Evaluation of the ZX101™ Octane Analyzer

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Introduction

This report contains an evaluation of the new ZX101™ Octane Analyzer from Zeltex , Inc. The data described herein were collected by independent laboratories, with the exception of the precision data, which were collected by the author. All statics reported were calculated by the author using standard statistical functions in a commercial spreadsheet software package.

Background

Octane Testing

The octane number associated with a motor fuel is a measure of the performance of that fuel. The number does not correspond to the concentration of any one constituent in the fuel, but rather to the pre-ignition properties of the fuel as compared with *standard* fuel mixtures. The term "octane number" is derived from the fact that the standard fuels contain iso-octane.

The ASTM Standard Procedures for determination of octane numbers require the use of two Waukesha CFR engines©. The "Research Engine" runs at 600 rpm, with a controlled air mixture and temperature as defined in ASTM D 2699. The "Motor Engine" runs at 900 rpm, with a controlled air mixture and temperature, and controlled fuel temperature as defined in ASTM D 2700. Waukesha engines or "knock engines" necessarily consume the fuel sample and a series of standard fuels during the test procedure.

The octane number of a fuel is defined by the compression at which the knock intensity of that fuel is 50% of the maximum knock intensity for the engine. Pure iso-octane is defined as having an octane number of 100, while heptane is defined as having an octane number of 0. A series of standards containing heptane, iso-octane and toluene are used to define a scale between these two bounds. The Research Octane Number (RON) of a fuel is the octane number measured on the Research Engine. Similarly, the Motor Octane Number (MON) is that number determined by the Motor Engine. The octane number typically posted on the pump at a service station is the average of the RON and MON (called PON, or (R+M)/2).

In recent years, there has been a great deal of research aimed at the development of new, more sophisticated techniques for the determination of octane number in gasolines. The method receiving te most attention has been near-infrared spectroscopy. 1-3 Several commercial devices have been developed to date.4.5 This paper focuses on the ZX101™ Octane Analyzer from Zeltex, Inc.

The ZX101™

The ZX101™ is a portable, battery powered octane analyzer for use with gasoline. It consists of three primary components: the analyzer, a sample container and a light shield. The entire package in a carrying case weighs less than 5 kg. The instrument performs an octane number determination in less than a minute, and does not require the use of standard samples. The measurement is completely non-destructive.

The ZX101™ measures octane number via near-infrared transmission spectroscopy. The instrument contains a patented solid-state optical system, comprising 14 near-infrared emitting diodes (IREDs) with narrow bandpass filters, a silicon detector system and a fully integrated microprocessor. Figure 1 shows a schematic representation of the ZX101™. The sample holder is a sealed, flat-sided, reusable glass container with an optical pathlength of 75 mm. The sample volume is approximately 225 ml.

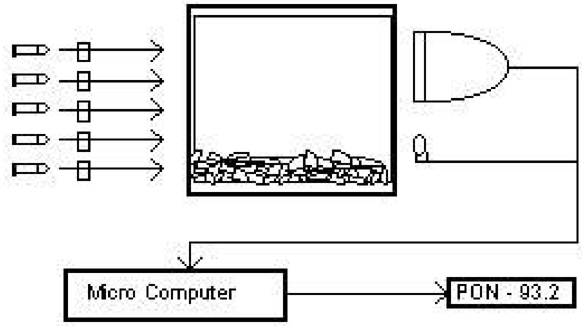

Figure 1
Schematic Diagram of ZX101C Optical System

To make an octane number determination, the user acquires a background signal from the empty sample chamber, measures the absorption spectrum of the sample twice, then acquires a second background signal. The entire process requires less than a minute, and can be performed by untrained, unskilled personnel.

Near-infrared spectroscopy

The near-infrared (NIR) spectral region is usually defined as that portion of the spectrum with wavelengths in the range 700 to 2500 nm. In this spectral region, overtone frequencies of molecular vibrations absorb light quite readily. Because the overtone absorption bands are typically wide and overlapping, spectroscopists cannot merely measure peak heights to perform quantitative analysis. Instead, multivariate regression analyses are utilized to correlate spectral features with concentrations or physical properties of interest.

The ZX101™ operates in the short-wavelength NIR, from 800 to 1100 nm wavelength. The instrument is factory calibrated to predict octane number (RON, MON and PON) from the absorption spectra of the fuels being tested. This prediction is accomplished through the use of a multivariate regression equations of the form:

$$\text{Octane number} = K_0 + K_1\,(OD1) + K_2\,(OD2)\ \ldots + K14\,(OD_{14}) + K_{15}\,(T_a)$$

where K_0 is a bias term, K_1 through K_{15} are slope coefficients, OD1 through OD_{14} are the absorbencies measured at each of the 14 wavelengths, and T_a is the ambient temperature at the time of the test.

The instrument can store up to 10 calibration equations, and is factory calibrated for RON, MON and PON of blended gasolines.

Features of the ZX101™

The ZX101™ has several features that safeguard against erroneous readings.

- *High Variance Warning* - triggered if repeat measures for a given sample exceed some preset value.
- *Temperature Warning* - triggered if the analyzer is used outside of the recommended temperature range (15° to 45° C).
- *Out of Range Warning* - triggered if the sample being tested is outside the range of the calibration range of the ZX101™.
- *Curve Checking* - triggered if the optical spectrum of the current sample is atypical of gasoline samples stored in the unit.

Limitations imposed by CFR engine testing

Quantitative NIR spectroscopy is a secondary technique, in that results are generated through regression equations that model the output of some primary method of analysis. In the case of octane testing, the primary method of analysis is the CFR engine.

A secondary method can never show better accuracy than the precision of the primary method. This is true because accuracy cannot be determined beyond the bounds set by the primary method. In the case of CFR engine testing, the limitations are as summarized in Table I. In this context, reproducibility describes the ability of a an engine to generate the same result for a given fuel after being shut down then restarted and used by a new technician. Repeatability describes the ability of an engine to generate the same result for a fuel sample in successive tests. The 95 % confidence interval corresponds to roughly two times the standard deviation of measurement (2σ) for large numbers of re-tests.

Table I: ASTM Specifications for CFR Engine Testing

	As per procedure	Reproducibility (95% confidence)	Repeatability (95% confidence)	At Octane number
RON	2699	± 0.7	± 0.2	95
MON	2700	± 0.9	± 0.3	85

Validation Studies

State Sponsored Octane Screening

An increasing number of state governments are requiring filling stations to undergo octane testing. Stations caught selling fuels with octane numbers significantly different from the values posted on the pump are fined, and in some cases closed down.

In a traditional test, gasoline samples are collected from various filling stations and brought back to the laboratory for testing on CFR engines. The testing is necessarily time consuming and expensive. For this reason, many states have begun using the ZX101™ to perform on-site octane screening. The ZX101™ makes octane determinations in seconds, and eliminates the tremendous expense of CFR testing.

During one recent survey, the State of Maryland (Jessup, MD) collected 161 gasoline samples from various filling stations. The samples were each measured with the ZX101™, and then tested on both the Research and Motor CFR engines. Figures 2, 3 and 4 contain scatterplots of the RON, MON and PON of these samples as measured by the ZX101™ and CFR engines. A statistical summary of the data is presented in Table II.

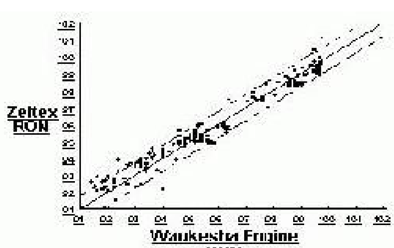

Figure 2
State of Maryland RON

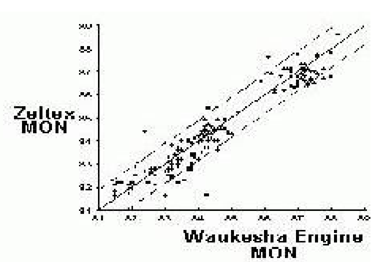

Figure 3
State of Maryland MON

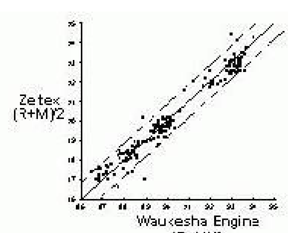

Figure 4
State of Maryland (R+M)/2

It is important to note that the properties of gasoline blends are engineered specifically for various climates through the use of additives. The gasoline samples tested by the State of Maryland represented a wide variety of fuels, with vastly different properties. For example, the sample set contained fuels with vapor pressures ranging from 10.6 (B-type mild-temperature gasoline) to 15.4 (higher than allowed in E-type cold-weather gasoline), and MTBE additive concentrations ranging from 0.2 to 16 volume %. While no statistical analyses were performed to correlate additive concentrations or vapor pressures with prediction errors, a cursory examination of the data does not indicate that any strong correlation existed.

In an independent survey, the Commonwealth of Virginia (Richmond, VA) collected 163 gasoline samples. As with the Maryland study, the samples were brought to the state laboratory and tested with the ZX101™ and CFR engines. Figure 5 shows the calculated PON as measured with the ZX101™ and the CFR engines. A statistical summary of the data is presented in Table II.

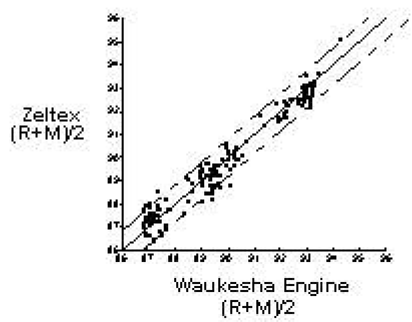

Figure 5
Commonwealth of Virginia (R+M)/2

The results of both of these validation studies show that the ZX101™ provides sufficient accuracy for the screening of gasoline samples from filling stations.

Octane Exchange Group

Laboratories that make use of CFR engines typically belong to one or more "Octane Exchange Groups" (OEG). These groups circulate gasoline samples to the member laboratories, and compile statistics about the octane numbers determined for similar samples by different laboratories. The purpose of the exchange groups is to allow laboratories to confirm that their engines are generating accurate data.

Zeltex ™ recently participated in one OEG's round-robin test. A set of 20 samples was provided to Zeltex ™ with no laboratory data. The samples were measured on the ZX101™, and the results returned to the OEG.

Later, the compiled laboratory values for RON and MON as determined by the OEG were returned to Zeltex™. Scatterplots for RON, MON and PON, as determined by both the ZX101™ and the OEG are shown in Figures 6, 7 and 8, respectively. A statistical summary of the data is presented in Table II.

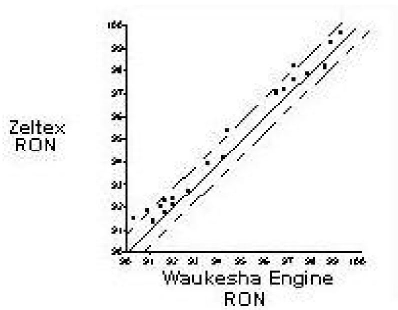

Figure 6
Octane Exchange Group RON

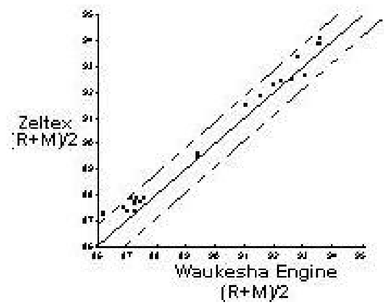

Figure 8
Octane Exchange Group (R+M)/2

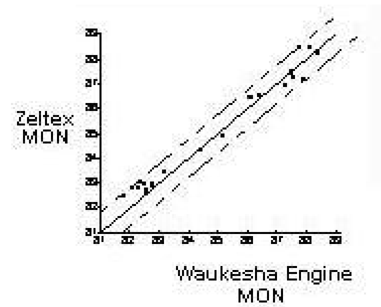

Figure 7
Octane Exchange Group MON

Because the initial calibration in the ZX101™ was performed with one set of CFR engines, it is possible that the instrument may produce results that have a relative bias to other sets of CFR engines. For this reason, the ZX101™ is generally slope and bias corrected upon installation to provide results that are compatible with the customer's CFR engines. The OEG round-robin test did not afford Zeltex ™ the opportunity to perform slope and bias correction, as it was a blind test. However, after the test was complete, and the analytical values for all the samples were known, slope and bias correction were performed. The statistical analysis the corrected data is summarized in the last section of Table II. Note that the slope and bias corrected data provide only a best-fit model for the ZX101™ predicted data to the CFR engine data.

Table II.
Table II: Summary of Validation Studies

Test Site	Test Type	Standard Error of Estimate	Correlation
Maryland	RON	0.55	0.97
	MON	0.59	0.95
	PON	0.46	0.98
Virginia	PON	0.49	0.98
OEG	RON	0.66	0.98
	MON	0.47	0.98
	PON	0.47	0.98
OEG (Slope and Bias corrected)	RON	0.45	0.99
	MON	0.39	0.99
	PON	0.30	0.99

Precision Studies

In order to assess the precision of the ZX101™, the author obtained an instrument from the manufacturer and performed two experiments. In the first test, a single user tested a single sample 25 times in succession. The second experiment utilized 5 different technicians to test a single sample 5 times each.

For each experiment, the mean, standard deviation and range were calculated. Tables III and IV summarize the results of these tests. The 95% confidence intervals are calculated using a Student's t distribution with 24 degrees of freedom ($\alpha/2 = 2.064$).

Table III: Precision Study; 25 retests by a single user

	RON	MON	(R+M)/2
Mean Value	98.4	87.9	93.2
95% Confidence	± 0.25	± 0.12	± 0.12
Maximum Reading	98.6	88.1	93.3
Minimum Reading	98.2	87.8	93.1

Table IV: Precision Study; 25 retests (5 by each of 5 users)

	RON	MON	(R+M)/2
Mean Value	98.5	87.9	93.2
95% Confidence	± 0.25	± 0.12	± 0.10
Maximum Reading	98.7	88.1	93.3
Minimum Reading	98.1	87.8	93.1

Summary

The ZX101™ was demonstrated to be an effective tool for the measurement of octane number in gasoline samples. Three independent studies provide validation of the instrument's utility.

The instrument is extremely easy to use, portable, fast and inexpensive. A typical analysis takes less than a minute and requires no standard fuels or experienced personnel.

In general, the users seemed extremely satisfied with the ZX101™, and had already integrated the instrument into their regular octane testing program. Many commented that the ZX101 provided tremendous cost savings by drastically reducing the number of CFR engine tests.

References

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7. State of Maryland, Comptroller of the Treasury, Motor Fuel Testing Laboratory, Jessup, Maryland. Thanks to Michael Jordon for sharing the results of his testing.

8. Commonwealth of Virginia, Department of General Services, Consolidated Laboratory Services, Motor Fuel Laboratory, Richmond, Virginia. Thanks to William Fowler for sharing the results of his testing.