Attachment 2

Responses to GC 16

1) Helium was used as the carrier gas for all gas analyses (with the exception of ammonia).

2) References of methods and a procedure from Varian are included in this attachment. These references were used for the internal method development in our laboratory.

3) A pulsed discharged helium ionization detector was used for all analyses. This detector was attached to a Varian 3800 GC. Details of the method and detection limits are given in the attached SOP.

4) There are no known interferences that would interfere with the CO analysis in the treatment bottles. This is indicated by the initial sample in which all results are non-detect for carbon monoxide. CO was only detected after incubation of the samples, and the retention time corresponded exactly to the standards at 4.81 ± 0.10 minutes.

5) Precision and accuracy studies were not conducted as part of the method development for this R&D study, nor was an MDL study conducted. These studies can be performed upon request. Attached is an evaluation of precision and accuracy based on the results of the check standards that were run over the course of this study. For these limited data, the warning limits were within 70% and 130% recovery.

PERMANENT GAS ANAYSIS USING PDHID

(SHAW ORG-011)

1.0 **Introduction:**

This document outlines principles to be used as guidance to generate data for the evaluation of permanent gases utilizing a pulsed discharge helium ionization detector (PDHID).

2.0 **Summary:**

A gas sample is analyzed by direct injection onto a GC (Varian 3800) equipped with a Valco PDHID detector. The concentration of the individual gas components is determined by comparison to a standard curve for each analyte.

3.0 **Scope:**

3.1 Target Compounds

Compound Formula	Molecular Weight
Hydrogen H_2	2
Oxygen O_2	32
Nitrogen N_2	28
Methane CH_3	16
Carbon Dioxide CO_2	44
Carbon Monoxide CO	28

3.2 The following quantitation limits (QL) in gas phase will be met.

Compound	Concentration (ppmv)	Method
hydrogen	100	low gas
oxygen	2000	high gas
nitrogen	2000	high gas
methane	500	low gas
carbon dioxide	2000	high gas
carbon monoxide	100	low gas

4.0 Equipment and Reagents:

4.1 Gas Chromatograph (GC) (Varian 3800) or equivalent equipped with a Valco pulsed discharge helium ionization detector (PDHID). The system is also equipped with a helium gas purifier to achieve helium carrier and makeup gas of 99.999% purity.

4.2 A tandem dual column system. Column One – Varian Pora Bond Q (10 meter, 0.32 inner diameter, 5 uM df). Column Two - Varian Molsieve 5A (10 meter, 0.32 inner diameter, 5 uM df). Carrier gas flows from the injector through Column One, to Column Two then to the detector.

4.3 Gas tight syringes capable of injecting up to 1,000 ul are used for large volume injections.

4.4 Data System to calculate the concentration from area counts. Varian Galaxie chromatography software is utilized.

4.5 Collection Vessels: Tedlar bags or gas tight serum vials serum vials (5 - 125 mL) with a butyl rubber-Teflon faced septum, or equivalent.

4.6 Syringes: Gas tight or plastic in various sizes up to with syringe valves to make up standard gas mixes.

4.7 Standards: Stock gas cylinders – 100% concentration of individual gases supplied by AirGas.

4.7.1 Gas Working Standards: Dilutions from the stock cylinders are prepared using gas tight syringes up to 1 liter in size. For example 1.0 ml of a pure gas (100%) is added to a 1-L tedlar bag filled with 999ml of helium to make a 1,000ppmv (0.1%) gas standard.

4.8 Inert Gas: Helium zero grade or better (less than 500 ppb THC) for making standards.

4.9 Containers for working standards: Tedlar® bags with a combination valve for hose fitting and syringe septum.

5.0 Schedule:

5.1 A sampling batch consists of one or more Sample Delivery Groups (SDG). An SDG is:20 samples or less.

5.2 Each SDG must include a set of quality control samples: sample blank, field duplicates if available, laboratory reagent blank, matrix spike, and matrix spike duplicate (only if sample available for analysis).

6.0 Interference:

6.1 Methane is a very common contaminant and occurs naturally in the atmosphere. Automobile exhaust contains high levels of the target compounds so care must be exercised to prevent contamination in transport. Care must be also exercised in the sample collection and analyses.

6.2 Due to the sensitivity of the PDHID detector, care must be taken using the gas tight syringes so not to introduce any oxygen or nitrogen from the atmosphere.

6.3 Moisture interferes with the low level analyses. Procedures to minimize the injection of moisture into the GC is advisable.

7.0 Sample Collection:

7.1 A tedlar bag is used for sample collection from a reaction vessel. Alternatively a sample can be drawn directly from a sealed serum vial reaction vial through a gas tight septum using a syringe.

7.2 Place in a Ziploc® bag or equivalent. Record the following information on a sample label: facility, sample identification number, sample type (groundwater or surface), sample date and time, preservative, collector's initials. Ship the samples on ice at $4 \pm 2\ ^{0}C$ to the laboratory.

8.0 Storage and Holding Times:

8.1 Refrigerate collected samples at $4 \pm 2\ ^{0}C$.

8.2 Holding time is <u>14 days</u> from sampling collection.

9.0 Analytical Guidance:

9.1 Standards: Three to five working standards that are evenly spaced are suggested. The low standard must be at or below the required quantitation limit to the highest concentration bracketing the samples The critical point is to bracket the concentration of the contaminants found in the samples. There are two methods that cover two different calibration ranges. The low gas method covers 100 ppmv to 5000ppmv range and the high gas

method covers 2000 ppmv up to 100,000 ppmv range.

9.2 Initial Calibration (IC): Using appropriate working standards for each of the two methods, create a calibration curve of concentration (ppmv) versus area counts, do not forced fit curve through the origin. Calibration is done using 100ul gas injections of individual gas mixtures. For the high gas method, calibration gas mixtures of H_2, O_2, N2, CH_3 and CO are made (in Tedlar bags) at 2,000, 10,000, 20,000, 50,000, 100,000 ppmv each gas. For the low gas method calibration gas mixtures of H_2, CH_3 and CO are made (in Tedlar bags) at 100, 200, 500, 1,000, 50,000 ppmv each gas.

9.3 Continuing Calibration Check (CCC): Using a mid-point standard, check the calibration at the beginning of each run batch and every 4 hours afterwards.

9.4 The sample must not be exposed to the atmosphere during the analysis. Air tight syringes must be used in transferring the sample.

9.5 Quantitation Limits (QL): The reporting limit of the sample (ppmv) is the calculation of the lowest gas standard used in the initial calibration.

10.0 Sample Analysis:

10.1 Analyze the sample by injecting a measured amount of the headspace (100ul) sample into the GC inlet with a gastight syringe. Smaller volumes down to 2 ul can be used if the 100 ul injection is above the linear curve. Concentrations are based on a 100 ul injection so if 2 ul are use it is considered a 50-fold dilution. If less then 2 ul is required to be in the linear range then the headspace must be further diluted – see below.

10.2 Dilutions: Headspace can be diluted if necessary by removing 400ul of the headspace with a gastight syringe into a prepurged Helium containing 40ml VOA vial to achieve a 1:100 dilution.

11.0 GC Instrument conditions

11.1 Column : Two columns in tandem are used for this analysis. The first column downstream of the injector is a Varian Pora Bond Q column (10meter, 0.32 m diameter, 5 uM df) The second column (upstream of the detector) is a Varian Molsieve 5A column (10meter, 0.32 m diameter, 5 uM df)

11.2 Temperatrue programs: The injector is at 200ºC, the detector at 240ºC and column temperature program set as follows. Initial temperature is 30ºC and is held for 2.5 min. The temperture is then ramped to 75°C at 15°C/min with no hold time. The total run time is 5.5 min. The linear flow rate of the carrier gas is 6.0 ml/min. There is no make up gas for the PDHID.

11.3 Method Variations:

11.3.1 Low Gas Method.

1) Split flow is set to 20

2) PDHID Range settings: Initial range is set at 10. At 1.10 min the range is switched to 9 and at 2.30 minutes the range is adjusted to 11.

11.3.2 High Gas Method.

1) Split flow is set to 60

2) PDHID Range settings: Initial range is set at 10. At 1.50 min the range is switched to 9 and at 2.30 minutes the range is adjusted to 10.

11.4 Retention time windows: Retention time windows are all set at ± 0.1 min from the initial calibration retention time.

12.0 Quality Control Requirements:

12.1 Initial Calibration (IC): The initial calibration must be performed and the acceptance criteria must be achieved before samples are analyzed. The acceptance criteria is a regression coefficient (r^2) greater than 0.995 and the lowest gas standard must have a signal/noise ratio greater than 5.

12.2 Continuing Calibration Check (CCC): The validity of the initial calibration is checked every 4 hours or 25 samples, whichever is more frequent, and at the end of the sample batch with the continuing calibration check. The acceptance criterion is less than 30% difference from the true value.

12.3 Laboratory Reagent Blank (LRB): An aliquot of a blank matrix that is handled exactly as a sample including exposure to all glassware, equipment, environmental conditions, and solvents that are used with other samples. The LRB is used to determine if the method analytes or interferences are present in the laboratory environment, the reagents, or the apparatus. The LRB criteria must be met before field or lab samples

are analyzed. A LRB is prepared and analyzed with each SDG and the acceptance criteria are: < 100ppmv for the low range and ; < 2000 ppmv for the high range.

12.4 Field or Trip Blank (FB): [For Field sampling only] An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, storage, preservation, and all analytical procedures. The purpose of the FB is to determine if method analytes or other interferences are present in the field environment. A FB is prepared and analyzed with each SDG and it must be below the lowest point in the standard curve to be reported as non detect.

12.5 Field Duplicates (FD1 and FD2): [For Field sampling only] Two separate samples collected at the same time and location under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with the sample collection, preservation, and storage, as well as with laboratory procedures. The acceptance criteria for field duplicates is less than 30% RPD.

12.6 Matrix Spike (MS): [For Field sampling only] The MS is analyzed exactly like a field sample to determine if the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The percent recovery will be based on the sample concentration as reported for the sample. The MS is prepared and analyzed with each SDG and the acceptance criteria recovery is between 75 - 125 %.

$$\% \text{ Recovery} = \frac{(\text{MS Concentration} - \text{Sample Concentration})}{\text{Theroetical Concentration}} * 100$$

12.7 Matrix Spike Duplicate (MSD): [For Field sampling only] A laboratory duplicate of the MS and analyzed with the MS. Analysis of the MS and MSD represent a measure of the precision associated with the laboratory, field procedures, and matrix effects. The acceptance criteria are recoveries between 750 - 125 % and agreement between the two spikes within 25 % RPD.

$$\%\text{RPD} = \frac{(\text{MS Concentration} - \text{MSD Concentration})}{((\text{MS Concentration} + \text{MSD Concentration})/2)} * 100$$

12.8 Secondary Standard-optional: A standard from another vendor used to check the primary working standard. This is down only when a secondary gas stock is available.

12.9 Method Detection Limit (MDL): Minimum concentration of a substance that can be reported with a 99% confidence that the concentration is greater than zero. A minimum of seven replicates of a low standard are analyzed and the MDL value is calculated on an annual basis, according to Shaw's standard MDL SOP determination.

12.10 Data must be flagged with a qualifier if a quality control sample fails the acceptance criteria. This must be explained in the narrative.

13.0 **Analytical References:**

13.1 Analysis of natural gas using dingle fapillary folumn and a pPulsed discahrge helium ionization detector, S.H Kim; S.M Nam; K.O. Koh; and Y.W. Choi , Bull. Korean Chem. Soc, Vol 20 No 7, May 1999

13.2 Gas chromatographic analysis of trace gas impurities in tungsten hexafluoride, J.B. Laurens; J. P de Coning, and J. McNeil Swinley, J. Chromatography , Vol 911 September, 2001

13.3 Fast isothermal separation of all permanent gases includeing CO2 by using a parallel setup of optimiazed PLOT columns, J. de Zeeuw and C. Duvekot, P-152 Varian Inc.; Middleburg, the Netherlands

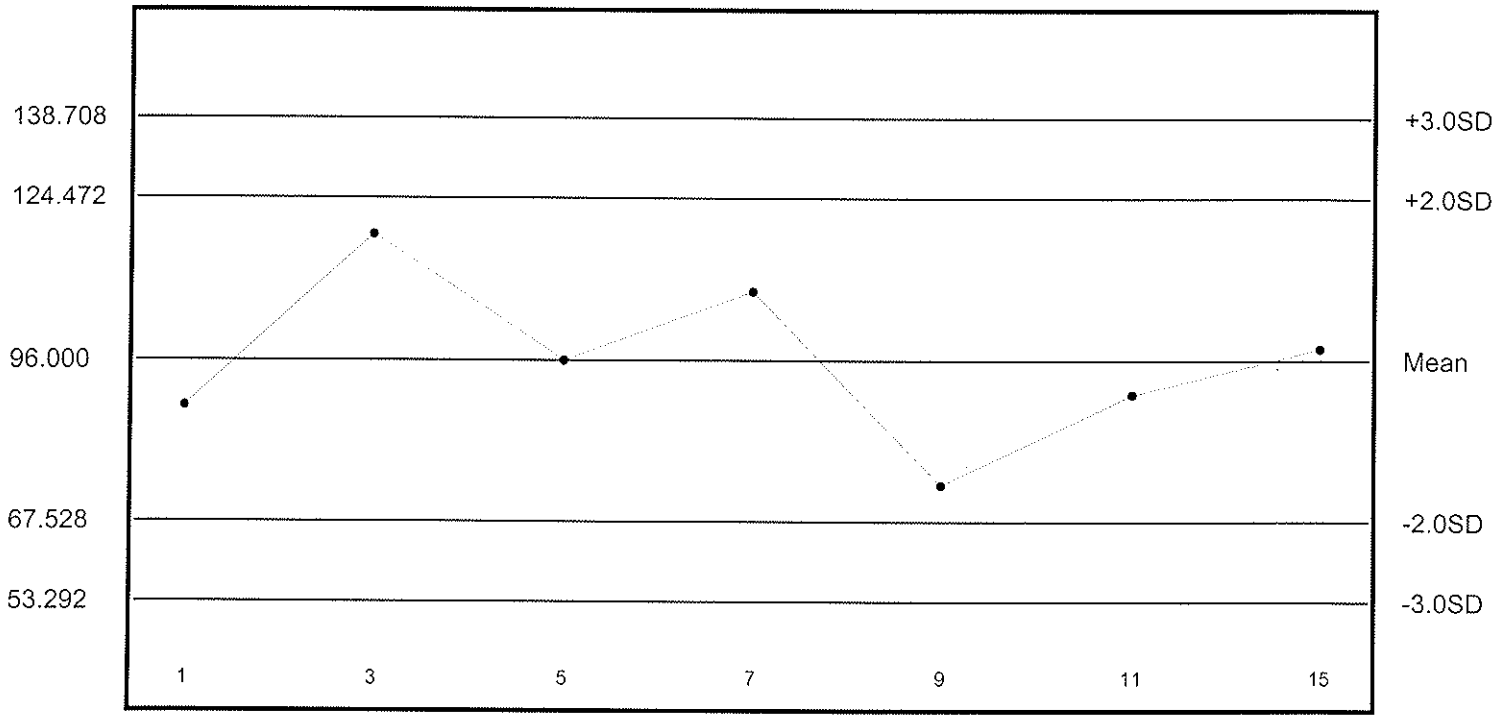
13.4 Method detection limit: 40 CFR, part 136, Appendix B

BLANK SPIKE RECOVERIES

Date	% recoveries observed H2 high	% recoveries observed H2 low	% recoveries observed methane high	% recoveries observed methane low	% recoveries observed CO high	% recoveries observed CO low
	7		7		7	
6/7/2007	88.00	80.00	94.00	120.00	92.00	70
6/7/2007	118.00	86.70	78.00	105.00	108.00	113
6/7/2007	96.00	90.00	138.00	78.00	110.00	105
6/7/2007	108.00	80.00	108.00	80.00	108.00	
6/12/2007	74.00	92.00	110.00	94.00	88.00	
6/18/2007	90.00	100.00	104.00	120.00	78.00	100
6/18/2007		100.00		97.50		112.00
6/25/2007	98.00	115.00	98.00	86.00	98.00	105

Spike recovery

hydrogen - high gas concentration

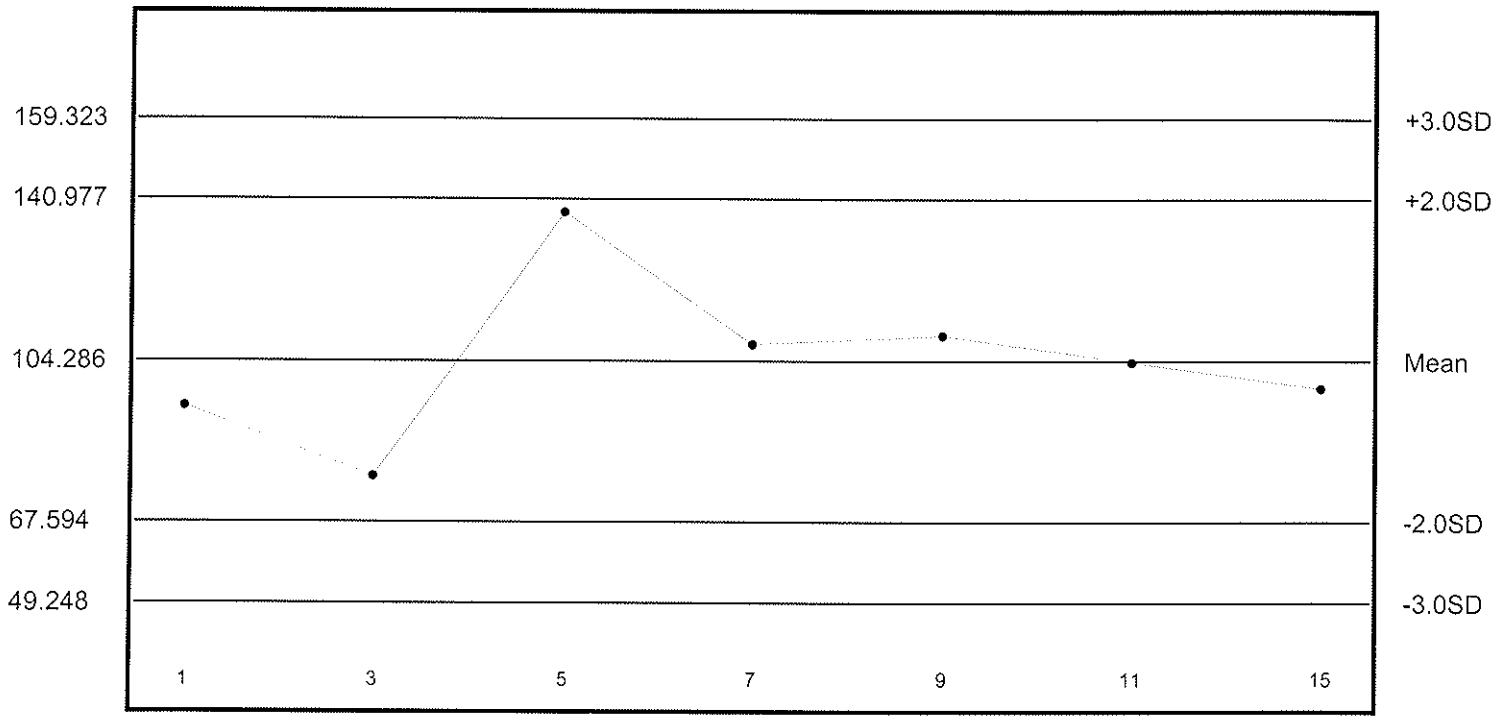


n= 7 Mean= 96.000 SD= 14.236 CV= 14.83% Min= 74.000 Max= 118.000

File:

Spike recovery

methane - high gas concentration



n= 7 Mean= 104.286 SD= 18.346 CV= 17.59% Min= 78.000 Max= 138.000

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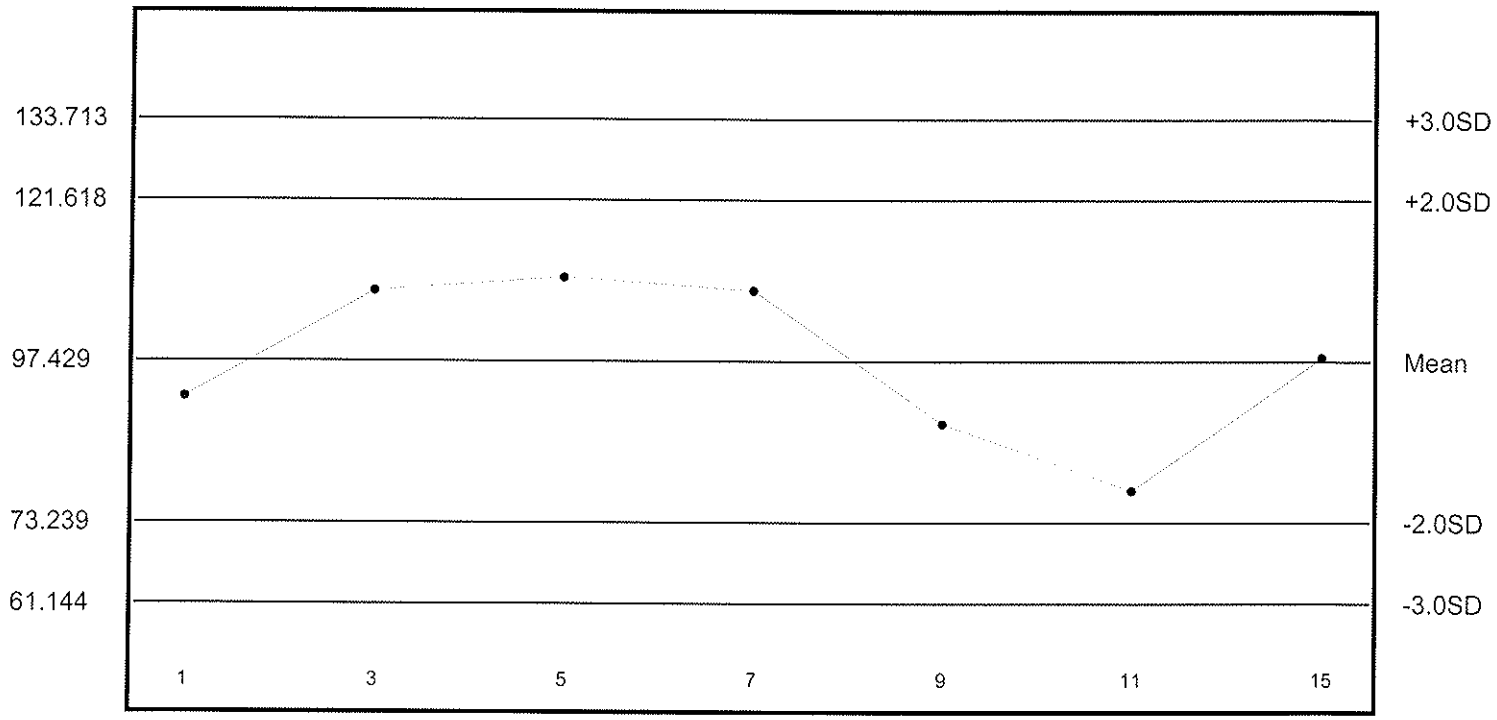
Spike recovery

carbon monoxide - high gas concentration

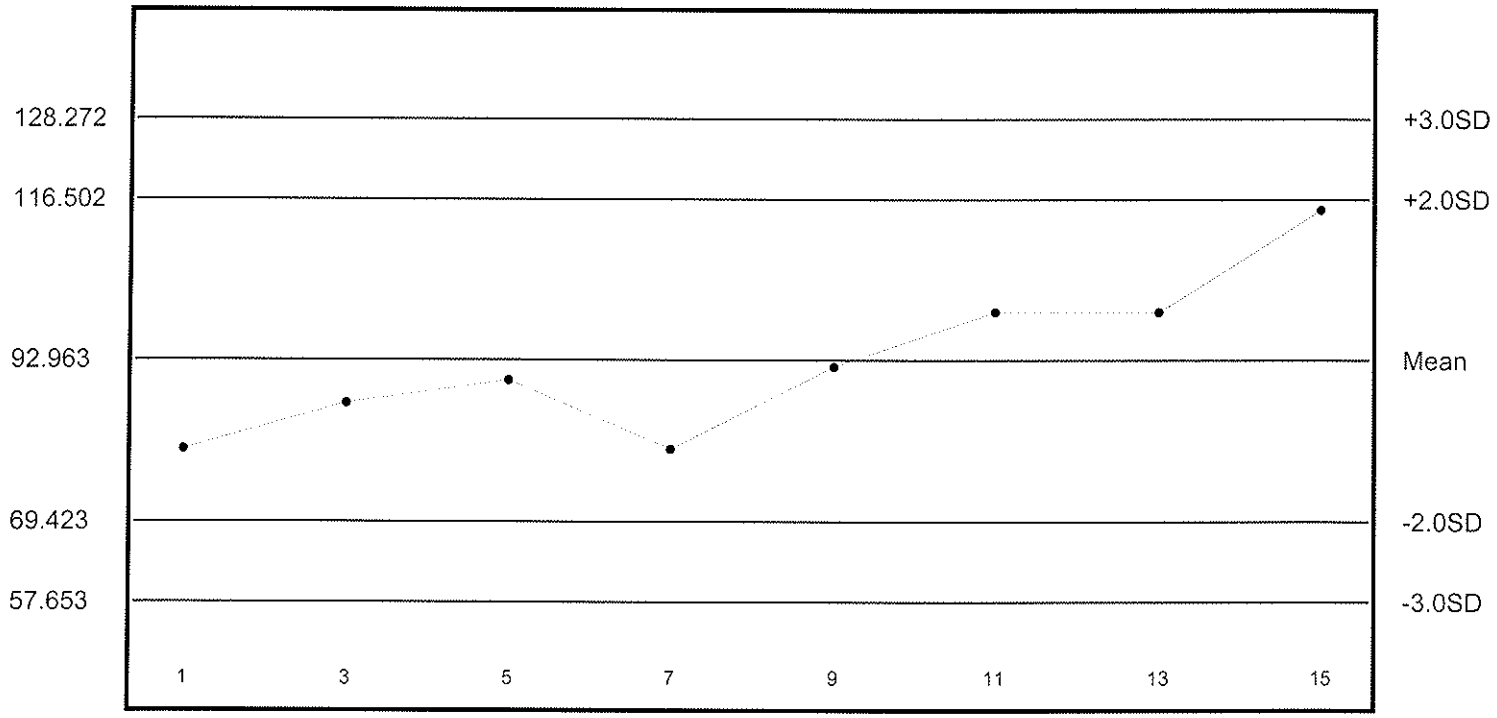


n= 7 Mean= 97.429 SD= 12.095 CV= 12.41% Min= 78.000 Max= 110.000

File:

Spike recovery

hydrogen - low gas concentration



n= 8 Mean= 92.963 SD= 11.770 CV= 12.66% Min= 80.000 Max= 115.000

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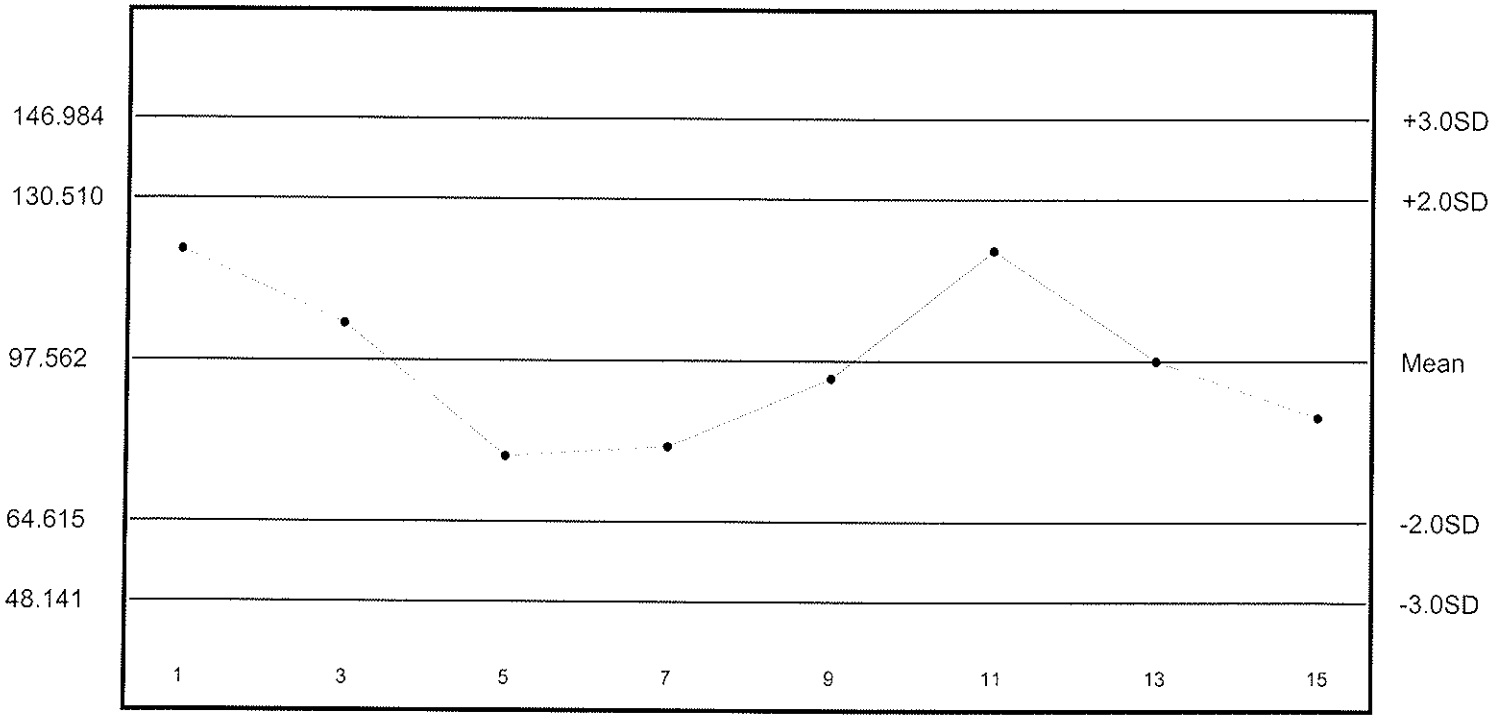
Spike recovery

methane - low gas concentration



n= 8 Mean= 97.562 SD= 16.474 CV= 16.89% Min= 78.000 Max= 120.000

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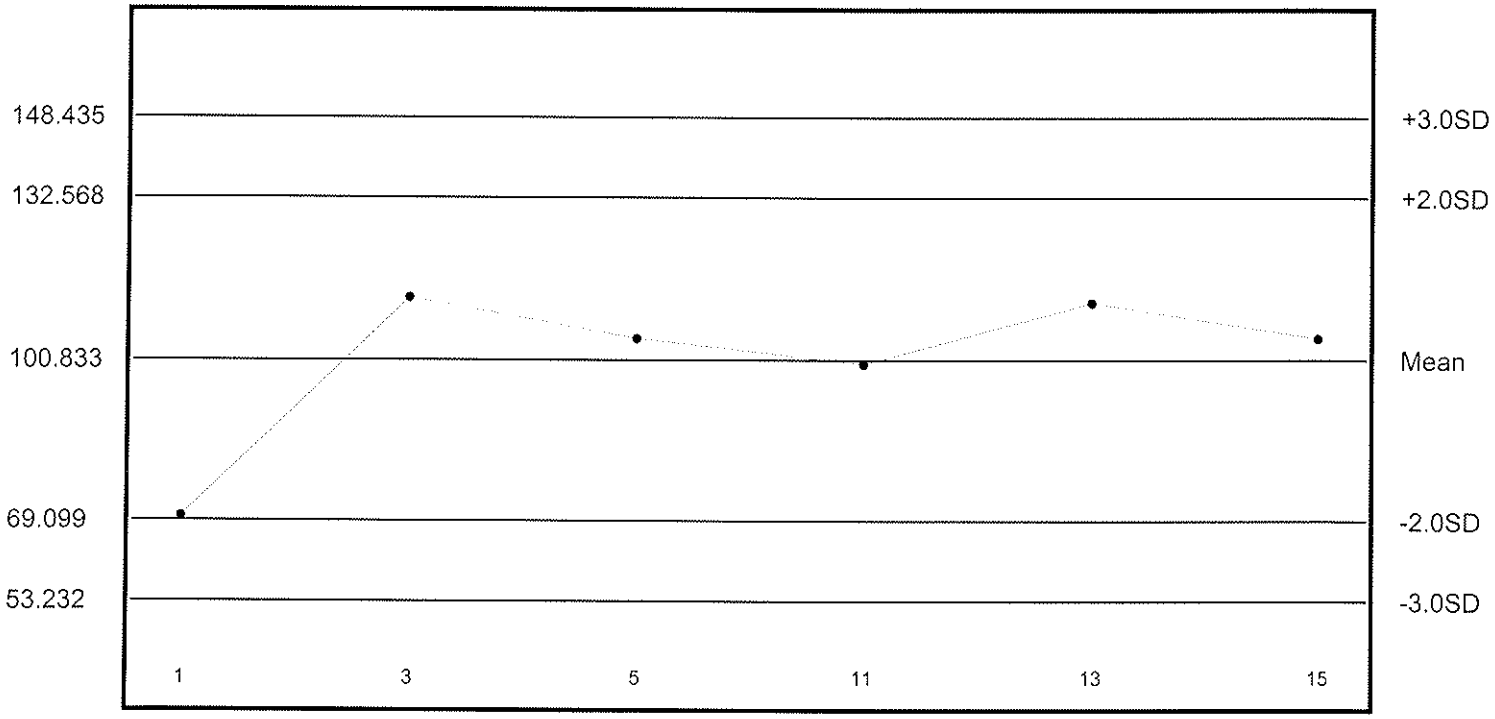
Spike recovery

carbon monoxide - low gas concentration



n= 6 Mean= 100.833 SD= 15.867 CV= 15.74% Min= 70.000 Max= 113.000

File:

Analysis of Natural Gas Using Single Capillary Column and a Pulsed Discharge Helium Ionization Detector

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Received October 2, 1998

Precise analysis of natural gas is important for determining the price due to calorific value, identification of source and gas quality. In natural gas, there are lots of components from C_1 to C_{10} hydrocarbons including isomers. Their physical properities are similar and the composition ratio of major against minor components is great. Therefore, good quantification is not easy in ordinarily analytical means.

The gas chromatic separation with high resolution capability and versatility has been used to characterize all the components of natural gas. The most recommended method is ASTM D-1945 and GPA standard 2261 multi-column technique, which consists of one ten-port valve, two six-port valves and several columns. Recently, an simpler technique using an alternative system with two GCs and three efficient columns, two capillary columns (PoraPLOT Q and FSOT) and one packed column (Hayesep Q), has been introduced.[1] In this system, the first GC is equiped with a thermal conductivity detector (TCD) and a flame-ionization detector (FID), and the second chromatograph is equiped with a TCD and a flame photometric detector (FPD). Using these techniques, the complex mixture of C_1 to C_{10} hydrocarbons are well characterized with good resolution and repeatability.[1,2] However, they require complicated equipments and sophisticated experimental skills and long analysis time. They do not seem to be suitable for industrial usage, such as distributer, small gas station, and dealer. The ratio of the major against the minor components in natural gas is almost third order. The amount of C_6 to C_{10} hydrocarbons is extremely small enough to be negligible in practical view. A simple analytical technique for C_1 to C_5 hydrocarbons might be appropriate economically for the suppliers.

In 1992, the pulsed discharge helium ionization detector (PDHID) was introduced by Went worth *et al.*[4] Attention has been paid to its advantages with simple configuration, convenience, high sensitivity and good versatility. The source of PDHID is a pulsed discharge in helium and responses to the helium ionization detector. As helium gas passes through the ionization chamber, analytes emanating the GC capillary are ionized by the helium metastables and photons, and transfer the signal to the electrometer. Since the ionization potential of the metastable helium is higher than that of all species except with argon ion, it can ionize all other compounds.[5] Therefore, PDHID has become a universal detector capable of detecting H_2, O_2, CO_2, H_2O as well as organic compounds ranging from light hydrocarbons to high molecular weight pesticides and metal complexes.[6-9] Its sensitivity for hydrocarbons is the order of 1 pg/s.[10]

This paper reports on the results of analysis for C_1 to C_5 hydrocarbons in natural gas. The experiment was developed, based on an economic and inexpensive structure which consisted of single column and single detector of PDHID in a gas chromatic system with a Y-piece split throttling port. This split port was employed for the measurement of the major components. Only small part of them flows to the column to prevent the sensitive detector from being overloaded as they are analyzed at the detector. Most is vented. We introduce a practical skill of measuring, in turn, the major and the minor in the single capillary column.

Experimental

Materials. Standard natural gas was purchased from Matheson(USA). The composition is given in Table 1.

Instrumentation. The experimental system is depicted in Figure 1. A gas chromatograph (DS 6200, Donam Systems. Inc, Korea) equipped with a PDHI detector and a GS-Q capillary column (J&W Scientific, USA) of 30 m length with I.D. 0.5 mm were used for this study. Before the natural gas was launched into the six-port sampling valve (Valco, USA), helium and natural gases were mixed at the preparation unit by the mass flow controllers (Brooks, Japan, flow range; 10-100 mL/min), and then the mixture gas was introduced into the GC column by the six-port valve equipped with 100 μL sampling loop to inject a constant amount of sample. For the major components (methane, ethane, and propane), a Y-piece split throttling port was set between the six-port valve and the column inlet. The split ratio was adjusted by a 1/16" micro needle valve on the Y-piece port,

Table 1. Composition of the standard natural gas

Component	Concentration[a] (mol %)
N_2	0.022
CO_2	0.000
CH_4	91.743
C_2H_6	4.190
C_3H_8	2.710
i-C_4H_{10}	0.655
n-C_4H_{10}	0.603
i-C_5H_{12}	0.067
n-C_5H_{12}	0.010

[a] Data from Matheson Gas Products

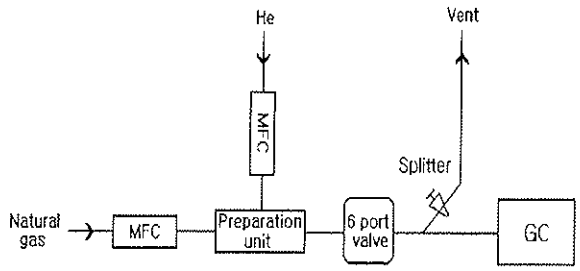

Figure 1. Schematic diagram of a injection system MFC: mass flow controller.

in order that the major components may not be saturated on the sensitive detector. There are two modes, split injection mode for the major and splittless injection mode for the minor. For the split injection mode, only a small amount is sent to the detector through the capillary column and most part is vented. For the splittless injection mode, no vent occurs and all the gas flows into the column. This skill allowed the major and the minor to be measured in the single capillary column, independently. 99.999% pure helium (Praxair, Korea) was used as carrier gas. For analysis of the major components the flow rate of the carrier gas was 27 mL/min, and the oven temperature was held initially at 160 °C for 2 min, then programmed to 240 °C at the increase rate of 40 °C/min. For the minor components (*i*-butane, *n*-butane, *i*-pentane, and *n*-pentane), the flow rate was 8 mL/min, and the oven temperature was held initially at 60 °C for 2 min, then programmed to 80 °C at the rate of 20 °C/min, and to 230 °C at the rate of 30 °C/min. The flow rate of helium gas for discharge was 30 mL/min.

Results and Discussion

Chromatogram in the split injection mode is illustrated in Figure 2. Each component exhibits the excellent peak shape. The retention time of methane, ethane, propane, *i*-butane, and *n*-butane (1.61, 1.71, 1.99, 2.47, and 2.68 min) shows good separation. Concentration of each component is 91.8 (methane), 4.2 (ethane), 2.7 (propane), 0.7 (*i*-butane), and

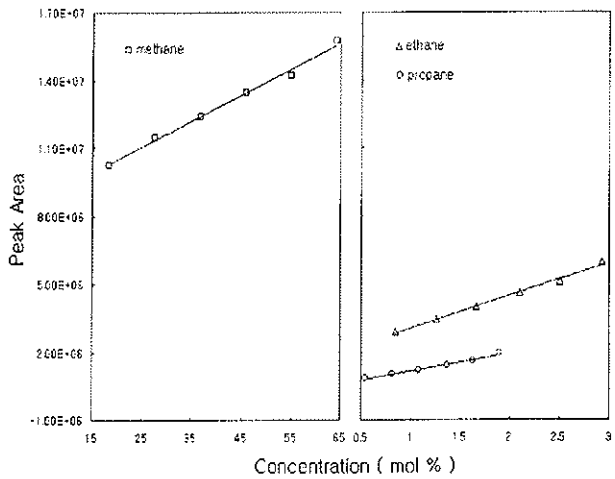

Figure 3. Calibration curves of the major components.

0.6 mol % (*n*-butane), respectively. The calibration curve for each component in the natural gas was obtained by changing the flow rates in the column but the total flow rate of helium and the natural gas was kept constant (50 mL/min). The flow rates of the natural gas were increased with 10, 15, 20, 25, 30, and 35 mL/min as the flow rates of helium were decreased with 40, 35, 30, 25, 20, and 15 mL/min, respectively. Keeping the total constant during GC temperature programming is important for good reproducible results of the gas analysis. The resulting chromatogram is illustrated in Figure 3. Good linearity (0.98-0.99 of correlation coefficient) for methane, ethane, propane was obtained.

The condition of analysis for the minor was the same as for the major except that the mode is splittless injection mode. The chromatogram of the minor components is shown in Figure 4. The major components were saturated as seen in the figure. Retention times of *i*-butane, *n*-butane are different from those in Figure 1, because the flow rate in the column inlet is changed by the splitter. The calibration curves (Figure 5) for i-butane, *n*-butane, *n*-pentane, *i*-pentane are linear (0.98-0.99 of correlation coefficients).

To investigate the precision of the analysis, relative stan-

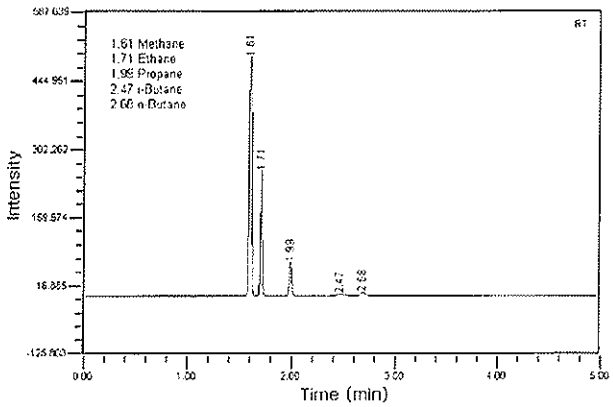

Figure 2. Chromatogram of the major components. GC conditions are in the text.

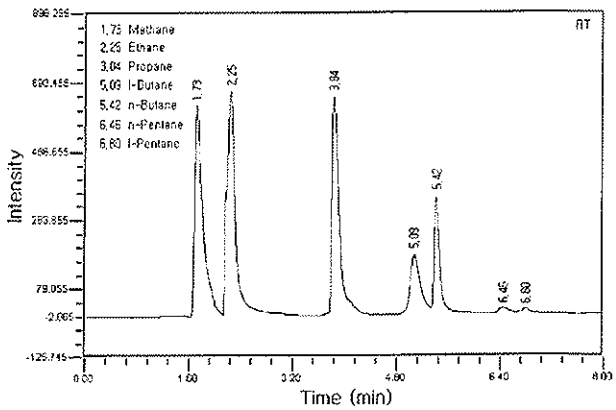

Figure 4. Chromatogram of the minor components. GC conditions are in the text.

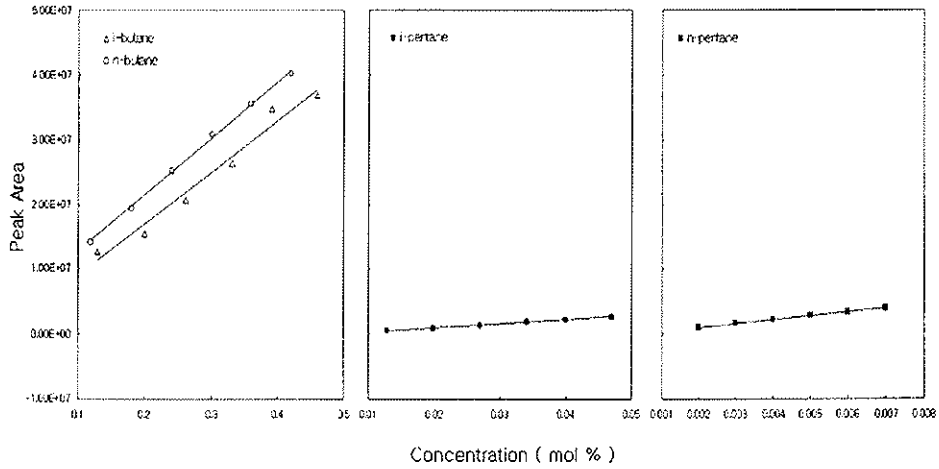

Figure 5. Calibration curves of the minor components.

Table 2. Repeatability of the natural gas analysis

Component	Repeatability (%RSD)[a]
CH_4	0.05
C_2H_6	0.91
C_3H_8	1.39
i-C_4H_{10}	0.54
n-C_4H_{10}	2.57
i-C_5H_{12}	6.79
n-C_5H_{12}	12.20

[a]Calculated from the results of six runs (methane, ethane, propane) and four runs (butane, pentane) within a day

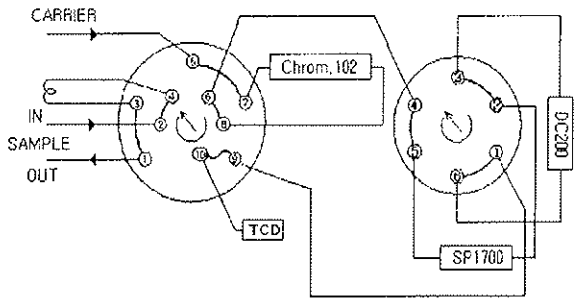

Figure 6. Valve diagram for analysis of natural gas.

dard deviations (RSD) were calculated from the results of six runs (for the major) and four runs (for the minor) within a day. For the RSD of the natural gas analysis, ISO 6568 suggests 0.1% for methane, 0.5-1% for more than 0.5 mol % composition, and 5-20% for less than 0.5 mol % composition. Resulting RSD values are given in Table 2. This method is not precise, but very convenient as compared with multi-column method (Figure 6 and Figure 7).

In conclusion, we can state that the single capillary column and PDHID system furnished with a splitter is convenient for monitoring major and minor components of natural gas. This method may be useful in practical places requiring for analyzing natural gas supplied home or to small factories. The skill is simple and the cost is cheap.

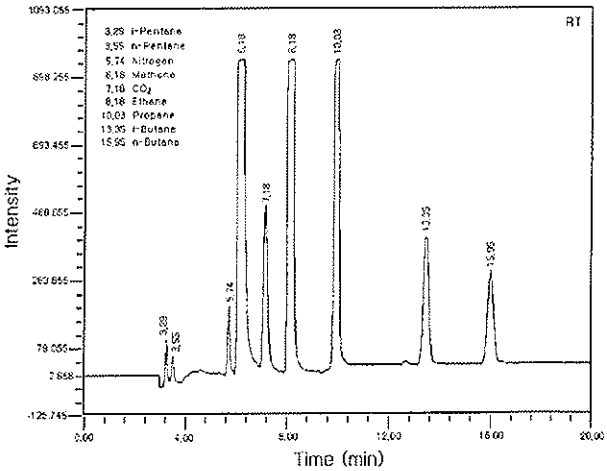

Figure 7. Typical gas chromatogram of natural gas by multi-column method (He carrier gas: 25 mL/min, isothermal at 80 °C, TCD: 100 °C).

References

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Gas chromatographic analysis of trace gas impurities in tungsten hexafluoride

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Abstract

Highly reactive fluorinated gaseous matrices require special equipment and techniques for the gas chromatographic analysis of trace impurities in these gases. The impurities that were analysed at the low-μg/l levels included oxygen, nitrogen, carbon dioxide, carbon monoxide, sulfur hexafluoride and hydrogen. This paper describes the use of a system utilising backflush column switching to protect the columns and detectors in the analysis of trace gas impurities in tungsten hexafluoride. Two separate channels were used for the analysis of H_2, O_2, N_2, CO, CO_2 and SF_6 impurities with pulsed discharge helium ionisation detection. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pulsed discharge helium ionisation detection; Detection, GC; Gases; Tungsten hexafluoride; Oxygen; Nitrogen; Carbon monoxide; Carbon dioxide; Sulfur hexafluoride

1. Introduction

Tungsten hexafluoride (WF_6) is a highly corrosive gas used by the electronics industry, which places a high demand on its purity. It is used in chemical vapour deposition to form high-purity coatings of tungsten on both metallic and non-metallic substrates such as silicon devices [1].

Several techniques for the analysis of gaseous impurities in corrosive matrices have been used in the past [2–11]. All these techniques lack the sensitivity towards the gaseous impurities H_2, O_2, N_2, CO, CO_2 and sulfur hexafluoride (SF_6) in WF_6 required by the electronics industry [12].

This paper describes the use of a dual-channel gas chromatograph, utilising pre-columns for the separation of the analytes from the matrix by retaining the latter. On each channel, a different analytical column is used in series with a pre-column for further separation of the analytes. Valves between the pre- and analytical columns are used to backflush the matrix while simultaneously quantifying the analytes using a pulsed discharge helium ionisation detection (PDHID) system on each side.

Following laboratory validation, the system was placed at-line in the WF_6 production plant at NECSA and has been in routine use for over a year. Continued evaluation of the performance of the system is included.

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2. Experimental

A Perkin-Elmer (Norwalk, CT, USA) Autosystem XL gas chromatograph, with PDHID systems (VICI, Schenkon, Switzerland) installed on both channels was used for the analysis of gaseous impurities in WF_6. All standard pneumatics of the gas chromatograph were bypassed as the analytical requirements placed stringent demands on the pneumatics. A custom inlet system had to be constructed to handle the introduction of the gas to the gas chromatograph (Fig. 1). The low-volume inlet manifold was constructed using 1.6 mm O.D. stainless steel tubing and two three-way stainless steel valves. This allowed for switching between calibration and sample gas while maintaining system integrity and simultaneously permitting the evacuation and disposal of excess sample. A detailed description of the inlet system was reported elsewhere [13].

To obtain a stable baseline on the PDHID system the helium carrier gas of 99.999% (5.0) had to be purified to 99.9999% (6.0) by using a zirconium alloy gettering system (HP2; VICI). An electronic-grade stainless steel regulator (Air Products, Kemptonpark, South Africa) was used with Cajon VCR connectors. Pre-cleaned 1.6 mm O.D. stainless steel tubing was used throughout and where connections had to be made, gold plated ferrules were used to ensure system integrity. Fixed restrictors in the tubing were used for flow control. This not only limited the number of connections but also prevented the ingress of air through gauges, needle valves and regulators.

The pre-columns used on both channels were 4 m×3.2 mm O.D. nickel columns packed with 10% Kel-F oil on Chromosorb T (250–500 μm). For the permanent gases (H_2, O_2, N_2 and CO) a 3 m×3.2 mm O.D. nickel column packed with Molecular Sieve 13X (150–180 μm) was used and for the condensable gases (CO_2 and SF_6) a 3 m×3.2 mm

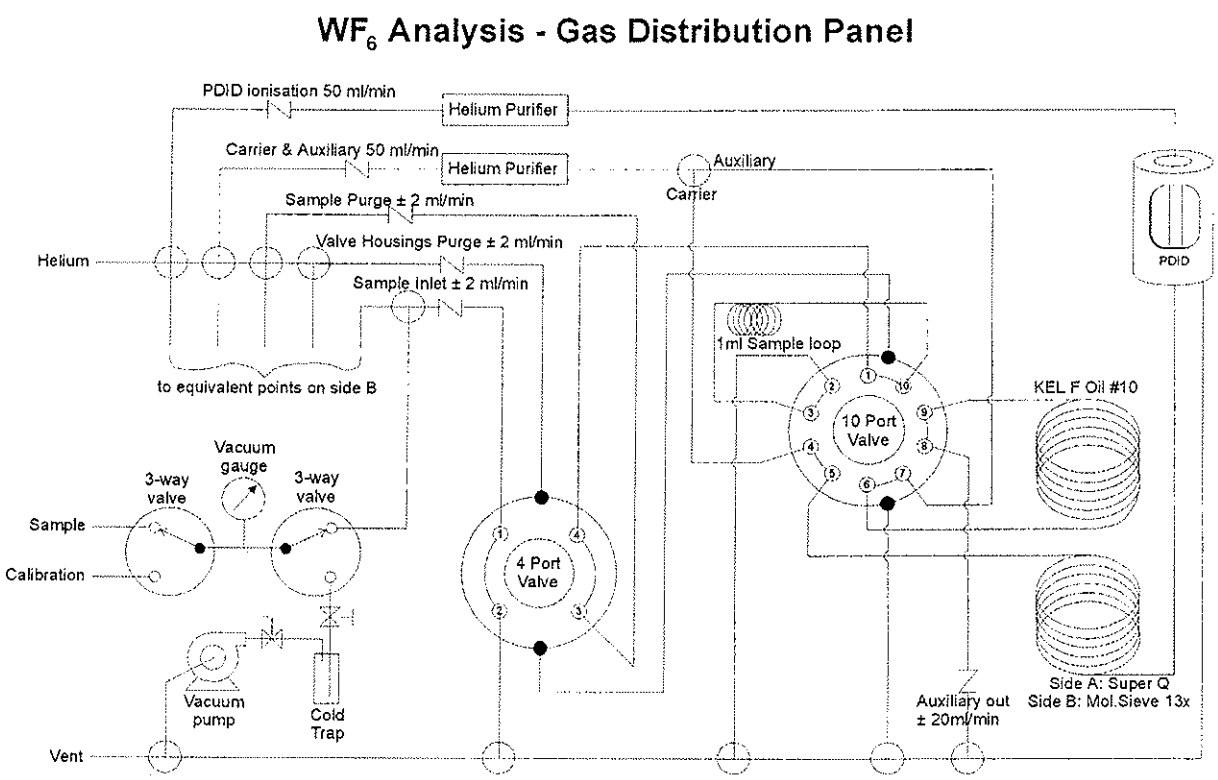

Fig. 1. A schematic diagram of the plumbing, valve and column configuration for the analysis of corrosive gases. The flow-rates indicated are approximate. The inlet system is shown in the bottom left corner of the schematic.

O.D. nickel column packed with Super Q (150–180 μm) was used. The columns were obtained from Chemlab (Johannesburg, South Africa). Dual channels allowed individual optimisation of the column flows and switching times.

An isothermal column oven temperature of 40°C and a constant flow of 18 ml/min was maintained during both the fore- and backflush cycles. Since PDHID shows some flow sensitivity the flow-rates through all columns must be carefully balanced. This was achieved by placing restrictors in both the supply and vent lines.

Ten- and four-port VICI rotary valves, manufactured from Hastalloy C22 with seats manufactured from a polymer composite, Valcon-E from VICI were used. The soft seat rotary valves, certified by mass spectrometry, had air-operated automatic actuators and helium purged housings.

The standard electronics of the Autosystem gas chromatograph were utilised for the detector, which was operated at 100°C. Data collection and processing was performed with PE Nelson Turbochrom software.

3. Results and discussion

A high-concentration static gas standard containing a nominal 50 μg/l H_2, O_2, N_2, CO, CO_2 and SF_6 in helium was used for setting up the system. The standard was obtained from Afrox (Germiston, South Africa). Representative chromatograms of the set-up gas standard are shown in Fig. 2.

The purity of the carrier gas is critical for the reliable quantitative analysis of impurities in the low- to sub-μg/l range. This application therefore precludes the use of programmable pneumatic control (PPC) or electronic pneumatic control (EPC) as this will degrade the quality of the carrier gas. Bearing in mind that the concentrations of O_2 and N_2 in the atmosphere are approximately 210 000 and 780 000 μg/l, respectively, the slightest leak will produce erroneous results.

A maximum allowable concentration of 7 μg/l (v/v) for the total gaseous impurities in WF_6 was required by industry, necessitating a very sensitive detector. The difference in chemical properties of the gas impurities required a universal detector. PDHID

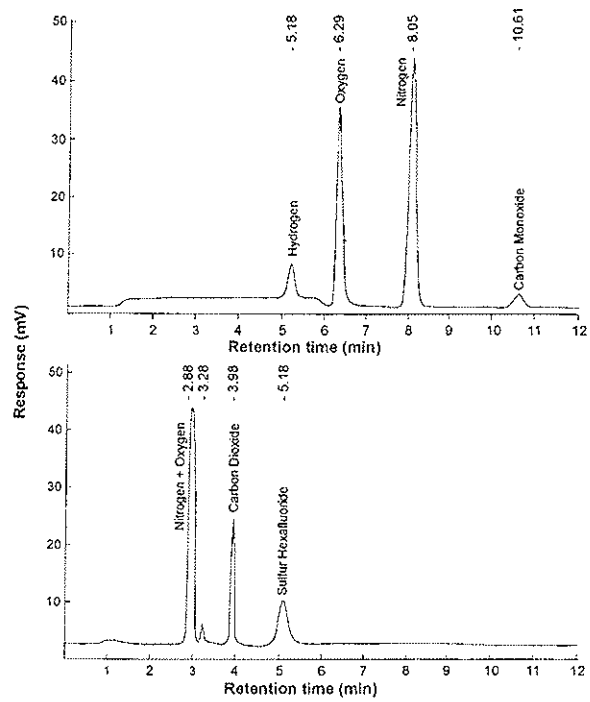

Fig. 2. The chromatograms recorded on both channels of the WF_6 system using the nominal 50 μg/l set-up gas mixture. In the lower panel, the unresolved O_2 and N_2 peak eluted at 3.05 min. The peak at 3.45 min is CO, which is usually not fully separated from O_2 and N_2 on this porous polymer stationary phase at these temperatures. However, adequate separation was obtained at these low concentrations.

has been shown to be one of the most sensitive universal detection methods in gas chromatography [14].

It is a prerequisite for the system to be dry since tungsten hexafluoride is readily hydrolysed by water, adsorbed to the inside of the transfer lines to give tungsten trioxide and hydrogen fluoride [1]. Tungsten oxides can cause blockages in the restrictors and transfer lines of the system:

$$WF_{6(g)} + 3H_2O_{(g)} \rightarrow WO_{3(s)} + 6HF_{(g)}$$

Chlorine trifluoride was used to dry the system, as erroneous oxygen values will be obtained unless the system is completely dry [13]:

$$4ClF_{3(g)} + 6H_2O_{(l)} \rightarrow 3O_{2(g)} + 12HF_{(g)} + 2Cl_{2(g)}$$

Previously either PTFE or nickel tubing has been

used for the column material [9]. In this case, where low levels of O_2 and N_2 have to be analysed, nickel is mandatory since PTFE tubing would allow permeation of atmospheric gases into the chromatographic system. An additional advantage lies in the passivity of nickel, and its alloys, towards reactive fluorinated gases. Nickel oxide is converted to nickel fluoride by ClF_3 between 25 and 180°C [15]. Deactivation of the sampling system by ClF_3 prior to the analysis of WF_6 renders the internal surfaces of all valves and connecting tubing very stable [13]:

$$6NiO_{(s)} + 4ClF_{3(g)} \rightarrow 6NiF_{2(s)} + 2Cl_{2(g)} + 3O_{2(g)}$$

The choice of the stationary phase is limited by the high reactivity of WF_6. PTFE and Kel-F supports, coated with Kel-F oils $[(C_2ClF_3)_n]$, were sufficiently inert and reversible in their behaviour to be used as packing materials [11,13,15,16]. Kel-F would be an ideal stationary phase but cannot perform the necessary separation at or above ambient temperature. Typically, a molecular sieve stationary phase is required to analyse permanent gas impurities and a divinylbenzene–styrene co-polymer stationary phase (Porapak, Hayesep or Super Q) for condensable gas impurities. These stationary phases cannot withstand this highly aggressive matrix gas. The aluminosilicate molecular sieves will trap these compounds, forming AlF_3 and SiF_4, and degrading the column with every injection. Divinylbenzene–styrene stationary phases will also be degraded by the matrix.

For these reasons a pre-column in combination with a backflush-to-vent valve switching technique was used. The corrosive matrix is prevented from coming into contact with the analytical column and the detector by reversing the flow direction of the carrier in the pre-column, after the impurities have eluted from it, but before the matrix elutes. The total volume of the pre-column, which is at least 10-times the sample loop volume, is introduced into the analytical column, making the additional helium purification essential.

Due to the presence of air, seemingly insignificant mistakes can have disastrous results. For instance, replacing the pressure regulator on the cylinder without purging it very well results in the air in the regulator mixing with the contents of the cylinder and changing the concentrations of the standards to such an extent that the entire cylinder becomes unusable as a calibration sample.

Molecular Sieve 13X was chosen in preference to Molecular Sieve 5A as SF_6 was also present in the WF_6 sample and could co-elute with hydrogen on the Molecular Sieve 5A.

Memory effects due to the matrix gas permeating the polymer sealing material of the rotary valves must be avoided. The four-port valve was installed ahead of the 10-port sampling valve to allow helium purging of the sample loop at all times except during actual sampling. The 10-port valve, on which the sample loop was mounted, was therefore exposed to the matrix gas for only 1 min per analysis cycle.

Critical to the success of this analysis is the switching (cutting times) of the 10-port valve. In order to determine the elution times of the matrix and the analytes on the pre-column a thermal conductivity detection (TCD) system was temporarily installed in-line between the pre- and analytical columns during the construction and testing phase (Fig. 2). Once the switching times were established, the TCD system was removed.

The statistical data for the calibration curves are tabulated in Table 1. Linear correlation coefficients

Table 1
Statistical data for calibration curves

	R^2	Detection limit ($S/N=3$)	Calibration range (μg/l)
Oxygen	0.9898	<10 ng/l	0.012–9
Carbon monoxide	0.9914	<500 ng/l	0.016–12
Nitrogen	0.9970	<10 ng/l	0.018–13.75
Hydrogen	0.9931	<10 ng/l	0.017–12.5
Sulphur hexafluoride	0.9866	<500 ng/l	0.018–13.25
Carbon dioxide	0.9974	<50 ng/l	0.017–13

were better than 0.99 is all cases except SF_6. The minimum detectable quantity found was in agreement with the literature. The PDHID response is linear over four orders of magnitude; therefore, a single-point calibration check was sufficient [14]. The stability of the system was measured as the difference between the calibration check and the mean. These data are shown in Fig. 3.

The gaseous impurities in WF_6 were determined using this system following deactivation and calibration. Chromatograms recorded on both channels for a representative WF_6 sample are shown in Fig. 4. Replicate analyses of a WF_6 sample with sub-μg/l levels of gaseous impurities yielded relative standard deviations (RSDs) of between 0.4 and 3.7% for the impurities.

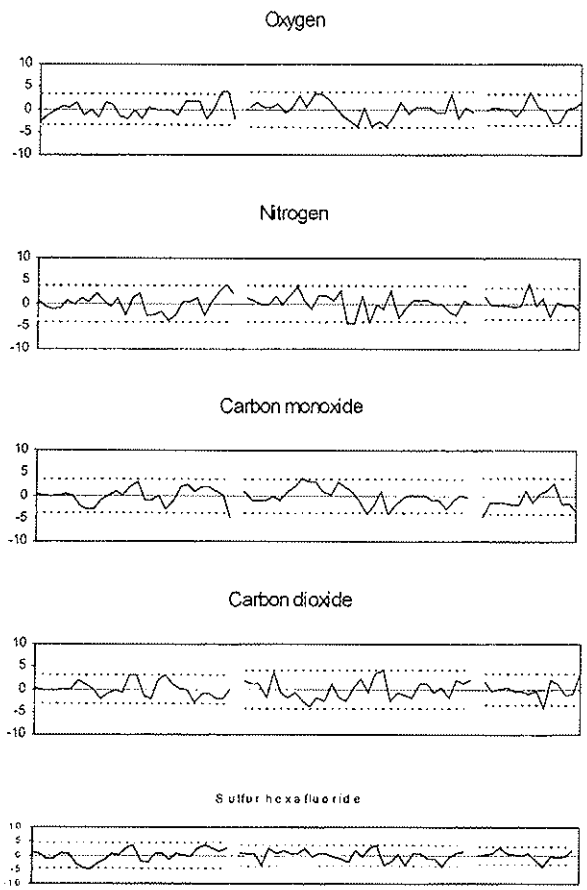

Fig. 3. Quality assurance charts showing the stability of the system using the difference between the calibration check and mean values, over a period of 70 weeks, within the limits of two standard deviations from the mean. Note that the QA charts consist of three parts corresponding to three different standard mixtures. The standards were replaced at regular intervals.

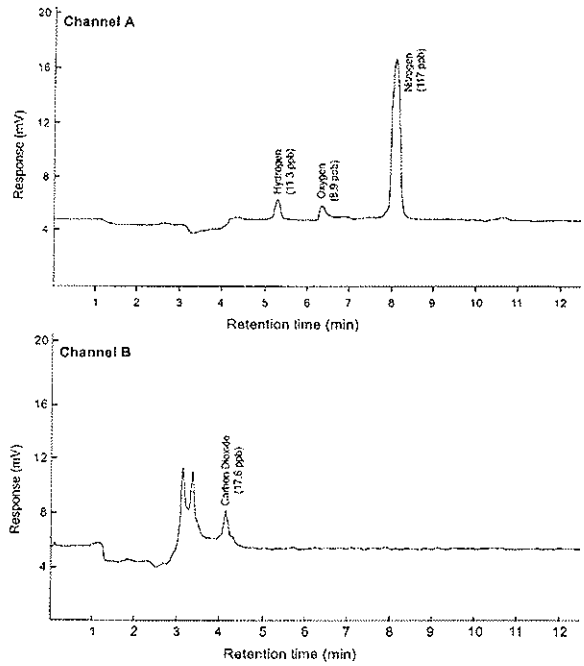

Fig. 4. Chromatograms recorded on both channels of the gaseous impurities in a WF_6 sample from the plant prior to the sample being dispatched to the client.

The enormous density difference between WF_6 and the contaminants allows for the "purification" of WF_6 in the sample container. If left until equilibrium has been reached, the headspace will contain a larger fraction of the contaminant gases. By carefully venting this headspace, the concentration of the gaseous impurities in the WF_6 can be reduced. The lowered values obtained following repetitive venting of the cylinder headspace, lead us to believe that the minimum detectable quantities are rather conservative. However, a certified static standard containing such low levels was not available.

4. Conclusion

A gas chromatographic system able to analyse trace impurities in a highly corrosive and aggressive matrix such as WF_6, was assembled, making use of a

backflush-to-vent column-switching technique. The specified level of allowable impurities necessitated the use of PDHID, which further required special measures to clean the carrier gas and avoid leaks.

The detection limits of below 10 ng/l and the RSD of less than 4% at sub-μg/l levels makes this system highly suitable for the analysis of trace gaseous impurities in WF_6. The entire system performs extremely well under plant conditions with long-term stability of less than 3% for the gas impurities.

Acknowledgements

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Fast isothermal separation of all permanent gases including CO2 by using a parallel setup of optimized PLOT columns

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Fast Isothermal separation of all permanent gases including CO2 using parallel setup of optimized PLOT columns

Summary
Analysis of permanent gases is usually done using adsorbents as stationary phase. These materials generate high retention for volatile components making separations possible at temperatures above ambient. Molecular Sieve separates all inert gases up to Carbon monoxide with high efficiency. For measuring Carbon dioxide a porous polymer type material is usually applied.
Practical solutions for permanent gas analysis are 2-column systems where the separation of CO2 from the other gases is done on a Porous polymer column and the first peak (containing the gases) is injected onto a molecular sieve column.
A new approach is to use a parallel set up of a molecular sieve column and a porous polymer. By tuning the retention, the dimensions and temperature of both columns it is possible to separate all the permanent gases in one run.
High resolution separation of permanent gases is obtained using a long
The system is very reliable and retention of the Molsieve column is virtually not affected by water or CO2. If contaminated, the system can be regenerated by heating at 300°C to remove contaminants

Background and possible solutions

The analysis of permanent gases is done in many industrial laboratories. Besides the permanent gases like hydrogen, oxygen, nitrogen and carbon monoxide also carbon dioxide and methane often have to be measured. Samples often also contain moisture. Ideal would be to have one column that is able to do all these components in one run, and with no sensitivity to moisture, but this is difficult. Molecular sieve type materials based on zeolites will separate all permanent gases, but will adsorb CO2

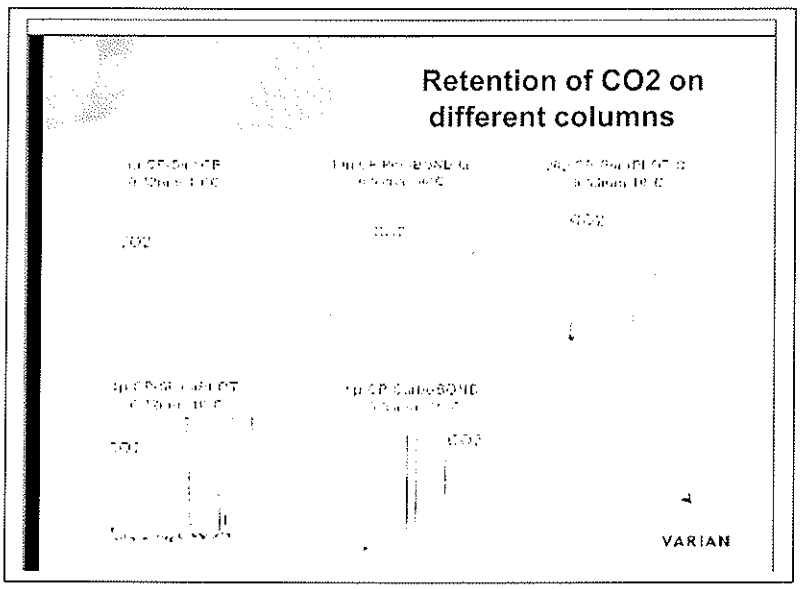

Fig. 1

and water very strong. Figure 1 shows a number of materials that elute Carbon dioxide with acceptable peak shape and retention;

Characteristics of different potential materials

CP-Sil 5 CB Thick film

Polydimethyl siloxanes can be coated with very thick films. Such thick films will separate CO2 from the permanent gases, however the permanent gases will elute as one single peak. Besides this, the efficiency of thick-film polydimethyl siloxane coating is very low due to a huge Cl-term.

Porous polymer adsorbents

Porous polymers have much more retention. The PoraPLOT series have the highest retention resulting in a retention factor of approx. 0.6 for carbon dioxide at 40°C. Porous polymers are highly inert and are not sensitive to water. The absolute retention however is not high enough to resolve gases like oxygen and nitrogen at temperatures above ambient. At analysis temperature of –50°C, the oxygen and nitrogen are separated, see figure 2. Oxygen elutes after nitrogen which is opposite of the elution found with a molecular sieve column. A 25 m capillary is required to obtain a base line separation. This application will work when both compounds are in similar concentrations.

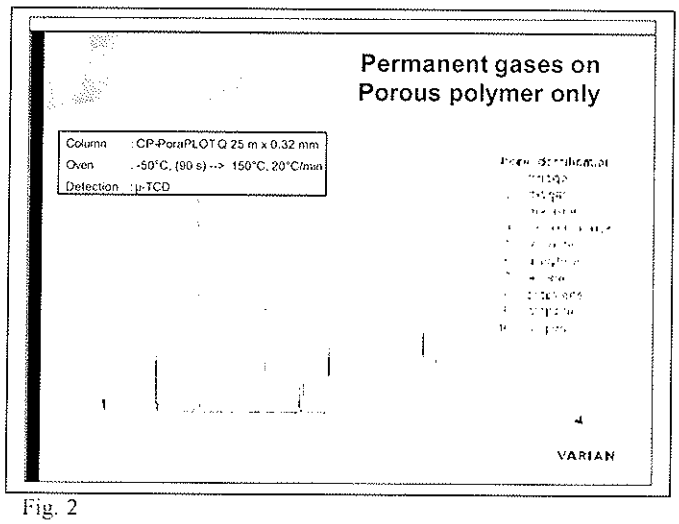

Fig. 2

Silica adsorbent

Silica has a large surface area which also retains carbon dioxide. The retention is however not sufficient to separate inert gases at ambient temperatures.

Carbon adsorbent

Carbon is an interesting material as it has a retention

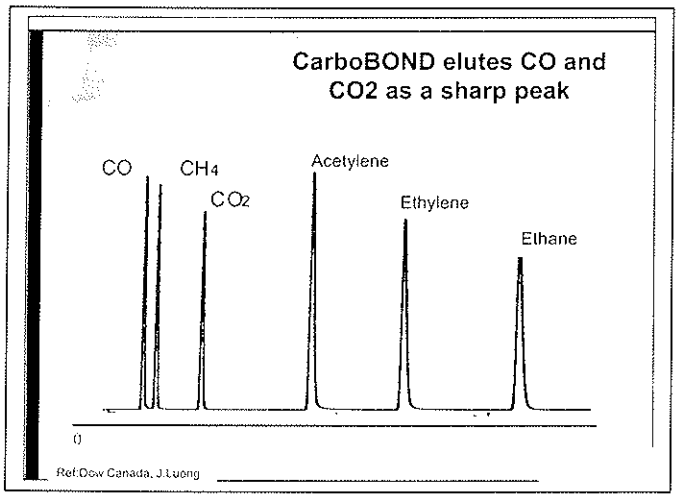

Fig. 3

between molecular sieves and porous polymers. Carbon is a highly non-polar material and it does provide a unique selectivity (separates all C2 isomers with highest possible resolution, see figure 3). Separation of CO and CO2 from the air peak is possible and with long columns also some separation is obtained between the oxygen nitrogen. Application for these components is only possible at temperatures around 30°C (which are not easy to maintain) and for similar concentration ranges. Fast separations are therefore not possible as well as separation of helium-neon and argon-oxygen; The retention of Carbon is not affected by moisture which allows introduction of water containing samples.

Molecular Sieve adsorbent

Molecular Sieves are zeolite based materials with a very high specific surface where the average pore size depend on the type of zeolite used. For permanent gas separations a pore size of 5A is commonly used. Volatile components with a molecular size < 5 A will diffuse in the pores and will be retained on the surface inside the pores. Components not able of entering the pores will only be retained by the outside of the molecular sieve particles (f.i. iso butane).

The retention for permanent gases is very high and even difficult separations can be realized using Molsieve 5A adsorbent. An example is the analysis of permanent gases and deuterated methanes on a 75 m column. To "see" the CHD3 isomer, minimal 94000 theoretical plates are required.

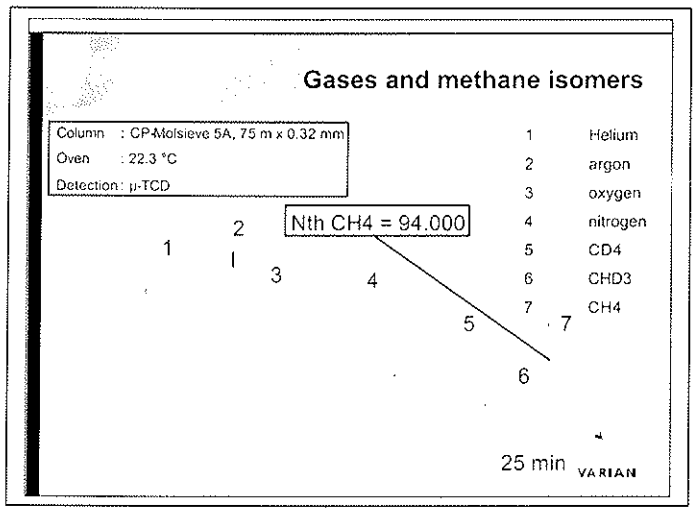

Fig. 4

Due to the high retention, carbon monoxide will elute after methane. Carbon dioxide and water are much stronger retained and will elute at temperatures > 200°C. Peak shape is however poor which makes quantification on a molsieve 5A not possible. If contaminated the molsieve 5A adsorbent can be regenerated by heating at 180- 300°C. the higher the temperature, the faster the regeneration will take place.

Switching system

As there is not a single adsorbent that is capable to separate all the permanent gases and elutes CO2, a widely used solution is a column switching system: The sample is introduced on a porous polymer column where the CO2 and water is separated from the "bulk" peak. This "bulk" peak elutes first and contains all the permanent gases. This fraction is introduced via a valve into a Molsieve column where all the components are separated; After the fraction is introduced the valve is switched and the retained water and CO2 on the PoraPLOT Q column elute straight to the detector, see figure 5. This set up is isothermal and requires a timed valve switching.

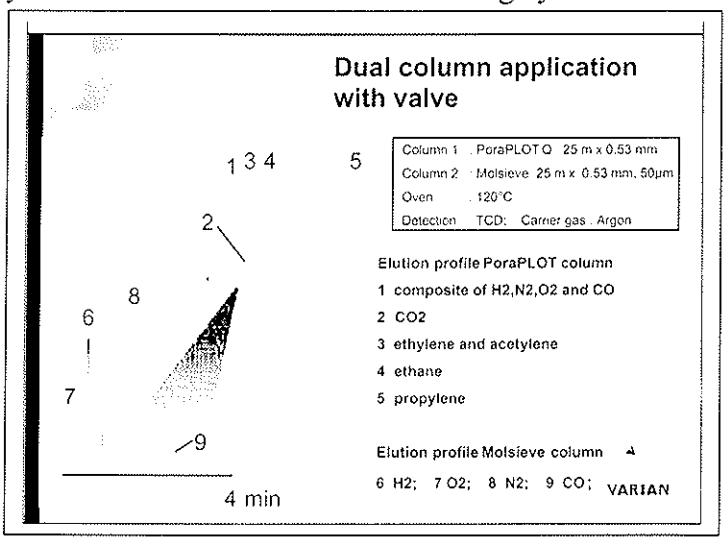

Fig. 5

New concept: Parallel setup of PLOT columns

An other approach to do this application is to inject on 2 columns at the same time. This can be done in different ways:

1. Two injector - two detectors (2 injections)
2. One injector - two detectors (1 injection)
3. One injector - one detector (1 injection)

For System 1 and 2 the calibration of detector sensitivity is an issue and installation of 0.53 mm columns in one injector is difficult. As detection is done with µ-TCD, the use of 0.53 mm is preferred to avoid dead volumes in the system.

Setup 3 needs optimization as two columns run parallel and detection is done with one detector. This is the system that is optimized with the Varian Select permanent Gas/CO2 columns.

Varian Select™ Permanent gases/CO2 and Select™ Permanent Gases/CO2 HR

The Select Permanent Gas/CO2 columns is a parallel setup of 2 PLOT columns of which the column dimensions (length, internal diameter and thickness of adsorption layer) have been optimized for fast isothermal analysis of permanent gas and CO2. Figure 6 shows the configuration of the columns. Depending on the column dimensions it is possible to do a fast separation of permanent gases or a high resolution separation of permanent gases.

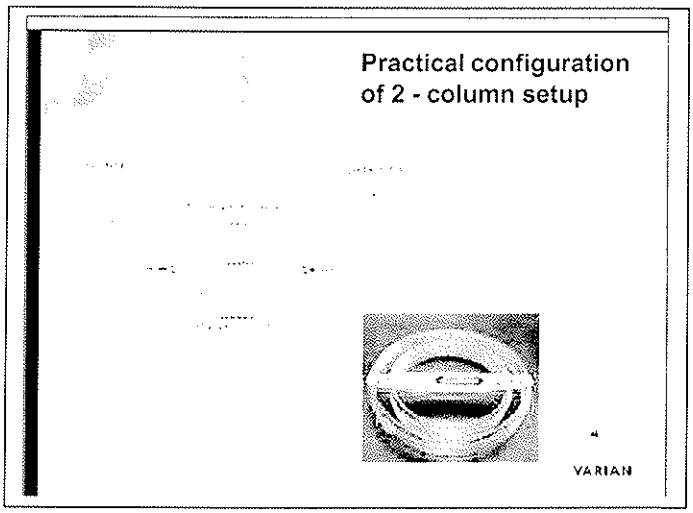

Fig. 6

Principle:

The sample is injected via one split/splitless injection port onto a parallel two column system. The adsorbents used are a PoraBOND Q and a Molecular Sieve 5A. Components are separated on the two columns and will elute to one detector. There are two configurations:

Select Permanent Gases/CO2

This Select column consists of a **short** Molsieve with thin layer and a **long** PoraBOND Q column. The permanent gases up to carbon monoxide that are separated on the molsieve adsorbent will elute before the first peak elutes from the PoraBOND column. After the CO has eluted, the composite peak elutes from the PoraBOND column followed by the methane and the CO2 peak. An example is shown in figure 7a. Note there are 2 methane peaks which we need for the calibration. This analysis can be speeded up significantly by operating under higher flows or running at higher temperature, see figure 7b.

Select Permanent Gases/CO2 HR

This is the high resolution configuration which is used for applications where besides CO2 also argon-oxygen and/or helium-neon separations are required. This configuration consists of a **short** PoraBOND Q column and a **long** Molsieve 5A. Due to the long molsieve column, the analysis times will be long, typically 20-25 minutes, see figure 8..

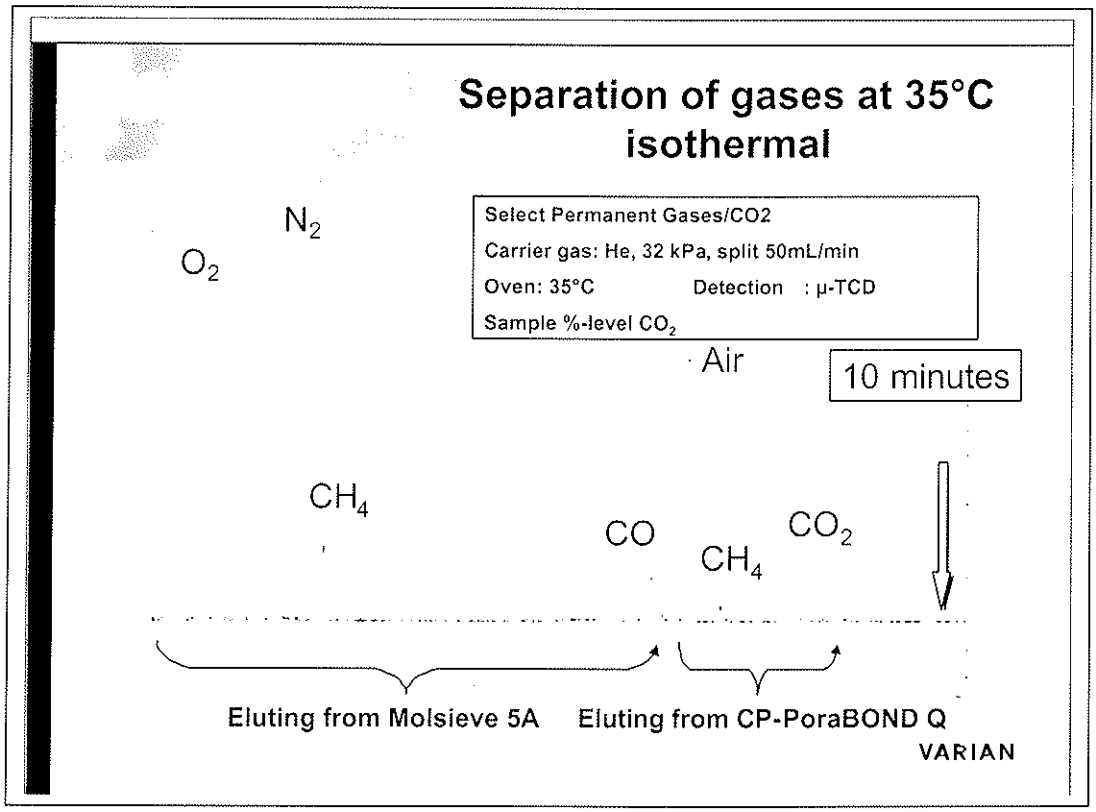
Separation of gases at 35°C isothermal
Select Permanent Gases/CO2
Carrier gas: He, 32 kPa, split 50mL/min
Oven: 35°C
Detection : µ-TCD
Sample %-level CO2
N2
O2
Air
10 minutes
CH4
CO
CO2
CH4
Eluting from Molsieve 5A
Eluting from CP-PoraBOND Q
VARIAN

Fig. 7a

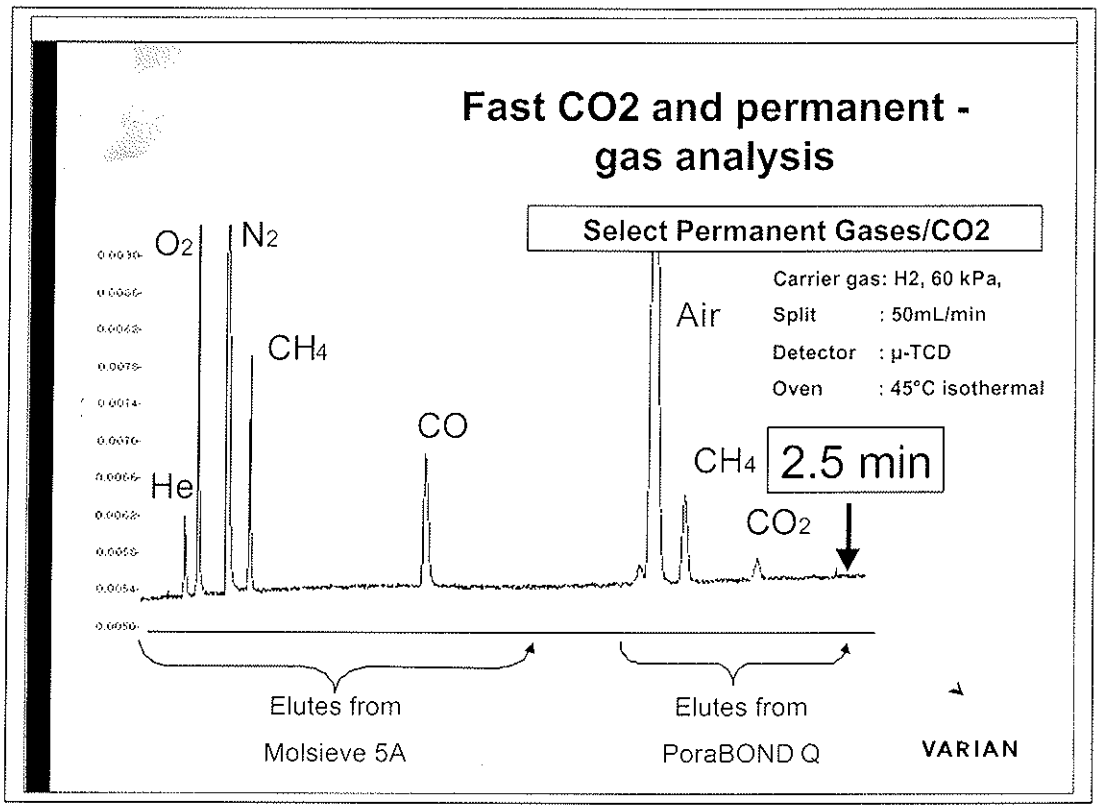
Fast CO2 and permanent - gas analysis
Select Permanent Gases/CO2
Carrier gas: H2, 60 kPa,
Split : 50mL/min
Detector : µ-TCD
Oven : 45°C isothermal
O2
N2
CH4
CO
He
Air
CH4
2.5 min
CO2
Elutes from Molsieve 5A
Elutes from PoraBOND Q
VARIAN

Fig. 7b

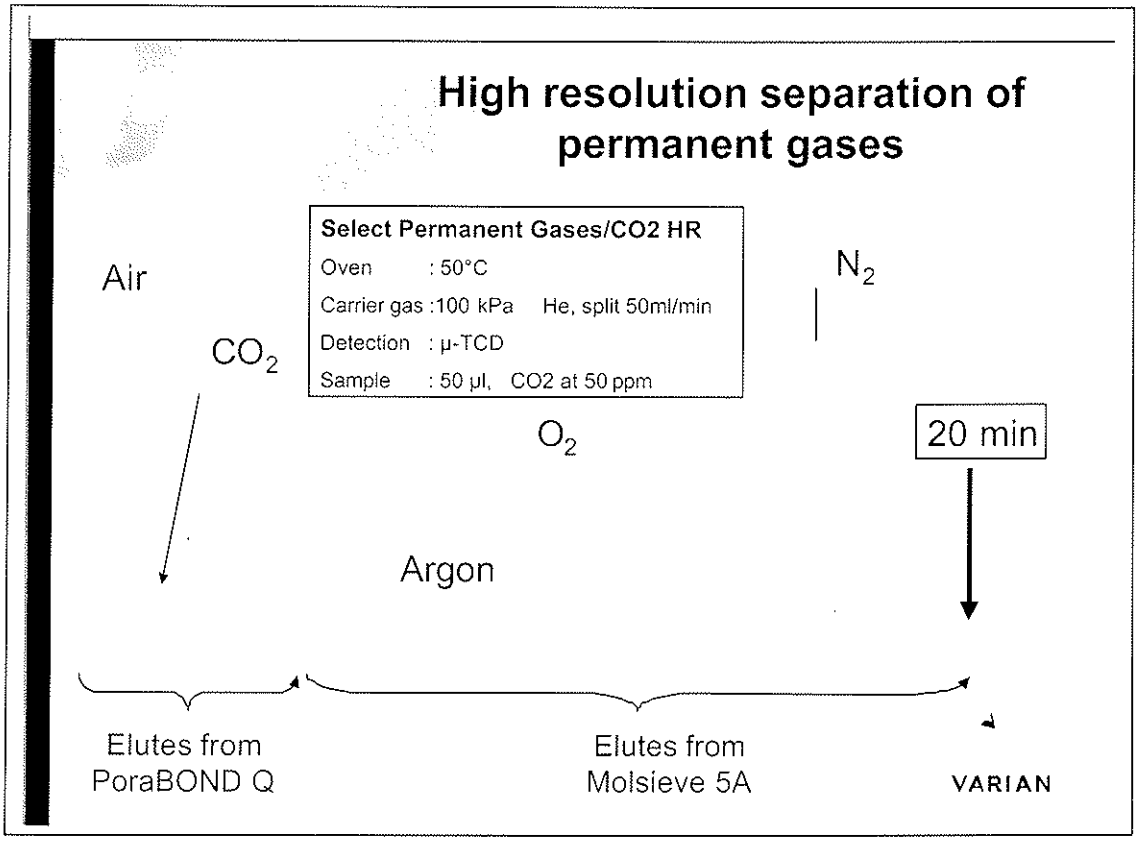

Fig. 8

Figure 8 shows the separation of the Select Permanent Gases/CO2 HR. This column is able to separate argon and oxygen with base line resolution. Also helium and neon are baseline resolved (see figure 9).
The short PoraBOND column allows a fast elution of CO2. The CO2 peak in figure 8 represents 50 ppm. The tailing peak is caused by water that is poorly injected because of the too low valve temperature.

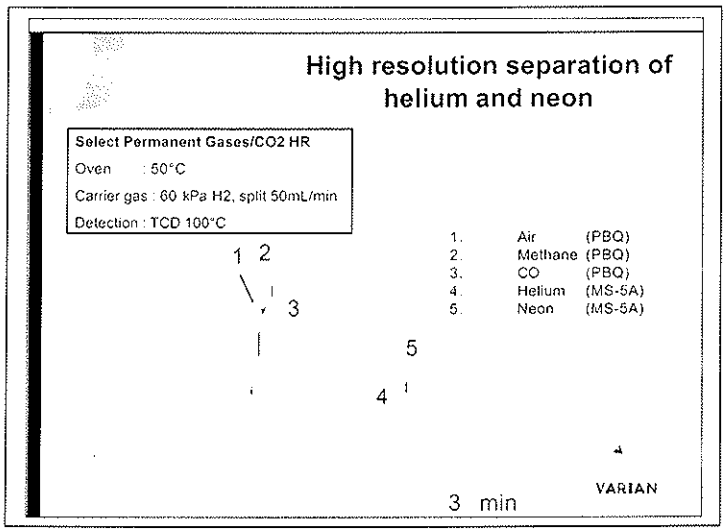

Fig. 9

Impact of water and CO2

One of the first questions using this concept is what happens with the water and the carbondioxide when it is introduced in the Molsieve column.
Molsieve materials will adsorb water and carbondioxide, but this is a reversible process. This means that molecular sieve materials always can be regenerated by heating at higher temperature. Once the Carbon dioxide and/or water is removed the original retention will be restored.

Practically regeneration is done when the retention times of the components are running out of the integration window. As there are only a few components to analyse, integration windows can be set quite large, meaning that a lot of water / CO2 can be introduced on the molsieve column before reconditioning is required. Experimentally it was found that the retention of molsieve was reduced by a factor 2 after approx. 2.5µl of water was injected onto the column, see figure 10 a,b and c. Table 1 show some calculations of equivalent amounts of water introduced. Practically many samples can be analyzed before regeneration is required. Impact of CO2 on retention of molsieve will be of comparable magnitude as water.

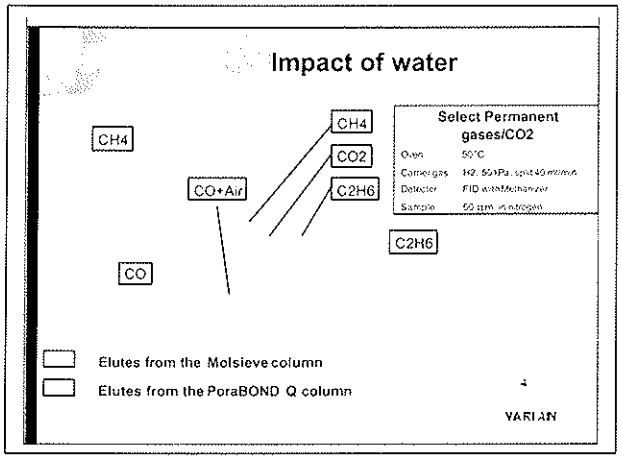

Fig. 10a

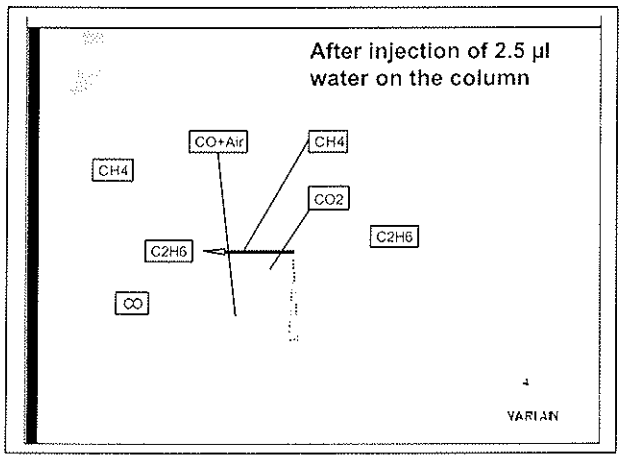

Fig. 10b

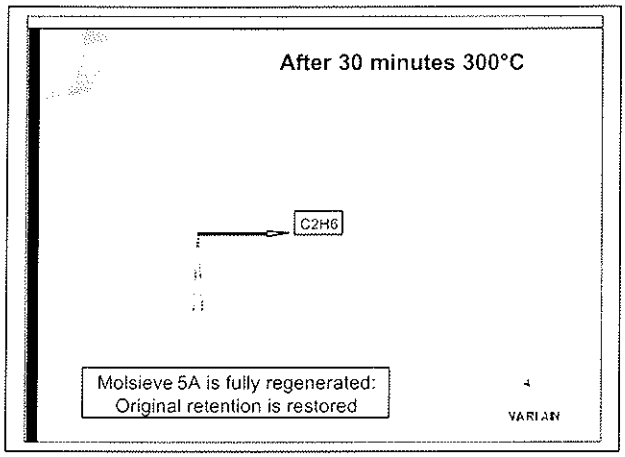

Fig. 10c

Table 1: Equivalent amounts of water representing 2.5 mg onto the molsieve column

Number of injections	Injection volume (µl, on to the column)	Water concentration (ppm)
2500	1	1000
250	10	1000
25	100	1000
25000	1	100
2500	10	100
250	100	100
25	1000	100
250000	1	10
25000	10	10
2500	100	10
250	1000	10

Influence of Oven temperature

As the two columns are operated parallel the oven temperature has strong impact on the peak elution of both columns. Especially when late eluting peaks elute from the shortest column, it is possible that a co-elution occurs in the detector. The separation of such peak pairs can esasily be achieved by changing the oven temperature by a few degrees. An example is shown in figure 10 where a sample containing ethane is analyzed on a Select Permanent gases/CO2 column. The ethane (peak 6) elutes late from the short Molsieve column and interferes with the peaks from the PoraBOND Q column when analyzed at 45°C. If a lower temperature is used ethane elutes later and like in

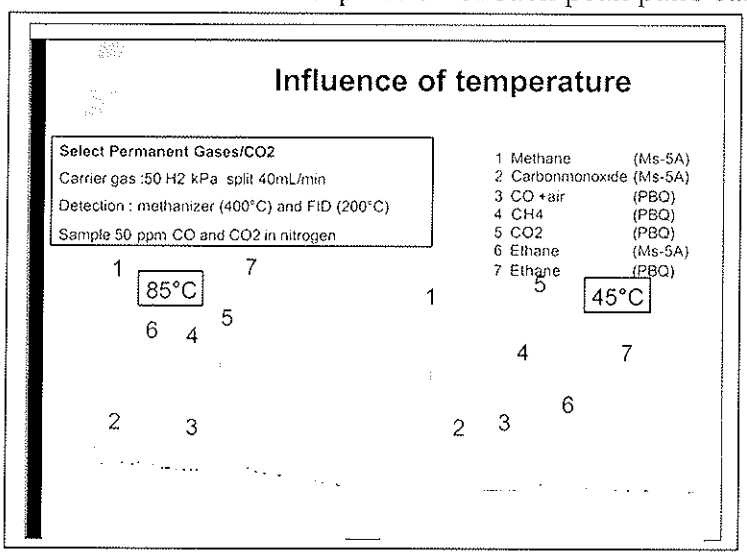

Fig. 11

figure 10, using a temperature of 85°C, ethane elutes much faster. By changing the oven temperature the elution of the compounds can be tuned, especially when compounds elute late from the shortest column.

Using the high resolution Select Permanent Gases/CO2 HR the risk of co-elutions is smaller. Figure 11 shows separations at 45°C and 65°C: no change in elution order occurs. In worst scenareo a sample containing C3-hydrocarbons or higher, run at a temperature around ambient will show peaks from the PoraBOND column after the helium-neon peaks from the Molsieve column. In that case also some adjustment of oven temperature will solve any co-elution issues.

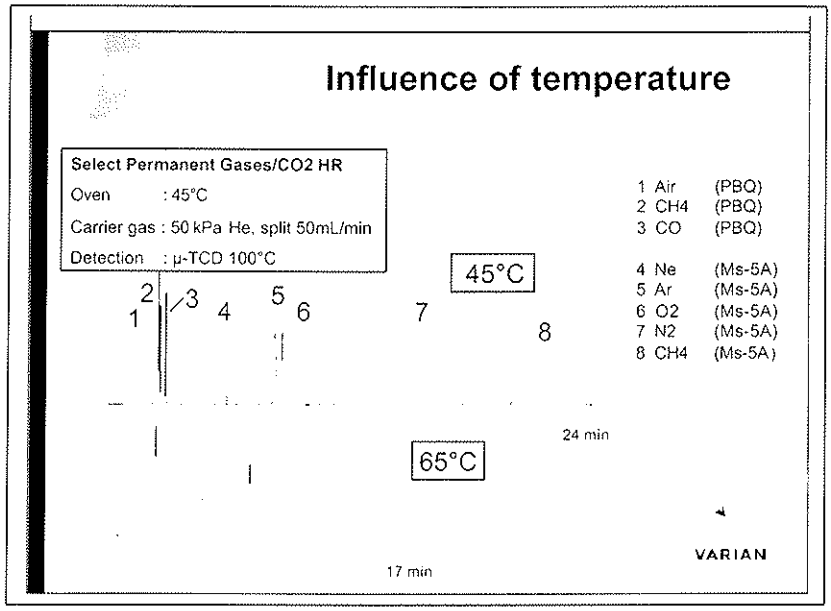

Fig. 12

Calibration

The sample is introduced and splitted over two columns. The split ratio between the two columns depend on the actual flow through both columns. To calibrate, methane can be used as this component is eluting from both columns. As the sensitivity of the detector is the same, the peak area for both methane peaks will represent the real split between the two columns.

Table 2 Typical flow rates

	Pressure (H2) (kPa)	Flow (ml/min)
Select Permanent Gases/CO2	32	4.8
Select Permanent Gases/CO2 HR	100	7.1

Stable Configuration up to 300°C

The columns that are chosen for this application have high mechanical and temperature stability. The PoraBOND Q as well as the Molsieve 5A columns can be heated to 300°C for reconditioning or regeneration. The stability of the in-situ prepared and bonded porous polymer results in long life times and virtually no particle release.

For the configuration a 5 and a 7 inch column cage is used which both conveniently fit on to the EZ-Grip, making a well organized setup of multi column systems possible, see fig.13.

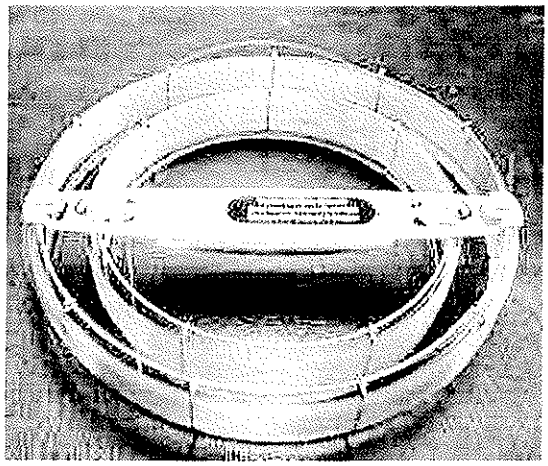

Fig. 13

Setting of Flows

Several gas chromatographs require column dimension to "calculate" and set the optimal flow. To make ssuch a system work with a parallel setup we have to give in a "virtual" column dimension to the data entry. This column dimension is calculated based on the flow resriction of both columns
Following dimensions can be used for this:

Select Permanent gases/CO2	: 30 m x 0.53 mm
Select Permanent gases/CO2 HR	: 40 m x 0.53 mm

Conclusion

A new approach for permanent gas analysis is introduced using a parallel configuration of optimized porous polymer and molecular sieve adsorbents. This results in a new product called: Select Permanent gases/CO2 for the fast isothermal analysis of permanent gases and CO2 in standard GC with μ-TCD technologies.
For high resolution separations a "HR" configuration is introduced which separates also the helium-neon and argon-oxygen components.
Due to the materials chosen, the Select Permanent Gases columns are mechanically very stable and can be used up to 300°C for fast regeneration and are well organized in the GC-oven due to the EZ-Grip. Like all PLOT columns, the Select Permanent Gases/CO2 columns are very durable.