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.

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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
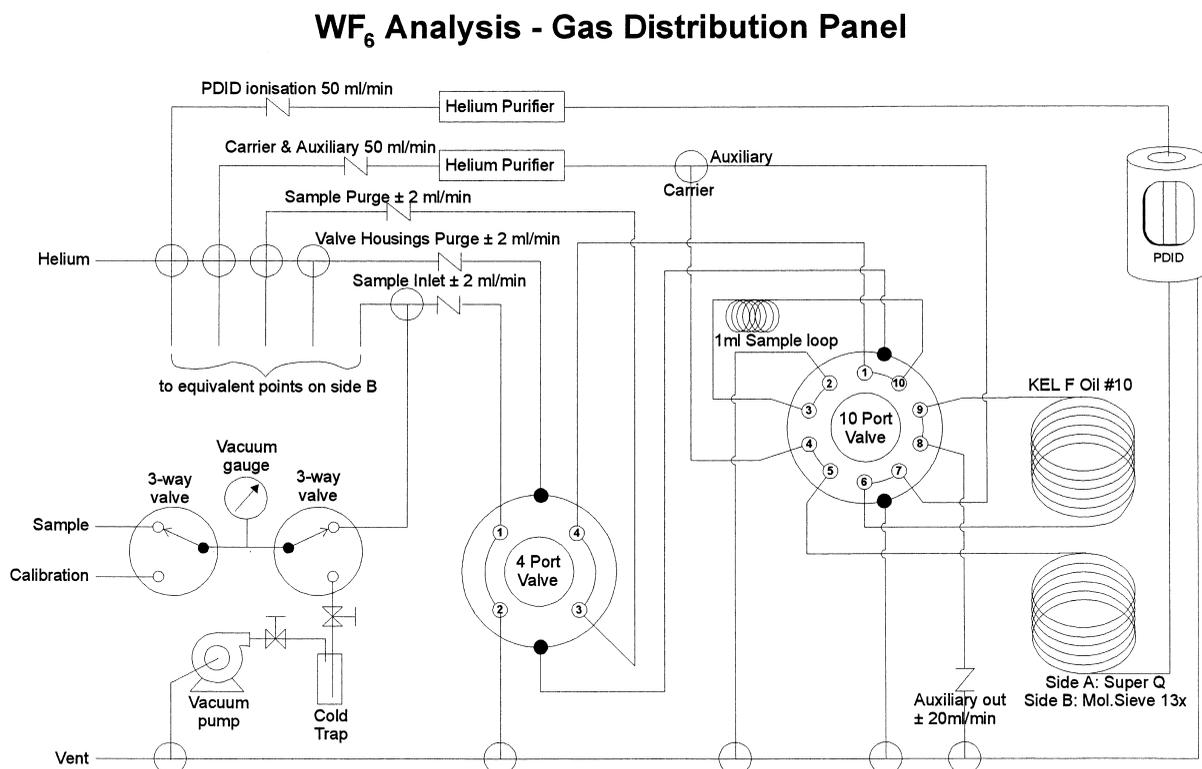

Fig. 1. A schematic diagram of the plumbing, valve and column configuration for the analysis of corrosive gases. The flow-rates indicated are approximate. The inlet system is shown in the bottom left corner of the schematic.

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
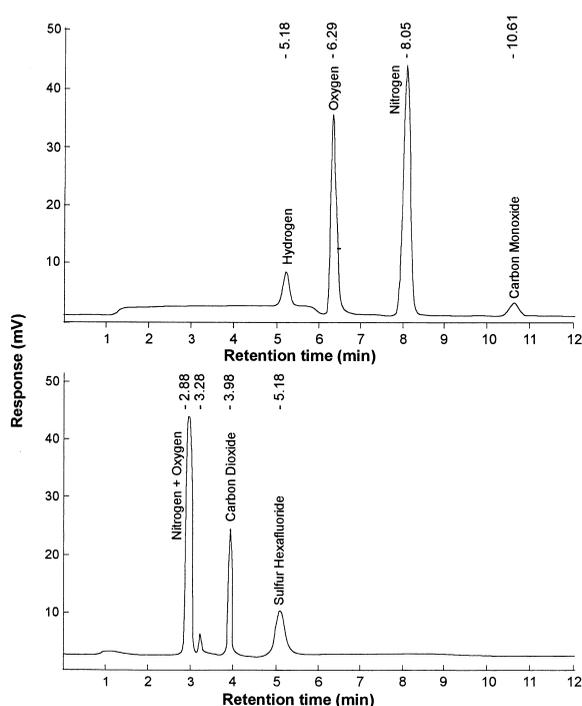

Fig. 2. The chromatograms recorded on both channels of the WF_6 system using the nominal 50 μg/l set-up gas mixture. In the lower panel, the unresolved O_2 and N_2 peak eluted at 3.05 min. The peak at 3.45 min is CO, which is usually not fully separated from O_2 and N_2 on this porous polymer stationary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

$$WF_{6(g)} + 3H_2O_{(g)} \rightarrow WO_{3(s)} + 6HF_{(g)}$$
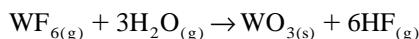
Chlorine trifluoride was used to dry the system, as erroneous oxygen values will be obtained unless the system is completely dry [13]:

$$4ClF_{3(g)} + 6H_2O_{(l)} \rightarrow 3O_{2(g)} + 12HF_{(g)} + 2Cl_{2(g)}$$
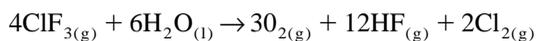
Previously either PTFE or nickel tubing has been

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

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.

levels of gaseous impurities yielded relative standard deviations (RSDs) of between 0.4 and 3.7% for the impurities.

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.
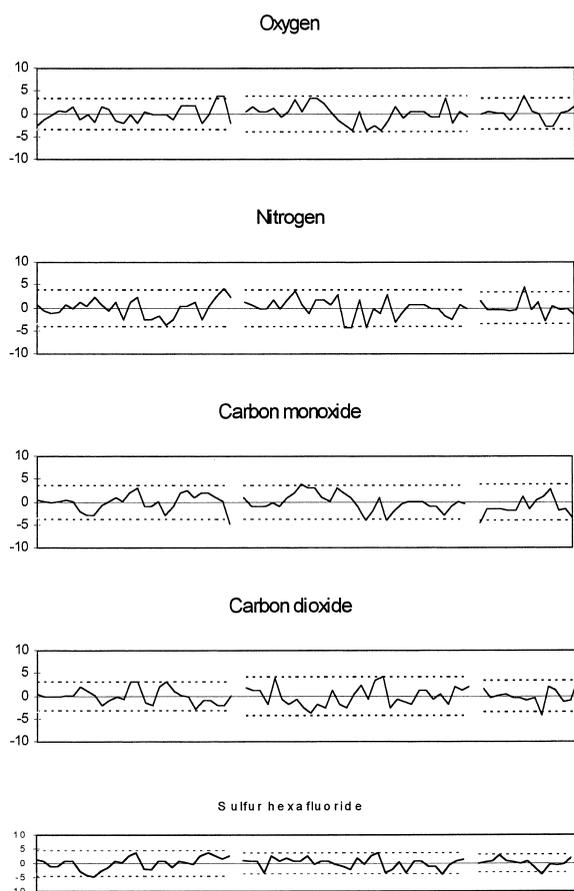

Fig. 3. Quality assurance charts showing the stability of the system using the difference between the calibration check and mean values, over a period of 70 weeks, within the limits of two standard deviations from the mean. Note that the QA charts consist of three parts corresponding to three different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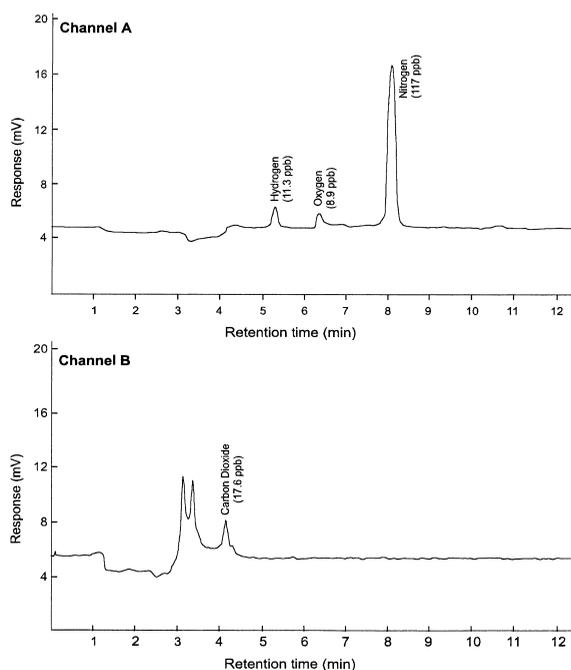
4. Conclusion

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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