An Advanced Base Deactivated Capillary Column for analysis of Volatile amines Ammonia and Alcohols.

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To analyze basic compounds at nano gram levels using gas chromatography, a basic surface modification is often required to reduce the impact of the acidic fused silica. Additionally, to separate volatile components, retention and efficiency at lower temperatures is required also. Base-modified polyethylene glycols have been available for some time, but are not very stable and they loose efficiency when used below 60C. Siloxanes are more challenging for base modification as the stability siloxane polymer should not be compromised. There are some solutions available, but there is room for improvement as present phases technologies are considered not optimal which translates in short column life times and non-reproducibility in amine response..

An advanced base deactivation technology has been made available several years ago by Restek corporation, where a new surface deactivation of fused silica was introduced. Such columns were commercialized under the names Rtx-5 amine and Rtx-35 amine. Similar approach was taken for designing a more stable column for volatile amines, not only by increasing the film thickness, but also by creating a direct link with the (base) surface deactivation. Additionally the number of cross-links (bridges) between polymer chains was optimized to make the polymer keeps efficiency as low as temperatures of 40 ºC. The higher degree of cross-linking was incorporated to make the column more resistant for amine/water mixtures.

The column, named Rtx Volatile amines, was tested with a series of amine samples and water matrices, to demonstrate performance. In this poster, several applications will be presented and discussed.

Introduction

The analysis of small chain amines is of great importance for the chemical industry as well as in pharmaceutical analysis. Volatile amines are building blocks or reactants for manufacture of many different classes of compounds. The analysis of small chain amines by capillary gas chromatography is challenged because of the high polarity and the basic nature of the amine compounds.
Any activity in the system will immediately impact amine peak symmetry and response.

Analysis of amines

Amines are generally known to be very difficult to analyze due to their basic character. With decreasing molecular size the influence of the amine group becomes larger which results in stronger adsorption characteristics. Most critical are the primary amines. Besides the basic character the amino group introduces a large dipole in the molecule. This dipole is responsible for strong interaction with silanol groups and siloxane bridges which often results in non-linear adsorption effects. This appears as strong tailing peaks in the chromatogram.

There are several gas chromatographic ways to do amine analysis. The packed column has been used widely with modified and mixed phases. Typical packings are the polyethylene glycol (PEG) mixed with potassium hydroxide or sodium hydroxide. These packings provide excellent peak shapes for amines. Also porous polymers with a basic modification can be used for this separation.

The best way to prevent the interaction of the strong dipole is to derivatize the amine or to deactivate the column in such a way that the interaction is minimized. Derivatization is not preferred as it is time consuming and all kinds of secondary effects like recoveries and matrix effects are introduced.

Practical amine analysis: priming

Practically in amine analysis, systems are often “primed”. Here a few repeated injections of a high boiling amine compound is performed. The high boiling amine will cover the active site, resulting in better chromatography. This deactivation is usually only temporarily as the amine will not remain at the active site. Amine priming must be repeated on regular basis. Advantage of the method is, that by injecting the whole chromatographic system is deactivated, including injection/detection port liners.

Capillary columns for volatile amine analysis: challenges

Columns for volatile amines must have a high degree of deactivation , combined with retention. Additionally they must be chemically resistant for tough matrix conditions. Amines are often analyzed together with water and alcohols. Also ammonia and water do have to be quantified.

Commercial available columns dedicated for volatile amines work fine when amines are in pure condition, but as soon as the matrix becomes tough, the chromatography becomes challenging. Figure 1 shows what typically happens when those columns are used for amine-water mixtures. The amine peaks rapidly show poor peak shapes. They split-up and elute with “chair” type shape. This makes quantification very unreliable and unpredictable, especially in a routine measurement environment.

To confirm these results, a standard deactivated thick-film Rtx column was tested using the same matrix. The same phenomena were observed, see figure 2. In order to get better stability, some

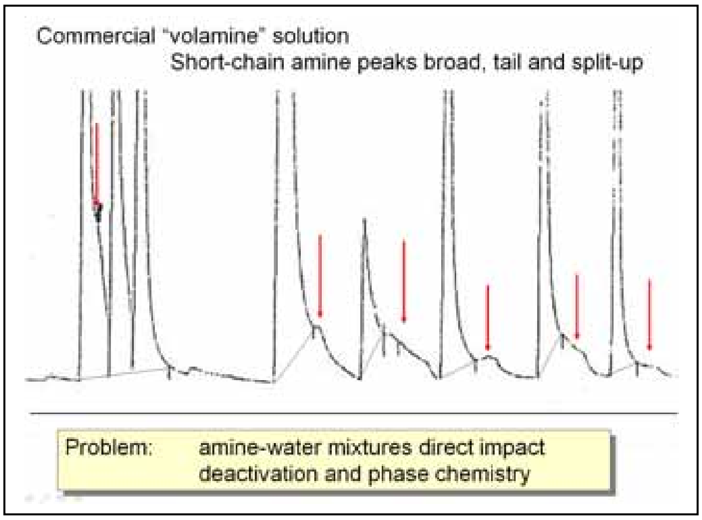

Figure 1; Peak shape of short chain amine on commercial column dedicated for volatile amines; Conditions table 1;

fundamental change was required. The impact of the fused silica surface as well as the stability of the stationary phase needed to be improved by using more robust surface deactivation and stable polymers.

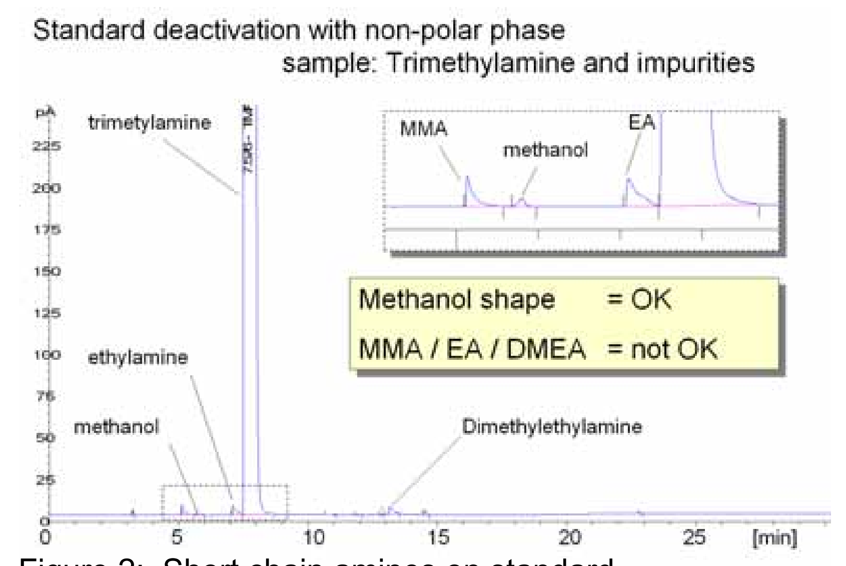

Figure 2: Short chain amines on standard deactivated column; conditions, table 1;

New Rtx Volatile Amine column

A series of columns were prepared using a deactivation technology that was explored when Restek developed the Rtx-5 and 35 amine columns. The base-deactivation of the surface greatly reduces the interaction of small chain amines, providing less adsorption and better peak shapes. Additionally, the stationary phase layer was bonded with the surface and was also more intensively cross linked to have better mechanical stability. As we have learned from the Rxi-deactivation technology, we made sure that remaining reactive silanols in the stationary phase were eliminated.

The resulting column was tested with a series of mixtures which results are shown in figures 3-7

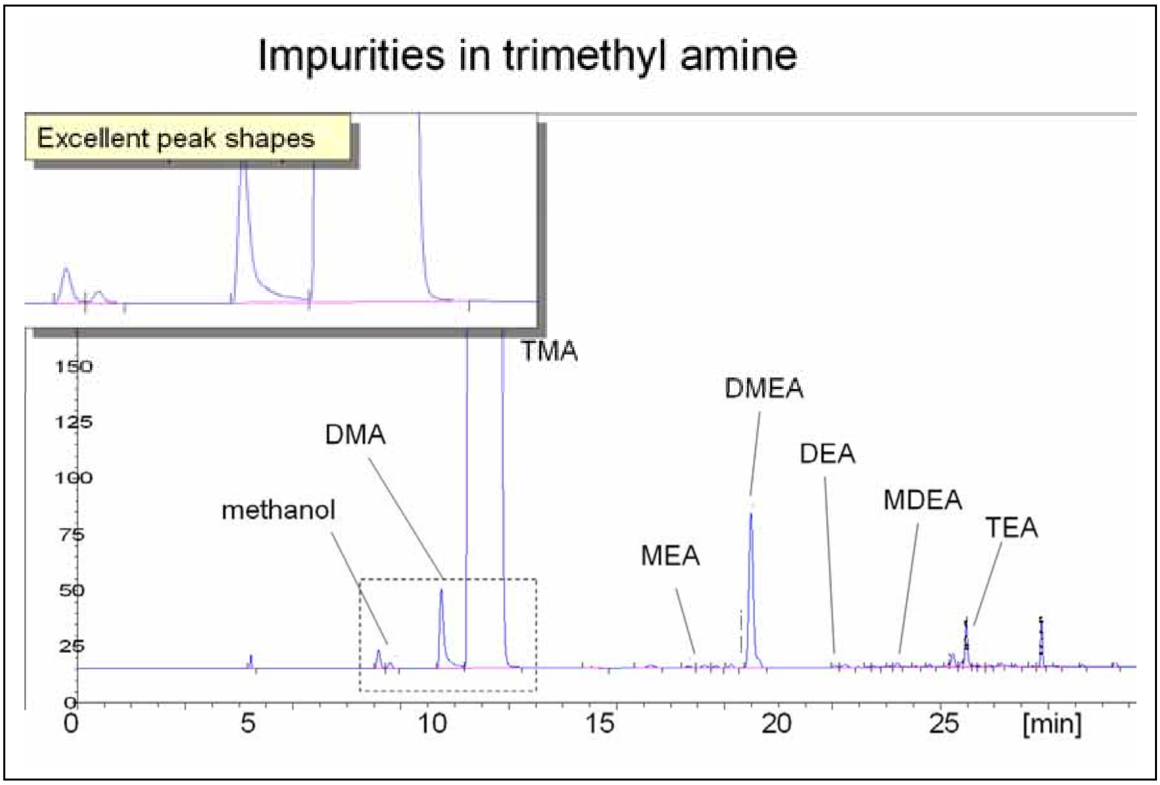

Figure 3: Impurities in trimethylamine; conditions: see table 1;

Figure 3 and 4 show the analysis of gas samples of amine compounds. These samples are the most simple and chromatography looks good. Figure 5 shows the same components, but now in water matrix. Usually when water is involved there are different matrix interactions which affect peak shape. The figure show an overlay of amines, 200-1000 ppm in water, of the first and 40th injection. Peak shapes are almost identical. This was a very promising result. Figure 6 shows a detail where there is a slight increase in tailing observed (blue trace). Figure 7 shows the analysis of 40% solution of monomethylamine in water. This mixture is known to be very difficult and is a perfect indicator for column stability.
The figure shows the first and 50th analysis. There is a small impact in peak shape, but this is minimal compared with the former chromatography solutions available.

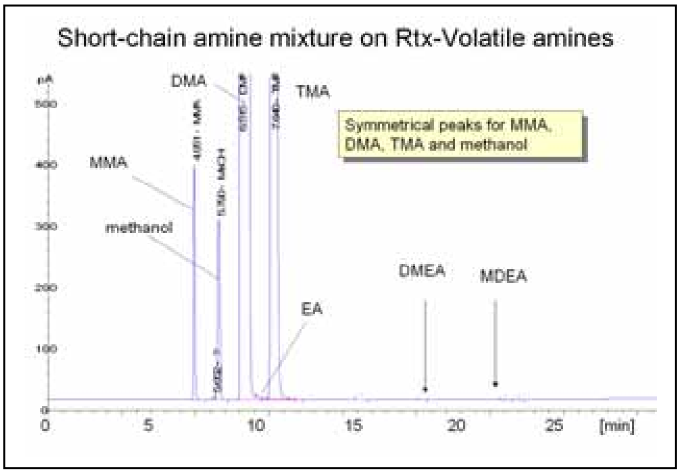

Figure 4: Short chain amines on Rtx-Volatile amines

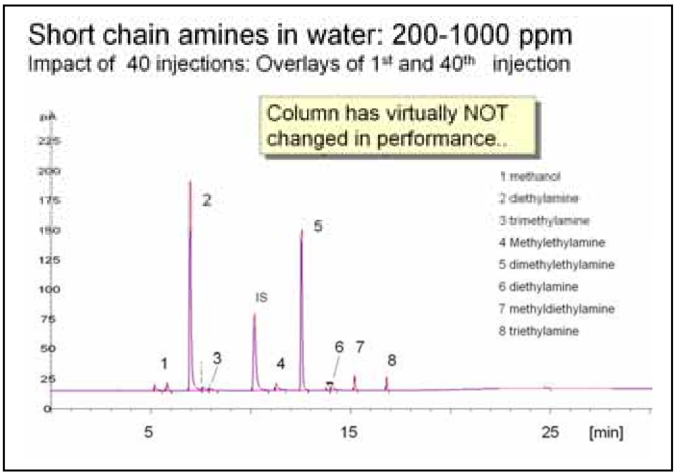

Figure 5: short chain amines in water matrix. Overlays of 1st and 40th injection; conditions: table 1

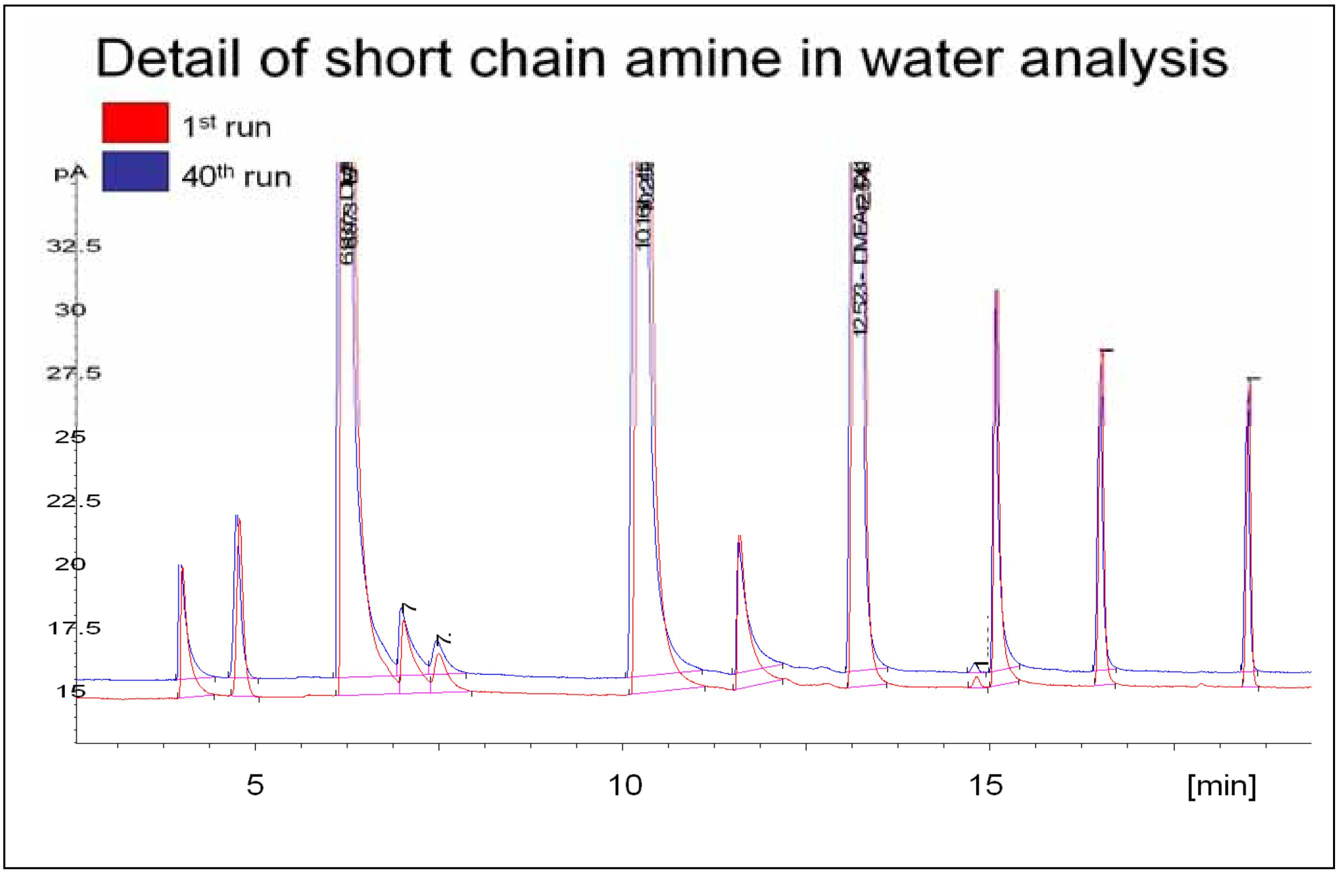

Figure 6: Detail of figure 5.

Table 1 Conditions for small chain amine amine testing

Column `	: 60 m x 0.32mm Rtx-Volatile amines
GC	: Agilent 6890
Injection	: Split; Spit 1:15 ; 30 ml/min
Injection volume	: 1.0µl, Fast plunger mode
Injection temp	: 220°C
Carrier Gas	: H2, flow = 2 ml/min; constant flow; 64.2 kPa velocity 35 cm/sec
Oven	: Initial 40°C – 10 min., 20°C/min to 250°C -10min isothermal
Detection	: FID, temp. 250C

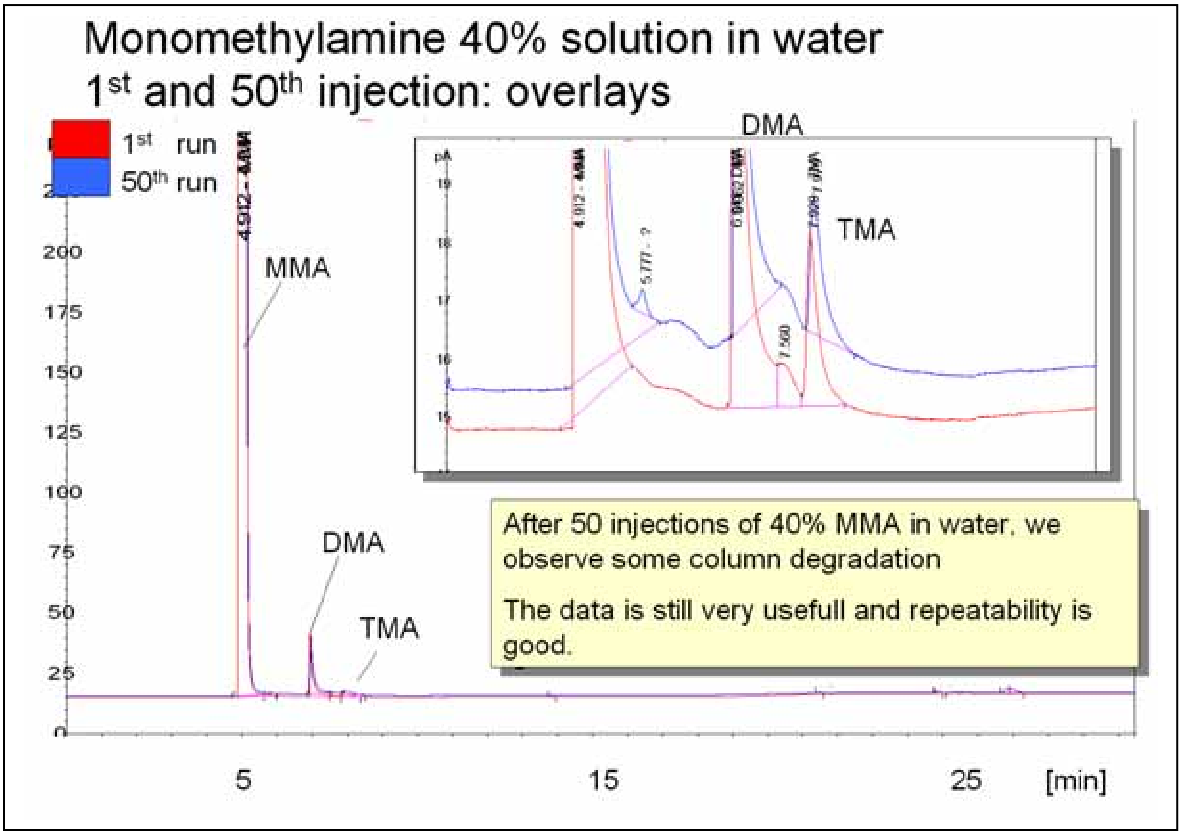

Figure 7: 40% mono-methylamine in water; conditions see table 1;

Table 2 Abbreviations and retention times

		Retention time [min]
MMA	monomethyl-amine	4.95
meOH	methanol	5.79
DMA	dimethyl amine	6.92
EA	ethyl-amine	7.11
TMA	trimethyl-amine	7.87
IPA	isopropyl amine (IS)	10.12
MEA	methyl-ethyl-amine	11.1
DMEA	dimethyl-ethyl-amine	12.5
DEA	diethyl-amine	14.0
MDEA	methyl-diethyl-amine	15.2

The Rtx volatile amines performs very good for polar amines, not only because of inertness and water tolerance, also for loadability. Figure 8-12 show several applications for impurity analysis in main amine compounds. Figure 13-15 show the separation of gases and water using TCD detection. Ammonia and water elute as sharp peaks. The column can also be used for measuring trace amounts of water in solvents, replacing Karl Fisher titration.

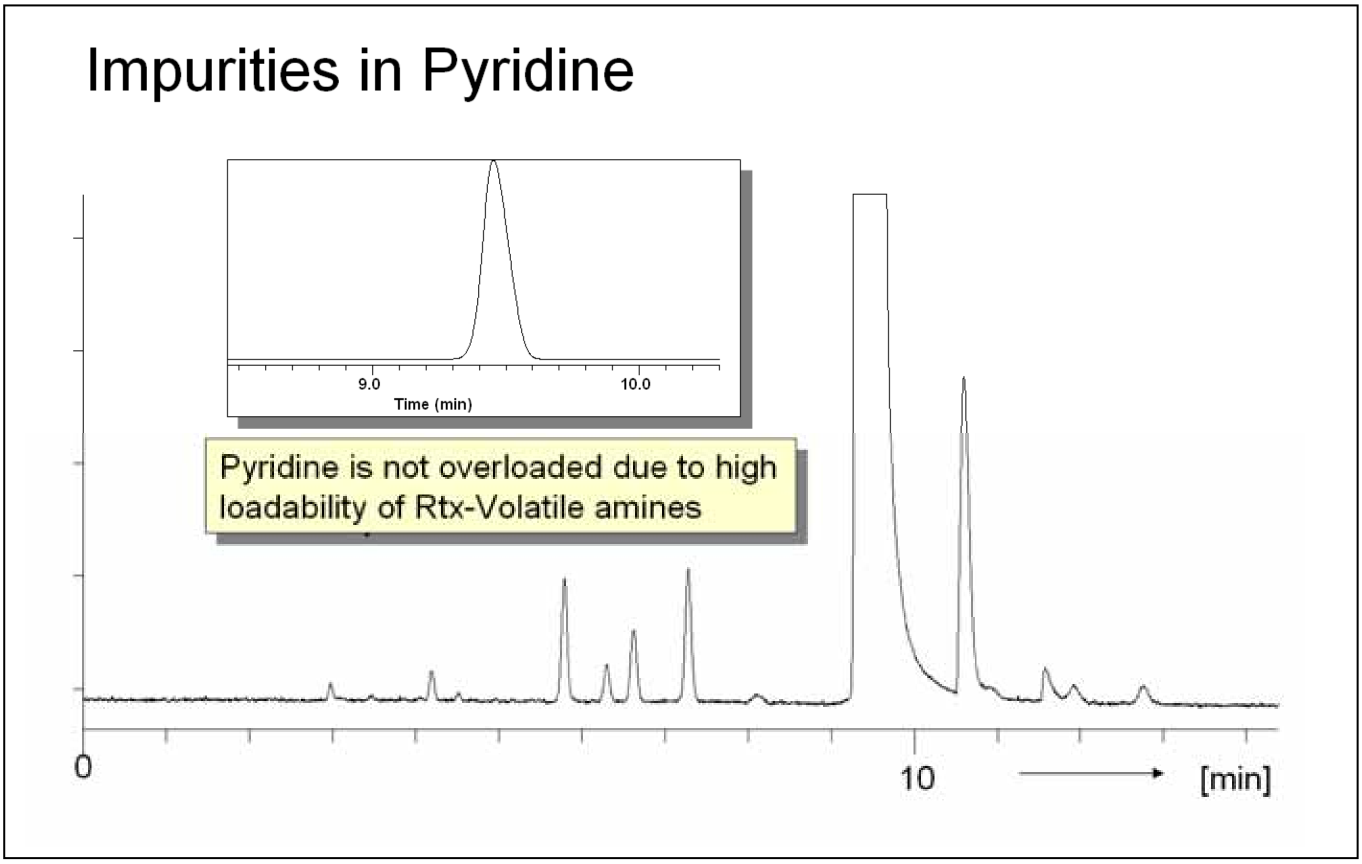

Figure 8: impurities in pyridine; conditions see table 3

Table 3 Conditions for impurity analysis

Column	: 60m x 0.32mm Rtx-Volatile amines
GC	: Agilent 6890
Oven	: 120 ºC
Carrier gas	: Hydrogen, 2 ml/min; 23 psi
Injection	: split, 1:15, 250 ºC, 1 µL
Detection	: FID, 250ºC

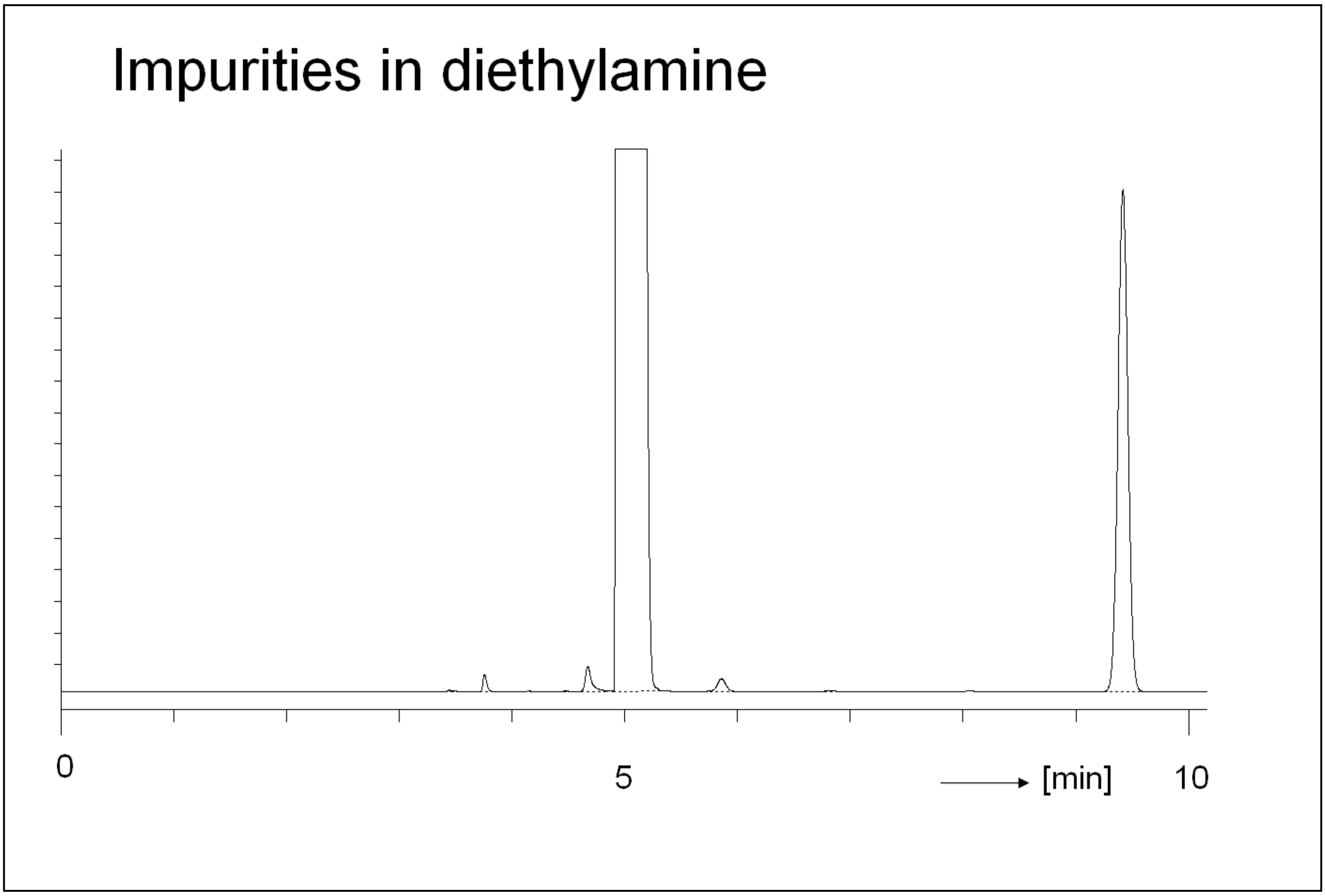

Figure 9: Impurities in diethylamine, conditions: table 3

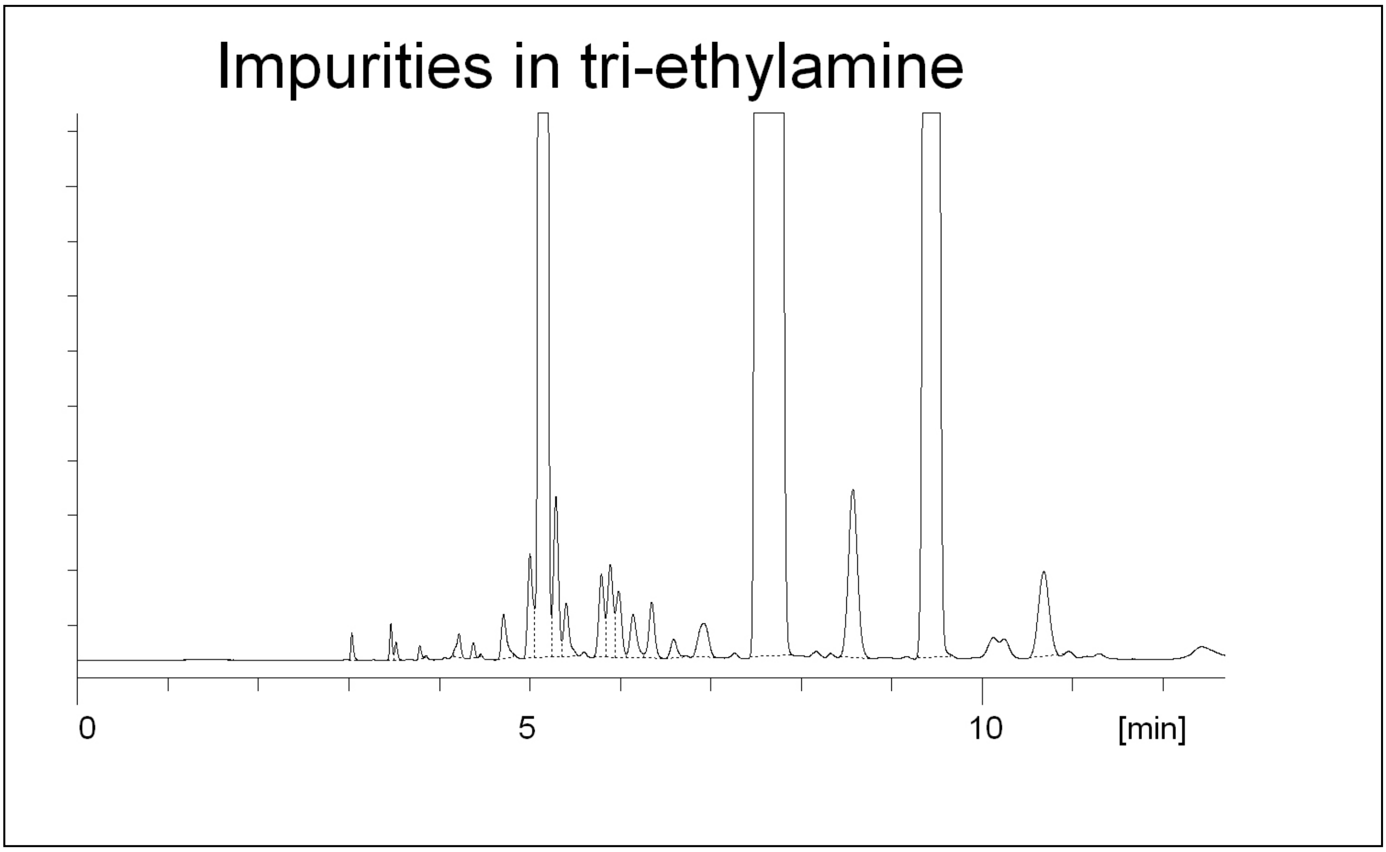

Figure 10 impurities in triethylamine, conditions see table 3

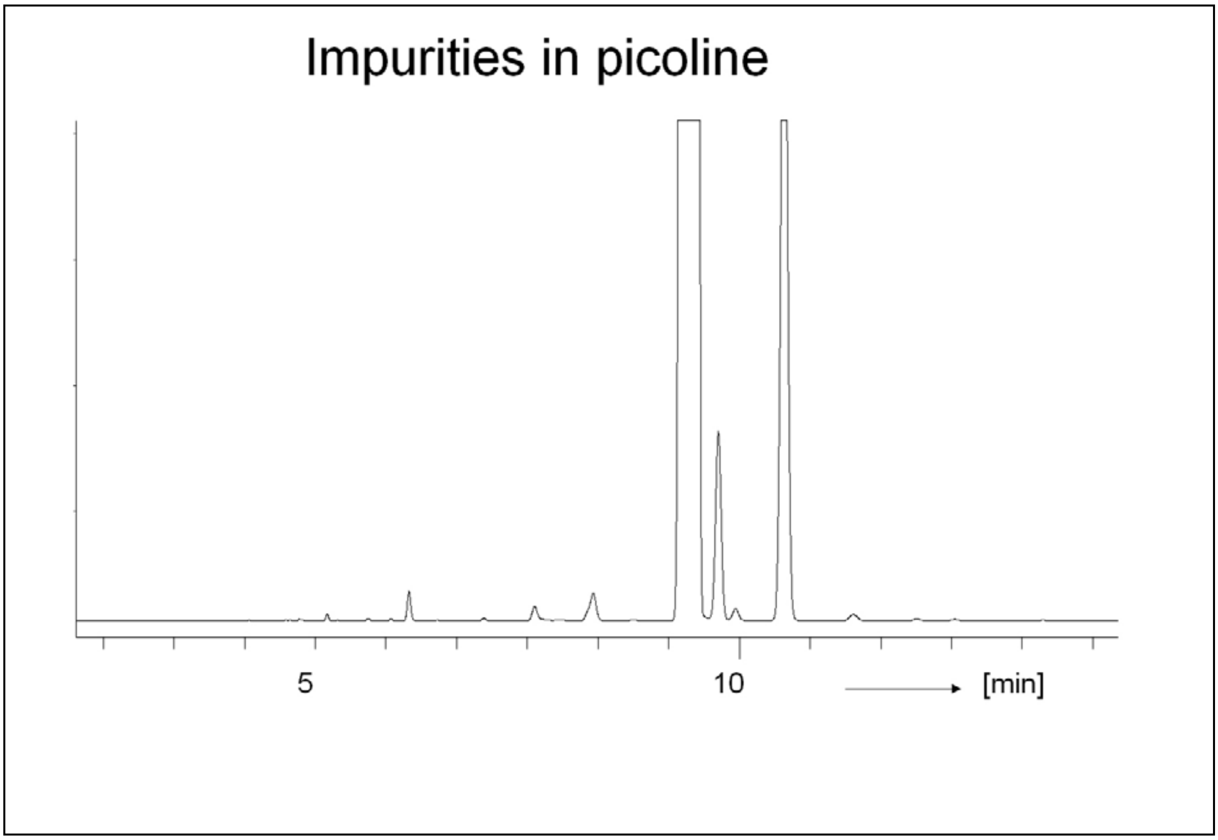

Figure 11: Impurities in picoline, conditions table 3;

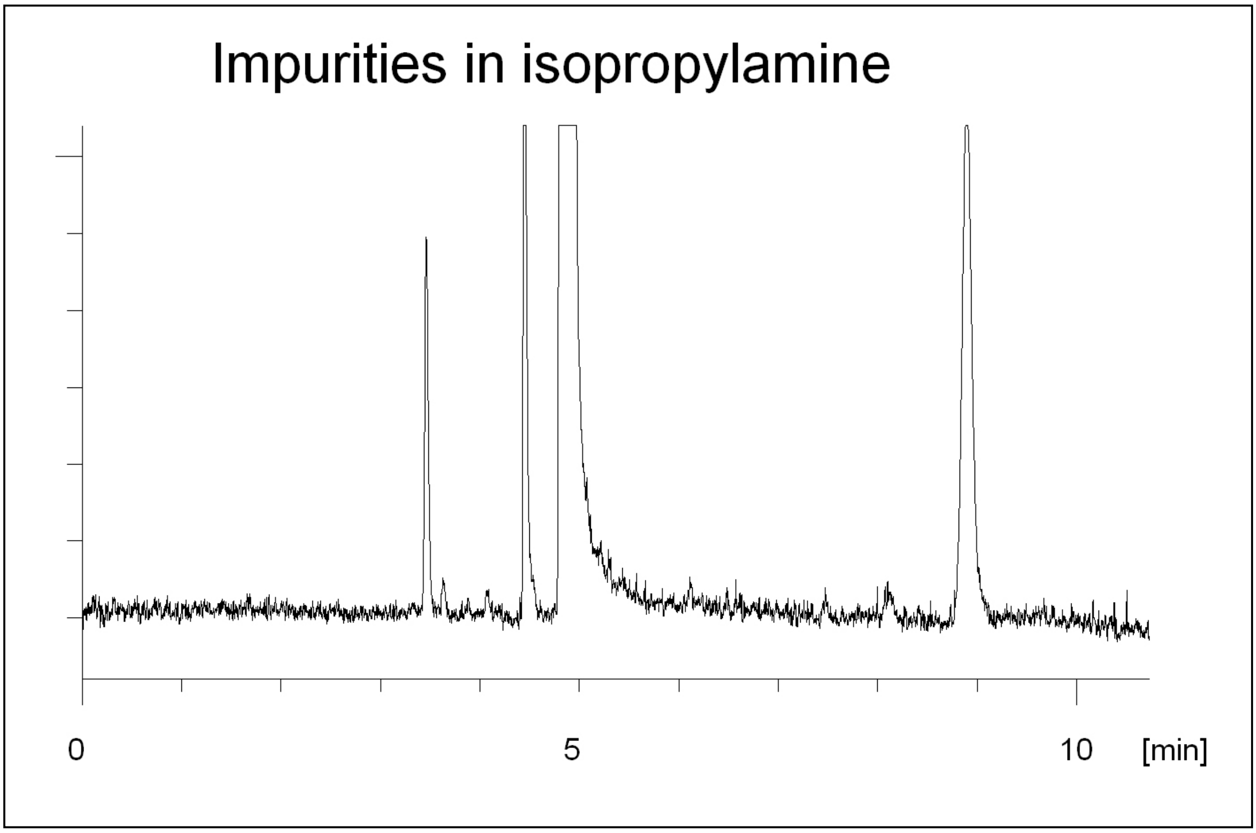

Figure 12 Impurities in isopropylamine, conditions table 3

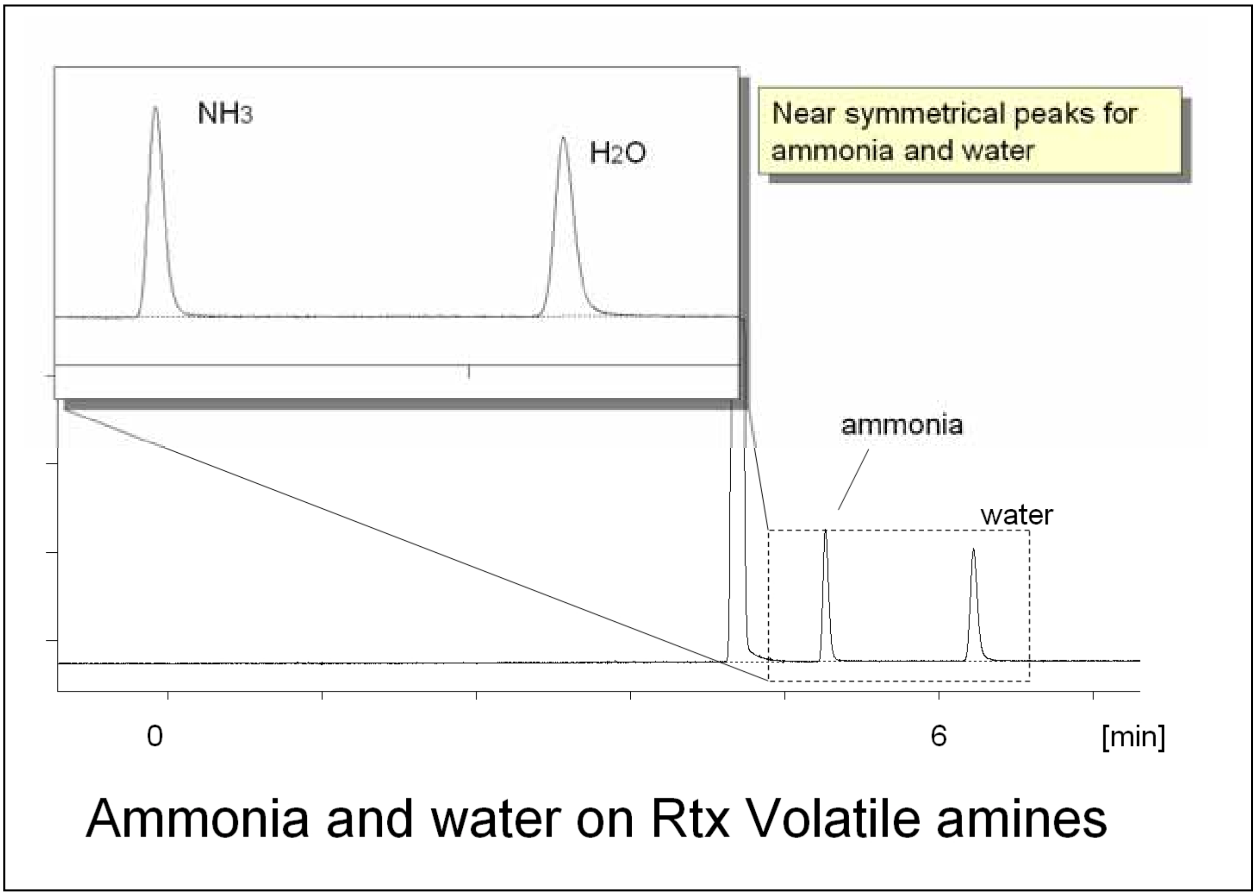

Figure 13:Ammonia and water;
Column: 60m x 0.32mm Rtx-Volatile amines; Oven: 45 ºC; Injection: split, 1: 10; Carrier: Helium, 150kPa; GC: HP5890; Detection: µ-TCD;

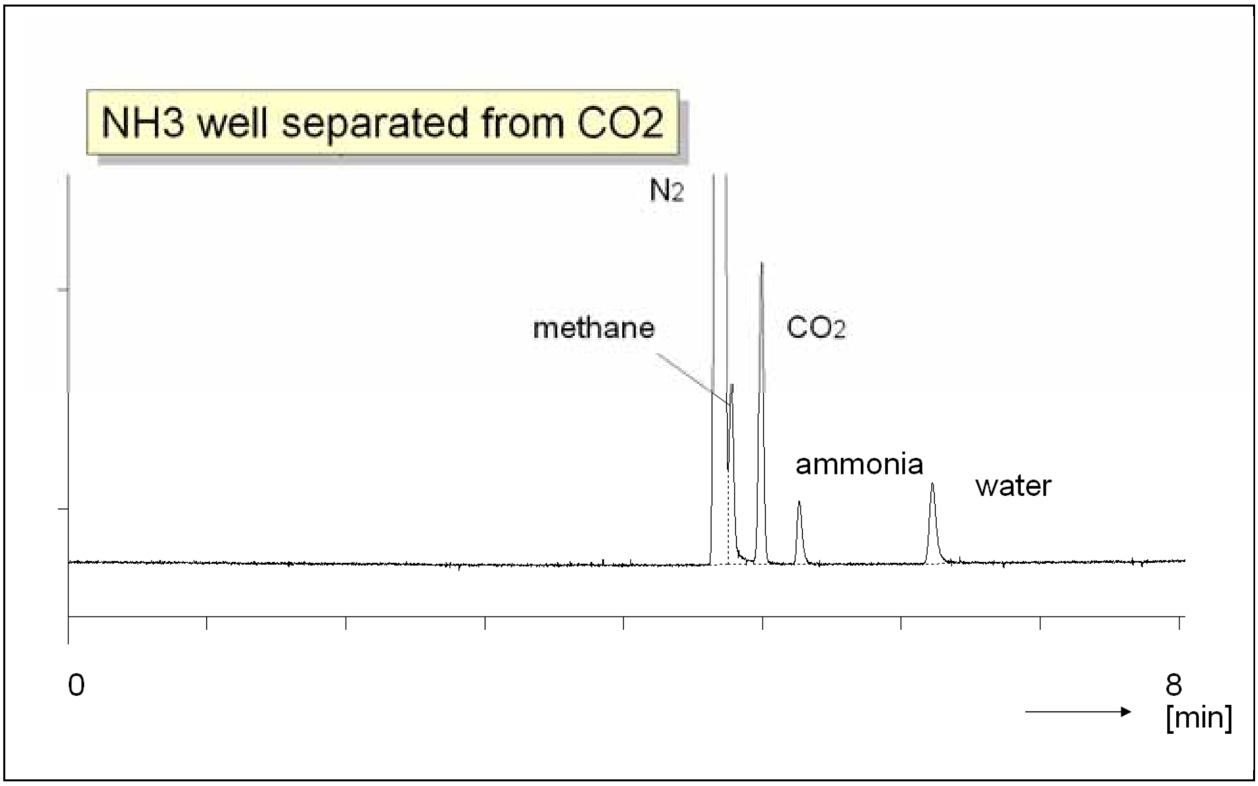

Figure 14: carbon dioxide and ammonia; conditions see fig. 13

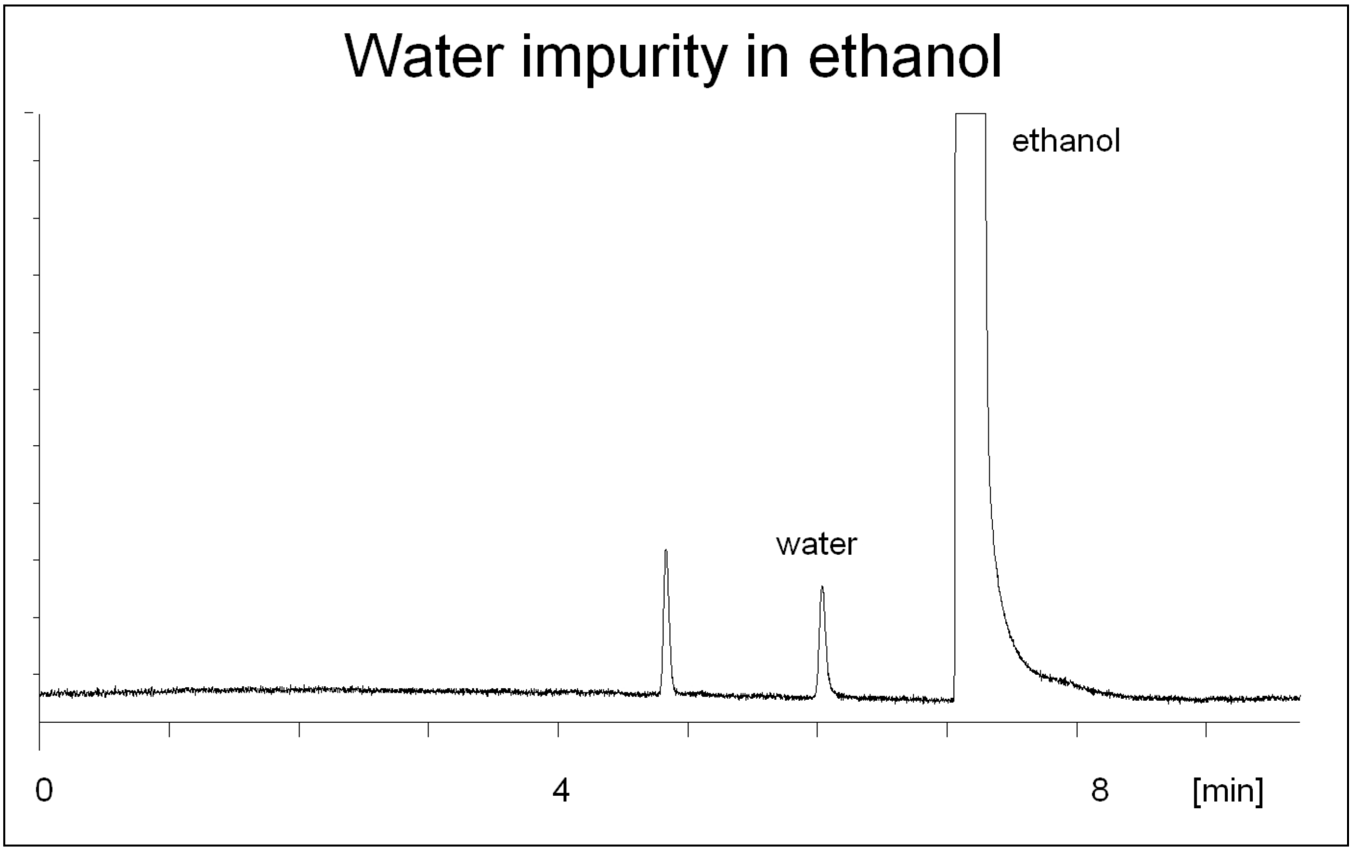

Figure 15: water content in ethanol; conditions fig 13, but oven at: 60 ºC

Summary

A new stable bonded stationary phase for amine application has been developed which is based on a non-polar stabilized polysiloxane. Because of the surface bonding and base deactivation of the fused silica surface, the Rtx-Volatile amines can handle direct liquid injections of water, with high level of short-chain amine like monomethylamine, dimethylamine and trimethylamine.

The new phase shows a very good peak shape for amines, alcohols, ammonia , CO2 and water and can be used at least up to 275°C.

Acknowledgement

Special thanks to Gilbert Baele,Taminco, Belgium, for testing the application and limitation of the base deactivation technology

Availability

#18076	Rtx-Volatile amines,	15m x 0.32mm
#18077	Rtx-Volatile amines	30m x 0.32mm
#18078	Rtx-Volatile amines	60m x 0.32mm

RESTEK