ADVANCED DETECTOR AND OPTICAL FABRICATION TECHNOLOGIES FOR IMPLEMENTING IMPROVED SPECTROSCOPIC INSTRUMENTATION

The Use of a CTIA Detector in Ion Mobility Spectrometry

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Abstract: *The ability to detect ions is of foremost importance in a wide number of chemical instruments. Over the last five years we have made significant progress implementing mass spectrometer detector arrays using concepts adapted from CTIA preamplifier array technology. These detectors demonstrate all the desirable characteristics of Faraday type detectors, with sensitivities approaching those of multiplier detectors, but are easily fabricated into long linear arrays - providing an important multiplex advantage for focal plane geometry mass spectrometers. Optimized single channel detectors have been developed with the ultimate goal of direct detection of single ions. Extremely high impedance CTIA amplifiers have been integrated with low capacitance collection elements to produce a detection system capable of direct measurement of charge with very high sensitivity.*

Key words: *Capacitive Trans Impedance Amplifiers (CTIAs), ion.*

1. INTRODUCTION

Adaptations of technology for astronomy are making dramatic impacts on many other areas of science and technology. This is probably most apparent in the field of modern chemical analysis. Low light level optical spectroscopies in the UV-visible and near IR regions (125 to 1100 nm) have advanced dramatically through the use of modern CCD and CID focal plane arrays. In atomic emission spectroscopy the venerable direct reader, using discrete photomultiplier tubes (PMTs), has been replaced by focal plane

J.E. Beletic et al.(eds.), Scientific Detectors for Astronomy 2005, 207-216.

arrays, often providing continuous wavelength coverage at higher resolution and improved sensitivity. Dispersive Raman spectroscopy has capitalized on the sensitivity and multiplex advantage of arrays, thus few scanning PMT based instruments are still employed. Although infrared focal plane arrays are gaining niche markets, total system costs have thus far limited their widespread adoption.

Capacitive Trans Impedance Amplifiers (CTIAs) are often employed as readout circuits in hybrid focal plane infrared arrays. This readout scheme has several desirable characteristics including a high degree of linearity and system gain determined by feedback capacitances, as well as the ability to provide high sensitivity for very small charge packets.

The ability to detect ions is of foremost importance in a wide number of chemical instruments. Mass spectrometers generally use a form of ion multiplier or, in cases where extreme accuracy is required (as in isotope ratio analysis), a Faraday cup or plate. Ion multipliers come in many configurations, but all utilize the principle of ion to electron conversion, which is accelerated onto a dynode to yield multiple secondary electrons. These secondary electron "packets" are subsequently accelerated into the next dynode (see Fig. 1). The process is repeated until a large, easily measured charge packet or steady state current is produced.

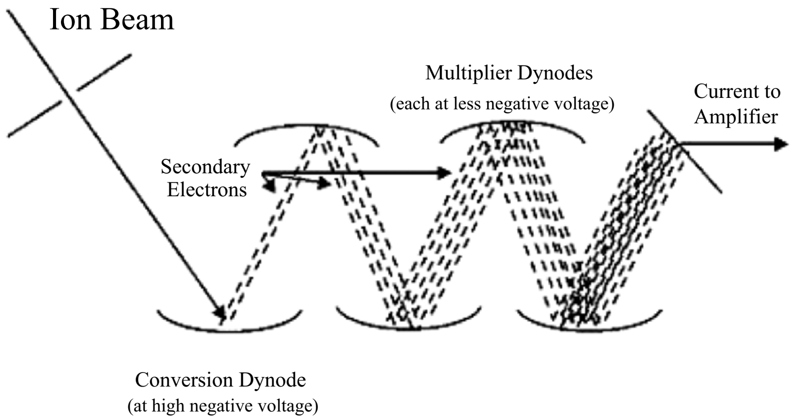


Figure 1. Ion multipliers use avalanche electron multiplication to increase current measured by 10^6 or more. However, this technique does not work at atmospheric pressure.

Although this approach is successful in many applications, limitations exist which prevent the detection of extremely large ions (the ion lands on the conversion electrode without ejecting an electron capable of causing secondary emission). Another possible difficulty is that the process does not provide the required precision and stability because the efficiency of the electron ejection process is influenced by ion mass and/or energy. Additionally, these charge multiplication techniques are not easily configured into large linear arrays suitable for focal plane mass spectrometers such as those using the Mattauch-Herzog geometry.

Over the last five years we have made significant progress implementing mass spectrometer detector arrays using concepts adapted from CTIA preamplifier array technology [1,2,3] These detectors demonstrate all the desirable characteristics of Faraday type detectors, with sensitivities approaching those of multiplier detectors. However they are easily fabricated into long linear arrays - providing an important multiplex advantage for focal plane geometry mass spectrometers.

In this manuscript, similar detector technologies are evaluated for their compatibility with Ion Mobility Spectrometry (IMS). IMS is widely utilized for the detection of chemical warfare agents, hazardous chemicals explosives, and even for elucidation of large biological molecules (see Fig. 2).

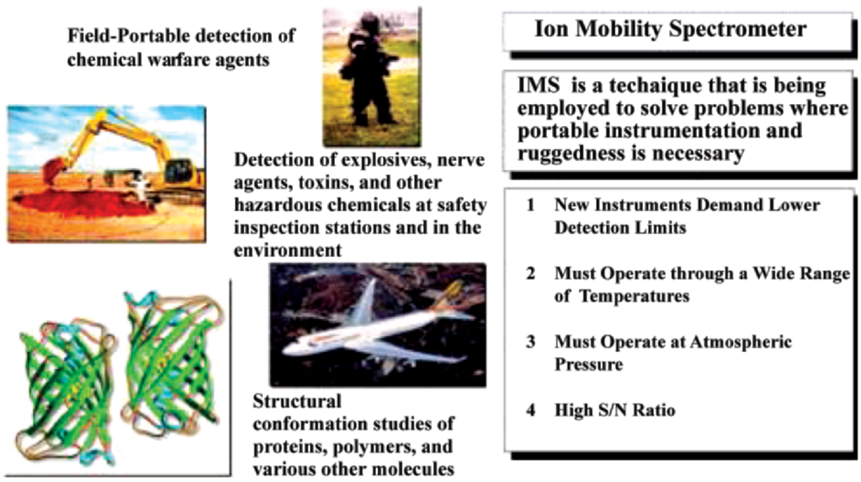


Figure 2. Ion mobility spectrometry is used today for a wide variety of ultra-trace field and laboratory analyses. One of the most common applications is screening for illicit explosives.

This technique, shown in Figures 3 and 4, involves ionizing the molecules of interest or a reagent gas, which subsequently transfers charge to analyte molecules. An ion shutter or gate pulses out a packet of ionized molecules accelerating them down a drift region over which a potential gradient is applied. The ions are collected as a function of arrival time at a Faraday plate or electrode.

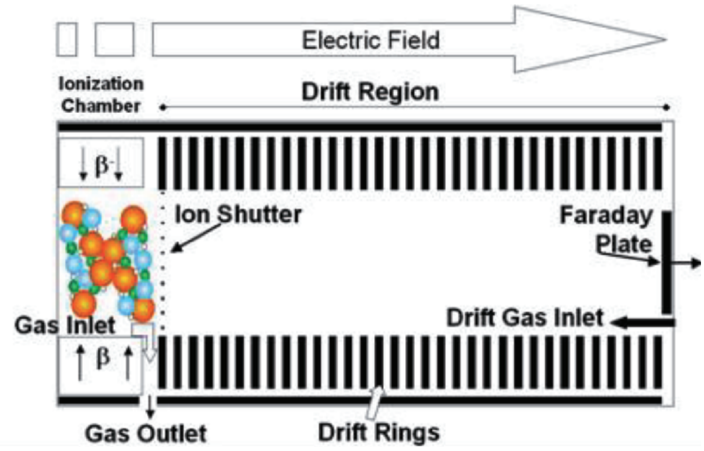


Figure 3. An ion mobility spectrometer consists of an ionization region where ions of analyte are generated, an ion shutter or gate to create a "pulse" of ions, a drift tube where different types of molecules are separated into discrete "packets," and a Faraday plate which collects the charge from individual ions.

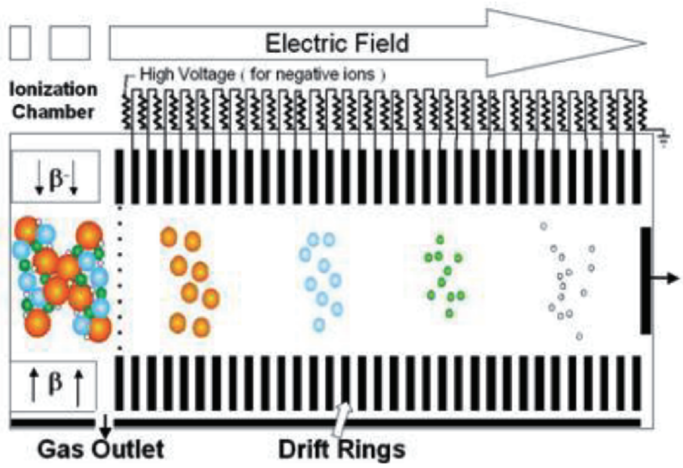


Figure 4. "Small" molecules migrate down the drift region faster than "big" molecules forming "packets" of ions of a single species.

Although this technique is similar to time of flight mass spectrometry, additional separation mechanisms are at work because the drift tube is usually operated at or near atmospheric pressure with a flow of drift gas (often air or nitrogen) from the detector end of the drift tube toward the ionization end. Hence the diffusion coefficient of the ion is also important. A more appropriate analogy of the process is atmospheric pressure ion viscometry. The equation in Fig. 5 relates the ion mobility (K) to the other operational parameters.

Relationship of Ion Mobility to Molecular Terms

Drift Velocity: $v_d = KE$ Mobility: $K = \frac{d}{t_d E}$

$$K = \frac{3}{16}\frac{e}{N}\sqrt{\frac{1}{m}+\frac{1}{M}}\sqrt{\frac{2\pi}{kT}}\left(\frac{1+\Delta}{\pi r^2 \Omega}\right)$$

E	Electric Field Strength	D	Drift Path Length
t_d	Drift Time	e	Unit Charge
m	Ion Mass (analyte)	M	Molecular Mass (drift gas)
N	Number Density	k	Boltzmann-Constant
T	Temperature	r	Minimum in Potential Curve
Ω	Collision Integral	Δ	Correction Term

Figure 5. Relationship of ion mobility to molecular terms.

The use of ion multipliers is problematic at pressures near atmospheric due to secondary electrons colliding with drift gas. IMS researchers have thus been forced to utilize direct electrometer measurements on the very small signals produced by the ion packets. Electrometer measurements use amplifiers with high input impendence to measure the voltage resulting from the flow of current through high-precision, high-value resistors (typically 10^{10} to 10^{12} **Ω**, see Fig. 6) or from the accumulation of charge on a small input capacitor.

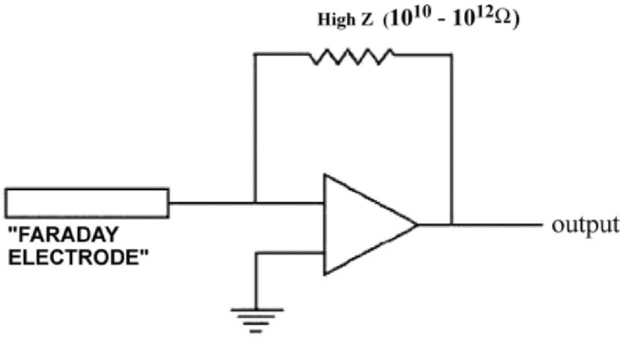


Figure 6. Conventional instruments use a high input impedance operational amplifier in a current to voltage circuit.

Limitations on the smallest detectable current arise from noise effects in the amplifying feedback resistor, the variable capacitance of the ion collector, the cables (inherent in the implementation of the discrete devices external to the operational amplifier), and from the amplifier itself. High-value feedback resistors are typically used to produce voltages from the small ion currents. For a $10^{12}\ \Omega$ feedback resistor, the thermal noise arising from thermally induced charge fluctuations amounts to about ± 1 femtoamp at room temperature. Additionally, the current commercially available operational amplifiers have a current noise of over 10 femtoamps at 10 KHZ bandwidths.

The other method for determination of charge is to measure the change stored on a capacitor. In conventional configurations, this approach suffers from the same noise fluctuations and detection limits as are obtained with a standard electrometer. Detection limits of several thousand ions have not yet been realized for portable ion mobility spectrometers which use this conventional technology. The CTIA approach, however, markedly reduces the detection limit.

2. MATERIALS AND METHODS

The CTIA employed for IMS applications was designed by Eugene Atlas and associates at Imager Laboratories (San Marcos, CA), and fabricated using 0.35 micron technology. Feedback capacitors were measured to be approximately 10 femtofarad (high sensitivity/small full well mode) and 990 femtofarad (for a total of 1,000 femtofarad in low sensitivity/large full well mode, see Fig. 7).

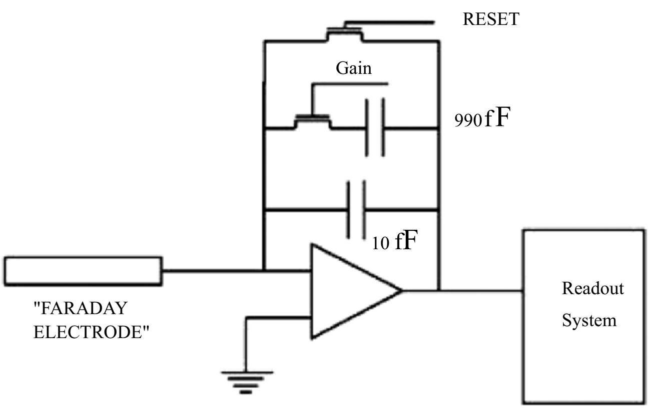


Figure 7. The CMOS-CTIA is fabricated using the 0.35 micron process as a high input impedance amplifier with 10 fF and switch selectable 990 fF feedback capacitors. Read noise using multiple nondestructive readouts is below three electrons.

This manuscript evaluates the application of CMOS-CTIA technology in miniature portable IMS systems designed for detection of explosives in the field. The IMS ionizer/drift tube/high voltage power supply and gate circuitry fit in a volume 2”×1.56”×4” with a drift tube bore of 0.46” (Fig. 8). Miniaturization of the IMS causes a loss in sensitivity over systems with large volume ionizers and larger, longer drift tubes. This is obviously an application requiring improvements in sensitivity, and this need has been met by the CMOS-CTIA technology.

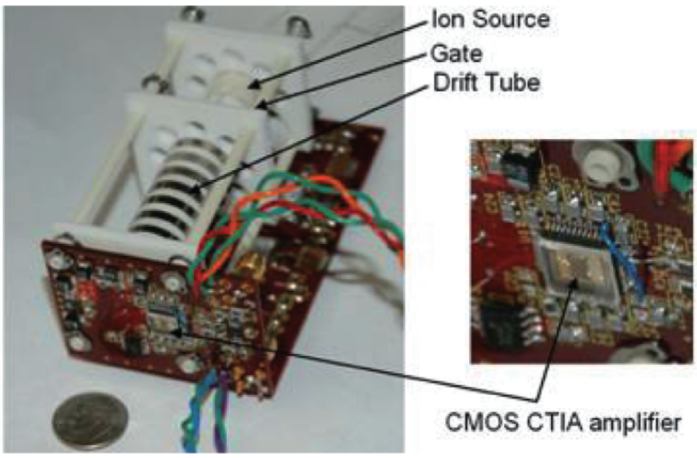


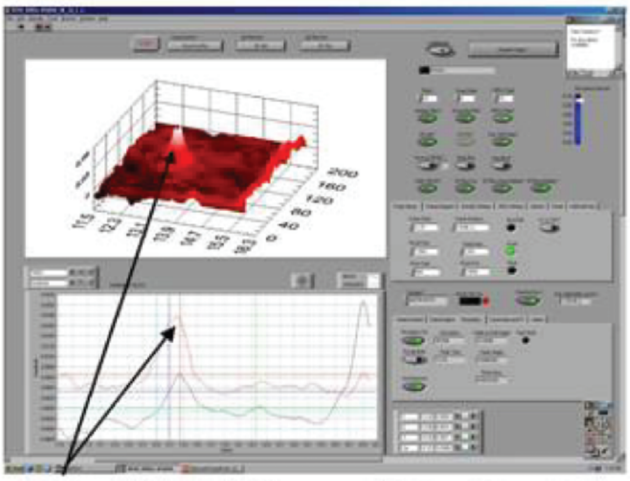
Figure 8. The miniature IMS system showing the motherboard containing the high voltage FET gating circuitry, divider string, and drift tube assembly. The detector and readout circuitry are mounted on a daughterboard at the detector end of the tube.

3. RESULTS AND DISCUSSION

Optimized single channel detectors have been developed with the ultimate goal of direct detection of single ions. Extremely high impedance CTIA amplifiers have been integrated with low capacitance collection elements to produce a detection system capable of direct measurement of charge with very high sensitivity. The small physical sizes of the collected elements and of the associated measurement circuitry resulted in a dramatic reduction in the input capacitance. Charge is accumulated on femtofarad-sized capacitors, whereas in a typical electrometer the input capacitance is tens of picofarads. The low relative capacitance produces a corresponding improvement in sensitivity. Read noise, using multiple nondestructive readouts [4,5], has been reduced to less than three electrons. Signals from a very low flux of ions can thus be reproducibly and quantitatively measured.

In addition to the high sensitivity, the ability to rapidly switch in additional feedback capacitance inherently gives the device a large dynamic range.

Detection sensitivity for explosives has been increased dramatically. Figure 9 shows a peak produced by 12.5 picogram of TNT. While the detection limit (signal 3× the rms of the noise) in a similar miniature drift system, using a conventional operational amplifier for current to voltage conversion, was calculated to be 10 nanograms, the detection limit in this case is below 0.9 picograms.



12.5pg TNT 96C, Filament, 1200 μs Pulse, B.C.

Figure 9. Showing the trace made by a 12.5 picogram sample of TNT. The detection limit is calculated to be approximately 0.9 pg. In the 3D trace, the left to right horizontal axis is drift time in milliseconds, and the front to rear horizontal axis is the scan number, with the sample being introduced at scan 82.

Unlike the operation of many focal plane arrays, integration times are very short (30-50 milliseconds), so dark current effects at room temperature are negligible. In fact, to evaluate operation in hostile desert environments, the detector was operated over a range of temperatures up to 80˚C. The device operated properly and the read noise increased to < 6 electrons.

This initial application of a CMOS-CTIA device designed for IMS indicates that such devices may play a major roll in improving the sensitivity of IMS systems, which could have a dramatic impact on detecting improvised explosive devices.

4. ACKNOWLEDGEMENTS

The authors would like to thank Eugene Atlas and his associates at Imager Laboratories (San Marcos, CA) for the design of the CTIA preamplifier die.

5. REFERENCES

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Jason Henning, whose personal best solving the rubik's cube is 70 sec, helped tremendously with preparation of the workshop and finalization of the proceedings. Thanks Jason!

The internet is not just for e-mail anymore. Internet phone was very popular with workshop participants as demonstrated by Peter Moore (top) and Javier Reyes, Gustavo Rahmer, Marco Bonati and Klaus Reif (bottom, left to right).