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Select Al2O3 MAPD : a new Inert Al2O3 column for the trace analysis of polar reactive hydrocarbons.

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Introduction

In petrochemical arena analysis of volatile hydrocarbons and impurities has become a routine application. In the C1-C5 range many unsaturated hydrocarbons are present (alkenes, alkynes) and also these have to be separated and quantified. As hydrocarbons are generally believed to be inert they will elute from a wide variety of stationary phases. Liquid type phases like 100% polydimethyl siloxanes will separate the saturated hydrocarbons, but selectivity is not present for separating the unsaturated hydrocarbons. Highly selective materials have been developed for the separation of unsaturated hydrocarbons and especially the adsorption chromatography has proven to be very effective. Materials like alumina [1-3] , silica[4] and carbon[5] have unique selectvities and are widely used. Also for the separation and quantification of polar impurities in hydrocarbons streams adsorbents like PoraBOND, PoraPLOT and Lowox have found wide application. Most widely used is the aluminium oxide. Aluminium oxides separate all C1-C5 hydrocarbons but has to be deactivated. The current alumina column show a lack of inertness towards reactive hydrocarbons cq, propadiene and methyl acetylene. This translates in a reduced response and a non reproducible response in time.
A new Al2O3 adsorbent is introduced called Select Al2O3 MAPD. The new material is intensively deactivated which provides highest response for reactive hydrocarbons and also generates a stable response in time.

Aluminium oxide

Alumina adsorbents in capillary columns have been introduced in 1963 and were commercialized in fused silica capillary columns in 1981. The alumina adsorbent has a very high activity and will retain components as light as ethane. To make the highly active alumina work as stationary phase in gas chromatography, it has to be deactivated. Deactivation can be done in many ways; however, the most practical and reproducible way is the deactivation with inorganic salts. Very popular is the KCl deactivated Alumina which provides a general non-polar alumina surface. Such a column will elute acetylene before the butane as seen in Figure 1. The alumina surface can be made more polar by deactivation with a salt with a higher charge, for instance sodium sulfate. The resulting alumina layer will elute the acetylene after the butane peaks indicating the higher polarity., see fig.2. Also the separation of trans-2-butene and 1-butene is much improved which is especially usefull for impurity analysis in butene streams.

The selectivity of alumina for hydrocarbons is very high. All C_1-C_4 hydrocarbons can be separated baseline. The resolution between the different hydrocarbons is sufficient to measure many traces of C_1-C_4 hydrocarbons in a matrix of any C1-C4 hydrocarbon. For this reason alumina is one of the most widely used columns in petrochemistry for analyzing hydrocarbon impurities in various light hydrocarbon matrices. Alumina columns have been developed in all dimensions, from 0.25 mm ID up to 0.53 and also in UltiMetal tubing.

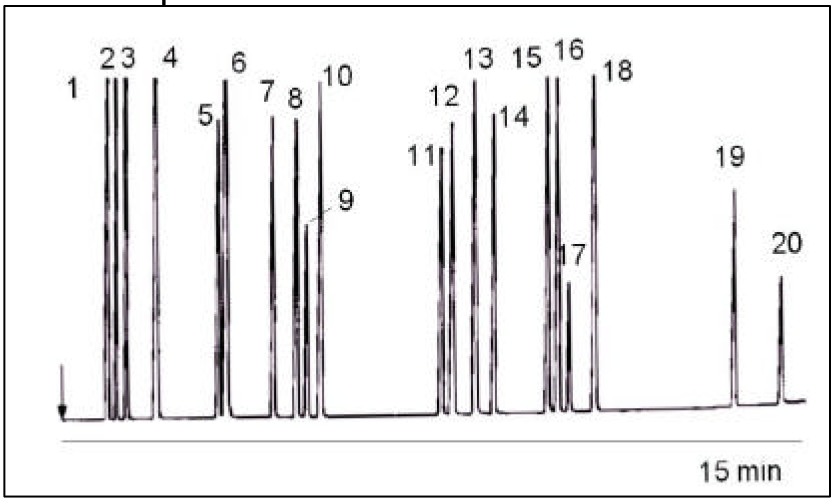

Figure 1: C1 - C6 hydrocarbons on Al2O3, KCl deactivated adsorbent PLOT
Column: 50 m x 0.32 mm fused silica, Al2O3/KCl df=5 um; Oven: 70 °C(4 min)-->180 °C, 10°C/min; Carrier gas: Helium; Injection:Split; Detection: FID; 1:methane; 2:ethane; 3:ethylene; 4:propane; 5:cyclopropane; 6:propylene; 7:acetylene; 8:isobutane; 9:propadiene; 10:butane; 11:trans-2-butene; 12:1-butene; 13:isobutene; 14:cis-2-butene; 15:isopentane; 16:methylacetylene; 17:pentane; 18: 1,3-butadiene; 19:ethylacetylene; 20:hexane

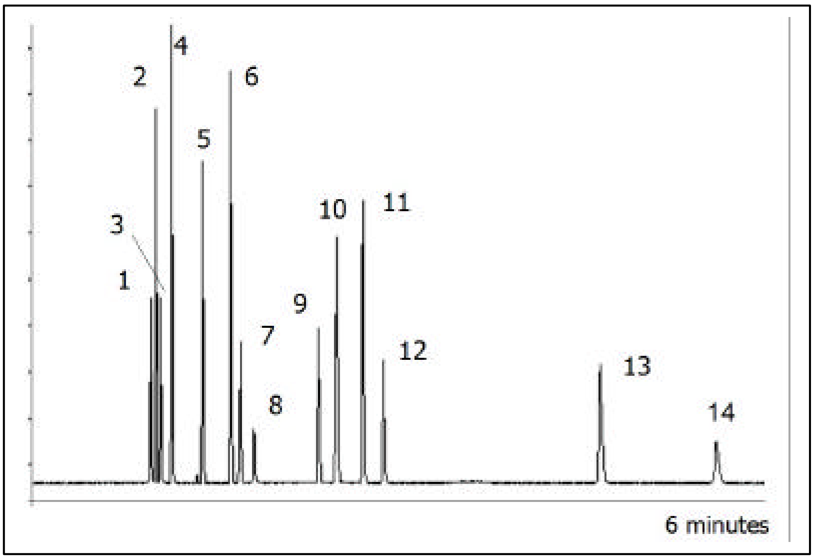

Figure 2: C1 – C4 hydrocarbons on Al2O3, Na2SO4 deactivated adsorbent PLOT
Column: 50 m x 0.32 mm fused silica, Al2O3/KCl df=5 um; Oven: 120 °C; Carrier gas: Helium; Injection:Split; Detection: FID; 1. Methane; 2. Ethane; 3.Ethene; 4.Propane; 5.Propene; 6.Butane; 7.Propadiene; 8.Acetylene 9. tr-2-Butene;; 10. Butene-1; 11. iso-Butene; 12. cis-2-Butene; 13. 1,3-Butadiene; 14.Methylacetylene;

Problems with alumina

Although alumina has unique separation characteristics, it also has limitations. The activity of the adsorbent will adsorb any moisture, carbon dioxide or other polar impurities in the sample. If moisture is brought on alumina, the retention times for hydrocarbons start to decrease. The reduction of retention time is due to water deactivating the sorbent involved. Water can simply be removed by heating up the column to 200 °C for 10-15 minutes. Water will elute and the column is then regenerated. If isothermal set-up is required, one could use a polar pre-column to retain water. A polyethylene glycol coated column with a 1.2 micron film works very well as the C1-C6 hydrocarbons will elute from this column before water elutes. Compounds with some degree of polarity (like a functional group) do not elute or are strongly retained(alcohols, esters ethers, bases, acids). Alumina has been used for analysis of CFC (Chloro-Fluoro-Carbons) which only worked for the fully substituted molecules. When a hydrogen was present the molecule was adsorbed.

Practically the application of Alumina is restricted to hydrocarbons.
Also on hydrocarbon analysis several unwanted interactions can occur. Figure 3 shows a reactivity issue when analyzing propadiene and methyl acetylene.

Figure 4 shows the behavior of an aluminium oxide column when used in a process environment running then same analysis over a period of 6 months. The response of propadiene relative to propane is plotted. During this period the response decreased with near 30%.

The absolute response to the reactive hydrocarbons varied strong from column to column and was much lower then theoretically would be expected. The

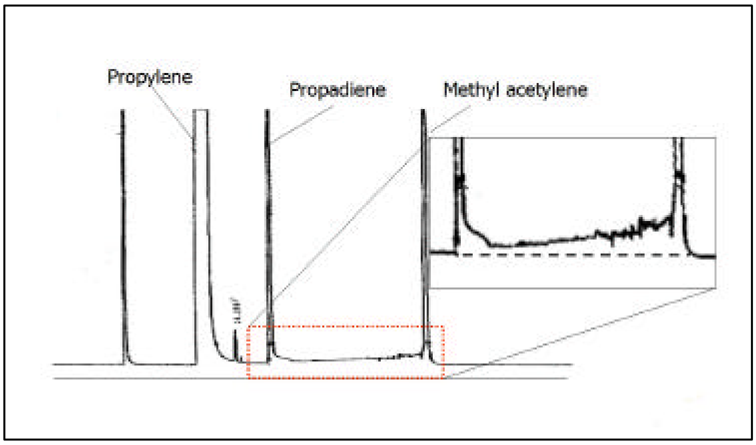

Fig. 3

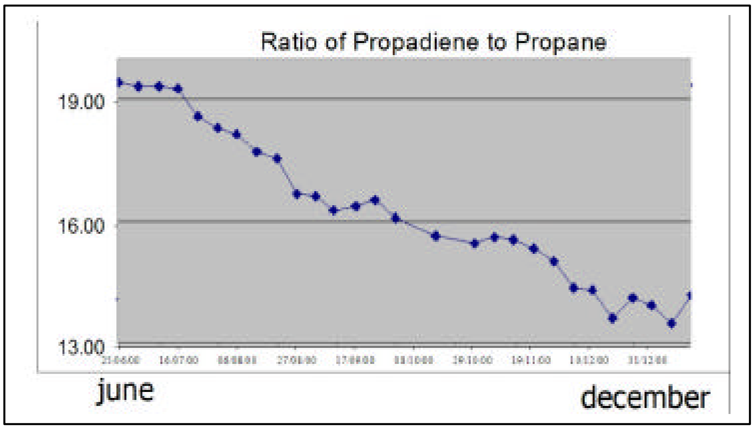

Fig. 4

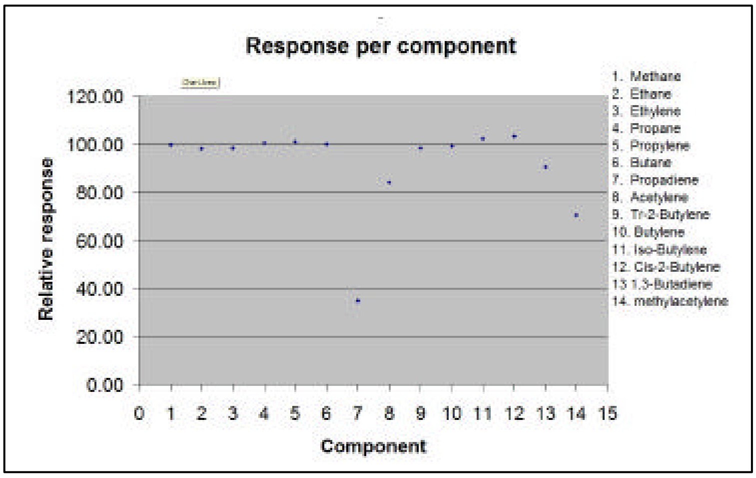

Fig. 5

typical response for all hydrocarbons is shown in figure 5: Propadiene (PD) response is approx. 35% and methyl acetylene (MA) is approx. 70%. Table 1 show the response factor for MA and PD relative to propane of 10 commercially available Al2O3 columns.

Table 1 : Response of MA and PD relative to propane

	Response MA (%)	Response PD (%)
Column 1 supplier 1	59	24
Column 2 supplier 1	63	24
Column 3 supplier 1	59	18
Column 1 supplier 2	73	66
Column 2 supplier 2	73	57
Column 1 supplier 3	64	32
Column 2 supplier 3	56	27
Column 3 supplier 3	63	24
Column 4 supplier 3	59	25
Select Al2O3 MAPD	93	84

The reactivity towards these hydrocarbons is related to their elution temperature and retention time. This is not a surprise, as longer elution times gives the component more chance to interact and also higher elution temperatures will not contribute to a better response.

Figure 6 shows the response of different hydrocarbons run on a polar type Al2O3 capillary but the analysis was done using different column flow rates With increased flow rate the response also increases significantly for propadiene and methylacetylene.

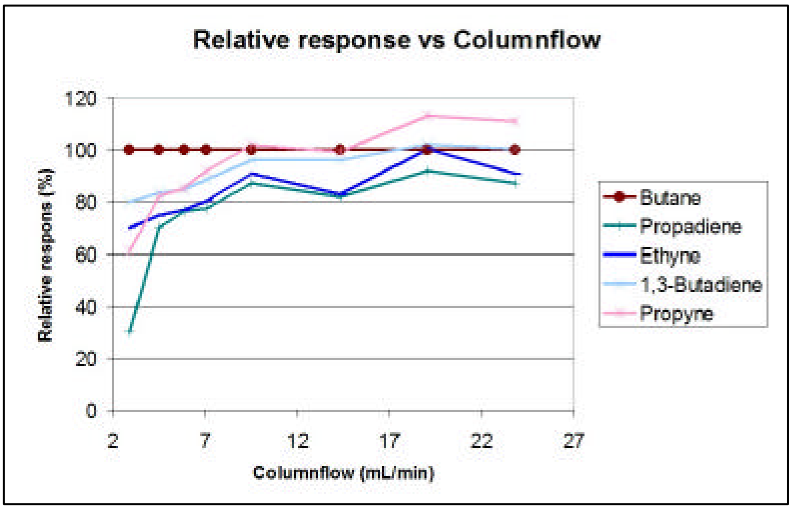

Fig. 6

A new Al2O3 column: Select Al2O3 MAPD

As it is not possible to operate columns at such high flow rates there is a clear room for improvement on the Al2O3 and challenge was to improve the response and stability for the reactive hydrocarbons methyl acetylene and propadiene.

The new alumina was given a special treatment and was deactivated much more intense than usually done with Al2O3/KCl and the Al2O3/Na2SO4 adsorbents. As a result the retention and reactivity was decreased and a highly stable column was obtained especially for methyl acetylene(MA) and propadiene(PD). The selectivity of the Select Al2O3 MAPD is close to the Na2SO4 selectivity although it is not exactly identical and small variations can occur. The response for propadiene is more than doubled, see figure 7.

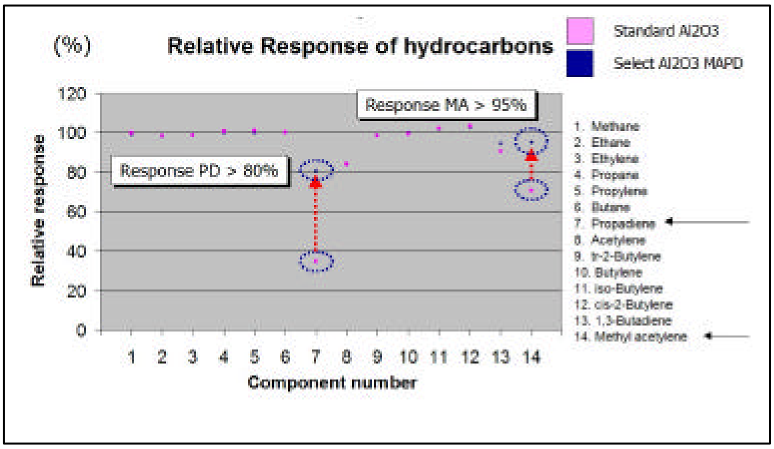

Fig. 7

Typical characteristics of this new column are:

Up to a factor 2 higher response for acetylene, methylacetylene and propadiene;

This is especially important when running traces. In many industrial hydrocarbon streams there are tight specifications on these reactive

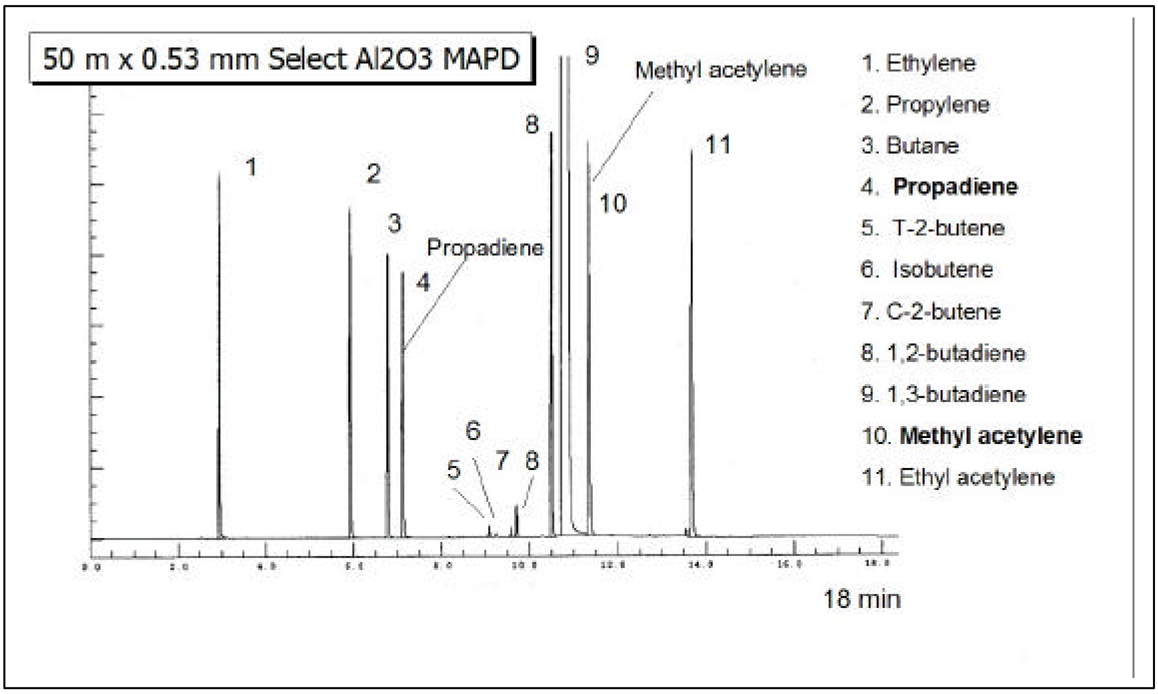

Fig. 8

hydrocarbons. Specification which are in the order of 1 – 3 ppm in a ethylene, propylene, butylene and butadiene product. Figure 8 shows an analysis of a 1,3 Butadiene stream. Note the high responses for the reactive hydrocarbons.

Improve detection limits up to a factor 2-3

As the signal produced for a propadiene peak is 2-3 times higher, so is the signal – noise ratio. As a result detection limits can be lowered with a similar factor. This makes the method more accurate and will also provides more accurate measurements.

No change of response in time

The Select Al2O3 MAPD was tested in a on-line analyzer measuring continiously light hydrocarbons including MA and PD over a period of 18 weeks, see fig.9 No change in response factor was observed during this period which was a welcome improvement for this hydrocarbon method.

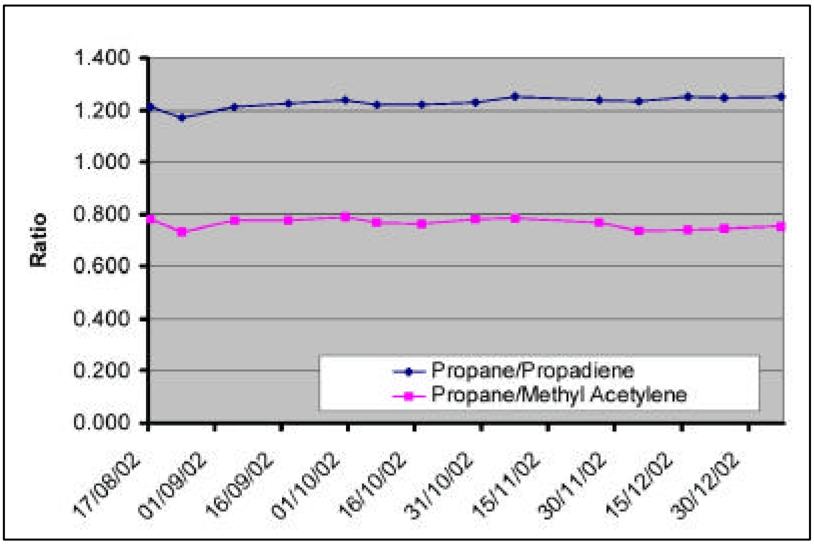

Fig. 9

Shorter run times

The run times for most hydrocarbon applications are shorter due to the lower retention of the column. Although the amount of Aluminium oxide in the column is the same, only the least active sites will participate in the retention process(the sites with highest activity are all deactivated). As a result the peak shape improves and peaks elute faster. The loadability was not found to be significantly lower.

Impact of water

Despite of the better inertness the Select Al2O3 MAPD remains senstive to water in the sample or the carrier gas. Water will be trapped on the alumina and will make components elute faster. Regeneration(water bake-out) is done by baking 5-10 minutes at 200 C. This can be done periodically or after each analysis. Regeneration will be approximate 2 times faster with the Select Al2O3 MAPD capillary. If an isothermal setup is preferred one can take a CP-Wax thick film pre-column, let the c1-C6 hydrocarbons go through and retain the water on the CP-wax column. After hydrocarbons are lead into the alumina column, a valve switch sent the later eluting water peak to vent or to the detector.

Application

This new alumina column can be used for all applications where C1-C10 hydrocarbons are analyzed and where there is an interest in quantitative analysis of reactive hydrocarbons like propadiene and methyl acetylene. Also compounds like acetylene, ethyl - and vinylacetylenes have least chance for reactions using this inert alumina.
We have seen good performance for % and impurity analysis see figures 10-14.

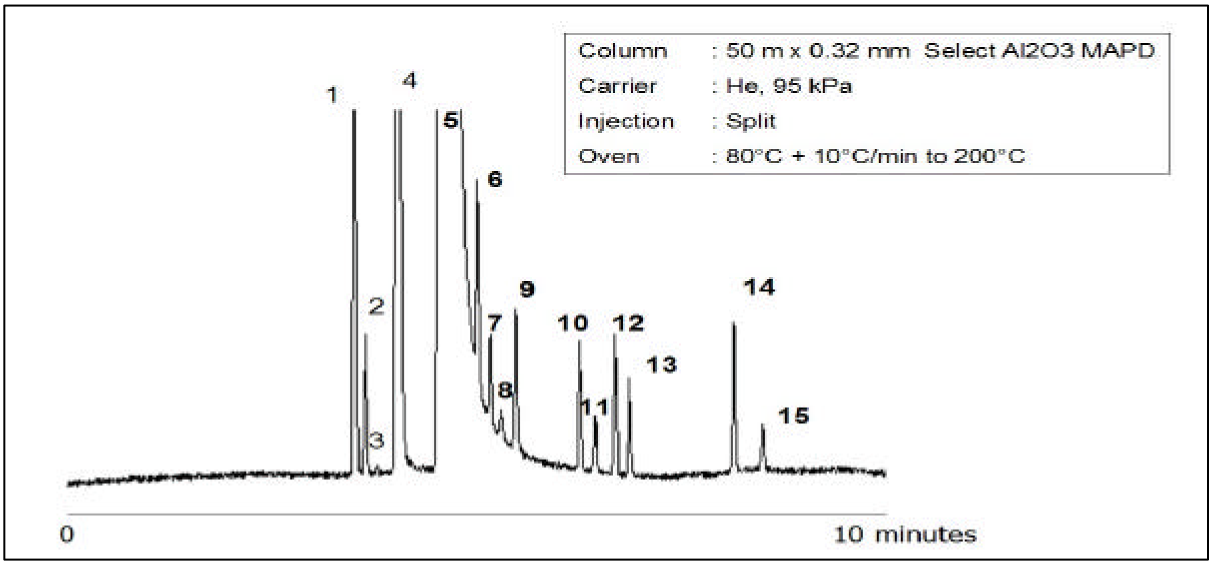

Fig.10: Impurities in propylene; 1 Methane; 2 Ethane; 3 Ethylene; 4 Propane; 5 Propylene; 6 Cyclopropane; 7 Butane 8 Propadiene; 9 Acetylene; 10 Trans-2-Butylene; 11 Butylene; 12 Iso-Butylene; 13 Cis-2-Butylene; 14 1,3-Butadiene; 15 Methylacetylene;

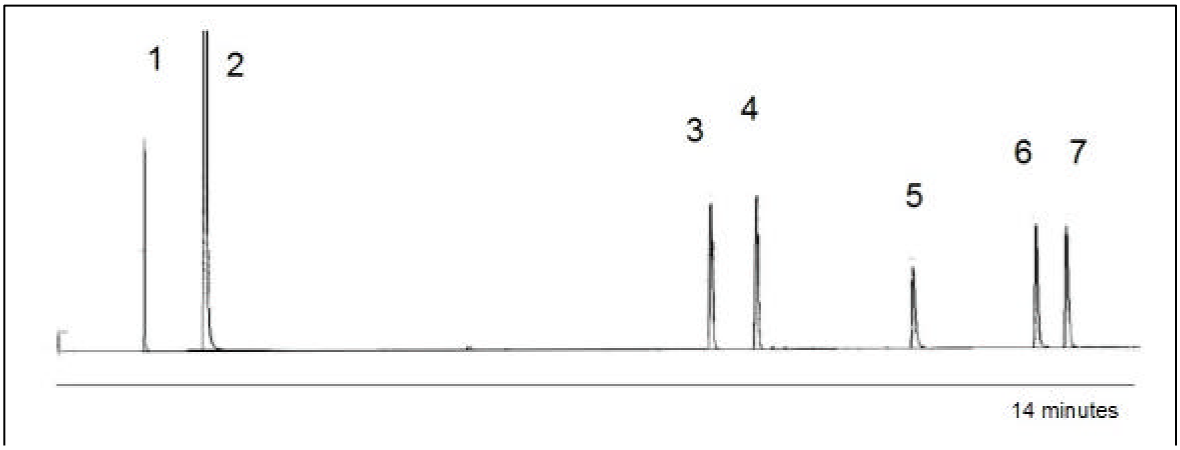

Fig 11 Elution of acetylenes
Column : 50 m x 0.53 mm Select Al2O3 MAPD; Oven: 40°C, 5min –> 160°C, 10°C/min –> 200°C, 20°C/min; Carrier gas : 4 psig, 4 min –> 11 psig, 0.5 psig/min
1 Ethane; 2 Propane; 3 Trans-2-butene; 4 Iso-pentane; 5 Methyl acetylene; 6 Vinyl acetylene
7 Ethyl acetylene; Ref: Jim Luong, Dow Chemical Canada

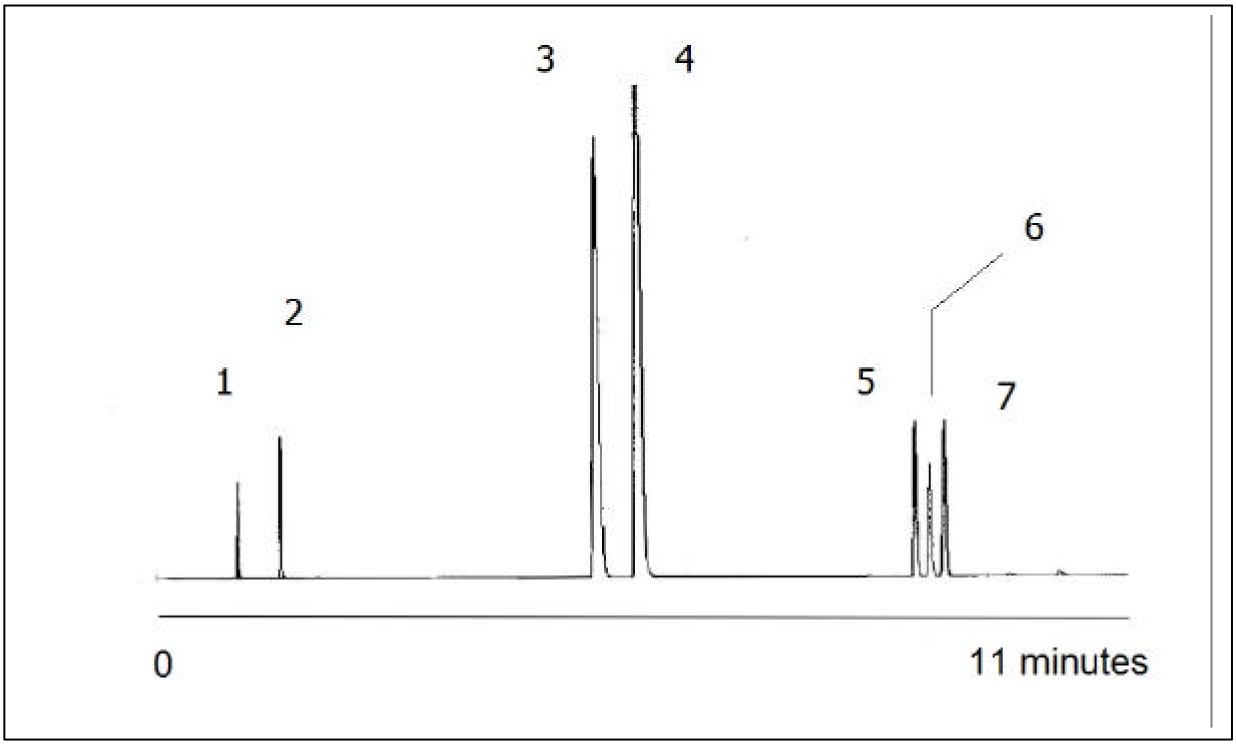

Fig.12
Column : 50 m x 0.53 mm Select Al2O3 MAPD; Oven: 40°C, 5min –> 160°C, 10°C/min –> 200°C, 20°C/min; Carrier gas : 4 psig, 4 min –> 11 psig, 0.5 psig/min
1 Methane; 2 Ethylene; 3 Iso-butane; 4 n-butane; 5 Iso-pentane; 6 Cis-2-butene; 7 n-pentane
ref: Jim Luong, Dow Chemical Canada

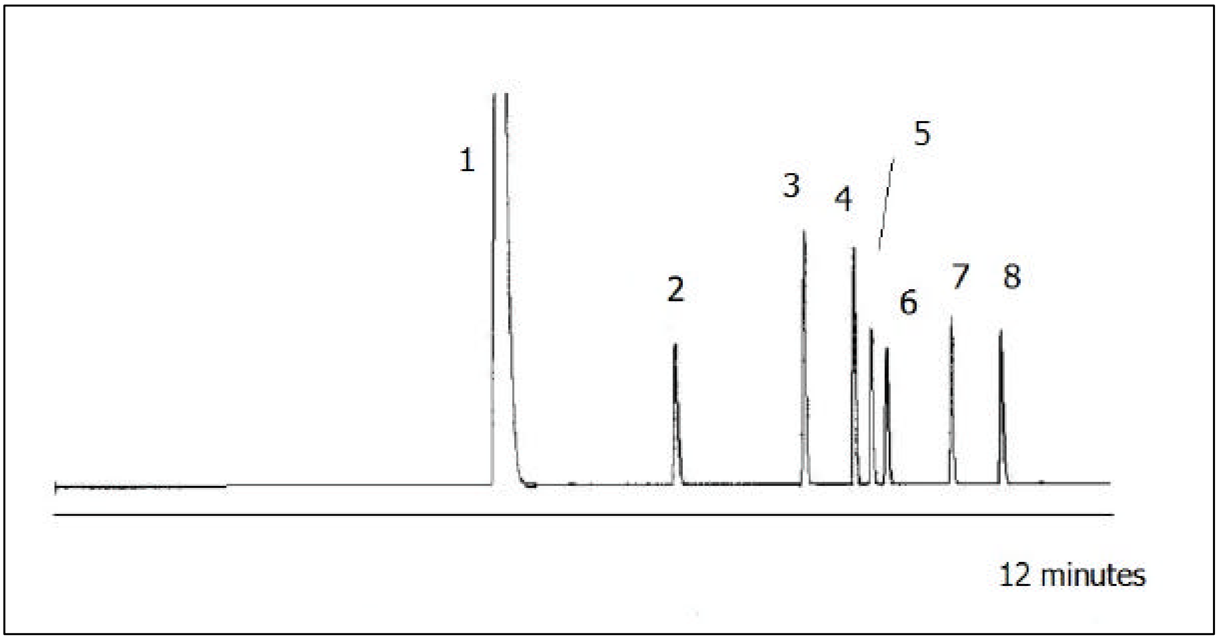

Fig.13
Column : 50 m x 0.53 mm Select Al2O3 MAPD; Oven: 40°C, 5min –> 160°C, 10°C/min –> 200°C, 20°C/min; Carrier gas : 4 psig, 4 min –> 11 psig, 0.5 psig/min
1 Propylene; 2 Propadiene; 3 Trans-2-butene; 4 Iso-butene; 5 Cis-2-butene; 6 n-pentane; 7 1,2 butadiene; 8 1,3-butadiene
ref: Jim Luong, Dow Chemical Canada

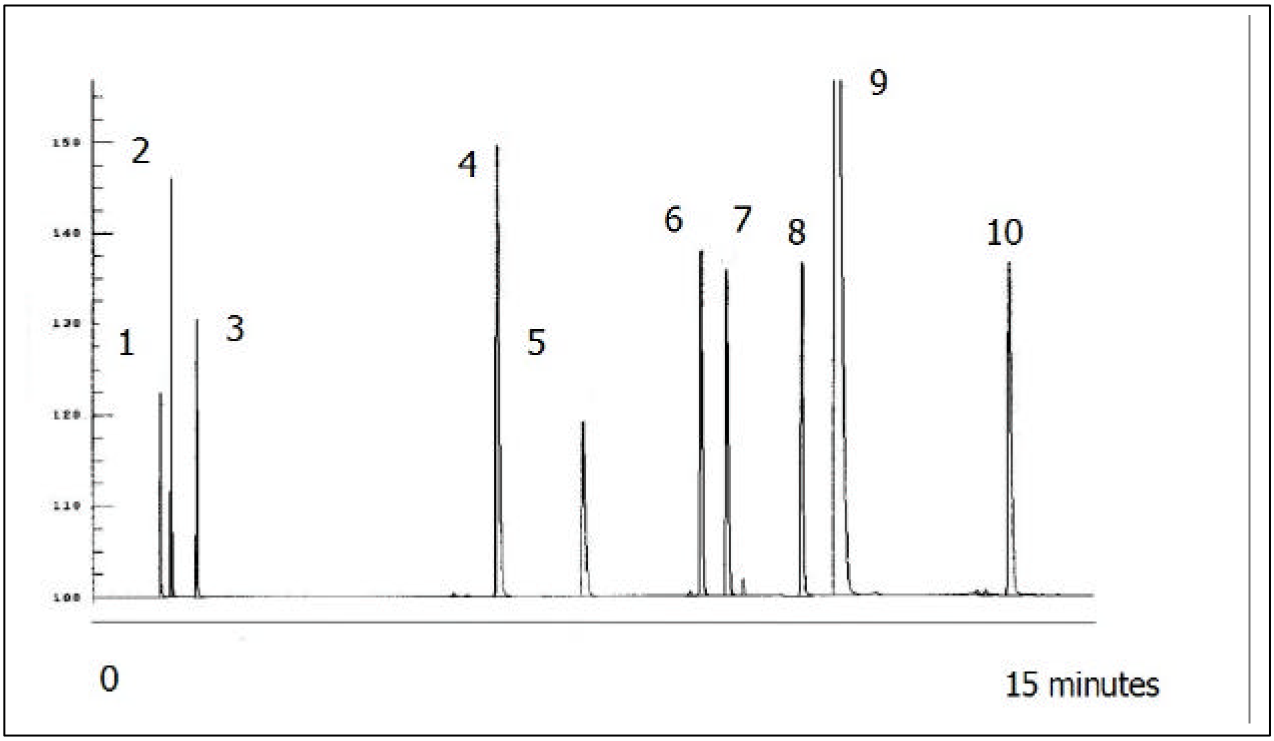

Fig.14
Column : 50 m x 0.53 mm Select Al2O3 MAPD; Oven: 40°C, 5min –> 160°C, 10°C/min –> 200°C, 20°C/min; Carrier gas : 4 psig, 4 min –> 11 psig, 0.5 psig/min
1 Methane; 2 Ethane; 3 Ethylene; 4 N-butane; 5 Propadiene; 6 1-butene; 7 Iso-butene
8 1,2-butadiene; 9 1,3-butadiene; 10 Ethyl acetylene
ref: Jim Luong, Dow Chemical Canada

Conclusion

A new Al2O3 PLOT columns is introduced with a better deactivation. The Varian Select Al2O3 MAPD shows improved inertness towards reactive hydrocarbons, especially propadiene and methylacetylene when analyzed down to ppm levels. Response for these components is much higher and also the response factor in time remains constant making the column very reliable in a analyzer environment.. The Select Al2O3 MAPD separates light hydrocarbons in the C1-C10 range can be used for similar applications as the existing Al2O3 columns. Nett benefit will be better detectivity and a consistent data.

References

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Acknowledgements

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Ordering Information

Capillary columns

Varian Select Al2O3 MAPD 50 m x 0.32 mm		CP7431
Varian Select Al2O3 MAPD 50 m x 0.53 mm		CP7432
Fused silica coupling		
Universal CP-QuickSeal	(10pc)	CP4787
Universal CP-QuickSeal Splitter	(5pc)	CP4798
Reamers		
For graphite and vespel ferrules		CP8427
Ferrules		
Graphite ferrules 1/16” for 0.53 mm	(10pc)	CR211108
Graphite ferrules 1/16” for 0.53 mm in HP-series	(10pc)	CR211168
Graphite ferrules 1/16” for 0.32 mm	(10pc)	CR211105
Graphite ferrules 1/16” for 0.32 mm in HP-series	(10pc)	CR211165
Graphite Vespel ferrules 1/16” for 0.32 mm	(10pc)	CR213105
Graphite Vespel ferrules 1/16” for 0.32 mm in HP series	(10pc)	CR213165
Graphite Vespel ferrules 1/16” for 0.53 mm	(10pc)	CR213108
Graphite Vespel ferrules 1/16” for 0.53 mm in HP series	(10pc)	CR213168
Gas Leak detector		
220 V Eur		CP80610
240 V UK		CP83610
110 V USA		CP87610
Filters		
Gas-Clean Oxygen filter		CP17970
Gas-Clean Moisture filter		CP17971
Gas-Clean Charcoal filter		CP17972
GC-MS Filter		CP17973
Connecting unit for 1 filter 1/4” tubing		CP7980
Connecting unit for 1 filter 1/8” tubing		CP7988
Connecting unit for 2 filter 1/4” tubing		CP738406
Connecting unit for 2 filter 1/8” tubing		CP738407
Connecting unit for 4 filter 1/4” tubing		CP7989
Connecting unit for 4 filter 1/8” tubing		CP736520
Flush head for Connection unit		CP7987
Column Cutting		
Tungsten Carbide Glass Knife		CP22674
Carborundum Glass file		CP22672

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