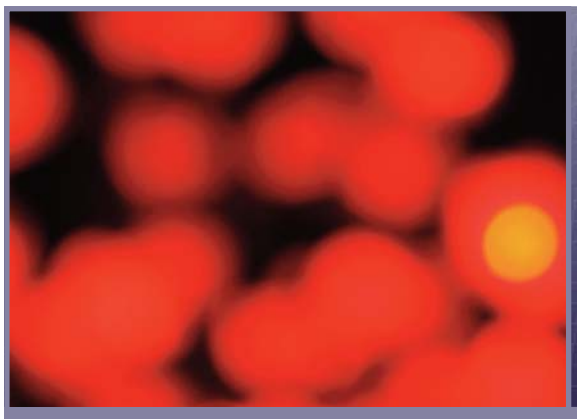

Fuel Analysis by Mid-Infrared Spectroscopy

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The analysis of fuels, especially gasoline and diesel automotive fuels, by a rapid, accurate, and easy-to-use method which can be applied also in the field is very important for the monitoring of fuel composition and quality at several points in the manufacturing process and distribution chain. Such a method is valuable in laboratories at refineries where fast, accurate results are needed, in small terminal and pipeline laboratories where it is not possible to perform all specified tests but monitoring fuel quality is necessary, at gas stations itself, and in mobile laboratories.
IR spectroscopy is the method of choice for such applications for several reasons discussed below.

Advantages of IR Spectroscopy

The IR spectrum contains direct molecular specific information so that many parameters can be determined simultaneously from one measurement.

The evaluation of the spectrum that leads to the final results can be performed automatically by microprocessors, so that the instrument can be automated. Thus IR instruments can be operated by personnel that have no background or training in analytical chemistry.

The measurement is very quick in comparison to other analytical methods, in the order of one minute per analysis.

The instruments to measure the IR spectrum can be made very compact, stable, and robust so that they are portable and may be used in harsh conditions and in the field. The IR analysers do not need any gas or other supply, as neither separation steps nor chemical reactions are required prior to the measurement.

No sample preparation is necessary, only an electrical power line is needed.

No other analytical technique combines all these advantages.

Principle of IR Spectroscopy

Infrared (IR) radiation is electromagnetic radiation with a wavelength between 0.7µm and 100µm. This range is further divided in the Near-IR (NIR) range (wavelengths 0.7µm to roughly 4µm), mid-IR (wavelengths 4µm to roughly 20 µm), and far-IR (wavelengths 20µm to 100 µm).

For analytical applications, mostly NIR and mid-IR spectroscopy are used.

In IR spectroscopy, IR radiation in the desired wavelength range is directed through the sample to be analysed, and the intensity of the transmitted radiation is measured as a function of wavelength. The process that leads to attenuation (absorption) of IR radiation by the sample is excitation of vibrations of molecules in the sample.

These vibrations can be excited only by radiation of wavelengths that match the energy difference between the ground and excited vibrational state.

These wavelengths are different for different molecules; furthermore there are usually different vibrations in a given molecule. This is why IR spectroscopy allows for the simultaneous determination of many different substances in one sample by one measurement over a certain wavelength range.

If a vibration is excited by radiation of a specific wavelength, then the intensity of the IR radiation passing through the sample at that wavelength decreases. The more molecules are present, the more vibrations can be excited, and the more the radiation decreases.

Therefore, the concentrations of many different substances can be determined quantitatively by IR spectroscopy.

Application to the Analysis of Fuels

Gasoline and Diesel fuels are complex mixtures of many different hydrocarbons and hydrocarbon types. They contain alkanes (paraffins), alkenes (olefins) and aromatics.

Moreover, driven in part by the desire to use renewable fuel sources, alcohols and ethers are blended into gasolines, and FAME from vegetable oils is very frequently a component in Diesel fuels.

Additionally, additives like MMT to increase octane numbers in gasolines or 2-EHN to increase the cetane number in Diesel fuels are used. Small quantities (<0.1 %) of such additives have a significant effect on some fuel properties.

In order to accurately determine the composition of complex mixtures, mid-IR spectroscopy can be very successfully applied to perform a quantitative analysis of gasoline and Diesel fuel.

In gasolines, it is important to know the concentrations of individual compounds, like benzene, ethanol or MTBE, but also total concentrations of different hydrocarbon types, like olefins and aromatics or the oxygen content.

With mid-IR spectroscopy, the lines of individual aromatics (like benzene, toluene, xylenes etc.) and oxygenates (like ethanol, methanol, MTBE, ETBE, etc.) can be resolved and used to calculate the concentrations of each compound, with no or minimal interference from other, chemically similar substances.

These individual lines as well as lines coming from certain hydrocarbon types (like olefins and aromatics) can then be used to calculate also the total concentrations of olefins, aromatics and oxygenates as well as the oxygen content of the gasoline sample.

Some additives like MMT which are present at concentrations typically only around 100 ppm can still be determined with mid-IR spectroscopy since the lines are very strong.

In Diesel fuels, the mid-IR spectrum allows to discriminate between single-nuclear and poly-nuclear aromatics. The FAME concentration can be measured with high accuracy using a very strong line. Unreacted vegetable oil and FAME have different mid-IR spectra, therefore with mid-IR spectroscopy, it is possible to detect if vegetable oil or FAME is present

in the Diesel sample.

2-Ethylhexylnitrate (2-EHN) is often used as additive, with concentrations typically between 50 ppm and 400 ppm. Even at this level, 2-EHN can be quantitatively determined with mid-IR spectroscopy.

Determination of Complex Parameters of Fuels

For monitoring fuel quality, not only the compositional analysis is of interest, but also the values of complex properties, like octane numbers for gasolines, cetane numbers of Diesel fuels or distillation properties are important.

Since these complex properties are correlated with the composition of the fuel samples, it is possible to calculate such complex properties from the IR spectrum. To be able to do that, a data base which contains the spectra or certain spectral regions of fuels samples and the values of the complex properties of interest as determined by a reference method (knock engine, distillation apparatus) is necessary.

Instruments for Fuel Analysis

Since the IR absorption for lighter molecules as present in gasoline is higher than for heavier molecules as present in Diesel fuel, different cells with different thickness need to be used for the different fuel types. Also, the methods to extract the information from the IR spectra are different for different fuel types.

Therefore, there used to be dedicated Gasoline and Diesel fuel IR analysers on the market.

This has changed with the ERASPEC from the Austrian manufacturer Eralytics GmbH. The ERASPEC is the first portable mid-FTIR spectrometer designed as a fully automated multi fuel analyser.

It uses an innovative technology to switch within a few seconds between a Gasoline and a Diesel/Jet fuel measurement cell.

The use of a small, integrated industrial PC board with large memory and high processing speed allows storing software for the analysis of different fuels types.

With these features, it is possible to perform quantitative analyses for Gasoline, Diesel fuel and Jet fuel using just one single portable analyser.

Highly accurate results for more than 40 fuel parameters, several important fuel properties, like Octane and Cetane numbers as well as Biodiesel (FAME) in conventional Diesel and Jet fuel are presented on a large full color touch screen in seconds.

The unmatched precision, speed and ease of operation make ERASPEC the preferred analyser for fuel compliance testing in the QC laboratory, fast at-line refining streams quality follow-up, fuel blending and research applications.

It follows in each detail the requirements of the latest international standards ASTM D5845, ASTM D6277, EN 238 and EN 14078

The heart of the system is a patented, rugged interferometer field-proven to be used also in challenging environments. The internal components are mounted on anti-vibration platforms and the portable aluminum instrument housing allows for field tests directly at the point of sale.

Additionally ERASPEC is an excellent solution for the global challenge posed by adulteration, smuggling and dilution in the fuel industry. With the touch of a button ERASPEC provides a detailed spectral analysis of fuels directly in the field to ensure the quality of fuels, to identify contaminations and to prevent impacts on public health, environment and engine components.

For more information on ERASPEC visit www.eralytics.com or send an email to office@eralytics.com.

Gasoline Analysis by ERASPEC (selected parameters)

Substance	Range	Repeatability	at:	Detection Limit
Benzene	0 - 10 Vol%	0.018 Vol%	@ 0.5 Vol%	0.06 Vol%
All other Aromatics	0 - 20 Vol%	0.2 Vol%	@ 5 Vol%	0.7 Vol%
MTBE	0 - 20 Vol%	0.08 Vol%	@ 6 Vol%	0.5 Vol%
ETBE	0 - 25 Vol%	0.1 Vol%	@ 9 Vol%	0.5 Vol%
Methanol	0 - 15 Vol%	0.05 Vol%	@5 Vol%	0.5 Vol%
Ethanol	0 - 25 Vol%	0.15 Vol%	@ 10 Vol %	0.5 Vol%
All other Oxygenates	0 - 25 Vol%	0.1 Vol%	@ 10 Vol%	0.5 Vol%
Total Oxygen	0 - 12 m%	0.04 ml%	@ 1.6 m%	0.09 m%
Total Olefins	0 - 80 Vol%	0.7 Vol%	@ 15 Vol%	0.5 Vol%
Total Aromatics	0 - 50 Vol%	0.8 Vol%	@ 33 Vol%	0.5 Vol%
Saturates	0 - 100 Vol%	1.1 Vol%	@ 45 Vol%	Not Applicable
Di-Olefins	0 - 15 Vol%	0.18 Vol%	@ 5 Vol%	0.2 Vol%
DCPD (Dicyclopentadiene)	0 - 15 Vol%	0.11 Vol%l	@ 5 Vol%l	0.5 Vol%
MMT (100µm-cell)	0 - 10000 mg/l	12 mg/l	@ 100 mg/l	30 mg/l
CMT (100µm-cell)	0 - 10000 mg/l	12 mg/l	@ 100 mg/l	30 mg/l
Manganese (by MMT)	0 - 2500 mg/l	3 mg/l	@ 100 mg/l	5 mg/l

Parameter	Range	Repeatability	at:
RON	70 - 110	0.4	@ 92 RON
MON	60 - 100	0.3	@ 82 MON
DENSITY	0.5 - 1.999 gcm^{-3}	0.0006 gcm^{-3}	@ 0.7800 gcm^{-3}

Diesel Fuel Analysis by ERASPEC (selected parameters)

Concentration of:	Range	Repeatability	at:	Detection Limit
Biodiesel (FAME)	0.3 - 40 Vol%	0.2 Vol%	0 - 10 Vol%	0.3 Vol%
Total Aromatics	0.5 - 60 Vol%	0.3 Vol%	@ 20%	0.5 Vol%
Polynuclear Aromatics (PNA)	0.5 - 50 Vol%	0.1Vol%	@ 5 Vol%	0.5 Vol%
Cetane Improver (2-EHN)	50 - 8000 mg/l	23 mg/l	0 - 800 mg/l	50 mg/l

Parameter	Range	Standard Deviation	Repeatability	at:
Cetane Number	20 - 80	0.32	0.8	@ 50
Cetane Index	20 - 80	0.25	0.7	@ 50
T90		0.4°C	1.0°C	@ 330°C
Density	0.5 – 1.999 gcm^{-3}	0.7800 gcm^{-3}	0.0006 gcm^{-3}	0.7800 gcm^{-3}

Jet Fuel Analysis by ERASPEC (selected parameters)

Parameter	Range	Repeatability	at:
Freezing Point	-25 - -75 °C	0.8°C	@ -55 °C
Flash Point	25 – 65 °C	0.8°C	@ 45°C
Smoke Point	19 – 29 mm	0.2 mm	@ 23 mm
Total Aromatics	0 – 60 Vol%	0.45 Vol%	@ 17 Vol%
Viscosity @ 20°C	1.2 – 2.1 mPas	0.03 mPas	@ 1.7 mPas
Viscosity @ -20°C	2.4 – 4.5 mPas	0.11 mPas	@ 3.7 mPas
FAME	0.08 – 6 Vol%	0.01 Vol%	0.3 Vol%
PNA	0.25 – 10 Vol%	0.08 Vol%	0.4 Vol%
Density	0.5 – 1.999 gcm^{-3}	0.0006 gcm^{-3}	0.7800 gcm^{-3}

NOTE: The range and repeatability for calculated parameters depend on the database used