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Gas chromatographic analysis of trace impurities in chlorine trifluoride

Johannes Bernardus Laurens^{a,*}, John McNeil Swinley^b, Johannes Petrus de Coning^c

^a*Department of Chemical Pathology, University of Pretoria, P.O. Box 2034, 0001 Pretoria, South Africa*

^b*Scientific Group, Johannesburg, South Africa*

^c*Department of Chemical Pathology, Medical University of Southern Africa, Pretoria, South Africa*

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Abstract

The gas chromatographic determination of trace gaseous impurities in highly reactive fluorinated gaseous matrices presents unique requirements to both equipment and techniques. Especially problematic are the gases normally present in ambient air namely oxygen and nitrogen. Analysing these gases at the low $\mu\text{l/l}$ (ppm) level requires special equipment and this publication describes a custom-designed system utilising backflush column switching to protect the columns and detectors. A thermal conductivity detector with nickel filaments was used to determine ppm levels of impurities in ClF_3 . © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorine trifluoride (ClF_3) is a gas used in the electronics industry which places a high demand on its purity. It is a very powerful oxidising agent, approaching the reactivity of fluorine itself and is used for etching and cleaning of apparatus. Its extreme reactivity and the accompanying energy release of the reaction can be sufficient to disrupt C–C bonds which may result in explosive reactions or fires [1,2]. ClF_3 offers the advantage that it can be stored as a liquid in steel cylinders at a relatively low pressure compared to fluorine.

Several techniques for the analyses of gaseous impurities in corrosive matrices have been used in the past [3–12]. None of these had the sensitivity

and selectivity required for this application. This paper describes a method using a pre-column to retain the ClF_3 matrix while allowing the gaseous impurities (O_2 and N_2) to pass through to an analytical column connected in series. The analytes are further separated by the analytical column and detected by thermal conductivity detection (TCD) while the residual matrix is backflushed to vent.

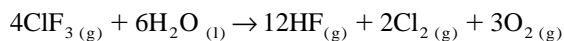
2. Experimental

A Varian 3400 gas chromatograph, equipped with a TCD system with nickel filaments was used. The industry required a total amount of O_2 and N_2 impurities of less than $288 \mu\text{g/l}$. While the same system may also be used for the determination of H_2 and CO , impurities such as CO_2 and SF_6 would

*Corresponding author.

require a dual channel system as described elsewhere [13]. The analytical requirements as well as the hazardous nature of ClF_3 necessitated the elimination of leaks from the system. All standard pneumatics of the gas chromatograph were bypassed and replaced with a custom-built inlet system. Pneumatic controls, needle valves, pressure and flow regulators are not fully leakproof and resistant to ClF_3 . All flow-rates were therefore regulated by in-line restrictors in the connecting tubing and where connections had to be made, gold plated ferrules were used for additional integrity.

Switching between calibration gas and samples can take several hours of sample purging before the previous gas mixture has been cleared from the lines connecting the cylinders to the GC inlet system. Loading a ClF_3 sample into a non-deactivated line will also result in the formation of excess oxygen originating from the reaction between adsorbed water inside the tubing and ClF_3 as it is readily hydrolysed [8].



An inlet manifold with a relatively large internal volume (6.4 mm tubing and six shut-off valves) was used initially. However, to reduce the deactivation time, a low-volume inlet manifold was constructed using 1.6 mm pre-cleaned tubing and two three-way valves. Deactivation takes place by loading the ClF_3 sample into the line a few times, evacuating the sample line after each sampling step to accelerate the deactivation. The sample inlet configuration appears in the lower left hand part of Fig. 1. This inlet configuration allowed the evacuation of the transfer lines up to the point where the sample or calibration gas was loaded into the sampling valve. Two 1.6 mm stainless steel Swagelok three-way valves were used to switch between the calibration and sample gases; and between the GC inlet or vent lines. No lubricant should be used on these valves as the ClF_3 will react with the lubricant and destroy the valve or block the tubing. A cold trap scrubber filled with liquid nitrogen was installed before the vacuum pump in order to prevent the pump from being damaged by the corrosive matrix. Furthermore ClF_3 cannot simply be vented to atmosphere due to its reactivity and toxicity to humans.

PTFE or nickel tubing has been used for the column material [9] but nickel had to be used because PTFE tubing would allow permeation of atmospheric gases into the chromatographic system causing false positive results. Nickel oxide on the inner tube walls is converted to inert nickel fluoride by the gas between 25°C and 180°C [14].



The choice of the stationary phase is limited by the high reactivity of ClF_3 . PTFE and Kel-F supports, coated with Kel-F oils [$(\text{C}_2\text{ClF}_3)_n$], were sufficiently inert and reversible in their behaviour to be used as packing materials [12,14–16]. This column lacks the selectivity to separate O_2 and N_2 at or above ambient temperature. Typically molecular sieve stationary phases are used to analyse permanent gas impurities but these cannot withstand the ClF_3 . Every injection will form AlF_3 , AlCl_3 and SiF_4 , etc., degrading the column.

A pre-column in combination with a backflush-to-vent valve switching technique was used (Fig. 1). A chemically resistant pressure transmitter with electronic readout was used to insure that the sample loop was filled to a reproducible pressure during both sample and calibration analysis. The matrix is prevented from reaching 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. A 4.5 m × 3.2 mm nickel column packed with Chromosorb T (250–500 μm) coated with 10% Kel-F oil was used as a pre-column and a 3 m × 3.2 mm nickel column packed with molecular sieve 13X (150–180 μm) was used as an analytical column. Both columns were obtained from Chemlab, South Africa. Since the volume of the pre-column is at least 10-times the sample loop volume, extra care must be taken to insure that carrier and backflushing gases are free of O_2 and N_2 .

A four-port valve was installed before the 10-port valve to allow constant purging of the sample loop with pure helium. This prevents high concentrations of the matrix gas from causing a memory effect on the 10-port valve as it was exposed to the matrix for only about 1 min per analysis. The soft seat rotary valves, manufactured from Hastalloy C22, certified

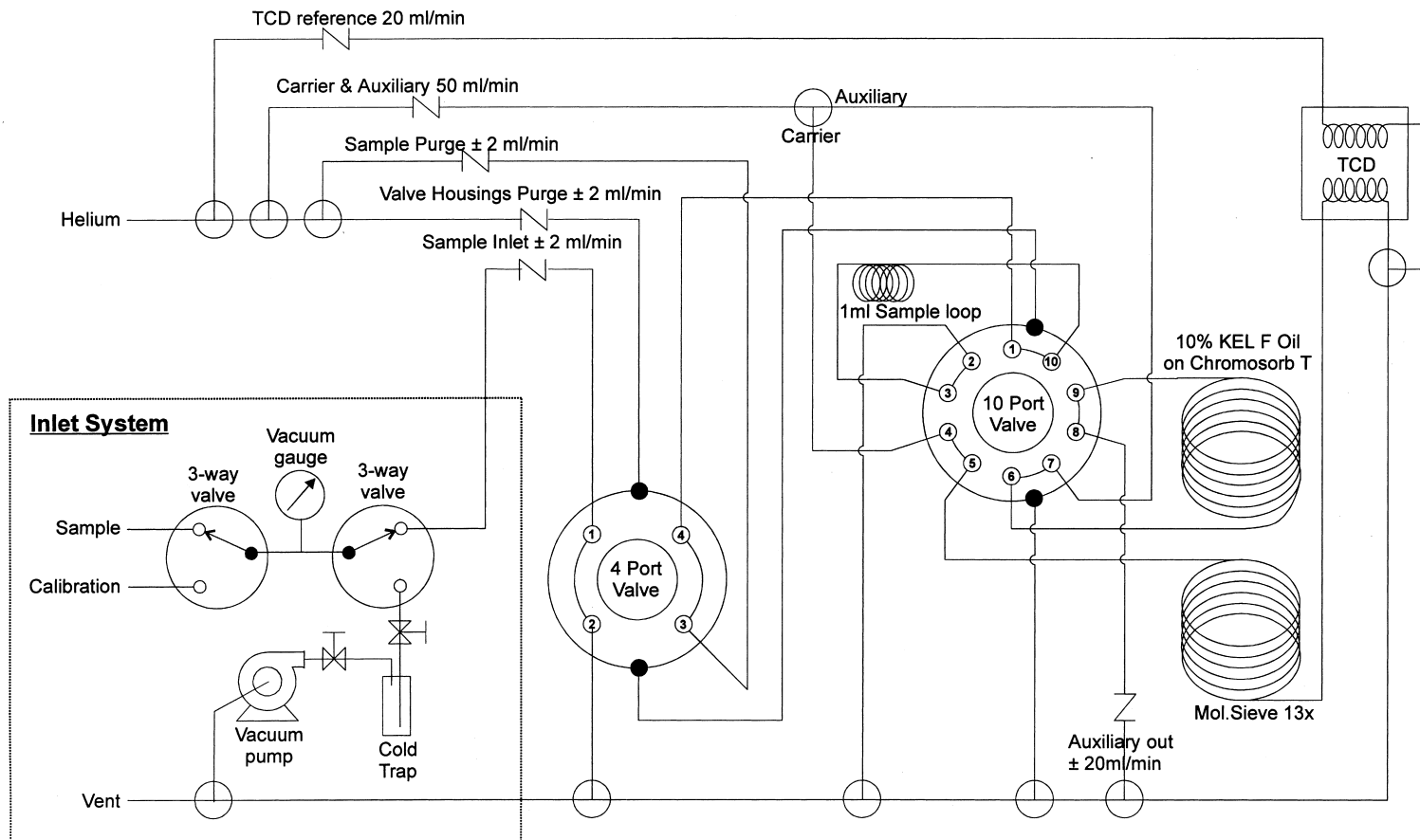


Fig. 1. A schematic diagram of the plumbing, valve and column configuration for the analysis of ClF_3 . The flow-rates indicated are approximate.

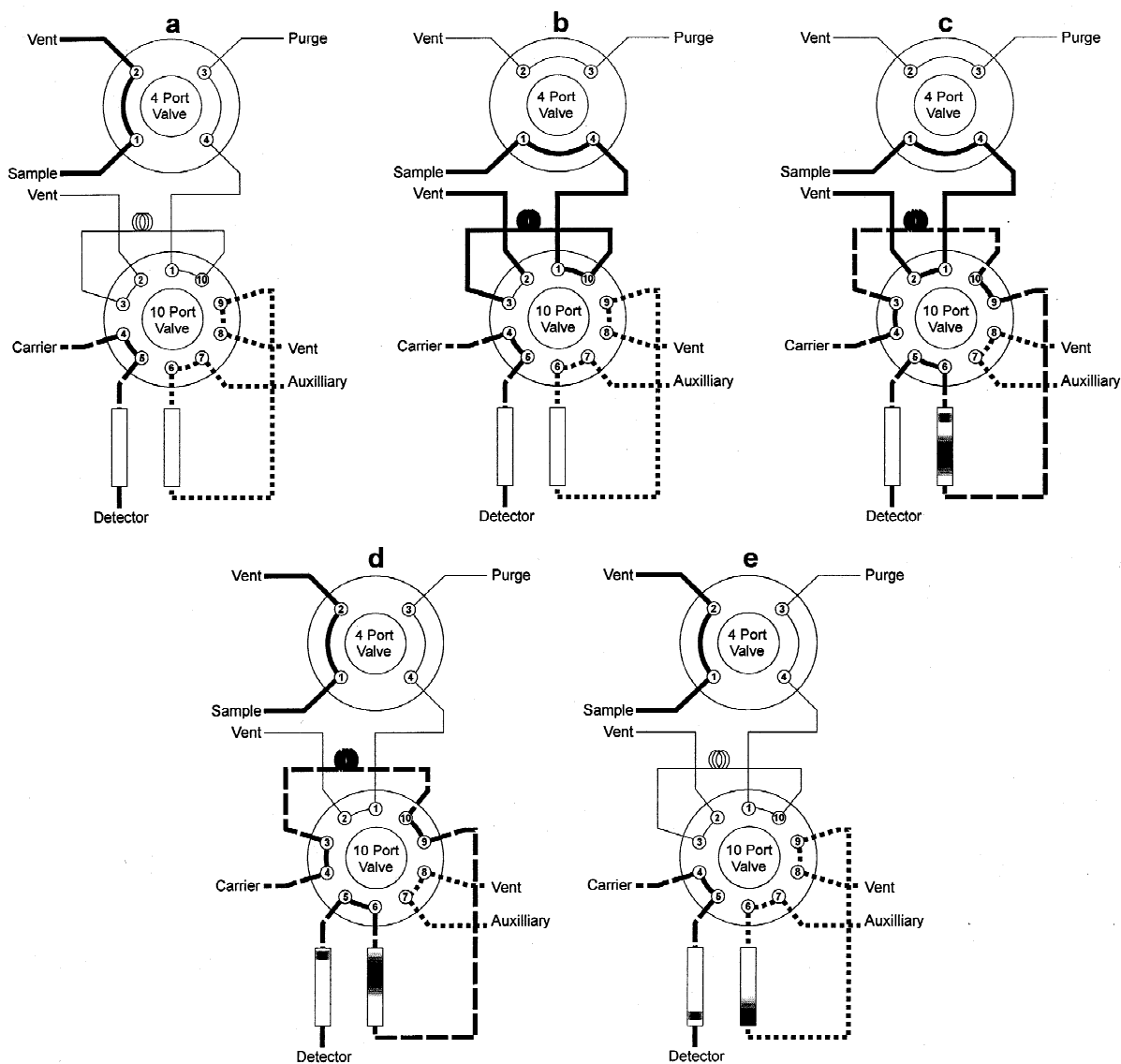


Fig. 2. (a) In the default position the sample flows through the four-port valve at a flow of approximately 2 ml/min to vent. The other side of the four-port valve is connected to the sample loop and is continuously purged with high-purity helium. Helium carrier gas flows through both columns, the pre-column being purged in the reverse direction by the auxiliary gas (high-purity helium) and the analytical column by the carrier gas (also high-purity helium). (b) At the beginning of the analysis the four-port valve switches allowing the sample loop to be filled with sample for at least 1 min to ensure that the loop volume is displaced at least two times. The 10-port valve stays in the same position as before. (c) The 10-port valve switches and the sample is introduced into the flow path. The sample flow is now directed to vent but almost immediately after the switching of the 10-port valve, the four-port valve switches back to its original position. See (d). The auxiliary flow is also directed to the vent line while the carrier gas flow through the sample loop, carrying the sample into the pre-column where the analytes are separated from the ClF_3 matrix. (d) With the four-port valve back in the original position the 10-port valve stays in the switched position. The two columns are now connected in series allowing the analytes to pass through the pre-column and the 10-port valve onto the analytical column while the matrix is retained by the pre-column. (e) As soon as all the analytes have passed through the 10-port valve it is switched back to the default position, disconnecting the columns and preventing the corrosive matrix to come into contact with the stationary phase of the analytical column. The carrier gas now proceeds to move the analytes through the analytical column, where they are separated and onto the detector for detection. The auxiliary gas reverses the flow through the pre-column backflushing the matrix to vent.

by mass spectrometry, had air-operated automatic actuators and helium purged housings (VICI, Switzerland).

The switching time of the 10-port valve is critical to the success of this analysis. The elution times of the matrix and the analytes on the pre-column were determined by installing the TCD system temporarily between the pre- and analytical columns. Once the switching times were established the TCD system was connected to the end of the analytical column [17]. The column switching sequence is shown in Fig. 2. Since TCD is flow sensitive, it required careful balancing of the flow-rates through the columns to prevent steps in the baseline whenever column switching occurs. This was achieved by restrictors in the vent lines.

A static, certified gas standard containing 51 $\mu\text{g}/\text{l}$

O_2 and 69 $\mu\text{g}/\text{l}$ N_2 in helium was obtained from BOC Afrox, South Africa and was used for setting up and calibrating the system. Data processing was done with a Spectra-Physics SP4290 integrator.

3. Results and discussion

Fig. 3 illustrates the deactivation with ClF_3 of the two inlet systems used. The oxygen concentration decreased with consecutive runs and finally reached a plateau after 12 injections on the large volume inlet manifold while the low volume inlet manifold required no more than four injections. Following deactivation the system remained stable for up to 8 h.

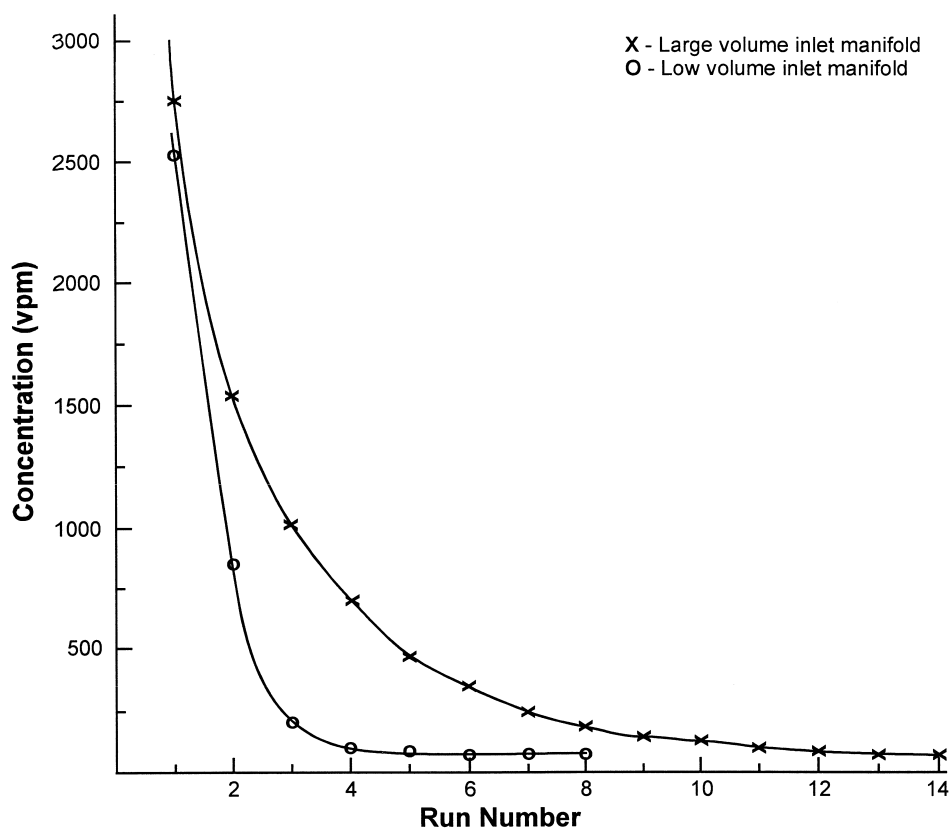


Fig. 3. The deactivation of the inlet systems by ClF_3 . The oxygen reached a plateau after 10 or more injections, using the large volume inlet manifold, while the nitrogen remained constant. By contrast the low volume inlet manifold required no more than four injections for deactivation.

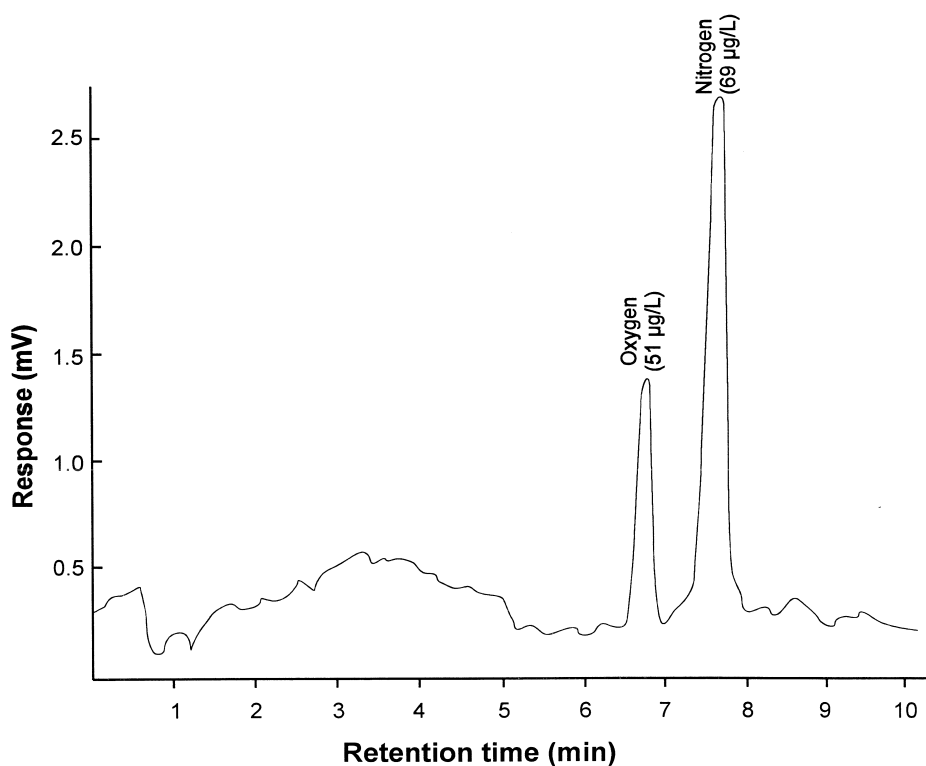


Fig. 4. Chromatograms using the certified calibration gas mixture. Column temperature, 40°C; carrier gas, helium at a flow of 20 ml/min. TCD at 200°C, range 0.05, attenuation 4, with helium reference flow of 20 ml/min.

Fig. 4 shows the chromatogram of the calibration gas mixture.

A typical result is shown in Fig. 5. The sum of the O₂ and N₂ concentrations in ClF₃ for five replicate injections (mean 94 µg/l) gave a relative standard deviation of 4.9%.

For gaseous impurity levels lower than the capabilities of TCD, pulsed discharge helium ionisation detection (PDHID) may be employed with relative ease and success [13]. The use of PDHID was evaluated for the determination of ppm levels, but was not extensively used as it far exceeded the analytical requirements that had to be met.

4. Conclusion

A gas chromatographic system able to analyse trace impurities in the highly corrosive and aggressive matrix of ClF₃, was assembled making use of a

backflush-to-vent column-switching technique. Special precautions had to be taken to clean the carrier gas and avoid leaks from the atmosphere into the chromatographic system and vice versa. In order to produce reliable and reproducible results, deactivation of the chromatographic system before analysis is extremely important.

The achieved sensitivity and reproducibility makes the system suitable for the determination of trace amounts of O₂ and N₂ in ClF₃.

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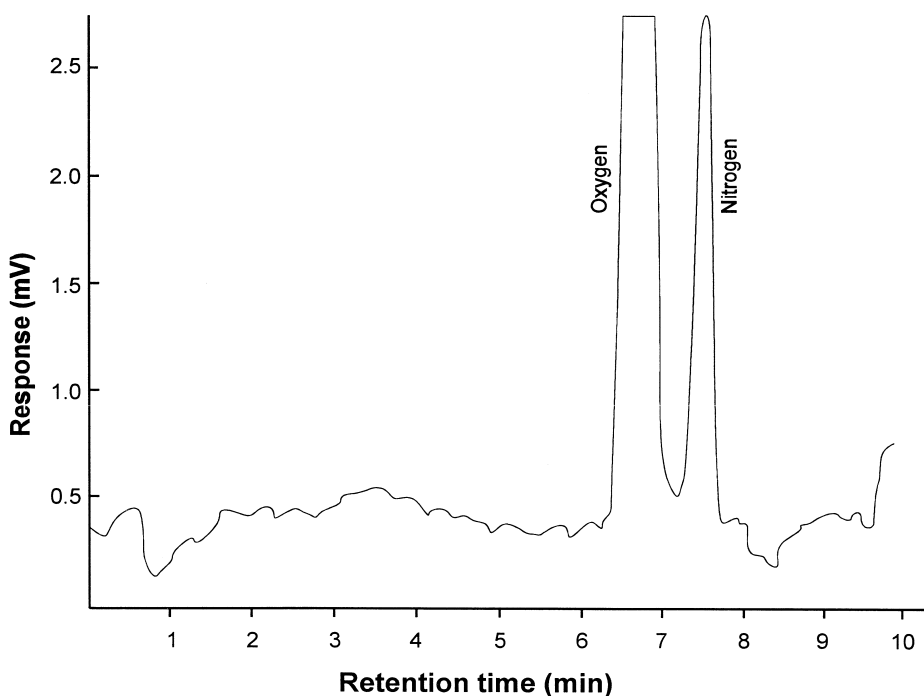


Fig. 5. Chromatograms of the gaseous impurities in ClF_3 .

in their laboratories and their permission to publish these results is kindly acknowledged.

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