

GC: A Review of the State-of-the-Art Column Technologies for the Determination of ppm to ppb Levels of Oxygenated, Sulfur, and Hydrocarbon Impurities in C₁–C₅ Hydrocarbon Streams

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Abstract

The determination of ppm to ppb levels of sulfur, oxygen-containing, and certain reactive hydrocarbons in bulk hydrocarbon feedstocks is important in the petroleum and petrochemical industry to minimize catalytic deactivation and improve product quality. Gas chromatography, coupled with selective or ultratrace universal detection (or both), is ideal in most cases for such analysis. However, to enhance selectivity and quantitation at the trace levels, optimized stationary phases are required. These phases are usually of the adsorbent type. This paper summarizes the performance of several state-of-the-art phases for the analyses of trace key hydrocarbons, sulfur, and oxygenated components.

Introduction

The determination of trace impurities by gas chromatography (GC) is a very common analysis in the petrochemical laboratory. Usually, these impurities, which can have a detrimental effect on catalytic deactivation or product quality (or both), consist of three types: hydrocarbons and sulfur- and oxygen-containing organo-molecules. Other impurities such as nitrogen- and heteroatoms- (arsenic, silicon, etc.) containing components may also have deleterious effects, but these are not addressed in this paper.

The analysis of trace hydrocarbons can be accomplished very effectively using selective adsorbents such as silica, alumina, and carbon. However, the analyses of trace sulfur compounds and oxygenates require a higher degree of inertness. For sulfur-containing compounds, a polydimethyl siloxane (PDMS) stationary phase for generic application or a silica-based stationary phase for special applications may be adequate.

Oxygenated compounds are highly polar, and additional spe-

cial selectivity and inertness is required. Aside from the more common polar liquid phases, it is shown that using a unique CP-Lowox adsorbent multilayer column technology, oxygenates can be selectively retained and quantitated at ppm levels. Using concentration techniques such as precolumn and stack injection, it is possible to determine ppb levels of oxygenated impurities in hydrocarbon streams with high accuracy. This paper summarizes and reviews the main approaches used for trace analysis of the three component types.

Experimental

Hydrocarbon impurities in hydrocarbon streams

In hydrocarbon feedstock streams, many types of hydrocarbons can be present. The presence or absence of hydrocarbon impurities provides information on final product quality and value or the applicability of feedstock streams/intermediate products to a petrochemical process. Because of its low detection limits, stability, and ruggedness, flame ionization detection (FID) is used most widely. Depending on the hydrocarbon impurity requiring analysis, certain column technologies can be used. Because these compounds are volatile, adsorption-type columns find wide application in the industry.

The most universally applicable phase for light hydrocarbon separation is alumina Al₂O₃. The latter phase was one of the first fused-silica porous-layer open-tubular (PLOT) columns developed, and it has found a wide application in petrochemical analyses, especially for light C₁–C₅ hydrocarbons, for which this phase exhibits unique performance.

Hydrocarbon separation using alumina adsorbents

Alumina adsorbents in capillary columns were introduced in 1963 (1) and were commercialized in fused-silica capillary columns in 1981 (2). The alumina adsorbent has a very high

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activity and retains components as light as ethane. Alumina requires deactivation to make its highly active surface a viable stationary phase in GC.

Deactivation can be accomplished in many ways; however, the most practical and reproducible approach is the deactivation with inorganic salts (3,4). A very popular deactivation procedure is the addition of KCl to the alumina that results in a general nonpolar and less active alumina surface, as demonstrated by the elution of acetylene ahead of butane (Figure 1). The alumina surface can also be made more polar than KCl deactivation by deactivating with sodium sulfate. Using sodium sulfate, the resulting alumina layer will elute acetylene after the butane peak, indicating a higher polarity of the phase. In addition, methyl-acetylene will be retained longer on a sodium sulfate-deactivated surface and will elute after 1,3-butadiene.

The selectivity of alumina for hydrocarbons is very high. All of the C_1 - C_4 hydrocarbons can be separated baseline. The resolution between the different hydrocarbons is sufficient to determine many trace C_1 - C_4 hydrocarbons in feedstock streams containing any C_1 - C_4 as the major component hydrocarbon (Figures 2 and 3). As a result, the alumina phase is one of the most widely used columns in the petrochemical industry for the analyses of hydrocarbon impurities in ethylene, propylene, and butylene feedstock streams.

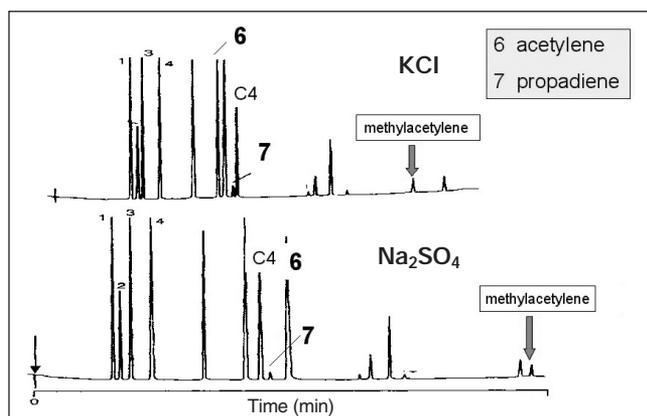


Figure 1. Selectivity of KCl and Na_2SO_4 -deactivated Al_2O_3 surfaces: the Na_2SO_4 -deactivated surface has more retention for polar hydrocarbons.

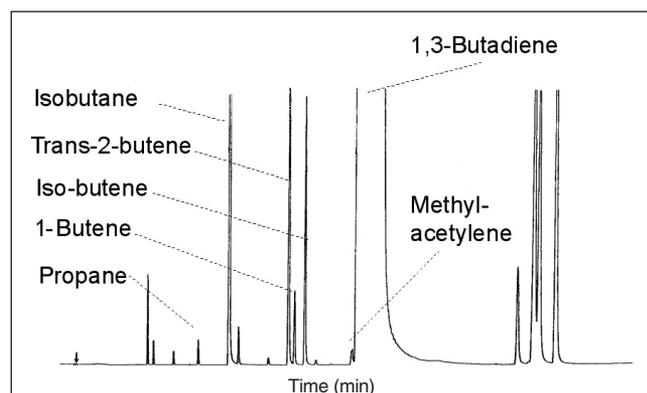


Figure 2. Impurities in 1,3-butadiene on Al_2O_3 -KCl; methylacetylene elutes in front of 1,3-butadiene.

For the majority of applications, the KCl-deactivated alumina can be used. This column, which now is also recommended in several methods standardized by the American Standards Testing Materials, will separate the majority of the C_1 - C_4 hydrocarbons and is ideal for impurity analysis (Figure 2).

In certain applications, greater column resolution may be required, particularly for cases in which the large feedstock hydrocarbon matrix component(s) may elute close to the impurities of interest and interfere with the analysis. In such cases, the major matrix component will appear as an "overloaded" peak. Under these conditions, the maximum resolution for butylene isomers is obtained by using a more active Na_2SO_4 -deactivated alumina column. For this application, the Na_2SO_4 -deactivated alumina is the optimum phase for impurity analysis, as the resolution between *cis*-2-butene and 1-butene is the greatest. Figure 3 shows an impurities analysis in 99.99% 1-butene. In the presence of the large 1-butene matrix peak, it is still possible to determine the other C_4 isomers. For an effective separation, the injection volume must be kept as small as possible. The large concentration of the "main" or matrix component, if not controlled, will influence the peak shape of the trace components that elute close to the main peak.

Characteristics of alumina phase

Capillary columns prepared with alumina phases are very rugged. Although alumina has unique separation characteristics, it also has some limitations that require attention. The activity of the adsorbent will adsorb any water, carbon dioxide, or other polar impurity in the sample or carrier gas stream. The adsorbed water will deactivate the surface, and, as a consequence, the column will have lower retention of the analytes (2). The water can be removed simply by heating the alumina capillary column to 200°C for 15 min. The water will desorb, and the column will be regenerated. When an analysis requires isothermal operating conditions, a polar precolumn that retains the water may be used. A column coated with 1-2- μ m film thickness of polyethylene glycol is very effective, as the C_1 - C_6 hydrocarbons will elute from the precolumn and the water will be retained on the precolumn. The water may be removed from the

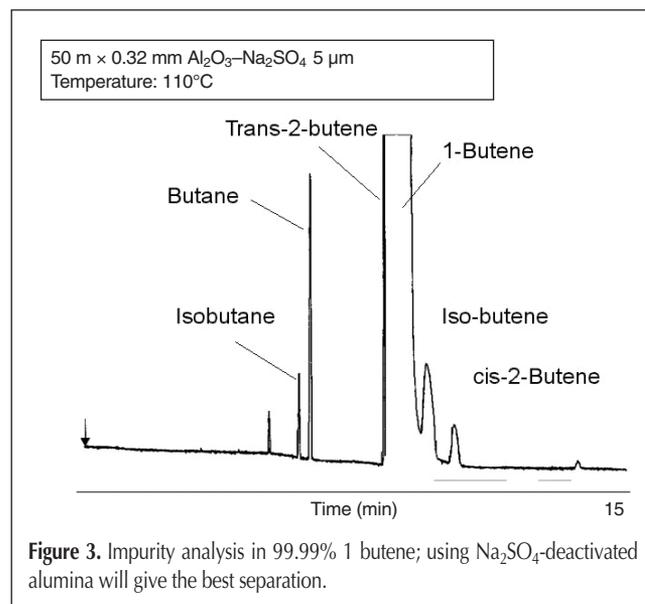


Figure 3. Impurity analysis in 99.99% 1-butene; using Na_2SO_4 -deactivated alumina will give the best separation.

precolumn by simple backflush or a vent-switching flow configuration (5). For more deleterious polar contaminants, the alumina column regeneration may take longer, but is possible. It was found that sulfur impurities present up to 2000 ppm did not seriously affect the stationary phase or the retention times of the trace impurities on alumina. Oxygen in the carrier gas will not harm the column. The maximum temperature of alumina phases should not exceed 200°C because above 200°C, recrystallization of the deactivation crystals will occur, causing irreversible changes in selectivity (4). Alumina layers coated in Ultimet tubing (Varian, Middleburg, the Netherlands) are very stable and find wide application in stressful environments (7).

In summary, the aluminum oxide phase has now been used by many laboratories in petrochemical and environmental analysis and is recognized to be the most effective phase capable of resolving most of the C₁–C₅ hydrocarbons with maximum separation efficiency.

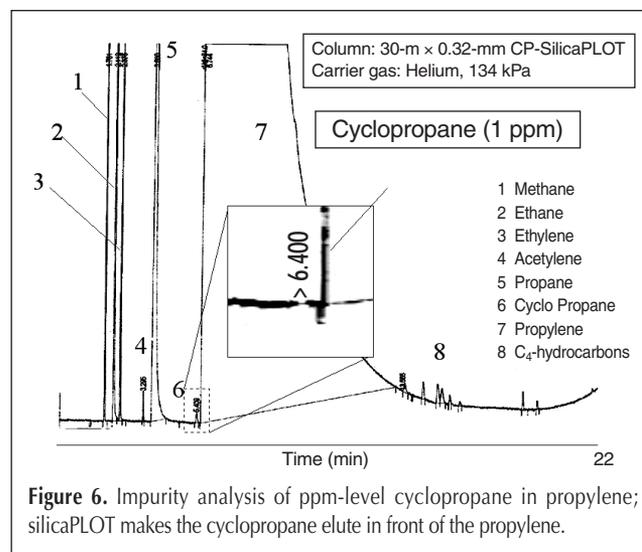
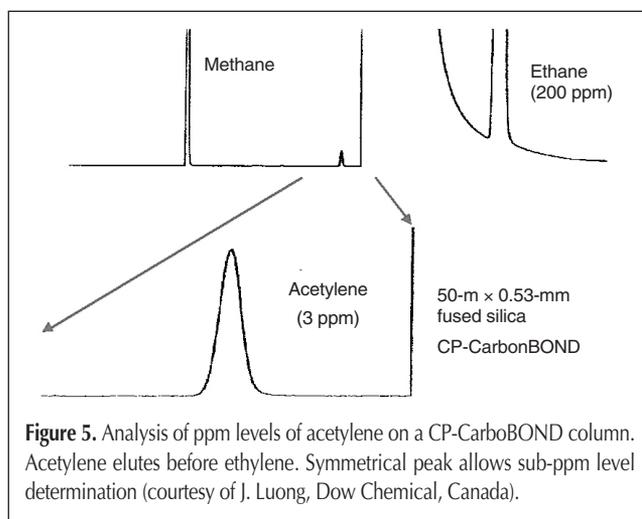
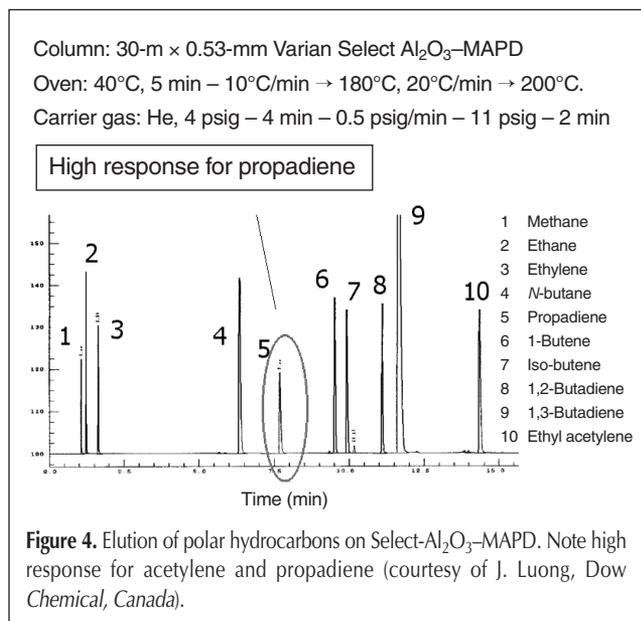
Trace analysis of methylacetylene, acetylene, and propadiene

Although alumina is the ideal adsorbent for most hydrocarbon analysis, it has some disadvantages because of its high surface activity, which results in an irreversible adsorption for the more “polar” hydrocarbons. These “polar” hydrocarbon compounds are typically methyl acetylene, acetylene, and propadiene. Although these compounds can be quantitated using alumina, the response of the detector for such components is lower than expected, based on their theoretical carbon number response using the FID. However, with frequent calibration, it is possible to obtain acceptable quantitation of these compounds. To improve the analysis using alumina for the determination of these compounds, a study was undertaken (8) to better understand the elution characteristics of these compounds as a function of column operating conditions. It was determined that the cause for the low response was an irreversible adsorption that can occur at higher column temperatures, which can be improved by reducing the elution temperatures. The lowering of the elution temperatures can be obtained in several ways: (a) with existing columns using higher carrier gas flow rates, (b)

lowering the GC oven temperature programs, and (c) using shorter columns. All of these actions will improve the analysis. In addition, a new alumina phase column called Select Al₂O₃–methylacetylenepropadiene (MAPD) (Varian) was developed that has an improved deactivated surface that exhibits a much lower retention for the hydrocarbons. The lower retention characteristics of this improved alumina phase allow the use of lower column temperatures and, thus, a higher response for the polar hydrocarbons. The results obtained with the improved phase are shown in Figure 4. The response for propadiene is much higher, allowing lower concentrations to be determined. This improved phase will yield a greater response for acetylene and methyl acetylene.

Acetylene in ethylene

The determination of acetylene in ethylene is an important analysis in the petrochemical industry. To separate the acetylene from ethylene adsorbents exhibits ideal selectivity. Aluminum oxide may be used; however, for any trace impurity analysis, it is important that the impurity elute significantly *in front* of the main component or that it elute significantly *after* the main component. In both cases, low concentration levels can be determined.



For the determination of trace acetylene in ethylene, two materials are of greater interest than alumina, silica and carbon. Using silica, the acetylene will elute *after* the ethylene peak (9). Separation is acceptable, but the acetylene elutes on the tail of the ethylene. This may be acceptable for the analysis of high ppm levels, but for trace analysis at lower concentrations, an improved separation is required. A highly unique selectivity is obtained with the carbon deposited adsorbents (10). These types of adsorbent materials have been used extensively for a long time in packed columns, under the name Carbosieve, as coated carbon materials. Several attempts have been made to commercialize capillary columns coated with Carbosieve materials, however, not with great success. Presently, two carbon types have found a practical application, the Carboxene and CarboBOND type of materials. Both materials exhibit comparable characteristics, as they are highly nonpolar and elute acetylene in front of ethylene. The main limitation for the application of the carbon-coated PLOT columns is the limited temperature range. Carbon-deposited layers become very active upon thermal exposure. Usually, application of these materials is limited to approximately 200°C, but up to this temperature, unique separations can be performed.

Figure 5 shows the analysis of ppm levels of acetylene in ethy-

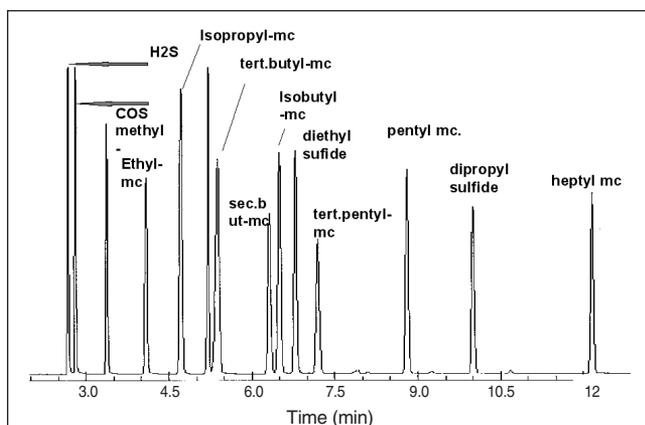


Figure 7. Separation of most common sulfur compounds on thick-film PDMS (CP-Sil 5 CB) using SCD detection (courtesy of J. Luong, Dow Chemical, Canada).

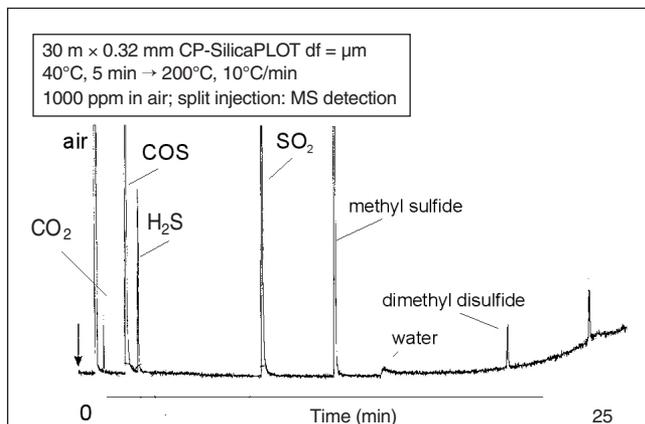


Figure 8. Separation of sulfur compounds on a silica PLOT column; COS and H₂S elute at high temperature and are well resolved. Also, SO₂ shows good peak shape.

lene. Because the acetylene elutes before the main ethylene peak, it can be determined to low concentration levels. Single-column analysis down to 500 ppb acetylene should be attainable.

Cyclopropane in propylene

In certain chemical processes, there is an interest in the determination of cyclopropane. This component is very volatile, and its determination requires special columns. Alumina adsorbents separate the cyclopropane, but it cannot be determined at ppm

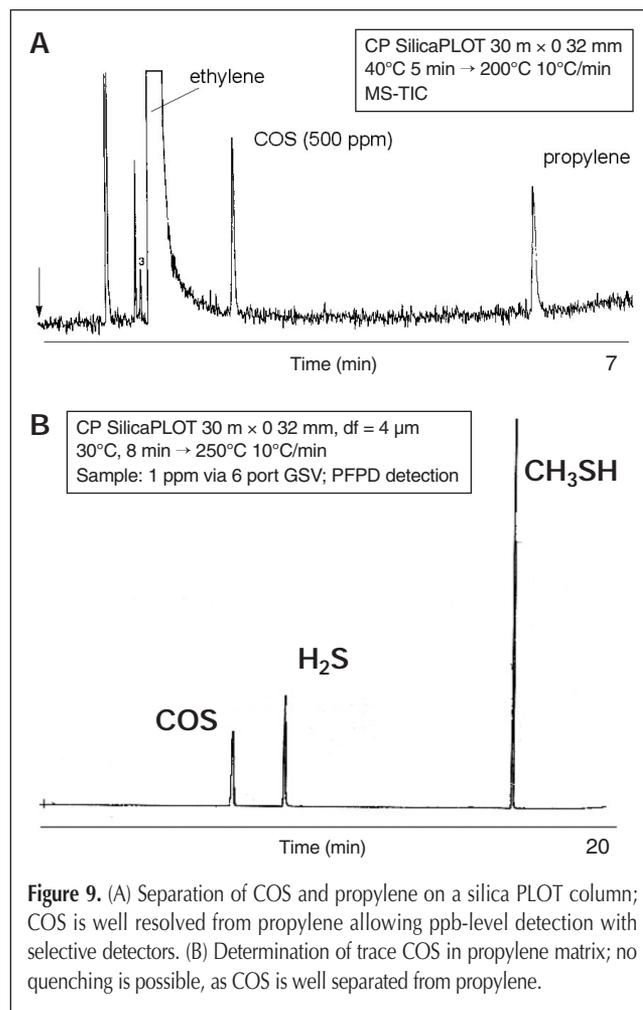


Figure 9. (A) Separation of COS and propylene on a silica PLOT column; COS is well resolved from propylene allowing ppb-level detection with selective detectors. (B) Determination of trace COS in propylene matrix; no quenching is possible, as COS is well separated from propylene.

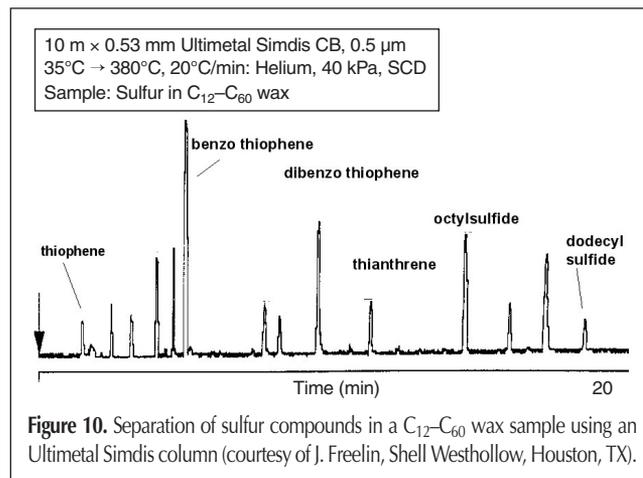


Figure 10. Separation of sulfur compounds in a C₁₂-C₆₀ wax sample using an Ultimetalsimdis column (courtesy of J. Freelin, Shell Westhollow, Houston, TX).

levels. An Al_2O_3 -KCl column coupled with a 50-m \times 0.32-mm CP-Sil 5 CB (Varian) with a 5- μm film was used successfully for such analysis (11). However, the analysis time was long and the cost of the required columns was high because it required using a 100-m coupled-column configuration. The same analysis can be performed using a single silica adsorbent, as shown in Figure 6. Because the cyclopropane elutes in front of the propylene, it can be determined at very low concentration levels. In this application, the oven was heated from 50°C (5 min) with 5°C/min up to 100°C, followed by a 20°C/min program to 225°C. The sample was introduced with a Valco sampling valve (VICI, Houston, TX) with a 250- μL sample volume into the splitter injector at a split ratio of 10:1. Even at the low concentration levels, the cyclopropane eluted in front of the propylene peak and could be quantitated accurately.

Sulfur impurities in hydrocarbon streams

Sulfur compounds exist in light feedstocks in a broad boiling point range varying from the very volatile sulfur gases to high-molecular-weight thiophenes. A number of sulfur compounds are very reactive, requiring an inert GC system for trace sulfur determination. The separation of sulfur compounds can be accomplished very well with GC, as these materials are relatively nonpolar and can be separated on different types of stationary phases. The main stationary phases used for separation of sulfur compounds are nonpolar phases based on polydimethylsiloxanes or PLOT columns coated with porous polymers or silica. The PLOT columns are mainly used for volatile sulfur compounds like carbonyl sulfide, hydrogen sulfide, and methylmercaptan, which are also the most reactive.

Detection of sulfur compounds

For the detection of sulfur compounds, several detectors can be used depending on the concentration levels to be determined.

High-ppm up to percent-level determinations can be accomplished with thermal conductivity detection (TCD). With microchip-TCD design, sulfur compounds can be determined to 10-ppm levels (see following section on sulfur in natural gas). Using micromachined technology for injection and detection devices, it is possible to have very short analysis times (< 200 s) with high sensitivity. Because detection is performed with a microchip-TCD (universal thermal conductivity detector), the selectivity of the column becomes very important in separating the sulfur compounds from the matrix.

The main disadvantage of the TCD is its limited sensitivity and its universal response. In addition, long-term exposure to reactive sulfur compounds (e.g., SO_2) limits its lifetime.

Sulfur *selective* detection is well developed and is used very broadly. Sulfur determination using chemiluminescence detection (SCD) allows low levels of sulfur compounds to be determined. Because of its equimolar response, the SCD has high selectivity and low detection limits at ppb levels. Alternatively, a pulsed flame photometric detector (PFPD) may be used (12). The PFPD also allows ppb levels to be determined. However, the response of this detector is quadratic, which can be accounted for with the data interpretation. Although these selective detectors have nearly six decades of selectivity, at ppb levels, the sulfur signal "quenching" effect from hydrocarbon background may yield a nonlinear response or interference from coeluting large amounts of hydrocarbon components (or both). To minimize interferences from the hydrocarbons, a column phase must be used that separates the sulfur components from the interfering background. Generally, as more selective detection systems are used, the selectivity of the column becomes less important; however, for trace sulfur compounds analysis, a good separation from the large hydrocarbon matrix components almost always will lead to a more accurate analysis.

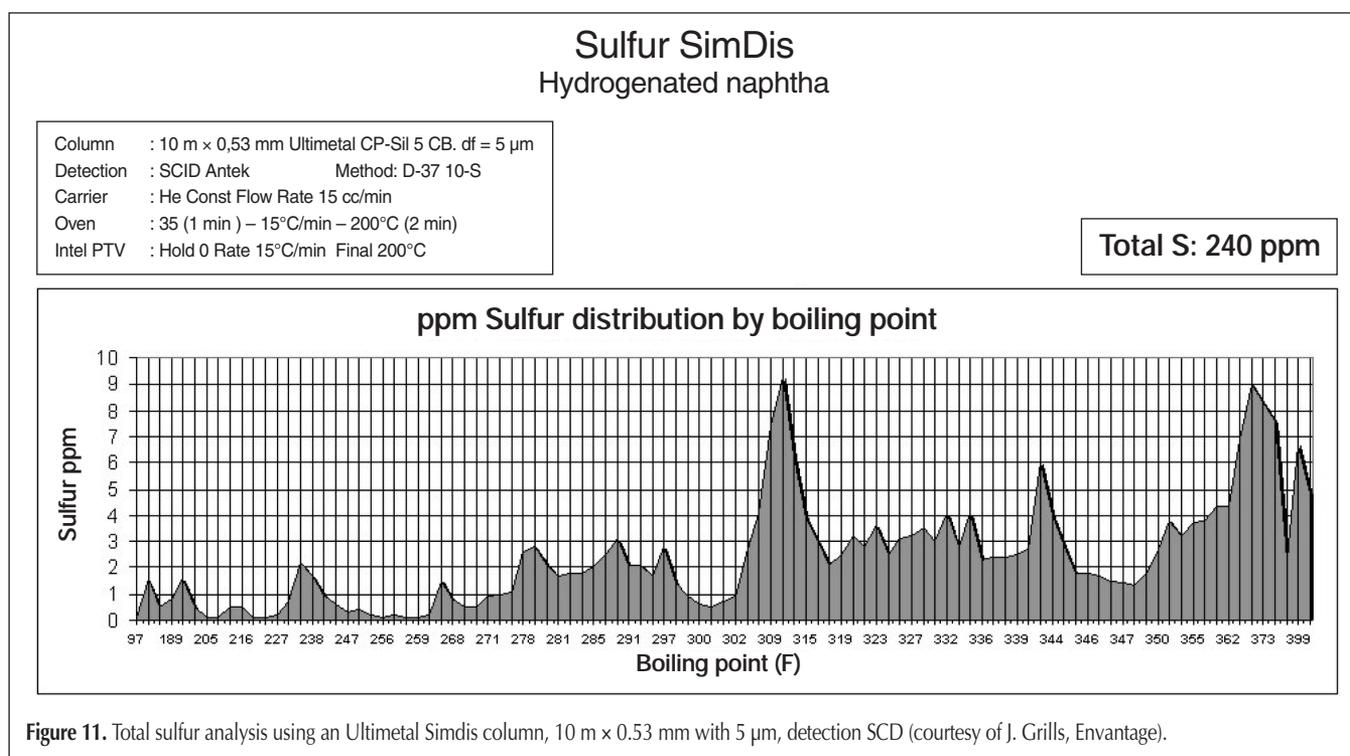


Figure 11. Total sulfur analysis using an Ultimetel Simdis column, 10 m \times 0.53 mm with 5 μm , detection SCD (courtesy of J. Grills, Envantage).

Sulfur analysis at ppm–ppb levels

Sulfur compounds need to be determined in a wide variety of hydrocarbon matrices. Although specific columns are available, many “generic” analyses have to be performed. For analyses of general sulfur compounds in up to C₇–C₈ hydrocarbons, a non-polar, such as 100% polydimethylsiloxane (PDMS), stationary phase will generally yield the best results. PDMS can be coated on deactivated fused-silica (or UltiMetal, or equivalent) surfaces, allowing ppb levels of sulfur compounds to be quantitated. For example, Figure 7 shows the separation of the C₁–C₇ sulfur compounds on a 5- μ m CP-Sil 5 CB phase at 30°C. However, this separation may be problematic for the analysis of H₂S, COS, and SO₂ at the specified temperature. Because these compounds, especially COS and SO₂, elute very closely together close to the column dead volume, the quality of the injection becomes a major issue. The optimum solution is to use PLOT columns as described next.

Determination of H₂S, SO₂, and COS

One option for the determination of H₂S, COS, and SO₂ is to use a selective stationary phase based on SiO₂ (silica) (10). Silica PLOT columns have the advantage that they elute not only the hydrocarbons, but also the sulfur compounds at low concentration levels. The sulfur compounds are retained and separated at temperatures as high as 80°C. This makes the separation of COS and SO₂ quite simple, as shown in Figure 8.

The silica PLOT column is also effective in the analysis of COS

in high-purity propylene using a selective detector (PFPD or SCD). In contrast, a similar analysis using a nonpolar PDMS liquid phase (CP-Sil 5 CB or equivalent) caused COS to elute at the same retention time as the propylene, which would cause sulfur signal quenching. Figure 9 shows the elution of COS, as well as propylene, on a silica adsorbent. Propylene is well separated, allowing good response at low levels for the selective detectors.

High-boiling sulfur compounds, sulfur simdis, and total sulfur analysis

To analyze the total sulfur content of hydrocarbon streams, it is necessary to elute all of the sulfur compounds, including those with a higher boiling point. Metal capillary columns are commercially available that possess a high degree of inertness for sulfur analyses. Figure 10 shows the sulfur impurities in a C₁₂–C₆₀ wax sample for which elution temperatures up to 380°C were required. Using the SCD in combination with thick-film polydimethylsiloxane stationary phase, it is possible to visualize the sulfur distribution. Figure 11 shows the fingerprint of a catalytically cracked naphtha sample containing a total of 240 ppm sulfur. The inert UltiMetal column used allows the higher boiling volatile compounds to elute.

Another example of using selectivity of the stationary phase is the analysis of thiophene in benzene with SCD. The analysis may be performed very well using a polyethylene glycol-type stationary phase (CP-Wax 52 CB or equivalent) at oven temperatures starting at 30°C with 10°C/min temperature programming to 125°C. The thiophene (11 ppb) elutes as a resolved peak with minimal interference, thus allowing low-level determination in the large benzene matrix (Figure 12).

A completely new approach for the determination of total sulfur was presented by Amirav (16), as shown in Figure 13. A PFPD detector was used, whereby the sample was introduced directly via a short 0.53-mm capillary coated with approximately 0.5- μ m film of polydimethylsiloxane. The 0.53-mm short column was coupled with a 1-m \times 0.1-mm capillary to create an acceptable pressure drop to allow control of the carrier gas flow. The sample was directly introduced in the PFPD, giving a response for sulfur. This method generated a total sulfur value within 100 s and can be used to approximately 5 ppm. Lower sulfur contents are difficult to attain because of the response of the matrix or major coeluting hydrocarbons.

Sulfur in natural gas

Natural gas is used widely for cooking and heating applications. One of the problems of natural gas is that it has no odor. As a result, very risky situations can occur that can lead to personal injuries. To avoid safety problems, an “odorant” is added to natural gas to allow detection of small gas leaks. Very low concentrations of sulfur compounds are added as odorant because the human nose is very sensitive for sulfur com-

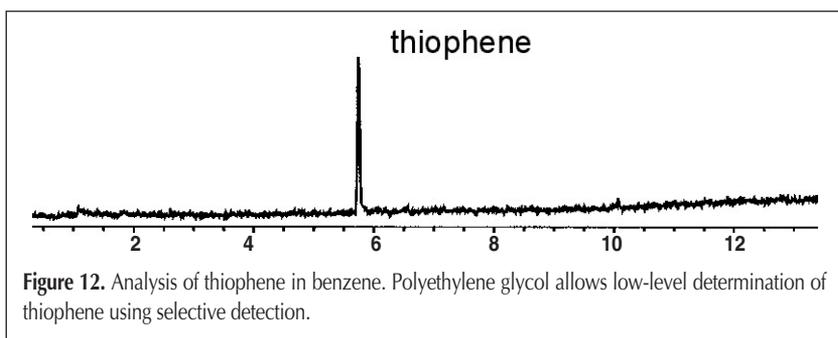


Figure 12. Analysis of thiophene in benzene. Polyethylene glycol allows low-level determination of thiophene using selective detection.

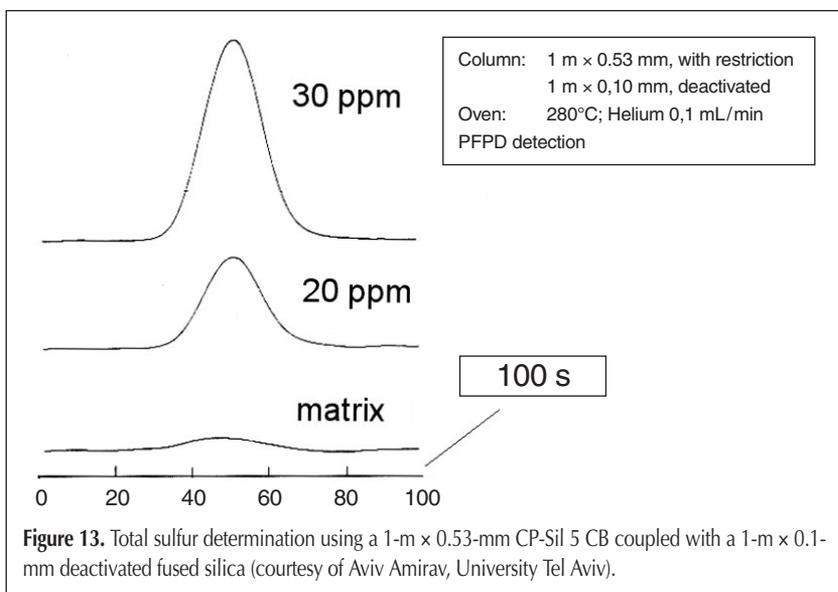


Figure 13. Total sulfur determination using a 1-m \times 0.53-mm CP-Sil 5 CB coupled with a 1-m \times 0.1-mm deactivated fused silica (courtesy of Aviv Amirav, University Tel Aviv).

pounds at fg levels. Several odorants may be added, such as methyl mercaptan, tetra hydrothiophene (THT), or butyl mercaptan (or all three). Consequently, rapid analyses are required for these sulfur components in natural gas at concentrations between 10–50 ppm. The TCD is a viable detector for these applications. For speed of analysis, a narrow-bore column would be ideal. The introduction of micromachined systems for injection, as well as detection (TCD), has led to the development of microGC technologies for very fast analysis of odorants in natural gas streams. Typically, an analysis with the chip technology takes approximately 50 s. Because the detector in such systems are TCD based (universal detection), the selectivity of the column becomes very important. Special stationary phases have been developed for tetra-hydro-thiophene (THT) and tert-butylmercaptan (TBM) to elute these components free from interference. Figures 14A and B show the separation of THT and TBM obtained using a fast technology used in the CP4900 micro GC (Varian).

Oxygenated impurities in hydrocarbon streams

Introduction

The determination of low levels of oxygenates may be performed using various technologies. These techniques include selective enrichment with adsorbents, multidimensional GC employing columns with different selectivity, or selective detectors such as the oxygen-specific flame ionization detection (O-FID) and atomic emission detection (AED). Although these techniques performed adequately, key limitations include difficulty to maintain and the high cost to implement.

The determination of ppm and sub-ppm levels of alcohols and aldehydes in different hydrocarbon matrices is a very important analysis in the petrochemical laboratory. The analysis of these “oxygenates” is important because the level of the oxygenates directly affects catalyst poisoning or product quality. Usually, this analysis is performed on high-polarity liquid phases, such as tri-cyano-ethoxy-propane (TCEP), or with the high maintenance O-FID, often with complex valve switching. With these methods, the detection limit is approximately 10 ppm. In 1995, a new adsorbent stationary phase material was introduced, called CP-Lowox (Varian), with an exceptionally high selectivity for oxygenates because of its multilayer technology. Methanol has a retention index higher than 1400 at temperatures > 200°C, which makes its determination possible at very low levels in ethylene, propylene, butene, and C₅ streams using standard FID detection. The CP-Lowox column has virtually no bleed, even at temperatures of 350°C. Many common oxygenates can be quantitated at sub-ppm and even at ppb levels. Besides methanol, a range of oxygenated compounds can be separated and quantitated such as alcohols, ethers, aldehydes, ketones, and esters.

Single-column separation of oxygenated compounds in hydrocarbon matrix

The most desirable approach to analyze trace level of oxygenates would be to inject the sample directly into a single column capable of resolving the oxygenates of interest with minimal interference from hydrocarbons with FID detection. To achieve this goal, a highly selective and stable stationary phase has to be used, and the column must have a high resolving power. Generally, this means long columns of small internal diameter, which result in relatively long analysis times. If there are only a few oxygenated compounds to be analyzed, the application of a single-column analysis becomes more realistic. The practical limitation on oxygenate levels that can be determined is approximately 5 ppm.

There are several stationary phases that are known to be selective for oxygenated components. Polyethylene glycols (PEGs), cyanosilicones, and the multilayer (CP-Lowox) phases are all used. Table I gives a comparison of these phases. It is clear that the CP-Lowox phase offers major advantages with respect to selectivity, temperature stability, bleed, trapping effect, stability, and chemical inertness.

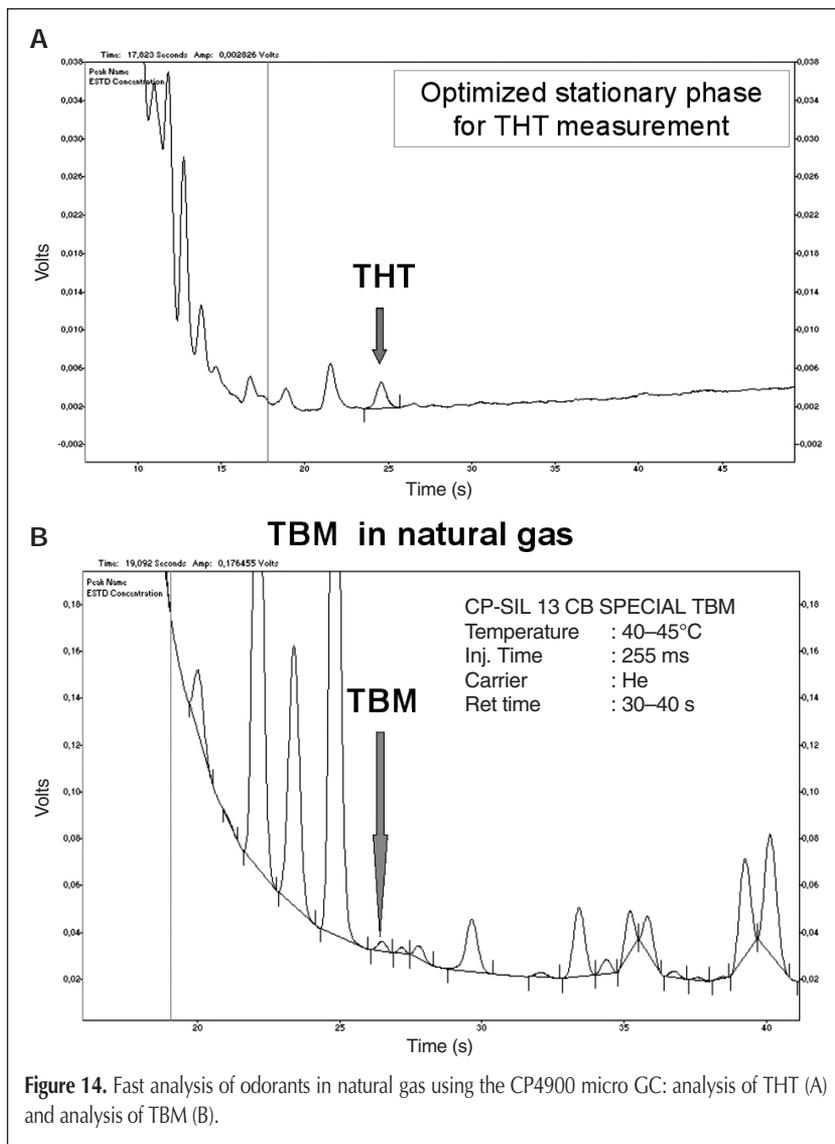


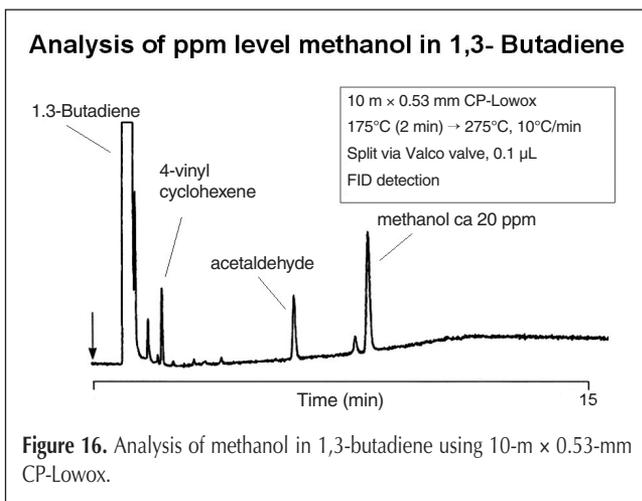
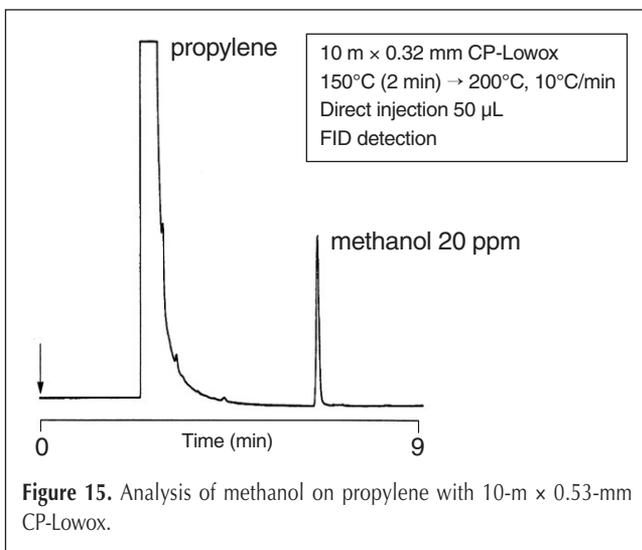
Figure 14. Fast analysis of odorants in natural gas using the CP4900 micro GC: analysis of THT (A) and analysis of TBM (B).

Analysis of methanol

Methanol in C_1 - C_3 stream. Methanol is a compound that is often present in light hydrocarbon streams. It is added to natural gas during its transportation to prevent freezing of piping, etc. Depending on the level of methanol and the matrix, several stationary phases can be used for the analysis. In the range of 1–100 ppm methanol in methane and ethylene, the methanol can be determined very simply using polar phases such as CP-Wax 52 CB or equivalent, TCEP, and CP-Lowox. If the same amount of methanol is analyzed in propylene, the CP-Wax 52 CB, or equivalent, phase will not be

Table I. Characteristics for Four Polar Phases Used for Oxygenes Analysis

	PEG	100% Cyano	CP-TCEP	CP-Lowox
Polarity	medium	high	high	very high
Selectivity	high	low	medium	very high
T_{max} (°C)	250	225	140	350
Bleed at T_{max} (pA)	10	10	15	1
Trapping effect	low	low	low	very high
0.53-mm Columns	yes	no	no	yes



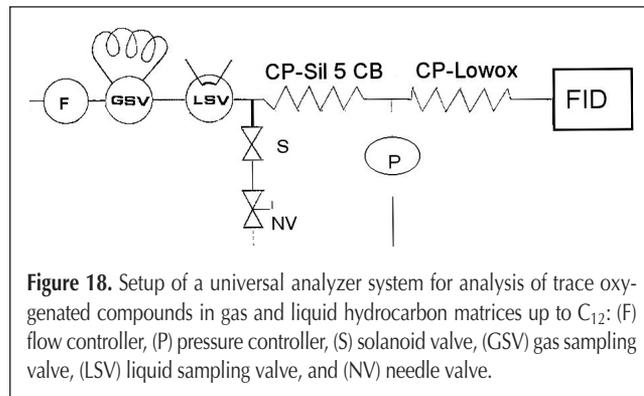
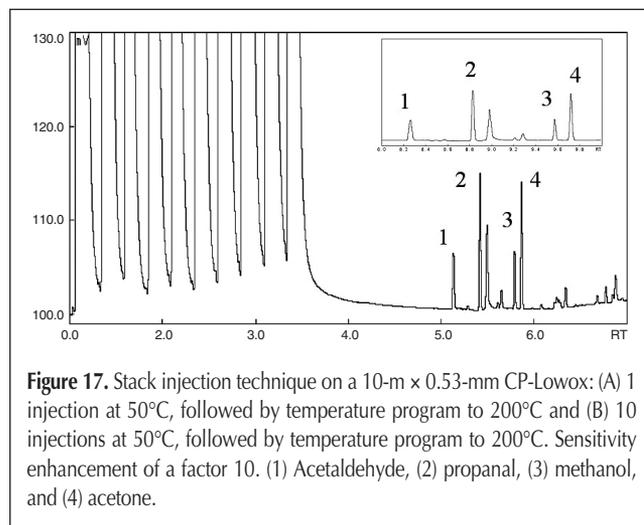
effective, as the large matrix hydrocarbon peak will mask the methanol peak. For the latter application, only TCEP and CP-Lowox will be effective.

In a range of 50 ppb–100 ppm methanol, no liquid phase will be effective, and the CP-Lowox adsorbent phase is the only phase that can separate methanol at these low levels. Figure 15 shows the analysis of methanol in pure propylene starting at 175°C.

Methanol in C_4 . The analysis of methanol in butadiene at the 100-ppm level is possible using the polar TCEP stationary phase. There is, however, a coelution on TCEP of methanol with 4-vinyl cyclohexene (4-VCH), a component that is often present in the 1,3-butadiene matrix. Although TCEP is a very polar and selective phase, the methanol determination is not possible. The separation on the CP-Lowox column is shown in Figure 16. The 4-VCH (peak 2) elutes very quickly and is well resolved from the methanol and other oxygenated compounds. Also note the excellent peak shape for methanol and acetaldehyde.

Stack injection

To determine low-level oxygenated compounds using a single column approach, a new technology was developed that is called “stack injection” (15). The analysis is conducted by performing successive injections of the same sample with a sampling valve while the oven is held at a constant low temperature. Light hydrocarbons, with very low k' values on this column, elute rapidly, whereas oxygenated compounds (higher k' value) from



the sum of all of the injections are trapped and refocused as a tight narrow band at the front of the CP-Lowox column. Enhancement of the sensitivity is proportional to the number of injections made. As an illustration, a stack of ten injections delivers a detection limit of 35 ppb (w/w) of methanol in pentane (Figure 17). The stack approach is applicable for a variety of polar compounds such as aldehydes, ketones, and alcohols. The technique is very easy to implement with a high degree of reliability. The concept of "stack injection" can be employed for other analytical applications when sample enrichment is required for sensitivity enhancement.

Oxygenates impurities in C_1 - C_{12} streams by multidimensional GC

The determination of oxygenated impurities in hydrocarbon streams up to C_{12} is possible using a setup as shown in Figure 18. Here, the injection is performed on a nonpolar precolumn

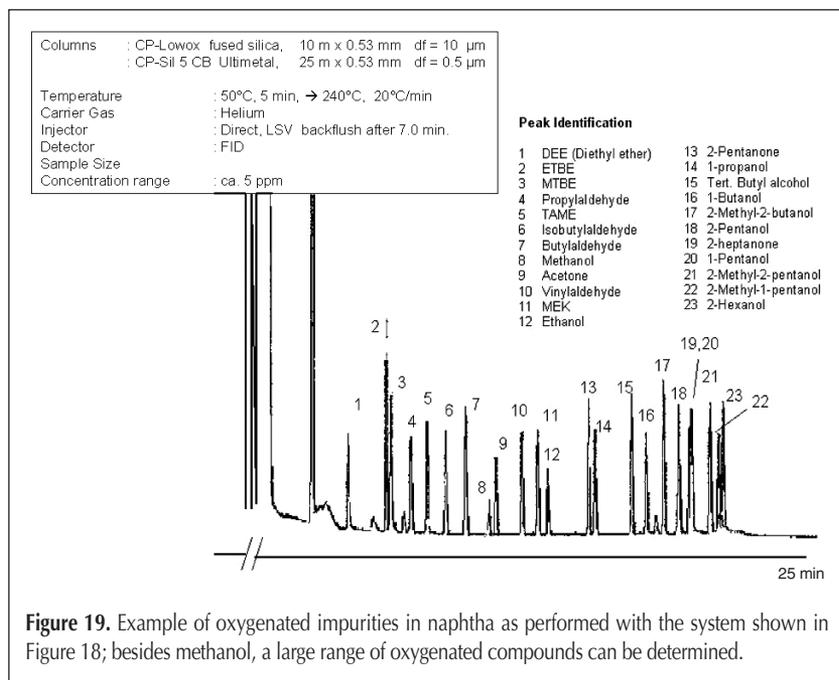


Figure 19. Example of oxygenated impurities in naphtha as performed with the system shown in Figure 18; besides methanol, a large range of oxygenated compounds can be determined.

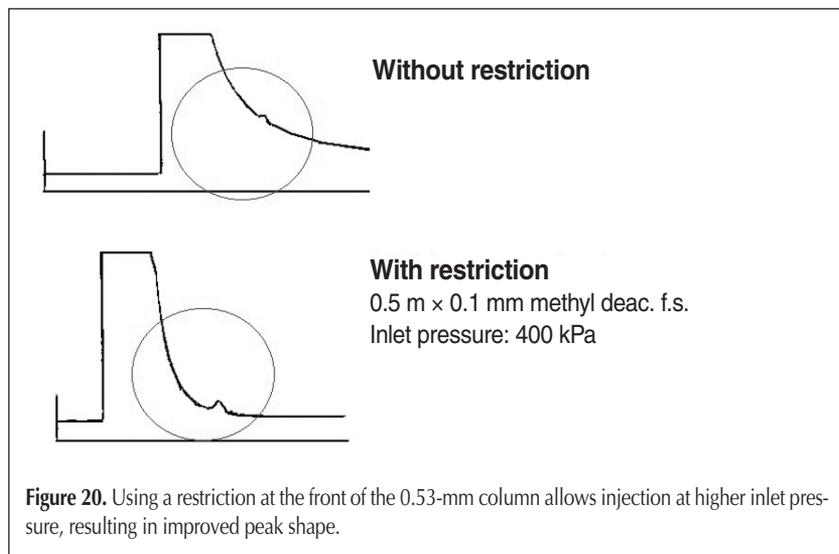


Figure 20. Using a restriction at the front of the 0.53-mm column allows injection at higher inlet pressure, resulting in improved peak shape.

coated with CP-Sil 5 CB. The oxygenated impurities will all elute together in the same range as the C_1 - C_6 fraction. This fraction is injected onto the CP-Lowox column, and all heavier components are backflushed. By injecting a large sample onto the precolumn, it is possible to determine ppb levels of oxygenates in naphtha streams using the described configuration (Figure 19). Such a system can be automated and is suitable for liquid, as well as gas, samples.

Injection of pressurized (gas) samples

Very often, oxygenates need to be determined in gaseous samples. The gas sample can be introduced directly into the CP-Lowox column using its normal inlet pressure of 10–30 kPa. The column can also be connected with a restrictor at the inlet, allowing a higher inlet pressure. The higher inlet pressure will compress the sample size and improve the injection, as shown in Figure 20. The peak shape of the major peaks will improve,

which will in turn improve the quantitation of impurities at low levels. The restrictor can either be a 3-m x 0.25-mm, 1-m x 0.15-mm, or 0.5-m x 0.1-mm fused-silica capillary, as long as it is properly deactivated.

Conclusion

GC is widely applied for trace impurity analysis in hydrocarbon streams. By selecting the optimal column, detectors, and system configuration, it is possible to determine trace levels of hydrocarbons, sulfur compounds, as well as oxygenated compounds. The applications presented in this paper have all been implemented in various laboratories and have produced reliable data.

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