ELIMINATION OF CONTAMINATING LEAKS AT INTERFACES IN GC AND GC-MS SYSTEMS

P. Wynne, R. Western, P. Dawes — SGE International Pty. Ltd. 7 Argent Place, Ringwood 3134, Australia.
Dan DiFeo Jr. — SGE, Incorporated. 2007 Kramer Lane, Austin, Texas 78758, USA.

INTRODUCTION

The connections between a GC column injector and detector are points at which leaks can develop. Mass spectrometers are particularly prone to air leaks that can also draw contaminants from the atmosphere into the instrument. While all unions are potential leak points, the most problematic is the seal at the transfer line interface of the mass spectrometer.

When conventional Vespel® / graphite ferrules are mated with stainless steel or brass components, the thermal coefficient of expansion of the ferrule is approximately ten times greater than the fittings. During thermal cycling, the ferrule is compressed against the sealing surfaces and the subsequent relaxation or 'creep' of the polyimide introduces leaks on cooling ***(Figure 1)***.

GC-MS systems must now be able to run without a specialist operator and it is therefore desirable that methods for achieving a stable seal between GC and MS require few intuitive skills.

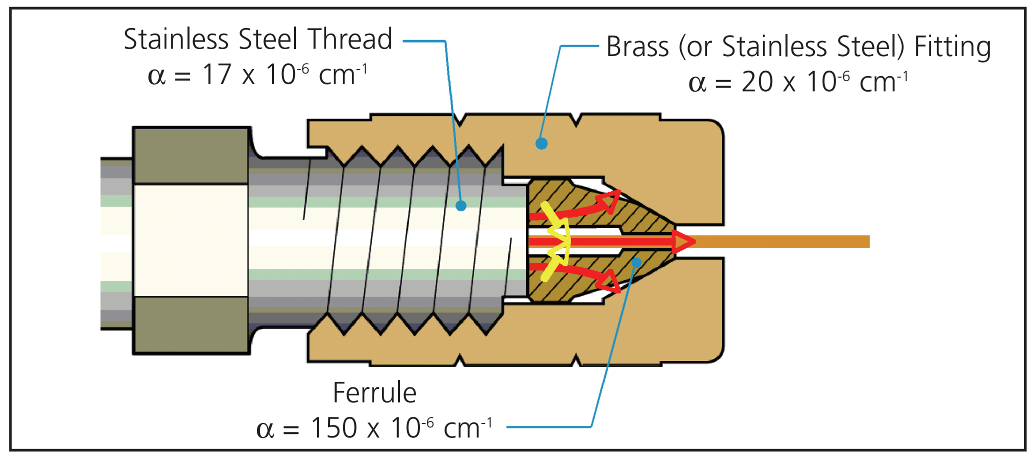

Figure 1. *Outward (red arrows) and inward creep (yellow arrows) of the Vespel ferrule due to the compression and relaxation during thermal cycling that results from the difference in the thermal coefficient of expansion (α) of materials.*

DISCUSSION

Changes in the MS ion-source pressure may be indicative of increased flow to the ion-source ***(Figure 2)***.

When the leak flow is much smaller than the column flow, the magnitude of the leak may be estimated from column flow using a nomogram (e.g. ***Figure 4***).

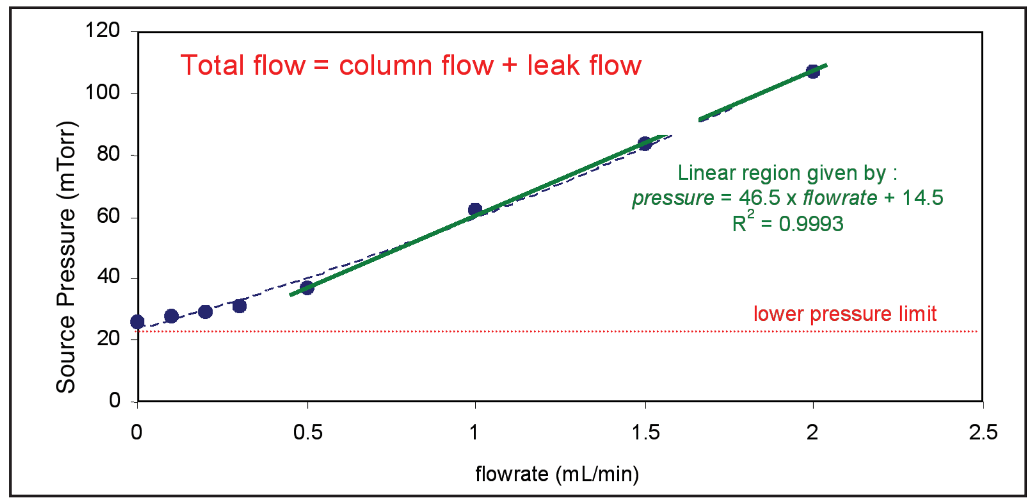

Figure 2. *The change in the mass spectrometer source pressure with flow rate of carrier gas (helium containing 1% v/v air) determined for an Agilent 6890 GC - 5973 MSD.*

From ***Figure 3b***, a typical air leak due to thermal cycling of the ferrule was gauged to be less than 0.02mL/min, which is equal to a pressure change of < 1mTorr (the limit of sensitivity for the vacuum gauge).

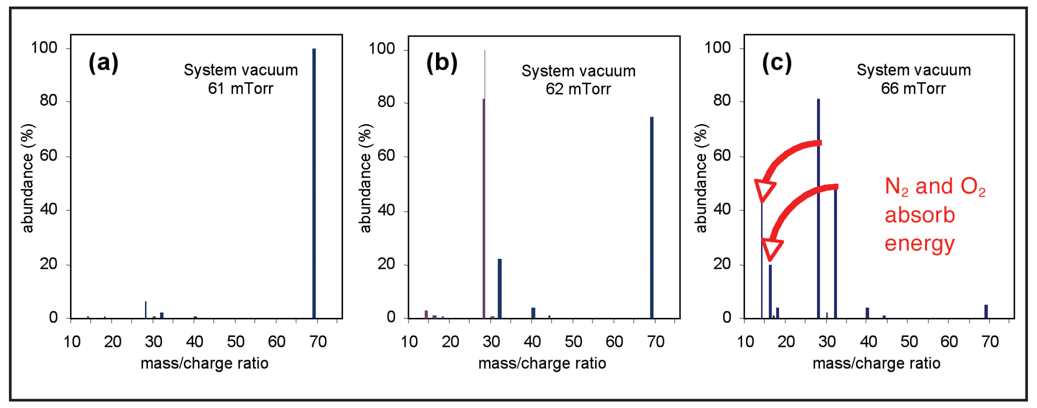

Figure 3. *The air and calibrant leak test for no-leak (a), ferrule deformation leak (b) and gross transfer line leak (c). The transfer line was fitted with a SilTite™ ferrule and nut in Figure 3a, Vespel/graphite ferrules in Figure 3b and 3c.*

Source pressure alone is not an adequate indicator of leaks. To overcome limitations in calculating flow rate changes from small changes in source pressure, determination of a nomogram that relates leak flow to the spectral abundance of air and calibrant is effective ***(Figure 4)***. In the example ***(Figure 3b)***, the leak is estimated to be less than 0.2% v/v of the total flow into the ion source for a column flow rate of 1mL/min.

An example of a gross leak through the GC-transfer line interface resulting from overtightening the ferrule is shown in ***Figure 3c***. The source pressure plot ***(Figure 1)*** shows the leak to be approximately 0.1mL/min or 10% v/v of the carrier gas flowrate.

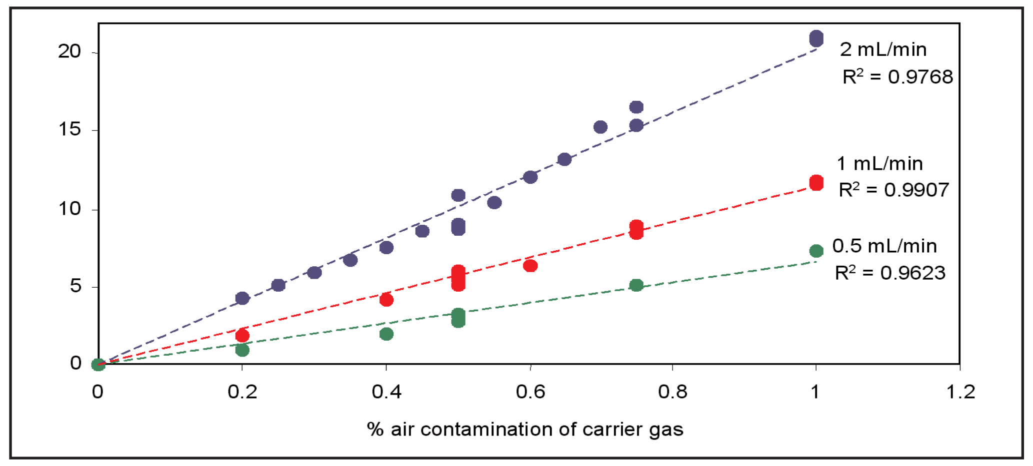

Figure 4. *A nomogram determined for an Agilent 6890 GC - 5973 MSD relating the change in the peak area ratio of nitrogen (m/z 28) to calibrant (m/z 69) with air contamination and flowrate of the carrier gas.*

Above a limiting flowrate, determined primarily by the pumping capacity of the instrument, the mass spectral responses of both the calibrant and the nitrogen are no longer linear with flowrate and are better estimated by fifth order polynomial functions ***(Figure 5 and 6)***. The effect is due to both buffering of high-energy electrons by the nitrogen and a concomitant decrease in the fragmentation of the calibrant. As a result, when a leak contributes more than a 1-2% of the flow into the ion-source, the nomogram approach to quantitative leak measurement becomes ineffective.

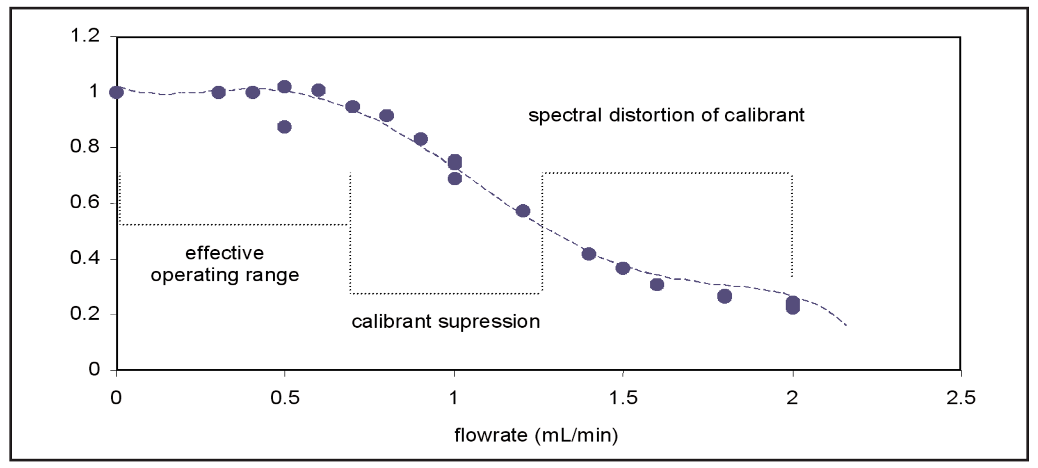

Figure 5. *The change in the normalized peak area of the calibrant gas (m/z 69) with flowrate of carrier gas (helium containing 1% v/v air).*

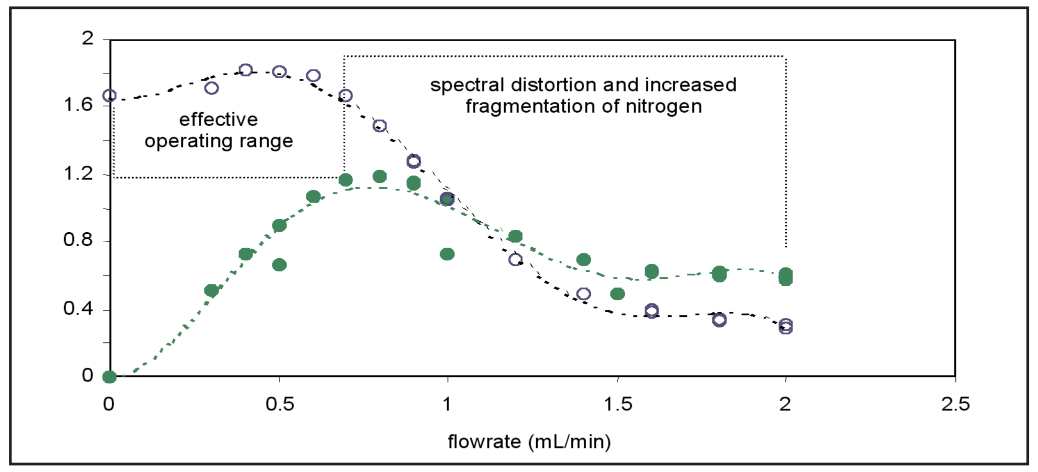

Figure 6. *The change in the normalized peak area (closed circles) and concentration corrected peak areas (open circles) of the nitrogen gas (m/z 28) with flowrate of carrier gas (helium containing 1% v/v air).*

A leaking transfer line interface does not impact on chromatographic performance as the leak is independent of the column flow but may lead to altered fragmentation or skewing of acquired spectra ***(Figure 7)***. This distortion of data is entirely consistent with buffering of the ion-source and loss of electron impact energy.

Effective closure of the interface between the GC column and MS transfer line is the most likely method of eliminating air leaks during routine operation. Preventing ferrule deformation due to thermal cycling is achievable by matching the thermal coefficient of expansion of the transfer line, interface nut and ferrule. SilTite™ ferrules and fittings, which are manufactured from stainless steel and therefore have the same coefficient of expansion as the mass spectrometer transfer line and GC injector interface, have proven to be effective at eliminating the leaks caused by relaxation of ferrules ***(Figure 3a*** compared with ***Figure 3b)***. Similar ferrule deformation on the injector interface may also be overcome by using SilTite ferrules and fittings.

Because SilTite ferrules do not compress or deform in the same way as Vespel ferrules, the torque required to achieve an effective seal is quantifiable rather than intuitive thereby reducing the incidence of over- or under-tightening interface fittings.

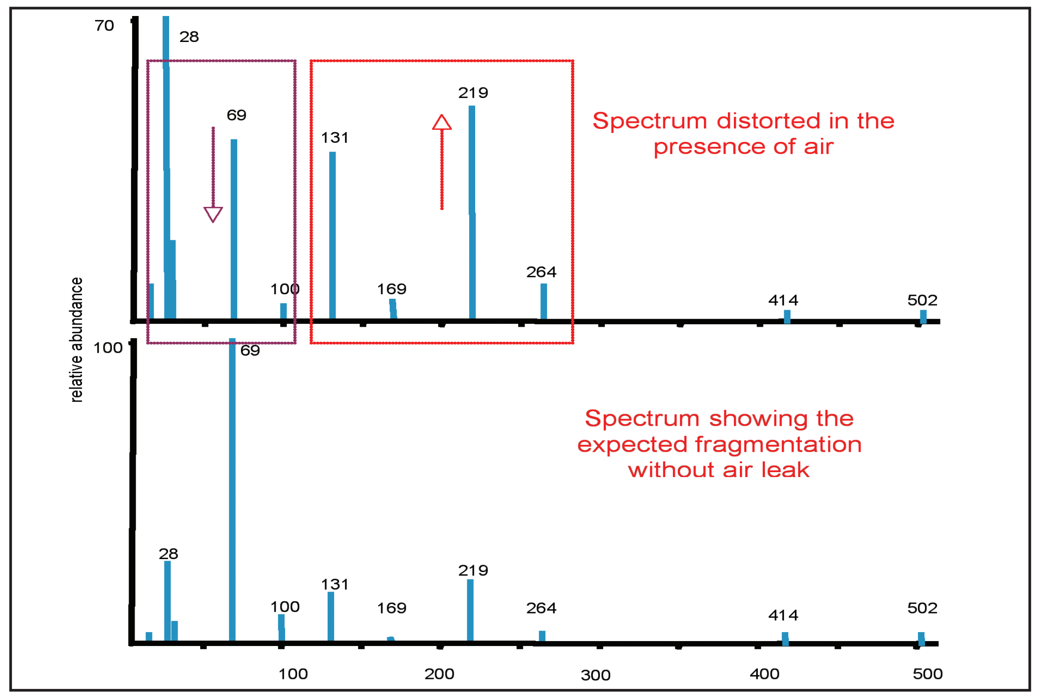

Figure 7. *Spectral distortion of perfluorotributylamine (calibrant) acquired in the presence of a significant air leak (top) compared with spectrum acquired under normal operating conditions (bottom).*

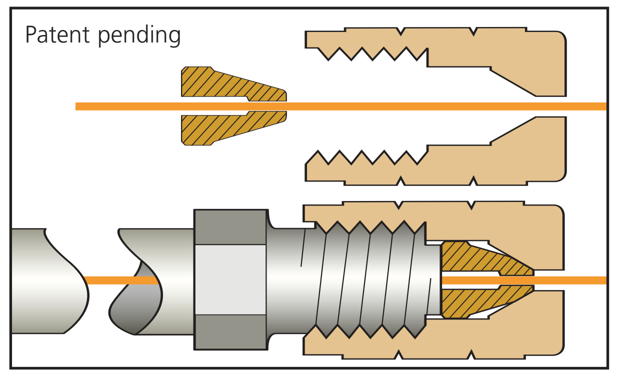

Figure 8. *The SilTite ferrule fits into the specifically designed SilTite nut. This allows a perfect seal every time with the MS interface.*

SEALING WITH SilTite METAL FERRULES

- A GC-MS can continue to operate in the presence of a transfer line leak
- The leak does not impact on chromatographic performance but can skew the mass fragmentation by absorbing electron impact energy
- Introduction of oxygen into the ion-source of the mass spectrometer can cause the high temperature oxidation of ion-source and ion-optic surfaces
- Oxidation of ion-optics can result in decreased instrument sensitivity
- Oxygen may reduce the operating lifetime of electron multipliers and filaments
- Effective closure of the interface between the GC column and MS transfer line reduces air leaks during routine operation
- SilTite ferrules and fittings have proven to be effective at eliminating transfer-line leaks
- SilTite ferrules and fittings are appropriate for novice users of mass spectrometers and do not require a special 'touch' to use

ETP electron multipliers

SGE

SGE, Incorporated
2007 Kramer Lane, Austin, Texas 78758, USA
Toll Free: (800) 945 6154 Tel: (512) 837 7190 Fax: (512) 836 9159
Email: usa@sge.com Web: www.sge.com

TP-0128-A