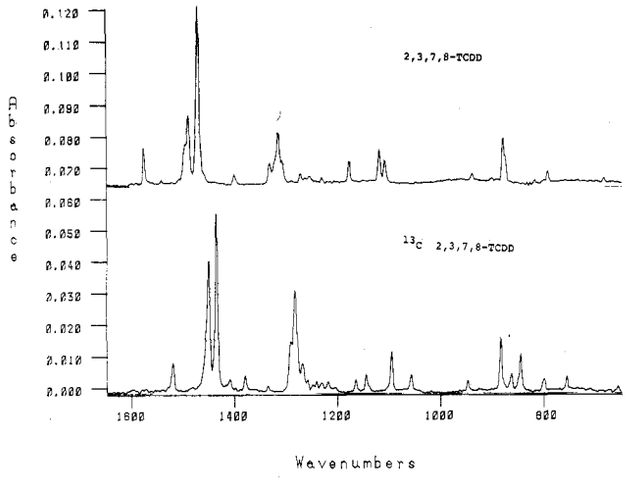

Figure 1. Gas chromatography/matrix isolation/Fourier transform infrared spectra of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (upper spectrum) and [$^{13}C_{12}$]-2,3,7,8-tetrachlorodibenzo-*p*-dioxin (lower spectrum).

equivalent parameter is available for GC/MS methods.

We are in the process of establishing accurate absorptivity values for the major spectral bands of both 2,3,7,8-TCDD and [$^{13}C_{12}$]-2,3,7,8-TCDD. Once these have been established and sensitivities have been further improved, GC/MI/FTIR may become an especially powerful method for isomer-specific dioxin determinations. The absorptivity and isotopic dilution/internal standard methods made possible by GC/MI/FTIR can be a cross-check on the accuracy of the quantitative data and the percent recovery of the internal standard can also be determined.

Thus it would appear that the GC/MI/FTIR technique can provide a reasonably sensitive but isomer-specific method of analyzing samples for environmentally hazardous compounds such as the dioxins and, eventually, the dibenzofurans. In fact, a combination of GC/MS and GC/MI/FTIR would likely enable more than the present-day 5–10% of the components found in a typical environmental extract to be identified or evaluated. The extremely high sensitivity of GC/MS could be used to detect very low-level contaminants, while the GC/MI/FTIR spectra could provide isomeric specificity for known components and, at least, functional group classification for currently unknown components.

We hope to report more fully on the results of our dioxin studies in progress using GC/MI/FTIR in a future article.

Registry No. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin, 1746-01-6; 2,3,7,8-tetrachlorodibenzo-*p*-dioxin-$^{13}C_{12}$, 76523-40-5.

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RECEIVED for review July 11, 1985. Accepted September 4, 1985. C.J.W. wishes to acknowledge partial support of this research by the Weldon Spring Endowment Fund as administered by the University of Missouri. Mention of products and manufacturers is for identification only and does not imply endorsement by the U.S. Environmental Protection Agency.

Detection of Mass 16 241 Ions by Fourier-Transform Mass Spectrometry

Sir: The last several years have seen greatly improved capabilities (*1–11*) for the analysis of large molecules by mass spectrometry (MS), including tandem MS (*9–11*). For such studies scanning type instruments have the disadvantage that even a nonvolatile sample must be continuously consumed in ionization, while the ions measured at any one time represent only a very narrow mass window; the resolution and scan range required for larger molecules exacerbate this problem. The time-of-flight (TOF) mass spectrometer used in plasma desorption studies (*2, 3, 11*) can measure ions of all masses produced in a pulsed ionization event, but here resolution has been limited to 1000–2000 because of the translational energy spread occurring in ionization and metastable and/or collisional ion dissociation. For tandem MS this energy spread reduces sensitivity and resolution even more seriously using sector (*9, 10*) and TOF (*11, 12*) instruments to separate ion dissocation products. The Fourier-transform mass spectrometer (FTMS) has several promising advantages (*13–17*): ions of all masses from an ionization pulse can be recorded simultaneously, the cyclotron frequency of an ion used to determine its mass is independent of the ion's translational energy, unusually high resolution (1/150000 at m/z 1180) can be achieved (*18*), ions produced at a low rate can be accumulated for measurement, and tandem MS

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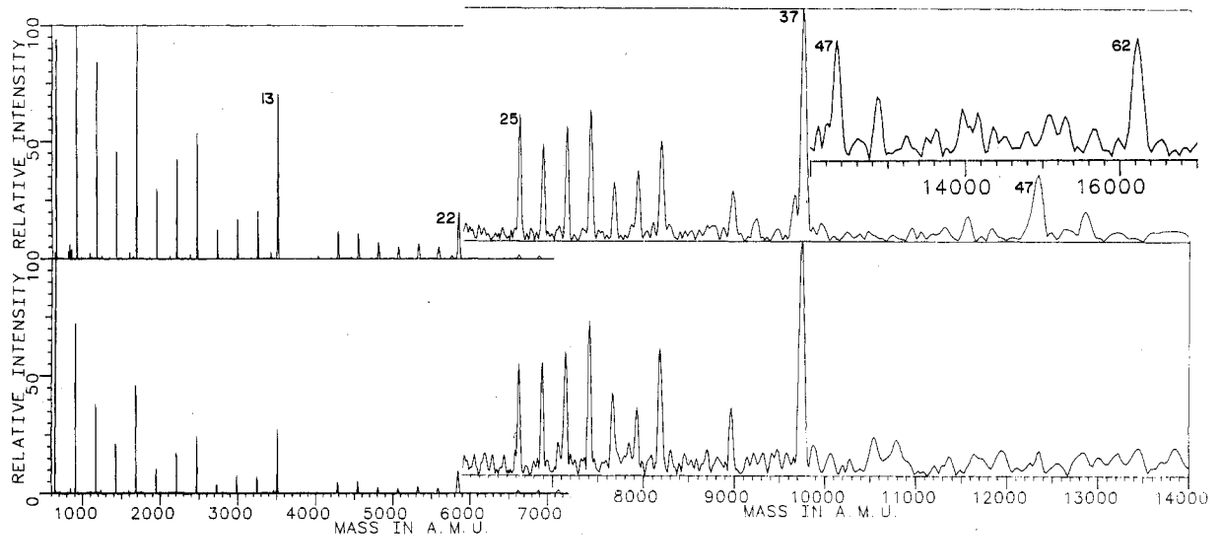

Figure 1. FTMS spectra of $Cs(CsI)_n^+$ (top) and $(CsI)_nI^-$ (bottom) produced by Cs^+ bombardment of CsI (values of n adjacent to peaks). Upper right data (positive ions) were measured separately. Without ion ejection the most abundant peak (not shown) for positive ions is at m/z 393 (for negative ions at 387); relative to this, the abundance of m/z 653 is 9.3% and m/z 9746 is 0.32% (negative ion m/z 647 is 7.0% and m/z 9740 is 0.20%).

measurements can be performed by sequential mass separations in the single analyzer (*19*). A key question (*20*), however, is whether ions will survive the FTMS residence times of 20–100 (or more) ms. This is orders of magnitude longer than such times for other MS instrumentation, increasing the opportunity for both metastable and collisional ion dissociation. Large molecular ion species formed by plasma desorption can dissociate extensively (>96% of dimer ions from insulin in 0.24 ms) (*11*). Recent FTMS evidence is encouraging; Castro and Russell have utilized FTMS with pulsed keV Cs^+ desorption ionization (DI) to measure the dimer ion of vitamin B_{12} at m/z 2792 (*21*), and Wilkins and co-workers (*8*) show that laser desorption-FTMS can produce ion masses of up to 6825 daltons from a polyperfluorinated ether. FTMS has measured m/z 1757 (*22*) and 2845 (*23*) ions from fast atom bombardment and m/z 1920 by tandem MS (*24*). We report here an independent investigation of the mass range of FTMS utilizing Cs^+ DI (*3*, *21*) to measure positive and negative cesium iodide cluster ions (*4*, *25–31*) of masses as high as 16241 daltons, the present low frequency limit of the detection system.

EXPERIMENTAL SECTION

Preliminary studies were done on a Nicolet FTMS-1000 instrument at Texas A&M (*21*, *32*). These were corroborated by the data of Figure 1 from a prototype FTMS-2000 instrument at Nicolet and Cornell, equipped with a 3-T magnet, single section cell, and improved detector electronics and shielding. Cesium iodide (MCB Chemicals Co.) in water was placed on the end of the direct probe, dried, and inserted along the magnetic axis to a position just outside, but not in contact with, the cell entrance. The sample was bombarded with cesium ions thermally emitted from a cesium alumina silicate ceramic (*21*, *32*, *33*), which is differentially pumped and positioned on the magnetic axis approximately 80 cm from the side of the ion cell opposite the probe. The Cs^+ beam had a kinetic energy of 10 keV and current density of $\sim 10^{-8}$ A cm^{-2} and was pulsed on for 1 ms. To increase the relative concentration of high mass ions in the cell, after a 1-ms delay the Cs^+ and Cs_2I^+ (or I^- and CsI_2^-) ions were ejected by applying for 1 ms each 40 V peak-to-peak signals corresponding to their cyclotron frequencies of 345.7 and 117.1 (or 362.6 and 118.9) kHz. The remaining ions were then excited for measurement with a 5-ms "chirp" frequency sweep. Data points (64K) were acquired over a 500-kHz bandwidth (corresponding to 92–17000 daltons) for 67 ms, followed by a 5-ms ion quench and 5-ms delay before repeating the sequence. Because of the high pressure and broad bandwidth recorded, the observed resolution was low: $\sim$1/1300 (half-height peak width/mass) at m/z 1000 and, as expected (*13–17*), 1/130 at 10000. Average mass accuracies were at least an order of magnitude better than these values. Other conditions were similar to those described earlier (*21*). Some of the low abundance peaks (Figure 1) are due to impurities, particularly chlorine; $Cs_2(CsI)_{n-1}Cl^+$ ions appear 91.94 daltons below the corresponding $Cs(CsI)_n^+$ ions.

RESULTS AND DISCUSSION

FTMS Mass Range. $Cs(CsI)_n^+$ ions of n = 47, 49, and 62, m/z 12344 (measured 12336), 12864 (12862), and 16241 (16233), are clearly detected (Figure 1) as are $(CsI)_nI^-$ ions of n = 37 and 47, m/z 9740 (9738) and 12338 (12348). The abundance of m/z 16241, relative to that of the most abundant ion m/z 393 (without its ejection), is 0.10%; this is probably lower than the actual value, as the output of the FTMS-2000 excitation amplifier decreases to <10% over a range of frequencies corresponding to masses of approximately 14000–17000 daltons. Thus up to such mass values there is no evidence of any inherent limitation to the novel detection system of FTMS, which utilizes ion image currents instead of collision with a multiplier surface. Although the latter in principle can detect every colliding ion, the FTMS-2000 can detect 100 ions with signal/noise = $\sim$3.

Mass Discrimination. Relative to previous reports with time-of-flight (*25*) and magnetic sector (*26–31*) instruments, the recent Campana study (*29*) utilizing a postacceleration detector shows much greater high mass abundances, with summed relative abundances of n = 23–37 (38–62) for $Cs(CsI)_n^+$ of 0.5% (0.11%) vs. the most intense peak and for $I(CsI)_n^-$ of 2.0% (1.2%). The corresponding FTMS values (Figure 1, peak areas) are 1.5% (0.28%) and 1.2% (0.1 ± 0.1%). Thus, despite the greater time for ion dissociation in FTMS, the relative discrimination for measuring high masses compares favorably to that of other instruments.

Extent of Ion Dissociation. Increasing residence times of $Cs(CsI)_n^+$ ions enhances differences in their resulting abundances, which have been related to their relative stabilities (*26–31*, *34*). For a magnetic sector instrument (*26*) with 0.3 keV ions (m/z 5000 lifetime $\sim$0.3 ms) the abundances of $Cs(CsI)_n^+$ ions for the "cubiclike" ("magic number") atomic arrangements (*24*, *32*) at n = 13 (3 × 3 × 3), 22 (3 × 3 × 5), 37 (3 × 5 × 5), and 62 (5 × 5 × 5) were substantially greater than those of the corresponding ions of the next higher n value, but comparable to those of the next lowest value. In such instruments any ions dissociating after $\sim 10^{-6}$ s are lost, lowering their abundance. In the FTMS experiment, dissociation

of these unstable ions will also lower their abundance, but the dissociation products will contribute to the spectrum, because any ions formed for ~5 ms after ionization will be detected; in Figure 1 the $Cs(CsI)_n^+$ ions of n = 22, 31 (3 × 3 × 7), 37, and 62 are much more abundant than nearby ions of lower, as well as higher, n values. However, also of appreciable abundance (Figure 1) are unusually labile cluster ions such as $Cs_{35}I_{34}^+$ (m/z 8966), of which 32% was found to undego metastable decomposition in the time period 0.1–0.2 ms (*27*).

The $(CsI)_nI^-$ ion data (Figure 1) show a striking resemblance in abundance to the positive ion data. The exchange of Cs for I^- has surprisingly little effect on the relative stabilities of the clusters.

CONCLUSION

It is apparent that the long ion residuence times of FTMS measurements does not preclude the detection of relatively high mass ions. This is consistent with the expectation that the intensity of an image current produced by ions of the same mass moving coherently should depend directly on the number (and charge) of ions, not on their mass.

Registry No. CsI, 7789-17-5.

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RECEIVED for review March 14, 1985. Resubmitted June 17, 1985. Accepted August 26, 1985. The Texas A&M research was supported by the National Institutes of Health (Grant GM-33780), U.S. Department of Energy (DE-AS05-82ER13023), and Texas Agriculture Experiment Station. Cornell research was supported by the National Institutes of Health (GM-16609) and Army Research Office (DAAG29-82-K-0179).

Mass Spectrometric Determination of Dipeptides after Formation of a Surface Active Derivative

Sir: Barber et al. (*1*) have described a mass spectrometry method that is related to secondary ion mass spectrometry (SIMS) but involves sputtering from a liquid rather than a solid surface. This method is particularly applicable to relatively polar substances that carry a negative or positive charge in solution. It has been demonstrated, however, that such a charge will not by itself ensure high sensitivity and that for materials with similar structures, sensitivity differences are determined largely by differences in surface activity (*2*, *3*). A reviewer of this paper has emphasized that hydrophobicity is an important aspect of the more general concept of surface activity.

It has been shown that surfactants may be used to control the composition of the liquid surface and that surfactants can function in a manner analogous to anion exchange resins—binding species of interest to the surface (*4*). Even in the case of small anions such as nitrate and sulfate, which in glycerol solution are entirely lacking in surface activity, high sensitivities can be obtained by using surface active reagents to bind these species to the liquid surface where they are readily sampled by the primary ion beam (*5*, *6*).

Great success has been reported in the analysis of peptides by sputtering from liquids such as glycerol (*7*), but sensitivities vary widely. In particular small relatively hydrophilic peptides

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