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Partial least squares analysis of rocket propulsion fuel data using diaphragm valve-based comprehensive two-dimensional gas chromatography coupled with flame ionization detection

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ABSTRACT

The chemical composition and several physical properties of RP-1 fuels were studied using comprehensive two-dimensional (2D) gas chromatography (GC × GC) coupled with flame ionization detection (FID). A "reversed column" GC × GC configuration was implemented with a RTX-wax column on the first dimension (^{1}D), and a RTX-1 as the second dimension (^{2}D). Modulation was achieved using a high temperature diaphragm valve mounted directly in the oven. Using leave-one-out cross-validation (LOOCV), the summed GC × GC–FID signal of three compound-class selective 2D regions (alkanes, cycloalkanes, and aromatics) was regressed against previously measured ASTM derived values for these compound classes, yielding root mean square errors of cross validation (RMSECV) of 0.855, 0.734, and 0.530 mass%, respectively. For comparison, using partial least squares (PLS) analysis with LOOCV, the GC × GC–FID signal of the entire 2D separations was regressed against the same ASTM values, yielding a linear trend for the three compound classes (alkanes, cycloalkanes, and aromatics), yielding RMSECV values of 1.52, 2.76, and 0.945 mass%, respectively. Additionally, a more detailed PLS analysis was undertaken of the compounds classes (*n*-alkanes, *iso*-alkanes, mono-, di-, and tri-cycloalkanes, and aromatics), and of physical properties previously determined by ASTM methods (such as net heat of combustion, hydrogen content, density, kinematic viscosity, sustained boiling temperature and vapor rise temperature). Results from these PLS studies using the relatively simple to use and inexpensive GC × GC–FID instrumental platform are compared to previously reported results using the GC × GC–TOFMS instrumental platform.

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1. Introduction

Although aerospace fuel commodities are produced to meet numerous specification requirements, even advanced kerosene-based fuels such as rocket propellant (RP-1) may possess wide variation in chemical composition, which may result in unacceptable or unexpected performance and fuel properties [1–4]. Variation may be due to original crude oil/feed stock composition and refinery operating conditions. Additionally, RP-1 chemical composition can vary depending upon post-refinery formulation. Investigation of RP-1 fuel properties and their relationship to their chemical composition must be performed in order to develop optimum fuels for specific applications [5–11]. Although there are current methods to analyze RP-1 and related fuels [3,6,7,11], more

informative, yet simpler and cost effective chemical analysis methods should be developed and investigated for routine application.

Gas chromatography (GC) coupled with flame ionization detection (GC–FID) is a traditional analytical platform to separate and analyze volatile and semi-volatile mixtures [12]. However, complex mixtures such as RP-1 fuels generally cannot be sufficiently separated with a single dimension of GC in order to provide the desired analytical insight. Comprehensive two-dimensional (2D) gas chromatography with flame ionization detection (GC × GC–FID) can improve upon the separation power of one dimensional GC and yield quantitative information [13–15]. With GC × GC, two "orthogonal" separation dimensions are implemented to increase peak capacity which substantially improves the information that may be gleaned from complex samples. Typically, the first GC × GC separation dimension (^{1}D) uses a column with a non-polar stationary phase, while the second dimension (^{2}D) uses a column with a polar stationary phase, providing complementary information. However, a "reversed column" GC × GC configuration

has been found to be more appropriate to provide optimized use of the 2D separation space to effectively separate the various compound classes in RP-1 and related fuels (*n*-alkanes, branched alkanes, mono- di- and tricyclic alkanes, and aromatics) [16,17]. The reversed column configuration uses a polar [1]D column followed by a non-polar [2]D column [18].

The modulator is the heart of the GC × GC instrument, interfacing the [1]D column to the [2]D column to accomplish a comprehensive two-dimensional separation. Here, we categorize three modulator designs: cryogenic-based "thermal" modulation [19–23], flow modulation [24–26], and diaphragm valve modulation [14,27,28]. While thermal modulation is popular, it can be expensive to implement and is generally not amenable to reduce to a simple platform because of the complexity involved with the cryogenic fluids. Flow modulation is becoming more popular with GC × GC, however, the injected pulse width onto the [2]D column is intrinsically quite large, resulting in a significant source of peak broadening and a relatively low [2]D peak capacity [29,30]. In comparison, diaphragm valve modulation is relatively simple and inexpensive to implement, while also providing a narrow injected pulse width onto the [2]D column with superior peak capacity even when a short modulation period is used (e.g., 1–2 s) [14,27,28,31–33]. The primary shortcoming of the diaphragm valve in the past has been the limited temperature range due to the O-rings within the valve, limiting the usage to a maximum of 175 °C if placed directly in the GC oven. This shortcoming was overcome to a reasonable extent by face mounting the valve on the top of the GC case to preserve the temperature sensitive O-rings within the valve, with a maximum temperature of 265 °C [28]. Recently, a state-of-the-art "high temperature" diaphragm valve with perfluoroelastomer O-rings has been developed that is capable of being placed directly in the GC oven; it can withstand temperatures up to 325 °C [34]. Recently, we reported the implementation and evaluation of this high temperature diaphragm valve with GC × GC–FID [35]. This high temperature diaphragm valve-based GC × GC–FID is implemented in this current study.

GC × GC–FID is well suited technique for when identification and quantification of every chemical compound is generally not possible and/or is an extremely laborious and impractical process for complex samples such as RP-1 fuels. Chromatographic-based ASTM methods often are rooted in this type of strategy. In this regard, it is advantageous to implement chemometric analysis of complex samples, specifically herein to discover important chemical/physical relationships between compositionally unique RP-1 fuels [16,17,36]. Partial least squares (PLS) analysis is well suited to quantitatively relate the GC × GC–FID data of complex samples, such as RP-1 fuels, with other forms of chemical/physical measurements.

PLS analysis provides the following two valuable outcomes. First, using a training set of samples, a linear correspondence of the chemical/physical properties can be modeled using the GC × GC–FID data, so subsequent analyses of GC × GC–FID data of new samples can be used to predict the modeled chemical/physical property without having to directly measure these properties on the new samples. Second, the underlying relationship between the chemical composition of the samples can be correlated to the modeled chemical/physical measurements, so a deeper understanding between chemical composition via the GC × GC–FID data and the chemical/physical measurements is provided [37–40]. To achieve both of these outcomes, leave-one-out cross validation is often performed (LOOCV) [16,17,37].

In this study, we seek to demonstrate the simple, yet highly capable GC × GC–FID instrumental platform, combined with PLS, to provide valuable information about the chemical composition of RP-1 fuels. Due to the potential for significant variation in chemical composition of RP-1 fuels as a result of variations that may

result during the distillation and blending processes, it is often beneficial to evaluate special laboratory blends where the analyst can control the make-up of the fuel [5–9]. Therefore, we study a set of fuels that have been well studied before, so as to provide validation of the instrument performance. Furthermore, we present implementation of a state-of-the-art high temperature diaphragm valve [34,35] as the modulator, with the valve mounted directly in the oven. To the best of our knowledge, this is the first application study using the high temperature diaphragm valve. With GC × GC–FID, we hope to obtain similar quantitative information as previously obtained while using GC × GC–TOFMS [16]. While GC × GC–TOFMS can yield substantially more qualitative information especially with the ability to identify analytes, instrumental cost is too high for routine implementation in many laboratory settings. Furthermore, GC × GC–TOFMS requires a large amount of upkeep, such as the systems associated with maintaining the vacuum, to keep it operational. When identification of analytes is not necessary or has already been performed, a FID can provide ample information and requires less maintenance and lower operational costs.

The following studies were performed. First, the summed GC × GC–FID signal of three compound-class selective 2D regions (alkanes, cycloalkanes, and aromatics) was simply regressed against previously measured (ASTM standard test method) values for these compound classes, and LOOCV was used for regression validation. Next, for comparison, using PLS analysis with LOOCV, the GC × GC–FID signal of the entire 2D separations was regressed against the same ASTM values for the same three compound classes. Using PLS, retention times are preserved and it is possible to determine how specific compounds influence the model by looking at the linear regression vectors (LRVs). Finally, PLS analysis was used to provide a more detailed study of compound classes (*n*-alkanes, *iso*-alkanes, mono-,di-,and tri-cycloalkanes, and aromatics) and of physical properties previously determined by ASTM methods (such as net heat of combustion, hydrogen content, density, kinematic viscosity, sustained boiling temperature and vapor rise temperature). Results from these studies using GC × GC–FID instrumentation are compared to previously reported results using GC × GC–TOFMS [16].

2. Experimental

Ten previously studied RP-1 fuel samples (listed in Table 1) were obtained from the Air Force Research Laboratory (AFRL) [5,6]. HPLC Grade hexane and acetone were obtained from Fisher Scientific and were used as solvent rinses prior to injection. Chromatographic data was obtained using a GC × GC–FID consisting of an Agilent 6890 GC (Agilent Technologies, Palo Alto, CA, USA) modified in-house with a high-speed, six-port diaphragm valve

Table 1
RP-1 fuel set. The NIST and ARFL numbers are provided for reference to previous studies [5,6].

NIST number	AFRL designation
11	LB080409-01
10	LB073009-06
9	LB073009-08
8	LB080409-05
7	LB073009-05
5	LB073009-01
4	LB073009-09
1	LB073009-02
2	LB073009-03
3	XC2521HW10