Environmental Health Perspectives
Vol. 36, pp. 85-96, 1980

Instrumental Aspects of Positive and Negative Ion Chemical Ionization Mass Spectrometry

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Differences in recording positive and negative ion chemical ionization mass spectra on a quadrupole mass spectrometer are discussed. An analog positive and negative ion electron multiplier detector is described which is well suited for a quadrupole instrument. This detector significantly reduces baseline noise in the negative ion mode and improves positive ion high mass sensitivity.

We have been involved in developing methodology to facilitate acquisition of positive and negative ion chemical ionization (CI) mass spectra on a quadrupole mass spectrometer. Operation of the ionizer under CI conditions provides a mixture of positive reagent ions and near thermal energy electrons. Accordingly, both positive and negative sample ions are produced simultaneously in large abundance in a CI ionizer.

With a quadrupole instrument, it is only necessary to reverse the ion accelerating potential and ionizer lens potentials to transmit ions of opposite charge to the mass analyzer. Unlike the situation in magnetic sector instruments, ions of identical m/e, but different polarity are transmitted with equal facility through a quadrupole mass filter without any change in operation. Detection of negative ions with an electron multiplier is the only inherant problem of a quadrupole instrument operated in the negative ion mode. Ions exiting a quadrupole mass filter will generally have less than 20 eV of kinetic energy and it is obvious that negative ions will not strike the cathode of a conventional positive ion electron multiplier.

The conventional approach to negative ion detection on a quadrupole instrument is to isolate the entire electron multiplier electrically at a high positive potential so that the cathode is at a sufficiently positive potential for efficient collection of the negative ions (Fig. 1). This methodology has the disadvantage that the anode (signal) of the electron multiplier and the preamplifier must also be isolated at this high positive potential. Therefore, complex preamplifier circuitry is required to reference the signal to ground potential. A special high voltage floating coaxial signal feedthru is required on the vacuum flange to prevent microphonic noise and charge leakage. The floated electron multiplier approach also has the problem that stray electrons in the vacuum system are efficiently detected, causing an increase in the baseline noise by a factor of approximately 30.

Our approach to negative ion detection is to convert the negative ions to secondary positive ions which are subsequently detected by a standard continuous dynode electron multiplier (CDEM) (*1*). Negative to positive ion conversions can be accomplished by impacting the primary negative ions on a conversion dynode maintained at a high positive potential. This negative ion detector is shown schematically in Figure 2 and was constructed by mounting a dynode opposite the cathode of a Galileo model 4770 continuous dynode electron multiplier. This approach eliminates the problems associated with floating the anode of an electron multiplier at a high positive potential. A further advantage of this negative ion detector is that stray electrons in the vacuum system do not efficiently produce positive ions when they im-

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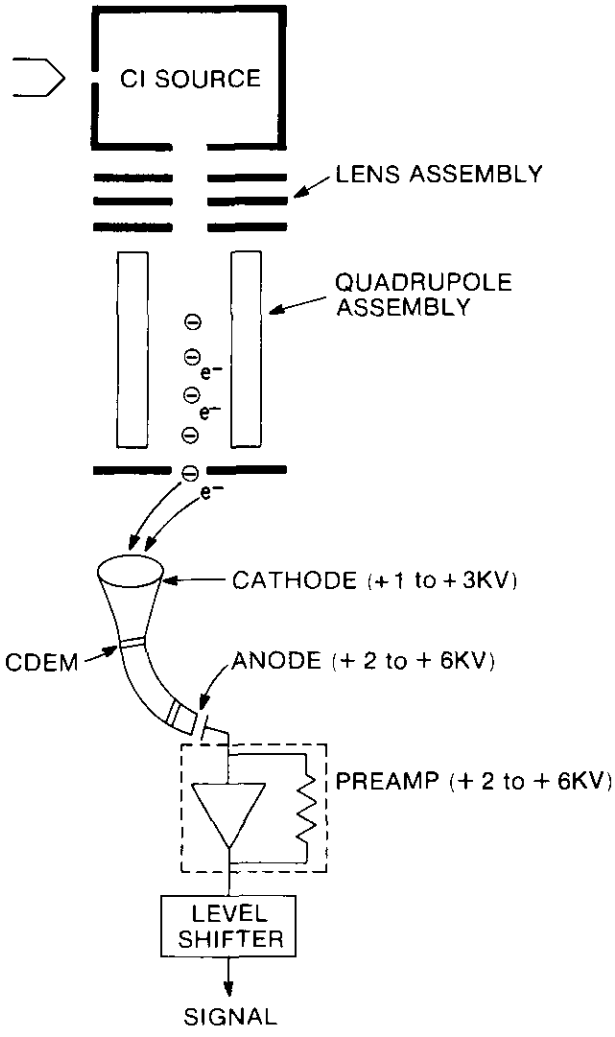

FIGURE 1. Off-ground negative ion continuous dynode electron multiplier.

pact the conversion dynode and the baseline noise is significantly reduced.

We believe the major mechanism responsible for this negative to positive ion conversion are: sputtering, fragmentation, and charge stripping.

In sputtering, the energy of the bombarding negative ions is transferred to the metal surface causing metal atoms to be vaporized from the surface. A fraction of these sputtered metal atoms lose electrons to form positive ions.

When polyatomic negative ions impact the dynode surface, they undergo extensive fragmentation. These fragments will consist of neutral species, negative ions, and positive ions. We feel that fragmentation becomes the major conversion process for large polyatomic ions (>200 amu).

As negative ions are accelerated toward the conversion dynode, two electrons may be stripped away to form positive ions. This constitutes charge stripping.

Figures 3 and 4 exhibit the gain as a function of m/e for a positive ion CDEM and a conversion dynode negative ion detector on a quadrupole mass spectrometer. Positive ion detection shows a reduction in gain for the high mass ions. Presumably this is due to poor secondary electron emission from impact of high mass ions on the cathode of the CDEM (*2*). On the other hand, negative ion detection using a conversion dynode shows an increase in gain for high mass ions. These data suggest that the larger organic negative ions are much more efficient in producing secondary positive ions when they impact the conversion dynode.

If two conversion dynodes of opposite polarity are properly positioned at the cathode of a CDEM, both positive and negative ions can be simultane-

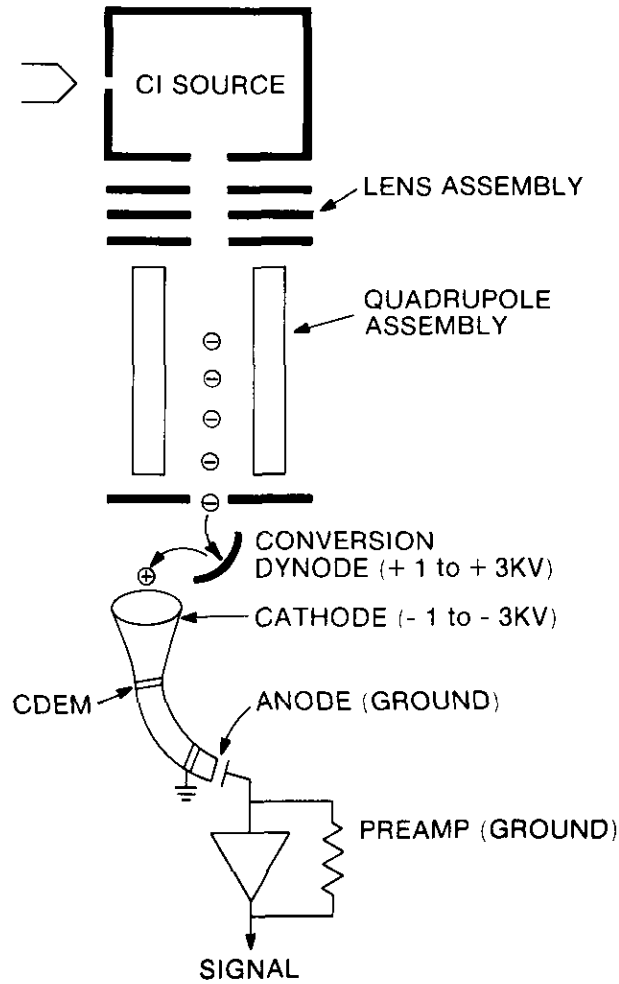

FIGURE 2. Conversion dynode negative ion detector.

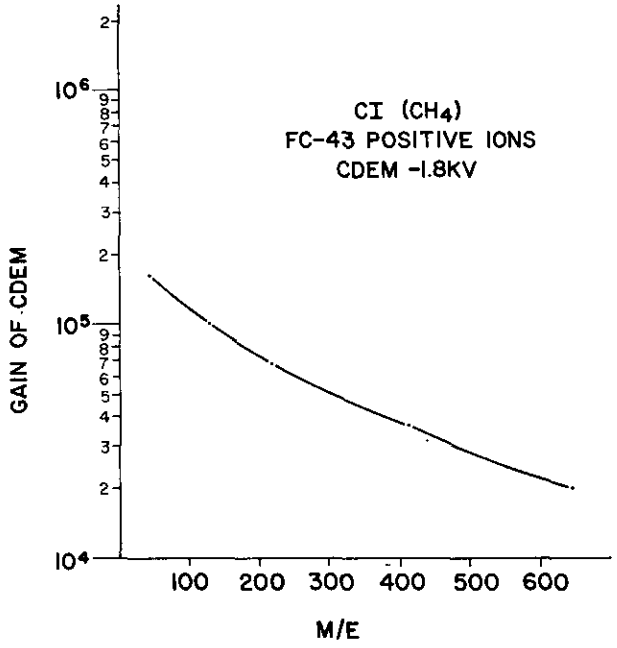

FIGURE 3. Positive ion gain vs. m/e for a CDEM.

ously attracted and detected without any change in the operating voltages (Fig. 5). Thus, selection of positive or negative ion spectra on a CI quadrupole instrument is accomplished by simply reversing the polarity of the lens and ion volume voltages.

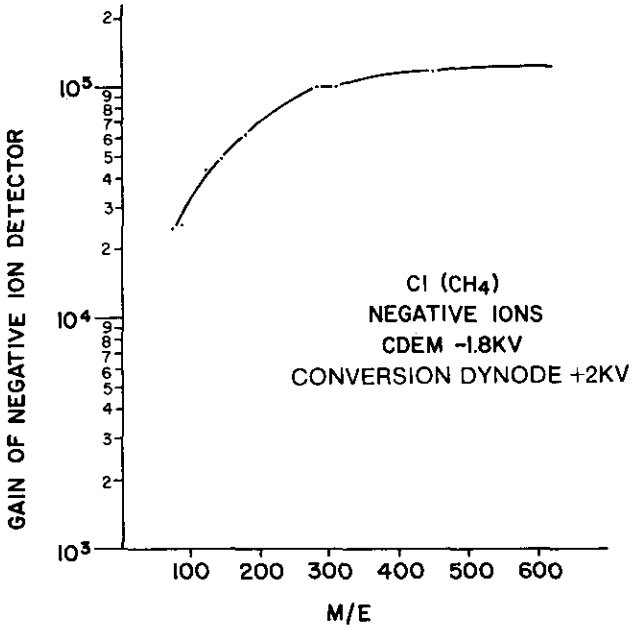

FIGURE 4. Negative ion gain vs. m/e for the conversion dynode negative ion detector.

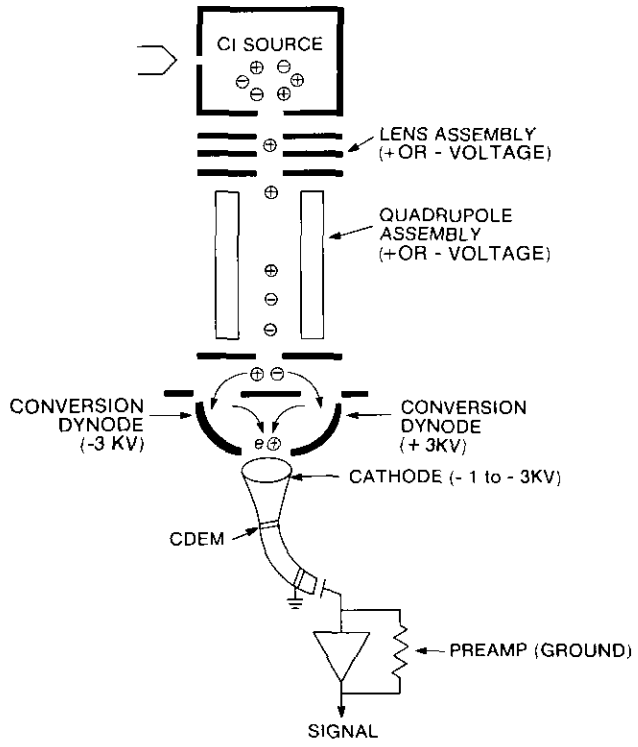

FIGURE 5. Simultaneous positive negative ion detector.

The use of a positive ion conversion dynode improves the gain and signal to noise ratio for high mass positive ions. Figure 6 shows an improve-

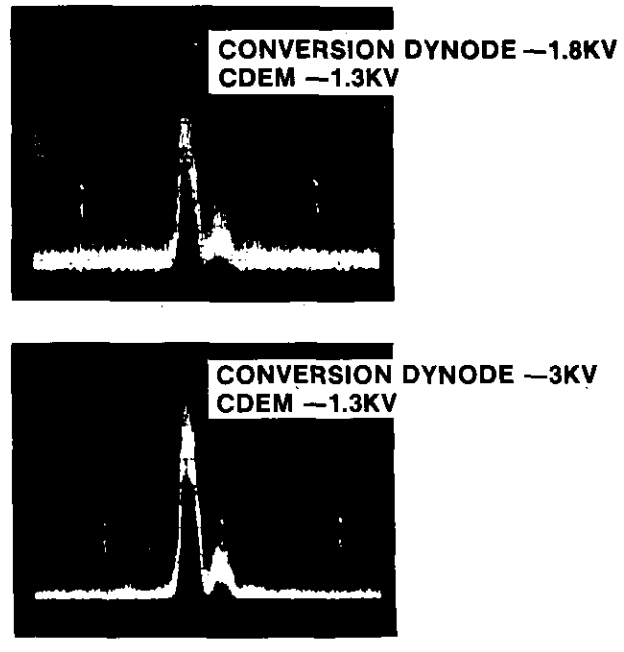

FIGURE 6. Comparison of positive ion signal/noise ratio for tris(perfluoroheptyl)-*syn*-triazine, m/e = 866.

ment in the signal to noise ratio by a factor of 4 for m/e 866 when the positive ion conversion dynode voltage is increased from −1.8 kV to −3.0 kV. The higher voltage on the dynode improves the conversion of positive ions to secondary electrons thereby increasing the overall gain of positive ion detection.

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