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Intercomparison of ethanol, formaldehyde and acetaldehyde measurements from a flex-fuel vehicle exhaust during the WLTC

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HIGHLIGHTS

- Ethanol, formaldehyde and acetaldehyde measurements were performed during the WLTC.
- Measurements from all the instruments were in good agreement.
- Non-methane organic gases resulted to be higher than non-methane hydrocarbons.

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ABSTRACT

An intercomparison exercise of the world-harmonized light-duty vehicle test procedure (WLTP) aiming at measuring ethanol, formaldehyde and acetaldehyde emissions from a flex-fuel light-duty vehicle using E85 was conducted in the Vehicle Emission Laboratory (VELA) at the European Commission Joint Research Centre (EC-JRC), Ispra, Italy. The instruments used during the intercomparison allowed online measurements of these compounds directly from the diluted exhaust. Measurements were done either in real time or immediately after the test. The measurement and analysis of exhaust emissions over the world-harmonized light-duty vehicle test cycle was done by means of Fourier transform infrared spectroscopy (FTIR), proton transfer reaction-mass spectrometry (PTR-Qi-ToF-MS), photoacoustic spectroscopy (PAS) and gas chromatography (GC). Results showed that online systems can perform measurements from the vehicle diluted exhaust assuring a good repeatability (within instrument variance) and reproducibility (between instrument variance) of the results. Measurements from all the instruments were in good agreement (|Z-score| < 2). Results showed that online systems can perform measurements from the vehicle diluted exhaust assuring the reproducibility and repeatability of the results. Results obtained measuring at the tailpipe using a FTIR were in good agreement with those acquired measuring at the constant volume sampler (CVS). Considering the low sensitivity of the current technique used to measure hydrocarbons emissions towards oxygenated compounds (flame ionization detector; FID), non-methane organic gases (NMOG) were calculated applying their FID response factors to the measured

Abbreviations: CARB, California Air Resources Board; CFR, U.S. Code of Federal Regulations; CH_3CHO, acetaldehyde; CLD, chemiluminiscence detector; CO, carbon monoxide; CO_2, carbon dioxide; cps, counts-per-second; CVS, constant volume sampler; EC-JRC, European Commission Joint Research Centre; EFs, emission factors; EPA, Environmental Protection Agency; EtOH, ethanol; EU, European Union; FFVs, Flex-Fuel Vehicles; FID, flame ionization detector; FTIR, Fourier transform infrared spectroscopy; GC, gas chromatography; HCHO, formaldehyde; HPLC, high pressure liquid chromatography; LDV, light-duty vehicle; LoD, limit of detection; ncps, normalized counts-per-second; NEDC, New European Driving Cycle; NDIR, non-dispersive infrared; NH_3, ammonia; NMHC, non-methane hydrocarbons; NMOG, non-methane organic gases; NO, nitrogen monoxide; NO_2, nitrogen dioxide; NOx, nitrogen oxides; PAN, peroxyacetyl nitrates; PAS, photoacoustic spectroscopy; PID, photo ionization detector; PTR-Qi-ToF-MS, Proton transfer reaction-mass spectrometry; RH, relative humidity; sccm, standard cubic centimeters per minute; SIT, sample integration time; THC, total hydrocarbons; UV-DAD, ultra violet diode array detector; VELA, Vehicle Emission Laboratory; WLTC, world-harmonized light-duty vehicle test cycle; WLTP, world-harmonized light-duty vehicle test procedure.

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emissions of ethanol, acetaldehyde and formaldehyde. NMOG resulted to be up to 74% higher than measured non-methane hydrocarbons (NMHC).

1. Introduction

Renewable energy sources contribute to climate change mitigation through the reduction of greenhouse gas emissions. For that reason European Union (EU) set out a target of at least 27% for the share of renewable energy consumed in the EU in 2030 [1]. Road transport is responsible for over 70% of transport greenhouse gas emissions and much of the air pollution in the EU [2]. To count towards the renewable energy targets, the contribution of biofuels, bio-liquids and biomass fuels will need to meet further sustainability and greenhouse gas emissions saving criteria. Ethanol remains the main biofuel used on spark ignition vehicles in EU [3] and in the United States, the Environmental Protection Agency (EPA) implemented a series of initiatives to promote the introduction of renewable fuels, with a target of 136 billion liters of renewable fuel to be blended with gasoline by 2022 [4].

Ethanol concentration in fuel blends is still an open issue in Europe. The latest version of the European gasoline standards (EN228) allows blending up to E10 (gasoline containing up to 10% of ethanol by volume), but modern gasoline vehicles can already run on blends containing up to 15% of ethanol [5]. Moreover, in Europe, Flex-Fuel Vehicles (FFVs; vehicles that can operate with standard gasoline and any ethanol containing blend) can run on standard gasoline (hereinafter E5, gasoline containing 5% ethanol) or on blends of ethanol and gasoline containing up to 85% ethanol during the summer (E85) or 75% during winter (E75, winter blend). Having a deep understanding of the impact that these ethanol containing fuel blends will have on vehicular emissions is hence of major importance.

Previous studies [6–9] have suggested that an increase in the ethanol content in the fuel blends reduces the emissions of some regulated gases (CO and total hydrocarbons (THC)) and CO_2. Those studies did not show strong trends for NOx emissions. However, despite promising benefits in terms of reducing regulated compounds and CO_2 emissions, it has been shown that higher ethanol concentrations in fuel blends lead to higher emissions of unburned ethanol, acetaldehyde and formaldehyde [6–9]. Formaldehyde and acetaldehyde are highly toxic and potentially carcinogenic [10–12]. They are also known for their impact on air quality, as they are precursors of ozone and peroxyacetyl nitrates (PAN) [13–15]. Therefore, given the possibility of having high ethanol concentration in fuel blends, it is crucial to study the emissions from FFVs for not only the regulated gases, but also the unregulated ones.

Flame ionization detector is generally used for measurement of THC in exhaust emissions. The FID response is calibrated for THC typically using propane. The response of most hydrocarbons in the FID is nearly identically to the one of propane. However, previous studies pointed out a different selectivity of the FID towards oxygenated compounds, such as ethanol, acetaldehyde and formaldehyde, which are commonly found in the exhaust of engines fuelled with ethanol blends [16,17]. To overcome this issue, the U.S. Code of Federal Regulations (CFR) requires the measurement of alcohols and aldehydes emissions for vehicles using blends with more than 25% oxygenated compounds by volume, and regulates the emissions of the so-called non-methane organic gases (NMOG) [18]. The EU regulation considers as "hydrocarbon emissions" what is measured by the FID, regardless the fuel blend used. Hence, the EU approach may lead to an incorrect estimation of actual emission of vehicles using ethanol blends.

It has hence become necessary to find suitable techniques to measure ethanol, formaldehyde and acetaldehyde emissions from vehicle exhaust using the new World harmonized Light-duty vehicle Test Procedure (WLTP). Therefore, in the present study four different analytical techniques: High Resolution Fourier transform infrared spectrometry (FTIR), proton transfer reaction-mass spectrometry (PTR-Qi-ToF-MS), photoacoustic spectroscopy (PAS) and gas chromatography (GC), present in six different instruments, were used to assess the feasibility of the measurement of ethanol, formaldehyde and/or acetaldehyde emissions from a FFV using E85 at the dilution tunnel over the cold start Worldwide harmonized Light-duty driving Test Cycle (WLTC) at 23 °C. These instruments were also compared to the United States and California Air Resources Board (CARB) conventional methods (Method 1001 for ethanol and Method 1004 for aldehydes). The differences observed between the actual hydrocarbon emissions measured using exclusively FID, as done at the moment in the EU, and incorporating additional measurements for ethanol, acetaldehyde and formaldehyde, are also presented.

2. Experimental and methods

A FFV was tested during an intercomparison exercise of the WLTP conducted in the Vehicle Emission Laboratory (VELA) at the European Commission Joint Research Centre (EC-JRC) Ispra, Italy. Six groups: AVL, HORIBA, Ionicon, LumaSense, Synspec and the Sustainable Transport Unit of the JRC, took part in the measurement and analysis of the exhaust emissions during the WLTC Class 3b vehicles (see Fig. S1). The technical description of the vehicle is available in Table 1. The vehicle was fuelled with E85 blend (85% Vol Vol^{-1} ethanol content, see Table S1 of the supplementary material for fuel specifications). Two tests were also performed with conventional E5 blend.

The VELA facility includes a climatic test cell with controlled temperature and relative humidity (RH) to mimic different ambient conditions (temperature range: −10–35 °C; RH: 50%). Tests were performed on a chassis dynamometer (inertia range: 454–4500 kg), designed for two and four-wheel drive LDV (two 1.22 m roller benches – MAHA GmbH, Germany). The emission exhaust is fed to a CVS (HORIBA, Japan) using a critical Venturi nozzle to regulate the diluted exhaust flow rate (CVS flow range: 3–30 m^3 min^{-1}). A series of thermocouples monitored the temperature of the oil, cooling water, exhaust, and ambient conditions. The tests were conducted at test cell temperature of 23 ± 0.5 °C,

Table 1
Vehicle specifications.

Features	FFV
Combustion type	Spark Ignition
Year of registration	2012
EU emission standard	Euro 5
After-treatment	Three Way Catalyst
Fuel system	Direct Injection
Engine power (kW)	132
Engine displacement (cm^3)	1596
Vehicle total mass (kg)	2110
Odometer at test start (km)	20010
Inertia class (kg)	1804