ARTICLE

Drugs on money and beyond: tandem mass spectrometry in the forensic sciences

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Tandem mass spectrometry (MS/MS) is widely recognised as an ideal technique to identify target compounds in hostile matrices, often described as "fast and dirty".[1] In parallel with the forensic mainstream, scientists with the authors' company have pioneered the use of MS/MS as a tool for forensic investigation. Using MS/MS instruments as highly selective detectors allows sample introduction with no prior clean-up and no chromatographic separation. This has been well proven by the number of applications to which thermal desorption (TD)-MS/MS instruments have been applied, perhaps the most extreme being the contents of a domestic vacuum cleaner. Finding traces of drugs inside a vacuum cleaner can only lead to the conclusion that at some time it was used to clean up these traces. This leaves the user to provide an explanation, although some quite bizarre explanations have been offered!

The speed afforded by the TD-MS/MS technique also offers advantages to the forensic investigator, as fewer handling steps are required and the possibility of contamination is reduced. Samples are introduced by thermally desorbing material into the Atmospheric Pressure Chemical Ionisation (APCI) corona discharge region of a tandem mass spectrometer (Figure 1). Because the thermal desorption process is comparatively rapid, the instruments are operated in selected reaction monitoring (SRM) mode to permit sufficient data to be collected. The process provides confirmation of molecular mass, through the selection of a precursor ion and at least two structurally significant product ions derived from fragmentation of this precursor. In accordance with Valid Analytical Measurement (VAM) recommendations,[2] monitoring two gas-phase ion transitions of this type provides a degree of identification equivalent to that obtained from a conventional electron impact gas chromatography/mass spectrometry (EI GC/MS) instrument. The major advantage of the TD-MS/MS technique is that the analytical process is complete within seconds rather than minutes. This allows many more exhibits or regions of an exhibit to be analysed than time or cost would normally allow.

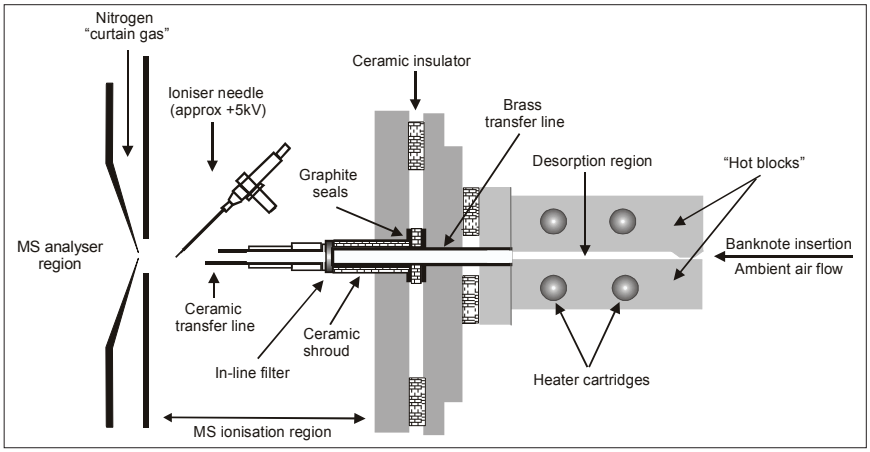

Figure 1. Schematic representation of the multipurpose thermal desorber coupled to an APCI source. Reproduced with permission.

The thermal desorption technique was initially applied to dust collected on filters using a portable "Dustbuster" vacuum cleaner. This system allowed samples to be collected at sites remote from the analytical laboratory by relatively unskilled operators. Once returned to the laboratory, the filters could be analysed for a range of controlled substances, cutting agents, explosives or environmental contaminants.

The most publicised application of TD-MS/MS has been the detection of drugs on banknotes. The combination of materials found on banknotes, ink, dust, finger grease, cosmetics etc., makes a very complex substrate but an ideal application for TD-MS/MS. Early examinations relied on vacuuming the notes themselves and collecting the debris which fell off them when they were shaken. Particulate matter was trapped on filters and subsequently analysed by TD-MS/MS. This method was nicknamed "Shake and Vac". Although this work demonstrated that it was possible to distinguish money associated with drug dealing from money in general circulation, it soon became apparent that there was a background of drug traces on banknotes and that there is little value in simply reporting their presence.

The thermal desorption inlet was modified to allow the introduction of individual banknotes and improve the quality of information obtainable (Figure 2).

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Figure 2. Analysis of a single banknote; requiring less than two seconds.

Using bespoke software the frequency, amount and pattern of drugs contamination may be assessed (Figure 3). From these data an experienced analyst can readily discern money closely associated with drug dealing or trafficking. The technique has now been applied to over one million banknotes in thousands of civil and criminal cases, including two cases at the Court of Appeal in the UK, and is now widely accepted as a fully mature forensic technique.

Of course, for the results to be used in this way, the findings have to be compared with those from a background database of banknotes taken from general circulation. To this end, we have analysed tens of thousands of banknotes withdrawn from banks in more than a hundred different geographical locations. The difference between background diamorphine contamination and banknotes from casework can be striking (Figure 4). Recently, two different mathematical models have been proposed to mimic the distribution of heroin traces in this background population.[3] The two models were found to be in close agreement, predicting an upper limit (at 99.9% confidence) of contamination

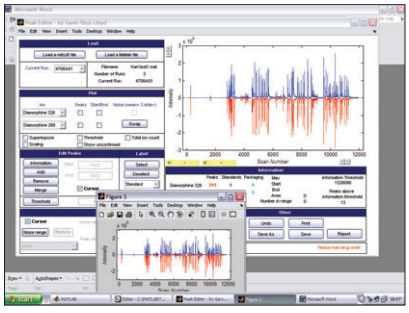

Figure 3. Bespoke software used to interpret TD-MS/MS data.

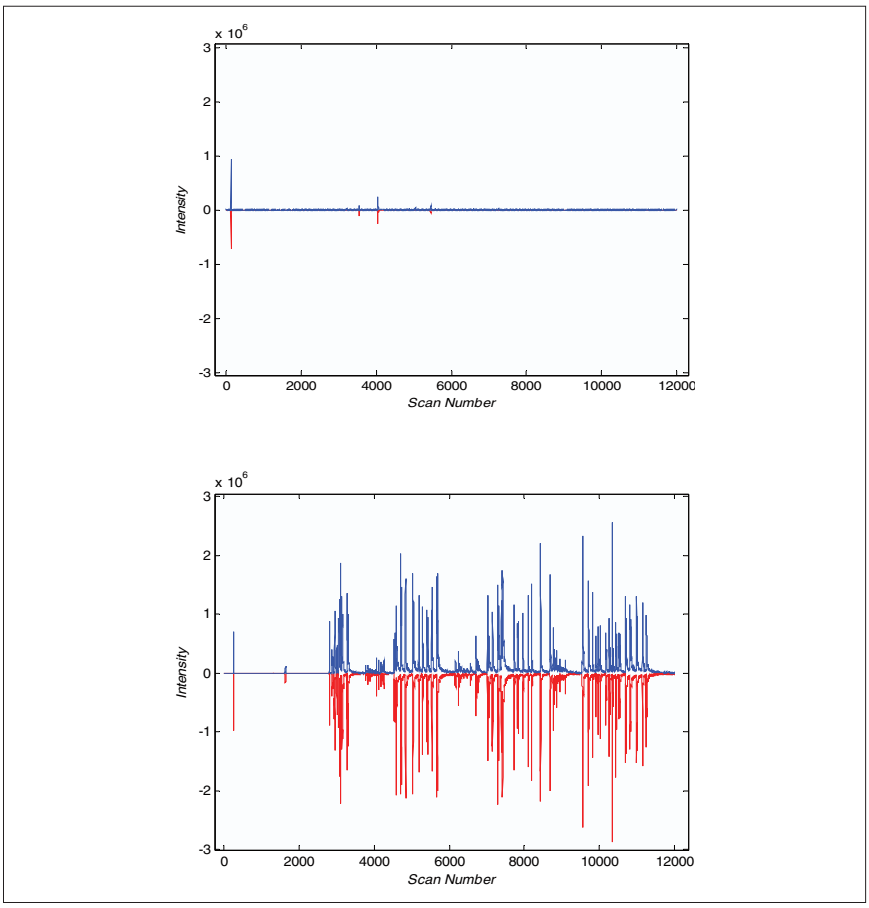

Figure 4. Product ions of protonated diamorphine (*m/z* 370), shown in blue (*m/z* 328) and red (*m/z* 268) for 128 banknotes taken from general circulation (top) and 71 banknotes from casework (bottom).

on banknotes from general circulation between 9 and 10%. The percentage contamination in case studies may then be calculated and compared to the background distribution using a simple statistical test. This presents a simple method by which the prosecuting authorities can ascertain whether or not the contamination present in a quantity of seized notes is consistent (or not) with the money forming part of the background distribution.

In collaboration with the University of Bristol Centre for Chemometrics, the method is currently being extended to encompass a wider range of drugs of abuse.

The TD inlet system is extremely versatile, allowing many exhibits to be analysed either directly, by introduction into the heated zone, or indirectly by collection of dust. One example is the analysis of clothing. The technique can be used to determine which areas of an item of clothing are contaminated with controlled drugs: pockets, sleeves, cuffs etc. This detailed information can then be used to infer the kind of activity that might produce a given distribution and may indicate whether the wearer was carrying, using or repackaging drugs. The technique can also be used to detect traces of drugs present in sweat and on the skin. From a single cotton wool swab it is possible to screen for 16 compounds in a few seconds. Screening for both drugs and their known metabolites makes it possible to ascertain whether traces resulted from physical contact or from ingestion. Trials with known drug users show a very high correlation between sweat samples analysed by TD-MS/MS, immunoassay and high performance liquid chromatography (HPLC) analysis of saliva and urine. The collection of sweat is, however, much less invasive and carries a much lower risk to the collector.

Figure 5. TD-MS/MS instrument mounted in a van.

The laboratory-based TD-MS/MS instruments have now been adapted into a transportable instrument (Scentinel®). A tandem mass spectrometer is mounted in a wheeled chassis together with all its ancillary equipment requiring only mains electricity, from a single power socket, or a generator, to operate. The software has also been greatly simplified to allow operation and interpretation by non-expert users. A vehicle-mounted system has now been deployed (Figure 5). This eliminates the need to remove exhibits from a crime scene for analysis and results in a vast increase in the speed with which results are obtained. This real-time sampling can be used, for example, to direct the course of an investigation when searching premises for drugs or explosives. The speed at which results can be reported also carries great value as scenarios can be presented to a suspect before they have time to think up a story/alibi. Although primarily a trace detection technique, TD-MS/MS can also assist in the analysis of bulk drug seizures. It is frequently necessary, for example, to establish that all the tablets in a particular batch contain ecstasy. Normally, a statistically significant proportion of the tablets would be selected, ground up, solvent extracted, cleaned up, filtered and diluted for analysis by GC/MS. Using TD-MS/MS, the surface of a tablet can be abraded with a toothpick, which can then be thermally desorbed without sample clean-up to establish the presence of the target compound. The savings in cost and time are enormous.

The detection of trace amounts of explosives on aircraft boarding passes has obvious analogies with the detection of drugs on paper money. Concomitant with forensic use, TD-MS/MS instruments have, therefore, been used in security applications. The high sensitivity and selectivity afforded by MS/MS gives it many advantages over other security screening devices such as X-ray scanners. For example, TD-MS/MS is currently believed to be the only technique that can reliably detect some of the peroxide explosives increasingly used in terrorist bombings.

The flexibility of TD-MS/MS, allied to its minimal method development time permits its rapid deployment for the detection of new threat compounds or materials, for example chemical or biological warfare agents.

Surprisingly, the analogy between banknotes and boarding passes extends to a "background" of aircraft passengers carrying traces of explosives. This includes "nuisance alarms" from people who have had legitimate contact with explosives through mining and military employment and people who use nitroglycerine for the treatment of heart conditions. Although such nuisance alarms can be inconvenient the alternative might be unimaginable.

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