

# Comparison of Mass Spectra Obtained with Low-Energy Ion and High-Energy Californium-252 Fission Fragment Bombardment

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**A direct comparison is made of the mass spectra of several involatile compounds obtained by using  $^{252}\text{Cf}$  fission fragment ionization and low-energy ion bombardment using kiloelectronvolt  $\text{K}^+$  and  $\text{Cs}^+$  ions. The comparisons were made on the same samples mounted on the same foils and mass determinations were made by using the time-of-flight principle. A very high degree of similarity was observed in the spectra obtained by the two ionization methods for all the compounds investigated.**

Two important new methods for obtaining the mass spectra of involatile organic compounds are fission fragment mass spectrometry (1, 2) and low-energy ion bombardment mass spectrometry (3-5). In these techniques the compound of interest is desorbed and ionized directly from a thin solid layer by bombardment with ions in two distinctly different energy ranges, i.e., either  $\sim 80$  MeV  $^{252}\text{Cf}$  fission fragments (1, 2) or 1-20 keV ions produced in an ion gun (3-5). Up to the present time it has not been possible to compare closely the relative properties and merits of these two techniques since virtually no determinations of the spectra of the same compound by the two techniques have been made. Furthermore, in the measurements on different compounds which have been made with the two methods, different types of mass spectrometers and methods of sample preparation have been used. Both of these factors can affect the validity of any comparisons which might be made. We also point out that while fission fragment mass spectrometry has been demonstrated to produce significant quasi-molecular ion yields from a wide range of large, involatile, and fragile molecular species (2), the mass spectral data base for low-energy ion bombardment is much more limited. Indeed, no spectra of compounds with a mass greater than 350 have hitherto been reported in the literature.

Here we report a direct comparison of mass spectra obtained by using fission fragment induced ionization at The Rockefeller University and with low-energy ion bombardment at The University of Manitoba. Of central importance is the fact that the comparisons at the two institutions were made on the same samples mounted on the same sample foils using similar techniques for mass determination, i.e., time-of-flight mass spectrometers. Measurements were made on the following compounds: alanine, arginine, sucrose, tetrabutylammonium iodide, adenosine 5'-monophosphate, adenylyl-(3' $\rightarrow$ 5')-cytidine (ApC), and vitamin B<sub>12</sub> (cyanocobalamin). For all these compounds both positive and negative ion mass spectra were obtained.

## EXPERIMENTAL SECTION

The two mass spectrometers used in the study will not be described in detail since complete descriptions are given elsewhere (5, 6). Instead we will point out features of the instruments which

may be relevant to the spectra comparisons. In the Manitoba instrument we typically employ 2-20 keV  $\text{K}^+$  or  $\text{Cs}^+$  pulsed ion beams with a pulse duration of approximately 10 ns and bombard the sample from the side facing the flight tube. The length of the flight tube is 1.5 m. The ion beam strikes the sample foil at an angle of incidence of 20° with a beamspot diameter of approximately 2 mm. In the Rockefeller instrument, fission fragments bombard the sample foil (diameter 12 mm) from the side facing away from the flight tube and thus pass through the foil before reaching the sample. The flight tube in the fission fragment apparatus has a length of 3 m and employs an electrostatic particle guide (7) to enhance the transport efficiency of ions to the detector.

Ions are accelerated in both instruments by highly transparent (90% transmission) plane grid electrodes placed in close proximity to the plane sample foil. In the ion bombardment device a single grid is employed with a spacing between the sample foil and the grid of 2 mm. In the fission fragment device two grids are employed with a spacing between the sample foil and first grid of 4.5 mm and an equal spacing between the first and second grids. Typically, sample ions were accelerated to an energy of between 2.5 and 5.0 keV in the ion bombardment mass spectrometer and to 6.5 keV in the fission fragment mass spectrometer, except in the case of the positive ions from vitamin B<sub>12</sub>, where an ion energy of 10 keV was employed in both instruments. The differences in configurations and voltages cause the sample ions to be extracted into the field free flight tube two or three times faster in the ion bombardment mass spectrometer than in the fission fragment mass spectrometer.

Different ion flight timing circuits are employed in the two instruments. The time-to-amplitude converter utilized in the ion bombardment instrument (Ortec, Oak Ridge, TN, Model 467) is a single stop device which can yield distorted time-of-flight spectra. The spectral distortion of primary concern is the loss of high mass events in the presence of intense low mass events. Considerable care was thus exercised to ensure that the primary pulsed beam was kept to a low enough intensity to ensure minimal spectral distortion. In the fission fragment instrument a multistop time-to-digital converter (8) with a very low deadtime ( $>10$  ns) is used. The flight times of up to 15 secondary ions per primary fragment may be measured with this device, and thus it does not give rise to spectral distortion of the kind mentioned above.

The compounds of interest were dissolved in mixtures of methanol and water and electrosprayed (9) on aluminized polyester film (0.00025 in. thick). Typically the sprayed samples had a thickness of 10  $\mu\text{g}/\text{cm}^2$ . The compounds studied were obtained from Sigma Chemical Co. except for sucrose (Fisher Scientific Co., Pittsburgh, PA) and tetrabutylammonium iodide (Aldrich Chemical Co., Milwaukee, WI) and used without purification.

The experimental procedure used for the comparisons was as follows: The samples were prepared at Manitoba and spectra were taken there with the pulsed low-energy ion bombardment mass spectrometer. The sample foils were then packed in shipping containers so that the faces with the samples adhering to them were free of contact. The sample foils were sent by post to Rockefeller where spectra were taken with the fission fragment mass spectrometer. Thus the same samples on the same sample foils were used in both studies. The average time interval between the two analyses of a sample was about 1 week.

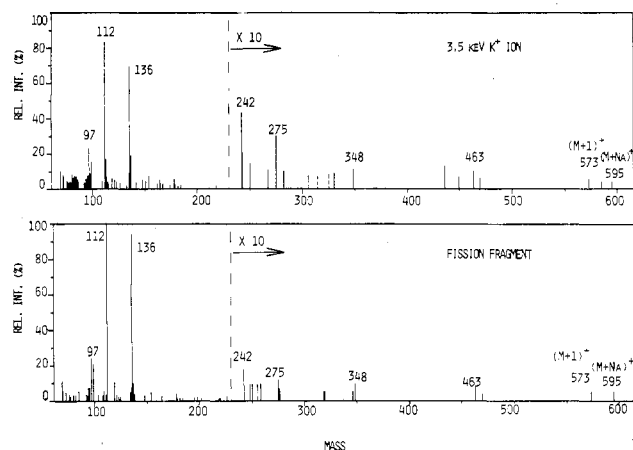


Figure 1. Adenylyl-(3'→5')-cytidine positive ion spectra: upper, 3.5-keV  $K^+$  ion bombardment; lower,  $^{252}\text{Cf}$  fission fragment bombardment.

For determination of the background, spectra were taken with both machines on a bare foil taken from the batch of foil which provided the sample foil. Considerable backgrounds were observed from the bare foil in the low mass region (>150 daltons) in both the positive and negative ion spectra for both instruments. In the positive fission fragment spectrum large ion intensities were observed at  $m/z$  1 ( $H^+$ ),  $m/z$  23 ( $Na^+$ ),  $m/z$  39 ( $K^+$ ), and  $m/z$  63 together with numerous peaks of smaller intensity. The low-energy ion bombardment spectrum was rather different, with large peaks at  $m/z$  23, 27, 29, 41, 43, 57, and 149. The most intense peaks observed from the bare foil in the ion bombardment negative spectrum were  $m/z$  1 ( $H^-$ ),  $m/z$  16 ( $O^-$ ), and  $m/z$  17 ( $OH^-$ ). The ions at  $m/z$  16 and 17 are present in relatively low intensity in the fission fragment negative spectrum, and the most intense ions are observed at  $m/z$  1 ( $H^-$ ) and  $m/z$  25 ( $C_2H^-$ ). In addition, numerous differences in ions of smaller intensity are observed. We do not understand the cause or significance of these differences. These backgrounds were subtracted from the sample spectra making use of the arbitrary criterion that sample peaks must have approximately twice the intensity of the background peak at the same  $m/z$  value to be retained in the net spectrum. The ubiquitous ions  $H^+$ ,  $Na^+$ ,  $H^-$ ,  $O^-$ ,  $OH^-$ , and  $C_2H^-$  were generally omitted from the spectral comparisons because of their uncertain origin.

For the fission fragment spectra all of the data with the exception of those for ApC and vitamin  $B_{12}$  were recorded in channels 3.125 ns wide, and the plotted intensities are the result of 5 channel sums about the peak centroids. Because of the greater length of the spectrum, ApC data were recorded at 5 ns/channel, and the intensities are the result of 3 channel sums about the peaks. The ion bombardment mass spectra were recorded at 9.2 ns/channel with the exception of that for vitamin  $B_{12}$ , which was recorded at 13.1 ns/channel. The plotted intensities for alanine, arginine, and sucrose were obtained from 5 channel sums, while ion intensities for the other compounds were simply obtained from the peak heights. We found that the peak shapes for different ion species from a particular compound could differ markedly, but in the same way for both methods of ionization. The method for deriving the intensities outlined above puts emphasis on peak heights, thus tending to underestimate the total intensity under broad peaks. However, since very similar broadening effects are observed with both modes of ionization, the comparisons are meaningful.

## RESULTS AND DISCUSSION

We have determined the positive and negative mass spectra with both modes of ionization for the eight compounds alanine, arginine, sucrose, guanosine, 5'-adenosine monophosphate, adenylyl-(3'→5')-cytidine, tetrabutylammonium iodide, and vitamin  $B_{12}$ . We state at the outset that a very high degree of similarity is found in the spectra obtained by the two ionization methods for all the compounds, and in particular the relative intensities of high-intensity ions and of quasi-molecular ions agree well. Since the totality of the data

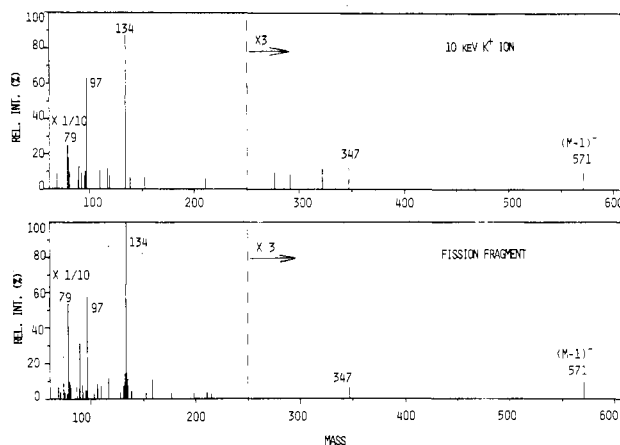


Figure 2. Adenylyl-(3'→5')-cytidine negative ion spectra: upper, 10-keV  $K^+$  ion bombardment; lower,  $^{252}\text{Cf}$  fission fragment bombardment.

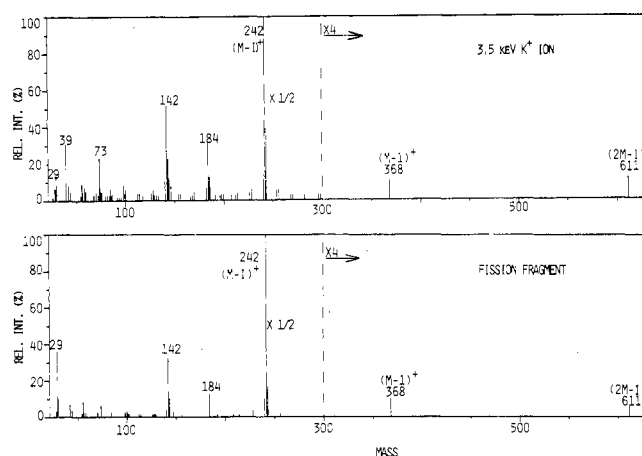


Figure 3. Tetrabutylammonium iodide positive ion spectra: upper, 3.5-keV  $K^+$  ion bombardment; lower,  $^{252}\text{Cf}$  fission fragment bombardment.

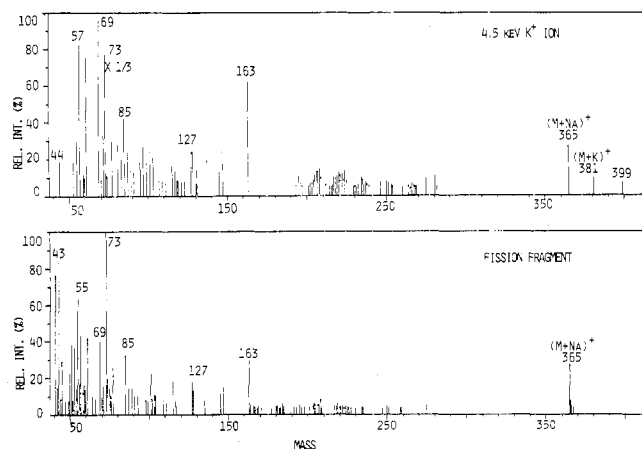
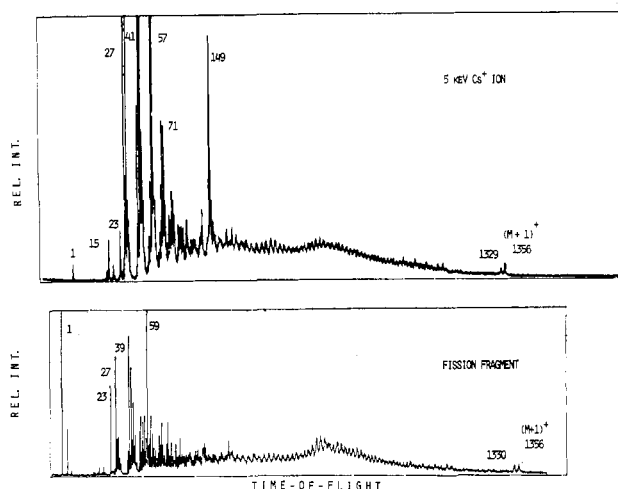


Figure 4. Sucrose positive ion spectra: upper, 4.5-keV  $K^+$  ion bombardment; lower,  $^{252}\text{Cf}$  fission fragment bombardment.

comprises 32 spectra, it is unrealistic to publish full spectra for all these compounds. Consequently, we adopt the expedient of giving representative histogram spectra of three compounds obtained with the two methods. Further examples are given elsewhere (10). The representative spectra given are for positive ApC (Figure 1) negative ApC (Figure 2), positive tetrabutylammonium iodide (Figure 3), and positive sucrose (Figure 4). The intensities in each pair of spectra are normalized at an appropriate quasi-molecular ion. The spectra of ApC and tetrabutylammonium iodide are repre-



**Figure 5.** Direct time-of-flight spectra for the positive ions from vitamin B<sub>12</sub>: upper, 5.0-keV Cs<sup>+</sup> ion bombardment; lower, <sup>252</sup>Cf fission fragment bombardment.

sentative of the best agreement obtained between the two ionization methods, while that for sucrose represents the poorest agreement. The agreement for the other spectra generally lie between those shown.

For the positive ApC spectra (Figure 1) we observe with both modes of ionization the (M + 1)<sup>+</sup> and (M + Na)<sup>+</sup> quasi-molecular ions, as well as intense fragments at *m/z* 112 (cytidine base + 2), 136 (adenine base + 2), 463 (loss of the cytidine base from the (M + 1)<sup>+</sup> ion), 242, and 348. In the negative ApC spectra (Figure 2) we find numerous corresponding ions including the (M - 1)<sup>-</sup> quasi-molecular ion at *m/z* = 571, the adenine base moiety at *m/z* = 134, and the intense PO<sub>3</sub><sup>-</sup> anion at *m/z* = 79. The positive spectra of the quaternary ammonium salt tetrabutylammonium iodide are given in Figure 3. A less direct comparison of the spectra of this compound has been made previously (11). We find that the relative intensities of most of the major ions agree to within a factor of 2. As the example of a compound for which the correspondence between spectra is not so close, we show the spectra of the positive ions from sucrose (Figure 4). We find many similarities for ions which have been shown to be significant (6), e.g., the fragments at *m/z* 69, 73, 85, 127, and 163, and the (M + Na)<sup>+</sup> quasi-molecular ion at *m/z* = 365. However, we also note several differences between the spectra, as with the absence of the (M + K)<sup>+</sup> quasi-molecular ion at *m/z* 381 in the fission fragment spectrum and the difference in the pattern of small peaks between *m/z* 200 and 300. We believe these latter peaks to be due to impurities or contamination of the sprayed sample foil since they did not occur for independently prepared samples of sucrose measured with the fission fragment apparatus. We further find that many of the peaks for which substantial differences are noted between the two methods correspond to ions having large mass defects and are thus inorganic in origin.

The central achievement of the fission fragment method has been its ability to produce significant quasi-molecular ion yields in very large, polar, and fragile molecular species. The comparison was thus extended to include vitamin B<sub>12</sub> for which we show direct time-of-flight data for the positive ions in Figure 5. The compound yields the protonated quasi-molecular ion together with a rather extensive and unusual decomposition spectrum. We note that even for a molecule as complex as vitamin B<sub>12</sub> the direct data show remarkable similarities in detail, especially above mass 150. A peak is observed at *m/z* 1330 in the fission fragment spectrum and *m/z* 1329 in the ion bombardment spectrum which probably correspond to the loss of the cyanide ligand attached to the central cobalt atom. The discrepancy of about 1 amu is

consistent with the estimated error in the mass determination of this broad, complex high mass peak. Some differences do exist, as for instance the observation of a large peak at *m/z* 149 in the ion bombardment spectrum and its relative absence in the fission fragment spectrum. We point out, however, that an impurity ion is consistently observed in the ion bombardment spectra at *m/z* = 149 and is only seen with weak intensity in the fission fragment spectra. Further discrepancies are to be seen in the low mass region. However, several of these may be associated with background ions.

Within the range of molecular weights and degree of volatility of the compounds included in this comparison, the spectra obtained with fission fragment induced ionization and low-energy ion bombardment ionization are highly similar. This agreement applies to both positive and negative ions. Further experimental comparisons are required to determine whether this trend will continue to hold true for some of the very large molecular species (*m/z* > 2000) which have been examined with fission fragment mass spectrometry. The consistent similarity of the observed patterns of ions indicate that the major processes for the formation of ions by these two ionization modes may be closely related. Superficially this is surprising since the major energy loss process for fission fragments (electronic stopping) is entirely different from that for low-energy ions (nuclear stopping) (12).

The relative analytical utility of the two techniques is, of course, of interest, but we are of the opinion that this is not yet established. However, we can give some of the factors which are involved. Since both methods yield similar mass spectra for a given compound, the factors will be primarily those of a practical nature. A problem exists in containing the <sup>252</sup>Cf radioactivity, and this requires rather stringent precautions. This problem does not exist with low-energy ion bombardment. The sensitivity of the fission fragment method is ultimately limited by the maximum flux of fission fragments which is allowed to pass through the sample, and this is limited by the necessity of keeping the <sup>252</sup>Cf source strength within practical limits. On the other hand, with a pulsed ion beam the number of ions in each pulse may be increased to a large value. In the present apparatus it has been straightforward to produce a flux of pulsed ions 2-3 orders of magnitude more intense than that available from the strongest practical californium source. The ion beam is also readily focused to a small diameter on the sample foil, which implies that it is necessary to coat only a small area of sample foil with sample, which could yield an improvement in the working sensitivity. However, increasing the bombarding ion flux may at some point produce sample charging effects having deleterious consequences. Finally, the question of the relative sensitivities of the two methods depends critically upon their intrinsic sensitivities for ionization, that is, on their intrinsic ion production yields. Unfortunately, reliable information on these yields is not presently available.

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## Fluorescence Photoselection of Matrix Isolated Polycyclic Aromatic Hydrocarbons

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**The analytical utility of fluorescence photoselection for distinguishing overlapping spectral bands in mixtures of matrix isolated polycyclic aromatic hydrocarbons is explored. The use of a polarizer to selectively pass the fluorescence of one component from a mixture of fluorophores after excitation by a polarized (laser) source results in significantly improved spectral discrimination. Potential applications, as well as the limits of applicability, are discussed.**

The detection of individual polycyclic aromatic hydrocarbons (PAHs) in complex samples, such as "synthetic fuels", represents a challenging problem to the analytical chemist. Recently, highly sensitive low-temperature fluorometric procedures (1-8), coupled with laser excitation (2-8), have been successfully exploited for the analysis of complex mixtures of trace amounts of PAHs and derivatives. Selective excitation (2-4), site selection (5-7), and time resolution (7, 8) techniques have proven especially effective as analytical procedures, providing a high degree of selectivity. However, because there are numerous situations in which these methodologies cannot be applied or are of limited usefulness, we have explored the use of photoselection techniques for improvement of selectivity in the low-temperature fluorometric characterization of multicomponent samples.

Although it is well-known that the fluorescence from PAHs in rigid media is partially polarized, especially when a polarized excitation source is used (e.g., a laser), the analytical advantages that can be extracted from this phenomenon have not been delineated. In a mixture in which the fluorescence from each compound is preferentially polarized in different directions, enhanced spectral selectivity for a particular compound intuitively may be expected if a polarizer is oriented to selectively pass the emission from the component of interest. However, in order to intelligently interpret or utilize the phenomenon of polarized emission and absorption, the results of the theory which is used to interpret experimental measurements of the polarization of electronic transitions must be understood.

In general, the theories assume that the sample molecules either are preferentially oriented in one direction or are oriented randomly (9). Samples which are prepared by matrix isolation procedures (1) (in which a vaporized sample is mixed with a large excess of diluent gas and deposited on a cryogenic

surface) are characterized by random orientations of sample molecules if a "conventional" matrix, such as argon or nitrogen, is employed (10). Hence, this paper will not consider sample preparation techniques which produce oriented solute molecules. The results of this paper will therefore be applicable to samples which are isolated in "conventional" matrices or frozen in low-temperature glasses but will not necessarily apply to samples prepared in crystalline hydrocarbons, Shpol'skii frozen solutions, or mixed crystals.

### THEORY

In order for a radiation-induced transition to be observed between initial and final states with wave functions  $\Psi_i$  and  $\Psi_f$ , respectively, the electric dipole transition moment

$$\vec{M}_{i,f} = \int \Psi_i \vec{r} \Psi_f d\tau \quad (1)$$

must have a nonvanishing value, because the probability for a transition is proportional to the square of  $M_{i,f}$  (9, 11-13). Here,  $\vec{r}$  is the electric dipole vector and  $\tau$  symbolizes the set of internal coordinates required for locating each electron of the molecule. Because  $\vec{M}_{i,f}$  is a vector with components along the molecule-fixed  $x$ ,  $y$ , and  $z$  axes, the integral in eq 1 can often be separated into three independent integrals of the form (12, 13)

$$\vec{M}_{i,f} = \hat{i} \int \Psi_i x \Psi_f d\tau + \hat{j} \int \Psi_i y \Psi_f d\tau + \hat{k} \int \Psi_i z \Psi_f d\tau \quad (2)$$

where  $\hat{i}$ ,  $\hat{j}$ , and  $\hat{k}$  are unit vectors directed along the  $x$ ,  $y$ , and  $z$  molecular axes, respectively. Thus, a transition is electric-dipole-allowed if one of the three integrals in eq 2 does not vanish, which can be determined by group theoretical analysis if the symmetry of the wave functions is known (9, 12, 13).

Transitions are generally polarized in the sense that the three integrals in eq 2 are not necessarily equal (12). For example, if the first integral has a finite value while the other two are equal to zero, the transition is said to be polarized along the  $x$  molecular axis (9, 12, 13). In some cases for which the molecular symmetry is sufficiently high or low and where  $x$  and  $y$  jointly form the basis for an irreducible representation, the integrals involving  $x$  and  $y$  are not independent of each other and neither integral is equal to zero (12, 13). For this situation, the transition is said to be polarized in the  $xy$  plane.

Of particular interest is the orientation of the transition moment relative to a molecule-fixed coordinate system. In general, the orientation cannot be determined from group