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QCM virtual multisensor array for fuel discrimination and detection of gasoline adulteration

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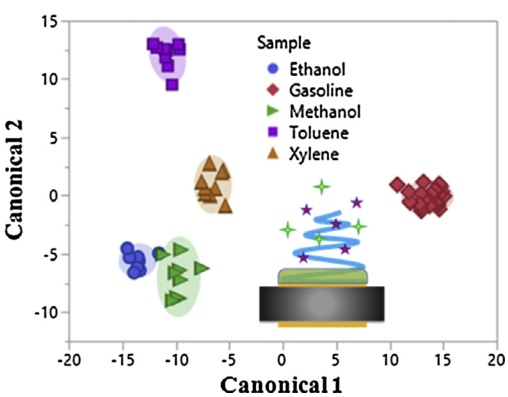
GRAPHICAL ABSTRACT



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ABSTRACT

Herein, a simplistic quartz crystal microbalance (QCM) approach for discrimination of petroleum based fuels is presented. In this regard, a quartz crystal microbalance (QCM) virtual multisensor array (V-MSA) was employed to discriminate between different petroleum based fuels and to detect gasoline adulteration with high accuracy. First, an ionic liquid based V-MSA was used to discriminate between four fuel types (petroleum ether, gasoline, kerosene, and diesel). Subsequently, the system was used to successfully discriminate between three gasoline grades as a precursor for studies of gasoline adulteration. Finally, the system was used to detect and determine the nature of several gasoline adulterants at different v/v ratios (1%, 10%, 20% and 40%). Excellent accuracy (100%) was achieved for each study extolling the potential of this approach. This report represents the first example of a QCM sensor array utilized for detection of gasoline adulteration.

1. Introduction

Petroleum based fuels have been the energy source of choice for meeting energy requirements worldwide. In this regard, gasoline,

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and diesel have proven to be globally important fuels, for transportation purposes [1,2]. As a result, illegal adulteration of such fuels can be a lucrative endeavor. This illegal activity is typically spurred by price disparities between petroleum based fuels and commonly available adulterants, such as industrial solvents [3,4]. In this regard, the cost difference is normally driven by differential taxation between fuels and potential adulterants [3,4]. Unfortunately, adulteration can have significant economic and environmental impacts. Such impacts include increased toxic emissions, lost taxes, and consumer vehicle malfunctions [3–8]. Thus, there is a need for simplistic cost effective methods for detection of fuel adulteration.

Numerous analytical techniques have been employed to detect fuel adulteration. In fact, the American Society for Testing and Materials International (ASTM) has documented several methods that have been accepted as global standards [3]. These include a number of physicochemical property based tests as well as more sophisticated analytical approaches. In this regard, relative density measurements, and evaporation/distillation methods are among the simplest approaches. However these approaches are often not sufficient for detecting low level adulteration or adulteration with naturally occurring fuel constituents such as hydrocarbon solvents [3]. More complex analytical methods such as gas chromatography-mass spectrometry (GC–MS) or implementation of dye markers are more reliable [3,9]. However, these approaches are typically expensive, time consuming or require significant expertise to achieve accurate results [3,8]. Due to these limitations, researchers are developing novel systems or application of novel techniques for detection of fuel adulteration. In this regard, all advanced research can be divided into two main categories 1) application of new techniques to traditional analytical approaches or 2) implementation of new instrumental approaches. With regard to the former category, the vast majority of reports in literature employ statistical analyses of data to enhance traditional approaches such as distillation and gas chromatography based methods [10–14]. In each case, statistical techniques are employed to simplify data analyses and enhance accuracy of detection. This approach addresses some of the limitations of traditional techniques such as the requirement for lengthy analysis time. With regard to the latter category, several new methods have been developed for detection of gasoline adulteration which are mostly based on applying new instrumental approaches. In this regard, several types of spectroscopy and spectrometry based methods have been reported recently [8,15–24]. In the present study, an alternative method for fuel discrimination and detection of gasoline adulteration, based on the quartz crystal microbalance (QCM), is introduced. Similar to some of the spectroscopy based methods, advantages of this approach include, lack of sample preparation, and prompt nondestructive analyses.

The QCM is a simple yet sensitive analytical tool primarily used as a mass detection device. However, as a physical event transducer, this device is particularly amenable to the fabrication of sensors and sensor arrays [25–37]. In this regard, a gas phase QCM sensor is typically comprised of a chemosensitive layer immobilized onto the quartz crystal resonator surface (QCR). The chemosensitive adlayer, which directly affects sorption properties, imparts sensitivity and selectivity to the sensor. As a gravimetric transducer, the QCM converts the sorption event into a quantifiable electronic signal. When several sensors employing different chemosensitive adlayers are utilized in tandem, a multisensor array (MSA) is developed. MSAs represent the most prevalent examples of QCM sensor arrays in literature [29–31,35,38–45], however such systems suffer from limitations when trying to discriminate numerous closely related highly complex mixtures. Recently, we introduced an alternative scheme called a virtual sensor array (VSA) based on the dynamic operation of a single sensor that utilizes harmonics, film thickness, and viscoelasticity to generate differential responses [36,37]. While powerful for discriminating closely related pure analytes, using single chemosensitive material, this scheme can also suffer some accuracy limitations when analyzing multiple highly complex mixtures [37]. To address the limitations experienced by the MSA and VSA schemes, we introduced a new scheme that combines the MSA and VSA scheme, termed a virtual multisensor array (V-MSA) [37]. This new scheme is based on dynamic operation of multiple sensors, and exhibits multifold enhancement of data density when compared to its component schemes. It was found that enhanced data density was a key factor in accurate discrimination of volatile complex mixtures [37]. Hence, we further explore the utility of this newly reported sensing scheme (V-MSA) by assessing its potential for fuel discrimination and detection of gasoline adulteration.

Herein, a new approach for fuel discrimination based on employing the quartz crystal microbalance is introduced. In this regard, the development and implementation of a QCM V-MSA, employing organic salts (OSs) as recognition elements, for discrimination of pure and adulterated fuel samples is described. OSs, particularly Ionic liquids and Group of Uniform Materials based on Organic Salts (GUMBOS), have proven promising chemosensitive adlayers for gas phase QCM sensors and sensor arrays [29–34,36,46–48]. Moreover, OSs exhibit viscoelasticity and favorable sorption properties, which are vital for fabrication of V-MSAs [34,49,50]. As a proof of concept, this system was initially employed to discriminate between four petroleum based fuels, specifically petroleum ether, gasoline, kerosene and diesel, which represent the most chemically distinct complex mixtures assessed. Subsequently, this array was used to discriminate more closely related complex mixtures represented by gasoline grades (Exxon Regular, Exxon Plus, Exxon Supreme). Finally, the system was utilized to detect adulteration of gasoline by common industrial solvents (methanol, ethanol, xylenes, and toluene) with varying adulterant concentration (v/v ratios 1%,10%,20%,40%). This study is the first report of a QCM sensor array for applications in fuel discrimination and detection of gasoline adulteration.

2. Experimental section

2.1. Reagents and materials

Four OSs, named 1-octyl-3-methylimidazolium bromide ([C_8MIm][Br]), 1-decyl-3-methylimidazolium bromide ([C_{10}MIm][Br]), 1-dodecyl-3-methylimidazolium bromide ([C_{12}MIm][Br]), 1-hexadecyl-3-methylimidazolium bromide ([C_{16}MIm][Br]) were used to prepare coatings on the QCRs utilized in these studies. These ILs were synthesized using previously documented procedures [51,52]. Fuel samples were purchased from a local Exxon Gas station in Baton Rouge, Louisiana, and contain 10–15% ethanol. Dichloromethane was obtained from Malindkroft fine chemicals. Xylenes were obtained from Fischer Scientific while toluene, anhydrous methanol, and anhydrous ethanol were obtained from Sigma Aldrich, all with specified purity >98.5%. All materials were used as is, without any further purification.

2.2. Preparation of stock solutions

Stock solutions of [C_8MIm][Br], [C_{10}MIm][Br], [C_{12}MIm][Br], and [C_{16}MIm][Br] (1 mg mL^{-1}) were prepared in dichloromethane (DCM) using 20 mL borosilicate glass scintillation vials.