



Impact of Air Leaks on the Productivity of GC and GC/MS Systems

Application Note

Environmental

Author

Ken Lynam
Agilent Technologies, Inc.

Abstract

Agilent 7890A GC dual-channel FID, Agilent 7890B GC, and Agilent 5977A Series GC/MSD System carrier lines fitted with three-way valves attached to a pure helium line and a 1,000 $\mu\text{L/L}$ oxygen-doped helium cylinder were used to simulate systems with air leaks. Column bleed, retention time drift, endrin/DDT breakdown, background noise, and electron multiplier voltages were monitored with and without oxygen in the carrier gas. Detrimental effects of oxygen in the carrier gas were observed almost immediately and persisted on both systems. Electron multiplier voltage climbed to 2,350 volts and the filament ruptured after 15 days of cumulative exposure to oxygen doped in the helium carrier.

Introduction

In gas chromatography, air leaks can cause a cascading series of deleterious effects on system components and chromatographic results. Establishing and maintaining leak-free connections in GC systems is a basic yet critical aspect of gas-phase analysis. Leak-free systems provide consistent, reliable data and can improve productivity by increasing intervals between required maintenance.

At elevated temperatures, generally higher than 260 °C, polysiloxane-based GC columns bleed and lose stationary phase, depending on the substituent group linked to the polymer [1]. In the presence of oxygen, bleed increases dramatically at elevated temperature [2,3]. Increased column bleed in turn leads to a shift to shorter retention for peaks of interest and an early demise of the GC column.



Agilent Technologies

Liner activity is also impacted by the presence of oxygen in the flow path. Oxygen can strip deactivation layers from glass liners, leaving more active sites onto which polar analytes can sorb. This leads to increased tailing, poor peak integration, and inaccurate results. The need for more frequent inlet maintenance, along with system downtime, is a direct consequence of leaks, especially for analyses of active analytes, such as chlorinated pesticides.

In GC/MS, air leaks in the flow path produce high levels of noise, increased bleed, shorter filament lifetime, more frequent source cleaning, and reduced electron multiplier life times. Cumulative effects of oxygen-contaminated carrier are illustrated in this application note to underscore the need to establish and maintain leak-free systems to the fullest extent possible.

Materials and Methods

System 1 consisted of a dual-channel FID Agilent 7890A GC equipped with a dual-tower Agilent 7693 Automatic Liquid Sampler and two inert split/splitless inlets. An inline three-way valve was installed in the carrier line leading to the rear inlet. One leg of the valve was plumbed to a pure helium (99.9999%) source, and the other was plumbed to a helium cylinder containing 1,000 µL/L oxygen. This installation enabled switching back and forth between pure helium and helium doped with oxygen to evaluate how lasting any effects might be. The front inlet was plumbed to the same pure helium source as the pure helium leg of the three-way valve on the rear inlet. Inlet maintenance and testing sequences were run simultaneously to ensure as close to a one-to-one comparison as possible.

System 2 consisted of an Agilent 7890B GC and an Agilent 5977A Series GC/MSD System equipped with a single-tower 7693 Automatic Liquid Sampler and an inert split/splitless inlet. An inline three-way valve was installed in the carrier line leading to the front inlet. One leg of the valve was plumbed to a pure helium source and the other was plumbed to a helium cylinder containing 1,000 µL/L oxygen. This installation enabled switching back and forth between pure helium and helium doped with oxygen to evaluate how lasting the effects might be.

FID conditions

Column:	Agilent J&W DB-1701, 20 m × 0.18 mm, 0.18 µm (p/n 121-0722)
Carrier:	Helium (front) versus 1,000 µL/L O ₂ in helium (rear), constant flow 1.36 mL/min at 125 °C
Oven:	125 °C (0.34 min) to 275 °C (7.3 °C/min, 10.1 min hold)
Inlet:	Pulsed splitless, 45 psi 0.32 min, 1 µL at 250 °C, total flow 54.4 mL/min, 3 mL/min switched septum purge, gas saver off, 50 mL/min purge flow after 0.33 min
Sample:	CLP pesticide mix 4 µg/mL or endrin/DDT 20 µg/mL
Inlet liner:	Ultra Inert splitless single taper with wool (p/n 5190-2293)
Dual FIDs:	300 °C at 40 mL/min H ₂ , 400 mL/min air, He constant collision and makeup 31 mL/min

GC/MS with Agilent J&W DB-1701 conditions

Column:	Agilent J&W DB-1701, 20 m × 0.18 mm, 0.18 µm (p/n 121-0722)
Carrier:	Helium versus 1,000 µL/L O ₂ in helium, constant flow 1.36 mL/min at 125 °C
Oven:	125 °C (0.34 min) to 275 °C (7.3 °C/min, 10.1 min hold)
Inlet:	Pulsed splitless, 45 psi 0.32 min, 0.5 µL at 250 °C, total flow 63.9 mL/min, 3 mL/min switched septum purge, gas saver off, 60 mL/min purge flow after 0.33 min
Sample:	CLP pesticide mix 4 µg/mL or endrin/DDT 20 µg/mL or semivolatiles mx
Inlet liner:	Ultra Inert splitless single taper with wool (p/n 5190-2293)
MSD temps:	Transfer line 280 °C, source 300 °C, quad 180 °C
Mode:	Full scan, 10 to 450 amu

GC/MS with Agilent J&W DB-5ms Ultra Inert conditions

Column:	Agilent J&W DB-5ms UI, 20 m × 0.18 mm, 0.36 µm (p/n 121-5523UI)
Carrier:	Helium versus 1,000 µL/L O ₂ in helium, constant flow 1.58 mL/min at 40 °C
Oven:	40 °C (2.5 min) to 330 °C (25 °C/min, 10.9 min hold)
Inlet:	Pulsed splitless, 45 psi 1.4 min, 0.5 µL at 300 °C, total flow 64.6 mL/min, 3 mL/min switched septum purge, gas saver off, 60 mL/min purge flow after 1.42 min
Sample:	CLP pesticide mix 4 µg/mL or endrin/DDT 20 µg/mL or semivolatiles mix
Inlet liner:	Ultra Inert splitless single taper with wool (p/n 5190-2293)
MSD temps:	Transfer line 325 °C, source 300 °C, quad 180 °C
Mode:	Full scan, 10 to 550 amu

Additional supplies

Vials:	Amber silanized screw top (p/n 5183-0716, 100/pk)
Vial caps:	Green screw (p/n 5185-5861, 500/pk)
Vial inserts:	Glass/polymer feet, 250 µL (p/n 5181-8872)
Septum:	Advanced Green (p/n 5183-4759)
Seals:	Ultra Inert Gold Seal with washer (p/n 5190-6145, 10/pk)
Ferrules:	Short, 0.4 mm, conditioned polyimide/graphite (p/n 5062-3508, 10/pk)
Magnifier:	20x Magnifier loop (p/n 430-1020)
Standard:	GC/MS semivolatiles analyzer check-out mix (p/n 5190-9473)
Syringes:	Blue line, 10 µL, PTFE tip plunger (p/n G4513-80220)

Sample preparation

The CLP organochlorine pesticide mix in toluene:hexane (0.2 mg/mL) was purchased from Supelco (Bellefonte PA, USA). The solution was serially diluted in Ultra Resi Grade IsoOctane (VWR, USA) to a working standard concentration of 4 µg/mL. This solution was used first for FID and later on for mass spectral experiments.

4,4' DDT and endrin inlet challenge solution in hexane (0.2 mg/mL) was obtained from AccuStandard (New Haven, CT, USA). The challenge solution was diluted in Ultra Resi Grade IsoOctane to a working standard concentration of 20 µg/mL. As before, this solution was used first for FID and subsequently for mass spectral experiments.

The semivolatile check-out mix in CH₂Cl₂ (10 µg/mL) was purchased through Agilent (Santa Clara, CA, USA). This mix was diluted 1:10 in Ultra Resi Grade IsoOctane to a working concentration of 1 µg/mL, and was used exclusively for mass spectral experiments.

Results and Discussion

GC/FID

A 7890A GC dual-channel FID, a 7890B GC, and a 5977 Series GC/MSD system were set up with a three-way valve in the carrier line to enable switching between pure helium, and helium doped with 1,000 µL/L oxygen to simulate an air leak. Oxygen in helium at 1,000 µL/L is representative of a 5% by volume air leak into each respective system. This approach was chosen to rapidly demonstrate the deleterious effects of having oxygen in the carrier gas.

Organochlorine pesticides included in US EPA 8081 [4] were chosen as a test case for the dual-GC-FID system. DB-1701 columns (14% (cyanopropyl-phenyl) methylpolysiloxane phase) were used to demonstrate the effects of having oxygen in the carrier, with respect to endrin/DDT breakdown, bleed profiles, and retention time stability.

Figure 1 shows a typical FID trace for US EPA 8081 pesticides on a 20 m × 0.18 mm, 0.18 µm Agilent J&W DB-1701 column. The nominal concentration of the pesticide mix in this chromatogram was 4 µg/mL.

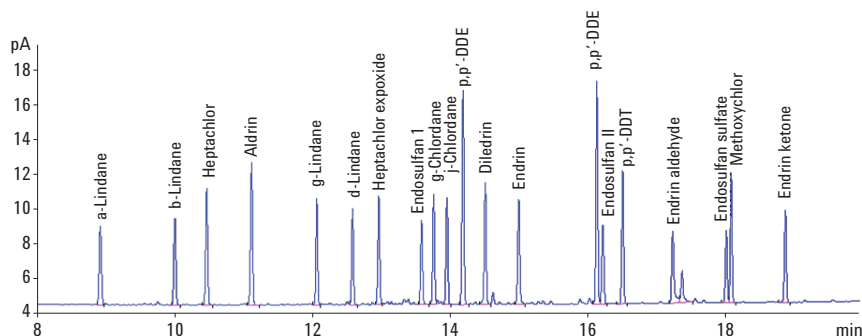


Figure 1. FID chromatogram of US EPA 8081 pesticides.

Almost immediately, oxygen in the carrier gas was observed to have a subtle impact on the column bleed performance with temperature cycling on the DB-1701 stationary phase. There was an increase in bleed on the oxygen-exposed column as the oven temperature climbed to 275 °C. The effect persisted, even after purging with pure helium carrier, indicating permanent column damage. Figure 2 is an overlay of blank injection FID chromatograms with and without oxygen in the carrier.

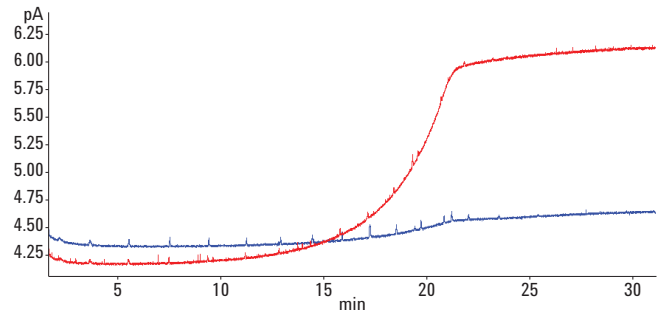


Figure 2. FID blank injection trace with (red trace) and without (blue trace) oxygen exposure.

The endrin/DDT challenge solution was prepared at a concentration of 20 µg/mL to obtain degradation products by FID. A series of 30 challenge injections was made on freshly serviced inlets with new liners. The front inlet was attached to a pure helium source, and the rear inlet was attached to an oxygen-doped helium cylinder. Figure 3 is an overlay of the 30th endrin/DDT injections using pure helium carrier versus the oxygen-doped carrier. According to US EPA 8081, inlet servicing is required when endrin/DDT breakdown reaches 20%. After only 30 challenge injections, endrin breakdown using the oxygen-doped carrier gas reached 39.8% while the channel plumbed with pure helium was still operating in the acceptable range, with endrin breakdown at 16.8%.

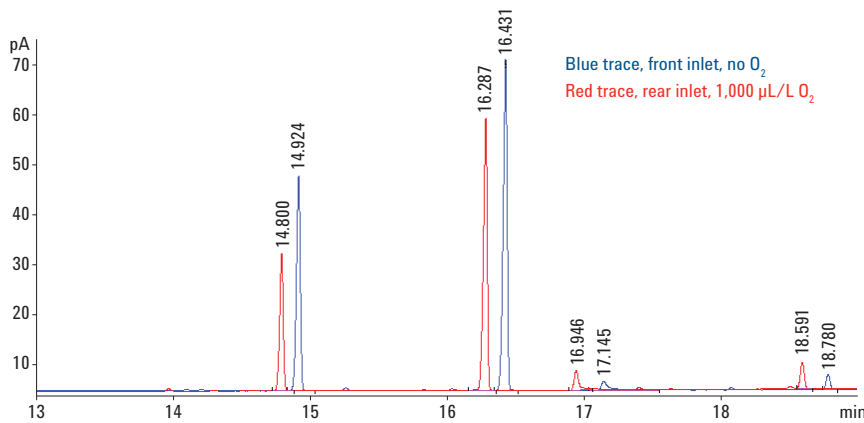


Figure 3. FID chromatogram of endrin/DDT breakdown, after 30 challenge injections with (red trace) and without (blue trace) oxygen in the carrier gas.

GC/MS

a 7890B GC with a 5977 Series GC/MSD system was set up with a three-way valve in the carrier line to enable switching between pure helium, and 1,000 $\mu\text{L/L}$ oxygen-doped helium to simulate an air leak. The three-way valve was switched back and forth between the oxygen-doped and pure helium carrier gas. At first, the oxygen-doped carrier was inline only during acquisition sequences. Gradually, exposure to oxygen-doped carrier gas was increased to overnight, then weekends, and finally for five days continuously until auto tune no longer functioned. The cumulative total of oxygen exposure for the GC/MS was 15 days before the system would no longer tune. The highest EMV (electron multiplier voltage) obtained was 2,350 volts, at which time source cleaning and filament

replacement were required to return the instrument to normal function with pure helium. Figure 4 shows the increase in EMV over the time of these experiments.

GC/MS testing on a DB-1701 column gave similar results to those seen by GC-FID for the endrin/DDT challenge solution at 20 $\mu\text{g/mL}$. On initial exposure to oxygen-doped carrier, an increase in bleed and a shift to shorter retention was seen, just as it had been by GC-FID. A significant increase in signal background, even at low temperature, was seen in the GC/MS signal on exposure to oxygen that was not evident in the FID signal. Figure 5A is an overlay of the 1st and 20th injections using pure helium, and Figure 5B is an overlay of the 1st and 20th injections on initial exposure to oxygen-doped helium.

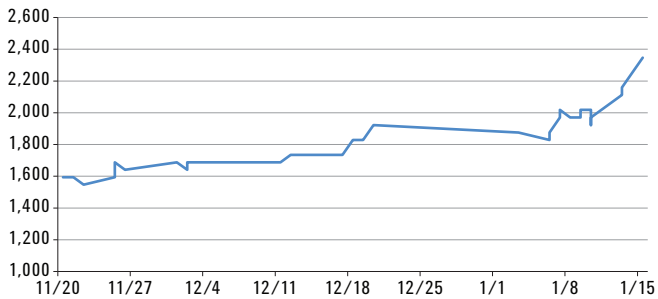


Figure 4. Electron multiplier voltage plot versus cumulative oxygen exposure.

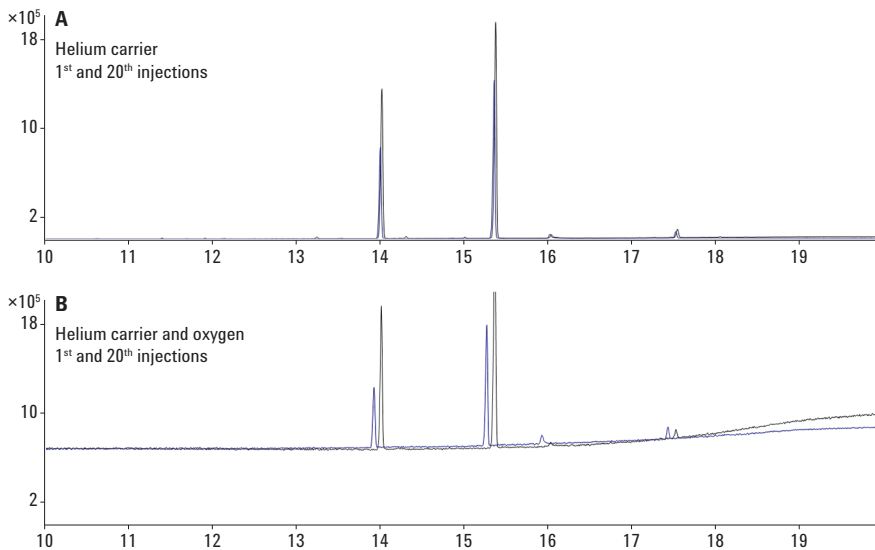


Figure 5A and 5B. First and 20th initial sequence injection total ion chromatograms with and without oxygen in the carrier. Note higher background, bleed and shorter retention in 5B.

GC/MS testing was conducted on a DB-5ms UI column with a 1 µg/mL GC/MS semivolatiles analyzer check-out mix. Here, the impact of oxygen in the carrier gas was readily apparent in that the high signal background all but wiped out the analyte signal. At a level of 1 µg/mL, this represents an alarming loss of sensitivity. Figure 6 is an overlay of the total ion chromatograms for an injection of 1 µg/mL GC/MS semivolatiles mix with oxygen in the carrier and without oxygen in the carrier.

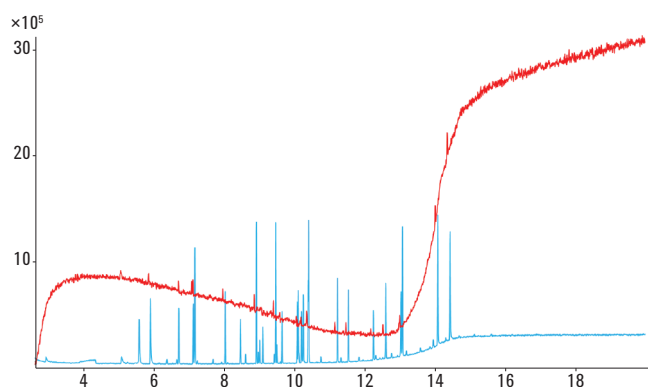


Figure 6. Total ion chromatogram overlay of 1 µg/mL semivolatiles mix with (red trace) and without (blue trace) oxygen in the carrier.

Conclusions

Air leaks into GC and GC/MS systems have a dramatic and cumulative effect on system performance. Permanent column damage, retention time drift to shorter retention, and increased inlet activity are characteristic of oxygen exposure at elevated temperature in both GC and GC/MS systems. All of these effects were observed. Dramatic signal loss, high background noise and rapid increase in electron multiplier voltage were seen on the GC/MS system.

The conditions used in these experiments were chosen to simulate an air leak of approximately 5% air into the system, and to rapidly visualize the deleterious effects. Both GC column and liner lifetimes were shortened, requiring more frequent maintenance. Under these conditions, after 15 days of cumulative exposure to oxygen, electron multiplier voltage climbed to 2,350 volts and the filament failed, dictating a

major service event in just over two weeks. Having to clean the source and replace a filament twice a month would most certainly have a dramatic impact on system productivity. All of these deleterious effects build a strong case for doing everything possible to keep air and the oxygen it contains out of GC and GC/MS systems.

References

1. P.R. Dvornic "High Temperature Stability of Polysiloxanes" pp. 419-431, Gelest Catalog 3000-A. Gelest, Inc. Morrisville, PA, USA (2004).
2. A.A. Reese, A.K. Vickers, C.George "GC Column Bleed: a MASS PerSPECTive" Agilent Technologies, Inc. Publication number B-0442 (2001).
3. Anon. What are the major causes of GC capillary column performance degradation? Internal publication, Agilent Technologies, Inc. (2007).
4. Anon. Method 8081B. United States Environmental Protection Agency, Washington, DC, USA (2007).

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc., 2014
Printed in the USA
February 27, 2014
5991-4110EN



Agilent Technologies