

Preliminary VOC Exclusion Studies Update

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Work to date

- Demonstrated feasibility of extracting remaining semi-volatiles from dried paint films
- Used TGA to determine relative weight loss (proportional to vapor pressure) as function of temperature for several semi-volatiles
- Worked with industry to develop paint matrices to use in future studies

EPA and AQMD

preliminary compound exclusion concepts

- ◆ Pre-screening for neat compounds
 - ◆ Method 24 or alternative evaporative test method
- ◆ Subsequent testing on fully formulated coatings
 - ◆ Laboratory formulated 'zero' VOC paint
 - ◆ Add dibutyl phthalate and candidate compound to test matrix
 - ◆ Perform extraction at 20, 40 and 60 minutes to check linearity
 - ◆ Verify percent retained is \leq percent of dibutyl phthalate retained

ACA Comments

- Film extraction too complicated, not accurate, only appropriate for latex architectural coatings
 - Use pentaethylene glycol instead of dibutyl phthalate
- Use TGA or Method 24 as second step instead of film extraction
- Open to lower temperatures more representative of AIM coatings applications
- Correlate to AQMD's ambient solvent evaporation results
- Utilize fully-formulated coating or resin

Recent work at Cal Poly, SLO

- ◆ Method 24 evaporation studies with subsequent GC analysis
 - ◆ Studies to determine if trans-esterification is occurring with dibutyl phthalate/polyethylene glycol mixtures
- ◆ TGA studies using both resin and fully formulated coatings

Method 24 Studies

- Added 0.1 g analyte + 0.1 g dibutyl phthalate to weighed pan
 - To date tested with glycerol, pentaethylene glycol and Velate 368
- Tested with no added solvent, 3 mL H₂O and 3 mL methanol
- Heated for one hour at 110°C
- Extracted pan with methanol/acetone mixture
- Added EGDE internal standard and analyzed using ASTM D6886 conditions
- Determined ratio analyte/diBuPh initial and post-heat, and determined ratio post heat/initial

Glycerol/dibutyl phthalate

glycerol/dibutyl phthalate					
	initial	post heat	post/initial		
sample	gly/dibuph	gly/dibuph		average	st dev
pan 1	1.49	1.58	1.06	1.08	0.02
pan 1	1.49	1.61	1.08		
pan 2	1.17	1.30	1.11		
pan 2	1.17	1.27	1.08		
pan 3 H2O	0.81	0.95	1.17	1.13	0.04
pan 3 H2O	0.81	0.89	1.10		
pan 4 H2O	0.95	1.10	1.16		
pan 4 H2O	0.95	1.04	1.09		
pan 1 MeOH	1.00	1.66	1.67	1.27	0.24
pan 2 MeOH	1.00	1.43	1.43		
pan 3 MeOH	1.00	1.04	1.04		
pan 1 MeOH	1.00	1.25	1.25		
pan 2 MeOH	1.00	1.15	1.15		
pan 3 MeOH	1.00	1.07	1.07		

Tetraethylene glycol/dibutyl phthalate

EG4/dibutyl phthalate					
	initial	post heat	post/initial		
sample	EG4/dibuph	EG4/dibuph		st dev	st dev
pan 1	1.09	1.05	0.97	1.00	0.04
pan 1	1.09	1.07	0.98		
pan 2	1.08	1.08	1.00		
pan 2	1.08	1.15	1.06		
pan 3 H2O	1.34	1.43	1.07	1.05	0.04
pan 3 H2O	1.34	1.47	1.10		
pan 4 H2O	0.93	0.95	1.02		
pan 4 H2O	0.93	0.95	1.02		
pan 1 MeOH	0.97	0.98	1.01	1.01	0.03
pan 1 MeOH	0.97	1.02	1.05		
pan 2 MeOH	0.97	1.00	1.03		
pan 2 MeOH	0.97	0.94	0.97		
pan 3 MeOH	0.97	0.99	1.02		

Velate 368/dibutyl phthalate

Velate 368/dibutyl phthalate					
	initial	post heat	post/initial		
sample	VE368/dibuph	VE368/dibuph		ave	st dev
pan 1	0.990564183	0.24013845	0.242426	0.267539	0.019812
pan 1	0.990564183	0.259727329	0.262201		
pan 2	1.136516549	0.31541892	0.277531		
pan 2	1.136516549	0.327312588	0.287996		
pan 3 H2O	1.099362072	0.374438355	0.340596	0.428798	0.100984
pan 3 H2O	1.099362072	0.377707897	0.34357		
pan4 H2O	1.07117042	0.569327836	0.531501		
pan4 H2O	1.07117042	0.535075689	0.499524		
pan 1 MeOH	0.994613154	0.091606943	0.092103	0.182301	0.083285
pan 1 MeOH	0.994613154	0.085866943	0.086332		
pan 2 MeOH	0.994613154	0.187691204	0.188708		
pan 2 MeOH	0.994613154	0.175323381	0.176273		
pan 3 MeOH	0.994613154	0.2731267	0.274606		
pan 3 MeOH	0.994613154	0.274297794	0.275783		

Could transesterification be occurring with glycols and dibutyl phthalate?

- Made up sample with known ratio of EG4/diBuPh
- Analyzed by GC to determine EG4/diBuPh ratio
- Ran D2369 on same sample
- Analyzed after heating (extracted pans with acetone, added EGDE in MeOH) and EG4/diBuPh ratio remained constant
- Conclusion: no transesterification occurring, results are indicating true amounts of dibutyl phthalate and glycol

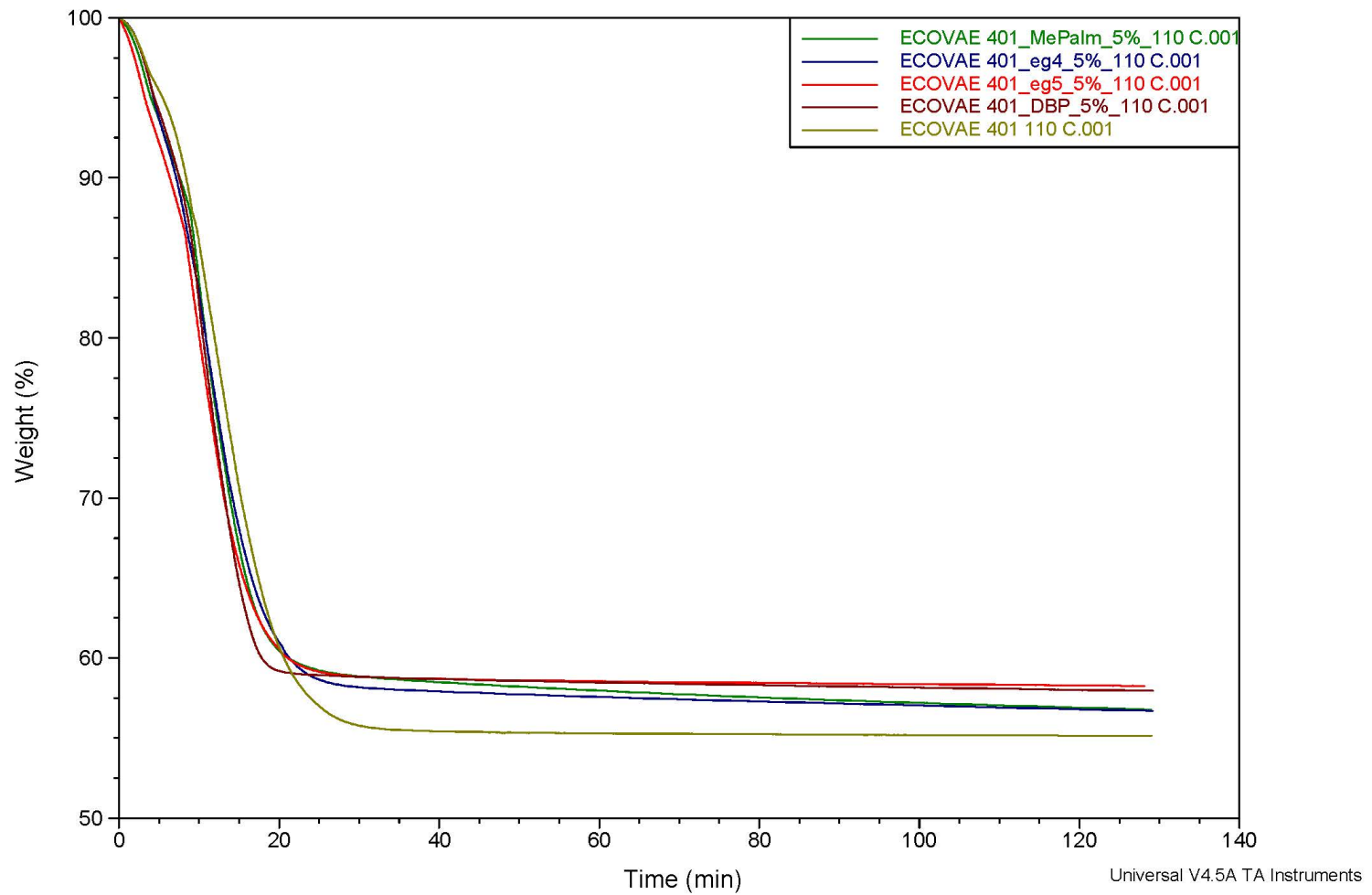
TGA studies with resin and fully formulated paint

- ◆ Samples prepared by combining 5% analyte by weight with either resin or formulated paint
- ◆ Resin tested: EcoVAE (Celanese) vinyl acetate/ethylene emulsion
 - ◆ 55% solids, MFFT 0°C, formulated for use in very low or “zero” VOC architectural DIY coatings – very similar to resin used in specially prepared “zero VOC” paint formulations
- ◆ Paint tested: flat and semi-gloss coatings prepared by Kelly-Moore specially for this project (described in previous presentation)

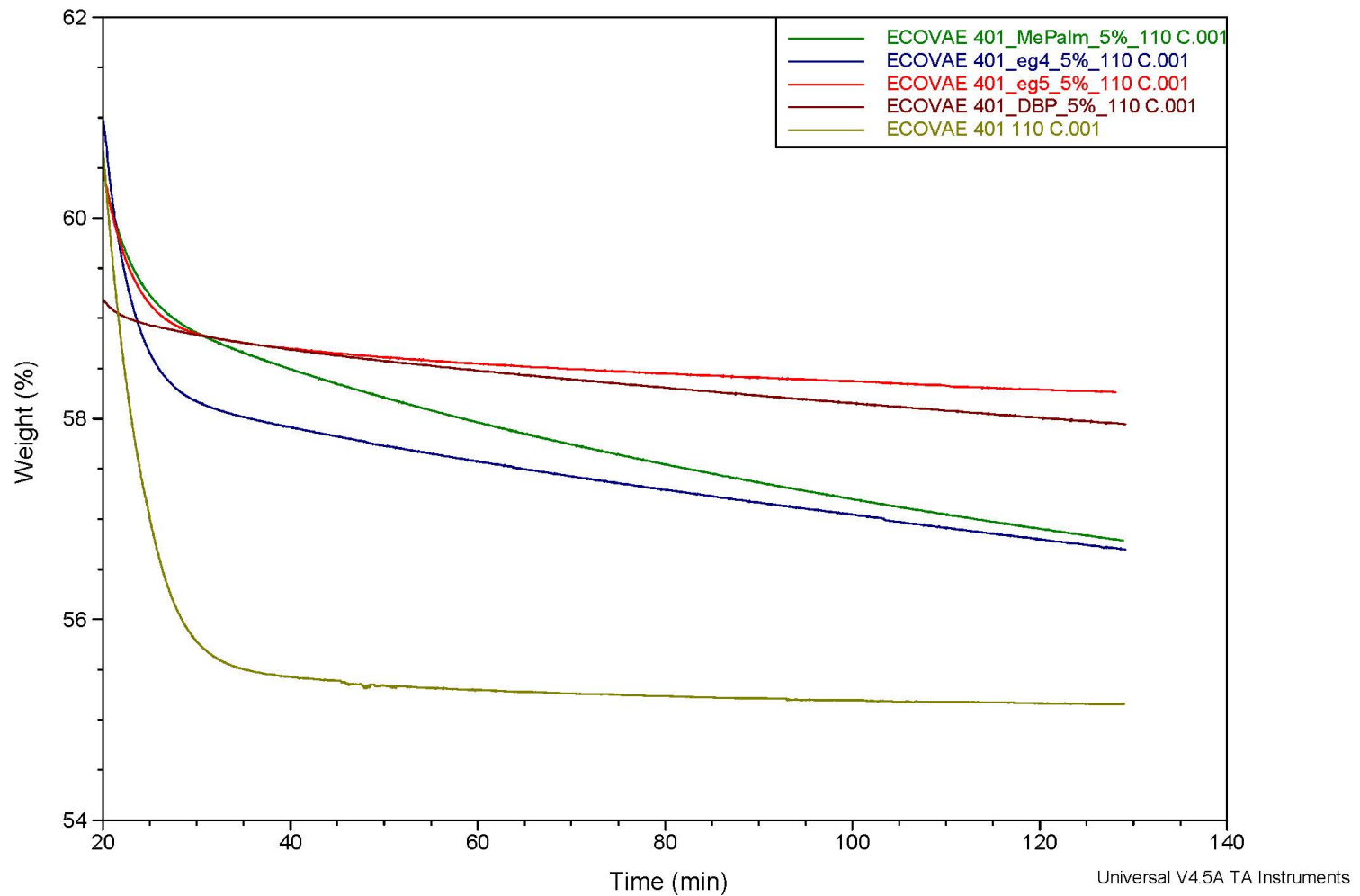
TGA testing

- ◆ Sample prepared by combining 5.00% analyte (by weight) with resin or paint in 40 mL septum-capped jars.
- ◆ Ceramic beads added to aid in mixing. Sample mixed for 15 minutes on mechanical shaker, sonicated for at least 20 minutes, then mixed on shaker again. Sample stirred by hand in between.
- ◆ 50 ± 1 mg sample used in open standard TGA pan
- ◆ Sample heated from ambient to 110°C at $10^{\circ}\text{C}/\text{min}$ then held at 110°C for two hours with 10 mL/min nitrogen flow

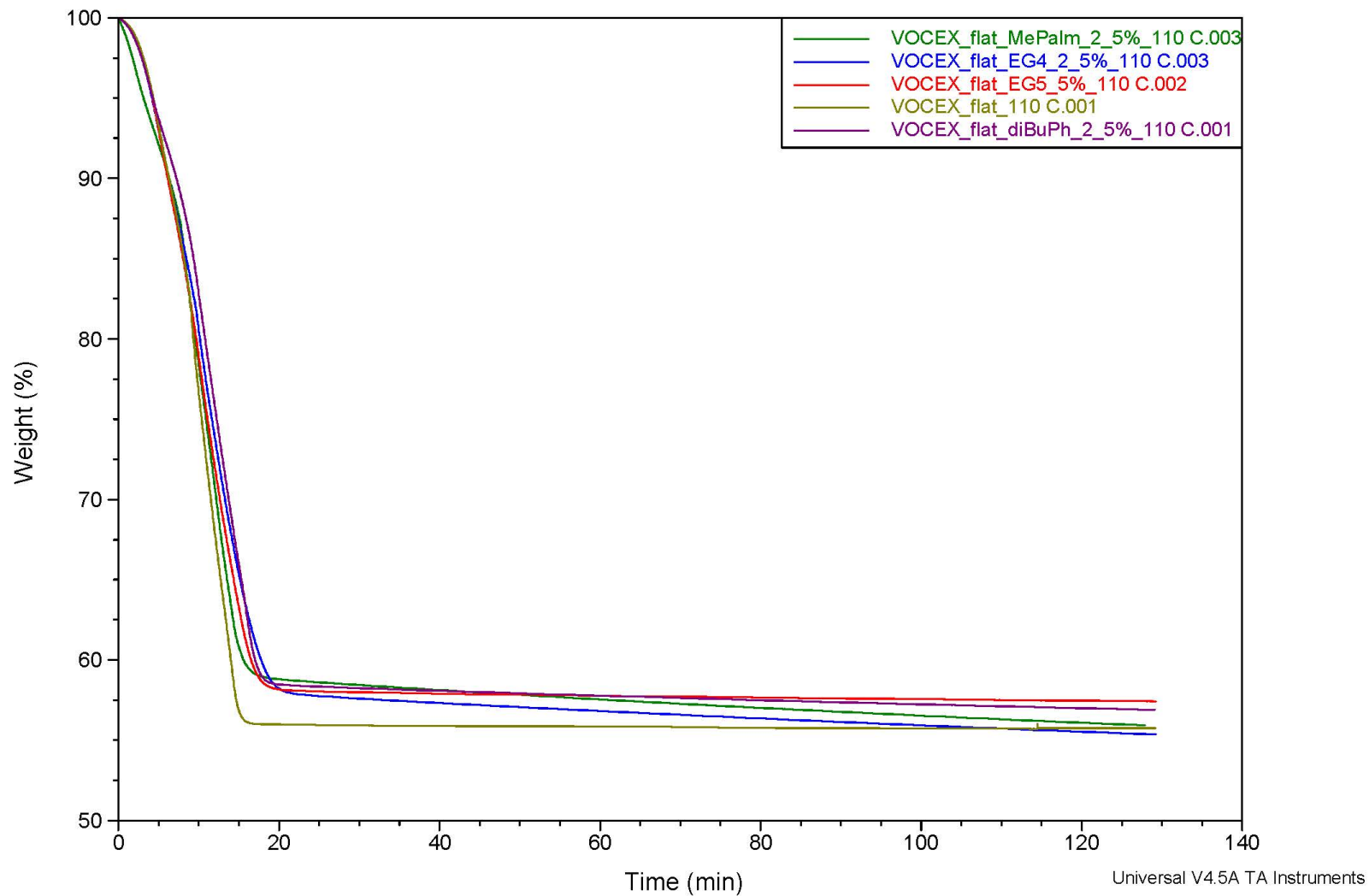
TGA results using resin



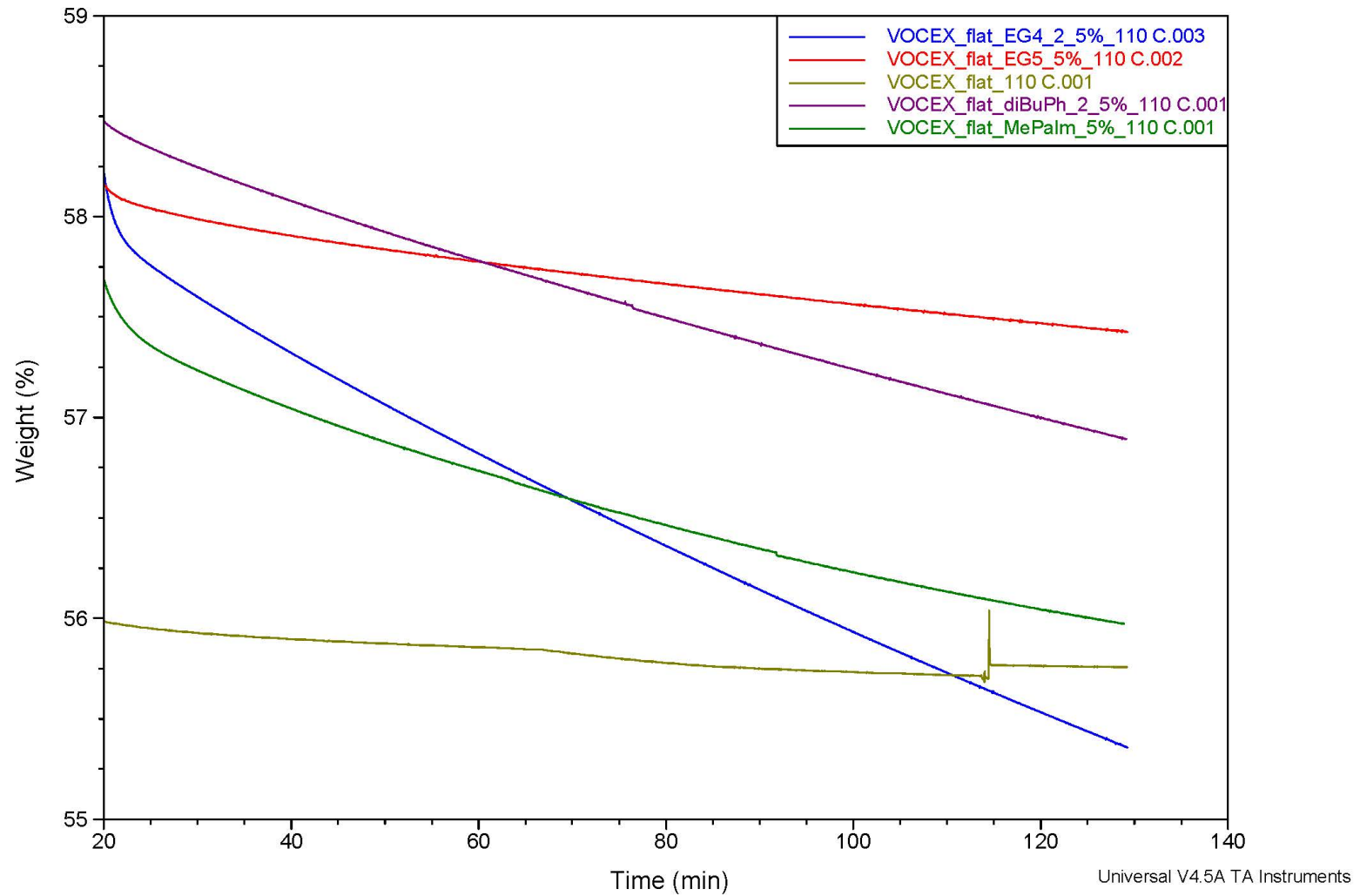
TGA resin expanded



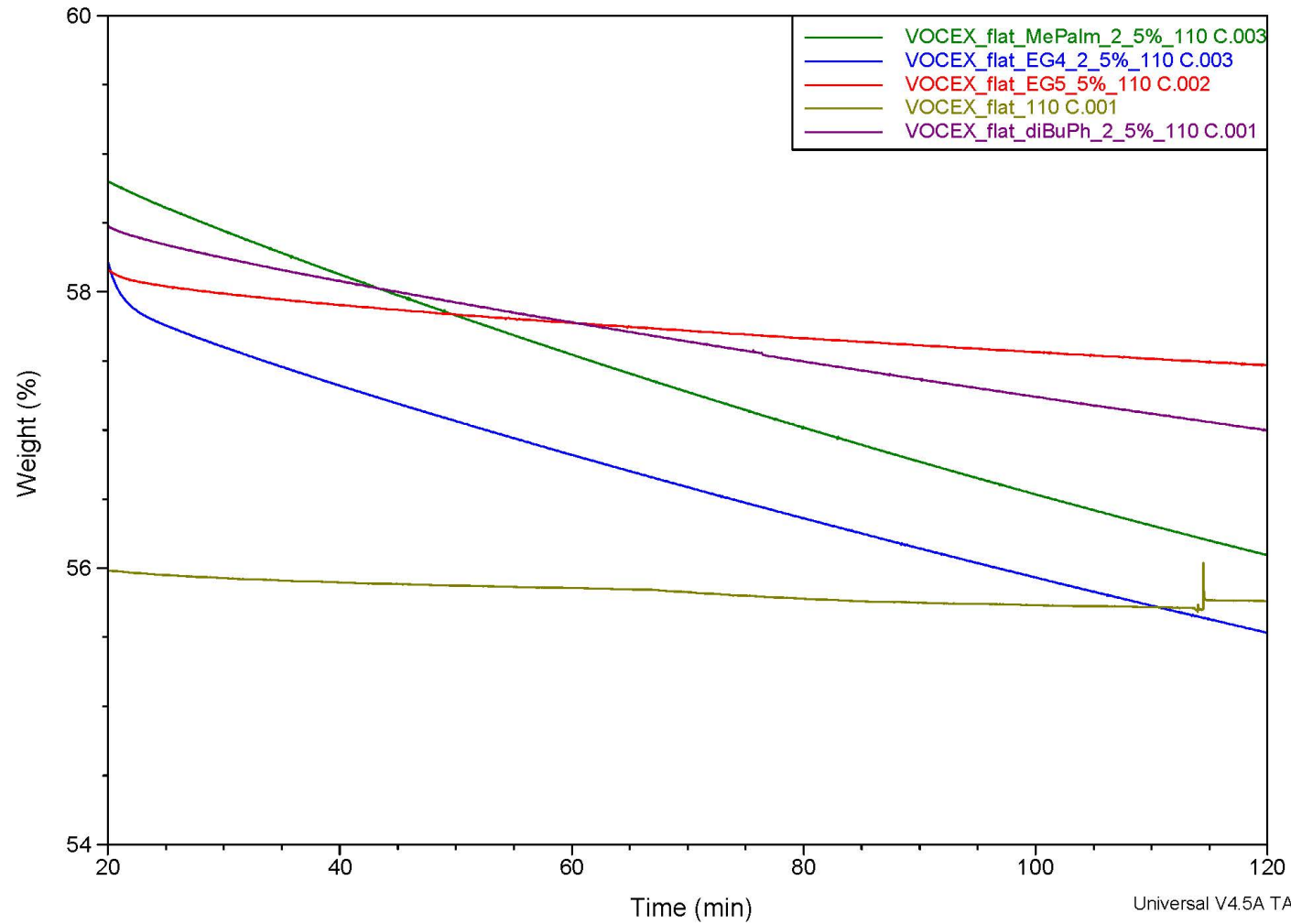
TGA results using flat paint



TGA flat paint expanded



TGA flat paint expanded 2nd run



Summary

- Method 24 testing on mixtures of analyte/dibutyl phthalate gives accurate relative volatility information
- TGA testing on resin or paint containing one analyte allows comparison between analytes at conditions most similar to EPA Method 24
- EG5 less volatile than methyl palmitate in all cases, EG4 slightly more volatile than methyl palmitate in TGA, equal volatility to diBuPh using Method 24
- Film extraction is much more complicated with difficulties insuring complete extraction of analytes
- Much work has been done trying to develop methods for possibly only a very few compounds