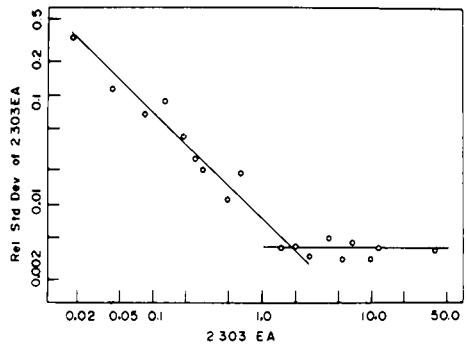

Figure 4. Analytical precision vs. sample absorbance. Results are determined from a constant 64 point data range.

comparison of results. The relative precision vs. ($2.303EA$) plot in Figure 4 indicates a contribution from noise sources which are constant and proportional with respect to absorbance. The constant noise, dominant at small A, may be interpreted as arising from fluctuations in the laser intensity which occur on a time scale shorter than t_c. This kind of noise leads to minimal correlation between data points and results in the greatly improved precision of the regression analysis approach. The proportional contribution which appears to dominate at higher sample absorbances arises from drift in the laser power on time scales longer than t_c. This drift causes the signal to change from experiment to experiment in proportion to the sample absorbance. From the plot of Figure 4, one may postulate the effect on precision of having a larger solvent or background absorbance. Increasing the background by an order of magnitude, for example, would raise the proportional noise contribution by an equal amount, but not enough to make a measurement of the solvent blank proportional noise limited. Therefore, one would expect equivalent detection limits as observed with the smaller background.

The regression analysis method of thermal lens measurement averages the more significant, short-term noise of the light-regulated laser. With lasers having poorer long-term power stability or samples having very large background absorbance, the improvement in precision over a sample $\Delta I_{bc}/I_{bc}$ measurement would not be as significant. For these situations, a differential thermal lens technique has been developed (*13*) which is immune to background drift but not to short-term noise. Combining the differential measurement with time resolution might result in an instrument which produces optimal precision independent of sample background.

LITERATURE CITED

(1) Gordon, J. P.; Leite, R. C. C.; Moore, R. S.; Porto, S. P. S.; Whinnery, J. R. *J. Appl. Phys.* **1965**, *36*, 3-8.
(2) Dovichi, N. J.; Harris, J. M. *Anal. Chem.* **1979**, *51*, 728-731.
(3) Imasaka, T.; Miyaishi, K.; Ishibashi, N. *Anal. Chim. Acta* **1980**, *115*, 407-410.
(4) Harris, J. M.; Dovichi, N. J. *Anal. Chem.* **1980**, *52*, 695A-706A.
(5) Haushalter, J. P.; Morris, M. D. *Appl. Spectrosc.* **1980**, *34*, 445-447.
(6) Brannon, J. H.; Magde, D. *J. Phys. Chem.* **1978**, *82*, 705-709.
(7) Carman, R. O.; Kelley, P. L. *Appl. Phys. Lett.* **1968**, *12*, 241-243.
(8) Hu, C.; Whinnery, J. R. *Appl. Opt.* **1973**, *12*, 72-79.
(9) Mark, J. B. Jr.; Rechnitz, G. A.; Grienke, R. A. "Kinetics in Analytical Chemistry"; Wiley-Interscience: New York, 1968.
(10) Mieling, G. E.; Pardue, H. L. *Anal. Chem.* **1978**, *50*, 1611-1618.
(11) Whinnery, J. R. *Acc. Chem. Res.* **1974**, *7*, 225-231.
(12) Daree, K. *Opt. Commun.* **1971**, *4*, 238-241.
(13) Dovichi, N. J.; Harris, J. M. *Anal. Chem.* **1980**, *52*, 2338.
(14) Bevington, P. R. "Data Reduction and Error Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969; Program 11-5.

RECEIVED for review September 2, 1980. Accepted October 22, 1980. This material is based upon work supported by the National Science Foundation under Grant CHE79-13177. Fellowship support (N.D.) by the Phillips Petroleum Co. and the American Chemical Society, Division of Analytical Chemistry (sponsored by General Motors), is acknowledged.

Matrix-Assisted Secondary Ion Mass Spectra of Biological Compounds

Lilian K. Liu,[1] Kenneth L. Busch, and R. G. Cooks*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Secondary ion mass spectrometry (SIMS) can be used to analyze nonvolatile or thermally fragile biomolecules when the sample is sputtered from a metal-supported ammonium chloride matrix. Sugars, nucleotides, nucleosides, and peptides form intact protonated or cationized species, and useful fragmentations are also observed. The spectra obtained by this version of the SIMS technique are similar but not identical with those obtained by field, plasma, and laser desorption techniques. Ionization of these large molecules in SIMS apparently occurs by the processes previously shown to operate for simpler species. In particular, direct ejection from the solid produces the intact cation for thiamine hydrochloride, while cationization by sodium, silver, and copper is observed for sucrose. Protonation to form $(M + H)^+$ occurs for several samples including arginine hydrochloride and the tripeptide glycylglycylglycine.

[1] On leave from the Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China.

Ionization of intact molecules of nonvolatile organic samples can be achieved by using several desorption techniques (*1*), among them the ion-induced sputter process which forms the basis of secondary ion mass spectrometry (SIMS) (*2*). Such difficult samples have traditionally been analyzed by field desorption (FD) (*3*) and more recently by laser desorption (LD) (*4*), plasma desorption (PD) (*5*), and electrohydrodynamic ionization (EHD) (*6*). Along with SIMS, these techniques circumvent the requirement for sample vaporization. SIMS analysis of compounds such as the amino acids, small peptides, and some drugs and vitamins has already been successful (*7, 8*). We now show that the capabilities of SIMS are enhanced if the organic sample is mixed with ammonium chloride and that protonated or metal-cationized molecular ions can be observed for intact mononucleotides, peptides, sugars, and other nonvolatile and thermally labile compounds. Several of these samples have not been successfully analyzed by SIMS by use of preparation methods which omit the salt.

Other reports of matrix-enhanced ionization have appeared. A urea matrix has been utilized for the analysis of underi-

0003-2700/81/0353-0109$01.00/0

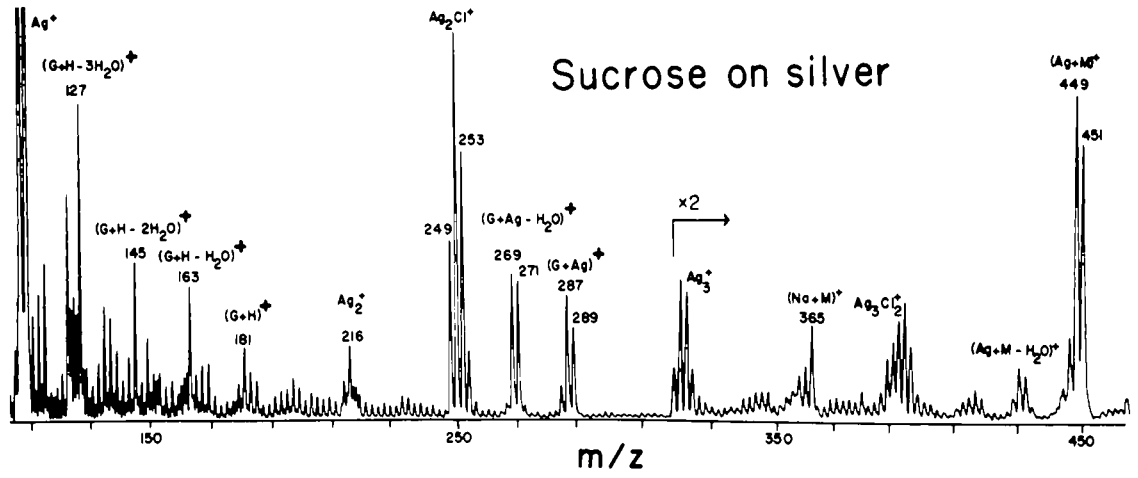

Figure 1. The positive ion SIMS spectrum of sucrose obtained with an ammonium chloride matrix contains cationized intact molecules $(Ag + M)^+$ and $(Na + M)^+$ and cationized and protonated glucose fragments $(G + Ag)^+$ and $(G + H)^+$. Losses of water from these ions are observed.

vatized amino acids in a fast evaporation ion source (*9*). Thermally fragile molecules have been ionized from an oxalic acid matrix (*10*). In a field desorption study, addition of *p*-toluenesulfonic acid has been shown to result in an increased absolute intensity of protonated molecular ions of zwitterionic compounds (*11*). In SIMS, isolation of hydrocarbons in an argon matrix at very low temperatures has been reported (*12*). Use of ammonium chloride as reported here allows the creation of an isolation matrix at room temperature. This simplifies spectra since it eliminates high mass ions formed by intermolecular reactions (*13*, *14*).

EXPERIMENTAL SECTION

Spectra were obtained with a commercial Riber SIMS instrument (Model SQ156L) equipped with a quadrupole mass analyzer, a Channeltron electron multiplier, and pulse counting electronics. Samples were prepared by adding an excess of the finely ground ammonium chloride (5- to 10-fold excess) and burnishing the mixture onto a 1-cm^2 metal foil support (usually silver). Alternatively, a thin film of the salt could be burnished onto the metal foil, and the solid sample spread over this coating. A primary ion beam of Ar^+ (5 kV energy) was used to bombard the sample. Total ion currents were held within the 10^{-10}–10^{-9}-A range (beam diameter ca. 1 mm^2) to minimize damage to the sample. No correction of the spectra for background was made. All compounds and salts were commercially available and were used without additional purification.

Total sample sizes utilized in these experiments were approximately 1 mg or less uniformly spread over a surface area of 1 cm^2. A beam diameter of 1 mm^2 thus sputters a maximum of 10 μg of sample into the gas phase as positive or negative ions and neutrals. Only the positive ions were extracted into the mass analyzer. Absolute ion count rates for typical samples were 500–1000 counts/s for the most abundant peaks. On the basis of a transmission efficiency of 10^{-4}, this represents a secondary ion yield for these samples of about 1%. A full spectrum of thiamine hydrochloride could be obtained with a 50-ng total sample, which translates to 0.5 ng sampled by the argon ion beam. Detection limits for the other compounds investigated here are estimated to be about 10 times higher. Under optimum conditions, detection limits in the low picogram range have been demonstrated for this instrument (*2*). Reproducibility of the spectra shown here is ±10% from the same sample foil and ±20% for different foils prepared in the same manner. The detailed effect of the matrix on the spectral behavior and detection limits of these compounds over a wide range of concentrations have not been studied. The ammonium chloride matrix produces an intense beam of NH_4^+ ions, and the sodium chloride matrix produces Na^+. Typically the mass range scanned by the quadrupole did not include these masses.

RESULTS AND DISCUSSION

The disaccharide sucrose was used to investigate the capabilities of this sample preparation technique. SIMS analysis of sucrose without the addition of ammonium chloride has not been successful under our experimental conditions, but when sputtered from this matrix the spectrum shown in part in Figure 1 is obtained. An abundant cationized molecular ion $(Ag + \text{sucrose})^+$ is observed. Ions which form by dehydration of this ion occur in lower abundance. A favored fragmentation of the cationized species $(Ag + M)^+$ is glycosidic cleavage with cation transfer to the glucose moiety and subsequent dehydrations. The protonated form of the intact sugar molecule is not observed, but ions corresponding to glycosidic cleavage of this ion do appear. A similar spectrum is obtained by mixing sucrose, silver nitrate, and ammonium chloride and then burnishing the mixture onto a platinum foil.

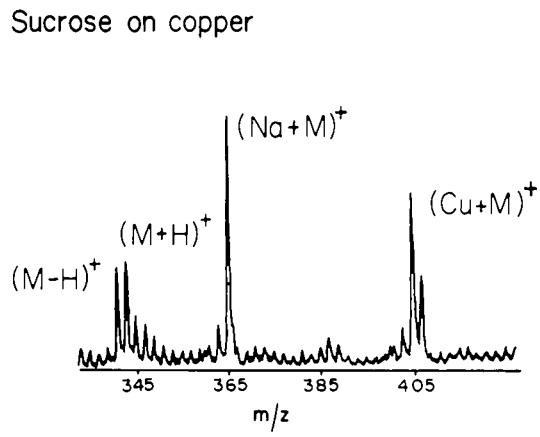

Figure 2. SIMS analysis of sucrose from a copper metal support produces abundant $(Cu + M)^+$ ions. Both $(M + H)^+$ and $(M - H)^+$ ions of sucrose are observed.

Additional experiments were performed with copper, tin, platinum, and iron (steel) metal supports to evaluate the ability of this preparation method to facilitate the formation of cationized species of sucrose. In another experiment, barium acetate was admixed with ammonium chloride. No attachment of tin, platinum, barium, or iron was observed, but copper did cationize sucrose when used as the metal support. The high mass region of the SIMS spectrum of sucrose using a copper foil support is shown in Figure 2. In addition to the $(Cu + \text{sucrose})^+$ ion, fragments due to glycosidic cleavage with cation transfer are observed. Particularly noteworthy is the similar abundance of both $(M + 1)^+$ and $(M - 1)^+$ ions. In addition to the copper cationized species, an ion $(Na + \text{sucrose})^+$ is observed, due to a sodium-containing contaminant of the sample or of the metal support. This adduct appears intermittently under normal conditions, but

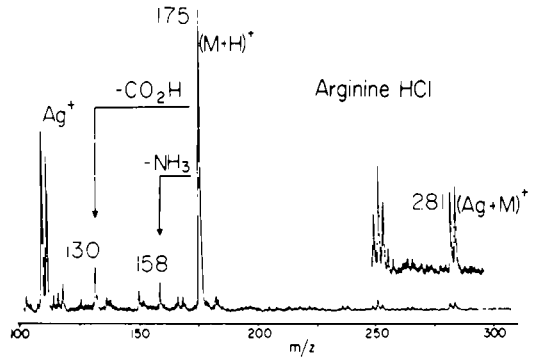

Figure 3. The SIMS spectrum of arginine hydrochloride contains an abundant $(M + H)^+$ ion and a smaller silver-cationized ion $(Ag + M)^+$. Fragment ions include $(M + H - COOH)^+$, $(M + H - NH_3)^+$, and the ion corresponding to the loss of the guanidyl group.

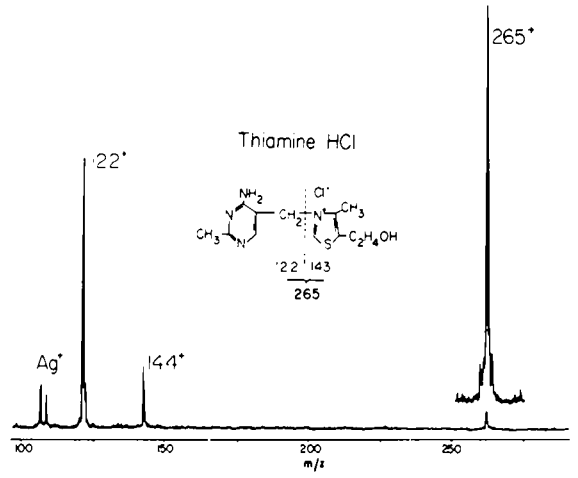

Figure 4. Thiamine hydrochloride analyzed from a silver-supported ammonium chloride matrix produces fragment ions at m/z 122, m/z 123, m/z 144, and an intact cation C^+ at m/z 265.

when sodium chloride is purposefully added to the ammonium chloride matrix, cationization by sodium is greatly increased, and both sodium-cationized molecules and sodium-containing fragments can be seen. Addition of potassium to the intact molecule has been observed but is apparently not as facile as sodium attachment.

Underivatized sucrose has been a test compound for mass spectrometric techniques designed to analyze nonvolatile or thermally unstable molecules. It is instructive to compare the SIMS spectrum of sucrose with those obtained by field desorption (*15–17*), laser desorption (*4*), plasma desorption (*18*), and electrohydrodynamic ionization (*6*). None of the mass spectra obtained by these various techniques contains a molecular ion $M^{+}\cdot$. Rather, abundant protonated or cationized (typically with sodium or potassium) molecular ions are formed. The ions observed in the SIMS spectrum $[(M + H)^+$, $(Na + M)^+$, and $(K + M)^+]$ parallel these results; cationization of sucrose by transition metals $[(Ag + M)^+$ and $(Cu + M)^+]$ is so far unique to SIMS.

The fragmentations observed in SIMS are, however, analogous to those reported in spectra obtained by other desorption techniques. Dehydration from $(M + H)^+$ has been reported in FD, and dehydration from $(Ag + M)^+$ is observed in the SIMS spectrum. Cationized species observed in the LD spectrum, however, do not undergo dehydration. Glycosidic cleavage to yield protonated and metal-containing ions has been consistently reported (FD, EHD, and LD). The $(M - H)^+$ ion which appears in the SIMS spectrum of sucrose sputtered from a copper support has not been reported in any of these other spectra but is observed in the SIMS spectra of other organic compounds. Otherwise, the spectra are amazingly similar considering the different ionization methods used to obtain them. The implications of this similarity have been discussed (*1*).

In accordance with the sucrose results, the monosaccharides glucose and galactose form abundant $(Ag + sugar)^+$ ions from which the expected dehydrations occur. A feature common to the SIMS spectra of all the sugars is the presence of ions two mass units below the abundant sugar ions, as seen in Figure 1.

Experiments with oxalic acid, urea, or *p*-toluenesulfonic acid matrices in sucrose analysis were unsuccessful in that neither protonated nor cationized sucrose was observed, although characteristic glycosidic cleavage fragments were observed. No improvement over analysis from a bare metal support was evident. However, an abundant cationized sucrose ion $(Na + M)^+$ could be obtained when sucrose was analyzed from a sodium chloride matrix on a silver support, along with a lower abundance of the silver-cationized ion $(Ag + M)^+$. Cationized (Na and Ag) fragment ions resulting from glycosidic cleavage were also observed in this spectrum. Thus we conclude that both ammonium chloride and sodium chloride can be used to create a suitable matrix.

Figure 3 is a portion of the positive ion SIMS spectrum of arginine hydrochloride mixed with ammonium chloride on a silver support. The protonated molecule at m/z 175 is an abundant ion in the spectrum, and formation of the cationized molecule $(Ag + M)^+$ also occurs. Fragment ions at m/z 130 and m/z 158, which might correspond to $(M + H - COOH)^+$ and $(M + H - NH_3)^+$ are noted. Loss of the guanidyl moiety produces an ion at m/z 116. The low mass region of the spectrum contains fragments at m/z 43, 59, 60, 69, and 83. A low abundance fragment correspondingly to cationized guanidine (m/z 166) is also observed. The SIMS spectrum of arginine obtained by Benninghoven without a salt mtrix (*7*) contains a base peak $(M + H)^+$ and a fragment $(M - COOH)^+$ of about 50% relative abundance. This loss stands in contrast to the loss of $(M + H - COOH)$ observed here from arginine hydrochlorine. Our SIMS spectra of glycine and serine, however, contain $(M + H)^+$ and $(M - 45)^+$ ions. In SIMS studies of other amino acids obtained without a matrix (*19*), silver-cationized molecules and fragment ions $(M - 45)^+$ have been noted. The $(M + H)^+$ ion of free arginine also appears in the FD mass spectrum (*20*) but is only 30% as abundant as the base peak $(M + H - NH_3)^+$. The ion at m/z 116 is observed with a relative abundance of 30% but the ion $(M + H - COOH)^+$ does not appear in the FD mass spectrum of arginine (*20*). The protonated molecular ion is clearly identified in both the field desorption and the SIMS spectra, although the fragmentations are somewhat different.

Figure 4 is the positive ion SIMS spectrum of thiamine hydrochloride. The intact cation of this quaternary salt can be observed at m/z 265, as expected from SIMS analyses of other quaternary compounds (*21*). Cleavage between the methylene carbon and the quaternary nitrogen forms the base peak ion at m/z 122. Fragmentation with proton transfer to the remainder of the molecule generates the ion at m/z 144, while transfer in the other direction yields the ion at m/z 123. The spectrum shown in Figure 4 was obtained with a 5-fold excess of ammonium chloride. By reduction of the proportion of the matrix salt relative to the vitamin, additional fragmentations from the cation at m/z 265 were observed. Thiamine has been analyzed by field desorption (*22*) and plasma desorption methods (*23*). Field desorption produces only the cation at m/z 265 at the optimum emitter current, but fragmentation to form m/z 143 is reported to occur at a slightly higher emitter current. The plasma desorption spectrum has a base peak at m/z 122, and ions at m/z 123, m/z 144, and m/z 147 are also reported. Interestingly, a

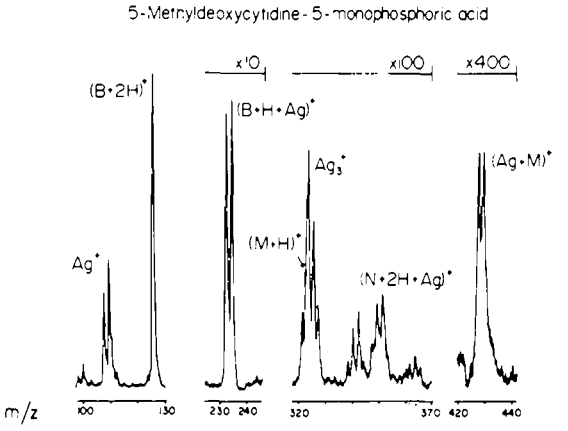

Figure 5. The silver-cationized molecular ion $(Ag + M)^+$ of a mononucleotide is observed in the matrix-assisted SIMS spectrum (5-methyldeoxycytidine-5′-monophosphoric acid). Fragments related to the neutral base (B + H) and the neutral nucleoside (N + H) are also observed.

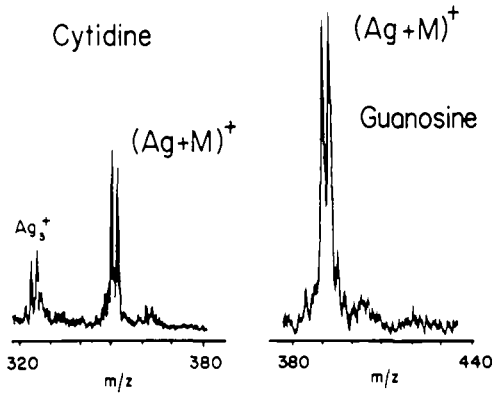

Figure 6. Silver-cationized ions $(Ag + M)^+$ can be formed for the nucleosides cytidine and guanosine.

protonated ion at m/z 266 is produced. However, the cation at m/z 265 has also been reported (*24*). Each of these mass spectrometric methods provides an equally useful mass spectrum of thiamine hydrochloride.

A portion of the positive ion SIMS spectrum of the mononucleotide 5-methyldeoxycytidine-5′-monophosphoric acid is shown in Figure 5, and partial spectra of two nucleosides, cytidine and guanosine, are shown in Figure 6. Both the cationized molecular ions $(Ag + M)^+$ and the protonated ions $(M + H)^+$ are formed by these compounds, although fragment ions corresponding to the protonated neutral bases $(B + 2H)^+$ form the base peaks in all of the spectra. Ions which represent silver-cationized base molecules $(B + H + Ag)^+$ are also consistently observed in these SIMS spectra. Similar species are observed in the field desorption mass spectra of these compounds (*25*), except that alkali rather than transition metals form the cationized species.

When the tripeptide glycylglycylglycine $(Gly)_3$ is sputtered from a silver support in the presence of ammonium chloride, both protonated and silver-cationized molecular species are formed. The protonated species fragments more readily than does the silver-cationized molecule. Losses of 57 and 75 daltons are observed from both the protonated and silver-cationized ions, and a less abundant fragment ion $(M + H - CO_2)^+$ is produced only from the protonated molecule. Loss of 57 (C_2H_3NO) is rationalized as elimination of a single glycyl unit with proton transfer to the remainder of the molecule. Loss of 75 corresponds to the ion formed by subsequent dehydration of this dipeptide product. Interestingly, no such dehydration occurs from the protonated or silver-cationized molecular species. Silver attachment to a monomeric glycine

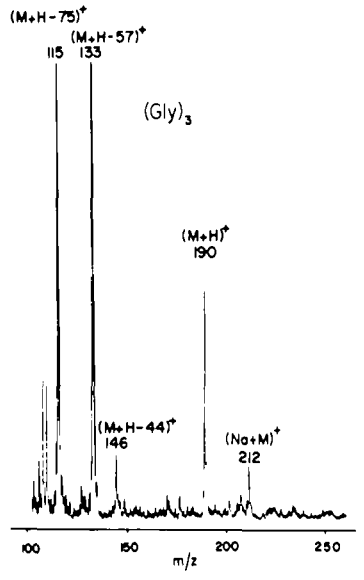

Figure 7. The tripeptide glycylglycylglycine, $(Gly)_3$, analyzed from an ammonium chloride matrix on a platinum support produces cationized $(Na + M)^+$ and protonated $(M + H)^+$ ions, and abundant fragment ions at m/z 115 and m/z 133.

unit is observed. When the same tripeptide is sputtered from an ammonium chloride matrix on a platinum support, only the protonated molecule and its associated fragments are observed as shown in Figure 7. Since platinum is sputtered much less efficiently than is silver, it is not observed either as the atomic species or in combination with the organic sample. Previous SIMS analysis of this tripeptide directly from a silver support (*7*) produced a spectrum with a base peak $(M + H)^+$ and a fragment ion $(M - COOH)^+$ of about 50% relative abundance. No other fragments and no cationized species were reported.

CONCLUSIONS

Ammonium chloride has a marked effect in the enhancement of SIMS spectra, but the reasons are not entirely understood. The matrix may act to reduce the sample–metal interaction energy, allowing the transfer into the gas phase of an intact molecular ion of low internal energy. Protonation or cationization can then take place in the selvedge. Alternatively, the matrix may act to reduce the probability of near-surface neutralization of sputtered ions. Although ammonium chloride forms a convenient room temperature matrix from which organic molecules can be sputtered, it is not inert; it can protonate molecules more basic than ammonia. For example, when sputtered directly from a bare metal support, phenanthroline produced the $M^{+\cdot}$ ion by charge exchange. Use of an ammonium chloride matrix results in exclusive formation of protonated molecule $(M + H)^+$.

These results further demonstrate the capability of SIMS to provide qualitatively useful mass spectra of nonvolatile or thermally fragile molecules (*2*, *7*). The technique is relatively simple and sample preparation is more straightforward than in competitive methods. Matrix-assisted SIMS yields spectra which show noteworthy similarities to those obtained by other desorption methods, although the formation of transition-metal adducts is at present unique to SIMS (*26*). In light of these and other recent results (*27*), continued application to a variety of biological materials is assured.

Note Added in Proof. Cationization of sucrose by Ag^+ has now been observed in laser desorption: Zakett, D.; Hemberger, P. H.; Schoen, A. E.; Cooks, R. G., to be submitted for publication.

By use of time-of-flight SIMS, vitamin B_{12} and other nonvolatile compounds have been ionized successfully without

use of a matrix: Standing, K. G., paper presented at University of Münster, Oct 1980.

LITERATURE CITED

(1) Daves, G. D., Jr. *Acc. Chem. Res.* **1979**, *12*, 359-365.
(2) Day R. J.; Unger, S. E.; Cooks, R. G. *Anal. Chem.* **1980**, *52*, 557A.
(3) Schulten, H.-R. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *32*, 97-283.
(4) Posthumus, M. A.; Kistemaker, P. G.; Meuzelaar, H. L. C.; Ten Noever de Brauw, M. C. *Anal. Chem.* **1978**, *50*, 985-991.
(5) MacFarlane, R. D.; Torgerson, D. F. *Science* **1976**, *191*, 920-925.
(6) Stimpson, B. P.; Evans, C. A., Jr. *Biomed. Mass Spectrom.* **1978**, *5*, 52-63.
(7) Benninghoven, A.; Sichtermann, W. K. *Anal. Chem.* **1978**, *50*, 1180-1184.
(8) Sichtermann, W.; Junack, M.; Eicke, A.; Benninghoven, A. *Fresenius' Z. Anal. Chem.* **1980**, *301*, 115-116.
(9) Gaffney, J. S.; Pierce, R. C.; Friedman, L. *J. Am. Chem. Soc.* **1977**, *99*, 4293-4298.
(10) Gaffney, J. S.; Friedman, L. Annual Conference on Mass Spectrometry and Allied Topics, 1977, paper WD-6.
(11) Keough, T.; Destefano, A. J. Annual Conference on Mass Spectrometry and Allied Topics, 1980, paper MAMOC6.
(12) Jonkman, H. T.; Michl, J.; King, R. N.; Andrade, J. D. *Anal. Chem.* **1978**, *50*, 2078-2082.
(13) Lancaster, G. M.; Honda, F.; Fukuda, Y.; Rabalais, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 1951-1958.
(14) Barber, M.; Vickerman, J. C.; Wolstenholme, J. *J. Chem. Soc. Faraday Trans. 1* **1980**, *76*, 549-559.
(15) Moor, J.; Waight, E. S. *Org. Mass Spectrom.* **1974**, *9*, 903-912.
(16) Schulten, H.-R. *Methods Biochem. Anal.* **1977**, *24*, 313-448.
(17) Prome, J. C.; Puzo, G. *Org. Mass Spectrom.* **1977**, *12*, 28-32.
(18) Chait, B. T.; Field, F. H. Annual Conference on Mass Spectrometry and Allied Topics, 1980, paper FAMOB10.
(19) Colton, R. J.; Murday, J. S.; Wyatt, J. R.; DeCorpo, J. J. *Surf. Sci.* **1979**, *84*, 235-248.
(20) Winkler, H. U.; Beckey, H. D. *Org. Mass Spectrom.* **1972**, *6*, 655-660.
(21) Day, R. J.; Unger, S. E.; Cooks, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 501-502.
(22) Sammons, M. C.; Bursey, M. M.; Brent, D. A. *Biomed. Mass Spectrom.* **1974**, *1*, 169-171.
(23) Becker, O.; Fürstenau, N.; Knippelberg, W.; Krueger, F. R. *Org. Mass Spectrom.* **1977**, *12*, 461-64.
(24) Krueger, F. R.; Wien, K. *Adv. Mass Spectrom.* **1978**, 1429.
(25) Schulten, H.-R.; Beckey, H. D. *Org. Mass Spectrom.* **1973**, *7*, 861-867.
(26) Grade, H.; Cooks, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 5615-5621.
(27) Eicke, A.; Sichtermann, W. K.; Benninghoven, A. *Org. Mass Spectrom.* **1980**, *15*, 289-294.

RECEIVED for review August 6, 1980. Accepted October 27, 1980. This work was supported by the National Science Foundation CHE-78-08728 and MRL Program DMR-77-23798. L.K.L. thanks the National Science Council of the Republic of China for a fellowship.

Direct-Linked Gas Chromatography–Fourier Transform Infrared–Mass Spectrometer System

Charles L. Wilkins,* Gary N. Giss, Gregory M. Brissey, and Steven Steiner

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588

Initial results of the joint use of complementary infrared and mass spectral information obtained from a directly linked gas chromatograph–Fourier transform infrared–mass spectrometer combination are presented. It is demonstrated that the efficacious and unambiguous qualitative analysis of model mixtures can be accomplished in situations where mass spectral or infrared information alone would not be adequate.

Reports over the past decade have documented the successful development of rapid and sensitive Fourier transform (FT-IR) spectrometers capable of making on-line measurements of infrared spectra of eluents from gas chromatograph columns (*1–8*). Recently, Kuehl and Griffiths have observed (*9*) that the sensitivity of GC/FT-IR systems has reached the point that they are viable as an alternative or complement to mass spectrometry for qualitative mixture analysis of mixtures containing components sufficiently stable and volatile for separation by GC. This reiterates the early suggestion by Low and Freeman (*10*), substantiated by the later results of others (*11*, *12*), that a direct linkage of GC/FT-IR and MS might yield an invaluable tool for mixture analysis. The use of multisource data of the type such a chemical information system can provide has been shown to be a powerful identification and structure elucidation tool (*12–15*). A pyrolysis GC system using a combination of trapping, mass chromatographic separation, elemental analysis, and on-the-fly infrared spectrometry has shown the validity of the multiinstrument system concept (*16*). More recently, we have presented a preliminary account of our investigation of the first general direct-linked GC/FT-IR/MS system (*17*). Subsequently, Hirschfeld has discussed preliminary experiments along these lines (*18*). In the present paper we describe more fully the results of our initial studies of a general-purpose on-line GC/FT-IR/MS chemical information system.

EXPERIMENTAL SECTION

Instrumentation. Figure 1 is a block diagram of the system components. A Kratos MS-5076 high-resolution mass spectrometer, operating under control of a NOVA 4X computer using Kratos DS-55 software, was linked via a heated glass-lined stainless steel transfer line to a Nicolet 7199 GC/FT-IR system controlled by a Nicolet 1180 computer and using Nicolet GC/FT-IR software. A Varian 3700 gas chromatograph with a 6 ft × $^1/_4$ in. o.d. copper column, packed with 5% Bentone 34 and 5% didecyl phthalate supported on 60–80 mesh acid washed firebrick was used for all separations. The column was operated between 50 and 100 °C with He as carrier gas at a flow rate of 40–70 cm^3/min.

The GC effluent was split with an adjustable microvalve (a "T" configuration Scientific Glass Engineering Inc. MNVTU microvalve) in order to properly match the sample requirements of both the mass spectrometer and the FT-IR. This valve, which could be adjusted to route between 0 and 100% of the effluent to either the mass spectrometer or the infrared instrument (20 full turns of valve control to cover this range), was adjusted by first closing it to the mass spectrometer (i.e., 100% effluent routed to the FT-IR). The valve was then carefully opened during elution of test samples to obtain an acceptable total ion current at the mass spectrometer detector. Less than half a turn proved necessary in all cases. Transfer lines were 1.6 mm o.d., 0.7 mm i.d. stainless steel glass-lined tubing. The line to the MS-5076 had a volume of 0.4 cm^3 and the line to the FT-IR light pipe had a volume of 0.2 cm^3. Transfer lines and the FT-IR light pipe were heated with heating tape (450 °C limit) to approximately 200 °C. The FT-IR transfer line and light pipe were controlled with a Chromel/Alumel thermocouple as a sensor. The MS-5076 transfer line was con-

0003-2700/81/0353-0113$01.00/0