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EVALUATION OF A NOVEL ION DETECTION SYSTEM ON A MAGNETIC SECTOR MASS SPECTROMETER

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OBJECTIVE

This paper describes a new detector for a magnetic sector mass spectrometer. The new detector provides enhanced mass specificity for accurate quantification. The expected and observed performance of this detector is compared.

INTRODUCTION

A double focusing magnetic sector mass spectrometer can be used to select and record the response from target compounds at high resolution and with high sensitivity. The high resolution enables many chemical background masses to be eliminated and consequently allows a lower detection level to be achieved. However, high resolution alone does not insure that all ions detected are of the target compound of interest. Background ions may be detected which are due to contaminants in the source or reference compound. Scattered ions from high abundance ion beams in close proximity to the selected mass may also be detected and which may give rise to a ubiquitous background. If an interference compound is present in the sample, different in mass from the analyte by less than the mass peak width, then this can also lead to erroneous measurements. The presence of such interferences may be recognised by the reporting of incorrect isotope ratios, although this method is not guaranteed. This situation is typically remedied by increasing the system resolution, with a corresponding reduction in sensitivity.

A new detector has been developed and constructed with the intention of automatically recognising the presence of such interference ions and background ions. The new detector separately monitors the high and low mass halves of the mass transmission window by splitting the ion beam and diverting the two halves to two discrete detection systems. If a selected mass is the only component present, then the ion beam will be split symmetrically between the two detectors and will give rise to two equal signals. However, if an interference ion (of higher or lower mass) is present, this will skew the response and produce an asymmetry between the two signals.

Figure 1 shows the new detector system fitted to an AutoSpec Premier. The new detector is positioned downstream of the standard detector. It consists of a knife edge beam splitter and reflection electrode, and two additional standard detectors. When monitoring a single mass centred on the collector slit the two detectors each record half the ion signal. The two outputs are summed and the combined output is equal to that recorded using the standard detector. In addition the two outputs are compared to determine their symmetry.

The degree of asymmetry seen between the two detectors is a direct indication of the difference in mass between the ion beam detected and the mass monitored. In order to characterise this aspect of the new detection system, a theoretical model of an ion beam will be developed. This will then be compared to the actual behaviour of the detection system.

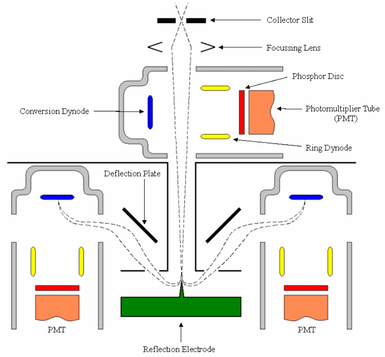

Figure 1: AutoSpec Premier with the New Detection System

THEORY

In the development of the theoretical model, the first consideration is the intensity distribution of the ion beam itself. A simple model of an ion beam profile on a magnetic sector instrument is a uniform distribution (rectangle - figure 2a). When this ion beam model is profiled by scanning it across an imaging slit (the collector slit - figure 2b), this idealised profile gives a triangular peak shape. This is shown in figure 2c. In this example, the ion beam width is 50ppm, the collector slit width is 50ppm and the resulting peak width is 100ppm. This corresponds to a mass spectrometer resolution of 10,000 at base.

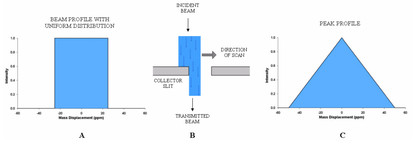

Figure 2: Simple Model of Ion Beam Profile

However, in practice the actual tuning profile seen is more complex, often being of the appearance of that seen in figure 3a. This shows a peak profile with 10,000 resolution (10% valley definition).

An ion beam distribution which yields a tuning profile more like that seen in practice is a cosine distribution as shown figure 3b. The corresponding peak profile is shown in figure 3c. This is compared to a real tuning peak profile in figure 3d. As can be seen, this model accurately reflects what is seen in practice.

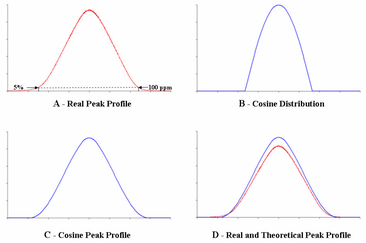

Figure 3: Actual and Cosine Model Peak Profiles

This theoretical model is now transposed onto the new split detection system. The resultant tune profile is generated by considering each half of the imaging slit is a separate slit. The two profiles are summed to provide the same profile as seen in the previous examples. The two detector traces and their sum can be seen in Figure 4.

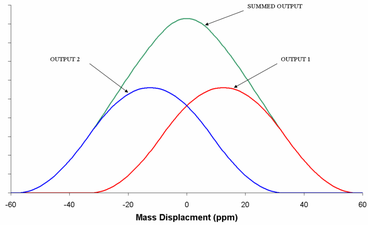

Figure 4: Theoretical Split Detector Profile

This tuning profile effectively represents a continuous distribution of mass displacements of the ion beam with respect to the central mass. When the ion beam is in the exact centre of the monitored window, the detected signal is at its maximum and the signal recorded by each detector is the same (Figure 5a). If the ion beam is displaced to higher or lower mass, the recorded summed intensity drops and a difference is seen between the two signals (Figure 5b). This difference is a function of the displacement in mass, and is referred to as the symmetry.

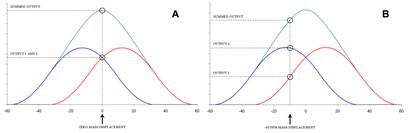

Figure 5: Examples of Mass Displacement on Split Profile

The symmetry is expressed as a percentage, being 100% when the detected signals are perfectly matched. As the difference between them increases, the symmetry drops towards 0%. The symmetry of the trace shown in figure 4 has been calculated as a function of mass displacement and is illustrated in figure 6. This measurement of symmetry, for this beam profile, is approximately a linear function of mass displacement.

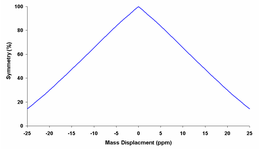

Figure 6: Symmetry Profile of Theoretical Model

This represents an ideal situation. However, there are a range of factors which can effect the accuracy of the symmetry value. Most important of these is the minimum increment in mass positioning. During a voltage switching Selected Ion Recording (SIR) acquisition the magnetic field is static and the mass is selected by varying the accelerating voltage. On the AutoSpec Ultima, the accelerating voltage is set using an 18 bit DAC. Each DAC step corresponds to a mass increment of 3.8ppm (1,000,000 / 2^{18}). The DAC steps can be clearly seen in the peak profile illustrated in figure 7 trace A.

The AutoSpec Premier allows this 18 bit DAC to be used over reduced voltage ranges. For example the accelerating voltage DAC may be set to control the voltage within the range 4000V to 8000V (8000V being the maximum instrument voltage). Within this range, the voltage can be set to the 18 bit precision which, over the total voltage range, equates to 19 bit specificity. This allows the mass to be selected in 1.9ppm increments.

Alternatively, the accelerating voltage maybe set to control the voltage over a 10% range. This provides 0.38ppm specificity.

The peak profiles acquired using these two additional modes of operation are shown in traces B and C respectively in figure 7. The improvement in mass selection can clearly be seen.

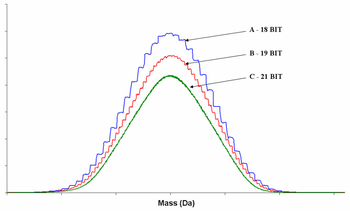

Figure 7: Peak Profiles Using a Range of Mass Increments

During a typical VSIR analysis, in which the effective DAC resolution is 19 bit, the maximum error in the setting of the mass of 1.9ppm. Figure 8 shows the symmetry profiles of the theoretical ion beam model when it is displace by +/- one DAC step.

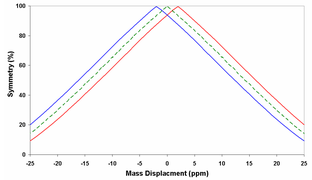

Figure 8: Symmetry Profile for +/- 1 DAC Step

For example, if this symmetry was 50% with a bias to low mass, then from figure 9a, it can be seen that the peak described is displaced to low mass by between 12 and 16ppm. If the symmetry is better than about 90%, then it is not possible to conclude that the measurement is in error. However, if the symmetry is less than 90%, then in this ideal case (illustrated in figure 9b) it can be concluded that this measurement is from an incorrect mass or is interfered with. It can be seen from figure 9b that a difference in mass of only 5ppm will give rise to a symmetry of 90% or less.

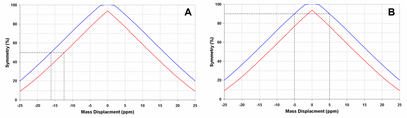

Figure 9: Relating Symmetry to Mass Displacement

METHODS AND MATERIALS

The new detection system has been fitted to a standard AutoSpec Premier (Waters, Manchester, UK). The new detection system is mounted in a separate housing and fitted to the end of the collector housing.

In order to evaluate the level of variability of the symmetry with respect to mass displacement, Perfluorokerosene (PFK) is infused into the ion source and an experiment was contrived whereby the 330.98241 Da peak is monitored along with several additional mass channels displaced from the central mass. These additional mass channels were displaced between -0.5 and +0.5 beam widths with respect to the central mass, in 0.1 beam width increments. As this experiment was run with a beam width of 50ppm (peak width 100ppm), the range of masses were from -25 to +25 ppm in 5ppm increments. The scan to scan variability of the symmetry measurements for all these mass channels was assessed and compared to the theoretical model.

An additional experiment was performed to see how well the new detector measures symmetry with a real unresolved interfering compound. A mixture containing Methyl Stearate and Butyl Stearate was used for this. The Methyl Stearate molecular ion mass is 298.28718 Da. Butyl Stearate can form a ^{13}C fragment which has a mass of 298.28271 Da, different in mass from the Methyl Stearate by just 4.5 mDa or 15ppm. At 10,000 resolution (10% valley definition), these two components are unresolved from each other. This experiment was repeated eight times.

RESULTS

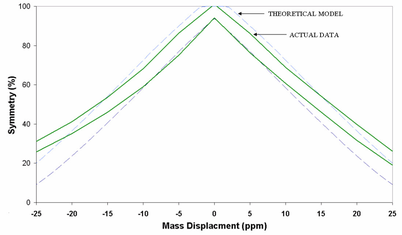

Figure 10: Comparison of Theoretical and Actual Symmetry Profiles

Figure 10 shows the resultant symmetry variability seen from monitoring a single mass in increments of 5ppm. The maximum and minimum values of symmetry have been calculated as being +/- 2 standard deviations of the range of values measured. The theoretical model shown in figure 8 is overlaid for the purpose of comparison with the data acquired.

As can be seen, the measured data shows less variability than that predicted. A possible reason for this is that the peak to peak variation in mass setting only corresponds to 1 DAC step and not 2 DAC steps as surmised.

The acquired data matches the profile of the theoretical model down to a symmetry of around 50%. Below this value, the symmetry measure for the acquired data is higher than that predicted. A possible reason for this is that the model used for the peak profile is less accurate near the extremities of the peak. This is more apparent on the low mass side of the peak than the high mass side. In figure 10 this is reflected by a greater deviation between the acquired data and the theoretical model for the low mass side of the peak.

Figure 11 shows chromatograms of the two analytical masses in the Methyl Stearate experiment. The two major components are identified.

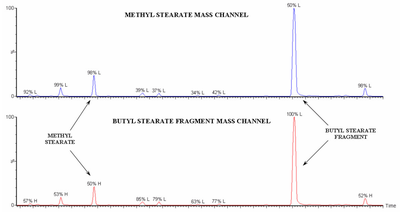

Figure 11: Chromatograms from Methyl Stearate Experiment

For the Methyl Stearate experiment, the data presented previously predicts that when the two major analytes are viewed on their corresponding mass channel, the chromatographic peaks should have a symmetry value between 94% and 100%. Actual data obtained (n=8) results in a mean symmetry value of 96.3% (SD = 2.7%) and 96.1% (SD = 2.8%) for Methyl Stearate and the Butyl Stearate fragment respectively. This is an acceptable match with theory.

The interfering components in the Methyl Stearate experiment are separated by 15ppm which, from the data shown in figure 10, should yield a symmetry value of 50% +/- 4%. The interfering mass, for the eight injections, gave a mean symmetry value of 50.9% (SD = 2.0%) and 52.0% (SD = 3.2%) on the Methyl Stearate and the Butyl Stearate fragment mass channels respectively. Again, this matches with the theoretical predictions.

For all this data, the signal intensities are assumed to be sufficiently intense so that ion statistical variation in measurement do not significantly contribute to symmetry measurements. For weak signals, ion statistical variation will contribute to this variation in observed symmetry.

CONCLUSIONS

- The symmetry measured by the new detection system has been shown to be approximately as expected.
- A symmetry of less than 90% indicates the presence of an interfering species, or the measurement of ions with a difference in mass of 5ppm or more for 10,000 resolution.

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