21 Tesla FT-ICR Mass Spectrometer for Ultrahigh-Resolution Analysis of Complex Organic Mixtures

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Introduction

FT-ICR mass spectrometry has become the method of choice for detailed chemical characterization of natural complex mixtures. The high mass-resolving power, mass accuracy, and dynamic range of FT-ICR enable resolution and confident elemental formula assignment for tens of thousands of unique components in complex organic mixtures. Here, we present complex mixture characterization on the newly developed NHMFL 21 T FT-ICR mass spectrometer.

Experimental

A broad range of samples with different origins and complexities was selected, and ESI and APPI ionization were used. All samples were analyzed in triplicate by 9.4 T FT-ICR MS and 21 T FT-ICR MS.

Results and Discussion

Ultrahigh mass-resolving power ($m/\Delta m_{50\%} > 2,700,000$ at m/z 400) and mass accuracy (80 ppb rms) enable resolution and confident identification of tens of thousands of unique elemental compositions. We demonstrate 2.2-fold higher mass-resolving power, 2.6-fold better mass measurement accuracy, and 1.3-fold more assigned molecular formulas compared to our state-of-the-art 9.4 T FT-ICR mass spectrometer. Analysis of a heavy petroleum distillate exemplifies the need for ultrahigh-performance mass spectrometry (49,040 assigned molecular formulas for 21 T versus 29,012 for 9.4 T) and extends the identification of previously unresolved Oo, SsOo, and NOo classes. Mass selective ion accumulation of an asphalt volcano sample yields 462 resolved mass spectral peaks at m/z 677 and reveals previously unresolved mass differences, as shown in **Fig. 1**. This direct comparison reveals the continued need for higher mass-resolving power and better mass accuracy for comprehensive molecular characterization of the most complex organic mixtures.
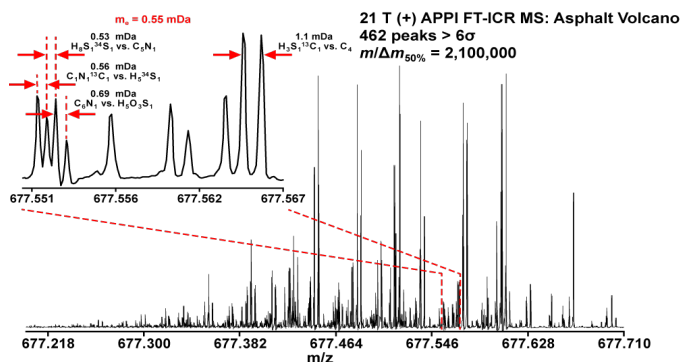

Fig.1 Mass scale expanded segment of 21 T (+) APPI FT-ICR mass spectrum of an asphalt volcano sample after ion trap isolation. Inset illustrates the need for ultrahigh mass-resolving power to resolve ions with a mass difference on the order of the mass of an electron (m_e = 0.55 mDa).

Conclusions

The NHMFL 21 T FT-ICR mass spectrometer exhibits predicted improvements in mass accuracy and mass-resolving power over our 9.4 T mass spectrometer. More molecular formulas are assigned at higher confidence level, at ultrahigh mass-resolving power, and with large ion populations. Performance improvement for heavy petroleum analysis illustrates the need for high magnetic field for thorough chemical characterization.

Acknowledgements

References

[1] Smith, D. F., *et al.*, Analytical Chemistry, **90**, 2041-2047 (2018).