Electronic Supplementary Information

Analysis of *in vivo* Plant Volatiles Using Active Sampling and TD-GC×GC-TOFMS

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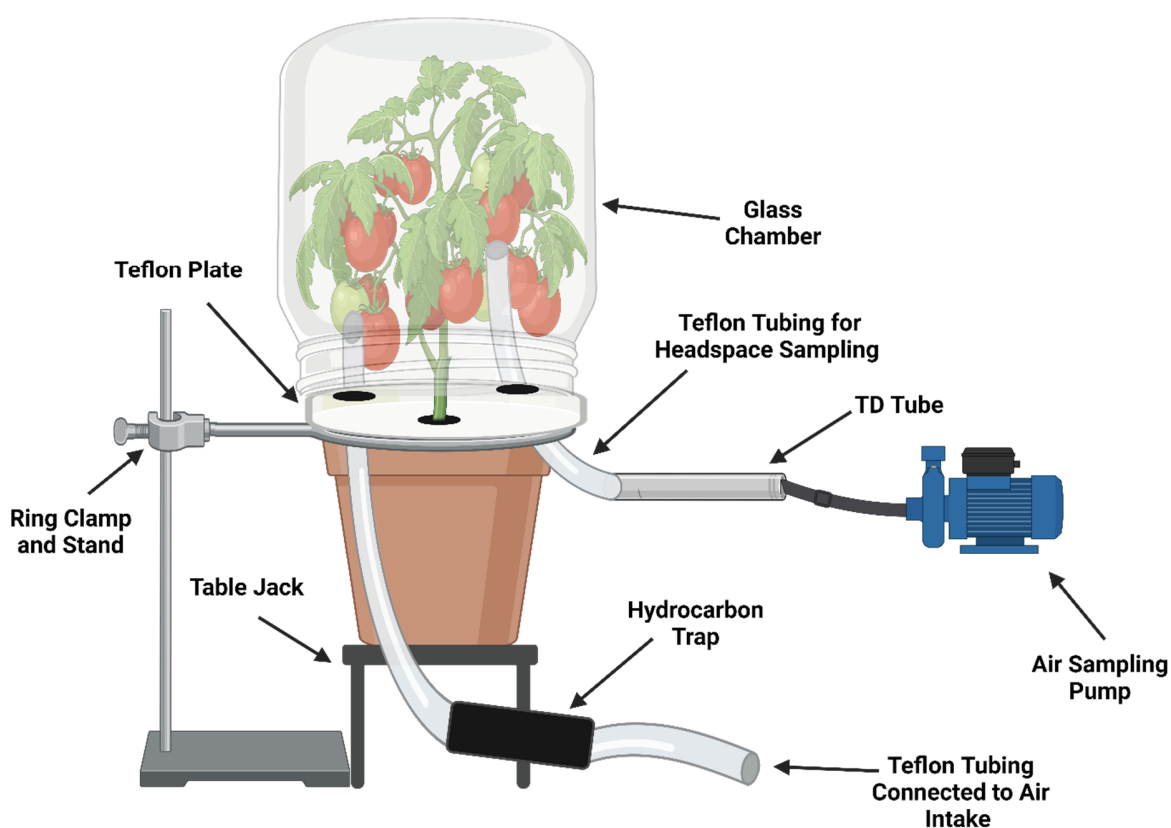
Figure S1. *in vivo* active plant sampling system with a thermal desorption tube.
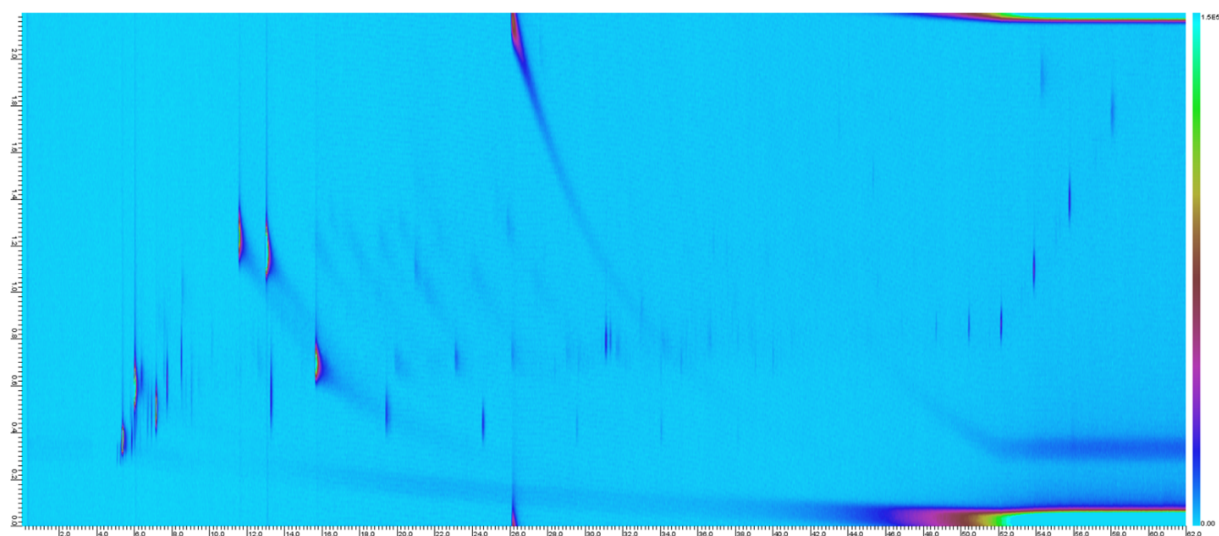
Figure S2. GC×GC-TOFMS TIC contour plot of the clean *in vivo* plant sampling system.

Horwitz Calculation

A solution containing n-nonane-d$_{20}$ was used to estimate the precision of the method based on the Horwitz Ratio. A solution of n-nonane-d$_{20}$ diluted in methanol was prepared at a concentration of 10 ng/µL. 4µL of this solution was manually spiked onto a thermal desorption tube using a 10 µL syringe. The Horwitz Ratio calculation requires the predicted relative standard deviation (PRSD$_R$), which is calculated based on analyte concentration (C), expressed as a dimensionless w/w ratio.

$$PRSD_R(\%) = 2C^{-0.15}$$

Calculation of C, based on the concentration of n-nonane-d$_{20}$ and the density of methanol at the laboratory temperature proceeds as follows:

for n-nonane-d$_{20}$:

$$\left(\frac{10\ ng}{1.0\ \mu L}\right) \times (4.0\ \mu L) \times \left(\frac{1\ g}{10^9\ ng}\right) = 4.0 \times 10^{-8} g$$

for methanol:

$$\left(0.7913\frac{g}{mL}\right) \times (4.0\ \mu L) \times \left(\frac{1\ mL}{10^3\ \mu L}\right) = 3.1652 \times 10^{-3} g$$

thus,

$$C = \frac{4.0 \times 10^{-8}\ g}{3.1652\ \times 10^{-3}\ g} = 1.2637 \times 10^{-5}$$

and,

$$PRSD_R(\%) = 2(1.2637 \times 10^{-5})^{-0.15} = 10._9\ \%$$