



Full Length Article

Rapid detection of fuel adulteration using microfabricated gas chromatography

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ABSTRACT

Rapid and accurate quality control for fuel adulteration is a major economic and health concern. Current technology lacks capability to provide speedy and accurate point of sale (POS) solutions. Most of the work done on portable solutions rely on absorbance spectroscopy, which provide a qualitative solution with a trade-off between speed and accuracy. This paper demonstrates a technique based on micro gas chromatography (μ GC) for portable, fast, and accurate analysis of diesel fuels adulterated with kerosene. The separation columns are fabricated using microelectromechanical systems (MEMS) technology. The columns are 1 m-long and consist of an embedded array of pillars. Two different stationary phase coating were examined to explore the efficacy of the proposed technique. The analysis relies on aggressive pressure and temperature programming of the chip to obtain partially separated chromatograms. When analyzed with well-established chemometrics methods such as Principal Component Analysis and Partial least Squares Regression a linear relationship between the chromatograms and diesel purity was determined. The separation column could discriminate as little as 5% added kerosene to diesel fuel with only four seconds of chromatogram analysis.

1. Introduction

Fuel adulteration is a common problem in many countries that lack quality control laws or methods. It potentially provides considerable economic incentives to unscrupulous individuals in the fuel supply chain mainly due to the different pricing structures of different available fuels. Countries mostly effected are developing economies like Brazil, India, Kenya, Nigeria and Morocco [1–4] to name a few. Owing to the different energy policies between countries, the prevalent form of fuel adulteration is diverse [4]. Typical adulterants are in the form of solvents, industrial wastes, heavier hydrocarbon-based oils, and other distillate hydrocarbon-based fuels. However, the most predominant form of fuel adulteration is found in fuels used in automobile such as diesel and gasoline. The fraud is committed by adding a fuel of inferior quality and price. Kerosene, for instance, is used in several countries as a household fuel for domestic consumption and is thus heavily subsidized by local governments. To make adulteration economically viable, the range of kerosene percentage in mixtures is usually between 10% and 30%. Anything below 10% is not profitable and any mixture above 30% can easily be detected by considerably deteriorated engine performance [5].

The two primary effects of adulteration of diesel can be described

from both economic and environmental standpoints. Engines running on adulterated diesel will perform with decreased efficiency causing long-term damage. The incomplete combustion of an incompatible fuel releases harmful pollutants. It has been shown that blended adulterated fuels can cause increased content of hydrocarbons, nitrogen oxide derivatives and carbon monoxide in tailpipe emissions [6]. Such adulterants have been shown to be carcinogens. Automobile engines are tuned to operate optimally for a fuel type. However, unauthorized blended fuels combust at different conditions and in turn do not burn as efficient. They also tend to increase carbon content deposition in the fuel lines reducing the lifetime of the engine and incurring frequent maintenance costs. Diversion of kerosene for adulteration can create a supply shortage for domestic consumption too. It was reported by India's National Council of Applied Economic Research (NCAER) that 38.6 percent of subsidized kerosene was being used in petrol and diesel adulteration [7].

To maintain fuel quality standard and to monitor adulteration, ASTM International (formerly known as American Society for Testing and Materials) has defined standardized testing of metrics and methods such as flash point, cetane number, conductivity, distillation, and density. These methods use various properties of hydrocarbon fuels to qualify

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Table 1
This table highlights published works on some of the portable and potentially portable solutions for fuel adulteration detection.

	Analytical Technique	Measured metric	Fuel type	Adulteration Concentration tested	Ref
Adsorption spectroscopy & refractometry	FTIR (Fourier Transform infra-red spectroscopy)	Spectrogram analysis	Diesel	0–50%	[3]
	UWB (Ultra-wideband radar)	Dielectric constant	Diesel	2%	[8]
	Handheld refractometer	Refractive index	Diesel	5, 10, 15%	[30]
	Meta material sensor-based refractometer	Permittivity	Diesel	10, 20, 30%	[31,32]
	Micro cavity-based sensor	Refractive index	Gasoline	10, 20, 30, 40, 50%	[33]
	Wavelength-dependent excess permittivity sensor	Permittivity	Diesel	5, 10, 15%	[34]
	Fiber optic sensor	surface plasmon resonance (SPR) wavelength	Diesel	0, 20, 40 and 80%	[11]
	Prototype for optical sensor	Refractive index	Diesel	5, 10, 15%	[35]
	Metal clad planar wave guide	Refractive index	Diesel	10 to 50%	[36]
	Long fiber grating sensor	Refractive index	Diesel	10 to 50%	[37]
Other	Near infra-red (NIR) spectroscopy	Spectrogram analysis	Gasoline	0.2 to 100%	[1]
	Fluorescent test strips	Viscosity (Fluorometric)	Diesel	10%	[38]
	Ultrasound	Sonogram analysis	Diesel	10–50%	[39]
	QCM	Mass variation	Gasoline	1, 10, 20 and 40%	[40]
	Electronic nose	Functionalized sensor array	Gasoline	Up to 25%	[41]
	Colorimetric sensor	Colorimetric microfiber	Gasoline	10 to 20%	[42]

and quantify sample characteristics to enforce quality. However, these tests are either time consuming or performed on laboratory bound equipment. It is not possible or feasible to test and monitor for fraud at the point of sale with these methods. To overcome this deficit, portable, reliable and faster techniques for adulteration detection are under development as summarized in Table 1, most of which rely on spectroscopy.

Rapid testing was demonstrated using FTIR (Fourier Transform infrared) spectroscopy to classify adulterated gasoline [3]. A non-invasive technique using radar as the detection medium was demonstrated by Venkoparao et al. (2001) to measure dielectric constant of adulterated fuel [8]. Refractive index is a good measure of viscosity of liquids and thus can be used for this purpose owing to different viscosities of different fuels of binary mixtures. In another work, commercial hand-held refractometers was calibrated to determine the kerosene content in diesel [9]. Others have developed fiber optic sensors to measure the surface plasmon resonance wavelength that can be correlated with the refractive index [10,11]. Other methods such as fluorometry, colorimetry, and electronic noses are less researched for fuel adulteration detection. It is notable that adsorption spectroscopy suffers from temperature dependence which makes it harder to calibrate any device for quantitative or qualitative applications. Fluorometry requires adding chemical markers to the adulterants for quality control. This is an added cost in manufacturing process. Portable and rapid techniques for adulteration detection and quantification are still deficient.

Even though fuels such as diesel and gasoline are singular products, they are a mixture of hundreds of different hydrocarbons. As such, separation methods such as gas chromatography (GC) provide more analytical information of the samples that is both qualitative and quantitative. This has made GC the gold standard procedure for quality control. Recent advances in the development of microfabricated gas chromatograms (μ GCs) have brought the powerful analytical technique to the field. There has been significant progress by our group and others to develop microfabricated separation columns on a silicon substrate and functionalize them with different stationary phases [12–22]. Research has shown that these columns can separate and identify the constituents of gaseous mixtures and can be integrated with other microsystem components to realize a fully functional GC [23,24]. The bulk of the ongoing research, however, is on comprehensive separation of all analytes in a mixture. However, as the sample complexity increases, the full separation of all analytes using MEMS-enabled columns

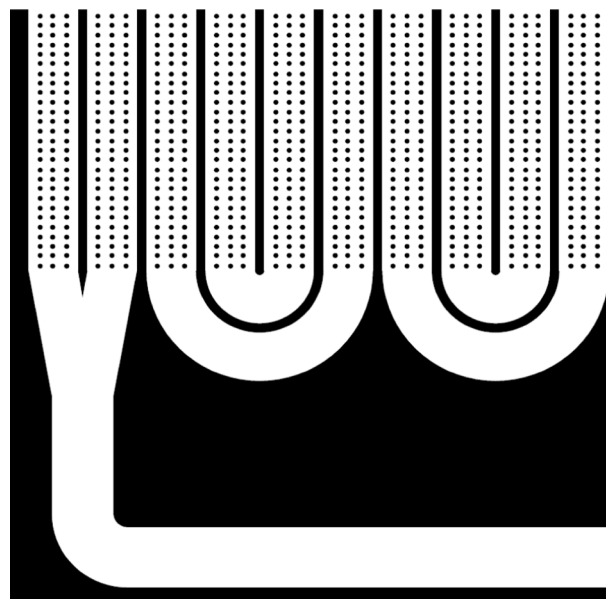


Fig. 1. Mask layout segment for separation column.

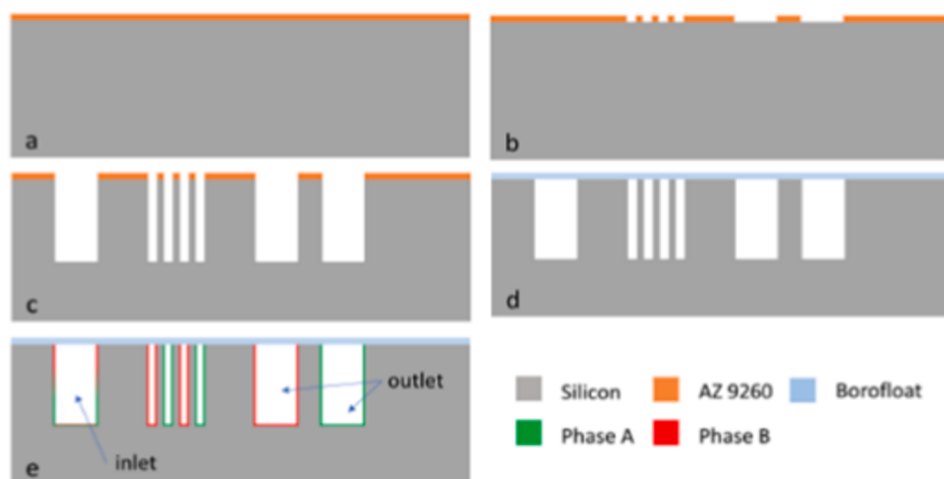


Fig. 2. Fabrication steps, a) Photoresist application on silicon wafer b) Photolithography, c) Column-etching with Deep reactive ion etching (silicon wafer), d) anodic bonding of borofloat glass wafer with silicon substrate, e) Coated Column.

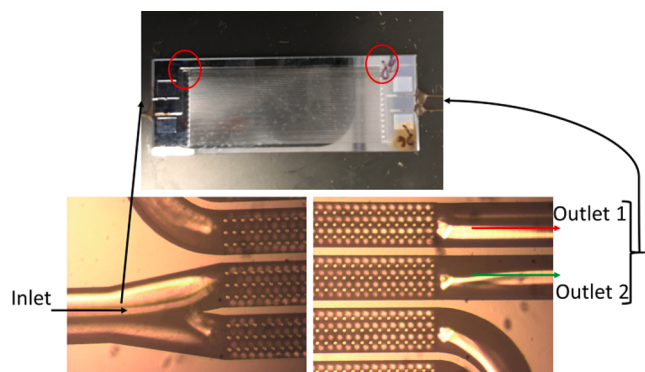


Fig. 3. Fabrication results showing micro separation column (top). Zoomed in pictures show the inlet and outlets of the chip after coating.

becomes more challenging as these columns are typically 50 cm-2 m long compared to 15–30 m-long fused silica capillary tubing used in conventional GCs. In this paper, we show, for the first time, that such MEMS separation columns and subsequently, handheld μ GCs, are very powerful in analyzing fuel adulteration in just a few seconds. The concept behind our approach is that for adulteration, the determination of all the compounds in the intended fuel is not necessary. This means instead of a full chromatographic analysis; we can just evaluate the profile or pattern of the partially separated analytes and distinguish the profile between a pure sample and its corresponding altered counterpart.

2. Materials and methods

2.1. Column design and fabrication

The design of the μ GC chip follows our previously published semi-packed architecture [25]. Each channel consists of 20 μ m pillars with a pitch size of 20 μ m in a row and 35 μ m between each row. The overall length of each channel is 1 m, with the width set as 200 μ m. The chip inlet bifurcates into two semi-packed channels each of which has its own outlet (Figs. 1 and 2). Each column is coated with a different stationary phase enabling us to evaluate the effect of the phase on detecting adulteration in fuel samples. This was done to reduce chip to chip and wafer level variation among the two channels. The column mask design and fabrication process flow are illustrated in Figs. 1 and 2. The fabrication result is shown in Fig. 3. The wafer is spun with photoresist (PR)

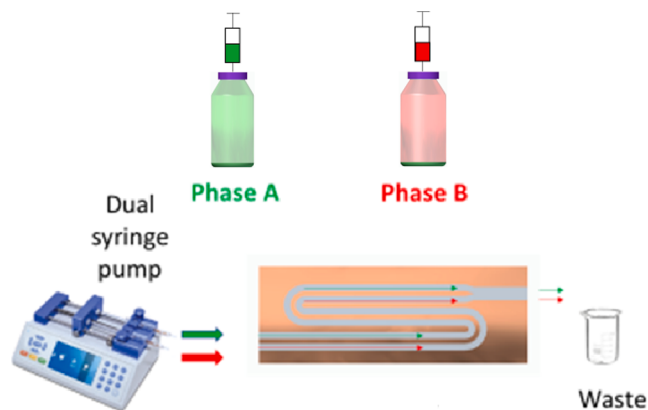


Fig. 4. The coating process is shown here. The two stationary phases are prepared in a solution of acetone. They are loaded in a syringe pump and injected at a rate of 20 μ L through the outlet to coat both the columns simultaneously.

AZ9260 @ 2000 rpm for 60 s after HMDS priming. The PR was soft baked for 2 min and 30 s at 110°C. The wafer was then rehydrated for 30 min. A PR thickness of 8.2 μ m was achieved. The mask design is transferred on the wafer via lithography with MA-6 (Karl Suss) mask aligner. After development of the pattern with AZ400k (1:3 dilution, 3 min) the wafer was dried with nitrogen. Using deep reactive ion etching (DRIE) the design was etched to a channel depth of 250 μ m. Plasma ashing was then performed to clean the wafer of left-over PR after acetone, IPA and DI water cleaning. Then the silicon wafer was bonded with a borofloat wafer using a Karl Suss, SB-6 anodic bonder. After dicing short fused silica capillary columns were connected to the device channels and sealed with epoxy. Two Room temperature Ionic Liquids (RTILs) were chosen as the stationary phases. While a further analysis with more traditional stationary phases would provide more insight into role of stationary phases, it would be a divergence from the investigation into micro GC's capability to detect fuel adulteration. This could be a topic of interest for future research. We chose two different stationary phases with different polarities to investigate their effect on diesel purity identification. ([P66614][NTf2]) trihexyltetradecyl-phosphonium bis (trifluoromethylsulfonyl)imide is denoted as Phase A, and ([BPyr][NTf2]) 1-butylpyridinium bis(trifluoromethylsulfonyl)imide is named Phase B. The columns were coated using a modified static coating process. 15 mg of each phase was dissolved in 1 ml acetone. To coat the columns, we use a dual syringe pump. The coating process is illustrated in Fig. 4. We load the phases in syringes and connect them to the outlet

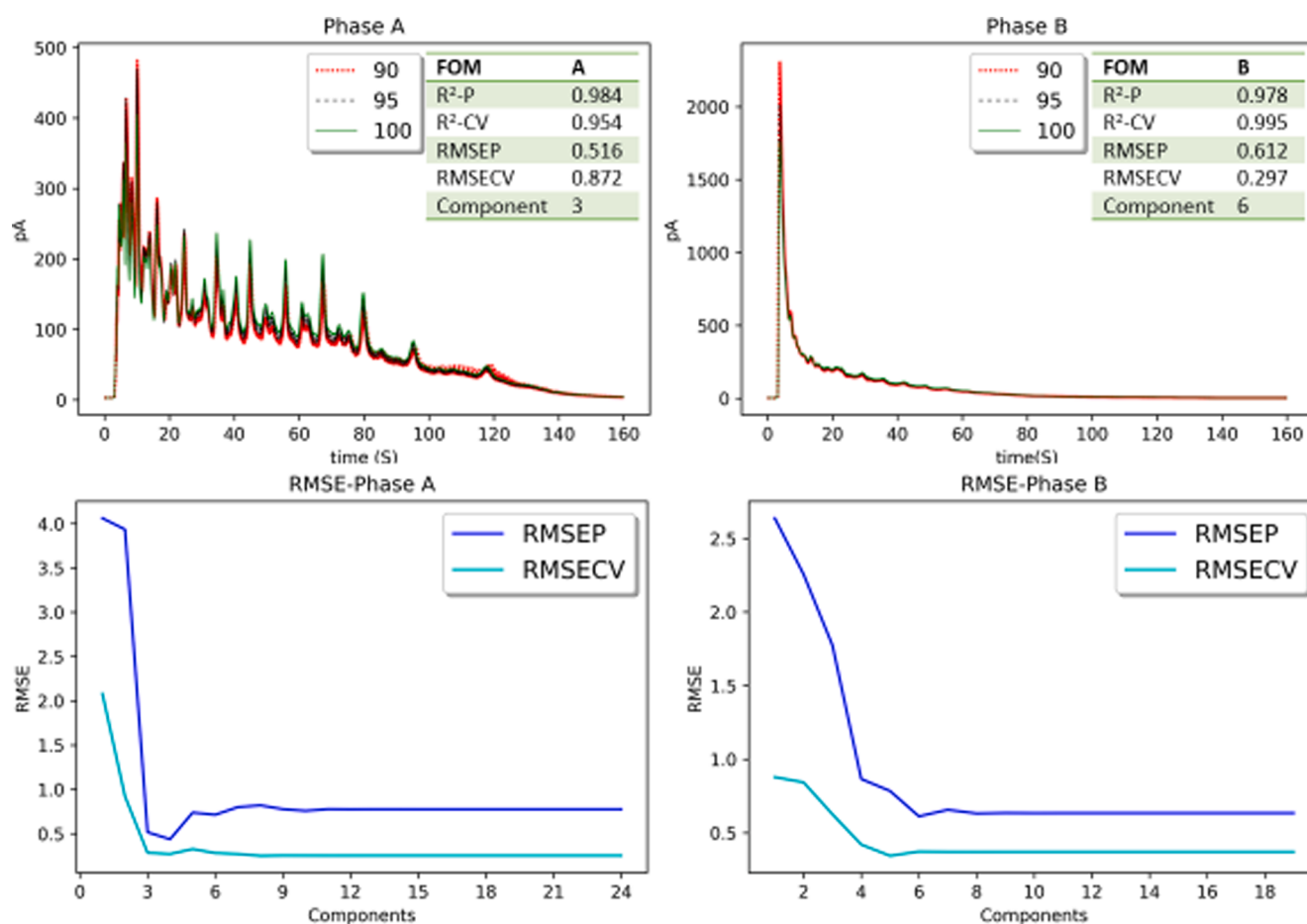


Fig. 5. Data analysis for 160 s. The FOM table shows the performance of the PLS model. Both Phase A and B show R^2 -P values greater than 0.9, affirming that the model can predict adulteration content fairly accurately.

of the device. We start injecting the phase solutions simultaneously through the outlets starting at 20 $\mu\text{L}/\text{min}$. After the columns are filled with the solution, we increase the rate to 40 $\mu\text{L}/\text{min}$. We further increase the injection rate to 60 $\mu\text{L}/\text{min}$ with 100 μL remaining in the syringe to make sure to fill any residue uncoated parts. After the injection is completed, we connect the inlet of the device to an empty vial connected to a nitrogen cylinder. The device is submerged in a bath of water in a hotplate at 45 $^{\circ}\text{C}$. This evenly heats up the device while the nitrogen gas dries the acetone. The columns were conditioned with Thermofischer's Heratherm oven at 150 $^{\circ}\text{C}$.

2.2. Experimental setup and data analysis

Diesel and kerosene were bought from "Briggs and Stratton" and "Crowne". They were mixed in volumetric ratios of 95/5 and 90/10% (v/v). Pure diesel was used as the control sample. All three different samples were kept refrigerated before, and after running the experiments, to keep their integrity intact. All testing was done with an Agilent 7890A GC which is equipped with an autoinjector and a flame ionization detector (FID). The fabricated columns were connected to the GC inlet. One of the outlets was connected to the FID. The inlet temperature was kept at 280 $^{\circ}\text{C}$ and the FID at 300 $^{\circ}\text{C}$. Ultra-high purity helium was chosen as the carrier gas. The tests were performed with a fast GC approach utilizing aggressive pressure and temperature programming. The run conditions were 80 $^{\circ}\text{C}$ initial temperature with 100 $^{\circ}\text{C}/\text{min}$ temperature ramp with a final temperature of 150 $^{\circ}\text{C}$ (with 1 min hold time) run at 40 psi carrier gas pressure. The injection was performed in split mode at a split ratio of 200:1 with an injection volume of 0.3 μL . The data were obtained from Agilent ChemStation software. Each

sample was run 11 times, with a total of 33 runs for all testing samples. Apart from the training samples, separate blind samples were taken for testing the trained models. The blind samples were prepared and put in unlabeled GC vials by a person who did not run the data analysis. The person performing the testing was not privy to the unlabeled samples values till after analysis was complete. This was done to prevent any observer bias in data analysis. We also ran 100% kerosene and 100% diesel samples at a 5 $^{\circ}\text{C}/\text{min}$ temperature ramp with 30 $^{\circ}\text{C}$ initial temperature with a hold time of 0.5 min and 150 $^{\circ}\text{C}$ final temperature for both phases. This was done to illustrate the constituent differences in the fuels. Principal Component Analysis (PCA) and Partial Least Squares Regression (PLSR) were then performed on the chromatographic data. PCA is used for exploratory multivariate data analysis. The original data is reduced to a set of uncorrelated principal components that can show the differences between observations. PCA and PLSR are widely used tools in chemometrics for calibration [26,27]. PCA is a dimensionality reduction technique. This is useful to visualize variations in higher dimensional data. PCA algorithm works by reducing original dataset of vectors and projects them onto a lower dimension vector while retaining the maximum variation possible from the original data set. PCA indicates that chromatographic patterns can be used to qualitatively discern adulterated and pure diesel. To quantitatively determine adulteration content, we use PLSR; a widely used technique for chemometric calibration. PLSR is an iterative algorithm that relates two groups of variables to each other, namely predictor (raw chromatograms) and response (concentration). Figures of merit (FOM) are indicators used to evaluate the accuracy and usefulness of the developed models. Root mean squared error gives an average distance of the calibration error from zero. Root mean squared error of cross validation (RMSECV) and

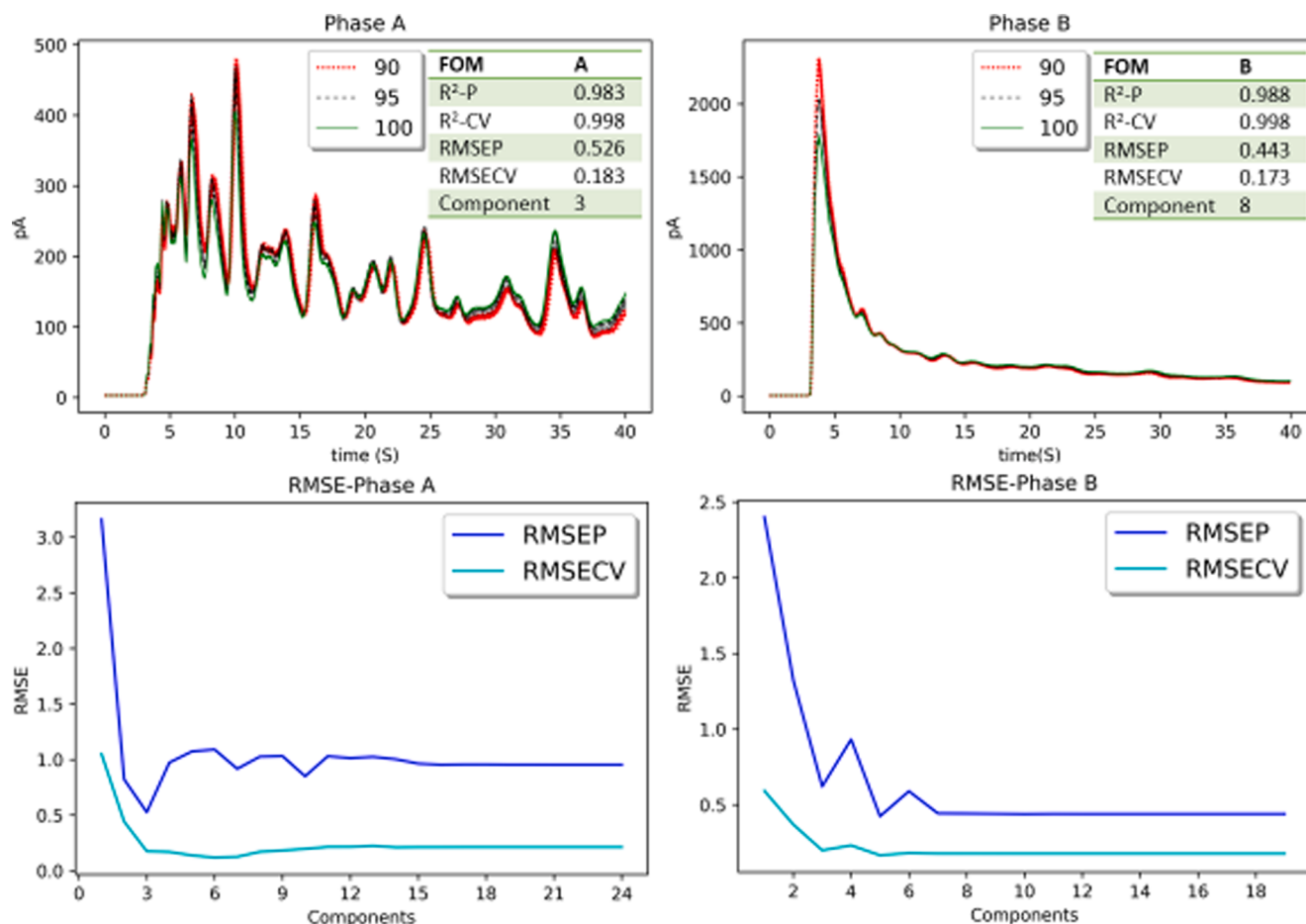


Fig. 6. Data analysis for the first 40 s of the chromatogram. Both Phase A and B shows RMSEP value $\sim 0.5\%$ (v/v) and R^2 -P over 0.9. Both models are effectively able to predict the adulteration content.

root mean squared error of prediction (RMSEP) are two metrics measured on the train and test set respectively. RMSECV gives a measure of how well the model can calibrate to training data. RMSEP gives the measure of model performance to unseen data [1].

3. Results and discussion

The choice of the stationary phase plays an important role in gas chromatography. Stationary phases exhibit varying selectivity depending on the type of analyte. Interactions between the analytes and the phases of similar polarities are highest. It increases the residence time in the stationary phase compared to analytes with a phase of opposing polarity. In our case, Phase B is more polar than Phase A [19]. The plate number of the columns were calculated with a solution of naphthalene in acetone with an isothermal run of 100 °C at different carrier gas pressures. The columns tested after conditioning showed an optimal operating pressure of around 20 psi. Phase A column had a plate number of 2117 @ 20 psi while Phase B showed a plate number of 1126 @ 25 psi.

GC analysis usually relies on peak retention time index to identify chemicals in the sample. In this way, a fully resolved chromatogram can identify any compound in the mixture assuming there is no co-elution. For complex samples, slow temperature programming and longer columns are required to identify the majority of the compounds of interest. However, even these methods fail to separate very complex samples and novel techniques such as multidimensional GCs have to be used for comprehensive detection of all analytes. For portable systems this increase their size, weight and power consumption. In most applications, it is not required to have a completely resolved chromatogram since most

of the information provided by the analysis is not required. A partially resolved chromatogram can provide enough information for the specific application. We investigated the chromatograms from the stand point of pattern recognition instead of the usual retention time index analysis. As stated previously, the GC was run in an aggressive temperature programming and pressure regime. It can be seen from the chromatogram (Figs. 5–7) that phase A does a decent job of separating the major hydrocarbons even in these conditions. Although it is incomplete, the separation can still be interpreted by a human observer. Phase B, however shows no appreciable separation whatsoever. It clearly cannot retain any of the low to mid boiling range analytes and releases them with a very short residence time in the stationary phase. This information is not useful for human interpretation by looking at retention time indexes. Diesel is primarily composed of non-polar alkanes with polar compounds accounting for less than 0.1% in mass [28]. These non-polar compounds and are not easily separated by Phase B (more polar) which would be an ineffective stationary phase to perform any reasonable separation of diesel or diesel-kerosene mixture. However, closer inspection of the data shows a trend among both phases for the purity of diesel (Fig. 8).

As mentioned above, PCA was used to determine if the chromatographic patterns contain sufficient information to discriminate between the samples. Before performing PCA, the data was preprocessed by scaling to unit variance after removing the mean. The data is then centered. The results of the PCA is shown in Fig. 9. For both phases, the first two principal components (PC) explain approximately 90% of the variance explained in the data. The first two components can discriminate between diesel sample and altered ones. It also illustrates the run-

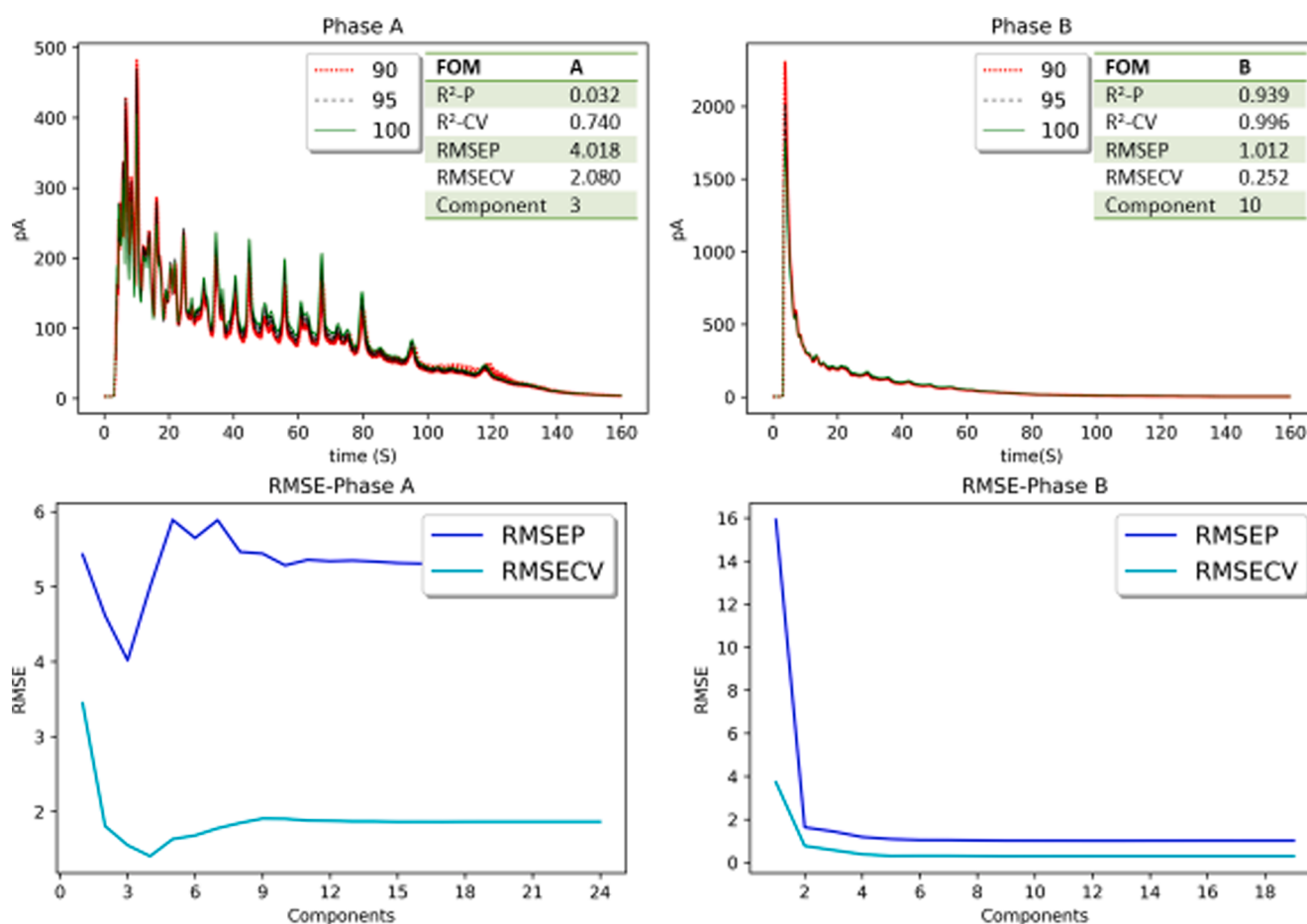


Fig. 7. Data analysis for first 4 s. We calculated high RMSE values for phase A chromatogram for both cross validation and prediction. The R^2 -P was also low (0.032) indicating inability of the model to predict adulteration percentage with only 4 s of data. Phase B shows RMSEP of 1.012% (v/v) and an R^2 -P value greater than 0.9 which shows the model can predict the adulteration content with 4 s of data.

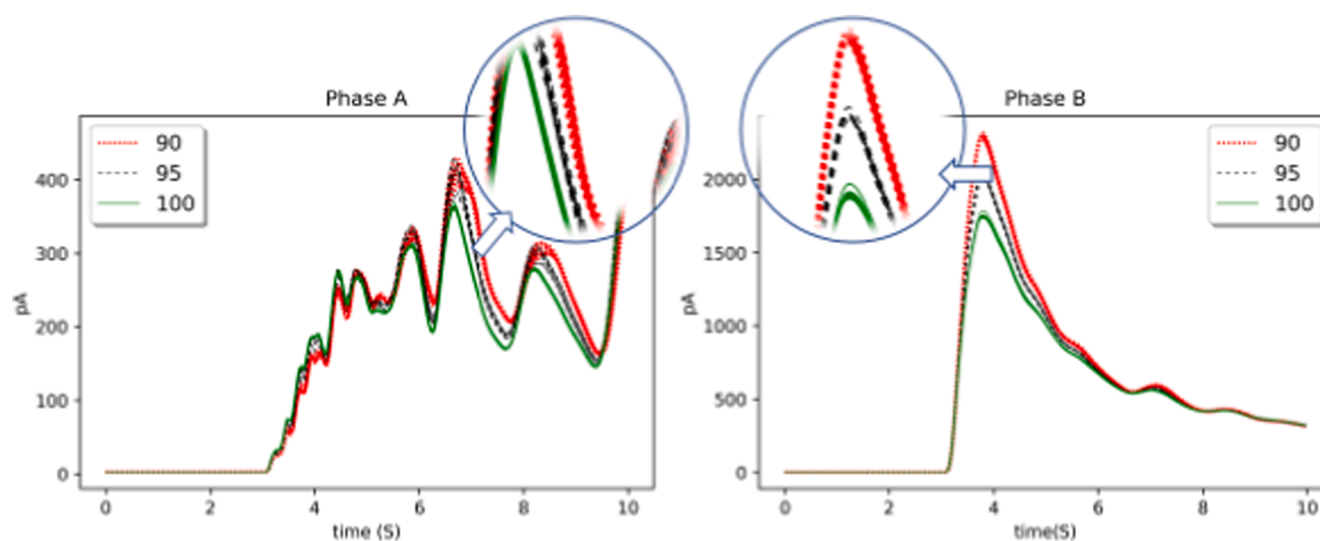


Fig. 8. Chromatogram overlay showing three different diesel concentrations of 90 to 100% (v/v) in the first ten seconds. Each concentration has 11 runs.

to-run variation of the GC for the same concentrations. This can be attributed primarily to noise from GC instrumentation (gas flow control, temperature programming and data acquisition). The results show that PCA can be used to qualitatively judge the purity of fuel and give a decision on possible adulteration of diesel and warrant further

investigation.

Fig. 5 FOM table displays the PLSR results of the analysis for 160 s. 11-fold Cross-Validation (CV) technique was applied to train the model to validate the model accuracy and its ability to generalize to unseen data. The R^2 -CV (Cross-Validation) fit for the observed versus the

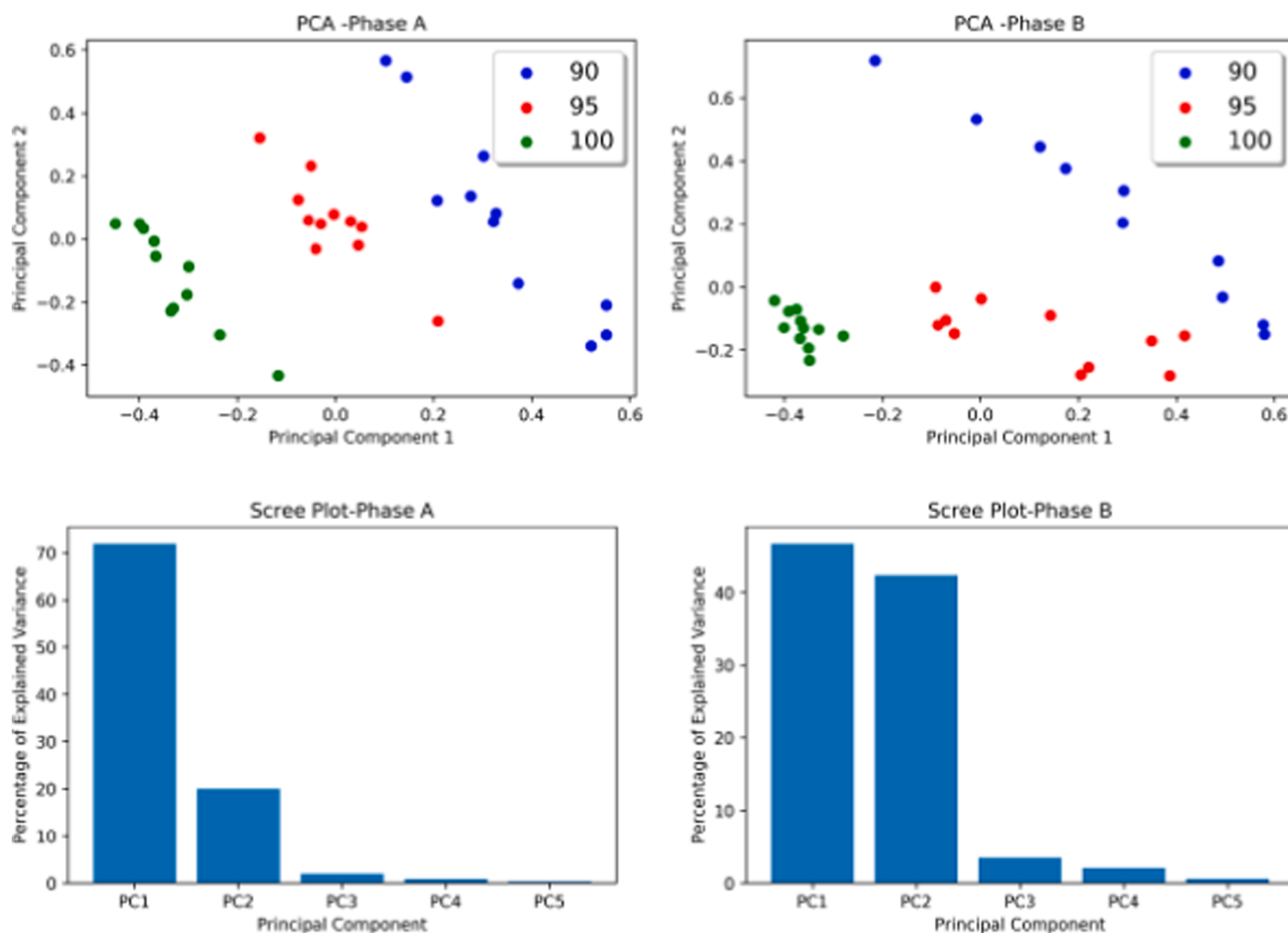


Fig. 9. PCA and scree plot for chromatograms from both phases. The PCA was performed on the full chromatogram obtained for both the phases. They show the chromatograms can be differentiated by PCA. The first two principal components account for ~90% of the variance explained in the data.

predicted results is greater than 0.9 for both phase A and B while the RMSECV shows a low value (0.516 for phase A and 0.612 for phase B). The model was tested using the blind sample data. The R^2_P fit was found to be greater than 0.9 and the RMSEP (root mean square error of prediction) was found to be less than 1. This shows the developed model generalizes well to unseen data. One of the most important requirements

of point-of-sale (POS) and process monitoring devices is the speed of analysis. To get a faster decision on the content of diesel adulteration, we trained the model on progressively smaller segments of the chromatographic data. By reducing the segment of the chromatogram used for building the model, a faster decision can be made on the sample content. We trained and tested the model on chromatographic data from

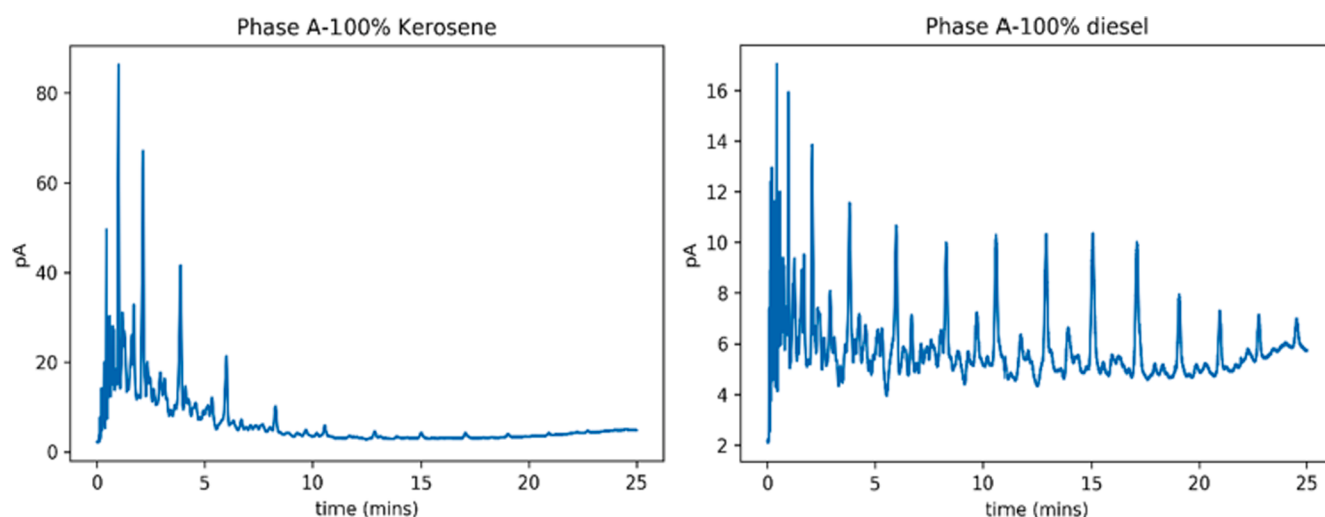


Fig. 10. Chromatograms showing the difference in hydrocarbon content of diesel and kerosene. GC conditions at 5 °C/min ramp rate from 30 °C to 150 °C @ 25 psi.

the two phases in the range of 3.5 s to 160 s segments, respectively. Figs. 5–7 show the results of 160 s, 40 s and 4 s analyses. The rest of the data is included in the supplementary section. Working with smaller segments of the chromatogram reduces the total information available to build the model. In our analysis, however, the data reduction was seen to have no major impact on model accuracy if more than 4 s of the chromatogram is used. The model for phase A fails for the first 4 s of chromatographic data showing a high RMSEP and RMSECV value and a R^2 -P value of 0.032. For phase B, the model performance was good with R^2 -P value of 0.939 and an RMSEP error of 1.012% (v/v). The data was not sufficient for accurate predictions of diesel purity at 3.5 s for Phase B. The results show that small segments chromatographic data can be used to determine diesel adulteration with kerosene. This method of analysis works well for diesel/kerosene blends because of the difference of boiling points of the major hydrocarbons of the two fuels. While kerosene is composed of lighter compounds, diesel is composed of heavier hydrocarbons. In adulterated diesel with kerosene, a more comprehensive GC analysis would show a higher ratio (Fig. 10) of low boiling compounds compared to pure diesel. Taking the early segments of the chromatogram works because the low boilers are first to elute. The kerosene compounds can be used as a marker in the chromatograms for the detection of diesel purity. This method should also work for diesel adulteration with lighter organic solvents. In our analysis, Phase B outperforms Phase A for rapid detection even though it cannot generate well-separated peaks in the chromatographic data.

The data presented in this paper show that adulterated diesel with kerosene can be quantified with an RMSEP of $\sim 1\%$ (v/v) or less. Compared to other portable devices such as IROX 2000 which has a prediction error of less than 2% with a total analysis time of 3 min with the device warm up time of 10 min [3], our technique can reach a decision within seconds with less than a minute warm up time. Our approach also reduces system complexity in terms of computing hardware and memory (considering only the first few seconds of chromatographic data are needed). Refractometric detection methods while being the least complex suffer from temperature dependence issues. Compared to spectroscopic and refractometric methods which analyze the bulk content, our approach provides some separation of the sample thereby creating a chromatographic pattern with more information about the sample. This can lead to a more accurate quantitative analysis of the sample. Our technique matches the speed of detection (in the order of seconds) compared to aforementioned techniques.

4. Conclusion and future work

We demonstrated a method that can detect 5% adulteration levels of kerosene in diesel in 4 s. In traditional GC analysis, partially resolved chromatograms are not very useful in making an analytical observation on the chemical composition of a sample. Here, we show a partially resolved chromatogram coupled with chemometric techniques can qualify and quantify adulterated diesel with kerosene. This technique holds potential to be applied for a wide range of applications. Quality control and fraud detection in fuels can be performed using this technique. In our future work, we intend to work on different column topologies, stationary phases and operating conditions on a portable platform. Multiple columns on one single device can reduce the footprint while eliminating the need for multiple injections and column multiplexing. On the analysis end, additional techniques such as data fusion of chromatograms from multiple columns can be used to improve the accuracy of the sensor. Fuel adulteration is not limited to diesel. Biodiesel, gasoline and ethanol are also some of the commonly adulterated fuels. However, the stationary phases used in this experiment may fail to discriminate those samples. One of the advantages of using RTILS is that they can be tuned with proper selectivity for the desired markers of the adulterated compounds [29]. Implementation of this method at POS and process control using μ GCs can ensure online tracking of fuel quality.

CRedit authorship contribution statement

Mustahsin Chowdhury: Conceptualization, Investigation, Formal analysis, Methodology, Writing - original draft, Software. **Azam Gholizadeh:** Conceptualization, Investigation, Writing - review & editing, Visualization. **Masoud Agah:** Conceptualization, Methodology, Supervision, Writing - review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2020.119387>.

References

- [1] Barra I, Mansouri MA, Bousrabat M, Cherrah Y, Bouklouze A, Kharbach M. Discrimination and quantification of moroccan gasoline adulteration with diesel using fourier transform infrared spectroscopy and chemometric tools. *J AOAC Int* 2019;102:966–70.
- [2] Lawal Y. Kerosene adulteration in Nigeria: causes and effects. *Am J Social Manage Sci* 2011;2:371–6.
- [3] Teixeira L, Oliveira F, Dossantos H, Cordeiro P, Almeida S. Multivariate calibration in Fourier transform infrared spectrometry as a tool to detect adulterations in Brazilian gasoline. *Fuel* 2008;87:346–52.
- [4] Gawande AP, Kaware JP. Fuel adulteration consequences in India: a review. *Sci Revs Chem Commun* 2013;3:161–71.
- [5] Sharma R, Gupta AK. Detection/estimation of adulteration in gasoline and diesel using ultrasonics. In: 2007 International Conference on Industrial and Information Systems. IEEE; 2007. p. 509–12.
- [6] Tharby R. Catching Gasoline and Diesel Adulteration 2002.
- [7] R. Committee, Committee on Pricing and Taxation of Petroleum Products, 2006, February. URL: <http://petroleum.nic.in/sites/default/files/Report1.pdf>. Last accessed: 9/20/2020.
- [8] Levitas B, Matuzas J, Viswanath G, Basalingappa V, Venkoparao V. UWB based oil quality detection. In: 2011 IEEE International Conference on Ultra-Wideband (ICUWB). IEEE; 2011. p. 220–4.
- [9] Alvarez-Segura T, Torres-Lapasio J, Ortiz-Bolsico C, Garcia-Alvarez-Coque M. Stationary phase modulation in liquid chromatography through the serial coupling of columns: a review. *Anal Chim Acta* 2016;923:1–23.
- [10] Kulkarni S, Patrikar S. Fiber optic detection of kerosene adulteration in petrol. *International Conference on Photonics, Metamaterials & Plasmonics: Pmp-2019*. 2019.
- [11] Verma RK, Suwalka P, Yadav J. Detection of adulteration in diesel and petrol by kerosene using SPR based fiber optic technique. *Opt Fiber Technol* 2018;43: 95–100.
- [12] Regmi BP, Chan R, Agah M. Ionic liquid functionalization of semi-packed columns for high-performance gas chromatographic separations. *J Chromatogr A* 2017; 1510:66–72.
- [13] Wang J, Ma J, Zellers ET. Room-temperature-ionic-liquid coated graphitized carbons for selective preconcentration of polar vapors. *J Chromatogr A* 2020;1609: 460486.
- [14] Sun J, Guan F, Zhu X, Ning Z, Ma T, Liu J, et al. Micro-fabricated packed gas chromatography column based on laser etching technology. *J Chromatogr A* 2016; 1429:311–6.
- [15] Li Y, Zhang R, Wang T, Wang Y, Wang Y, Li L, et al. A micro gas chromatography with separation capability enhanced by polydimethylsiloxane stationary phase functionalized by carbon nanotubes and graphene. *Talanta* 2016;154:99–108.

- [16] Hou L, Feng F, You W, Xu P, Luo F, Tian B, et al. Pore size effect of mesoporous silica stationary phase on the separation performance of microfabricated gas chromatography columns. *J Chromatogr A* 2018;1552:73–8.
- [17] Han B, Wu G, Huang H, Liu T, Wang J, Sun J, et al. A semi-packed micro GC column for separation of the NAFLD exhaled breath VOCs. *Surf Coat Technol* 2019; 363:322–9.
- [18] Luo F, Zhao B, Feng F, Hou L, You W, Xu P, et al. Improved separation of micro gas chromatographic column using mesoporous silica as a stationary phase support. *Talanta* 2018;188:546–51.
- [19] Regmi BP, Chan R, Atta A, Agah M. Ionic liquid-coated alumina-pretreated micro gas chromatography columns for high-efficient separations. *J Chromatogr A* 2018; 1566:124–34.
- [20] Shakeel H, Agah M. High density semipacked separation columns with optimized atomic layer deposited phases. *Sens Actuators, B* 2017;242:215–23.
- [21] Chan R, Agah M. Semi-packed gas chromatography columns with density modulated pillars. *J Microelectromech Syst* 2018;28:114–24.
- [22] Shakeel H, Wang D, Heflin JR, Agah M. Improved self-assembled thiol stationary phases in microfluidic gas separation columns. *Sens Actuators, B* 2015;216: 349–57.
- [23] Garg A, Akbar M, Vejerano E, Narayanan S, Nazhandali L, Marr LC, et al. Zebra GC: A mini gas chromatography system for trace-level determination of hazardous air pollutants. *Sens Actuators, B* 2015;212:145–54.
- [24] Sun J, Xue N, Wang W, Wang H, Liu C, Ma T, et al. Compact prototype GC-PID system integrated with micro PC and micro GC column. *J Micromech Microeng* 2019;29:035008.
- [25] Akbar M, Wang D, Goodman R, Hoover A, Rice G, Heflin JR, et al. Improved performance of micro-fabricated preconcentrators using silica nanoparticles as a surface template. *J Chromatogr A* 2013;1322:1–7.
- [26] Bro R, Smilde AK. Principal component analysis. *Anal Methods* 2014;6:2812–31.
- [27] Wold S, Sjöström M, Eriksson L. PLS-regression: a basic tool of chemometrics. *Chemometrics Intell Lab Syst* 2001;58:109–30.
- [28] Smit E, De Goede S, Rohwer ER. Class separation of the trace polar species present in diesel using hydrophilic interaction chromatography and high resolution mass spectrometry. *Energy Fuels* 2018;32:8944–54.
- [29] Armstrong DW, He L, Liu Y-S. Examination of ionic liquids and their interaction with molecules, when used as stationary phases in gas chromatography. *Anal Chem* 1999;71:3873–6.
- [30] Kanyathare B, Peiponen KE. Hand-held refractometer-based measurement and excess permittivity analysis method for detection of diesel oils adulterated by kerosene in field conditions. *Sensors (Basel)* 2018;18.
- [31] Rawat V, Nadkarni V, Kale SN. High sensitive electrical metamaterial sensor for fuel adulteration detection. *Defence Science Journal* 2016;66.
- [32] Bakır M, Karaaslan M, Unal E, Karadag F, Alkurt FÖ, Altıntaş O, et al. Microfluidic and fuel adulteration sensing by using chiral metamaterial sensor. *J Electrochem Soc* 2018;165:B475–83.
- [33] Mishra V, Tiwari V, Patel PN. Nanoporous silicon microcavity based fuel adulteration sensor. *Silicon* 2015;8:409–15.
- [34] Kanyathare B, Peiponen KE. Wavelength-dependent excess permittivity as indicator of kerosene in diesel oil. *Appl Opt* 2018;57:2997–3002.
- [35] Kanyathare B, Kuivalainen K, Rätty J, Silfsten P, Bawuah P, Peiponen K-E. A prototype of an optical sensor for the identification of diesel oil adulterated by kerosene. *J Eur Opt Soc-Rapid Publ* 2018;14.
- [36] Yadav GC, Prakash S, Sharma G, Kumar S, Singh V. Detection of kerosene adulteration in automobile fuel with a novel metal clad planar waveguide. *Opt Laser Technol* 2019;119.
- [37] Mishra V, Jain SC, Singh N, Poddar G, Kapur P. Fuel adulteration detection using long period fiber grating sensor technology; 2008.
- [38] Gotor R, Tiebe C, Schlischka J, Bell J, Rurack K. Detection of adulterated diesel using fluorescent test strips and smartphone readout. *Energy Fuels* 2017;31: 11594–600.
- [39] Leghrib R, Ouacha E, Zouida A, Faiz B, Amghar A. Monitoring automobile fuel adulteration using ultrasound technique for environmental issues. *Measurement* 2020;150.
- [40] Speller NC, Siraj N, Vaughan S, Speller LN, Warner IM. QCM virtual multisensor array for fuel discrimination and detection of gasoline adulteration. *Fuel* 2017;199: 38–46.
- [41] Wiziack NKL, Paterno LG, Fonseca FJ, Mattoso LHC, Gouma P. A Combined Gas and Liquid Chemical Sensor Array for Fuel Adulteration Detection 2011:178–9.
- [42] Lee J, Balakrishnan S, Cho J, Jeon S-H, Kim J-M. Detection of adulterated gasoline using colorimetric organic microfibers. *J Mater Chem* 2011;21.