



Correlation of rocket propulsion fuel properties with chemical composition using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry followed by partial least squares regression analysis

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ABSTRACT

There is an increased need to more fully assess and control the composition of kerosene-based rocket propulsion fuels such as RP-1. In particular, it is critical to make better quantitative connections among the following three attributes: fuel performance (thermal stability, sooting propensity, engine specific impulse, etc.), fuel properties (such as flash point, density, kinematic viscosity, net heat of combustion, and hydrogen content), and the chemical composition of a given fuel, i.e., amounts of specific chemical compounds and compound classes present in a fuel as a result of feedstock blending and/or processing. Recent efforts in predicting fuel chemical and physical behavior through modeling put greater emphasis on attaining detailed and accurate fuel properties and fuel composition information. Often, one-dimensional gas chromatography (GC) combined with mass spectrometry (MS) is employed to provide chemical composition information. Building on approaches that used GC–MS, but to glean substantially more chemical information from these complex fuels, we recently studied the use of comprehensive two dimensional (2D) gas chromatography combined with time-of-flight mass spectrometry (GC × GC–TOFMS) using a “reversed column” format: RTX-wax column for the first dimension, and a RTX-1 column for the second dimension. In this report, by applying chemometric data analysis, specifically partial least-squares (PLS) regression analysis, we are able to readily model (and correlate) the chemical compositional information provided by use of GC × GC–TOFMS to RP-1 fuel property information such as density, kinematic viscosity, net heat of combustion, and so on. Furthermore, we readily identified compounds that contribute significantly to measured differences in fuel properties based on results from the PLS models. We anticipate this new chemical analysis strategy will have broad implications for the development of high fidelity composition–property models, leading to an improved approach to fuel formulation and specification for advanced engine cycles.

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1. Introduction

The chemical composition of a kerosene fuel is complex, and changes in composition have been widely demonstrated to impact fuel properties and performance [1–4]. However, achieving precise control over the chemical composition of distillate fuels such as RP-1 (MIL-DTL-25576E) is challenging due to variations in crude oil

composition and place of origin, refinery and post-refinery operating conditions, or even the date and time the material was refined, treated, and formulated to meet the detail specification requirements. A better understanding of fuel composition and how it relates to fuel performance and properties is expedient for a number of reasons. Indeed, it has become increasingly important to gain a better understanding of fuel composition, and an assessment of the potential sources of fuel composition variation is paramount to maintain control of fuel performance [5–11]. It is also beneficial to relate new chemical analysis technologies to the benchmarking ASTM methods for characterizing properties and compositions of fuels such as RP-1. For such assessments, it is often beneficial

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Table 1

RP-1 fuel set, where the RP-1 sample number is used herein, while the NIST and AFRL numbers are provided for reference to previous studies of interest.

RP-1 sample	NIST number [6]	AFRL designation [5]
1	11	LB080409-01
2	10	LB073009-06
3	9	LB073009-08
4	8	LB080409-05
5	7	LB073009-05
6	5	LB073009-01
7	4	LB073009-09
8	1	LB073009-02
9	2	LB073009-03
10	3	XC2521HW10

to evaluate special laboratory blends (where the analyst has some control over the chemical composition, see Table 1) as well as to assess the performance of “field” fuels [5–9].

Gas chromatography coupled with mass spectrometry (GC–MS) is an established instrumental platform of the chemical analysis laboratory. GC–MS has proven itself as a powerful tool for the study of the chemical composition of complex samples including but not limited to fuels [5–10,12–14]. Nevertheless, GC–MS can be made substantially more powerful by adding another dimension of separation, that is, by performing comprehensive two-dimensional (2D) gas chromatography prior to time-of-flight mass spectrometry detection (GC × GC–TOFMS) [15–23]. GC × GC–TOFMS is well suited for the analysis of complex mixtures of volatile (and/or semi-volatile) compounds, such as are present in fuels [15–17,19–24]. With GC × GC–TOFMS, the 2D separation commonly involves the first separation dimension performed using a non-polar stationary phase column and a separation run time of 30–60 min [15,16,24] followed by a polar stationary phase column, providing a complementary separation relative to the first column, so chemical compounds not separated on the first dimension at a given retention time have the opportunity to be separated on the second dimension. However, for the current study of RP-1 fuels, which contain primarily *n*-alkanes, *iso*-alkanes, cyclic alkanes, and relatively fewer aromatics, it was deemed necessary to apply a “reversed column” GC × GC format in order to provide better selectivity [24], with the first dimension separation using a polar phase (RTX-wax) and the second dimension separation using a non-polar phase (RTX-1). GC × GC–TOFMS provides a considerable amount of data for a given complex sample (e.g., typically ~300–400 MB compressed per sample run). It has become clear there are also significant challenges to readily glean useful information from this significant amount of data, which is why powerful chemometric software methods are used for analysis [15–27].

Even though GC × GC–TOFMS is a powerful instrumental platform for fuels analysis, it is critical to develop and apply data analysis software to convert the immense data into readily interpretable and useful information. For this purpose, multivariate data analysis methods have been developed, broadly referred to as “chemometrics”. Chemometrics is ideally suited to reveal similarities and/or differences between sets of GC × GC–TOFMS data [15–17,20–22,27]. Specific to this study, the partial least-squares (PLS) regression analysis was used to associate differences in measurable information for each fuel sample, in this case chemical and physical property data, to chemical composition differences as provided by the signal intensity differences, from one compound peak to the next, in the GC × GC–TOFMS data. Details on PLS theory can be found elsewhere [28–31]. Briefly, PLS analyzes two data matrices (X-block and Y-block, respectively) and calculates loadings referred to by the number of latent variables (LVs). Using PLS, models are constructed to account for variance (ideally, the relevant chemical differences) in both the GC × GC–TOFMS data,

i.e., the signal intensities (which constitute the X-block) and the respective measured property values (which constitute the Y-block). Thus, PLS modeling ideally provides a one-to-one correspondence between the measured values (plotted on the *x*-axis as the benchmark method) relative to the predicted values (plotted on the *y*-axis using the GC × GC–TOFMS data in the PLS model).

In this study, we sought to demonstrate the potential of the GC × GC–TOFMS instrumental platform, combined with PLS analysis, to provide useful information in the chemical analysis of RP-1 samples. By doing so, our goals were to demonstrate the feasibility of being able to (1) build PLS models to relate chemical composition data obtained from the GC × GC–TOFMS to measured fuel performance quantities (e.g., density, kinematic viscosity, net heat of combustion, and so on), and then to (2) assess the quality of those models for subsequent prediction of fuel chemical and physical characteristics without making direct measurements. Eventually, this chemical analysis approach will provide insight into addressing (3) the overall goal of optimizing fuel composition to meet desired fuel property and performance characteristics. To begin to address these goals by use of GC × GC–TOFMS with PLS analysis, a key focus is to be able to elucidate chemical compounds or compound classes responsible for observed differences between fuels (e.g., type, feedstock) or differences in their measured physical properties. Specifically we report the use of GC × GC–TOFMS with PLS to model and predict measured fuel properties (density, kinematic viscosity, net heat of combustion) [6].

2. Experimental

Several RP-1 fuel samples were obtained from the Air Force Research Laboratory (AFRL), and have been studied in prior reports [5,6], as listed in Table 1. All chromatographic data were obtained using the GC × GC–TOFMS consisting of an Agilent 6890N GC (Agilent Technologies, Palo Alto, CA, USA), a thermal modulator (4D upgrade, LECO, St. Joseph, MI, USA), and a Pegasus III TOFMS (LECO, St. Joseph, MI, USA). Aliquots of the RP-1 fuel samples were introduced to the GC × GC–TOFMS instrument via a 7683B auto-injector (Agilent Technologies, Palo Alto, CA, USA). The following experimental conditions were applied. The auto-injector was set to a 1 μl injection, using a 200:1 split injection with helium carrier gas. Acetone was used for the solvent rinse. Isobaric mode was used with an inlet pressure of 35 psig (241 kPa). The GC oven initial temperature was set to 40 °C for 2 min and ramped to 225 °C at a rate of 6 °C/min where the final temperature was maintained for 3 min. The GC inlet temperature was set to 225 °C and the transfer line temperature was set to 235 °C. The thermal modulator offset was 20 °C, with a hot pulse time of 0.59 s and a cool time of 0.35 s. The primary column (first separation dimension) for the GC × GC used a RTX-wax (polar) stationary phase: 30 m length, 250 μm i.d., and 0.5 μm film thickness. The modulation period was set to 2.5 s (i.e., the secondary column separation time). The secondary column (second separation dimension) used a RTX-1 (non-polar) stationary phase: 1.2 m length, 100 μm i.d., and 0.18 μm film thickness. The secondary column oven temperature control was not applied, so the secondary column oven was open and at the same nominal temperature as the primary column oven. The mass spectrometer electron energy was set to –70 eV and the detector voltage was set to 1600 V. The ion source temperature was set at 225 °C. The data acquisition parameters were set with a 120 s acquisition delay, mass-to-charge ratio (*m/z*) scan range of 35–334 amu at unit resolution, and acquisition rate set of 100 Hz.

There were replicate GC × GC–TOFMS chromatographic data collected for each RP-1 sample, and each set of replicates were analyzed separately using the PLS procedure (described below). Results for both replicates are provided herein, overlaid in figures,

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