Estimation of Select Specification Tests for Aviation Turbine Fuels Using Fast Gas Chromatography (GC)

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The quality of aviation turbine fuels is measured largely by specification tests, which are routinely conducted for every large fuel supply purchased by the United States Air Force. Because military operations insist on more mobility than ever before, fuels are often purchased locally where the military is located. To test the fuels being purchased from unfamiliar sources, the military is examining mobile laboratories. With modern instrumentation such as gas chromatography (GC) with microbore columns and multiple detectors, compositional data can be easily and quickly obtained and related directly to specification test properties. By investigating composition−property relationships, a single GC experiment can be used to estimate several properties. In this work, the development and validation of specification test prediction using compositional data obtained via fast (<5 min) GC is presented. Simple correlations and relationships between properties and composition are suggested as possible ways to predict specification results without the expense and time required for testing. In this initial work, the properties investigated were simulated distillation, flash point, freeze point, and sulfur content. Results indicated that these tests could be reasonably predicted in minutes using correlations to fast GC data. Instrumentation developed for predicting specification tests was delivered to a field location and used to predict the specification results of locally purchased and captured fuels in wartime. These same fuels were also analyzed in regional laboratories, for validation of results.

Introduction

Aviation fuels have been an important component of the success of the gas turbine engine, which was first introduced by Han von Ohain in 1939. While early proponents of the gas turbine engine claimed to be able to fly these craft on any fuel ranging from peanut butter to whiskey,[1] there has always been a need to carefully control the quality of the fuel being used in gas turbine engines. Although the gas turbine engine may have, at one time, been more tolerant of fuel impurities than gasoline or diesel reciprocating engines, today's advanced turbine engines are not nearly as tolerant. Impurities in fuel can disable advanced turbine engines, interfere with the cooling of avionics and weapons systems, and disturb the control and gauging systems on board. Obviously, in-flight failures caused by aircraft fuel are more serious and potentially life-threatening than gasoline or diesel fuel failures on ground vehicles. Thus, fuel quality in an aircraft system is critical and is largely controlled by the fuel specification system.

Military and civilian fuel specifications are controlled under standards MIL-DTL-83133E (for military fuels) and ASTM D1655-01 (for commercial aviation).[2] These two specifications detail properties for JP-8, which is military aviation fuel, and Jet A, which is the primary commercial aviation fuel. The current specification properties for JP-8 and Jet A are listed in Table 1.[3] Although the military normally uses JP-8 jet fuel, the expeditionary (mobile) nature of today's Air Force, and the military in general, make it necessary to purchase local fuel from nearby sources. The benefit of not having to transport fuel is then offset by the inability to carefully control the quality of fuel purchased. Although fuel samples of locally purchased fuel can be sent to regional laboratories for specification testing, there is a benefit to operate mobile laboratories to measure important specification properties.

The specification tests, while all important to fuel performance, are often conducted using tests methods that are 20−50 years old. Some of these tests do not take advantage of today's modern analytical laboratory and may also be difficult to perform in the field. Standard ASTM-D86, for example, is a test designed to obtain a fuel's boiling range and most typically uses large glassware and mantle heaters.[4] Standard ASTM D2386, which is the test for freezing point, requires that fuel be cooled to temperatures below −47 °C.[4] It also requires operators to watch a solution carefully to determine at which temperature the last solid crystal

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<div align="center">**Table 1. Military JP-8 and Commercial Jet A Specification Tests and Ranges**[a]</div>

property	Value		ASTM test method
	Jet A or Jet A-1	JP-8	
		Composition	
acidity, total	0.10 mg KOH/g (max)	0.015 mg KOH/g (max)	D 3242
aromatics	25 vol % (max)	25 vol % (max)	D 1319
olefins	-	5 vol % (max)	D 3227
sulfur, mercaptan	0.003 mass % (max)	0.001 mass % (max)	D 3227
sulfur, total	0.30 mass % (max)	0.3 mass % (max)	D 1266, D 1552, D 2622, D 4294, or D 5453
		Volatility	
distillation			D 86
volume percent recovered			
initial boiling point, IBP	205 °C, max	report	
10	205 °C, max	205 °C (max)	
20		report	
50	report	report	
90	report	report	
final boiling point, FBP	300 °C (max)	300 °C (max)	
distillation yields			
residue	1.5 vol % (max)	1.5 vol % (max)	
loss	1.5 vol % (max)	1.5 vol % (max)	
flash point	38 °C (min)	38 °C (min)	D 56 or D 3828
density at 15 °C	775−840 kg/m^3	775−840 kg/m^3	D 1298 or D 4052
vapor pressure at 38 °C (kPa (max))			D 323 or D 5191
		Fluidity	
freezing point	−40 °C (max) (Jet A), −47 °C (max) (Jet A-1)	−50 °C (max)	D 2386, D 4305, D 5501, or D 5972
viscosity at −20 °C	8.0 mm^2/s (max)	8.0 mm^2/s (max)	D 445
		Combustion	
net heat of combustion	42.8 MJ/kg (min)	42.8 MJ/kg (min)	D 4529, D 3338, or D 4809
one of the following requirements:			
1. luminometer number	45 (min)	-	D 1740
2. smoke point	25 mm (min)	25 mm (min)	D 1322
3. smoke point	18 mm (min)	19 mm (min)	D 1322
naphthalenes	3.0 vol % (max)	-	D 1840
		Corrosion	
copper strip, 2 h at 100 °C (max)	No. 1	No. 1b	D 130
		Stability	
thermal stability, 2.5 h at 260 °C:			
filter pressure drop	25 mmHg (max)	25 mmHg (max)	D 3241
tube deposit, less than	<Code 3	<Code 3	D 3241
		Contaminants	
existent gum	7 mg/100 mL (max)	7 mg/100 mL (max)	D 381
particulates	1 mg/L (max)	1 mg/L (max)	D2276
water reaction, interface rating (max)	1b	1b	D 1094
water separation index modified	70	70	D 1094

[a] Data taken from ref 3. See the current version of D 1655 for complete requirements.

disappears in the fuel as it is cooled, then heated. The flash point is a test in which samples must be heated to temperatures above 50 °C to measure fuel volatility. All of the tests can be well-conducted by technicians in laboratories under controlled conditions; however, because of excess power requirements, utilities, or bulky or breakable equipment, the tests are difficult to perform in a mobile laboratory. Although many of these tests have been miniaturized[5] and modernized[6] to some degree, they still entail conducting each performance test with a single piece of equipment.

In this contribution, we describe work that has been conducted to measure multiple specification properties for aviation fuel quickly with a single, rapid analytical measurement. This measurement will incorporate advanced laboratory instrumentation (gas chromatography (GC)), which can be more readily transported and used in mobile laboratories. The goal of this testing is to conduct one fast (less than 5 min) GC experiment and to obtain accurate specification test results for multiple specification test properties. The specification test properties investigated in this initial work were distillation range, freeze point, flash point, and sulfur content. Empirical relationships with many fuels were developed for these properties and then validated using additional measurements made from fuels not used in the correlation development. After conducting the correlations of composition (as measured by GC) and properties, this instrumentation was sent to a military location to predict specification test results for the U.S. military. These correlations and the field usage of this technique demonstrate the ability of fast GC to quickly and accurately measure specification test properties with less time and equipment.

Background

A. Specification Test Prediction. Jet fuels are comprised of thousands of individual compounds. Prop-

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(6) Product information (available at http://www.petrolab.com).

erties of fuels, as measured by specification tests, are likely be related to the concentrations of these compounds and any interactions these compounds might have with each other. Therefore, it seems reasonable that properties may be directly related to composition, although the relationships may be complex. Chemometric procedures are continuing to be a popular way to define the complex relationships between composition and properties. The thermal stability of jet fuels, which is an extremely complex property that may be related to the trace composition of chemical constituents, has been attempted using chemometrics.[7] Analysis of variance (ANOVA) techniques with GC $\times$ GC data (two-dimensional gas chromatography) have also been used to predict the fuel types (e.g., Jet A vs JP-7 vs JP-5) of unknown petroleum samples.[8]

In addition to GC data as the source for chemometric procedures, spectroscopy has been used for the prediction of fuel properties. Near-infrared (NIR) spectroscopy-based predictions of octane number, aromatic content, API gravity, and vapor pressure have been conducted for gasoline[9] and crude oil.[10] Jet fuels and kerosenes were examined using NIR spectroscopy for viscosity, density, flash point, and other properties.[11,12] Fourier transform infrared (FTIR) spectroscopy has also been used, along with chemometrics, to predict the Reid vapor pressure in commercial gasoline.[13] Nuclear magnetic resonance (NMR) spectroscopy has been used to predict aromatic content, octane number, and other properties, based on the proton NMR spectra.[14] In all of these cases, advanced laboratory instrumentation was used to predict property tests (density, viscosity, flash point, vapor pressure, etc.), in part, because of the potential to conduct multiple property measurements with one laboratory analysis. In addition, some of these analytical procedures may have been automated or may have been capable of on-line measurement, making the techniques of interest to fuel manufacturers and suppliers.

While chemometrics may indeed hold the ultimate answer to the prediction of these relationships, a simpler approach is described in this contribution. Because GC in nonpolar columns represents, in essence, a distillation, the use of simple GC retention would seem appropriate for flash point and distillation range. Indeed, in the case of simulated distillation, routines are available that predict single-plate distillation from GC data for mixtures from crude oils to finished gasolines.[15] The flash point is directly related to the relative amount of low boiling (volatile) components available in a product. Thus, it would seem straightforward to use simpler relationships of composition to predict proper-

ties without resorting to the development of more-complex chemometric procedures.

A great deal of understanding about the low-temperature properties of fuels already exists. Several authors have reported that the freezing point of aviation fuel mixtures is dependent upon n-alkane concentrations[16,17] and, specifically, the higher n-alkane concentrations in fuel. Thus higher n-C18 concentrations in fuel are more important than elevated C12 concentrations. This observation makes sense, with regard to the differences between diesel and jet fuel and the relative n-alkane concentrations in each. Thus, this work assumes the primary importance of these components and measures their concentration in a fast and reasonably accurate way to estimate the freeze point.

Gas chromatography is a versatile and convenient technique, in that general analysis can be conducted so that all components are measured. In addition, specific components can be measured if a detector exists that responds selectively to the property of interest. In the jet fuel specification, sulfur content is an important property, relating to emissions, catalyst poisoning, thermal stability, and general fuel quality. Sulfur detection by specification tests are conducted by techniques (such as X-ray fluorescence) which are appropriate for determining the differences between a specification "pass" and a "fail": that is, less than or greater than 0.3 wt % sulfur in fuel. Chromatographic detectors for sulfur are designed for low parts per million (ppm) determinations of individual sulfur levels; because the specification limit is 3000 ppm by weight, chromatographic detectors have more-than-adequate sensitivity to measure the sulfur content in fuel. The summation of a low resolution chromatographic determination of sulfur is directly related to total sulfur measurement.

In these four examples, (distillation range, flash point, freeze point, and sulfur content), we have selected properties that are directly related to and appropriate for GC measurement as an initial specification test prediction. Although other programs are being addressed to use these data with chemometric routines, it is clear that past experience about fuel properties and chromatography can reasonably predict some specification properties.

B. Fast Gas Chromatography. Fast GC analysis is useful for field determinations of jet fuel. Depending on the resolution required for a particular GC separation, analysis times can be greatly decreased using this technique rather than conventional GC. The need to analyze complex mixtures using GC is often a balance between the ability to separate adjacent peaks in a chromatogram (resolution) and analysis time. Especially in complex mixtures, analysts can use longer columns and much slower programming rates to increase resolution; however, there is a penalty to be paid in time of analysis. Because petroleum samples are arguably the most complex samples known, much work has been performed to provide the greatest possible resolution without the consideration of time. Some petroleum analyses that may take 2−4 hours and longer have been

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reported.[18] However, because better resolution is frequently unnecessary for some analyses, there is a definite application for faster analysis.

The history, methods, and applications for conducting fast analyses via GC are delineated in several excellent reviews.[19-23] In these works, the authors discuss the typical ways to shorten analysis time: (a) decrease the column length; (b) increase the carrier gas flow rate; (c) use multichannel columns;[23] and (d) provide rapid heating of the column with heating rates up to 1200 °C/min and higher.[19] Fast GC, in these instances, is best-described as conducting analyses as fast as is possible to provide *sufficient* separation of the compounds of interest. Often, in the search for maximum resolution, compounds can be over-separated, which usually lengthens the time of analysis which can be possible. Fast GC could be described as that separation which can produce the desired analytical information in the shortest time.

In petroleum analyses, and specifically for aviation fuels, there are a good many separations where complete resolution is not needed. Fingerprinting of different types of fuels (diesel, gasoline, aviation fuels, kerosene, etc) can be performed quickly to characterize the mixtures in useful ways.[24] Simulated distillation[25] is one good example of a chromatographic analysis that has low resolution but can be conducted very fast ($\ll$5 min). Fortunately, excellent resolution is not usually necessary to obtain the critical information about distillation range;[24] therefore, this application is a good example of fast GC where limited resolution is required. One must decide, therefore whether the speed of analysis allows enough resolution to provide compositional information about the fuel, which can be related to the results of the specification tests.

Experimental Section

The goal of this program was to conduct a rapid, single GC experiment using flame ionization detection and sulfur-specific detection, and to relate these results empirically to specification test results for total sulfur, distillation range, flash point, and freeze point. The instrumentation developed was to be transported for military installations in the field for use as a specification test predictor for the properties listed.

A. Fast Gas Chromatography Instrumentation. The fast GC system was developed to provide a 5-min analysis of the fuel in question with sufficient resolution for specification test prediction. Two fused-silica capillary columns were used with a two-holed ferrule into the injector of a gas chromatograph (Agilent model 6890). The first column, which is a 7.0-meter microbore HP-5 (0.1 mm inner diameter (ID), 0.17 μm film thickness; Agilent Technologies), was connected to a flame

ionization detector (FID). The second column was a wide-bore 30-m model HP-5 (0.32 mm ID, 0.25 μm film thickness, Agilent technologies) which was connected to a sulfur-specific flame photometric detector (FPD) on the GC. The columns were chosen because of their nonpolar nature, which ensured that compounds would elute essentially by boiling point, which is an important and necessary feature for these predictions. The detectors were also chosen to make use of the excellent linearity of the FID signal and the specificity of the FPD for sulfur detection. An Agilent Chemstation was used to monitor both signals from the two detectors simultaneously. Because the first column was a microbore (0.10 mm ID), peaks are typically much narrower than more-traditional columns (0.25 mm). Thus, the data rate for the FID was 100 Hz, instead of the more-common rate of 20 Hz. The FPD was operated at 20 Hz. An auto sampler was also used with this chromatographic system.

The conditions of temperature programming and pressure programming the GC system were chosen to balance the speed of analysis and the splitting of sample in the two dissimilar columns. The inlet pressure for the two columns was chosen to optimize (or nearly so) the separations being conducted in the microbore column to the FID. In this case, the average linear velocity was fixed at 41 cm/s in constant flow through the column. This setting resulted in a nominal initial inlet pressure of 29.4 psi, which increased throughout the analysis to maintain constant column flow. The wide-bore column to the FPD was not used optimally, resulting in poor resolution from the second column separation. However, because the analysis being conducted was total sulfur measurement, the need for optimal resolution per unit time was only required in the first column. A high split ratio (200:1) was used for all analyses in this study. All of these important flow rates were controlled using electronic pressure control features within the GC system.

The separations performed in the laboratory and used to develop the correlations were conducted in helium carrier gas. However, because this system was to be used in a mobile laboratory, no gas bottles were desired. The exclusive use of gas generation would allow the system to be more mobile and would not significantly detract from the resolution of the separations. Therefore, a nitrogen-air separation system (Domnick Hunter, Ltd., model UHPA0601W) was obtained to provide pure nitrogen for the carrier gas and makeup gas for each detector. It also provided dry, filtered air for the FID and FPD systems. A hydrogen generation system (Matheson/Airgas, Chrysalis model) was also used to provide hydrogen gas from the electrolysis of water for the FID and FPD systems. While hydrogen could have been used for carrier gases to increase speed and resolution, the safety aspect of using hydrogen in high-split ratio injections for a forward-operating mobile laboratory was not desirable.

Sample preparation required a constant dilution of the fuel to be analyzed. In this case, each fuel was diluted 1:20 in hexane solvent. Simulated distillation requires a standard of normal alkanes (C5 through C17) to be analyzed, to determine the retention times of each of the alkanes. In addition, Jet A fuel with 1700 ppm (by weight) of sulfur was used to calibrate the sulfur detector. Dilutions of this solution in hexane were performed using syringes, which were made available for the mobile laboratory.

B. Correlation Development. The goal of this program was to develop empirical correlations of GC data to specification test results so that one injection could be used to predict specification test results. Fuels from several test programs being analyzed by specification tests were used to develop the correlations to the properties of simulated distillation (distillation range), flash point, freeze point, and sulfur content. Table 2 lists the appropriate specification property and ASTM test method for each of the tests. Specification test results were

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Table 2. Specification Tests Used To Correlate to Fast Gas Chromatography (GC)

specification property	ASTM method	description
distillation range	D2887	simulated distillation, a GC-based method that can provide volatility data in place of the one plate D86 distillation data
flash point	D56, D93	ability of fuel vapors at specific temperatures to ignite when exposed to a flame
freeze point	D2386	temperature at which visual solids disappear upon warming
sulfur content	D1266, D2622	weight percent of sulfur-containing organics in fuel

Table 3. Specification Limits for Volatility, as Measured via ASTM D86

	Volatility Limit				
	JP-8	Jet A	JP-7	JP-5	Avgas(100/130)
initial boiling point, IBP	report		182 °C (min)		report
T 10% rec. max	186 °C (max)	186 °C (max)	196 °C (min)	205	75 (min)
T 20% rec. max	report		206 °C (min)		report
T 50% rec. max	report	report	report	Report	report
T 90% rec. max	report	report	260 °C (max)	Report	report
final boiling point, FBP	330 °C (max)	300 °C (max)	288 °C (max)	300 °C (max)	290 °C (max)
residue	1.5 vol %	1.5 vol %	1.5 vol %	1.5 vol %	
loss	1.5 vol %	1.5 vol %	1.5 vol %	1.5 vol %	

performed according to ASTM test methods by qualified quality control laboratories.

Results and Discussion

A. Development of Correlations and Validation of Predictions. The results of chromatographic determinations were related directly to specification test results for a collection of fuels. Training sets of fuels analyzed for the properties of interest were developed. Other fuel samples were then used to validate the correlations; fuels from the validation set were not used in the training set for the development of the correlation. The fuels used for training were Jet A or JP-8 fuels, with as wide a range of properties as the specification would allow. In some cases, off-spec fuels (diesel fuels or gasolines) were added to the training set to allow a broader range of property values with which to compare.

A.1. Simulated Distillation. In simulated distillation, the chromatographic column replaces the distillation apparatus of Standard Method ASTM D-86. In doing so, the distillation changed from a single-plate distillation to a more complete multiple-plate distillation using chromatography. This information is generally different than the specification results from distillation, which are primarily derived from Standard Method ASTM D-86. Several researchers have investigated the relationship of simulated distillation (D2887) data with D-86 data.[26] In fact, relationships exist for converting D2887 to D86 data and are used routinely in available software for conducting these methods on GC systems.[15] Also, specification test levels for military jet fuel are available for D2887 data as well as D86 data. The existing specification levels for D86 distillation data are given in Table 3.

The use of simulated distillation for predicting D86 data is well-documented. The purpose of this work was to use Standard Method D2887 to predict specification-grade fuels, and also to predict D86 data from the D2887 data. Figure 1 shows a plot of the retention time versus *n*-alkane boiling point. Using the cumulative area of the chromatographic tracing along with the boiling points

for individual *n*-alkanes, one may construct a cumulative distribution for boiling range, as shown in Figure 2. The cumulative distribution of the peaks eluting from the FID analysis is compared to the total FID response to obtain the area percentage of the chromatogram (essentially, the percentage recovered), which was then related to the temperature to recover that fraction by comparison to Figure 1.

The retention time at which a percentage of the area was achieved was related to the boiling temperature by comparison with Figure 1 to generate a cumulative distribution, with respect to temperature. Through examination of this curve, it is possible to find the cut points (percentage recovered at various temperatures), as shown in Figure 2. With the cumulative distribution, one can predict the percentage of recovered fuel.

Unfortunately, it clear from Figure 2 that Standard Method ASTM D86, which is the current specification test for boiling range, does not agree precisely with Standard Method D2887, except near the midpoint of the cumulative distillation plot. This observation is well-established in the literature[15,26] and empirical correlations now exist to perform the routines to transfer the D2887 chromatographic information to D86 data for comparison to the specification tests. However, the commercial product was unavailable to use at the time; therefore, a less-sophisticated adjustment (using the average deviation from the D86 to D2887 data for a
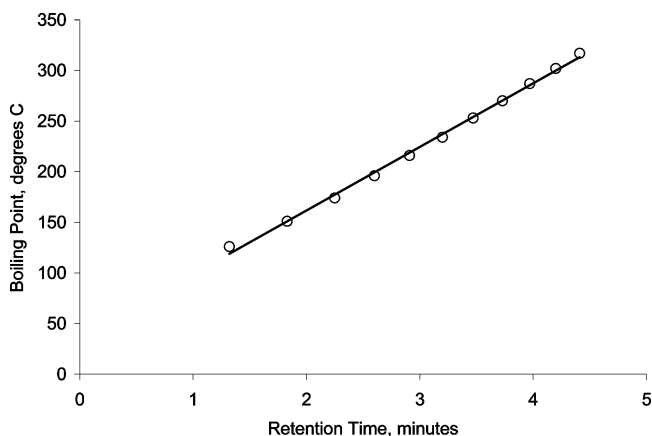
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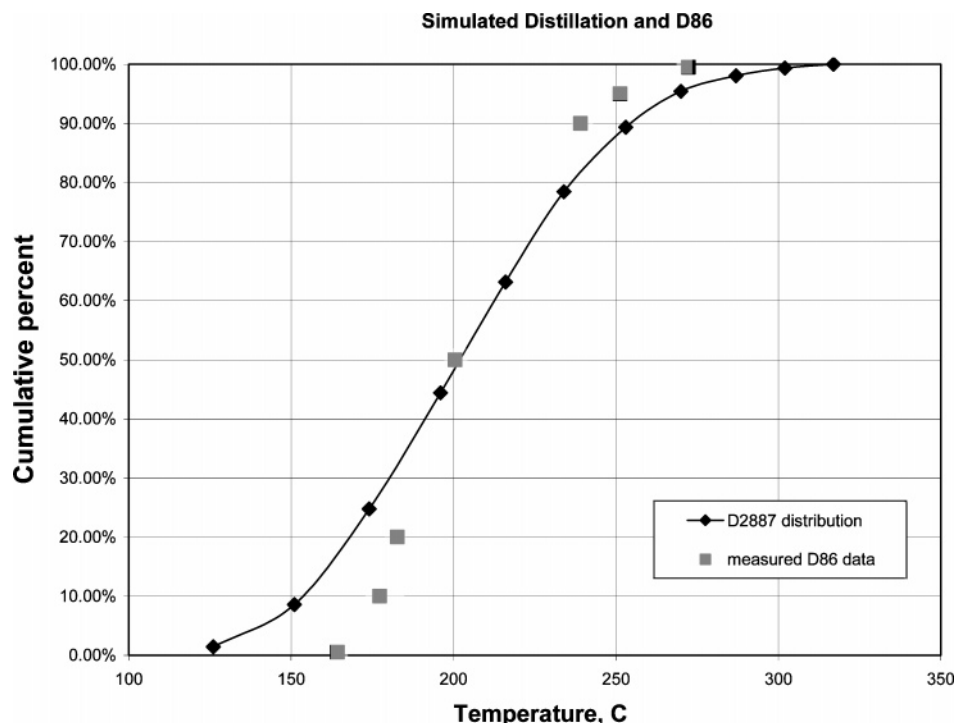

Figure 1. *n*-Alkane boiling points plotted against retention time from heptane (C7) through heptadecane (C17).

Figure 2. Curve showing the cumulative distribution of the boiling range distribution as predicted by Standard Method ASTM D2887 for one of the fuels used in the training set. The squares represent the D86 distillation temperatures as measured by the specification tests.

particular recovery point) was established with the training set and evaluated using the validation set. Additional commercial software will be incorporated in the future.

This work describes an empirical relationship of the cumulative chromatographic response (percentage recovered), compared to measured D86 responses for a large training set of fuels. These fuels were taken mostly from Jet A and JP-8 samples from the United States. The size of the training set was 99 fuels tested by D86 distillation. To relate the GC simulated distillation predictions to the D86 measurements, a relationship between the two data sets was developed using the $n = 99$ training set for each distillation recovery tested (10%, 50%, and 90%). Another set ($n = 33$) of data (not included in the training set) was then used to evaluate the accuracy of this prediction.

The results of the predictions for simulated distillation are shown in Figure 3. The results generally fall within 10 °C of the measured D86 temperature for 10%, 50%, and 90% recovery. The predominance of points below the $y = x$ line indicates a slight bias. By incorporating other software routines to change the D2887 data to D86 data, we may improve these correlations. Also, some jet fuel specifications (JP-5, JP-8) provide D2887 (simulated distillation) specification limits for the 10% recovered temperature (186 °C for JP-8). However, GC-based simulated distillation is a proven technique and can be conducted readily in the fast GC analysis.

To conduct simulated distillation, a normal alkane standard must be analyzed to determine the relationship between retention time and boiling point for the normal alkanes under the instrumental conditions selected. These standards need not be run if the chromatographic columns used are identical to those used in the current experiments. However, from a
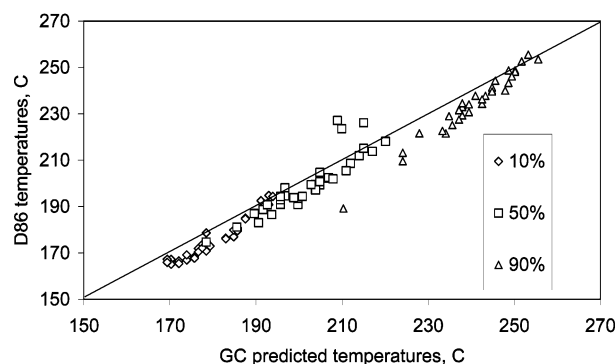

Figure 3. Gas chromatography (GC) predictions of ASTM D86 distillation data using the modified simulated distillation method. The predictions are compared to actual ASTM D86 data for a set of data that was not used to develop the correlations.

practical viewpoint, all columns are slightly different and the determination of retention times for alkanes is more straightforward after examining a standard mixture.

A.2. Flash Point. The flash point was determined simply by summing the area of the peaks eluting before the C9 *n*-alkane (see Figure 4). Although other compounds contribute some volatility, these compounds represent the great majority of the volatile compounds; that is, compounds that would be in the vapor phase at the temperatures indicated. Because the FID for this GC system provides a constant response factor for most of the volatile compounds, this semiquantitative estimation works reasonably. Several aromatic compounds have different response factors than the aliphatic compounds; because higher or lower concentrations of aromatic compounds, compared to aliphatic compounds, will change the volatility without changing the area response of this collection of peaks, there is error
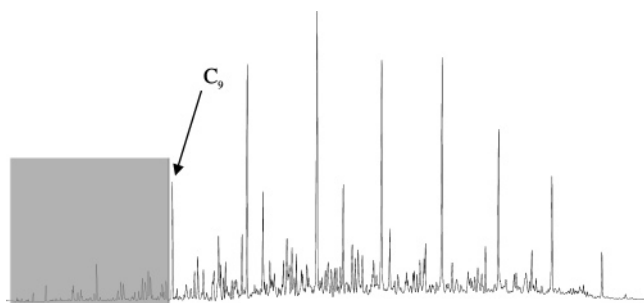
Figure 4. Calculation of flash-point area (small box) versus the total chromatographic area (large box). This ratio is then related to the ASTM measured flash point.
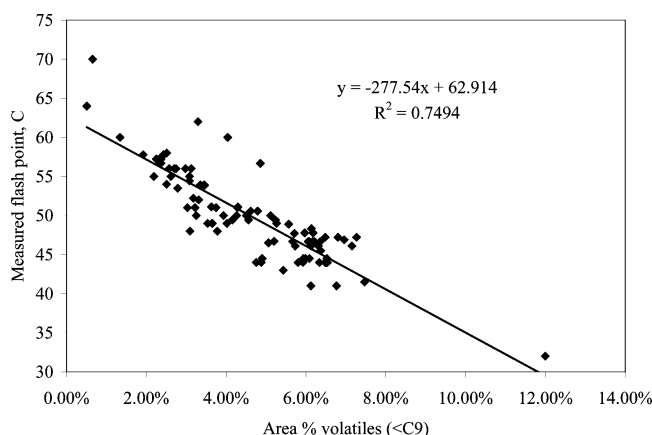

Figure 5. Area-percent response of hydrocarbons, relative to the total hydrocarbon response measured by a flame ionization detector (FID) ($n = 116$).
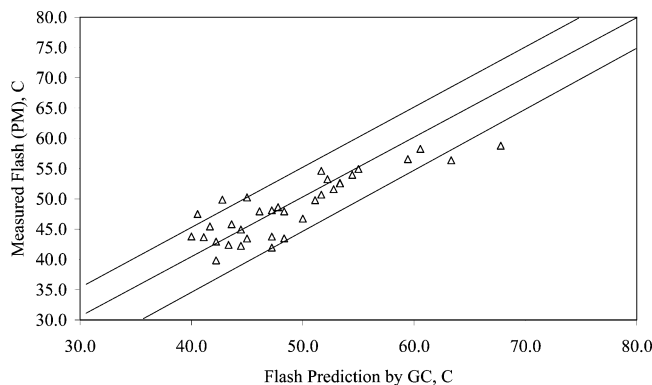

Figure 6. Actual versus predicted flash-point temperatures for World Survey program fuels.

associated with this measurement. Improvements could be made if retention times were tracked and aromatic compounds were distinguished from aliphatic and response factors for each class were calculated. However, because this technique needed to be field-portable and simple, the aromatic and aliphatic compounds were lumped together and used in this estimating fashion.

The calibration of this estimate is shown in Figure 5, where the area percentage of the chromatographic response is plotted against known measurements of flash point temperature. This correlation was used to predict the flash points of other fuels, not included in the training set. These results are shown in Figure 6.

Flash-point testing is normally performed using Standard Methods ASTM D56 (Flash Point by Tag Closed Tester) or ASTM D93 (Flash Point by Pensky Martens Closed Cup Tester). The development of the correlation
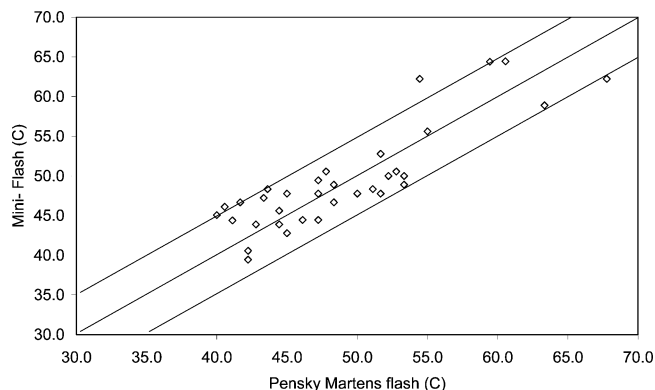

Figure 7. Comparison of two ASTM flash point tests methods (Mini flash versus Pensky Martens Flash).

did not distinguish between these two techniques, even though they generally show a slight bias. Several of the fuels examined in this effort were performed by both techniques (Standard Methods D56 and D93). Figure 7 shows the differences between the two techniques and the level of accuracy for the same sample measured by the same laboratory.

It is apparent that the ASTM methods themselves have some inherent error, with regard to the flash point. The great majority of the fuels tested by both methods show agreement to within 5 °C. The GC prediction technique is generally accurate to 5 °C, with some notable exceptions, as observed in Figure 6. The conclusion from these figures is that simple GC area percent calculations can be used to predict the flash point almost as well as the ASTM methods, and they can be conducted at different laboratories or via different methods. The error associated with the estimation by GC is not significantly different than that of the ASTM tests themselves. This is interesting, given the fact that the correlations were performed using the ASTM tests, with their associated errors. The fact that the GC-based calculations provide little additional error to this measurement is indication of its suitability as an estimator or screening tool.

A.3. Freeze-Point Predictions. Prediction of the freezing point is an important and useful measurement to perform for field applications, because of the difficulty of supporting the cryogenic or subambient conditions necessary for conducting the freeze-point test. It is an important measurement to be made in the field, because an accurate measurement of the freeze point could allow aircraft to be operated at temperatures closer to the fuel's measured freeze point, rather than at temperatures closer to the specification test limit. Currently, aircraft must be operated at temperatures above the fuels specification freeze point, rather than the measured freeze point.

In this application, we recognize the close relationship between freezing point and normal alkane concentration. This relationship has been shown in both diesel and jet fuel samples:[27] the higher the concentration of heavier normal alkanes, the higher the freezing temperature. Heavier *n*-alkanes, being the most likely components to freeze at high temperatures, have a tendency to align and agglomerate. Thus, a relationship

(27) Zabarnick, S.; Widmore, N.; Vangness, M. *Energy Fuels* **2002**, *16*, 1565−1570.

between *n*-alkane concentration in the fuel and the measured freeze point was anticipated. The higher *n*-alkanes were weighted to be more important in this relationship and the best, but non-unique, weighting relationship was determined empirically as a power-law equation. The higher *n*-alkanes were higher weighted by considering the boiling point of each carbon number alkane, as shown below in eq 1.

$$W_n = A(T_{mp,n} - T_c)^P \quad \text{(for each n-alkane)} \quad (1)$$

where W_n is the weighting factor for each *n*-alkane (C8−C20), A is a pre-exponential factor, $T_{mp,n}$ is the melting temperature of each *n*-alkane, T_c is the constant temperature used to reduce the power-law term, and P is a power-law factor.

The variables A and P—the pre-exponential factor and the power-law factor, respectively—are solved by successive iteration based on a minimization of error (prediction minus measured) using initial estimates for A and P. By multiplying these weights by the area-percent (approximately the weight-percent) concentrations for each normal alkane, one obtains a relationship that describes a value that gives the *n*-alkane concentrations weighted toward the heavier normal alkanes, taking into account both concentration and carbon number.

$$X = \sum_{n=20}^{n=8} W_n[C_n] \quad (2)$$

where $[C_n]$ is the area percent concentration of the *n*-alkane and X is the weighted *n*-alkane concentration factor.

This value, summed between the C8 and C20 weighted *n*-alkane concentrations, could then be compared empirically with measured freeze points. The weighting factor and concentrations for each normal alkane were summed and, using linear regression, were compared to the measured freeze point to obtain a slope and intercept for the linear relationship. With the slope and intercept, an estimation of the predicted freeze point was determined. By repeating this spreadsheet calculation with different values for T_c, A, and P, and then minimizing the residual between the measured and predicted values, we obtain the relationship in eq 3:

$$T_{fp} = [\sum_{n=20}^{n=8} 5.0 \times 10^{-14}(T_{mp,n} - 200)^{7.07} \times$$
$$[C_n]][\text{slope}] + \text{intercept} \quad (3)$$

where the slope and intercept were determined by the previously described relationships. These A factors, P values, slopes, and intercepts were calculated to minimize errors for 91 fuels for which freeze-point data were available. These final relationships, as described by eq 3, were used to predict the freeze points for an independent set of fuels. Figure 8 shows the agreement for these 38 fuels for which data were available.

In these data, it is apparent that the freeze-point predictions can differ by 5−7 °C from the measured freeze-point values. This prediction is probably not precise enough to be used to determine minimum in-flight temperatures. A field technique that could ac-
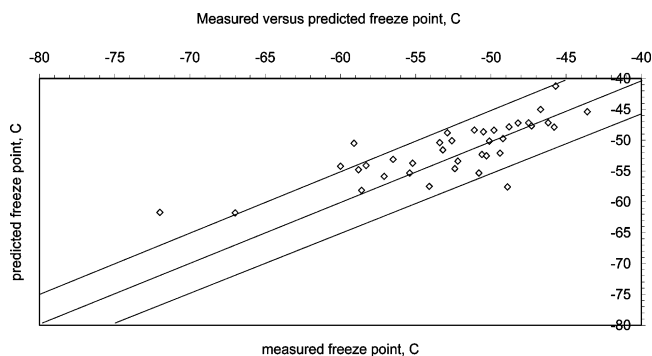

Figure 8. Measured versus predicted freeze point for a weighted concentration of normal alkanes using empirical data.

curately predict the freeze point would allow aircraft to fly at a temperature just above the freeze point of the particular fuel being used, instead of the specification limit of the fuel. Further work is need to improve these predictions using GC data.

Clearly, the higher normal alkanes are important factors in determination of the freeze point. The weighting factors used show the importance of the C15 through C20 normal alkanes, although the concentration effect also has an important role. That is, the low concentrations of heavily weighted C20 may not be as important as the high concentrations of C16 or C15 in the fuel. Also, the concentrations of alkanes less than C11 were determined to be virtually unimportant, no matter their concentration. These observations are apparent in the determination of the freeze point for diesel fuels as compared to jet fuels, because diesel fuel *n*-alkane concentrations, especially for C18 through C11 and above, are quite high. Freeze-point predictions for diesels are often greater than 0 °C; although not an accurate freeze point, this value shows the importance of the higher *n*-alkanes in freeze-point prediction.

A.4. Sulfur Content. Sulfur content is perhaps the most directly measured property for GC, because a sulfur detector is available as one of the two detectors on the system. Although the column connected to this system was not a microbore column, the column velocity and flow were so high that experiments could be performed within ~5 min, which is the length of time of the micobore separation. Although some resolution is lost in operating the column at this excessive flow rate, our goal was only to measure the total sulfur content of the fuel sample, meaning that the area response of the flame photometric detector (FPD) could be summed and that resolution of individual components was not an issue. The two chromatograms in Figure 9 show the simultaneous collection of FID data, representing the microbore GC separation of the hydrocarbon components of the fuel, and the sulfur signal from the low resolution separation in the second column.

The calibration of this system was performed using a single fuel sample. The fuel (Code POSF-2959) is a high-sulfur fuel that was measured using standard microcoulometry tests (ASTM D3120) to be 1700 ppm (wt/wt). Calibration was performed using syringes to dilute this sample. Every jet fuel sample analyzed had to be accurately diluted using syringes, or some other accurate dilution technique. The calibration curve,
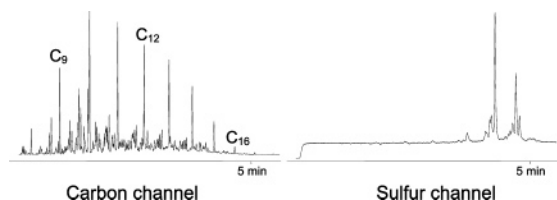
Figure 9. Simultaneous carbon and sulfur channels using the flame photometric detector in parallel with the FID for experiments with a duration of <5 min. Sulfur signal is summed to obtain a total sulfur concentration, compared to a calibration curve.
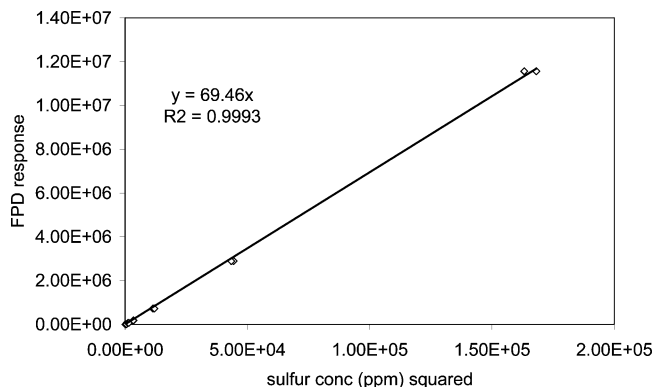

Figure 10. Sulfur calibration for the flame photometric detector (FPD) based on the square of the sulfur concentration.
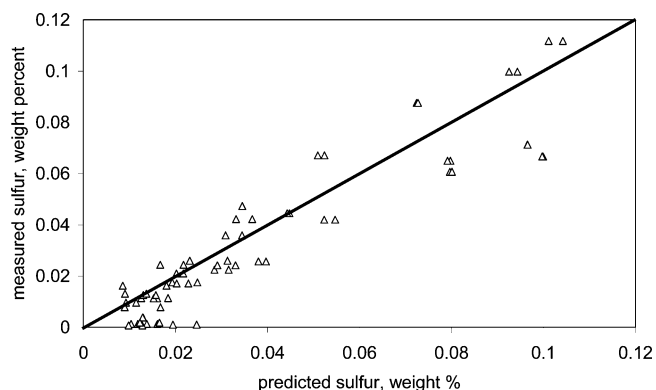

Figure 11. Predicted (by GC−FPD) versus measured (ASTM D2622) sulfur content for 38 fuels from the World Survey program.

based on the response of the square of the concentration, is shown in Figure 10.

Using this calibration curve, each of the unknown fuels was diluted using hexane or similar solvents and analyzed. The results in Figure 11 show the amount of sulfur measured by FPD response, compared to specification test results for Standard Method ASTM D2622, which is the X-ray fluorescence method. These data were obtained for the same set of fuels as previously mentioned, i.e., the survey set of 38 samples, from military bases and airports around the world.

Although the agreement may not be perfect in this plot, one must consider that the specification test results for sulfur are those determined using Standard Method ASTM 2622 (sulfur by X-ray fluorescence). This test is not particularly precise, and it is designed to be able to determine the differences between fuels that are of the near-specification limit of 0.3 and those that are above the specification limit. GC is more suited toward low-

level determinations of the amount of sulfur in a sample; indeed, the fuel sample itself is diluted by a factor of 50 before analysis begins. In any case, the technique is very capable of screening for nonspecification levels of sulfur in many different types of samples.

B. Use of Specification Test Prediction in the Field. The GC−FID−FPD system was outfitted so that it could be operated in the field from a near-automated fashion. Thus, a wireless laptop computer for system control, along with the correlations described here, was developed for the system.

The GC system also contained autosampling capability, so that the operator had only to dilute 20 μL of the sample in 1000 μL hexane, put the vial in the autosampler, and run the method. Each experiment was conducted within 5 min or less. The data analysis was not automated at this stage of development of the project. Therefore, data files were integrated manually to obtain (1) the total FID response for the entire chromatogram, excluding solvent; (2) the integrated sum of response for compounds up to normal C9; (3) the area of each *n*-alkane; (4) the total sulfur response; and (5) the CSV output of all peaks to be used in calculation of the simulated distillation profile

With these five pieces of information, the flash point, freeze point, simulated distillation, and sulfur content could all be predicted using the correlations previously described. All results were automatically printed out in summary format.

Although the specification data generated was an estimate from GC data, it provided a screening tool (with one 5-min automated chromatographic experiment and ~5 min for data analysis) for determining whether an unusual fuel was present. If the specification properties predicted were questionable or failing, the fuel sample could then be sent to a local or regional laboratory for routine specification analysis. This screening technique could save time and expense for an army quickly moving across a battlefield, by obtaining fuel from local unfamiliar or captured sources.

This instrumentation was provided for use in the screening of fuels for specification tests. Table 4 gives examples of results obtained from captured and locally purchase fuel samples. Specification predictions were made using the fast GC data and comparisons to the regional quality assurance laboratory were also obtained.

These data indicate that the great majority of specification properties of fuels tested were successfully predicted using the GC analysis. The instrument, as expected, was especially good at determining diesel fuel versus jet fuel, which is an important consideration when examining captured fuel. Flash-point predictions quickly and easily reveal the differences between JP-8, diesel fuel, and aviation gasoline. Fuels for trucks that may have catalytic conversion systems designed for lower-sulfur diesel are readily measured for sulfur. The system is relatively automated. It is also interesting to note that the volumes of fuels needed for testing are relatively low. Full specification tests for JP-8 generally require more than 1 gallon of fuel. Chromatographic analysis requires on the order of microliters of fuel, which may improve the speed and ease of sample shipment and storage.

Table 4. Specification Test Prediction by Fast GC in the Field[a]

fuel type	sample location[b]	Freeze Point (°C) specification test	GC	Flash Point (°C) specification test	GC	Sulfur Content (wt %) specification test	GC
TS-1	A	−53	−56.3	32	26.1	NA	<0.01
Diesel 1	A	pp, −22; cp, −25[c]	−30.9	42	41.5	0.07	0.045
AvGas	B	−65	−65.4	NA	−197	0.01	<0.01
AvGas	B	−65	−65.5	NA	−197	0.01	<0.01
AvGas	B	−63	−65.4	NA	−198	0.03	0.0331
AvGas	B	−63	−65.4	NA	−197.7	0.03	<0.01
AvGas	B	−62	−64.5	NA	−197	0.02	<0.01
AvGas	B	−62	−65.4	NA	−197	0.02	<0.01
AvGas	B	−66	−65.4	NA	−198	0.01	<0.01
AvGas	B	−66	−65.4	NA	−197	0.01	<0.01
Diesel 1	C	NA	134	NA	58.6	NA	0.06
Diesel 1	C	NA	146	NA	58.3	NA	0.09
MoGas	C	NA	−64.6	NA	−113	NA	<0.01
MoGas	C	NA	−64.6	NA	−107	NA	<0.01
Diesel 2	D	pp, −9; cp, −7[c]	101.2	71	56	0.69	0.4
Diesel 2	D	pp, −9; cp, −8[c]	140.9	75	58.8	0.61	0.297
JP8	E	−52	−52.1	44	26.7	0.1	0.14
JP8	F	−47	−49.4	48	42.2	0.01	0.11
JP8	F	−49	−47.5	NA	41.9	0.006	<0.01
JP8	F	−46.8	−49.9	NA	39.3	0.005	<0.01
JP8	F	−47	−49.3	NA	38.3	0.005	<0.01
JP8	F	−48.2	−51	NA	38.7	0.005	<0.01
JP8	F	−48.3	−51.7	NA	39.7	0.005	<0.01
JP8	F	−48.6	−52.3	NA	29.5	0.003	<0.01
JP8	F	−49	−52	NA	28.9	0.003	<0.01
JetA1	G	−50	−55	58	51.2	0.14	0.14
JP8	H	−52	−53.6	46	40.5	0.05	0.05
JP8	I	−48	−50.6	45	41.9	0.05	0.05
JP8	J	−49	−50.7	44	43.4	0.1	0.1
JP8	D	−52	−52.5	46	25.9	0.001	<0.01
JP8	D	−47	−55.4	44	23.8	0.002	<0.01

[a] NA = measurement not applicable. [b] All samples were taken from undisclosed locations outside the continental United States. [c] The pour point (pp) and cloud point (cp) are given because the freeze point is out of range.

Conclusions

Gas chromatography (GC) can be useful in quickly and accurately measuring compositional data that can then be used for specification test prediction. The predictions for distillation temperatures, freeze point, flash point, and sulfur content are generally within the range of accuracy for many of the specification tests if analyzed by multiple laboratories. Commercial simulated distillation software can greatly improve the predictions made to ASTM D86 data. However, the military is currently considering the use of an alternate simulated distillation specification test limit. The freeze point is typically accurate within 7 °C, and the flash point is typically accurate to within 5 °C. The sulfur content, as measured by chromatography, may be more accurate than the specification sulfur test, which is based on a specification limit of 0.3% sulfur. The GC method can handle low levels of sulfur better than the current X-ray spectrometry method (ASTM D2622) does. Thus, as a screening tool, and considering that only simple correlations were used for relating composition to properties, this estimation for jet fuel properties seems acceptable for screening purposes.

There are already many important specification or nonspecification tests that can be measured or estimated using compositional data from GC analysis. Using gas chromatography−mass spectroscopy (GC−MS) or liquid chromatography (LC), it is likely that many more specification tests could be predicted from two or three analyses on advanced instrumentation. A gas or liquid chromatograph in a mobile laboratory allows for a versatile laboratory that is capable of a wide variety of test methods, including estimations of current specification tests, as well as advanced tests that are related to additive concentration or thermal stability.