Electronic Supplementary Material (ESI) for Analyst.


Support Information

# A new insert sample approach to paper spray mass spectrometry: paper substrate with paraffin barriers.

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HPLC-UV analysis

“The chromatographic analyses were performed using a liquid chromatography system (Infinity 1290, Agilent, USA), consisting of aquaternary solvent pump delivery (1290 Quat Pump), a thermostated auto-sampler (1290 Sampler) and a refractive index detector (RID). RID and the column oven were set at 45°C. The column used was a BioRad Aminex HPX-87H (300 x 7.8 mm, 9 µm) equipped with a Biorad Aminex Cation-H guard column (30 x 4.6 mm). The mobile phase was $H_2SO_4$ 5 mM used in isocratic mode. The flow rate of the mobile phase was 0.6 mL/min and the total run time was 60 min. The column and detector temperatures were maintained at 45°C, while the auto-sampler was set in 4°C. The injection volume of samples and standards was 10 µL. Agilent Open Lab with Data Analysis software (version A.01.01) was used for the operation of the LC system and to the data processing.”

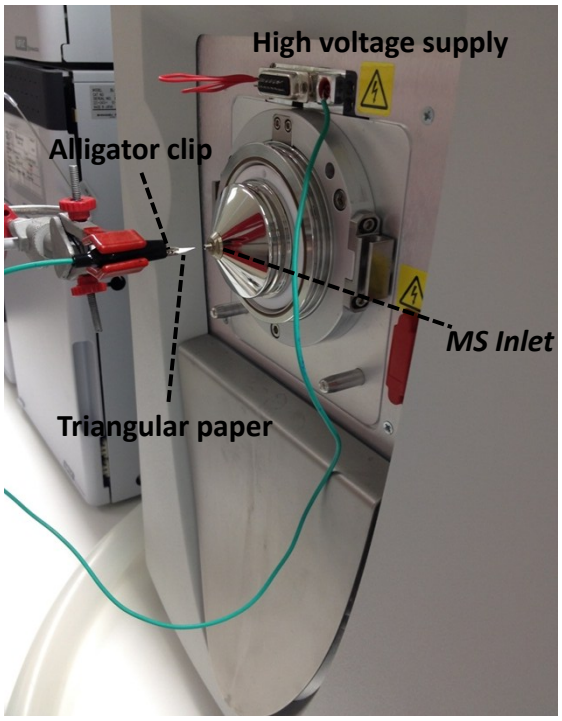


**Figure S1**. PS-MS homemade prototype device.

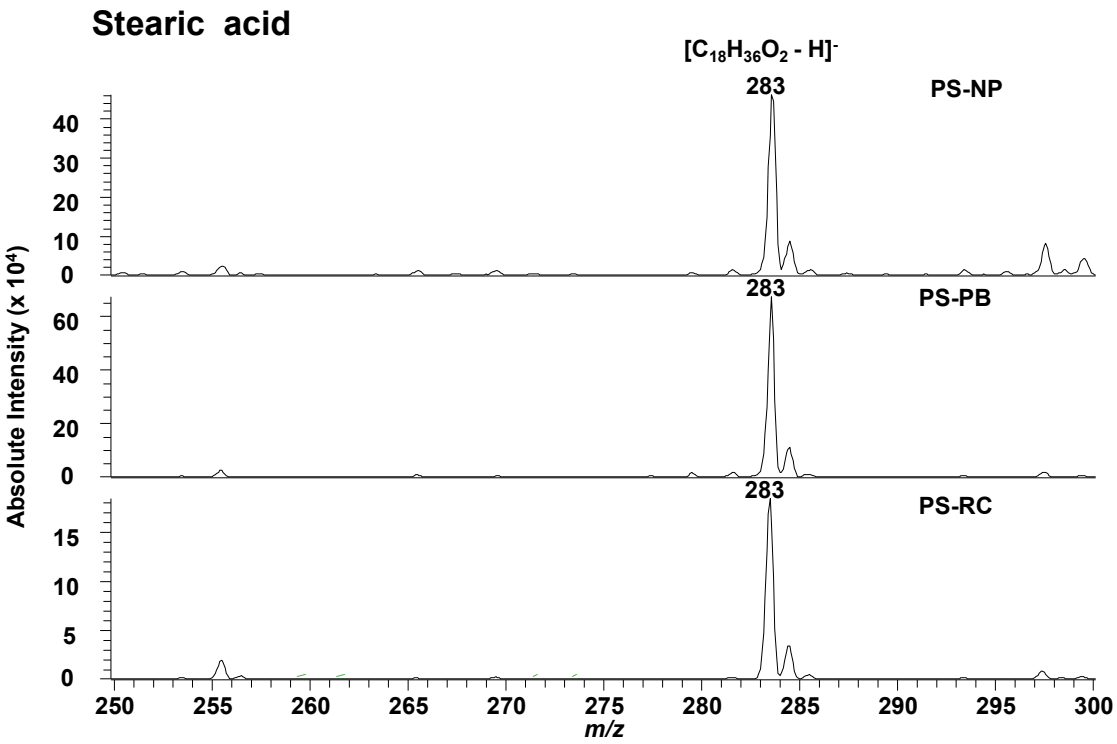


**Figure S2**. PS (-) MS of stearic acid in different type of substrate.

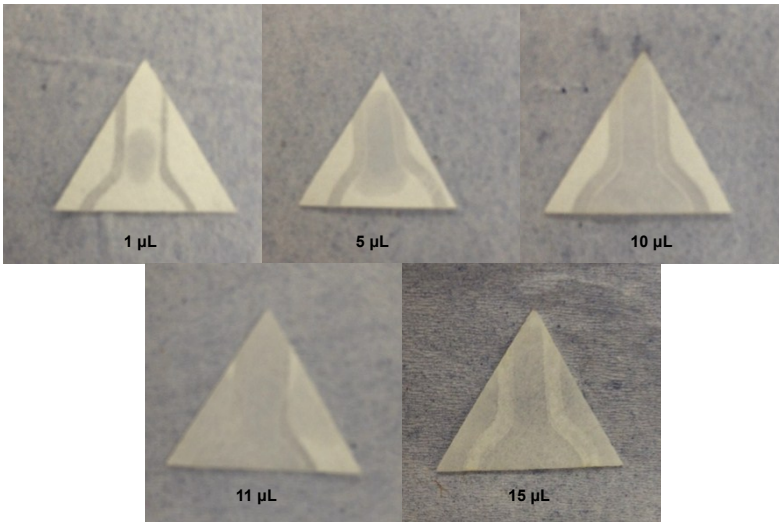


**Figure S3**. Optical images showing the overflow on paraffin channel after applying 10 µL of solvent.

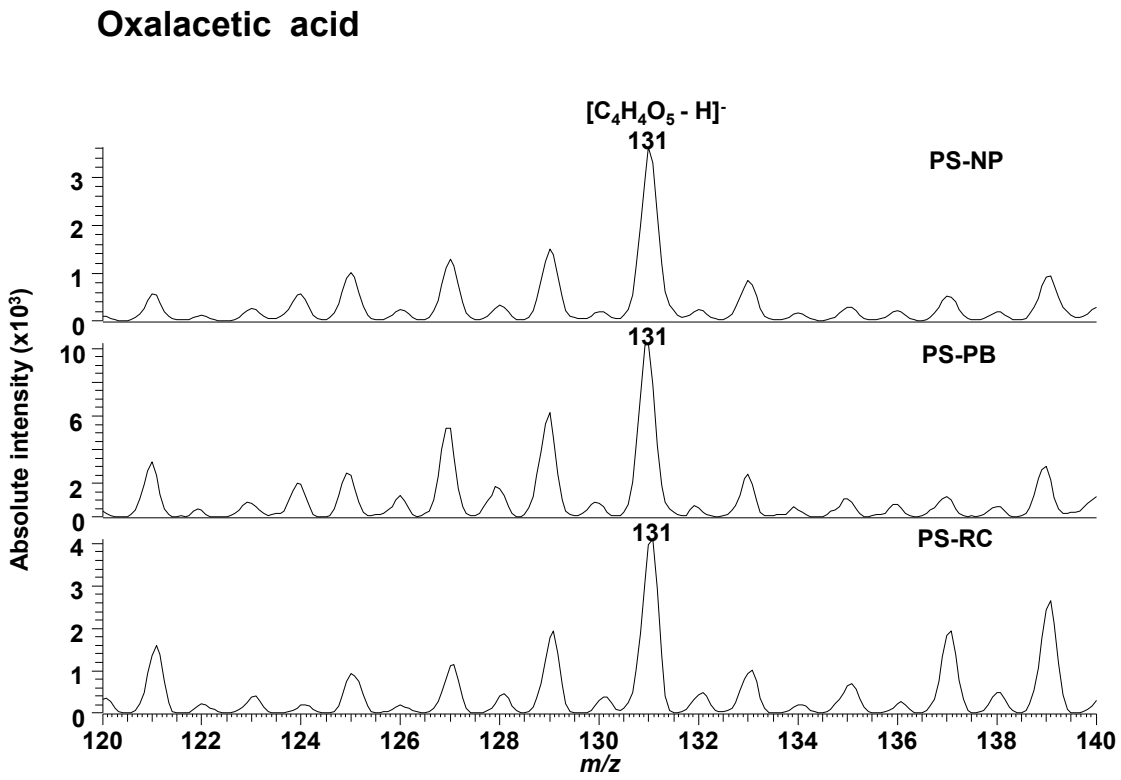


**Figure S4**. PS (-) MS of oxaloacetic acid in different type of substrate.

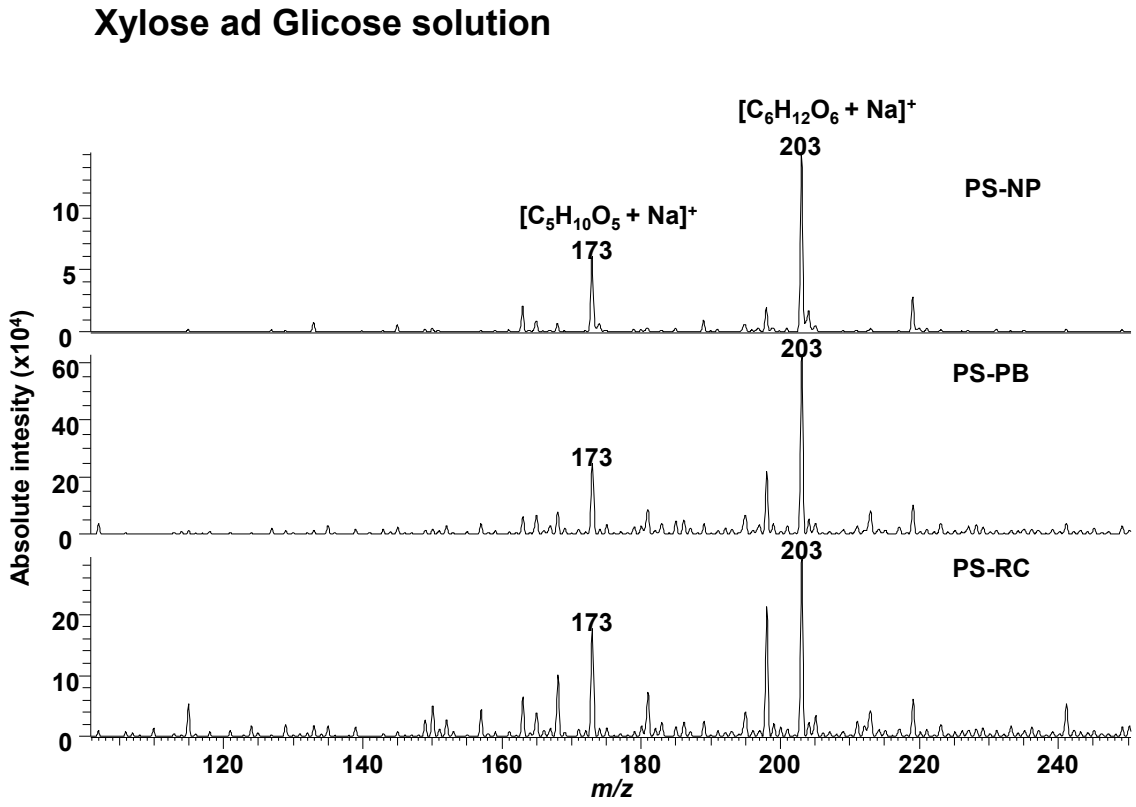


**Figure S5**. PS (+) MS of xylose and glucose in different type of substrate.

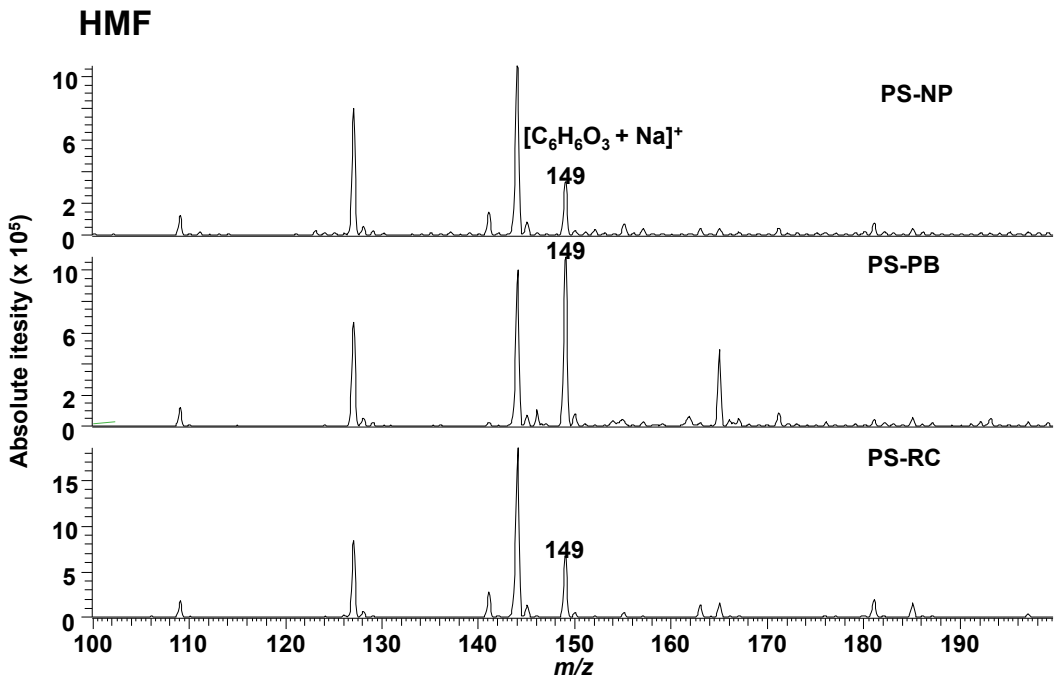


**Figure S6**. PS (+) MS of HMF in different type of substrate.

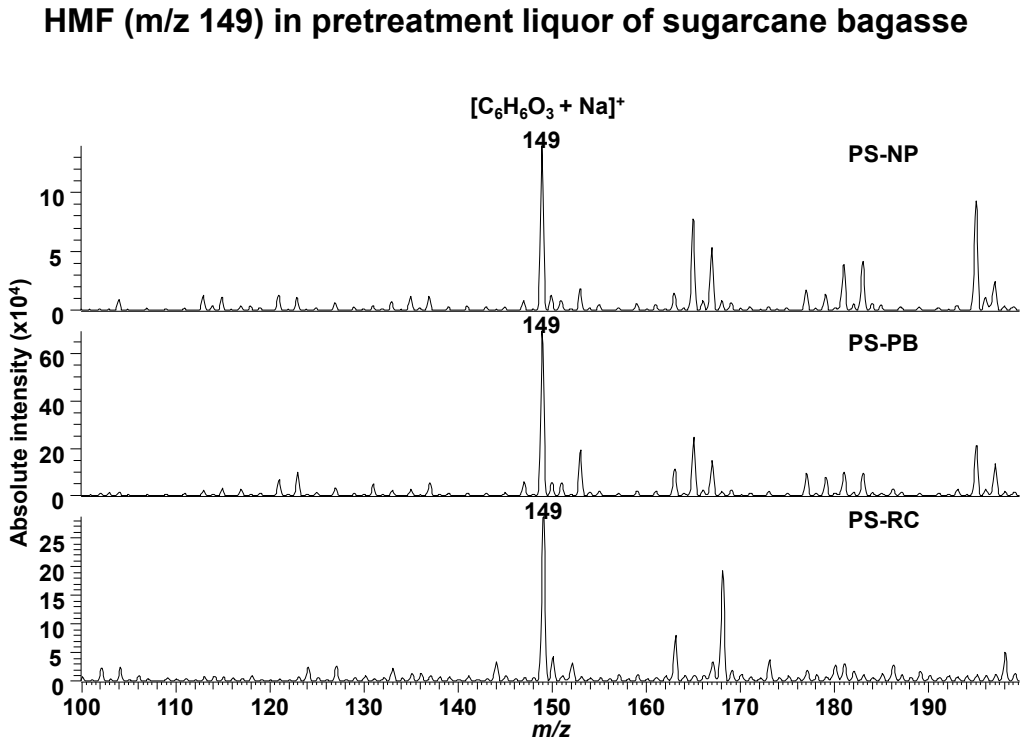


**Figure S7**. PS (+) MS of HMF in pretreatment liquor of sugarcane bagasse in different type of substrate.

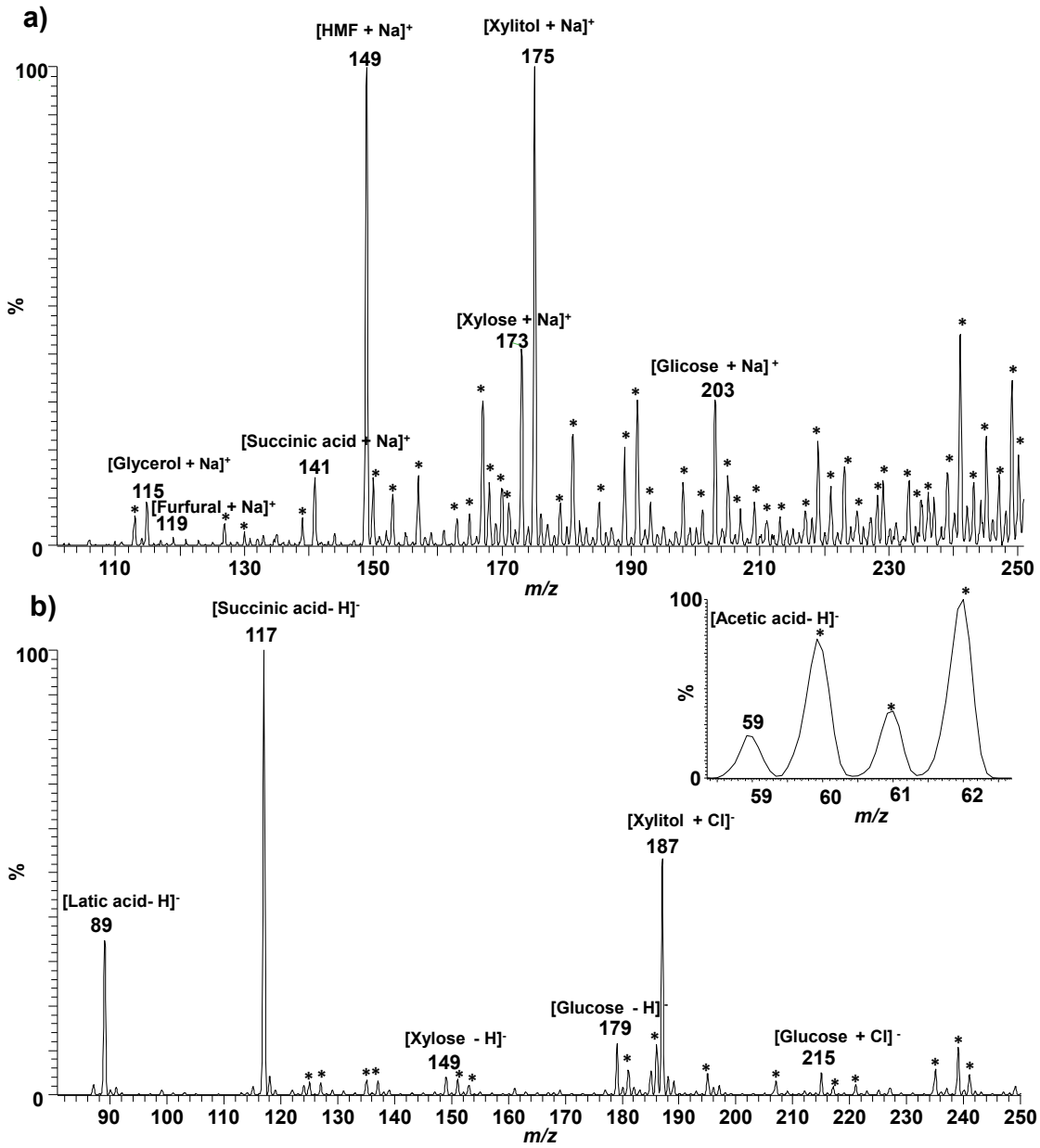


**Figure S8.** Paper spray mass spectrum of a mix of standards of lactic, succinic and acetic acid and xylitol in positive (A) e negative (B) mode.

**Table S1**. Ratio of the absolute intensity of ions detected by PS-PB, PS-NP and PS-RC.

| Analyte | *PS-PB/ PS-NP*[*] | *PS-PB/PS-RC*[*] |
|---|---|---|
| **Stearic acid** | 11.3 | 3.7 |
| **Oxaloacetic acid** | 2.8 | 2.5 |
| **Xylose** | 4.5 | 1.5 |
| **Glucose** | 4.4 | 2.1 |
| **HMF** | 3.2 | 1.6 |
| **HMF in pretreatment liquor of sugarcane bagasse** | 5.0 | 2.4 |

- Ratio between the absolute intensity of each *m/z* detected.