



Analysis of Gases via Gas Chromatography

Part 1: Nitrous Oxide

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Gas chromatography (GC) is a technique that deals with gas separations. Practically the components to separate must be brought in the gaseous phase to be able to be transported by the carrier gas. In order to do that, the temperature of the sample and column can be increased. Today's gas chromatographs can be used up to 500 °C, meaning that it is possible to analyse components with boiling points around 700 °C. The component must be thermally stable. This works fine for hydrocarbons but more polar molecules will decompose.

Nitrous oxide (N_2O), is commonly known as "laughing" gas but is also used as a component in fuels in rockets and as an aerosol propellant. N_2O is, in itself, a stable gas and can be analysed relatively easy via gas chromatography. Often it is confused with "nitric oxide", (NO). NO is a very reactive gas. When oxygen is preset, it will immediately oxidize into NO_2 . NO_2 can be easily recognized as it has a dark brown colour. Also NO_2 shows reactivity, meaning that

the analysis of NO and NO_2 via gas chromatography is not commonly done (see for details [1]).

Retention in GC: Use of Adsorbents

The first need for measurement of nitrous oxide via GC is to use stationary phases that show retention. Because the N_2O is a gas under ambient conditions, it will not be retained by liquid stationary phases. Even on the thickest film Rtx-1, the nitrous oxide will co-elute

with nitrogen, oxygen, methane and CO_2 . If sub-ambient conditions are used, it is possible to separate all gases, but the setup is not easy to maintain and is expensive.

An easier way is to use a different type of stationary phase. Adsorbents provide very high retention, which allow separation of gases at temperatures above ambient. The most popular adsorbent for nitrous oxide is the porous polymer. Such materials are available in packed as

well as capillary (PLOT) configurations. Figure1 shows a separation of 25 ppm nitrous oxide using a porous polymer PLOT column using mass spectrometric detection.

In mass spectrometry one needs to be aware that the fragments are relatively small and there can be similar masses for different components. N_2O will show one unique fragment and that is m/z 30 (NO). CO_2 and N_2O will both show m/z 28 (CO and N_2) and m/z 44 (CO_2

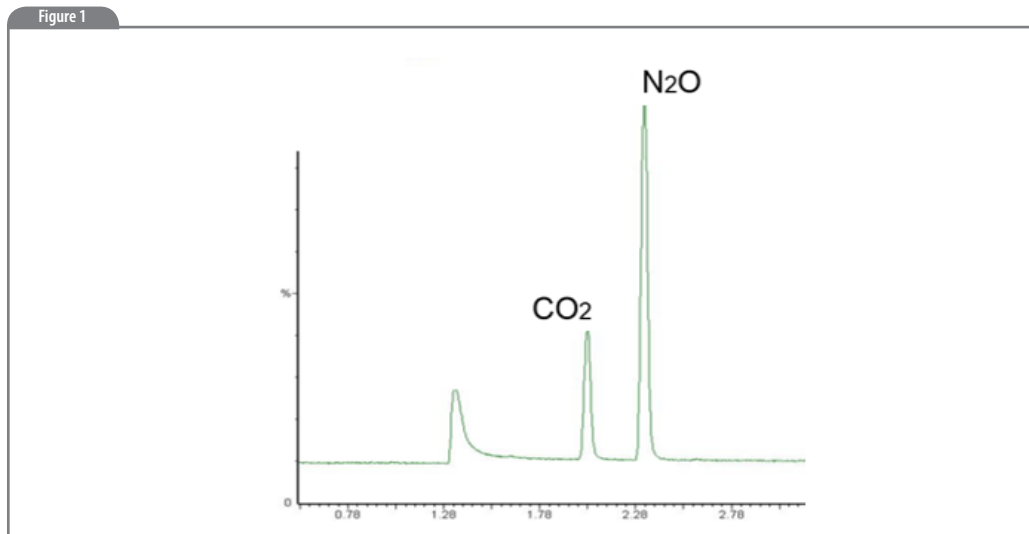


Figure 1: Separation of nitrous oxide and carbon dioxide on capillary PLOT. Column: 30/0.25 Rt Q-BOND, Oven: 27 °C; Carrier gas: He, 20 psi; Injection: split, Detection: MS. N₂O at 25 ppm.

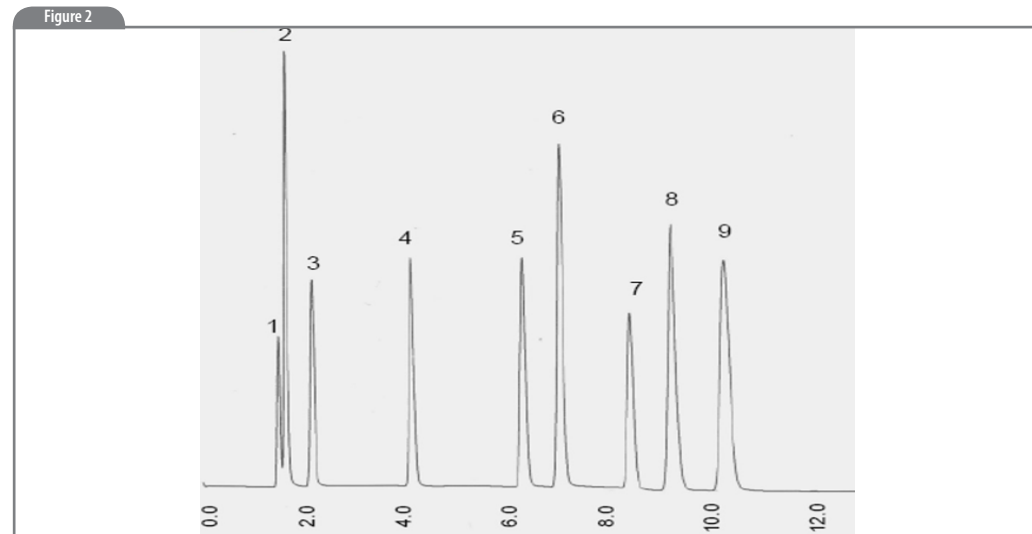


Figure 2: Separation of gases on ShinCarbon. Column: 2 m x 1 mm Shincarbon, 80/100; Oven: 35 °C, 2 min, 25 °C/min to 200 °C; Injection: Split 10:1; Carrier gas: He, 8 mL/min; Injection 1 mL. Detection: TCD; Peaks: 1 = O₂, 2 = N₂, 3 = CO, 4 = CH₄, 5 = CO₂, 6 = N₂O, 7 = C₂H₂, 8 = C₂H₄, 9 = C₂H₆.

and N₂O). CO₂ has m/z 32 as a unique mass. An additional challenge for a bias on masses 28 and 32 is air (N₂ = m/z 28 and O₂ = m/z 32). Air bias can be caused by sample, gas purity or leaks.

In order to achieve sufficient separation between CO₂ and N₂O it is important to have a narrow injection band, see “sample introduction” discussion below.

An alternative material that can be used is the Shincarbon. Shincarbon is a carbon molecular sieve with very high retention. It is presently only available as a packed column. Figure 2 shows the separation. Also here a split injection is used that employs

a 1 mm micro-packed column. The way to do this is explained under ‘Sample Introduction’. An easier way to run the Shincarbon application is to use a 0.53 mm ID micro-packed MXT capillary. This column has an outside diameter < 0.8 mm and can be installed in any capillary gas chromatograph using the standard ferrules [2].

An interesting application for N₂O is also shown in Figure 3. Here N₂O is analysed in a matrix of argon at 5 ppm level. Detection was done using a relatively new detector type, the Plasmadetek [3]. The separation was done on AluminaBOND/Na₂SO₄. The N₂O has quite some retention at

40 °C and elutes as a sharp peak. This column may be of interest especially if larger amounts of CO₂ are present in the sample. At high CO₂ levels, the porous polymer as well as the Shincarbon, will show a big risk that the N₂O peak will be masked by the CO₂. The alumina adsorbent will completely adsorb the CO₂, meaning the N₂O peak will elute completely free. In time, the CO₂ may also impact the retention of the alumina, meaning that the adsorbed CO₂ has to be removed by high temperature conditioning (12 hours 200 °C).

Figure 4 shows nitrous oxide eluting form a molsieve 5A adsorbent. Because N₂O is a linear molecule, it

will fit in the pores of zeolite-based molsieves and gets retained. The 5A molsieve retains the N₂O quite a lot, and it needs temperatures well above 150 °C to elute the N₂O. Because of the high retention, the nitrous oxide will be very well separated from other permanent gases. In a similar way to alumina, carbon dioxide will be totally adsorbed.

Sample Introduction

Because gases do not have high retention, the injection band must be as small as possible to minimize peak broadening. This means that the best injection is to use small sample loops or use a split injection.

Figure 3

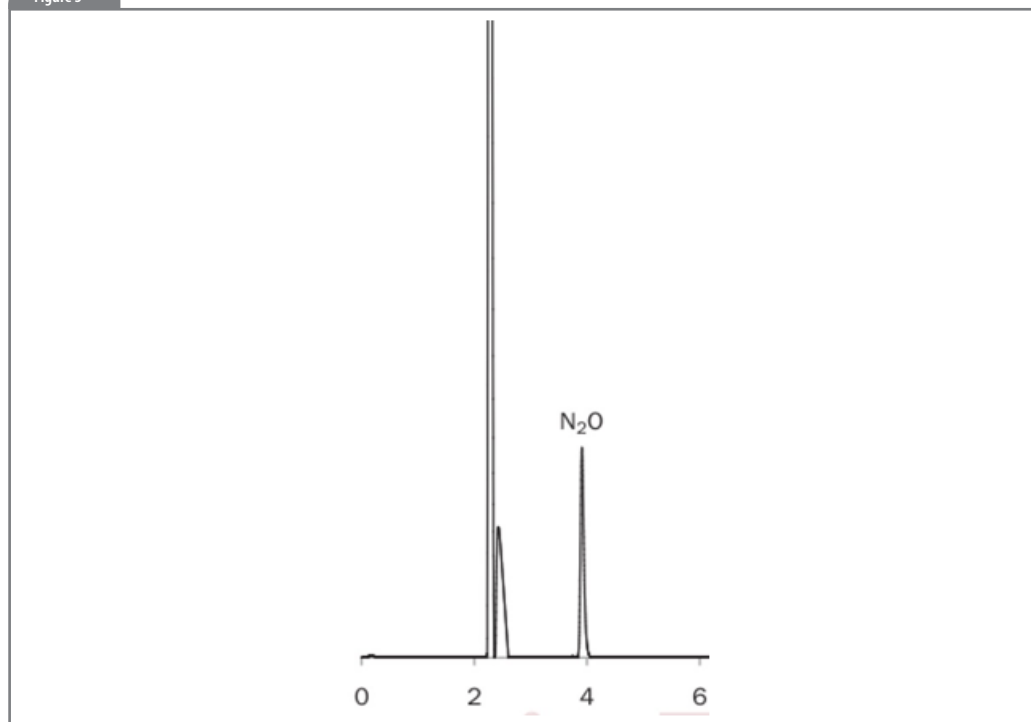


Figure 3: Nitrous oxide on Alumina BOND / Na_2SO_4 . Column: 30 m x 0.53 mm Rt Alumina BOND / Na_2SO_4 ; Helium, 4 mL/min; Oven: 40 °C; sample: 60 μL ; Detector: PlasmaDetek PED; sample: 5.4 ppm N_2O . Chromatogram courtesy: L. Paradis, LDetec.

For capillary columns the split injection is done using a split/splitless injector. Such injectors are standard in most capillary GC instruments. This injector contains a liner. Generally, for gas injections a liner with a small diameter is preferred, typically 1 mm (see Figure 5). Because of the small diameter, the carrier gas velocity in the liner is very high, which benefits the injection band width. The liner does not need wool because there is

no solvent evaporation. This is also the reason why the injector does not have to be heated very high. The injection port can be set at the same temperature as the oven.

Split Injection on Packed Columns

It is also possible to do a split injection using a packed column. The easiest way is to use the 0.53 mm micro-packed column because this can be installed directly in any

Figure 4

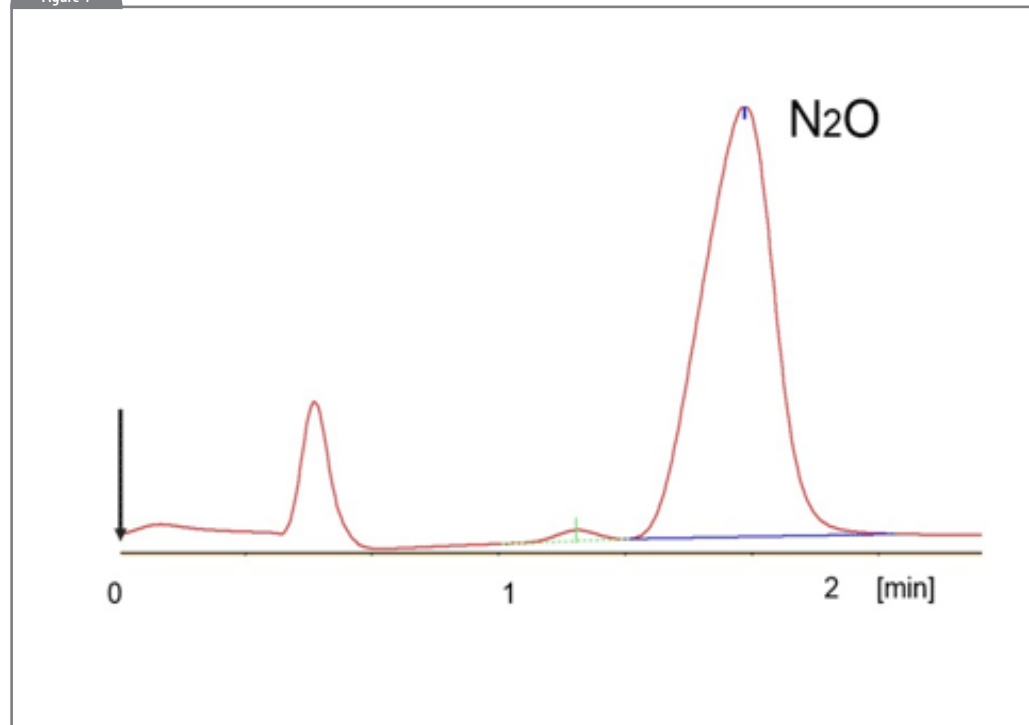


Figure 4: Nitrous oxide on Molsieve 5A. Packed column with molecular sieve 5A; Oven 160 °C.

split injection port [2]. If the packed column has a larger diameter, it is possible to connect the inlet of the packed column with a short transfer line, as shown in Figure 6.

All that is needed is a short piece of deactivated 0.53 mm ID MXT® column tubing, appropriate compression reducing unions and appropriate ferrules. The same setup can usually be used for the detector side as well. To minimize dead volume effects

the 0.53 mm transfer tubing can be positioned best just inside the inlet /outlet of the packed column. The outside diameter of this MXT® tubing is 0.78 mm, meaning it can be used for packed columns with ID 1–4 mm.

Detection of Nitrous Oxide

Detection of nitrous oxide cannot be done with a flame ionization detector. With thermal conductivity detection it is possible but sensitivity is not very

Figure 5



Figure 5: Example of 1 mm ID liner for gas injections.

Figure 6

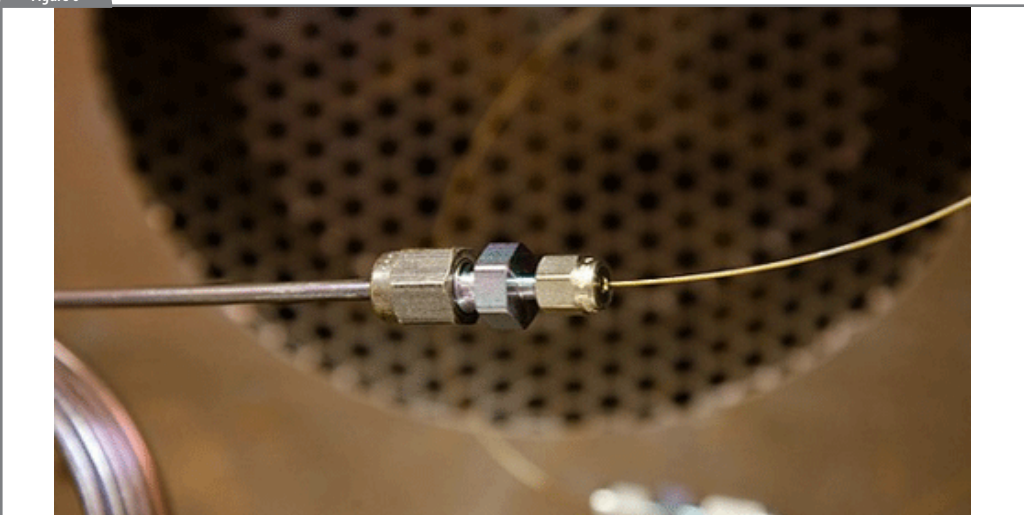


Figure 6: Installation of a packed column in a capillary GC. Connections made using a reducing union and 10 – 15 cm x 0.53 mm deactivated MXT tubing.

high. Mass spectrometry will work at ppm levels. For lowest detection limits, the Pulse Discharge (PDD), PlasmaDetek (PED) and Electron Capture (ECD) detectors typically seem to be the most promising.

References

- [1] <http://blog.restek.com/?p=4583>
- [2] <http://blog.restek.com/?p=1045>
- [3] http://www.lidetek.com/uploads/PDF/chromatomag_v2_2014.pdf
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Jaap de Zeeuw studied six years of chemistry and graduated in 1979. Jaap has 37 years' experience in GC capillary technology and has developed many PLOT columns as well as bonded-phase columns. He is also the originator of simple concepts for fast GC-MS using a high vacuum inside the capillary column. He has published more than 100 publications in the field of GC on column technology and application. He worked for 27 years for Chrompack/Varian and for the last nine years has served as an international specialist on gas chromatography for Restek in The Netherlands.