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Mass spectrum measurement using a one-dimensional focal plane detector

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Abstract

The objective of a focal plane detector (FPD) is to measure as accurately as possible the spectrum incident on it and therefore the central problem to be resolved is to relate the measured spectrum to the incident spectrum. This is a non-trivial task when the FPD is preceded by a microchannel plate electron multiplier (MCP) or other distorting element but an understanding of the characteristics can help to harness the power of the array. The measurement process for a one-dimensional array of discrete counters is analyzed and where the measured spectrum depends linearly on the incident spectrum, the measurement process has been modeled using simple matrix algebra. This model has been exploited in a number of ways outlined in this paper including the correction of non-uniformity and its extension to the non-linear region is under consideration. (Int J Mass Spectrom 215 (2002) 195–209) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mass spectrometry; Detector; Uniformity; Ion detector; Electron detector; Deconvolution

1. Introduction

Over the last 30 years or so since the development of microchannel plate electron multipliers (MCPs), reliable electronics and integrated circuits, mass spectrum measurement using arrays of detectors has become increasingly attractive since they can enable the parallel measurement of a much larger fraction of a mass spectrum than a single detector. This much greater measurement efficiency has been the driving force behind the development of detector arrays but alongside this development is the need to develop an understanding of their performance. At the present time it is possible to incorporate all the pulse sensing electronics, data storage, control logic and bus interface on a single silicon ship for an array of better than 25 μm spatial resolution. This is not just an achievement of scale. There are also significant performance advantages. It will be seen that a very important feature of such integration is that the detector input capacitance is very low. This is very difficult to achieve except by integration. A non-integrated detector input anode requires a connection to the sensor circuitry, and the connection itself has a capacitance typically several times greater than that of the anode. This may inhibit access to the region of stable operation (RSO).

Dispersion in space is only one of the techniques used in mass spectrometry but it is dominant in electron energy, UV and X-ray measurement and there is some overlap in development of focal plane detectors in these areas, especially in electron energy spectroscopy. This overlap will ensure the continuing drive

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in the development of detector arrays to the benefit of mass spectrometry. In this paper the performance issues of a one-dimensional array of ion counters will be considered and it will be shown that operating conditions can be achieved which are close to ideal when detector input anodes, along with sensing electronics are integrated on a single silicon chip.

A schematic of a spatially dispersive mass spectrometer with a single slit detector and a detector array is shown in Fig. 1 [1,2]. By replacing the single slit detector with an array of detectors a much larger fraction of the spectrum can be measured. The example of Fig. 1(b) shows a 'discrete detector' array, i.e., an array of discrete or independent detectors which enables truly parallel ion detection. An ion falling on the MCP initiates a pulse of electrons from a small area of the MCP exit which falls on the anodes and is detected (an event). Since the early 1970s, the development of such detectors has been enabled by the advent of the MCP and the development has been driven by the need for high efficiency detectors in UV spectroscopy [3], X-ray spectroscopy [4,5], electron energy spectroscopy [6–8], mass spectrometry [9–13]. The need has been felt particularly in space-borne experiments. There are many types of detector array which have been discussed and compared elsewhere [2] and some are included in the present volume.

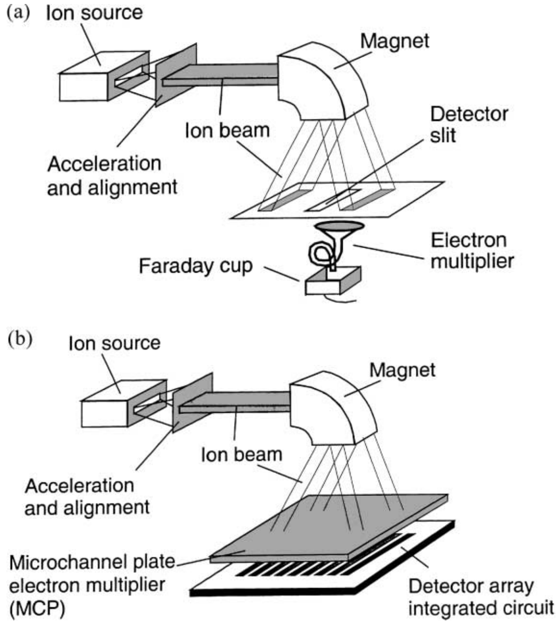

Fig. 1. Simplified schematic of a magnetic sector mass spectrometer incorporating (a) a single slit detector, (b) a discrete detector array integrated circuit (array IC). The slit of the single detector is replaced by a one-dimensional array of metal strips (anodes) each of which has approximately the same dimensions as the single slit. Each anode collects charge from the MCP output and forms the input to an integrated detector circuit.

In addition to the development of an integrated detector array, an algorithm for the correction of non-uniformity has been developed [14]. This is vital since non-uniformity is always present in arrays of detectors. In its simple form this algorithm gives an excellent correction when the incident ion intensity does not vary sharply in the direction of dispersion, i.e., when incident peaks cover several anodes. For rapidly varying intensities other deconvolution methods are currently under study to overcome the otherwise intractable problems.

The following issues are considered in this paper:

(a) The objectives of mass spectrum measurements.
(b) The signals measured.
(c) The measurement.
(d) The ideal measurement conditions.
(e) Data processing.

2. Measurement of mass spectra

2.1. Objectives of the measurement

The detector system will be regarded as everything after the focal plane of the mass spectrometer, i.e., from the front face of the MCP. To the detector, a random or systematic fluctuation in the incident spectrum is not noise, it is signal. It is the job of the instrument designer and the user to provide the optimum spectrum in the focal plane and it is the job of the detector to measure it. However, all measurements are imperfect, and in order to relate or transform *measured* to *incident* spectra it is useful to understand the origins of the imperfections. Throughout this paper the measured spectrum will be distinguished from the incident spectrum. A perfect detector would give the incident spectrum. The measured spectrum is imperfect.

A prevalent idea seems to be that detector arrays should approach the ideal of a 'direct sampling' array (e.g., a CCD for photons) in which a single ion should be seen by a single detector so that the array *samples* the peak profile directly (i.e., without a preceding MCP). Hence, if the sampling frequency were sufficiently high then the peak could be recovered accurately. However, mass spectrum peaks are often narrow and from sampling theory one should sample at twice the maximum frequency component of the incident peak which may be technically very demanding for a narrow beam since a spatial resolution better than the detector spacing or the MCP channel diameter may be required.

Although a spectrum could be scanned across an array, each detector recording a convolution of the incident spectrum and its own detector function, the efficiency advantage of parallel detection would be compromised and therefore the spectrum is usually static over the array. Inevitably, arrays of detectors are frequently viewed as simply a collection of single detectors. However, to take this view is to disregard the characteristics on which some of the power of the array rests. The measured spectrum is not a convolution of the incident spectrum with a single detector in the normal sense nor is it a straightforward sampling of the incident spectrum but a more complex object incorporating the non-uniformities of all the detectors and the MCP as well as inaccuracies in the MCP mounting. Behind this complexity there is a simplicity which can be exploited to advantage if the detector array function is properly understood, and the 'problems' of multiple counting of a single ion by more than one detector can be turned to advantage. For example, accurate ion intensities can be measured for isotope ratio experiments even in the presence of detector non-uniformity if the 'region of stable operation' can be accessed.

From the point of view of the detector, it should ideally do no more nor less than give the incident spectrum. However, this is a tall order since it implies very high resolving power and dynamic range. For a highly resolved incident spectrum, a discrete detector array cannot measure peak profiles due to the MCP channel size, the array spatial resolution and the width of the MCP output pulse. Similarly the MCP output gain distribution depends on the local incident intensity and may be differentially shifted for peaks of different intensity. Therefore, it is essential to recognize these problems and overcome them. A single slit detector can approach the ideal goal closely except in one respect, namely at the expense of an enormous loss of efficiency.

It is often not the peak profiles which are needed by a mass spectrometer user. For example, it may be that the identities of mass peaks are known and only the accurate ratios of the peak intensities are needed as is the case in some isotope ratio measurements. On the other hand, a user may wish to know both the positions and intensities of peaks to infer the molecules present in the ion source but again, the exact profile of the peak is not required since it only reflects the properties of the source slit and the ion optics, etc. In many such applications it may be unnecessarily demanding to insist that we measure the incident peak profiles exactly. The peak profiles are of no great interest unless they give information on partially resolved peaks. However, the question of whether the measured peak heights or the peak areas give the best measure of the relative peak intensities arises and this is not immediately obvious for a detector array. In spite of the latter comments, it is very important to develop detector arrays which can measure profiles accurately since they are needed for example when a mass spectrometer is used for ion energy measurement. Also identical arrays are needed in electron energy spectroscopy where the profiles may contain a great deal of information.

When a spectrum is recorded by scanning it across a single slit, the resolving power of the detector can be simply varied by varying the slit width, there is no problem of non-uniformity, and non-linearity of the detector response can be simply corrected (up to a point) by calibration. With a detector array on the other hand, the efficiency is very much greater, but there is no slit, there is always non-uniformity, and non-linearity is more difficult to correct since it is largely a local MCP phenomenon. Non-linearity may also result from the pulse-pair resolution of the detector circuitry but the maximum count rate per detector of the detector array considered here is at least 100 times better than the MCP and is ignored for the present.

2.2. Signals measured

The problem of non-uniformity complicates the measurement of mass spectra using an array of detectors. However, even with a perfectly uniform array neither the relative heights nor the relative areas of two peaks will give the correct relative intensities of the two peaks unless the conditions are correct. For example, a peak of constant height stepped across an array may show a height variation dependent on its position directly above or between two detector anodes [15]. Along with other performance issues this can be best understood in terms of the distribution of voltage pulse heights induced on the detector anodes by the MCP pulses which will be referred to as the pulse height distribution (PHD). This is after all what is being measured by the detector circuitry.

An incident ion spectrum is not measured directly. Each ion falls on the MCP, or more commonly a stack of two MCPs, and produces a shower of typically about 10^6 electrons (an event) which is registered by the detector array. A measured peak is an accumulation of many single events. A single event may be recorded by one or more detectors depending on several factors including the gain of the MCP and the discrimination levels of the detectors [16].

2.2.1. The MCP

A MCP pulse is output in typically around 1 ns. The electrons fall on detector anodes and induce voltage pulses whose magnitudes are determined by the gain and the profile of the electron pulse which falls on the anodes as well as the anode capacitance. A schematic of a MCP is shown in Fig. 2(a). It consists of a plate typically of thickness 0.5 mm and composed of many small tubes (typically straight tubes of diameter about 10 μm) each of which is at an angle of around 10° to the vertical and has an internal coating of a low work function material. A voltage (typically ≤1 kV) is applied between the metallised front and rear surfaces of the MCP.

An ion entering a MCP channel causes the release of secondary electrons which are accelerated down the channel, each electron releasing further electrons resulting in a pulse of G (gain) electrons being emitted at the MCP exit within about 1 ns. The firing of a MCP channel is analogous to the sudden discharge of a capacitor and the capacitor must be recharged by current in the channel wall. Typically the recharge time is about 10^{-2} s but can vary greatly depending on the type and condition of the MCP.

Fig. 2(b) shows that the electron pulse initiated by a single event can become wide on reaching the

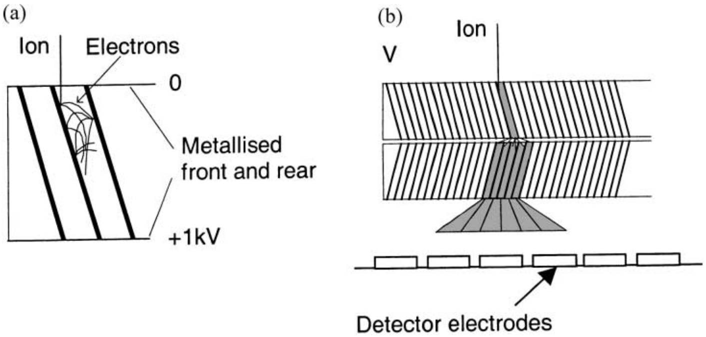

Fig. 2. Multiplication of electrons by an MCP. (a) A particle entering a MCP channel emits one or more electrons which are accelerated along the channel to give further collisions and multiplication of the signal; (b) a single event leads to a wide electron pulse at the MCP exit with further spreading on travelling to the array. The channels are arranged to slope in opposite directions to reduce ion feedback and optimize the incident ion detection efficiency.

array although the profile is not known precisely. A number of channels of the second MCP are activated by one channel of the first MCP and it has been observed that the electron pulse emerging from the second MCP can have a diameter of >100 μm [16]. Much work has been carried out on the performance of single MCPs and MCP stacks operated under various conditions, e.g., [16–25]. There is greater spreading for a larger gain MCP pulse as space charge repulsion (mutual electrostatic repulsion of the electrons) is greater. Also the greater the separation between the MCP output and the detector anodes, the greater the spreading of the electron pulse. An attractive field will help to confine the electrons and give less spreading. A voltage pulse on a given anode will be capacitatively coupled to adjacent anodes thus spreading the effect of the pulse somewhat.

2.2.2. *Pulse gain distribution for a single MCP plate*

The gain distribution of a single MCP plate is typically a quasi-exponential decay (average gain about 10^4) as shown in Fig. 3. As the MCP supply voltage is increased the distribution shifts to higher gains but the effect known as 'ion feedback' limits the maximum operating voltage. At high supply voltages (typically ≈ 1 kV) ions formed from residual gas are accelerated back up a MCP channel, collide with the channel wall and may initiate secondary electron pulses. This degrades the performance and may lead to a continuous discharge.

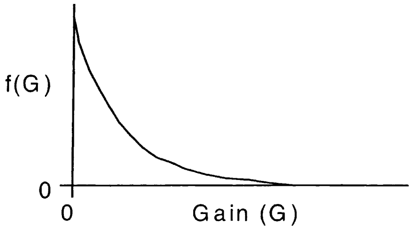

Fig. 3. Schematic of the MCP pulse gain distribution in arbitrary units ($f(G)$) of a single MCP plate. The gain shows a quasi-exponential fall-off for a single plate.

2.2.3. *Pulse gain distribution for a double MCP stack*

If two MCPs are arranged as in Fig. 2(b), ions formed from residual gas in the second MCP are stopped at the interface between the MCPs before they acquire sufficient energy to release secondary electrons thus reducing ion feedback effects. Each incident ion of the mass spectrum initiates an electron pulse from the first MCP plate and the input of each channel of the second MCP receives sufficient electrons to drive it to saturation. When the channel is saturated its output is independent of the initiating event and the gain distribution is peaked (Fig. 4). If the detector anode capacitances are sufficiently low then the voltage PHDs induced on detector anodes will lie above the noise level (Fig. 5(a)) and it can be seen that in this case all events could be detected if the discrimination level (DL) were placed below the PHD. This is the *region of stable operation* [2] discussed in the next section. Thus, the measured noise level would be minimal, inherent in the random arrival of the ions, and purely random. These are the ideal conditions for isotope ratio experiments. There would be no region of stable operation (explained in the next section) if the incident beam were too wide or if the incident intensity were too high.

In practice the PHD has been observed to extend to lower voltages than the ideal peak shown in Fig. 4 as the incident ion intensity increases [2,24] but this has been omitted from the figure to simplify the

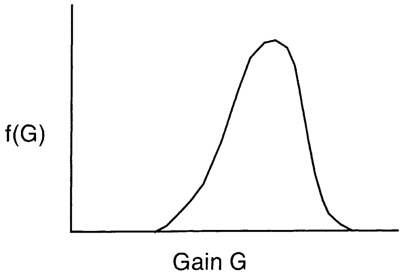

Fig. 4. An idealized schematic of the gain distribution ($f(G)$) of a stack of two MCP plates. Typically the FWHM of the gain distribution is about ±50% of the modal gain. If the MCP supply voltage is reduced then the peak moves to lower gain and the profile eventually changes to a quasi-exponential fall-off.

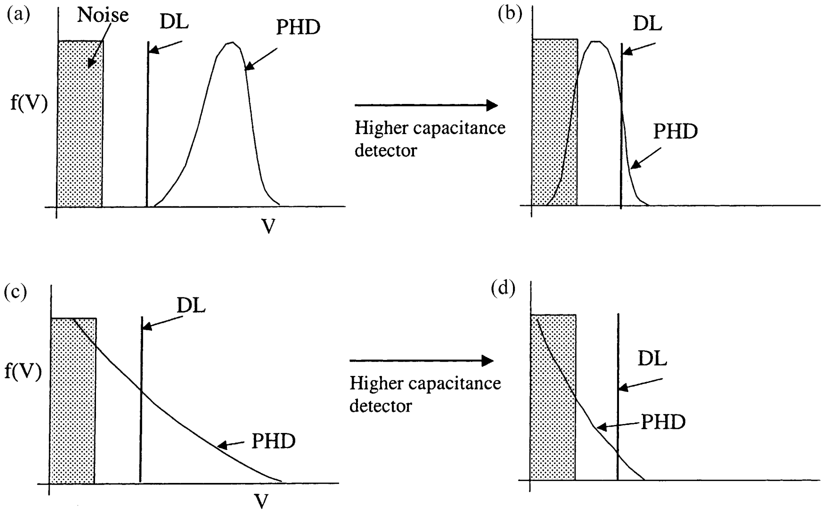

Fig. 5. Idealized schematics of the pulse height distributions on the detector anodes at the center of (a) and (b) a narrow incident beam; (c) and (d) a wide incident beam.

discussion. At sufficiently low incident intensities, Fig. 4 is a reasonable approximation for a MCP in good condition.

2.3. Measurement

Most ions hitting the inside of a MCP channel initiate an electron pulse and there is a distribution of gains for many such pulses. Each MCP pulse falls on the detector anodes and induces voltages whose magnitude diminishes the more remote the anode is from the pulse center. Hence, on each anode there is a PHD and it is these pulses which are being measured by the detector circuitry. If the height of a given voltage pulse is above the DL of a detector then the detector registers a single count, otherwise no count is registered. All detectors are set to have the same DL although in practice there is always a degree of non-uniformity due to manufacturing tolerances.

Schematic representations of PHDs on the detector at the center of an incident ion beam are shown for a number of situations in Fig. 5. The following cases are illustrated

- (a) and (b) refer to a narrow incident beam;
- (c) and (d) refer to a wide incident beam;
- (a) and (c) show the PHD for a low anode capacitance;
- (b) and (d) show that if the capacitance of a detector anode is increased the PHD shifts to lower values.

It can be seen that in cases (b), (c) and (d) the DL cannot be placed completely below the PHD without introducing noise into the measurement. However, in case (a) this is possible and hence for small fluctuations of the operating conditions the measured signal on the central detector will not be affected. The ideal of case (a) cannot be achieved for a wide incident beam since the PHD on the anode at the center of a peak includes the effect of pulses from remote events and hence extends to low values. Case (a) corresponds to the ideal of operation in the RSO and it should be noted that

- case (a) is achievable only for very low anode capacitance or high multiplier gain. However, if a very low capacitance can be achieved the central anode would measure the total incident intensity accurately even in the presence of non-uniformity, i.e., the peak height and not the integral of the measured peak profile is the correct measure of the peak intensity. Note that as the MCP performance degrades with age and usage, it may remain possible to make good measurements as long as the RSO can be accessed;

- at high local incident particle fluxes the PHD shifts to lower values [23] since the MCP cannot increase its output indefinitely and its gain distribution shifts to lower values, i.e., the MCP response becomes non-linear. For large shifts case (a) will not be achievable. If the pulse pair resolution of the array circuitry is not adequate at higher intensities this results in detector non-linearity but is not included in the present discussion since its pulse pair resolution is better than 10^{-6} s.
- non-uniformity always influences the edges of measured peaks.

The presence of a RSO can be concisely demonstrated by plotting a measured peak height as a function of both DL and MCP supply voltage on a two-dimensional contour diagram [2]. A flat area indicates the presence of a RSO. Alternatively the RSO appears as a flat region if an ion peak is plotted as a function of the DL at a constant MCP voltage (Fig. 6). As the DL is increased the peak maximum remains approximately constant since the PHD lies above the DL. At the onset of the peak rise (when the DL is within the PHD) the non-uniformity at the peak edges is clearly seen [26].

The 'flat' region in Fig. 6 in fact shows a slight increase as the DL is lowered. This may be inherent in the MCP gain distribution or result from low voltage pulses due to MCP non-linearity.

There is often concern expressed about the fact that a single ion may be measured by more than one detector since it is thought that this must cause a problem in estimating the total intensity of an incident beam. In fact this enables the central anode to integrate the incident beam intensity for a narrow incident beam if the RSO can be accessed and is arguably the ideal situation for the measurement of relative ion intensities such as isotope ratios using a detector array. In addition of course an array can measure several different peaks simultaneously.

2.3.1. Non-uniformity

Non-uniformity may arise from several sources including the MCP, the detector input circuitry and the accuracy of the alignment between the MCP and the detector anodes. Non-uniformity is always present to some degree due to manufacturing tolerances. As already explained, peak heights may be measured accurately even in the presence of non-uniformity but

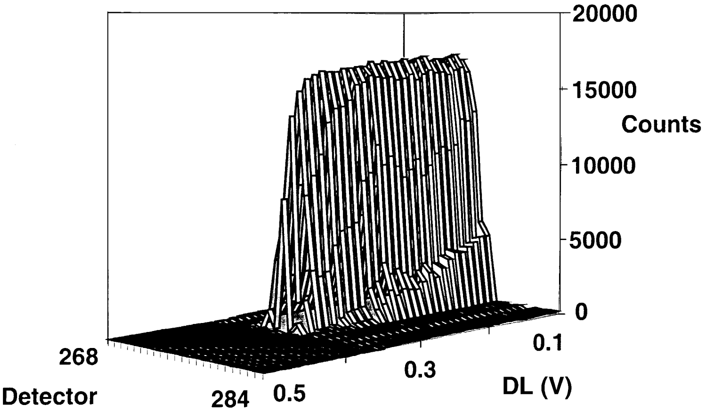

Fig. 6. An ion peak is plotted as a function of the DL at a fixed MCP voltage of 2.2 kV. As the DL is decreased from a voltage level above the PHD the peak height rises rapidly and shows a flat region when the DL is substantially below the PHD and therefore in the RSO. Each peak was accumulated for a period of 10 s with an ion flux of about 1500 ions s^{-1} at the peak maximum. At the onset of the peak rise (when the DL is within the PHD) the non-uniformity at the peak edges is clearly seen [26].

where peak profiles are needed then there should be a correction for non-uniformity. A correction algorithm is outlined in the next section which corrects all sources of non-uniformity. The limitations of the algorithm are also discussed.

In terms of pulse height distributions and discrimination levels, the problem of non-uniformity can be viewed as follows. When the discrimination levels of two detectors are unequal (Fig. 7) then the relative number of events recorded may be incorrect. This gives detector non-uniformity. The detectors at the edges of the measured peaks cannot be in the RSO and hence non-uniformity effects will always influence the *measured* peak fall-off even for narrow incident peaks. The MCP may also be non-uniform.

In Fig. 7 the DL values for two detectors are shown. The detectors need not be adjacent but could be anywhere on the array and for simplicity of illustration the same PHD is assumed on each detector. In Fig. 7(a) it can be seen that both detectors will correctly measure the signal intensity since the PHD is above both. However, when the discrimination levels of two detectors are unequal and at least one lies within the PHD then the relative number of events recorded on the two detectors is incorrect. Thus, the detector non-uniformity is reflected in the measured peak profiles. Fortunately the error due to non-uniformity is a systematic error and a correction can be made.

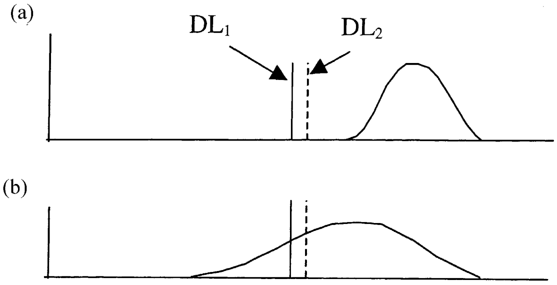

Fig. 7. An illustration of the effect of non-uniformity. (a) The pulse height distribution lies above the discrimination levels (solid and dashed vertical lines) of two detectors. The DLs do not coincide due to non-uniformity but the ions would still be counted correctly on both detectors. (b) If the pulse height distribution were not entirely above one or both of the DLs then this non-uniformity would result in an incorrect relative fraction of the PHD being measured. The detectors need not be adjacent. For simplicity the PHD is assumed to be the same for both detectors.

2.4. Ideal measurement conditions

In order to achieve reproducible mass peak intensities, measurements should be made in an operating region where the signal measured is independent of the conditions so that for small fluctuations in the conditions there is little change of signal. This is the RSO, which can only be achieved if the PHD can be set above the DL. For the type of detector considered here a RSO exists only if

- there is a low detector input capacitance or high multiplier gain;
- the incident ion beam is narrow;
- the incident ion intensity is in the linear operating range since the PHD shifts to lower values at high intensity.

If the RSO cannot be accessed then the DL cannot be set below the PHD and any non-uniformity or non-linearity of multiplier, detector response will inevitably appear in the measured spectrum. If the peak profile is needed then the peak must necessarily be sampled at several points on the incident profile hence the incident peak must be wide. Therefore, the RSO cannot be accessed by the central detector and in any case the detectors at the edges of a measured peak can never access the RSO. This is where the non-uniformity correction becomes essential.

There is great potential for impenetrable complexity in discussing the array performance. However, the final result can be simply stated—for accurate peak intensities, measurements should be made in the RSO and peak heights must be used. For the best peak profiles the incident ion intensity must not change rapidly over the distance of a detector anode width (i.e., an incident peak must cover several anodes) and a good non-uniformity correction should be made.

As hinted, working in the RSO will not only enable the accurate measurement of peak intensities, it will also optimize the stability and reproducibility of the measurements. The following plea was sent by Dr. J. Villinger when he discovered that a special issue of IJMS was to be devoted to detectors and measurement, which illustrates the problems faced by instrument manufacturers due to the current state of detector technology.

> I want to see a paper explaining why all detectors I experienced in whatever operating mode have a reproducibility error of at least 5–7% at the best. I mean, even in counting mode you have an output drift of 5% or more per day when you operate the multipliers with more then 10,000 ions per second. Only at very low count rates, less than 1000, you have good stability. I bring up this question, as this is very painful in our quantitative applications where you have to work with users demanding less than 2% drift over the day. Somehow multipliers seem to be only stable at low and constant output, so we have to drive our instrument sensitivity according to the concentrations we have to measure and try and keep count rates below 100,000 pulses per second.

There is a sense of mass spectrum measurement as a black art here rather than the logical deterministic exercise one would hope for. The discussion has focused on an integrated array of ion counters and has attempted to show how the problems can be minimized. The question arises of the relevance of these arguments to other types of detector, e.g., arrays of analogue detectors or single detectors.

For a single ion counter behind a single slit (or circular orifice in the case of a quadrupole mass spectrometer) the issues are similar, i.e., the PHD must lie above the DL or any fluctuation of the conditions will be imposed on the measured spectrum unless they can be averaged out. Therefore, low detector input capacitance, high multiplier gain and low incident ion intensity are essential. However, there is no non-uniformity for a single detector and also if the PHD lies above the DL at the measured peak center then it also lies above it at the measured peak edges and therefore the relative peak areas can be taken as a good measure of the relative peak intensities. In short, when the RSO is not accessible, reproducibility over a period of a day would require all conditions to be very stable over this period as well as no change in the MCP characteristics. The alternative is to work within the RSO for all ion peaks and this will not be possible if the incident ion intensity is too high.

In the case of analogue detectors, non-uniformity of arrays and non-linearity of the MCP will present a similar problem as that described for the array of counters. However, for analogue detectors there is no RSO of the type already defined.

2.4.1. Detector anode dimensions

Of the many design trade-offs, those of the detector anode length and width deserve careful consideration. There is a tendency to consider that greater length and smaller width are desirable. However, a higher detector input capacitance negates the amplifying effect of the MCP and this has serious performance implications for the array of counters.

Consider a one-dimensional array with anodes 2 mm long (perpendicular to the direction of dispersion) and about 25 μm wide (in the direction of dispersion). The capacitance of such an anode on the surface of a silicon chip could be around 0.5 pF. An anode of width about 25 μm may collect typically about a third of the electrons from a MCP pulse centered above it. Therefore, a MCP pulse with a gain of say 3×10^6 will give a voltage pulse (calculated from $V = Q/C$) of $(10^6 \times 1.6 \times 10^{-19})/(0.5 \times 10^{-12}) = 0.2$ V. Pulses of this order can be easily detected using the simple sensors. If the MCP gain distribution is such that the lowest voltage pulses lie above about 0.1 V then the RSO should be accessible. It can be seen from these hand-waving approximations that an anode capacitance of about 0.5 pF or less should enable access to the RSO. This low capacitance is very difficult to attain unless the anodes are integrated with the electronics. Even contact pads, needed when the anode is not integrated, can add several times 0.5 pF. The figures may well vary widely for different technologies. The possible effect of a doubling of an anode capacitance is illustrated in Fig. 8 and it should

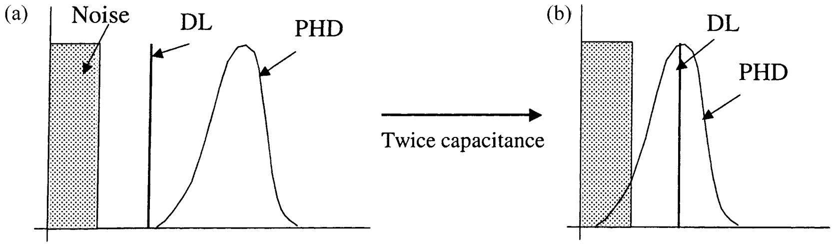

Fig. 8. The possible effect of using a longer detector anode is shown. If the ideal situation shown in (a) can be achieved with a detector anode of a given length, then doubling this length in an attempt to collect more ions will not achieve its goal and will compromise the performance. (b) The anode length is doubled, the capacitance is therefore doubled but the charge collected from each MCP pulse remains the same. Therefore, the PHD shifts to lower values.

be noted that

- to a first order there can be little improvement by decreasing the width of anodes since an anode half as wide will have roughly half the capacitance but will collect only about half as many electrons in a given pulse;
- doubling the anode length may result in more MCP pulses landing on the anode but the capacitance will double and the same number of electrons will be collected in a given pulse. Therefore, the pulse distribution will shift to lower values and in the case illustrated by Fig. 8 no more events will be counted.

It can be seen that in the case of Fig. 8, if all conditions were the same except that the detector anode length (and hence capacitance) were doubled then there would be a performance advantage to the shorter anode. This can be understood from Fig. 8(b) where the PHD would encompass twice as many events if the incident ion beam is longer than the detector anode length (perpendicular to the direction of dispersion) but only half of them would be detected because the PHD would shift to lower values. This special case is chosen simply as a means of illustrating the possibility that there may not be an increase in the detected signal in spite of the increased anode length, but the advantage of working in the RSO would be compromised. It may be a very good trade-off to have short anodes to reduce capacitance. This trade-off deserves serious consideration at the design stage.

3. Processing

A mathematical model of the measurement made by the detector array opens up the possibility of powerful data processing methods. The following model enables the correction of non-uniformity and also enables forward deconvolution of measured spectra.

3.1. Non-uniformity

It turns out that in order to correct measured data for non-uniformity it is not necessary to know from where the non-uniformity originates although this has been considered [14]. A mathematical representation of the measurement process is needed and simple matrix algebra provides the necessary mathematical framework. Consider an experiment in which a square profile ion beam of unit intensity is incident above the detector anode at one extreme of the array. The *measured* peak is entered in the first column of a matrix. The incident beam is then placed above the next anode and the new *measured* peak is entered in the next column of the matrix with the peak center on the diagonal. This is repeated for all anodes to give the '**A**' matrix representing the action of the array.

Consider the general matrix multiplication $\mathbf{Ab} = \mathbf{c}$ where $\mathbf{A}$ is any square matrix and $\mathbf{b}$ and $\mathbf{c}$ are any column matrices of the same dimension. The column matrix $\mathbf{c}$ is a weighted sum of the columns of $\mathbf{A}$ where the weighting factor for the ith column of $\mathbf{A}$ ($\mathbf{A}^{(i)}$) is b_i.

Therefore,

$$\mathbf{c} = \sum_i \mathbf{A}^{(i)} \mathrm{b}_i$$

This is clearly a satisfactory representation of the measurement process if **b** represents the incident spectrum and **c** represents the measured spectrum since b_i is the incident intensity on anode i and $\mathbf{A}^{(i)}$ is the peak which is seen for unit incident intensity above anode i.

Therefore, we can model the measurement by

$$\mathbf{c} = \mathbf{Ab}$$

Ideally, for a uniform array, all rows and columns of **A** should have the same profile. Such an ideal symmetric matrix is represented by **U** where in practice the columns of **U** contain an average of the measured peak shapes (with the maxima on the diagonal). We can write

$$\mathbf{A} = \boldsymbol{A}\mathbf{U}$$

$$\mathbf{AU}^{-1} = \boldsymbol{A}\mathbf{UU}^{-1} = \boldsymbol{A}$$

enabling calculation of $\boldsymbol{A}$ for any **U**. Therefore we can write

$$\mathbf{c} = \boldsymbol{A}\mathbf{Ub}$$

$$\boldsymbol{A}^{-1}\mathbf{c} = \boldsymbol{A}^{-1}\boldsymbol{A}\mathbf{Ub} = \mathbf{Ub} = \mathbf{ccorr}$$

and **ccorr** is the corrected spectrum which would be seen with a uniform detector array represented by **U**. Therefore, $\boldsymbol{A}^{-1}$ is the correction matrix we require. It should be noted that **U** could equally well have been the unit matrix. In the latter case

$$\mathbf{A} = \boldsymbol{A}\mathbf{I}$$

$$\mathbf{A} = \boldsymbol{A}$$

and the correction matrix is $\mathbf{A}^{-1}$. This of course corresponds to the direct recovery of the incident spectrum from the measured spectrum and follows immediately from $\mathbf{Ab} = \mathbf{c}$ since

$$\mathbf{A}^{-1}\mathbf{Ab} = \mathbf{A}^{-1}\mathbf{c} = \mathbf{brec}$$

where **brec** is the recovered incident spectrum. Calculations show **ccorr** to be of better quality than **brec**. It can be seen that information on non-uniformity of the MCP is contained in the rows of **A** and the columns contain information on the non-uniformity of the array integrated circuit. This algorithm and the properties of the rows and columns has been illustrated in a previous publication [14] where it was also shown that it can be extended to the correction of non-uniformity in two-dimensional imaging devices.

A further insight into the **A** matrix (rows labeled i and columns labeled j) may be gained by considering an incident beam with a square profile one detector wide and of fixed intensity. The jth column of the array shows the signal measured on detectors i with the beam incident above the detector j. The ith row shows the signal measured on the detector i when the beam is incident above detectors j. Another way of stating the latter is that a column shows the signal measured by different detectors with the beam incident above a given segment of the MCP and a row shows the signal on a given detector when the beam is incident on different parts of the MCP.

It should be noted that if the total integrated signal is very low, then the model will not be accurate. This can be seen in the extreme case of a single incident ion resulting in the recording of a single count on say two detectors. In this case the measured spectrum is not equal to **Ab**. The best statistical solution to this problem is under study.

3.2. *The* **A** *matrix*

When the **A** matrix is found then all acquired data can be corrected if the physical and electrical conditions remain the same and the characteristics of the detector components (MCP and array IC) do not change. The **A** matrix has some interesting properties which assist in its computation. If the array is uniformly illuminated the 'spectrum' measured **c** does not have a flat profile but is jagged due to non-uniformity. This jagged profile is given by

$$\mathrm{c}_i = \sum_j \mathrm{A}_{ij}$$

This immediately provides a useful constraint on **A** since the uniform illumination experiment is relatively easily carried out. If the MCP is uniform and the non-uniformity is due to the array then each *row* of the **A** matrix has the same profile but with its maximum centered on the diagonal and the area under the profile of row i equal to c_i. The assumption of MCP uniformity has proved to be a good one in recent experiments to measure electron energy spectra (Fig. 9). Since a single detector anode measures the output from many MCP channels it is reasonable to anticipate that this will to some extent average out any channel-to-channel MCP non-uniformities. If conditions should change, it is relatively straightforward to recompute the **A** matrix automatically by performing a uniform illumination experiment.

The non-uniformity of the array IC is clearly evident in the data of Fig. 9(a). This graph shows part of the measured energy spectrum of secondary electrons emitted from a copper surface bombarded with high energy electrons [27]. From the point of view of the detector, the measurement of electrons is almost identical to the measurement of ions. Each electron from a hemispherical energy analyzer hits the MCP and initiates an electron pulse which is registered by one or more detectors if the pulse gain is sufficient.

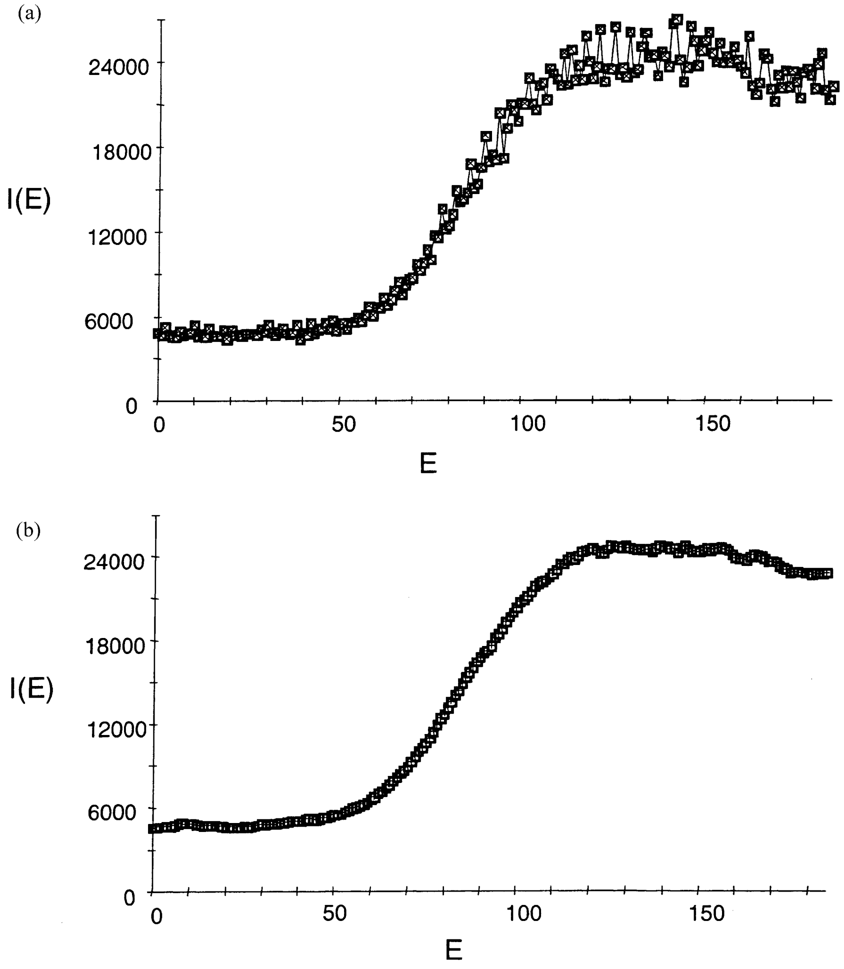

Fig. 9. (a) Electron energy spectrum—raw data; (b) data corrected for non-uniformity.

Fig. 9(b) shows the raw data of Fig. 9(a) corrected for non-uniformity using the above algorithm. In these experiments the **A** matrix was found by carrying out a uniform illumination experiment and making an educated estimate of the row profile based on experience and simulations carried out previously [28]. The estimate was good first time as can be seen from the data quality in Fig. 9(b). This is not an arbitrary procedure since the quality of the correction can established by a visual inspection or statistical analysis of the corrected data itself. It is emphasized that the algorithm does not smooth the data by some sort of averaging method but corrects a systematic error. The correction of the data in Fig. 9 is excellent and was reproduced on other data taken with the same detector on the same day. At the present time there has been no systematic study of the variation of **A** with parameters such as age and usage of the MCP, etc.

3.3. Limitations and developments

If the experimental conditions change, for example if the MCP ages, the MCP supply voltage is changed or the DL is changed, etc. then a new **A** matrix must be measured. This has proved to be relatively straightforward if the MCP response remains uniform since it is simply necessary to make a uniform illumination measurement and find the row profiles of the **A** matrix. Experiments will be carried out in future to gain more experience on how the **A** matrix changes with age, usage, etc. of the MCP. Such measurements would provide a concise summary of the change of the detector characteristics.

3.3.1. Deconvolution

Although the correction algorithm provides a good way of removing the effects of non-uniformity from measured spectra, the recovery of the incident spectrum from $\mathbf{A}^{-1}\mathbf{c}$ has been less successful. However, forward deconvolution [29] is enabled by the matrix model and is providing encouraging results (to be published). For a measured ion peak **c**, the trial **t** which minimizes $\chi^2 = \sum_i (c_i - (\mathbf{At})_i)^2/\sigma_i^2$ (where σ_i^2 is the variance of the measured signal on the *i*th detector), may be computed and taken as the best estimate of the incident spectrum **b**. Fig. 10 shows the results of forward deconvolution for two measurements. The bold vertical stems show the incident beam **t** found by minimizing χ^2 and the crosses show the raw data (measured spectrum). As a test of the deconvolution, the circles computed from **At** show good agreement with the measured spectrum. Thirty-eight such measurements were made by moving a peak of constant height across the array. Each deconvolution gave equally good results. The **t** column matrices found in this way recovered much of the resolution lost in the measurement and the incident beam can be seen to be between one and two detector anodes wide. However, the peak intensities as computed from **t** showed

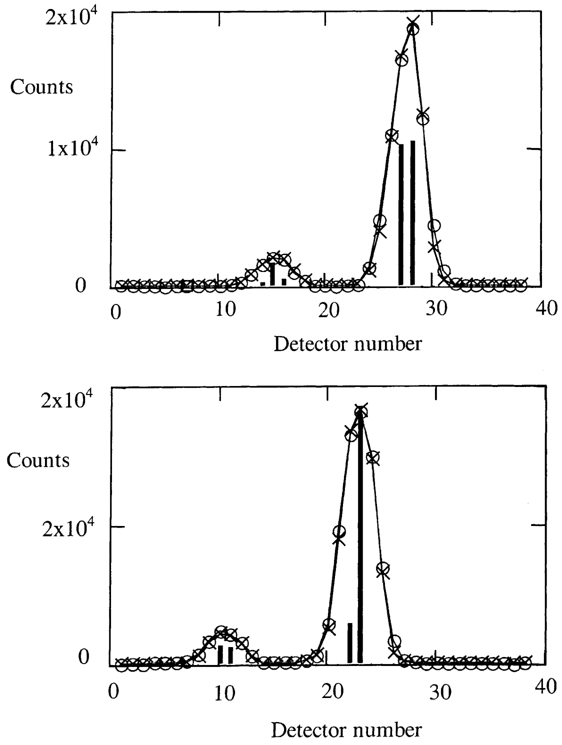

Fig. 10. A spectrum was moved across the array. Crosses show the measured spectrum **c**. Bold vertical lines show the incident spectrum **t** (see text) recovered by forward deconvolution and the circles show the reconstituted data **At**. The incident spectrum is clearly between one and two detector anodes wide. Thirty-eight such spectra were measured.

a variance several times greater than that expected if the peaks were indeed of constant intensity as they were moved across the array. Further work will be carried out to investigate this.

A measured spectrum is always a histogram with the number of elements (n) equal to the number of detectors and in the event that the array response varies significantly over the dimension of a single detector (25 μm), the algorithm of Section 3.1 recovers less accurately an incident spectrum with structure within a single detector width. However, by working forwards, **A** matrices of any dimension may be used since they can be constructed both conceptually and experimentally. For example, it is possible to step an ion beam of say half the anode width across the array and construct an $\mathbf{A}'$ matrix of dimension $2n$ and we can see that

$$\mathbf{A}'\mathbf{b}' = \mathbf{c}'$$

exactly as above where $\mathbf{b}'$ and $\mathbf{c}'$ are column matrices with $2n$ elements. However, since the actual measured spectrum **c** has only n elements the appropriate pairs of elements in $\mathbf{c}'$ must be added together to give the measured **c**. In this case the $\mathbf{t}'$ which minimizes

$$\chi^2 = \sum_i \frac{\left(c_i - \sum_{j=2i-1}^{2i}(\mathbf{A}'\mathbf{t}')_j\right)^2}{\sum_{j=2i-1}^{2i}(\mathbf{A}'\mathbf{t}')_j}$$

would give a recovered incident spectrum of $2n$ elements from a measured spectrum of n elements. The value of this method remains to be investigated.

3.3.2. Non-linearity

The algorithms presented in this section assume that the detector is working in the linear region. Therefore, the MCP gain distribution and hence the PHD should not be a function of the incident intensity and the latter must be low enough to ensure that this is the case. Where peaks of widely different intensity are to be measured with high accuracy this is critical since the most intense beam may be further into the non-linear range than the less intense beam and the intensity ratio will be incorrect. The problem is not unique to arrays of ion counters of course but for single detectors (or direct sampling arrays not preceded by a MCP) it is straightforward to correct up to a point. With an array preceded by an MCP, correction is more difficult since non-linearity is a local MCP effect. It should be noted that this problem arises for all arrays preceded by a MCP.

4. Conclusions

The measurement of mass spectra using an array of independent ion counters integrated on a silicon chip and preceded by a MCP has been considered. The measurement process has been analyzed and where the measured spectrum depends linearly on the incident spectrum the measurement process has been modeled using simple matrix algebra. The performance issues are non-trivial but it has been shown that there exists a RSO which enables accurate measurement of relative peak heights even in the presence of non-uniformity. The conditions for the existence of a RSO include low detector input capacitance, a low incident ion intensity and narrow incident peaks. There is no RSO when broad ion beams are being measured but in this case a non-uniformity correction algorithm is presented. A forward deconvolution and maximum entropy procedure is under consideration to improve the data processing and its use in the correction of non-linearity is being studied.

A new detector array is under development at Aberystwyth which will contain about 1000 detectors with a spatial resolution of 25 μm and will be designed to maximize uniformity.

Spatial dispersion is only one of the means of dispersing ions in mass spectrometry. However, it is the dominant means in the dispersion of electrons, UV, X-rays, etc. and detector arrays will remain an important area of research driven by the needs in several areas.

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