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The development of a micro-Faraday array for ion detection

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Abstract

A micro-Faraday array detector was evaluated for use as an ion detector for mass spectrometry. This charge-integrating detector was based upon the merging of technologies from the fields of CCDs and infrared (IR) multiplexers. Measurements were performed by exposing the detector to an Ar^+ ion beam of low flux. The array detector responds to both positive and negative charges and preliminary results indicate a detection limit of 100 ions. Current data indicate that the linear dynamic range of the device is over five orders of magnitude. The capability of the device to perform specialized charge read out modes could theoretically both lower the detection limit by a factor of seven and increase the linear dynamic range to nine orders of magnitude using non-destructive read outs. (Int J Mass Spectrom 215 (2002) 131–139) © 2002 Published by Elsevier Science B.V.

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1. Introduction

Over the last 20 years, focal plane array detectors have brought a revolution to ultraviolet, visible, and very near-infrared (IR) optical spectroscopies [1–4]. These devices have dramatically changed spectroscopic fields such as atomic emission, Raman, molecular fluorescence, astronomy, and many imaging applications by allowing simultaneous observation of the entire spectral region or selected sub-regions, providing increased sensitivity, increasing dynamic range, and greatly improving background correction.

Recently, an increasing number of near- and mid-IR focal plane arrays have become available [5]. The IR-sensitive materials are not, however, suitable for implementing the required readout circuitry. Today's IR focal plane arrays have been constructed by placing IR-active photon to charge conversion materials on top of silicon readout multiplexers. The multiplexers used in IR-detector arrays are capable of reading very low levels of charge, with extraordinarily low dark charges and low readout noise. A new generation of highly promising mass spectrometric detectors could be realized by employing a combination of technologies developed for visible CCDs and IR multiplexer arrays [6]. Such detectors could be implemented in configurations ranging from a single

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element suitable for quadrupole and time of flight instruments to linear arrays optimized for sector-based instruments and even *XY* arrays for imaging applications.

The workhorse of ion detectors employed in mass spectrometry for years has been the electron multiplier [7]. To a lesser extent, traditional Faraday cups and Faraday plates [8] are used in select applications. These detector technologies are based on concepts developed before WWII. Considerable research and resources that have been poured into modern ionization techniques such as thermospray, electrospray, MALDI, and more recently, nanospray [9–11]. These new ionization sources have placed new demands on detection capabilities, including an increased range of mass-to-charge-ratios (m/z), efficient detection of high m/z compounds, the ability to detect very few ions of a specified m/z in a matrix of many other m/z ions, and the ability to quantify the results over many orders of magnitude. Whereas research is being conducted to address each of these detector-dependent figures-of-merit separately, the micro-Faraday array detector described here has the potential to provide improvements in all of these areas.

Applications that require high throughput, constant gain, and high precision, such as isotope ratio mass spectrometry, are well suited for the current configuration of the technology available in the micro-Faraday array detector. Isotope ratio studies [12,13] often require a precision of lower than 0.001% R.S.D. This level of precision cannot be achieved with electron multipliers in analog mode. While some modern instruments now utilize electron multipliers in isotope ratio studies [14], precision is sacrificed to gain a lower detection limit. The problem with using electron multipliers as detectors in sector instruments performing isotope ratio studies is that, because of several factors, the stability of the detector decreases. The performance of the electron multiplier degrades over time as ions both coat and sputter away the ion to electron conversion material. These detectors can be mass dependent, yielding different gains across the mass spectrum. This changing detector performance also challenges the ion counting mode, as the discriminator level must be continuously reset. Because the performance of the electron multiplier can rapidly and drastically change, their ability to perform high precision measurements is problematic and sometimes impossible.

To obtain the desired high precision, Faraday plates and Faraday cups are often employed. Although high precision measurements can be made with these detectors, they are relatively insensitive and cause detection limits to be high. The current state-of-the-art detection limit using a Faraday cup is around 6000 ions per second in the most sophisticated and expensive ion detection schemes [15], which corresponds to 1 fA of current. Highly sophisticated electronics are required to measure this small current with any certainty. Electrometers use amplifiers with extremely high input impedance to measure the voltage resulting from the flow of current through high precision high-value resistors (typically $10^{12}\ \Omega$ or more) or from the accumulation of charge on a small input capacitor. Limitations on the smallest detectable current by such methods arise from noise effects in the input resistor and from the variable capacitance of the ion collector and cables inherent in the device. For a $10^{12}\ \Omega$ input resistor, the noise arising from thermally induced charge fluctuations amounts to about ± 1 fA at room temperature.

The noise in the rate of charge measurements arises from voltage fluctuations in the amplifier of the electrometer. These fluctuations cause relatively poor detection limits. Low detection limits are desirable for applications where either the sample is limited (extraterrestrial studies [16,17]) or when it is advantageous to study the smallest amounts of the sample possible (nuclear studies [18,19]).

Initial results are presented for the case of a multiplexer developed for a linear IR-array to read out flat, finger-shaped micro-Faraday “cup”. Future directions for using optimized multiplexers and CCDs are also considered. This detector technology holds promise to provide detectors capable of extraordinarily linear operation from single to hundreds of millions of ions per second.

Table 1
Performance of the CTIA as evaluated at the Steward Observatory at 4 K

Parameter	CTIA performance
Noise	27 e^-
Transimpedance	4.4 μV/e^-
Detector offset (no input charge)	2 μV
Power dissipation	32 μW
Parts per wafer	82

The normal operation of the multiplexer for mass spectrometry use is at 233 K.

2. Device description

The device consisted of gold, finger-shaped Faraday electrodes wire bonded to a capacitative transimpedance amplifier (CTIA) developed by Eric Young (Steward Observatory). This particular amplifier was originally constructed for use as a low-noise IR detector for astronomy. The performance characteristics of the CTIA evaluated at 4 K are shown in Table 1. In these investigations, exploring the device capability as a mass detector, the device was operated on a Peltier cooler at a temperature of 233 K. The Faraday-fingers, described below, serve as the charge collection input to an amplifier connected to the low-noise multiplexer charge read out. There is 1 A per charge collection element. The feedback loop of the amplifier contains a 36 fF capacitor used to accumulate and integrate the input charge. The measured charge is output as a voltage by the multiplexer. The predicted performance of the output for this device is 4.4 μV per input charge, and it is able to integrate both positive and negative charges. This arrangement is shown in Fig. 1.

The collection elements were produced by standard lithographic techniques and can be made extremely small (down to 10 μm), and closely spaced (10 μm) in large numbers. The small physical size of the collection elements and associated measurement circuitry results in dramatically reduced input capacitance and allows the accumulation of charge on femptofarad feedback capacitors rather than on the tens-of-picofarad capacitors typical of an electrometer system. Lowered capacitance produces a corresponding improvement in sensitivity. The signal required to overcome the limiting amplifier noise drops from thousands of electrons per second to only a relatively few ions in a

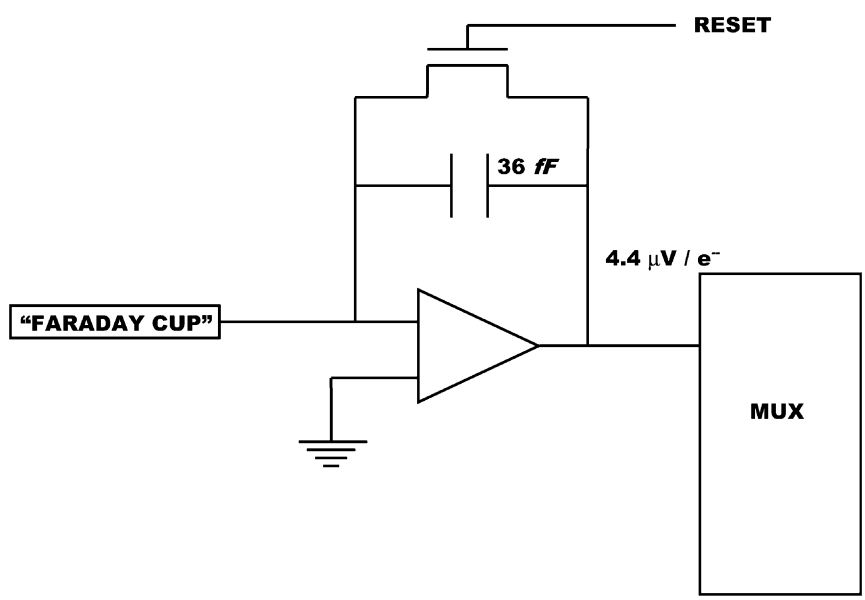

Fig. 1. Effective circuit of an individual detector element.

given integration period. The array detector device described herein does not measure current, but rather measures charge, so that a few ions can be detected over a long integration period. With this arrangement, signals from a very low flux of ions can, therefore, be reproducibly and quantitatively measured.

The detector fingers were divided into three sizes to allow for evaluation of the effect of the electrode input capacitance on read out performance. The top ends of each element are wire-bound to the CTIA. The CTIA device is a 32 pixel-wide array detector on 175 μm centers. Detector fingers are bonded to multiplexer pixel positions 0–25. The detection elements at pixel positions 26 through 31 remained unbonded. An image of the individual detector elements is shown in Fig. 2. Each finger is 145 μm wide and is separated from the next finger by 10 μm gaps and a 10 μm guard electrode. The electrode fingers are made from gold 7 μm thick over a 1 μm buffer layer of titanium deposited on a silica-glass substrate. Spectral Instruments (Tucson, AZ) constructed the read out electronics and provided the control software.

Multiple read out modes are available with this particular multiplexer device. The background charge can be separately determined and subtracted from measurements, as in normal CCD operation. To do this, the charge is reset, after which a read operation is performed to determine the “background” charge, an exposure is initiated, and a second read operation is performed to determine the “ion charge”. The entire cycle can be repeated. The device can also be read in a manner similar to that of charge-injection devices

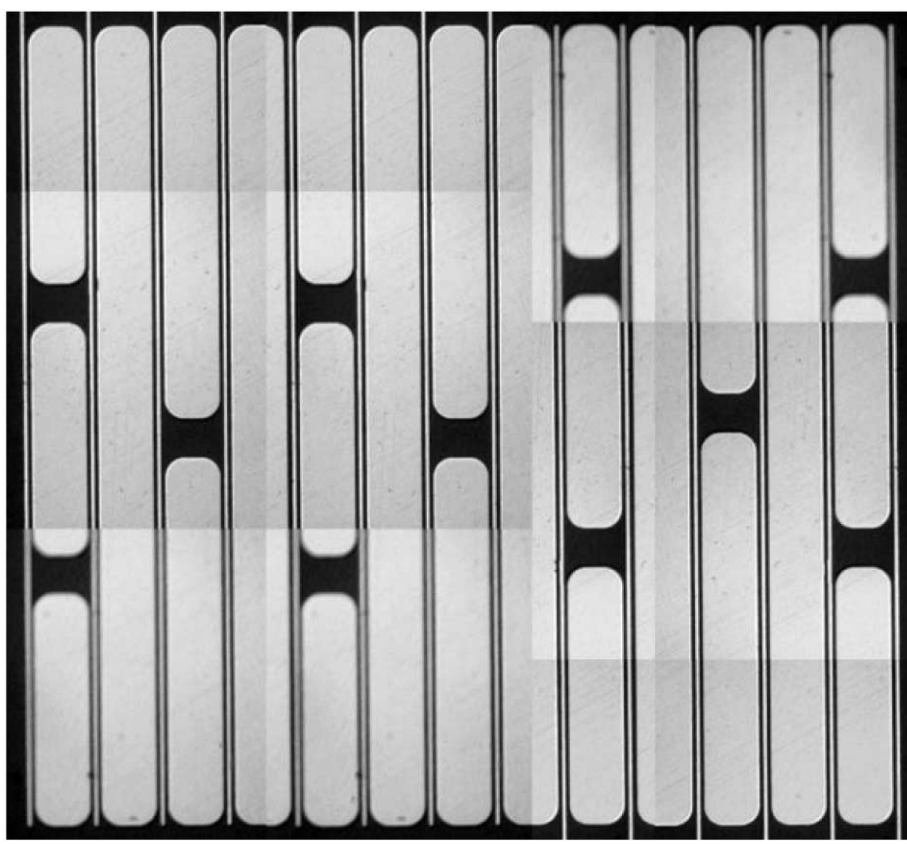

Fig. 2. Visual image of individual detector elements. Pixels are 5, 2.45 and 1.60 mm long and 145 μm wide, with 10 μm spacing. There is also a 10 μm guard electrode present between each detector element.

(CIDs) [20,21]. Using the technique developed by Denton of "random access integration" (RAI) the charge integration time between destructive read outs is varied under computer control so that detector elements receiving low ion fluxes are integrated for a longer period of time. This, in effect, optimizes the integration time for each individual detector element. The ability to perform non-destructive readouts has allowed CIDs used in optical emission spectroscopy to be operated with a linear dynamic range exceeding ten orders of magnitude.

3. Experimental setup

Characterization of this ion detector was conducted according to the experimental setup described below and as illustrated in Fig. 3. The ion source used in the characterization studies was an ion gun (Vacuum Generators AR6; power supply, Vacuum Generators 400A). Ar^+ ions were directed onto a single micro-Faraday finger detector element using a 100 μm pinhole in a stainless steel mask (Edmund Industrial Optics). The mask was held at ground potential. The energy of the Ar^+ ions used was 2000 eV before the pinhole. Additional masks and baffles all held at ground were also introduced into the vacuum chamber between the ion gun and detector to reduce stray signal and ion beams. The 100 μm pinhole mask was attached to an XYZ translation stage for mobility. The ion gun was mounted on a bellows fitted with a kinematic-type micrometer device to allow redirection of the beam onto the pinhole as the mask was moved across the detector array. With this arrangement, the ion beam can be isolated to any individual pixel of the detector. The gun, operated at its minimum settings, produced an excessive flux, so the ion beam was defocused, alleviating the need to constantly

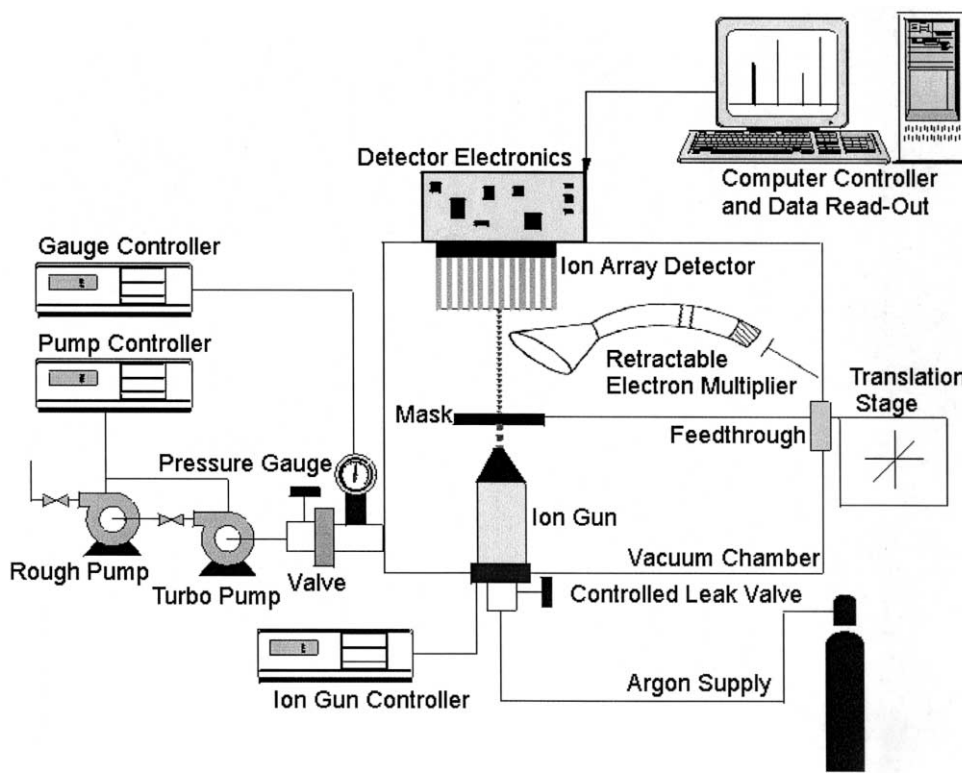

Fig. 3. Schematic of the experimental setup used for preliminary characterization of the detector.

redirect the beam as the pinhole was moved over a small range. The ion beam flux was measured by placing an electron multiplier between the mask and the array detector on a retractable stage for insertion and removal without breaking the vacuum.

4. Results

4.1. Detector array response

The camera's first exposure showed an image in which every pixel of the multiplexer was saturated. Even the pixels above detector element 25, which were not connected to the multiplexer, showed the saturation response. Because the pinhole only allowed exposure of one pixel to a high flux of ions, the device was not working as expected. The problem was that the silicon device was responding to light from many sources, including the filament of the pressure gauge, the ion gun filament, and the view ports in the vacuum chamber.

Measures were taken to eliminate the response caused by light on the detector. The multiplexer chip was covered with an opaque epoxy, baffles were introduced into the chamber to reduce the exposure to light from the ion gun filament, opaque caps were placed on all view ports into the vacuum chamber, and the Bayard–Alpert pressure gauge was turned off while exposures were taken.

After minimization of the detector response to light, the reset level voltage was adjusted so the background-subtracted count was close to an output signal of 0 ADUs for a background exposure of 1 s. The reset level is ∼500 ADUs, and the background charge subtracted from the ion charge level is between 5–20 ADUs. An ADU is an arbitrary detector unit or a measure of output intensity when the system gain is unknown. The detector showed the ability to respond to argon ions (Ar^+) as is shown in Fig. 4. When electrons from a filament were allowed onto a detector element, a negative signal was observed with respect to the reset level, just as the positive ions produced a positive voltage response. These observations show that the detector is charge sensitive and

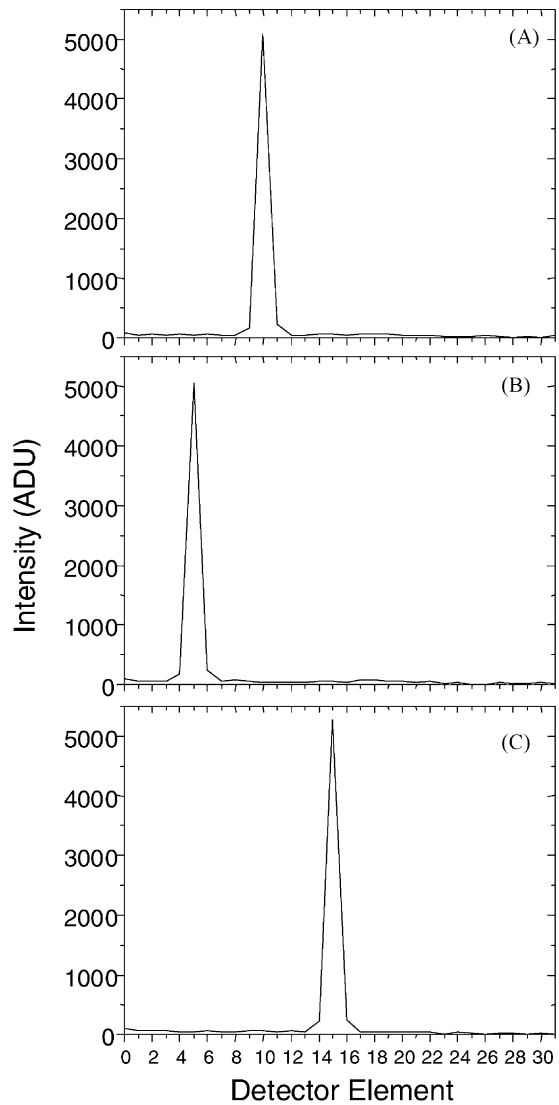

Fig. 4. Detection response to the 100-μm Ar^+ ion beam on the three different sizes of detector elements. (A) Full-length pixel, (B) half-length pixel, (C) third-length pixel.

can simultaneously detect both positive and negative ions on separate detection elements in the same array.

4.2. Effect of input capacitance

To evaluate the effect of Faraday cup input capacitance on the multiplexer performance, three sizes of

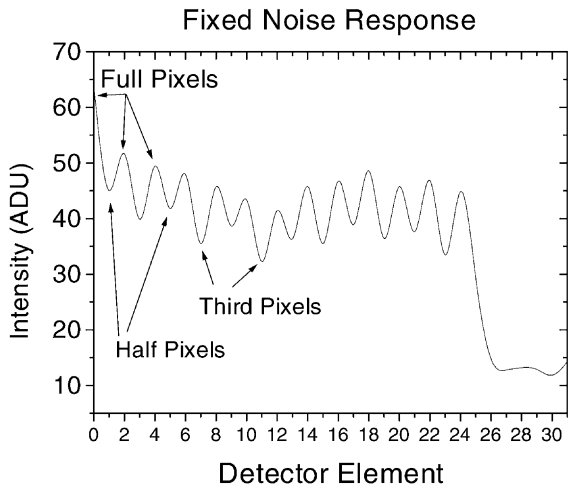

Fig. 5. Fixed pattern response of the array due to different capacitances of the detector elements (integration of a "background" exposure for 1 s).

fingers were fabricated, as shown in Fig. 2. A repeating pattern of full-length (5 mm), half-length (2.45 mm), full-length, and third-length elements (1.60 mm) was evaluated. The result of the different input capacitances is shown in Fig. 5. Fig. 5 is the averaged spectrum of 10 background exposures of 1 s each, followed by a voltage reset.

Fig. 5 shows that higher input capacitance results in higher apparent background signal. The difference is more pronounced between the full-length detector elements and the half- or third-length elements and is less pronounced between the half-length elements and third-length elements. This type of detector response is termed "fixed pattern response"; it is reproducible and is not a true noise source. In this case, inhomogeneity was purposely introduced to determine the effect of finger capacitance. The fixed pattern response can be corrected by subtraction in a manner similar to background charge correction. A background exposure is subtracted from the ion exposures to result in a theoretically flat-field-corrected image. Variations in the background thereafter must be due to noise.

The response of the array detector with ion illumination on full-length (A), half-length (B), and third-length (C) detector elements is shown in Fig. 4. Varying the electrode capacitance and size by up to a factor of three did not seem to have any detrimental effects.

4.3. Detector performance

A plot of camera signal vs. ion gun emission current, at a constant integration time, was linear over five orders of magnitude without incorporating RAI. The upper limit is determined by the full-well capacity of the device. The linear range could be increased by changing the integration time to accommodate both large and small ion fluxes. We anticipate that linear response can be achieved across more than nine orders of magnitude by using RAI with integration periods of 1 ms and 10 s. Crosstalk between pixels was negligible at ion counts nearly equal to the full-well capacity. Crosstalk is a phenomenon where the read out of adjacent pixels is affected by charge accumulated on a neighboring pixel; it is caused by the interaction of electronic components in the integrated circuit.

The detection limit of the device was determined from the mean–variance data plot [22] shown in Fig. 6. Repeated cycles consisting of device reset, background signal measurement, and ion signal measurement were performed. Non-destructive readout

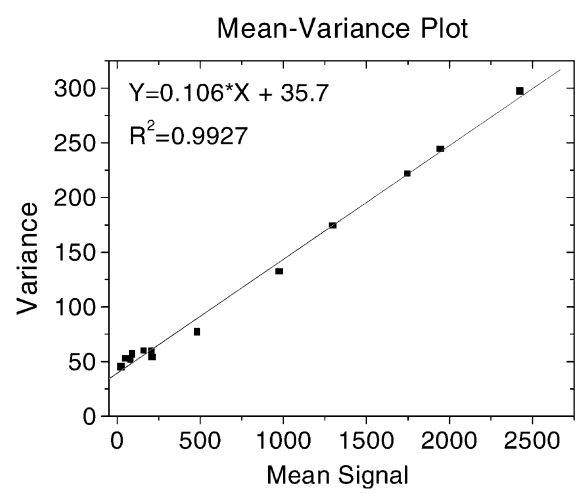

Fig. 6. Mean–variance plot for the micro-Faraday finger detector.

(NDRO) of the signal was not used in this detection limit study. The read noise of the detector, which includes the CTIA, read out electronics, and support circuitry, was found to be 56 electrons by the mean–variance method [22] for the ion-background data. The read noise for a single reading was thus 56/1.414 electrons, but in practice, a subtraction must be performed, resulting in the 56 electron value and a detection limit of approximately 110 ions at a 2σ confidence interval.

Preliminary data indicate that the detection limit of the micro-Faraday finger array can be reduced by using the NDRO of the device. In this mode, after collection of charge, the charge is repeatedly converted to a voltage without affecting the accumulated charge from the ion signal. This allows ensemble averaging to reduce the mean square read noise. Initial studies indicated that read noise could be reduced by a factor of at least seven, to give a practical 2σ detection limit of 16 ions. Without using NDROs, the read noise magnitude will restrict the detection limit.

5. Discussion

5.1. Current work

The micro-Faraday array detector described herein has several advantages over modern state-of-the-art electrometers used on magnetic sector instruments. First, it must be emphasized that the array detector described here is an integrating device. Second, the micro-Faraday array detector is capable of simultaneous determinations without scanning, giving a multiplex advantage. Third, the small physical size of the array elements can lead to superior m/z resolution.

The detection limits of electrometers are fixed by their sensitivities to ion currents arriving at the detector, whereas the micro-Faraday finger array signals can be gated to integrate small fluxes over the period of time necessary to accumulate a detectable charge. The micro-Faraday detector is a charge-integrating device and is able without using NDROs to measure the charge from 100 ions, whether collected over 1 ms or over 10 s.

Detecting ions with an integrating multichannel device will allow an entire spectrum to be acquired without mass analyzer scanning or detector movement. Similarly, simultaneous detection and high dynamic range measurements will reduce sample size requirements necessary to complete an entire mass spectrum. This reduction should allow for a complete mass spectrum to be taken on sample sizes orders of magnitude less than that of a single channel instrument with the same detection limit.

Mass resolution will be limited by crosstalk between array elements. The present array displayed negligible crosstalk between elements with just-below-full-well charge on one element and nearly zero charge on the adjacent element. This may or may not become an issue as attempts are made to improve mass resolution in the second-generation array detector, which has smaller Faraday elements.

Isotope ratio precision will be greatly improved by enabling RAI. The detector dynamic range is expected to exceed nine orders of magnitude, assuming crosstalk can be controlled when it appears.

5.2. Future work

A second-generation detector with 1024 elements is being constructed. This device will employ a different charge-to-voltage read out than the multiplexer used on the first-generation device.

Faraday element geometry will be explored to determine the optimum shape and collection efficiency of the detector element. To minimize secondary electrons, which may escape from the finger electrodes, the geometry of the electrodes will be channel shaped and possibly recessed like a cup or trap. The goal is to collect all secondary ions and electrons without allowing any to escape. If charge escapes from the collector electrodes in the form of secondary electrons or secondary ions, the measurement efficiency and accuracy will be reduced. By retaining the secondary species produced, detector efficiency could increase. Use of electrode coatings

will also be explored to minimize secondary ion emission.

Because the detector is based upon measuring charge, and not measuring kinetic energy, as is the case with electron multipliers, ions with high mass-to-charge ratios should be detected without degradation of efficiency. Because the kinetic energy of high-mass ions is reduced, the detection efficiency of the electron multiplier falls off dramatically as the mass-to-charge ratio becomes very large (over 1 million). The charge-measuring detector described herein should not have this problem.

6. Conclusions

The preliminary characterization of the micro-Faraday array detector shows promising results for use in mass spectrometry. The detector boasts a low detection limit of around 100 ions during an integration period using destructive read outs, and initial studies demonstrate that by using NDROs, the detection limit is reduced by a factor of seven. The device responds to both positive and negative charges without requiring detector modification. Additional experiments to determine the ion detection efficiency, mass dependence, and charge-state dependence are currently underway to fully characterize the detector performance.

Acknowledgements

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