

Further Applications of NALDI-TOFMS

Mark F. Wyatt,¹ Shujing Ding,¹ Bridget K. Stein,¹ A. Gareth Brenton,¹ R. Hugh Daniels,² and Christopher M. Williams¹

¹EPSRC National Mass Spectrometry Service Centre (NMSSC), Institute of Mass Spectrometry, School of Medicine, Swansea University, Singleton Park, Swansea SA2 8PP, U.K.

²Nanosys Inc., 2625 Hanover Street, Palo Alto, CA 94304, U.S.A.

Summary

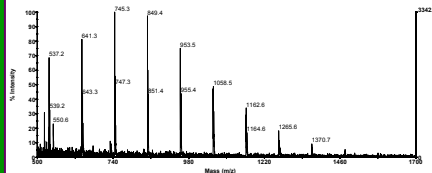
- Non-polar compounds and metal complexes have been analysed using NALDI technology.
- NALDI has greater sensitivity than MALDI.
- Porphyrins can be observed as $[M + H]^+$, M^{2+} or M^{+} species depending upon compound functionality.
- Polymers may be cationised.
- NALDI may out-perform other mass spectrometry techniques.
- More fragmentation may occur with NALDI compared to MALDI.

Introduction & Current Study

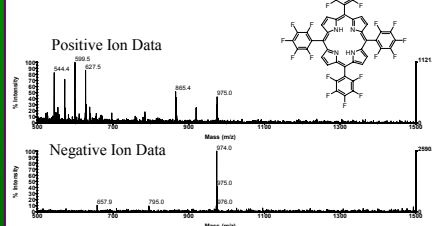
- Nanotechnology-assisted laser desorption/ionisation time-of-flight mass spectrometry (NALDI-TOFMS)^{1,2} is an important new analytical technique, which has the advantage over MALDI of not requiring a matrix.
- The sample is deposited directly onto the plate, saving analyst time.
- The nanostructured silicon surface³ has an upper mass limit of approximately 2000 Da, and the NALDI plates were designed with relatively small, polar, organic molecules in mind.
- The full capability of this technology can be explored with the variety of samples received at the NMSSC, and our collaborative studies have focused on non-polar molecules and metal complexes.
- Data was acquired using an Applied Biosystems Voyager DE-STR spectrometer, operated in positive and negative ion, reflectron mode.
- The NALDI plates fit directly into the Opti-ToF holder.
- A range of samples were analysed by NALDI, and comparisons are made with data acquired by MALDI, EIC/CI and ESI.

Polymers

- A mixture of polystyrene (MW=600) and $Cu(NO_3)_2$ leads to the observation of a copper cationised polymer series.

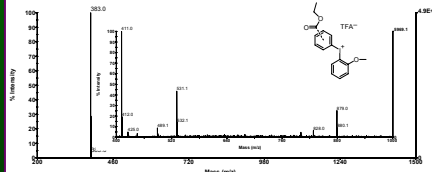


Fluorinated Porphyrin



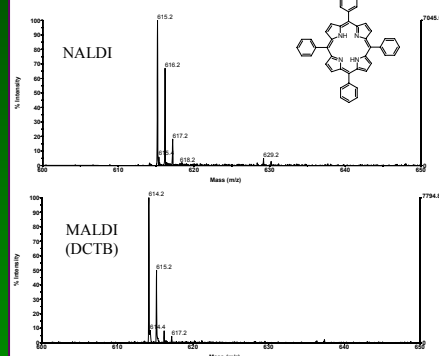
- Greater intensity M^{2-} species observed compared to M^{+} .

Hypervalent Iodide Compounds



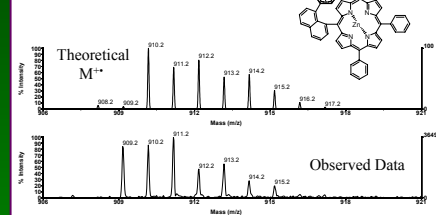
- Very intense monomer (m/z 383) observed for ortho isomer.
- Very low intensity dimer (m/z 879) observed with increased laser power.
- Similar NALDI data observed for meta and para isomers.
- Dimer only observed for meta and para isomers with MALDI (DCTB) and ESI.

Free-base Porphyrins



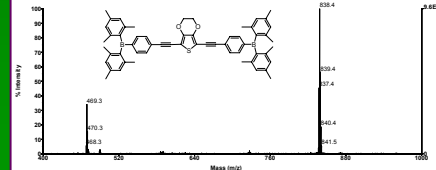
- $[M + H]^+$ observed with NALDI, compared to M^{2+} usually observed with MALDI (DCTB).
- NALDI can show 1000 times greater sensitivity than MALDI; data acquired for a 10amol/μL of this sample.

Metal-porphyrin Complex

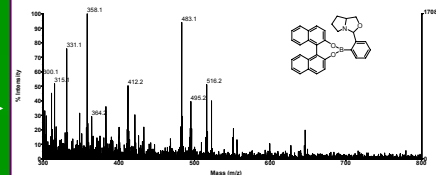


- A mixture of the $[M - H]^+$ and M^{2+} species were observed in NALDI.
- A metal atom is complexed within the cavity of the porphyrin and this may be preventing the formation of the $[M + H]^+$ species.

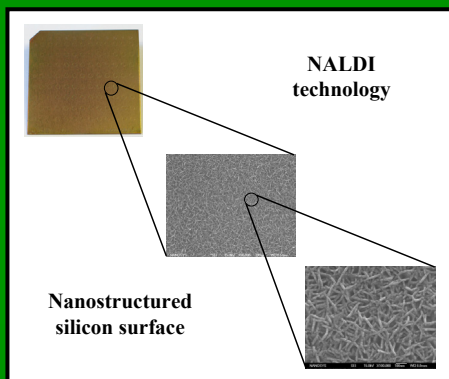
Boron Compounds



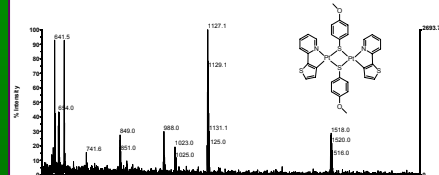
- Fragmentation observed with NALDI, compared to only M^{2+} (m/z 838) observed with MALDI (DCTB).



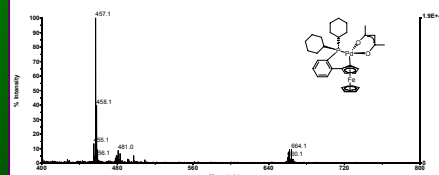
- Low intensity M^{2+} (m/z 483) species observed.
- NALDI data is higher quality than MALDI (DHB) data, comparable to ESI data, and slightly lower quality than EIC/CI data.



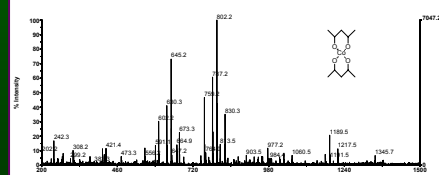
Organometallic/Coordination Compounds



- Several species observed with NALDI, compared to only M^{2+} (m/z 988) observed with MALDI (DCTB).



- Fragmentation observed with NALDI, compared to only M^{2+} (m/z 664) observed with MALDI (DCTB).



- Very complex spectrum observed for an apparently simple compound.
- NALDI data is identical to MALDI (DCTB) data.

Conclusions and Future Work

- High quality data can be acquired for non-polar compounds and metal complexes using NALDI technology.
- NALDI has greater sensitivity than MALDI; at least 1000 times more for two porphyrin compounds.
- Porphyrins can be observed as $[M + H]^+$, M^{2+} or M^{+} species depending upon compound specific functionality.
- Polymers may be cationised; a salt will usually be required.
- NALDI may out-perform other mass spectrometry techniques, but more compounds must be characterised to fully evaluate capabilities of the technology.
- More fragmentation may occur with NALDI compared to MALDI; extra structural information is provided.
- Boronic, sulphonic and carboxylic acid compounds, and fullerenes were attempted in negative ion mode; only background ions were observed.

Acknowledgements

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References

1. "CA-NALDI™: Rapid One-Step Small Molecule Analysis"; corporate poster no.1 presented at the 54th American Society for Mass Spectrometry (ASMS) Conference in Seattle WA, USA, 2006.
2. "CA-NALDI™: Rapid One-Step Small Molecule Analysis"; corporate poster no.2 presented at the 54th American Society for Mass Spectrometry (ASMS) Conference in Seattle WA, USA, 2006.
3. E. P. Go, J. V. Apon, G. Luo, A. Saghatelian, R. H. Daniels, V. Sahi, R. Dubrow, B. F. Cravatt, A. Vertes, and G. Siuzdak *Analytical Chemistry*, 2005, 77, 1641-1646.