RRMC
Radiobioassay & Radiochemical Measurements Conference

The University of Iowa

Purity of DGA Normal for Po Separations

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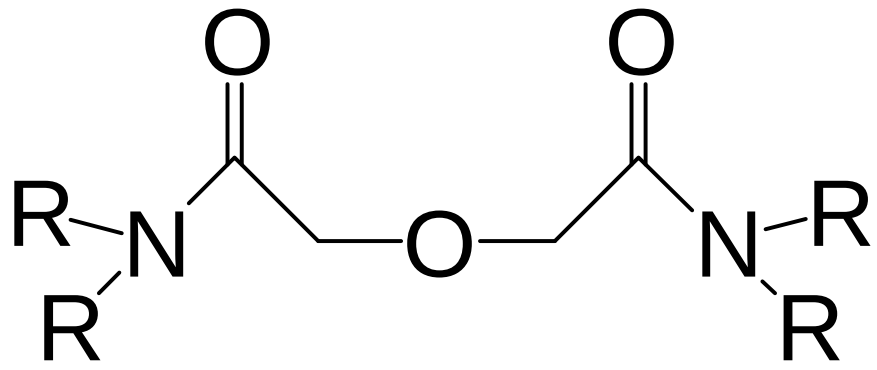
DGA Applications

Rare Earth Separations[1]

Trivalent Actinides[1]

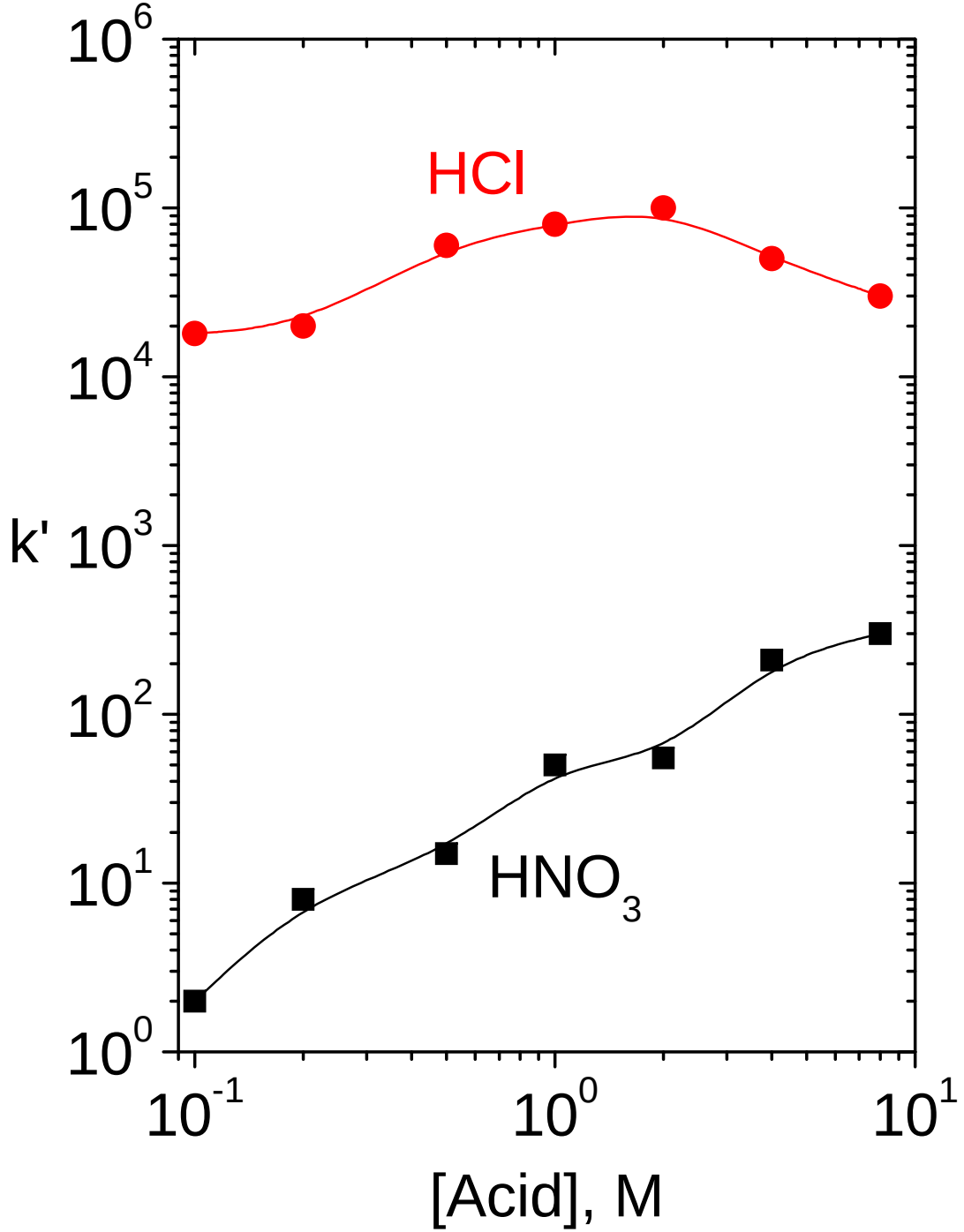
Removal of alpha emitters from Ra[2]

Polonium Separations[3]



[1]Horwitz, McAlister, Bond, Barrans, Jr., *Solv. Extr. Ion Exch.*, 23, 319 (2005)
[2]Maxwell, Culligan, Hutchinson, Utsey, McAlister, *J. Radioan. Nucl. Chem*. 300(3), 1159 (2014)
[3]Mawwell, Culligan, Hutchinson, Utsey, McAlister, *J. Radioan. Nucl. Chem*. 298(3), 1977 (2014)

k' Po on DGA Resin



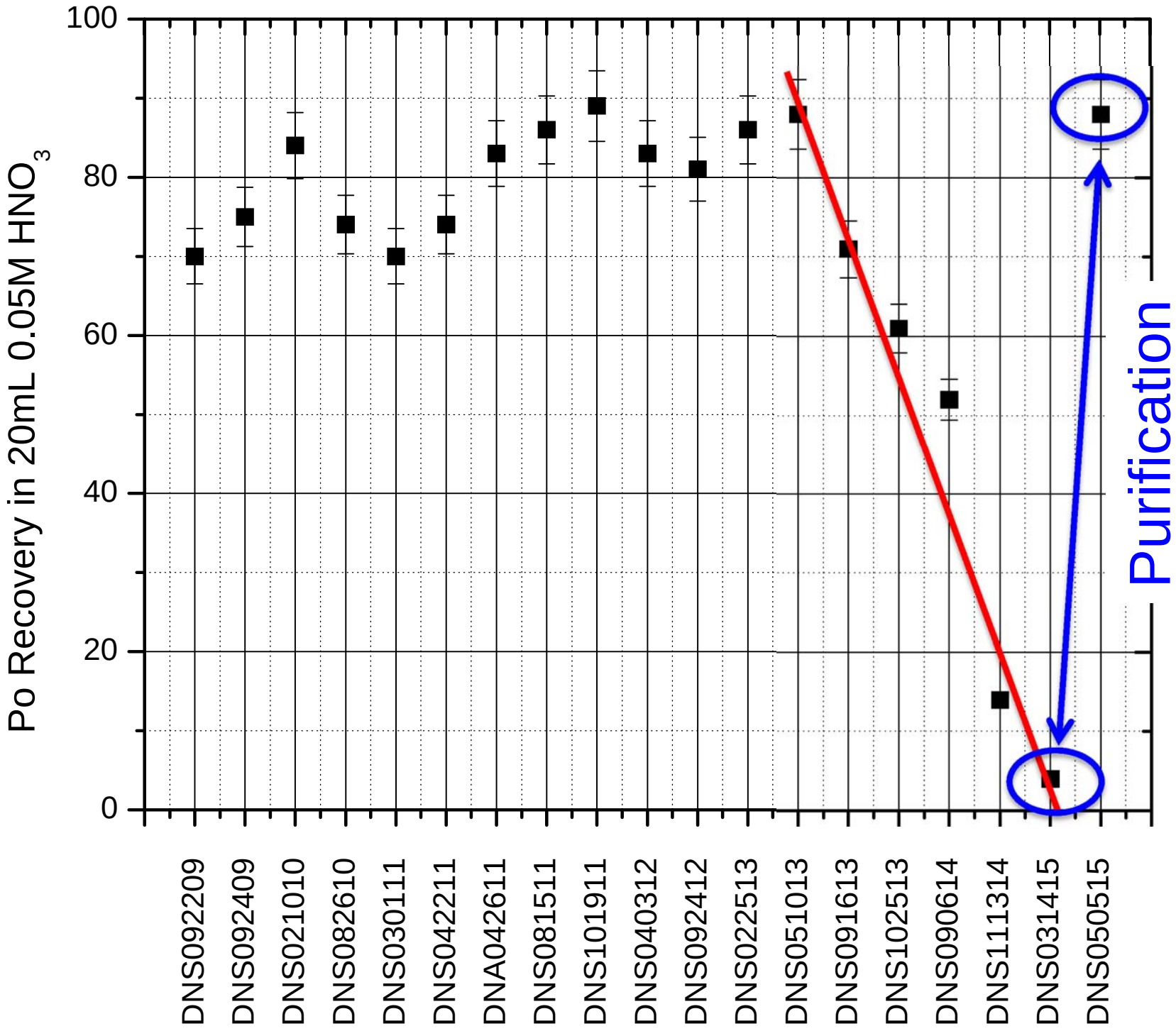
DGA Quality Control

2009 and earlier: Elution of Eu-152 Tracer
Periodic LC-MS

2010-2015: Separation of Am-241 and U-233

2015 and later: Add Po QC test

Polonium Recovery on TODGA



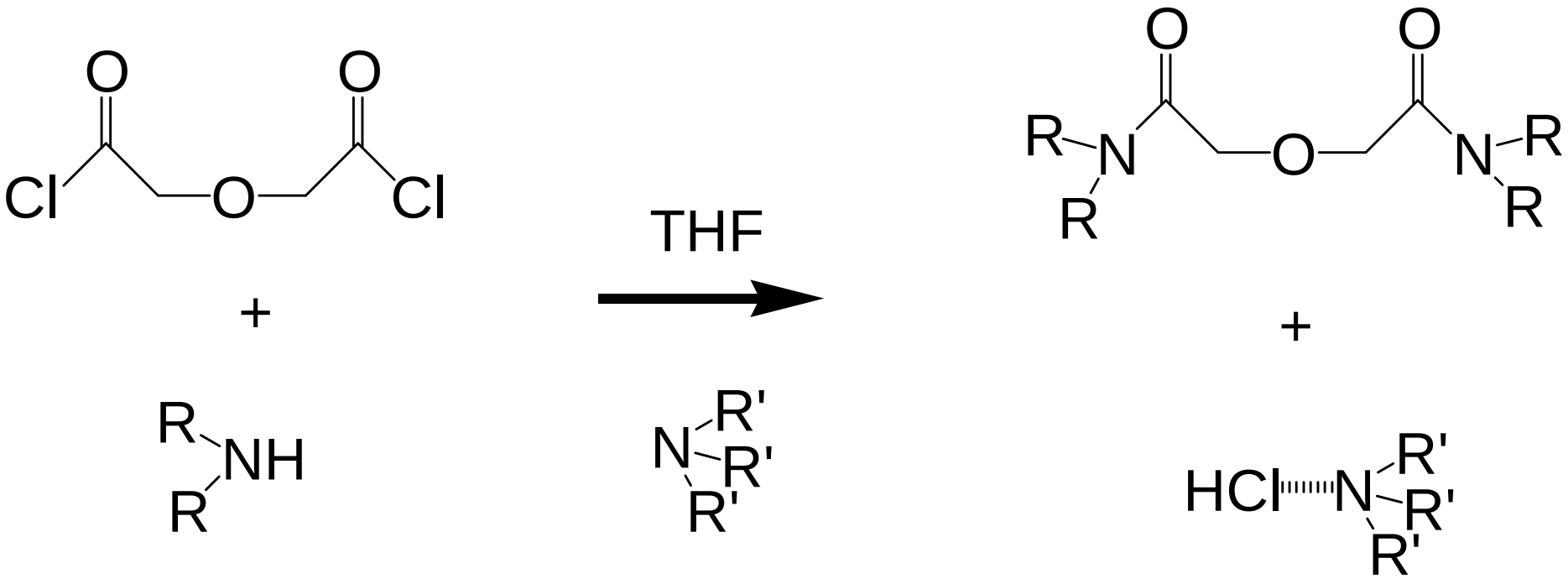
What Changed?

Can we purify?

How do we prevent?

Only Po???

Synthesis of DGA from Diglycolyl chloride (DGC)



Horwitz, McAlister, Bond, Barrans, Jr., *Solv. Extr. Ion Exch.*, 23, 319 (2005)
Sasaki, Sugo, Suzuki, Tachimori, *Solv. Extr. Ion Exch.*, 19, 91 (2001)

Raw Materials

Purchased a large amount of DGC in 2011

- Synthesis Chemist noted darkening of material over time
- Dark material was not a problem in the past
- Dark material persists into final product
- Impurity is heat/pH sensitive

Supplier began packing Dioctylamine in plastic (was glass)

- Plastic containers frost over (amine + air/moisture)

Po issue not observed with TEHDGA

- Is dioctylamine the source of the issue?

Improved Synthesis and Purification

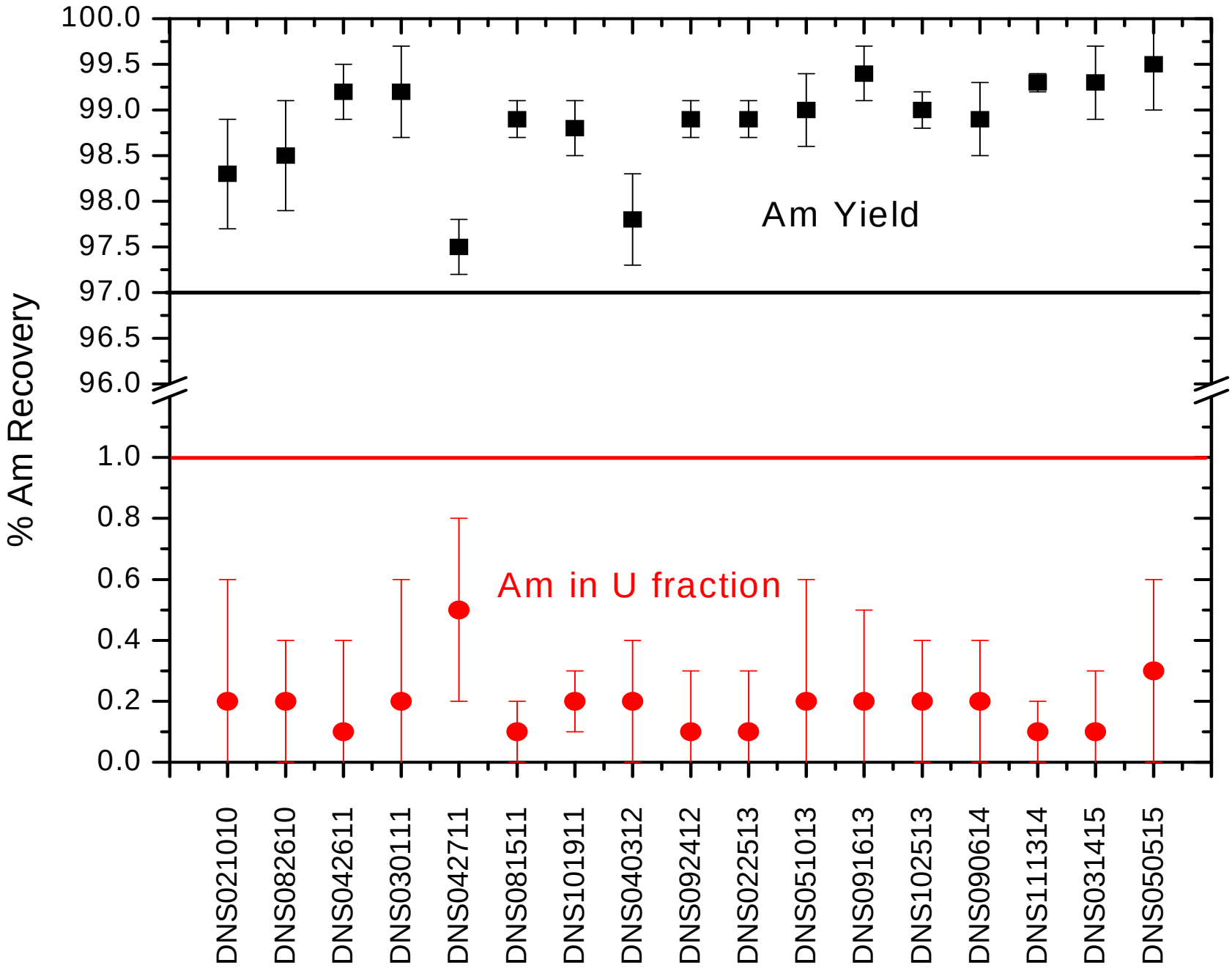
Distill Diglycolylchloride

Distill Dioctylamine

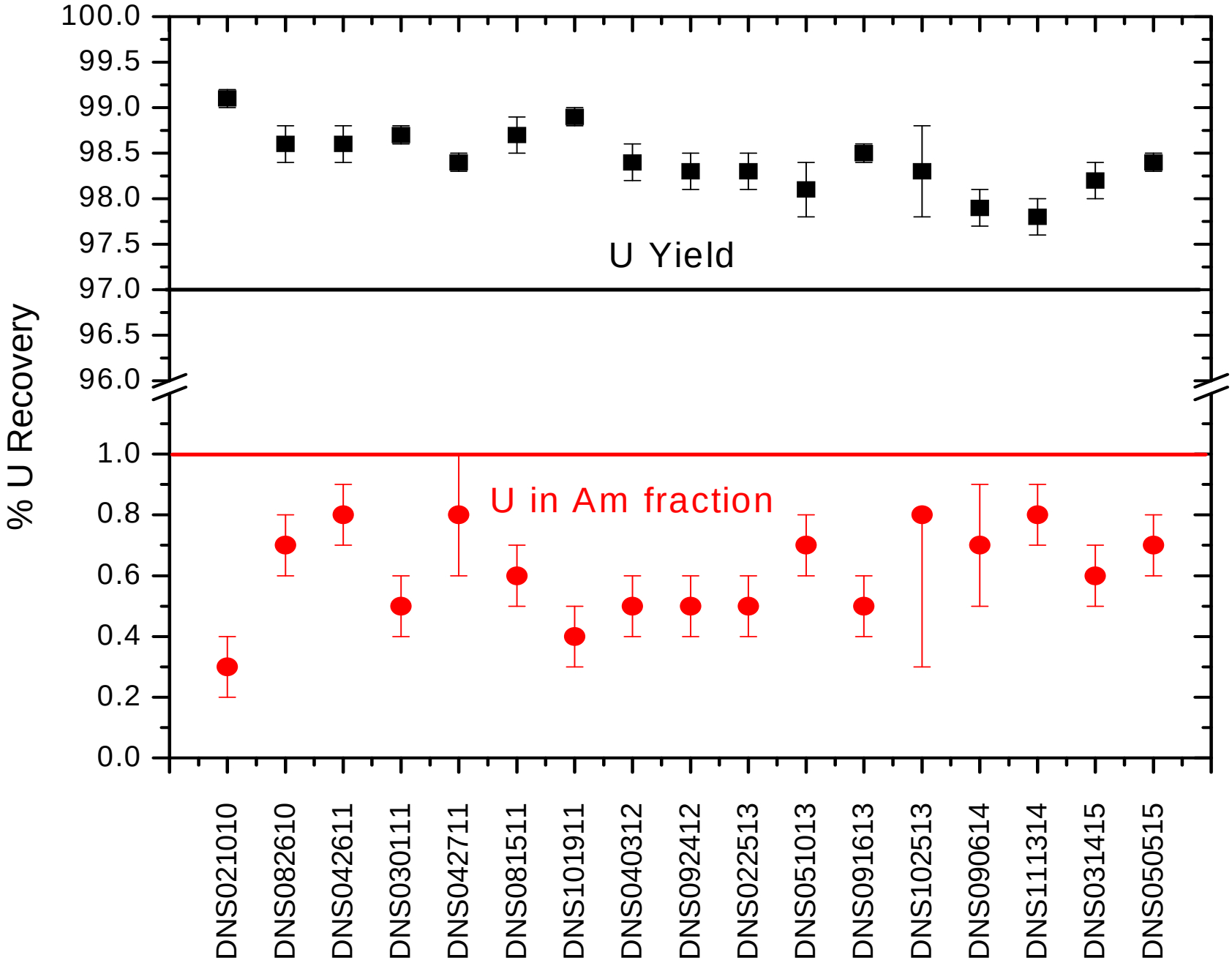
Dry Solvent

Test Po recovery.
Additional purification as necessary.
Full batch and standard QC.

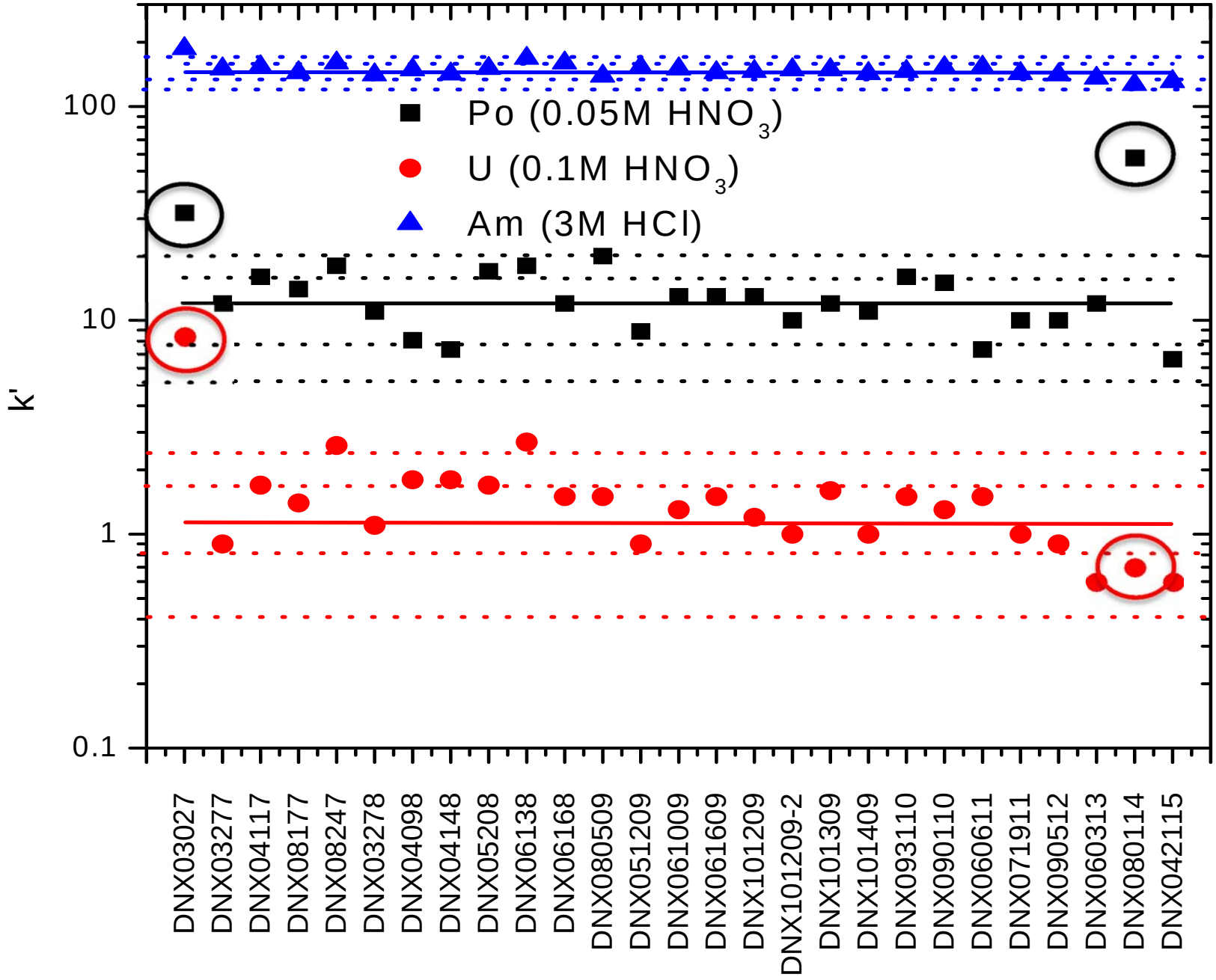
Am in Standard DGA QC



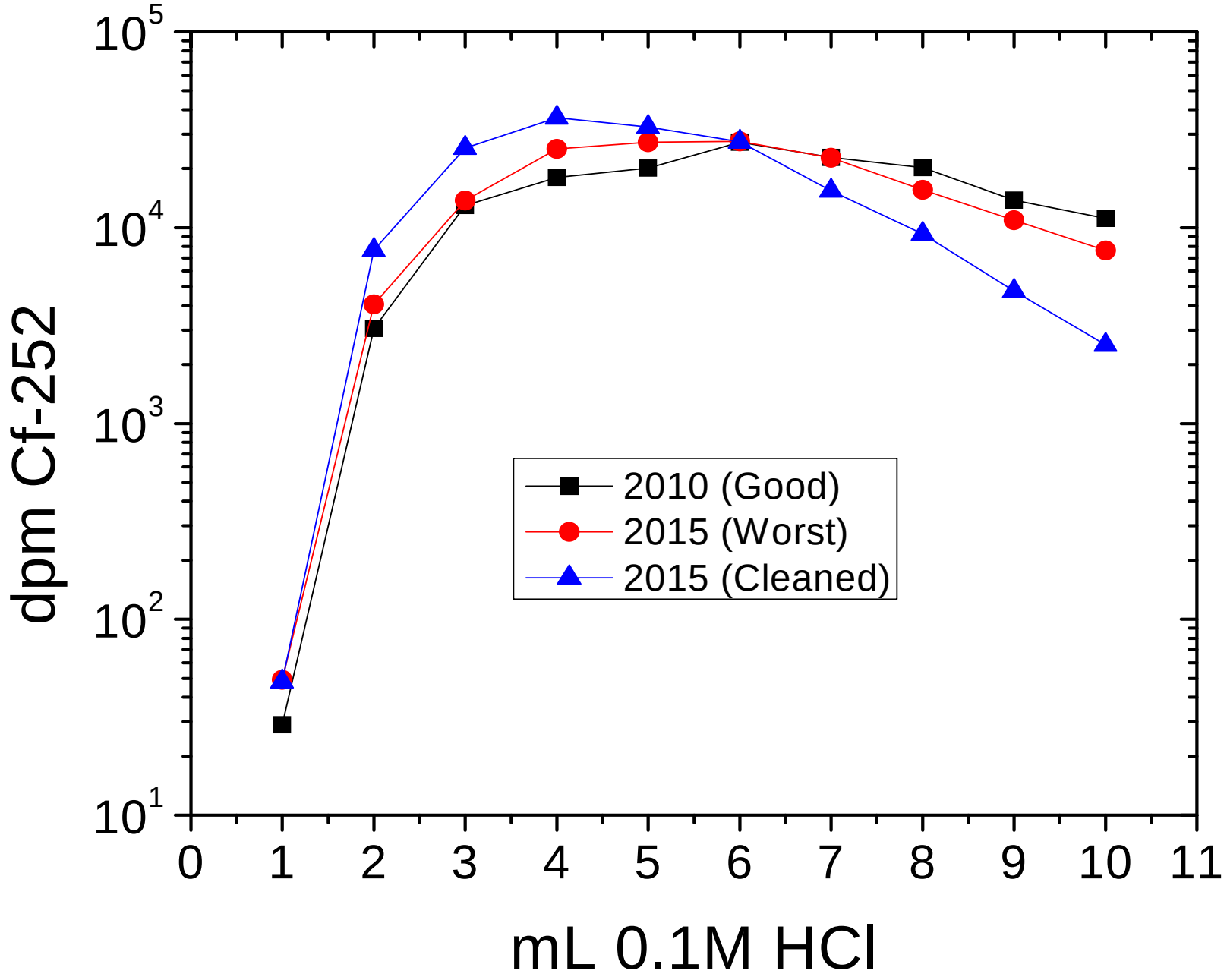
U in Standard DGA QC

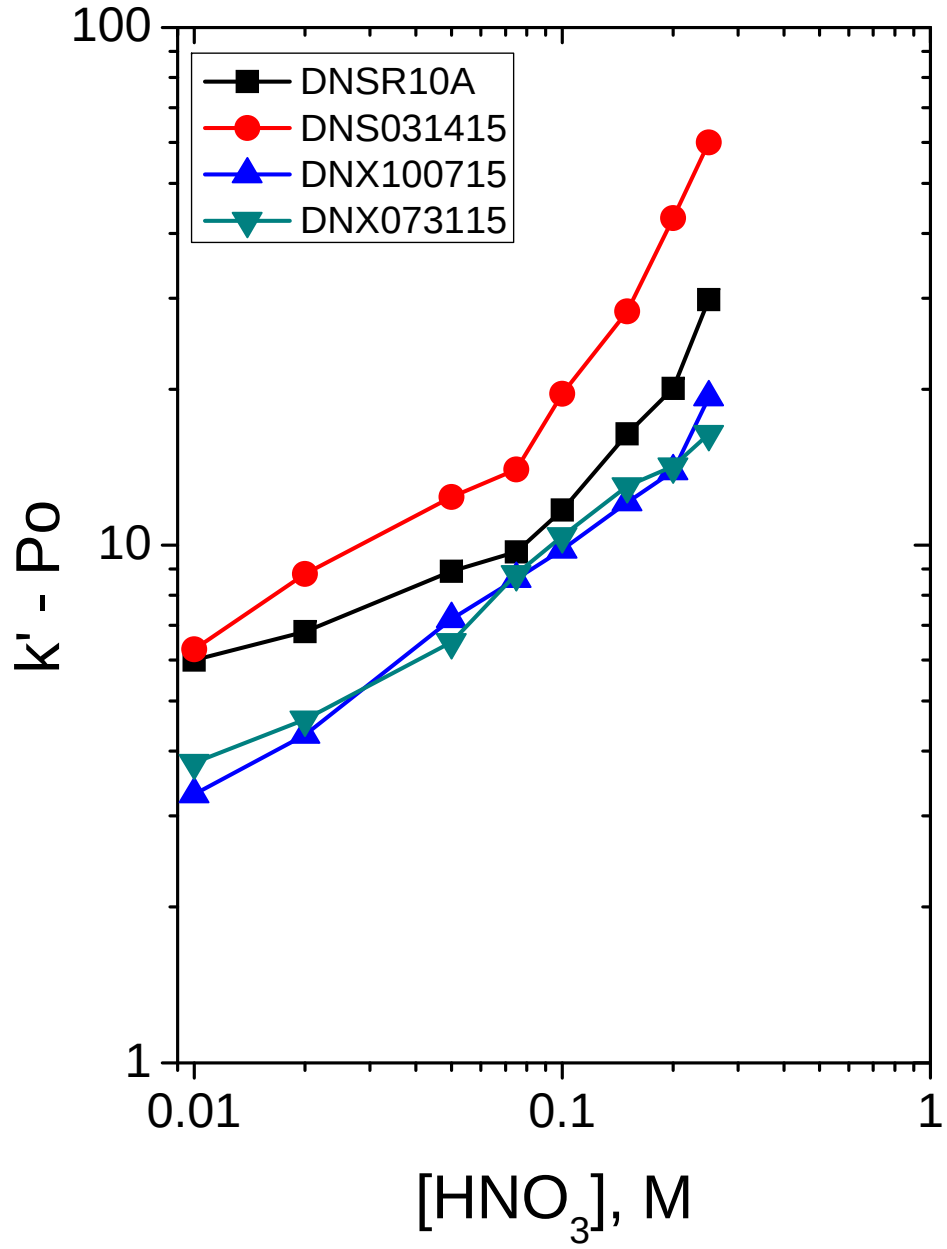


k’ on DGA Resin Lots

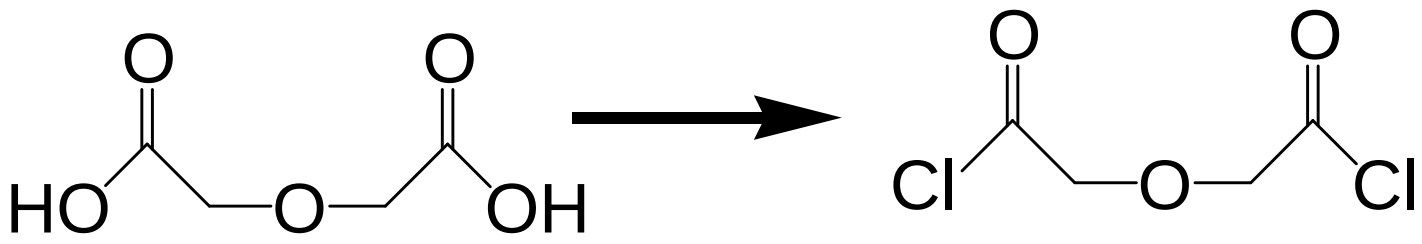


Elution of Cf-252 from 2mL DGA, Normal Cartridges




100
10
1
0.01
0.1
1
k' - P0
[HNO3], M
DNSR10A
DNS031415
DNX100715
DNX073115

Synthesis and Degradation of DGC

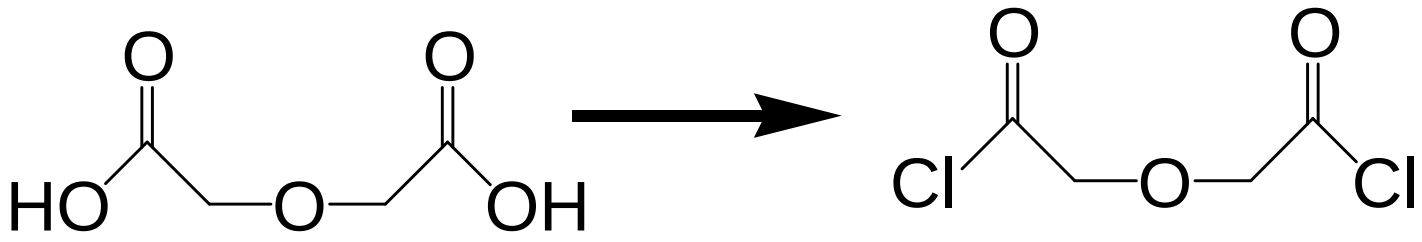


$SOCl_2$ → SO_2 HCl

Aged samples of SO_2Cl_2 develop a yellow hue, possibly due to the formation of S_2Cl_2.

S_2Cl_2 has been used to introduce C-S bonds.

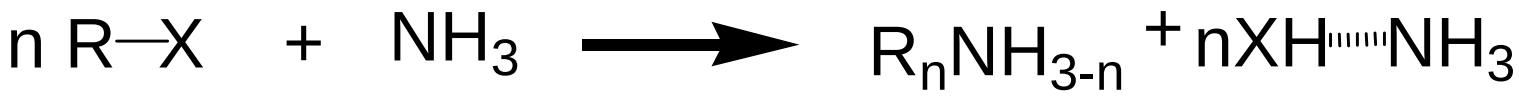
Synthesis and Degradation of DGC



$PCl_3 \longrightarrow H_3PO_4$

$PCl_5 \longrightarrow POCl_3 \quad HCl$

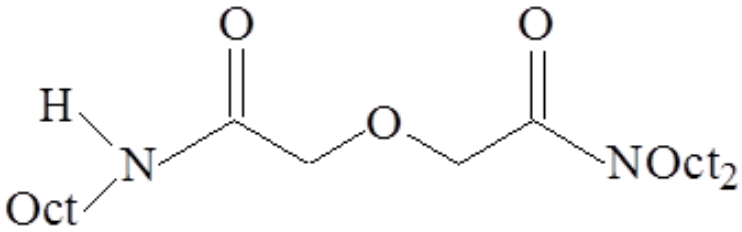
Synthesis and Degradation of Dioctylamine

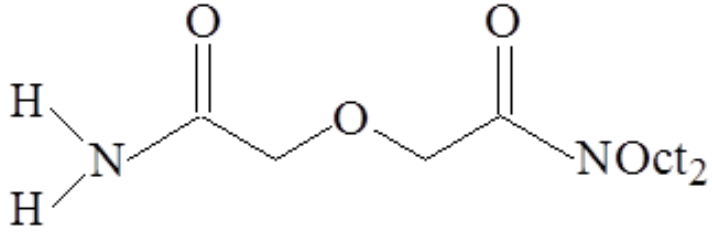


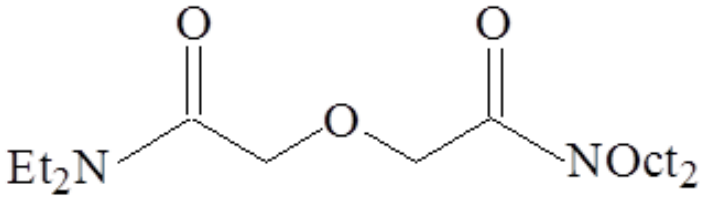
Octylamine impurity?

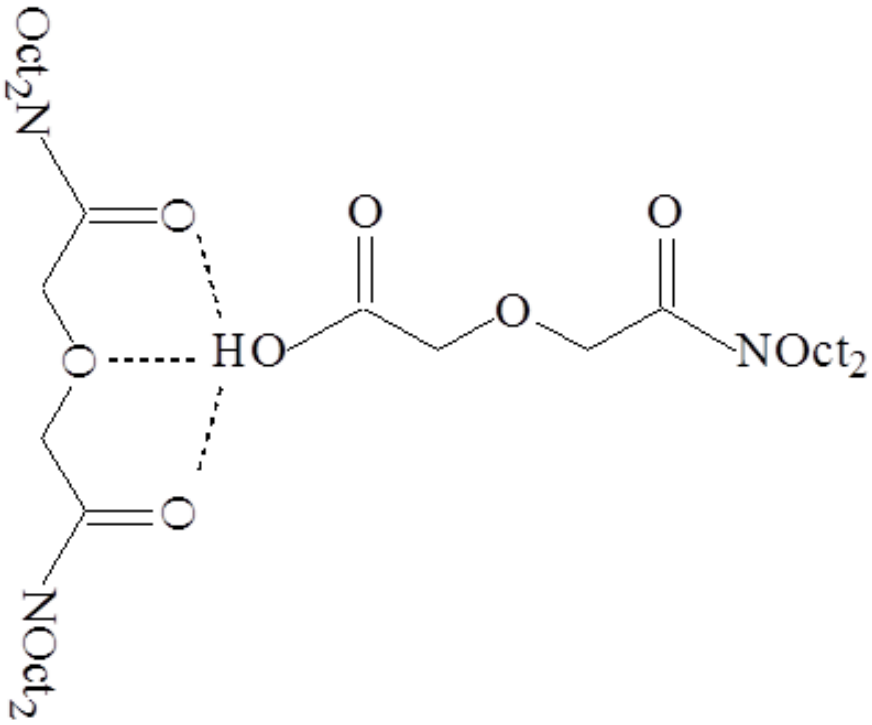
Hydrolysis/Oxidation by air/water?

Common DGA Impurities by LC-MS



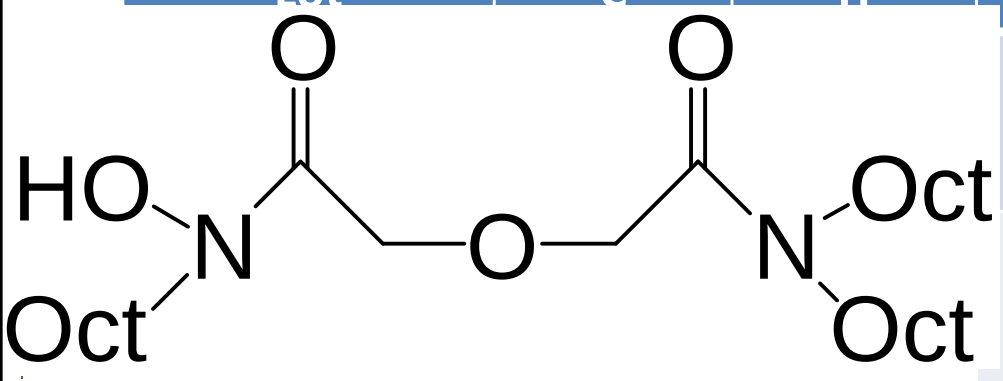






Elemental Analysis of DGA Lots

Lot	(74.4%) C	(12.5%) H	(8.3%) O	(4.8%) N	S	P
Impurity from Column	67.7	11.8	14.3	5.5	<0.05	<25ppm
DNX073115 (NEW DGC)	74.8	12.9	8.4	4.8	<0.05	<25ppm



C = 69.4% O = 13.2%
H = 11.6% N = 5.8%

Summary

- DGA Synthesis and Purification Improved
- DGA QC updated with Po testing
- DGA lots from 2010-2015 tested retroactively
  - Standard Separations
  - Po Separations
    - Only separation affected by impurity
  - Other customer separations (as comments received)
  - Data available upon request