PetroSpec APPLICATION NOTE

Why Regulatory Bodies Trust PetroSpec's GS1000 for Field Enforcement

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Since the start of the Federal reformulated fuel program in January 1995, which included requirements for maximum amounts of benzene and oxygenates in gasoline, US EPA (United States Environmental Protection Agency) and CARB (California Air Resources Board) field agents have used PetroSpec mid-IR analyzers to enforce their regulations. After one year evaluations of all analytical field instruments for benzene and oxygenate content, the PetroSpec instruments were selected as the sole analytical instrument for field evaluations. PetroSpec units are capable of simultaneously evaluating benzene, toluene, xylene, oxygenate, total aromatic, olefin, saturate, octane (RON and MON), T50 and T90, DI, E200 and E300, and VOC levels.

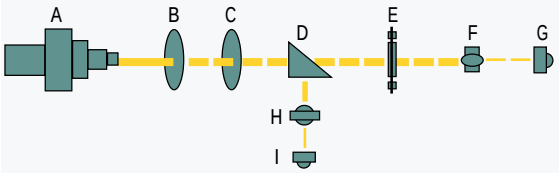
So, why do the EPA and CARB continue to use PetroSpec instruments in the field? First, the PetroSpec analyzer is the only instrument specifically designed for the rigors of field use. The hardware includes a temperature controlled, vibration dampened, state-of-the-art filter based optical bench, which creates a stable, rugged, and highly accurate optical system. The instrument also includes outlier statistics that indicate whether a selected prediction model is appropriate for analyzing a particular sample. Additionally, the PetroSpec comes equipped with the most comprehensive mid-IR fuel calibration set available; Windows-compatible software is also supplied so on-site calibration updates can be performed by the user.

ACCURATE FIELD MEASUREMENTS REQUIRE STABLE INSTRUMENTS

The EPA's instruments are transported via van to each inspection site, subjecting them to a constant environment of vibrations and jolts. Typical FTIR spectrometers cannot tolerate this rough environment because even small vibrations misalign the optics; large vibrations can destroy an FTIR's alignment so severely that the instrument must be returned to the factory for repair. Realignment in the field takes time, requires technically skilled personnel, and sacrifices overall accuracy of the equipment.

To eliminate problems caused by field-handling and rigorous use, PetroSpec's mid-IR instruments are designed around a dual beam, filter based optical bench. 18 individual optical filters isolate spectrum portions that correspond to specific chemicals of interest. Each of these filter measurements is actually a ratio between the internal air reference and the sample reading. Because wavelengths and the instrument's alignment do not change over time, this ratio method eliminates errors resulting from electronic and light source variations. Furthermore, unlike typical mid-IR instruments, the optical bench designed by PetroSpec is not susceptible to humidity and requires no drying agents.

Figure 1. *Dual beam optical design; reference spectrum taken each cycle*



A	*Mid-Infrared Source*	F	*Lens*
B	*Chopper Wheel*	G	*Detector (Fuel Properties)*
C	*Filter Wheel*	H	*Lens*
D	*Beam Splitter*	I	*Detector (Reference Spectrum)*
E	*Fuel Cell*		

In field use, it is critical that an instrument maintain accuracy in any weather conditions — whether the bitter cold of winter or the oppressive heat of summer. PetroSpec's units' temperature controlled optical bench extends the ambient operating range of these instruments. Because this feature is of particular importance to the EPA, the agency examined effects of ambient temperature on the PetroSpec GS1000 Portable Gasoline Analyzer, both with and without temperature control. Known oxygenated fuels were tested on two units in a temperature controlled room. The instruments were equilibrated at ambient room temperature, turned on and measurements taken at 0, 15, 30, and 60 minutes. The temperatures studied were 10, 20, 40, 72 and 90^{0}F.

The first result the EPA observed is that both in-

struments warmed up in approximately 30 minutes, even at very cold ambient temperatures. This time frame allows all optics to reach an equilibrium temperature and meets the guidelines stated in the instrument operating manual.

However, as shown in the graph below, a significant difference was found in the effective ambient operating temperatures of the two instruments. Without temperature control, accurate results were produced for an operating temperature range from 40° to 90°F. With temperature control employed, however, this operating range was extended down to 10°F.

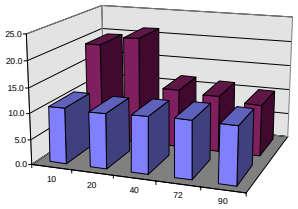


Figure 2. *MTBE results at different ambient temperatures; instruments with or without temperature control*

DEVELOPMENT OF CALIBRATION FUEL SETS

While hardware is an important factor in the instrument's stability and accuracy, it is also critical to develop an accurate calibration set in order to produce the most accurate results. Most spectroscopic instruments are calibrated by the user, using fuel with property values pre-determined by the user using standard ASTM methods. A complete and reasonably accurate user calibration can take years to accomplish and requires a high level of technical expertise. Because most calibration sets are based on sample results determined using ASTM methods, the errors inherent in these analyses are introduced into the spectroscopic calibration.

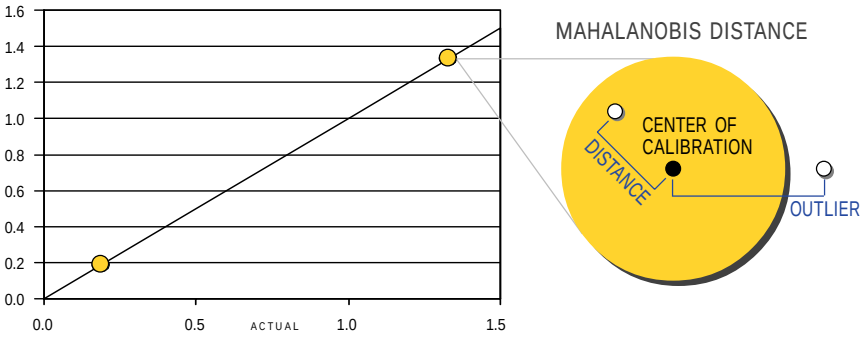
The PetroSpec analyzer is pre-calibrated with synthetically produced, judiciously selected calibration samples, offering a unique advantage over other spectroscopic instruments. PetroSpec established the critical wavelengths to independently measure each chemical of interest and to determine naturally occurring chemicals in the fuels that interfere with the chemical analysis. This extensive research has produced over one hundred gravimetrically prepared fuels, each containing a unique combination of chemicals to be analyzed and using the chemicals that interfere with the analysis.

As a leader in spectroscopic-based petroleum analysis equipment, PetroSpec has developed virtually all ASTM methods in this area. In the development of our calibration fuel sets, PetroSpec also utilized the added expertise of many key scientists in the petroleum community, including BP-Amoco, Shell, Chevron-Texaco and Ethyl Corporation. These companies supplied both concepts and fuels for this calibration.

Universal acceptance of the instrument became a guiding point from the outset of PetroSpec's research and development process. Therefore, it was critical that the instrument arrive to the customer precalibrated, making PetroSpec's initial development of an accurate and reproducible fuel-based calibrations set essential. The development and fine tuning of the calibration fuel set has been ongoing since 1989.

Once an instrument is programmed with PetroSpec's factory calibration fuel set, it is also important that this calibration reflect the composition of users' fuel. The calibration can only be expected to predict fuel samples that have similar chemical compositions to those in original calibration fuel matrix. Below is a concrete example of this limitation using our benzene method ASTM D-6277. One can easily detect the amount of benzene in a gasoline mixture by measuring the benzene absorption at 673 cm^{-1}. To quantify the amount of benzene in gasoline, a set of synthetic samples are prepared in which the amount of benzene in the fuel is precisely known. In the figure below, samples including 0.20 and 1.38 volume percent benzene are included, establishing a calibration curve (or line). From this calibration set, only benzene analysis of sample containing between 0.20 and 1.38 volume percent can be interpolated correctly. Samples outside the range of samples in the calibration set are an extrapolation and thus are not valid.

Figure 3. *Benzene ASTM D 6277*



To determine if a test fuel is outside the range of the calibration fuel set, an outlier analysis based on the Mahalanobis distance is incorporated into every PetroSpec analysis. The Mahalanobis distance determines scalar distance between 1) the center of mass of spectral data composing the calibration fuel set, and 2) the spectral data composing the fuel sample. The spectral data from the calibration fuel sample set spans an n-dimensional space (shown in yellow, above). The center of that space is determined. If the distance from the center of the calibration to the sample is greater than the limit of the calibration space, the sample is considered an *outlier*. In such a case, the PetroSpec instrument automatically alerts the user that an outlier has been determined. The calibration set must be expanded (updated) to yield a result that can be trusted.

All PetroSpec IR based fuel analyzers include software that allows users to include the outlier results in future calibrations. This is accomplished by either adjusting one of the universal calibrations included in the original factory-installed set, or by developing a completely new calibration. Up to 10 new property calibrations can be programmed.

OTHER COUNTRY REGULATORY AGENCIES THAT USE PETROSPEC INSTRUMENTS

Various government-run oil companies, including Pemex (Mexico), YPF (Argentina), and Petrobras (Brazil), use PetroSpec equipment. In Asia, the Thailand and Malaysian governments rely on PetroSpec units for field testing, and customs agencies in France, Greece and Italian employ PetroSpec's portable instruments in their European fuel evaluation programs.