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# energy&fuels

# A Rapid and Versatile Method to Determine Methanol in Biofuels and Gasoline by Ambient Mass Spectrometry using a V-EASI Source

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ABSTRACT: Methanol is an organic compound commonly used as a solvent in the synthesis of fuel for internal combustion engines. However, the adulteration of fuels (biofuels and gasoline) with methanol is commonly practiced throughout world, and regulations to control the content of methanol in these fuels have been imposed. Although methanol in fuels can be analyzed by numerous analytical techniques, the traditional methods have some disadvantages, such as interferences, incomplete reactions, and lengthy analysis. Thus, the present work proposes a rapid and versatile methanol determination method using a simple derivatization of the sample with nicotinoyl chloride and subsequent fast analysis by ambient mass spectrometry using venturi easy ambient sonic-spray ionization (V-EASI-MS), without preseparation, taking into account all parameters of linearity, limits of detection, quantification, accuracy, and precision based on ISO 5725. We were able to develop a powerful method to quantify methanol in fuels which can be used as an alternative method to detect adulteration by government agencies.

# 1. INTRODUCTION

Methanol (CH<sub>3</sub>OH) can be applied as an industrial solvent and is also used as a reagent to obtain products such as formaldehyde, as a feedstock to produce fuel additives (for example, methyl *tert*-butyl ether (MTBE)), or directly as fuel in internal combustion engines. Methanol is an extremely volatile primary alcohol containing only one carbon. Its low molecular weight and physical-chemical characteristics present a challenge to analytical techniques for its detection and quantification.<sup>1</sup>

The main methods used for methanol detection presently are colorimetry,<sup>2,3</sup> cyclic voltammetry,<sup>4,5</sup> spectroscopy,<sup>6–11</sup> and gas chromatography coupled with mass spectrometry.<sup>12,13</sup> However, these techniques are usually time consuming and sometimes require accessories such as an automated liquid insertion system or headspace.<sup>14</sup> Detection of methanol traces by colorimetric analysis has been performed using chromotropic acid to produce a colored complex. In this procedure, methanol is oxidized by potassium permanganate to formaldehyde, which reacts with the salt of chromotropic acid, resulting in a purple color, as measured by colorimetry; moreover, this method is subject to interferences and incomplete reactions, and although selective, it is not specific.<sup>2</sup>

Methanol has similar properties to ethanol, such as color, odor, and density; for this reason, the most important techniques to analyze contaminated fuel (ethanol and gasoline) with methanol is from gas chromatography (CG) with a flame ionization detector (FID) and/or mass spectrometer (MS), producing methods that require a few minutes for each analysis.<sup>12,15</sup>

In Brazil, the price of methanol is presently half the market price of ethanol and more slightly over a third that of gasoline, and it is not subject to taxes levied on the sale of fuels; for this reason, there have been several cases of ethanol fuel and gasoline adulteration with methanol discovered since 2010.<sup>16</sup> The use of methanol as a fuel is prohibited in Brazil because the methanol in fuels can generate mechanical problems and causes in serious health problems for users, especially problems for gas station attendants due to its higher toxicity from its higher concentration.<sup>17</sup> Government agencies establish limits of methanol that are set according to the origin of fuel, e.g., 0.2% (w/w) methanol in biodiesel and 0.5% (v/v) methanol in ethanol and gasoline.<sup>18,19</sup> For solving the task of identifying methanol in fuels, the Brazilian Petroleum Agency (ANP) in partnership with laboratories involved in quality control of fuels have developed an official method that employs GC-FID to determine methanol in ethanol fuel and gasoline.<sup>20</sup>

In the field of mass spectrometry, easy ambient sonic-spray ionization (EASI) is a potential tool that can be used in the development of methods aiming to control the quality of fuels, as was showed previously by Alberici and co-workers.<sup>21</sup> EASI is based on sonic-spray ionization (SSI), which is a soft ambient ionization technique that generates ions directly from samples in their native environment with no or minimal sample preparation.<sup>22</sup> EASI is useful in the analysis of labile molecules and complex mixtures, because generally one ion is formed for each molecule. No high voltage or heating is applied in the capillary of the sprayer, so thermal or electrochemical changes which occur in other techniques are minimized or eliminated.<sup>23,24</sup> The V-EASI technique presents the same principles

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of ionization as EASI but without an electric pump, because it incorporates a suction system based on the venturi effect, i.e., narrowing in the flow of a fluid in a closed system that causes an increase of pressure and speed at this point, so that when a tube is connected, the fluid is aspirated into the system.<sup>25</sup>

Thus, this work aimed to develop a faster method to identify and quantify methanol in fuels using a rapid and versatile V-EASI-MS analysis based on the simple derivatization of methanol and direct solution insertion in the mass spectrometer using V-EASI. Methanol was derivatized with nicotinoyl chloride to have reactivity with hydroxyl alcohols and an amino group, which favors the formation of protonated molecules. A derivatization procedure also was described by Cooks and co-workers to increase sensitivity and detection of compounds not readily ionized by soft ionization techniques.<sup>26</sup> Therefore, the analytical method presented here produces results more quickly and with the same quality criteria as the standardized methods.

#### 2. MATERIALS AND METHODS

**2.1. Materials and Procedure for Sample Preparation.** We obtained ethanol fuel, gasoline, and biodiesel at service stations in the Campinas region, São Paulo, Brazil. All samples used in the development of this new method were analyzed according to official standards, i.e., by EN  $14110^{27}$  for biodiesel and ABNT-NBR  $16041^{20}$  for ethanol fuel and gasoline, and no methanol was detected in any of the samples. Standard solutions were prepared using these same samples in a concentration range from 0.100% to 1.000% (v/v) of methanol (HPLC-grade, Merck SA, Rio de Janeiro, Brazil), and all of the samples were used for evaluation of linearity. Samples of ethanol, gasoline, and biodiesel were also doped with methanol and used for determination of precision and accuracy at three concentrations, i.e., 0.200% (v/v), 0.500% (v/v), and 0.800% (v/v).

The standards and samples were prepared from an aliquot of  $100 \,\mu$ L of sample and  $10.0 \,\mu$ L of 1-propanol (99.9%, Sigma-Aldrich, São Paulo, Brazil, used as an internal standard (IS)). Then, derivatization was performed using 100 mg of nicotinoyl chloride (97%, Sigma-Aldrich, São Paulo, Brazil). The mixture was shaken and then left at rest for 30 s, followed by dilution for a final solution of  $1000 \,\mu$ L with tetrahydrofuran (99.8%, Tedia, Rio de Janeiro, Brazil).

**2.2. Analytical Method.** The analyses were performed by V-EASI coupled with a single quadrupole mass spectrometer (LCMS2010, Shimadzu) in the positive ion mode. The system was set to run with a nebulization gas flow of 5 L min<sup>-1</sup> at a temperature of 250 °C, an analyzer block at 250 °C, and a detector voltage of 1.40 kV. Detection was performed by the selected ion monitoring (SIM) mode with the selection of m/z 138 and 166 related to the methyl ester of nicotinic acid (Figure 2) and the propyl ester of nicotinic acid (internal standard), respectively.

For the analysis, a valve for liquids commonly used in highperformance liquid chromatography was used, operating with a 5  $\mu$ L injection loop, connected to the sample suction capillary, without a column, as shown in Figure 1. For each injection, the signal produced in the MS has the form of a peak similar to those obtained by liquid chromatography, so the results were processed through the LCMS Solutions 3.70.390 software (Shimadzu Co.). The SIM mode allowed for the analyses of the sample and internal standard simultaneously.

**2.3. Method Validation.** The proposed method was validated based on the International Organization for Standardization (ISO 5725).<sup>28</sup> The validation parameters were evaluated for selectivity, linearity, detection and quantification limits (LOD and LOQ), and precision and accuracy, determined for the three different matrices, i.e., ethanol fuel, gasoline, and biodiesel.

The limit of detection (LOD) is defined as the lowest amount of analyte present in a sample that can be detected. It is calculated at the standard deviation of 10 independent low-spiked blank matrix samples.



**Figure 1.** (a) The system with a liquid valve coupled with the V-EASI source and (b) a scheme of the valve used in liquid injections, where the positions refer to loading of the sample (Position 1) and direct injection to V-EASI (Position 2).

The standard deviation is divided by the slope of linear regression of the calibration curve and calculated according to the formula

$$LOD = (3s)/b$$

where s is the standard deviation of 10 independent low-spiked matrix samples and b is the slope of the linear regression.

The limit of quantification (LOQ), defined as the lowest amount of analyte in a sample that can be quantified with acceptable accuracy under the established experimental conditions, was determined according to the formula

LOQ = (10s)/b

where s is the standard deviation of 10 independent low-spiked matrix samples and b is the slope of the linear regression.

Linearity is demonstrated by the ability to obtain analytical responses directly proportional to the concentration of an analyte in a sample. The determination was calculated by the ordinary least-squares method.

Precision was determined from a dispersion of a set of results by calculating the relative standard deviation (RSD) of the measurement series at different concentrations and at different periods. Accuracy was determined as the degree of agreement between the individual results, obtained by the method under study, in relation to a reference value accepted as true. In this work, due to the unavailability of samples at the different concentrations, the preparation used was done by the method of adding the analyte, in which known quantities were added to the samples.



**Figure 2.** Reaction of methanol and nicotinoyl chloride, forming methyl ester of nicotinic acid.



**Figure 3.** (a) Chronogram containing a set of sequential analyzes (triplicate analytical curve, blank samples, and samples doped at three concentration levels) with methanol peaks (red) and internal standard (blue) in the same matrix of ethanol fuel. (b) Zoom of overlay of one repetition of analytical curve with samples (red) and internal standard (blue). (c) Zoom of overlay of five repetitions of ethanol fuel without methanol.

# 3. RESULTS AND DISCUSSION

Although methanol is used in MS as a solvent to dissolve samples and favors ionization as a proton donor, it is not essentially ionized by ambient ionization techniques, so derivatization was applied. The reaction of methanol with an acyl chloride forms a readily ionizable derivative, which may be detected by ambient ionization-MS. Here, methanol was derivatized with nicotinoyl chloride, which reacts with the hydroxyl group of alcohols and has an amino group to favor the formation of protonated molecules that form an ester of hydrochloric acid (Figure 2). The presence of hydrochloric acid promotes the protonation, and consequently, the molecule can be analyzed by V-EASI-MS. In order to reduce the effects of derivatization on the quantification, 1-propanol was used as an internal standard, chosen because it is a primary alcohol that is not present in the samples. 1-Propanol reacts with the nicotinoyl chloride to form protonated propyl ester of nicotinic acid.

Article



Figure 4. Mass spectra of ethanol (a), gasoline (b), and biodiesel (c) acquired between m/z 100–200 Da.

# Table 1. Limits of Detection and Quantification for the Determination of Methanol in Ethanol, Gasoline, and Biodiesel

matrix	limits of detection (%, v/v)	limits of quantification (%, v/v)
ethanol	0.006	0.020
gasoline	0.009	0.026
biodiesel	0.010	0.030

The peaks produced using a liquid injection valve can be quantified in the same way as the peaks generated in a chronogram. The peaks of the IS and ethanol samples generated in a representative analysis are shown in the ion chronogram of Figure 3. Peak areas were determined for the analyte (ion of m/z 138) in red and the internal standard (ion of m/z 166) in blue, shown in Figure 3a. The expanded region (Figure 3b) shows the analysis of the ethanol sample (red) doped with concentrations













(c)

Figure 5. Analytical curves of methanol at the concentrations of 0.000%, 0.100%, 0.300%, 0.500%, 0.700%, and 1.000% for (a) ethanol, (b) gasoline, and (c) biodiesel.

of methanol at 0.000%. 0.100%, 0.300%, 0.500%, 0.700%, and 1.000% and that of the internal standard (blue). Note that the peaks formed in sequence are symmetrical, which facilitates the determination of their areas. Even using an internal standard, the respective area of each peak is proportional to the concentration, but at higher concentrations the IS corrects the ionic suppression.

**3.1. Selectivity.** Selectivity is a parameter that shows if the method suffers from interference caused by other components of the matrix. MS has the ability to discriminate compounds based on m/z and is therefore a very selective technique. The green rectangle in Figure 3a shows the analysis of ethanol without methanol, which was analyzed five times. Note that there is no sign of the protonated ion of methyl ester of nicotinic

Table 2. Interday and Intraday Precision Results in Ethanol, Gasoline, and Biodiesel at Three Levels of Methanol in the Fuel Samples

matrix	concentration (%)	GC/FID method (CV %) ( <i>n</i> = 3)	V-EASI/MS interday (CV %) $(n = 5)$	V-EASI/MS intraday (CV %) $(n = 3)$
ethanol	0.200	0.5	6.8	1.8*
	0.500	1.2	8.8	4.6
	0.800	0.6	5.3	1.6
gasoline	0.200	0.3	6.1	4.6
	0.500	0.4	6.3	0.9
	0.800	0.7	6.1	4.1
biodiesel	0.200	2.2	7.2	3.6
	0.500	1.6	3.1	3.7
	0.800	0.2	4.5	5.1

"An outlier was removed from the calculation of this value, and the intraday imprecision was calculated with n = 2.

Table 3. Summary of Results Obtained by Standard Methods (GC/FID) and the Proposed Method (V-EASI/MS) for the Accuracy of Ethanol, Gasoline, and Biodiesel for Three Levels of Methanol Addition in the Fuel Samples

matrix	nominal concentration (%, v/v)	GC/FID method (%, v/v)	recovery (%)	V-EASI/ MS method (%, v/v)	recovery (%)
ethanol	0.200	0.190	95	0.194	97
	0.500	0.478	96	0.497	99
	0.800	0.754	94	0.803	100
gasoline	0.200	0.216	108	0.215	108
	0.500	0.527	105	0.503	101
	0.800	0.835	104	0.814	102
biodiesel	0.200	0.185	93	0.195	98
	0.500	0.486	97	0.512	102
	0.800	0.801	100	0.830	104

acid (m/z 138). The high signal-to-noise ratio produced by V-EASI-MS analysis contributed to a stable baseline in the mass region of the quantification ion, although many other compounds may be present in the sample. In addition, Figure 4a-c shows the V-EASI-MS spectra of ethanol, gasoline, and biodiesel without methanol addition in the full scan mode, where we set the instrument to analyze at m/z = 100-200 Da. The figures show that we found several ions related to other constituents of the fuels but found no ions with m/z 138 (derivatized methanol) and 166 (derivatized internal standard). These results reinforce the selectivity of this method.

**3.2. Limits of Detection and Quantification (LOD and LOQ).** The LOD and LOQ were determined from low-spiked blank matrix samples doped with methanol (Table 1). The limit of detection was obtained with a standard deviation of 10 measurements divided by the slope multiplied by 3, whereas the LOQ was multiplied by 10. The lowest LOD and LOQ were found for ethanol, probably because it is a less complex chemical sample than gasoline and biodiesel, so the matrix effect is less significant. For all matrices, the method was able to determine satisfactory LOD ( $\leq 0.010\%$ , v/v) and LOQ ( $\leq 0.030\%$ , v/v). The LOD and LOQ values in all matrices are lower than in other methods previously described in the literature, such as cyclic voltammetry (LOD of 0.045% in ethanol)<sup>4</sup> and near-infrared spectroscopy (LOD of 0.51% in ethanol).<sup>10</sup>

**3.3. Linearity.** The linearity was determined from analytical curves using a concentration of methanol in the three fuels at 0.000%, 0.100%, 0.300%, 0.500%, 0.700%, and 1.000%, and the analytical curves are shown in Figure 5a–c. For all curves, the linear correlation coefficients were above 0.990, which indicates that the method was linear in this range of concentrations. The method presents a linear dynamic range from 0.100% to 1.000%, which can be used for quantitative analysis without the need to use a preseparation system such as a chromatographic column.

**3.4. Precision.** The precision of the method was evaluated through the analysis of three levels (0.200%, 0.500%, and 0.800% of methanol in the fuel samples) with interday (n = 3) and intraday (n = 5) analysis. The results are described in Table 2 as CV%. The imprecision analysis of the three sample fuels was performed in a range of CV% from 0.9% to 8.8%. The highest imprecision was found in ethanol, possibly because ethanol also reacts with the derivative agent used, promoting competition in relation to the derivatization of methanol and consuming it in greater quantity than other fuels.

**3.5. Accuracy.** For the accuracy determination, we prepared 10 solutions for each matrix at three different levels (0.200%, 0.500%, and 0.800% of methanol in the fuel samples). The accuracy was obtained by the ratio between the average concentration determined experimentally and the corresponding theoretical concentration, and the results are expressed as a percentage of recovery (Table 3). Note that we obtained recoveries in the range of 97–108%. Values in the range of 100 ± 10% are acceptable at this concentration level.<sup>29</sup>

The summary of validation results for the concentration level of 0.5% of the matrices used for the comparison to other analytical techniques is presented in Table 4.

The results presented in the Table 4 indicate that the proposed method presents better accuracy and precision compared to cyclic voltammetry, while compared to gas

Table 4. Comparison of Parameters Obtained in the Validation of Ethanol, Gasoline, and Biodiesel and Other Analytical Techniques

	proposed method			Pereira et al., Fuel , (2016) <sup>4</sup>	Fernandes et al., Talanta (2008) <sup>10</sup>	Mittelbachet al., Chromatographia (1996) <sup>12</sup>	
method		direct V-EASI/MS		cyclic voltammetry	near-infrared spectroscopy	GC/FID	GC/MS
fuel	ethanol fuel (with 0,5% of methanol)	gasoline (with 0,5% of methanol)	biodiesel (with 0,5% of methanol)	ethanol fuel (with 5% of methanol)	gasoline (with 10% of methanol)	biodiesel (with 0.2% of methanol)	biodiesel (with 0.2% of methanol)
LOD	0.006	0.009	0.010	0.05	0.51	0.01	0.001
LOQ	0.020	0.026	0.030	0.15	1.50	0.03	0.003
linearity	$r = 0.998 \ (n = 15)$	$r = 0.995 \ (n = 15)$	$r = 0.993 \ (n = 15)$	N/A	$r = 0.999 \ (n = 5)$	$r = 0.999 \ (n = 5)$	$r = 0.999 \ (n = 5)$
precision	8.8% (n = 5)	6.3% ( <i>n</i> = 5)	3.1% (n = 5)	16% (n = 3)	0.29% ( $n = 4$ )	7.1% (n = 5)	1.0% (n = 5)
accuracy	99% ( <i>n</i> = 3)	101% (n = 3)	102% (n = 3)	120% (n = 3)	99% ( <i>n</i> = 2)	96% ( <i>n</i> = 5)	98% (n = 5)

chromatography, the precision and accuracy values are equivalent. This shows that the V-EASI quantification method can be implemented to substitute other techniques.

# 4. CONCLUSION

We were able to develop and validate a new method to quantify methanol in ethanol, gasoline, and biodiesel samples by ambient mass spectrometry with a V-EASI source. The method is versatile and fast compared to other methodologies using the GC-FID technique. The quality criteria of validation, such as selectivity, linearity, precision, accuracy, and limits of detection and quantification, proved to be equivalent to the official standard methods. The V-EASI-MS analysis was more selective, without suffering interference from other components of the matrix which frequently occurs in the official methods (ABNT 16041 or ASTM D5501<sup>30</sup> for ethanol fuel and gasoline, and EN 14110 for biodiesel). Another very important aspect of the V-EASI-MS method is its short analysis time, with measurements being performed in approximately 30 s, whereas in the Brazilian (NBR 16041, NBR 15343, 2015), American (ASTM D5501-12 (2016)), and European (EN 14110, 2019) standard methods the analysis times are around 30 min for gasoline, 15 min for ethanol, and 50 min for biodiesel. Thus, the determination of methanol in fuels by V-EASI-MS is much faster than and presents quality criteria that can be alternative to those of the Brazilian, American, and European standard methods, with good potential to be a new method to detect fuel adulteration.

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# Notes

The authors declare no competing financial interest.

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