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### **DATASHEET EOC-SI-R7000 Series Raman Process Analyzer System**



### 1. System introduction

The EOC-SI-R7000 series online Raman analysis system provide on-line analysis for the mixture composition of contents. The EOC-SI-R7000 series online Raman system can provide fast, accurate and stable detection methods for the composition and properties of various homogeneous liquid mixtures. By building a corresponding quantitative analysis model, the system can be widely used in various types of companies. Continuous or intermittent production process, real-time online detection of its product composition and content, and provide key measurement information for advanced control and real-time optimization.

Due to in process application features, the EOC-SI-R7000 series analysis system can be directly used outdoors in the hazardous area or in the analysis cabin in a form of positive pressure explosion-proof. When the process sampling point is relatively close to the control room or operation room (distance ≤200m), the host of the analysis system can also be installed in the control room or operation room in non-explosion-proof form, and connect to the on-site Raman probe.

#### Advantages of Raman spectroscopy:

- Vivid peaks
- fast, efficient and accurate analysis
- Non-contact sample
- No sample consumable
- No need for sample pretreatment
- On-site maintenance free
- No effect on water or gas
- Flexible sampling and easy to use

#### Raman Effect

The Raman effect exists in all molecules: gas,Liquid or solid, every molecule has a corresponding Raman spectrum. Raman spectroscopy can reflect both the molecular vibration information of molecular groups, such as C = C, C-C, C = O, benzene rings, etc., and the structural information of isomers. Since the Raman spectrum has the characteristic of directly reflecting the structure and content information of the measuring sample, we can use this feature to obtain the composition content or attributes of the sample by establishing a mathematical model between the Raman spectrum and the corresponding sample.

## 2. Working principle

The working principle of the online Raman analysis system is shown in Figure 1. The monochromatic excitation light emitted by the laser illuminates the sample to be measured in the sampling tube through a special optical fiber and a Raman probe. The excited Raman scattered light is collected by the probe, and transmitted to the spectrometer for spectroscopic and analog-to-digital conversion by a special optical fiber. The Raman spectrum data is pre-processed and calculated in the analytical model to obtain the composition content or quality index of the corresponding measuring sample.

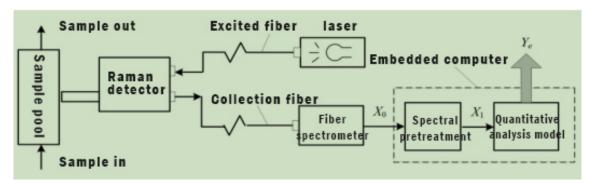


Figure 1. Online Raman analysis principle

## 3. System composition

The hardware of the analysis system is mainly composed of on-site sampling cabinet and main cabinet. According to the number of detection channels, it is

divided into two types: single channel and multi-channel. The system components are shown in Figures 2 and 3 respectively.

For single-channel systems, there is only one sampling loop in the sampling cabinet. For a multi-channel system, it can take the form of multiple sampling cabinets, every one of which has only one sampling circuit; or a sampling cabinet with multiple sampling circuits inside. The specific configuration depends on the actual process pipeline conditions.

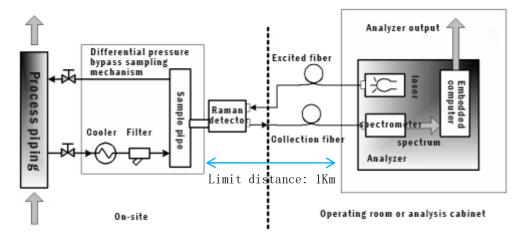


Figure 2. Single channel Raman Analysis system

The on-site sampling cabinet is shown in Figure 4. It is a passive intrinsically safe device (except for flameproof temperature and pressure transmitters), which can be placed directly at the process site near the sampling point. After the process pipe is properly trepanned, the sampling pipe line will be led out, and connected to the sampling cabinet through the flange. The liquid to be measured flowing through the process pipeline is driven by the pressure difference between the front and back of the process pipeline, enters the sampling cabinet through the sampling pipeline, and finally returns to the process pipeline. For high temperature liquids, water cooling is adopted in the sampling cabinet to cool down. In addition, the sampling cabinet is also equipped with an instrument air interface to maintain a slight positive pressure in the sampling cabinet and protect key components such as Raman probes from contamination.

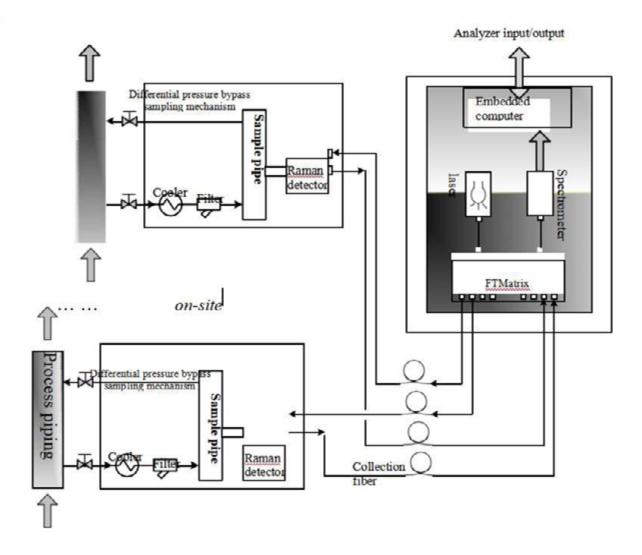


Figure 3. Multi-channel Raman Analysis system





Figure 4. On-site sampling cabinet of Analysis system

The main cabinet is divided into two types: positive pressure explosion-proof type and non-explosion-proof type, as shown in Figure 5. Positive pressure explosion-proof host cabinet is suitable for outdoor storage in the process site or the analysis cabin near the sampling point. Because the distance to the sampling point is short, the required optical fiber is short, the Raman signal is relatively strong, the signal-to-noise of the analysis system is relatively high, and the detection limit is low. However, the investment is relatively large, and special cooling equipment is required to ensure that the temperature in the main cabinet can meet the requirements for the normal operation of various optical and electrical components.

Non-explosion-proof host cabinet, suitable for placing in DCS cabinets or operation rooms, especially suitable for samples with strong Raman signals, such as aromatic hydrocarbons and gasoline. When the sampling point is far away from the DCS cabinet, the strength of the Raman signal weakens significantly, so the distance between the main cabinet and the sampling cabinet is required to be less than 200 meters. The investment of the non-explosion-proof main cabinet is relatively small, no special analysis cabin or refrigeration equipment is needed, and the surrounding environment of the main cabinet is relatively clean and tidy; and standard cabinets can be used with large installation space, which is not only suitable for single-channel inspection applications but also suitable for multichannel detection applications.



Figure 5. Main cabinet of analysis system:

(A). single-channel positive pressure explosion-proof type;

(B). Multi-channel non-explosion-proof

For a single-channel analysis system, a set of separate optical equipment is set up in the main cabinet, including lasers, spectrometers, etc. The multi-channel system applies time-division multiplexing technology to multiple detection channels, so that every channel can share the same laser and spectrometer (but Raman probes still need to be set up independently), thereby reducing the allocation cost of the optical equipment in every detection channel.

## 4. Application area

Petroleum and chemical	Pharmaceutical	Wine-making	
Chemical synthesis	Isomer conversion	Alcohol concentration	
Polymerization	Response monitoring	Concentration of ethyl hexanoate	
Composite material	Synthesis and crystallization of drug intermediates	Concentration of ethyl lactate	
Adsorption separation device	Quality control		
Distillation equipment	Raw material inspection		
Oil blending	Intermediate product detection		
Aqueous solution	Final product inspection		

## 5. Technical parameters

Sheet 1. EOC-SI-R7000-532 Parameters

Spectral parameters			
Excitation light source	532nm Narrow Linewidth Stabilized Laser		
Excitation power	1200 mW (Output power can be set in software)		
Spectral detection	$200 \sim 3300 \text{ cm}^{-1}$		
range			
Resolution	6 cm <sup>-1</sup>		
Wavelength stability	≤0.1 cm <sup>-1</sup>		
Spectral stability	$\sigma/\mu < 0.5\%$ (COT 8 hours)		
Temperature stability	Spectral shift $\leq 1 \text{ cm}^{-1} (10\text{-}40 ^{\circ}\text{C})$		
Spectral intensity	$<\pm 3\%$ (in 5 ~ 40 °C)		
change	₹3% (III 3~40 C)		
Detector			
Type	Ultra-high sensitivity and rapid cooling CCD		
Detector cooling	-10 °C		
temperature	-10 C		
Detection range	200-1100 nm		

Effective Pixels	2048*64			
Dynamic Range	50000: 1			
Pixel size	14 ×200 μm			
ADC solution	16bit			
F/#	≥2.0			
Analysis system				
Measurement object	Liquid homogeneous mixture			
Measurement	Mixture component mass content (w %)			
parameters				
Measurement accuracy	Measuring range $0 \sim 100\%$ , Routine analysis repeatability error $\leq \pm 0.05\%$			
	(Dedicated signal amplification processing, with the lowest detection limit			
	50 ppm)			
The sampling period	sampling time: $10 \sim 120$ s, Warm-up time: 5 minutes			
	Sample working pressure ≤5.0 MPa			
Test Conditions	(Surface pressure)			
	Differential pressure in and out of the			
	sampling tube ≥0.10 MPa			
	If the sample temperature is higher than 80 °C, the water cooling mechanism			
	needs to be automatically introduced in			
Instrument working	temperature: $-10 \sim 40  ^{\circ}C$ , humidity $\leq 85  \%$			
environment				
E1i	Main cabinet explosion-proof mode: positive pressure explosion-proof			
Explosion-proof grade	(optional),			
	Explosion-proof grade: Exp II CT6, Protection class: IP 65			
Remote monitoring	Remote display of current spectrum, analysis results and system status via			
function	Ethernet			
Analog signal output	DC 4 ~ 20 mA Current output (optional)			
System status output	Passive relay contact (optional)			
Digital communication	Modbus or OPC Protocol (Ethernet)			
MTBF	≥ 12 Months			
Else	Main cabinet power supply: AC220 V / 50Hz, Power: ≤1000W			
	Main cabinet size:			
	• Positive pressure explosion-proof type: 900 * 450 * 2100mm,			
	weight: 150 kg			
	• Non-explosion-proof type: 800 *800 *2100mm, weight: 150kg			
	Tron-explosion-proof type: 600 600 2100mm, weight: 130kg			

Spectral parameters			
Excitation light source	785nm Narrow Linewidth Stabilized Laser		
Spectral detection	$200 \sim 2000 \text{ cm}^{-1}$		
range	200 ~ 2000 Cm		
Resolution	C1		
Wavelength stability  Analysis system	≤0.1 cm <sup>-1</sup>		
Measurement object	Liquid homogeneous mixture		
Measurement	Mixture component mass content (w %)		
parameters	Wixture component mass content (w /0)		
	Measuring range 0 ~ 100%, Routine analysis repeatability error ≤±0.05 %		
Measurement accuracy	(Dedicated signal amplification processing, with the lowest detection limit		
771 1: : 1	50 ppm)		
The sampling period	sampling time: $10 \sim 120 \text{ s}$ , Warm-up time: 5 minutes		
	Sample working pressure ≤5.0 MPa		
Test Conditions	(Surface pressure)		
	Differential pressure in and out of the		
	sampling tube ≥0.10 MPa		
	If the sample temperature is higher than 80 °C, the water cooling mechanism		
	needs to be automatically introduced in		
Instrument working	temperature: $-10 \sim 35$ °C, humidity $\leq 85$ %		
environment			
Explosion-proof grade	Main cabinet explosion-proof mode: positive pressure explosion-proof		
	(optional),		
	Explosion-proof grade: Exp II CT6, Protection class: IP 65		
Remote monitoring	Remote display of current spectrum, analysis results and system status via		
function	Ethernet		
Analog signal output	DC 4 ~ 20 mA Current output (optional)		
System status output	Passive relay contact (optional)		
Digital communication	· /		
MTBF	$\geq$ 12 months		
Else	Main cabinet power supply: AC220 V / 50Hz, Power: ≤1000W		
	Main cabinet size:		
	Positive pressure explosion-proof type: 900 * 450 * 2100mm, weight:		
	150 kg		
	Non-explosion-proof type: 800 *800 *2100mm, weight: 150kg		

## **Applications**

## Fast, on-line analyze circulating liquid in adsorbent tower of PX unit

Para-xylene (PX) is an important chemical raw material. The terephthalic acid prepared from it can be used in the chemical and pharmaceutical industries. At the same time, it is also an important intermediate for the production of polyester fibers. At present, PX is mainly prepared by separating the mixed xylenes. Among a variety of separation processes, the simulated moving bed adsorption separation process has become a mainstream process for separating mixed xylenes due to its high production efficiency and good separation effect, and has been widely used.

At present, PX adsorption separation processes that have been widely used in industry include Parex process developed by American company UOP, Eluxyl process developed by French IFP. To ensure product purity and yield, an online Raman analysis system needs to be installed to achieve fast and accurate analysis of the PX adsorption and separation process. The online Raman analysis system was previously monopolized by American Process Instrument company and French Jobin Yvon company (referred to as JY company). Among them, JY is the designated supplier of French IFP, and its software is suitable for Eluxyl process.

In order to break source dependence on importing products and realize the localization of key analysis equipment, our company combined the development and application experience of more than ten years to develop the first online Raman analysis system for the pumping circulation line of adsorption towers in China, and owns independence Intellectual property. At present, the system has been successfully applied to the PX process of a refinery. The main analysis items: quality percentage of toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, and p-diethylbenzene in the circulating liquid.

The system consists of a on-site sampling cabinet and a positive pressure explosion-proof host cabinet. The sampling cabinet is placed directly at the process site, while the main cabinet is of a positive pressure explosion-proof type and placed in a special analysis cabin. The raw spectrum measured by the online Raman system is shown in Figure 6. Imported high-performance key optical components not only improves inspection Sensitivity, and significantly reduced noise levels, making the spectral signal-to-noise ratio above 2000: 1.

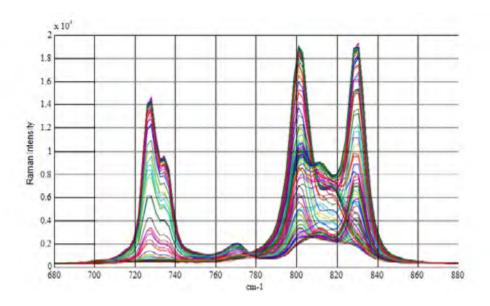


Figure 6 Raman spectrum of circulating fluid measured on site

To check the accuracy of the Raman analysis results of the circulating fluid, the process workshop collected a set of circulating fluid samples (24 samples) on July 5, 2016, and performed chromatographic analysis. By detecting the Raman spectrum of these samples and substituting them into the Raman quantitative analysis model, the Raman analysis values of each sample composition can be obtained. The comparison between Raman analysis and chromatographic analysis is shown in Figure 7. It can be seen that based on the self-developed circulating fluid quantitative analysis model, the online Raman system not only has fast analysis speed, on-site maintenance free, but also has high analysis accuracy.

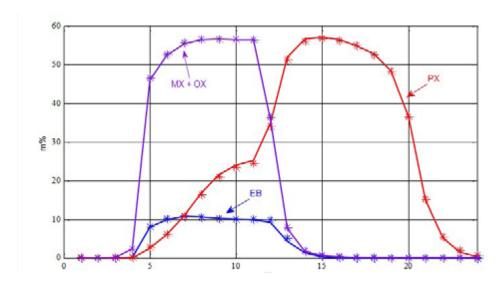


Figure 7 Comparison of quantitative analysis results of circulating fluid
(The solid line is the Raman analysis value, "\*" is Chromatographic value)

In order to investigate the repeatability of the online Raman analysis systems, we focus on 10 continuous operating cycles (each run cycle is about 30 min) fluctuation of the concentration distribution curve of the adsorption tower. It can be seen from Fig. 8 that for each key component, the fluctuation of the concentration distribution curve is small, and the repeatability of the analysis results is good.

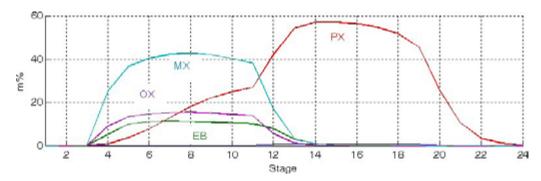


Figure 8. Fluctuation analysis curve of the concentration of the circulating liquid in the adsorption tower for 10 consecutive cycles

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In summary, the online analysis system for the pumping circulation line of the adsorption tower has the following distinctive features: its main technical indicators have reached the international advanced level, and the stable and reliable on-site operation won the full recognition of the refinery.

- Fast analysis speed. Due to the strong Raman characteristic and characteristic peak height of the aromatic hydrocarbon molecules, and the high sensitivity of the localized online Raman system, the spectrum acquisition time is only 5s and the analysis period is 9s.
- On-site maintenance free. The Raman spectrum detection method is noncontact, the on-line analysis system does not require complicated on-site maintenance work, and the daily maintenance of the sampling device is close to "maintenance-free".
- Analysis model is maintenance-free. The material components of the pumping circulation line of the adsorbent tower are complex, and the component variation range is large. Traditional modeling methods require a large number of

training samples. In order to overcome its limitations, we introduced a spectral analysis technique to build a quantitative analysis model based on the functional relationship between the characteristic peaks of each component and their content. This modeling method only needs to collect 1 representative set of circulating fluid samples, no calibration is required in daily use, and it can automatically adapt to large changes in the composition of the circulation line.

High analysis accuracy. The domestic Raman analysis system fully considers the influence of external measurement conditions (such as laser power and wavelength fluctuations, etc) on the analysis results, which makes its repeating measurement accuracy greatly improved. At the same time, it considers the influence of non-aromatic and C10 aromatics (except for PDEB) on the analysis results, so as to significantly improve the accuracy, and the deviation from the chromatographic value of manual sampling decrease significantly. Taking the PX content in the circulating fluid as an example, when the actual PX content varies from 0 to 60%, the analysis mean square error is only 0.38%.

#### Online analysis of the purity in PX device

As an important chemical raw material, the purity of PX products is strictly regulated at home and abroad: the purity of superior PX products is not less than 99.70% (mass fraction), and the purity of first-class products is not less than 99.50% (mass fraction). Currently, the standard method for measuring the purity of PX is gas chromatography, which specifies that at 95% confidence level, the repeatability error should not be greater than 0.04% (mass fraction) and the reproducibility error should be not greater than 0.09% (mass fraction).

The PX production process requires real-time, online testing of the purity of PX products. Although traditional gas chromatography has been applied to online detection, it has the disadvantages of complex operation, slow detection speed, and complicated equipment maintenance. The actual application effect is not ideal. The Raman spectrum detection method has the advantages of simple operation, maintenance-free, accurate and fast, clean and environmental protection, especially suitable for online detection in industrial processes. So our company developed an online Raman analyzer for the purity of PX products, and added it into on-site operation at a large industrial PX facilities in March 2015. The test object is the bottom liquid of the PX finished product tower T203.

In order to improve the detection sensitivity and shorten the fiber length, the mainframe of the Raman analyzer is placed in a standard analysis cabin in a positive pressure explosion-proof manner. Part of the measured spectrum is shown in Figure 9. The real-time dynamic trend of PX product purity is shown in Figure 10. After calculation, the repeatability error of this online Raman meter is 0.0044% (mass fraction), which is 10 times lower than the repeatability error specified by the national standard method SH / T 1486.2-2008.

Based on routine manual sampling chromatographic analysis data, the process shop evaluated the accuracy of the PX purity online Raman analysis system. The scatter distribution of PX Raman analysis and chromatographic analysis is shown in Figure 11. After calculation, the standard prediction error of this online Raman instrument is 0.0064%, and the maximum error is about  $\pm 0.02\%$ , which is lower than the reproducibility error of chromatographic analysis.

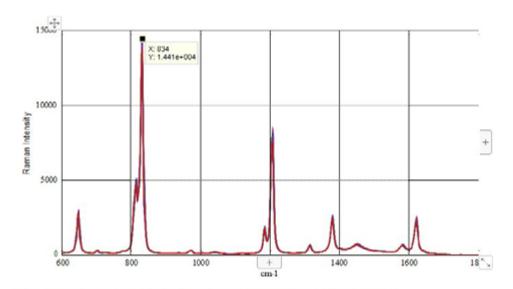
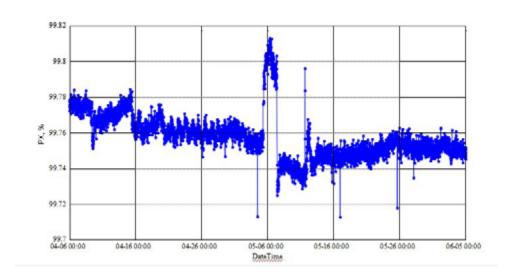


Figure 9 Raman spectrum of PX finished product measured on site



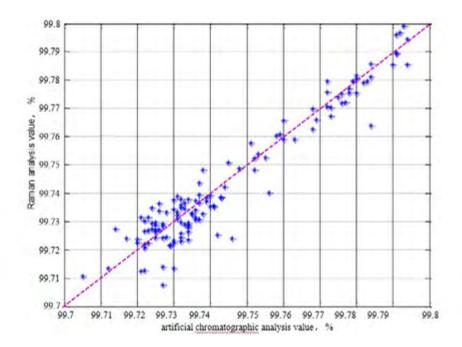


Figure 11 PX Raman analysis value vs artificial chromatographic analysis value

It can be seen that for online analysis of high-purity PX products, Raman spectroscopy has demonstrated its superiority. Long-term continuous on-site operation shows that the localized online Raman meter not only runs reliably and stably, has good repeatability and fast detection speed (sampling cycle is 2 min); moreover, the analysis and detection accuracy can fully meet the requirements of national standards.

In fact, the Raman analysis method has obvious technical advantages for the purity analysis of petrochemical products. For constant purity analysis, it is expected to replace conventional gas chromatography. Especially for the online analysis of the purity of aromatic products, the technical advantages of Raman analysis are more prominent because of its strong Raman signal and good characteristics.

# Online analysis of octane number in reformed gasoline from catalytic reforming unit

Catalytic reforming equipment uses naphtha as raw material, and improves its octane number through reforming reaction. The main operation goal of reforming is to achieve a balanced coordination between reformed gasoline octane number and liquid

yield. In order to optimize the operating conditions to improve the economic benefits of equipment, on-line detection of critical parameters such as reformed gasoline octane number is essential.

For reformed gasoline, because its octane number is mainly determined by the content of linear paraffins, sidechain paraffins, naphthenes, alkenes and aromatics in the oil, and these groups have corresponding Raman characteristic peaks in the Raman spectrum. In practice, it is only necessary to establish a regression model of these characteristic peaks and octane number. Based on this theory, we designed and developed a set of online Raman analysis system for gasoline octane number based on the actual needs of reforming equipment in a refinery.

The system consists of on-site sampling cabinets and non-explosion-proof mainframe cabinets. The sampling cabinets are placed directly at the process site, while the mainframe cabinets are placed between DCS cabinets near the process site. The raw gasoline stable spectrum measured by the online Raman analysis system is shown in Fig. 12. It can be seen that the fluorescence background has less interference and the signal-to-noise ratio is high.

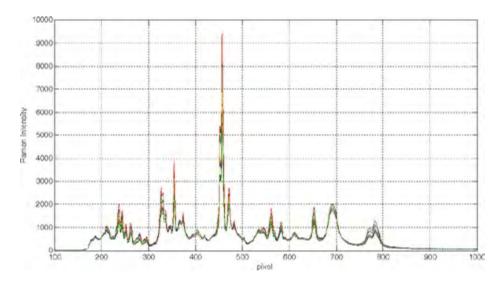


Figure 12 Original spectrum of partially reformed gasoline samples

As an important indicator of the anti-knock performance of gasoline, the research find that the octane number (RON) is closely related to the chemical composition of gasoline, especially the molecular structure of hydrocarbons in gasoline. Due to the complexity of gasoline composition, in order to establish a RON quantitative analysis

model, some representative daily analysis oil samples need to be collected. From the Raman spectra and laboratory analysis values of these oil samples, combined with gasoline Raman characteristic peak analysis, regression models of these characteristic peaks and RON can be established.

In order to evaluate the consistency between the online analysis value of the Raman system and the data of manual analysis, the reforming process workshop took the stable bottom liquid as the detection object, and organized a model comparison work on March 27, 2014. The comparison between the gasoline octane number values by online Raman analysis and the manual sampling analysis is shown in Figure 13.

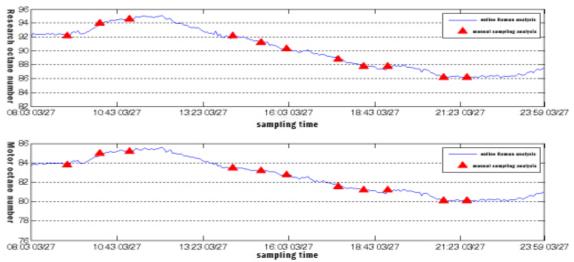


Figure 13 Stabilized gasoline octane number comparison of online Raman value and experimental analysis value

The experimental operation mode is to obtain different reaction products by artificially changing the reaction temperature under the condition that the feed properties of the reforming reaction are basically unchanged. It can be seen from Figure. 13 that the online Raman analysis value can fully reflect the influence of operating conditions on the gasoline quality index, and has a high degree trend consistency with the sampling analysis data.

Based on this, the refinery examined the long-term repeatability and trend of the model, combined with daily sampling to analyze oil samples, and evaluated the model's agreement. After long-term on-site operation, it is shown that:

- (1) The online analysis system has the advantages of fast analysis speed, short sampling period, no need for complex sample pretreatment, flexible sampling, convenient use, in-site maintenance free, and environmental friendly during the analysis process, etc;
- (2) By comparing actual test data with daily analysis data, the online analysis system can well reflect the impact of various operating conditions on the octane number, and the repeatability error does not exceed 0.05 octane number. The standard error of prediction is 0.31 octane number, and the average absolute value error is 0.26 octane number.
- (3) The online operation data of the analysis system is consistent with the changing trend of laboratory sampling analysis data and equipment process conditions (such as reaction temperature), which can meet the actual needs of subsequent online advanced control systems and optimization of operating conditions.

# On-line analysis of key indicators of finished gasoline from gasoline pipeline blender

Gasoline pipeline blender equipment uses catalytic gasoline, reformed gasoline, alkylated oil, naphtha, MTBE, and a small amount of non-aromatic component oils as raw materials. The proportion of component oils is adjusted to produce the finished gasoline according to market demand. Focused gasoline quality indicators in the blending process include: The research octane number( RON), anti-knock index, aromatic content, olefin content, oxygen content, etc.

For on-line detection of the above quality indicators, Raman spectroscopic analysis technology not only has the common advantages of fast spectroscopic detection speed and on-site maintenance free, but also has the characteristics of Raman spectroscopy which can directly reflect the main groups (such as aromatic hydrocarbons, alkene, isoparaffin, ether / alcohol, etc.). So it is particularly suitable for the analysis of the above-mentioned key indicators of gasoline. By taking the blender equipment of gasoline pipeline in a refinery as an example, the application of the above Raman spectroscopy analysis method in actual production will be introduced as below.

The refinery has adopted a gasoline pipeline blending process. The component oils include: desulfurized refined catalytic gasoline (referred to as "catalytic gasoline"), heavy component reformed gasoline (referred to as "reformed gasoline"), non-fragrant gasoline(referred to as C5 and C6 non-aromatic produced by reforming equipment), naphtha and MTBE. Except for naphtha and MTBE, other component oils come directly from the production equipment, without buffering in the middle tank. In order to achieve the card edge control of blended gasoline quality, the overall structure of the gasoline pipeline blending optimization control system used is shown in Figure 14. As the key to optimizing the implementation of the control system project, the fastness and accuracy of the blended gasoline online analyzer AT10 is very important.

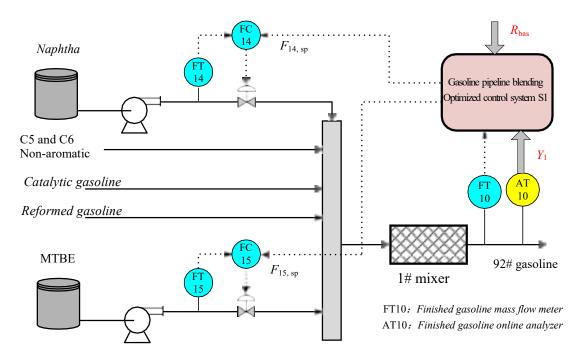


Figure 14 Structure of the optimal control system for the gasoline blending process

#### **Establishment of Quantitative Analysis Model for Finished Gasoline**

We first analyzed the oil samples in combination with the finished gasoline collected in daily production, and measured to obtain the original Raman spectra of these oil samples. In order to establish a quantitative analysis model of aromatics, olefins, and oxygen content, the corresponding Raman spectral characteristic bands were obtained by correlation analyzing the artificial analysis data of aromatics, olefins, and oxygen content in training samples collected by the refinery analysis center. Based on the above characteristic spectrum segment, i.e. based on the above training samples, a regression algorithm can be used

to establish a high-precision quantitative analysis model

As an important indicator for the anti-knock performance of gasoline, RON, anti-knock index are closely related to chemical composition of gasoline. So the Raman characteristic peaks related to the above composition are selected as model inputs, and a nonlinear regression method is introduced to establish a Raman quantitative analysis model of RON and anti-explosion index.

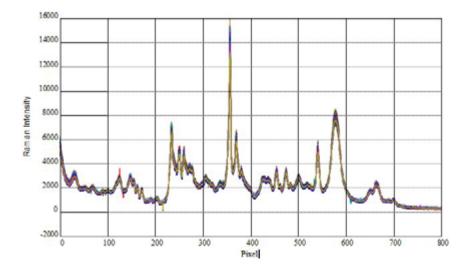
In order to verify the accuracy of the above analysis model, the analysis data was compared with a large number of finished gasoline samples collected daily by the analysis center. The comparison results are shown in Table 3 . The Raman analysis model evaluation of the finished gasoline indexes. It can be seen that the average error between the Raman analysis value and the laboratory analysis value of each index is as follow: RON, anti-knock index  $\leq 0.3$ , aromatics / olefin content  $\leq 1.0$  V%, and oxygen content  $\leq 0.10$  m%.

Table 3. Raman analysis model evaluation of various indexes of finished gasoline

Analysis attributes	RON	Antiknock index	Aromatic content, V%	Olefin content, V%	Oxygen content, m%
Raman method measuring range	80 ~ 110	70 ~ 100	0 ~ 60	0 ~ 60	0~10
Raman repeatable error	≤±0.05	≤±0.05	≤±0.2	≤±0.2	≤±0.04
Raman mean error	≤±0.27	≤±0.22	≤±1.0	≤±1.0	≤±0.10
National standard analysis	GB/T 5487	GB/T 503	G	B/T 11132	SH/T 0663
Repeatable errors allowed by national standard	0.2	0.3	1.3	1.8	0.05
Reproducibility error allowed by national standard	0.6	1.1	3.7	5.6	0.22

## Application of quantitative analysis model for finished gasoline

The online Raman analysis system embedded with the quantitative analysis model of the finished gasoline was put into operation at the actual site of the gasoline blending installation in December 2015. It can simultaneously analyze 5 key quality indicators such as the finished gasoline RON. The raw spectrum of the blended gasoline obtained by partial continuous measurement is shown in Figure 15. For the step change of MTBE and naphtha flow, the dynamic response of the RON Raman analysis value of the finished gasoline is shown in Figure 16. The increase in high-octane MTBE flow lead to increase of gasoline RON significantly, gasoline RON decreases accordingly while the increase in low-octane naphtha flow.



It can be seen that the response of the gasoline RON Raman analysis value is fast, and it has a simple and clear corresponding relationship with the main optimization variables. The on-site operation results show that the online Raman system not only has the advantages of fast analysis speed, on-site maintenance free and so on, but also reaches a high level in measurement repeatability and accuracy.

Based on the above Raman analyzer, we have developed the corresponding gasoline blending optimization software. By adjusting the MTBE and naphtha blending amounts in real time, the software maximizes economic benefit for refinery on the premise of ensuring the "card edge" control of gasoline quality indicators.

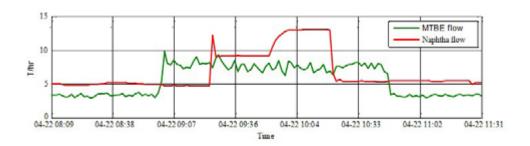


Figure 16. Dynamic response of the key indicator RON of gasoline blending

#### Application of quantitative analysis model for liqueur production

We first analyzed the liqueur samples of the finished liqueur collected in the daily production of Wuliangye Group, and obtained the original Raman spectra of these samples. In order to establish a quantitative analysis model for alcohol content, ethyl hexanoate, ethyl acetate and ethyl lactate content, combining with the data of the alcohol content, ethyl hexanoate, ethyl acetate and ethyl lactate content of training samples collected by the winery analysis center artificially, the corresponding Raman spectral characteristic bands were obtained by correlation analysis. Based on the above characteristic spectrum segment, i.e. based on the above training samples, a regression algorithm can be used to establish a high-precision quantitative analysis model.

As important indicators of liquor, alcohol content, the chemical composition of ethyl hexanoate, ethyl acetate and ethyl lactate are closely related. So the Raman characteristic peaks of the above composition are selected as the model input, and a nonlinear regression method is introduced to establish a Raman quantitative analysis model of alcohol content, ethyl hexanoate, ethyl acetate, and ethyl lactate index.

In order to verify the accuracy of the above analysis model, the analysis data was compared with a large number of finished liquor samples collected daily by the analysis center. The comparison results are shown in Table 4. The Raman analysis model evaluation of various indicators of liquor. It can be seen that the average error between the Raman analysis value and the laboratory analysis value of each indicator is very good.

Table 4. Raman analysis model Evaluation of various indexes of liquor

Analysis	Alcohol	Ethyl	Ethyl acetate	Ethyl lactate
attributes	content	hexanoate		
Raman method	3 ~ 100	0.01 ~ 10%	0.01 ~ 10%	0.01 ~ 10%
measuring range				
Raman repeat	≤±0.05	≤±0.05	≤±0.05	≤±0.05
error				
Raman mean	≤±0.27	≤±0.22	≤±0.22	≤±0.22
error				

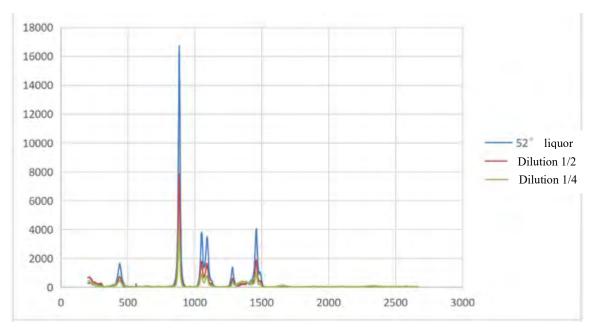


Figure 17. Spectrum of liquor by Raman spectra method