Supporting Information: Research on Cluster Hollow Fiber Membrane Proton Transfer Reaction Mass Spectrometry (CHFM-PTR-MS) and Its Application in Odorous Gas Detection

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Table of Contents

Table S1. Concentrations and uncertainties of the VOCs in standard gas

Standard gas	Compound	Concentration（ppmv）	Uncertainty
1	Methyl Mercaptan	0.99	3%
	Methyl Sulfide	0.98	3%
	Carbon Disulfide	1.02	3%
	Ethyl Sulfide	0.95	3%
	Dimethyl Disulfide	0.98	3%
2	Methyl Acrylate	1.06	3%
	Ethyl Acrylate	1.07	3%
	Styrene	1.11	3%
	Cumene	1.12	3%

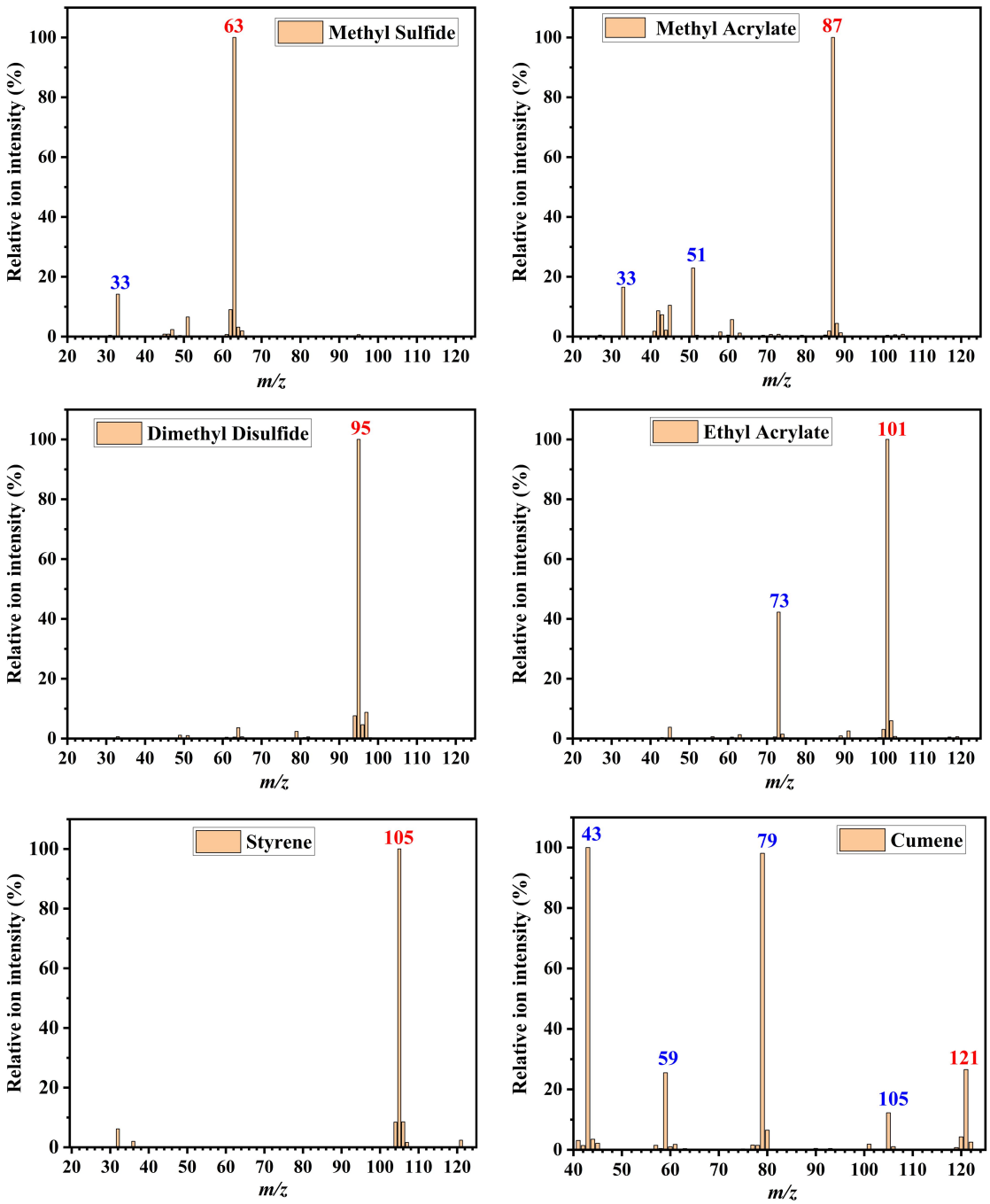

Figure S1. Mass spectrum of six test compounds detected by direct injection PTR-MS (*E/N*=167.3 Td). Air background had been deducted. Water cluster ions $H_3O^+(H_2O)$ and $H_3O^+(H_2O)_2$ were skipped. From Figure S1, most of the tested compounds in the spectrum are dominated by protonated characteristic ions, except for cumene. Cumene contains many fragment ions under the current *E/N* condition, which is also the reason for its low sensitivity. Considering the detection sensitivity of most substances, we are unable to further reduce the *E/N* value. If only cumene needs to be detected in some certain scenarios, the *E/N* can be appropriately reduced to obtain a better sensitivity.

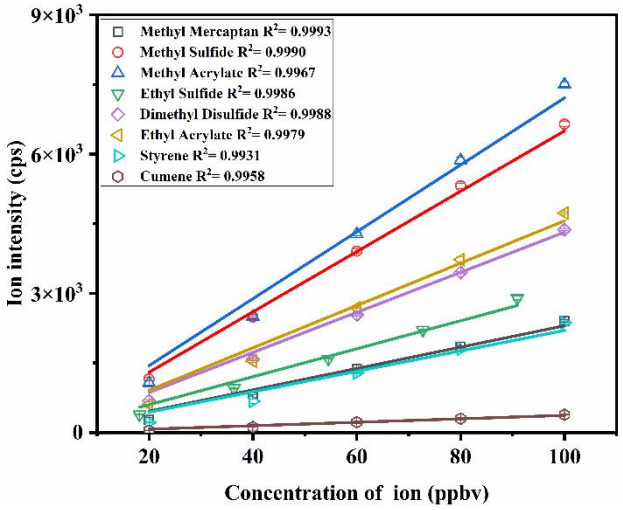

Figure S2. Calibration curves of traditional direct injection PTR-MS.

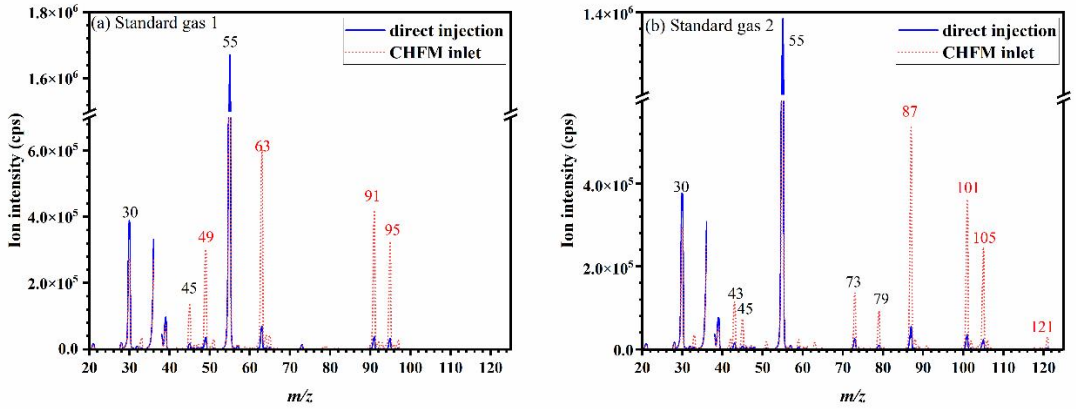

Figure S3. Mass spectrum comparison between CHFM-PTR-MS and direct injection PTR-MS. The detection concentration is 0.95-1.12 ppmv, and the mass ranges of the mass spectrum are *m/z* 20-125, skipping the $H_3O^+(H_2O)$.

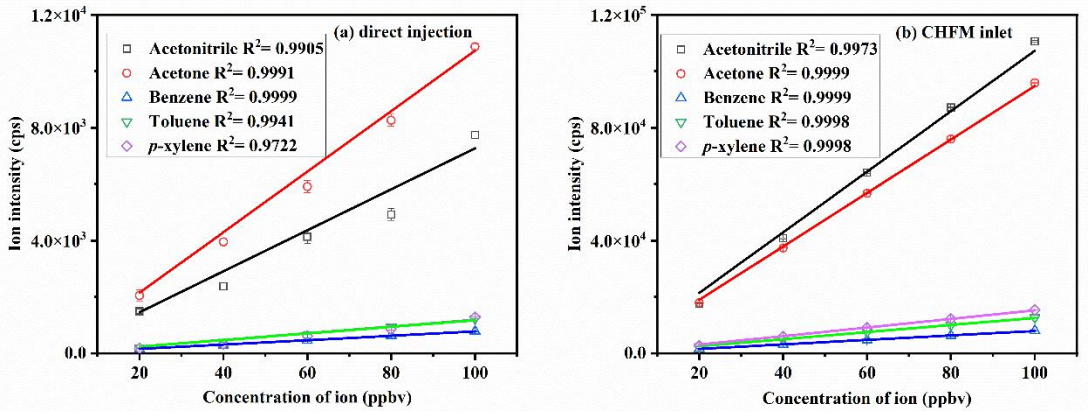

Figure S4. Calibration curves of (a) traditional direct injection PTR-MS and (b) CHFM-PTR-MS.

Table S2. Improvement in sensitivity and LOD for other five test compounds

Compound (*m/z* for MH^+)	Sensitivity (cps/ppbv)			LOD (ppbv)		
	ST	SD	SD/ST	LT	LD	LT/LD
Acetonitrile (42)	72.7	1072.6	14.8	0.174	0.017	10.2
Acetone (59)	107.3	947.4	8.8	0.445	0.053	8.4
Benzene (79)	7.7	79.2	10.3	2.642	0.176	15.0
Toluene (93)	11.9	125.4	10.5	0.850	0.088	9.7
p-xylene (107)	11.7	152.4	13.0	1.542	0.157	9.8

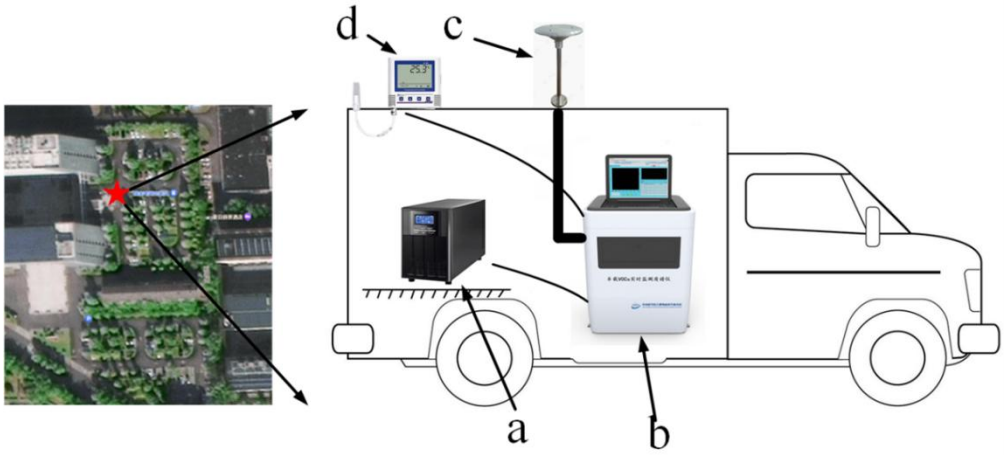

Figure S5. Odorous gas application site (Left) and vehicle platform (Right). The location shown in the figure is the Interdisciplinary Research Building of the Hefei Institutes of Physical Science, Chinese Academy of Sciences. The red star marks the site of the odorous gas application, which is located at the waste disposal area outside the experimental building. The right side of the figure shows a schematic diagram of the vehicle platform, which includes the following components: (a) Battery. (b) HFM-PTR-MS. (c) Sampling head. (d) Temperature and humidity sensor.

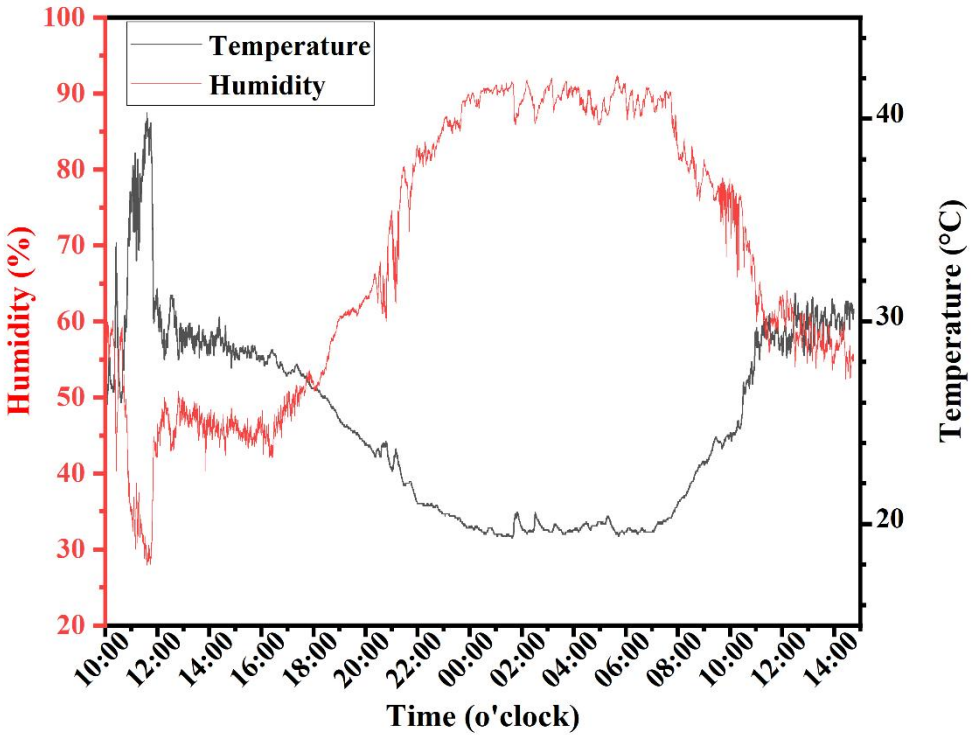

Figure S6. Temperature and humidity during the application.