# Examining internal gas compositions of a variety of microcircuit package types & ages with a focus on sources of internal moisture

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## ABSTRACT

The primary cause of corrosion, stiction or other failure mechanisms within hermetically sealed enclosures has historically been viewed as due to increases in internal moisture concentrations. It has historically been postulated that the primary source of moisture in these enclosures is the failure to achieve hermeticity at seal, or the loss of hermeticity post-seal. This postulation is the basis for failure analysis and mitigation both in the appropriate standards like MIL-STD-883 and in industrial QA procedures. Empirical observation of many data sets over the past 20+ years shows that this postulation does not always hold up in practice. The purpose of the current work is to test this postulation through the analysis of archival microelectronic packages and data sets of various ages.

Internal gas composition data for three different sets of packages totaling 165 units is reviewed. Of these, 63 were noncompliant (>0.50v%) on internal moisture, but only 8 (12.7%) showed an internal gas composition "signature" consistent with air leaking into the enclosure. These data suggest that leaks play a minor role in gas composition change within enclosures and that outgassing from materials is the principal contributor to internal moisture concentrations and the failure modes they induce.

## Keywords

microelectronic packages, moisture, hermeticity, outgassing, leaks, permeation, corrosion, failure modes

## 1. INTRODUCTION

Moisture threatens reliability of devices in sealed enclosures by causing corrosion or electrical instability of microcircuits, fogging of optics, or stiction of moving parts in micro and nano machines. Materials outgassing and/or failure to achieve or maintain hermeticity elevates moisture in enclosures. Much attention has been focused on leaks due to lack of hermeticity as a principal cause of elevated moisture. A recent description of leak mechanisms[1] confirms that leak avoidance is critical for cavities sealed under vacuum, and depicts Fick's Law diffusion as the means of moisture ingress for enclosures with no pressure differential with the outside.

New capabilities for helium leak detection approaching $1x10^{-13}$ cc atm/sec have extended fine leak detection by more than four orders of magnitude.[2] These new capabilities have focused moisture control efforts on leak avoidance. However, little real data have been published differentiating between hermeticity loss and materials outgassing as root causes of elevated moisture. This paper reviews internal gas analysis data for 200 units of various types, providing insight into the prevalence of mechanisms leading to excessive moisture in device enclosures.

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An important benchmark for understanding what is really occurring within a hermetically sealed cavity is the composition of natural air as shown in Table 1.

Table 1. Chemical composition of natural air.

| Species | Content, v % | Comment |
|---|---|---|
| **Nitrogen** | 78.08 | Constant in natural air |
| **Oxygen** | 20.95 | Constant in natural air; $N_2/O_2$ ratio = 3.7 |
| **Argon** | 0.93 | Constant in natural air; $O_2$/Ar ratio = 22.5 |
| **Water** | 0.10 – 3.0+ | Variable, depends on temperature , humidity, pressure |
| **Carbon Dioxide** | 0.038 | Any amount in enclosures >≈0.04% is not from air |
| **Neon** | 0.0018 | Not from air if detected in enclosures |
| **Helium** | 0.0005 | Not from air if detected in enclosures |
| **Methane** | 0.0002 | Not from air if detected in enclosures |
| **Hydrogen** | 0.00005 | Not from air if detected in enclosures |

If air has leaked into an enclosure sealed in pure inert gas(es) not containing Ar, the internal gas content should show the $O_2$ and Ar components of air in roughly their natural ratio. Absolute concentrations will be less than those in ambient air (i.e. "diluted") if the leak has not yet caused the enclosure cavity to reach equilibrium with outside air. Moisture content will vary depending on temperature and humidity of ingressed air and whether materials outgassing has contributed to moisture levels within the cavity. Carbon dioxide in an enclosure exceeding roughly 0.04v%[3] is not from air and clearly indicates outgassing, as does the presence of any volatile organic compounds. Helium (if originally present) retained in any unit would argue against a significant leak mechanism.

### 1.1 Impacts of Ambient Temperature and Relative Humidity on Internal Moisture Concentration

Figure 1. Maximum water vapor content within a cavity due to air leaks of 25%. 50% and 75% relative humidity (RH).

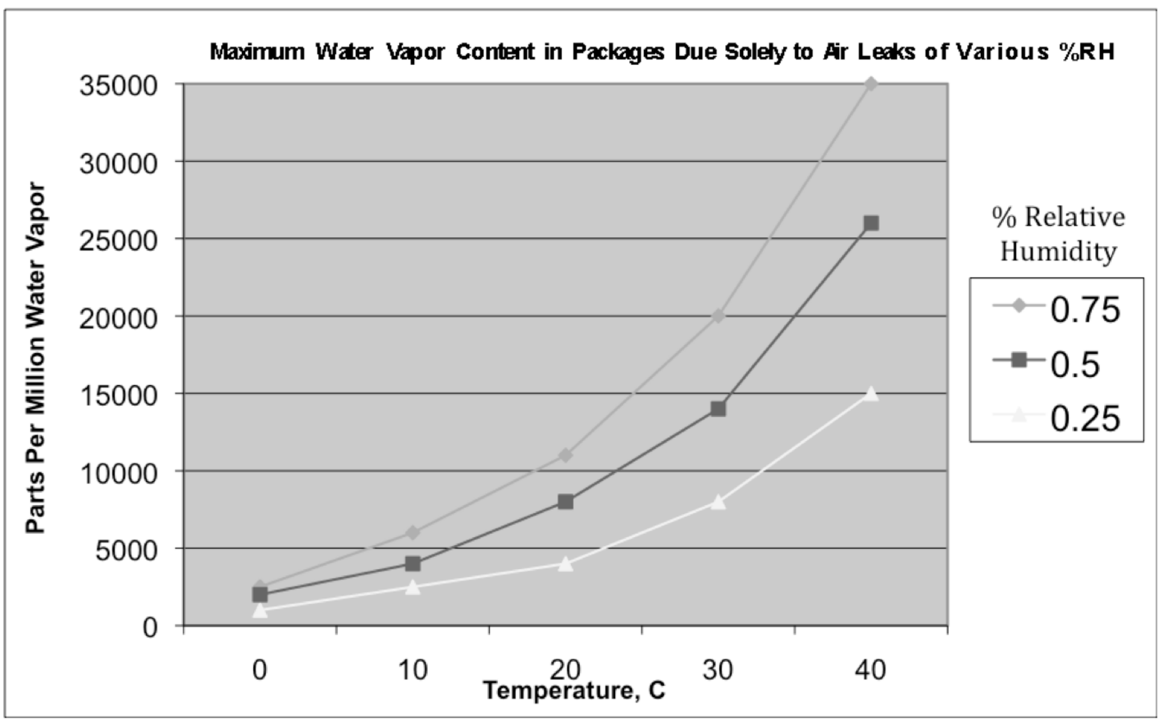


Figure 1 shows the maximum internal water vapor concentration at equilibrium within a cavity open to the external atmosphere via a leak. At cool temperatures and "nominal" levels of RH, a package will never become non-compliant to specification, or reach dangerous levels of water vapor, simply by leaking. It must be cautioned that:

a) under those temperature conditions, any significant outgassed water vapor may push the cavity into dew point or fogging conditions. While this is not good, it is a materials control problem, not a leak problem.

b) this point may be incorrect for stiction issues. Micromechanical devices can be sensitive to stiction at much lower levels of relative humidity.

At higher levels of temperature and RH, easily reachable in service conditions, packages can leak to non-compliant and/or dangerous levels of moisture. However, prior work on leak modalities into cavities where the cavity pressure is equal to that of the external ambient indicates that systems under these conditions should be modeled using Fickian diffusion.

Pre-existing internal concentrations of water vapor at time zero, or increasing concentrations of water vapor within the cavity due to outgassing during the package's lifetime, (either or both caused by poor materials selection and process control) take a package to dangerous conditions sooner. As a result, there is less margin of safety if non-hermeticity is present or develops.

The key point is that it is quite possible to engineer and control materials and processes (M&P) to achieve dry packages at time zero, so as to create the most protection for the package. It is much harder to engineer and control M&P to be as certain of leak prevention, as it is to be certain of dry initial conditions. Consequently, leak rates and associated testing ought to be the secondary line of defense against moisture problems, while the primary line of defense ought to be M&P selection and process control. This contention is supported by the results of the current work.

## 2. SAMPLES & ANALYSIS

Three different groups of internal gas analysis data and samples were reviewed. The data were generated via test methods in MIL-STD-883, Test Method 1018.

### 2.1 Sample Groups/Data

Sample Group 1

This group contained 15 microcircuit packages built 10-20 years ago by Harris Semiconductor (now Intersil Corporation). The units were never placed in service and were stored for their entire lifetime in a plastic bag in a desk drawer. Eight were TO metal cans, having a nickel lid seam welded to a gold-plated header with eight pins entering through glass-to-metal seals. Seven were gold-plated Kovar flatpacks or DIPs of various sizes and lead counts with braze sealed lids. Most units had cavity volumes ≤0.1cc. The units were analyzed by Oneida Research Services in June 2008 per Test Method 1018. The analytical focus for this group was to determine if the concentration of internal moisture was elevated after long storage lifetimes by poor hermeticity (leaks) or by materials outgassing within the cavity.

Sample Group 2

This group contained 71 units from a Test Method 5011[4] qualification study of polymeric adhesives.[5] Study of this group evaluated adhesive suitability, so moisture from material outgassing would likely be present. The focus was to determine if poor hermeticity contributed to elevated moisture content.

Sample Group 3

This group contained 114 units from a private database (author R. K. Lowry's) compiled from many different clients. The group comprised microcircuit packages of a wide variety of styles and cavity volumes. Clients had obtained gas analysis data on the units for a variety of reasons including pre-shipment inspections, materials and process qualifications, DPA, failure analysis, and engineering studies. Details necessarily remain proprietary, but reviewing the gas analysis results with a focus on causes of elevated moisture content is instructive.

**2.2 Data**

Internal gas composition data for all sample groups came variously from three different commercial service laboratories, each with suitability for Test Method 1018 procedures. Except for Group 1, the choice of laboratory was by clients and not authors of this paper. Data were not compared for inter-laboratory differences. The study focus was to generally discern causes for noncompliance to the expectation of 0.50v% maximum internal moisture, as defined by MIL-STD-883.

**2.3 Data Analysis**

Numerical values in gas analysis reports were rounded to two decimal places and tabulated as volume percent (v%), where 1v% = 10,000 ppmv. No entry in a cell in the data tables indicates that the species reported either as <0.01v% or as not detected.

## 3. RESULTS AND DISCUSSION

Table 2 summarizes the aggregate results for moisture compliance:

Table 2. Non-compliance to the 0.50v% moisture limit of the three sample groups

| Group | Total Units | Units >0.50v% $H_2O$ |
|---|---|---|
| 1, "Old" units | 15 | 0 |
| 2, 5011 Qual units | 71 | 18 |
| 3, Consultant's database | 114 | 41 |
| Total | 200 | 59 (29.5%) |

The first reaction to 29.5% of units noncompliant on moisture is alarm, justifiably if results were solely from pre-shipment inspections or process control measurements. But this study includes units that might have moisture control problems anyway, so the high incidence of noncompliance is not surprising.

Results for each of the three sample groups were tabulated and their overall gas composition "signatures" considered in detail for the likely causes of internal moisture.

**3.1 Group 1, "Old" Units**

Tables 3 and 4 summarize results for the TO cans and braze units.

Table 3. Internal gas composition for eight TO cans, all about 20 years old.

| Year sealed | | | All units pre-1990 | | | | | |
|---|---|---|---|---|---|---|---|---|
| Approx. age | | | All units 18+ years | | | | | |
| S/N | 3-1 | 3-2 | 3-3 | 3-4 | 3-5 | 3-6 | 3-7 | 3-8 |
| 1014.2 Gross Leak | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass |
| 1014.2 Fine Leak Rate x 1E-9 atm cc/sec | 8.8 | 6.4 | 5.8 | 6.0 | 5.4 | 5.0 | 4.6 | 4.8 |
| Nitrogen, v% | 99.90 | 99.90 | 99.90 | 99.90 | 99.90 | 99.90 | 99.90 | 99.80 |
| Oxygen, v% | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Argon, v% | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Water, v% | 0.04 | 0.03 | 0.03 | 0.02 | 0.05 | 0.03 | 0.02 | 0.08 |
| Carbon Dioxide, v% | 0.08 | 0.05 | 0.04 | 0.02 | 0.06 | 0.04 | 0.12 | 0.08 |
| Hydrogen | | | | | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Helium** | | | | | | | | |
| **Fluorocarbon** | | | | | | | | |
| **Ammonia** | | | | | | | | |
| **Organics** | | | | | | | | |

Table 4. Internal gas composition for seven braze seal units, age from 10-19 years old.

| | **18 leadd braze seal DIPs** | | | | **40 lead braze DIP** | **84 lead PGA** | **16 lead Flatpack** |
|---|---|---|---|---|---|---|---|
| **Post seal treatment** | no bake | 1 hr p.s. bake | 1 hr p.s. bake | no bake | 1/2 hr bake | none | None |
| **Year sealed** | 1989 | 1989 | 1989 | 1989 | 1991 | 1998 | 1990 |
| **Approx. age** | 19 y | 19 y | 19 y | 19 y | 17 y | 10 y | 18 y |
| **S/N** | 4-1 | 4-2 | 4-3 | 4-4 | 4-5 | 4-6 | 4-7 |
| **1014.2 Gross Leak** | Pass | Pass | Pass | Pass | Pass | Pass | Pass |
| **1014.2 Fine Leak Rate x 1E-9 atm cc/sec** | 5.6 | 4.8 | 4.4 | 4.0 | 4.6 | 9.6 | 9.6 |
| **Nitrogen, v%** | 98.60 | 98.50 | 99.00 | 97.60 | 96.80 | 94.20 | 99.90 |
| **Oxygen, v%** | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| **Argon, v%** | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| **Water, v%** | 0.01 | 0.02 | 0.02 | 0.02 | 0.04 | 0.04 | 0.02 |
| **Carbon Dioxide** | 0.05 | 0.07 | 0.03 | 0.02 | 0.02 | 1.11 | 0.06 |
| **Hydrogen** | 1.33 | 1.37 | 0.91 | 2.33 | 3.13 | 4.65 | <0.01 |
| **Helium*** | | | | | | | |
| **Fluorocarbon*** | | | | | | | |
| **Ammonia*** | | | | | | | |
| **Organics*** | | | | | | | |

All 15 TO99 cans and braze seal units are clearly free of significant moisture, from either materials outgassing or ingress through leaks, throughout their entire lifetimes.

These units had eutectic substrate attach and no polymeric materials inside, which helps achieve and maintain moisture outgassing control over long periods of time.

The findings in Tables 3 and 4 were gratifying. Robust M&P rendered these package styles both dry and truly hermetic for long periods of time of practical significance to device reliability. The materials and technology remain available today.

The need for robust M&P cannot be over emphasized. As package internal volumes decrease, the necessity for a truly hermetic seal rapidly increases. For example, a device with an internal volume of 0.1 cc cannot exceed leak rates of $10^{-10}$ sccm if service lives exceeding 10 years are to be reached. [1]

### 3.2 Group 2, 5011 Adhesive Qualification Units

All units in this group contain polymeric substrate attach materials which require careful choice and robust pre-seal processing to insure moisture control. There were 71 total units, of which 18 were noncompliant and 53 compliant on moisture. Table 5 summarizes results for the noncompliant units.

Table 5. Noncompliant units in 5011 adhesive qualification study.

| **Seq. S/N** | **5-1** | **5-2** | **5-3** | **5-4** | **5-5** | **5-6** | **5-7** | **5-8** | **5-9** |
|---|---|---|---|---|---|---|---|---|---|
| **Study ID** | C3-45 | A22-14 | A38-2 | C6-B5 | C5-19 | C5-20 | C5-B8 | C2-63 | A38-1 |
| **Nitrogen** | 74.00 | 90.90 | 59.00 | 93.10 | 90.90 | 90.20 | 95.20 | 95.40 | 95.30 |
| **Oxygen** | 19.40 | 0.02 | 0.52 | 2.39 | | | | | |
| **Argon** | 0.83 | 0.11 | 0.68 | 0.16 | | 0.18 | 0.04 | | .11 |
| **Water** | 1.68 | 2.50 | 11.70 | 1.68 | 0.68 | 0.91 | 1.10 | 0.54 | 2.33 |
| **Carbon Dioxide** | 0.41 | 0.88 | 3.93 | 0.48 | 3.71 | 6.37 | 0.16 | 0.27 | 2.02 |
| **Hydrogen** | | | | | 0.33 | 0.29 | 0.09 | | .03 |
| **Helium** | | 4.83 | | 2.19 | 4.01 | 1.68 | 3.41 | | |
| **Fluorocarbon** | 3.65 | 0.76 | 24.00 | | | | | | |
| **Ammonia** | | | | | 0.07 | 0.09 | | | |
| **Organics** | | 0.01 | 0.14 | | 0.33 | 0.24 | | 3.82 | 0.20 |

Table 5, continued

| **Seq. S/N** | **5-10** | **5-11** | **5-12** | **5-13** | **5-14** | **5-15** | **5-16** | **5-17** | **5-18** |
|---|---|---|---|---|---|---|---|---|---|
| **Study ID** | C2-64 | C5-18 | A22-4 | A22-5 | A22-6 | A22-12 | A22-13 | A37-1 | A38-3 |
| **Nitrogen** | 95.20 | 91.80 | 91.50 | 91.30 | 91.20 | 92.60 | 91.20 | 99.00 | 96.00 |
| **Oxygen** | | | | | | | | | |
| **Argon** | 0.06 | | 0.03 | 0.03 | 0.03 | 0.03 | 0.02 | | 0.07 |
| **Water** | 0.52 | 0.71 | 0.96 | 1.13 | 0.98 | 0.96 | 0.86 | 0.63 | 1.71 |
| **Carbon Dioxide** | 0.27 | 3.12 | 0.73 | 0.78 | 0.76 | 0.69 | 1.24 | 0.21 | 2.08 |
| **Hydrogen** | | 0.32 | | | | | | | 0.02 |
| **Helium** | | 3.80 | 6.69 | 6.75 | 6.99 | 5.65 | 6.57 | | |
| **Fluorocarbon** | | | | | | | | | |
| **Ammonia** | | 0.04 | | | | | | | |
| **Organics** | 3.99 | 0.20 | 0.04 | 0.04 | 0.04 | 0.03 | 0.09 | 0.09 | 0.16 |

S/Ns 5-1, 5-2, and 5-3 contain components of air and fluorocarbon. This defines these units as "variable" or "one-time" leakers, as discussed later. These units are a special case of induced non-hermeticity. They are most likely hermetic except during stresses of burn in or leak test.

S/N 5-4 contains $O_2$ and Ar in a ratio that, while not identical to air, probably identifies it as a leaking device. Its He content is less than half that of a brother unit (data not shown), and it contains no FC. However, its $CO_2$ content at 0.48v% is too high to be explained by air ingress alone, so outgassing is also occurring in this unit. The 14 remaining noncompliant units S/Ns 5-5 through 5-18 contain no detectable $O_2$ and negligible Ar (though three have somewhat elevated Ar). All contain some level of volatile organics, and most contain $CO_2$ at concentrations far above that of natural air. These units are noncompliant due solely to materials outgassing.

None of the 53 compliant units contain $O_2$ and most contain no Ar. Absence of $O_2$/Ar indicates that up to the time of analysis none of the units had begun to acquire moisture by air ingress.

Units with polymeric materials tend to have levels of $CO_2$ and organics that track with moisture content. This is reflected in Table 6, showing that on average compliant units contain only about one-third as much as much $CO_2$ and hydrocarbons as noncompliant units, further indicating outgassing as the source of moisture in units in this group.

Table 6. Comparison of gas compositions between compliant and noncompliant units.

| | Number of units | Average $H_2O$ v% | Average $CO_2$, v% | Average HC, v% |
|---|---|---|---|---|
| **Noncompliant, >0.50v% $H_2O$** | 18 | 1.75 | 1.60 | 0.69 |
| **Compliant, <0.5v%** | 53 | 0.23 | 0.66 | 0.22 |

Twelve of the 53 compliant units contained moisture between 0.40-0.50v%. Any loss of hermeticity, or any additional outgassing, would quickly push those units above the recommended maximum moisture content. This underscores the importance of qualifying polymeric materials and their processing with respect to their moisture behavior.

Thus in Group 2, 17 of 18 noncompliant units contain moisture due solely to outgassing from materials. One unit showed evidence of air ingress, however outgassing also contributed to its total moisture content.

### 3.3 Group 3, Database of Miscellaneous Part Types

This was a group of 114 units of a wide variety of package styles and sizes. It had 41 units (from 31 different lots) noncompliant on moisture content. The gas composition "signatures" of the 41 noncompliant parts fell into four distinct categories, shown in Table 7.

Table 7. Categories of nonconforming units among 100 unit (31 sample group) database.

| Category | Status | No. Units |
|---|---|---|
| **1. Nonconforming units with components of air** | Non-hermetic enclosure | 7 |
| **2. Nonconforming units with no components of air** | Outgassing materials | 20 |
| **3a. Nonconforming units with components of air and FC** | Probable one-time leaker | 9 |
| **3b. Nonconforming units with no air, but FC** | Definite one-time leaker | 5 |
| **Total** | | 41 |

Category 1 is that of probable leakers, in which $O_2$ and Ar are present. Seven of the 41 noncompliant units exhibit this "signature", as summarized in Table 8.

Table 8. Apparent non-hermetic units, those with air and no FC.

| | Gp 23 | Gp 27 | Gp 28 | Gp 42 | Gp 44 | Gp 31 | Gp 31 |
|---|---|---|---|---|---|---|---|
| | **FP** | **FP** | **TO-OC-4** | **TO257-132** | **Weld unit** | **Cer FP-1** | **Cer. FP-2** |
| **S/N** | **8-1** | **8-2** | **8-3** | **8-4** | **8-5** | **8-6** | **8-7** |
| **Nitrogen** | 93.90 | 96.80 | 90.40 | 78.30 | 81.66 | 77.50 | 76.90 |
| **Oxygen** | 3.55 | 1.63 | 4.11 | 18.60 | 16.44 | 20.50 | 21.20 |
| **Argon** | 1.15 | 0.14 | 0.40 | 0.82 | 0.62 | 0.93 | 0.96 |
| **Water** | 1.04 | 0.80 | 1.96 | 1.68 | 1.02 | 0.81 | 0.86 |
| **Carbon Dioxide** | 0.32 | 0.40 | 2.07 | 0.66 | 0.03 | 0.28 | 0.13 |
| **Hydrogen** | 0.03 | | 0.01 | | | 0.01 | 0.01 |
| **Helium** | | 0.24 | 1.08 | | | | |
| **Fluorocarbon** | | | | | | | |
| **Ammonia** | | | | | | | |
| **Organics** | | | | | | | |

S/N's 8-4 through 8-7 contain more-or-less stochiometric air. The others contain $O_2$ and Ar in "diluted" amounts, with $O_2$/Ar ratios from 3.1 to 11.6, unlike that of natural air. But the $O_2$/Ar presence probably indicates at least some air ingress (though the He in units 8-2 and 8-3 begs that question). Outgassing contributed to the levels of moisture in all units except 8-5, as $CO_2$ is elevated far above that of natural air in the others. These seven units are classified as containing at least some moisture due to air ingress, per the considerations of this study.

Category 2 was a group of 20 units that are noncompliant, but contain negligible or no components of air, and no fluorocarbon. Not all the results are shown, but all the units had gas composition signatures like the typical examples in Table 9.

Table 9. Typical results for the 27 nonconforming units containing no air or FC.

| | **C2-63** | **C2-64** | **C5-18** | **C5-19** | **A22-4** | **A22-5** | **Metal Can C** | **06-TO-143** | **06-TO-214** | **T-1** | **T-2** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **S/N** | **9-1a** | **9-1b** | **9-2a** | **9-2b** | **9-3a** | **9-3b** | **9-4a** | **9-4b** | **9-5** | **9-6a** | **9-6b** |
| **Nitrogen** | 95.40 | 95.20 | 91.80 | 90.90 | 91.50 | 91.30 | 94.20 | 94.30 | 92.90 | 96.00 | 96.40 |
| **Oxygen** | | | | | | | | | | | |
| **Argon** | | 0.06 | | | 0.03 | 0.03 | 0.02 | 0.01 | 0.13 | | |
| **Water** | 0.54 | 0.52 | 0.71 | 0.68 | 0.96 | 1.13 | 0.73 | 1.03 | 2.69 | 1.50 | 1.21 |
| **Carbon Dioxide** | 0.27 | 0.27 | 3.12 | 3.71 | 0.73 | 0.78 | 0.12 | 0.13 | 1.16 | 0.01 | 0.01 |
| **Hydrogen** | | | 0.32 | 0.33 | | | 0.27 | 0.01 | 0.19 | 0.15 | 0.12 |
| **Helium** | | | 3.80 | 4.01 | 6.69 | 6.75 | 4.71 | 4.56 | 2.90 | 2.31 | 2.29 |
| **Fluorocarbon** | | | | | | | | | | | |
| **Ammonia** | | | 0.04 | 0.07 | | | | | | | |
| **Organics** | 3.82 | 3.99 | 0.20 | 0.33 | 0.04 | 0.04 | | | | | |

S/N's 9-1a and 9-1b are brother units whose gas compositions are very similar. While they are barely noncompliant, it is clear that excess moisture is from organic compounds in the enclosures. S/N's 9-2a and 9-2b are also brother units with a similar situation, but much more $CO_2$. These units have also retained their He. S/N's 9-3a and 9-3b are another set of brother units, with higher moisture yet lower organics and lower $CO_2$. Clearly, the differences between S/N groups 9-1, 9-2, and 9-3 are the post-seal outgassing behavior of the organic materials inside the enclosures. Failure to properly cure these materials allows post-seal outgassing to elevate enclosure moisture content.

S/N's 9-4 through 9-6 are a variation on the theme. Organics do not seem to play a role in their gas compositions, yet all are noncompliant, exceeding the moisture limit by factors ranging from 1.5x to 5.4x. This is attributed to poor pre-seal baking of package piece parts, failing to permanently remove adhered moisture, which subsequently outgassed from part surfaces.

Category 3 is a group of 14 units that are noncompliant and contain fluorocarbon. Within this group, subgroup 3a has 9 that also contain components of air, and subgroup 3b has 5 that do not contain components of air. Table 10 shows typical results for these kinds of units.

Table 10. Typical results for noncompliant units that contain fluorocarbon and no air (S/Ns 10-1 through 10-4), and those that contain fluorocarbon and air (S/Ns 10-5 through 10-6c).

| | **FP3** | **T10-06-3** | **T10-06-4** | **T3-4** | **A22-14** | **A38-2** | **SB-AP-23** | **SB-AP-87** | **SB-AP-95** |
|---|---|---|---|---|---|---|---|---|---|
| **S/N** | 10-1 | 10-2a | 10-2b | 10-3 | 10-4 | 10-5 | 10-6a | 10-6b | 10-6c |
| **Nitrogen** | 93.60 | 93.80 | 94.10 | 93.60 | 90.90 | 59.00 | 81.30 | 80.00 | 72.00 |
| **Oxygen** | | 0.01 | 0.01 | | 0.02 | 0.52 | 15.30 | 16.20 | 8.91 |
| **Argon** | 0.02 | 0.09 | 0.07 | | 0.11 | 0.68 | 0.70 | 0.72 | 0.40 |
| **Water** | 0.86 | 3.22 | 2.75 | 0.86 | 2.50 | 11.70 | 1.18 | 1.13 | 1.07 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Carbon Dioxide** | 0.15 | 0.30 | 0.29 | 0.15 | 0.88 | 3.93 | 0.22 | 0.61 | 0.96 |
| **Hydrogen** | | 0.04 | 0.02 | 0.55 | | | | | |
| **Helium** | 4.57 | 2.49 | 2.71 | 4.57 | 4.83 | | 0.03 | 0.09 | 0.36 |
| **Fluorocarbon** | 0.29 | 0.07 | 0.10 | 0.29 | 0.76 | 24.00 | 1.28 | 1.25 | 16.30 |
| **Ammonia** | | | | | | | | | |
| **Organics** | | | | | 0.01 | 0.14 | | | |

### 3.4 Pressure-Sensitive Leakers

Three units in Group 2 and 14 units in Group 3 resemble those with glass-to-metal seals having variable leak rates,[6] e.g. units with leaks apparently induced by external thermal or physical stresses such as clamping during burn-in which temporarily breaks the oxide-sealed surfaces in glass-to-metal seals. Table 11 contains data typical of units with pressure sensitive leaks described in that study.

Table 11. Noncompliant units, which contain FC in the pressure-sensitive leaker study.

| | **Gp 49** | **Gp 49** | **Gp 50** |
|---|---|---|---|
| | **Clarke 425** | **Clarke 432** | **Clarke 20** |
| **Nitrogen** | 94.60 | 92.10 | 82.20 |
| **Oxygen** | | 0.34 | 2.58 |
| **Argon** | 0.53 | 0.05 | 0.17 |
| **Water** | 0.77 | 0.78 | 0.81 |
| **Carbon Dioxide** | 0.04 | 0.03 | 1.06 |
| **Hydrogen** | | | |
| **Helium** | 3.90 | 6.70 | 12.20 |
| **Fluorocarbon** | 0.08 | 0.04 | 0.88 |
| **Ammonia** | | | 0.13 |
| **Organics** | 0.01 | 0.02 | |

Because of this characteristic, noncompliant units in Sample Group 2 or 3 that contain fluorocarbon and/or a gas signature like that in Table 10 are not counted as “on-the-shelf” or “in-service” units with moisture elevated by normal air ingress.

### 3.5 Moisture From Chemical Reactions

Within-enclosure chemical reactions, such as $H_2$ outgassing[7] and $H_2O$ production by reaction with surface-exposed oxides[8], or reaction of $H_2$ and $O_2$ in the presence of nickel as a catalyst producing $H_2O$[9], are special cases of the outgassing mechanism rather than a consequence of air ingress. Those mechanisms may have contributed to excess moisture in some of the samples, but they were not studied in detail.

### 3.6 Peculiar Data

Not all gas compositions are readily explainable. Table 12 shows some examples to challenge the reader. The data on the explanted hermetic biomedical device was obtained from a lawsuit filing in public record. The device contained negligible air, or at least not enough to explain 33v% $H_2O$. (Not all data were reported in the filing). How can so much water be inside this unit? The large TO’s, A and B, are brother units. A has the right amount of Ar for air, but no $O_2$. The level of moisture is too high to be explained purely by air ingress. Was the $O_2$ consumed by some kind of chemical reaction that produced water? The organic substance reported was specifically methanol, which implies a chemical reaction of $O_2$ with $CH_4$ to make water and methanol (no balanced reaction is evident unless $H_2$ is available). Unit B also has much water but a completely different gas signature. The LCC is noncompliant by a small amount, but has 23 times as much $CO_2$ as air. Where did all the $CO_2$ come from, and is that the explanation for noncompliance? Proposed explanations for these data are solicited from the reader.

Table 12. Peculiar hermetic enclosure gas compositions.

| | Explanted Biomed device | Large TO A | Large TO B | 48 ld LCC |
|---|---|---|---|---|
| **Nitrogen** | nr | 70.60 | 87.20 | 98.40 |
| **Oxygen** | 0.17 | | | |
| **Argon** | nr | 0.91 | | |
| **Water** | 32.91 | 24.70 | 10.10 | 0.67 |
| **Carbon Dioxide** | nr | 0.40 | 0.06 | 0.91 |
| **Hydrogen** | nr | | 0.04 | 0.07 |
| **Helium** | 13.55 | | 2.56 | |
| **Fluorocarbon** | nr | | | |
| **Ammonia** | nr | | | |
| **Organics** | nr | 3.77 | | |

nr=not reported

## 4. RESULTS & CONCLUSIONS

### 4.1 Results

1) Fifteen TO can and braze seal units more than 20 years old maintained negligible internal moisture due to robust materials processing that prevents both outgassing and air ingress.

2) Seventy-one units from a Test Method 5011 adhesive qualification study had 18 units noncompliant on moisture content. One of these contained an internal gas signature consistent with air ingress. Air ingress did not account for all the moisture in that unit.

3) One hundred fourteen units of a wide variety of package styles and sizes had 41 units noncompliant on moisture content. Seven contained an internal gas signature consistent with air ingress, but only one of these contained air exclusively.

Table 13 summarizes the results with respect to sources of internal moisture.

| Sample Group | Number of Units | Noncompliant Units | Noncompliant: Air ingress | Noncompliant: outgassing exclusively | Noncompliant: variable leak |
|---|---|---|---|---|---|
| **1. Units 10-20 years old** | 15 | 0 | 0 | 0 | 0 |
| **2. 5011 Adhesive Qual** | 71 | 18 | 1[a] | 14 | 3 |
| **3. Consultant's database** | 114 | 41 | 7[b] | 20 | 14 |
| **Totals** | 200 | 59 | 8 | 34 | 17 |
| **Percentages** | | 29.5% of units are noncompliant | 13.6% of the noncompliant units | 57.6% of the noncompliant units | 28.8% of the noncompliant units |

a. This unit showed evidence of outgassing also.
b. Only one of these units showed air ingress exclusively.

### 4.2 Conclusions

Overall, 57.6% of noncompliant units in this study contained elevated moisture due solely to materials outgassing with no evidence of air ingress. An additional 28.8% of the units behaved as variable leakers, a condition not attributed to simple air ingress during storage or service. Only 13.6% of noncompliant units showed evidence of air ingress, and only one of those appeared to contain air exclusively with no evidence of outgassing.

Piece part and materials selection and robust processing are the essential first line of defense for internal moisture control of sealed enclosures. Concern for hermeticity becomes important only after materials and processes are in place to assure that product is dry as-sealed and is as free as possible of outgassing.

It is recognized that certain package types, sealing equipment, suppliers of materials and equipment, and seal processes may be unique special causes of hermeticity issues. Engineers must address these special causes, while maintaining control of materials outgassing, as an integral part of investigating and eliminating special causes of hermeticity failure.

It is recognized that this is a small dataset. Much larger databases are available. The authors solicit inputs from anyone who can share data with the community as a whole to enlarge this study.

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