## **Supplementary Information**

#### Direct Analysis and Quantification of Metaldehyde in Water using Reactive Paper Spray Mass Spectrometry

Simon Maher<sup>a\*</sup>, Fred P. M. Jjunju<sup>a</sup>, Deidre E. Damon<sup>c</sup>, Hannah Gorton<sup>d</sup>, Yosef S. Maher<sup>c</sup>, Safaraz U. Syed<sup>e</sup>, Ron M. A. Heeren<sup>e</sup>, Iain S. Young<sup>b</sup>, Stephen Taylor<sup>a</sup> and Abraham K. Badu-Tawiah <sup>c\*</sup>

<sup>a</sup>Department of Electrical Engineering & Electronics, University of Liverpool, Brownlow Hill, Liverpool, L69 3GJ, UK.

<sup>b</sup>Institute of Integrative Biology, University of Liverpool, Crown Street, Liverpool, L69 7ZB, UK.

<sup>c</sup>Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, 43210, USA.

<sup>d</sup>Northumbrian Water, Leat House, Pattinson Road, Washington, NE38 8LB, UK.

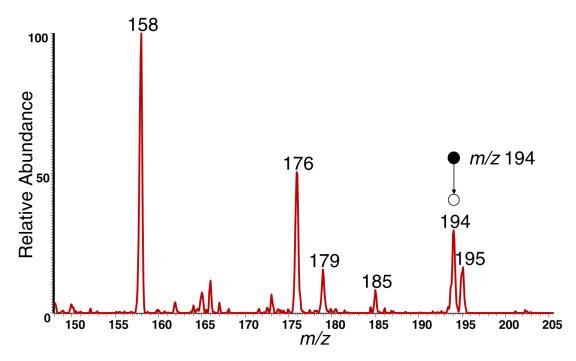
<sup>e</sup>M4I, Maastricht Multimodal Molecular Imaging Institute, Maastricht University, Faculty of Health, Medicine and Life Sciences, Universiteitssingel 50, 6229 ER Maastricht, The Netherlands.

To whom correspondence should be addressed:

\*Dr Simon Maher, Department of Electrical Engineering & Electronics, University of Liverpool, Brownlow Hill, Liverpool, L69 3GJ, UK, Telephone: +44 (0)151 794 9517. Fax: +44 (0)151 794 4540. E-mail: s.maher@liv.ac.uk

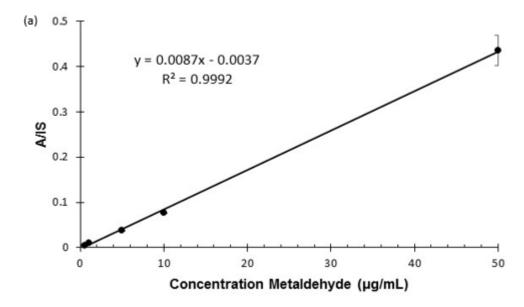
\*Professor Abraham Badu-Tawiah, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210, USA. Telephone: +1 614 929 4276. Fax: +1 614 292-1685. E-mail: badutawiah.1@osu.edu

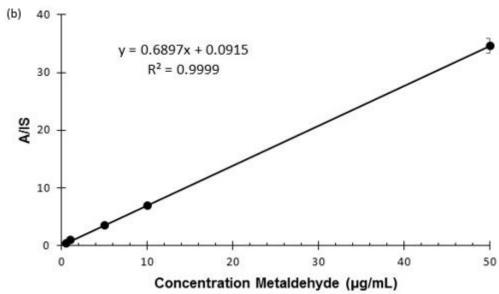
#### 1. Characterization of Metaldehyde Detection using PS-MS



Supplementary Figure S1: Positive ion mode paper spray mass spectrum of metaldehyde recorded using a benchtop ion trap mass spectrometer. 5  $\mu$ g of the analyte in 1  $\mu$ L deionized water was spotted onto filter paper and ionized in air by application of a positive electric potential (3.5 kV) using methanol as the paper spray solvent. The figure shows the CID data for the precursor ion at m/z 194.

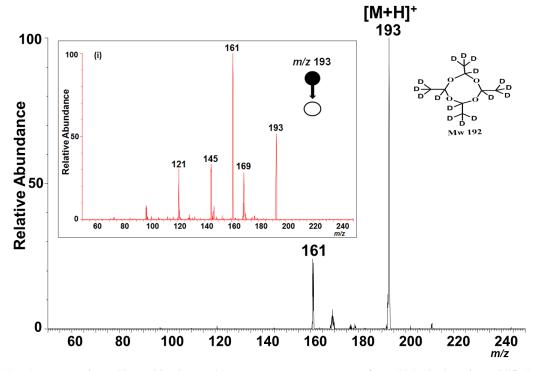
#### 2. Neutral PS-MS calibration curves





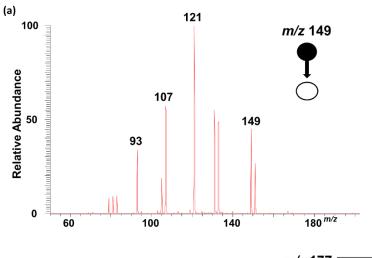
Supplementary Figure S2: Calibration curve for quantification of metaldehyde in water using PS-MS/MS when analysing (a) sodiated ion types and (b) ammoniated ion types produced in neutral MeOH spray solvent. Error bars indicate standard deviation from three replicates.

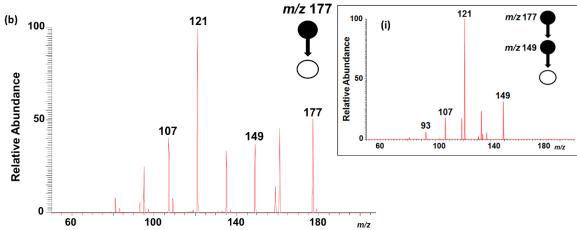
### 3. Characterization of acidified Metaldehyde-d<sub>16</sub>



Supplementary Figure S3: Positive ion mode paper spray mass spectrum of metaldehyde- $d_{16}$  using acidified spray solvent. Inset (i) shows CID data for the precursor ion at m/z 193.

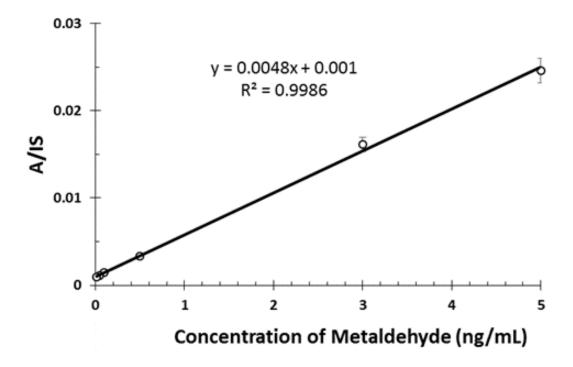
# 4. Comparison of m/z 149 from solution and generated from gas phase fragmentation





Supplementary Figure S4: Comparison of CID of m/z 149 formed (a) directly from the solution with (b) the fragmentation of gas-phase m/z 149 formed from the MS2 of m/z 177 (insert (i)).

#### 5. Reactive PS-MS calibration curve



Supplementary Figure S5: Calibration curve for quantification of metaldehyde in water using PS-MS/MS when analyzing protonated ion types produced in acidified spray solvent. Error bars indicate standard deviation from three replicates.