

# Using Mass Spectrometry to Detect Ethanol and Acetaldehyde Emissions from a Direct Injection Spark Ignition Engine Operating on Ethanol/Gasoline Blends

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## ABSTRACT

Ethanol and acetaldehyde emissions from a direct ignition spark ignition were measured using mass spectrometry. Previous methods focused on eliminating or minimizing interference from exhaust species with identical atomic mass and fragment ions created in ionization process. This paper describes a new technique which exploits the fragment ions from ethanol and acetaldehyde. A survey of mass spectra of all major species of exhaust gas was conducted. It was found that ethanol contributes most ions in mass number 31 and that no other gas species produces ions at this mass number. Acetaldehyde detection suffers more interference. Nevertheless, it was estimated that detection at mass number 43 is possible with 10% error from 2-methylbutane.

This new technique was validated in an engine experiment. By running the engine with pure gasoline and E85, the validity of the technique can be checked. Two conditions were investigated: idling (1200 rpm, 1.5 bar NIMEP, retarded ignition timing) and medium load (1500 rpm, 3.8 bar NIMEP, MBT ignition timing). The results from both conditions confirmed that ions were only detected when E85 was used. Furthermore, the measured ethanol concentrations agree with results obtained using gas chromatography. However, acetaldehyde was overestimated greatly. It was possibly caused by ions with atomic mass 44 being miscounted or by the fact that the interference from 2-methylbutane was much bigger than calculated. Further investigation is required.

## INTRODUCTION

Ethanol has been increasingly used as a transportation fuel in the world. Most of it is blended with gasoline. In the US, most gasoline in the market contains 10% ethanol. High concentration blends (E85) are sold in Brazil, Sweden and in some states in the US. Thailand, Columbia and Costa Rica are making ethanol from sugarcane or cassava, and blended it with gasoline to be sold locally [1, 2].

Compared with gasoline, ethanol has a superior anti-knocking property. Its heat of vaporization is about 3 times as high as gasoline. Both characteristics are highly desirable for direct injection spark ignition engine downsizing strategies which could significantly reduce fuel consumption of vehicles without compromising performance. When ethanol/gasoline blend is burnt in an internal combustion engine, oxygenates are produced as unburned fuel or partial oxidation products. Exhaust gas studies found that ethanol and acetaldehyde are the main oxygenate species. Acetaldehyde is carcinogenic if inhaled. It is also an ozone precursor which contributes

to smog formation [3]. Jacobson et al. [4] pointed out that ethanol in atmosphere is further oxidized to acetaldehyde, increases the atmospheric acetaldehyde inventory.

The higher the ethanol content in fuel, the more organic gas emission from an internal combustion engine. At present, the US EPA and CARB emission regulations for E85 (85% ethanol and 15% gasoline by volume) requires speciated measurement of ethanol and carbonyls [5]. The dominating carbonyl species is acetaldehyde. The CARB test procedure recommends water impinge sampling followed by gas chromatograph (GC) analysis for ethanol measurements. The carbonyl measurement was performed through acidified 2,4-dinitrophenylhydrazine cartridge sampling and high performance liquid chromatography (HPLC) analysis. These methods are sensitive to very low concentration and free of interference from other species, but require considerable manual handling and lengthy analysis time. Another method to measure ethanol concentration was the use of photoacoustic sensors (PAS) [6]. It was approved by CARB as the equivalent as the water impinger method. PAS has a simplified sampling method and the result is available online, which is similar to conventional emission analyzers. However Loo et al. [7] reported that compensation for ammonia and carbon dioxide was required to get accurate ethanol concentration. Fourier Transform Infra Red Spectroscopy (FTIR) can also be used to detect ethanol and acetaldehyde, but it is subject to interference from other species. In summary the challenge for ethanol and acetaldehyde measurements is to isolate these species for analysis from a complex mixture of exhaust gas, which may contain hundreds of components. Chromatography is an effective means to resolve the mixture but the analytical procedures are relatively complex and time consuming. Attempting to analyze the mixture without separation has a cross interference problem; however, the measurements are quicker. Mass spectroscopy could be seen as a happy medium. It discriminates different species by their atomic masses, yet the measurements are as quick as FTIR or PAS methods.

In mass spectrometry, a gas mixture is admitted to a high vacuum chamber where it is ionized. Ions are then separated by their mass-to-charge ratio by various means depending on the types of mass analyzer, e.g. quadrupole, magnetic sector and time-of-flight. Separating exhaust gas species by mass does not guarantee that the measurements are interference free. Firstly, Ethanol and nitrogen dioxide have a nominal atomic mass of 46. Similarly carbon dioxide and acetaldehyde have an atomic mass of 44. Secondly, during the ionization process a gas molecule can split into smaller fragments, adding another source of interference. To minimize the effect of fragment ions, most mass spectrometers used in exhaust gas analysis utilize chemical ionization. Chemical ionization is a low energy process, which yields fewer fragments. Ekstrom and Adelsund [8] devised a technique to detect ethanol and acetaldehyde using chemical ionization with three different ionization levels. Different ionization levels were chosen to avoid ionizing interfering species. Despite this effort, ethanol was found to be interfering with acetaldehyde, hence compensation had to be applied.

This study proposes a completely opposite approach. Instead of minimizing fragments and hence interference, we attempt to identify ethanol and acetaldehyde from their fragment ions. In fact, fragment ions produced in the ionization process is so repeatable and unique that it is used in Gas chromatography-mass spectrometry (GC-MS) system to identify unknown species in a sample. The development of this new technique is divided into two stages: The first stage is to utilize exhaust speciation data obtained from gas chromatography and investigate the distribution of fragment ions from major organic gas species. The second stage is to validate any detection scheme from the first stage in a well designed engine experiment.

## EXPERIMENT

### MASS SPECTROMETER

The mass spectrometer employed in this study was a Pfeiffer Omnistar GSD300. It has an oil-free vacuum system (a turbomolecular pump backed by a diaphragm pump) to achieve a hydrocarbon-free background, which is essential for detecting trace organic gases. Gases were ionized by electron impact at 60 eV. The ions are then analyzed by a quadrupole mass filter (Pfeiffer QMS200). A DC voltage and a radio frequency voltage are applied to the four rods. Depending on the combination of DC and AC voltage, ions of only one mass-to-charge ratio ( $m/z$ ) will pass through the rods [9] and reach the Faraday cup detector. The operating parameters of the mass spectrometer are given in Table 1.

**Table 1 Operating parameters of Pfeiffer Omnistar mass spectrometer**

<b>Ion source</b>	Tungsten filament
<b>Filament current</b>	1 mA
<b>Quadrupole rod diameter</b>	6 mm
<b>Quadrupole rod length</b>	100 mm
<b>Mass scan range</b>	0-50 amu
<b>Mass scanning speed</b>	1 amu/s
<b>Resolution, adjustable</b>	0.5-2.5 amu
<b>Peak ratio reproducibility</b>	0.5%

### ENGINE SETUP

The engine is a GM naturally aspirated DISI Ecotec 4-cylinder engine [10] which is modified for single cylinder operation. Cylinder no. 1 is the only active cylinder with the intake and exhaust separated from the remaining three cylinders, which are under wide-open-throttle (WOT) motoring operation. The engine is equipped with a charge motion control valve at the intake port to provide a swirling charge motion; see Fig. 1. The valve is closed (swirl-enabled) for all the experiments in this study. The engine specification is shown in Table 2.

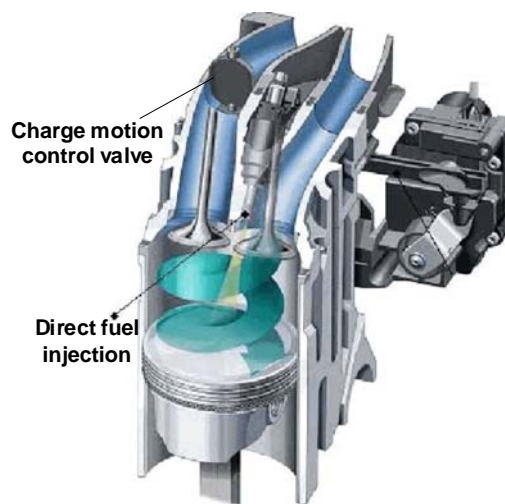


Fig. 1. Charge motion and injector arrangement; adapted from [10]

**Table 2 Engine specification**

<b>Displacement per cylinder</b>	550 cc
<b>Bore</b>	86 mm
<b>Stroke</b>	94.6 mm
<b>Compression ratio</b>	12.0
<b>IVO/IVC</b>	0° after TDC/60° after BDC
<b>EVO/EVC</b>	44.5° before BDC/ 10.5° after TDC
<b>Injector Center Line</b>	47° from horizontal
<b>Nominal cone angle</b>	52°
<b>Injection pressure</b>	40 to 120 bar

The engine coolant temperature (ECT) was controlled using a heater in a 80-L coolant tank. To control the injection pressure, the engine fuel pump was not used. Instead, premixed ethanol/gasoline blends were supplied from individual accumulators pressurized by high pressure nitrogen at 70 bar. Another study on hydrocarbon emission [11] has shown that low and stable emissions are achieved at 70 bar injection pressure. The fuel line was arranged so that the residual fuel could be evacuated by a PTFE dry pump. The flushing process was validated by observing the change in fuel pulse width under stoichiometric condition when the fuel was switched from gasoline to E85.

A Kistler 6125A piezoelectric pressure transducer with flame arrester and a Kistler 510 charge amplifier were used for in-cylinder pressure measurements. In-cylinder pressure was pegged to the manifold absolute pressure at BDC in the intake stroke.

## FUEL

An emission certification gasoline Haltermann HF473 was used in this study. Its fuel properties are summarized in Table 3. E85 was made by blending anhydrous ethanol (Pharmco-Aaper 200 proof, 99.98% pure) 85% by volume and 15% by volume of Haltermann gasoline. The fuel was blended just before it was pumped into the accumulator for testing.

**Table 3 Haltermann gasoline properties**

<b>Property</b>	<b>Value</b>
Density (ASTM 4052)	741 kg/m <sup>3</sup>
Reid vapor pressure	62 kPa
Sulfur (by weight)	28 ppm
Oxygen (by weight)	<0.01
Hydrogen / Carbon ratio	1.826
Lower heating value (ASTM D3338)	43.04 MJ/kg
Research Octane No.	97.4
Motor Octane No.	89
Aromatics	27.1% liquid vol.
Olefins	0.6% liquid vol.
Saturates	72.3% liquid vol.

## EXHAUST GAS SAMPLING

Exhaust gas was sampled from a mixing tank 2 m from the exhaust port. This eliminated any spatial and temporal variation of exhaust gas species. The exhaust sample was conveyed to a 1 m fused silica capillary with an internal diameter of 0.15 mm. It was estimated the response time of the sampling system was about 5 seconds [12]. To avoid condensation in the capillary, the capillary was heated and controlled to  $150 \pm 1^\circ\text{C}$ . During sampling, the pressure of the vacuum chamber in the mass spectrometer was between  $3.5\text{--}3.7 \times 10^{-6}$  mbar.

## MASS SPECTROMETER CALIBRATION

A mass spectrometer does not measure gas species concentration directly. It measures ion current at the Faraday cup detector. To quantify the concentration of a gas species, the mass spectrometer has to be calibrated. A 1000 ppm ethanol (balanced with nitrogen) mixture was created in a 5 L heated cylinder at  $70^\circ\text{C}$ . Two absolute pressure transducers (MKS Baratron 629B) were instrumented to measure low (up to 13.3 kPa) and high gas pressure (up to 400 kPa). The cylinder was initially evacuated, and then 0.11 ml of pure ethanol (Pharmco-Aaper 200 proof) was injected into the cylinder, which resulted in a vapor pressure of 1.050 kPa. The cylinder pressure increased to the measured value as soon as injection was completed. The value remained stable, which indicated that there was no fuel condensation and that the evaporation was complete. Nitrogen of ultra high purity (99.999%) was admitted to the cylinder to just above atmospheric pressure. At this point, the nominal concentration of ethanol was 10,000 ppm which was 10 times higher than the desired pressure. A mechanical fan was used to fully mix the gases for 5 minutes. A second stage dilution was applied by evacuating the cylinder to 10.49 kPa and filling it with nitrogen again to 104.1 kPa. A mechanical fan was used again to mix the gases. This two stage dilution was the key to high accuracy in the final blend. Attempting to create the mixture in one pass would have required very low ethanol pressure at which the limited resolution of the absolute pressure transducer would have led to a large error. The final ethanol concentration was  $996.9 \pm 5.3$  ppm. This error was determined using error of propagation analysis with a 95% confidence interval.

The mass spectrometer sampled the gas mix via a heated capillary inlet (at  $150^\circ\text{C}$ ). The ion currents at amu 31, 43, 44, 45 and 46 were recorded. 40 samples were averaged to calculate the gain [ppm/A]. The advantage of blending a calibration gas in-house is that the interference between gases can be studied quickly by customized blending.

## RESULTS

### THEORETICAL BASIS

Mass spectrometry does not offer positive identification for a specific species in exhaust gas for several reasons:

- There could be several species present which have identical masses, so they are detected at the same time.
- In Electron Impact (EI) ionization, gas molecules are bombarded by a high-energy electron beam (60 eV). A molecule can split into smaller fragments, so a molecule can give a response on masses other than the nominal molecular mass.

- The mass spectrometer used has a quadrupole mass filter, which differentiates charged molecules by their mass to charge ratio ( $m/z$ ). A molecule can be charged multiple times in the ionization process, so the mass spectrometer can register responses at  $m/z = 40, 20$  and  $10$  for a gas molecule with  $\text{amu} = 40$ .

Each gas has a mass spectrum, which is unique and reproducible, similar to a fingerprint. In GC-MS, a gas mixture is first separated into individual components. The mass spectrum of an unknown component can be identified by comparing the measured mass spectrum to a mass spectrum library. This identification is not possible if a gas mixture is analyzed in the mass spectrometer, as there is no chromatographic separation. Therefore the task of MS detection is to ensure that a peak in a spectrum is only due to one gas component, and nothing else. This section will establish that ethanol can be detected without interference from other exhaust gas species.

A typical ethanol mass spectrum is given in Fig. 2. The abscissa of Fig. 2 is relative abundance. The ion currents are normalized to that of the most abundant one. Notice that ethanol has a nominal atomic mass of 46, but the ethanol molecular ion is not the most abundant ion. Cleavage of the C-C bond next to the oxygen usually occurs during ionization (see Fig. 3). Of all the potential ions, the  $\text{CH}_2\text{OH}^+$  fragment with an atomic mass of 31 has the highest frequency. For acetaldehyde, hydrogen next to the carboxyl group is usually stripped away yielding  $\text{CH}_3\text{O}^+$ . The whole carboxyl group can break off, forming a  $\text{CHO}^+$  ion. This is why the peaks at  $m/z=43$  and  $29$  are amongst the highest in the mass spectrum (Fig. 4).

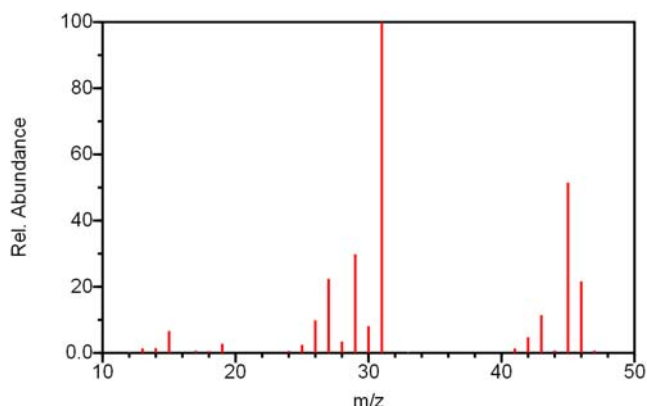


Fig. 2. Mass spectrum of ethanol. The ordinate is relative abundance. The most abundant ion is assigned with 100% relative abundance. Other ions are scaled according to the most abundant one.

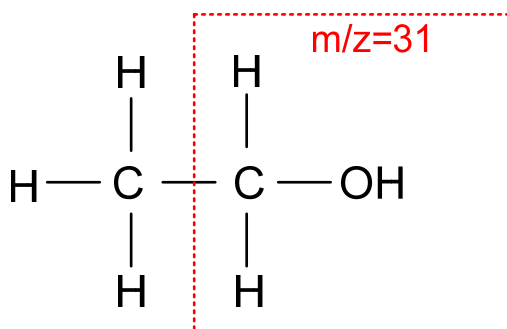


Fig. 3. Most common mode fragmentation of ethanol in ionization process

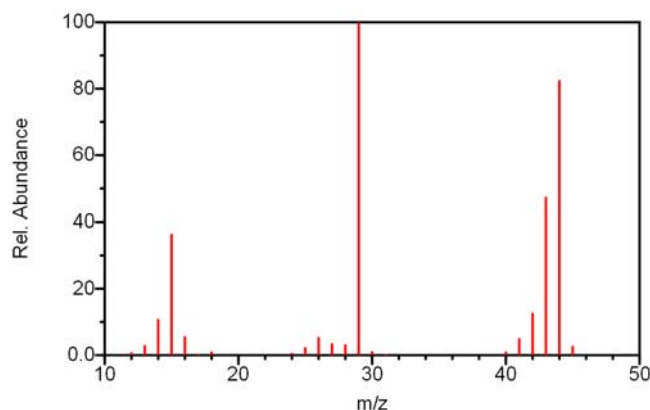


Fig. 4. Mass spectrum of acetaldehyde

A positive detection of ethanol and acetaldehyde requires that their mass spectra do not overlap with the mass spectra of other exhaust gas species. Ekstrom et al. [8] pointed out that nitrogen dioxide ( $\text{NO}_2$ ) may interfere with ethanol and carbon dioxide may interfere with acetaldehyde. In addition, ethanol and acetaldehyde can interfere with each other as both species have peaks from  $m/z = 41$  to  $45$ . Other hydrocarbons in the exhaust may create fragment ions that overlap with ions produced from ethanol and acetaldehyde. To investigate the extent of interference, an extensive survey of exhaust gas species was conducted. Exhaust gas from the same engine was speciated using gas chromatography from a previous study [13]. Major organic gas species that had an ethanol concentration of at least 10% were selected. Combustion products such as nitrogen dioxide and carbon dioxide were also included in the survey, as their mass spectra cover the range where interference is possible.

The mass spectrum data (relative abundance) of the selected species were obtained from National Institute of Standards and Technology online chemistry database [14]. The survey was restricted to mass numbers 27, 29, 31 and 42 to 46 inclusively. These are the mass numbers where ethanol and acetaldehyde yields the most ions. The results of the survey are summarized in Table 4. Firstly, there is no mass number which has ions coming from a single species. However at  $m/z = 31$ , ions from ethanol dominate — contribution from ethane, formaldehyde and acetaldehyde is negligible. It should be noted that Table 4 only gives the relative abundance of ions. The overall effect on the measured concentration is a product of relative abundance and the concentration of an interfering species. Acetaldehyde and formaldehyde are partial oxidation products of ethanol. Previous research [15, 16] shows that their mole concentrations are 5-10 times smaller than that of ethanol. Ethane concentration is smaller still (1/7 to 1/32 of ethanol) depending on the ethanol content of the fuel. Therefore, this survey indicated that ethanol can be uniquely detected at mass number 31 for all practical purposes.

Acetaldehyde is a different story. Eight other species contributed ions at mass number 29, similarly at mass number 42. Mass numbers 43 and 44 have relatively less interference. The four species which interfere with the detection of acetaldehyde in mass number 43 are shown in Fig. 5. The mole concentrations were measured using gas chromatography when the engine was firing at 1500 rpm, 3.8 bar NIMEP fueled with E85. The speciation of other exhaust components is given in Appendix. Although 2-methylbutane has very low concentration compared with acetaldehyde, it contributes 10% of the total ion current. This is because 2-methylbutane has the highest relative abundance at mass number 43. In contrast even ethanol is 6 times more concentrated than acetaldehyde, its ion contribution is modestly higher than that of acetaldehyde. The ion current contributions from propene and 2,2,4-trimethylpentane are negligible. A possible detection scheme is to ignore the interference of 2-methylbutane (it may introduce an error up to 10%), so that the total ion current is

due to ethanol and acetaldehyde. Since ethanol concentration can be determined from mass number 31, the ion current due to acetaldehyde at mass 43 can be isolated.

**Table 4 Relative abundance of selected exhaust gas species**

	Mass to charge ratio (m/z)							
Exhaust gas species	<b>27</b>	<b>29</b>	<b>31</b>	<b>42</b>	<b>43</b>	<b>44</b>	<b>45</b>	<b>46</b>
<b>Ethane</b>	33.23	21.52	0.5	0	0	0	0	0
<b>Propene</b>	38.73	0	0	70.36	2.3	0.1	0	0
<b>2M Butane</b>	51.34	46.75	0	81.94	99.99	4.48	0	0
<b>2M Propene</b>	21.72	10.91	0	3.6	0.1	0	0	0
<b>Benzene</b>	2.62	0	0	0	0	0	0	0
<b>Toluene</b>	1.79	0	0	0	0.1	0.1	1.49	0.99
<b>1,2,4 TM Benzene</b>	5.36	0.58	0	0.15	0.09	0.35	0.11	0
<b>2,2,4 TM Pentane</b>	5.29	8.49	0	1.29	18.49	0.6	0	0
<b>Formaldehyde</b>	0	99.99	0.5	0	0	0	0	0
<b>Carbon dioxide</b>	0	0.1	0	0	0	99.99	1.2	0.4
<b>Nitrogen dioxide</b>	0	0	0	0	0	0	0	37.03
<b>Ethanol</b>	22.41	29.85	99.99	4.74	11.44	0.71	51.49	21.63
<b>Acetaldehyde</b>	3.59	99.99	0.3	12.79	47.49	82.59	2.79	0



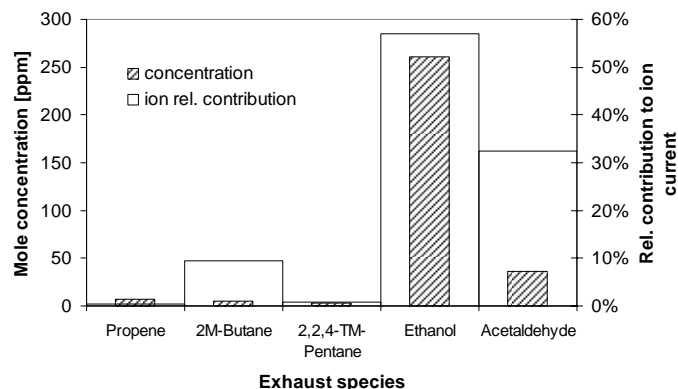


Fig. 5. Mole concentration of exhaust species and their relative ion contribution at mass 43.  
Engine was running at 1500 rpm, 3.8 bar NIMEP, stoichiometric, E85

Detecting acetaldehyde at mass number 44 is a possibility. As shown in Fig. 6, interfering species which are common at both mass number 43 and 44, have diminished effect at mass 44 due to smaller relative abundance. For instance, the relative contribution of ethanol to ion current decreases from 57% to 15%. The biggest obstacle is carbon dioxide. Since it is a combustion product, the mole concentration in the exhaust is between 12-13%, depending on ethanol fuel content. This high concentration in effect overshadows acetaldehyde, even though the relative contribution of ion current of acetaldehyde is the highest amongst all organic gases. To successfully detect acetaldehyde at mass number 44, the mass spectrometer must have very high resolution to resolve ion current to ppm level.

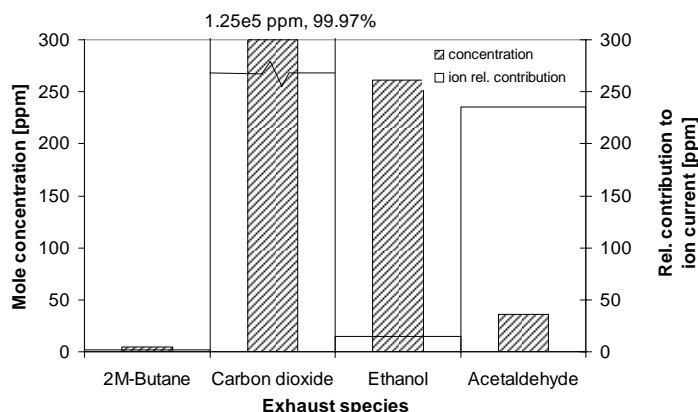


Fig. 6. Mole concentration of exhaust species and their relative ion contribution at mass 44.  
Engine was running at 1500 rpm, 3.8 bar NIMEP, stoichiometric, E85

## ENGINE TESTS

The preceding section has established methods of detecting ethanol and acetaldehyde using mass spectrometry. These methods were put to test in a series of engine experiments. Exhaust gas was sampled to the mass spectrometer in a mixing tank about 2 m from the exhaust port. The capillary inlet was heated to 150°C to prevent hydrocarbon and water condensation. The vacuum chamber in the mass spectrometer was baked and evacuated for 3-4 hours before the experiment, to achieve low background readings. The background mass

spectrum only consisted of peaks at 17, 18 and 28 mass numbers. The engine was run with pure gasoline and E85 under idling (1200 rpm, 1.5 bar NIMEP, 15 CAD before TDC ignition timing) and medium load conditions (1500 rpm, 3.8 bar NIMEP, MBT timing). The air/fuel mixture was stoichiometric. Fuel injection occurred in the intake stroke (120 CAD before BDC) to create a homogenous mixture. Sampling began once the engine output and exhaust temperature were stable. This usually took about 10 minutes.

Figures 7 and 8 compare the mass spectra of exhaust gas when the engine was fueled with gasoline and E85. Unlike the spectra in Figures 1 and 3, these spectra are continuous because they were obtained by incrementally varying the voltages of quadrupole mass filters. A discrete spectrum is usually obtained by reporting the maximum peak ion currents with the corresponding mass numbers. When gasoline was used, the ion current at mass number 31 was lower than  $1 \times 10^{-14}$  A, which was near the detection limit. However the ion level increased to the order of  $1 \times 10^{-12}$  when the engine switched over to E85. This finding holds for both medium load and idling conditions. Therefore the results support the proposed theory that ethanol can be uniquely detected at mass number 31. Ions are detected in mass number 43 in both gasoline and E85, which confirms that multiple exhaust species contribute ions at mass number 43. Two exhaust species which contributes ions at mass number 43, 2-methylbutane and 2,2,4-trimethylpentane, are found in higher concentration in gasoline exhaust than E85 exhaust. So even though there is no acetaldehyde when gasoline is used, the ion current level is similar to when using E85. Hence acetaldehyde cannot be detected exclusively at mass number 43. Apart from mass number 31 and 43, there are marked difference in ion current in mass numbers 19, 26, 41 and 42.

The concentration of ethanol is determined by taking the measured ion current at mass number 31 and dividing it by the gain (A/ppm) as determined in calibration. At medium load, there is  $290 \pm 75$  ppm of ethanol in the exhaust gas. The measurement uncertainty includes both the uncertainty in the gain and ion current. It is relatively large because the variation in ion current was 25%. Only 3 mass spectra were recorded, so it is expected that more measurements will increase the precision. Ethanol was measured at 261 ppm [13] using the gas chromatography under the same engine conditions. Since both measurements are comparable, it is concluded that ethanol can be quantified successfully with this method.

Assuming the ion contribution to mass number 43 ( $I_{43}$ ) is predominantly from ethanol and acetaldehyde, it can be expressed mathematically as:

$$I_{43} = C_e G_{e,43} + C_a G_{a,43} \quad (1)$$

where,  $C_e$  and  $C_a$  are the mole concentration of ethanol and acetaldehyde respectively.  $G_{e,43}$  is the ion current (gain) at mass number 43 per ppm of ethanol.  $G_{a,43}$  is ion current at mass number 43 per ppm (gain) of acetaldehyde.  $G_{e,43}$  and  $G_{a,43}$  were determined in calibration.  $I_{43}$  and  $C_e$  are measurements. By rearranging Eq. 1 and making  $C_a$  be the subject, the mole concentration of acetaldehyde is determined to be 1550 ppm. This value is 43 times bigger than the gas chromatography measurements (35.8 ppm). This gross overestimation suggests that there are other ions from other species in mass number 43. Merely removing the interference of ethanol is insufficient. Perhaps, the interference from 2-methylbutane is significant, and ignoring it leads to a large error. Another explanation is limited mass resolution of the mass spectrometer. This is a big peak at mass number 44. If the mass spectrometer cannot resolve ions between mass numbers 43 and 44,  $I_{43}$  may include the ion contribution to mass number 44. Recall that carbon dioxide contributes most ions to mass number 44, and it is one of the most abundant exhaust species, so any miscounting of mass 44 ions as mass 43 will inflate  $I_{43}$  significantly. Further investigation is required to identify the cause of the problem.

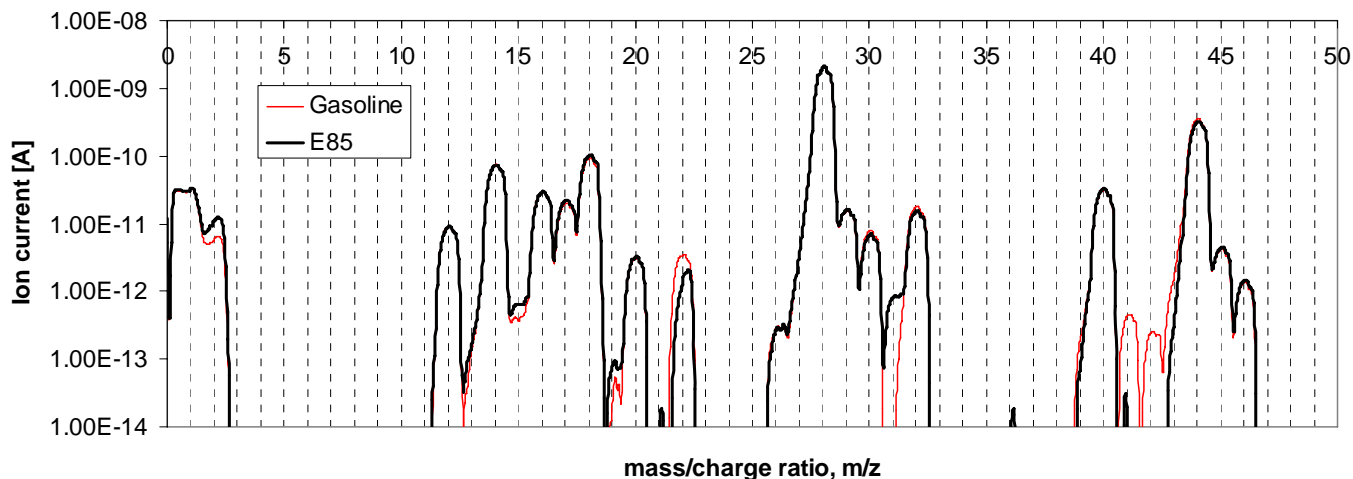


Fig. 7. Mass spectrum of exhaust gas when the engine was under medium load

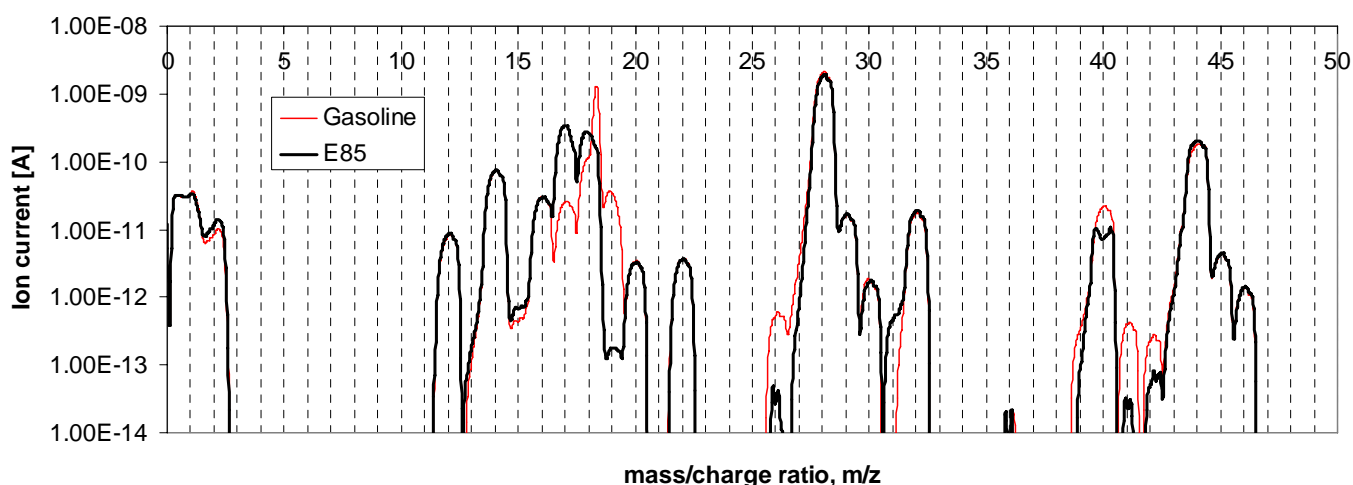


Fig. 8. Mass spectrum of exhaust gas while engine idle

## FUTURE WORK

Whilst this new technique has been shown to detect ethanol in the exhaust successfully, few areas need to be addressed before it can be applied in practice. Firstly, more runs will be required to establish repeatability. Secondly, the calibration can be done in multiple concentrations to check for linearity. Thirdly, mass resolution could be refined so that ions in mass 43 and 44 can be resolved. The interference seen in acetaldehyde may be eliminated. Finally, transient tests will be conducted to see if the system is fast enough to detect emission changes expected in a legislative driving cycle.

## CONCLUSIONS

A novel technique to detect ethanol exhaust gas using mass spectrometry has been developed. This method utilizes fragment ions of ethanol generated in the ionization process. An extensive survey of exhaust species had identified that virtually all ions with mass number 31 come from ethanol. Engine experiments on pure gasoline

and E85 confirmed that ethanol could be uniquely detected at mass number 31. Furthermore the measured ethanol concentration was comparable to previous results obtained using gas chromatography. Therefore, it is concluded that this new ethanol detection is not subject to interference from other exhaust species, which are often encountered in other online measurement techniques.

A similar technique was proposed for detecting acetaldehyde. The study of exhaust gas species indicated that 2-methylbutane and few other species interfered with the detection. Experimental results proved that the interference was severe — the measured concentration was over 43 times of the values measured using gas chromatography. Apart from interference from other exhaust species, another source of error stemmed from the limited resolution of the mass spectrometer. Ions at mass number 44 might have been miscounted as ions at mass 43. Further investigation is required in order to apply this new technique for acetaldehyde detection.

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## DEFINITIONS/ABBREVIATIONS

BDC: Bottom dead center

CAD: Crank angle degree

CARB: California Air Resources Board

DISI: Direct injection spark ignition

EPA: Environmental Protection Agency

MBT: Minimum ignition advance for best torque

NIMEP: Net indicated mean effective pressure

PTFE: Polytetrafluoroethylene

TDC: Top dead center

## APPENDIX

Speciated exhaust gas components measured using gas chromatography. Engine was running at 1500 rpm, 3.8 bar NIMEP, stoichiometric, E85

Component	Mole concentration [ppm v/v]
Ethanol	261.14
Methane	82.16
Ethylene	68.60
Ethyne	36.31

Acetaldehyde	35.79
Toluene	12.09
Ethane	8.14
Propene	7.00
2M-Butane	5.00
2M-Propene	4.28
Benzene/1M-CycloPentene	2.94
1,2,4-TM-Benzene	2.78
2,2,4-TM-Pentane	2.55
1M-3E-Benzene	1.13
2,3,4-TM-Pentane	1.09
2,3,3-TM-Pentane	1.09
1,3,5-TM-Benzene	0.87
Pentane	0.85
1,3-Butadiene	0.61
1M-4E-Benzene	0.60
Unidentified	0.54
t-2-Butene	0.53
2,3-DM-Butane	0.52
2M-Propane	0.49
1M-2E-Benzene	0.49
2,4-DM-Hexane	0.49
2M-Pentane	0.44
2M-2-Butene	0.43
CycloPentadiene	0.41
2,2,5-TM-Hexane	0.41
2,4-DM-Pentane	0.40
Hexane	0.39
E-CycloPentane	0.38
1,2,3-TM-Benzene	0.32
E-Benzene	0.30
3M-Pentane	0.29
Indan	0.25
2,3-DM-Hexane	0.24
Styrene	0.23
n-PropylBenzene	0.23