應用手冊

Identification of Organometallic Compounds Using Field Desorption Ionization on the GCT

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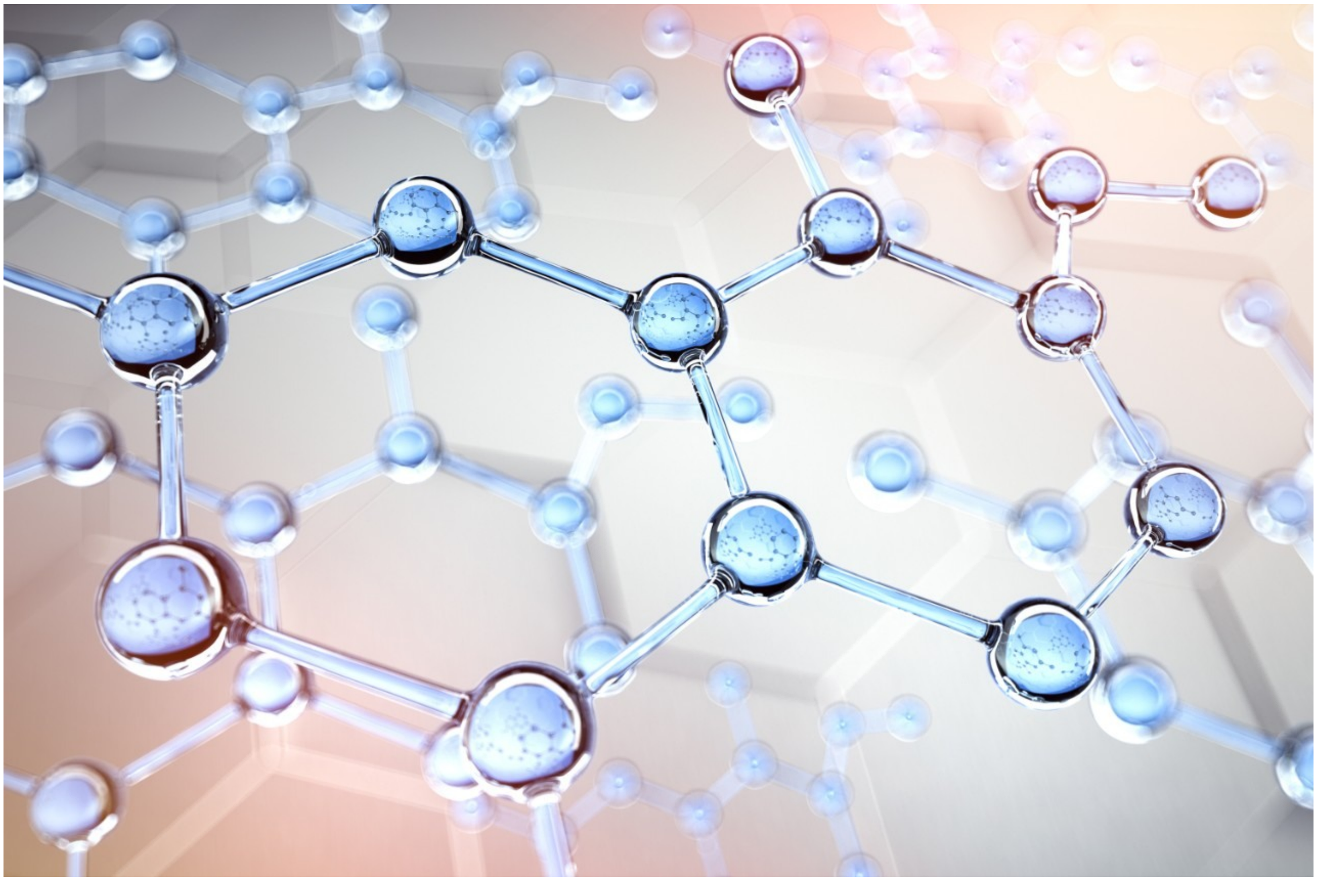

Abstract

Field Desorption is an established ionization technique which has been historically associated with magnetic

sector instruments. The technique provides a soft method of ionization for compounds that are nonvolatile yet thermally unstable preventing the formation of molecular ions from GC analysis or probe desorption. In this application note we will show that through the use of a Waters Micromass GCT (GC Time-of-Flight) Mass Spectrometer, compounds such as organometallics can be routinely analyzed to produce molecular ion distributions and exact mass data (regularly within the 5ppm publication criteria).

Introduction

Field Desorption (FD) is used primarily for the analysis of non-polar or thermally unstable compounds not amenable to other ionization modes. This ionization process is very soft, producing mainly molecular ions (M^+) with few fragment ions. In FD, the sample is loaded directly onto an FD emitter (typically 10 μm tungsten covered with carbon microneedles, dendrites). An electric current is passed through the emitter wire to raise its temperature. The emitter is placed in close proximity to a set of extraction electrodes held at high voltage (10-15 kV). This produces very high electric fields around the tips of the carbon dendrites. Under the influence of these fields, quantum tunneling of a valence electron from the molecule takes place to give an ion radical.

The analysis of organometallic complexes by mass spectrometry is particularly challenging. Due to the weak bonds around the coordination metal, molecular ion information is often absent. Using traditional ionization techniques such as EI^+(Electron Impact) and CI^+(Chemical Ionization), spectra are often dominated by lower mass fragmentation ions.

Traditionally, analysis has been completed using Fast Atom Bombardment (FAB) on a magnet sector instrument. However, FAB is becoming less routine due to the expense of purchasing and running a magnetic sector instrument. More recently, atmospheric ionization sources such as electrospray have been utilized. Certain solvents necessary to dissolve the organometallic can cause the dissociation of a ligand before the compound has been infused into the electrospray source.

In this application note, the analysis of an organometallic complex is described. Spectra from EI^+, CI^+, FI (Field Ionization), electrospray, and FD are shown for the organometallic complex illustrated in Figure 1. The routine exact mass measurement capability of the GCT is also demonstrated.

Waters Micromass GCT Mass Spectrometer.

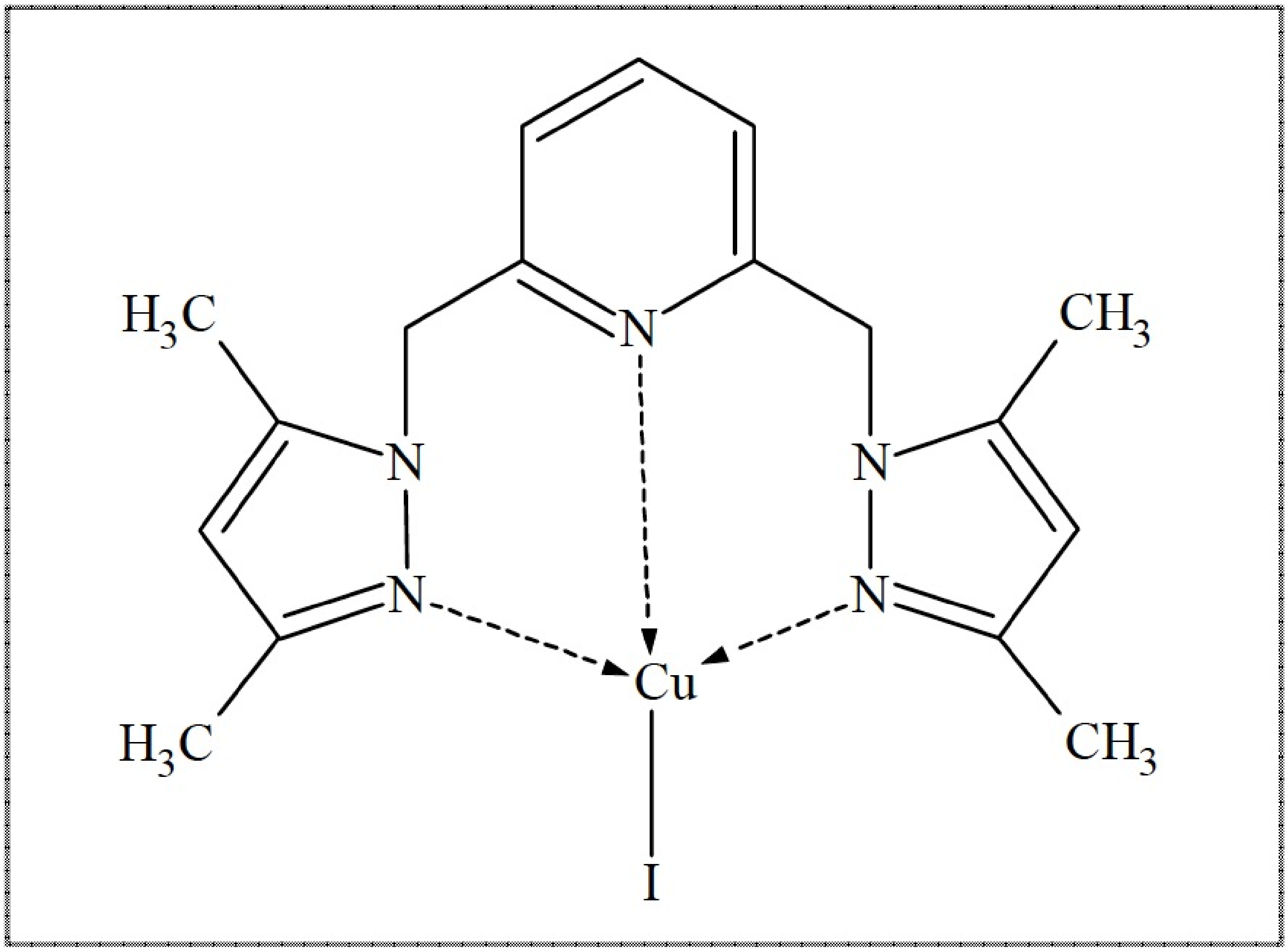

Figure 1. The structure of a specific organometallic molecule called “Organometallic A”.

Experimental

All of the samples were analyzed on a GCT MS instrument using either EI^+, CI^+, FI, or FD. Each sample was dissolved in dichloromethane (DCM) to yield a solution of approximately 1 mg/mL. Electrospray analysis of Organometallic A was completed on a Waters Micromass LCT Premier Mass Spectrometer.

Heated Probe

The samples analyzed by EI^+ and FI were introduced into the ion source via the solids probe lock and subjected to the following thermal gradient: 20 °C for 0.5 min., heated at a rate of 150 °C /min.to 650 °C with a hold time of 2 min.

Desorption Chemical ionization (DCI)

The samples analyzed by CI^+ were introduced into the chemical ionization source via the insertion probe lock and subjected to the following gradient. 0 A for 0.5 min., ramped to 1.5 A at a rate of 0.5 A/min. with a hold time of 2 min.

EI^+

The ion source was operated at 180 °C with an electron energy of 70 eV and a trap current of 250 µA. Spectra were acquired over an applicable mass range using an integration time of 0.45 s and a delay of 0.05 s (2 spectra/s).

A single point lock mass of 218.9856 Da (perfluorotributylamine) was infused into the ion source continuously during the analysis.

CI^+

The ion source was operated at 100 °C with an electron energy of 70 eV and an emission current of 100 µA. Spectra were acquired over an applicable mass range using an integration time of 0.95 s and a delay of 0.05 s (1 spectrum/s). The reagent gas used was methane at a source pressure of $2x10^{-4}$ mbar. A single point lock mass of 286.0027 Da (2,4,6-tris(trifluoromethyl)-1,3,5-triazine) was infused into the ion source continuously during the analysis.

FI^+

An extraction voltage of 12 kV was used with a flash off current of 6 µA during the acquisition delay. Spectra were acquired over an applicable mass range using an integration time of 1.2 s and a delay of 0.2 s. A single point lock mass of 201.9609 Da (chloropentafluorobenzene) was infused into the ion source continuously during the analysis.

Electrospray

The source temperature was set at 100 °C with a desolvation temperature of 150 °C and a desolvation gas flow of 150 mL/min. The capillary voltage was 2500 V, while the cone voltage was 30 V. Spectra were acquired over an applicable mass range using an integration time of 1.0 s and a delay of 0.1 s. A single point lock mass of 556.2771 Da (leucineenkephalin) was infused into the ion source continuously during the analysis.

FD

An extraction voltage of 12 kV was used with the emitter current being manually ramped to desorb the sample from the emitter surface. Spectra were acquired over an applicable mass range using an integration time of 1.2 s and a delay of 0.2 s for all of the FD experiments. A single point lock mass of 58.0419 Da (acetone) was infused into the ion source continuously during the sample analysis.

Results and Discussion

Figures 2 through 6 illustrate the mass spectra of Organometallic A analyzed by different methods of ionization. Table 1 provides exact mass information including the measured and expected mass, the mass error and the elemental composition of the significant ions within the spectrum.

The EI$^+$ spectrum (Figure 2) shows the organic ligand, 295.1808 Da with an exact mass error of 3.9 ppm, in addition to a number of fragment ions.

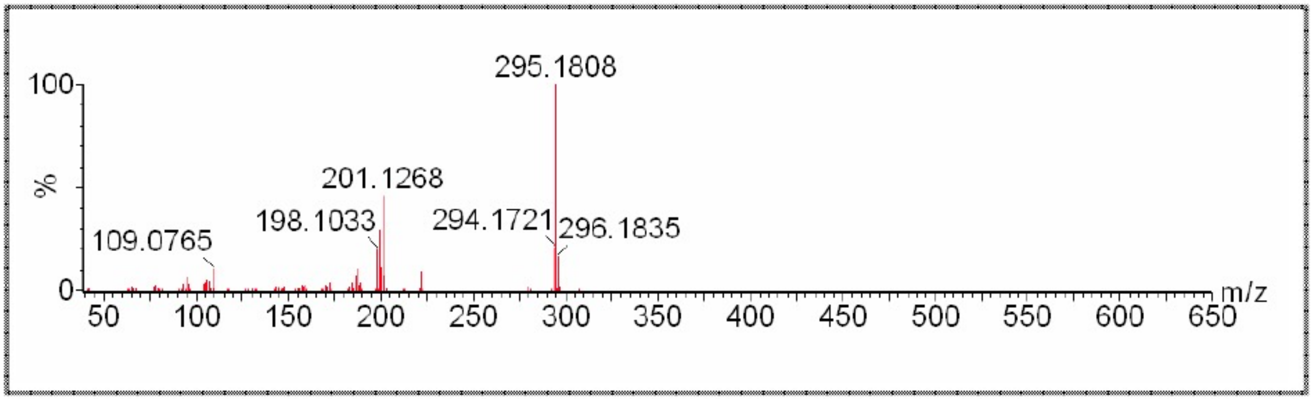

Figure 2. EI$^+$ spectrum of Organometallic A.

The CI$^+$ spectrum (Figure 3) contains both a protonated adduct and $(C_2H_5)^+$adduct, confirming the organic ligand structure.

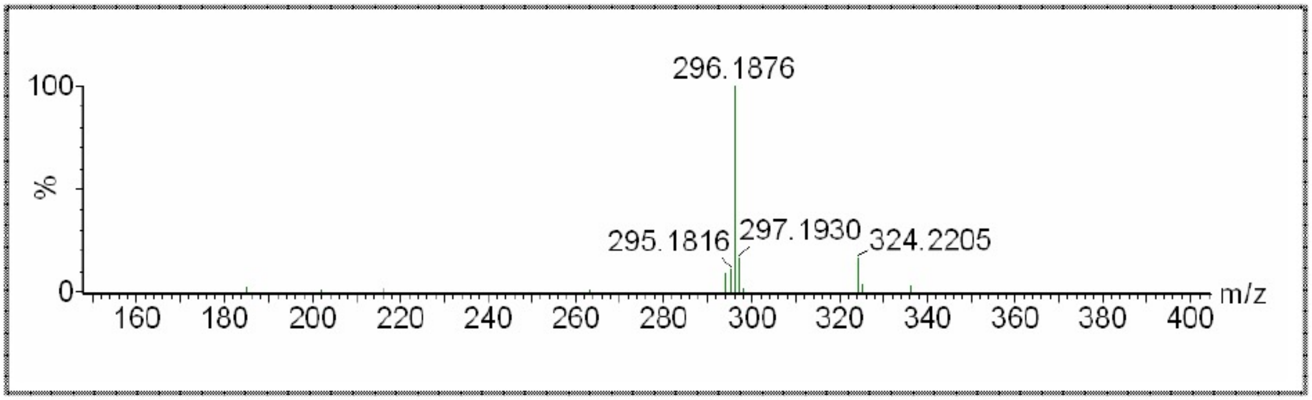

Figure 3. CI$^+$ spectrum of Organometallic A.

FI+ (Figure 4) also produces the organic ligand, suggesting that the thermal energy required to volatilize the compound causes the molecule to fragment prior to reaching the ionization region.

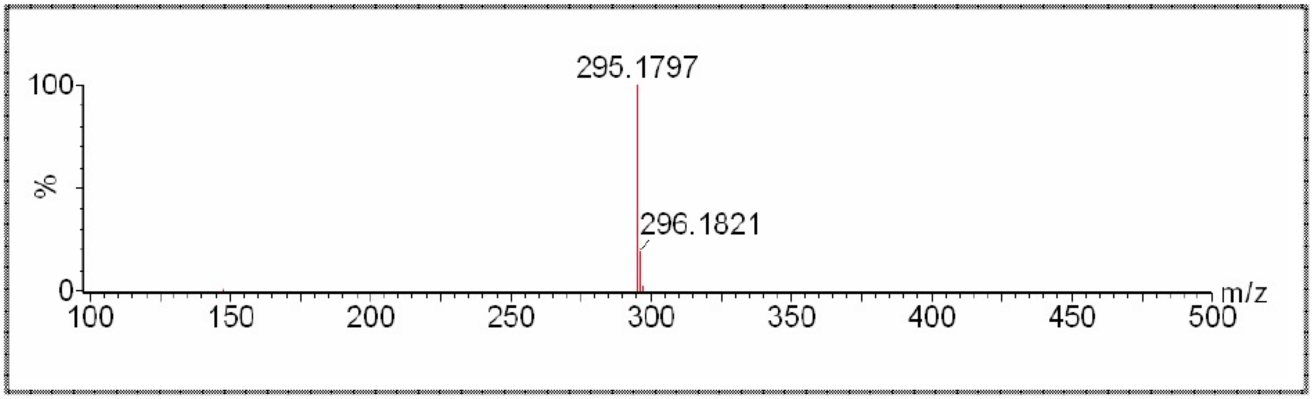

Figure 4. FI+ spectrum of Organometallic A.

Electrospray ionization (Figure 5) of this molecule is complicated by the fact that the compound is soluble in DCM while a protonating solvent is required for electrospray. The compound was therefore dissolved in DCM and diluted with methanol prior to infusion to a concentration of 200 pg/µL. No molecular ion is apparent (due to the solvent exchange requirements of the ionization technique) while a mass for the (M–I)+ fragment is observed at 358.1099 Da, an exact mass error of 1.7 ppm. A protonated fragment ion of the organic ligand is observed at 296.1861 Da with a sodiated adduct also seen at 318.1666 Da.

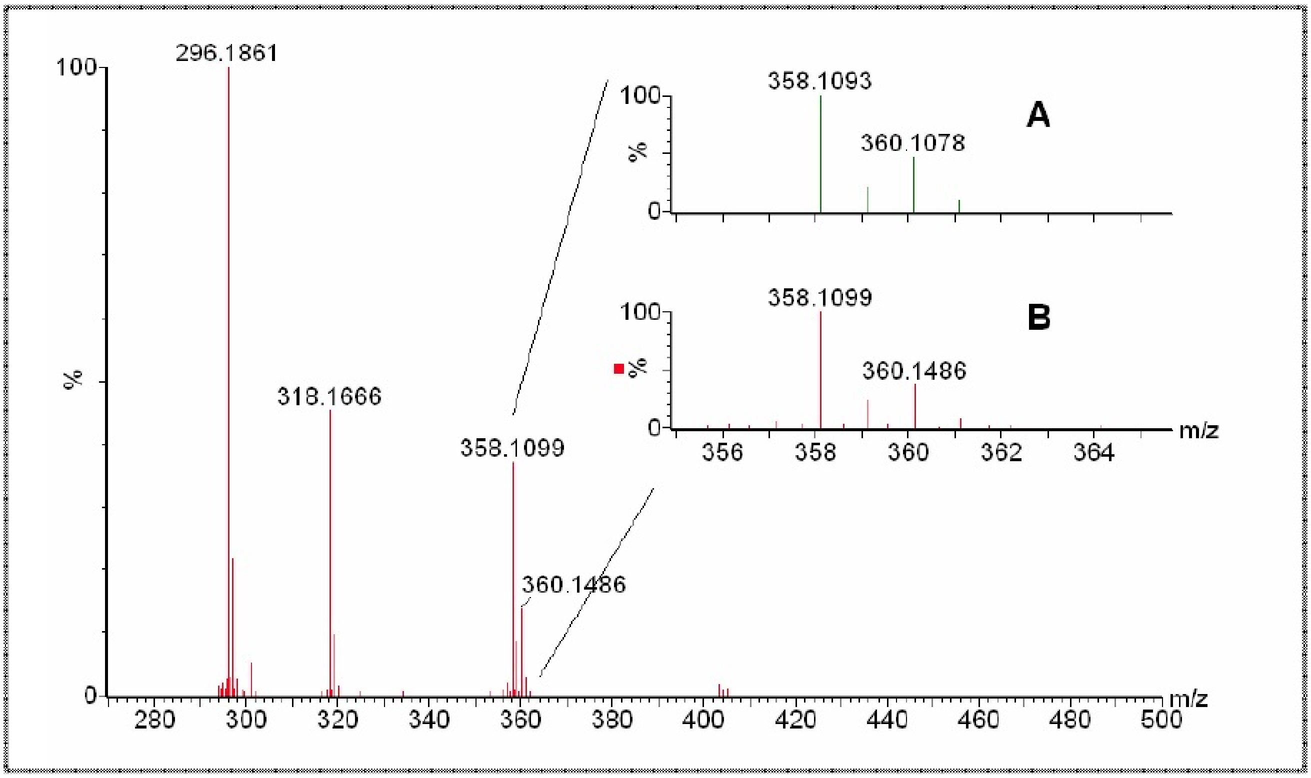

Figure 5. Electrospray spectrum (B) and isotope model (A) of Organometallic A.

The FD$^+$ spectrum (Figure 6) shows the molecular ion isotope pattern in addition to a number of fragment ions. Also illustrated is the isotope pattern expected for $C_{17}H_{21}N_5CuI$. The fragment ions observed include the loss of the iodine atom at 358 Da and the loss of copper from this fragment resulting in the 295 Da of the organic ligand seen in the EI$^+$ and FI$^+$ spectra.

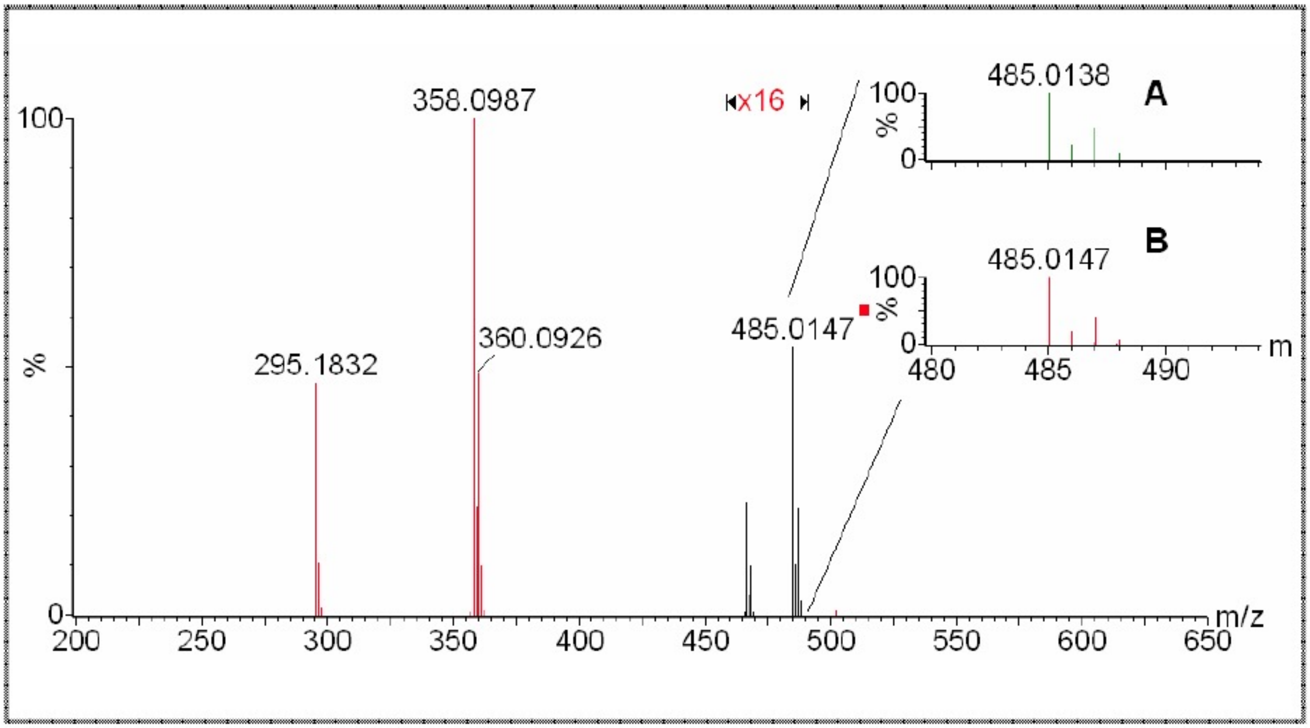

Figure 6. FD spectrum (B) and isotope model (A) of the molecular ion of Organometallic A.

A selection of mass spectra are provided for two of the organometallic compounds is described in Table 1. Also included is the isotope model for each compound under investigation. Figures 7 and 8 (FD Samples 1 and 4) illustrate an excellent molecular ion isotope pattern match for three different organometallic complexes.

Sample	Experimental exact mass (Da)	Calculated exact mass (Da)	Exact mass difference (mDa)	Exact mass difference (ppm)	Molecular ion formula
EI+	295.1808	295.1797	1.2	3.9	$C_{17}H_{21}N_5$
CI+	296.1876	296.1875	0.1	0.3	$(C_{17}H_{21}N_5+H)^+$
	324.2205	324.2188	1.7	5.2	$(C_{17}H_{21}N_5+C_2H_5)^+$
FI	295.1797	295.1797	0.0	0.0	$C_{17}H_{21}N_5$
Electrospray	358.1099	358.1093	0.6	1.7	$C_{17}H_{21}N_5{}^{63}Cu$
FD	485.0147	485.0138	0.9	1.9	$C_{17}H_{21}N_5{}^{63}CuI$

Table 1. Experimentally determined and calculated exact mass data of the high mass ions obtained using EI+, CI+, FI, and FD for Organometallic A.

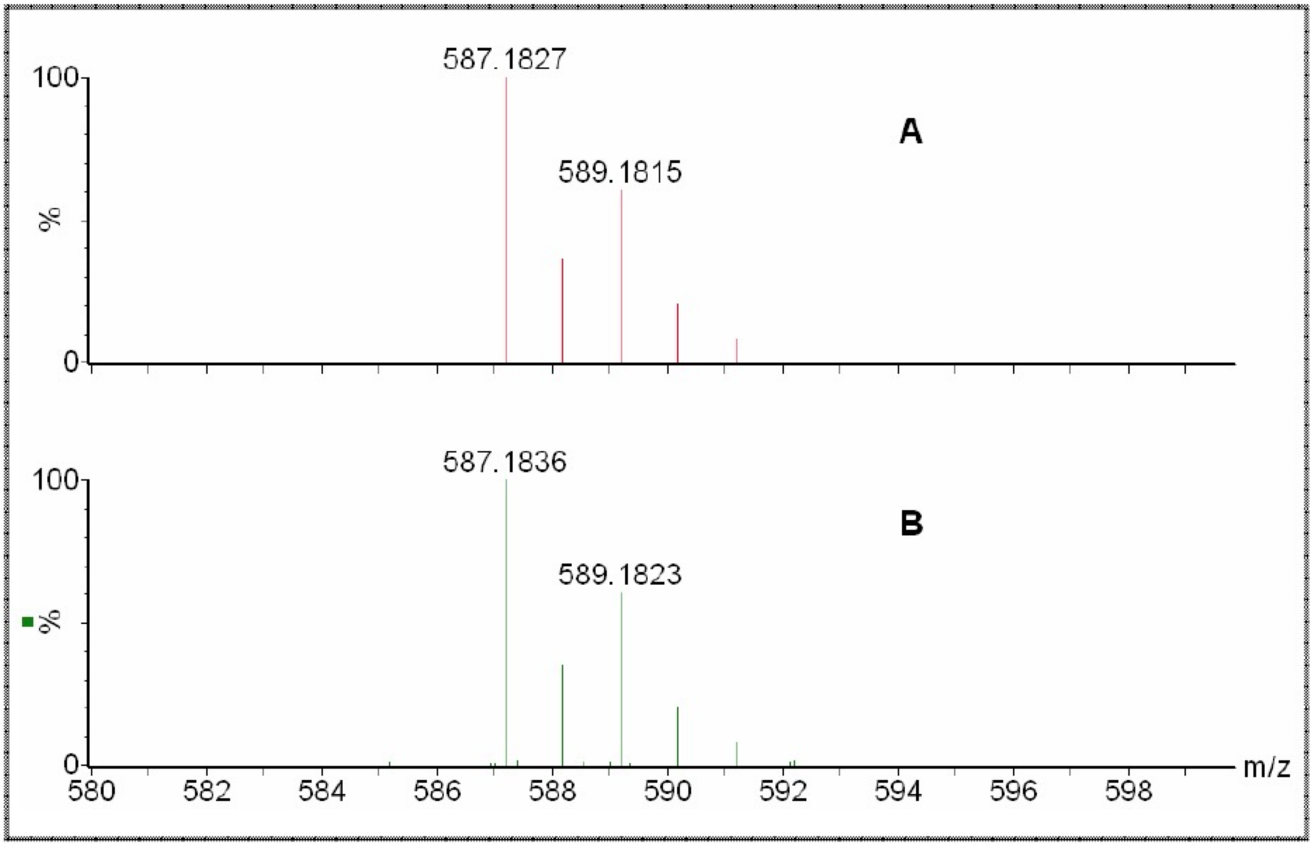

Figure 7. FD spectrum (B) and isotope model (A) of the molecular ion of organometallic Sample 1.

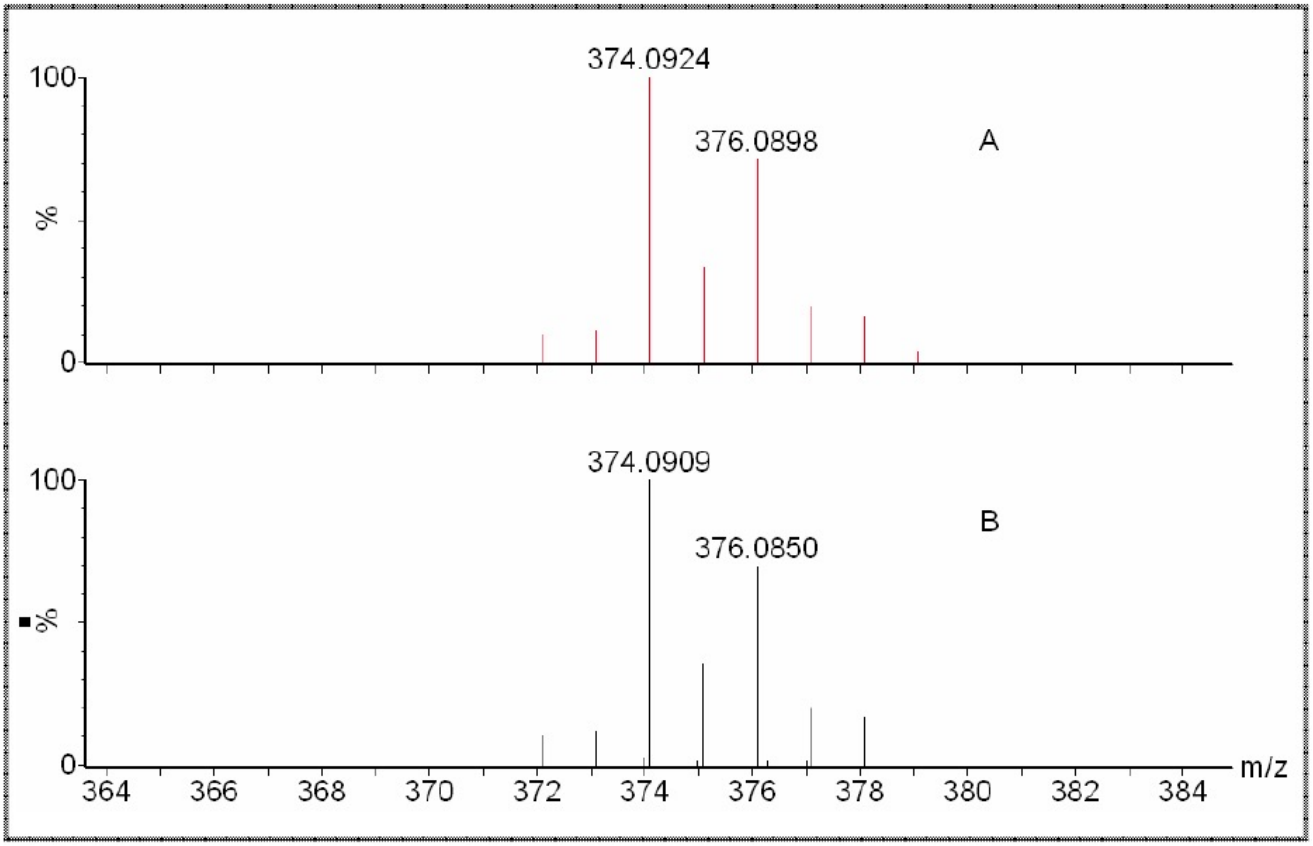

Figure 8. FD spectrum (B) and isotope model (A) of the molecular ion of organometallic Sample 4.

The expected and calculated masses for the molecular ions, as well as the exact mass error are provided in Table 2.

Sample	Experimental exact mass (Da)	Calculated exact mass (Da)	Exact mass difference (mDa)	Exact mass difference (ppm)	Molecular ion formula
FD Sample 1	587.1836	587.1827	0.9	1.5	$C_{30}H_{40}N_2O_2S_2{}^{63}Cu$
	589.1823	589.1809	1.4	2.4	$C_{30}H_{40}N_2O_2S_2{}^{65}Cu$
FD Sample 2	497.2204	497.2229	-2.5	-5.1	$C_{28}H_{38}N_2O_2{}^{63}Cu$
	499.2244	499.2211	3.3	6.6	$C_{28}H_{38}N_2O_2{}^{65}Cu$
FD Sample 3	682.1683	682.1707	-2.4	-3.6	$C_{36}H_{30}{}^{10}BN_8{}^{35}Cl{}^{63}Cu$
FD Sample 4	374.0909	374.0922	-1.3	-3.4	$C_{18}H_{26}N{}^{35}Cl_2{}^{48}Ti$

Table 2. Experimentally determined and calculated exact mass data of the molecular ions obtained using FD for a range of organometallic compounds.

Conclusion

With the analysis of Organometallic A, we were able to show that EI^+, CI^+, FI, and electrospray could only produce mass spectral information on fragments of the molecule. However, a molecular ion was obtained using FD. A selection of organometallic compounds were analyzed by FD on the Waters Micromass GCT Mass Spectrometer, showing the technique to be routine, obtaining molecular ion and exact mass information to confirm the identity of these thermally labile compounds. Additionally, the molecular ion isotope patterns were used to help confirm the elemental composition determined by theexact mass data.

Acknowledgment

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