Investigation of Surface-Assisted (SA) LDI-TOFMS for the Characterization of Organometallic and Coordination Compounds

David Thomas, Mark F. Wyatt, Bridget K. Stein and A. Gareth Brenton

EPSRC National Mass Spectrometry Service Centre (NMSSC), Swansea University, Swansea, SA2 8PP, U.K.

Overview

- Recent research has focussed on the use of MALDI-TOFMS to characterize organometallic/coordination/highly conjugated compounds.
- 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) matrix very effective for these compounds, with radical molecular ions observed.
- DCTB has low vacuum stability, so only a few samples can be prepared and analysed at a time. Additionally, sample preparation procedures are generally time consuming compared to other mass spectrometry techniques.
- Aim is to identify a surface that would emulate performance of DCTB matrix, while affording higher throughput of analyses.
- Six organometallic/coordination/highly conjugated compounds were studied and a range of metallic, oxide and carbon based surfaces were investigated.
- No surface matched DCTB for quality of data. A compromise between data quality and speed of analysis may be unavoidable.
- 3 x 0.2 µL layer spotting technique achieved better quality data than 1 µL spot of the same sample solution.

Introduction

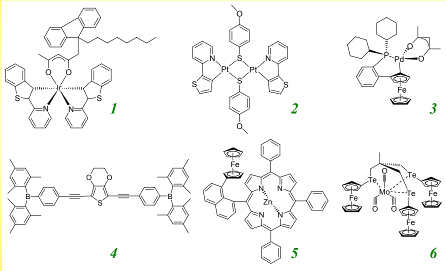
MALDI-TOFMS is a very powerful analytical technique, which can be applied to a wide range of samples classes. Generally, sample preparation involves dissolution of the sample and the matrix, preferably in the same solvent. The solutions are mixed, with the matrix in large excess; then 0.5-1 µL is placed onto a sample plate. The solvent evaporates to leave a layer of co-crystallised sample and matrix. Certain samples, such as those containing metals or a high degree of conjugation, are, in general, observed as radical ions; they have lost (or gained) an electron. Such samples constitute a considerable proportion of those received at the NMSSC, and previous work has shown the matrix DCTB to be highly effective.[1]

However, the sample preparation procedure as described above is very time consuming. In addition, the DCTB matrix sublimes relatively quickly in the vacuum of the instrument, so only a few samples may be prepared at a time. Replacement of the matrix by a suitable surface, *i.e.* one that promotes the generation of radical ions, while maintaining the quality of the data obtained, would speed up sample preparation and analysis, leading to improved laboratory efficiency and the possibility of automated analysis. Initially, compounds that are known to work by traditional preparation methods will be tested until we have a proven methodology, which can then be applied to the samples that require it.

Materials and Instrumentation

- DCTB matrix purchased from Fluka (U.K.).
- HPLC-grade dichloromethane purchased from Fisher (U.K.).
- MALDI-TOFMS measurements obtained with a Voyager DE-STR instrument (Applied Biosystems, U.S.A.).
- Gold and stainless-steel target plates purchased from Applied Biosystems.
- Copper, brass, nickel and aluminium sheet purchased from Goodfellows (U.K.).
- Quickmass™ sample slides (Nanohorizons, U.S.A.) kindly donated by Rachel Martin (Shimadzu, U.K.).
- Magnesium (Mg) ribbon purchased from Sigma-Aldrich (U.K.).
- Samples submitted to the NMSSC by:
  - *1* N. R. Evans and A. B. Holmes, University of Cambridge, U.K.
  - *2* J. Weinstein, University of Nottingham, U.K.
  - *3* J. Amin and C. J. Richards, Queen Mary, University of London, U.K.
  - *4* J. C. Collings and T. B. Marder, University of Durham, U.K.
  - *5* P. J. Scaife and A. N. Cammidge, University of East Anglia, U.K.
  - *6* S. Jing and C. P. Morley, Swansea University, U.K.
- 6B and 8B Staedtler pencils purchased from WHSmiths (U.K.).

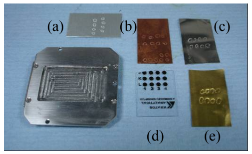
Samples



1 *2* *3* *4* *5* *6*

Surfaces and Sample Plate Modification

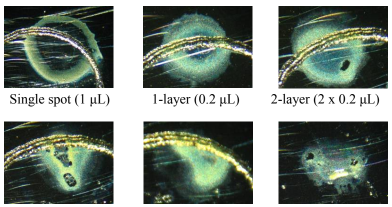
- Gold and stainless steel welled sample plates were used as received.
- Blank stainless steel plate had a recess machined into it to accommodate metal sheets and Quickmass™ slides, which were secured with tape.



(a) Aluminium
(b) Copper
(c) Nickel
(d) Quickmass™
(e) Brass

- MgO surface was created by smoking; Mg ribbon was ignited and waved below the inverted plate.
- Carbon surface was created by rubbing the pencil onto plate.[2]

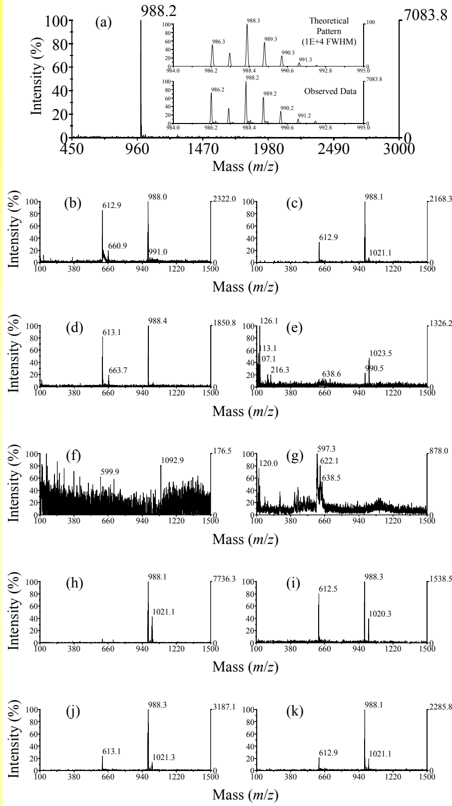
Sample Deposition



Single spot (1 µL) | 1-layer (0.2 µL) | 2-layer (2 x 0.2 µL) | 3-layer (3 x 0.2 µL) | 4-layer (4 x 0.2 µL) | 5-layer (5 x 0.2 µL)

- Larger volume (1 µL) single spot dried to leave an outer ring of sample.
- Multiply spotted layers of a smaller volume (0.2 µL) dried to leave a more homogeneous layer of sample.
- Increases in quality of data were observed when going from the single spot to the 3-layer spot.
- No further increases in quality of data were observed when going from the 3-layer spot to the 5-layer spot.

Results for *1* with 3-layer prep. ($M^{+\bullet}$ = *m/z* 988.3)



(a) DCTB matrix
(b) Gold surface
(c) Stainless steel surface
(d) Aluminium surface
(e) Copper surface
(f) Nickel surface
(g) Brass surface
(h) 6B pencil surface
(i) 8B pencil surface
(j) Quickmass™ surface
(k) MgO surface

- A similar trend of results was observed for sample *4*.
- Low intensity radical molecular ions were observed for samples *2*, *3* and *5* on the gold, stainless steel, aluminium, Quickmass™ and pencil surfaces.
- A radical molecular ion was only observed for sample *6* with DCTB.
- No radical molecular ions were observed for any of the samples in negative ion mode.

Observations and Discussion

- The observation of radical molecular ions compares favorably with data from other LDI-MS studies of organometallic and coordination compounds.
- Radical molecular ions have also been observed for transition metal phenanthroline and bypyridine compounds,[3] while only metal adduct ions have been observed for a range of transition metal acetylacetonate complexes.[4,5]
- Charge-transfer mechanism:[6] Matrix$^{+\bullet}$ + Analyte → Matrix + Analyte$^{+\bullet}$ occurs if the ionization energy of the matrix is greater than that of the analyte.
- The work function of a surface is approximately half the ionization energy, so the surfaces studied are comparable with DCTB matrix.
- The results obtained do not follow the order for the surface work functions; *e.g.* higher quality data was obtained for the carbon surface over the copper surface, even though copper has the higher work function.
- Impurities in the pencil lead will result in a lower work function than that of pure carbon.
- Vastly different results observed when the surface was the only variable, so the properties of a surface do affect the desorption/ionization process.
- No surface matched DCTB for quality of data, but sample characterization was still achieved from several surfaces, and a compromise between data quality and speed of analysis may be acceptable, possibly unavoidable.
- The 3-layer spotting technique led to a thicker sample layer and higher quality of data compared to when a larger amount of sample was deposited.
- This thicker layer could reduce electron emission from the substrate surface, resulting in higher signal intensities.[7]
- The MgO surface was dusty/powdery and rapidly (after 12 analyses) contaminated the source region and extraction grid.

Conclusions and Future Work

- No surface matched DCTB for quality of data. A compromise between data quality and speed of analysis may be unavoidable.
- 3 x 0.2 µL layer spotting technique achieved better quality data than 1 µL spot of the same sample solution.
- The properties of a surface do affect the desorption/ionization process, but the observed data could not be related to the work function of a surface.
- The effects of sample concentration will be explored.
- Copper oxide, titanium oxide and titanium nitrate are some of the surfaces still to be investigated. These dusty/powdery surfaces will have to immobilised to prevent the rapid contamination of the source region and extraction grid.

References

1. Wyatt, M. F.; Stein, B. K.; Brenton, A. G. *Anal. Chem.* **2006**, *78*, 199-206.
2. Black, C.; Poile, C.; Langley, J.; Herniman, J. *Rapid Commun. Mass Spectrom.* **2006**, *20*, 1053-1060.
3. Balasanmugam, K.; Day, R. J.; Hercules, D. M. *Inorg. Chem.* **1985**, *24*, 4477-4483.
4. Pierce, J. L.; Busch, K. L.; Cooks, R. G.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 2597-2602.
5. Rholy, K. E.; Heffren, J. S.; Douglas, B.E. *Org. Mass Spectrom.* **1984**, *19*, 398-402.
6. McCarley, T. D.; McCarley, R. L.; Limbach, P. A. *Anal. Chem.* **1998**, *70*, 4376-4379.
7. Knochenmuss, R. *Anal. Chem.* **2004**, *76*, 3179-3184.