

Field Desorption Mass Spectrometry of Organic Acids and their Salts

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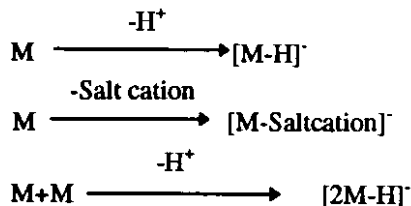
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Summary: Negative field desorption mass spectra of 30 organic acids (mostly simple sulfonic acids) or their salts has been reported in this paper. Most of the acids studied give rise to the formation of simple negative ions i.e. $[M - H]^-$ or $[M - \text{salt cation}]^-$. Very low fragmentation of the parent molecules is observed. Addition of additive such as LiCl enhances the intensity of ion signals. Cluster of these molecules are also observed but their intensity is very low.

Introduction

Negative ion field desorption mass spectrometry (NFD MS) introduced by H.D. Beckey in 1969 [1] is widely applied in analyzing various polar organic compounds [2,3]. Sulfonic acids are very important source materials for industries like dyes, textiles and surfactants. These acids and their salts are thermally labile and/or less volatile to be analyzed by conventionally mass spectrometric techniques. However, some sulfonic acids and their sulfonate have been studied by positive mode of field desorption mass spectrometry [4]. Alkyl benzene sulfonic acids encountered in the environmental pollution have also been collected by L. Prokai in his review on field desorption mass spectrometry [5]. Roellgen and his coworkers [6,7] reported the analysis of some of sulfonic acids using negative field desorption mass spectrometry. In this report NFD mass spectra of some 30 organic acids or their salts are reported and discussed. Majority of the compounds gave intensive molecular ion peaks or

quasimolecular ion peaks via the following mechanisms.



Where M means molecules studies in the given table.

Fragment ions from the matrix material which is polyethylene glycol (PEG 4000) are rarely observed. Lithium chloride (LiCl) used as additive give intensive peaks for their ions of Cl^- and LiCl_2^- .

Results and Discussion

The compounds studies are reported in the table. The study show that monosulfonic acid gave

Table Organic acids and their related compounds

S.No.	Name of compounds	Mol. wt	Heating masses their assignment and % intensities (in current parentthesis) (mA)
1	1-naphthalene sulfonic acid	208	19 415 [2M-H] ⁻ (10), 207 [N-H] ⁻ (100)
2	1,5 naphthalene disulfonic acid	288	20 287 [M-H] ⁻ (7), 207 [M-HSO ₃] ⁻ (4), 143 [M-2H] ⁻ (100), 135 [KSO ₄] ⁻ (5), 127 [I] ⁻ (62), 89 [PEG] ⁻ (38), 85 [PEG] ⁻ (11)
3	1,3,5 naphthalene trisulfonic acid	368	17 207 [H-2HSO ₃ +H] ⁻ (22), 193 [HS ₂ O ₄] ⁻ (100), 135 [KSO ₄] ⁻ (10), 89 [PEG] ⁻ (33).
4	4-amino-azobenzene-3,4' disulfonic acid + LiCl	357	18 196 [M-2HSO ₃ +H] ⁻ (5), 178.5 [M-2H] ⁻ (100), 89[PEG] ⁻ (20), LiCl ₂ , Cl ⁻
5	Methyl orange	327	0-20 304 [M-Na] ⁻ (100).
6	Methyl orange + LiCl	327	16 346 [M-Na+LiCl] ⁻ (14), 340 [M-Na+HCl] ⁻ (4), 304 [M-Na] ⁻ (100), Cl ⁻ , LiCl ₂
7	Sulfadimidin Sod. Salt	300	15 577 [2M-Na] ⁻ (4), 555 [2M-2Na+H] ⁻ (17), 277 [M-Na] ⁻ (100)
8	7-Iodo-8-hydroxy quinoline 5-Sulfonic acid Sod. Salt.	373	16 350 [M-Na] ⁻ (64), 224 [M-Na - I +H] ⁻ (62) 127 [I] ⁻ (100), 89 [PEG] ⁻ (90).
9	Guaiacol Sulfonic acid Pot. Salt	242	15-18 203 [M-K] ⁻ (100), 89[PEG] ⁻ (38)
10	6-Hydroxy naphthalene-2-Sulfonic acid Sod. Salt.	246	18-25 447 [2M-2Na+H] ⁻ (3), 223 [M-Na] ⁻ (100)
11	3-Amino 1,5-naphthalene disulfonic acid	303	16 150.5 [M-2H] ⁻ (100), 99[PEG] ⁻ (90)
12	3-Amino 1,5-naphthalene disulfonic acid + Glycerol	303	16 207 [M-HSO ₃ NH ₂ +H] ⁻ (5), 150.5 [M-2H] ⁻ (100), 135 [KSO ₄] ⁻ (5), 91 [G-H] ⁻ (11)
13	Taurocholic acid sod. salt.	537	23 514 [M-Na] ⁻ (100), 109 [CH ₃ CH ₂ SO ₃] ⁻ (38)
14	Sodium cumene sulfonate	222	24 421 [2M-Na] ⁻ (10), 399 [2M-2Na+H] ⁻ (5), 199 [M-Na] ⁻ (100), 97 [HSO ₄] ⁻ (21)
15	1-dodecane sulfonic acid sod. salt.	272	0-30 249 [M-Na] ⁻ (100)
16	camphore sulfonic acid	232	17.5 231 [M-H] ⁻ (100)
17	P-Anisic acid	152	16 151 [M-H] ⁻ (100)
18	P-Toluic acid	136	15 135 [M-H] ⁻ (100)
19	Gallic acid	170	14 339 [2M-H] ⁻ (17), 169 [M-H] ⁻ (100)
20	Pencillin-G	334	15 667 [2M-H] ⁻ (30), 333 [M-H] ⁻ (100)
21	Cholic acid + LiCl	408	31 443 [M+Cl] ⁻ , LiCl ₂ , Cl ⁻ , Li ₂ Cl ₃ ⁻
22	Methyl red+LiCl	269	19 304[M+Cl] ⁻ (78), 268[M-H] ⁻ (100), Cl ⁻ , LiCl ₂ ⁻
23	Mucic acid	210	21 [M-H] ⁻ (100)
24	Gentisinic acid sod salt.	176	21 153 [M-Na] ⁻ (100)
25	P-aminosalicylic acid sod. salt	175	16 152 [M-Na] ⁻ (100)
26	Glycocholic acid sod. salt	487	1-26 464 [M-Na] ⁻ (100)
27	Glucuronic acid sod. salt	216	22 193 [M-Na] ⁻ (100), 175 [M-Na-H ₂ O] ⁻ (93), 149 [M-Na-CO ₂] ⁻ (18), 89 [PEG] ⁻ (22)
28	Vaniline + C ₂ H ₅ OH	152	10 151 [M-H] ⁻ (100)
29	L-adrenaline	183	19 182 [M-H] ⁻ (100)
30	2,6-dihydroxynaphthalene	160	26 319 [2M-H] ⁻ (100), 159 [M-H] ⁻ (5)

intensive parent molecular ion peak by proton abstraction process while di and tri sulfonic acids were fragmented by the elimination of their one or two sulphate groups. Methyl orange which is a sodium salt of sulfonic acid gave [M - Na]⁺ ion by cation (Na⁺) abstraction process. Derivatives of sulfonic acids showed less fragmentation than pure sulfonic acids. Sulfadimidine sodium salt gave dimer at m/z = 577 with very weak ion signal. Inorganic anion i.e. I⁻ ions gave the base peak while analyzing 7-iodo-8-hydroxy quinoline-5-sulfonic acid-Na-salt. This shows the sensitivity of NFD MS towards the halide ions. Methyl orange, guaiacol sulfonic acid -potassium salt and 6-hydroxy-naphthalene-2-sulfonic acid-sodium-salt

desorb at wide range of temperatures. Divalent ions [M - 2H]⁻ at m/z = 150.5 is highly interesting for 3-Amino- 1,5-naphthalene disulfonic acid. It is also noted that if glycerol instead of PEG 4000 is used as a matrix encourages fragmentation of the above compound. This shows that PEG 4000 is suitable matrix in NFD mass spectrometry (compare Fig. 1,2).

Both taurocholic acid-sodium salt and sodium cumene sulfonate gave [M-Na]⁻ ions which are the base peaks of the spectra. 1-dodecane sulfonic acid sodium salt give a single peak spectrum at m/z = 249 and at a wide range of temperatures i.e. at 0-30 mA. Camphore sulfonic

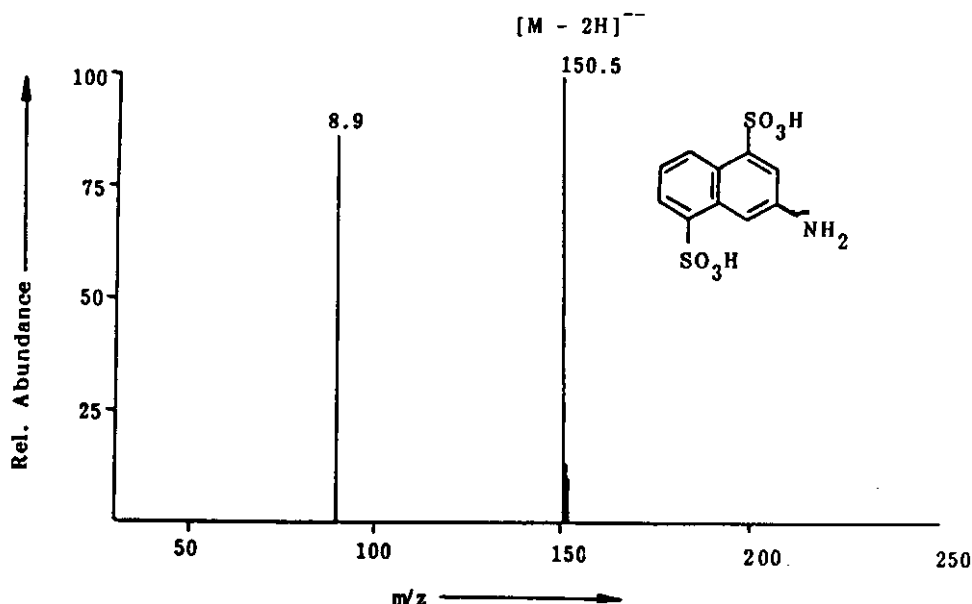


Fig. 1: NFD mass spectrum of 3-amino 1,5-naphthalene disulfonic acid (mol. wt=303) mixed with PEG 4000 and water in the ratio of 1:4:3.

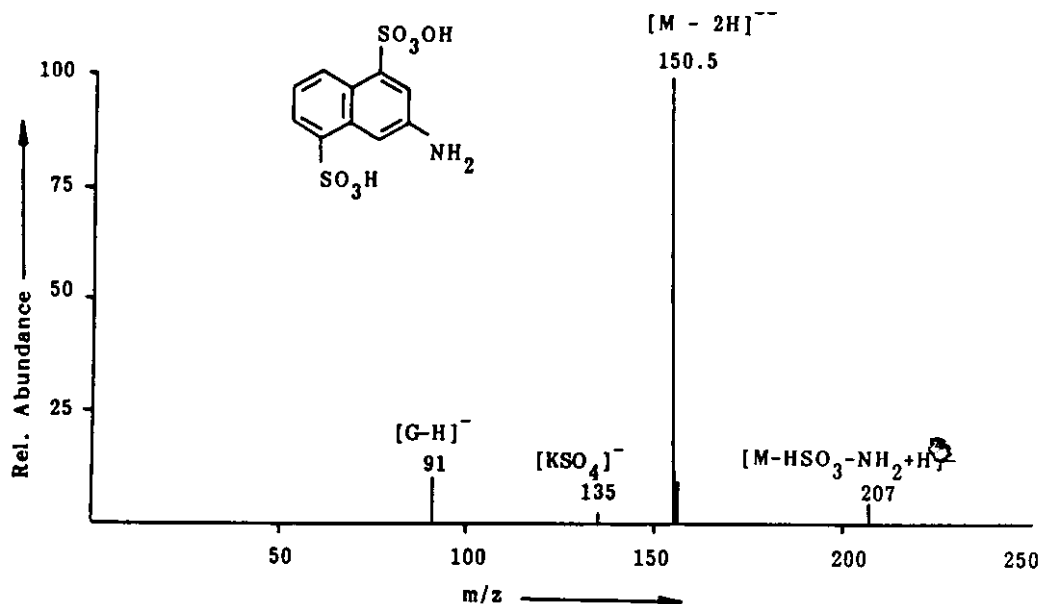


Fig. 2: NFD mass spectrum of 3-amino 1,5-naphthalene disulfonic acid (mol. wt=303) mixed with glycerol and water in the ratio of 1:4:3.

acid gave only a monomer at $m/z = 231$ due to its stability in structure. P-anisic acid and P-toluic acid also gave monomers without any fragmentation. Gallic acid containing three hydroxy groups gave dimer in addition to the monomer which can be

explained in terms of hydrogen bonding. Pencillin-G which do not have a sulfonic group also gave dimer at $m/z = 667$ with a significant intensity. Pure cholic acid and methyl red showed no sensitivity to NFD emitter but gave intensive ion

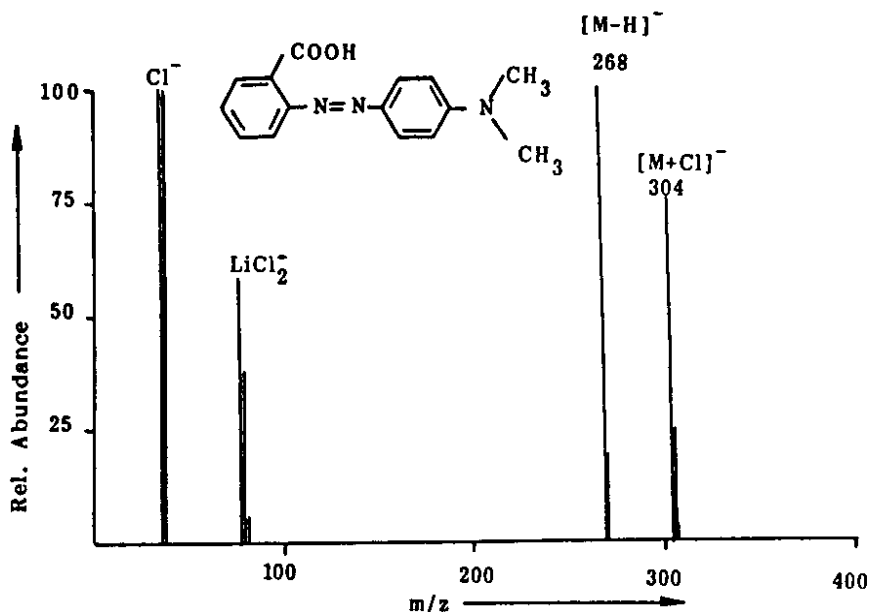


Fig. 3: NFD mass spectrum of methyl red (mol. wt=269) mixed with LiCl, PEG 4000 and water in the ratio of 1:0.2:4:3.

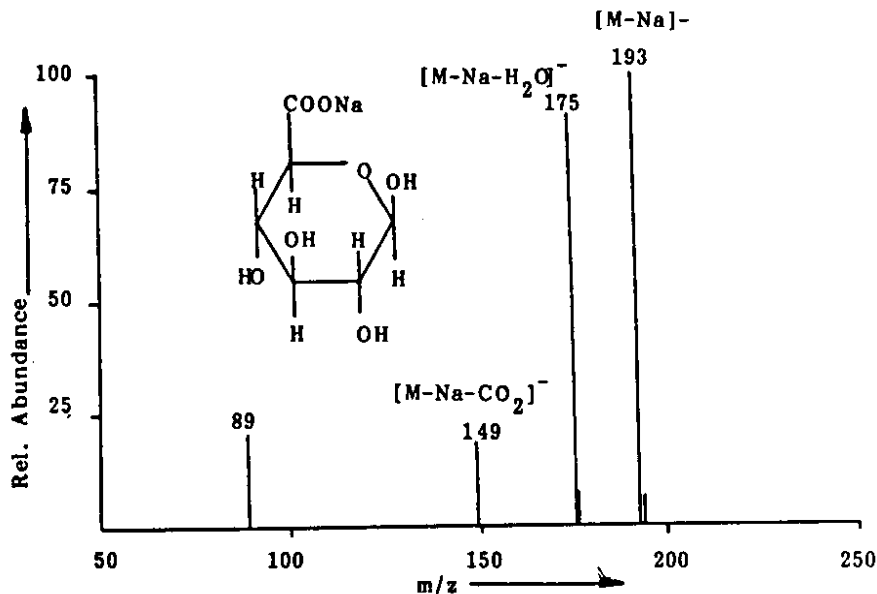


Fig. 4: NFD mass spectrum of glucuronic acid - sodium salt (mol. wt=216) mixed with PEG 4000 and water in the ratio of 1:4:3.

signal when lithium chloride added to them as additive. In addition to the sample ions, intensive peaks for Cl^- , LiCl_2^- and Li_2Cl_3^- are also observed (Fig. 3). Mucic acid which is a dicarboxylic acid gave only monomer. Gentsinic acid-sodium-salt

and P-aminosalicylic acid sodium salt gave monomers of quasimolecular ions by eliminating their cations. Glycocholic acid-sodium salt which does not contain sulfonic group give only monomer. Glucuronic acid sodium salt gave

extensive fragmentation (Fig. 4). PEG 4000 showed fragment ions at $m/z = 89$ of little intensity. Vanillin and L-adrenaline gave only monomers. Dimer of 2,6-dihydroxy naphthalene form the base peak. Study of all 30 compounds shows that addition of Lithium Chloride (LiCl) retains water molecules from desorption as a result, often improves the desorption conditions of the sample layer and crystallization of the sample layer material is prevented. Addition of PEG 4000 give rise to the growth of field enhancing protuberances observed by optical microscopy [8]. The length of the protuberances formed during the field induced disintegration of the sample layer on the surface of emitter decreases with increasing viscosity. In case of highly viscous solutions the increase in best cathode temperature (BCT) is also observed. Most of the sulfonic acids studied gave rise to the formation of ions clustered with the acids themselves. However, the potassium or sodium salts of the sulfonic acids generated the unclustered sulfonic acids anions.

Ion formation in the NFD MS is based on the desolvation mechanism [9]. However, the desolvation of negative ions from the viscous electrolytic solutions, prepared by mixing a high molecular weight polymer with the aqueous sample solutions, is possible only at field strength below the onset of electron emission. That is why we observed $[M-H]^-$ ions instead of M^- ions. Therefore it can be concluded that NFD MS is insensitive to most non acidic compounds and hence a high selectivity exists for the detection of organic acids and their salts from a mixture of non acidic components.

Experimental

A single focusing 60° sector mass spectrometer was used for obtaining NFD mass spectra. It was equipped with a home built FI/FD ion source. Smooth $10 \mu\text{m}$ W wires without field enhancing microneedles (activated) emitters were used. A potential of -4KV (10^9 V/m) was applied to the emitter (called cathode) and the counter electrode was grounded (zero potential). Vacuum

of $10^{-4} - 10^{-6}$ hpa was maintained in the ion source using ordinary rotary and diffusion pumps. Mass range of the mass spectrometer was about 700. Masses were scanned by varying the magnetic field strength with the help of Hall voltage. The distance between cathode and counter electrode was about 7 mm. Channeltron was used for collecting the ion signals. Polyethylene glycol (PEG 4000) was used to make the solution viscous. $10^{-8} - 10^{-6}$ gram sample was loaded on the emitter for one measurement. The sample mixture was in the ratio of 1:4:3 V/V for sample: PEG: H_2O respectively. Spectra was recorded on a chart recorder.

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