Confirmation of the chemical formula of heat/light sensitive compounds using field desorption coupled with high-resolution mass spectrometry

Related product : Mass spectrometer (MS)

Introduction

Field desorption (FD) is a soft ionization technique useful for producing molecular ions in an MS ion source. The combination of high-resolution time-of-flight mass spectrometry (HRTOFMS) and FD is useful for direct MS measurement of a sample, and provides information for identifying the chemical formula of synthetic compounds and confirming the molecular weight. Since FD-HRMS vaporizes and ionizes a sample rapidly in a vacuum, and does not use a gas chromatograph, it has advantages for measuring unstable compounds, such as those sensitive to heat and light.

The FD emitter consists of carbon whiskers on a tungsten wire, and is inserted into the ion source using a probe. After coating the emitter with a sample solution and installing the probe to MS, FD measurement is performed by turning on the high voltage in the mass spectrometer. The most common method for coating the FD emitter is using a micro-syringe. This application note reports the syringe sampling procedure, and measurement results of example compounds that are sensitive to heat and light.

Measurement

Two bis(diazo) compounds sensitive to heat and light were measured. The corresponding chemical structures are shown in Figure 1. The sample was dissolved in tetrahydrofuran to concentration of 10 mg/mL (Sample solution).

Table 1 shows the details of the measurement conditions for FD-HRMS analysis. The sampling procedure and tools are illustrated in Figure 2.

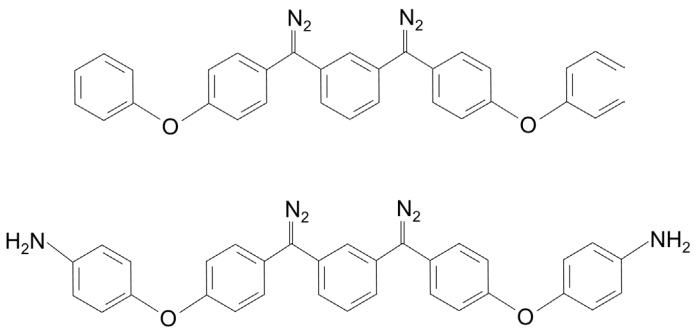


Figure 1. Chemical structures

Table 1. Measurement and analysis conditions

HRMS	
Sampling method	Syringe
Sample volume	4μL
TOFMS	JMS-T2000GC (JEOL)
Ionization	FD+ : -10 kV, 40 mA
Cathode voltage	-10 kV
Emitter current program	0 mA →25.6 mA/min →40 mA
Monitor ion range	*m/z* 35-1600

Sampling Procedure

1. Set the probe on the probe stand.
2. Pull up 4 μL of sample solution using the micro-syringe, and set the micro-syringe on the syringe stand.
3. Move the tip of the micro-syringe close to the emitter.
4. Push the plunger to make droplet of sample solution, then coat the emitter with the sample droplet.

Table 2. The features of syringe sampling with tool

Sampling operability	Requires familiarity with sampling
Sample volume	Approx. 4 μL/measurement
Merits	・Requires smaller sample volume ・Good for analytes in solvents with low boiling temperatures

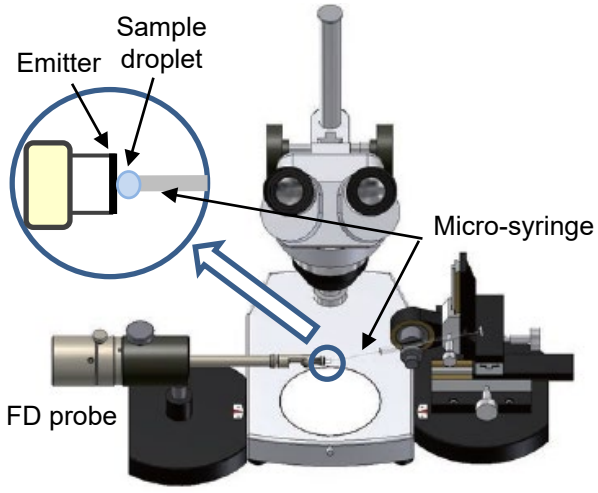
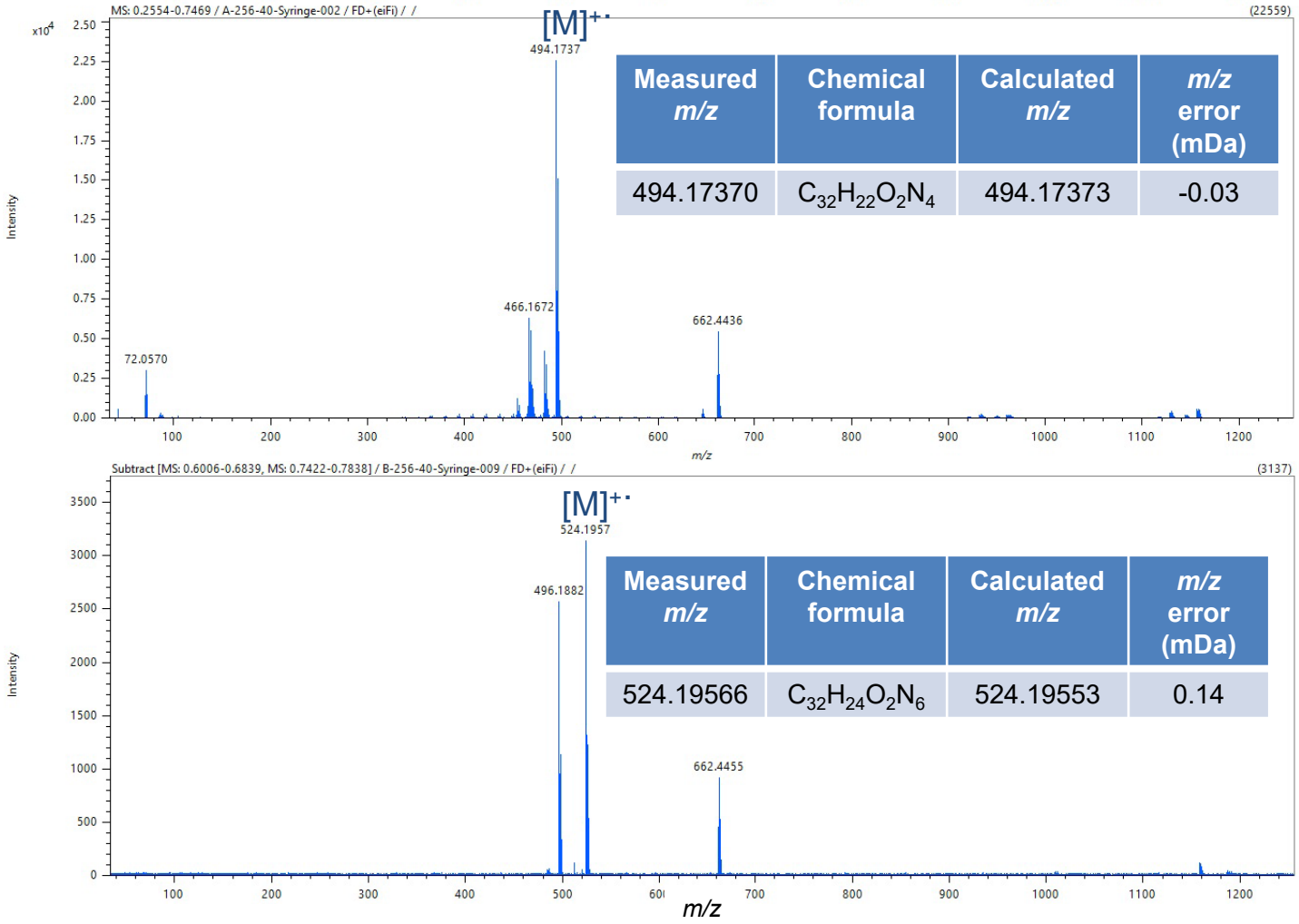


Figure 2. Scheme of syringe sampling tool

Result

FD-HRMS mass spectra were shown in Figure 3. The molecular ion $[M]^{+\cdot}$ was primary component detected from each sample. Some impurities or reacted compounds were also detected, though peak intensity was notably less than the molecular ion peak. The accuracy of the *m/z* measured for both molecular ions was less than 1 mDa of error.



Measured *m/z*	Chemical formula	Calculated *m/z*	*m/z* error (mDa)
494.17370	$C_{32}H_{22}O_2N_4$	494.17373	-0.03

Measured *m/z*	Chemical formula	Calculated *m/z*	*m/z* error (mDa)
524.19566	$C_{32}H_{24}O_2N_6$	524.19553	0.14

Figure 3. FD mass spectra and estimated chemical formulae calculated from the exact mass of the molecular ions

The advantages of the syringe-sampling method are shown in Table 2. Although the method requires some familiarity with the sampling operation, only a small sample volume is required, because it can be dispensed with a micro-syringe. The method can also result in less contamination at the emitter, because the sample is applied only to the emitter wire. It is also possible to get a higher concentration of sample on the emitter by repeatedly applying the sample solution. Using an air tight micro-syringe for sampling is advantageous when using highly volatile solvents.

Summary

In this application note, we reported the FD-HRMS measurement results of two heat/light sensitive compounds using a micro-syringe sampling method. Since FD measurement takes only 1 to 3 minutes from applying sample to completion of measurement, it is a useful analytical method that can help rapidly determine the chemical composition and molecular weight of sample compounds, even if the target compounds are sensitive to heat and light.

Acknowledgement

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