Use of Leak Detection Techniques in the Development of a Hermetic Terminal Seal Design

***J.W. Baker*, B.J. Stein, P.M. Shah, N.D. Isaacs**

Mine Safety Appliances Company

INTRODUCTION

PURPOSE OF PRESENTATION

Present some nuances associated with standard helium mass spectrometry leak detection and introduce the use of photoacoustic infra-red analysis as a leak detection method

TRANSPORTATION OF LITHIUM-ION CELLS

- Regulated by DOT
- Requirements for shipping listed in 49 CFR (Chapter I, Sub-Chapter C, §173.185)
- Li ion cells with >1.5 g equivalent Li content must meet the requirements of United Nations, ***Transport of Dangerous Goods Manual of Tests and Criteria*** (Fourth Revised Edition, ST/SG/AC.10/11/Rev.4, Section 38.3)

U.N. MANUAL OF TESTS AND CRITERIA

Requirements for Testing Cells (Section 38.3.4)

Tests

1. Altitude Simulation
2. Thermal Test
3. Vibration
4. Shock
5. External Short Circuit
6. Impact
8. Forced Discharge

Cells are subjected to tests 1 through 6 and 8

Tests 1 through 5 must be conducted in sequence on same cell

• THERMAL TEST

- Cycle Between Temperatures

  - 40 °C to +75 °C

  Dwell at Temperature: 6 h small cell (≤12 g equiv. Li), 12 h large cell (>12 g equiv. Li)

  Maximum 30 minutes between Temperatures

  11 Temperature Cycles to Be Completed

- Requirements

  No Mass Loss

  No Leakage

  No Venting

  No Disassembly

  No Rupture

  No Fire

  Cell at Not Less Than 90% of Pre-Test Potential

Definition: Mass Loss

$$ML(\%) = \frac{(M_1 - M_2)}{M_1} \times 100$$

Cell Mass (g)	Mass Loss Limit (MLL)
<1	0.5 %
>1 but <5	0.2 %
≥5	0.1 %

M_1 mass before test, M_2 mass after test

• TERMINAL SEAL DEVELOPMENT

- Original Terminal Seal Designed for Controlled Temperature Operation (+5 °C to +45 °C)

  U.N. Thermal Test Induced Leaks in Cells with Original Terminal Seal Design

- Improved Terminal Seal Developed

  Hermetic Crimp Seal

  Successfully Passed U.N. Test Requirements

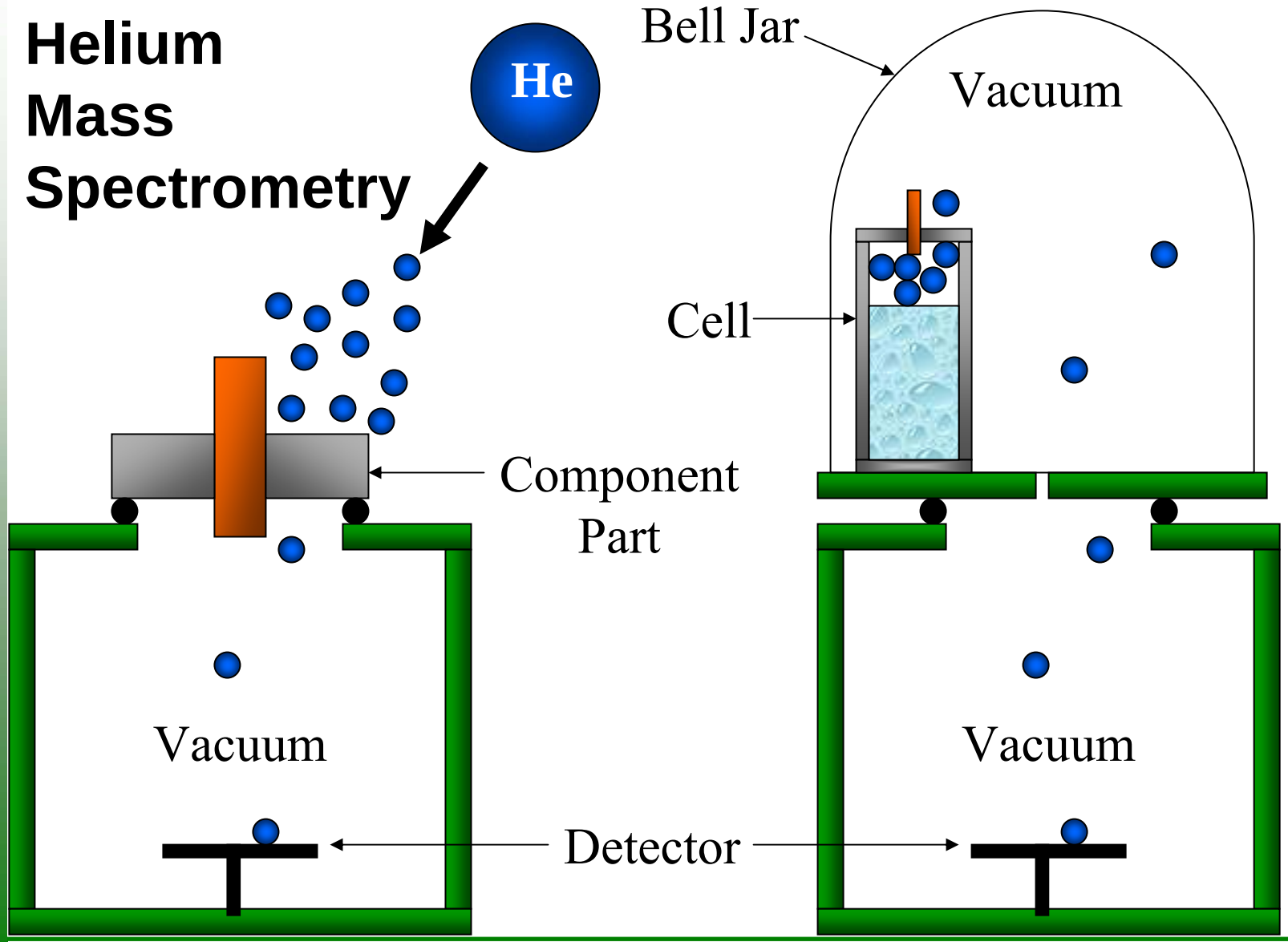
  Patent Application in Process

  Cannot Discuss Design Details

- **He-MS LEAK DETECTION**
  - Description
  - Special Considerations for Measurements
- **PA-IR LEAK DETECTION**
  - Description of Analysis Technique
  - Type of Materials Analyzed
  - Use in Leak Detection
- **SUMMARY**

He-MS LEAK DETECTION

He-MS LEAK DETECTION



• EVOLUTION OF THE TECHNIQUE

- Test Original Seal Design Component Parts
  - Subject Parts to U.N. Thermal Test
  - Evaluate Parts with He-MS

    Specification: 1×10^{-8} atm•cm^3/s He
  - Parts Found to be Hermetic at Room Temperature
  - Some Cells Leaked Electrolyte at Terminals During Thermal Cycling
- Modify He-MS Test Method
  - Expose Parts in Temperature Steps that Exceed U.N. Temperature Range
  - Evaluate Parts at Test Temperature w/ He-MS (part not brought back to room temperature for evaluation)

• TESTING PARTS AT TEMPERATURE

- Original Terminal Seal Design

  Leakage occurred at low temperature (-10 °C) after sufficient high temperature (+60 °C) exposure

- Experimental Variations with Design

  Some variations leaked at specific temperatures but were hermetic when returned to room temperature

  Final variation hermetic over the range -40 °C to +75 °C

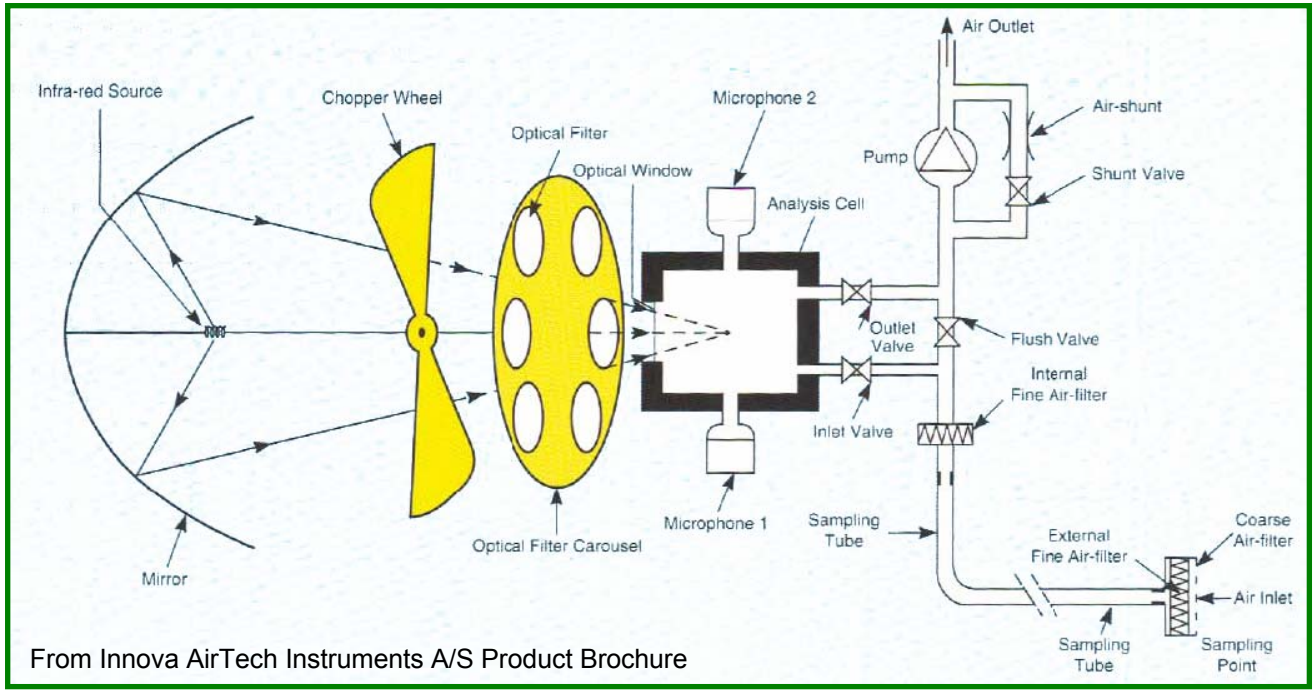
- Concern with He-MS Technique

  A leak could be produced in a cell during the U.N. Thermal Test which might not produce a failing result

  He-MS may not detect such a leak

PA-IR LEAK DETECTION

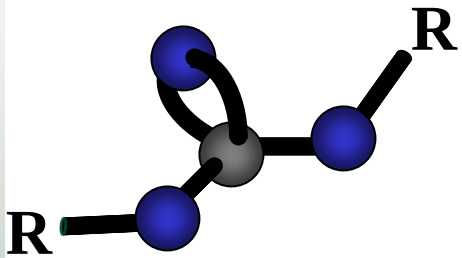
PHOTOACOUSTIC INFRA-RED



From Innova AirTech Instruments A/S Product Brochure

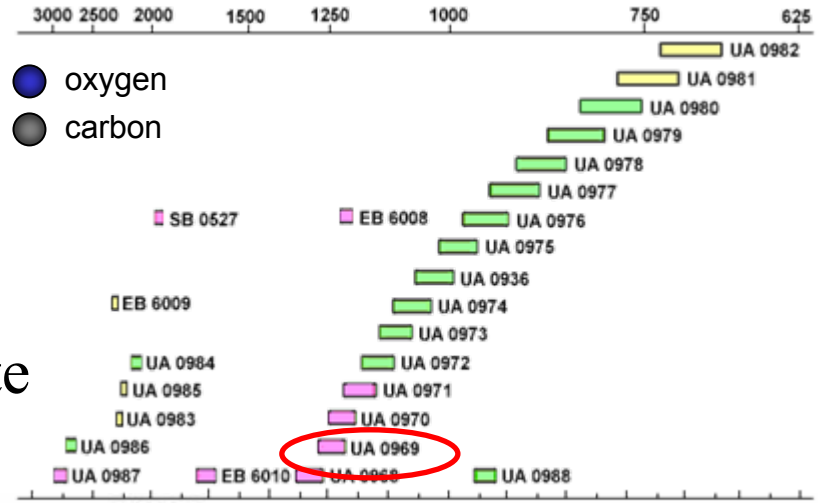
- Gas sample drawn into sample chamber
- IR light pulsated when passing through chopper
- Optical filter narrows wavelength
- Pulsating IR raises and lowers gas temperature creating acoustic signal
- Acoustic signal directly proportional to concentration

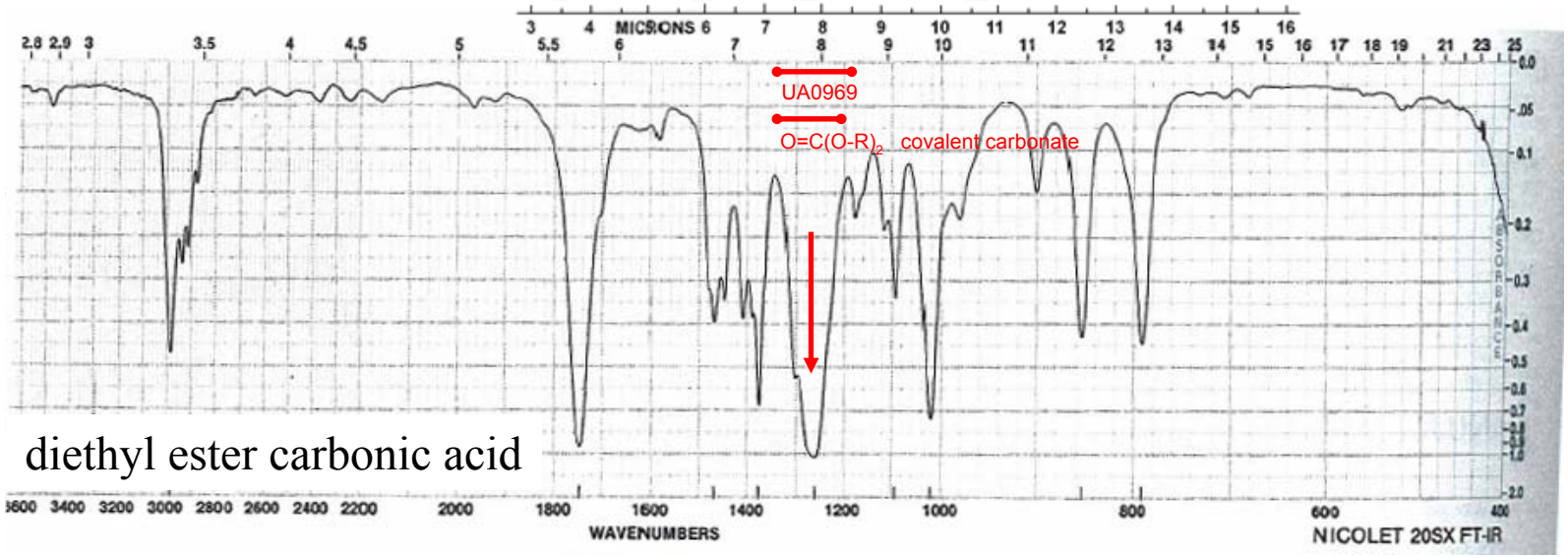
FILTER SELECTION



oxygen
carbon

Covalent Carbonate Functional Group





diethyl ester carbonic acid

• INTERFERENCES

- Water Vapor

  All analyses performed and samples prepared in dryroom

- Other Materials

  Any Material with IR Absorbance at Same Wavelength

  Laminated Bag Material (pouch cell bag) Inner Layer Outgases

  Check Empty Bag for Background

• CALIBRATION

- Qualitative

  Method Intended as ***Qualitative*** Comparison Tool to Evaluate Significant Change in Leakage of Seals

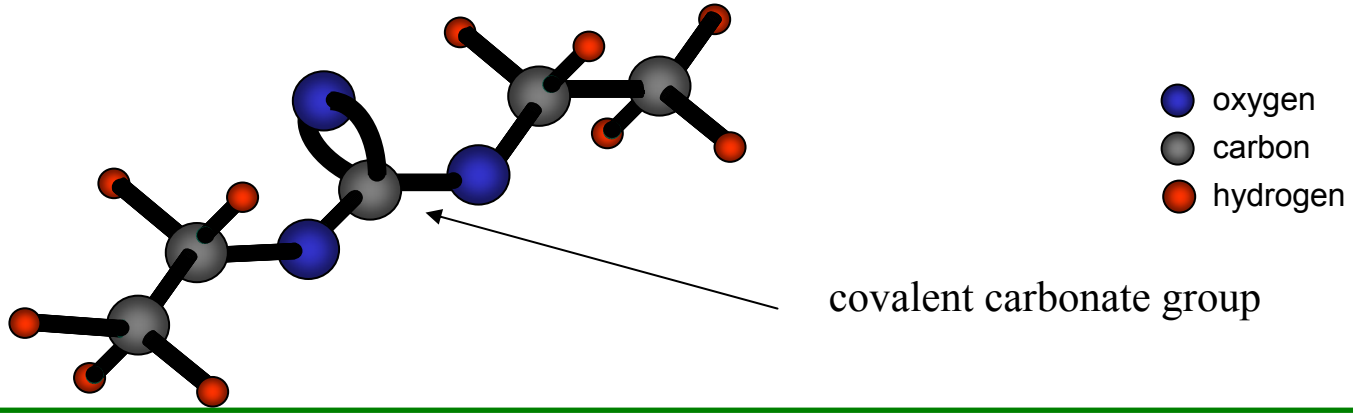
- Standards

  Volatile material

  diethyl ester carbonic acid or diethyl carbonate (DEC)

  99 ppb DEC in zero grade air

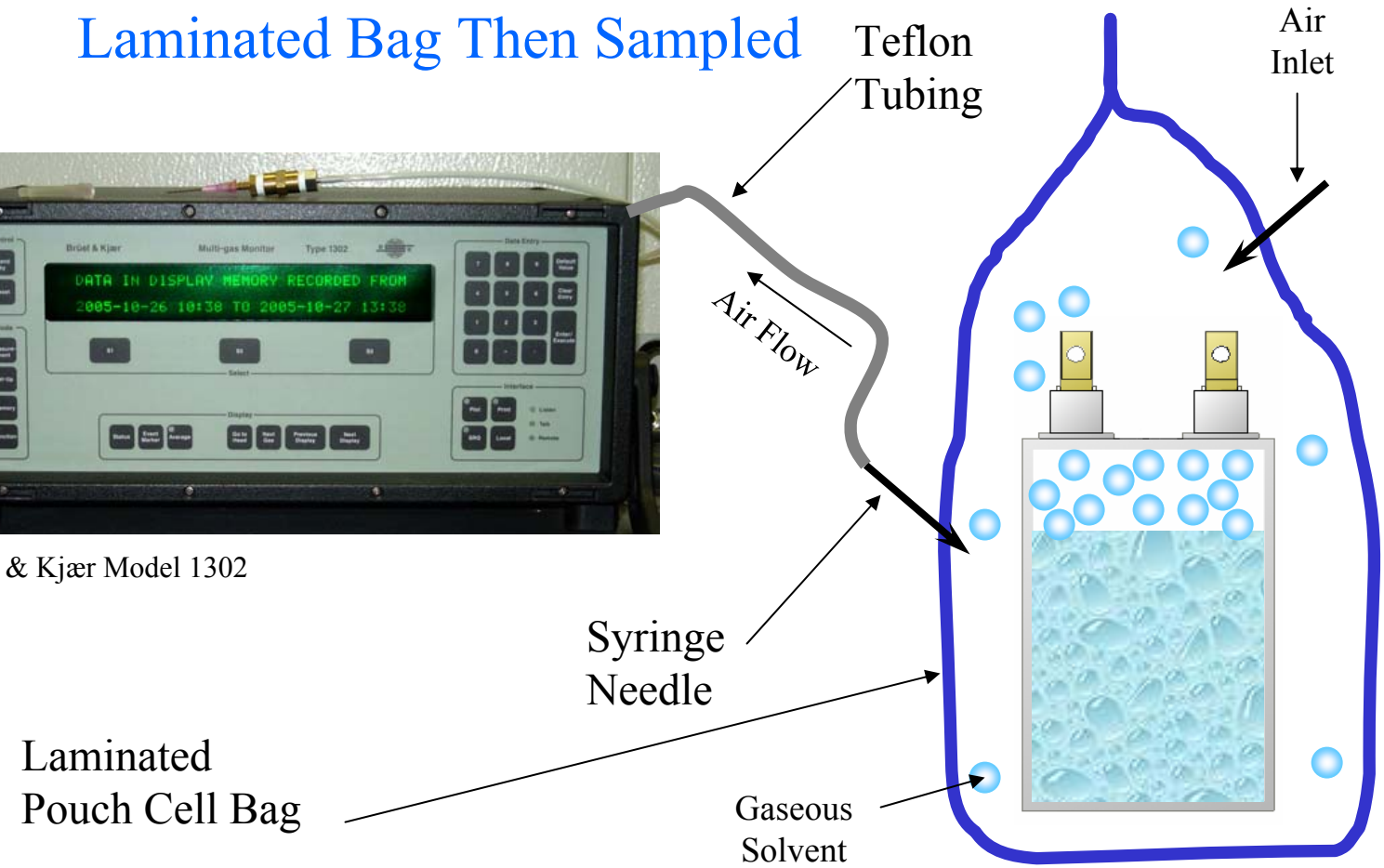
  5,000 ppb DEC in zero grade air



USE AS LEAK DETECTOR

Cell Exposed to U.N. Thermal Test Conditions in Laminated Bag Then Sampled

Brüel & Kjær Model 1302



TERMINAL SEAL DEVELOPMENT

Evaluate Terminal Seal Design Change 10 Ah Cell

Fast Test: Temperature Shock

5 Cycles with 1 hour dwell, < 10 sec for temperature change

Sample	After -10 °C to +55 °C (ppb DEQ)	After -30 °C to +75 °C (ppb DEQ)	After -40 °C to +75 °C (ppb DEQ)
Dryroom Air	2	2	2
Empty Bag	---	6	---
Design Evaluation 1	5	6	481
Design Evaluation 2	43	215	---
Design Evaluation 3	6	6	676
Old Design	5	8520	---

No visible leakage

visible leakage

PA-IR analysis detected leakage of solvent which occurred over different temperature ranges indicating an inconsistent seal design, cells built with this seal design eventually showed leakage under +5 °C to +45 °C use conditions

Implications are that readings in the calibration range (99 ppb+) of the instrument, and possibly lower, are indicative of significant leakage

DEQ = DEC Equivalent

• ANALYSIS FOR NEW TERMINAL SEAL DESIGN

- Experimental 10 Ah Cells

  3 Cells with Original Seal Design

  3 Cells with New Seal Design

- Expose to U.N. Thermal Test

  (-40 °C to +75 °C, 6 h dwell, 11 cycles, 30 min ramp)

Sample	MLL (%)	Δ Mass (%)	PA-IR (ppb DEQ)	Comment
Dryroom Air	---	---	**1**	
Empty Bag	---	---	**6**	
Orig. Design 1	0.1	0.003	**6030**	faint odor, visible leakage at terminal
Orig. Design 2	0.1	-0.002	**7820**	strong smell, visible leakage at terminal
Orig. Design 3	0.1	0.009	**3700**	very faint smell, visible leakage at terminal
New Design 1	0.1	0.002	**26**	
New Design 2	0.1	0.008	**24**	
New Design 3	0.1	0.000	**25**	

DEQ = DEC Equivalent

Mass Loss Insignificant, within error of balance

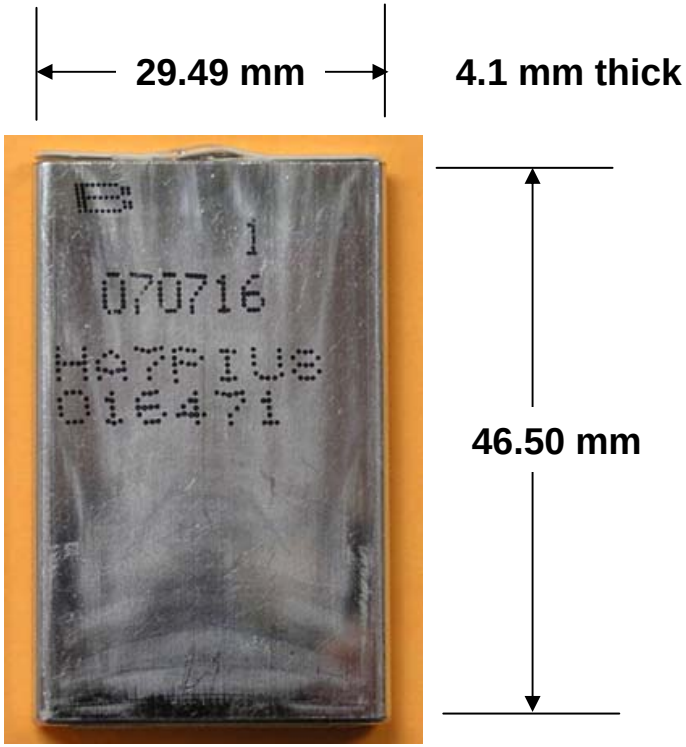
ANALYSIS OF COMMERCIAL CELL

Sanyo Model UF463048P

Lithium Ion

680 mAh

14 g



SANYO UF463048P RESULTS

- Expose Cells to U.N. Thermal Test

(-40 °C to +75 °C, 6 h dwell, 11 cycles, 30 min ramp)

Sample	MLL (%)	Δ Mass (%)	PA-IR (ppb DEQ)
Dryroom Air	---	---	**1**
Empty Bag	---	---	**2**
Sanyo at room temp	---	---	**51**
Sanyo 1	0.1	-0.012	**606**
Sanyo 2	0.1	-0.013	**498**
Sanyo 3	0.1	-0.012	**498**
Sanyo 4	0.1	-0.012	**460**
Sanyo 5	0.1	-0.010	**486**
Sanyo 6	0.1	-0.013	**356**

Significant Mass Loss and greater than much larger MSA cells but within acceptable limits of U.N. Thermal Test

DEQ = DEC Equivalent

SUMMARY

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- **IMPROVED CRIMP TYPE TERMINAL SEAL DEVELOPED**
  - Hermetic from -40 °C to +75 °C
  - Pass DOT/U.N. Cell Test Requirements for Transport of Dangerous Goods
- **Qualitative Method Developed to Evaluate Cell Leakage**
  - PA-IR Leak Detection More Sensitive Tool For Complete Cells
  - He-MS Leak Detection Good for Parts and Subassemblies

Identified the Need for Testing at Temperature

ACKNOWLEDGEMENTS

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