Navy Energetics ManTech Center

Evaluation of a Manufacturing Capability for XU-238

Presenter Patrick Greer, PhD

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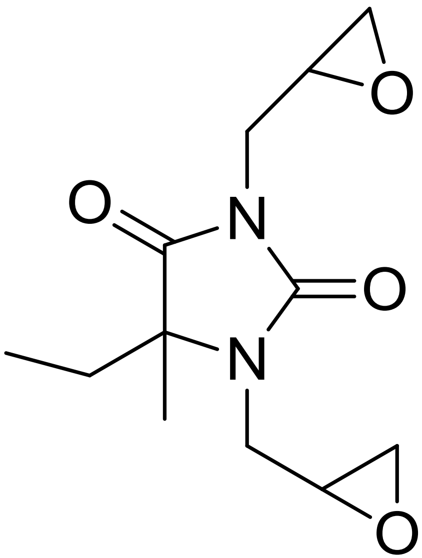
Request from NSWC CAD/PAD Branch:

1,3-diglycidyl-5-ethyl-5-methylhydantoin (XU-238)



- Light yellow viscous liquid
- MW = 254.28 g/mol
- MF = $C_{12}H_{18}N_2O_4$
- BP = >100^{o}C at high vacuum

- XU-238 is an epoxy resin used as a bonding agent in EC-08 propellant.
- EC-08 is used in MK 109 Canopy Jettison Rocket Motor (CJRM) and F-16 CJRM.
- The current CONUS supplier is producing XU-238 and indicated marginal interest in future production.
- CAD/PAD's annual requirement is 8-lb/year.
- IHEODTD was asked to produce a 50g lot for suitability testing in propellant formulation work.

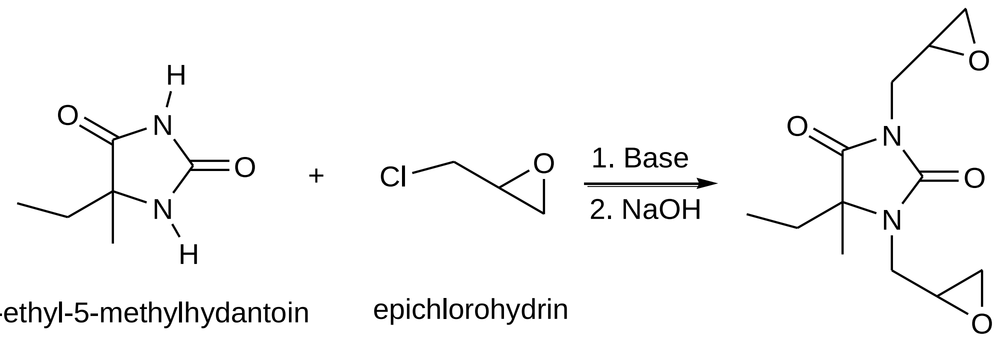
Mil Spec – MIL-R-82657 (OS)

Property	Minimum	Maximum
Specific gravity, 25°C	1.205	1.225
Viscosity, cps, 25°C	550	850
Hydrolyzable chlorine, wt%	-	0.5
Epoxy assay, g/g, mole	95	107
Water content, wt%	-	0.2

- Material was tested via MIL-R-82657 – "Resin, Epoxy, Trifunctional" dated 31 January 1977.
- The material was only tested for epoxy and water content as called out in NAVAIR Drawing No. 1560AS122 (highlighted blue in the table).
- Each test was done in triplicate with the average value reported.

Synthesis

- Synthetic route used was described in a 1967 Great Britain patent, #1148570, “N,N’-diglycidyl compounds and process for their manufacturing and use”.



5-ethyl-5-methylhydantoin

epichlorohydrin

XU-238

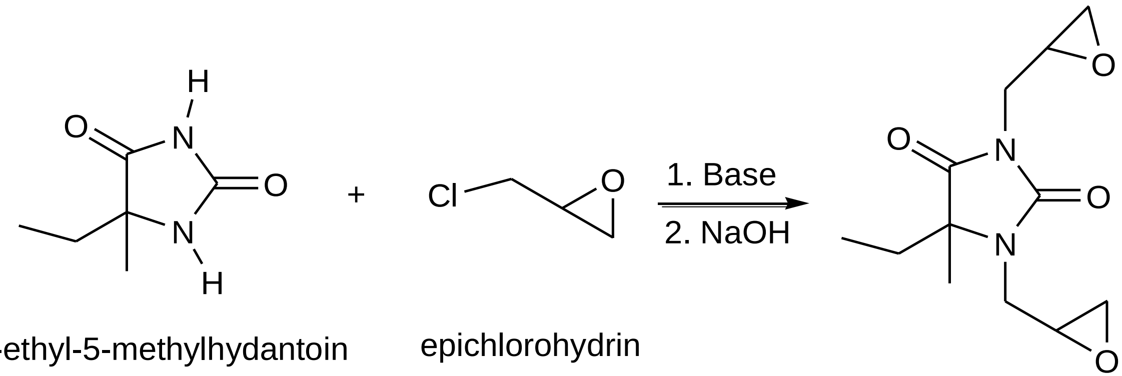
$C_{12}H_{18}N_2O_4$
MW = 254.28

Base: Triethylamine or Benzyltrimethylammonium chloride

- Steps for the procedure are listed below:
  - Epichlorohydrin is both reactant and reaction solvent, with a high mole ratio of epichlorohydrin:hydantoin.
  - Reactants are heated with a base to reflux.
  - Excess epichlorohydrin is removed under vacuum; reaction mixture cooled below reflux; followed by solid sodium hydroxide (NaOH) addition and stirred.
  - Water is removed under vacuum and the resulting residue is filtered removing solids. Epichlorohydrin was used to rinse the filter bed.
  - The filtrate is further dried under vacuum to remove traces of water and epichlorohydrin giving a clear yellow viscous liquid.

Not a scale up friendly process

Synthesis



5-ethyl-5-methylhydantoin + epichlorohydrin → XU-238

XU-238

$C_{12}H_{18}N_2O_4$
MW = 254.28

Base: Triethylamine or Benzyltrimethylammonium chloride

- All reagents were commercially available but 5-ethyl-5-methylhydantoin is expensive and may be not be readily available in large quantities from common CONUS chemical vendors.
  - 50g cost $1080.00 ($21.60/gram) from Sigma-Aldrich (bulk order).
- Due to time constraints, triethylamine was not tested nor was optimization of the molar ratio of excess epichlorohydrin studied.

Synthesis – 1g Scale

- Two runs were completed on 1 gram scale with modifications to the patent's procedure.

- The high mole ratio of epichlorohydrin:hydantoin was maintained.

- Reactants were heated with benzyltrimethylammonium chloride and the reaction progress was monitored by HPLC.
  - Hydantoin compound was converted to an intermediate once the reaction reached reflux.

- Reaction was cooled below reflux followed by solid NaOH addition. Heating continued until the intermediate was not observed by HPLC. White solids (assuming NaCl) immediately precipitated during NaOH addition.

- White solids were filtered using a Celite bed to help quickly filter the reaction mixture. Acetone was used to rinse the filter bed instead of epichlorohydrin.

- Excess epichlorohydrin/acetone was removed under vacuum and heating resulting in a clear yellow viscous liquid.

- Crude yields for both runs were 86% and ~100% with expected yield of 1.78g.

- Both runs passed epoxide testing.

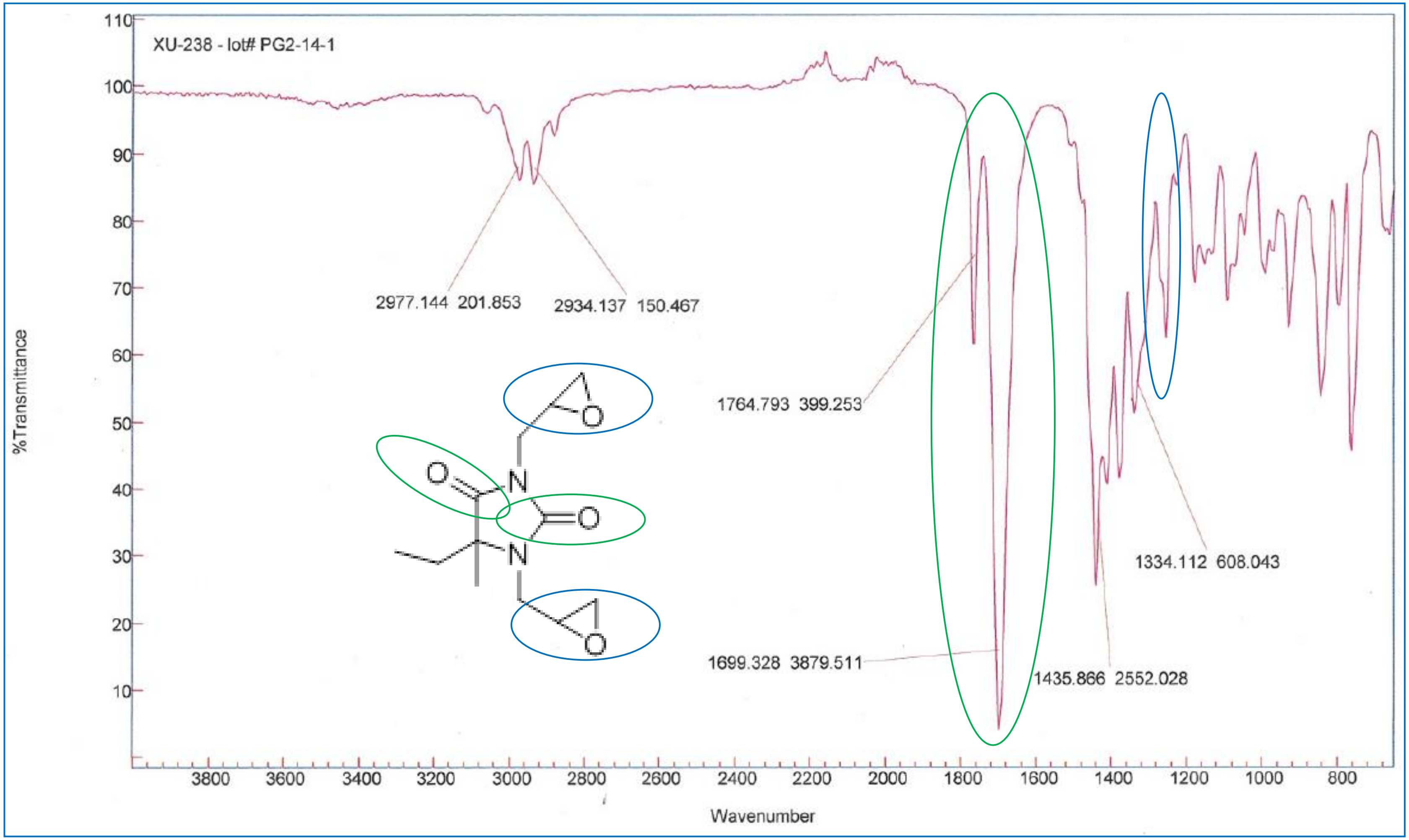
- Not enough material was available water content testing.

Test	Spec.	PG2-6-1	PG2-14-1
		Crude	Crude
Epoxide Eqv. (eq./100g)	0.71 - 0.81	0.76	0.75
Water (Wt. %)	0 - 0.1	N/A	N/A

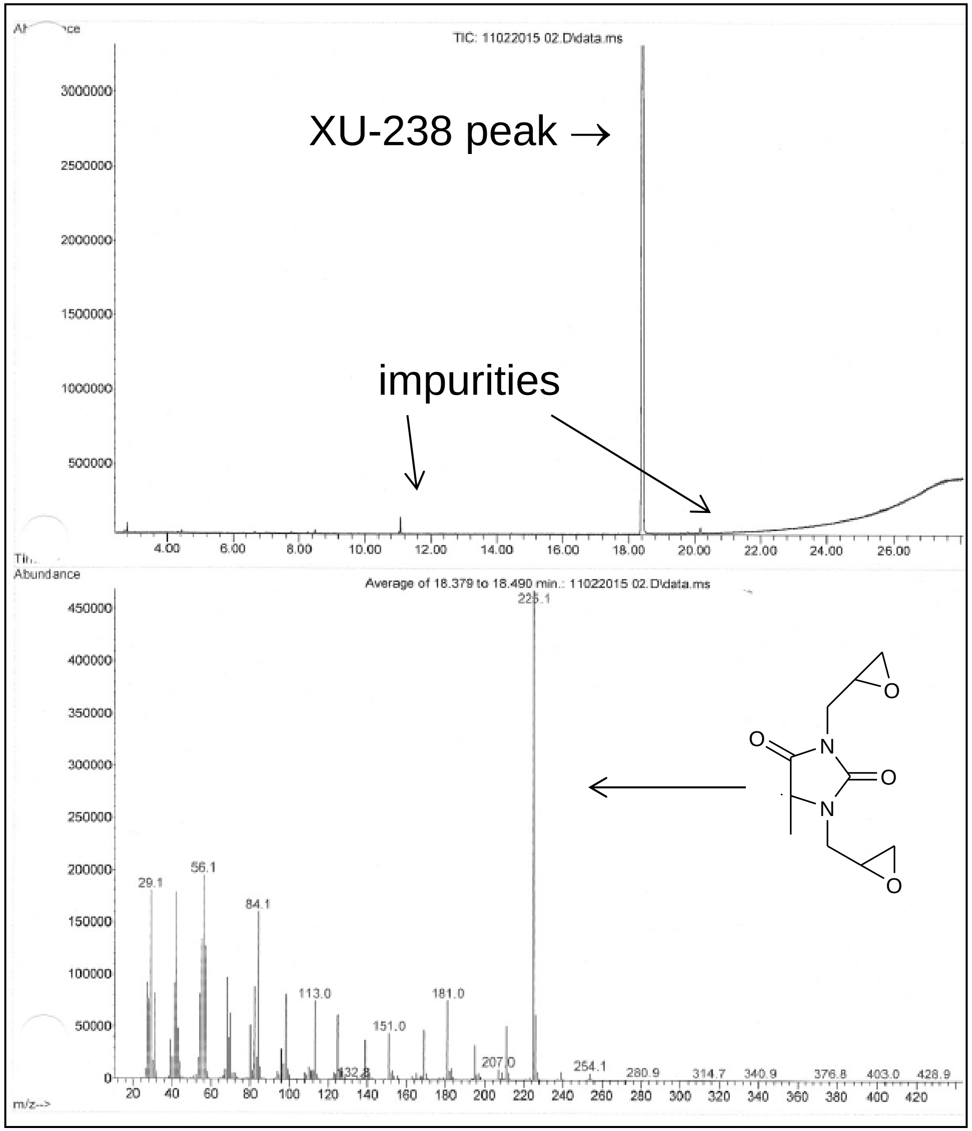
Key: Pass | Fail

Analytical Data - IR

- Infrared (IR) analysis shows peaks for the carbonyl group (1764 and 1700 cm^{-1}) and epoxide ring (~1250 cm^{-1}).

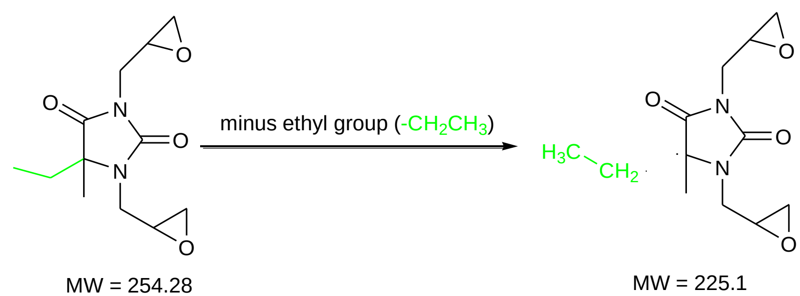


Analytical Data – GCMS



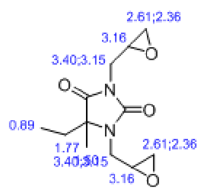
- GC-MS shows crude material to be clean with a few minor impurity peaks.

- The mass fragment peak at 225 indicates XU-238 minus the ethyl group.

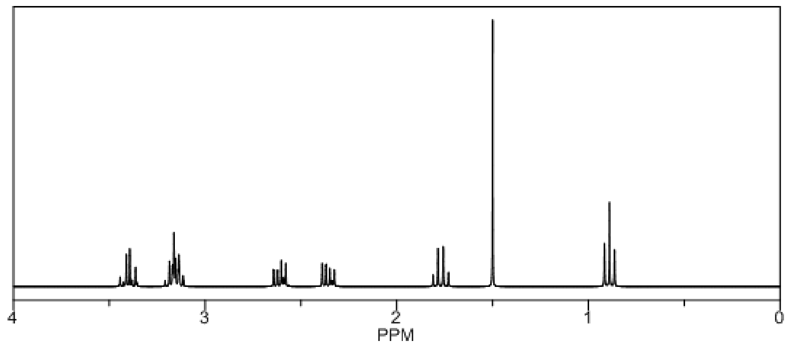


Analytical Data – HNMR

ChemNMR ¹H Estimation



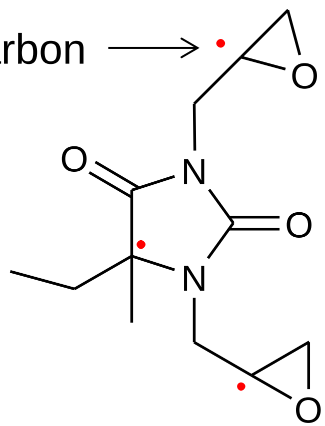
Estimation quality is indicated by color: good, medium, rough



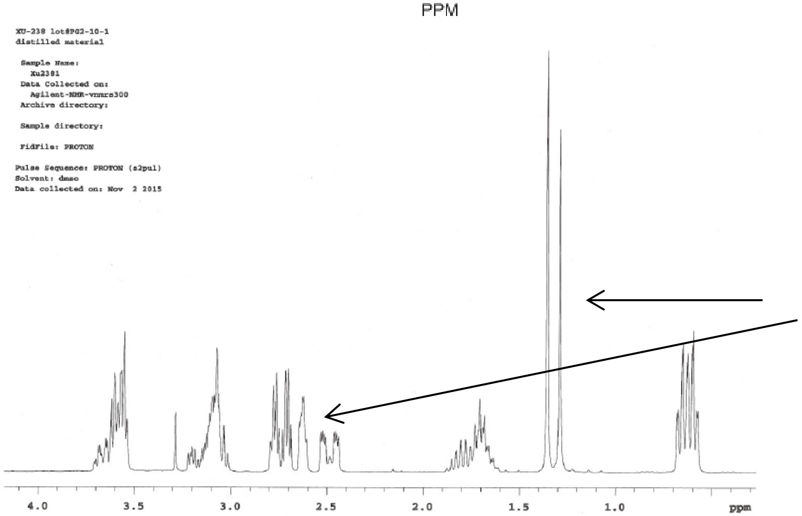
^{1}H NMR ChemDraw™ predictor result for XU-238.

- Does not take into account for chiral carbon atoms shown by red dots.

chiral carbon



The presence of chiral carbons produces racemic and/or diastereomers products. Mixture may contain up to 8 different conformations of XU-238



Diastereomers produce extra peaks in the HNMR.

Epichlorohydrin and the hydantoin were purchased as racemic mixtures thus producing diastereomers.

Synthesis – 5g Scale

- Only 1 run was completed on 5g scale using the procedure developed on 1g scale.
  - The high mole ratio of epichlorohydrin:hydantoin was maintained.
  - By HPLC, the hydantoin compound was converted to the intermediate once the reaction reached reflux.
  - Reaction was cooled below reflux followed by solid NaOH addition. White solids (assuming NaCl) immediately precipitated during NaOH addition.
    - Added NaOH in portions, small exotherm was observed (~2^{o}C) with each addition.
  - White solids were filtered using a Celite bed followed by acetone rinses to remove any leftover product.
    - Acetone washes removed the bulk of the product during filtration.
    - The Celite bed was re-filtered on a fresh bed of Celite with extra washes of acetone – <100mg of product was obtained.
  - Excess epichlorohydrin/acetone was removed under moderate vacuum and heating, then further treated with high vacuum resulting in a clear yellow viscous liquid.
  - Crude yield was obtained but data is not available. Expected yield was 8.94g.
  - Material was sent for epoxy and water content testing
    - Passing results were obtained.
    - IR and GCMS matched with previous results.

Test	Spec.	PG2-16-1
		Crude
Epoxide Eqv. (eq./100g)	0.71 - 0.81	0.74
Water (Wt. %)	0 - 0.1	0.02

Synthesis – 10g Scale

- Four 10g scale runs were completed using the procedure developed on 5g scale.
  - Same reaction conditions and isolation procedure were applied to each run with no problems observed.
  - Expected mass yield was 17.89 grams per batch. A total of 71.5g of a light yellow viscous liquid was obtained.

Batch #	Crude wt. (g)	Crude yield %
1	18.96	106
2	18.89	106
3	20.74	116
4	20.46	114

  - IR data from each run matched very well with previous lots.

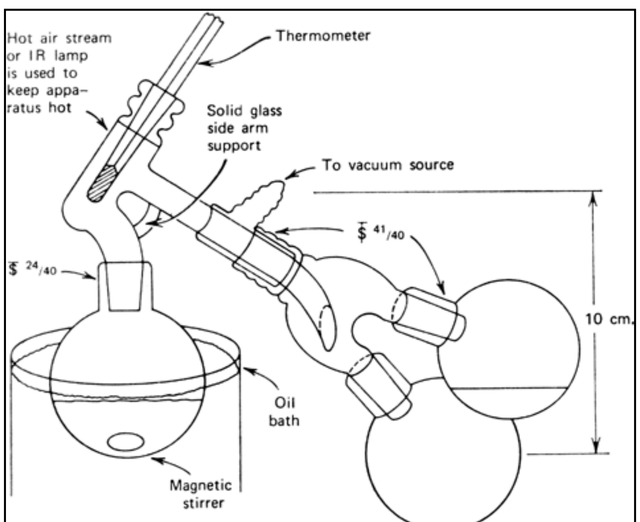
- Crude material was not tested for epoxy and water content.
  - High crude percent yields indicate that epichlorohydrin and/or acetone may still be present because of the viscous nature of XU-238.
  - Epoxy testing requires ~2.2g and water content requires 6g of XU-238 for three trials. Concerned about using too much material for testing and not able to deliver the 50g deliverable if testing failed.
  - A distillation technique was needed to further purify the material for passing Mil Spec results.

Short Path Distillation

- Literature search on different types of hydantoin compounds have describe the use of distillation for purification.

- Short path distillation is a technique to distill high boiling, thermally sensitive compounds at low vacuum pressures and temperatures.
  - Quick method to determine the boiling point of a compound and to observe any decomposition.

- A short path distillation technique was tested on a sample of XU-238 to determine if pure XU-238 could be obtained and at what percent recovery.



XU-238 - 55 Gallon Drum

- Summer 2015 - During an inventory inspection, a full 55 gal drum of XU-238 was discovered.

- XU-238 was purified using short path distillation.
  - A clear light yellow viscous liquid was collected at >100ºC at low vacuum pressure.
  - A 69% recovery was obtained from 21.3g of starting XU-238.
  - Further optimization was not studied at the time.

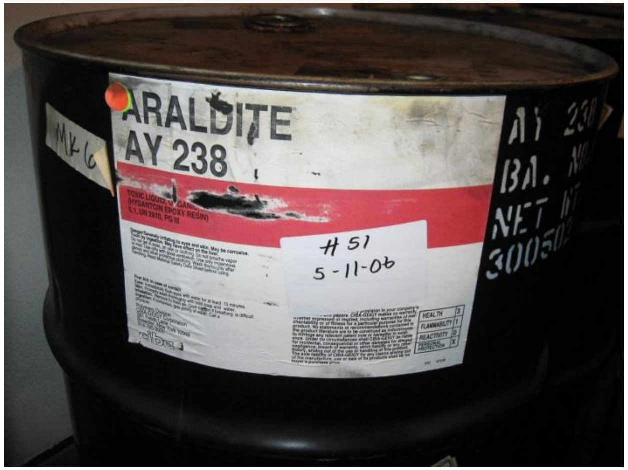
- Material was tested for water content and epoxy:

Test	Spec.	Drum XU-238	
		Sampled Crude	PG2-10-1 Pot Distillation
Epoxide Eqv. (eq./100g)	0.71 - 0.81	0.66	0.78
Moisture (Wt. %)	0 - 0.1	0.03	0.02

- Drum material remains in storage awaiting for further distillation experiments to optimize the process.

  - If future distilled lots pass tests, material will be sent for formulation study for suitability.

  - The distilled material will also be re-packaged, purged with an inert gas and stored for future use.

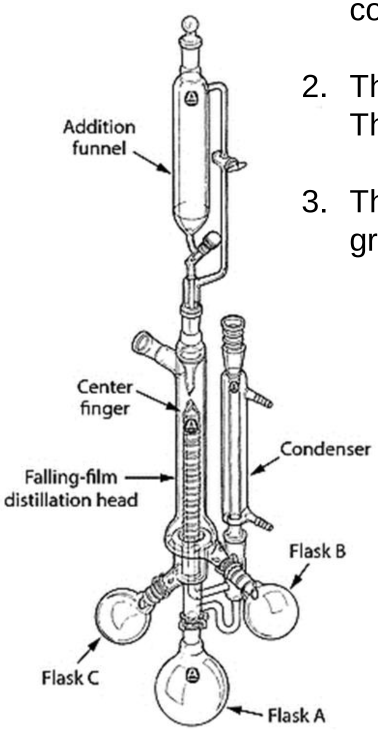


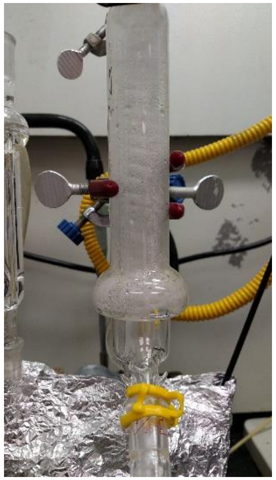
Falling Film Distillation

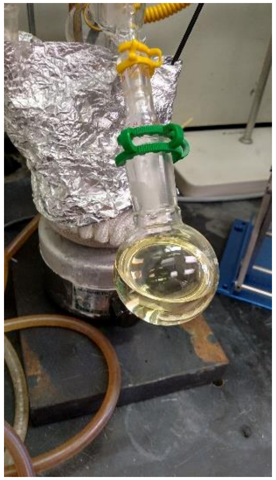
- A disadvantage of short path distillation is that not all material in the flask gets distilled.
  - Higher distillation temperatures are needed to “drive” the process but may decompose material at the same time.

- Falling film distillation adds the material to a heated center finger for a brief period of time, avoiding potential decomposition. The material being distilled is typically added at room temperature with or without vacuum pressure.

1. Flask A is filled with the solvent desired and heated to reflux. The boiling solvent vapor maintains a constant temperature at the center finger which is the distillation temperature.
2. The material is added by addition funnel or pump and allowed to drip onto the heated center finger. The volatilized material will condense on the outer air-cooled wall and collect in Flask B.
3. The high boiling material will remain on the center finger and flow down the spiral into Flask C by gravity.







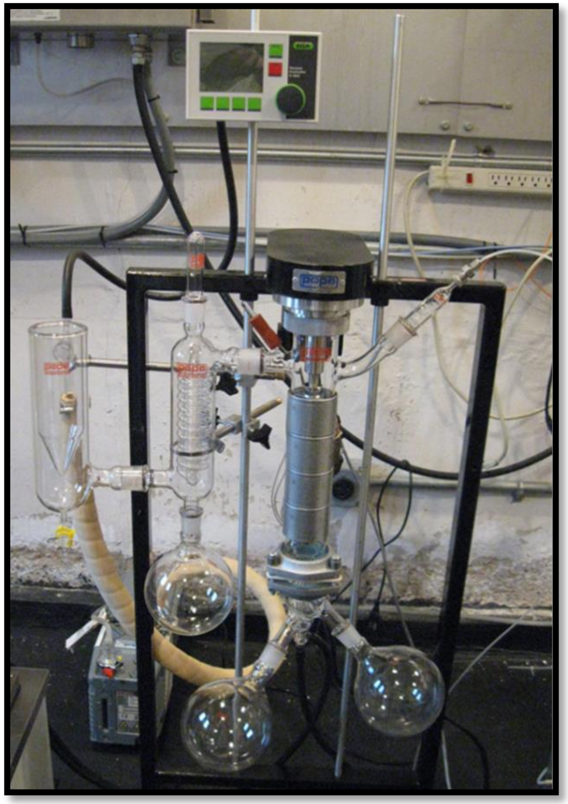
Falling Film Distillation

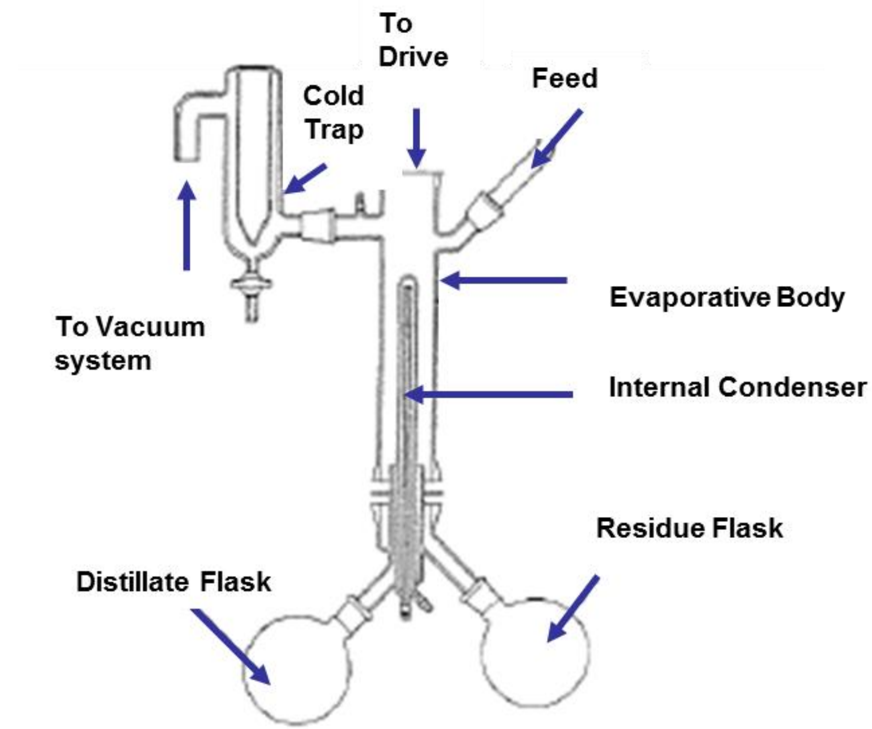
Falling film - clip 1.mp4

Falling film - clip 2.mp4

- 68g of crude XU-238 was distilled with 64g of purified XU-238 collected (93% distillation recovery).
- Very little crude XU-238 was leftover in the fee`d flask, most material was in the feed line.
- Distilled material was light yellow viscous liquid matching all previous analytical data.
- No decomposition losses.

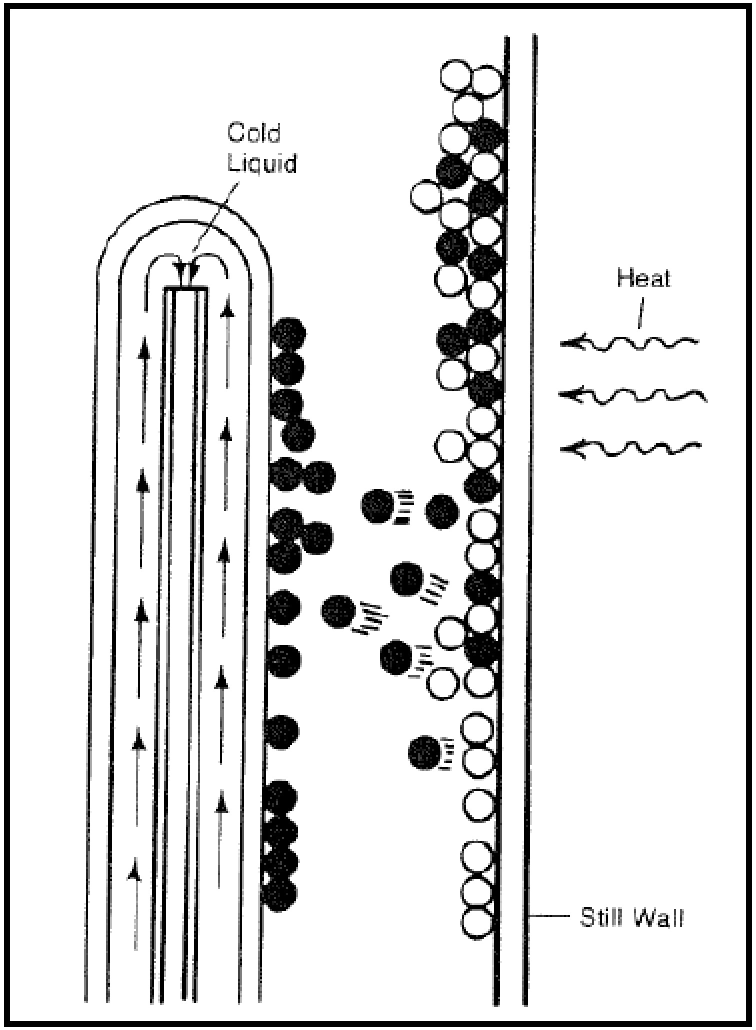
Wiped Film Evaporator (WFE)

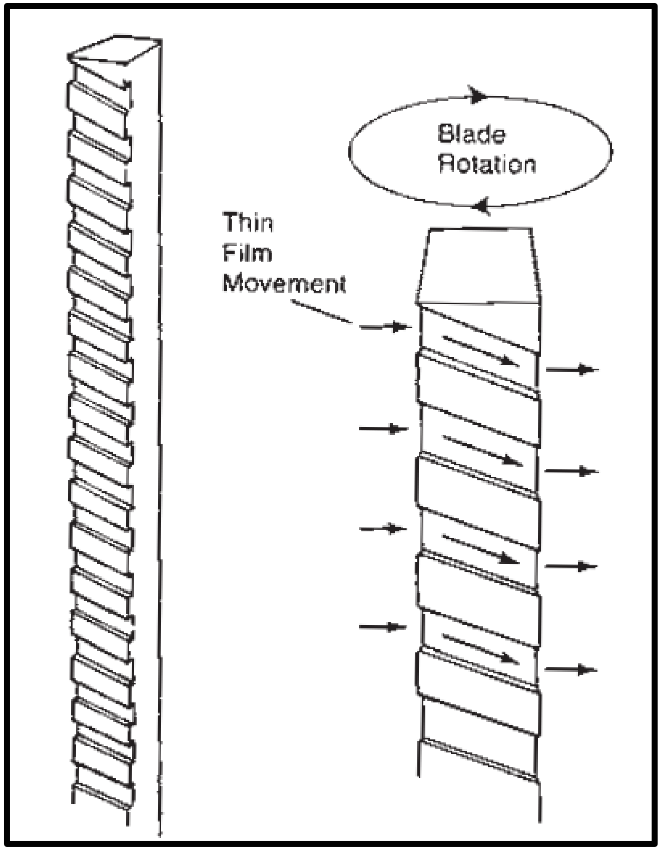




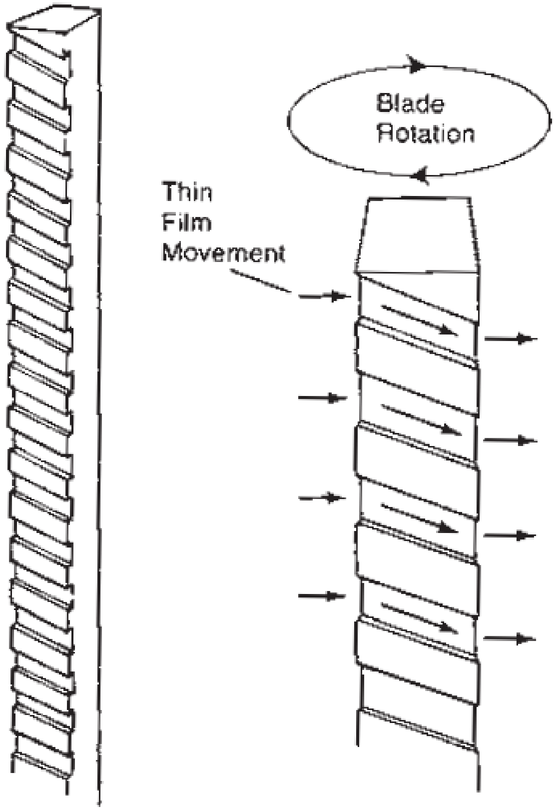
- WFE is used for heat sensitive materials.
- Wiper blades create a thin film of material that moves down the column.

WFE Theory


Cold
Liquid
Heat
Still Wall


Blade
Rotation
Thin
Film
Movement

Wiper Blades in Motion



Note: Heating jacket and internal condenser are not shown in video.

WFE 07-14-15 007.avi

Future Work

- Perform WFE experiments on drum XU-238 material and future synthetic lots. Submit passing material samples for formulation work.
- Examine reaction parameters to further optimize the process with current infrastructure.
  - Optimize the epichlorohydrin - hydantoin ratio to lower the amount of epichlorohydrin.
  - Test triethylamine as the base and compare any differences in the process.
  - Examine the use of GC analysis for reaction monitoring.
  - Submit XU-238 lots for formulation suitability.
  - Plan for potential scale-up synthesis.
- Find reliable CONUS vendors for the 5-ethyl-5-methylhydantoin reagent.
  - Possibly explore the synthesis to produce material in-house.