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HUMAN HEALTH | ENVIRONMENTAL HEALTH

VOLUME 11 | November 2009
INDIA ANALYTICAL SCIENCES

Dear Readers

In every volume of FRESH we have incorporated variety of instrumentations and applications related to the industry types. We have also listened to the requests from various readers to include specific applications and product notes related to ongoing analytical issues.

The previous issue of FRESH was dedicated to environmental applications which are the burning issues of today's world. PerkinElmer application teams are continuously working on to provide the solutions in various industrial, research and academic segments.

This edition of FRESH is dedicated to the Petroleum and Hydrocarbon industries. The challenges in this area are enormous due to global economy; limited reserves of the crude and regulations for the consumption. Since this segment is governed by the methodologies of UOP, ASTM etc. norms the reliability of the results is the key factor.

PerkinElmer's range of instrumentation and technology provide the solutions to Petrochemical industry right from the crude to various byproducts. Some of the applications related to the hydrocarbon and fuel analysis are covered in this issue. We are eager to get comments and suggestions from you.

FOR CLEANER FUEL

WHAT'S **Fresh** inside...

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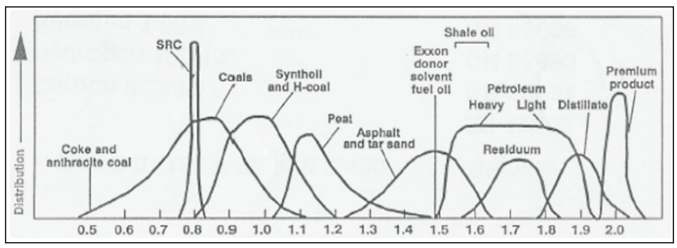
Crude oil process optimization with EA 2400 Series II Organic Elemental Analyzer

Organic Elemental Analyzer is common tool in the Oil and Petroleum Industries. The PerkinElmer 2400 Series II CHNS/O Elemental Analyzer (2400 Series II) is a powerful instrument for the rapid determination of carbon, Hydrogen, Nitrogen, Sulphur and Oxygen content in the organic and other types of materials. It has the capability of handling wide variety of samples; including solids, liquids, volatiles and viscous samples.

Based on the classical Pregl-Dumas method samples are combusted in pure oxygen environment. With the resultant combustion gases measured in the automated fashion.

Crude oil contains a mixture of hydrocarbons. The most common ones are linear aliphatic alkanes, cycloalkanes, aromatic hydrocarbons and many others. Each of these molecules will affect the physical properties of the crude oil. Hydrogen to Carbon (H/C) mole ratio is an indirect quality measure of the fossil fuel. Higher H/C mole ratio fraction will have lower un saturation in the hydrocarbon molecules and offer higher combustion efficiency.



Hydrogen/carbon mole ratio

Typical H/C Ranges and Average Values for Hydrocarbons from Various Sources

Type	Range	Average
Premium Product	1.95 - 2.05	2.00
Distillate	1.80 - 2.00	1.90
Light Crude	1.70 - 1.90	1.80
Heavy Crude	1.50 - 1.75	1.63
Asphalt and Tar Sands	1.25 - 1.65	1.45
Peat	1.00 - 1.45	1.10
Synthoil and H-Coal	0.80 - 1.20	0.97
Coals	0.50 - 1.10	0.84
Solvent Refined Coal	0.76 - 0.84	0.80

H/C Mole ratio varies with the source of hydrocarbon

The short chain aliphatic alkanes (from 5 to 8 carbon atom chain) from crude oil are typically processed in to petrol whereas the longer chain(9-16 carbon atom chain) into diesel fuel and kerosene. Higher molecular weight aliphatic alkanes and heavier paraffinic wax are often used as lubricants and heat transfer applications.

Cycloalkanes or more commonly known as napthenes is usually cracked to higher value linear chain products. The cracking process involves the use of Pt (Platinum) catalyst. In the napthenes cracking reaction chamber. The Pt catalyst will have carbon built up over time. The carbon deposited will greatly reduce the

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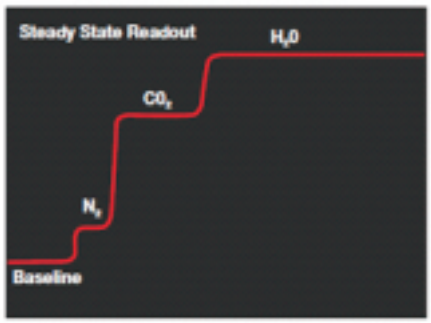
Pt catalyst used in Naphtha cracking process covered with carbon (-4.3% wt/wt) deposit in the reaction chamber.

conversion efficiency of the Pt Catalyst. Periodically the Pt catalysts in the reactor need to be regenerated to improve the conversion efficiency. On the other hand premature regeneration of the Pt catalyst will cause undesirable loss due to down time in the process. EA 2400 Series II is commonly utilized to monitor the degree of carbon built up on the Pt catalyst in the Naphtha cracking process. Oxygen content in the crude petroleum is important in the refining process because it relates to the amount of hydro-processing required to remove oxygen as water. Hydro processing is necessary because these compounds may lead to the formation of coke or sludge which inhibits the refining process and results in the costly down time.

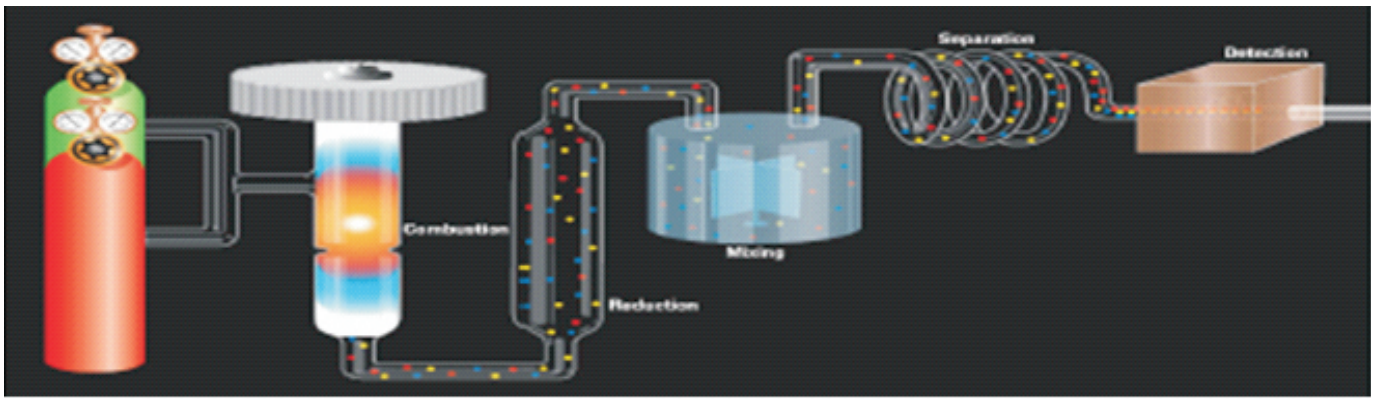
Oxygen is found in the petroleum primarily in the form of carboxylic acids, furan derivatives, alcohols, ketones and esters. EA 2400 Series II can be switched over to oxygen only mode for the accurate determination of oxygen content in the crude oil. Another petroleum related area where oxygen content is important is found in characterization of gasohol. Gasohol is a blend of gasoline and ethanol and found largely in Brazil. The composition of Gasoline and ethanol can be ascertained by determining the oxygen content using hetero element calculations.

PerkinElmer 2400 Series II CHNS/O elemental Analyzer comes with wide variety of sample encapsulation system. The capsules are available for solids, liquids and volatiles made up of Tin, Aluminum. The different sealers are designed for volatile liquids like gasoline and kerosene as well as thicker liquids like paraffinic wax and bitumen.

The PerkinElmer
2400 CHN Elemental Analyzer



The stand alone system with printer and micro balance makes the laboratory equipped with the solution for the elemental analysis for petroleum crude.



The EA2400 CHNS/O Schematic

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A Novel Analysis of Highly Volatile Solvents using the PerkinElmer Optima 7300 DV with a Total Consumption Sample Introduction System

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Introduction

The analysis of volatile solvents for trace metal contamination is important for a variety of reasons. Inorganic contaminants can damage the refinery process and certain catalysts can be poisoned making the chemistry of the process inefficient. These contaminants may also be harmful to the products the solvents are used in. They may cause premature breakdown or wear of mechanical equipment. Perhaps most importantly, these contaminants may be discharged into the environment causing harmful effects to ecosystems.

Traditionally the analysis of volatile solvents has been difficult on an optical ICP. The volatility and vapor pressure of the samples would extinguish the plasma and also deteriorate the pump tubing. Thus samples required either dilution in a less volatile solvent or the use of a chilled spray chamber. These remedies raised the detection limits or made the analysis too cumbersome to be practical.

In addition, elements such as silicon can produce different sensitivities depending upon the organic form of the analyte. It is believed these variations are caused in part due to varying transport efficiencies in the spray chamber. By utilizing a system that is nearly 100% transport efficient these speciation effects can be reduced or eliminated.

Experimental

A PerkinElmer® Optima™ 7300 DV ICP-OES was used for this analysis. The Optima 7300 DV incorporates a cassette mounted torch for easy maintenance and the plasma can be viewed either axially or radially. Axial viewing allows for the best possible detection limits, while radial viewing demonstrates the longest linear range.

Various volatile solvents were analyzed using the Optima 7300 DV for a range of analytes including silicon. Due to varying aspiration properties, these solvents would traditionally exhibit sensitivities dependent upon their individual volatility and viscosity. This would require samples to be matrix matched with the standards. Data in this report was collected on each solvent using one calibration curve in one solvent – heptane. Matrix-matched standards were not used or needed.

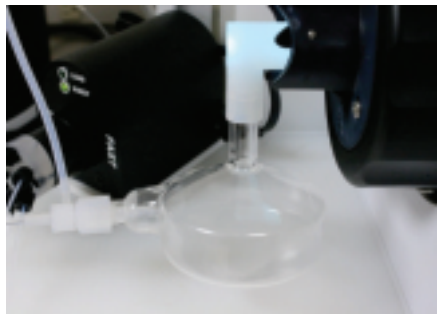

Fig1. A large volume cyclonic spray chamber was used. Due to the "total consumption" nature of the system, no drain was required.

A chilled spray chamber is normally required to analyze these samples by plasma emission. In order to aspirate these solvents at room temperature (i.e. no cooling of the spray chamber), a unique sample introduction system developed by Elemental Scientific Incorporated was used. This sample introduction system, called the microFAST OS, incorporates a low flow syringe pump. This syringe pump eliminates the need for peristaltic pump tubing. The neat organic samples and standards are then drawn into a loop on an inert injection valve. When this valve switches, the sample is transported into a PFA nebulizer by a solvent carrier stream driven by a reciprocating continuous low flow dual syringe pump system. This system operates continuously at a very low rate of 5 to 40 microliters per minute. At such a low flow rate, the aerosol transport efficiency dramatically increases. Essentially 100% of the sample enters the ICP injector, minimizing any elemental speciation effects.

With this high transport efficiency, it is important that the plasma maintain optimal and stable power. The PerkinElmer Optima 7300 DV incorporates true solid state RF power generation opposed to power generation from traditional PA tubes. This solid state RF stability is critical when aspirating solvents of varying vapor pressure. Power stability translates into less matrix effects from solvent variations. Additionally the patented use of a shear gas keeps the interface free of any carbon deposits that may obstruct the optical path.

Results

The calibration was prepared by weight in heptane using organo-metallic standards. The calibration curve was acquired with a blank and 3 standards: 25 ppb, 50 ppb, and 100 ppb. A 500 ppb cobalt solution was used as an internal standard. Five different solvents were analyzed for a variety of analytes. Solvents included hexadecane, butane, gasoline, hexane, and naphtha. Most samples were analyzed neat; however, the butane and hexadecane were diluted 1:5 in heptane to aid in aspiration.

Table 1. Detection Limits calculated by analyzing seven samplings of the heptane blank.

Analyte	Detection Limit (ppb)
Ag 328.068	1.5
Al 308.215	7.8
B 249.677	5.4
Ba 233.527	0.5
Ca 228.802	2.4
Cd 228.802	1.1
Cr 267.716	1.0
Cu 327.393	1.4
Fe 238.204	0.6
Mg 285.213	1.1
Mn 257.610	0.3
Mo 202.031	2.6
Ni 221.648	10.4
Pb 220.353	13.9
Sb 206.836	10.0
Sn 189.927	4.0
Ti 334.940	1.3
V 290.880	0.8

Normally when analyzing solvents, a smaller diameter injector is required to limit the amount of solvent loading into the plasma. This restricts the sensitivity of the analysis. When using the microFAST OS, a larger diameter injector can be used to increase the sensitivity of the analysis, thereby lowering detection limits.

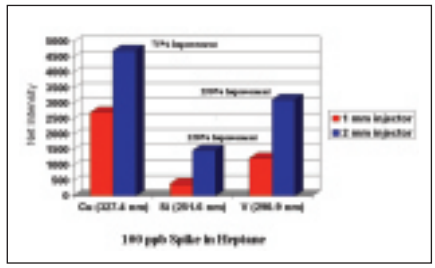

Fig2. Sensitivity improvement compared to injector diameter.

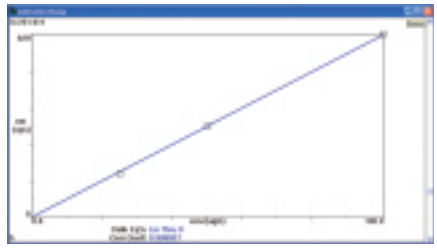

Fig3. Calibration curve of Si in heptane at 25 ppb, 50 ppb, 100 ppb.

In certain applications, silicon is an important analyte in organic solvents. Trace levels can be difficult due to contamination, low sensitivities, and interferences. Typically low level silicon is analyzed by ICP-MS; however, ICP-MS analysis can be problematic in organic matrices due to carbon interferences. Seven solvents were analyzed for silicon at low detection limits using the Optima 7300 DV and the microFAST OS Sample introduction system.

Table 3. Silicon was measured in various volatile solvents and spiked with 50 ppb.

Sample Type	Si result in ppb	50 ppb Spike %Recovery
Gasoline	52	100
Gasoline Duplicate	52	99
Naptha	15	122
Xylene	20	118
MEK	<2	113
Toluene	13	124
Xylene (Reagent Grade)	<2	120
Xylene (Paint Store Variety)	27	115

Conclusion

The use of the Optima 7300 DV for the direct analysis of neat organic solvents has a variety of advantages over traditional systems.

- By aspirating the sample neat, there is limited sample preparation thus limiting contamination possibilities.
- The reduced sample flow rate eliminates the effects of solvent loading on the plasma.
- Detection limits are improved by reducing the spectral interferences, improving the sensitivity, and eliminating contamination from the diluents.
- Throughput can be improved by employing a single calibration curve for a variety of solvents.
- Elements such as silicon exhibit uniform sensitivity regardless of the chemical species.
- By eliminating waste from the instrument and the need for peristaltic pump tubing, the cost of each analysis is reduced.

Table 2. Samples were spiked by weight with 160 ppb organo-metallic multi-element standard. Samples were then analyzed against a calibration curve made in heptane.

	Butane (1:5)		Naptha		Gasoline		Hexane		Hexadecane (1:5)	
Analyte	Conc. ppb	Spike % Recovery	Conc. ppb	Spike % Recovery	Conc. ppb	Spike % Recovery	Conc. ppb	Spike % Recovery	Conc. ppb	Spike % Recovery
Al 308.215	<50	102	<10	97	<10	95	<10	103	<50	96
Ca 317.933	<5	103	1	100	1	89	4	99	30	99
Cd 228.802	<5	104	<1	98	<1	91	<1	102	<5	98
Cr 267.716	<5	105	1	100	<1	99	1	102	5	101
Cu 327.393	<5	103	2	99	8	97	1	103	10	101
Fe 238.204	<5	103	1	99	11	94	<1	101	5	99
Mg 285.213	<5	102	2	98	<1	99	2	102	10	97
Mn 257.610	<5	104	1	99	<1	98	1	102	5	100
Mo 202.031	<15	102	<3	99	<3	84	2	101	10	97
Pb 220.353	<75	102	<1	94	11	91	16	86	15	94
Ti 334.940	<5	104	<1	100	<1	91	<1	104	<5	102
V 290.880	<5	105	<1	100	<1	88	<1	103	5	101
Zn 206.200	<5	102	23	101	29	92	<1	98	<5	97

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High-Speed Refinery Gas Analyzers (HS-RGA)

PerkinElmer-Arnel's family of High-Speed Refinery Gas Analyzers consists of two offerings:

- Model 1117 High-Speed Refinery Gas Analyzer
- Model 1317 High-Speed Refinery Gas Analyzer

They are based on the PerkinElmer® Clarus® 600 Gas Chromatograph (GC) and incorporate special column sets to accommodate the use of hydrogen carrier gas to optimize throughput.

The Model 1117 Refinery Gas Analyzer is a three-channel system, providing guaranteed analysis of helium, hydrogen, oxygen, nitrogen, CO2, CO, H2S, C1 through C5 hydrocarbons including olefins and C5=, C6+ composite in less than 7.5 minutes using two Thermal Conductivity Detectors (TCD / TCD) and a Flame Ionization Detector (FID).

The Model 1317 High-Speed Refinery Gas Analyzer, also a three-channel system, provides guaranteed gas sample analysis of helium, hydrogen, oxygen, nitrogen, CO2, CO, H2S, C1 through C5 hydrocarbons including olefins and C5=, C6+ composite in less than 7.5 minutes using two TCDs and an FID as well as the additional capability of sampling pressurized liquids through the use of a liquid sampling valve.

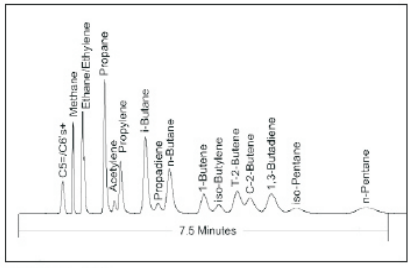
The analyzers are built upon the same robust and proven design of previous PerkinElmer-Arnel analyzers with the added benefit of improved productivity and throughput. These new models extend the PerkinElmer-Arnel family of refinery gas analyzers for customers who need precision, speed of analysis and throughput.

The Model Arnel 1117 Analyzer meets methodology requirements as described in: ASTM D1945, ASTM D1946, ASTM D2597, UOP 539-86, UOP 709, DIN 51872-4.

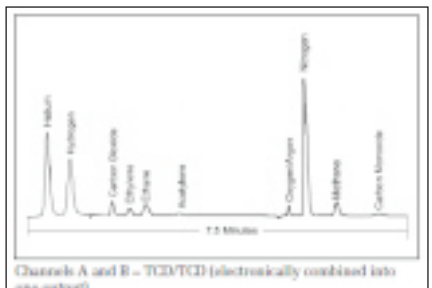
The entire valving is plumbed with sulfur-resistant materials to enhance H2S detection. Following are the brief details about the analyzer and its performance.

- Guaranteed detection ranges/concentration levels:

	Min (%)	Max (%)
Channel A (TCD)		
He and H_2	0.01	100
Channel B (TCD)		
H_2S	0.02	100
All other components	0.01	100
Channel C (FID)		
C_5=/C_6+ composite	0.01	40
All other components	0.01	100



Channel C – FID.



Channels A and B – TCD/TCD (electronically combined into one output).

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Trace Sulfur Impurities in Petroleum Liquids Using the Sulfur Chemiluminescence Detector

Introduction

PerkinElmer-Arnel offers a family of turnkey analyzers that measure trace levels of sulfur compounds in liquid-phase petrochemicals, including liquefied petroleum gas (LPG), naphtha and gasoline. Analyzer Models 4026, 4027 and 4227 incorporate a sulfur chemi-luminescence detector (SCD) for analysis of these liquids. Key performance features of the SCD for these petrochemicals include high sensitivity, > 104 dynamic range, equimolar sulfur response, lack of carbon interference and simple calibration.

Features of SCD

- Trace-level analysis of H2S, COS, SO2, mercaptans, aromatic sulfur compounds and sulfides
- Typical samples include LPG, gasoline, naphtha and liquidolefins
- Programmable Pneumatic Control (PPC) and non-PPC configurations
- Additional PID channel for aromatics and FID channel for hydrocarbons and oxygenates or total hydrocarbons such as methane are available
- Worldwide service and support

Analyzer models

Model 4026

The Model 4026 (Figure 1) analyzes liquids and compressed gas liquids such as LPG using a liquid sampling valve (LSV) connected directly to a capillary column and configured with the SCD for trace-sulfur measurement. This design provides the highest reliability and, especially for the lightest most active sulfur compounds, the best chromatography. The valve is shown in the off or fill position. Sample is injected by turning the valve rotor clockwise. When the rotor turns, the liquid contained in the groove between ports "S" and "W" is placed in the carrier flow path or ports "C" and "P". Pressurized liquids immediately flash to a gas in a vaporization zone and then enter the column.

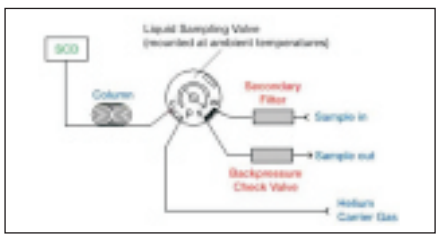


Fig 1. Model 4026 analyzer, incorporating a liquid sampling valve.

It is important to keep pressurized liquids as liquid when they are in the LSV's sample groove. If the sample vaporizes while in the groove, sampling precision is very poor. The LSV is mounted outside the column oven in order to keep the liquid as cool as possible and a spring-regulated check valve provides backpressure to the sample while in the sampling groove. This pressure prevents low vapor pressure components from vaporizing in the groove.

A secondary particulate filter, which is included, helps to prevent valve damage and is designed to be a backup filter should the operator's primary filter fail.

Model 4027

The Model 4027 (Figure 2) analyzes liquid samples via syringe injection to a capillary column.

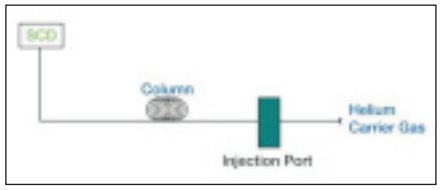


Fig 2. Model 4027 analyzer, incorporating an injection port.

Model 4227

The Model 4227 (Figure 3) adds an LSV and capillary column system to Model 4027 to also analyze pressurized liquids.

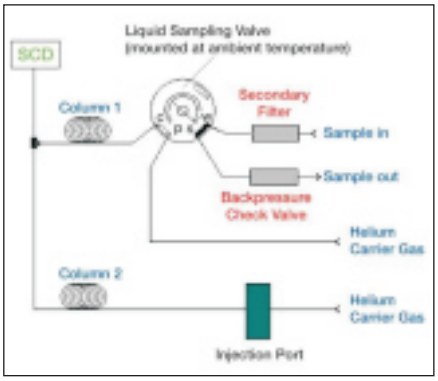


Fig 3. Model 4227 analyzer, incorporating a liquid sampling valve and injection port.

Column-temperature programs

The actual starting temperature and temperature program used in the analyzer depend upon the components to be analyzed. The liquid sampling valve is at ambient temperature and not in the analyzer's column oven. Therefore, the column oven temperature can be programmed to whatever is required to accomplish the analysis. If a separation of COS and SO2 is required, the analyzer must be configured with either the liquid nitrogen or liquid CO2cryogenic-oven cooling option.

Minimum detection limit (MDL)

Practical sulfur compound detection limits are < 10 ppb for liquid samples. Figure 4 presents an example chromatogram of a liquid standard comprising trace level sulfur compounds in toluene. The SCD has a selectivity of > 108gS/gC i.e., one gram of sulfur generates a signal that is 108greater than the signal generated by a gram of carbon. Even with this great selectivity, a very high concentration of a single hydrocarbon will generate a small signal. For example, consider analyzing a sample of 10 ppb (molar) methylmercaptan in propane. The weight of the sulfur in the methylmercaptan (32) and the weight of the carbon in propane (3 x 12 = 36) are such that this sample contains ~108more carbon than sulfur on a weight basis. With a selectivity of > 108, pure propane will generate a peak of the same size as the sulfur impurity. With more carbon in the component, pure butane would generate a larger peak.

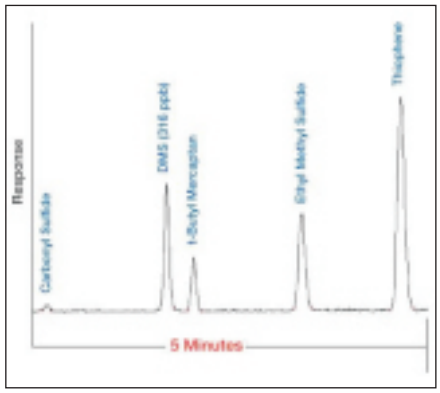


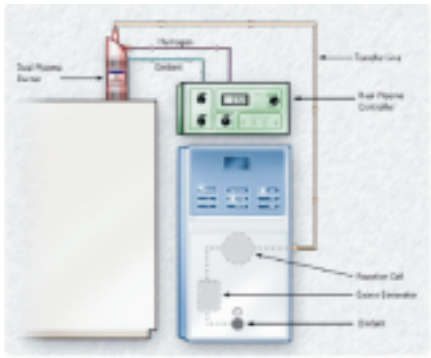
Fig 3. Model 4227 analyzer, incorporating a liquid sampling valve and injection port.

Specifying a custom analyzer

Although the Model 4026, 4027 and 4227 analyzers cover most common samples, some sample combinations are better served by a custom adaptation of a standard model. Some examples include: the analysis of a sample with heavy components that might condense, a requirement to add an autosampler or the inclusion of an FID channel for another analysis to be combined with the SCD channel. These models all have an unused detector location and, depending upon the samples to be analyzed, it is possible to add a second analysis or a second application.

Routine maintenance

The SCD is a trace-level detector with remarkable characteristics. This remarkable performance requires extremely clean gases, a working vacuum pump and a clean, active burner. All of these SCD analyzers require sulfur filters. Filter use depends upon the quality of your supply gases. The SCD generates ozone and this gas is pulled to the vacuum pump. The chemical traps supplied in the optional one-year maintenance kit protect the pump by trapping the ozone. Over long periods of use, SCD burner ceramics can deactivate. The ceramics are also deactivated if exposed to a hydrogenrich atmosphere, due to loss of burner air. Sensitivity is recovered by the replacement of the SCD's ceramics. The best way to assure optimum system performance is to hold to a rigorous preventative maintenance schedule.



The Schematic diagram of the SCD detector connected to GC

Model 3062 reporting software

Model 3062 reporting software can be utilized to provide customized reports and calculations using the full capabilities of Microsoft®Excel® and TotalChrom®data-handling software. It can also be used to translate the resulting report into many languages.