TECHNICAL NOTE

Gas Chromatography

# Comparison of Packed vs. PLOT Columns in Arnel Light Hydrocarbon Analysis

## Overview

As leaders in the manufacturing of high performance Refinery Gas Analyzers (RGAs), we constantly test technologies that could improve our products. One technology that we tested is the Porous Layer Open Tubular (PLOT) column.

Although catalog chromatograms make it look like PLOT columns are ideally suited to refinery gas analysis, they have practical flaws when used to analyze real samples. Compared to packed column analyzers, PLOT column instruments:

- Are poisoned by $H_2O$, $CO_2$, $H_2S$ and $NH_3$
- Require long run time to elute $C_5$ and $C_6$ components
- Require closer monitoring by higher-level operators
- Have poor detection limits
- Are more fragile
- Have higher initial costs and operating cost

## For Arnel RGAs, Packed Columns Are Better

PerkinElmer's packed column RGAs have produced consistent results for years with minimum maintenance. Because PLOT columns cannot meet this requirement, we continue to use packed columns.

## $Al_2O_3$ Column Poisoning

The $Al_2O_3$ PLOT column is poisoned by $H_2O$, $CO_2$, $H_2S$, other sulfur compounds and $NH_3$ (typical components in refinery streams). As the column poisons, the retention times for all components move. With severe poisoning, *the retention order changes.*

Poisoning by $H_2S$, other sulfides and $NH_3$ is not reversible. If your samples contain these components, you will have to constantly adjust your calibration and eventually replace the column.

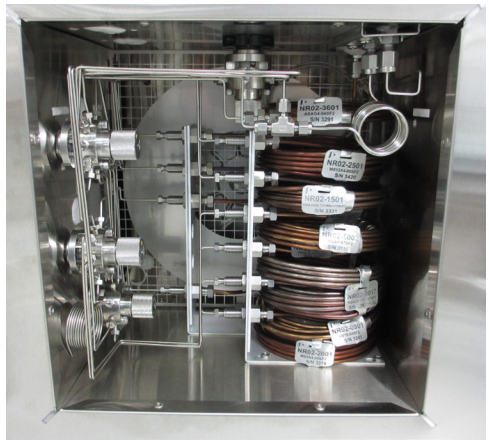

*Figure 1.* Model Arnel 1157 RGA.

$H_2O$ and $CO_2$ poisoning is reversed by conditioning the column at a high temperature. There are two conditioning approaches: One approach is to ramp the column up to the conditioning temperature for ~15 minutes after every analysis. This assures fairly stable retention times. However, the total analysis time is greatly extended by the conditioning and cool down times. Also, temperature cycling may loosen capillary connections.

A second approach is to tolerate small retention time shifts and condition the column on a schedule. This approach keeps run times shorter but requires more skilled operators and still runs the risk of peak retention time collapse.

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## KEY ADVANTAGES OF PACKED COLUMNS

- **Poisoning:** Not poisoned by ammonia or sulfur compound
- **Run Time:** Fastest packed RGA column available
- **Detection Limits:** No column overload issues eliminate need for split injector
- **Ruggedness:** Engineered with stainless steal
- **Operator Interaction:** Easy to use for all operators
- **Running Costs:** Lower consumable costs and energy consumption

## Long Run Times

Although refinery samples often contain $C_5$ olefins and heavier components, the process engineer is usually only interested in these components as a single "$C_{5=}$, $C_{6+}$" group. Packed column analyzers use a "pre" or "cut" column and backflush all of these components as a single peak. Thus, the analysis is complete when n-pentane elutes.

Injection of a refinery sample onto a PLOT column requires that the analyzer run until all components elute. Even running at elevated temperatures, PLOT column analyses that include heavy components can take twice as long as packed column analyses. Also, oven cool down must be added to the total analyses time.

## Guard Column Problems

Some analysts try to eliminate the poisoning problems by installing a short "guard column" in front of the analytical column. The idea is that guard column will absorb the problem components such as water and $CO_2$ before they reach the PLOT column. Unfortunately, any guard material selected has selectivity to more than just the components of interest. Thus, components of interest are also absorbed.

Even more of an issue is that the operators don't have a reliable method to know when the guard column is saturated and must be replaced. Compounding the problem is the fact that the absorption ratios will change as the column is saturated. Analyzed components will change in response without any way for the operator to know that the saturation has occurred.

## Split Injection Port Problems

Capillary columns require split injection ports. A change in the split ratio after external standard calibration will cause significant error. This is especially true when results are not normalized. A split ratio that is too low will overload a column. A split ratio that is too high will raise the detection limits.

PLOT columns overload very easily and require small samples and high split rates. Besides the obvious detection limits problem, high split rates lower reproducibility and consume a large amount of carrier gas.

## Poor Light Gas Detection Limits

Molecular sieve $H_2$, $O_2$, $N_2$, $CH_4$, CO) and porous polymer ($CO_2$ and $C_2$'s) PLOT column components are detected by TCD's Splitting the sample to avoid PLOT or micropacked columns overload and obtain good separations causes poor detection limits. The poor detection limits lead to poor dynamic ranges. 1/8" packed column analyzers use 1cc or greater sample loops. Thus, packed column analyzers have better detection limits for these gases.

## Problems Protecting A Molecular Sieve PLOT Column

A molecular sieve column must be protected from poisoning by the use of a porous polymer column that is backflushed to vent. Because performance may be affected by backflushing a capillary column, packed columns are always used as the guard column. Packed column lights gas channels provide both simplicity and improved sensitivity. The poisoning of the molecular sieve is a subtler problem when using molecular sieve PLOT columns. Capillary columns have a lower capacity to absorb impurities before their performance degrades. A packed column molecular sieve can last much longer before reconditioning.

## Greater Operator Interaction

All these problems mean that the operator responsible for a PLOT based analyzer must be aware of potential problems. The operator must also be able to solve these problems. While having a skilled operator may not be an issue during the day, the third shift operator is often not as skilled.

## Higher Costs

PLOT columns require split injectors. Packed column analyzers do not require injection ports. Thus, packed column analyzers can reduce on initial costs. They also save carrier gas because there is no split flow.

Packed column analyzers are rugged and run isothermally. PLOT columns are more fragile and require temperature programming. To some degree, all PLOT columns suffer from material flaking off of the column wall. This loose material is pushed through the column causing spikes at the detector. Temperature programming means that fittings over time must be retightened. Handling will cause a broken column.

## Summary

While PLOT columns have excellent separation ability for certain samples (such as ethylene and propylene streams), real world refinery samples are better analyzed using packed columns. Packed column RGAs are extremely rugged, flexible, are not poisoned by the sample, run faster, have greater dynamic range and require basically no maintenance.

**PerkinElmer, Inc.**
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
**www.perkinelmer.com**

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