Improve Trace Analysis of Acetylene, Propadiene, and Methyl Acetylene Impurities with Higher Capacity Alumina MAPD Columns

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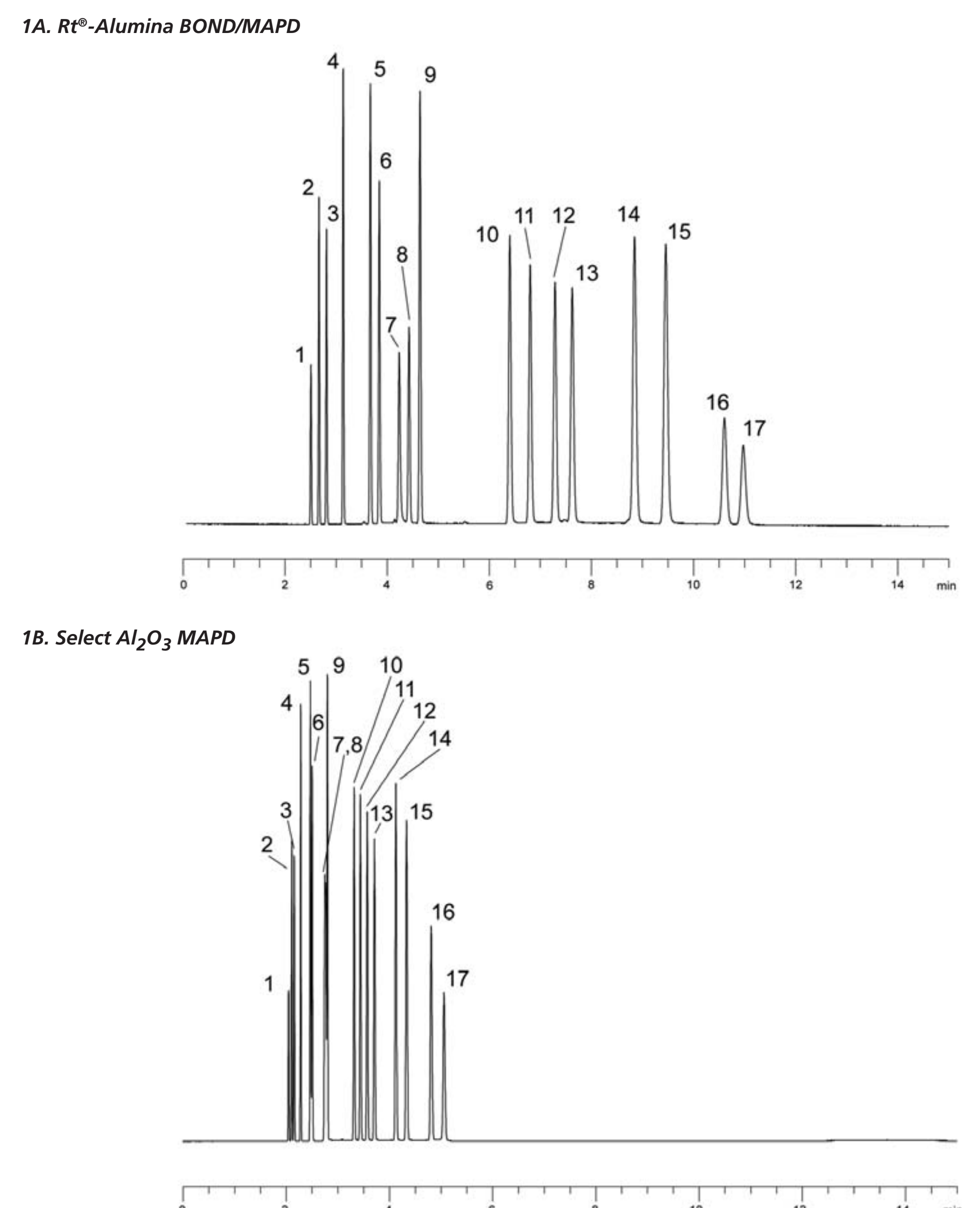
When analysing trace impurities in petroleum gases, such as propylene, ethylene, or 1,3-butadiene, column capacity (loadability) is an important factor in obtaining accurate data. Phase overload results in peak tailing, which can be problematic when trace level impurities elute near the main component where they may be obscured by the larger peak. Peak tailing can be further exacerbated by residual activity on the adsorbent surface. Using a higher capacity column with an appropriate deactivation is a good strategy for reducing tailing and improving accurate quantification of low level polar impurities in volatile petroleum streams.

MAPD alumina PLOT columns are commonly used for these applications because the selectivity of alumina makes it very useful for separating C1-C5 hydrocarbons. Although selectivity is very good for these compounds capacity is often poor, which limits the amount of sample that can be injected. Larger sample volumes can be desirable when less sensitive detectors (e.g. TCDs) are used or when trace levels of impurities, such as acetylene, propadiene, or methyl acetylene, must be detected in order to prevent damage to polymerisation catalysts.

New Rt®-Alumina BOND/MAPD columns have an improved deactivation, increased capacity, and greater absolute retention compared to other commercially available MAPD PLOT columns. As shown in a comparison of absolute retention, all peaks are well resolved on the Rt®-Alumina BOND/MAPD column and no coelutions are observed (Figure 1). Greater retention increases the separation space, which reduces the likelihood of coelution and can lessen the impact of tailing. Absolute retention was compared using an isothermal oven temperature of 130°C; however, several critical compounds were not resolved on the Select Al_2O_3 MAPD column at this temperature, so optimized conditions for each column were used for capacity evaluations.

To assess capacity, each column was tested at the temperature shown on the manufacturer's QA protocol in order to achieve comparable retention and adequate resolution. A range of sample volumes of a QA test mix were analysed on each column using a 6-port sampling valve and 5µL to 250µL sample loops. Peak tailing was measured for the analytes that were most likely to exhibit tailing and be sensitive to poor capacity in actual impurity testing. As shown in Table I, much less peak tailing was observed on the Rt®-Alumina BOND/MAPD column. Symmetrical peaks were obtained across a wide sample volume range, indicating that the column deactivation was highly effective and also that capacity was greater on the Rt®-Alumina BOND/MAPD column. Linearity was also assessed, as shown in Figure 2, and excellent correlations were achieved for all target impurities across the test range.

When analysing impurities, such as acetylene, propadiene, and methyl acetylene in petroleum gases, column capacity is an important consideration. Rt®-Alumina BOND/MAPD columns offer higher capacity than other commercially available MAPD columns and are recommended for analysing polar impurities in light hydrocarbon streams. Greater capacity improves data accuracy due to better peak symmetry and a wide linear range.



Columns: 50m x 0.53mm ID x 10µm; Sample: PLOT column QA test mix (DCG# 547267); Injection: 5µL, split, 200°C; Split vent flow rate: 80mL/min.; Oven: 130°C, isothermal; Carrier gas: helium, (4.4psi, 30kPa); Detector: FID, 200°C. Peaks: 1. Methane, 2. Ethane, 3. Ethylene, 4. Propane, 5. Cyclopropane, 6. Propylene, 7. Acetylene, 8. Propadiene, 9. n-Butane, 10. trans-2-Butene, 11. 1-Butene, 12. Isobutene, 13. cis-2-Butene, 14. Isopentane, 15. n-Pentane, 16. 1,3-Butadiene, 17. Methyl acetylene.

***Figure 1:** Rt®-Alumina BOND/MAPD columns have greater absolute retention than Select Al_2O_3 MAPD columns, resulting in greater capacity through increased separation space.*

Rt®-Alumina BOND/MAPD (130°C)

Tailing Factor (USP)			
Sample Size (µL)	**Propadiene**	**Acetylene**	**Methyl Acetylene**
5	1.038	1.227	1.083
10	1.040	1.219	1.130
25	1.058	1.248	1.216
50	1.085	1.292	1.388
100	1.094	1.316	1.546
250	1.177	1.481	2.224

Select Al_2O_3 MAPD (100°C)

Tailing Factor (USP)			
Sample Size (µL)	**Propadiene**	**Acetylene**	**Methyl Acetylene**
5	1.073	1.298	1.908
10	1.098	1.478	2.743
25	1.165	1.902	4.555
50	1.304	2.580	6.871
100	1.448	3.241	9.208
250	1.979	4.882	15.476

Table I: *Higher capacity is also demonstrated by comparing peak symmetry. Rt®-Alumina BOND/MAPD columns produce more symmetrical peaks, even when more material is injected.*

2. Rt® - Alumina BOND/MAPD Linearity

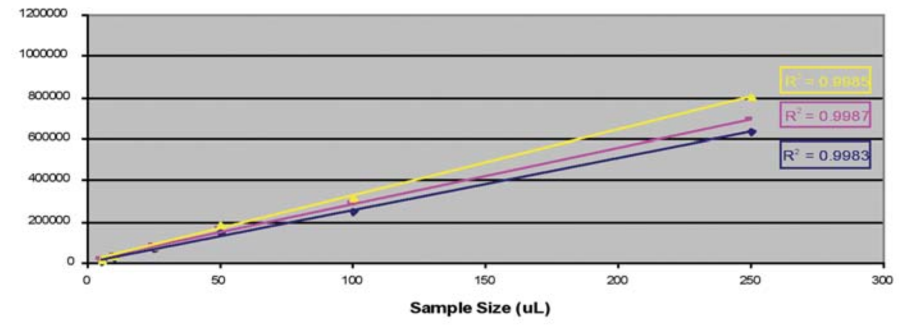


Figure 2: *Higher capacity results in a wide linear range and accurate quantification, even at levels that can produce tailing and incomplete separations on other MAPD columns.*
(yellow = methyl acetylene, pink = acetylene, blue = propadiene)

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