

**Quantitative response in ion mobility spectrometry with atmospheric pressure chemical ionization in positive polarity as a function of moisture and temperature**

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4 1 QUANTITATIVE RESPONSE IN ION MOBILITY SPECTROMETRY WITH  
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6 2 ATMOSPHERIC PRESSURE CHEMICAL IONIZATION IN POSITIVE POLARITY AS A  
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9 3 FUNCTION OF MOISTURE AND TEMPERATURE  
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24 ABSTRACT

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26 Response to fourteen chemicals from five chemical families spanning the range of proton  
27 affinities was quantitatively determined using an ion mobility spectrometer at ambient pressure  
28 from 30°C to 175°C in purified air with moisture from 1 to 1×10<sup>4</sup> ppm. Drift times and reduced  
29 mobility coefficients for the reactant ion in positive polarity, the hydrated proton formed using a  
30 <sup>63</sup>Ni ion source, were compared to computational models showing hydration value ranges from  
31 ~2 to ~6.5. Peak intensities and drift times for protonated monomers and proton bound dimers  
32 for alcohols, aldehydes, acetates, ketones, and organophosphates, obtained over the ranges of  
33 temperature and moisture, permitted the calculation of response factors with atmospheric  
34 pressure chemical ionization. Formation of product ions could be described by heat of formation  
35 for the displacement of water from the hydrated proton and temperature-controlled hydration  
36 levels. Findings provide a broad framework to understand the importance of moisture and  
37 temperature in quantitative response in ion mobility spectrometers.

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39 Key Words

40 Ion mobility spectrometry, moisture, response factors, temperature, proton affinity

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4 **42 1. Introduction**

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7 43 Ion mobility spectrometry (IMS) is a measurement method of central importance today within  
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9 44 commercial aviation security and military preparedness[1,2] Quantitative Response [3] of with  
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11  
12 45 emerging importance in clinical breath analysis[4] with analyzers operated at ambient pressure,  
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14 46 often in purified air atmospheres. Response is such instruments, often hand-held or benchtop  
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16 47 analyzers is based on chemical ionization at ambient pressure[5] using gas phase protons in  
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19 48 positive polarity or  $O_2^-$  or  $Cl^-$  in negative polarity[6]. Ions derived from sample neutrals are  
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21 49 characterized in electric fields through ion swarm velocities (or coefficients of mobility,  $K_o$ ) in  
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23  
24 50 constant electric fields or in oscillating fields by differences in mobility coefficients ( $\Delta K_o$ )  
25  
26 51 between extremes of field strength[7]. Whether conventional IMS or the more recent differential  
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28  
29 52 mobility spectrometry (DMS), the processes of ion formation are common to both with similar  
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31 53 parameters of operation. In addition, the principles of ion formation[8] and separation (either by  
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33  
34 54  $K_o$  in IMS  $\Delta K_o$  in DMS) encompass similar principles for the influences of moisture and  
35  
36 55 temperature of the supporting atmosphere[9]. These two parameters are known through decades  
37  
38 56 of experience to govern the appearance of mobility spectra, the magnitude of  $K_o$  and  $\Delta K_o$ , and  
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40  
41 57 the response to substances. While moisture and temperature can be well-regulated and  
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43 58 monitoring in research instruments, portable or in-field instruments are designed to provide  
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46 59 relatively stable conditions within a range of moisture and temperature. At present, there is no  
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48 60 supporting resource to frame expectations for response with changes in these two parameters and  
49  
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51 61 no supporting systematic experimental and computational finding over a broad range of analyte  
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53 62 reactivity in Atmosphere pressure ionization (API)[10].

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55 63 Atmosphere pressure ionization mass spectrometry (API-MS) [10]has provided some insight into  
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58 64 the influence of API response through quantitative response with compounds from a range of gas  
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4 65 phase basicities (GB)[11]. Compounds with strong basicity (e.g., amines)[12,13] exhibited  
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6 66 response independent of temperature or GB magnitude; that is, the heat of reaction between an  
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9 67 amine and  $H^+(H_2O)_n$  was so favorable that product ions were formed on each collision. Other  
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11 68 substances showed some positive relationship between GB and quantitative response in API MS;  
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14 69 still others exhibited strong anomalies between the association of GB with API response. They  
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16 70 attributed the differences to the influence of hydration in the reactant ion and structure of  
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19 71 substances and their strength of interaction with the reactant ions. In a second companion work,  
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21 72 the association between API MS response and GB of substances was strengthened with increased  
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24 73 temperature of the ion source. This increase was attributed to dehydration of the reactant ion and  
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26 74 product ions, removing hydration as a secondary influence on API response and GB. Although  
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29 75 the principles of their findings are broadly valuable, extension of their findings to IMS or DMS  
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31 76 instruments was complicated by differences in technology and practices such as ion lifetimes in  
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34 77 the supporting atmosphere which can be as large as 15 ms in IMS drift tubes compared to a ms  
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36 78 or below in API MS. The aim of this investigation is to provide experimental data as a  
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39 79 framework for building an understanding of the role of moisture and temperature on response  
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41 80 with a conventional IMS drift tube.

42  
43 81 Although the lack of systematic treatment of moisture and temperature in IMS and DMS is  
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46 82 noted, exploration has occurred on a limited basis and some understandings can be gleaned from  
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48  
49 83 their findings. Meyer and Borsdorf [14] showed that increase moisture in negative polarity  
50  
51 84 altered the drift times of halides formed by dissociative reactions with  $O_2^-$ . Their findings in  
52  
53 85 positive polarity paralleled findings from Sunner and Kebarle where response with amines at  
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56 86 80°C was little affected by moisture while response with other compounds was significantly  
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58 87 lessened with increases in moisture. At slightly lower temperature of 70°C, Puton, et al [3]

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4 88 found response to amines was affected by moisture more than 10% RH. Similarly, Safaei, et al  
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7 89 [15] found that a DMS analyzer at ambient temperature could be operated with excessive levels  
8  
9 90 of moisture for the detection of ketones, although levels in excess of  $1 \times 10^3$  ppm showed  
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11 91 unwelcome suppression of response due to decreased reaction efficacy in the initial step of ion  
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13  
14 92 formation between the analyte neutrals and hydrated protons.  
15  
16 93 None of these studies in IMS or DMS have provide a broad measure of the combination of  
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18 94 temperature and moisture with substances representative over a relatively broad range of proton  
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21 95 affinities, or heats of reactions between hydrated protons and neutral analyte. The goal for this  
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24 96 work was an exploration of quantitative influences of moisture and temperature suitable to  
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26 97 inform a range of investigations or applications of ion mobility spectrometry.  
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## 31 99 **2. Experimental**

### 32 33 100 *2.2 Instrumentation*

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36 101 The ion mobility spectrometer included a drift tube built in-house using stacked stainless-steel  
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38 102 rings with Teflon insulators. The total length of the drift tube was 205 mm with 18 mm for the  
39  
40  
41 103 ionization region, 48 mm for the reaction region, and 139 mm for the drift region. The ionization  
42  
43 104 region has an internal diameter of 19.5 mm, Teflon insulator diameter of 39 mm and contains a  
44  
45 105  $10 \mu\text{Ci } ^{63}\text{Ni}$  ionization source.  
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48 106 A model 5890 series II gas chromatograph (Agilent Technologies Inc., Santa Clara, CA) was  
49  
50 107 used to pre- fractionate sample and deliver effluent into the ionization region. A split/splitless  
51  
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53 108 injector was equipped on the gas chromatograph. Nitrogen was used as a carrier gas passing  
54  
55 109 through a 15 m RTX 200 capillary column (Restek Corp., Bellefonte, PA), which then passed  
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4 110 through a transfer line consisting of a 50 cm aluminum clad capillary column. The transfer line  
5  
6 111 was heated to 180 °C. (see supplementary data Fig S1.)  
7  
8

9 112 The spectrometer drift gas was compressed air initially purified through a Whatman Zero Air  
10  
11 113 Generator (Parker Hannifin Corp., Cleveland, OH) and then passed through a 1.5 m long x 60  
12  
13 114 mm ID column containing 5Å molecular sieves to remove additional moisture by flow rate of  
14  
15 115 550 ml min<sup>-1</sup>. A Panametrics Moisture Monitor Series 35 (Billerica, MA) was placed in series  
16  
17 116 with the purified air after the sieve tower to monitor the moisture supplied to the drift tube.  
18  
19 117 Initial measurements were made at moisture levels of ~1 to 5 ppm; additional water was metered  
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21 118 into air flow between the sieve tower and the moisture meter.  
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### 26 119 27 28 120 2.3 *Chemicals* 29 30

31 121 The chemicals were purchased in pure form (98% or greater) from Sigma Aldrich (St. Louis,  
32  
33 122 MO) include of trimethyl phosphate, triethyl phosphate, tripropyl phosphate, tributyl phosphate,  
34  
35 123 2-heptanone, 2-nonanone, butyl acetate, pentyl acetate, hexyl acetate, 1-octanol, 1-decanol,  
36  
37 124 heptanal, octanal, and nonanal. Deionized water for the humidity generator was from Barnstead  
38  
39 125 nanopure water system (APS Water Services Corporation, California) with purity level of 18  
40  
41 126 MΩcm<sup>-1</sup>.  
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### 46 127 47 48 128 2.4 *Procedures* 49

#### 50 129 *Ion Mobility Spectrometry.* 51

52  
53 130 Experiments were carried out in this range at ambient pressure (660 Torr). Gas temperature was  
54  
55 131 monitored at the drift tube and drift gas in range of 30 to 175°C, respectively. The electric field  
56  
57 132 from the source end to the shutter was held constant in all experiments at 32 Vmm<sup>-1</sup>. Mobility  
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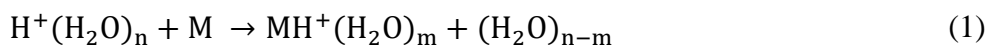
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4 133 spectra were obtained by monitoring ion intensities as a function of drift time. Each recorded  
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6 134 spectrum was the average of  $\sim 2 \times 10^3$  individual points per spectrum, and twenty averaged spectra  
7  
8  
9 135 were recorded, and their average constituted the spectrum for each electric field strength.  
10  
11  
12 136 Resolving power for reactant ion was calculated as 35.  
13

14 137

### 16 138 2.5 *Studies on levels of hydration.*

18  
19 139 The hydration value of the reactant ion was modeled using well-established enthalpies based on  
20  
21 140 API-MS[16]. Initial measurements were made at moisture levels of  $\sim 1$  to 5 ppm. The reactant  
22  
23 141 ion was examined across a range of moistures and temperatures from approximately 1 to  $1 \times 10^4$   
24  
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26 142 ppm and 30 to 175°C.  
27

28  
29 143 Spartan 10 software (Wavefunction, Inc., Irvine, CA) was used with density functional theory  
30  
31 144 (DFT) and the 6-311+G(dp) basis set for both optimization and energy and frequency for a  
32  
33 145 selected member of the different analytes (Eq. 1).  
34



36  
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38 146 These calculations were performed from hydration value  $n=1$  to  $n=6$  [15].—Results show the  
39  
40  
41 147 initial formation of the hydrated proton has a standard reaction enthalpy of  $-691 \text{ kJ mol}^{-1}$  (See  
42  
43 148 supplementary data Fig. S2). Standard reaction enthalpy is plotted as a function of  $n$  for  
44  
45  
46 149 representative chemicals at 100°C. Values for these thermodynamic parameters changed little  
47  
48 150 when calculated for 50°C and 150°C.  
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50  
51 151

### 53 152 2.6 *Studies of response with different moisture levels and temperature.*

54  
55 153 The analytical responses for fourteen chemicals from five different families—examined for peak  
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57  
58 154 intensity as a function of moisture. The solutions were diluted in HPLC grade methanol and  
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4 155 acetonitrile to concentrations ranging from 25 ppb to 25 ppm. Chemical were introduced into the  
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7 156 gas chromatograph as a pre-separated sampling system and only one chemical was entering the  
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9 157 spectrometer at a time. Responses for peak height were compared across multiple moisture levels  
10  
11  
12 158 and temperatures ranging from  $\sim 1$  to  $\sim 4 \times 10^3$  ppm and 50 to 150°C. A range of concentrations  
13  
14 159 were selected spanning the instruments limit of detection to source saturation. Each  
15  
16 160 concentration was measured in triplicate providing an average and standard deviation. In  
17  
18  
19 161 addition, reduced mobility values were examined across moisture levels for the reactant ion and  
20  
21 162 the selected chemicals using 2,6-di-tert-butyl pyridine as a standard to calculate the  $K_o$  values  
22  
23  
24 163 [17](see supplementary data Fig S3.) to no better than  $\pm 0.02 \text{ cm}^2 \text{V}^{-1} \text{cm}^{-1}$ .  
25  
26 164

### 27 28 29 165 **3. Results and Discussion**

#### 30 31 166 *3.1. Change in Reactant Ion as a Function of Moisture*

32  
33 167 Reduced mobility coefficients for the reactant ion peak in purified air at ambient pressure were  
34  
35  
36 168 influenced by moisture over extremes from 1 to  $\sim 1 \times 10^4$  ppm<sub>v</sub> as seen in Figure 1 with plots for  
37  
38  
39 169 seven temperatures. At low moisture and elevated temperature, the reactant ion peak was  
40  
41 170 resolved into the hydrated proton (the most abundance species) and lesser abundances of  
42  
43 171 hydrated ammonium and trace levels of nitric oxide. At elevated levels of moisture, only a  
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46 172 single ion peak was observed either through peak convolution or suppressed of formation of the  
47  
48 173 lesser ion populations. Decreases in moisture at all temperatures resulted in increased  $K_o$ , or  
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51 174 decreased drift times, linearly with the normal log plots of Figure 1. At 30°C,  $K_o$  increased from  
52  
53 175 1.75 to 1.95  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  and similar changes in  $\Delta K_o$  for all other temperature. Some variability  
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56 176 was observed in slopes without a systematic change with temperature.  
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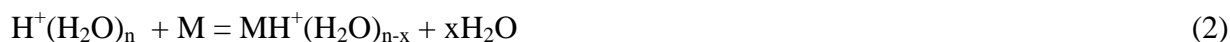
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4 177 The increases in  $K_o$  with decreases in moisture (at a given temperature) are consistent with a  
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7 178 decrease in the level of hydration (n) in  $H^+(H_2O)_n$  and values for n, calculated from models of  
8  
9 179 ion distributions from API MS studies [15] are shown in Figure 2. Values for n ranged from  
10  
11  
12 180 near 2 at 1 ppm moisture (175°C) to nearly 6 at  $1 \times 10^4$  ppm moisture (30°C). At any given  
13  
14 181 value for temperature and moisture, a distribution for n exists, for example n is 2 to 3 at 5 ppm  
15  
16 182 moisture, and ~4 at  $4 \times 10^3$  ppm moisture. Further detailed descriptions of the distributions are  
17  
18  
19 183 given in supplementary data (Fig S4). In general, the net weighted value for n changed roughly  
20  
21 184 by a step of 1 over the moisture extremes at any temperature. Although moisture and  
22  
23  
24 185 temperature are known to control the level of hydration (n) for the hydrated proton ( $H^+(H_2O)_n$ ) in  
25  
26 186 air at ambient pressure, this is the first systematic collection of  $K_o$  values for both parameters.  
27  
28  
29 187 These findings are consistent with that early reference with increases in mobility from 1.98 to  
30  
31 188  $2.30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ .

32  
33 189 While moisture and temperature affect the mobility of the reactant ions, changes also occur in the  
34  
35  
36 190 reactivity where increased values of n result in significantly increased proton affinities of  
37  
38 191  $H^+(H_2O)_n$ . This increase in proton affinity will affect quantitative response to analytes as  
39  
40  
41 192 described below.

### 42 43 193 44 45 194 *3.2. Quantitative Response as a Function of Moisture*

46  
47  
48 195 Response to an analyte (M) in an IMS drift tube at ambient pressure with a beta emission ion  
49  
50 196 source occurs through chemical ionization with reaction that could be described best as a  
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52  
53 197 displacements where the association of M with  $H^+(H_2O)_n$  as shown in Equation 2 results in the  
54  
55 198 loss of one or more  $H_2O$ . In these studies, the level of moisture was constant throughout the  
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58 199 reaction and drift regions, thus, the formation of a protonated monomer ( $MH^+(H_2O)_{n-x}$ ) may be

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4 200 reversed and response can be understood as the initial formation of the product ion and then the  
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7 201 resilience of the ion against back reaction to M with  $H^+(H_2O)_n$ :



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11  
12 202 Given sufficient vapor concentration and reaction time, a proton-bound dimer,  $M_2H^+$  (Eq. 3) can  
13  
14 203 be formed:



18  
19 204 While proton bound trimers or tetramers might be formed in the ion source volume of the  
20  
21 205 analyzer, ion residence in the drift tube exceeds lifetimes of such ions and these higher adducts  
22  
23  
24 206 are not observed in mobility spectra.

25  
26 207 Quantitative response to analytes at 150°C are shown in Figure 3 for the protonated monomers of  
27  
28  
29 208 triethyl phosphate and 1-octanol respectively. All plots have features well-known for API  
30  
31 209 sources with ion mobility spectrometers with onset of response (or limit of detection, LOD) or  
32  
33  
34 210 appearance of a protonated monomer at low mass, governed largely by the collision probability  
35  
36 211 for [M], reaction enthalpy, and time for mixing (or reaction) of  $H^+(H_2O)_n$  and M. Repeatability  
37  
38  
39 212 on average was better than 5% RSD as seen in error bars for data points. Plots for triethyl  
40  
41 213 phosphate show similar detection limits from 0.06 ppm from 80 to  $4 \times 10^3$  ppm with slightly  
42  
43 214 better LODs for 5.4 and 26 ppm. The high proton affinity and strong reaction enthalpy for this  
44  
45  
46 215 compound (and other phosphate or organophosphorous compounds) favor a stable protonated  
47  
48 216 monomer with little back reaction by water displacement (Equation 4). The slopes of the  
49  
50  
51 217 response curves (i.e., sensitivities) were comparable over the range of moisture levels each  
52  
53 218 reaching a non-linear region and then a plateau in response where the ion source is saturated.

54  
55 219 In contrast, response with the relatively low proton affinity of octanol at the extreme of proton  
56  
57  
58 220 affinities here shows low LOD only at low moisture (4.1 ppm) with a decade loss in LOD by 94

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4 221 ppm moisture. The change in slope ( $\Delta I/\Delta \text{mass}$ ) or sensitivity of response was significantly  
5  
6 222 affected by increased moisture with decreased sensitivity and displacement toward higher mass.  
7  
8  
9 223 Above 120 ppm moisture, product ions were not observed in the mobility spectra. At these  
10  
11 224 levels of moisture, the proton affinity of the hydrated proton was too large for the production of a  
12  
13  
14 225 protonated monomer or the reverse displacement by water controlled the lifetime of the product  
15  
16 226 ion. Octanol was representative of all alcohols (and aldehydes) which were chosen for low  
17  
18  
19 227 proton affinity to bracket performance with the high proton affinity phosphates. Ketones and  
20  
21 228 acetates with proton affinities between the extremes showed quantitative response intermediate  
22  
23  
24 229 between the extremes, described in detail at reduced temperatures below.

25  
26 230

### 27 28 29 231 3.3. *Quantitative Response as a Function of Temperature*

30  
31 232 Response curves were obtained also at temperatures of 50 and 100°C with representative plots  
32  
33 233 shown in Figures 4 to 6 for compounds with high, intermediate, and low proton affinities. As  
34  
35  
36 234 temperature is reduced to 100°C, response for an organophosphate (Figure 4) exhibited  
37  
38 235 similarities to that at 150°C (Figure 3a); however, significant differences can be seen with  
39  
40  
41 236 worsened LODs at 0.50 and  $4.5 \times 10^3$  ppm moisture. Otherwise, levels of saturation and slopes  
42  
43 237 are comparable at moistures of ~100 ppm and below. Response for compounds of intermediate  
44  
45  
46 238 proton affinity (2-nonanone, Figure 5) was similar without response at moisture above 500 ppm  
47  
48 239 above which response was suppressed until 4000 ppm where response was nil.

49  
50  
51 240 The influence of temperature is seen in the significantly lessen response for octanol with  
52  
53 241 decreased slopes to 100 ppm moisture, and no response above 100 ppm moisture. The other  
54  
55 242 chemical class with low proton affinities, aldehydes showed the strongest changes as a function  
56  
57  
58 243 of temperature and moisture where any response was observed only at 1 and 25 ppm. Even

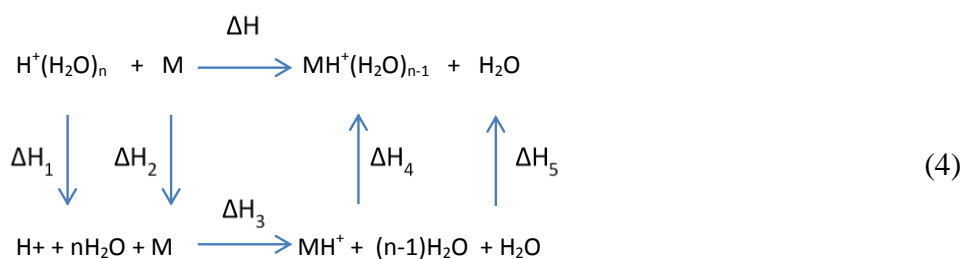
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244 spectra at these levels were distorted without extraction of quantitative response. At 50°C for  
245 alcohols, response was observed only at the lowest moisture level of 1 ppm. The changes in  
246 response with moisture and temperature with compounds spanning a range of proton affinities  
247 can be understood through enthalpies for reactions shown in Equations 4 and 5, and are  
248 described in detail below.

249  
3.4. *Standard Enthalpies and Free Energies of Reactions*

251 The proton transfer between  $H^+(H_2O)_n$  and analyte M in an atmosphere containing water vapor  
252 of Eq. 1 may be examined in detail with the Hess cycle of Equation 4.



253 The equations show stepwise relationships for the release of one water molecule as for the  
254 calculated thermodynamic data,  $\Delta H^\circ$  in Figure 7a and  $\Delta G^\circ$  in Figure 7b. In the cycle shown in  
255 Equation 6,  $\Delta H_2$  and  $\Delta H_5$  are zero,  $\Delta H_1$  is the enthalpy to fully dehydrate the proton and  $\Delta H_3$  is  
256 the negative of the proton affinity of M.  $\Delta H_1$  is obtainable from the NIST compilation for  
257 different values of n, n = 1 being for the proton affinity of water, 691 kJ mol<sup>-1</sup>, which is lower  
258 than for any of the analytes.  $\Delta H_3$  is the negative of the proton affinity of M and  $\Delta H_4$  is the  
259 enthalpy of hydration of  $MH^+$ .  $\Delta H_1$  is common to the reactions of all the analytes so for the  
260 overall reaction the differences observed in their behavior is dependent on the sum of  $\Delta H_3$  and  
261  $\Delta H_4$ , that is the proton affinity of M and the enthalpy of hydration of  $MH^+$ .

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4 262 In general, the enthalpy of hydration of  $MH^+$  is the inverse of the proton affinity of M: the more  
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6 263 tightly bound the proton to M, the lower will be charge transfer to a water solvation shell. Other  
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9 264 things being equal, as  $\Delta H_3$  becomes more positive  $\Delta H_3$  becomes less negative and  $\Delta H$  for the  
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11 265 overall reaction becomes more exothermic. This is confirmed by comparison of the calculated  
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14 266 enthalpies of reactions in Figure 7a with the proton affinities of the analytes listed in Table 1.  
15  
16 267 The calculated reaction enthalpy  $\Delta H$  between alcohol and aldehyde, and phosphate for  $n = 1$   
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19 268 when no solvation occurs is ca.  $110 \text{ kJ mol}^{-1}$ , which is essentially the same as the proton affinity  
20  
21 269 difference. For  $n = 4$  the reaction product is  $MH^+(H_2O)_3$ , and the difference becomes much  
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24 270 smaller, roughly  $40 \text{ kJ mol}^{-1}$ , indicating a much higher solvation for protonated alcohols and  
25  
26 271 aldehydes than for the phosphates. At all water concentrations, the ketones and acetates with  
27  
28  
29 272 intermediate proton affinities show intermediate enthalpy changes.  
30  
31 273 Previous computations show that this value of  $n$  occurs at  $\sim 500$  ppm moisture at  $150^\circ\text{C}$  and at  $\sim 1$   
32  
33 274 ppm moisture at  $50^\circ\text{C}$ . This computation is consistent with experimental results; at  $150^\circ\text{C}$   
34  
35  
36 275 response for aldehydes and alcohols was lost when the moisture level exceeds 500 ppm. At  
37  
38 276  $50^\circ\text{C}$  response was seen for aldehydes and alcohols at 1 ppm moisture, but the spectrum was  
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40  
41 277 distorted, and quantitative data was not extrapolated from this result (see supplementary data Fig  
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43 278 S7).

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### 47 48 280 3.9. Summary of sensitivity of response in IMS.

49  
50 281 The findings in this study are summarized in Figure 8 where sensitivity (slopes of response  
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52  
53 282 curves) are shown for three temperatures of the range of moistures. Several patterns in  
54  
55 283 sensitivity of response can be observed. At elevated temperatures ( $150^\circ\text{C}$ ), high and  
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58 284 intermediate proton affinity compounds exhibit response over the entire range of moisture with  
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4 285 slightly lessened and proportional decrease in sensitivity with increased moisture. Compounds  
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7 286 with low proton affinities alcohols and aldehydes lose response above 500 ppm moisture. As  
8  
9 287 temperature (Fig. 8b) is decreased to 100°C, a division in trends of sensitivity arises between  
10  
11 288 intermediate and high proton affinity compounds. Increases in moisture have little impact on  
12  
13  
14 289 high proton affinity compounds while intermediate proton affinity compounds exhibit loss in  
15  
16 290 response at high moisture levels. In the low proton affinity category, response for aldehydes is  
17  
18  
19 291 lost by 100 ppm and alcohols by 500 ppm moisture. At low temperature of 50°C, sensitivity  
20  
21 292 with low proton affinity chemicals is severely degraded for aldehydes and alcohols by 50 ppm  
22  
23  
24 293 and lost over 100 ppm. Sensitivities for intermediate proton affinity compounds were halved by  
25  
26 294 100 ppm (compared to low moisture) and lost above 500 ppm.

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### 31 296 3.5. *Change in analyte drift time ( $K_o$ values) as a function of moisture*

32  
33 297 Another impact of increased moisture in the drift tube was a shift in drift time for analyte ion  
34  
35  
36 298 peaks as shown in Table 1. Chemicals with proton affinities above 900 kJ mol<sup>-1</sup>  
37  
38 299 (organophosphates) showed no peak shifts in drift time as a function of moisture. Chemicals  
39  
40  
41 300 with medium proton affinities (ketones and acetates: 830 to 860 kJ mol<sup>-1</sup>), shifted to slower drift  
42  
43 301 times only when the moisture was increased above 100 ppm. The remaining chemicals with low  
44  
45 302 proton affinities (aldehydes and alcohols: ~800 kJ mol<sup>-1</sup>) shifted to slower drift times even with  
46  
47  
48 303 small increases in moisture. Above a moisture level of 100 ppm no response was seen for these  
49  
50 304 chemicals, thus shifts in drift time could not be determined.

51  
52  
53 305 The organophosphate monomers showed a decrease in mobility of 2 to 3% when the moisture  
54  
55 306 was changed from 1 ppm to 4×10<sup>3</sup> ppm (see supplementary data Fig S5). A linear regression  
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57  
58 307 was plotted, and a one-tailed test was performed on this regression for all the chemicals and p-

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4 308 values were obtained (Table 1). The three smaller monomers showed a statistically significant  
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7 309 change in  $K_o$  using at an alpha level of 0.05, and tributyl phosphate was significant at an alpha  
8  
9 310 level of 0.1. The  $K_o$  values for the dimers were also examined across the range of temperatures.  
10  
11 311 The dimers showed no statistical change in  $K_o$  with an increase in moisture. There was no  
12  
13  
14 312 change in  $K_o$  even when  $K_o$  was examined across temperatures. This result suggests that these  
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16 313 dimers do not hydrate at the conditions studied. These results are consistent with Mäkinen et al  
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18  
19 314 [6]. Further studies could look at the mobility of dimers across a range of chemical families to  
20  
21 315 see if this holds true for other chemical families as well.  
22  
23  
24 316 The acetate and ketone monomers also showed a dependence on moisture with respect to  
25  
26 317 reduced mobility. The monomers showed 2.5 to 3% decreases in mobility when the moisture was  
27  
28  
29 318 changed from 1 ppm to 500 ppm (see supplementary data Fig S6). A linear regression was  
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31 319 plotted, and a one-tailed test was performed on this regression for all the chemicals and p-values  
32  
33 320 were obtained (Table 1). The change was significant at an alpha level of 0.05 for all the acetates  
34  
35  
36 321 and ketones except for 2-heptanone. This is most likely due to the high errors observed as the  
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38 322 slope for 2-heptanone was the greatest for all chemicals examined. At an increased moisture  
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40  
41 323 level, the formation of dimers was suppressed so this relationship was not examined for the  
42  
43 324 dimers.  
44  
45 325 The  $K_o$  of the alcohols changed by 3% from a change in moisture from 1 ppm to 100 ppm, but a  
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48 326 statistical test was not performed on the alcohols due to there being few data points (see  
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50 327 supplementary data Fig S7). The Aldehydes were not examined for a change in  $K_o$  because of  
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52  
53 328 the lack of response at 25 ppm moisture and above.  
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#### 57 330 **4. Conclusions**



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4 331 In this study, the influence of moisture from 1 to  $4 \times 10^3$  ppm and temperature from 50 to 150°C  
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6 332 was shown to affect sensitivity of response with chemicals from three categories of low,  
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8 333 intermediate, and high proton affinity. These parameters are synergetic in influence through the  
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10 334 extent of hydration of the reactant ion and subsequent change on proton affinity of  $H^+(H_2O)_n$ .  
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12 335 Changes in proton affinity of the hydrated proton influence sensitivity of response and limits of  
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14 336 detection significantly with low proton affinity chemical such as aldehydes and alcohols. Only  
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16 337 minor impacts were observed with high proton affinity compounds, demonstrated here with  
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18 338 organophosphates although comparable behavior would be anticipated with amines. Compounds  
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20 339 of strong yet intermediate proton affinity, here acetates and ketones, should behavior between the  
21  
22 340 extremes with response possible into the hundreds of ppm moisture only. The findings here  
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24 341 compliment and reinforce findings with DMS for use in environmental monitoring and  
25  
26 342 demonstrate that the deleterious effects of moisture on ionization chemistry can be compensated  
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28 343 somewhat with temperature; nonetheless, moisture should be kept below 100 ppm for response  
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30 344 to a broad range of compounds. Alternatively, selectivity to high proton affinity chemicals could  
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32 345 be improved with suppressed response to compounds of lesser proton affinity with elevated (and  
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34 346 controlled) moisture levels.  
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#### 48 349 **Declaration of interest statement**

49  
50 350 We declare that we have no financial and personal relationships with other people or  
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52 351 organizations that can inappropriately influence our work.  
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415

418 Table 1. Drift times (in ms) of selected compounds at three levels of moisture.

<i>Chemical Name</i>	<i>Moisture (ppm)</i>			<i>Proton Affinity</i> (kJ mol <sup>-1</sup> )	<i>Slope</i>	<i>P-Value*</i>
	5	80 to 100	4000			
<i>Tributylphosphate</i>	21.8	21.8	21.7	915*	-0.008	0.058
<i>Triethylphosphate</i>	16.3	16.5	16.5	909	-0.015	0.036
<i>2-Nonanone</i>	17.1	17.4	17.8	854*	-0.021	0.049
<i>2-Heptanone</i>	15.1	15.3	15.8	845*	-0.022	0.080
<i>Pentyl Acetate</i>	15.9	15.9	16.4	839*	-0.015	0.022
<i>Butyl Acetate</i>	14.9	14.9	15.3	837*	-0.016	0.021
<i>Nonanal</i>	16.3	16.6	NA	802*		
<i>Heptanal</i>	15.4	15.8	NA	799*		
<i>1-Decanol</i>	16.0	16.6	NA	801*		
<i>1-Octanol</i>	14.3	15.1	NA	799		

419 \*Proton affinities estimated based on isomers or similar chemicals.

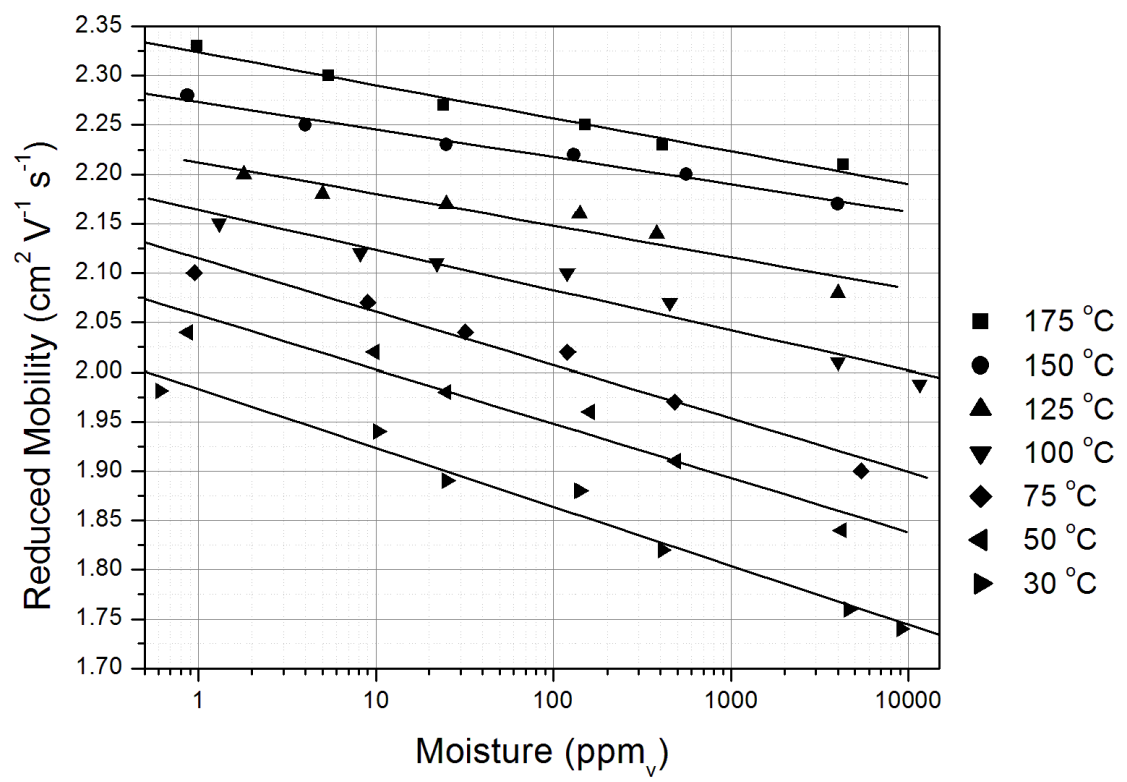
420 Alcohols and aldehydes show no response at  $4 \times 10^3$  ppm.

421 Error levels for drift times are  $\pm 0.2$ ms. NA reported for aldehydes and alcohols at  $4 \times 10^3$  ppm moisture due to no  
422 response seen at this moisture level.

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10 427 1. Reduced mobility coefficients ( $K_o$ ) for the reactant ion peak with moisture and temperature.  
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12 428 2. Level of hydration (n in  $H^+(H_2O)_n$ ) with moisture and temperature and calculated from distribution  
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15 429 curves derived from experimentally determined enthalpies.  
16  
17 430 3. Response curves at 150°C for a) triethyl phosphate and b) octanol at several moistures.  
18  
19 431 4. Response curves at 100°C for trimethyl phosphate at several moistures.  
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21 432 5. Response curves at 100°C for 2-nonanone at several moistures. No response was seen at  $4 \times 10^4$  ppm  
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23 433 moisture.  
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25 434 6. Response curves at 100°C for 1-octanol at several moistures. No response was seen at 500 ppm  
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27 435 moisture.  
28  
29 436 7. Spartan calculations of (a)  $\Delta H^\circ$  and (b)  $\Delta G^\circ$  for the reaction  $H^+(H_2O)_n + M \rightarrow MH^+(H_2O)_m +$   
30  
31  $(H_2O)_{n-m}$  where  $m=1$  for five chemicals. Calculations at 50, 100, and 150°C were comparable and  
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33 437 results only at 150°C are shown.  
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35 438  
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37 439 8. Sensitivity of the instrument towards the chemicals studied at three temperatures 150°C (left) 100°C  
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39 440 (middle) and 50°C (right).  
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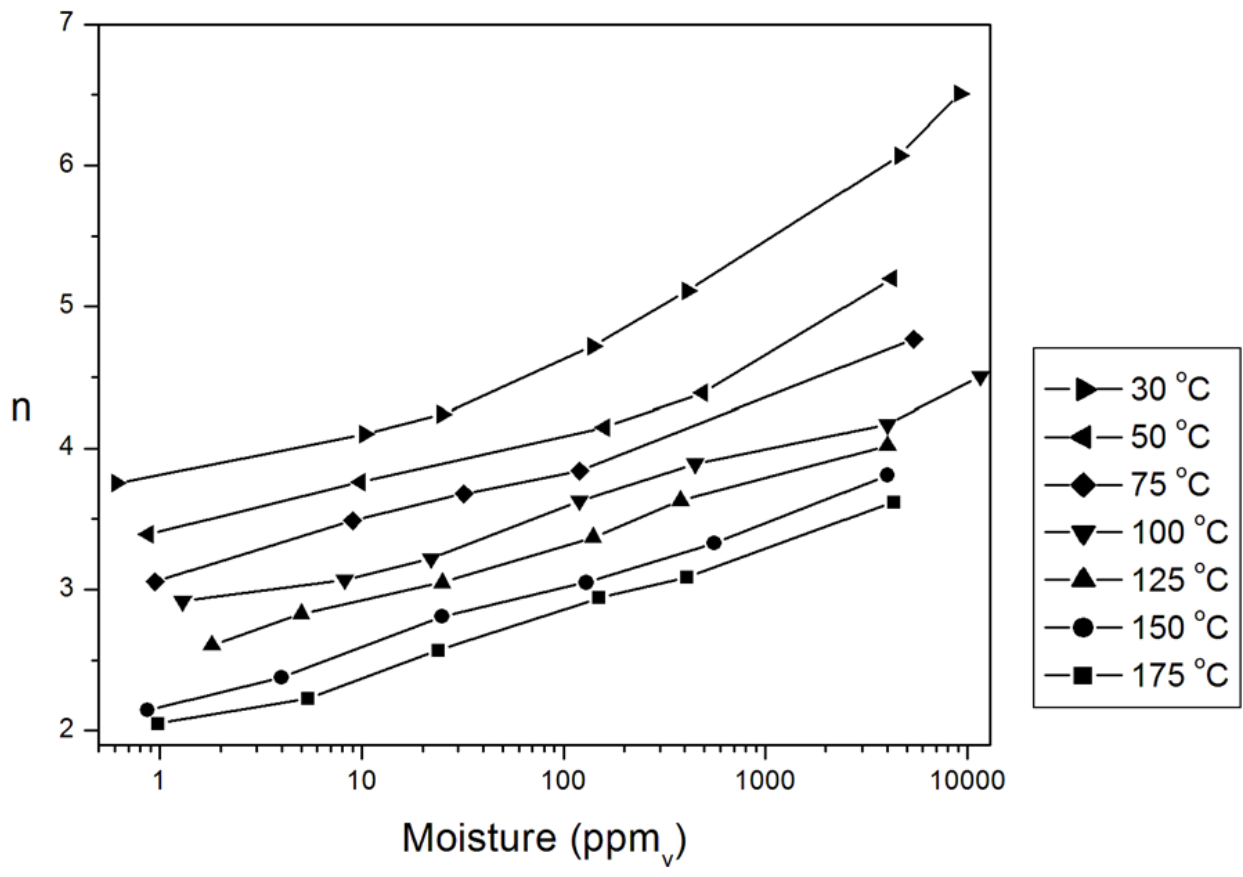
Figure 1.





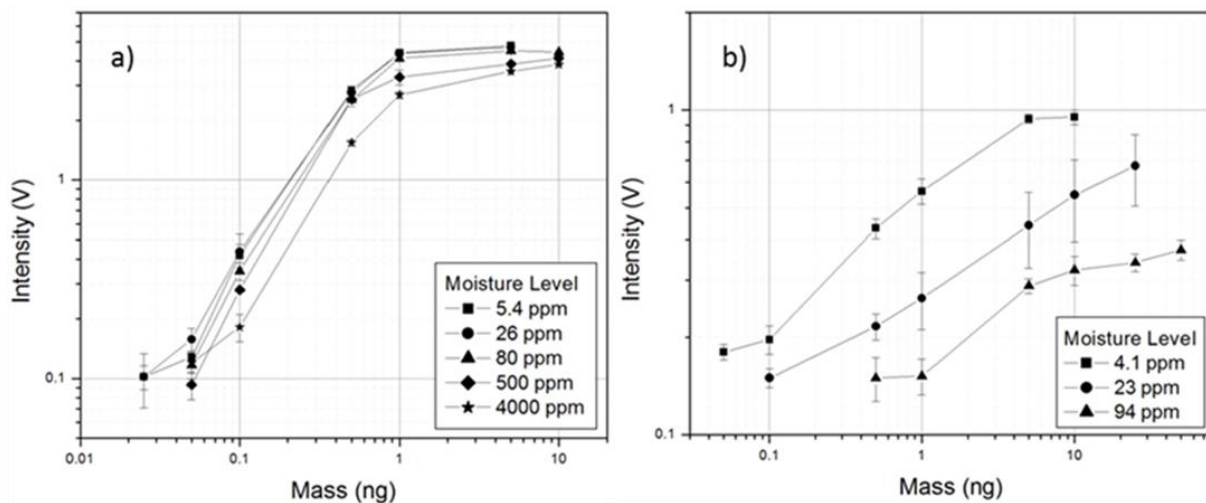
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Figure 2.



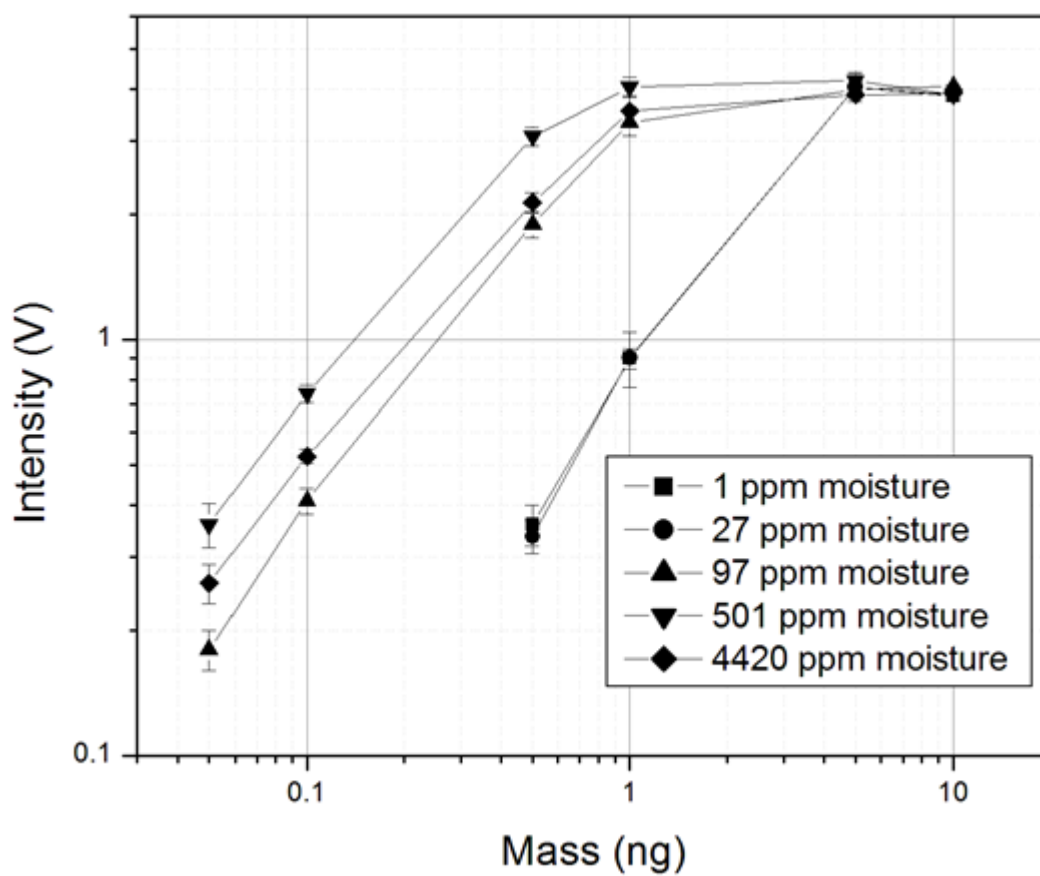
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Figure 3



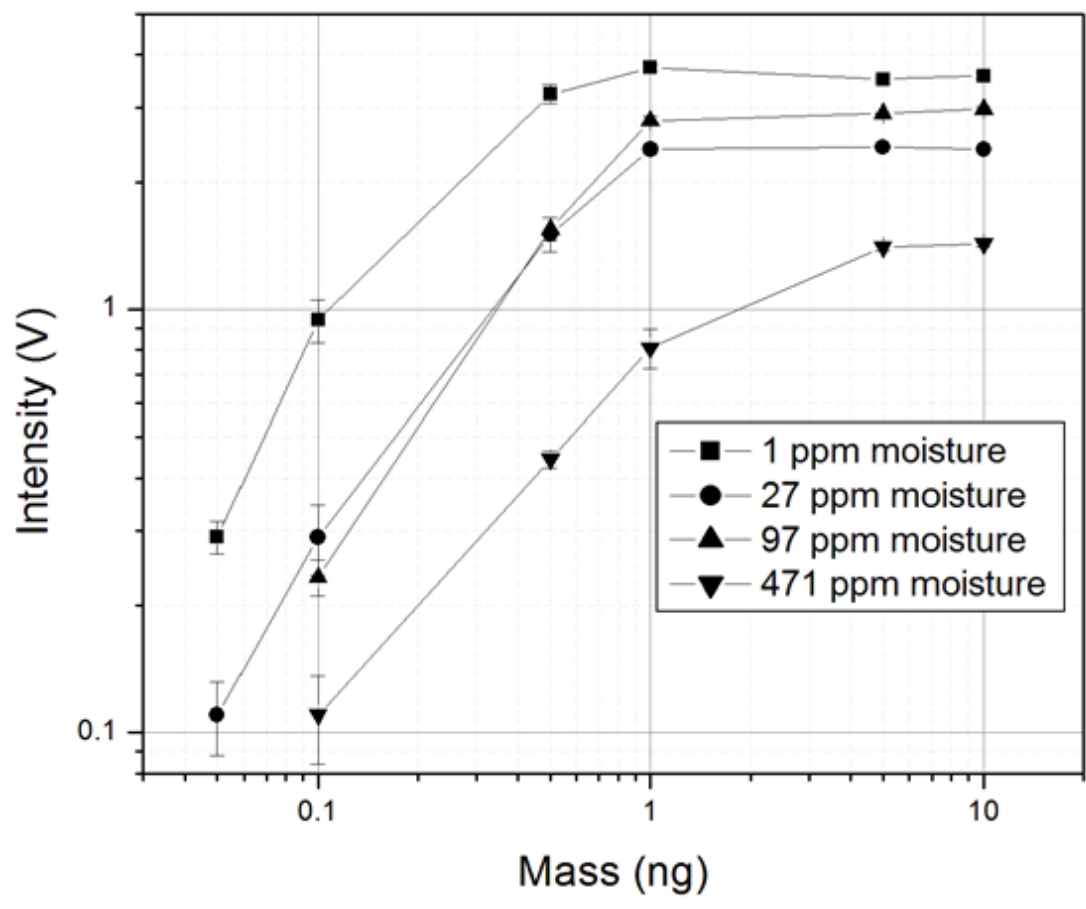
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Figure 4



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Figure 5.



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Figure 6.

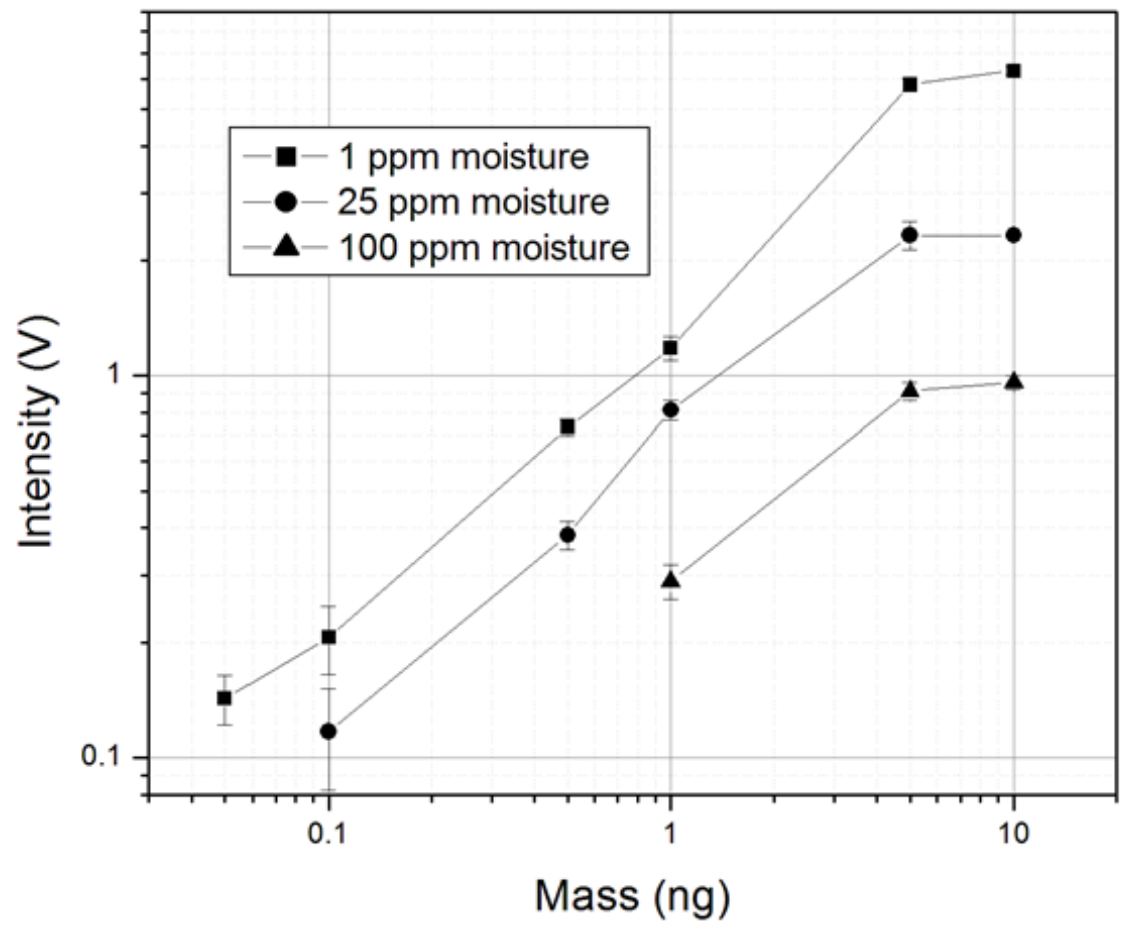
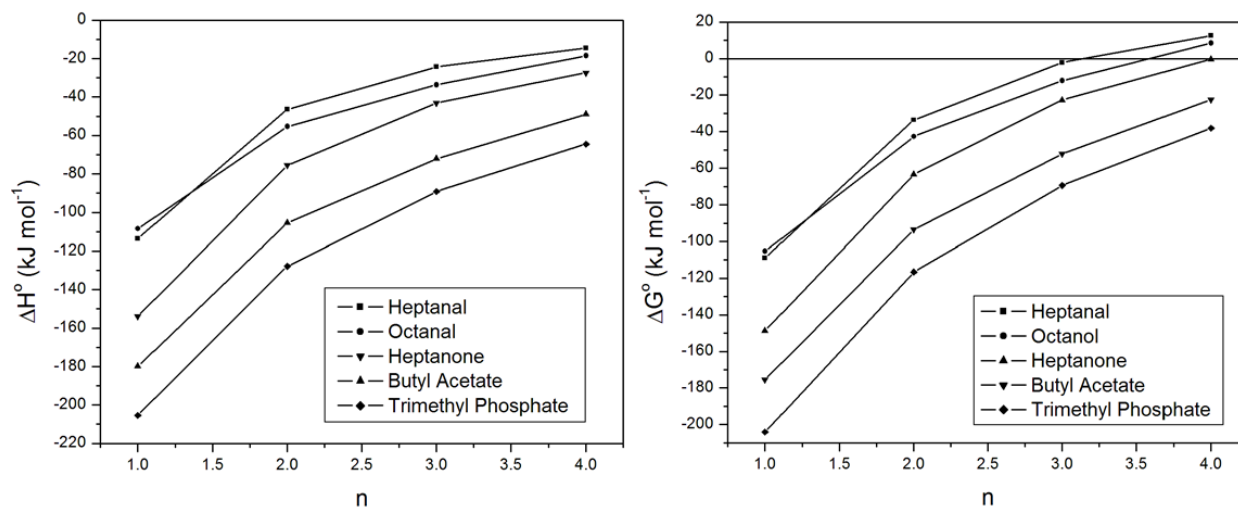


Figure 7



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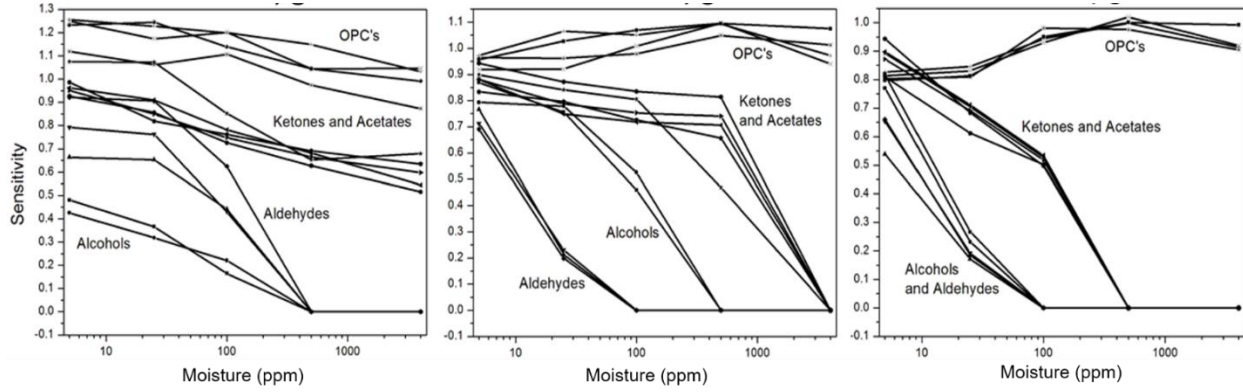
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Figure 8



1 **Supplementary data**

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3 QUANTITATIVE RESPONSE IN ION MOBILITY SPECTROMETRY WITH  
4 ATMOSPHERIC PRESSURE CHEMICAL IONIZATION IN POSITIVE POLARITY AS A  
5 FUNCTION OF MOISTURE AND TEMPERATURE

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8 Zahra Safaei<sup>1,2</sup>, Timothy J. Willy<sup>3</sup>, Gary A. Eiceman<sup>2</sup>, J.A. Stone<sup>4</sup>, M.  
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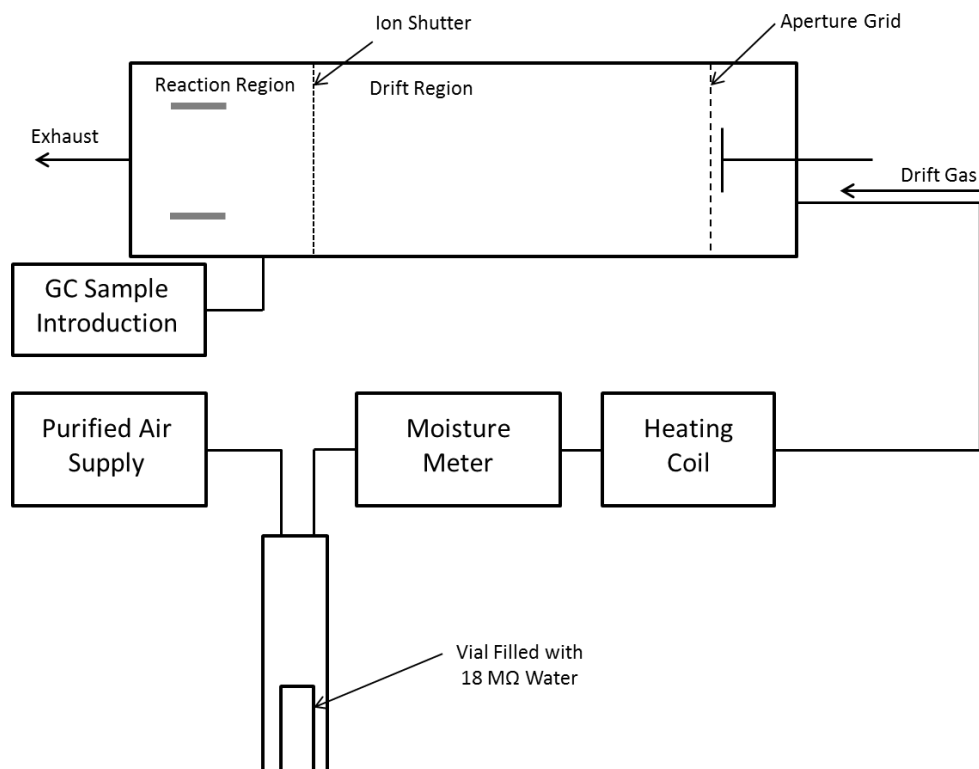
17 *<sup>4</sup>Department of Chemistry, Queens University, Kingston, Ont. K7L 4J1, Canada*

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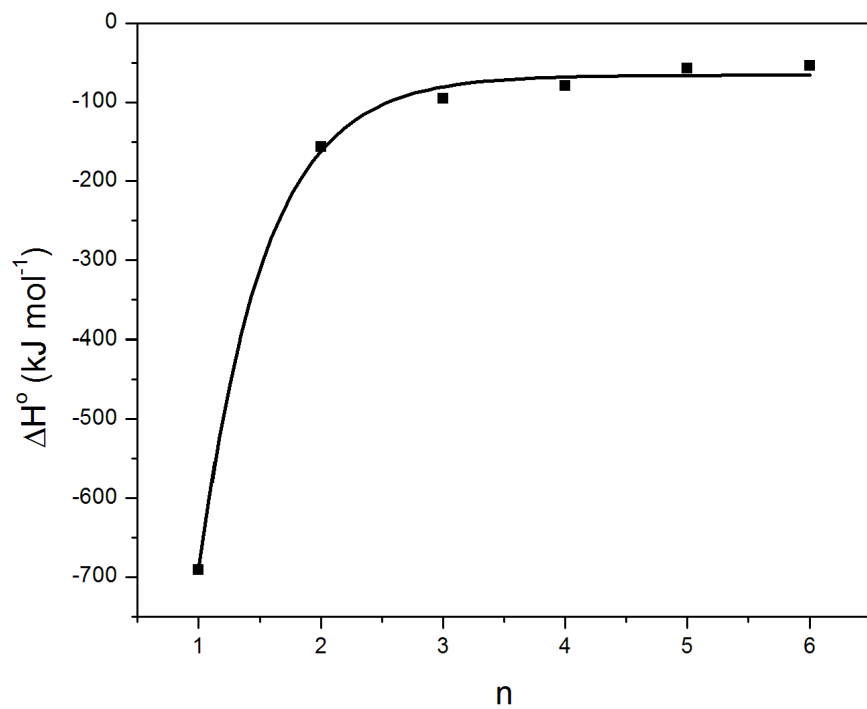
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 22 Fig. S1. Diagram showing the experimental design and drift tube used to add  
 23 moisture and sample to the drift gas. Moisture in the vial evaporates into the test  
 24 tube through a small opening and is carried into the drift tube by a purified air  
 25 flow. Moisture levels can be controlled by changing the size of the opening in the  
 26 vial.

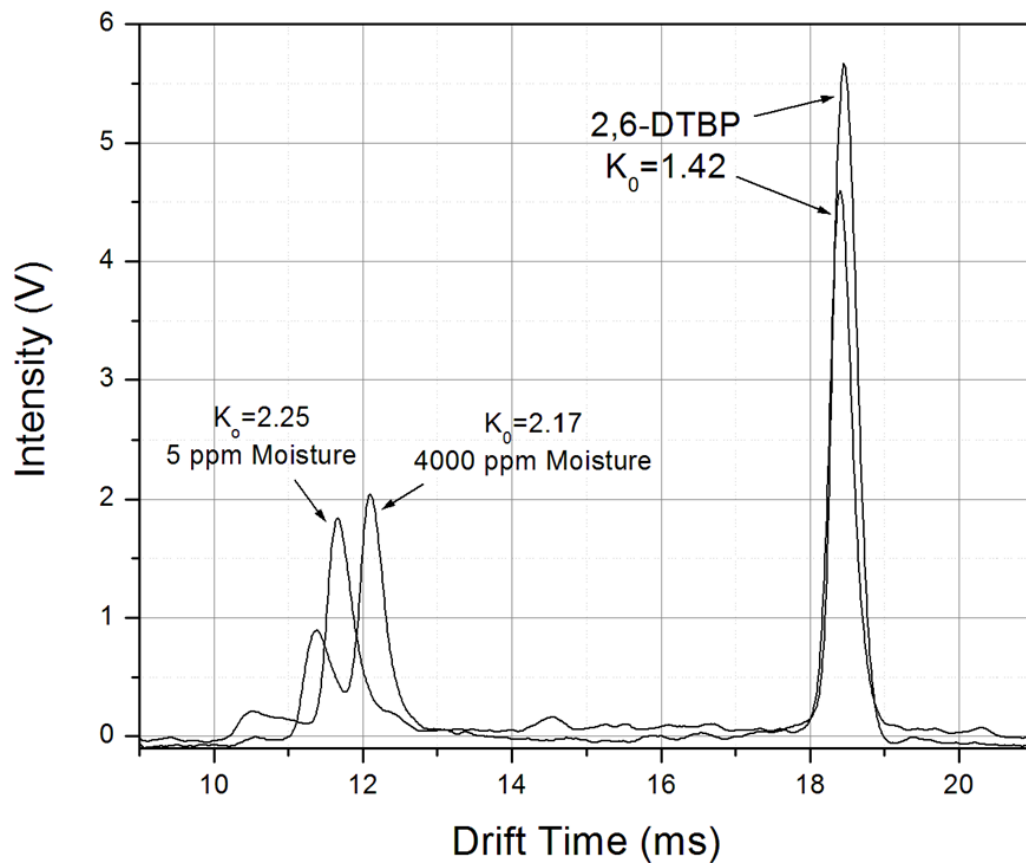
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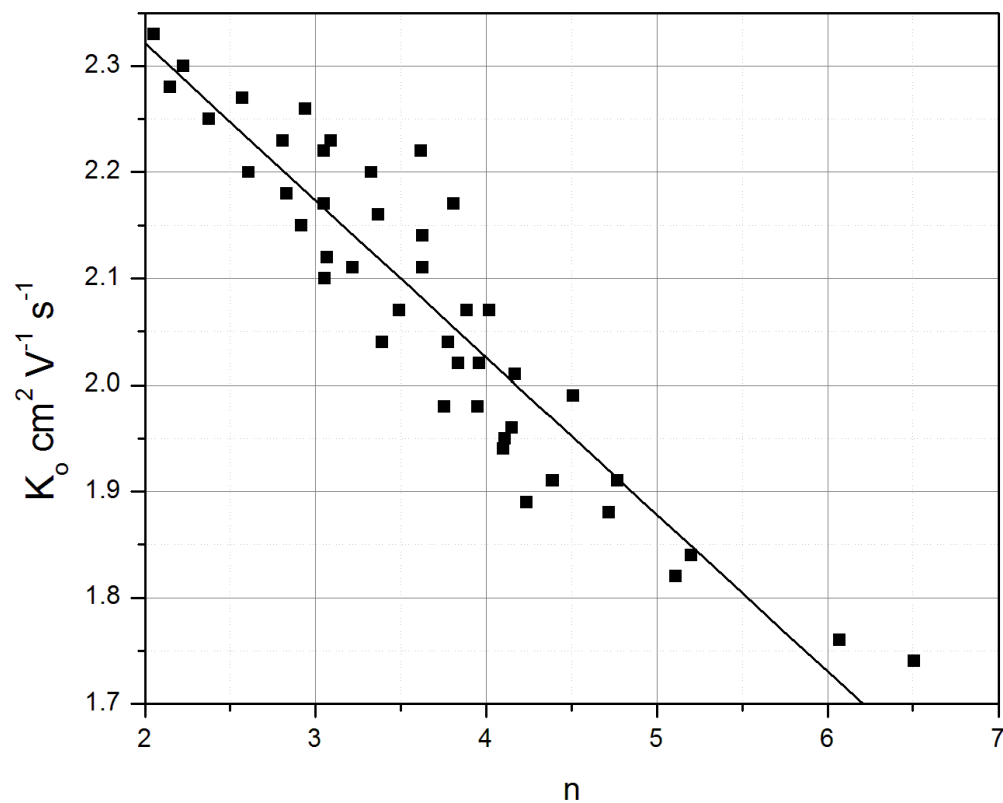
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30 Fig. S2. Plot of  $\Delta H^\circ$  for increasing n values for reaction 2 with n=1 to n=6 Values  
31 for  $\Delta H^\circ$  were obtained from Spartan 10 software.

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34 Fig. S3. Two spectra for the reactant ion with reduced mobility values at the lowest  
35 and highest moisture levels. 2,6-di-tert-butyl pyridine (2,6-DTBP) was used as a  
36 reference for the  $K_0$  ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) values.  
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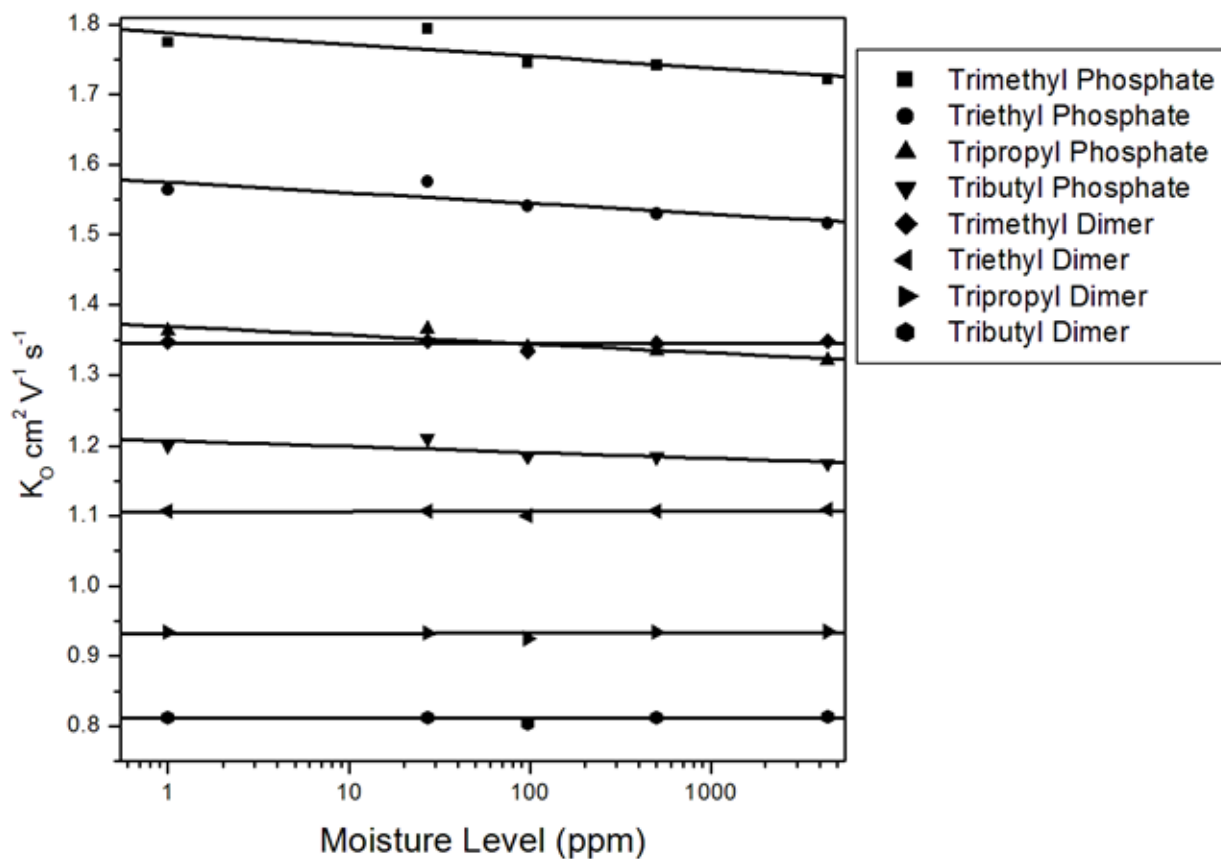
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39 Fig. S4. Plot of  $K_0$  for the reactant ion with respect to computational values for  $n$ .

40 The calculations for  $n$  were performed using models done by Kebarle. The  $R^2$

41 value was 0.87 and the slope was  $-0.147 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \text{n}^{-1}$ .

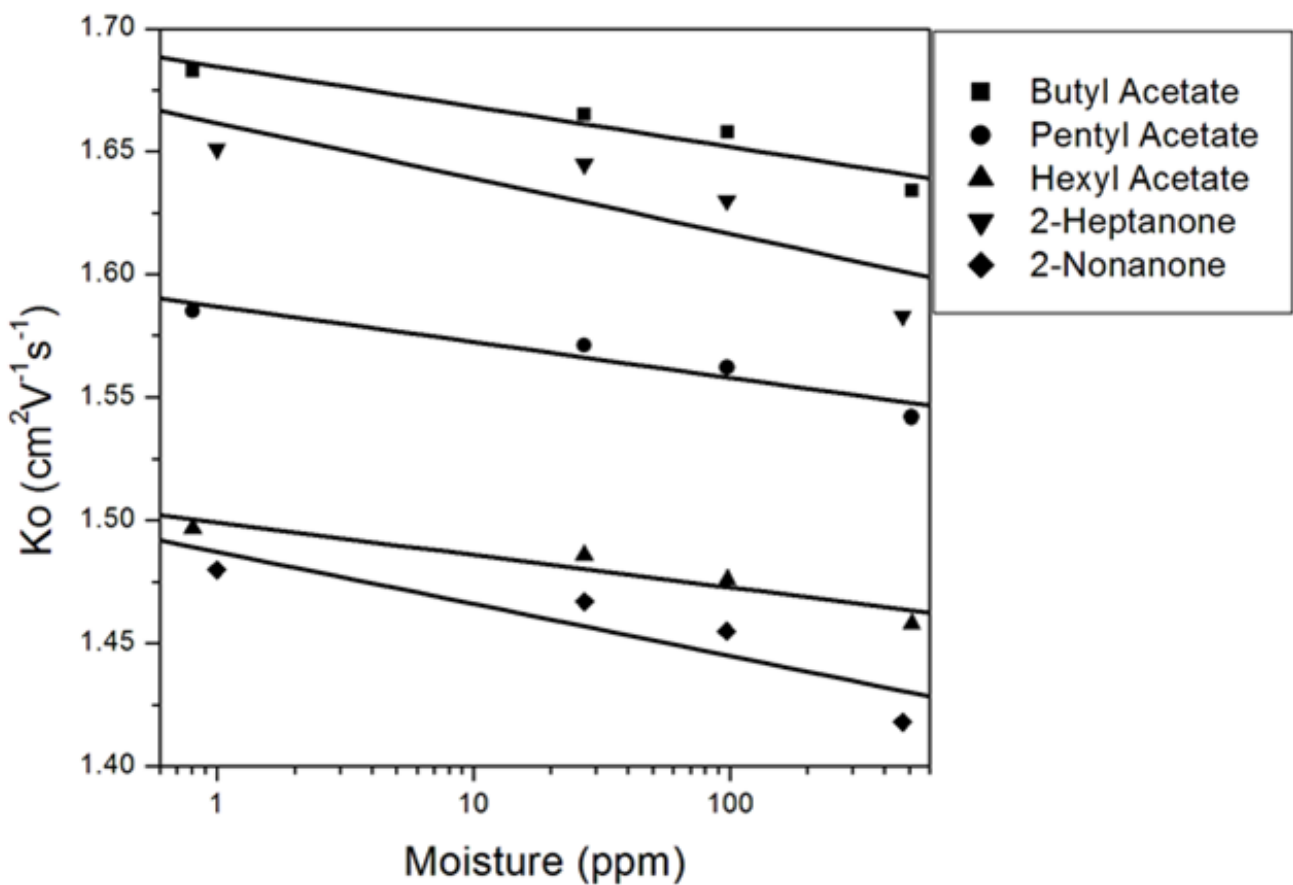
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 44 Fig S5. Graph showing change in  $K_o$  as a function of moisture for  
 45 organophosphorus compounds. The monomers of the three smaller compounds  
 46 showed a statistically significant difference in  $K_o$  as a function of moisture using  
 47 an alpha level of 0.05. Tributyl phosphate showed no statistically significant  
 48 change at an alpha level of 0.05 but was significant at an alpha level of 0.1. The  
 49 dimers for all the compounds showed no significant change.

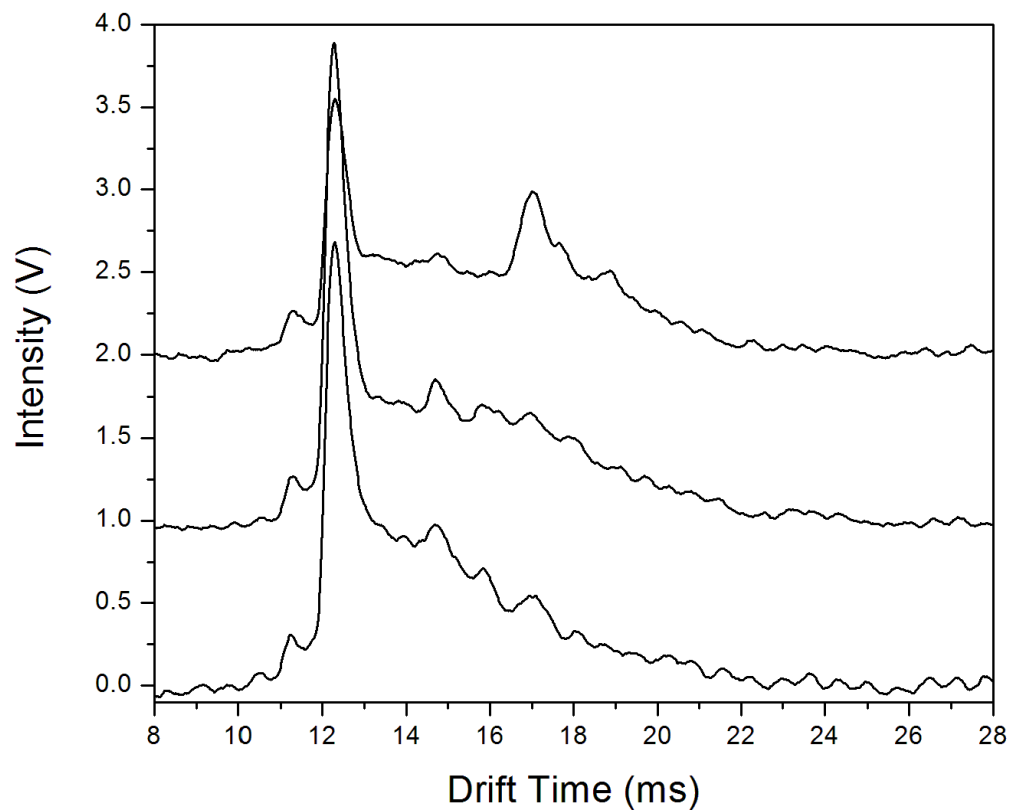
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 53 Fig S6. Graph showing change in  $K_o$  as a function of moisture for the monomers of  
 54 acetates and ketones. All chemicals show a statistically significant difference in  $K_o$   
 55 as a function of moisture. The formation of dimers was suppressed at elevated  
 56 moistures, so this relationship was not examined for the dimers.

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64 Fig. S7. Response of 10 ppb of nonanal (top), octanol (middle), and heptanal  
65 (bottom) at 50 °C and 1 ppm moisture.

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31 Conflict of Interest and Authorship Conformation Form  
32

- 33
- 34 ○ All authors have participated in (a) conception and design, or analysis and  
35 interpretation of the data; (b) drafting the article or revising it critically for  
36 important intellectual content; and (c) approval of the final version.  
37
  - 38 ○ This manuscript has not been submitted to, nor is under review at, another  
39 journal or other publishing venue.  
40
  - 41 ○ The authors have no affiliation with any organization with a direct or indirect  
42 financial interest in the subject matter discussed in the manuscript  
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