# Eichrom Resin Shelf-life

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eichrom®

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# Eichrom Quality System

- ISO 9001:2008

  -quality management systems standards

  -demonstrate the ability to consistently provide product(s) that meet customer requirements.

  -aim to enhance customer satisfaction

  -effective application of the system

  -continual improvement of the system

- Produce and conform to procedures governing:

  -sourcing or producing quality raw materials

  -converting raw materials into finished products

  -testing finished products for initial quality

  -re-testing products to evaluate quality after a time period

# Resin Shelf-life testing

- Started with Sr Resin in 2008 due to customer comments

- Extended to TEVA, TRU, UTEVA, DGA in 2009-2010 to support agencies desiring to stockpile resins for emergency preparedness.

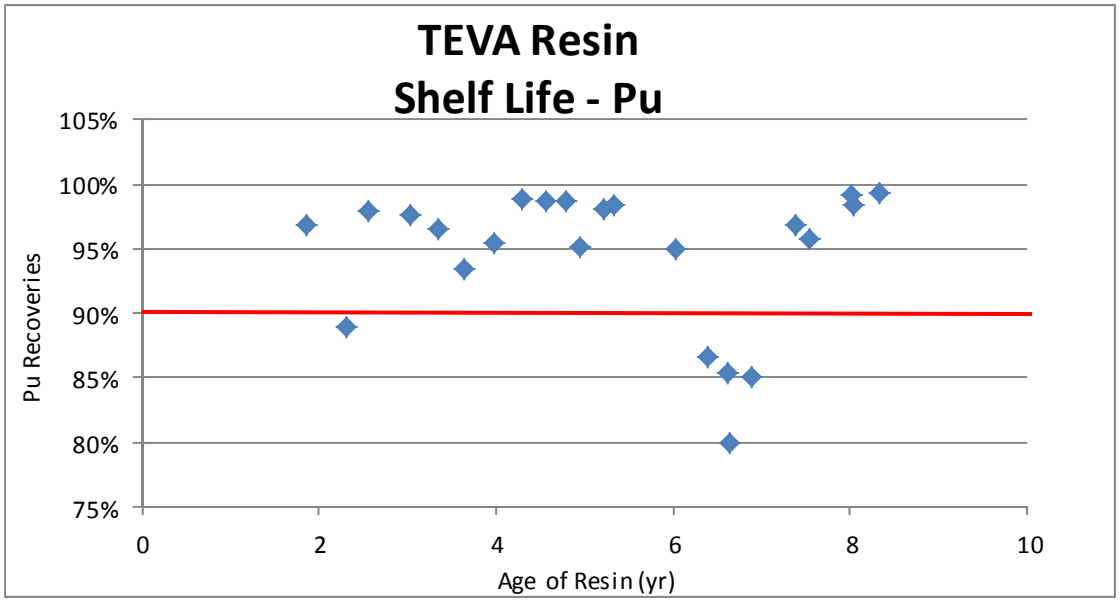
- Has resulted in numerous improvements:
  - Raw material purification
  - Production techniques
  - Quality control testing procedures

- Prior to 2005, QC
  - Batch Uptake Measurements
  - Limited column separation testing

- In 2005-2007, QC
  - Cartridge/Column Separations
  - At least 2 analytes

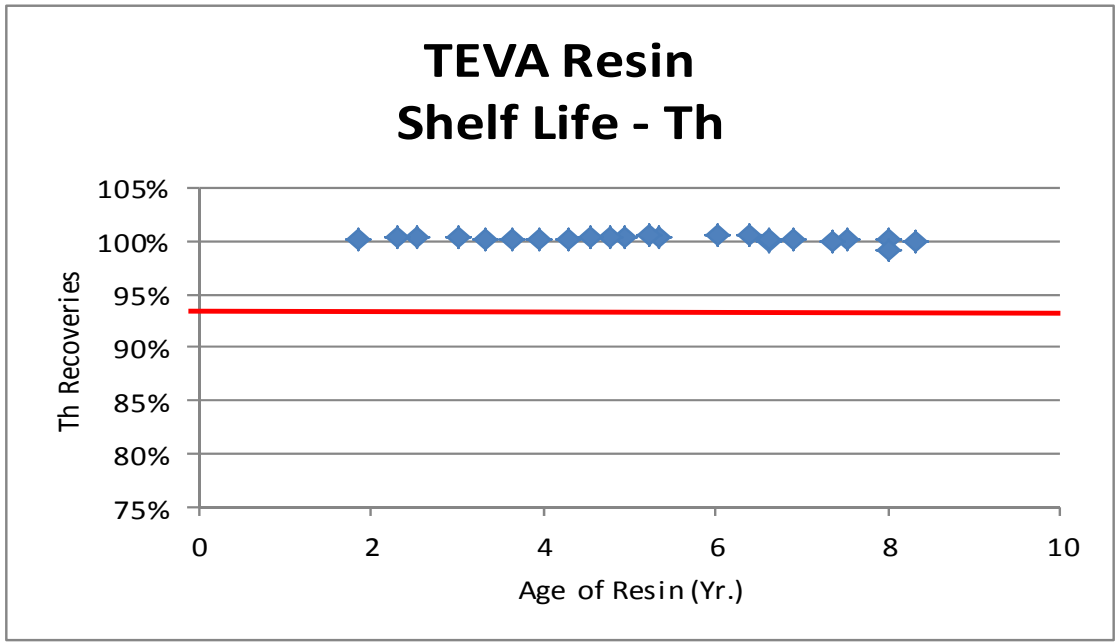
Good News!!!

# TEVA



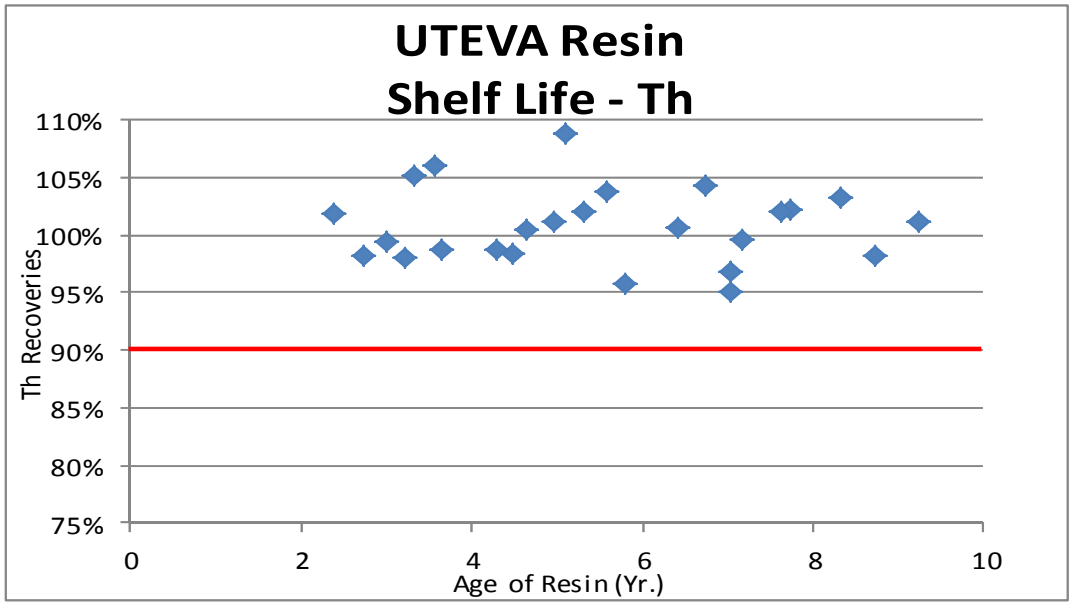

Recovery in 0.02M HCl-0.02M HF

Performed in 2010 on lots from 2001-2008.



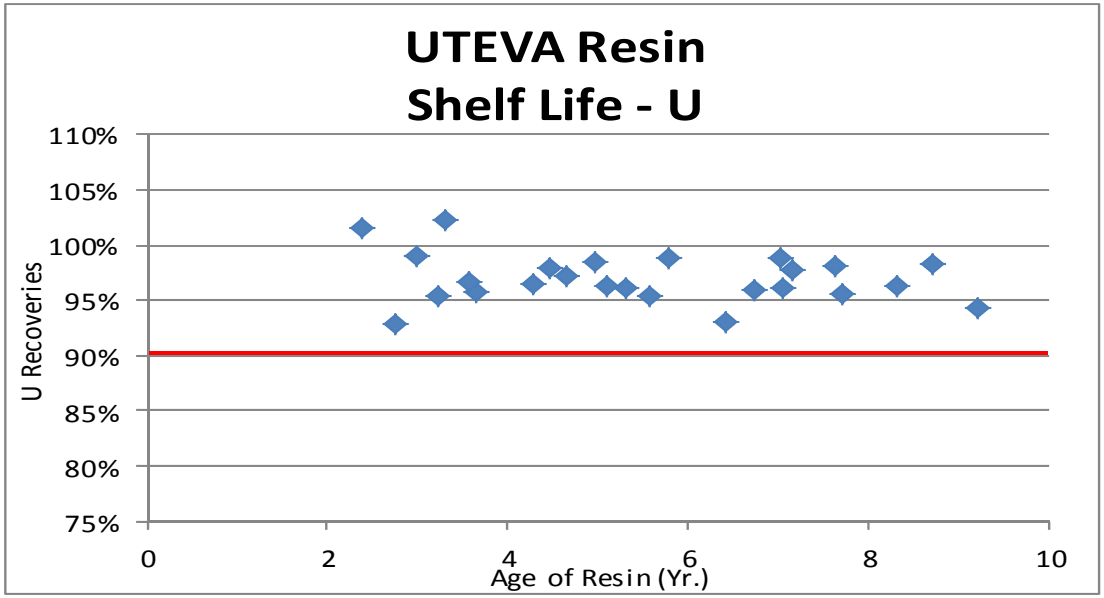

Recovery in 6M HCl

# UTEVA



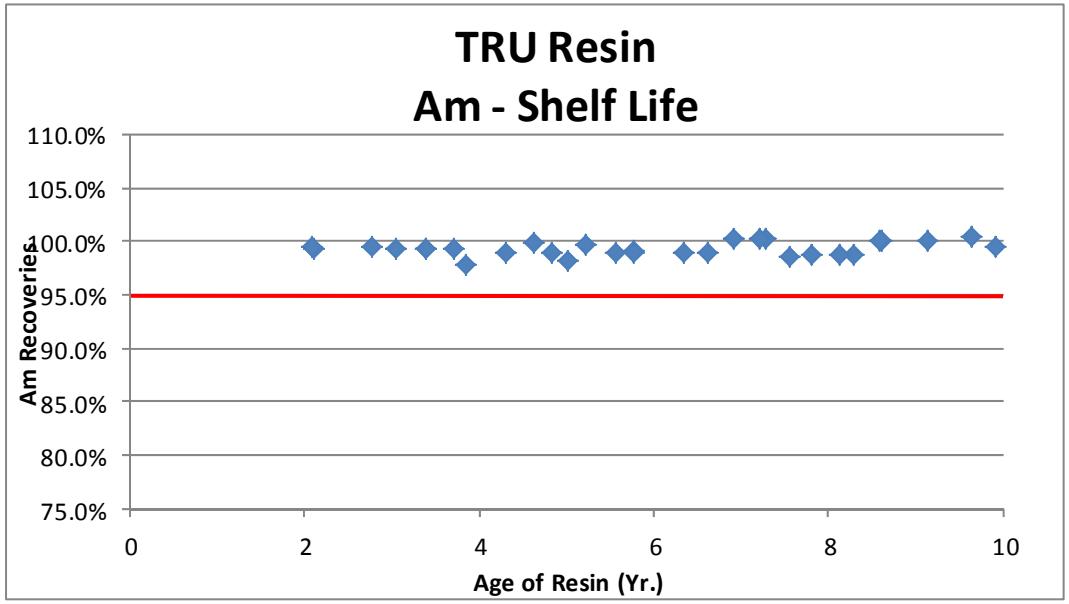

Recovery in 5M HCl-0.05M Oxalic Acid.

Performed in 2010 on lots from 2001-2008.



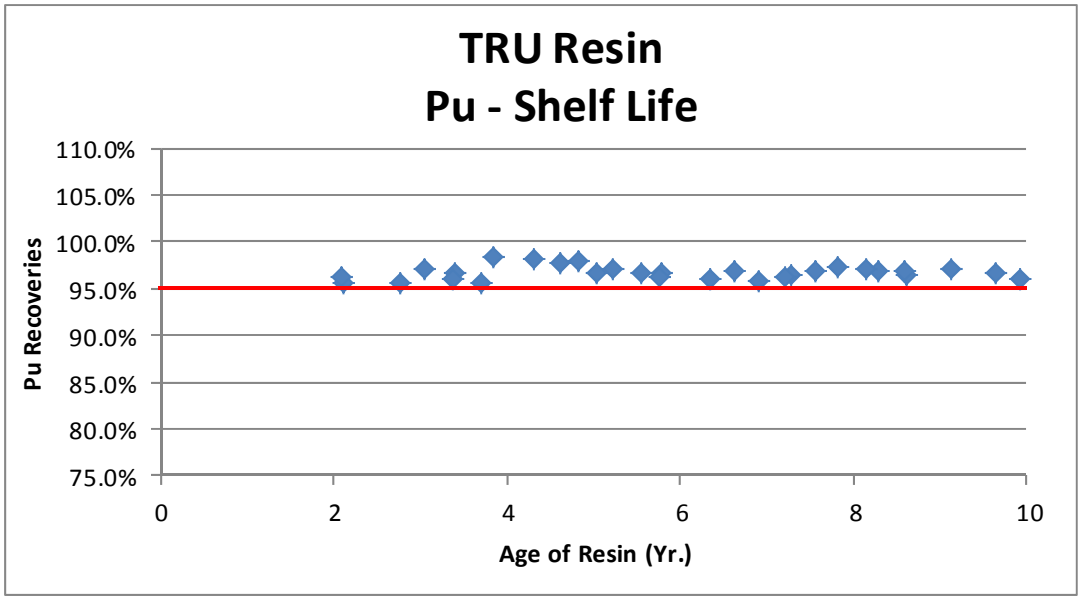

Recovery in 1M HCl

# TRU Resin



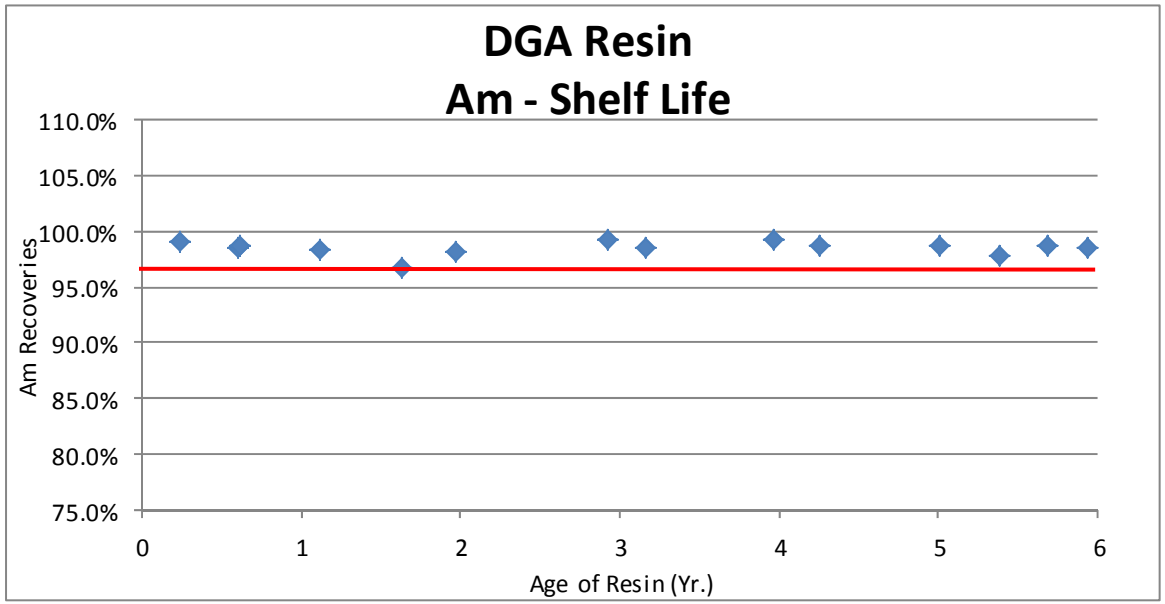

Recovery in 4M HCl

Performed in 2009 on lots from 2000-2008.



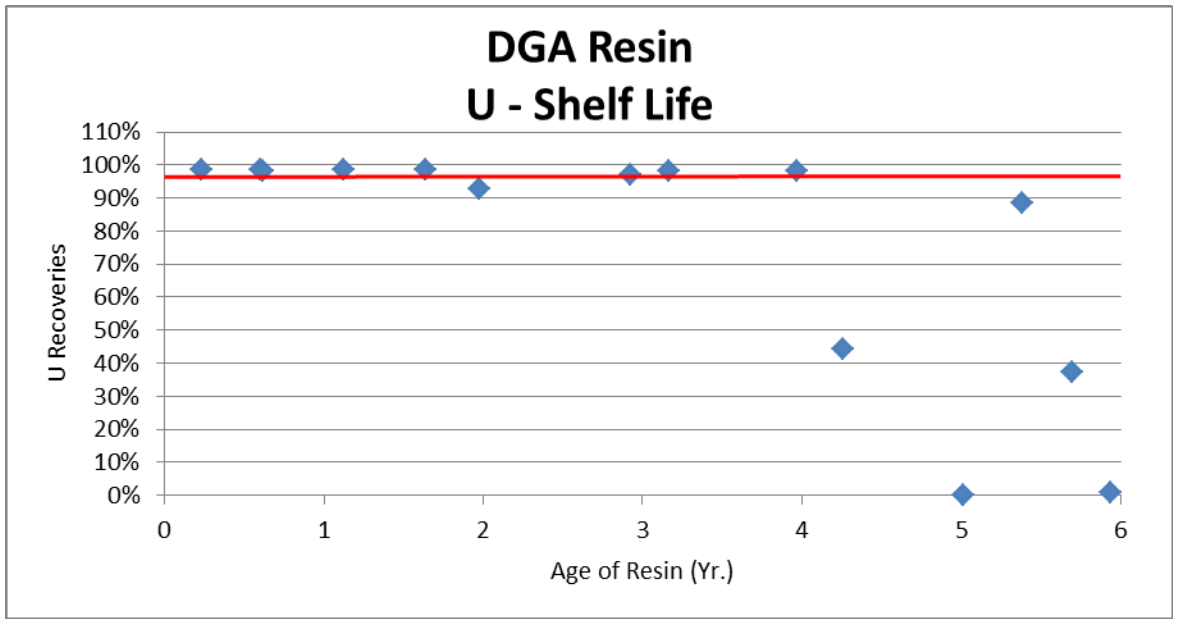

Recovery in 0.1M ammonium bioxalate

# DGA Resin




Recovery in 0.1M HCl

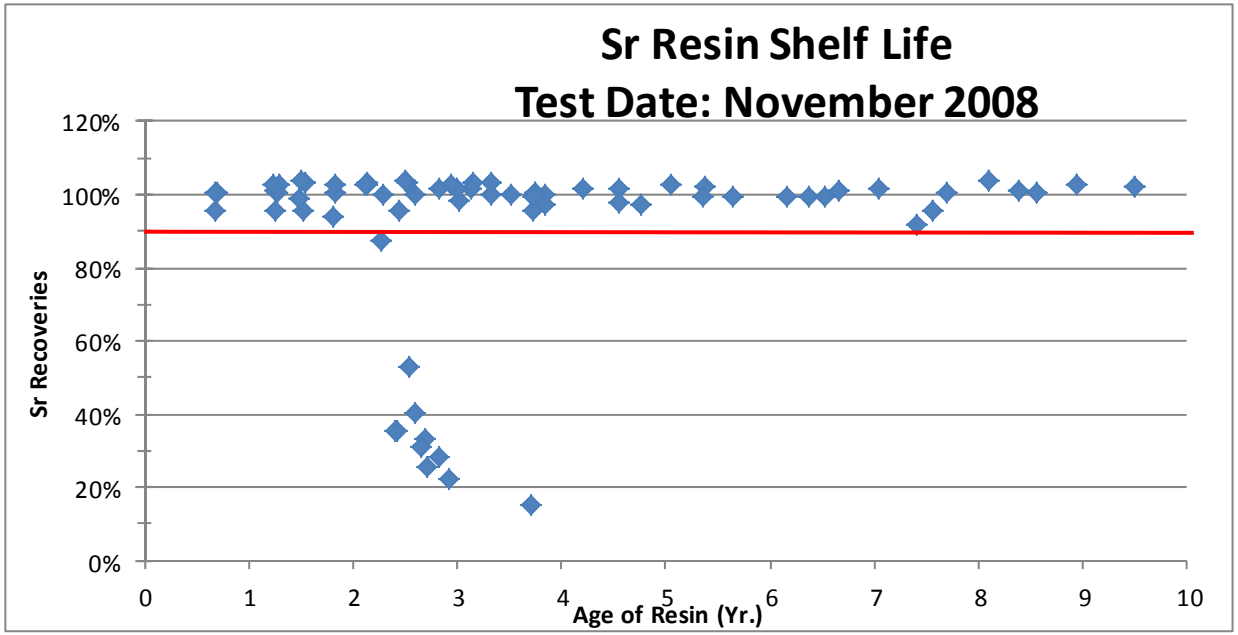
Performed in 2010 on lots from 2004-2010.




Recovery in 0.1M $HNO_3$

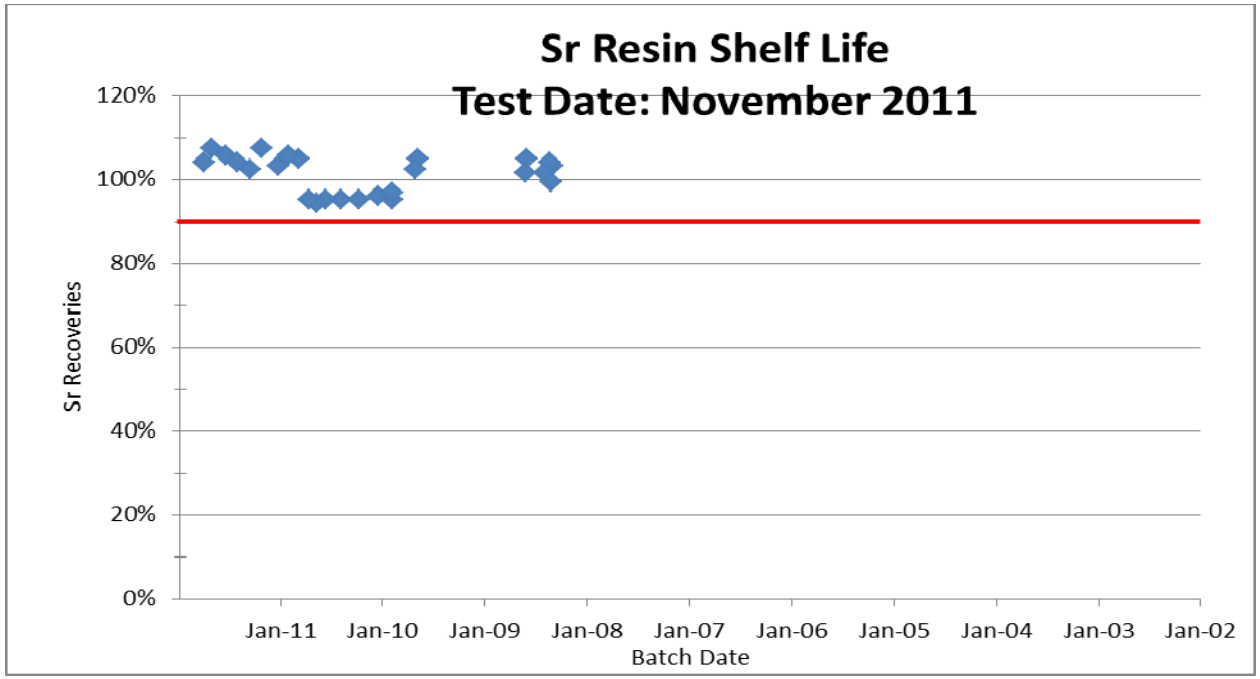
# Sr Resin

# Sr Resin




Recovery in 0.05M $HNO_3$

1998-2007 lots




Recovery in 0.05M $HNO_3$

2008-2011 lots

# Parameters Correlating with failures

1) Bulk Resin (not columns or cartridges)

2) Failure at >1.5 years from production date

3) Exposure to high (>30°C) or low temperature (<4°C).

Testing points to physical issue, not chemical degradation

- loss of 1-octanol diluent (smell)
- waxy/solid crown ether
- re-forumulating resin with recovered crown

# Frequencies of Failures

Original Testing (2008)
December 2005 – June 2006 MAJOR failures

**-8 out of 11 failed after 2 years**

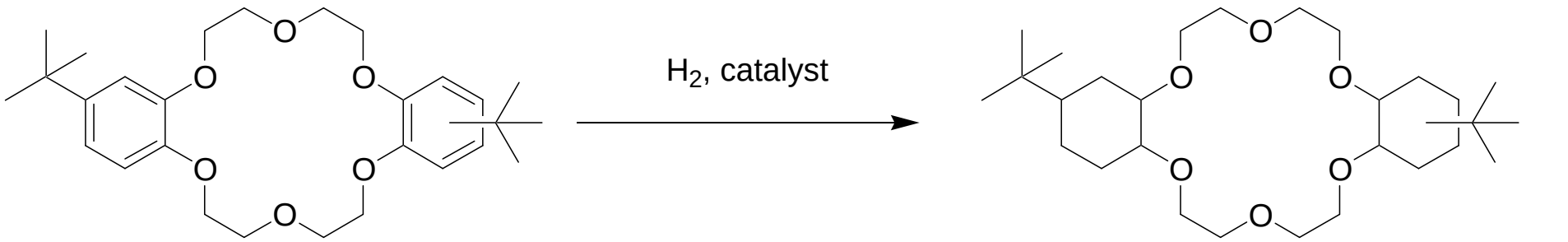
-2007 no failures

2011 Testing

No failures for 2008-2011 lots

Subsequent Testing
2008 2 failures
2009 2 failures
2010 1 failure so far
2011 no failures to date
2012 1 failure
2013 no failures to date
2014 no failures to date

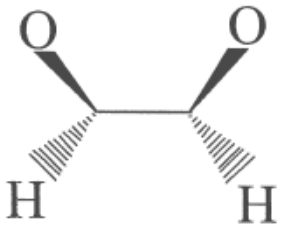
# Sr Resin Production



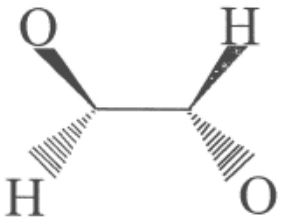

4,4'(5')-di(t-butylbenzo)18-crown-6

4,4'(5')-di(t-butylcyclohexano)18-crown-6

2 isomers with different connectivity of *t*Bu group.

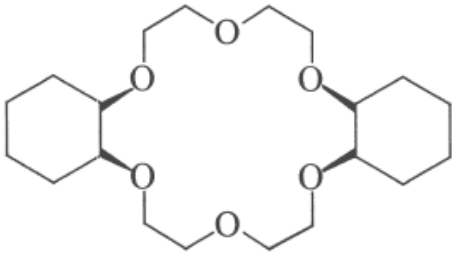



cis

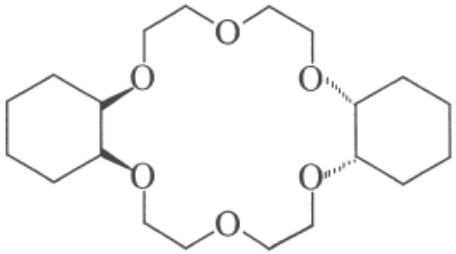



trans

40 possible stereoisomers

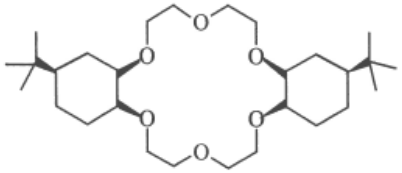


cis-syn-cis-dicyclohexano-18-crown-6

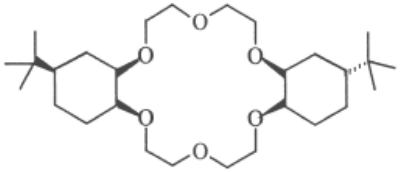


cis-anti-cis-dicyclohexano-18-crown-6

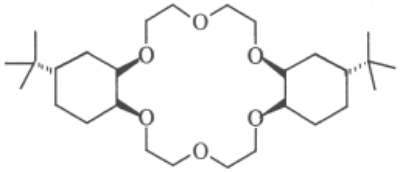
12 cis-cis isomers are predominant.



4(z),4'(z)-cis-syn-cis

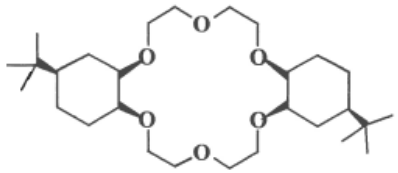


4(z),4'(e)-cis-syn-cis

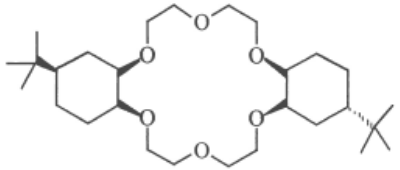


4(e),4'(e)-cis-syn-cis

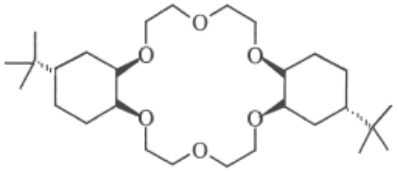
9 cis-cis isomers are responsible for Sr retention



4(z),5'(z)-cis-syn-cis



4(z),5'(e)-cis-syn-cis



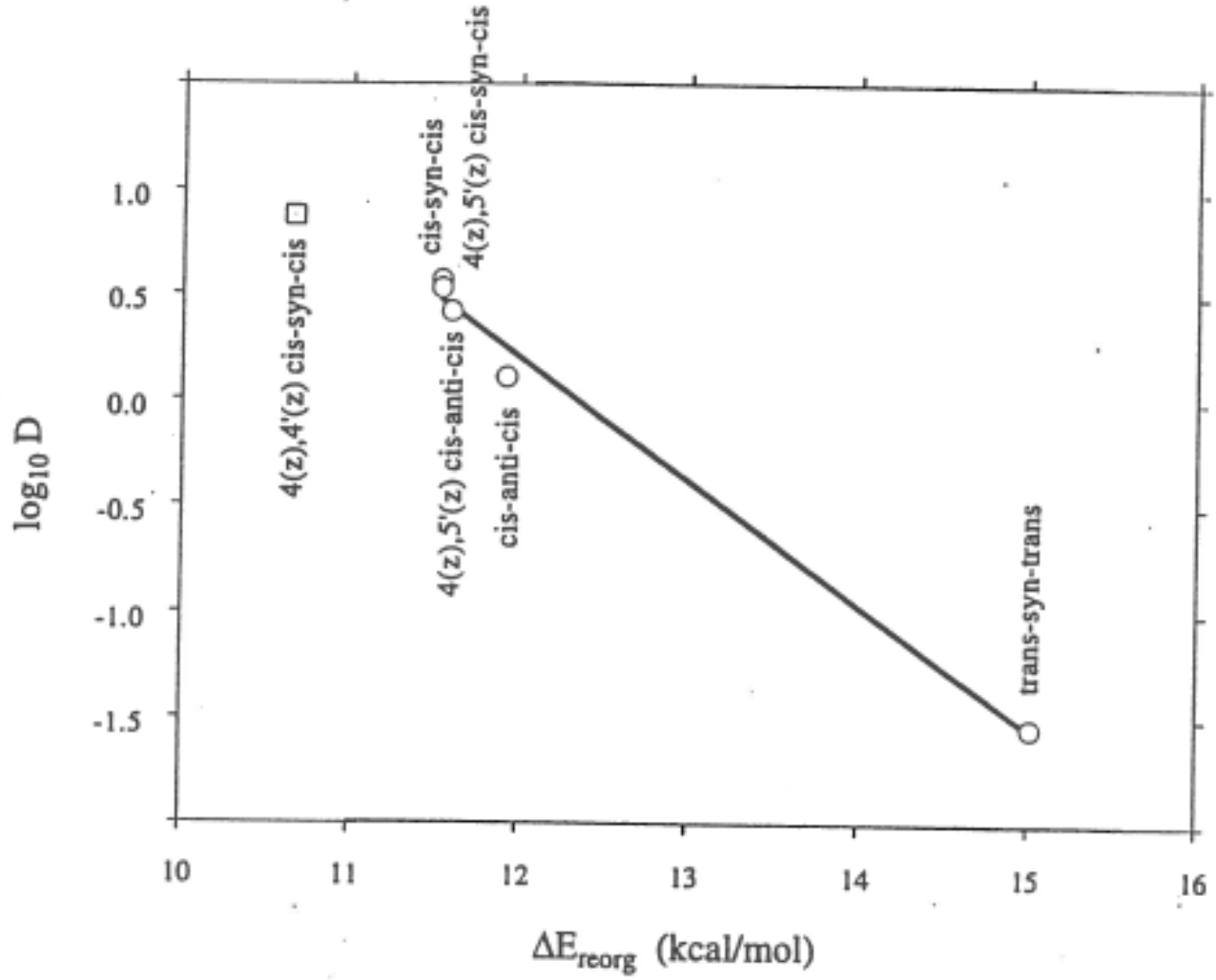
4(e),5'(e)-cis-syn-cis

A. Pawlak, “Crown Ether Stereoisomerism: Implications in Metal Ion Extraction and Ionic Liquid Design, Ph.D. Dissertation, The University of Wisconsin-Milwaukee, May, 2014.

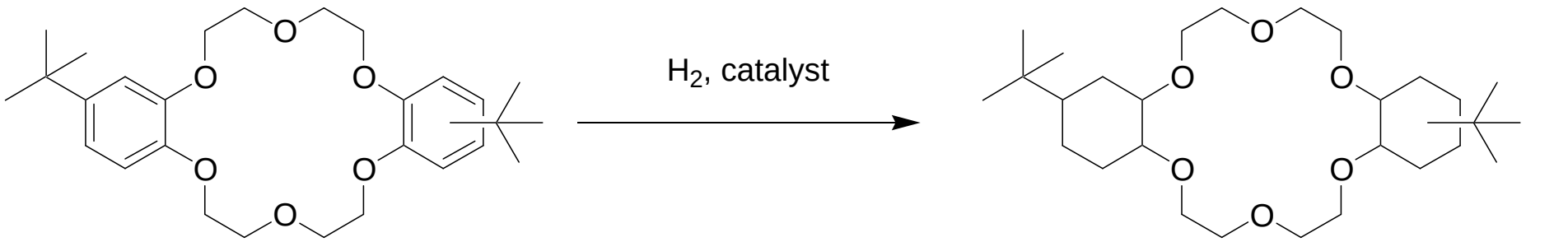
**Table 1.** Predicted $D_{sr}$ at 0.1 M ligand concentration for the n-octanol::1 M nitric acid system.

| | | | |
|---|---|---|---|
| 4(z),4'(z) *cis-syn-cis* | 9.50±1.6 | 4(z),5'(z) *cis-syn-cis* | 3.00±0.5 |
| 4(z),4'(e) *cis-syn-cis* | 5.79±1.0 | 4(z),5'(z) *cis-anti-cis* | 2.77±0.5 |
| 4(e),4'(e) *cis-syn-cis* | 4.93±0.8 | 4(e),5'(e) *cis-anti-cis* | 2.52±0.4 |
| 4(z),5'(e) *cis-syn-cis* | 4.57±0.8 | 4(e),4'(e) *cis-anti-cis* | 0.052±0.009 |
| 4(e),5'(e) *cis-syn-cis* | 3.67±0.6 | 4(z),4'(z) *cis-anti-cis* | 0.064±0.010 |
| 4(z),4'(e) *cis-anti-cis* | 3.21±0.5 | 4(z),5'(e) *cis-anti-cis* | 0.022±0.004 |
| *cis-syn-cis* | 3.00±0.5 | *trans-syn-trans* | 0.028±0.005 |
| *cis-anti-cis* | 1.79±0.3 | *trans-anti-trans* | 0.0004±0.0001 |
| 18-crown-6 | 0.77±0.13 | | |

M. Dietz, et al. "Comparison of Column Chromatographic and Precipitation Methods for the Purification of a Macrocyclic Polyether Extractant, Sep. Sci. Tech., 34(15), 2943-2956 (1999)


log10 D
1.0
0.5
0.0
-0.5
-1.0
-1.5
10
11
12
13
14
15
16
ΔEreorg (kcal/mol)
4(z),4'(z) cis-syn-cis
4(z),5'(z) cis-anti-cis
cis-syn-cis
4(z),5'(z) cis-syn-cis
cis-anti-cis
trans-syn-trans

# Sr Resin Production




4,4'(5')-di(t-butylbenzo)18-crown-6

4,4'(5')-di(t-butylcyclohexano)18-crown-6

1) Small test batch – Dw Sr from 3.1M $HNO_3$

2) Blend crown lots to consistent Dw Sr value (120-130)

3) Full batch - Dw Sr from 3.1M $HNO_3$
- Gravimetric Recovery/Blank Residue
- Stability in 8M $HNO_3$
- Sr Recovery from Ca/Ba/Y matrix

# Recommendations

1) If stockpiling, consider  Sr Resin cartridges or columns

2) Exposure to high (>30°C) or low temperature (<4°C).

3) Tightly seal resin bottles and repackage into smaller containers as necessary.