A New High Retentive and Selective GC column for the Separation of CFC, based on Alumina Adsorbent

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Chloro-Fluoro Carbons (CFC), also known as Refrigerants or Propellants, are highly volatile compounds which can be analyzed via gas chromatography. Their production, application and especially release is controlled carefully as they have a direct impact on the ozone layer. For the separation via GC, we meet some challenges as due to their volatility, a stationary phase is required with very high retention. In gas liquid separations films up to 10 micrometer can be coated, but such thick-films coated columns have low efficiency, due to the huge contribution to mass transfer in the liquid phase.

A more elegant solution is to use adsorbents for the separation. Alumina coated PLOT columns were developed and applied already 25 years ago with limited success due to high activity of the alumina materials used. Porous polymers also did not provide the correct selectivity and showed severe band broadening.

The use of alumina was recently revisited for hydrocarbon separations and during this project a procedure was developed to reduce the activity of the alumina significantly, making this adsorption material applicable for a large range of CFC type compounds.

The resulting AluminaBOND – CFC column was tested with a series of halogenated components well although the column still showed some reactivity.

In this poster the data will be presented on application, linearity and limitation of using new generation modified alumina.

Backgrounds

The analysis of the different chlorofluorocarbons (CFCs) has become a priority analysis in the environmental field as several CFCs are held responsible for the breakdown of the ozone layer in the upper stratosphere [1]. CFCs have been used for a long time as blowing agents, propellants and also as cleaning agents. As the FCCs were used widely an investigation was started to find alternative compounds [2]. The hydrofluorocarbons (HFCs) show to be very promising but are also not without risk. The HFCs are highly effective absorbers of infrared radiation which would contribute to global warming.

CFC compounds and nomenclature

The CFC compounds are also known under names as "Arcton", "Freon", "Frigen" or "Genetron" are individually identified by a CFC code based on the "rule of 90" [3]. To derive the chemical formula for a certain CFC you have to add "90" to the CFC number. From the resulting number you can deduct the structure.

For example: CFC 12. Adding 90 will result in "102". The number "102" indicates: 1 carbon, 0 hydrogen, 2 fluorine. The two open positions are for chlorine, so the structure is CCl₂F₂.

Other common CFCs elute in order of increasing boiling point. More physical and chemical properties of CFCs can be found in [4]
Separation of CFC compounds

CFC are highly volatile compounds. The analysis of these compounds can therefore be done by gas chromatography. One of the requirements to make a separation of volatile compounds possible is to use a stationary phase which provides sufficient retention for the compounds to be measured. Separations of CFCs have been done with packed columns as these columns can be packed with adsorbents or with liquid phases with a very low phase ratio making a separation possible. The separation obtained was mainly on selectivity combined with a high k values. The plate number of the packed column is very low. With the introduction of the chemically bonded phases on capillary columns the selectivity could be combined with a high theoretical plate number offering more perspective in resolution. Many of the CFCs with boiling points above ca - 30 °C could be separated on thick film non-polar capillary columns like Rtx-1. The separation of CFCs with such low boiling points requires higher retention. This could be obtained by applying sub ambient conditions, however this is for many users not a practical alternative. With the introduction of the porous layer open tubular (PLOT) columns and the high selectivity of the adsorbents used, the separation of many volatile CFCs was possible at oven temperatures above ambient [5]. Porous polymers showed interesting properties for CFC, but were not able to provide the right selectivity. Besides that, several CFC showed severe band broadening depending on type and pore size distribution of the porous polymer used. Very good results were obtained with alumina as stationary phase. However, the high catalytic activity of this material caused a non reproducible retention behavior, especially for the partially halogenated CFC compounds. Noy reported issues using Al2O3/KCl type columns [6]. In this publication he referred to decomposion of methylene chloride and CFC-22.

Alumina as adsorbent

Alumina has shown to be a superior material for retaining volatile hydrocarbons. The selectivity allows all isomers to be base line resolved at temperatures above ambient. Alumina is highly retentive and to control retention, the alumina surface must be deactivated with inorganic salts, like KCl or sodium sulfate. The application of alumina for separation of polar analytes has not been successful, however, neutral components like halogenated compounds, can be separated quite successfully. As the activity of the alumina causes unwanted interactions, we increased the salt deactivation and surface coverage of alumina, resulting an alumina column that shows improved behavior towards sensitive compounds.

Testing with 1,2 butadiene

One of the probes that was used for testing activity of alumina is 1,2 butadiene. This component can form dimers and trimers when analyzed using alumina. The analysis of butadiene was performed using a commercial alumina column, 50m x 0.32mm Al2O3/KCl and also on a new CFC deactivated column of similar dimensions. Also the Na2SO4 deactivated alumina was tested. The columns were run isothermally at 150 °C, injecting pure 1,2 butadiene sample. In the butadiene, an impurity called “X” is eluting which makes a marker on the level of decomposition observed.
Figure 1: 1,2-butadiene on Na2SO4 deactivated alumina; Column: 50m x 0.32mm; Oven: 150ºC; Carrier: H2, 156 kPa, 23 psi; Injection: Split, 1:30; Sample: 1,2 butadiene, 40 μl

Figure 2: 1,2-butadiene on commercial KCl deactivated Column; Conditions see figure 1

Figure 3: 1,2-butadiene on new Alumina BOND CFC column; Conditions, see fig.1

New Rt-Alumina BOND CFC

Reactivity of RT-Alumina BOND CFC surface is much less...

# Also note higher efficiency

By Proper alumina surface and deactivation, the (re)activity can be reduced significantly
Using sodium sulphate, immense activity was observed, see figure 1. As can be seen there is a big reaction platform visible showing dimmers and trimers being formed while the butadiene is traveling through the capillary. Next column tested was the commercial Al2O3/KCl column, under similar conditions, see figure 2. The performance is much better compared to Na2SO4, but still a lot of decomposition is observed. Figure 3 shows the new Rt-AluminaBOND CFC, also under same conditions. Results have much improved. Figure 2 and 3 are both recorded with similar sensitivity settings, clearly showing much less reactivity of the Alumina BOND CFC column. Impurity marked with "X" can be used as a reference for visual interpretation.

It’s clear that the level of dimerization depends on the activity of the surface and the deactivating salt. Next step is to test this column for the application of CFC compounds.

**Separation of CFC**

In order to have a column with most flexibility for CFC applications, a 30m x 0.53mm column dimension was chosen. Most CFC compounds are gases and are injected via gas sampling loop or gastight syringe. The column needs to offer highest loadability and minimum injection peak broadening, especially if low levels have to be analyzed and direct injection is applied. Additionally, if there are sensitive components, it may be interesting to use higher flow rates to elute such components at lower elution temperatures.

![Rt AluminaBOND CFC Good Peak shape for halogenated compounds](image)

**Figure 4** Halogenated hydrocarbons on Rt-Alumina BOND CFC

Column: 30m x 0.53mm Rt-AluminaBOND CFC; Carrier: H2, 8 ml/min, 34 kPa, 5 psi; Oven: 135°C; Injection: Split 20:1; 170 mL/min; Detection: FID: 220°C; Peak Identification: 1: 1,1 dichloroethylene; 2:Methylene chloride; 3:Tr-1,2 dichloroethylene; 4:Tetrachloromethane; 5:unknown; 6:Cis-1,2 dichloroethylene; 7:Trichloroethylene; 8:1,1,1-trichloroethane; 9: Chloroform
Figure 4 shows a series of halogenated components that are showing good chromatography using the deactivated alumina. Peaks elute symmetrical and there is no sign of reactivity. Also the methylene chloride, peak 2, which was reported by Noij to decompose, elutes as a sharp symmetrical peak on the modified alumina surface.

As the separation is performed with gas – solid chromatography which is an adsorption process, the eluting peak symmetry will be a function of injected amount. In adsorption components will start to tail when overloaded. Fig. 5 shows the injection of 200, 80 and 6 nanograms of methylene chloride. As absolute injected amount reduces, the eluting peak becomes more symmetric.

The retention of the alumina is very high which allows highly volatile compounds to be retained. Figure 6 shows the separation of volatile halogenated compounds at 135°C, including vinyl chloride. Again, no sign of decomposition.

To test response of halocarbons after actvation, the same sample was analyzed after the alumina was exposed to its maximum temperature of 200°C for 16 hours. Figure 7 shows the chromatograms obtained. There is virtually no change in response and retention, showing the stability of the alumina surface. Figure 8 and 9 show practical applications of the alumina BOND technology. Different CFC components are analyzed and resolved using alumina BOND

![Overloading Impact of Methylene Chloride on Rt AluminaBOND CFC](image)

Figure 5  Impact of sample load on peak shape of CFC; Test component methylene chloride; Test conditions similar as in figure 4
technology. As can be seen from the chromatograms, no decomposition is occurring, also for the CFC-22 which was also challenging bas reported in [6].

**Figure 6:** Volatile halogenated hydrocarbons; Conditions: see fig. 4; Peak identification: 1: Dichlorodifluoromethane; 2: Chloromethane; 3: Vinylchloride; 4: Trichlorofluoromethane; 5: Chloro ethane

**Figure 7:** Impact of high temperature conditioning. Conditions and peak identification, see Figure 4; Black: before conditioning; Red: after 16 hrs at 200 °C

**RT-Alumina BOND CFC**
16 hrs 200°C: No change in retention or response
Figure 8: Impurities in R134a; Column: 30m x 0.53mm Rt-Alumina BOND CFC; Carrier gas: He; Oven: 80°C for 6 min., 10°C/min to 140°C, 140°C hold for 2 min.; Injection: gas sampling, 500 μl
Peak Identification: 1: R 115 = Chloropentafluoroethane; 2: R 12 = Dichlorodifluoromethane; 3: R 22 = Chlorodifluoromethane; 4: R 134a = 1,1,1,2 Tetrafluoroethane;
Chromatogram courtesy: André Hähnel, Westfalen AG

Figure 9: Separation of CFC; Column and conditions see fig.8
Despite of the promising results obtained, alumina still has limitations.

The alumina still shows reactivity for certain halocarbons that have a desire to form a more stable molecule. CFC compounds that can split-off a HCl molecule seem to be challenging. Figure 10 shows some examples of HCl decomposition of 1,2-dichloroethane and 2-chloropropane. During analysis, the degradation products are formed.

![Graph showing decomposition of 2-chloropropane and 1,2-dichloroethane](image)

**Figure 10:** Limitation of alumina; decomposition of 2-chloropropane and 1,2 dichloroethane while moving through the column. While releasing a HCl molecule, these compounds are transferred into propylene and vinyl chloride

**Conclusion**

A new highly selective adsorbent based on alumina is developed which makes trace CFC analysis possible. The selectivity of alumina allows the separation of many CFC type components using temperatures above ambient.

The deactivated alumina adsorbent can be used for the separation of a wide range of commercially used Chloro-Fluoro Carbons. Although much improved, some reactivity remains halogenated compounds that can split off hydrochloric acid.
References


Availability

The Rt Alumina BOND CFC is standard available as:

#19763 RT AluminaBOND - CFC, 30m x 0.53mm

Also 50m x 0.32mm can be supplied if higher efficiency is required.