Results for Radical Ions by MALDI-TOFMS

Mark F. Wyatt,† Suzanna D. Kean,‡ Bridget K. Stein† and A. Gareth Brenton†

 EPSRC National Mass Spectrometry Service Centre (NMSSC), School of Medicine,† and School of Engineering,‡ Swansea University, Swansea, SA2 8PP, U.K.

Overview

Recent research has focussed on the use of MALDI-TOFMS to characterise organometallic/coordination/highly conjugated compounds. Recent investigations showed that greater accuracy is achieved when radical ions are calibrated with radical ion standards, and that a general benchmark of ±5 ppm accuracy could be realised.

Porphyrazine-based standards have been identified and accurate mass measurements were made for five analytes; mean mass accuracy errors ranged from 0.1–1.7 ppm and all measurements had ±5 ppm accuracy.

Technique is especially useful for instances when only MALDI ionises an analyte or when MALDI is the only ionisation mode available.

Introduction

Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOFMS) is a very powerful analytical technique, which can be applied to a wide range of sample classes, including organometallic, coordination, and highly conjugated compounds. Such samples constitute a considerable proportion of those received at the NMSSC and are, in general, observed as radical ions; they have lost (or gained) an electron. Previous work has shown that the matrix DCTB to be highly effective.1

Accurate mass measurement increases the certainty of analyte identification, and background literature and general operational guidelines are available.2,3 At the NMSSC, computer-assisted peak matching on a magnetic sector instrument with an electrospray (ESI) source4 is preferred for the wide range of samples received. Alternative sources are used where ESI is not appropriate, and while these systems generally give excellent results, some samples specifically require MALDI ionisation.

However, a method needed to be developed for accurate mass measurement of radical ions by MALDI-TOFMS. Initial studies showed that greater accuracy is achieved when radical ions are calibrated with radical ion standards.5 Tetradeuterated porphyrins were identified as potential calibration standards and used in this study to measure five compounds that had previously been measured by peak matching. Here we present a proven methodology, which can be applied to samples that require a MALDI source or when MALDI is the only technique available.

Materials and Instrumentation

- DCTB, 5,10,15,20-tetratetraphenylporphyrin (Standard 1), boron trifluoride diethyl etherate, and tetrachloro-2-methoxy-4-nitrochlorobenzene were purchased from Fluka (U.K.).
- DIME-deuterium dichloromethane was purchased from Fisher (U.K.).
- 5,10,15,20-tetra-4-methylphosphorylporphyrin (Standard 2), 4-ethylbenzaldheyde, and 4-isopropylbenzaldheyde were purchased from Sigma-Aldrich (U.K.).
- Pyrrole was purchased from Acros (U.K.).
- Samples were submitted to the NMSSC by: J. S. C. Jha and R. W. Boyle, University of Hull, U.K.
- J. P. J. Scalise and A. N. Cammidge, University of East Anglia, U.K.
- J. C. Collings and T. B. M. R. Dermer, Durham University, U.K.
- J. Amin and C. J. Richards, Queen Mary, University of London, U.K.

- MALDI-TOFMS measurements were acquired with a Voyager DE-STR instrument (Applied Biosystems, U.S.A.). Data were acquired using positive ion, reflection mode. Delay time = 100 ns; acceleration voltage = 20 kV, and grid voltage = 65.5 V. Every acquisition was an accumulation of 2 × 25 laser shots, and the laser power was optimised for each.

Accurate Mass Measurement

- Five measurements were made on four separate days.

Results for 1

- Intensity of the m/z 774.5 ion was insufficient for accurate measurement.

Results for 4

- Initial characterisation provided a good isotope distribution match.

Results for 5

- Initial characterisation provided a good isotope distribution match.

Conclusions

Porphyrazine-based calibration standards have been used for the accurate mass measurement of radical ions by MALDI-TOFMS.

Mean mass accuracy errors ranged from 0.1–1.7 ppm and all individual measurements had ±5 ppm accuracy.

Extra care must be taken when accurately measuring ions which do not comprise the lowest mass isotope of all elements in the species.

References