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Conical torch allows direct analysis of pure and hydro-alcoholic solutions of methanol and 1-propanol in ICPOES

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3 Analytical performance of the Conical torch in inductively View Article Online  
4 coupled plasma optical emission spectroscopy operating DOI: 10.1039/DOJA00368A  
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13 methanol and 1-propanol solutions

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28 **Abstract**

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This work explores, for the first time, the strengths and weaknesses of the Conical torch in ICP-OES operating methanol and 1-propanol solutions ranging from 30% to 100% w w<sup>-1</sup>. To this end, Conical torch performance has been evaluated considering: (i) plasma fundamental properties; (ii) plasma robustness; (iii) carbon-based background emission; and (iv) analytical figures of merit. For the sake of comparison, a Fassel torch has been employed as a reference. Results show that the discharge for the Conical torch is highly robust and plasma characteristics (i.e., excitation temperature and electron number density) are mostly unaffected by the introduction of pure and hydroalcoholic solutions of methanol and 1-propanol. In contrast, the discharge for the Fassel torch is severely affected by organics introduction and it is not feasible to operate methanol solutions above 30% w w<sup>-1</sup>. Because torch geometry and improved gas flow patterns, the Conical torch affords higher emission signal (2-fold) than the

Fassel torch. Nevertheless, the detection limits for both torches are comparable, which is due to the increase in both (carbon-based) background emission and signal noise for the Conical torch. From these results and considering that the Conical torch requires less r.f. power (35%) and argon consumption (55%) than the Fassel one, it is beyond doubt that the former torch is more advantageous for those applications requiring the analysis of alcohol solutions (i.e. extraction procedures and chromatographic separations).

**Keywords:** Conical torch, matrix effects, methanol, 1-propanol, inductively coupled plasma, optical emission spectrometry

## Introduction

Most of the applications involving inductively coupled plasma-optical emission spectrometry (ICP-OES) are focused on the analysis of liquid samples containing either acid and/or salt matrices. Nevertheless, there are circumstances in which the analysis of organic/hydro-organics matrices might be required such as: (i) samples of organic nature (e.g. petroleum products, spirits, etc.);<sup>1,2</sup> (ii) samples treated with organic solvents (e.g. analyte extraction);<sup>3,4</sup> and (iii) chromatographic mobile phases in hyphenated applications.<sup>5</sup>

The analysis of organic/hydro-organic matrices by ICP-OES is challenging due to the occurrence of both spectral and non-spectral interferences.<sup>6</sup> In general, spectral interferences by organics are easy to deal with since the most sensitive analyte wavelengths in ICP-OES are found below 300 nm whereas carbon-based molecular emission is located in the high UV and visible regions. Non-spectral

interferences are, however, more troublesome and can arise from changes on

(i) nebulization and aerosol transport to the plasma. Mainly because of the lower surface tension and the higher volatility usually shown by organics with regard to acidic solutions, the former generates finer aerosols and affords higher aerosol transport to the plasma.<sup>7,8</sup> Therefore, higher analyte emission signals might be expected when operating organics; (ii) plasma excitation conditions. Plasma fundamental properties (excitation temperature, electron density, etc.) are usually deteriorated by the high solvent load afforded by organics, thus negatively affecting analyte emission (i.e. signal suppression).<sup>9,10,11</sup> In fact, organics could extinguish the plasma and compromise long-term plasma performance due to the formation of carbon deposits within the torch;<sup>12</sup> and, (iii) analyte ionization/excitation mechanisms. It has been observed that carbon species affect differently atomic and ionic populations present in the plasma and, hence, emission signals in ICP-OES.<sup>13,14,15</sup> To improve plasma tolerance and mitigate both spectral and non-spectral interferences in ICP-OES,<sup>16</sup> different strategies have been proposed: (i) optimization of experimental conditions to improve plasma robustness (i.e. increase r.f. plasma power and decrease both the nebulizer gas flow rate and the sample uptake rate);<sup>4,7,8</sup> (ii) decrease injector inner diameter;<sup>1,16</sup> (iii) changes on the rim shape of both intermediate and injector tubes of the (Fassel) torch;<sup>17</sup> (iv) selection of non-conventional sample introduction systems (i.e. spray chamber cooling, desolvation system, electrothermal vaporization, etc. );<sup>1,4,7,16</sup> and (v) oxygen addition.<sup>2,16</sup> However, most of the approaches are not easy to apply in routine analysis and entail more complexity and additional costs.

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3 Recently, a new Conical ICP torch has been presented as an alternative to the  
4 conventional (cylindrical) Fassel design.<sup>18,19,20,21</sup> Because of its geometry, the new  
5 torch is able to produce a plasma with 4 times higher power density (leading to  
6 higher excitation/rotational temperature, higher electron density, and higher  
7 robustness) compared with that generated with the Fassel torch, while  
8 consuming 50 to 70% less argon and up to 800 W less power.<sup>18,19,20</sup> Despite  
9 operating at lower argon flow and r.f. plasma power, the Conical torch shows  
10 comparable figures-of-merit and lower Na-based matrix effects than those of the  
11 Fassel torch in both axially- and radially-viewed ICP-OES.<sup>18,21</sup> Given its analytical  
12 features, the use of the Conical torch may be advantageous for the direct analysis  
13 of organic matrices without requiring complex experimental arrangements.  
14 Nonetheless, no previous attempts to operate such matrices have been reported  
15 so far.

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17 The goal of this work is to evaluate the analytical performance of the Conical torch  
18 operating organic solutions in axially-viewed ICP-OES. To this end, pure and  
19 hydroalcoholic solutions of methanol and 1-propanol have been introduced into  
20 the plasma. These solvents have been selected attending to its wide use in  
21 analytical applications and its different physicochemical properties (e.g. viscosity,  
22 volatility, carbon to oxygen ration, etc.) that allow the assessment of the main  
23 problems arising from organic introduction in ICP-OES (i.e. spectral and non-  
24 spectral interferences).<sup>6,16</sup> Conical torch performance has been evaluated in  
25 terms of: (i) plasma characteristics (i.e. excitation temperature and electron  
26 number density) and robustness (Mg II/Mg I ratio); (ii) carbon-based background  
27 emission; and (iii) analytical figures of merit (i.e. sensitivity, repeatability and limits  
28 of detection). To evaluate the strengths and weaknesses of the Conical torch  
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operating organic solutions, a conventional Fassel torch has also been employed as a reference.

## Experimental

### Reagents and solutions

Pure and hydroalcoholic solutions (30% w w<sup>-1</sup> and 60 w w<sup>-1</sup>) of methanol and 1-propanol and 1.0% w w<sup>-1</sup> nitric acid were tested to investigate the analytical capabilities of the Conical torch in dealing with organic matrices. All the solutions were prepared using deionized water (in-house system) and analytical grade organic solvents (Sigma-Aldrich, Steinheim, Germany). Multielemental standard solutions (Al, B, Ca, Cr, Cu, Fe, Ga, Mg, Mn and Mn) for each matrix were prepared by diluting aliquots from the corresponding 1000 µg mL<sup>-1</sup> monoelemental reference solutions (ICP standard, TraceCERT, EMD Millipore Corp., USA). Because of differences in wavelength sensitivity, Ca, Mg, Mn and Na concentration was fixed at 0.5 mg L<sup>-1</sup>, whereas, for the remaining elements, it was 10 mg L<sup>-1</sup>. Blank solutions for each matrix were prepared to perform studies on plasma tolerance and carbon-based background emission.

### ICP-OES instrumentation

The experimental setup is schematically shown in Figure 1. The lens stack was placed in front of the torch to observe the plasma in axial viewing (i.e., head on) and achieve higher sensitivity. Therefore, the obtained signals represent

integrated emission from the whole length of the central channel of plasma. A flow of air was implemented in front of the torch at a suitable distance to divert the tail, thus reducing self-absorption and protecting the optical lenses from thermal damage and sample deposition.<sup>20</sup> The focal distance of the lens stack with respect to the plasma was carefully adjusted to maximize signal intensity for each torch. An optical fiber was used to transfer the collected light to the entrance slit of a monochromator (Triax550, HJY, USA) which was connected to a charge-coupled detector (CCD3000, Spectrum-One, HJY, USA). The CCD was cooled with liquid nitrogen to minimize dark current noise. Table 1 shows the geometrical parameters of both Conical and Fassel torches. Further description of the experimental arrangement can be found elsewhere.<sup>18,19,20</sup>

Plasma operating conditions employed throughout this work for both torches are shown in Table 2. For the Conical torch, r.f. power and plasma gas flows previously used for aqueous introduction were selected to operate organics as well. For the Fassel torch, however, standard operating conditions for aqueous introduction are not suitable to deal with organics and, hence, they were partially modified. Thus, according to the literature, plasma r.f. power was increased from 1000 W to 1400 W whereas the intermediate gas flow was set at 1.0 L min<sup>-1</sup> instead of 0.2 L min<sup>-1</sup>.<sup>8,16,22</sup>

Emission lines employed in this work are listed in the Supplementary material (Table S1, Electronic supplementary information). To evaluate plasma characteristics operating organics, excitation temperature (i.e. Boltzmann plot with Fe atomic lines)<sup>23</sup> and the electron number density (i.e. Stark broadening of the H<sub>β</sub> 486.133 nm line) were monitored.<sup>24</sup> Plasma robustness was assessed by means of the Mg II 280.270 nm/Mg I 285.213 nm line intensity ratio.<sup>25</sup> Carbon-



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3 based background was evaluated by using atomic carbon (C I 247.856 nm),  
4 cyanide radical, CN, (378-388 nm) and the diatomic carbon, C<sub>2</sub>, (473-484 nm)  
5 emission.<sup>22</sup> For all the tests, 10 consecutive integrations of the desired  
6 wavelength were acquired. The integration times were adjusted considering the  
7 sensitivity of the target lines. Limits of detection were calculated based on the 3 $\sigma$   
8 criterion. To this end, background signal and its relative standard deviation  
9 (RSD<sub>BG</sub>) were determined as suggested by Sadler et al.<sup>26</sup> Finally,  
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## Results

Plasma discharge using the Conical torch was directly ignited and sustained for pure and hydroalcoholic solutions of methanol and 1-propanol without any major trouble operating the standard experimental conditions usually employed for aqueous solutions. Neither special ignition procedure<sup>27</sup> nor modification of the standard sample introduction system (i.e. spray chamber cooling, desolvation, etc.)<sup>8</sup> were required. In fact, the discharge was highly stable even at sample uptake rates (Q<sub>i</sub>) as high as 1.5 mL min<sup>-1</sup>. This fact is highly remarkable considering that an r.f. plasma power of just 900 W and a plasma gas flow of 7 L min<sup>-1</sup> were employed.

Fig 2. shows plasma images operating pure and hydroalcoholic solutions of 1-propanol for the Conical torch at a nebulizer gas flow (Q<sub>g</sub>) of 0.3 L min<sup>-1</sup>. A 1.0% w w<sup>-1</sup> nitric acid solution is included as a reference. The images were captured with a Nikon D90 camera mounted with a 105 mm AF MICRO NIKKOR lens. For comparison purposes, all the images were captured at the same distance and with identical camera settings such as exposure, shutter speed, ISO, etc. As it can be observed, the shape and position of the discharge were mostly unaffected

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3 when increasing the content of 1-propanol. Differences on the length of the  
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5 plasma in the axial direction between 1.0 w w<sup>-1</sup> nitric acid and 1-propanol  
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7 solutions were lower than 5%. Similar findings were also noticed operating pure  
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9 and hydroalcoholic solutions of methanol (Fig. S1, Electronic supplementary  
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11 information).

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14 Though plasma experimental conditions were specifically selected to operate  
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16 organics (e.g. plasma r.f. power 1400 W, etc.), the analysis of pure and  
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18 hydroalcoholic solutions using the Fassel torch is clearly more challenging,  
19  
20 particularly operating with the methanol ones.<sup>6,8</sup> Thus, the discharge was highly  
21  
22 unstable operating methanol solutions below 60% w w<sup>-1</sup> and was extinguished for  
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24 more concentrated solutions. Pure and hydroalcoholic solutions of 1-propanol,  
25  
26 however, can be operated without any major difficulty. Interestingly, it was  
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28 observed that plasma was moved downstream and was contracted for all alcohol  
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30 matrices in comparison with the reference solution (Fig. 2 and Fig. S1). For  
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32 instance, the length of the plasma in the axial direction for pure 1-propanol was  
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34 approximately 20% lower than for 1.0 w w<sup>-1</sup> nitric acid. This phenomenon, known  
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36 as thermal pinch effect, is usually related to the increase in plasma thermal  
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38 conductivity by the atomization of solvent molecules which cools the peripheral  
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40 regions of the plasma, giving rise to a smaller and hotter plasma.<sup>28,29</sup> Therefore, it  
41  
42 could be concluded that the discharge for the Conical torch is apparently more  
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44 robust against organics than the Fassel one. In fact, once the plasma was  
45  
46 extinguished for the Fassel torch operating with organics, the sample introduction  
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48 system had to be gently rinsed out with 1.0% nitric acid to remove any alcohol  
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50 traces present so that the plasma could be re-ignited.  
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## Plasma characteristics

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It is well-known that organics have a significant influence on fundamental properties of the plasma compared to non-organic solutions. Depending on matrix characteristics and plasma operating conditions, either positive or negative effects have been reported.<sup>8,9,10,11,13,29</sup> In this work, the influence of organics on plasma characteristics have been evaluated by means of the excitation temperature and electron number density. In addition, the Mg II 280.270 nm/Mg I 285.213 nm line intensity ratio was employed to evaluate plasma robustness against organic matrices.<sup>25</sup> The results are shown in Table 3.

As expected from visual plasma observations (Fig. 2), organics had a limited effect on plasma thermal properties for the Conical torch. Using this experimental setup, neither excitation temperature nor the Mg II/Mg I ratio were significantly affected by the presence of organics in the plasma. Nevertheless, the introduction of organic solvents into the plasma led to an increase (about 2-fold) in electron number density which could be attributed to the increase in the hydrogen amount by the atomization of organics<sup>6</sup>. For the Fassel torch, however, organics exert a significant influence on plasma characteristics. Thus, when operating 30% w w<sup>-1</sup> methanol, the plasma excitation temperature was apparently unaffected, but both electron number density and the Mg II/Mg I ratio increased. From these data, it is not easy to get conclusions about the effect of the introduction of 30% w w<sup>-1</sup> methanol solution on plasma characteristics in the Fassel torch, particularly given the high uncertainties obtained when measuring the different plasma parameters. With regards to pure and hydroalcoholic solutions of 1-propanol, these matrices resulted in higher excitation temperatures, electron densities and Mg II/Mg I ratio

values than the reference solution. These results are consistent with the *thermal pinch effect* previously noticed when introducing 1-propanol matrices.

Table 3 also reveals, that, as expected from previous works in the literature,<sup>18,21</sup> when operating the 1.0% w w<sup>-1</sup> nitric acid solution, the Conical torch showed higher excitation temperatures (about 1000 K higher), electron number densities and Mg II/Mg I values than the Fassel design due to the high power density derived from plasma size reduction.<sup>18</sup> As regards to 1-propanol introduction, because of the *thermal pinch effect* for the Fassel torch, plasma excitation temperature and the Mg II/Mg I ratio for both torches were very similar. From the data shown in Table 3, it is clearly demonstrated that the discharge for the Conical torch is mostly unaffected by methanol and 1-propanol solutions than for the Fassel design and, hence, it is more suitable for those applications in which the analysis of organic matrices is required. In fact, no changes on the standard experimental conditions for the Conical torch operating inorganic solutions are required to deal with organic matrices.

### Carbon-based background emission

As it was shown in Fig. 2, as expected, the introduction of organics into the plasma affords a characteristic radiation emission from different carbon-based molecular species, irrespective of the torch employed.<sup>6,29</sup> Thus, violet radiation emission by CN was located at the boundaries of the plasma tail-plume as a result of air entrainment. On the other hand, green radiation emission by C<sub>2</sub> was found at the center of the plasma and at the outer plasma region close to the torch walls due to solvent vapor diffusion around the base of the plasma. Radiation emission

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3 from both species are directly related to the carbon content of each matrix. The  
4 higher the carbon content, the higher the molecular emission that was registered.  
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6 To gain further insight into carbon-based background emission for both torches,  
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8 emission from C (C I 247.856 nm), CN and C<sub>2</sub> (average signal in the 378-388 nm  
9 and 474-484 nm, respectively) have been monitored for all the matrices tested in  
10 this work.<sup>6</sup> Table 4 shows C, CN and C<sub>2</sub> signal ratios between organics and the  
11  
12 1.0 w w<sup>-1</sup> nitric acid solution for both Conical and Fassel torches at a Q<sub>g</sub> equal to  
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14 0.3 L min<sup>-1</sup>. As it would be expected, irrespective of the torch configuration,  
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16 carbon-based background emission increased with the alcohol content and they  
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18 were higher for 1-propanol than for methanol solutions due to its higher carbon  
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20 content. Finally, it is important to point out that the behaviors described above  
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22 were magnified when increasing Q<sub>g</sub> values due to the higher amount of aerosol  
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24 introduced to the plasma.

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27 In general, carbon-based background emission by organics was higher for the  
28  
29 Conical torch in comparison with the Fassel design. For instance, the average C,  
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31 CN and C<sub>2</sub> background emission was, respectively, 1.3-, 1.5- and 1.4-fold higher  
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33 for the Conical torch than for the Fassel design (Fig. 3). These findings can be  
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35 attributed to the different characteristics of the discharge generated by each  
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37 torch.<sup>18,19</sup> Because of the torch geometry and gas flow patterns, the plasma  
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39 formed by the Conical torch is more compact and is closer to the exit of the  
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41 injector tube. Consequently, the sample is directly introduced into the plasma  
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43 central channel, giving rise to higher emission by carbon-based molecular bands  
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45 in this region. Furthermore, as shown in the literature<sup>20</sup>, the Conical torch is  
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47 relatively immune to rotational flow patterns in front of the injector tube, which  
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49 again causes the sample to directly go through the central channel of the plasma  
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rather than its periphery. For the Fassel torch, however, the plasma is generated farther away from the injector tube tip and rotational flow patterns in front of the injector tube are common, thus allowing solvent vapor diffusion at the base of the plasma.<sup>29</sup> This is likely the main reason why the discharge for the Fassel torch is less robust against organics since solvent vapor diffusion affects the plasma induction zone and eventually leads to plasma extinguishment.

### Emission signal

Fig. 4 shows the influence of  $Q_g$  on the Mg II 280.802 nm emission signal for the Conical and Fassel torches operating pure and hydroalcoholic solutions of methanol and 1-propanol. Irrespective of the matrix considered, the Mg II 280.802 nm emission signal for the Conical torch showed a maximum at a  $Q_g$  of 0.3 L min<sup>-1</sup>. This typical behavior of maximum can be explained on the basis of  $Q_g$  effect on: (i) aerosol generation and transport; (ii) sample residence time; and (iii) plasma characteristics. When increasing  $Q_g$ , aerosol generation and analyte transport are favored (i.e. higher emission signal) but these effects are counterbalanced by the lower sample residence time in the plasma and the lower energy available for analyte excitation/ionization due to the solvent load increase.<sup>7,8</sup> For the Fassel torch, however, it is not feasible to operate organics at  $Q_g$  values lower than 0.3 L min<sup>-1</sup> because plasma becomes unstable and it is easily extinguished. In addition, the optimum  $Q_g$  for 1.0% w w<sup>-1</sup> nitric acid differs from that obtained when operating alcohol solutions. Thus, Mg II 280.802 nm emission signal for the reference solution is maximum at 0.4 L min<sup>-1</sup> whereas for organics it was found to be maximum at 0.3 L min<sup>-1</sup>. These findings point out, once again, the higher robustness of the discharge for the Conical torch in

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3 comparison to the Fassel one. With regards to matrix effects for both torches, it  
4 is observed that Mg emission signal increased with the alcohol content and, for a  
5 given alcohol content, higher signals were obtained by methanol solutions than  
6 those by 1-propanol. These results are totally expected considering the influence  
7 of physicochemical properties for each matrix on aerosol generation and  
8 transport (i.e. surface tension, volatility, etc.) and plasma robustness operating  
9 organics.<sup>4,7,8</sup> Finally, due to the limited aerosol diffusion at the base of the  
10 plasma,<sup>18</sup> the Mg II 280.802 nm emission signal for the Conical torch was higher  
11 than for the Fassel design. For instance, the average signal improvement for all  
12 the matrices tested operating the Conical torch at a  $Q_g$  of 0.3 L min<sup>-1</sup> was 1.7-fold.  
13 Because organics matrix effects in ICP-OES might depend on both wavelength  
14 and analyte characteristics (i.e. atomic vs. ionic),<sup>8,13,14,15</sup> the influence of  $Q_g$  on  
15 the emission signal of different elements has also been investigated (Table S1).  
16 Similar findings to those shown in Fig. 4 for Mg II 280.802 nm were observed . In  
17 general, for a given matrix, signal enhancement afforded by the Conical torch in  
18 comparison with the Fassel design was mostly independent of wavelength  
19 characteristics (Fig. 5). Several authors have pointed out that the presence of  
20 carbon in the plasma could increase the emission of atomic lines for hard-to-  
21 ionize elements (i.e. As, Se, etc.) due to a charge transfer reaction mechanism  
22 between carbon ionic species and analyte atoms.<sup>13,14,15</sup> Unfortunately, this  
23 phenomenon could not be investigated in detail since analyte wavelengths for the  
24 elements affected by this interference lie in the far to mid-UV region and the  
25 spectrometer used in the this work could only operate in the mid- to near UV and  
26 visible regions (>250 nm).  
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## Signal precision

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The repeatability was determined by analyzing ten replicates of the different analyte wavelengths. In general, relative standard deviation ranged from 3 to 6%, regardless of the matrix and torch configuration. To investigate long-term signal stability, different analyte wavelengths were monitored for a period of 1 hour at 5 minutes intervals for methanol and 1-propanol solutions. Fig. 6 shows the normalized emission signal ( $I_{\text{nor}}$ ) over time for different analyte wavelengths operating pure methanol. Similar findings were observed for methanol 30% and 60% w w<sup>-1</sup> solutions. Considering signal repeatability for these emission lines (4% RSD, 10 replicates),  $I_{\text{nor}}$  values below 0.92 or higher than 1.08 (*i.e.* exceeding an uncertainty range of  $\pm 8\%$ ) indicate no signal drift. Dashed lines in Fig. 6 represent this range. As it can be observed, no drift on analyte emission was registered, even for those wavelengths located nearby carbon-based molecular background emission bands, thus confirming Conical torch suitability for long-term analysis of methanol-containing solutions. On this regard, it is important to highlight that the use of Conical torch simplifies the development of analytical applications requiring methanol since, unlike the Fassel torch, there is no need of using non-conventional sample introduction system (e.g. desolvation)<sup>3,4,8</sup> or specific experimental conditions<sup>16</sup> for dealing with such matrix. For 1-propanol solutions, however, emission signal shows drift over time. In general, no changes on signal emission are usually registered when introducing 1-propanol solutions for 5 minutes, however after that time, the signal starts to decline, thus affecting long-term precision. In this regard, the higher the alcohol content, the faster the deterioration of the analyte emission. For instance, at a sample uptake rate of 0.5 mL min<sup>-1</sup>, the continuous introduction of a pure 1-propanol solution was



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3 approximately limited to 30 minutes. This behavior is mostly related to carbon  
4 deposits formation over time on the tip of the injector tube for the Conical torch. View Article Online  
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7 Nevertheless, it was observed that carbon deposits could be removed by  
8 introducing a 1.0% w w<sup>-1</sup> nitric acid solution. Thus, after the continuous  
9 introduction of a pure 1-propanol solution for 15 minutes, carbon deposits are  
10 completely removed after nebulizing 1.0% w w<sup>-1</sup> nitric acid for 5 min. Similar  
11 findings were observed for the Fassel torch but the formation of carbon deposits  
12 takes much longer, probably because of the cylindrical-shape of the injector tube  
13 tip with a narrower face, and the effect of the intermediate gas which pushes the  
14 plasma farther away from the injector tip. These results highlight the significance  
15 of the injector torch tip design on the formation of carbon deposits and, hence, as  
16 far as the Conical torch is concerned, this issue may be mitigated by redesigning  
17 the shape of the injector tube tip. In either case, regardless of the torch design,  
18 oxygen addition is advisable to guarantee accuracy and precision on a long-term  
19 basis for the analysis of carbon rich matrices such as 1-propanol.<sup>2,16</sup>  
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### Limits of detection

Table 5 shows the LoD for the Conical torch operating all the matrices investigated. Results reveal that, except for Al I 396.152 nm and Na I 589.592 nm, LoD for all the matrices were similar. It was noticed that organics raised up RSD<sub>BG</sub> with regard to the reference solutions and, hence, the beneficial effect of organics on emission signal is partially counterbalanced (Fig. 4 and Fig. 5). As regards to Al I 396.152 nm and Na I 589.592 nm, these wavelengths are located nearby the spectrum region where CN and C<sub>2</sub> molecular bands radiate and,

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3 hence, signal-to-background ratios for these elements were significantly  
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5 deteriorated when increasing matrix carbon content, thus negatively affecting  
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7 LoDs.  
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10 Fig. 7 shows the LoDs ratio between Fassel and Conical torches at the optimum  
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12  $Q_g$  for methanol 30 % w w<sup>-1</sup> and 1-propanol solutions (i.e. 0.3 L min<sup>-1</sup>). Despite  
13  
14 the higher signals afforded by the Conical torch, LoDs for both torches were, in  
15  
16 general terms, similar. It was observed that the  $RSD_{BG}$  for the Conical torch was  
17  
18 higher than for the Fassel torch, thus negatively affecting LoDs. Probably,  
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20 because the aerosol is more efficiently introduced into the plasma,  $RSD_{BG}$  is  
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22 partially deteriorated for the Conical torch when compared to the Fassel design.  
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24 Nevertheless, these results are highly remarkable considering the operating  
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26 conditions of the Conical torch in comparison with those of the Fassel design (i.e.  
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28 35% less plasma power and 55% less argon consumption) and the feasibility to  
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30 operate methanol rich matrices.  
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## 42 Conclusions

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44 Results in this work demonstrate that the Conical torch is totally suitable for the  
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46 direct analysis of pure and hydroalcoholic solutions of methanol and 1-propanol.  
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48 Unlike the conventional Fassel design, the discharge for the Conical torch is  
49  
50 highly robust and plasma characteristics (i.e. shape, excitation temperature, etc.)  
51  
52 are mostly unaffected by organics introduction. In fact, organics could be directly  
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54 analyzed by the Conical torch using the same sample introduction system and  
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56 experimental conditions as those employed for acid solutions. For the Fassel  
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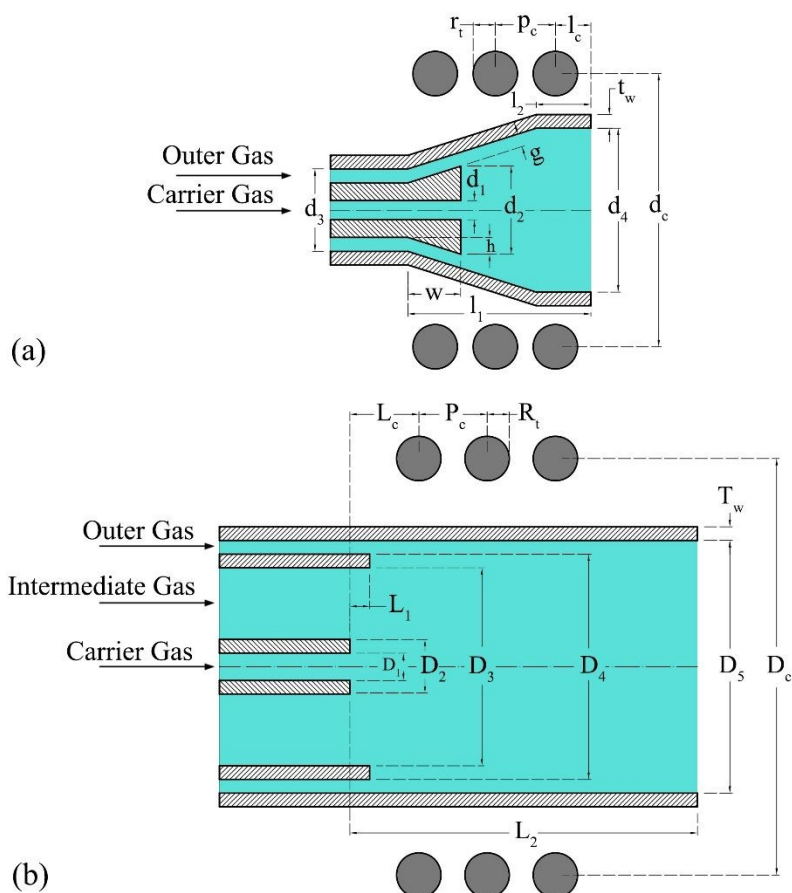
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3 torch, though plasma experimental conditions were specifically selected for  
4 organics introduction, it is not feasible to operate methanol solutions above 30 w  
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6 w<sup>-1</sup>. Because of the small size and high energy density of the discharge for the  
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8 Conical torch, it affords higher emission signals than the Fassel torch (2-fold).  
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10 Nevertheless, carbon-based molecular background emission and signal noise  
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12 are also enhanced and, consequently, limits of detection for both torches are of  
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14 the same order of magnitude. Additionally, considering that the Conical torch  
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16 operates pure methanol solutions and requires less r.f. power and argon  
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18 consumption than the Fassel design, it is beyond doubt that the former torch is  
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20 more advantageous for practical analysis.  
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### Conflicts of interest

There are no conflicts to declare.

### Acknowledgments

Financial support of Natural Sciences and Engineering Research Council (NSERC) of Canada and Dean's Strategic Fund by the University of Toronto are gratefully acknowledged. Guillermo Grindlay would like to thank the University of Alicante (ACIE19-05) for the financial support for this work.

**Table 1.** Geometrical parameter of the Conical and Fassel torch.View Article Online  
DOI: 10.1039/D0JA00368A

	Conical Torch	Conventional Fassel Torch	
$l_1$	13.4 mm	$L_1$	1.5 mm
$l_2$	4 mm	$L_2$	25.5 mm
$l_c$	2.6 mm	$L_c$	5 mm
$p_c$	4.4 mm	$P_c$	5 mm
$d_1$	1–2 mm	$D_1$	2 mm
$d_2$	6.5 mm	$D_2$	4 mm
$d_3$	6 mm	$D_3$	14 mm
$d_4$	12 mm	$D_4$	16 mm
		$D_5$	18 mm
$d_c$	20 mm	$D_c$	30 mm
$r_t$	1.6 mm	$R_t$	1.6 mm
$t_w$	1 mm	$T_w$	1 mm
$w$	3.9 mm		
$h$	1.2 mm		
$g$	1 mm		

**Table 2.** Operating parameters for the Conical and Fassel torches in ICP-OES. View Article Online  
DOI: 10.1039/D0JA00368A

Parameter	Conical	Fassel
Frequency (MHz)	40	
RF power (W)	900	1400
Outer gas flow rate (L min <sup>-1</sup> )	7	15
Intermediate gas flow rate (L min <sup>-1</sup> )	-	1.0
Nebulizer gas flow rate, Q <sub>g</sub> (L min <sup>-1</sup> )	0.2-0.5	0.2-0.6
Injector tube i.d. (mL min <sup>-1</sup> )	1.0 (fused silica)	1.0 (alumina)
Sample uptake rate (mL min <sup>-1</sup> )	0.5	

**Table 3.** Excitation temperature, electron number density and Mg II/Mg I ratio for the Conical and Fassel torches operating different matrix solutions.  $Q_g$ : 0.3 L min<sup>-1</sup>

Matrix solution	Conical torch			Fassel torch		
	T <sub>exc</sub> (K)	Electron number density ( $\times 10^{15}$ cm <sup>-3</sup> )	Mg II/I	T <sub>exc</sub> (K)	Electron number density ( $\times 10^{15}$ cm <sup>-3</sup> )	Mg II/I
1.0% w w <sup>-1</sup> nitric acid	7500±400	4.6±0.3	7.2±0.3	6400±200	3.4±0.1	6.5±0.3
30% w w <sup>-1</sup> methanol	7200±400	8.9±0.2	7.6±0.4	5500±900	4.6±0.10	7.7±0.7
60% w w <sup>-1</sup> methanol	7900±500	8.1±0.2	6.9±0.3	-	-	-
Pure methanol	7500±300	7.3±0.2	6.7±0.3	-	-	-
30% w w <sup>-1</sup> 1-propanol	7000±200	7.8±0.2	7.7±0.4	7300±300	4.4±0.1	7.9±0.4
60% w w <sup>-1</sup> 1-propanol	7500±200	7.7±0.2	6.9±0.4	7000±300	4.3±0.1	7.4±0.3
Pure 1-propanol	7400±900	7.1±0.2	7.2±0.5	6800±200	4.7±0.4	7.9±0.5



**Table 5.** Limits of detection (ng mL<sup>-1</sup>) for different analyte wavelengths operating 1.0% w w<sup>-1</sup> HNO<sub>3</sub> and organics for the Conical torch.Q<sub>g</sub>: 0.3 L min<sup>-1</sup>

Analyte	Type	λ (nm)	1.0% w w <sup>-1</sup>	Methanol			1-propanol		
			HNO <sub>3</sub>	30%	60%	pure	30%	60%	pure
B	I	249.773 nm	30	19	10	9	14	16	18
Mn	II	257.610 nm	1.6	0.9	0.8	1.0	1.1	0.8	0.8
Fe	II	259.940 nm	6	4	3	3	4	3	3
Cr	II	267.716 nm	4	3	2	3	3	2	2
Mg	II	279.553 nm	0.12	0.08	0.07	0.07	0.07	0.07	0.08
Ga	I	294.364 nm	15	11	11	11	10	9	11
Cu	I	324.754 nm	3	3	2	1.6	1.9	1.9	1.6
Ca	II	317.933 nm	3	2	2	2.0	1.6	1.5	1.8
Al	I	396.1520 nm	8	9	11	20	9	13	30
Na	I	589.592 nm	5	7	11	34	6	23	70



## Figure captions

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**Fig. 1.** Schematics of the experimental setup.

**Fig. 2.** Plasma images operating 1.0% w w<sup>-1</sup> nitric acid and 1-propanol solutions for the Conical and Fassel torches. Q<sub>g</sub> 0.3 L min<sup>-1</sup>.

**Fig. 3.** Emission spectra for (A) C, (B) CN and (C) C<sub>2</sub> operating a pure 1-propanol solution for Conical and Fassel torches. Q<sub>g</sub> 0.3 L min<sup>-1</sup>.

**Fig. 4.** Influence of the nebulizer gas flow rate on Mg II 280.802 nm emission signal operating (A) methanol and (B) 1-propanol solutions for Conical (straight lines) and Fassel (dotted lines) torches. (\*) 1.0% w w<sup>-1</sup> nitric acid, (■) 30% w w<sup>-1</sup> alcohol; (▲) 60% w w<sup>-1</sup> alcohol and (●) pure alcohol.

**Fig. 5.** Emission signal ratio between Conical and Fassel torches for different emission wavelengths. Q<sub>g</sub> 0.3 L min<sup>-1</sup>.

**Fig 6.** Signal stability test for different emission lines operating pure methanol for the Conical torch. I<sub>nor</sub> values among dotted lines indicate no signal drift. Q<sub>g</sub> 0.3 L min<sup>-1</sup>.

**Fig. 7.** Limit of detection ratio between Fassel and Conical torches for different emission wavelengths. Q<sub>g</sub> 0.3 L min<sup>-1</sup>.

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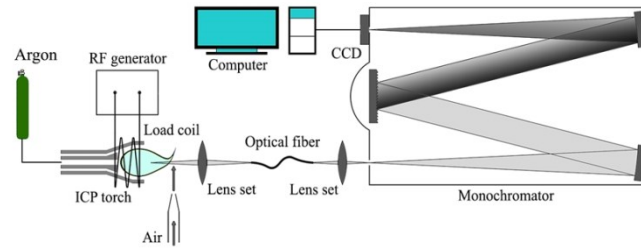


Fig 1

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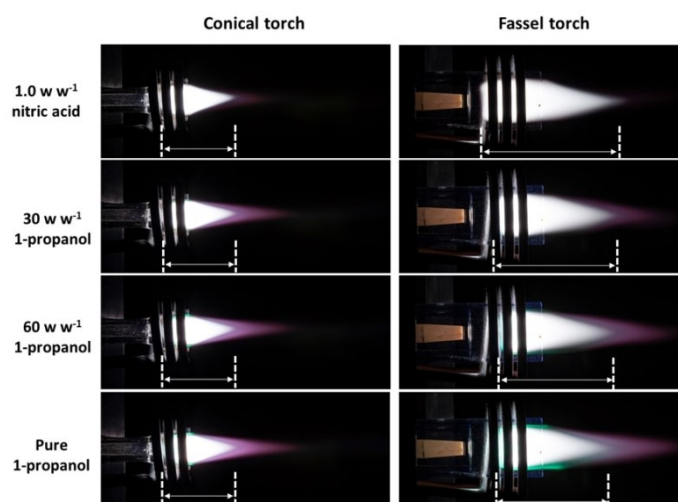


Fig 2

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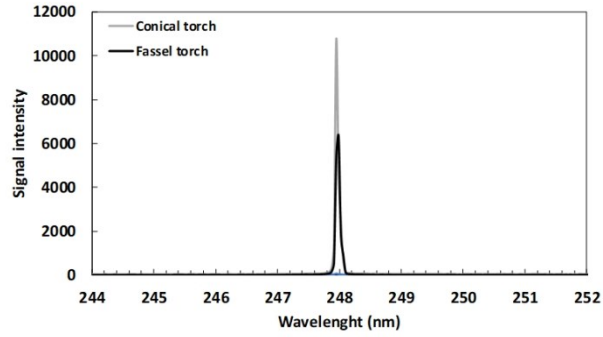


Fig 3.A

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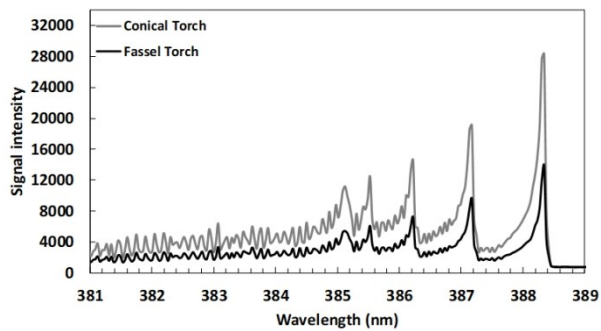


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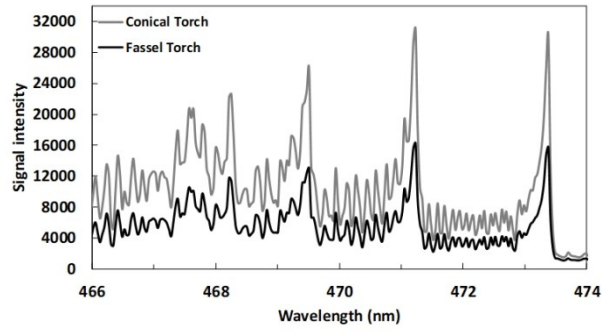


Fig 3.C

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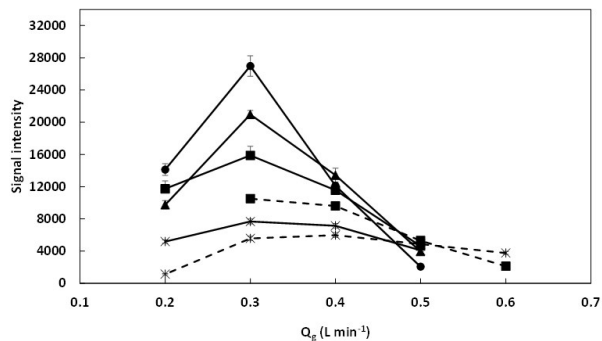


Fig 4.A

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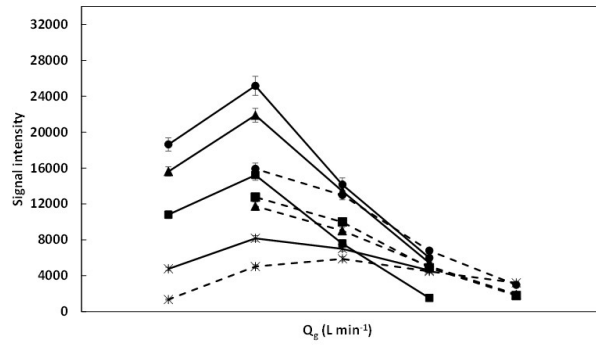


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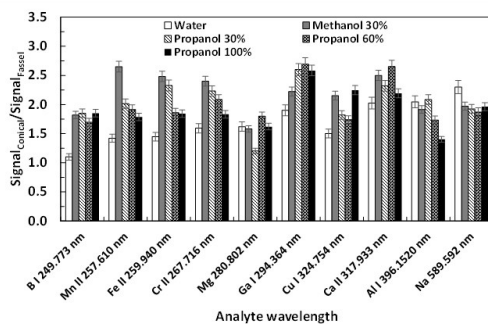


Fig 5

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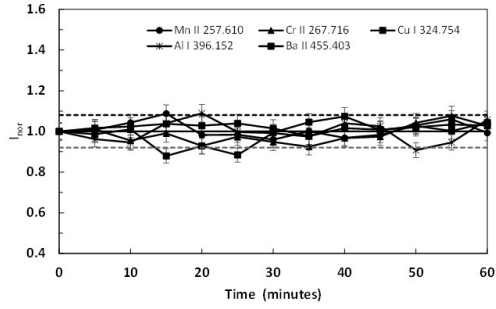


Fig 6

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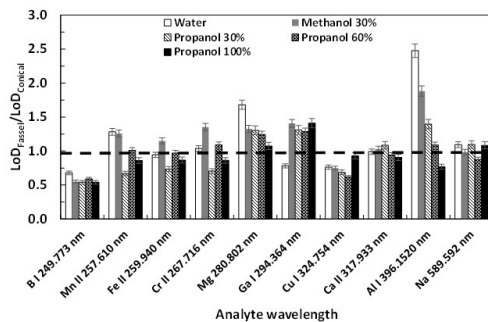


Fig 7

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