The Evaluation of a Novel Ion Detection System for a Magnetic Sector Mass Spectrometer

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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.

The new detector is described and illustrated (Figure 1). A series of analyses of extracts from complex matrices have been carried out to evaluate the performance of this detector compared to that of the conventional detector. Examples will be used to illustrate the additional information provided by the new detection system and how it may be used to recognise erroneous measurements and aid diagnosis of the cause of such errors.

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. This does not require that the existing detector be removed and consequently the AutoSpec may still be operated with its standard detector. When it is required to use the new detector, the standard detector is switched off and this allows the ion beam to pass through to the new detector. If the standard detector is switched back on the AutoSpec reverts to operating with this detector.

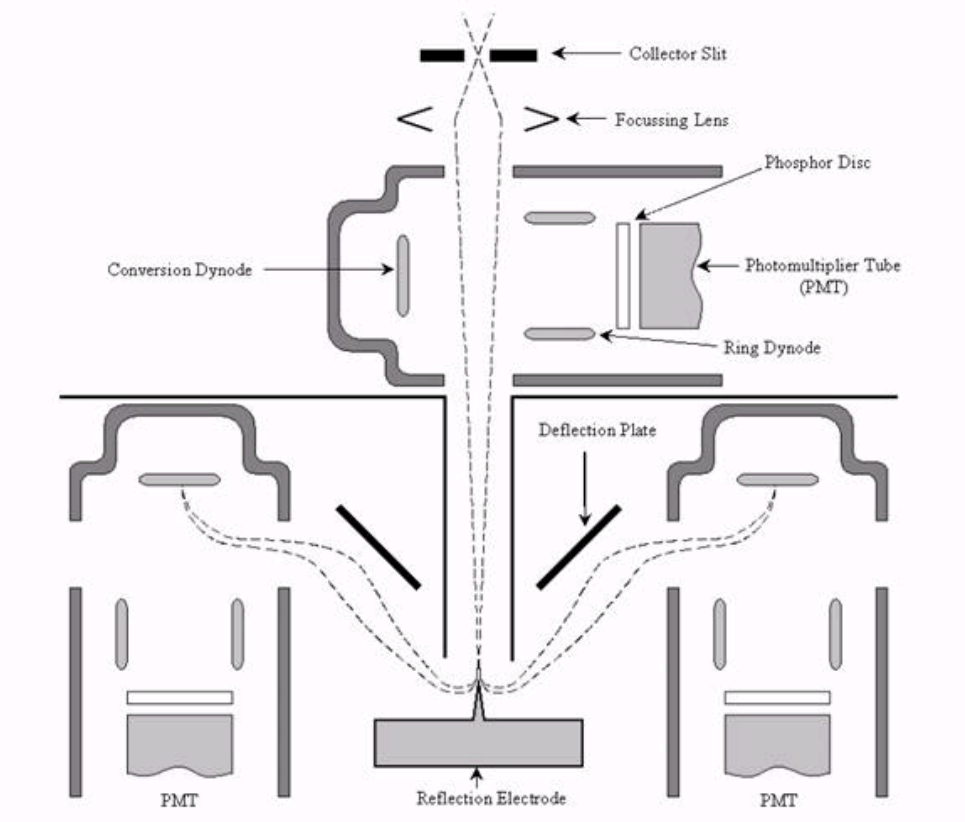

Figure 1. Waters Micromass AutoSpec Premier with the new detector system.

Figure 1 shows the new detector system fitted to a standard AutoSpec. 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 samples were first separated by GC using an Agilent 6890 with a J&W DB5-MS, 60m x 0.25mm i.d. capillary column. All samples were injected splitless (1ul), into a helium carrier gas, set at a constant flow rate of 1.0ml/min. The mass spectrometer was operated in positive ion EI mode at 10,000 resolution (10% valley definition). All data was acquired in the Voltage Switching Selected Ion Recording (SIR) mode of operation. Full experimental details will be presented. When data is acquired using the new detector, a measurement of symmetry is automatically determined for every chromatography peak on all mass channels.

Results and Discussion

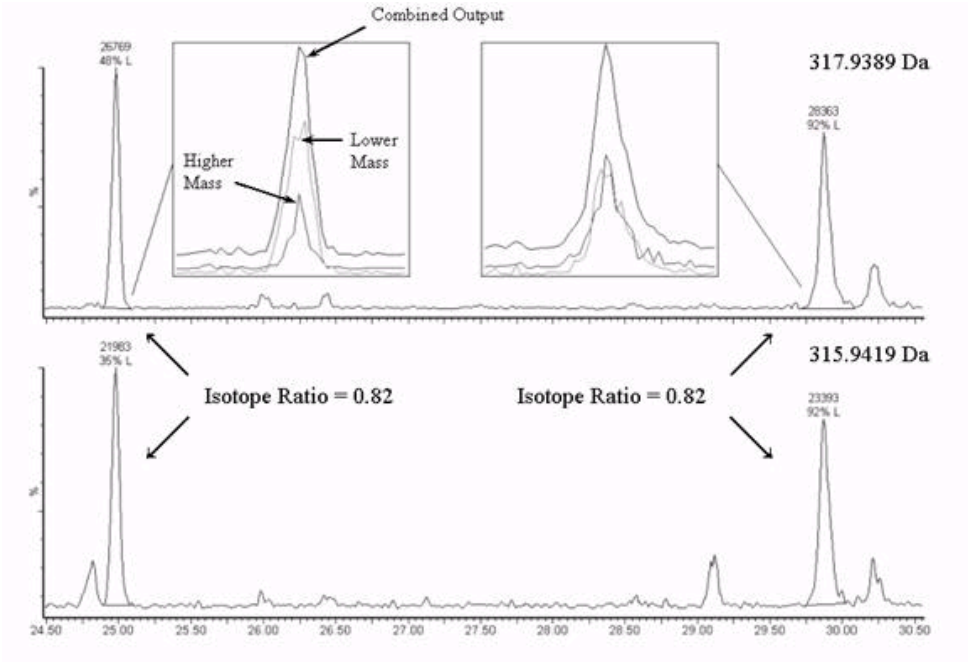

Figure 2: Ion chromatograms of masses 315.9419 Da and 317.9389 Da for ^{13}C 2,3,7,8 TCDF.

Figure 2 shows an example obtained from a trout extract analysed using the new split detector. The two traces show the chromatograms for m/z 317.9389 Da and 315.9419 Da respectively. The two peaks highlighted have retention times of approximately 25 and 30 minutes respectively. They are present on both isotopic mass channels and fall within the isotope ratio criteria required for the compound of interest. From the expected retention time, the analyte (^{13}C 2,3,7,8 TCDF) is assumed to be that eluting at approximately 30 minutes. The symmetry measurement of 92% confirms both mass channels to be within +/- 10ppm of the corresponding analytical mass for the second highlighted peak. The first peak however, shows symmetry values (48% and 35%) on both mass channels to be significantly lower than that expected. The signal is significantly higher on the low mass detector (as seen in the insert of Figure 2) indicating that the mass of this ion is lower than that of the analyte.

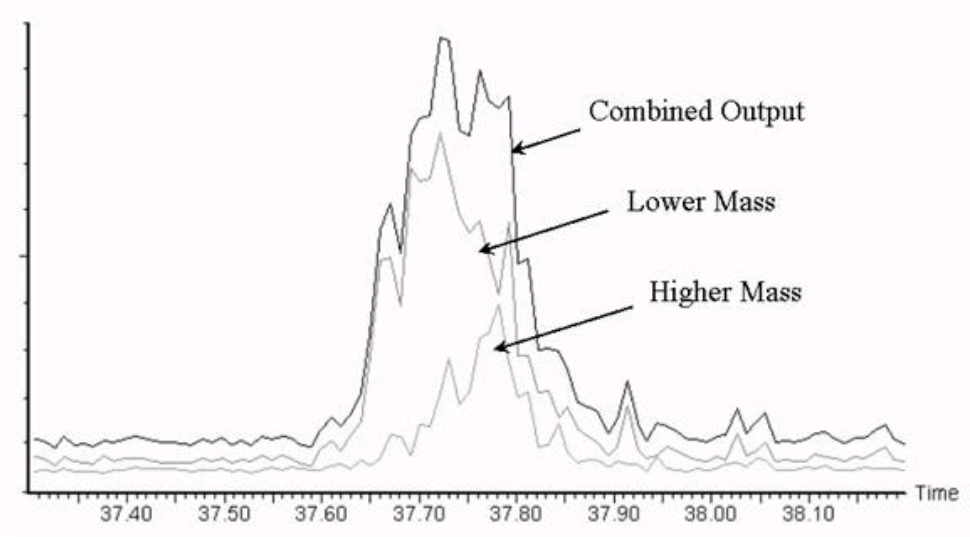

Figure 3: Ion chromatogram of mass 369.8919 Da for ^{13}C PeCDD.

Another example of data from the same sample is shown in Figure 3. This shows part of the chromatogram for m/z

369.8919 Da. Through the use of the new split detector we can clearly see that this peak is actually comprised of two components. The two components have some temporal separation but less than the chromatographic peak width. The interference elutes slightly before the analyte, at the start of the peak and the symmetry is biased towards low mass. The latter portion of the peak exhibits a lower level of interference and the symmetry of the two outputs is improved. Actual quantitation of this analyte was not recorded since the isotope ratio fell outside that required. Since it can now be seen from the two outputs that the interference has eluted before the analyte, and that the high mass detector output is significantly less effected by the interference, then it is possible to determine a better value for the analyte signal from the high mass detector output.

The data shown above illustrates two benefits to be gained by use of the split detector. Peaks that meet the isotope ratio criteria may be recognised to be from other substances with a mass difference as little as +/- 15 ppm with respect to that of the analyte. Secondly, where the isotope ratio criteria fails to be met, the cause of the problem may be recognised by the use of the split detector. In some cases an acceptable quantitative measurement may still be determined from the split detector outputs.

The extra information provided by the split detector when operated at an instrumental resolution of 10,000 (10% valley definition) allows interferences to be recognised which may otherwise require a resolution of up to 40,000 to eliminate.