Electronic Supplementary Material (ESI) for Analyst


# An In-Source Stretched Membrane Inlet for On-Line Analysis of VOCs in Water with Single Photon Ionization TOFMS

Keyong Hou,[a] Fanglong Li,[b] Wendong Chen,[ac] Ping Chen,[ac] Yuanyuan Xie,[ac] Wuduo Zhao,[ac] Lei Hua,[a] Kemei Pei[b] and Haiyang Li[a*]

[a] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China

[b] Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, 310018, China

[c] University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding Authors:

Haiyang Li, Dr. Professor
Dalian Institute of Chemical Physics, Chinese Academy of Sciences
Email: hli@dicp.ac.cn
Phone: +86-411-84379509
Fax: +86-411-84379517

The pressure in the ion source usually increases when solution passing through the HFM, which would lead to the instability of the ion signal. The pressure inside of the ion source was measured by a micropirani transducer (MKS, 925C) to investigate the effect of the pressure of the ion source. The mass spectrum was accumulated for 20 s at a repetition rate of 25 kHz in this experiment; the pressure was varied via adjusting the vacuum valve. Fig. S1 shows the relationship between the ion intensities of analyte molecules and the pressure in the ion source. The ion intensities for MTBE and ETBE were increased by 5-folds when the pressure was changed from 0.08 to 0.7 Pa, but the ion intensity almost keep constant when the pressure higher than 0.8 Pa.

During the sample analysis, the vacuum valve was completely closed, and the pressure of the ion source was maintained in the range of 1.1 Pa to 1.2 Pa. Consequently, the fluctuation of pressure on the stability of ion intensity would be very small.

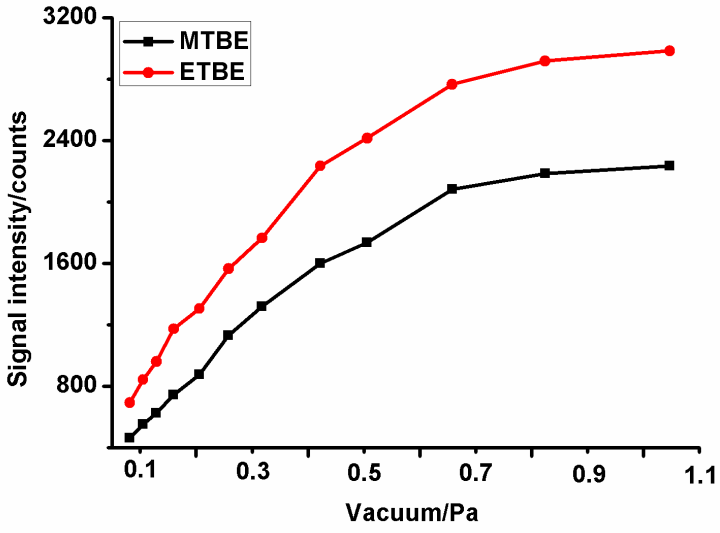
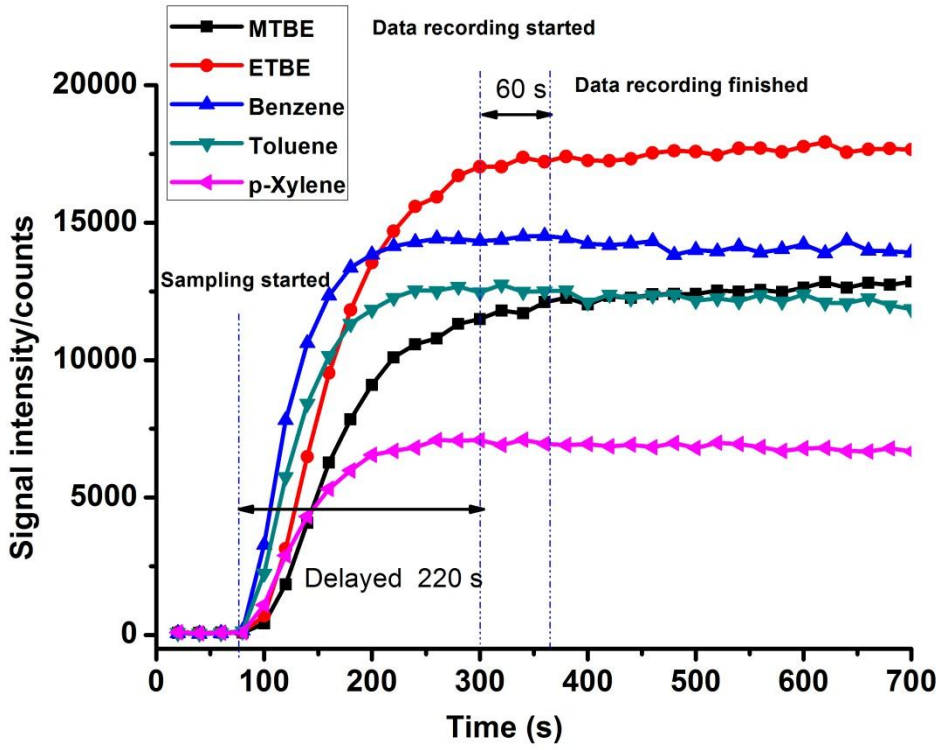



Fig. S1 Ion intensity vs. the pressure in the ion source

With membrane inlet, only steady state flow rate during pervaporation can be used for quantitative analysis, and the steady state also presented the maximum signal intensity. So, we recorded the data in steady state. Fig2S showed the response curve of the membrane inlet and the exact experimental procedure, MTBE need more time to get the steady state. The experimental procedure is : (1) turning on the peristaltic pump, the samples are passing through the HFM and the sampling process starts; (2) then simultaneously close valve C, after the sampling, there is a 220 s delay time before the data collection, and the spectra for quantitative analysis were accumulated for 60s.




FigS2. Experiment procedure labeled on the response curve.

We designed a small vacuum chamber to measure the relative photon intensity of VUV lamp. The inner volume of the chamber was 500 mL; the pressure inside the ion

source was measured by a micropirani transducer (MKS, 925C), and a 110 L $s^{-1}$ turbo pump connected with a vacuum valve was used to maintain pressure of the chamber at 1 Pa. The schematic diagram of the photon density measurement setup was show in Fig. S3a. The VUV lamp was placed on the top of the chamber and was sealed by the O ring. The VUV lamp window was put into the chamber, and a radius of 24 mm stainless steel Faraday plate was placed parallel, coaxially with the VUV lamp window. The photons emitted from VUV lamp shined on the Faraday plate, resulting in that the photoelectrons emitted from the Faraday disk. A picoammeter (Keithley 6487) was connected with Faraday disk to measure its current. A nickel mesh with 80% photon transmission was placed 2 mm above the Faraday plate, and worked at a voltage of 9 V. The Faraday plate was mounted on an insulator, and the bottom of which was connected to a slidable rod. The distance between the VUV lamp window and Faraday plate was adjusted by moving the slidable rod. When the distance is reduced from 15 mm to 7 mm, the detected current signal is from 2.8 nA increased to 5.7 nA, which was about 2-folds increase. The measured current *vs.* the distance between VUV lamp window and Faraday disk was shown in Fig. S3b.

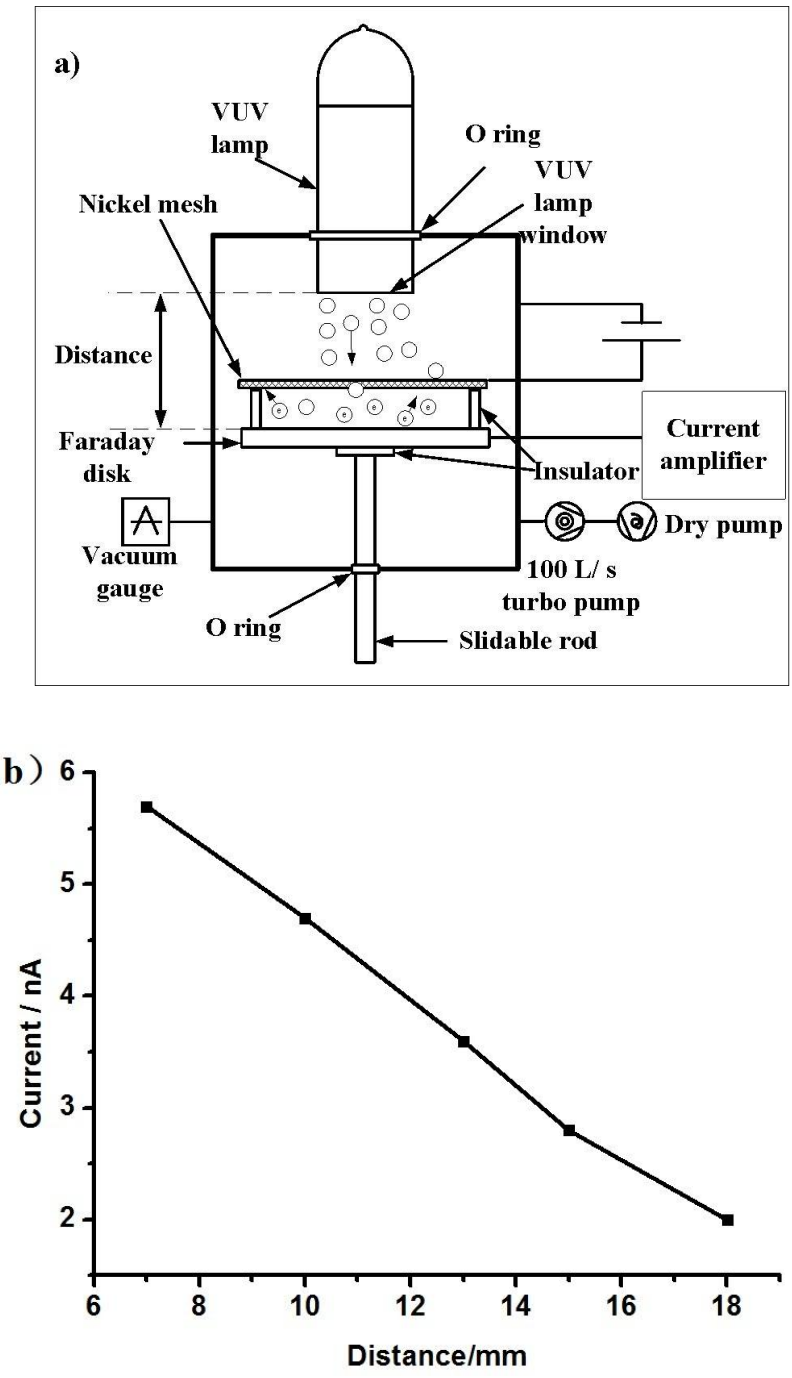



Fig. S3 a) Schematic diagram of the photon intensity measurement setup; b) Measured current vs. the distance between VUV lamp window and Faraday disk.

Fig S4 shows a complete response curve of MTBE, ETBE, benzene, toluene, and xylene with stretched in-source hollow fiber membrane inlet. The detail response time

was listed in Table S1. The rise and fall response times in our measurement are determined as the time of a signal from 10% to 90% of its maximum. All the data used in Fig. S4 were accumulated within 20 s at a repetition rate of 25 kHz. Taking the rise time of the original 8 cm HFM for example, the rise times of MTBE, ETBE, benzene, toluene, and *p*-xylene in the in-source design were 319 s, 265s, 118s, 142s and165s, respectively. Combining the in-source and stretching methods together was more effectively reducing the response time of HFM, the rise times of MTBE, ETBE, benzene, toluene and *p*-xylene were reduced to160 s,145 s,82 s,86 s and 103 s, respectively.

When the sample analysis is completed, the sample solution was changed to purified water, the signal was recorded continuously (Valve C keep close). The Fig. S4 showed that the fall time was even longer than the rise time. Combining the in-source and stretching methods together, the fall times of MTBE, ETBE, benzene, toluene and *p*-xylene were 282 s,275 s,124 s, 124 s and 146 s, respectively. The reason for the long fall time is due to the low gas conduction between the ion source and the mass analyser, the enriched sample was pumped out the ion source only through the 1 mm central hole skimmer electrode, which acts as a vacuum barrier to maintain the high vacuum pressure inside of the mass analyser. So, in the new design, we added another turbo-pump to quickly pump out the enriched sample in the ion source by opening valve C.

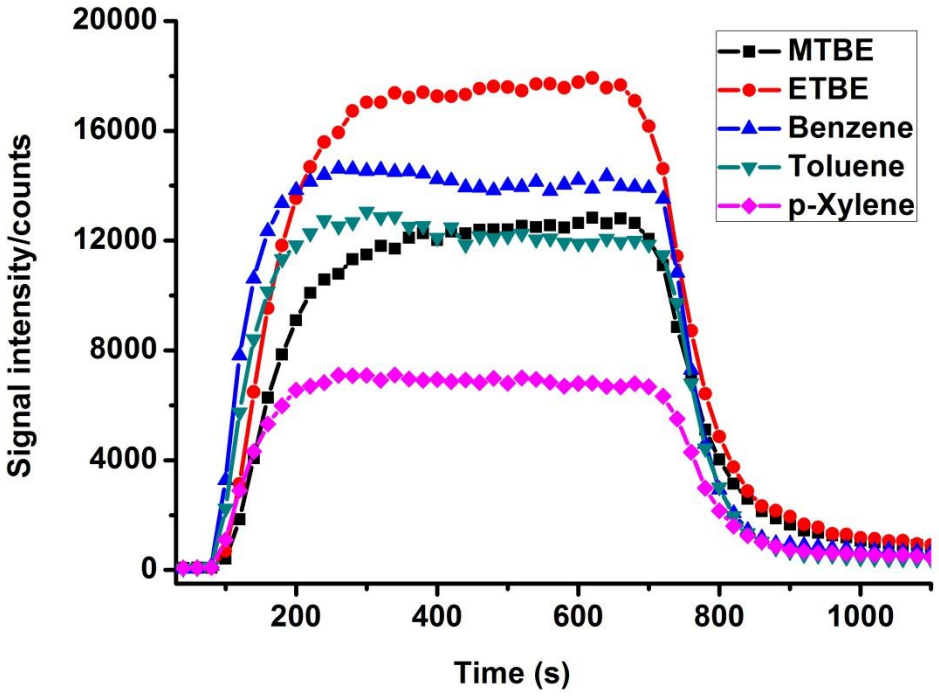



Fig. S4 Response curve of the stretched in-source HFM for compounds of benzene, toluene, p-xylene, MTBE and ETBE

Table S1 Rise Time and Fall Time for different geometries of HFM.

| Response Time | Membrane State | MTBE | ETBE | Benzene | Toluene | *p*-xylene |
|---|---|---|---|---|---|---|
| **Rise Time** | 8cm (stretched) | 160 | 145 | 82 | 86 | 103 |
| **In-source** | 8cm (Original) | 319 | 265 | 118 | 142 | 165 |
| **Rise Time** | 8cm (stretched) | 348 | 338 | 237 | 386 | 649 |
| **Out-source** | 8cm (Original) | 530 | 520 | 360 | 605 | 1120 |
| **Fall Time** | 8cm (stretched) | 282 | 275 | 124 | 124 | 146 |
| **In-source** | 8cm (Original) | 601 | 535 | 203 | 209 | 230 |
| **(Valve C closed)** | | | | | | |
| **Fall Time** | 8cm (stretched) | 1000 | 960 | 835 | 1152 | 2560 |
| **Out-source** | 8cm (Original) | 1190 | 1290 | 940 | 1560 | 2720 |
| **(Valve C closed)** | | | | | | |