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Novel reduced pressure-balance syringe for chromatographic analysis☆

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ABSTRACT

When withdrawing a fluid sample (for additional chromatographic analyses) from an apparatus operated at a reduced pressure, a typical syringe proves to be ineffective (even if it is equipped with a gas tight plunger). It simply does not create enough pressure differential to remove a fluid sample from a reduced pressure environment. We encountered such a situation as part of efforts to extend the operation of the advanced distillation curve protocol to reduced pressures. The problem was solved by the development of a pressure balance syringe that allows reliable and precise sampling from an apparatus operating at sub-ambient pressures. This new device uses an external vacuum source to evacuate a syringe barrel, allowing a user to withdraw fluid samples from environments with pressures as low as 0.5 kPa. To demonstrate the operation of the newly developed device, distillate analyses were performed on two fluids at low pressure: a predefined validation mixture, and a commercial soy based biodiesel fuel. The pressure balance syringe was used successfully for sampling in both cases. The use of the pressure balance syringe is not limited to reduced pressure distillations; indeed it can be used for a variety of applications in which chemical/compositional analyses are desired on a fluid contained in a reduced pressure environment.

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1. Introduction

In many applications, it is necessary for the researcher to withdraw small amounts of sample from an experimental or process apparatus (in the laboratory, or in the plant either on-line or at-line) for analytical testing, including chromatographic analysis [1]. This differs considerably from the more common laboratory circumstance of sample aliquot withdrawal from a vial. Often, the apparatus imposes serious constraints on how the withdrawal can be done [2]. At atmospheric pressure, a gas tight microsyringe is often the most effective method for extracting (precisely and with low uncertainty) small amounts of sample in preparation for chromatographic analysis [3]. Extracting fluid from an apparatus operating at reduced pressures (for example, between 0.5 and 2.5 kPa) with a typical gas tight plunger microsyringe is ineffective, however. A withdrawn plunger will not provide a large enough pressure differential to pull fluid from a low pressure environment into the barrel of the syringe. As part of a larger effort to modify the advanced distillation curve (ADC) method [4–7] to provide for reduced pressure volatility measurements [8], a device was developed to withdraw small amounts of fluid from a chamber operating at reduced pressures.

Details of the ADC method have been described elsewhere, therefore only a brief description of it will be presented here. The ADC is an improved method and apparatus for distillation curve measurement that is especially applicable to the characterization of complex fluids such as fuels [4–7,9–13]. It is a significant improvement over current approaches such as ASTM D-86 [14]. The ADC provides temperature, volume and pressure measurements of low uncertainty, and the temperatures obtained are true thermodynamic state points that can be modeled with an equation of state [15–17]. Such thermodynamic model development is simply impossible with the classical approach to distillation curve measurement, or with any of the other techniques that are used to assess fuel volatility or vapor liquid equilibrium. In addition, the ADC incorporates a composition explicit data channel for each distillate fraction (for qualitative, quantitative, and trace analysis). Sampling very small distillate volumes (5–25 μl) yields a composition-explicit data channel with nearly instantaneous composition measurements. Thus, the critical composition information accompanies the temperature data grid. Chemical analysis of the distillate fractions allows for determination of how the composition of the fluid varies with volume fraction and distillation temperature, even for complex fluids. These data can be used to approximate vapor liquid equilibrium (volatility) of complex mixtures, and present a more complete picture of the fluid under study. The ADC approach provides consistency with a century of historical data, an assessment of the energy content of each distillate fraction, and where needed, a corrosivity assessment of each distillate fraction [18–20]. Suitable analytical techniques

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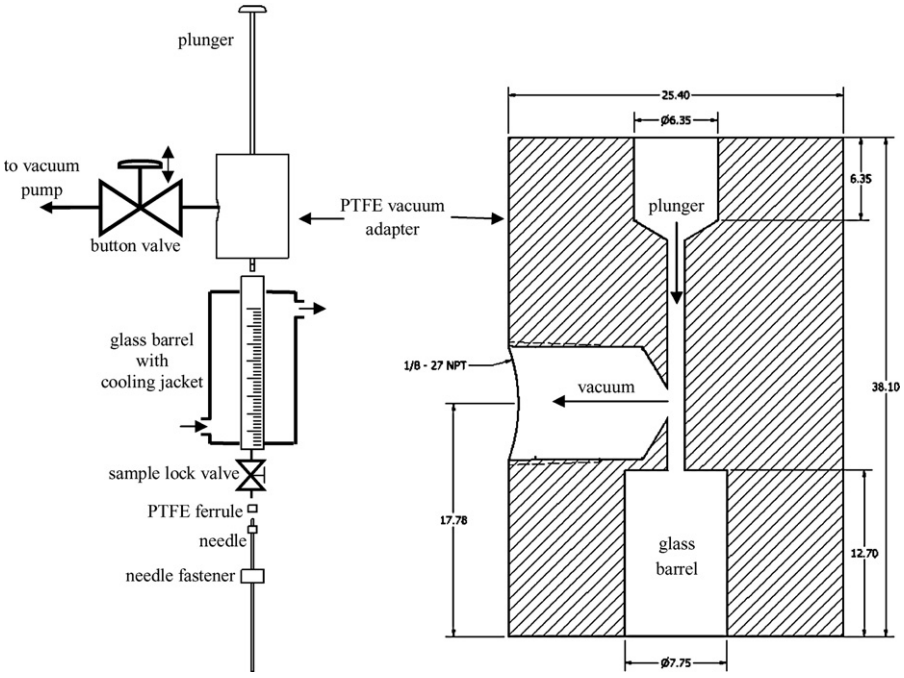

Fig. 1. Diagram illustrating the components of the new reduced pressure syringe. Also included is a detailed cross-section of the PTFE vacuum adapter. The dimensions given in the figure are provided in millimeters, and are considered to be typical.

include gas chromatography with either flame ionization detection (GC–FID), electron capture detection (GC–ECD) or mass spectral detection (GC–MS), element specific detection (such as GC with sulfur or nitrogen chemiluminescence detection, GC–SCD or GC–NCD), Fourier transform infrared spectrophotometry (FTIR), refractometry, and Karl-Fisher coulombic titrimetry [21,22].

Typically, when measuring the composition of distillate fractions using the ADC protocol, one withdraws between 5 and 20 μl of fluid at a special sampling adapter, just as the fluid emerges from the condenser. This volume is enough fluid for analysis, but not so much as to disrupt the volume measurements needed to construct a precise distillation curve. Sample withdrawal during an ADC measurement is typically done with a standard chromatographic syringe when operating at atmospheric pressure. Unfortunately, a standard syringe proved ineffective when operating the ADC at reduced pressures.

2. Method

2.1. Reduced pressure balance syringe design

The new reduced pressure-balance syringe uses an external vacuum source to evacuate the syringe barrel, creating the required pressure differential needed to withdraw the sample from an environment that is itself at reduced pressure. The device is a modified commercial 100 μl gas tight syringe that incorporates an adapter to allow for introduction and precise metering of the vacuum with a button valve. The apparatus, as well as a detailed cross-section of the adapter, is shown schematically in Fig. 1.

The commercial 100 μl gas tight syringe consists of a glass barrel with volumetric markings, a sample lock valve, and a replaceable needle sealed with a PTFE ferrule. Having a replaceable needle allows the user to select the appropriate needle size and tip, depending on the volatility and viscosity of the sample being withdrawn. The sample lock valve is important because it prevents liquid from being pulled back into the reduced pressure environment (i.e., the apparatus from which the sample has been withdrawn) once vacuum is shut off from the syringe adapter. The plunger consists of a metal rod with a PTFE tip, creating a snug fit in the glass barrel, allowing the liquid sample within the barrel to be easily ejected. It should be noted that the measured volumetric repeatability of the commercial syringe was within 1%, therefore, we expect the repeatability of the reduced pressure syringe to follow similarly.

The adapter, which provides a sealed bond between the vacuum connection and the syringe, was machined from 25 mm diameter PTFE rod. As illustrated in the cross-section drawing of Fig. 1, there is a hole in the bottom of the adapter for insertion of the glass barrel of the microsyringe. Above this hole, there is a narrow passage (aligned with the passage in the syringe barrel) through which the plunger passes. This passage provides a path for the plunger to expel the fluid that is pulled into the syringe barrel. An access port (threaded with 1/8-27 NPT, to allow connection of a toggle/button valve) supplies the vacuum to the syringe. The toggle valve allows the user to easily control the application of vacuum. To ensure a vacuum tight apparatus, all the holes were sized to provide an interference fit with the inserted parts.

We note that depending on the level of vacuum supplied to the syringe and the volatility of the sample being withdrawn, it is possible for the extracted sample to vaporize once inside the syringe barrel and be pulled into the vacuum pump. To alleviate this problem, an air jacket was fitted around the syringe barrel so that cold air from a vortex tube would chill the syringe below the boiling point of the compounds being withdrawn. This jacket is typically glass, to allow the syringe markings to be easily read. For clarity, the details of the air jacket are not shown in Fig. 1, but have been published elsewhere [23,24].

Prior to use, the jacketed syringe should be cooled with the vortex tube and cleaned by flushing it with solvent using the plunger. Alternatively, one can remove the plunger and use a commercial syringe cleaner operating under suction. With the sample lock valve closed, the user inserts the needle into the reduced pressure apparatus through a septum or other closure. This serves to prevent rapid increase in pressure of the apparatus. Once the needle tip is submerged in the fluid that is to be sampled, the user activates the vacuum button valve to evacuate the glass barrel, thus reducing the

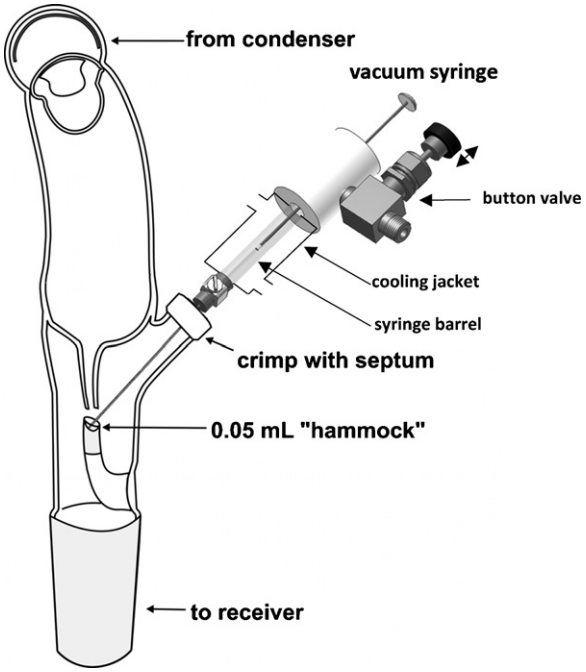

Fig. 2. Image illustrating the withdrawal of samples from the reduced pressure ADC apparatus. The method of operation is discussed in the text.

pressure in the barrel below the pressure extant in the apparatus. The sample lock is then opened, resulting in fluid traveling up the syringe barrel. Prior to removing the syringe from the apparatus, the user shuts off the vacuum to the syringe, and closes the sample lock. Once the syringe is removed, the sample can be easily expelled into a vial for subsequent analysis.

2.2. Demonstration of operation

To demonstrate the vacuum syringe's operation, analytical samples were withdrawn from the reduced pressure ADC apparatus and analyzed using GC–MS. The detailed operation of the ADC at reduced pressure is addressed elsewhere; only a brief description will be provided here [8]. This paper is concerned only with the low pressure sampling aspects; the reader is referred to our prior work for details about the ADC [4–7,21,22,25–28].

The required volume of fluid for the distillation curve measurement (200 ml) was placed into a boiling flask. Following sample degassing with vacuum, the pressure in the ADC apparatus was set with a pressure controller. After the pressure was stabilized, the flask was slowly heated with a model predictive temperature controller [27]. As heating continued, vaporization of the fluid occurred, and the volume of the distilled liquid was measured in a level stabilized receiver. The temperatures were recorded at selected volume fractions to construct the distillation curve (that is, the temperature data grid). Sample withdrawal (for chromatographic analyses) was done in the sampling adapter (following the condenser, but before the fluid dropped into the receiver) [8,25]. As seen in Fig. 2, the syringe needle was inserted through a septum into the apparatus. The needle tip was placed (to rest) in a calibrated volume hammock into which the condensed distillate fell. At selected volume fractions, the fluid in the hammock was pulled into the reduced pressure balance syringe, as discussed above. The vacuum source used for the syringe was the same vacuum pump used to evacuate the distillation apparatus, resulting in a pressure of ~0.01 kPa supplied to the syringe. Although the same pump was used for the syringe and distillation apparatus, the pressure in the syringe was always lower. We note that the uncertainty in this pressure is not an issue, provided the value remains below that extant in the apparatus being sampled. This was approximately two orders of magnitude lower than that maintained in the distillation apparatus by the pressure controller. Distillate samples (approximately 10 μl in volume) were pulled into the syringe and expelled into a septum capped vial containing a known mass of solvent. Upon reweighing the vial with the added sample, the vial was available for any applicable type of analysis, including GC–MS as illustrated below.

Table 1
A listing by retention time (t_R) of the components of the validation mixture identified by GC–MS. Also included are the actual mass fractions for each component.

Component	Mass fraction (%)	Retention time (min)
Toluene	16.1	2.9
m-Xylene	18.3	4.4
1,2,4-Trimethyl benzene	10.2	6.6
n-Dodecane	13.8	9.7
n-Tetradecane	14.3	12.2
n-Hexadecane	16.7	14.4
n-Octadecane	8.1	16.5
Squalane	2.5	–

Two different fluids were used to demonstrate the operation of the pressure balance syringe. One was a well characterized validation mixture created by combining various hydrocarbon compounds together; the other was a commercial soy based biodiesel fuel (B-100). The chemical makeup of the validation mixture is provided in Table 1. The biodiesel fuel sample was subjected to chemical analysis before the measurement of the distillation curve (GC–MS, scanning mode, 30 m × 0.25 mm capillary column with a 0.1 mm coating of the stationary phase, 50% cyanopropyl–50% dimethyl polysiloxane) [10,29–31]. The resulting chromatogram of the neat B100 sample is illustrated in Fig. 3, with the assignment of major components having an area percent in excess of 2% presented in Table 2.

The reduced pressure distillation of the validation mixture was performed at 2 kPa and that of the B100 was performed at 1 kPa. The uncertainty in the pressure maintained by the pressure controller was 0.02 kPa. The temperature data grids (temperature plotted against distillate volume fraction) were measured for both fluid samples. Using the vacuum syringe, ~10 μl samples of distillate were withdrawn for selected fractions as the fluid emerged from the condenser. These aliquots were added to vials containing a known mass of acetone, as described earlier. The resulting vials were then analyzed by GC–MS in scanning mode. A typical

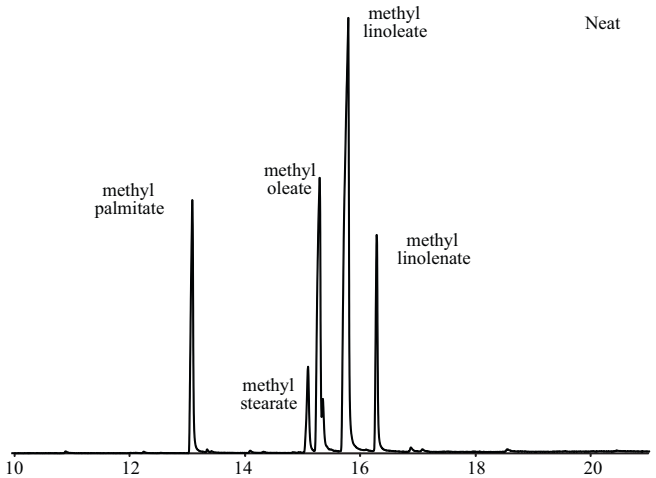

Fig. 3. Chromatogram of the neat biodiesel fuel sample. The *y*-axis is arbitrary units of intensity and the *x*-axis is time in minutes.

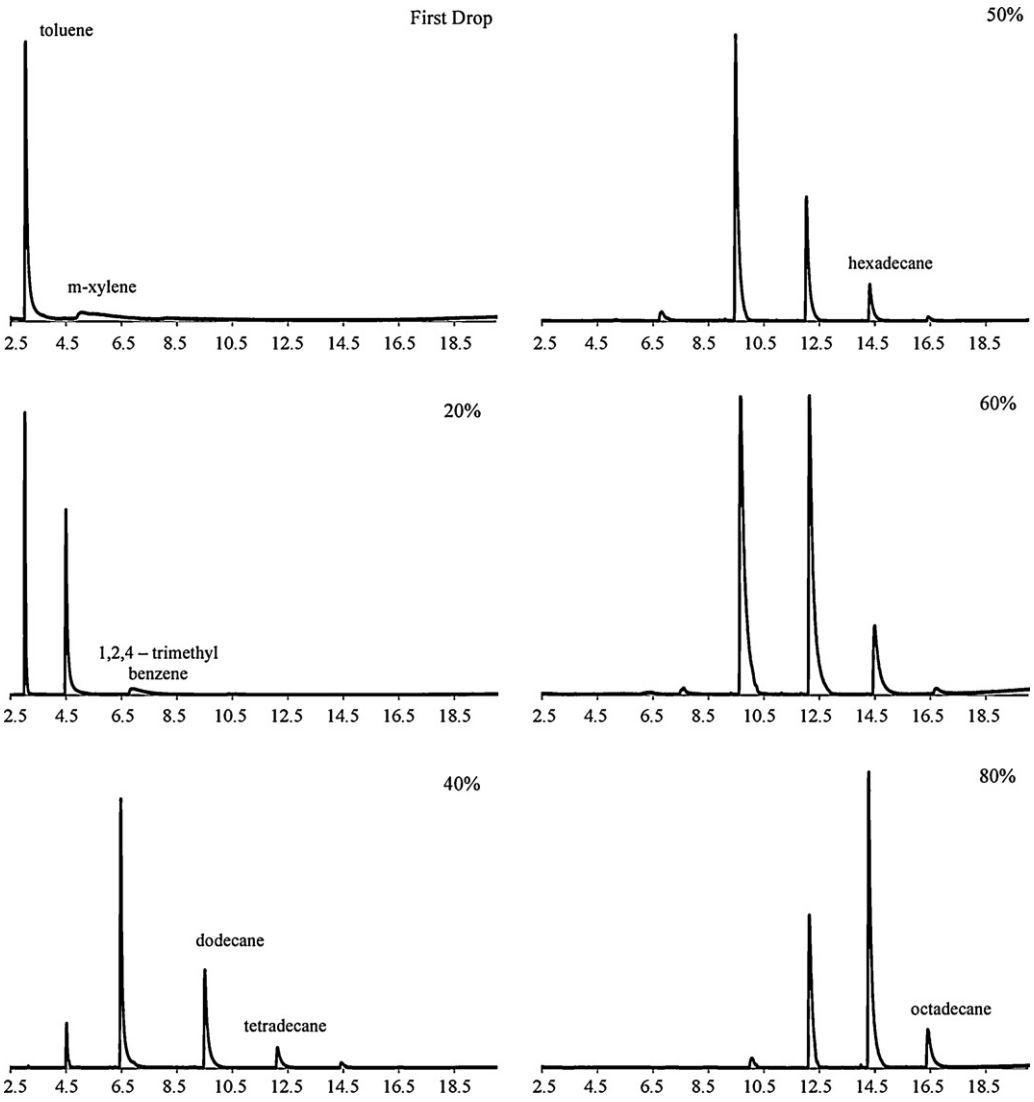

Fig. 4. Representative chromatograms of six distillate volume fractions of the validation test mixture. The component peaks are labeled in the first fraction that they were observed in. The *y*-axes are arbitrary units of intensity and the *x*-axes are time in min. The details of the chromatography are discussed in the text.

hydrocarbon analysis protocol was chosen for the validation mixture (30 m × 0.32 mm capillary column of 5% phenyl–95% dimethyl polysiloxane having a thickness of 0.25 μm, 75/1 injection split, injector at 300 °C, constant head pressure of 69 kPa (10 psig), column at 50 °C for 2 minutes followed by 12 °C per minute to 250 °C, three minute soak at 250 °C). The biodiesel fuel samples were analyzed with the same program and conditions used to analyze the neat sample (discussed above).

Table 2
A listing by retention time (t_R) of the components of the biodiesel fuel identified by GC–MS, having chromatographic peak area counts in excess of 2%. The area percents are uncalibrated and are intended only as a rough guide to the relative composition of the sample.

Component	Area %	Retention time (min)
Methyl palmitate	15.0	13.08
Methyl stearate	5.4	15.09
Methyl oleate	20.6	15.29
Methyl vaccenate	2.7	15.35
Methyl linoleate	45.5	15.79
Methyl linolenate	10.7	16.29

3. Results and discussion

Representative chromatograms for each fraction of both samples are shown in Figs. 4 and 5, respectively. The retention time (t_R) axis is in minutes for each chromatogram, and the abundance axis is presented in arbitrary units of area counts (voltage slices). The solvent (acetone) did not interfere with the sample and was removed digitally. Both Figs. 4 and 5 show that the lightest components decrease in concentration (peak area) as the distillation proceeds. In the validation mixture, the first drop of condensate is almost completely composed of toluene. By the 40% distillate volume fraction, toluene is completely removed. The ability to withdraw a sample rich in toluene demonstrates the utility of the pressure balance syringe to easily remove volatile components, even at reduced pressure. As the distillation progresses, the heavier components, n-hexadecane and n-octadecane, begin to emerge at higher concentrations. The small amount of squalane in the mixture could not be observed with our method due to its very high boiling temperature.

The syringe was able to easily withdraw distillate samples of the biodiesel fuel from the ADC apparatus operated at a pressure of 1 kPa. As seen in the chromatogram of the first drop, this fraction sample contains components spanning a wide range of volatilities

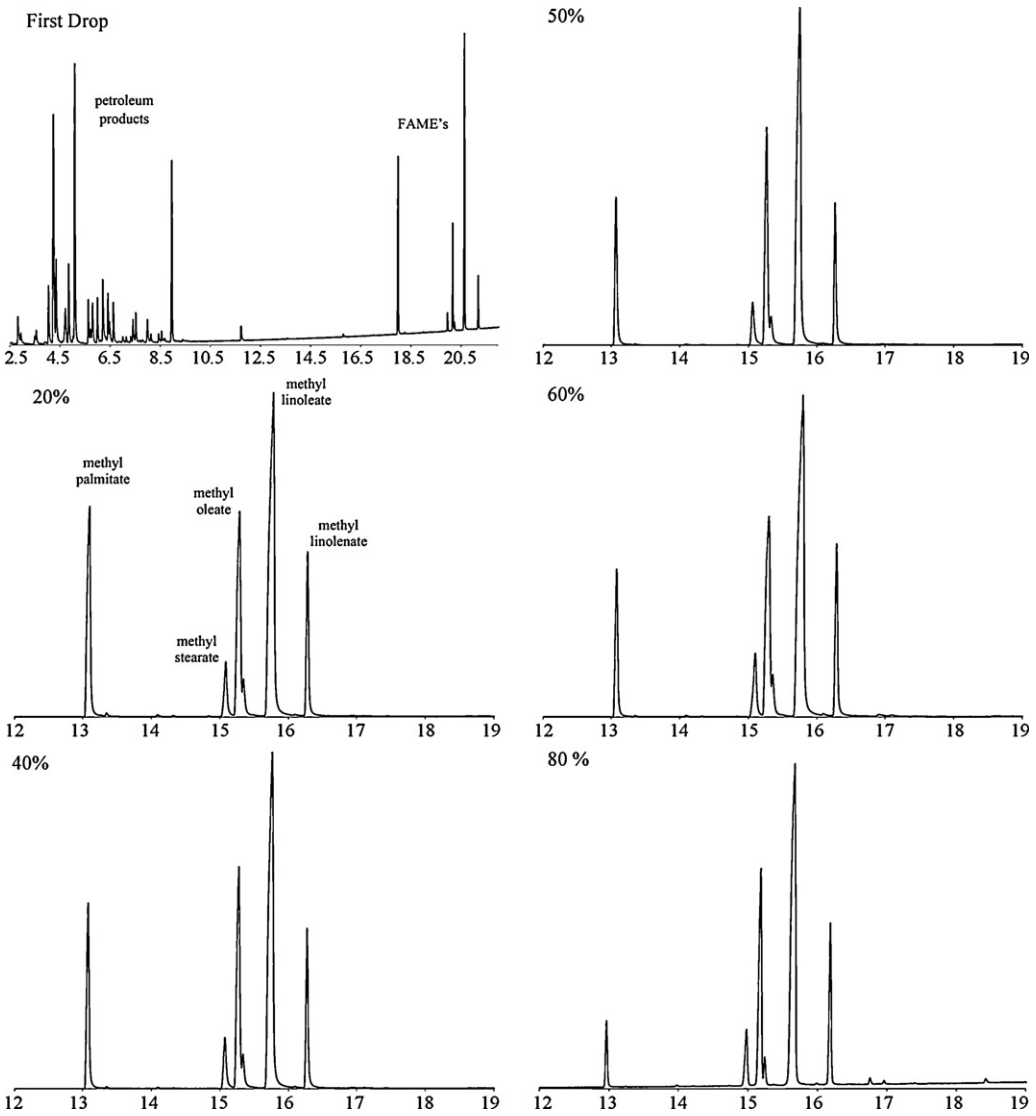

Fig. 5. Representative chromatograms of six distillate volume fractions of the biodiesel fuel. The component peaks are labeled in the first fraction that they were observed in. The *y*-axes are arbitrary units of intensity and the *x*-axes are time in min. The details of the chromatography are discussed in the text.

(from the petroleum contaminate to the individual FAME's). After the first drop, the evolution of the biodiesel fuel composition is not as striking as the validation mixture, due to the very similar boiling temperatures of the FAME's that are present. This is also indicated by the distillation curve, which spans only a change in temperature from beginning to end of ~6 °C [8]. This modest change in temperature mirrors the result of our atmospheric pressure distillation measurement [10,29,32]. Despite this, the concentration of methyl palmitate clearly decreases as the distillation progresses. These results demonstrate the ability of the pressure balance syringe to withdraw a viscous fluid from a chamber at pressures as low as 1 kPa.

4. Conclusion

A novel pressure balance syringe with the ability to extract small amounts of sample from an environment operating at reduced pressures has been developed. The design uses an external vacuum source to create a sufficient pressure differential to withdraw fluid samples from an apparatus operating at pressures as low as 0.5 kPa. The motivation of this work was to design a device to extract precise volumes (~5–20 μl) of distillate fractions during a reduced pressure distillation for further compositional analysis. The operation of the syringe was demonstrated by low pressure distillations of two different fluids. They included a validation mixture (at 2 kPa), and a biodiesel fuel (at 1 kPa) from which ~10 μl of distillate faction samples were extracted and analyzed using GC–MS. This work will lead to more complete reduced pressure VLE measurements using the reduced pressure ADC method, allowing for the analysis of low volatility fluids that show high boiling temperature at atmospheric pressure. The new device is not limited to reduced pressure distillations and may be useful for a variety of applications in which further chemical/compositional analyses are desired on a fluid contained in a reduced pressure environment.

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