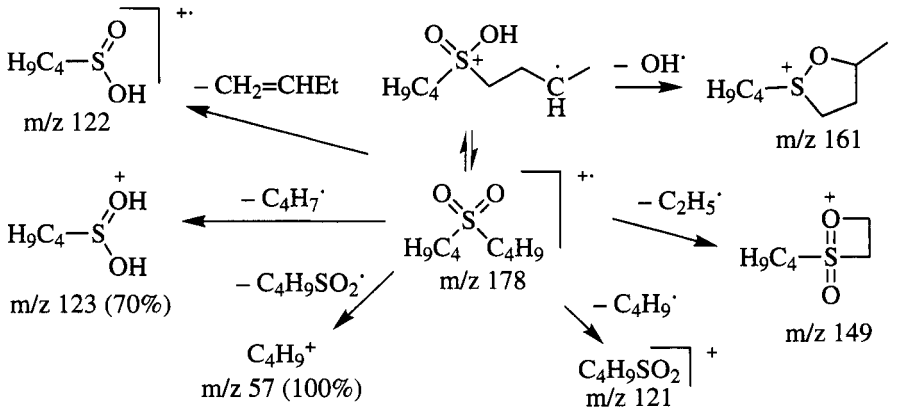
Fragmentation: Fragmentation of the S–C bond with the charge remaining on either side. Single and double H rearrangements to give $RS(O)OH^{+\cdot}$ and $RS(OH)_2^{+}$.

The probability of the double H rearrangement increases with increasing chain length. If one of the substituents is unsaturated, rearrangement to RS(O)O-alkene and fragmentation of the S–O bond yields the ion $RSO^{+\cdot}$.

Ion series: Dominating aliphatic fragments, C_nH_{2n+1} (m/z 29, 43, 57,...) and C_nH_{2n-1} (m/z 27, 41, 55,...). Usually one significant fragment corresponding to alk–$S(O)OH^{+\cdot}$ (from the series of m/z 80, 94, 108,...) or alk–$S(OH)_2^{+}$ (from the series of m/z 81, 95, 109,...) can be observed.

Intensities: Intensive peaks mainly aliphatic fragments in the lower mass range.

Molecular ion: Weak. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^{+}$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).



7.10.11 Cyclic Sulfones [4]

Fragmentation: Dominant eliminations of SO_2 (Δm 64, followed by loss of $CH_3^{\cdot}$), $HSO_2^{\cdot}$ (Δm 65, followed by loss of C_2H_4), or CH_2SO_2 (Δm 78). Weak fragment at $[M-17]^+$ due to $OH^{\cdot}$ elimination.

Ion series: Mainly unsaturated hydrocarbon fragments, C_nH_{2n-1} (m/z 27, 41, 55,...).

Intensities: Intensive peaks in the lower mass range.

Molecular ion: Moderate. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^{+}$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

S

7.10.12 Alkyl Aryl Sulfones [4]

Fragmentation: Isomerization of $M^{+\cdot}$ to ar–OS(=O)alk and formation of the phenoxy ion or the phenol radical cation with H rearrangement. The migration of the aryl group depends on the type of substituents. It is facilitated by electron donators and hindered by acceptors. Mainly in substituted or unsaturated alkyl derivatives also isomerization to ar–S(=O)O–alk(ene) and formation of ar–$S{=}O^+$ (m/z 125 if ar is phenyl). Single and double H rearrangements to give ar-$S(O)OH^{+\cdot}$ and ar–$S(OH)_2^+$. The probability of the double H rearrangement increases with increasing chain length. In some derivatives, SO_2 elimination from $M^{+\cdot}$ dominates. Substituents X of the alkyl group may migrate to the aryl group to yield X–ar–$S{=}O^+$ ions.

Ion series: Aromatic fragments, C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...), as well as S- and O-containing aromatic fragments at higher masses.

Intensities: Intensive peaks mainly in the higher mass range.

Molecular ion: Strong. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.13 Diaryl Sulfones [4,5]

Fragmentation: Predominant aromatic fragments of the type ar–O^+ and ar–SO^+ (m/z 125 if ar is phenyl), formed after migration of one of the aryl groups. The ar-SO_2^+ ion is unimportant; ar^+ is intense. Small fragments due to SO_2, $SO_2H^{\cdot}$, and SO_2H_2 eliminations (Δm 64, 65, and 66, respectively). With alkyl substituents in *ortho* position, $[M\text{-}OH]^+$ and $[M\text{-}H_2O]^{+\cdot}$ are formed, upon which SO elimination follows.

Ion series: Aromatic fragments, C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...) and the S- and O-containing aromatic fragments at higher masses. Usually, ar–SO^+ (m/z 125 if ar is phenyl) is very strong.

Intensities: Intensive peaks mainly in the higher mass range.

Molecular ion: Strong. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.14 Aromatic Sulfonic Acids [6]

Fragmentation: The most prominent fragment, $[M\text{-}HSO_3]^+$ (Δm 81), is formed in a two-step process. In the first step, $OH^{\cdot}$ elimination leads to a weak fragment ion $[M\text{-}OH]^+$ (Δm 17). If an alkyl group is present in *ortho* position, $[M\text{-}H_2SO_3]^{+\cdot}$ (Δm 82) is formed instead of $[M\text{-}81]^+$. Other important fragments are $[M\text{-}SO_2]^{+\cdot}$ (Δm 64), $[M\text{-}HSO_2]^+$ (Δm 65), and $[M\text{-}SO_3]^{+\cdot}$ (Δm 80).

Ion series: Aromatic fragments, C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...), and O-containing aromatic fragments at higher masses.

Intensities: Intensive peaks mainly in the higher mass range.

Molecular ion: Very strong. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.15 Alkylsulfonic Acid Esters [6]

Fragmentation: Loss of alkyl by fragmentation of the C–O bond with concomitant double H rearrangement to form the protonated sulfonic acid ion (m/z 97 for methanesulfonates), which then loses water. Loss of the alkoxyl residue (fragmentation of the S–O bond). Formation of an alkene ion from the sulfonate alkyl by a McLafferty-type rearrangement. In aryl esters, the phenoxy ion and the phenol radical cations dominate the spectrum.

Ion series: Besides $RSO_3H_2^+$ and RSO_2^+ (m/z 97 and 79 for methanesulfonates), for aliphatic esters mainly alkene fragments. In aryl esters, aromatic fragments,

C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...), as well as O-containing aromatic fragments at higher masses.

Intensities: Intensive peaks in the lower mass range.

Molecular ion: Small or negligible in alkyl esters; strong in aryl esters. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.16 Arylsulfonic Acid Esters [6]

Fragmentation: Dominating fragments resulting from cleavage of the S–O bond (leading to the ar–SO_2^+ ion), which loses SO_2 (m/z 155 and 91 for *p*-toluenesulfonates). In alkylsulfonates with longer chains, double H rearrangement to give the protonated acid (m/z 173 for *p*-toluenesulfonates).

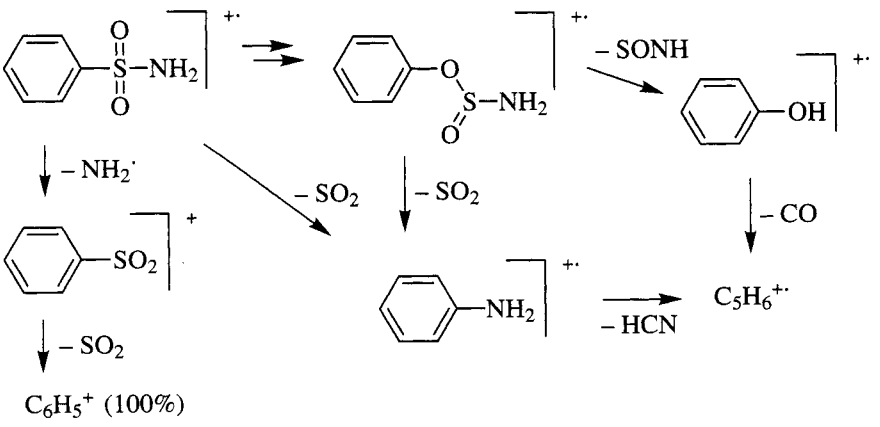
Ion series: Aromatic fragments, C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks mainly in higher mass range.

Molecular ion: Medium or weak. Characteristic ^{34}S isotope peak at $[M+2]^{+\cdot}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to $M^{+\cdot}$).

7.10.17 Aromatic Sulfonamides [6]

Fragmentation: In *N*-alkylamides, the C–C bond next to N is split preferably. In *N*-arylamides, besides $[M\text{-}SO_2]^{+\cdot}$ and $[M\text{-}HSO_2]^+$, the ions ar–SO_2^+ and ar'–NH^+ are formed.

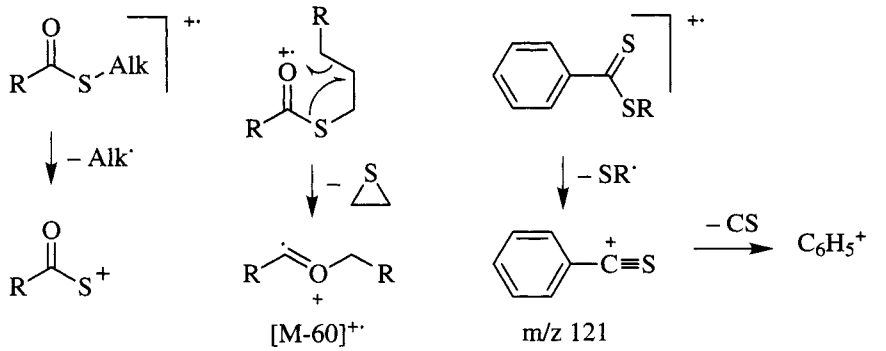


Ion series: Ions typical of the tosyl group: m/z 155, 91, and 65.

Molecular ion: In arylamides, $M^{+\cdot}$ is dominant.

7.10.18 Thiocarboxylic Acid S-Esters [7]

In contrast to esters, elimination of the alkyl radical from the thiol site is the major fragmentation process. Ethylene sulfide is eliminated from thioesters with longer alkyl chains. Aromatic dithiocarboxylic acid esters usually fragment in two steps to the aryl cation.



7.10.19 References

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7.11 Carbonyl Compounds [1-4]

7.11.1 Aliphatic Aldehydes [5]

Fragmentation: Cleavage of the bond next to CO. The fragmentation of the hydrocarbon chain is similar to that in corresponding alkanes. McLafferty rearrangement with localization of the charge on either side, giving rise to $C_nH_{2n}^{+\cdot}$ (m/z 28, 42, 56,...) and, often less important, to $C_nH_{2n}O^{+\cdot}$ ions (m/z 44, 58, 72,...). At least one product (often both) is significant. Elimination of water from the molecular ion to give $[M-18]^{+\cdot}$, occasionally very pronounced.

Ion series: Dominating consecutive fragments of the series of C_nH_{2n+1} and $C_nH_{2n-1}O$ (in both cases: m/z 29, 43, 57,...). Weaker fragments of the series C_nH_{2n-1} (m/z 41, 55, 69,...) and rearrangement products, C_nH_{2n} (m/z 28, 42, 56,...).

Intensities: Intensive peaks concentrated in the lower mass range. Local even-mass maxima from McLafferty-type reactions ($[M-44]^{+\cdot}$ when aldehyde not substituted in α-position).

Molecular ion: Only strong for molecules of low molecular weight; very weak for $C_{n>9}$. $[M-1]^+$ may be more relevant than $M^{+\cdot}$.

7.11.2 Unsaturated Aliphatic Aldehydes

Fragmentation: Cleavage of the bond next to CO, leading to $[M-1]^+$ (more significant than in saturated aldehydes), $[M-29]^+$, and m/z 29. No McLafferty rearrangement occurs if the γ-hydrogen atom is attached to a double bond or if there is a double bond in α,β-position.

Ion series: Fragments of the series of C_nH_{2n-1} and $C_nH_{2n-3}O$ (in both cases m/z 41, 55, 69,...).

Molecular ion: Stronger than in saturated aldehydes. Usually, $[M-1]^+$ is relevant.

C=X

7.11.3 Aromatic Aldehydes

Fragmentation: Characteristic $H^{\cdot}$ loss to yield the corresponding benzoyl ion, $[M-1]^+$, followed by decarbonylation to a phenyl ion, $[M-1-28]^+$, of lower intensity. To a small extent also decarbonylation of the molecular ion, leading to $[M-28]^{+\cdot}$. Weak signal at m/z 29 (CHO^+).

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks predominantly in the molecular ion region.

Molecular ion: Usually prominent. $[M-1]^+$ is strong.

7.11.4 Aliphatic Ketones

Fragmentation: Cleavage of the bond next to CO is the most important primary fragmentation. The charge can remain on either side. The acyl ions then lose CO. McLafferty rearrangement giving rise to $C_nH_{2n}O^{+\cdot}$ ions (m/z 58, 72, 86,...). Consecutive rearrangements occur if both alkyl chains contain a γ-H atom. Keto-enol tautomerism of the first rearrangement product is not a prerequisite for the second rearrangement to occur. Oxygen is sometimes indicated by weak signals at $[M-18]^{+\cdot}$ and m/z 31, 45, 59. Fragmentation of the hydrocarbon chain similar to that in the corresponding alkanes.

Ion series: Dominating consecutive fragments of the series C_nH_{2n+1} and $C_nH_{2n-1}O$ (in both cases: m/z 29, 43, 57,...), with maxima due to cleavage at the CO group to give acyl ions and their decarbonylation products. Weaker fragments in the series C_nH_{2n-1} (m/z 41, 55, 69,...). Even-mass maxima, $C_nH_{2n}O$ (m/z 58, 72, 86,...), due to alkene elimination (McLafferty rearrangement). Usually, m/z 43 (CH_3CO^+) is strong if an unsubstituted α-CH_2 group is present.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Relatively abundant, weak in long-chain and branched aliphatic ketones.

7.11.5 Unsaturated Ketones

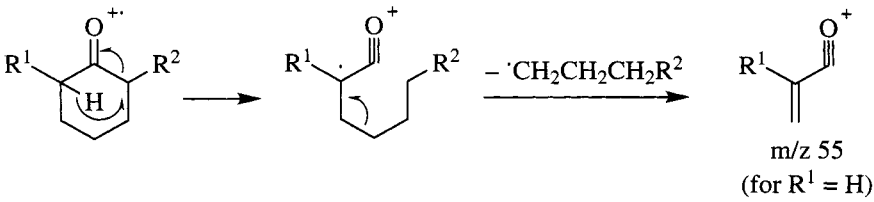
Fragmentation: Cleavage of the bond next to CO, more favorably on the saturated side, is the most important primary fragmentation. The acyl ion then loses CO. The McLafferty rearrangement occurs neither when the unsaturated substituents are in α,β position nor when the only available γ-hydrogen atom is attached to a double-bonded carbon.

Molecular ion: Relatively abundant.

7.11.6 Alicyclic Ketones

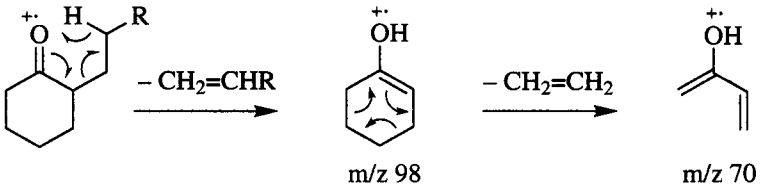
C=X

Fragmentation: Major primary fragmentation by bond cleavage next to carbonyl, followed by loss of alkyl residue.



m/z 55
(for R^1 = H)

Prominent McLafferty-type elimination of larger alkyl groups in position 2 or 6 as alkenes. This rearrangement is very favorable; even aromatically bonded H atoms can rearrange. For cyclohexanones, a consecutive retro-Diels–Alder reaction can occur:



m/z 98 m/z 70

Oxygen is sometimes indicated by a weak signal at $[M-18]^{+\cdot}$.

Ion series: Consecutive alkene fragments of the type of C_nH_{2n-1} or $C_nH_{2n-3}O$ (for both: m/z 41, 55, 69,...) with maxima due to alkyl loss after ring opening next to the carbonyl group and H transfer. Prominent even-mass maxima by elimination of substituents at position 2 or 6 as alkenes via sterically favored McLafferty rearrangements.

Intensities: Overall more intensive peaks in the lower mass range or even distribution of major peaks over the whole mass range. Local maxima from major fragmentation pathway.

Molecular ion: Abundant.

7.11.7 Aromatic Ketones

Fragmentation: Dominant α-cleavage to give the benzoyl ion, followed by decarbonylation to a phenyl ion of lower intensity. α-Cleavage in acetophenone also produces the acetyl cation (m/z 43). Even-mass maxima due to alkene elimination via McLafferty rearrangement. CO elimination from diaryl ketones through skeletal rearrangements.

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...).

C=X *Intensities:* Intensive peaks predominantly in the molecular ion region.

Molecular ion: Strong.

7.11.8 Aliphatic Carboxylic Acids

Fragmentation: Fragmentation of the C–CO bond leading to m/z 45 and to $[M-45]^+$. Loss of $OH^\cdot$ leading to $[M-17]^+$; may be followed by decarbonylation. Cleavage of the γ bond (relative to CO) leading to $^+CH_2CH_2COOH$ (m/z 73) if there is no branching on the α- and β-C atoms. Loss of $H^\cdot$ (not the carboxylic one) leading to $[M-1]^+$. Water elimination to give $[M-18]^{+\cdot}$ if the alkyl group

consists of at least 4 C atoms; may be followed by decarbonylation. McLafferty rearrangement to m/z 60 (acetic acid) if there is no α-substituent.

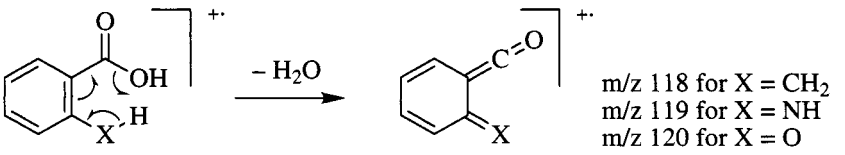
Ion series: Saturated and unsaturated alkyl ions mainly in the lower mass range (C_nH_{2n+1} and C_nH_{2n-1}, m/z 29, 43, 57,... and 27, 41, 55,...). With long-chain aliphatic acids, $C_nH_{2n-1}O_2$ series (m/z 59, 73, 87,...), exhibiting maxima for n = 3, 7, 11, 15,... (m/z 73, 129, 185, 241,...). Even-mass maxima, $C_nH_{2n}O_2$ (m/z 60, 74, 88,...), due to McLafferty rearrangements.

Intensities: Intensive peaks due to the above mentioned ions.

Molecular ion: Generally detectable. Easily protonated to $[M+H]^+$.

7.11.9 Aromatic Carboxylic Acids

Fragmentation: Pronounced loss of OH$^\cdot$, leading to $[M-17]^+$ and followed by decarbonylation (Δm 28) to a phenyl ion of lower intensity. Water elimination to $[M-18]^{+\cdot}$ if a H-bearing *ortho*-substituent is present. Some acids decarboxylate (Δm 44). Loss of CO (Δm 28) from $M^{+\cdot}$.



m/z 118 for X = CH_2
m/z 119 for X = NH
m/z 120 for X = O

Ion series: Aromatic hydrocarbon fragments, C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks predominantly in the molecular ion region.

Molecular ion: Strong.

7.11.10 Carboxylic Acid Anhydrides

Fragmentation: In the case of linear anhydrides abundant acyl ions due to cleavage next to carbonyl group. For cyclic anhydrides maxima due to decarboxylation (Δm 44), followed by decarbonylation.

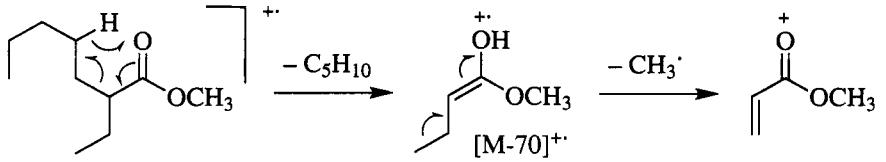
C = X

Molecular ion: Weak or absent (especially in linear aliphatic anhydrides), easily protonated to $[M+H]^+$. Relatively strong for phthalic anhydrides.

7.11.11 Saturated Aliphatic Esters

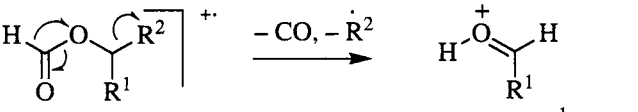
Fragmentation: Dominant fragmentation of the bonds next to the carbonyl C, leading to alk–CO^+ (m/z 43, 57, 71,...; decreasing intensity with increasing length of the alkyl chain) and followed by decarbonylation, as well as fragmentation to $COOR^+$ (m/z 59, 73, 87,...) and to alk^+ (m/z 15, 29, 43,...).

Alcohol elimination to $C_nH_{2n-2}O$ (m/z 42, 56, 70,...), followed by decarbonylation (Δm 28) or ketene elimination (Δm 42). Alkene elimination from the acid side via McLafferty rearrangements, leading to $C_nH_{2n}O_2$ (m/z 60, 74, 88,...). The larger alkyl group participates in the rearrangement if several γ-H atoms are available. In the following example, the alternative process leading to $[M\text{-}C_2H_4]^{+\cdot}$ is negligible.



Non-specific H rearrangements at the alcohol side (from $M^{+\cdot}$ or the McLafferty product) lead to $C_nH_{2n}O_2$ and to the corresponding alkene, C_nH_{2n} (m/z 28, 42, 56,...). In methyl esters of long chain acids, the ions $[(CH_2)_{2+4n}COOCH_3]^+$ (m/z 87, 143, 199,...) correspond to maxima. For esters of higher alcohols (at least C_3), double H rearrangement to the protonated acid, $C_nH_{2n+1}O_2$ (m/z 61, 75, 89,...). α-Substituted esters may lose the substituent and then CO (Δm 28) via alkoxyl rearrangement. In an analogous reaction, β-substituted esters may eliminate ketene (Δm 42).

Besides usual ester reactions, specific rearrangements can be observed in formates.



(m/z 31 for $R^1 = H$)

Ion series: C_nH_{2n+1} (m/z 29, 43, 57,...) for the alkyl groups at the ester oxygen (except for methyl esters). C_nH_{2n-1} (m/z 27, 41, 55,...). $C_nH_{2n-1}O_2$ (m/z 59, 73, 87,...), exhibiting maxima for n = 4, 8, 12,... (m/z 87, 143, 199,...) in case of the methyl esters of long-chain acids. Even-mass maxima for $C_nH_{2n}O_2$ (m/z 60, 74, 88,...) due to alkene elimination via McLafferty rearrangements on both sides of the carboxyl group. C_nH_{2n} (m/z 28, 42, 56,...) as H rearrangement product from the alcohol side.

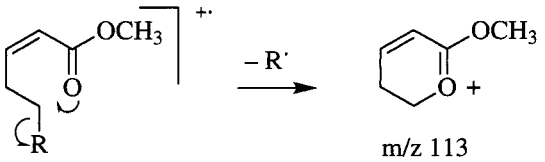
C=X

Intensities: Intensive peaks due to above mentioned ions from the lower mass range.

Molecular ion: Often of low abundance. Easily protonated to $[M+H]^+$.

7.11.12 Unsaturated Esters

α,β-Unsaturated esters: Loss of alk–O· followed by C=O elimination is the dominant fragmentation path. Also, loss of the δ-substituent yields a 6-membered oxonium ring:



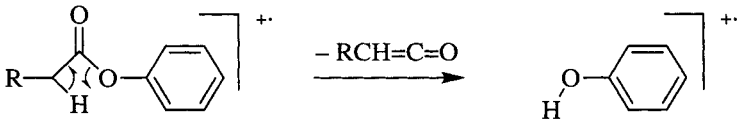
m/z 113

Significant difference between Z and E isomers of long-chain α,β-unsaturated esters: Single H rearrangement occurs with Z esters and double H rearrangements (leading to protonated acids) have been found for E esters.

β,γ-Unsaturated esters: Only slight qualitative, but significant quantitative differences have been observed as compared to α,β-unsaturated esters.

γ,δ-Unsaturated esters: Loss of the alcohol chain as a radical, R·, followed by ketene elimination.

Aliphatic enol esters and aryl esters: Formation of alk–CO^+ (m/z 43, 57, 71,...). Elimination of a ketene to give the enol/phenol radical cation. The rearrangement occurs prodominantly, but not exclusively, through a 4-membered transition state.



$[M-42]^{+\cdot}$ for R = H

7.11.13 Esters of Aromatic Acids

Fragmentation: Dominant loss of RO· to form the benzoyl ion, followed by decarbonylation (Δm 28) and further loss of acetylene (Δm 26). Ethyl esters also eliminate C_2H_4 (Δm 28) to give the acid radical cation, which then loses OH· to yield the benzoyl ion. In higher alkyl esters, besides the acid, the protonated acid is formed (double H rearrangement). In *ortho*-substituted aryl esters with an α-hydrogen atom on the substituent, an alcohol is eliminated from $M^{+\cdot}$. In the case of alkyl phthalates (other than dimethyl phthalate), alkenyl elimination to give the protonated ester acid, followed by alkene elimination from the other ester group, and subsequently water elimination to the protonated anhydride ion, which forms the base peak at m/z 149.

C=X

Ion series: Aromatic hydrocarbon fragments, C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Prominent maximum at the mass of the related benzoyl ion and its decarbonylation product.

Molecular ion: Usually strong.

7.11.14 Lactones

Fragmentation: The most prominent reaction is the loss of substituents (or H$^{\cdot}$) at the O-bearing C atom, followed by decarbonylation (Δm 28), decarboxylation (Δm 44, mainly in smaller molecules), and ketene elimination (Δm 42). Decarboxylation of $M^{+\cdot}$ is rarely significant. Competing reactions are several kinds of primary ring cleavages. Aromatic lactones show maxima due to two consecutive decarbonylations.

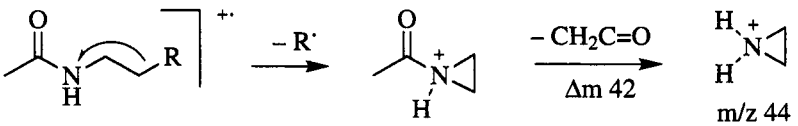
Ion series: No specific ion series. The acetyl ion (m/z 43) is often an important fragment.

Intensities: Maxima at the mass resulting from loss of substituents at the C atom next to oxygen. Otherwise, intensive peaks evenly distributed over whole mass range.

Molecular ion: Usually of low intensity and easily protonated to $[M+H]^+$ in aliphatic lactones; abundant in the case of aromatic lactones.

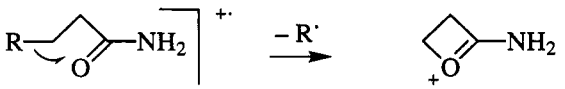
7.11.15 Aliphatic Amides

Fragmentation: Alkene elimination on the acid side via McLafferty reaction to yield the corresponding acetamide radical cation. Loss of alkenes on the amine side to give the ion of the desalkyl amide, often via double H rearrangement to the protonated desalkyl amide ion. Cleavage on both sides of the carbonyl group. Cleavage of the C–C bond attached to N, and the β,γ-C–C bond (relative to N; see scheme).



Cleavage of the bonds to the β-C (see scheme) and γ-C on the acid side.

C=X



Ion series: Even-mass fragments corresponding to $C_nH_{2n}NO$ (m/z 44, 58, 72,...) produced by cleavage of the bond next to CO on the acidic side. Odd-mass fragments (in secondary and tertiary amides), $C_nH_{2n-1}O$ (m/z 43, 57, 71,...), produced by cleavage of the bond next to CO on the amine side.

Intensities: Overall peak distribution maximizing in the low mass range. Local maxima from McLafferty and from γ-cleavage products.

Molecular ion: Significant. Strong tendency to protonate to $[M+H]^+$.

7.11.16 Amides of Aromatic Carboxylic Acids

Fragmentation: Amides of aromatic acids exhibit maxima due to amide bond cleavage yielding the benzoyl ion, followed by decarbonylation (Δm 28).

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks predominantly in the molecular ion region.

Molecular ion: Abundant. $[M\text{-}H]^+$ is significant in N,N-disubstituted anilides, weaker in monosubstituted derivatives, and absent from the spectrum of benzamide. It is formed exclusively by loss of *ortho*-hydrogens of the aromatic ring.

7.11.17 Anilides

Formanilides: Loss of CO (Δm 28) to give the aniline radical cation and consecutive HCN elimination (Δm 27).

Acetanilides: Ketene elimination to yield the aniline radical cation (often base peak), which consecutively eliminates HCN (Δm 27), and formation of the acetyl cation (m/z 43).

Trichloroacetanilides: Dominant loss of $CCl_3^{\cdot}$ (Δm 117).

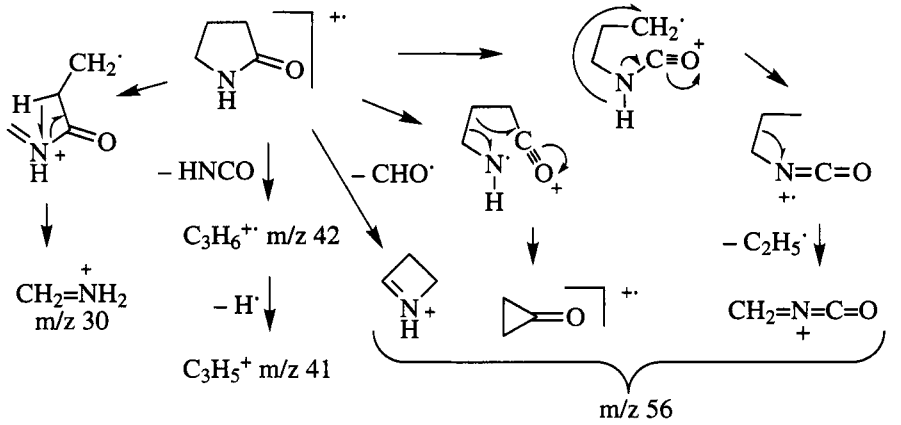
Pivalanilides: Besides reactions analogous to those of acetanilides (formation of the aniline radical cation, Δm 84), also formation of the *tert*-butylbenzene radical cation through elimination of HNCO (Δm 43).

7.11.18 Lactams

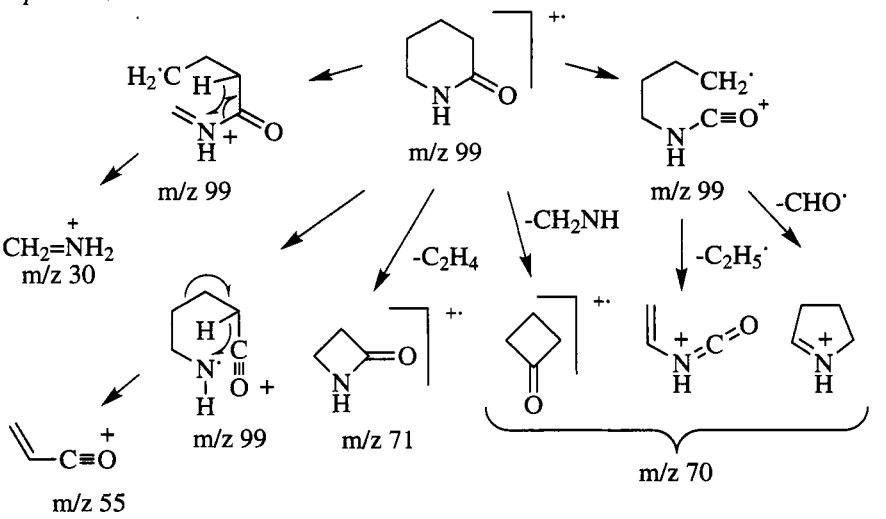
Fragmentation: Cleavage of the C–C bond at the N-bearing C atom. Cleavage of the CO–N bond, followed by loss of CO (Δm 28) or by further cleavage of the C–C bond next to N, giving an iminium ion. In 2-pyrrolidone and 2-piperidone, the signal at m/z 30 ($[CH_2{=}NH_2]^+$) is strong. The base peak of 2-pyridone is formed by CO elimination (Δm 28).

C = X

2-Pyrrolidone:



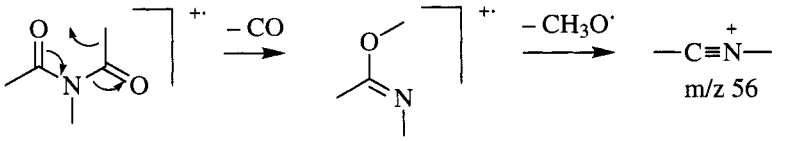
2-Piperidone:



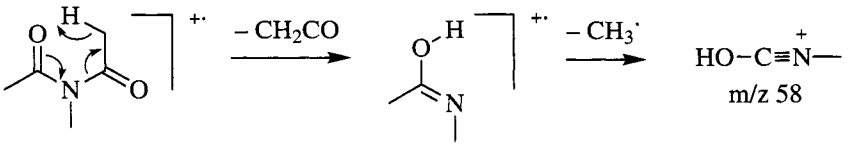
C=X *Molecular ion:* Often observable; more abundant than for the corresponding lactones.

7.11.19 Imides

Saturated acyclic imides: Consecutive CO (Δm 28) and alkoxy elimination:

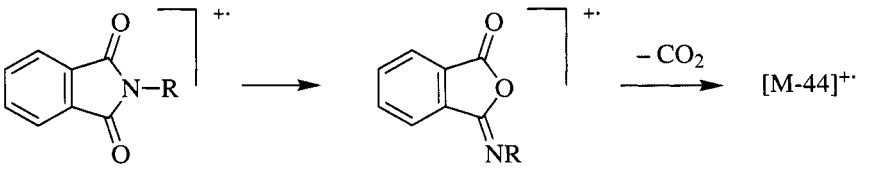


Ketene elimination:

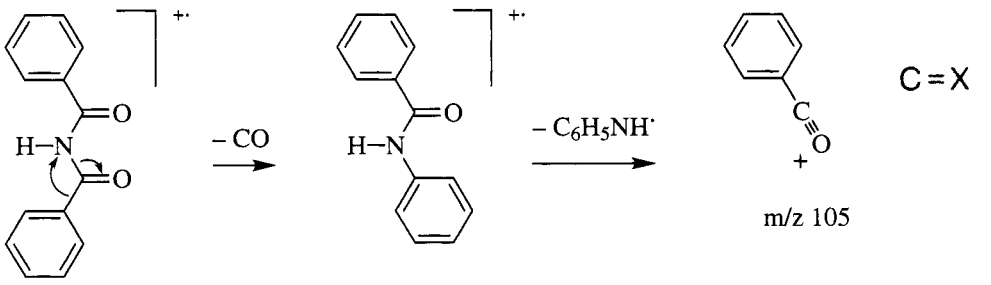


If the N-substituent chain is sufficiently long, cleavages of the C–C bond next to N with or without H rearrangement.

Cyclic imides: The spectra of saturated cyclic imides are almost identical to those of the corresponding diketones. Loss of HNCO (Δm 43) from succinimide, followed by CO elimination (Δm 28). Aroyl migration and loss of CO_2 from aromatic cyclic imides.



Dibenzoylamine: Loss of CO to *N*-phenylbenzamide:



7.11.20 References

[1] J.H. Bowie, Mass spectrometry of carbonyl compounds. In: *The Chemistry of the Carbonyl Group,* vol. 2; J. Zabicky, Ed.; Wiley-Interscience: London, 1970; p 277.

[2] S.W. Tam, Mass spectra of acid derivatives. In: *The Chemistry of Acid Derivatives, Part 1*; S. Patai, Ed.; Wiley: Chichester, 1979.

[3] D.G.I. Kingston, J.T. Bursey, M.M. Bursey, Intramolecular hydrogen transfer in mass spectra. II. The McLafferty rearrangement and related reactions, *Chem. Rev.* **1974**, *74*, 215.

[4] D.G.I. Kingston, B.W. Hobrock, M.M.Bursey, J.T. Bursey, Intramolecular hydrogen transfer in mass spectra. III. Rearrangements involving the loss of small neutral molecules, *Chem. Rev.* **1975**, *75*, 693.

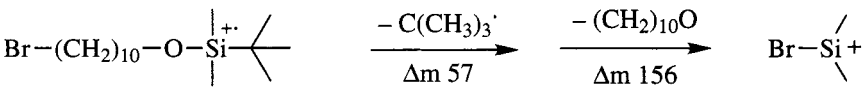
[5] A.G. Harrison, High-resolution smass spectra of aliphatic aldehydes, *Org. Mass. Spectrom.* **1970**, *3*, 549.

C=X

7.12 Miscellaneous Compounds

7.12.1 Trialkylsilyl Ethers [1,2]

Fragmentation: Loss of alkyl attached to Si (preferential loss of larger groups). Cleavage of the C–C bond adjacent to O, followed by alkene elimination. Loss of alkoxyl, followed by alkene eliminations. Elimination of trialkylsilanol. The $R_2Si{-}OR'$ cation has the tendency to attack, in an electrophilic manner and even over long distances, free electron pairs and π-electron centers, causing the expulsion of neutral fragments from the interior of the molecule via a rearrangement:



Ion series: $[C_nH_{2n+3}OSi]^+$ (m/z 75, 89, 103, 117,...). $[C_nH_{2n+3}Si]^+$ (m/z 45, 59, 73, 87,...). Occasionally, maxima at even mass due to elimination of trialkylsilanol.

Molecular ion: $M^{+\cdot}$ often of low abundance or absent, easily protonated to $[M+H]^+$. Typical isotope patterns owing to ^{28}Si, ^{29}Si, and ^{30}Si (see Chapter 2.5.5).

7.12.2 Alkyl Phosphates [3]

Fragmentation: Maxima due to alkenyl loss from $M^{+\cdot}$ via double H rearrangement, followed by successive alkene eliminations down to protonated phosphoric acid (m/z 99).

Ion series: PO^+ (m/z 47), $H_2PO_2^+$ (m/z 65), $H_2PO_3^+$ (m/z 81), often as non-specific P indicators.

Molecular ion: $M^{+\cdot}$ observable.

7.12.3 Aliphatic Phosphines and Phosphine Oxides

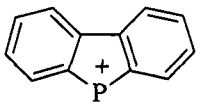
Ion series: Maxima of the ion series of $[C_nH_{2n+3}P]^+$ (m/z 48, 62, 76, 90,...) due to alkene eliminations.

Molecular ion: $M^{+\cdot}$ observable.

7.12.4 Aromatic Phosphines and Phosphine Oxides

Fragmentation: Maxima due to loss of an aryl group, followed by H_2 elimination to yield the 9-phosphafluorenyl ion (m/z 183).

Molecular ion: $M^{+\cdot}$ abundant, easily losing $H^{\cdot}$ to give $[M\text{-}1]^+$.



m/z 183

7.12.5 References

[1] D.G.I. Kingston, B.W. Hobrock, M.M. Bursey, J.T. Bursey, Intramolecular hydrogen transfer in mass spectra. III. Rearrangements involving the loss of small neutral molecules, *Chem. Rev.* **1975**, *75*, 693.

[2] H. Schwarz, Positive and negative ion chemistry of silicon-containing molecules in the gas phase. In: *The Chemistry of Organic Silicon Compounds*;.S. Patai,.Z. Rappoport, Eds.; Wiley: Chichester, 1989; p 445.

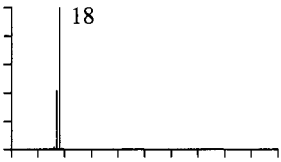
[3] D.G.I. Kingston, J.T. Bursey, M.M. Bursey, Intramolecular hydrogen transfer in mass spectra. II. The McLafferty rearrangement and related reactions, *Chem. Rev.* **1974**, *74*, 215.

7.13
Mass Spectra of Common Solvents and Matrix Compounds

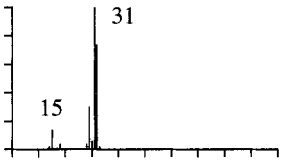
7.13.1
Electron Impact Ionization Mass Spectra of Common Solvents

The label {50} indicates that the intensity scale ends at 50% relative intensity and is subdivided in 10% steps. In these cases, the height of the base peak has to be doubled to bring it to 100%. All spectra represent positive ions only.

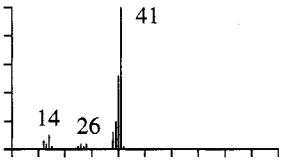
Water {50}



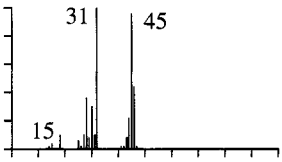
Methanol



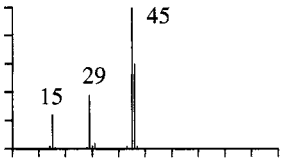
Acetonitrile



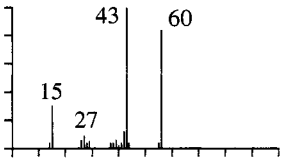
Ethanol {50}



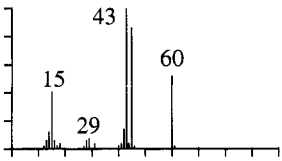
Dimethyl ether



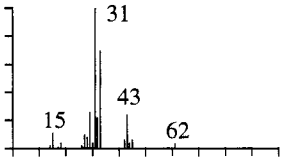
Acetone {50}



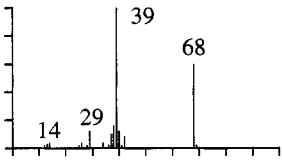
Acetic acid



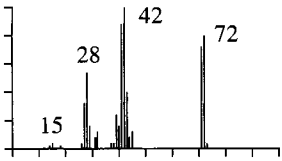
Ethylene glycol {50}



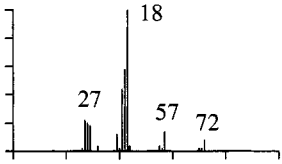
Furan



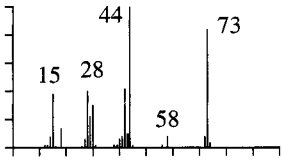
Tetrahydrofuran {50}



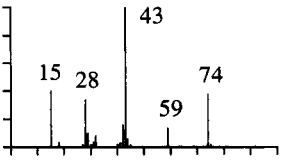
Pentane



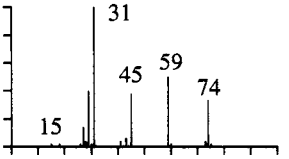
N,N-Dimethylformamide



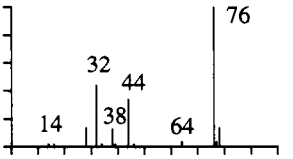
Methyl acetate {50}



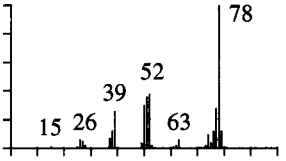
Diethyl ether



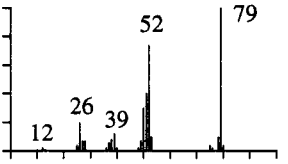
Carbon disulfide {50}



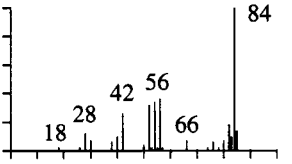
Benzene {50}



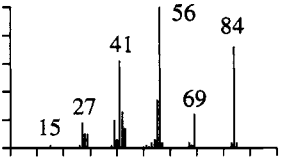
Pyridine



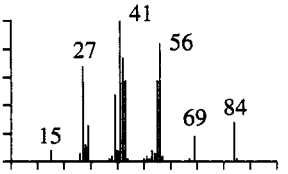
Benzene-d_6 {50}



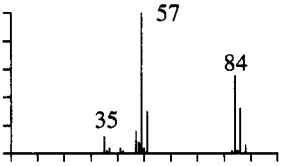
Cyclohexane



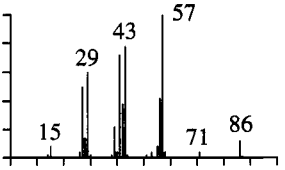
1-Hexene



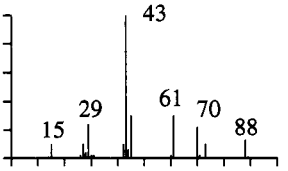
Methylene chloride



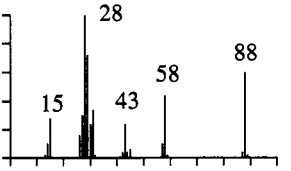
Hexane



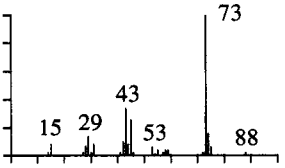
Ethyl acetate {50}



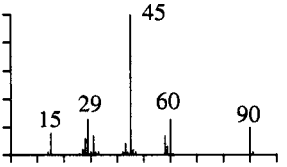
1,4-Dioxane {50}



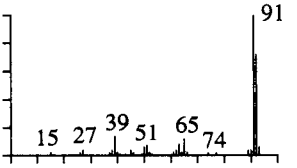
Tetramethylsilane {50}



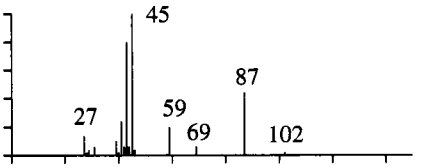
Dimethyl glycol {50}



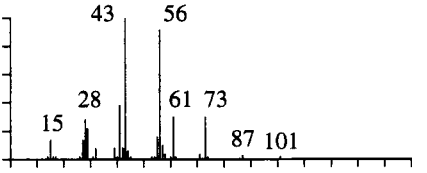
Toluene



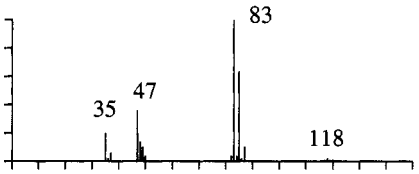
Diisopropyl ether {50}



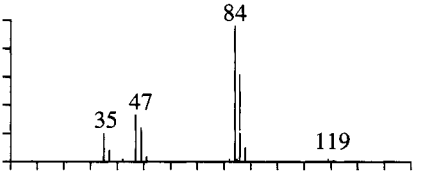
Butyl acetate {50}



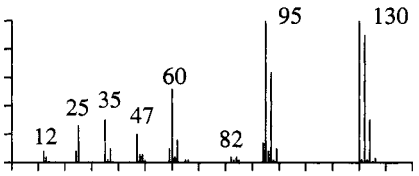
Chloroform



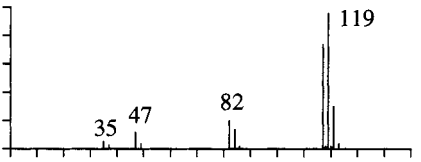
Chloroform-*d*



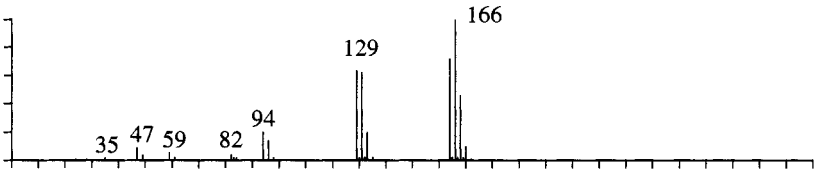
Trichloroethylene



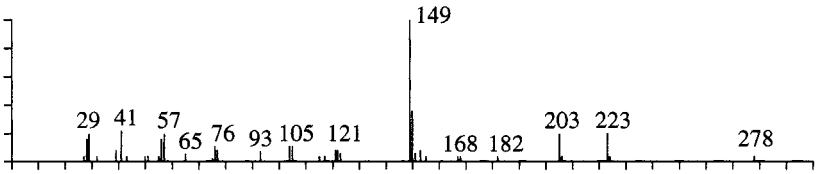
Carbon tetrachloride



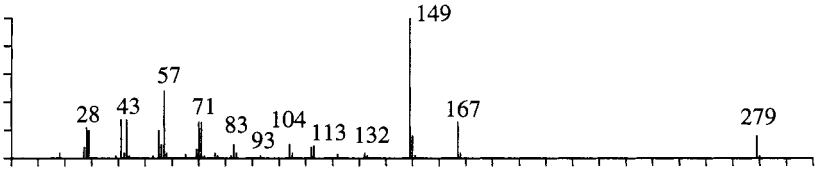
Tetrachloroethylene



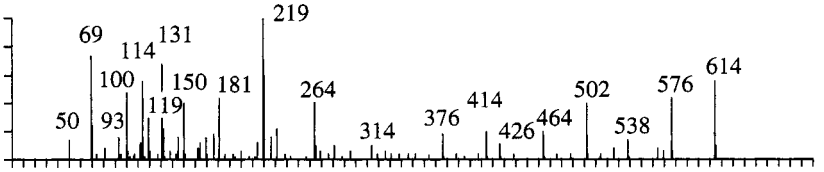
Dibutyl phthalate [25] (frequent impurity due to its use as polymer plasticizer)



Dioctyl phthalate (frequent impurity due to its use as polymer plasticizer)



Heptacosafluorotributylamine (calibration reagent)

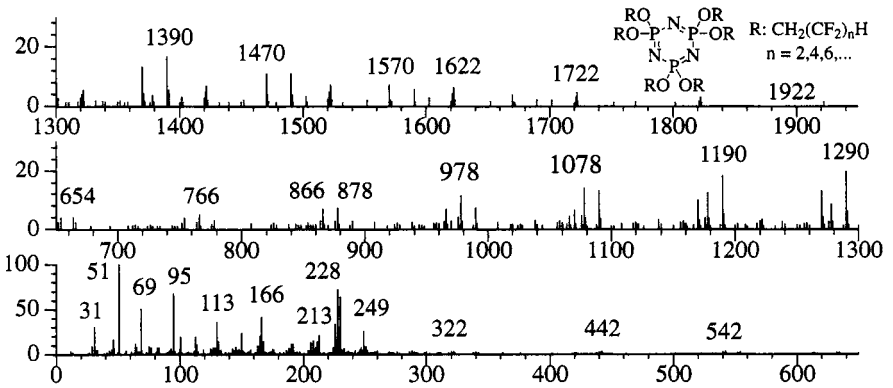


7.13.2 Spectra of Common FAB MS Matrix and Calibration Compounds

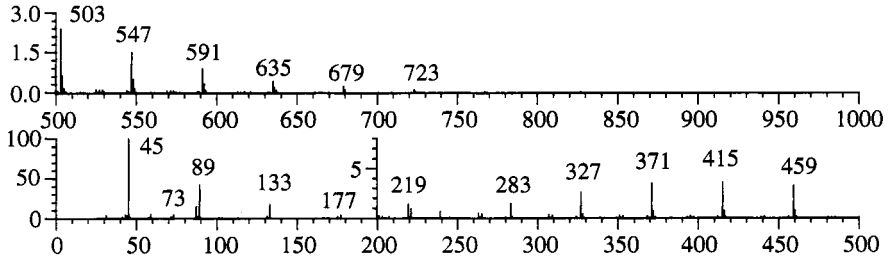
Fast atom bombardment (FAB) mass spectra (MS) usually exhibit protonated or deprotonated molecular ions, $[M\pm H]^{\pm}$, and protonated clusters, $[M_n+X_m\pm H]^{\pm}$ (n,m = 0,1,2,...), of the sample and matrix molecules, X. If there are even traces of metal salts in the sample, clusters of the type $[M_n+X_m+\text{metal cation}]^+$ occur in positive ionization mass spectra. Sodium (23 u) and potassium (39 u) ion adducts are most commonly encountered. The nature of the clusters is often revealed by the regular intervals at which they occur in the spectra.

Calibration Compounds in Positive Ionization FAB Mass Spectra

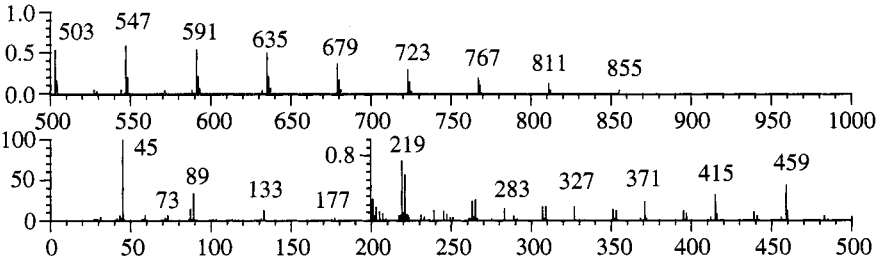
Ultramark 1621 (erroneously also referred to as "perfluoroalkyl phosphazine")



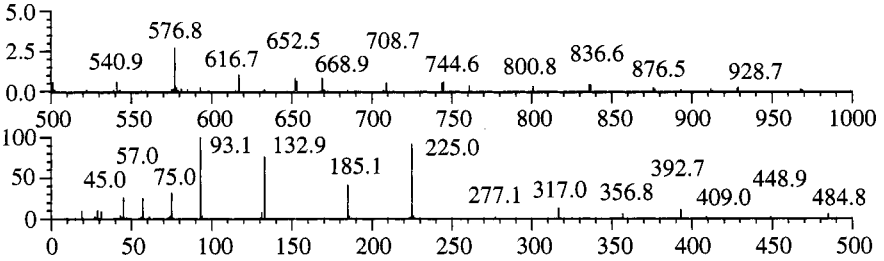
Polyethylene glycol 400 (often used as an internal reference for high resolution m/z determinations)



Polyethylene glycol 600 (often used as an internal reference for high resolution m/z determinations)

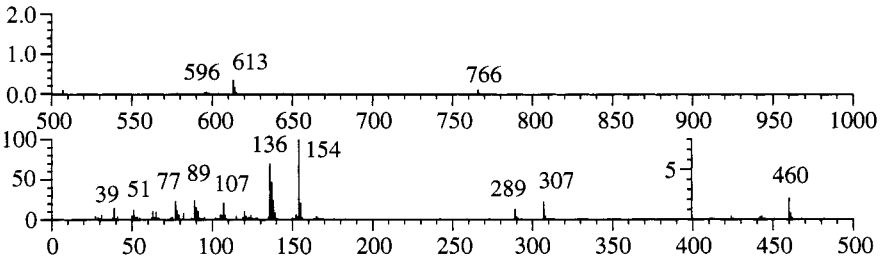


CsI (Cs^+, 132.9; I^-, 126.9) in glycerol (formation of $[glycerol_m\text{-}H_n\text{+}Cs_p\text{+}I_q]^+$)

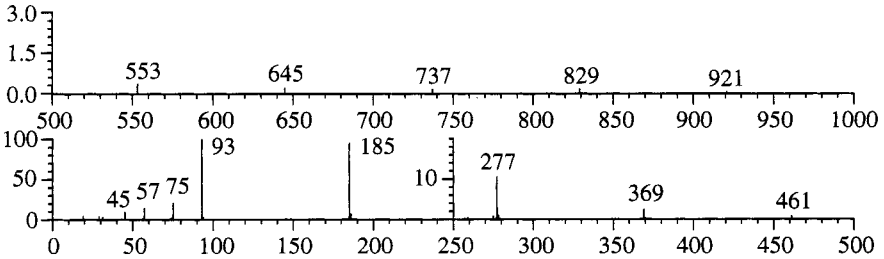


Matrix Compounds in Positive Ionization FAB Mass Spectra

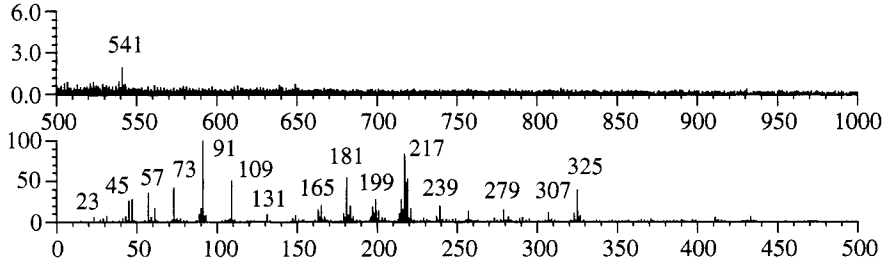
3-Nitrobenzyl alcohol (M_r 153)



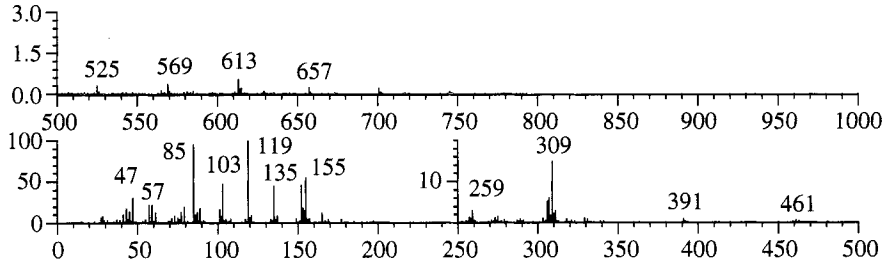
Glycerol (M_r 92)



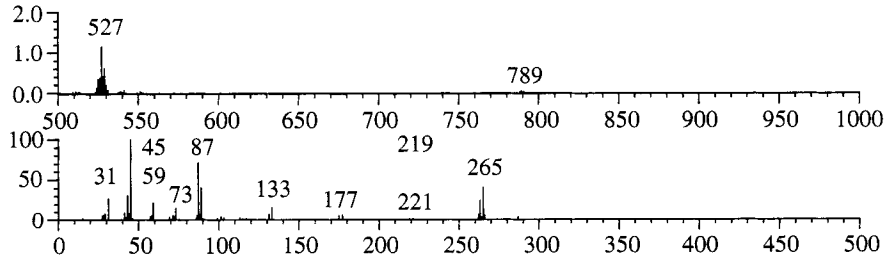
Thioglycerol (M_r 108. Note m/z 23 (Na^+), 131 ($[M+Na]^+$), 239 ($[2M+Na]^+$). Similarly, small K^+ impurities give signals at m/z 39, 147, 255)



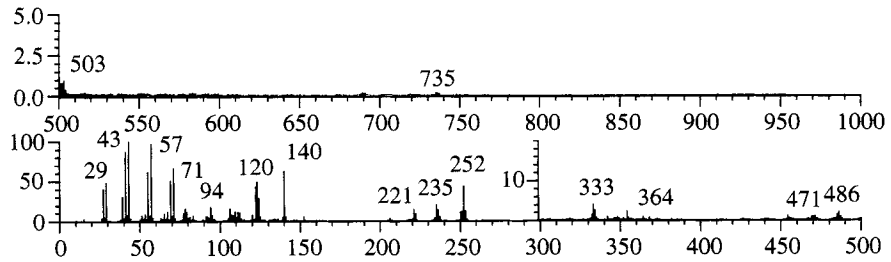
Magic bullet (dithiothreitol/dithioerythritol, $HSCH_2(CHOH)_2CH_2SH$; M_r 154)



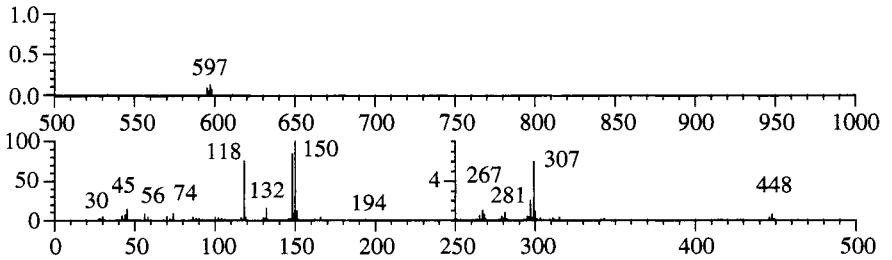
1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6, M_r 264. Also used as an additive; binds metal ions and reduces $[M+metal\ ion]^+$ in favor of $[M+H]^+$, which can be important for samples with exchangeable H^+, such as for peptides [1])



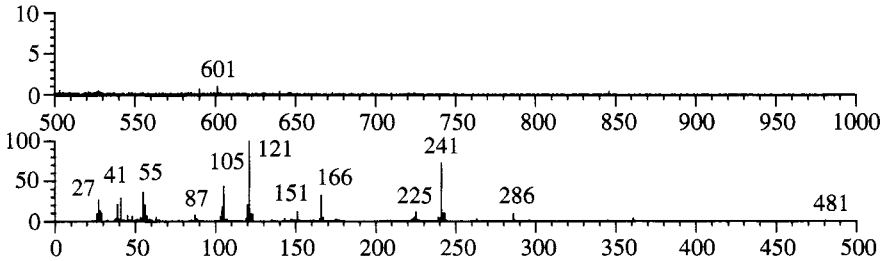
2-Nitrophenyl octyl ether (M_r 251)



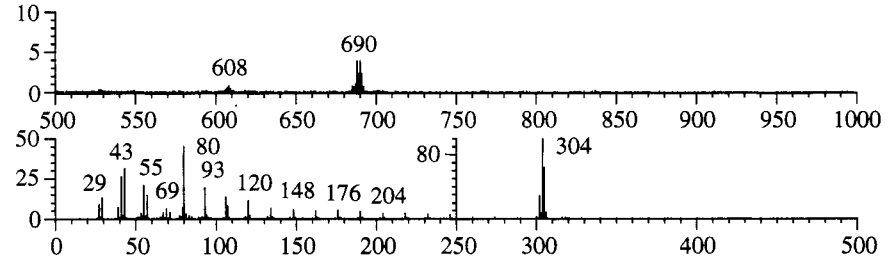
Triethanolamine (M_r 149)



Sulfolane (M_r 120) [2]

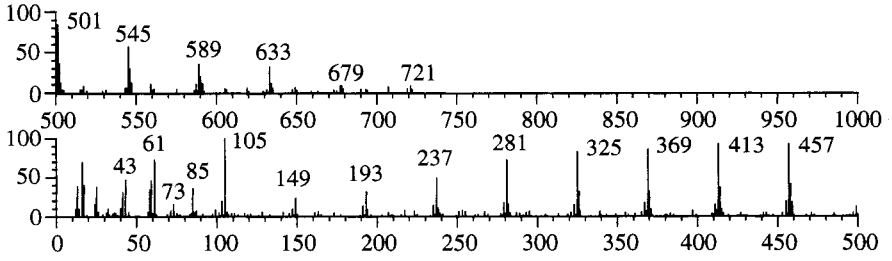


Hexadecylpyridinium bromide (M_r 385; hexadecylpyridinium = 304) in 2-nitrobenzyl alcohol

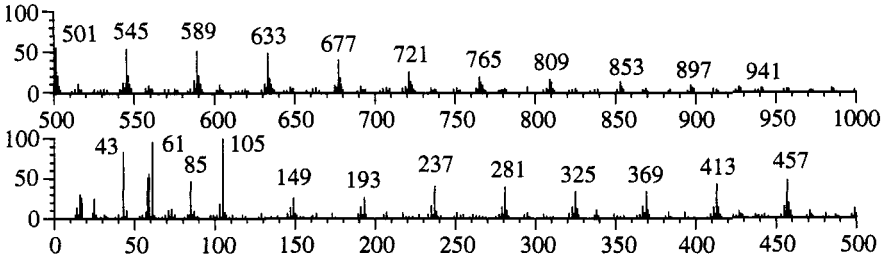


Calibration Compounds in Negative Ionization FAB Mass Spectra

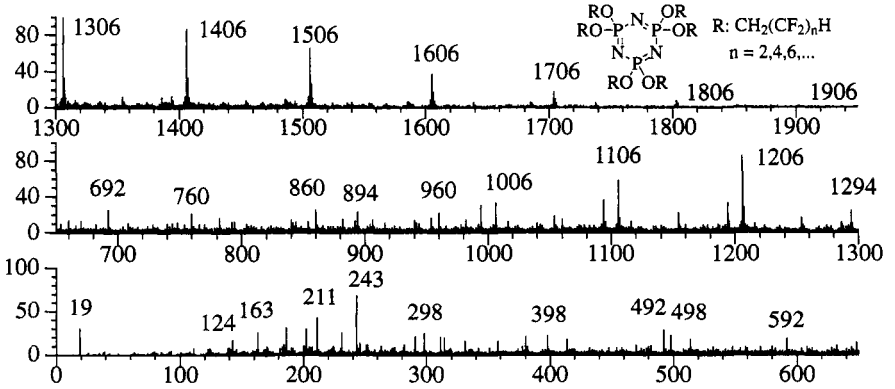
Polyethylene glycol 400 (often used as reference for high resolution MS)



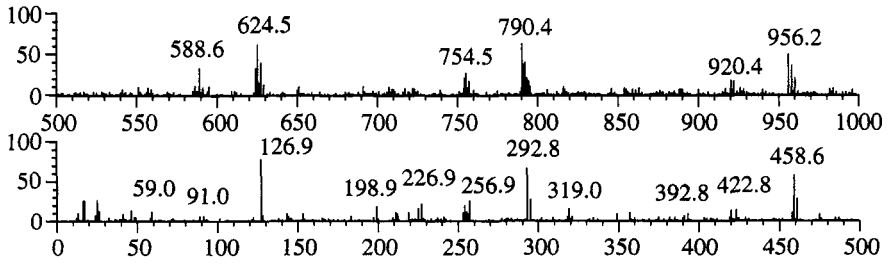
Polyethylene glycol 600 (often used as internal reference for high resolution MS)



Ultramark 1621 (erroneously also referred to as "perfluoroalkyl phosphazine")

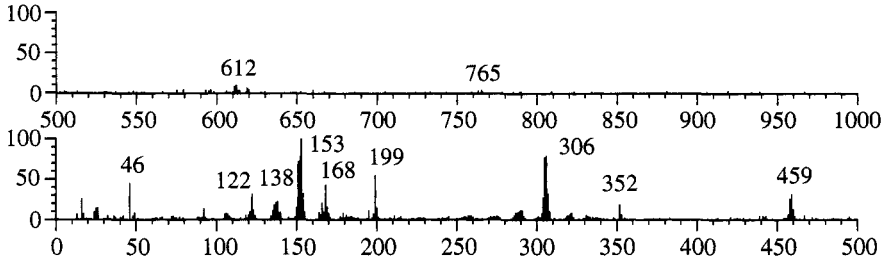


KI (K^+, 39.0; I^-, 126.9) in glycerol (formation of $[glycerol_m\text{-}H_n\text{+}K_p\text{+}I_q]^-$)

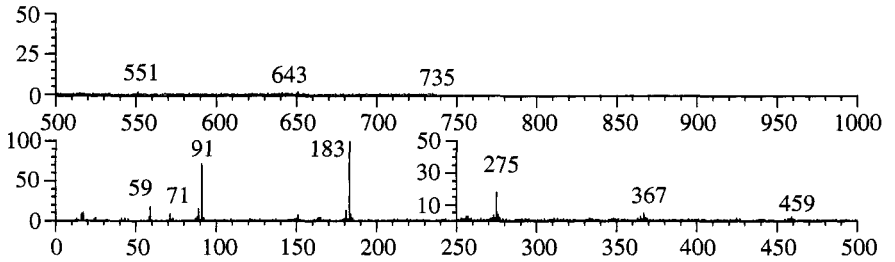


Matrix Compounds in Negative Ionization FAB Mass Spectra

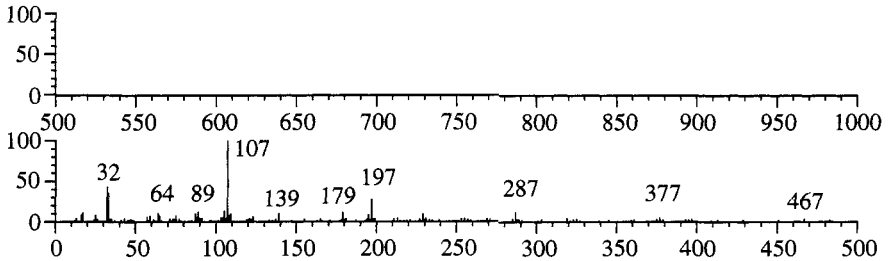
3-Nitrobenzyl alcohol (M_r 153)



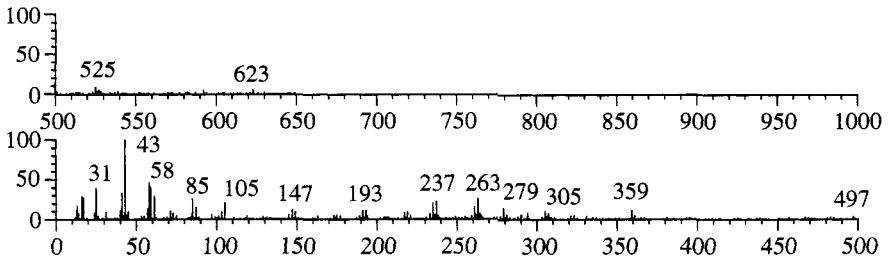
Glycerol (M_r 92)



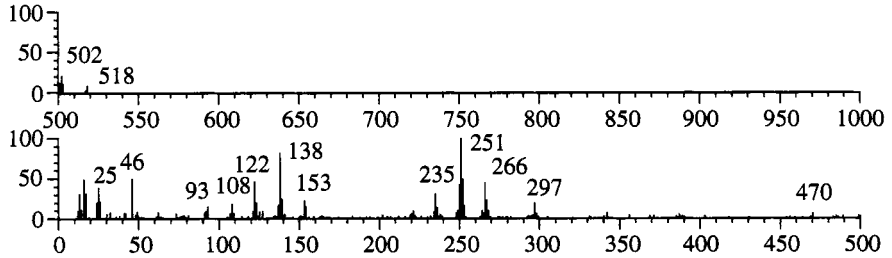
Thioglycerol (M_r 108)



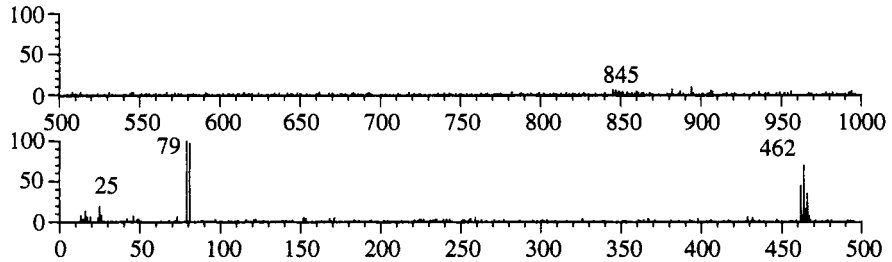
1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6, M_r 264)



2-Nitrophenyl octyl ether (M_r 251)



2-Nitrobenzyl alcohol solution of hexadecylpyridinium bromide (M_r 385; hexadecylpyridinium = 304; enhances detectability and reduces metal ion adducts of sample [3].)

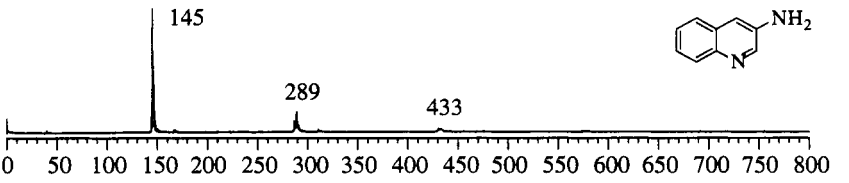


7.13.3 Spectra of Common MALDI MS Matrix Compounds

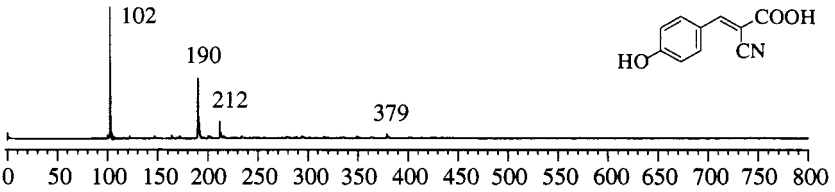
Matrix-assisted laser desorption ionization (MALDI) mass spectra (MS) usually exhibit protonated or deprotonated molecular ions, $[M\pm H]^{\pm}$, and protonated clusters, $[M_n+X_m\pm H]^{\pm}$ (n,m = 0, 1, 2,...), of the sample and matrix molecules, X. If there are even traces of metal salts in the sample, clusters of the type $[M_n+X_m+\text{metal cation}]^+$ occur in positive ionization mass spectra. Sodium (23 u) and potassium (39 u) ion adducts are most commonly encountered. The nature of the clusters is often revealed by the regular intervals at which they occur in the spectra [4].

Matrix Compounds in Positive Ionization MALDI Mass Spectra

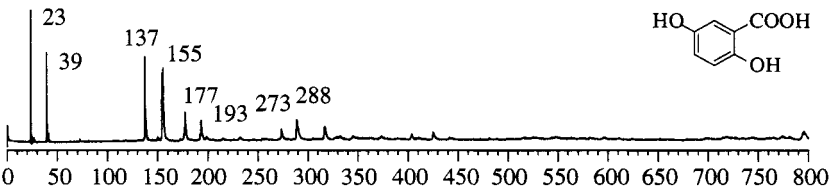
3-Aminoquinoline (M_r 144)



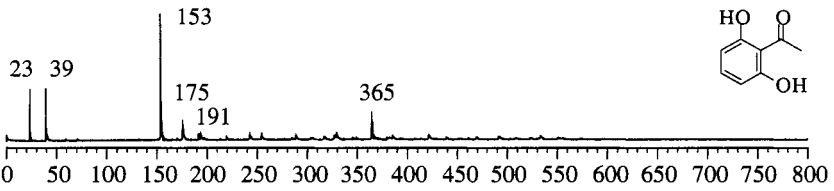
α-Cyano-4-hydroxycinnamic acid (M_r 189; m/z 212, $[M+Na]^+$)



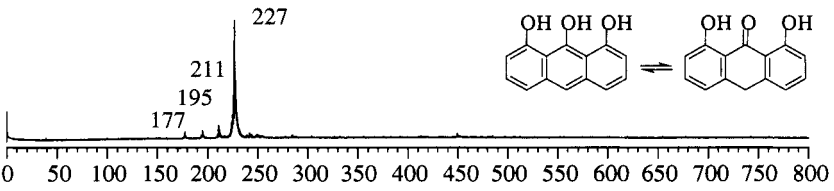
2,5-Dihydroxybenzoic acid (M_r 154; m/z 177, $[M+Na]^+$; m/z 193, $[M+K]^+$)



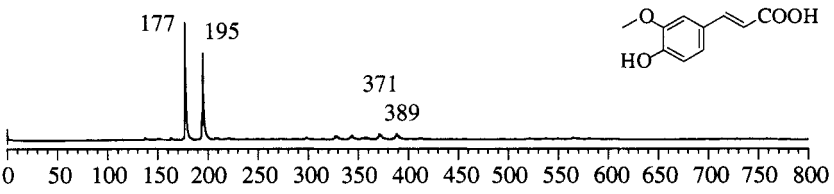
2,6-Dihydroxyacetophenone (M_r 152; m/z 175, $[M+Na]^+$; m/z 191, $[M+K]^+$; m/z 365, $[2M+Na+K-H]^+$?)



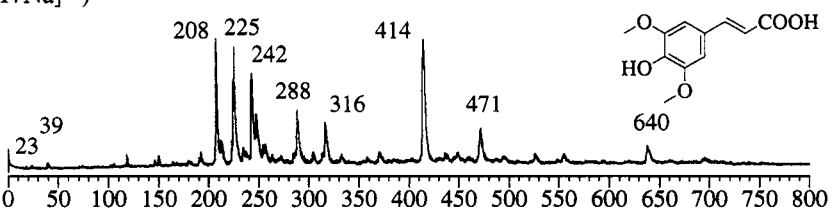
Dithranol (M_r 226)



Ferulic acid (4-hydroxy-3-methoxycinnamic acid; M_r 194)

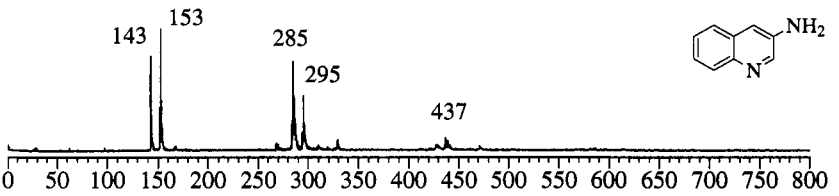


Sinapinic acid (3,5-dimethoxy-4-hydroxycinnamic acid; M_r 224; m/z 471, $[2M+Na]^+$)

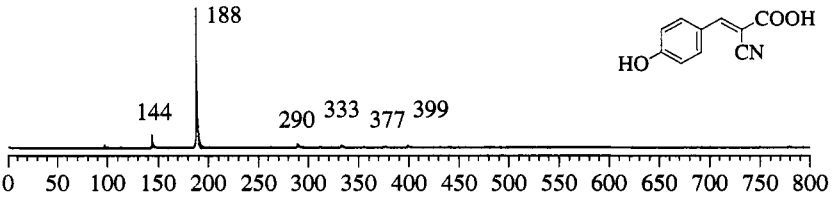


Matrix Compounds in Negative Ionization MALDI Mass Spectra

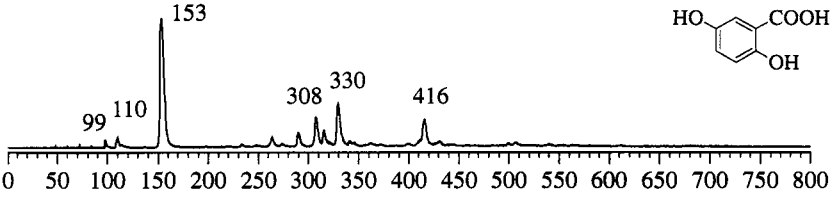
3-Aminoquinoline (M_r 144)



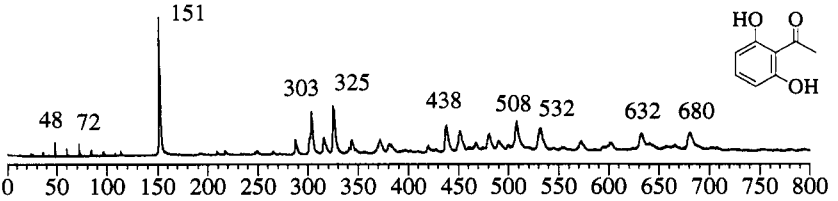
α-Cyano-4-hydroxycinnamic acid (M_r 189; m/z 399, $[2M+Na-2H]^-$)



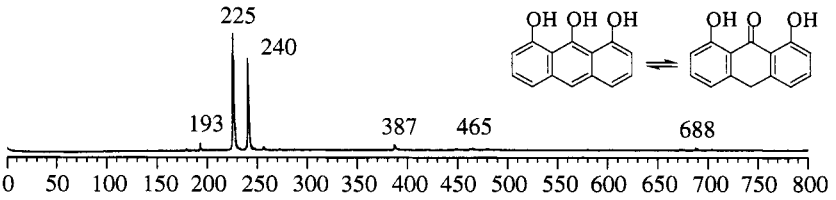
2,5-Dihydroxybenzoic acid (M_r 154)



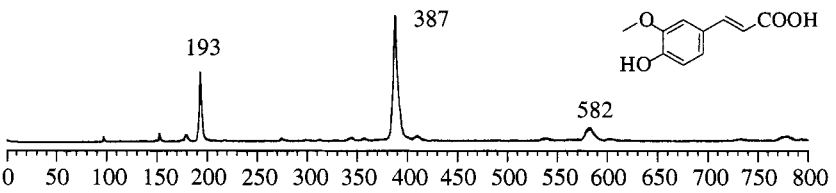
2,6-Dihydroxyacetophenone (M_r 152; m/z 325, $[2M+Na-2H]^-$)



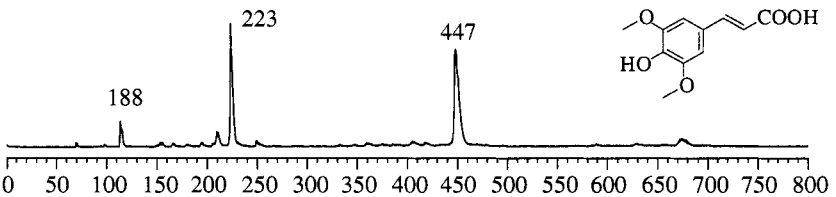
Dithranol (M_r 226)



Ferulic acid (4-hydroxy-3-methoxycinnamic acid; M_r 194)



Sinapinic acid (3,5-dimethoxy-4-hydroxycinnamic acid; M_r 224)



7.13.4 References

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[2] P.K. Singh, L. Field, B. Sweetman, Organic disulfides and related substances, J. Org. Chem. **1988**, *53*, 2608.

[3] Z.-H. Huang, B.-J. Shyong, D.A. Gage, K. R. Noon, J. Allison, *N*-Alkylnicotinium halides: a class of cationic matrix additives for enhancing the sensitivity in negative ion fast-atom bombardment mass spectrometry of polyanionic analytes, J. Am. Soc. Mass Spectrom. **1994**, *5*, 928.

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