

EPSRC National Mass Spectrometry Centre, Swansea

Application Note No 5

Application of solvent-free preparation methods for the analysis of organometallic and coordination complexes by MALDI-TOFMS

by M.F. Wyatt, EPSRC National Mass Spectrometry Service Centre (NMSSC), Swansea University, SA2 8PP, UK
<http://www.swan.ac.uk/nmssc/>

Introduction

Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) is an important and successful analytical technique for a wide variety of compounds. A traditional dried-droplet sample preparation technique relies on sample and matrix combinations that are soluble in the same volatile solvent or miscible solvents. However, many samples submitted to our Centre are insoluble or only soluble in less volatile solvents *e.g.* dimethyl sulphoxide. Development of a solvent-free MALDI method would complement other solvent-free ionisation techniques, offering a softer method of ionisation, and allowing analysis of compounds not suited to these other techniques.

Previous work in this area has focussed mainly on synthetic polymers,^{1,2} but has also been applied to biochemical samples.^{3,4} Preliminary investigations into the analysis of various first-row transition metal acetylacetonate complexes using assorted literature and NMSSC solvent-free methods were summarised in a recent conference poster.⁵

The preparation method of ball-milling the sample and matrix mixture, followed by 'smearing' onto the target plate,⁶ including our own variations,⁵ is evaluated here for vanadium (III) acetylacetonate ($V(acac)_3$), in order to establish a reliable protocol. In addition, two insoluble samples submitted to the NMSSC are examined as case studies.

Experimental methodology

Chemicals

$V(acac)_3$, 2,3,4,5,6-pentafluorobenzoic acid (PFBA), and 2,3,4,5,6-pentafluorocinnamic acid (PFCA) were purchased from Sigma-Aldrich. 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) was purchased from Fluka.

MALDI Sample Preparation

For $V(acac)_3$, 0.1, 0.2, 0.5, and 1 mg were added to both tapered plastic and flat-bottomed glass sample vials. 10 mg of DCTB matrix was added to each vial. One 3 mm steel ball was added to the plastic vials (Method *A*), and two balls to the glass vials (Method *B*).

Each vial was agitated for 4×15 seconds to ensure complete homogenisation, using a vortex mixer.

TIP! After each round of mixing, dislodge material from vial crevices with a thin, stiff object *i.e.* a straightened paperclip.

A small amount of loose material from each vial was then placed onto a stainless steel sample plate and smeared with the flat side of a microspatula. Material stuck to the ball from the plastic vials (Method *C*) was dabbed onto the plate and then smeared.

TIP! Use gentle pressure and a circular motion to smear until no loose powder remains.

For Case Study 1, 1 mg was mixed with 10 mg of DCTB matrix. For Case Study 2, 0.3 mg was mixed with 10 mg each of DCTB, PFBA, and PFCA matrices. Method *B* was followed for all case study preparations.

Mass Spectrometry

MALDI-TOFMS spectra were acquired using an Applied Biosystems Voyager DE-STR spectrometer (Framingham, MA, USA), which is equipped with a nitrogen laser ($\lambda = 337$ nm). The instrument was operated in positive and negative ion, reflectron mode. The accelerating voltage was 20 kV, while the grid voltage was maintained at 65.5 %. The delay time and laser fluence were optimised for each sample, but were kept constant for all data acquisitions for the $V(acac)_3$ complex.

Results and discussion

$V(acac)_3$

The positive ion MALDI-TOFMS data for the various preparations of $V(acac)_3$ are given in Table 1. Radical ions for the sample (m/z 348.1) were observed for all preparations, showing that for a range of sample loadings, any milling method, and method of sampling each mixture for analysis, may be viable. The relative intensities of ions were fairly consistent between preparations with identical sample amounts. However, the total ion count fluctuated randomly between all preparations, despite every acquisition parameter remaining constant. Re-analysis of the prepared plate revealed that a large increase in ion count and improvement in signal-to-noise ratio was observed when the laser was aimed at more translucent areas of the preparation, compared to opaque, powdery areas. This is a strange result, as translucent areas for a dried-droplet preparation usually indicate a low sample-to-

matrix ratio. It is clear that the smearing stage of the preparation is more critical than the milling stage.

Preparation Method	Sample (mg)	Relative Intensity (%)	
		V(acac) ₃ (M ⁺⁺)	DCTB (M ⁺⁺)
A	0.1	16	100
	0.2	46	100
	0.5	100	43
	1	100	9
B	0.1	30	100
	0.2	45	100
	0.5	84	37
	1	100	27
C	0.1	6	100
	0.2	23	100
	0.5	92	100
	1	100	40

Table 1. Positive ion MALDI-TOFMS data for various preparations of V(acac)₃ with DCTB.

Case Study 1

This sample was ferrocene fully substituted with mercury acetate groups. The data (see Figure 1) is very low intensity, but is sufficient for the major species to be identified. Positive radical ions for the fully substituted compound were observed at m/z 2771.7. The species at m/z 2255.8 and 2513.8 correspond to radical ions for compounds containing eight and nine mercury acetate groups respectively. These are not fragments, as the extra hydrogen is accounted for in the isotope patterns. The low mass species do not contain iron or mercury isotopes.

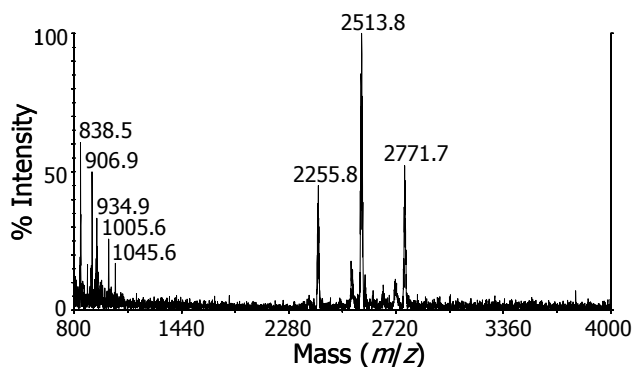


Figure 1. Positive ion MALDI-TOFMS spectrum for mercury acetate ferrocene compound with DCTB matrix.

Case Study 2

This sample was an erbium complex with three bis(pentafluorophenyl)phosphinate ligands (ErL₃). Only negative ions for the ligand were observed by the dried-droplet method with DCTB. However, a multitude of positive and negative species were observed up to m/z 6000 with the DCTB solvent-free method, suggesting oligomeric complexes. Two fluorinated matrices, PFBA and PFCA, were used, as they are more miscible with fluorinated samples.⁷ Spectra acquired with PFBA (see Figure 2) are much simpler to interpret, with an [Er₂L₅]⁺ species at m/z 2318.6 and an anticipated [ErL₄]⁻ species being observed. Similar results were observed with PFCA.

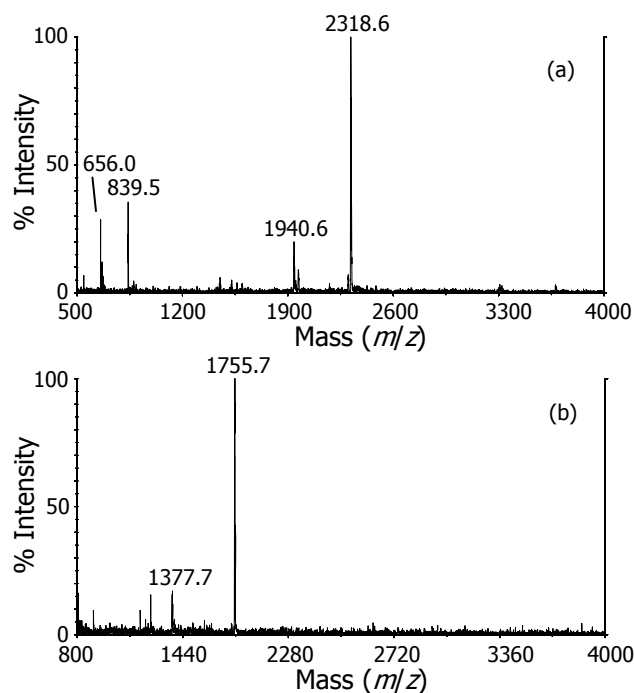


Figure 2. (a) Positive ion and (b) MALDI-TOFMS spectra for erbium bis(pentafluorophenyl)phosphinate compound with PFBA matrix.

Conclusions

Here we demonstrate that useful data can be acquired for insoluble organometallic and coordination complexes by MALDI-TOFMS via solvent-free preparation methods. The smearing technique of Hanton and Parees⁶ appears to be the critical step of such methods, and independent of the solids mixing route (A, B, or C).

References

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