

A Direct Technique for Obtaining Electron-Impact Mass Spectra of Polar, Involatile Compounds. Application to Underivatized Disaccharides

Sir:

Readily interpretable mass spectra of thermally unstable compounds of very low volatility have been obtained using a conventional electron ionization (EI) mass spectrometer by a simple technique.¹ The technique combines (a) rapid sample heating, shown by Beuhler et al.²⁻⁴ to effect vaporization of polar, thermally unstable compounds while minimizing decomposition, with (b) simultaneous detection of all ions formed by use of a photographic plate in the focal plane of a mass spectrometer of Mattauch-Herzog geometry.⁵ The result of this combination is a powerful technique for mass spectrometric analysis of involatile, thermally labile compounds.^{1,6}

The ability to analyze underivatized carbohydrates by mass spectrometry is severely limited by the thermal instability and extremely low volatility of these compounds.⁷⁻¹¹ Indeed, the difficulties are so pronounced and so well known that in 1969 Beckey selected the monosaccharide D-glucose as the first substance to test and exemplify the analytical potential of field desorption mass spectrometry.¹²⁻¹⁴ To illustrate the capability of the technique described here we have obtained mass spectra of the underivatized disaccharides sucrose (Figure 1a) and lactose (Figure 1b) using a conventional, unmodified EI mass spectrometer.

Samples of sucrose or lactose (10–20 μg) were adsorbed from aqueous solutions onto a coil (six turns, diameter ~ 1 mm) of rhenium wire¹⁵ (0.25 nm) which was then placed into the mass spectrometer ion source via a direct insertion probe until the wire was positioned directly in the electron beam. With the ion source maintained at 130 $^{\circ}\text{C}$, an ionization potential of 70 eV with 200 μA of electron current and an accelerating voltage of 6 kV, and instrument resolution ~ 3000 , a current was passed through the coiled wire bearing the sample causing the wire

to reach a temperature of >1200 $^{\circ}\text{C}$ within 0.1–0.2 s. The spectrum produced was obtained in digital form by processing the photoplate detector using a photodensitometer-computer system¹ and plotted (Figure 1a or 1b).

In addition to the disaccharide spectra (Figure 1) and those of peptide amides previously reported,¹ we have successfully obtained complete spectra of other, essentially involatile compounds including quarternary and transition metal-organic complex salts and a plant saponin. We have not yet succeeded in obtaining spectra exhibiting molecular ions for complex salts in which the species of interest is anionic, e.g., guanosine diphosphate monosodium salt. For compounds of molecular weight <600 , we have had little trouble in reproducibly obtaining spectra exhibiting protonated molecular (i.e., pseudomolecular, MH^+) ions. For larger compounds, results have been more variable; often we have failed to observe an ion corresponding to the entire molecule (i.e., MH^+). In these instances, the ions which are observed are readily assignable and characteristic of the compound structure. Repeated analyses of such larger, polar molecules have usually resulted in a complete spectrum being obtained.¹⁶ It must be emphasized that our experience is still quite limited and the technique has not been optimized. We are confident that it will prove quite general and permit analysis of polar compounds of mass >1000 .¹⁷

Spectra of relatively involatile compounds obtained by this technique (e.g., Figure 1, ref 1 and 6) invariably exhibit protonated molecular (MH^+) rather than molecular (M^+) ions. It is perhaps pertinent that similar results are obtained with field desorption mass spectrometry where relatively volatile compounds yield molecular ions (M^+), whereas less volatile compounds usually ionize via cationization (MH^+ , MNa^+ , etc.).^{13,14}

During the past few years impressive advances have been made in the mass spectrometry of polar, relatively nonvolatile compounds. Particularly noteworthy are results obtained using

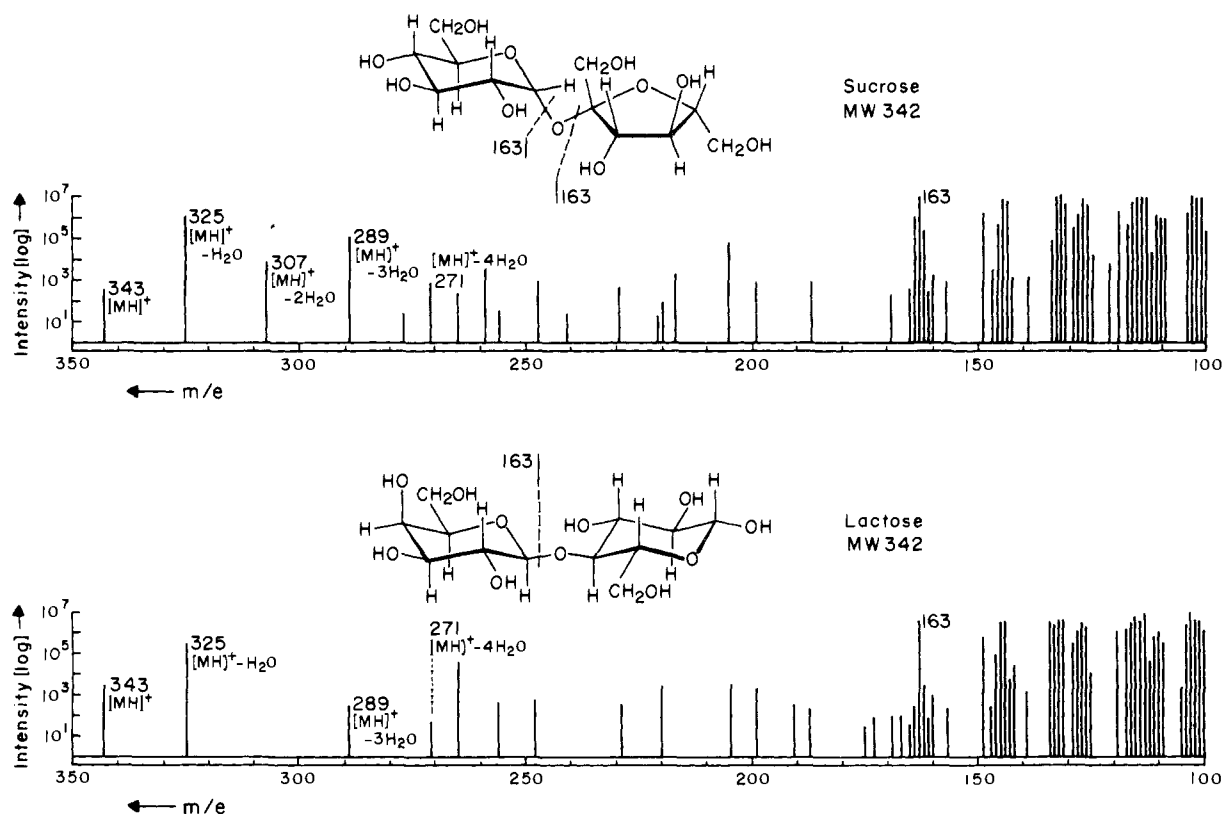


Figure 1. Mass spectra of (a) sucrose and (b) lactose obtained using a conventional electron ionization mass spectrometer by the techniques described in the text.

the newer techniques of field desorption,^{13,14} fission fragment induced desorption (²⁵²Cf desorption),^{18,19} and electrohydrodynamic ionization²⁰ mass spectrometries. By use of sample volatilization techniques first described by Beuhler et al.,^{2-4,21} together with adequate ion detection methods, the utility of the better established electron-impact and chemical ionization techniques for analysis of polar, unstable, "nonvolatile" compounds can be greatly extended.^{19,22-24} This is a discovery of major importance given the generally superior structural information contained in spectra produced using these relatively energetic ionization modes as compared with spectra produced using "soft" ionization methods.

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References and Notes

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- (15) We have used with equal success a loop of tungsten wire,¹ a rhenium ribbon, and a molybdenum photoetched mesh.
- (16) Since the initial report,¹ a complete spectrum of the heptapeptide amide *p*-Glu-Gln-Phe-Phe-D-Leu-Leu-MetNH₂ has been obtained which exhibits peptide backbone characterizing ions at *m/e* 908 (MH⁺), 760, 647, 534, 387, 240, and 112.
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Book Reviews

Anionic Surfactants. Part 1 (Surfactant Science Series. Volume 7). Edited by WARREN M. LINFIELD (Eastern Regional Research Center, USDA). Marcel Dekker, Inc., New York, N.Y. 1976. xi + 314 pp. \$35.00.

This first volume of a two-volume subseries on anionic surfactants is likely to be of most value to those interested in the chemical engineering of sulfonates and sulfates and in the chemistry associated with such processes, or to the technologist interested in the formulation of products based on these compounds.

Several chapters catalog and discuss industrial processes used to sulfonate or sulfate alkyl benzenes, monoalcohols, unsaturated fats, and lower alcohol or alkylphenol ethoxylates. Olefins, alkanes, and fatty acids will be discussed in Volume 2. Representative data on compositions and properties have been assembled. Indeed, a useful compilation of the extensive research at the Eastern Regional Research Center on anionics containing other polar functional groups comprises one chapter.

For the chemist, the chapter by Edwards represents a sound comprehensive analysis from the literature of the reaction intermediates and mechanisms involved in the sulfonation chemistry of monofunctional fatty intermediates. The sulfonation chemistry of the polyoxyethylene materials was not treated in detail and still needs clarification.

Notably absent, considering the broad title, are (1) a treatment of soaps comparable to those on sulfates and sulfonates and (2) a serious treatment of the physical chemistry of anionic surfactants.

The only real chemical problem I had with the book was a persistent misuse of the term "amphoteric". This term has historically had a clearly defined meaning. Specifically, it denotes a molecule which has the capacity to react both as an acid and a base (e.g., aluminum hydroxide or glycine). Both in the first chapter and elsewhere (e.g., pp 176, 182), it is applied to structures which are neither acidic nor basic,

e.g., a quaternary ammonio sulfonate containing a carboxylic amide link. This molecule is zwitterionic but neither acidic, basic, nor amphoteric. This mistake is noticeable elsewhere in the literature of surfactant technology as well.

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Topics in Carbon-13 NMR Spectroscopy. Volume 2. Edited by GEORGE C. LEVY (Florida State University). Wiley-Interscience, New York, N.Y. 1976. xii + 485 pp. \$27.50.

The first half of this volume is devoted to ¹³C NMR studies of naturally occurring molecules. Separate chapters deal with ¹³C NMR probing of peptide conformation and structure (R. Deslauriers and I.C.P. Smith), a sample of ¹³C NMR studies of small naturally occurring molecules such as terpenes, alkaloids, and coumarins (E. Wenkert et al.), an inclusive, pragmatic and highly instructive discussion of ¹³C NMR biosynthetic studies (A.G. McInnes, J.A. Walter, J.L.C. Wright, and L.C. Vining), and a lucid review of ¹³C NMR work on biopolymers including proteins, nucleic acids, and polysaccharides (R.A. Komoroski, I.R. Peat, and G.C. Levy). The second half of the volume presents reviews of wider variety of subject matter in ¹³C NMR spectroscopy. An exhaustive review of the application of ¹³C NMR to the study of organometallic and transition metal complexes is given (O.A. Gansow and W.D. Vernon) and is followed by a review of ¹³C spin-relaxation theory and applications to structure determination (F.W. Wehrli). An excellent discussion of the use of the computer in Fourier-transform NMR is given (J.W. Cooper) and the last chapter is a clear and unusually readable presentation of the theory of indirect (through bond) nuclear spin-spin coupling constants with special attention being given to ¹³C-H and ¹³C-X coupling (P.D. Ellis and R. Ditchfield). All contributions are written with a general scientific readership in mind. With the exception of the chapters