MS Tips No.36 Cold-Spray TOFMS: Analysis of Porphyrin Isomers in AccuTOF CS

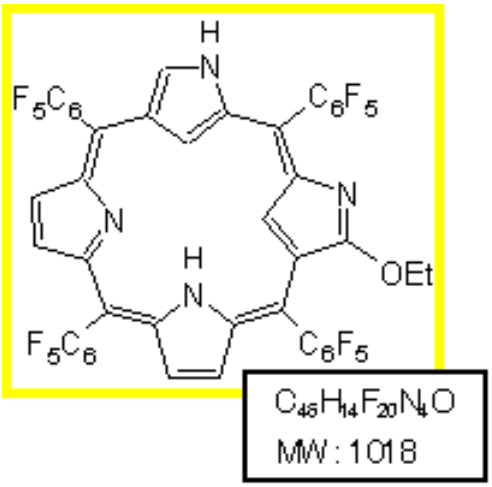
Dr. Furuta of Kyushu University has been studying membrane transport of proton and specific anions using porphyrin compounds. He has reported that multiple N-confused expanded porphyrin, which combines rotating and expanding characteristics of intramolecular pyrrole ring in N-confused porphyrin (NCP), an isomer of porphyrin, is effective for membrane transport.[1)-3)]

N-confused porphyrin is known to bond with a number of metal elements to form relatively stable complexes. An N-confused porphyrin metal complex has a carbon-metal bond within a ring, acting as an organic metal complex.

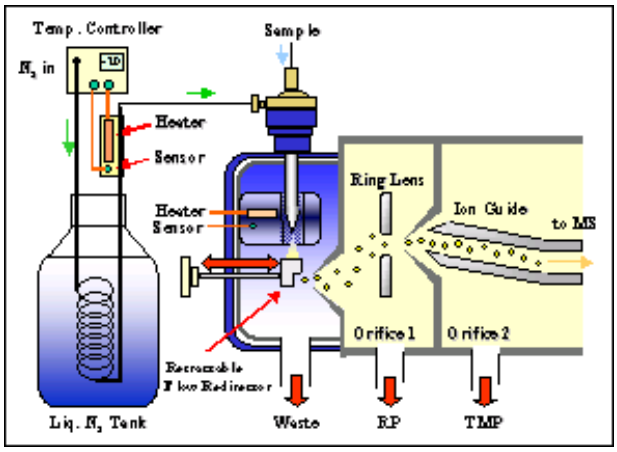
With confused pyrrole introduced into the ring, the complex will become unstable, and will be unfit for conventional ESI. Cold-spray ionization is more effective for such unstable samples. The figure below shows an outline of a cold-spray system.(For details of cold-spray ionization, see MS Tips No. 035.)

We used doubly N-confused porphyrin and its copper complex as samples to test the effectiveness of cold-spray ionization. We analyzed the samples in ESI and cold-spray, and compared the mass spectral data acquired under each set of conditions.

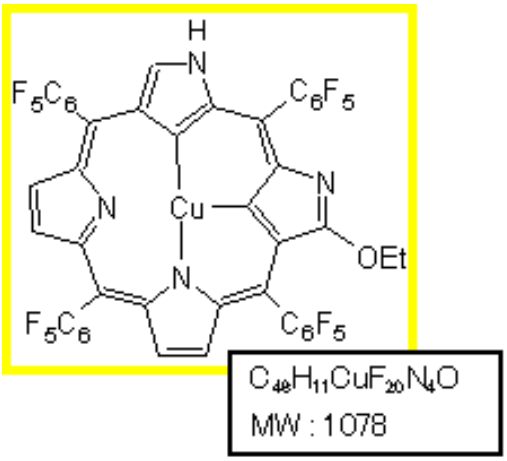
External view of AccuTOF CS



Doubly N-confused porphyrin (NCP)



Cold-spray system



Doubly N-confused porphyrin copper complex (NCP-Zn)

Results

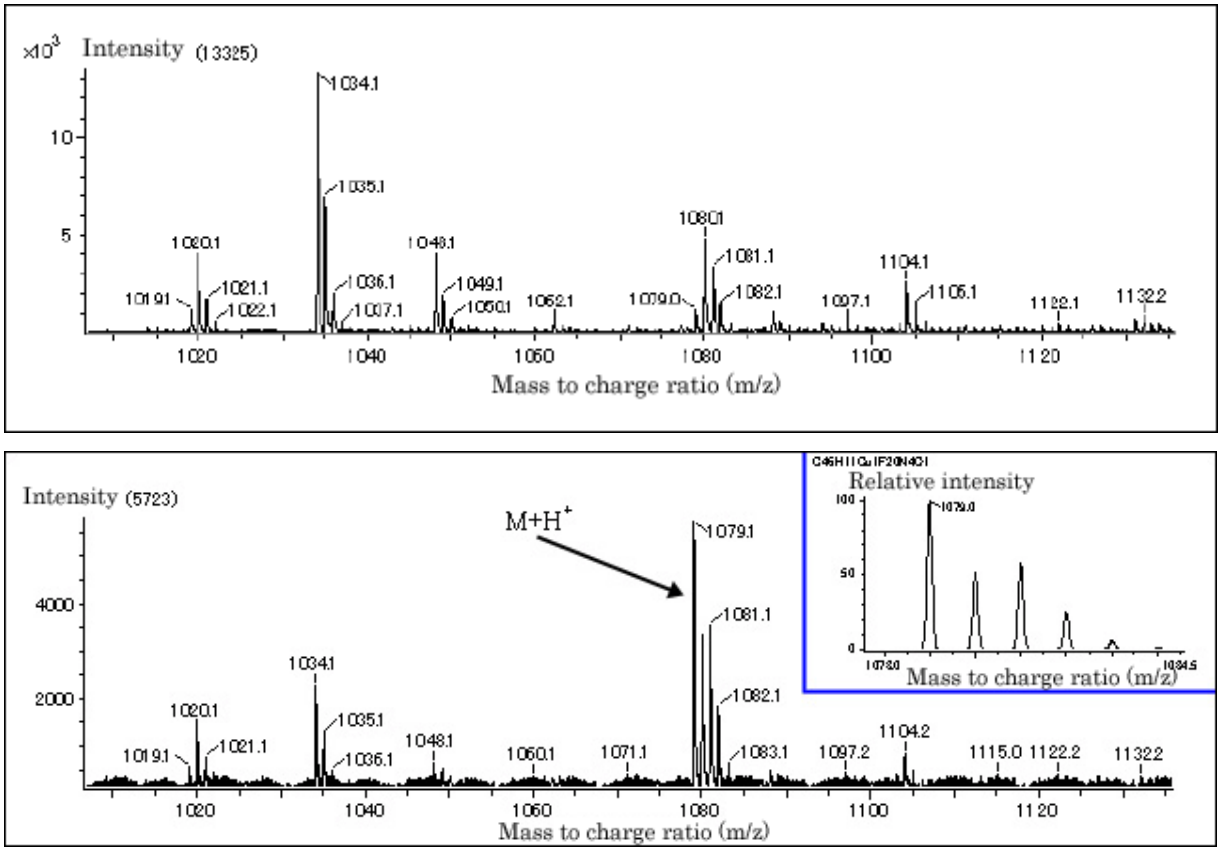
Both ESI and cold-spray detected the $M+H^+$ ion (m/z 1019) as the base peak of doubly N-confused porphyrin (MW: 1018).The spectral patterns acquired were nearly equal.

Only cold-spray detected the molecular ion of N-confused porphyrin copper complex. The isotopic simulation spectra showed an excellent agreement. While ESI detected an ion peak at the m/z nearby, the isotopic pattern of the spectrum acquired suggests that the composition contains no copper and is consequently an ion different from the target compound.

The results demonstrate that cold-spray will be a powerful tool in porphyrin chemistry, expected to have a wide range of applications including functional materials and reactive catalysts.

Conditions (N-confused porphyrin metal compound)	
Sample introduction	Infusion with syringe pump
Solvent	Chloroform
Flow rate	10 µl/min
Ionization	ESI and cold-spray
Coolant	Liquid nitrogen
Heater temperature	-10°C
Desolvating temperature control	250°C (ESI), OFF (cold-spray)
Orifice 1 temperature control	80°C (ESI), OFF (cold-spray)
Nebulizing gas	N_2 (1.0 L/min)
Dry gas	ON (ESI), OFF (cold-spray)

Needle voltage	2000 V
Ring lens voltage	15 V
Orifice 1 voltage	100 V
Orifice 2 voltage	5 V
Ion guide voltage	2500 V
Detector voltage	2800 V
Mass range	m/z 100 to 2000
Experiment time:	3min
Recording interval	5sec



Top: ESI mass spectrum of NCP-Zn

Bottom: Cold-spray mass spectrum and isotopic simulation mass spectrum of NCP-Zn

References

1. H.Furuta, H.Maeda, A.Osuka, M.Yasutake, T.Shinmyozu, Y.Ishikawa: Inner C-arylation of Doubly N-Confused Porphyrin-Pd Complex in Toluene; A Possibility of Pd3+ Intermediate,

Chem. Commun., 2000, 1143-1144

2. K.Araki, F.N.Engelmann, I.Mayer, H.E.Toma, M.S.Baptista, H.Maeda, A.Osuka, H.Furuta: Doubly N-Confused Porphyrins as Efficient Sensitizers for Singlet Oxygen Generation, Chem. Lett., 2003, 32, 244-245
3. S.Alagar, T.Ishizuka, A.Osuka, H.Furuta：Doubly N-Confused Hexaphyrin: A Novel Aromatic Expanded Porphyrin that Complexes Bis-Metals in the Core, J. Am. Chem. Soc., 2003, 125, 878-879