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# Determining Surface Energy of Porous Substrates by Spray Ionization

## Abstract

We have developed a new spray-based method for characterizing surface energies of planar, porous substrates. Distinct spray modes (electrospray versus electrostatic-spray), from the porous substrates, occur in the presence of an applied DC potential after wetting with solvents of different surface tension. The ion current resulting from the spray process maximizes when the surface energy of the porous substrate approaches the surface tension of the wetting solvent. By monitoring selected ion current (e.g., benzoyllecgonine,  $m/z$  290→168) with a mass spectrometer or total ion current with an ammeter, the solvent surface tension yielding the maximum ion current was determined to indicate the surface energy of the solid. Detailed evaluations using polymeric substrates of known surface energies enabled effective calibration of the approach that resulted in the correct estimation of the surface energy of hydrophobic paper substrates prepared by gas-phase silanization. A three-parameter empirical model suggests that the experimentally observed ion current profile is governed by differential partitioning of analyte controlled by the interfacial forces between the wetting solvent and the porous substrate.

## Keywords

Mass Spectrometry, Surface Energy, Paper Spray, Porous Surfaces, Electrostatic spray

## Disciplines

Materials Science and Engineering

## Comments

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**ABSTRACT**

We have developed a new spray-based method for characterizing surface energies of planar, porous substrates. Distinct spray modes (electrospray versus electrostatic-spray), from the porous substrates, occur in the presence of an applied DC potential after wetting with solvents of different surface tension. The ion current resulting from the spray process maximizes when the surface energy of the porous substrate approaches the surface tension of the wetting solvent. By monitoring selected ion current (e.g., benzoylecgonine,  $m/z$  290 $\rightarrow$ 168) with a mass spectrometer or total ion current with an ammeter, the solvent surface tension yielding the maximum ion current was determined to indicate the surface energy of the solid. Detailed evaluations using polymeric substrates of known surface energies enabled effective calibration of the approach that resulted in the correct estimation of the surface energy of hydrophobic paper substrates prepared by gas-phase silanization. A three-parameter empirical model suggests that the experimentally observed ion current profile is governed by differential partitioning of analyte controlled by the interfacial forces between the wetting solvent and the porous substrate.

**KEYWORDS:** Mass Spectrometry, Surface Energy, Paper Spray, Porous Surfaces, Electrostatic spray

## INTRODUCTION

The rapid spreading/penetration of a fluid (liquid or gas) on solid surfaces is an important phenomenon that is encountered in many practical applications including printing, water harvesting, oil recovery, and mass transfer.<sup>1-4</sup> Theoretical understanding of many of these processes relies on knowledge of interfacial forces, which are related to the adhesion between the solid substrate and the wetting liquid. Hence, the determination of the forces involved in the wetting process is important. Most wetting studies use contact angle measurements as the primary data, with small contact angles ( $<90^\circ$ ) indicating high wettability and large values ( $>90^\circ$ ) corresponding to low wettability. To facilitate the characterization of surface energies of porous fibrous materials with a complex interface such as cellulose substrates, this study focuses on the development of a novel method that relies on the measurement of ion current derived from electro spraying a suitable solvent from the planar substrate of interest. This new process was observed to provide higher resolution measurements on rough, porous materials than the conventional contact angle measurements.

Substrate-based ionization such as paper spray (PS) has become an inexpensive and facile technique for complex mixture analysis by ambient mass spectrometry (MS). PS-MS has been applied to quantify therapeutic drugs and their derivatives,<sup>5-9</sup> drugs of abuse,<sup>10,11</sup> chemical warfare agents,<sup>12-14</sup> and corrosion inhibitors<sup>15,16</sup> among other classes of compounds. Paper has not only proven to be an attractive sample collection, storage, and transportation strategy, but also requires only microliters of sample for analysis, easing the burden on the sample donor and collector. This attention has resulted in the development of modified paper substrates for the purpose of increasing analytical performance, such as wax printed,<sup>17</sup> silane treated,<sup>18,19</sup> silica coated,<sup>20,21</sup> paraffin barrier,<sup>22</sup> carbon nanotube coated,<sup>23-26</sup> and metal-organic framework coated paper.<sup>13,27,28</sup> Paper

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3 spray ionization inherently relies on the interaction between a raw sample and the (modified) paper  
4 substrate, as well as the extraction and ionization of a target molecule from the paper surface via  
5 a spray solvent. When the paper substrate is modified, these interactions are also altered, ultimately  
6 resulting in increased performance. Because of this, characterization of the modified paper surface,  
7 including surface energy, would help elucidate mechanism governing the observed increase in  
8 analytical performance. Surface energy is especially important because the paper surface not only  
9 acts as the ionization platform, but also the sample collection platform. Wetting properties of the  
10 sample on these new modified paper devices, influenced by surface energy, are of high importance  
11 as they control analyte stability,<sup>19</sup> analyte extraction and ionization.<sup>18</sup> More importantly, the  
12 widespread of any method will require reproducibility by others mandating quality control  
13 assessments. In this case, a means to certify that a selected paper treatment time will correspond  
14 to a specific hydrophobicity is needed to reduced batch-to-batch variations. Unfortunately, contact  
15 angle measurements are not suitable for characterizing anisotropic surfaces such as paper, because  
16 the equilibrium state of the liquid/solid contact is compromised by a third state, often air, filling  
17 the pores and capillary effects that cause variations in wetting states as the probing liquid displaces  
18 the air from the porous structure of the substrate.<sup>29</sup> Efforts to overcome these limitations still rely  
19 on a “corrected” contact angle measurement, which is not applicable if absorption of the solvent  
20 occurs especially with concomitant fiber swelling.<sup>30,31</sup> Therefore, an additional method of surface  
21 energy determination not relying on angle measurement may serve as a complementary technique  
22 in porous or fibrous surface analysis.

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50 We have previously shown that the surface energy of cellulose materials like paper can be  
51 lowered through surface grafting of silanes.<sup>18</sup> This process reduces wettability with an aqueous  
52 medium due to changes in surface chemistry and texture. The reduced wetting of the sample  
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3 facilitates increased sensitivity of PS-MS analysis from complex biological matrices via selective  
4 liquid/liquid extraction. This in-situ, selective partitioning capability is adopted here to estimate  
5 the surface energies of treated hydrophobic paper substrates. Precise and accurate quantification  
6 of the wetting properties of the treated paper is expected to enable efficient process optimization  
7 and reproducible implementation of this versatile material.  
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15 Specifically, the proposed spray method for determining surface energies of cellulose  
16 materials is based on the differential partitioning of a probe analyte (e.g., benzoylecgonine,  $\log P$   
17  $-0.59$ ) out of the paper substrate after wetting by a solvent of known surface tension. The  
18 hypothesis is that ion current derived from the wetted paper substrate will reach a maximum when  
19 the surface energy of this porous paper substrate approximately equals the surface tension of the  
20 liquid in contact with the paper. This is due to the occurrence of more efficient partitioning of the  
21 analyte between the solid and the liquid phase. By measuring the total ion current with a simple  
22 multimeter or the selected ion current with a mass spectrometer, this partitioning phenomenon can  
23 be monitored to indicate surface energy. This new approach overcomes major challenges  
24 associated with current contact and/or interface localization methods, including i) the limited  
25 resolution in contact angle measurement on fibrous or rough surfaces, and ii) dynamic nature of  
26 wetting on porous substrates leading to continuous change in wetting states over time. Results  
27 indicate that both total and selected ion currents derived from a particular substrate vary with  
28 surface tension of the wetting solvent, reaching a maximum near the surface energy of the porous  
29 substrate. Calibration with polymeric substrates of known surface energies enabled correct  
30 prediction of surface energies of unknown solid substrates. The experimentally recorded ion  
31 current distribution curves were reproduced by a three-parameter model that included partition  
32 coefficient, solvent surface tension and the solid surface energy of interest.  
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## MATERIALS AND METHODS

### Reagents, Standards and Solutions

Standard solution (1.0 mg/mL) of benzoylecgonine was obtained from Cerilliant (Round Rock, TX). (3,3,3-trifluoropropyl) silane and acetonitrile were purchased from Sigma-Aldrich (St. Louis, MO). Whatman filter paper (24 cm, grade 1), polycarbonate, polyacrylonitrile and ethyl acetate membrane filters were purchased from Whatman (Little Chalfont, England).

### Hydrophobic Paper Preparation

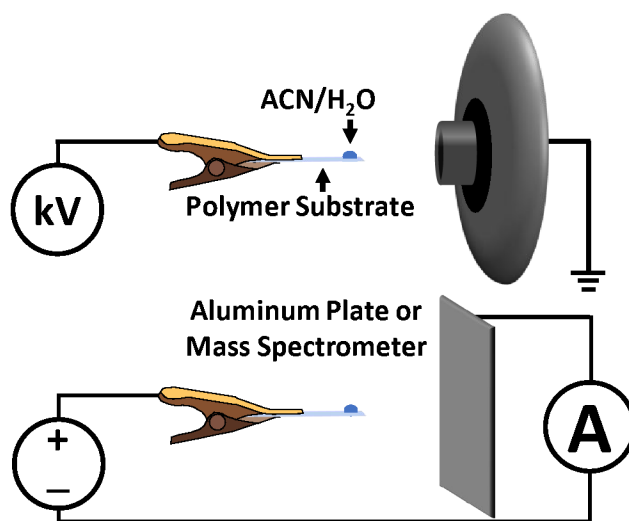
All paper rectangles were cut by hand using a paper trimmer. Pre-cut paper rectangles were treated in a vacuum desiccator with 0.5 mL trichloro(3,3,3-trifluoropropyl) silane. Untreated paper was not subjected to this reaction. The strips of paper/polymer rectangles were 4 mm base x 20 mm height.

### Paper Spray Ionization, Ion Current and Contact Angle Measurements

Electrospray from paper substrates occurs by applying a direct current (DC) voltage to the paper wetted by a suitable solvent in an experiment known as paper spray. The ion current derived from this ionization process was measured with a Fluke 287 multimeter, which was attached to a 3 × 2 inches aluminum plate. A DC voltage of 5 kV was applied to the paper substrate by an external power source (Figure 1). All experiments were performed using paper substrates on which 4 μL of 2 μg/mL (8 ng absolute amount) benzoylecgonine had been dried. The presence of a known



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3 chemical species allows a more selective means by which ion currents can be monitored through  
4 tandem mass spectrometry (MS/MS). Therefore, all ion current profiles presented in this work  
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6 tandem mass spectrometry (MS/MS). Therefore, all ion current profiles presented in this work  
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8 were collected via mass spectrometer unless otherwise specified. Here, product ion current  
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10 corresponding to the benzoylecgonine transition  $m/z$  290  $\rightarrow$  168 was recorded using a Thermo  
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12 Scientific Velos Pro LTQ linear ion trap mass spectrometer (San Jose, CA). MS parameters used  
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14 were as follows: 200°C capillary temperature, 3 microscans, and 60% S-lens voltage. Spray  
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16 voltage was 5 kV unless otherwise specified. Distance between the paper and mass spectrometer  
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18 inlet ranged from 1-3 cm depending on required energy needed for droplet vibration and ionization.  
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20 Thermo Fisher Scientific Xcalibur 2.2 SP1 software was used for MS data collection and  
21  
22 processing. Collision-induced dissociation (CID) was utilized for analyte fragmentation. Fragment  
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24 of benzoylecgonine ( $m/z$  290  $\rightarrow$  168) was monitored in the positive mode with collision energy of  
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26 of benzoylecgonine ( $m/z$  290  $\rightarrow$  168) was monitored in the positive mode with collision energy of  
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28 30 eV. Movies of hydrophobic PS spray plumes were recorded using a Watec camera (WAT-  
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30 704R). Color pictures were taken with a Canon PowerShot SX410 IS. Contact angles were  
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32 measured using a ramé-hart goniometer.  
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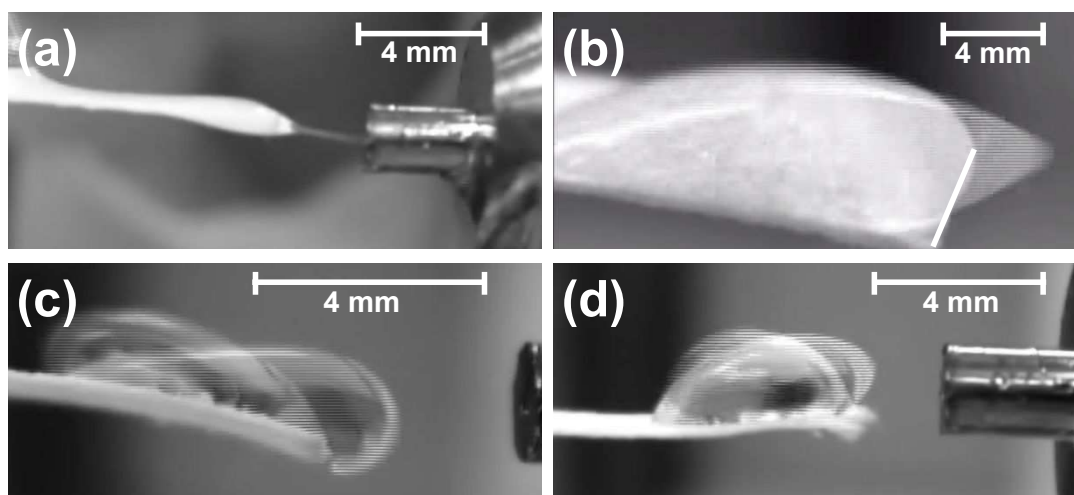
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3 **Figure 1.** Experimental setup using a mass spectrometer (top) or an aluminum plate with a  
4 microammeter detector (bottom). A rectangular strip of polymer substrate is affixed to an alligator  
5 clip, on which a DC voltage is applied. The solvent of choice (varying mixtures of acetonitrile and  
6 water) is applied to extract and ionize analyte pre-dried on the surface. The aluminum plate or  
7 mass spectrometer detects the incoming ion current.  
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## 19 **RESULTS AND DISCUSSION**

### 20 **Ionization Modes with Changing Surface Energies**

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25 Commercial application of modified paper substrates in analytical mass spectrometry will  
26 depend on proper characterization of properties including surface energies of the treated paper.  
27 Our initial attempts to use contact angle measurement with water produced inconsistent results on  
28 the anisotropic paper substrates (e.g., see Figure S1).<sup>29</sup> That is, although significant structural  
29 differences in treatment has been reported,<sup>32</sup> comparable contact angles were observed for the  
30 (3,3,3-trifluoropropyl) silane treated filter paper despite the fact that the modified paper substrates  
31 exhibited marked differences in wetting properties. This wetting process translates into variable  
32 ion yields, the limit of which is related to the surface energy of the substrate since  $\delta W = \gamma dA$  (where  
33  $W$  = work,  $A$  = area, and  $\gamma$  = surface tension).<sup>33</sup> Observations via camera revealed several spray  
34 modes when utilizing spray solvents with varying surface tension (Figure 2 and Videos S1-S4).  
35 When a solvent does not wet the treated hydrophobic paper during PS, a stable Taylor cone is not  
36 observed, and instead electrostatic spray<sup>34</sup> ionization occurs. This is due to capacitive charging in  
37 the applied solvent drop, causing molecules within the drop to align themselves with the applied  
38 electric field and accelerate.<sup>35,36</sup> The kinetic energy gained in this process results in macroscopic  
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3 vibration (surface instabilities) of the solvent drop (Figure 2b-d). Meanwhile, molecules that gain  
4 sufficient kinetic energy break through the liquid surface and are collected as ions by the  
5 multimeter or mass spectrometer. This voltage dependence has been confirmed, rather than relying  
6 solely on pneumatic effects (Figure S2). The extent of vibration, which depends on the magnitude  
7 of applied voltage<sup>37,38</sup> and the relative difference between surface tension of solvent and surface  
8 energy of paper determines collected ion intensities. We have used this interaction to determine  
9 the surface energy of treated hydrophobic paper samples when contact angle was insufficient.  
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41 **Figure 2.** Stills from Videos S1-S4. Acetonitrile/water droplets of varying ratios (see Table 1)  
42 resting on a paper strip treated for 2 hours when 5 kV is applied. (A) Droplet consists of solvent 7  
43 (pure acetonitrile, surface tension 29.3 mN/m). (B) Consists of solvent 5, surface tension 38 mN/m.  
44 (C) Consist of solvent 4, surface tension 40.5 mN/m. (D) Consists of solvent 1, surface tension  
45 62.4 mN/m.  
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Table 1. Reported surface tensions of acetonitrile/water mixtures. Those signified by a number are reported by Rafati et. al.<sup>39</sup>

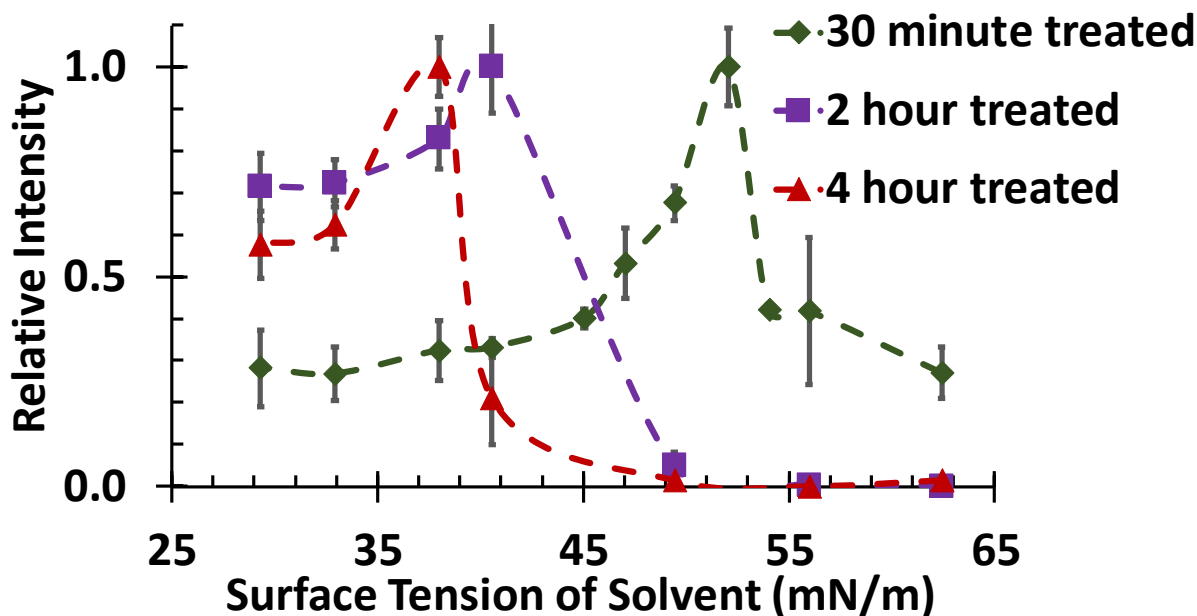
Solvent	Mole Fraction of Acetonitrile	Mole Fraction of Water	Does the solvent wet 2-hour treated paper?	Literature Surface Tension (mN/m) <sup>39</sup>
1	0.0149	0.9851	No	62.36
2	0.0298	0.9702	No	55.92
A*	0.0366	0.9634	No	54*
B*	0.0410	0.959	No	52*
3	0.0516	0.9484	No	49.39
C*	0.0620	0.9380	No	47*
D*	0.0710	0.9290	No	45*
E*	0.0814	0.9186	No	43*
4	0.0950	0.9050	No	40.54
5	0.1227	0.8773	Partially	37.97
6	0.2541	0.7459	Yes	32.92
7	1	0	Yes	29.3

\*Surface tensions estimated by interpolation. Used only on select treated papers or polymers

### Estimating Surface Energies from Surface Tension of Solvent and Maximum Ion Current

Ion intensities are dependent on the relative difference between the surface tension of the solvent and the surface energy of the paper because: (i) the solvent must dissolve/extract the target dried analyte from the paper surface through wetting; (ii) the surface tension of the solvent determines the spray mode, which ultimately influences (iii) the ionization efficiency of the analyte. These conditions imply that there is an optimal solvent surface tension for ion production from a given

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3 paper substrate with specific surface energy. This is because solvents with high surface tensions  
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5 are less likely to form a stable Taylor cone while solvents with low surface tension are expected  
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7 to suffer from unfavorable analyte partitioning and dilution in large area.  
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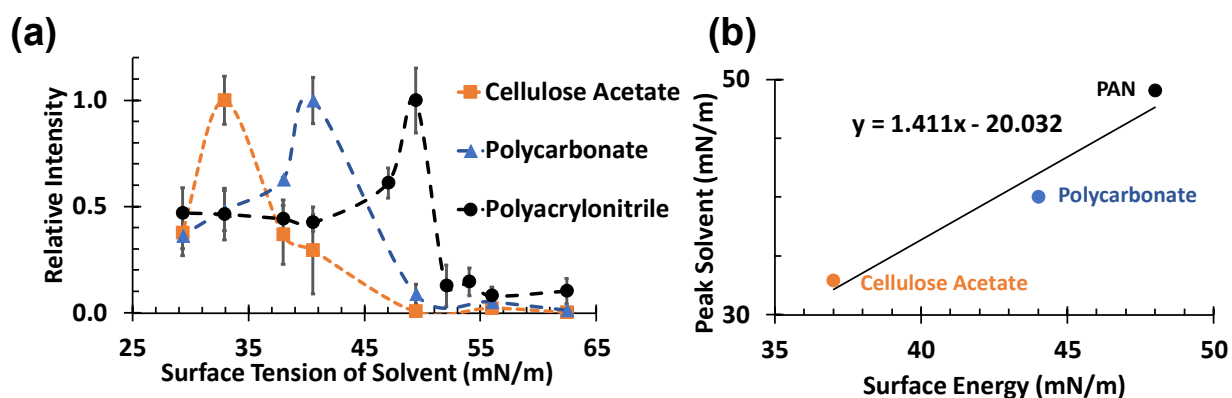
**Figure 3.** Experimental ion intensity varying with the change of surface tension of ACN/H<sub>2</sub>O spray solvents for silane treated paper. (Table 1) collected via mass spectrometer ( $m/z$  290  $\rightarrow$  168). Dotted lines connect experimental data and do not represent modeled data. Data was collected in triplicate, and error bars show one standard deviation.

To examine this possibility, we used solutions of known surface tensions that consisted of varying mole fractions of water/acetonitrile mixtures (Table 1).<sup>39</sup> These solution mixtures were used as spray solvents in electrostatic spray where neat benzoylecgonine (2  $\mu$ g/mL) analyte dried on the hydrophobic paper was ionized in the process. Because the electrostatic spray ionization of

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3 dry samples is a function of solubility and wettability, we anticipated a maximum ion signal to be  
4 recorded when the surface tension of the spray solvent approximately equaled the surface energy  
5 of the hydrophobic paper. This expectation has been met (Figure 3). Maximum/peak selected ion  
6 ( $m/z$  168) currents were observed at solvent surface tensions of 38, 40, and 52 mN/m for  
7 hydrophobic paper substrates prepared by 4 h, 2 h, and 30 min silane exposure times, respectively.  
8 Polymeric membranes of known surface energies were also employed: cellulose acetate (37  
9 mN/m), polycarbonate (44 mN/m), and polyacrylonitrile (PAN) (48 mN/m). The corresponding  
10 peak currents were observed at 33, 40, and 49 mN/m (Figure 4a), respectively, which correlated  
11 well with the known surface energies of the membranes (Table 2). These results suggest the  
12 position of the maximum current may be used to determine the surface energy of the  
13 paper/membrane from which the electrostatic spray is derived. Therefore, the three membranes  
14 were used as standards to estimate the unknown surface energies of treated paper (Figure 4b).  
15 Through interpolation, the surface energies of the as-prepared hydrophobic paper substrates were  
16 estimated to be 41, 42.5, and 51 mN/m for 4 h, 2 h, and 30 min treatment times, respectively (Table  
17 2). These results compare well to an earlier study, in which a Zisman plot determined the critical  
18 surface tension of a 2 hour treated silane paper to be  $\sim 44$  mN/m.<sup>18</sup> The decreased surface energies  
19 observed for increased silane treatment times is not surprising given that hydrophobicity is  
20 expected to increase with concomitant decrease in surface energies. It should be noted that this  
21 method is limited by the availability of commercial polymeric membranes that are suitable for  
22 ionization. Because of this limitation, only three membranes could be used for the calibration  
23 shown in Figure 4b.

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53 While surface tension and composition of solvent is an influencing factor of ion intensity, it is not  
54 the sole contributor to the ion profile found in Figures 3 and 4a. This is supported by contrasting the ion  
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profiles with Figure S3, which showed little surface effects. In Figure S3, 10 ng of benzoylecgonine was dried and reconstituted in each solvent found in Table 1. These solutions were analyzed by mass spectrometry via direct injection through electrospray ionization (5 kV spray voltage). Ion intensity derived from each solution was nearly constant, and a maximum intensity appears when pure acetonitrile is used (solvent 7). This clearly indicates that the surface also effects which solvent will produce a larger ion intensity using the paper spray experiment. This is further supported by the clear shifts of peak surface tension solvent shown in Figure 3 when the only changing parameter is the treatment time of the paper surface.



**Figure 4.** (a) Experimental ion intensity of benzoylecgonine varying with the change of surface tension of ACN/H<sub>2</sub>O spray solvents for commercial polymers (Table 1) collected via mass spectrometer ( $m/z$  290  $\rightarrow$  168). Dotted lines connect experimental data and do not represent modeled data. Data was collected in triplicate, and errors bar show one standard deviation. (b) Calibration of cellulose acetate polycarbonate, and polyacrylonitrile (PAN) with treated and untreated paper projected onto the line where peak surface tensions are used as values for the y-axis. The determined surface energies of paper substrates are provided in Table 2.

Table 2. Surface energy determination using peak surface tension solvent.

Surface name	Reported Surface Energy (mN/m)	Peak Tension (mN/m)	Surface Solvent	Calculated Surface Energy (mN/m)
Cellulose Acetate	37	33		--
Polycarbonate	44	40		--
Polyacrylonitrile	48	49		--
4 Hour Treated Paper	--	38		41
2 Hour Treated Paper	--	40		42.5
30 Minute Treated Paper	--	52		51

### Fitting a Model to Experimental Data

The ability to reproduce known surface energies of selected membranes gives high credence to the proposed method. We developed an empirical model to probe the theoretical validity of important factors considered in this study.

Optimum ion current is expected when solvent surface tension is approximately equal to the surface energy of the paper/polymer surface. All solvent mixtures used across each experiment are similar in composition, and thus evaporation rate post-Taylor cone is similar and would not



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3 contribute to an increase in signal at an intermediate mixture during ionization (as seen in figures  
4 3 and 4a). Therefore, it is hypothesized that evaporation rate is less important in determining the  
5 solvent surface tension that yields the highest ion signal when compared to wetting and partitioning  
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13 Three regions in the ion profile (Figure 3, 4a) can be distinguished: (1) the region before  
14 the maximum current, involving solvents with lower surface tension than the surface energy of the  
15 solid substrate, (2) the point at which the ion current is maximized; at this point, the corresponding  
16 solvent surface tension is expected to equal the surface energy of the paper substrate, and (3) the  
17 region after the peak current, where solvent surface tension is greater than surface energy of the  
18 substrate.  
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28 If we define the partition coefficient as:  
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$$31 \quad K = \frac{m_{\text{solvent}}}{m_{\text{paper}}} \quad (\text{Eqn. 1})$$

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35 where  $m_{\text{solvent}}$  is the moles of the target analyte in the spray/extraction solvent, and  $m_{\text{paper}}$  is the  
36 moles of target analyte on the paper surface. This term (K) is meant to describe not only the initial  
37 dissolution of target analytes from the blood spot, but also the total amount of analyte carried to  
38 the tip of the paper and present in the spray entering the mass spectrometer. Each region in the ion  
39 current distribution curve will have the following properties: (1) Solvent with low surface tension:  
40 high degree of wetting, high degree of paper-solvent-analyte interaction resulting in possible  
41 redistribution of analyte back into the paper substrate post-extraction, high evaporation rate (due  
42 to spreading) further increasing redeposition of the analyte onto the paper before spray can occur,  
43 and resulting in a decreased K value. (2) Solvent for the peak ion current must have surface tension  
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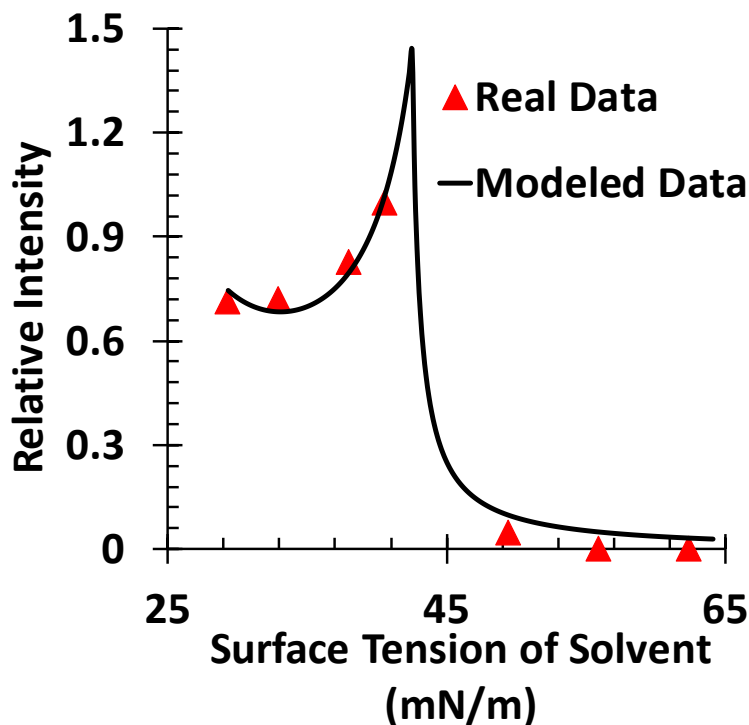
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3 that allows intermediate wetting, less paper-solvent-analyte interaction and less analyte re-  
4 deposition/redistribution post-extraction resulting in more efficient transfer to the mass  
5 spectrometer.<sup>5</sup> It will also have a moderate evaporation rate and large K value. (3) Solvent with  
6 high surface tension: low degree of wetting, low degree of paper-solvent-analyte interaction  
7 resulting in reduced extraction and low amount of re-deposition, low evaporation rate, and small  
8 K value.  
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11 Using the above reasoning, along with adding fitting parameters to correct for a changing  
12 K value and other parameters, we propose the following empirical equation to account for the  
13 shape of the ion current observed in Figure 3 and 4a:  
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$$I \approx \frac{aK}{|SE^2 - \gamma^2| + b\gamma - c} \quad (\text{Eqn. 2})$$

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30 where I is the number of desorbed molecules, which relates to ion intensity; a, b, c are fitting  
31 parameters; K is the partition coefficient; SE is the surface energy of solid substrate; and  $\gamma$  is the  
32 surface tension of solvent. This equation is expected to produce a maximum ion intensity near the  
33 peak surface tension solvent while correcting for partitioning effects pre-ionization. By setting K  
34 to 1 (note: changes in K will occur as solvent composition is varied, but for simplicity, we set K  
35 equal to 1, and any associated errors is compensated for by the fitting parameter a) and SE as 42.5  
36 mN/m, we fitted this equation to the data collected for 2 hour treated paper resulting in a good  
37 correlation with experimental data (Figure 5; also see Figures S4-S7). The mechanism modeled  
38 here describes only the desorption of molecules from the solid substrate and their subsequent  
39 transfer via droplets toward the instrument, whose quantity is proportional to the ion intensity at a  
40 single time point. Modeling was performed on relative data, with the assumption that other factors  
41 such as applied potential, ionization efficiency, charge deposition, or work functions associated  
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with the detector would scale the data to absolute quantities. The shape of this function, when plotted using the best fitting parameters, is as shown in Figure 5. This trend implies there is an actual peak surface tension that is approximately equal to the surface energy of the paper, which can be determined experimentally.



**Figure 5.** Data found on Figure 3a fitted with Equation 2 for 2 hour treated paper. Fitting parameters were found to be:  $a = 116.76 \text{ m}^2/\text{mN}^2$ ,  $b = 66.1 \text{ mN/m}$ ,  $c = 2728 \text{ mN}^2/\text{m}^2$ .

For high accuracy and selectivity, fragment ion ( $m/z$  168) currents from benzoylecgonine were monitored by a mass spectrometer to determine peak surface tensions. However, this method of determining surface energy of a rough, porous surface is not limited to the use of a mass

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3 spectrometer. Instead, a multimeter or microammeter can be paired with the membrane/paper  
4 strips to measure total ion current and subsequently determine the peak surface tension. Here, a  
5 multimeter attached to an aluminum plate was connected to a portable power source that supplied  
6 5 kV DC voltage; ion currents derived from the paper spray process were monitored for different  
7 solvents. Current profiles obtained from the multimeter measurements were similar to those  
8 recorded using the mass spectrometer, and peak surface tensions were found for polycarbonate,  
9 cellulose acetate, and 4-hour treatment paper that agreed well with MS values (Figure S8).  
10 Although not selective to specific analyte, this result indicates that surface energy is a key  
11 parameter in determining the performance of substrate-based spray ionization methods. The shape  
12 of the extracting liquid droplet is determined both by the surface tension of the liquid itself and the  
13 surface energy of the substrate upon which the drop rests (plus other external factors, e.g., gravity).  
14 The changes in droplet shape can in turn affect electrospray ion yield by changing charge density.  
15 For example, a liquid with lower surface tension will result in larger wetting area, leading to limited  
16 charge density at the droplet surface and a lower Laplace pressure that is not optimal for  
17 electrostatic spray. On the other hand, a liquid with very high surface tension would lead to droplet  
18 with small surface area, and thus high electrostatic pressure under the same surface charge. The  
19 Laplace pressure of the liquid will also be very high, making electrostatic spray difficult to occur.  
20 Consequently, a liquid deposited on a substrate with moderate surface tension will favor  
21 electrostatic spray, just as is predicted by Equation 2.  
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## 51 CONCLUSIONS

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3 In summary, comparing the extraction and ionization of benzoylecgonine from the porous  
4 substrates composed of cellulose acetate, polycarbonate and polyacrylonitrile allowed the  
5 estimation of surface energy of modified paper. The degree of wetting determines the mechanism  
6 of ionization in paper spray. An electrospray-based mechanism is observed for complete wetting  
7 conditions and ionization occurs via the formation of a Taylor cone. The solvent beads onto the  
8 surface if it is unable to wet the substrate; the application of DC potential causes the solvent drop  
9 to vibrate resulting in the generation progeny of smaller droplets via electrostatic spray  
10 mechanism. By adjusting the surface tension of solvent, the surface energy of the substrate from  
11 which the spray is derived can be determined. The subtle variations in interfacial forces arising  
12 from changes in solvent surface tension results in a measurable difference in ion intensities, which  
13 is quantified by a mass spectrometer or a simple multimeter. This spray ionization method was  
14 able to resolve surface energies of modified paper substrates (e.g., 41.0 and 42.5 mN/m) that are  
15 challenging to distinguish by contact angle measurements. The method is applicable to synthetic  
16 polymeric membranes. An empirical equation was proposed to provide an approximation for the  
17 observed experimental data.  
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## 42 **ASSOCIATED CONTENT**

### 43 **Supporting Information**

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45 The following files are available free of charge.

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47 Brief description of supporting information (PDF)

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51 Video S1: Solvent with surface tension 62 mN/m on treated paper (AVI)  
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3 Video S2: Solvent with surface tension 41 mN/m on treated paper (AVI)  
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6 Video S3: Solvent with surface tension 38 mN/m on treated paper. Footage of Taylor cone  
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8 formation was replayed at the end of the video at 10% speed. (AVI)  
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12 Video S4: Solvent with surface tension 29 mN/m on treated paper (AVI).  
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### Author Contributions

A.B-T and D.E.D designed the experiments. D.ED, Y.S.M, D.M.A, and J.B performed spray experiments. B.S.C performed contact angle measurements, S.M. and M.M.T helped with theoretical modeling. All authors discussed the results. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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### ABBREVIATIONS

PS, paper spray; MS, mass spectrometry; DC, direct current; MS/MS, tandem mass spectrometry; CID, collision-induced dissociation; PAN, polyacrylonitrile

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TOC

