

Supporting Information

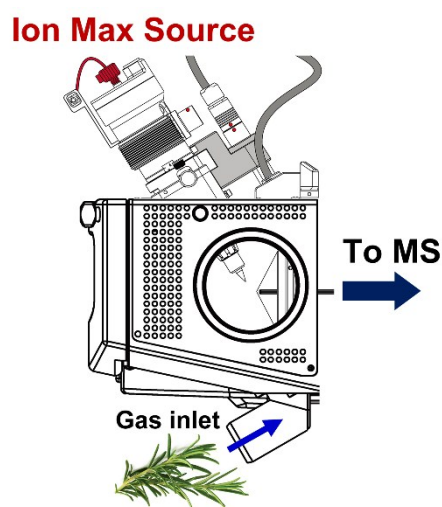


Figure S1. Schematic of the sampling system for SESI-MS analysis using the Ion Max source. The Ion Max source had a roughly enclosed structure and was slightly modified to facilitate sampling. Specifically, as seen in Figure 1a, the drain tube was removed from the source that turned the drain outlet into a sample inlet, then the volatilized analytes can be drawn into the source chamber without additional pump device. After colliding with the electrospray, the analytes can be ionized probably through the charge transfer reactions.

The Henry's Law calculation:

For a given species, the definition of Henry solubility H^{cp} (SI unit: $\text{mol m}^{-3} \text{Pa}^{-1}$) is:

$$H^{cp} = \frac{c_a}{p}$$

where c_a is the concentration (unit: mol m^{-3}) in the aqueous solution, and p is the partial pressure (unit: Pa) in the gas phase. According to Ref. 57, the H^{cp} value for N,N-dimethylaniline (DMA) is $0.17 \text{ mol m}^{-3} \text{Pa}^{-1}$.

To calculate the partial pressure of a given DMA solution, the mass concentration (c_m , g/mL) must be converted to the molarity concentration (c_a , mol/L). As the molar mass of DMA is about 121 g/mol, the conversion is:

$$c_a = \frac{c_m}{121 \text{ g} \cdot \text{mol}^{-1}}$$

then the partial pressure p of DMA vapor from a 1 ppb (i.e. 1 ng/mL) solution can be acquired:

$$p = \frac{c_a}{H^{cp}} = \frac{\frac{c_m}{121 \text{ g} \cdot \text{mol}^{-1}}}{0.17 \text{ mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}} = \frac{\frac{1 \text{ ng} \cdot \text{mL}^{-1}}{121 \text{ g} \cdot \text{mol}^{-1}}}{0.17 \text{ mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}} = 4.8 \times 10^{-4} \text{ Pa}$$

At atmospheric condition with a standard pressure of 101 325 Pa, the volume concentration of DMA can be calculated by the pressure ratio, which is **0.47 ppbv**.

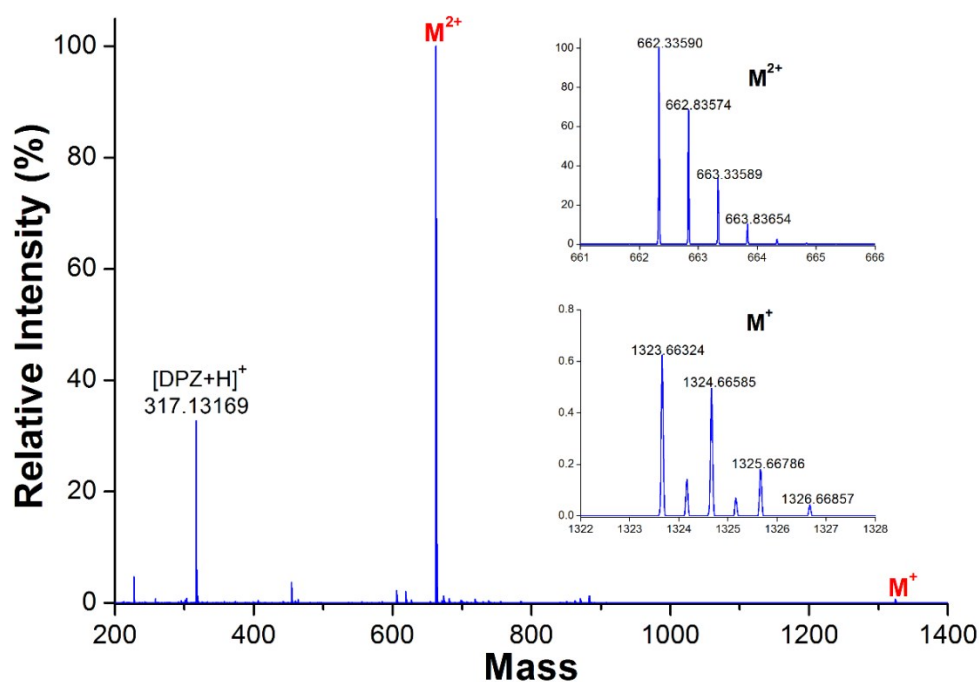


Figure S2. MS analysis of peptide using the SAP-ESI source. In this experiment, methanol with 0.01% hydrochloric acid was used as the spray solvent, and 3 μ L mixed aqueous solution of 9,9-dioxopromethazine and a synthetic peptide (Biotin-aminocaproic acid-RDFAAYRS-CONH₂, labelled as **M** in the spectrum) were injected directly from the gas inlet into the ion source. Dominated double-charged ions and few single-charged ions of the peptide can be observed in the mass spectrum.