Selectivity of the Isocyanate-Hydroxyl Reaction vs. Side Reactions as a Function of Catalysis

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SL2195

POLYURETHANES IN COATINGS

-Reactive two components

Two package	Polyisocyanate + Polyol
One package	Blocked isocyanate + Polyol

-Reactive one component — NCO prepolymer + moisture; Oxidative

-Nonreactive one component

Solution	Thermoplastic PU
Aqueous solution	High and low MW PU Thermoplastic and XL

D.Dietrich, Proceedings of the Third International Conference in Organic Coatings Science and Technology, Athens Greece 1977

ISOCYANATE REACTIONS

R-NCO

R-OH	$R\text{-}NH_2$
HOH	EPOXY
R-COOH	TRIMER
R-NHCONH-R	DIMER
R-NHCOO-R	CARBODIIMIDE

CATALYSIS PROBLEMS

HIGH SOLIDS COATINGS	WATERBORNE
POTLIFE/REACTIVITY	WATER REACTION
MOISTURE REACTION	POTLIFE
SOLUBILITY	GASING
NETWORK STABILITY	STABILITY
	GLOSS

Objectives of this Study

ENVIRONMETALLY ACCEPTABLE CATALYSTS

REACTION RATE OF CATALYSTS WITH OH

SELECTIVE CATALYSTS FOR OH

IMPROVED POTLIFE/REACTIVITY

REDUCED WATER REACTION

CATALYSTS USED

DIBUTYLTIN DILAURATE/DIACETATE
DIBUTYLTIN OXIDE
AMINES
LEAD COMPOUNDS
ZINC SALTS
MANGANESE SALTS

CATALYST PROPERTIES

POTLIFE / REACTIVITY
SELECTIVITY
DELAYED ACTION
LOW TEMPERATURE
HIGH TEMPERATURE
WATER
HIGH RATE (RIM)
EXTERIOR DURABILITY
RESISTANCE PROPERTIES
ENVIRONMENT - TOXICITY

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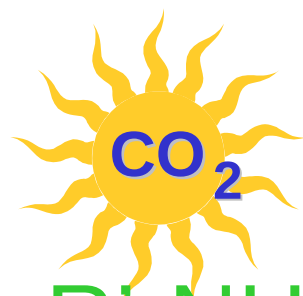
Isocyanate-Hydroxyl Reactions

$$ROH + R'NCO \rightarrow R'NHCOOR$$



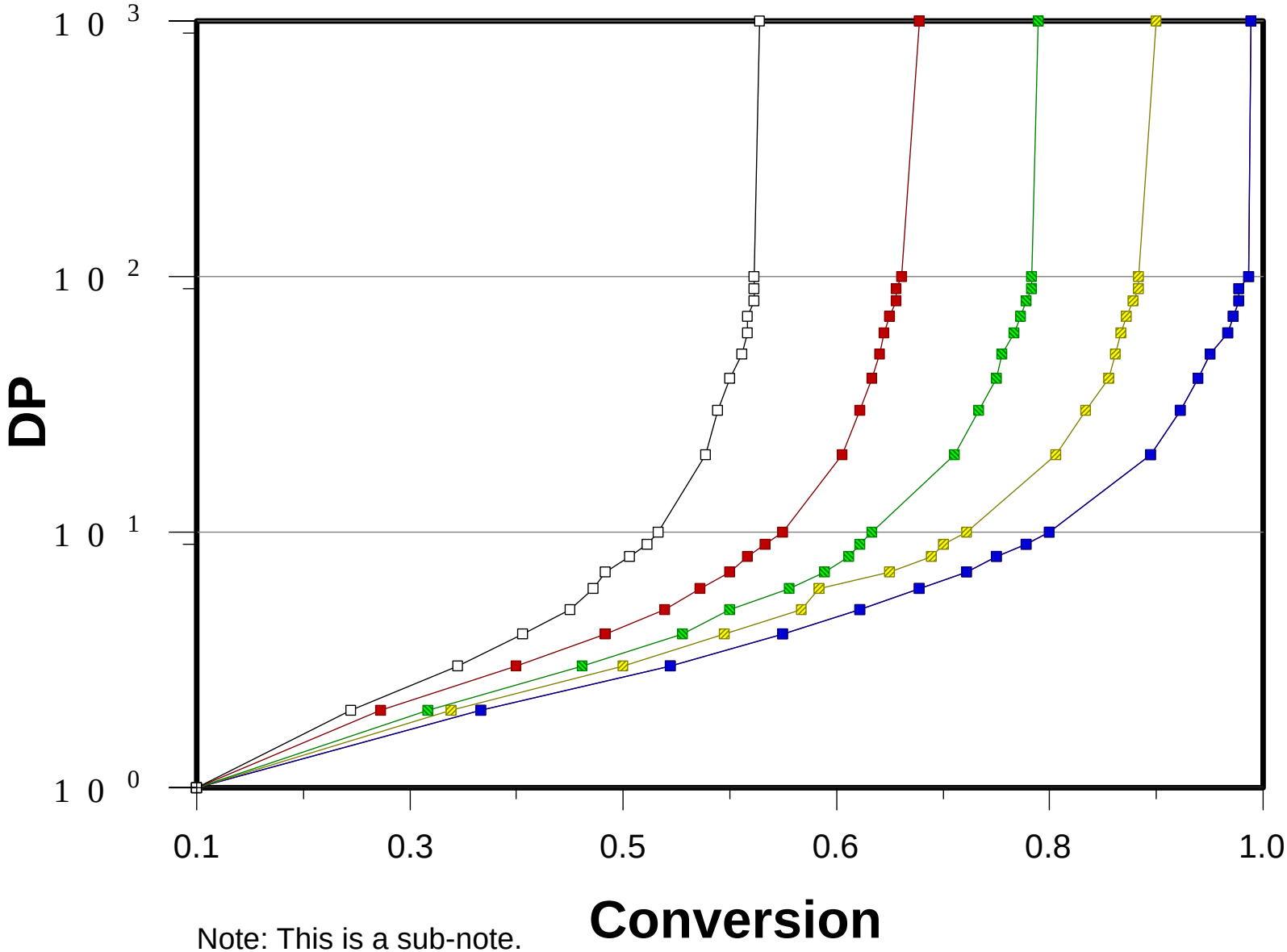
$$R'NCO + H_2O \rightarrow R'\text{-}NHCOOH \rightarrow R'\text{-}NH_2$$

$$R'NH_2 + R'NCO \rightarrow R'NHCONHR'$$

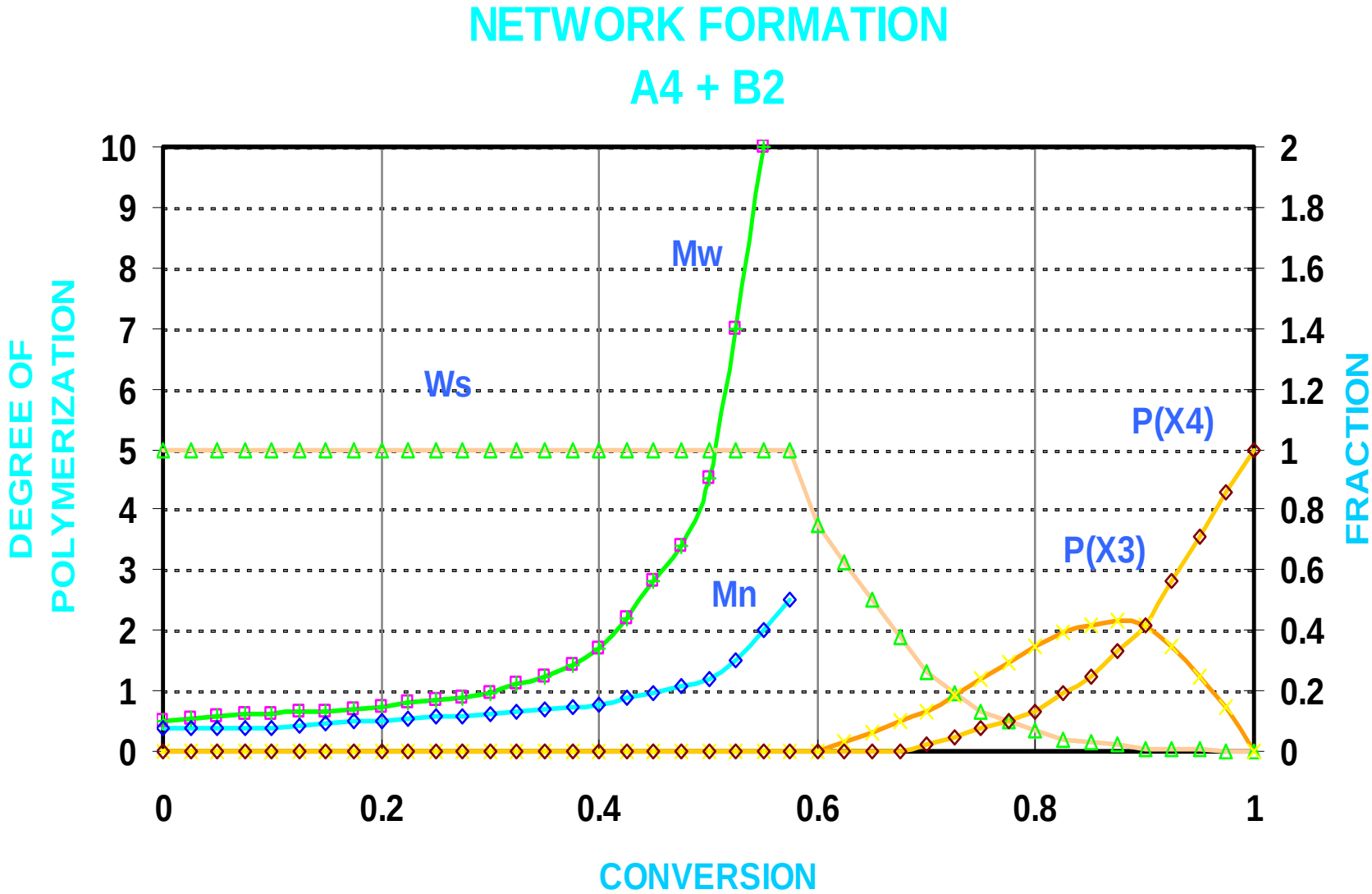
ADDITIONAL REACTIONS

MW AS A FUNCTION OF CONVERSION

CROSSLINKER DIFUNCTIONAL

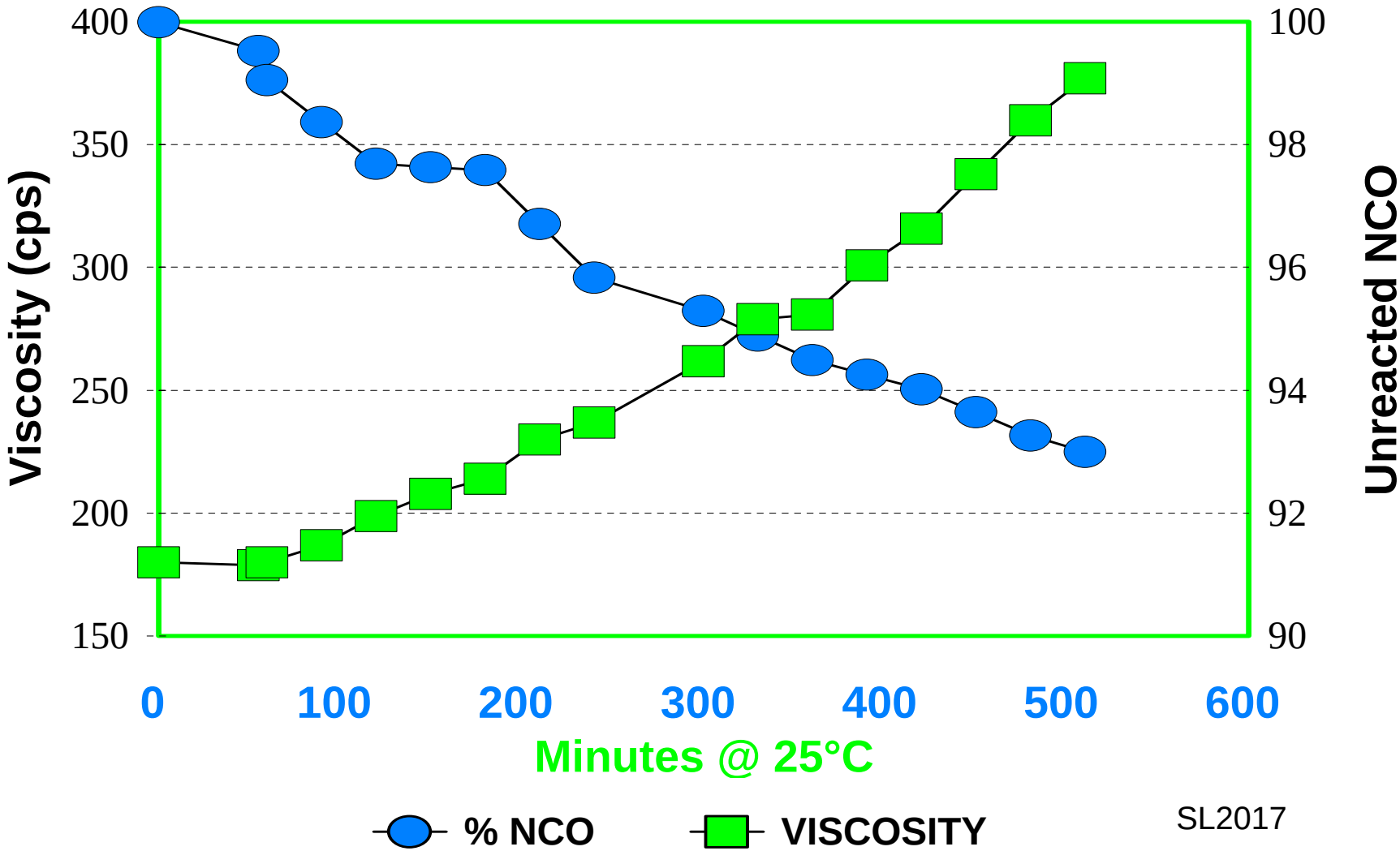


Note: This is a sub-note.


NETWORK FORMATION
A4 + B2
DEGREE OF POLYMERIZATION
FRACTION
CONVERSION
Mw
Ws
Mn
P(X4)
P(X3)
0
1
2
3
4
5
6
7
8
9
10
0
0.2
0.4
0.6
0.8
1
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0

PE/HDI-TRIMER

No Catalyst



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SCREENING OF CATALYSTS

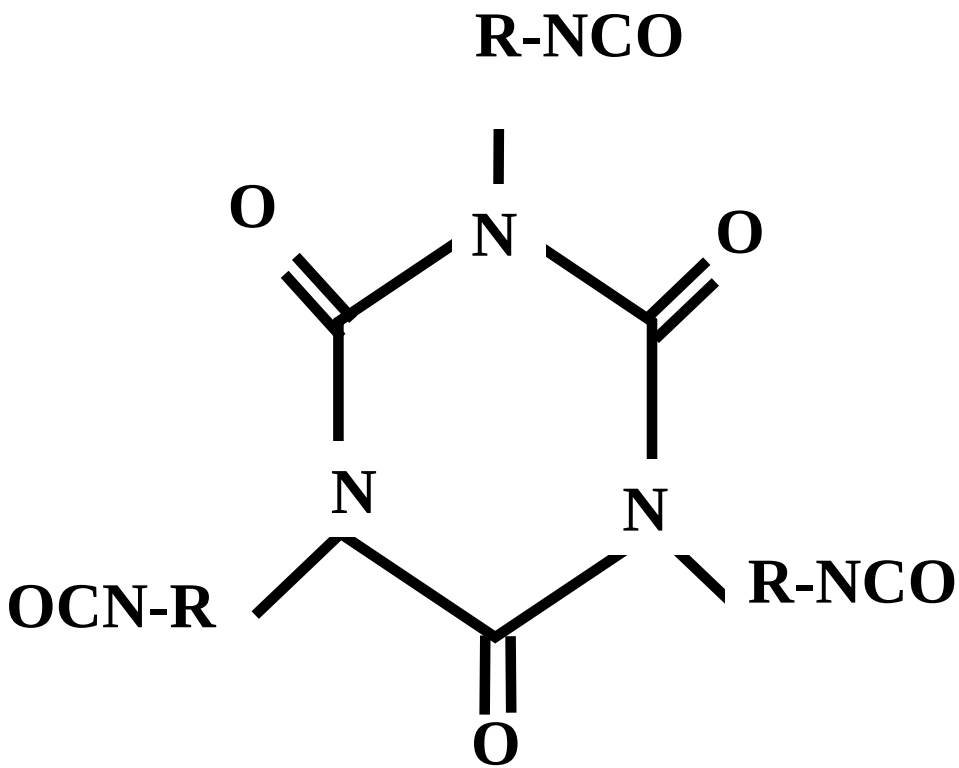
APPLICATION TESTS FORMULATION

- POTLIFE (2X VISC.
- GEL TIME
- TACK FREE
- DRY-THROUGH

MODEL SYSTEMS (ANALYTICAL)

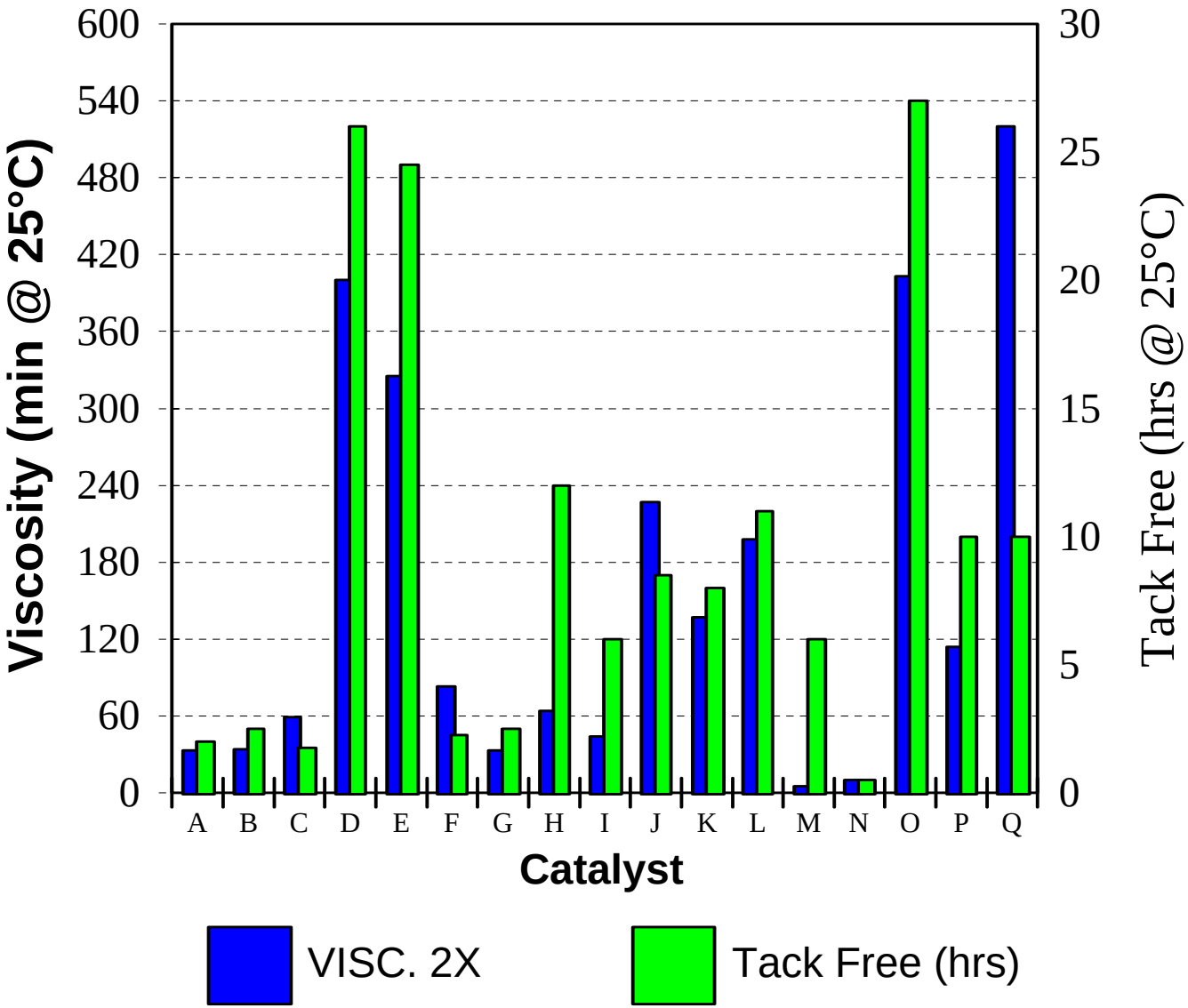
- DISAPPEARANCE OF NCO
- FORMATION OF URETHANE / UREA
- MW

HDI-TRIMER



Catalyst Study (HDI TRIMER)

Metal (0.0065% on Solids)

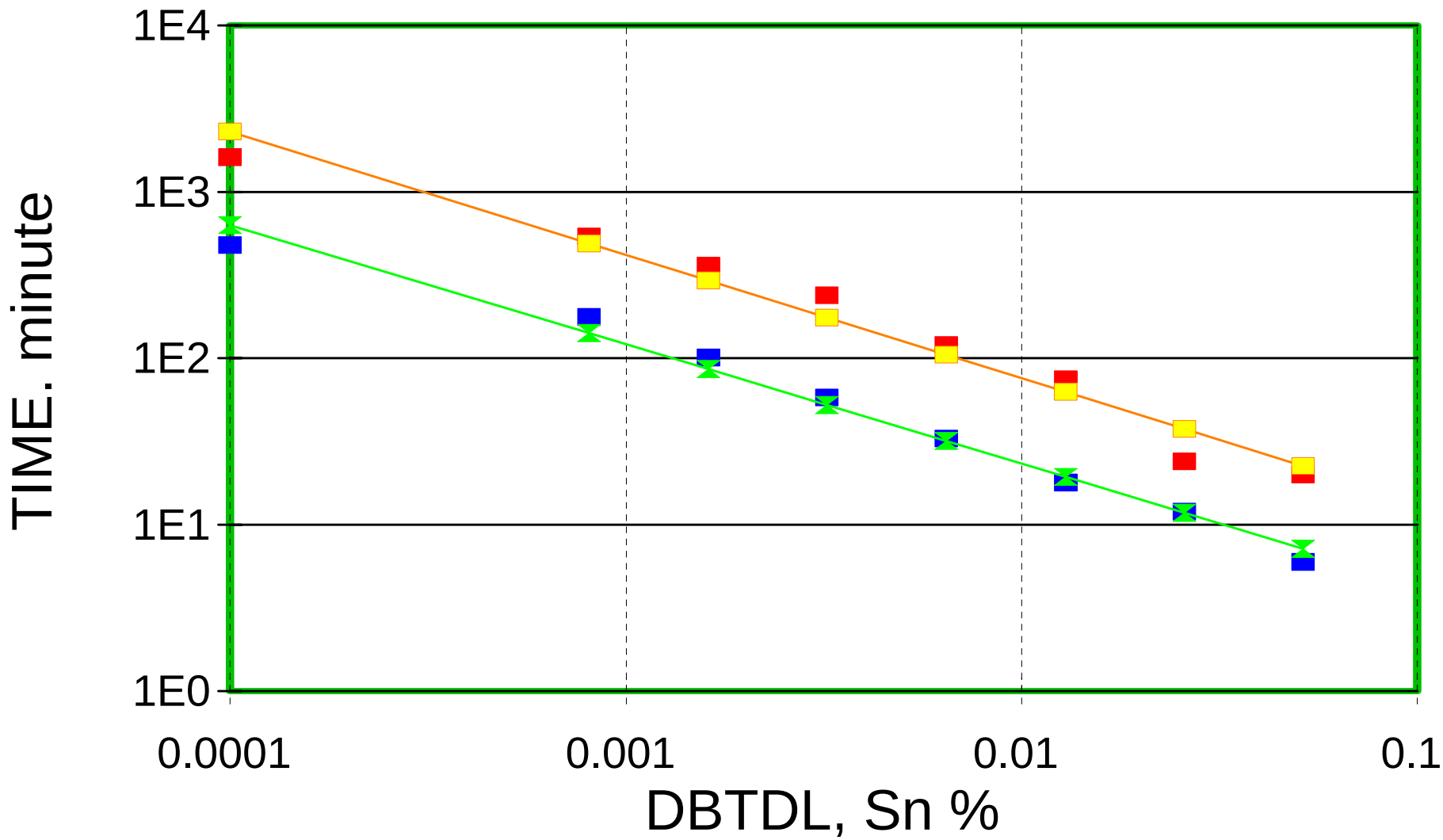


A: DBTDL
B: DBTDA
C: Mn Naph/PD
D: Mn Oct
E: Sn Oct/PD
F: Vn acac/PD
G: Vn acac
H: Bi Oct
I: Bi Naph
J: Zn acac/PD
K: Zn Oct
L: Co Oct
M: Zr acac
N: Zr acac/PD
O: Zr Oct
P: Al acac
Q:Al chelate/PD

SL2242

PE/HDI-TRIMER

CATALYST REACTION RATE



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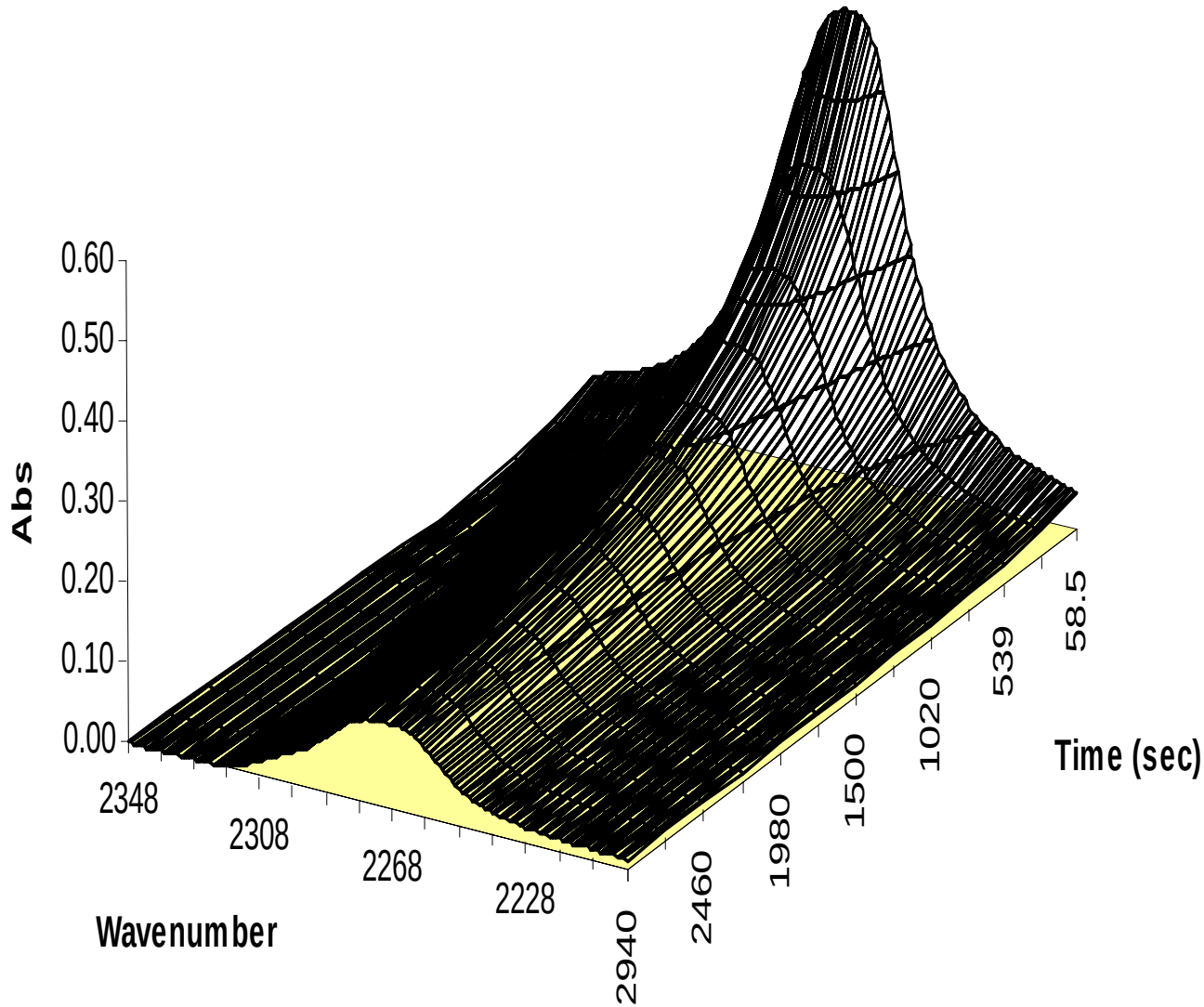
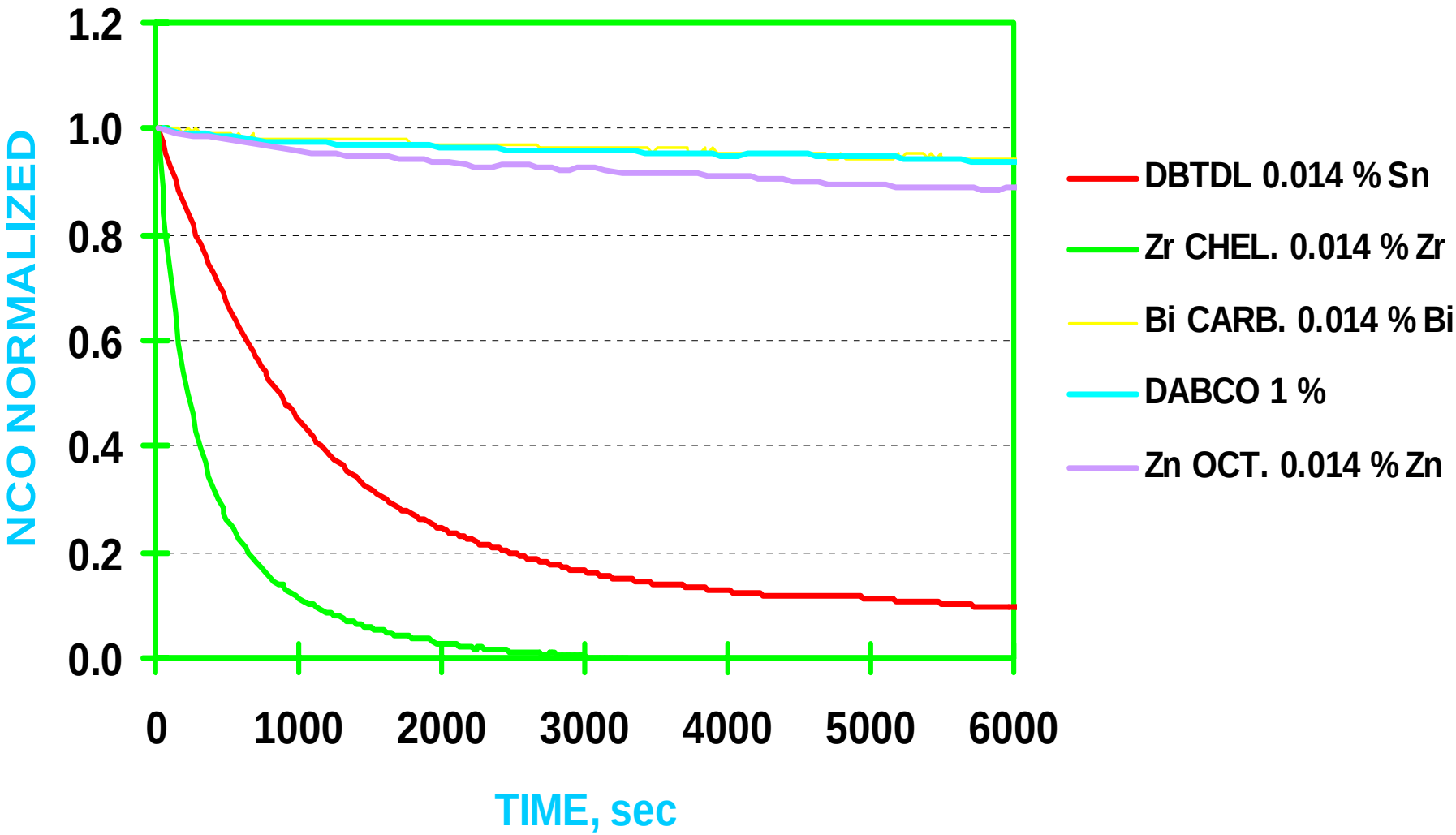
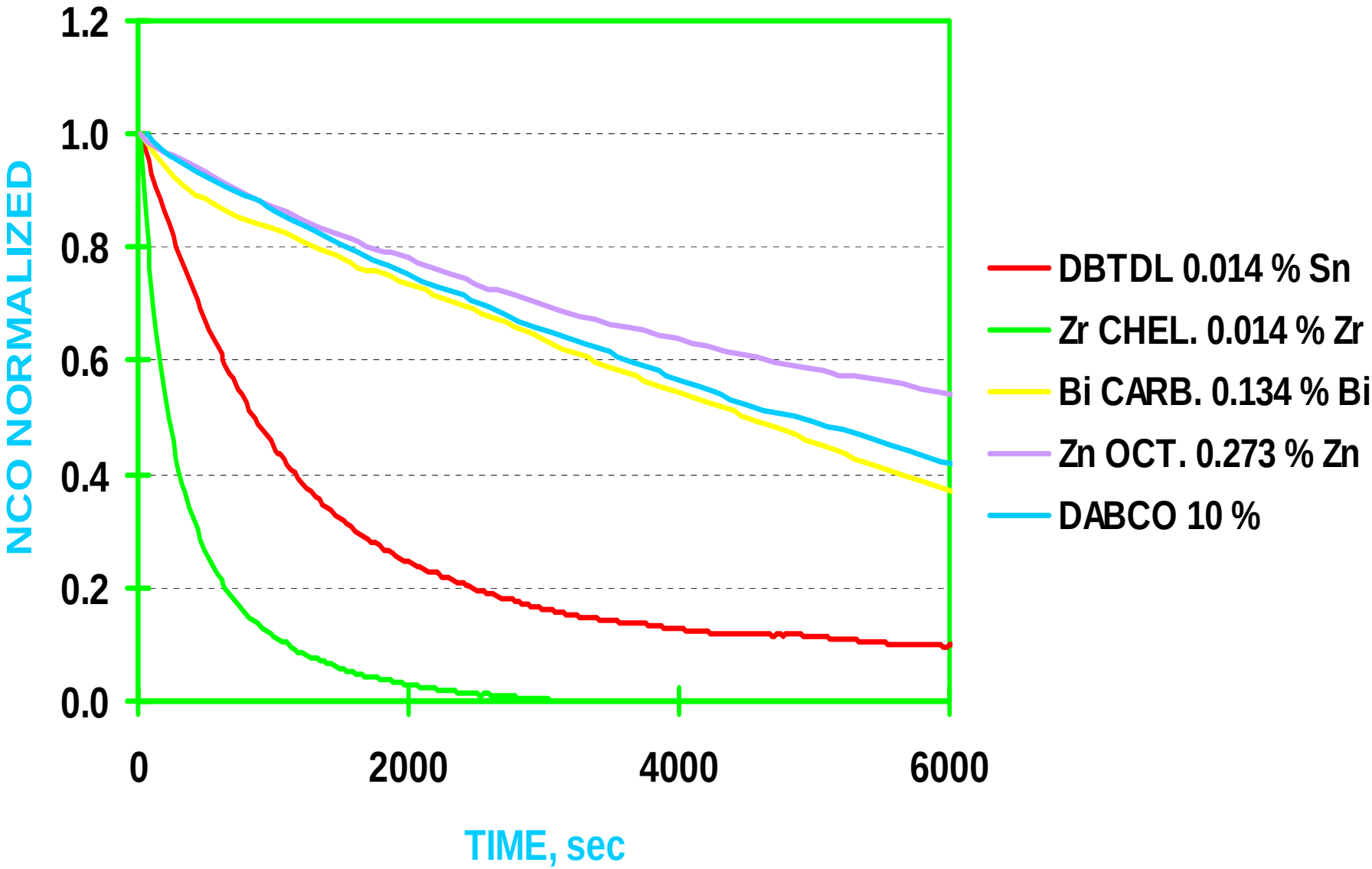
Isocyanate Peak Decay



HDI TRIMER / HYDROXYL
DBTDL 0.0140% Sn
n-BUTANOL

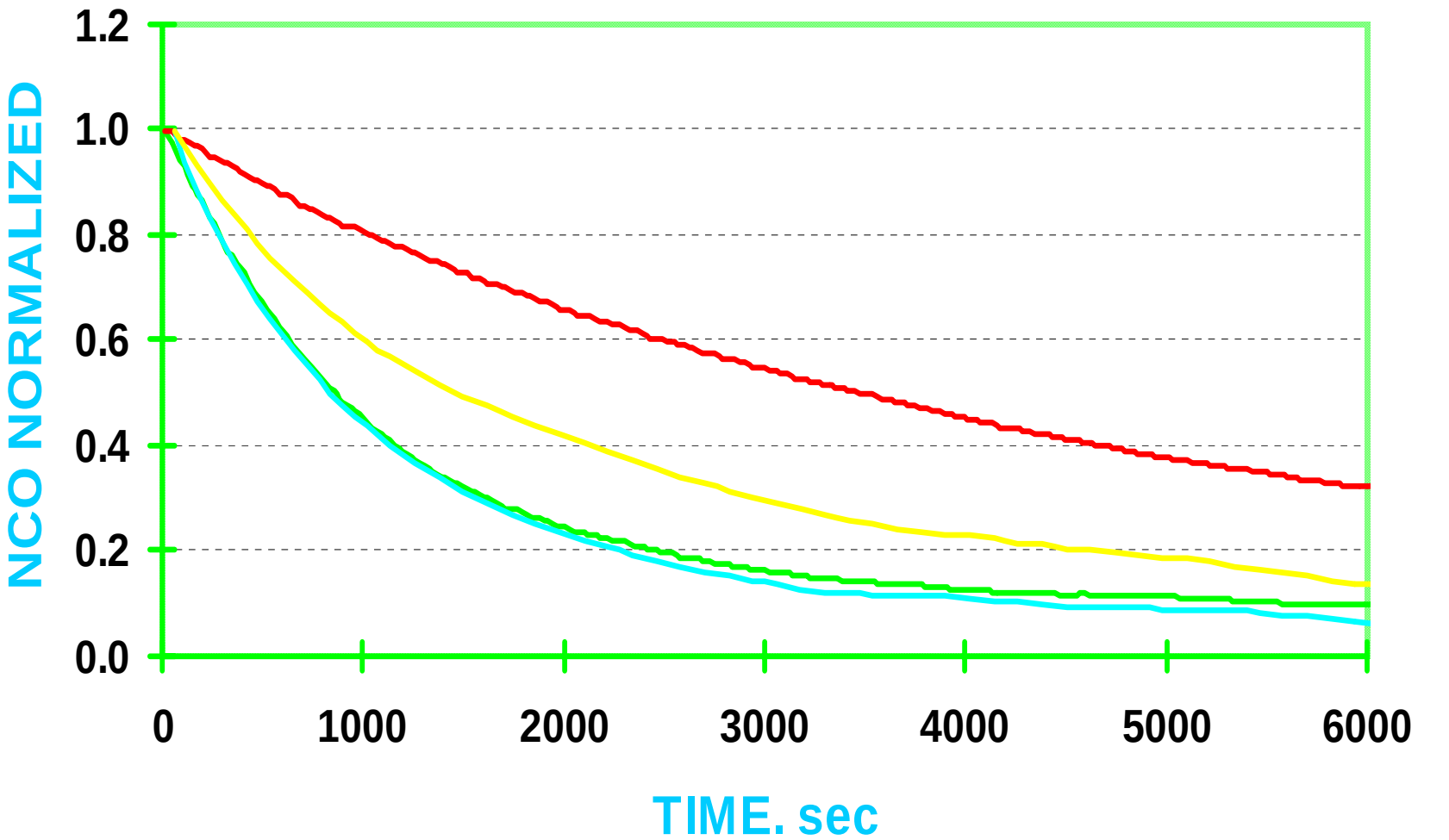


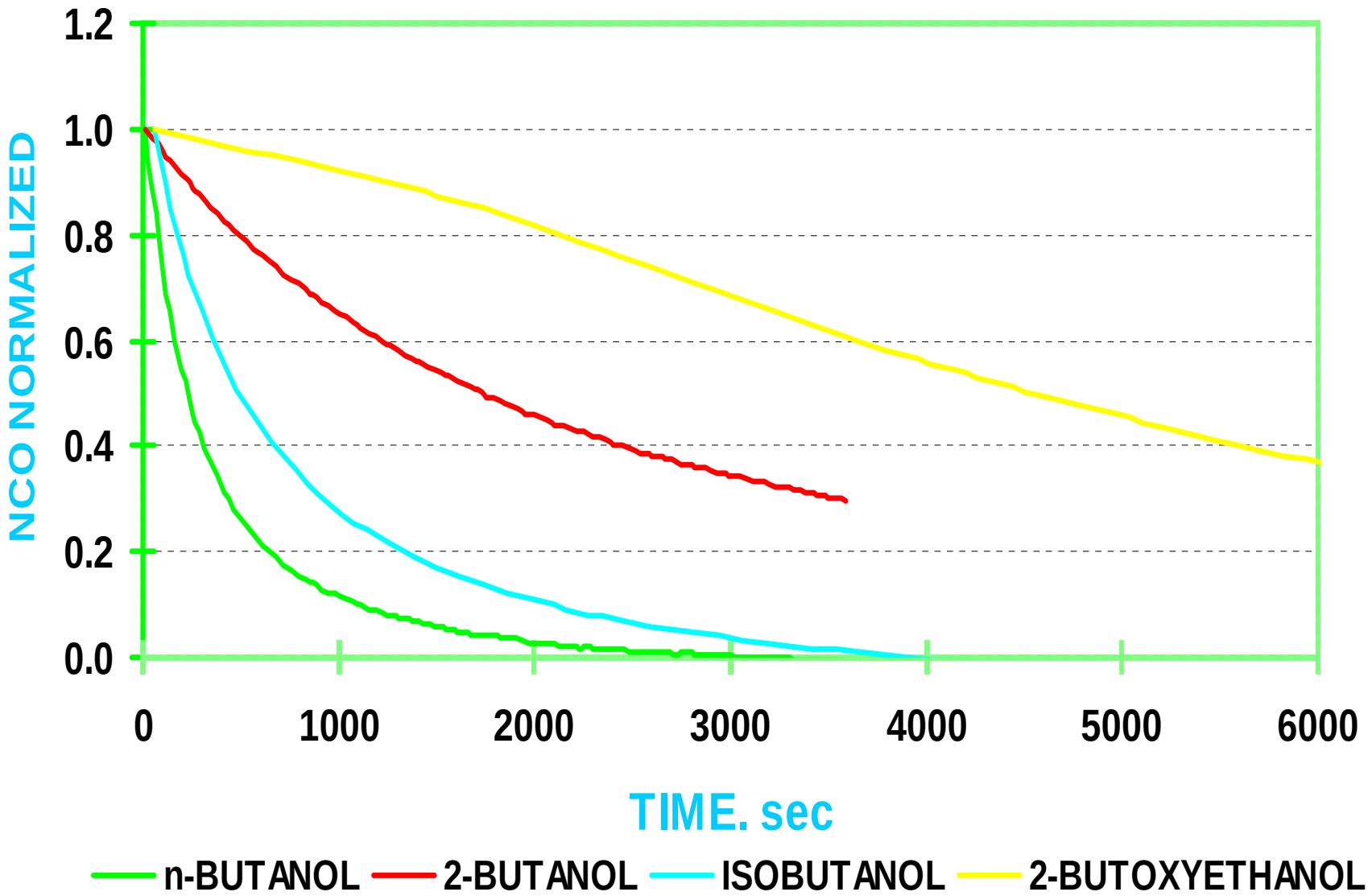
HDI TRIMER / n-BUTANOL

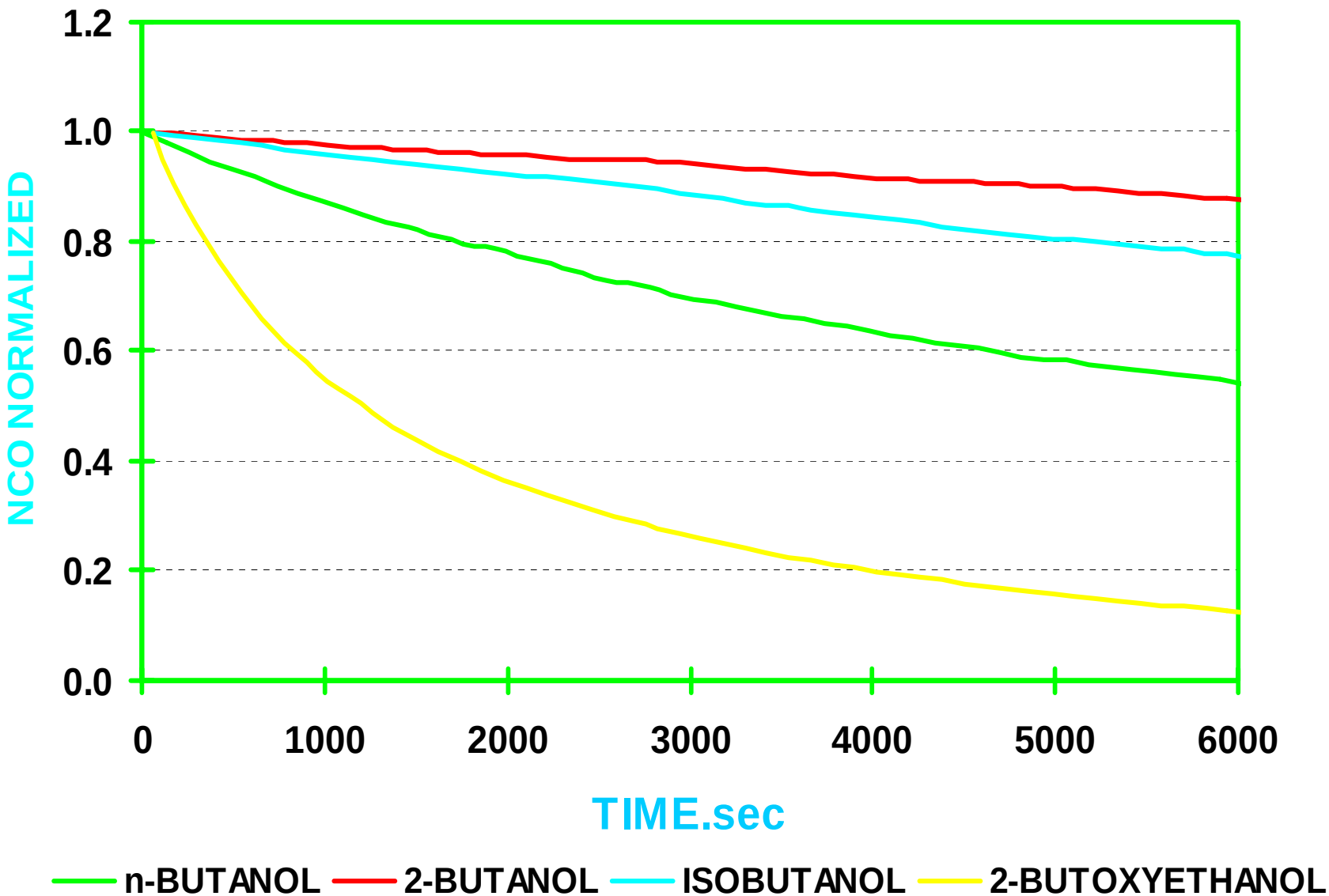


HDI-TRIMER - HYDROXYL

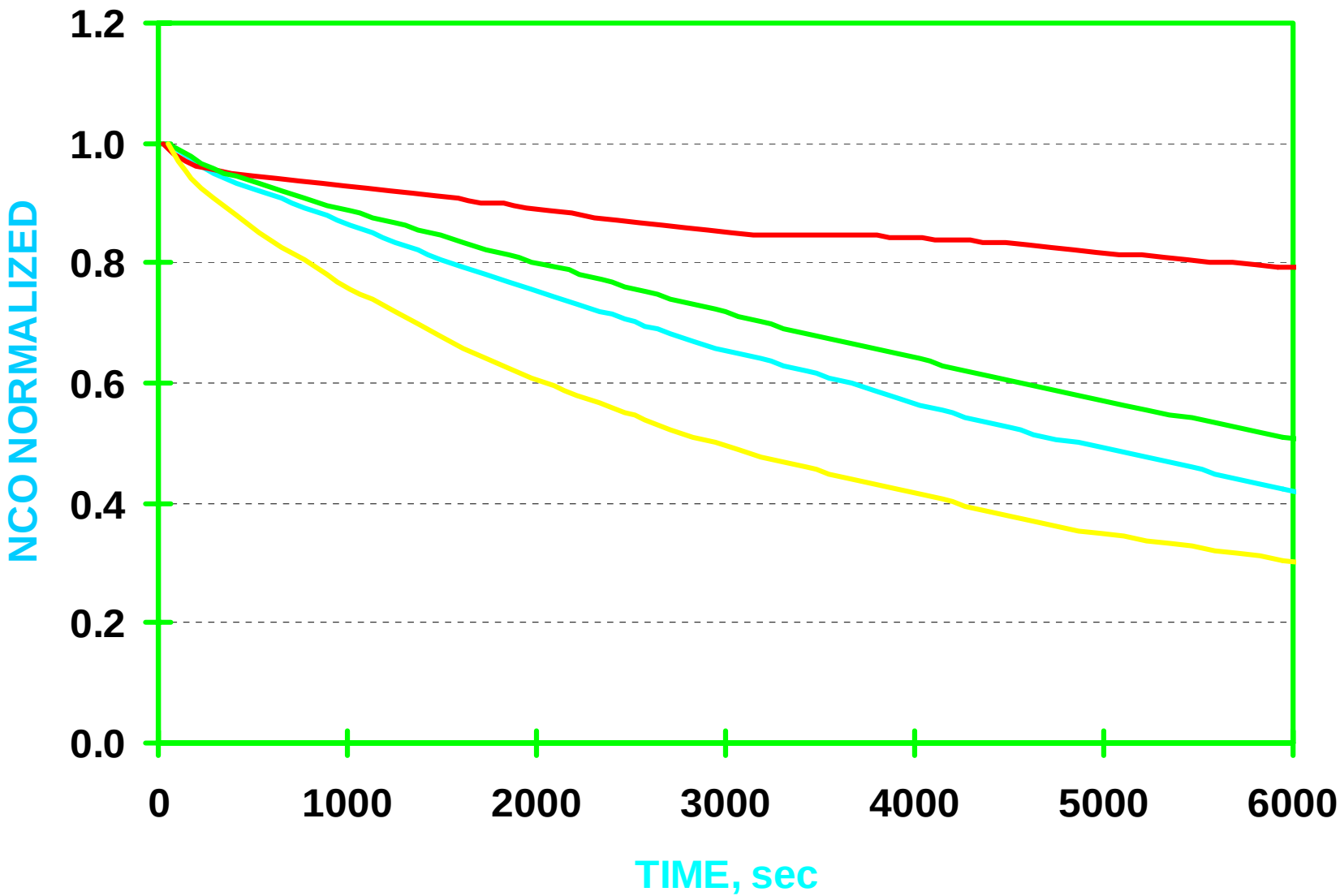
DBTDL 0.014% Sn

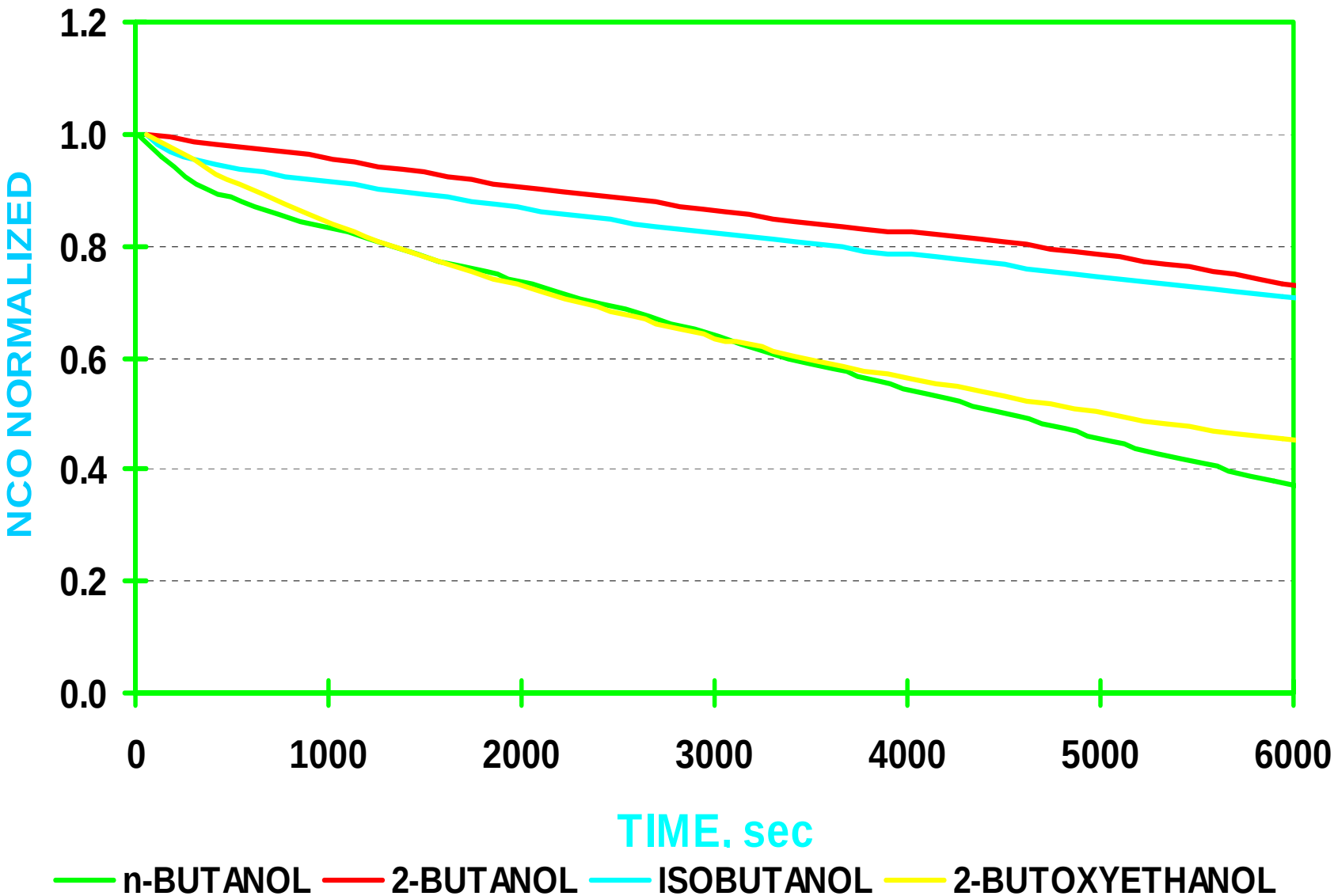



HDI TRIMER / HYDROXYL
Zr CHELATE 0.014% Zr
NCO NORMALIZED
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1000
2000
3000
4000
5000
6000
TIME. sec
n-BUTANOL
2-BUTANOL
ISOBUTANOL
2-BUTOXYETHANOL

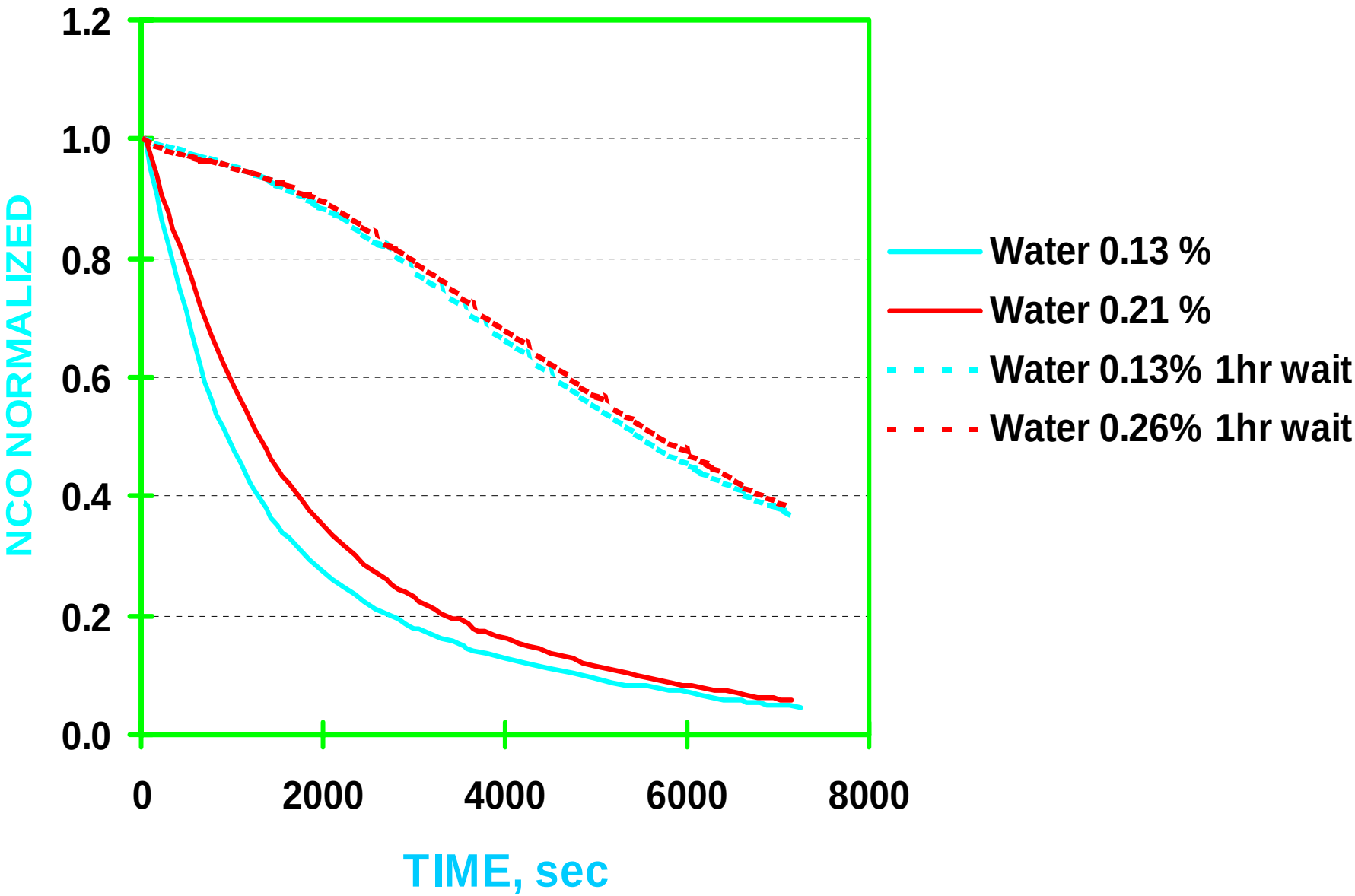

HDI TRIMER / HYDROXYL
Zn OCTOATE 0.272% Zn
NCO NORMALIZED
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1000
2000
3000
4000
5000
6000
TIME.sec
n-BUTANOL
2-BUTANOL
ISOBUTANOL
2-BUTOXYETHANOL

HDI TRIMER / HYDROXYL
DABCO 10%



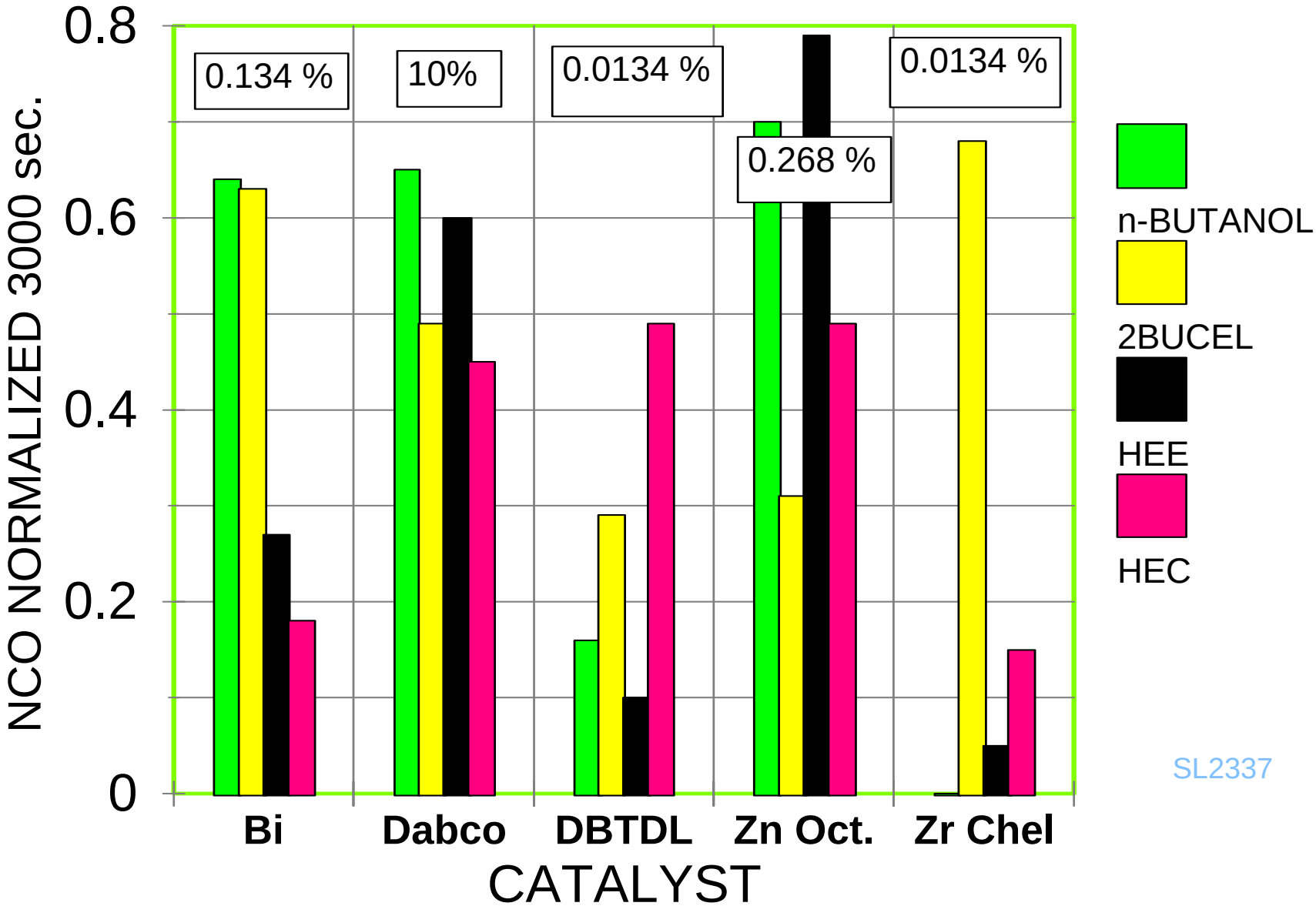

HDI TRIMER / HYDROXYL
Bi CARB. 0.134 % Bi
NCO NORMALIZED
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1000
2000
3000
4000
5000
6000
TIME. sec
n-BUTANOL
2-BUTANOL
ISOBUTANOL
2-BUTOXYETHANOL

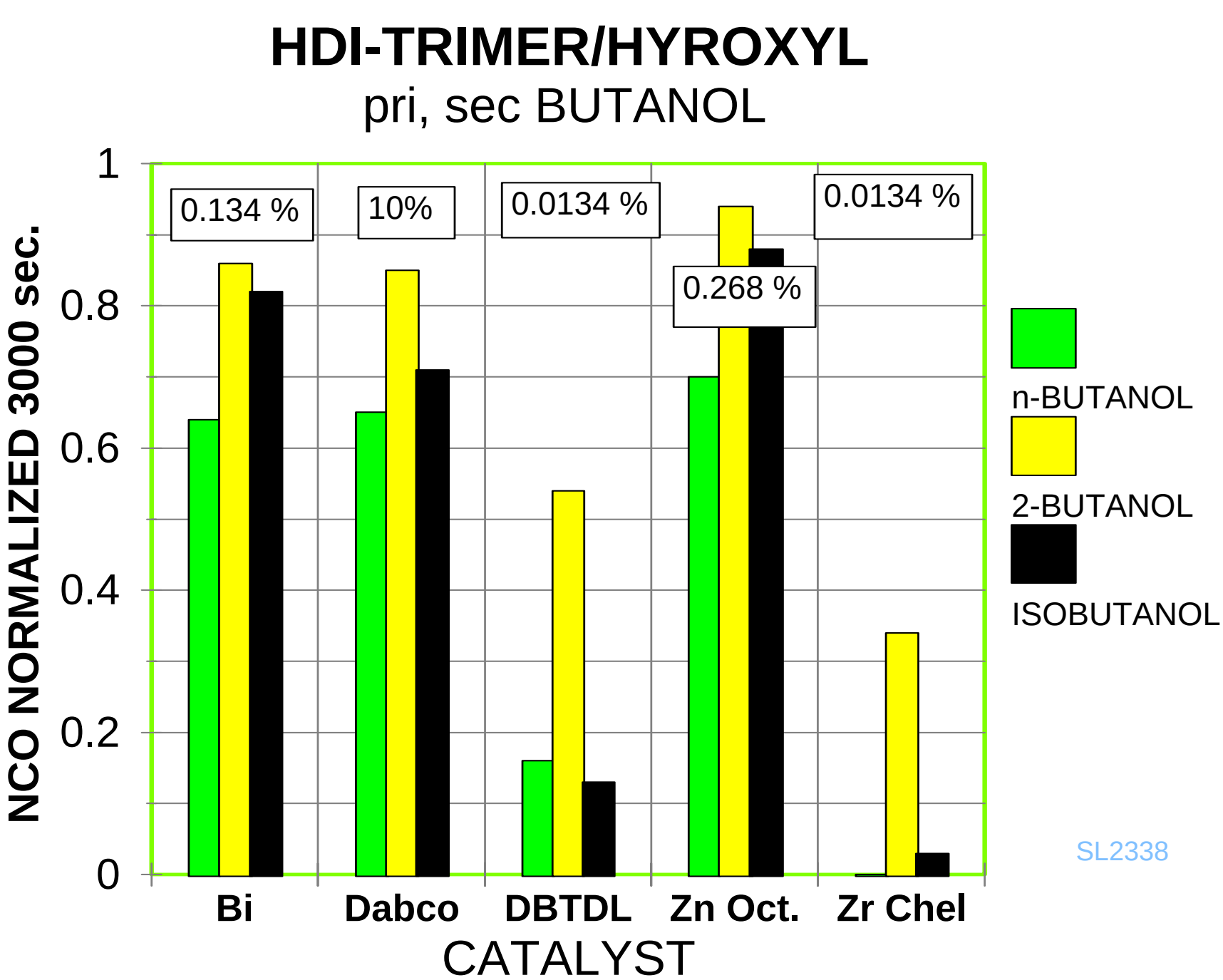
HDI TRIMER / 2-BUTOXYETHANOL
Zr CHELATE 0.028 % Zr, WATER EFFECT



HDI-TRIMER/HYROXYL

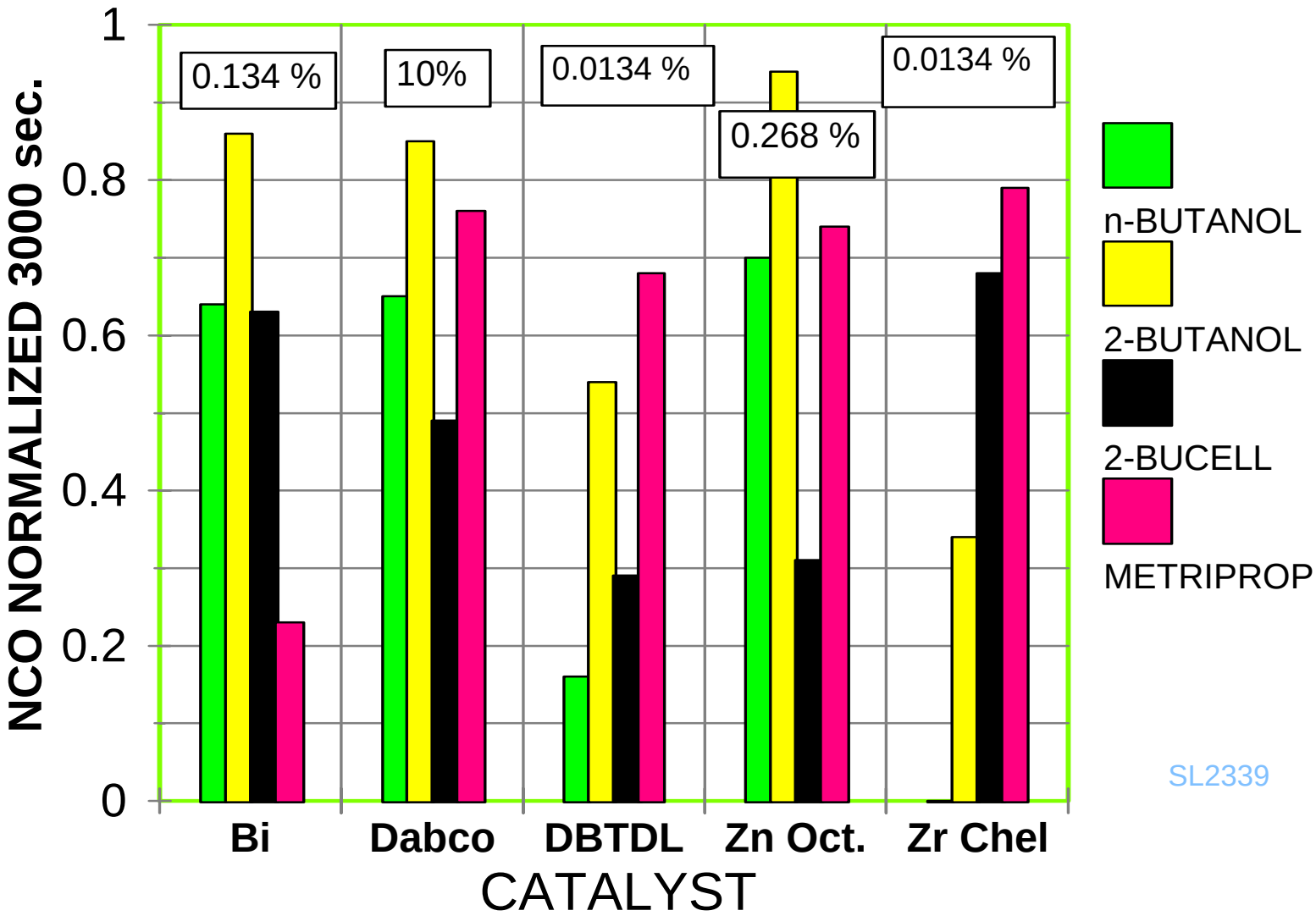
PRIMARY HYDROXL



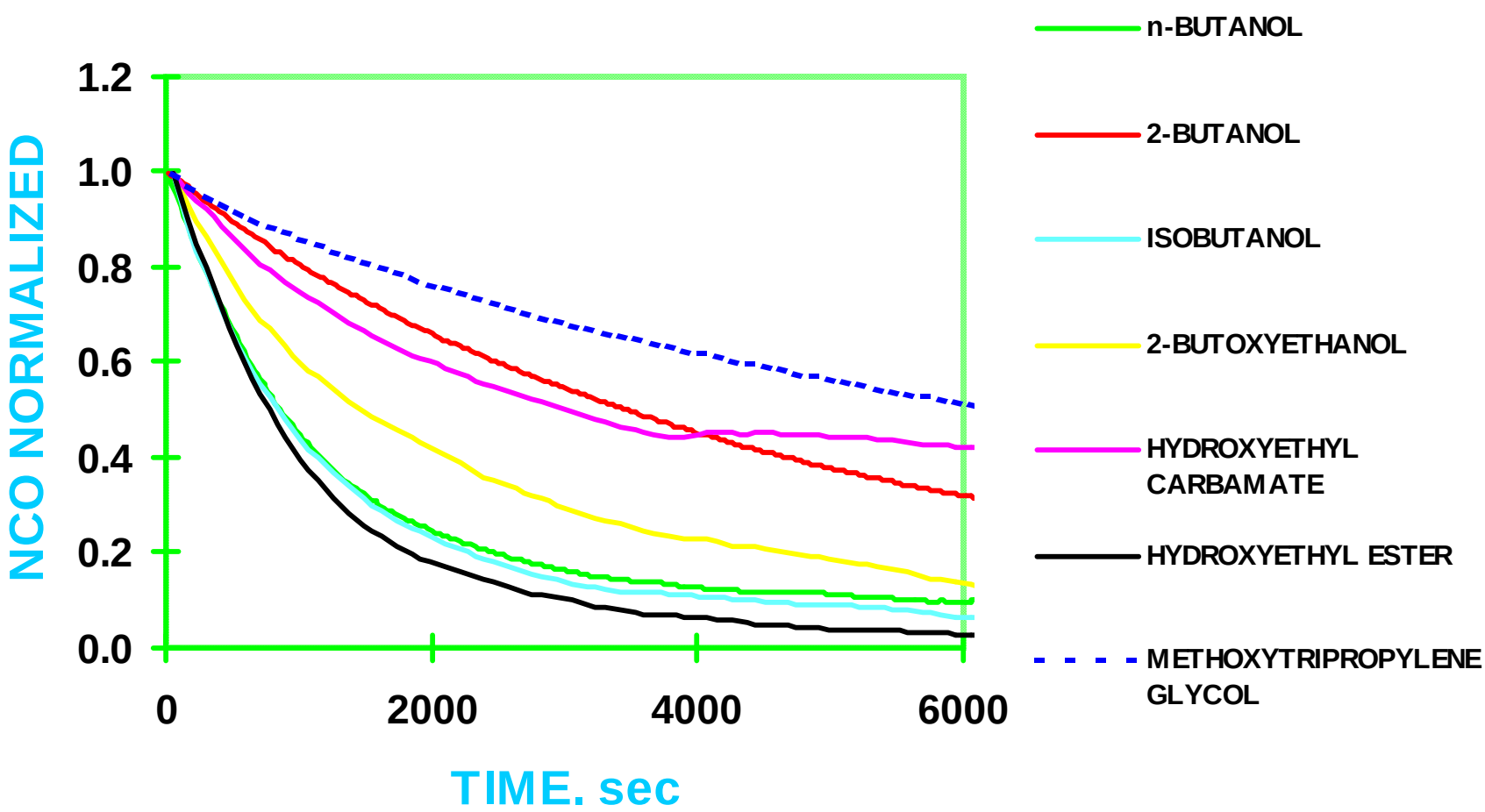

HDI-TRIMER/HYROXYL
pri, sec BUTANOL
NCO NORMALIZED 3000 sec.
1
0.8
0.6
0.4
0.2
0
0.134 %
10%
0.0134 %
0.268 %
0.0134 %
Bi
Dabco
DBTDL
Zn Oct.
Zr Chel
CATALYST
n-BUTANOL
2-BUTANOL
ISOBUTANOL
SL2338

HDI-TRIMER/HYROXYL

pri, sec BUTANOL, ETHER

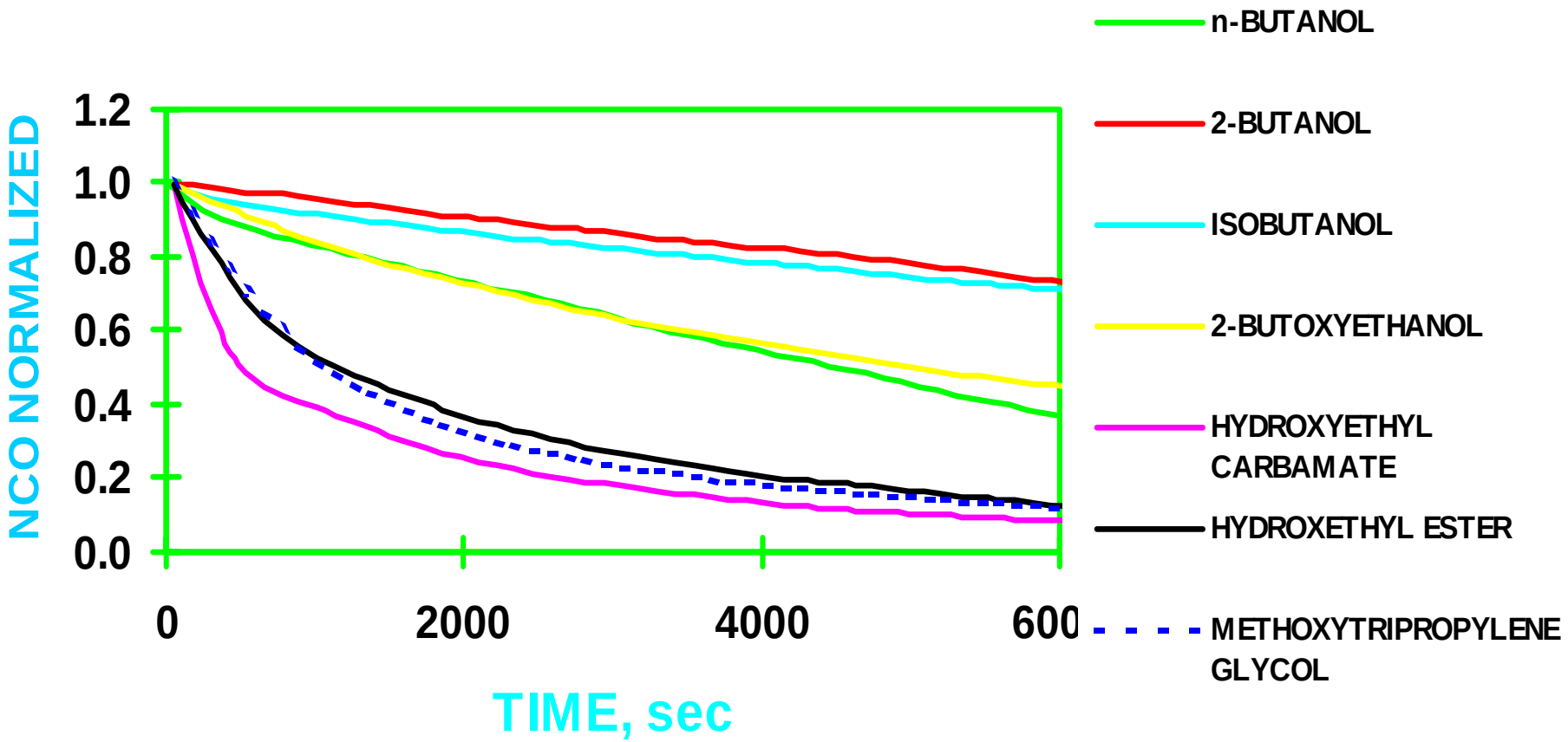


HDI-TRIMER - HYDROXYL
DBTDL 0.014% Sn



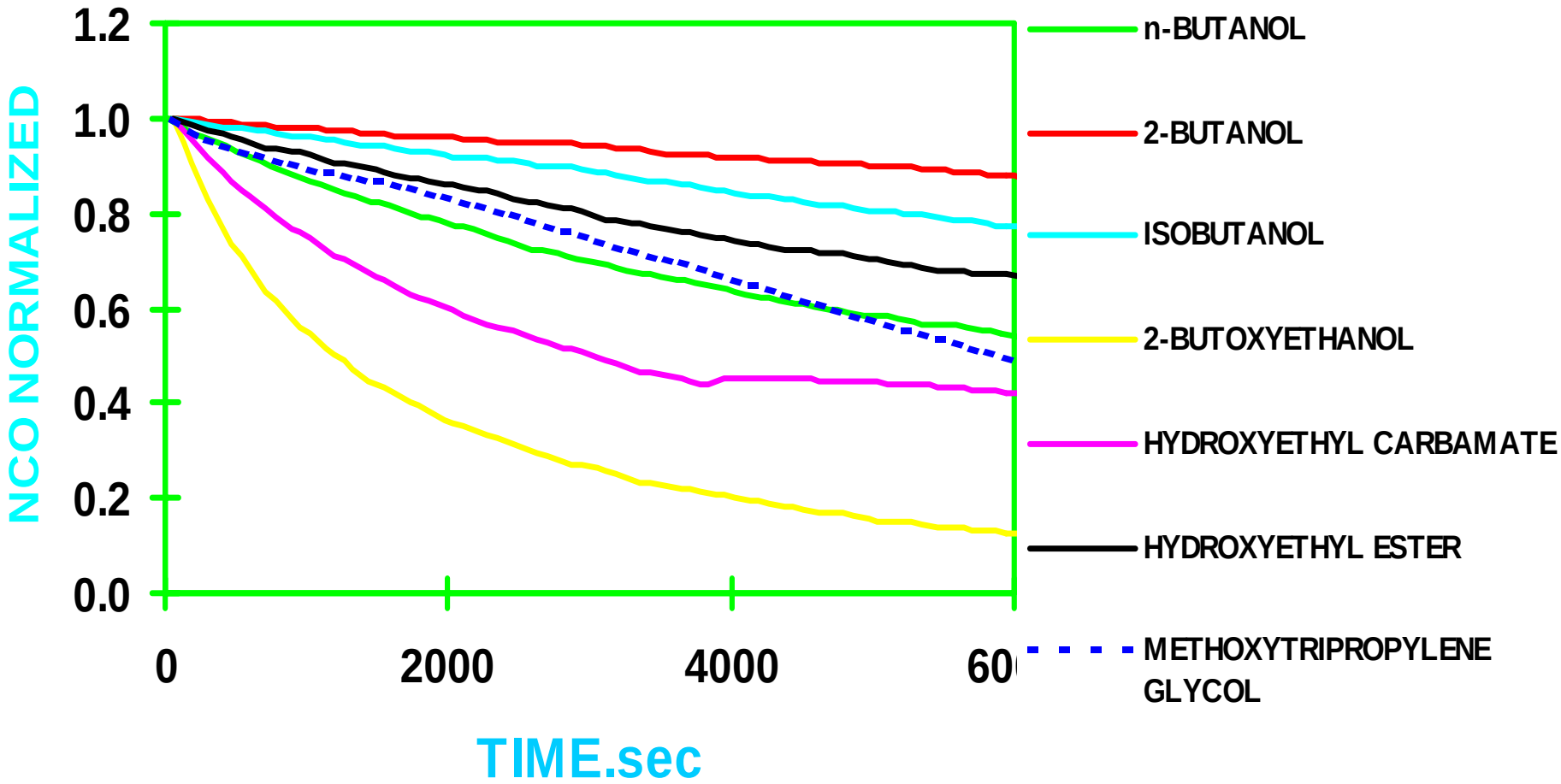
SL2340

HDI TRIMER / HYDROXYL
Bi CARB. 0.134 % Bi



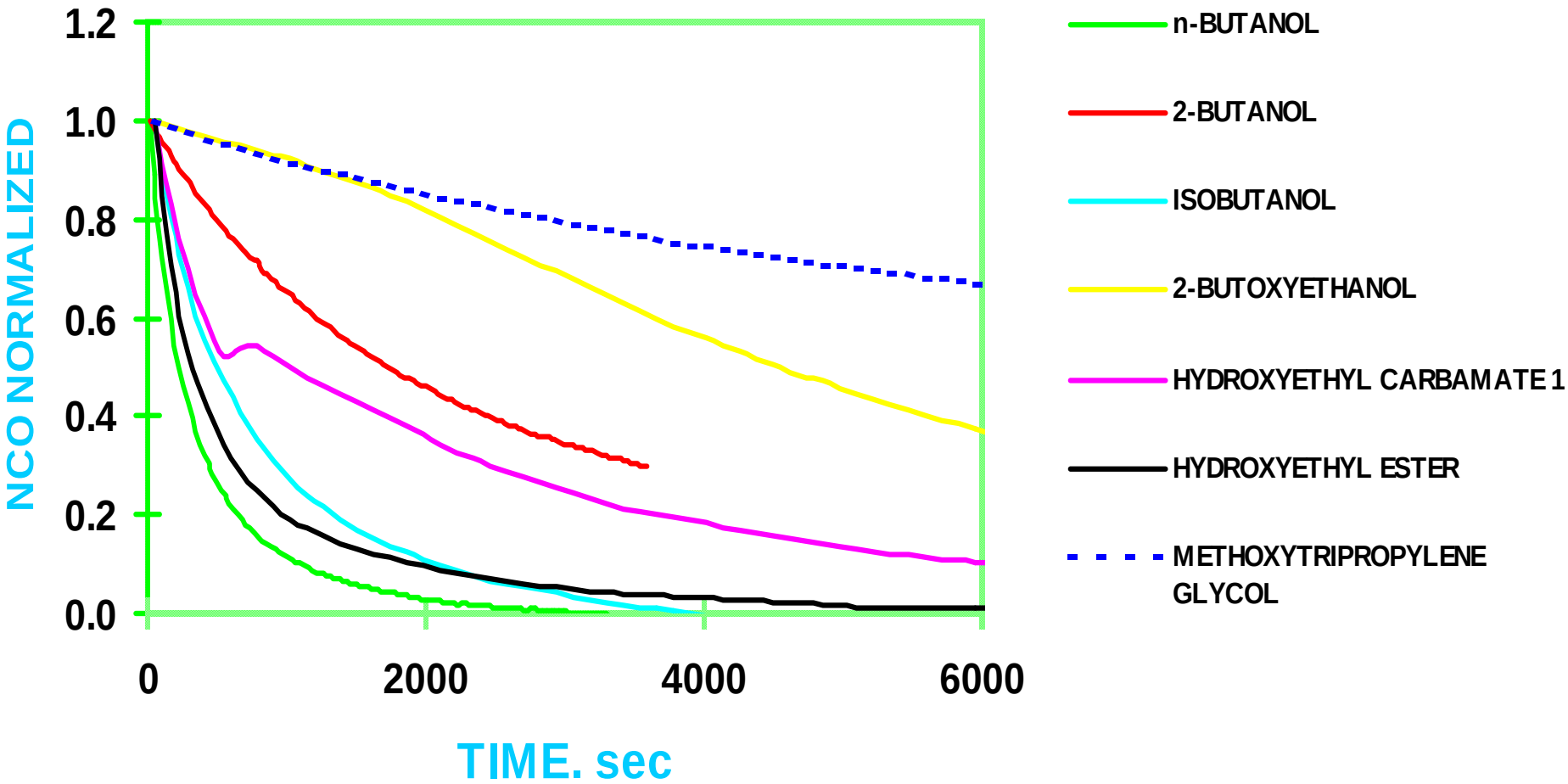
SL2341

HDI TRIMER / HYDROXYL
Zn OCTOATE 0.272% Zn



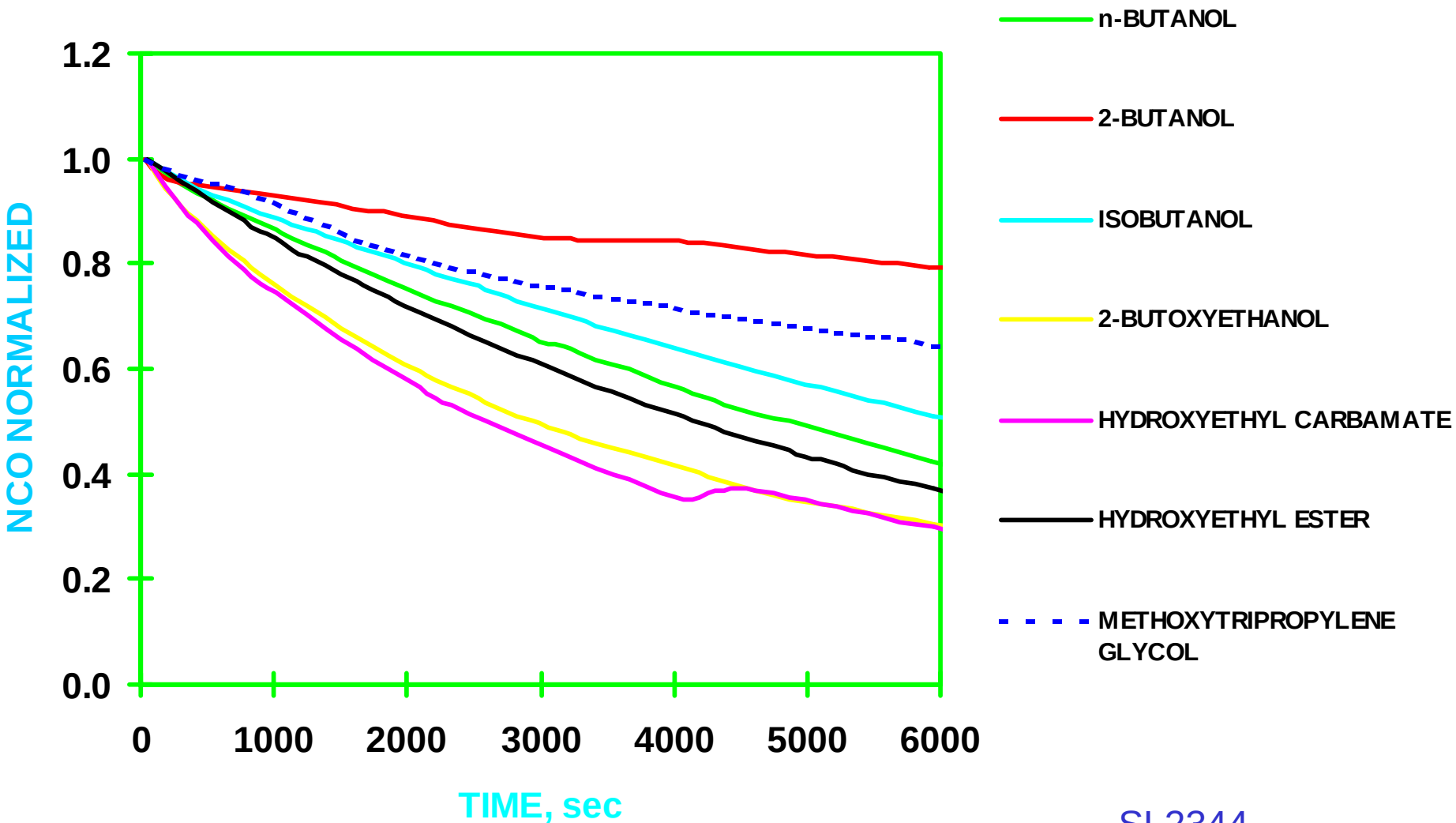
SL2342

HDI TRIMER / HYDROXYL
Zr CHELATE 0.014% Zr



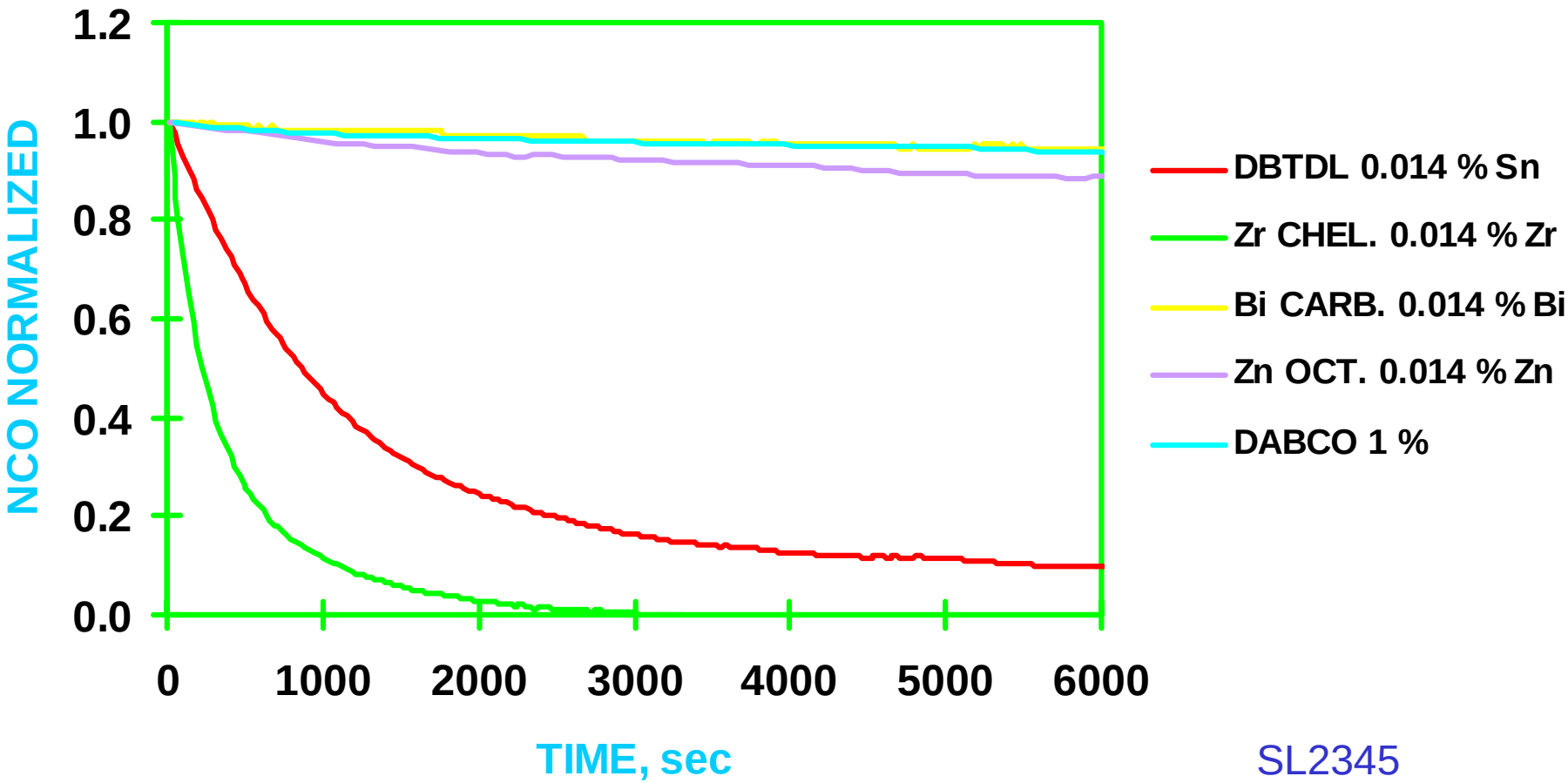
SL2343

HDI TRIMER / HYDROXYL
DABCO 10%



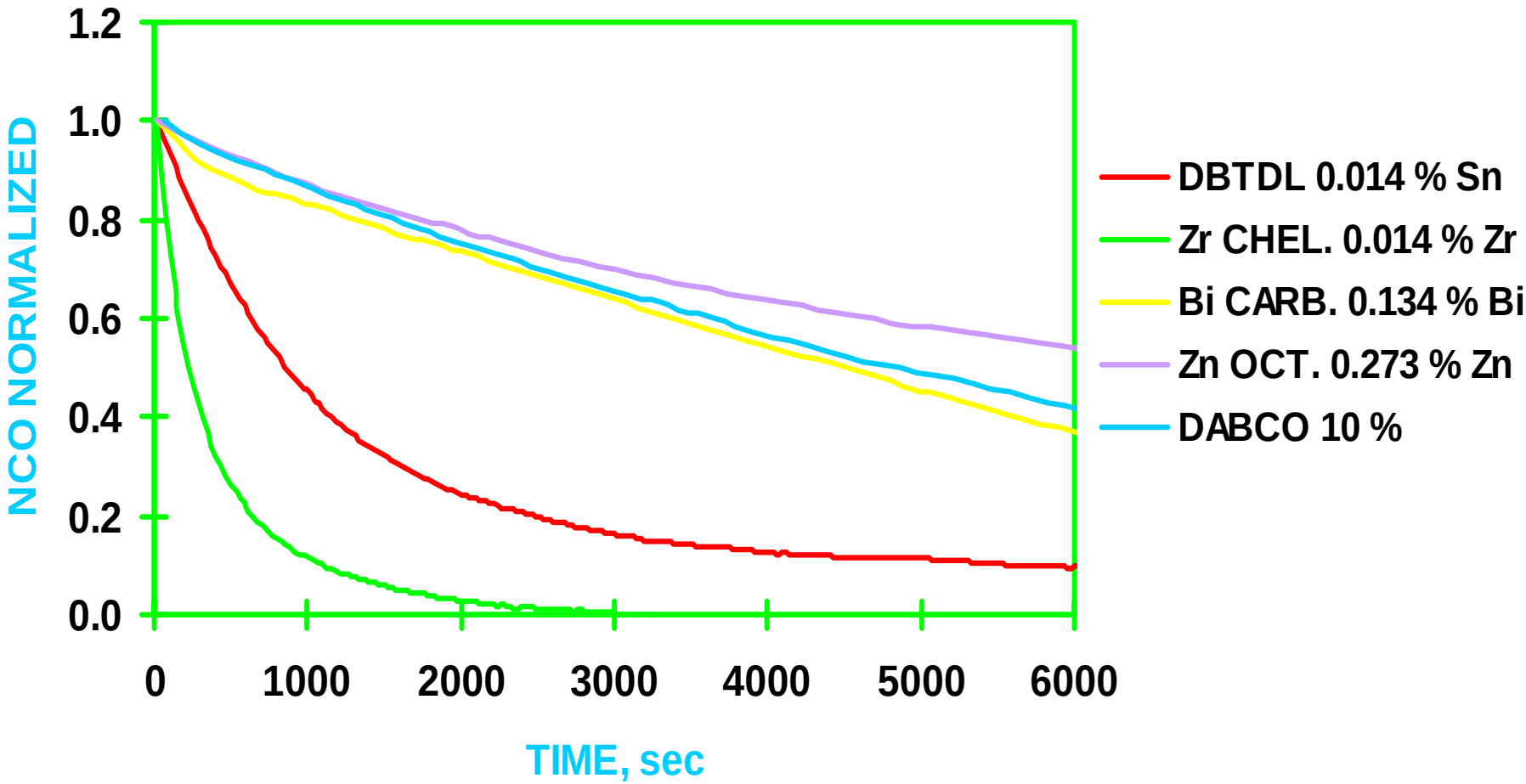
SL2344

HDI TRIMER / n-BUTANOL



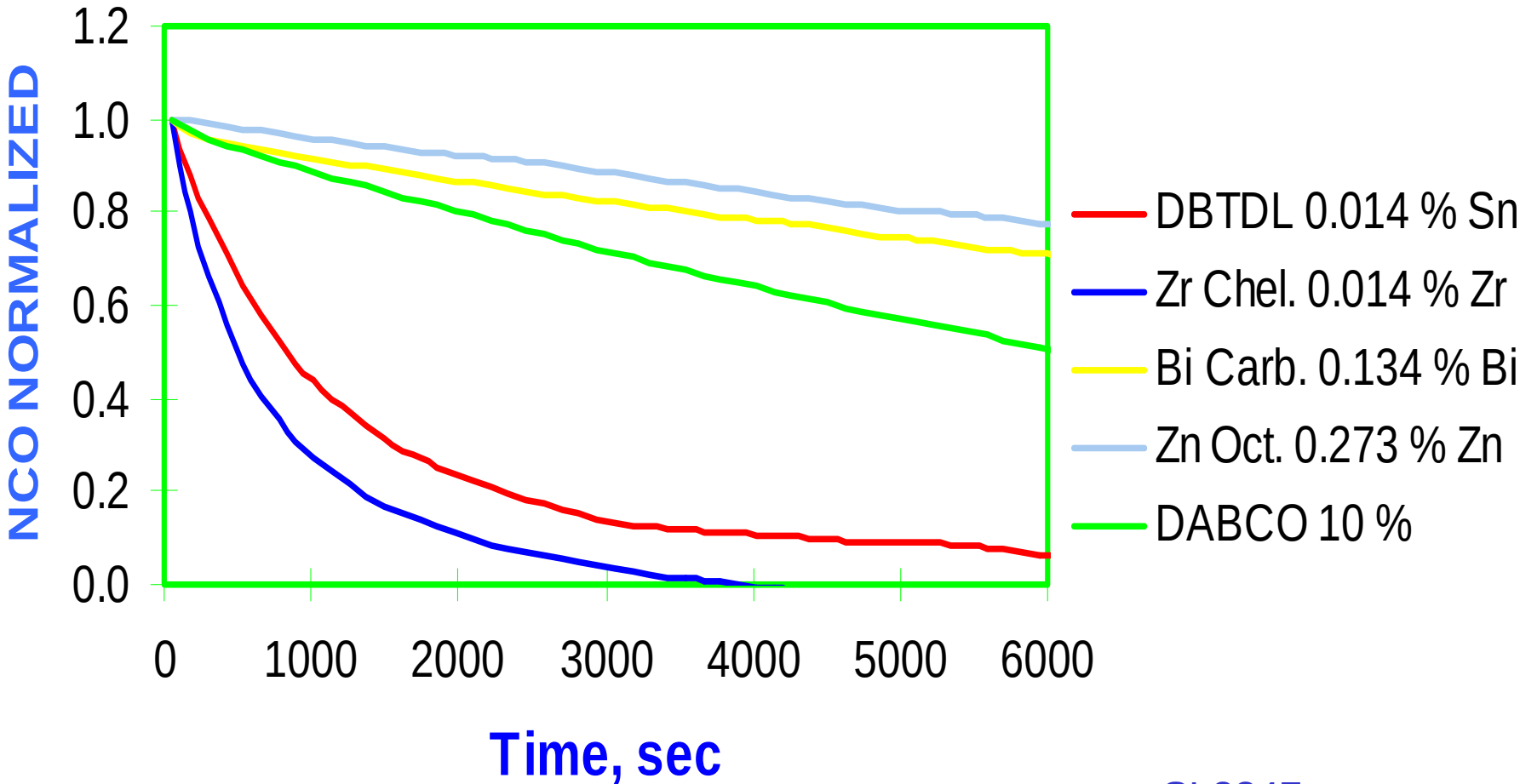
SL2345

HDI TRIMER / n-BUTANOL



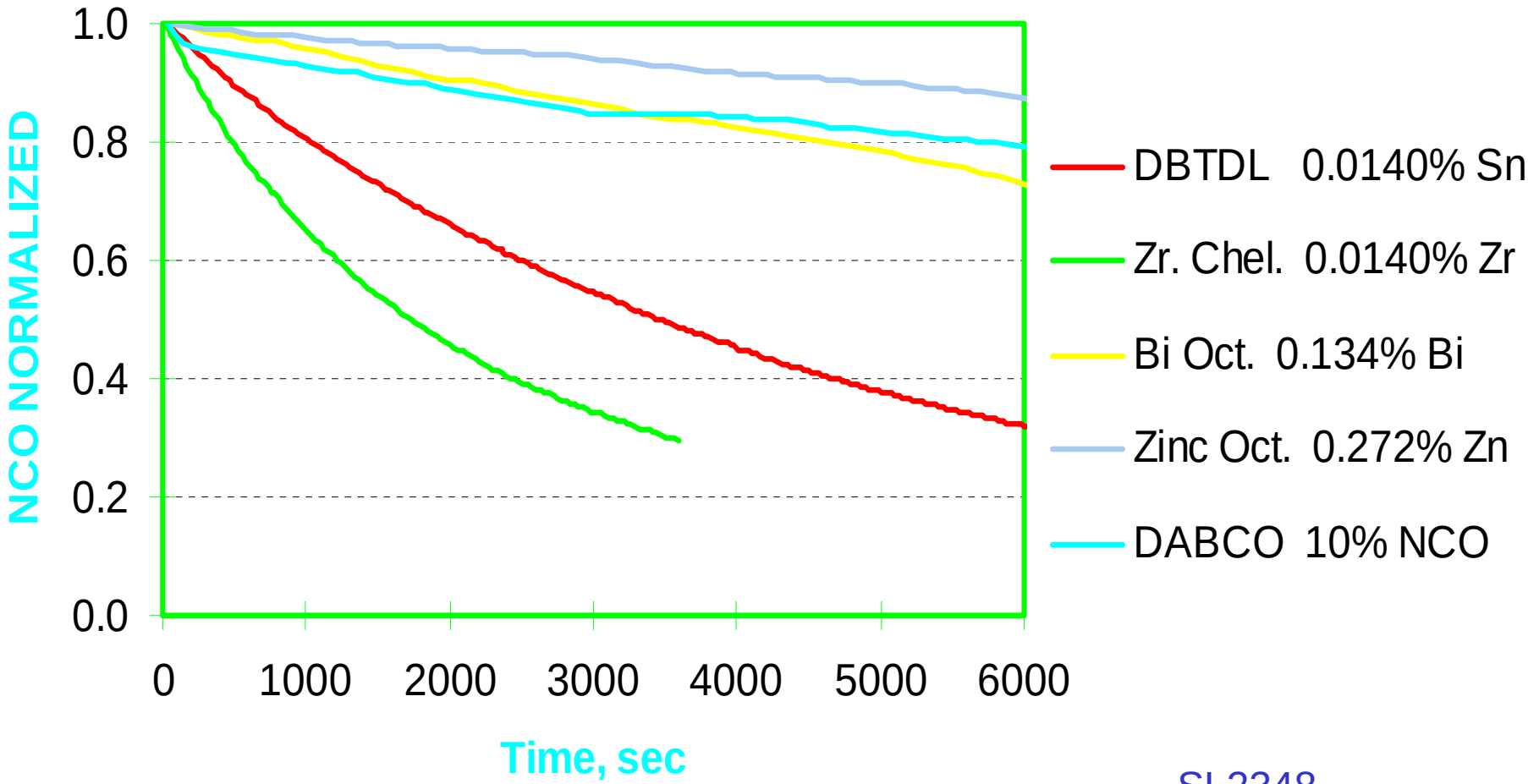
SL2346

HDI-TRIMER / ISOBUTANOL



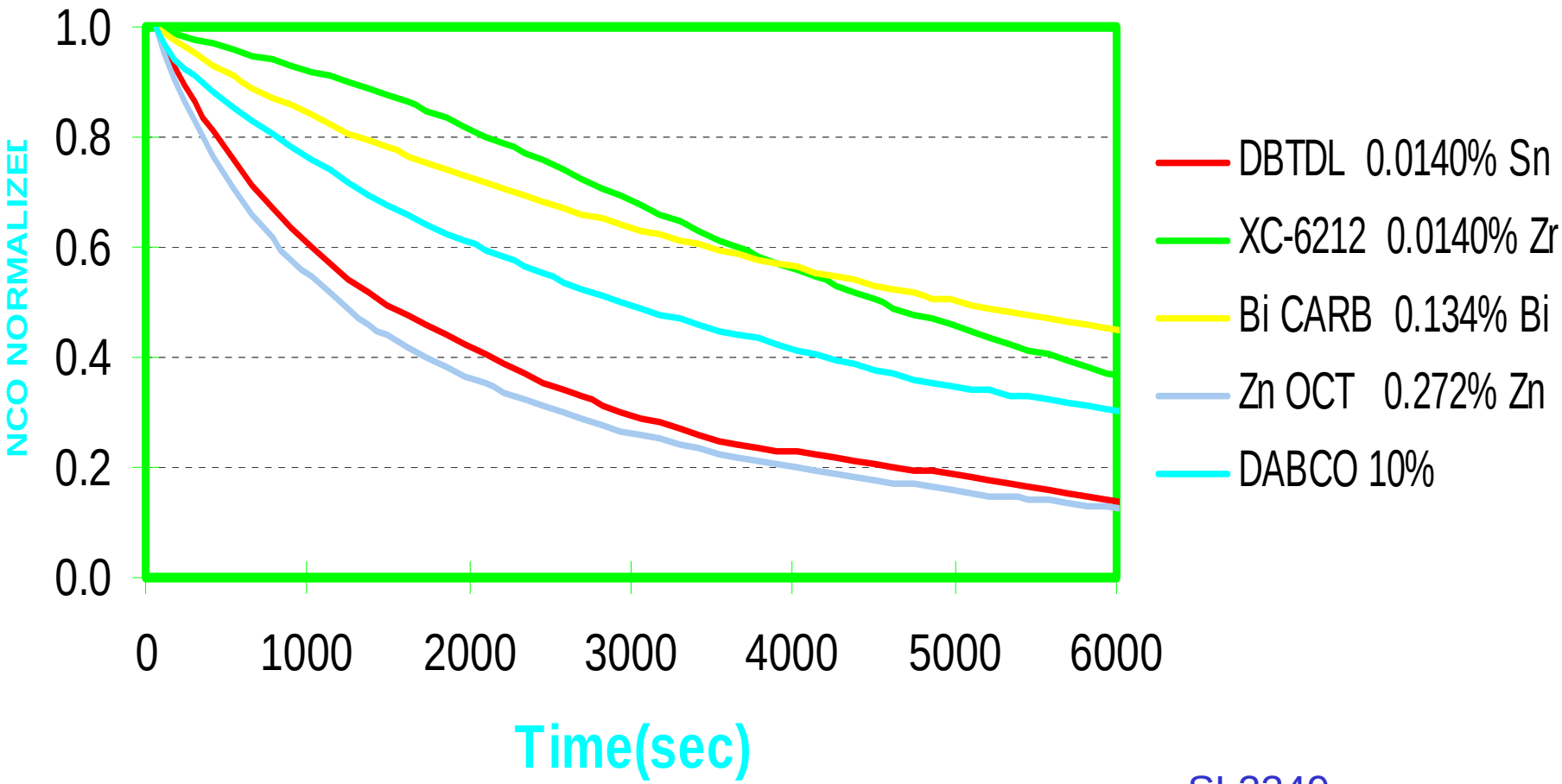
SL2347

HDI-TRIMER / 2-BUTANOL



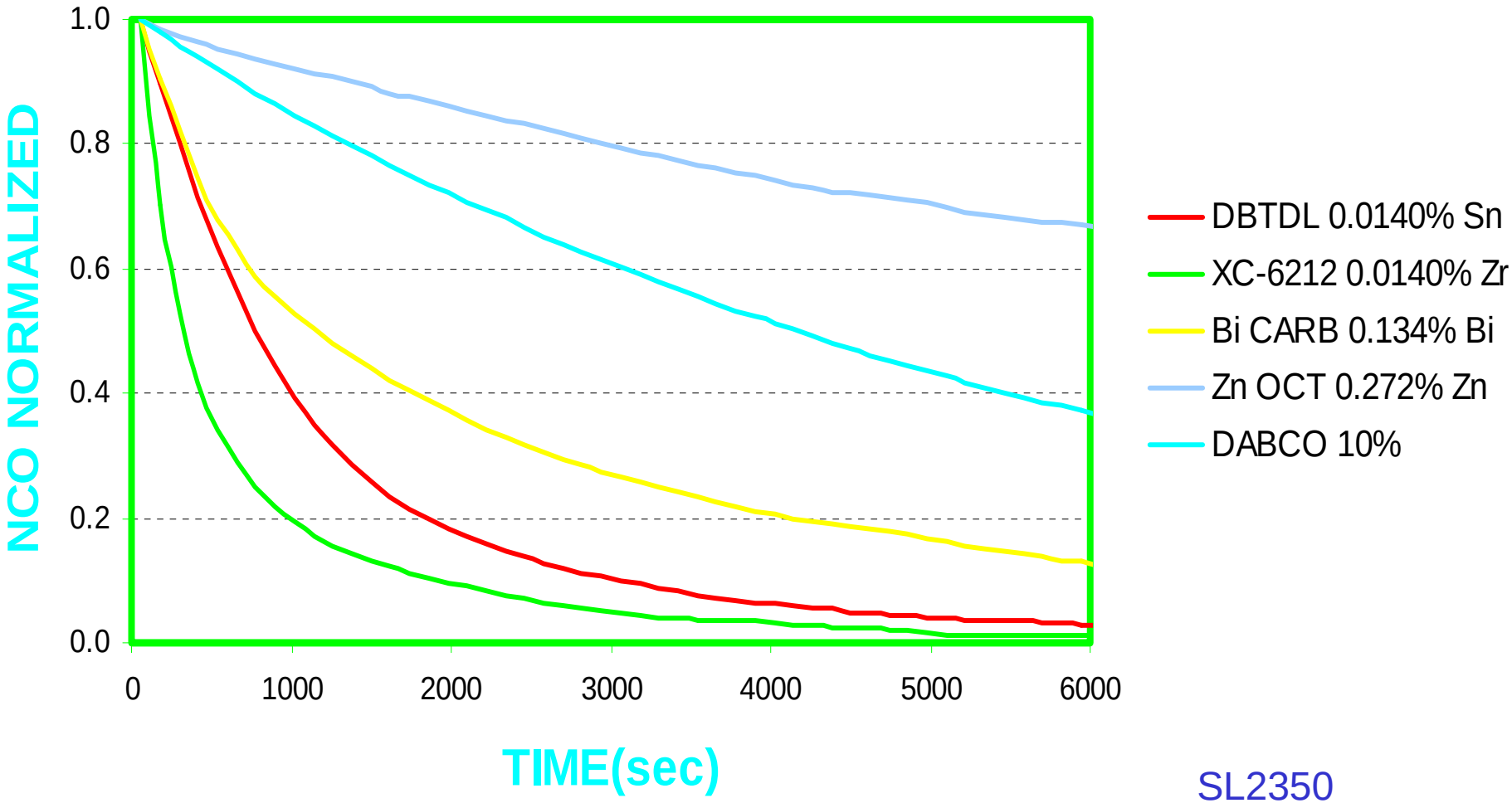
SL2348

HDI TRIMER / 2-BUTOXYETHANOL



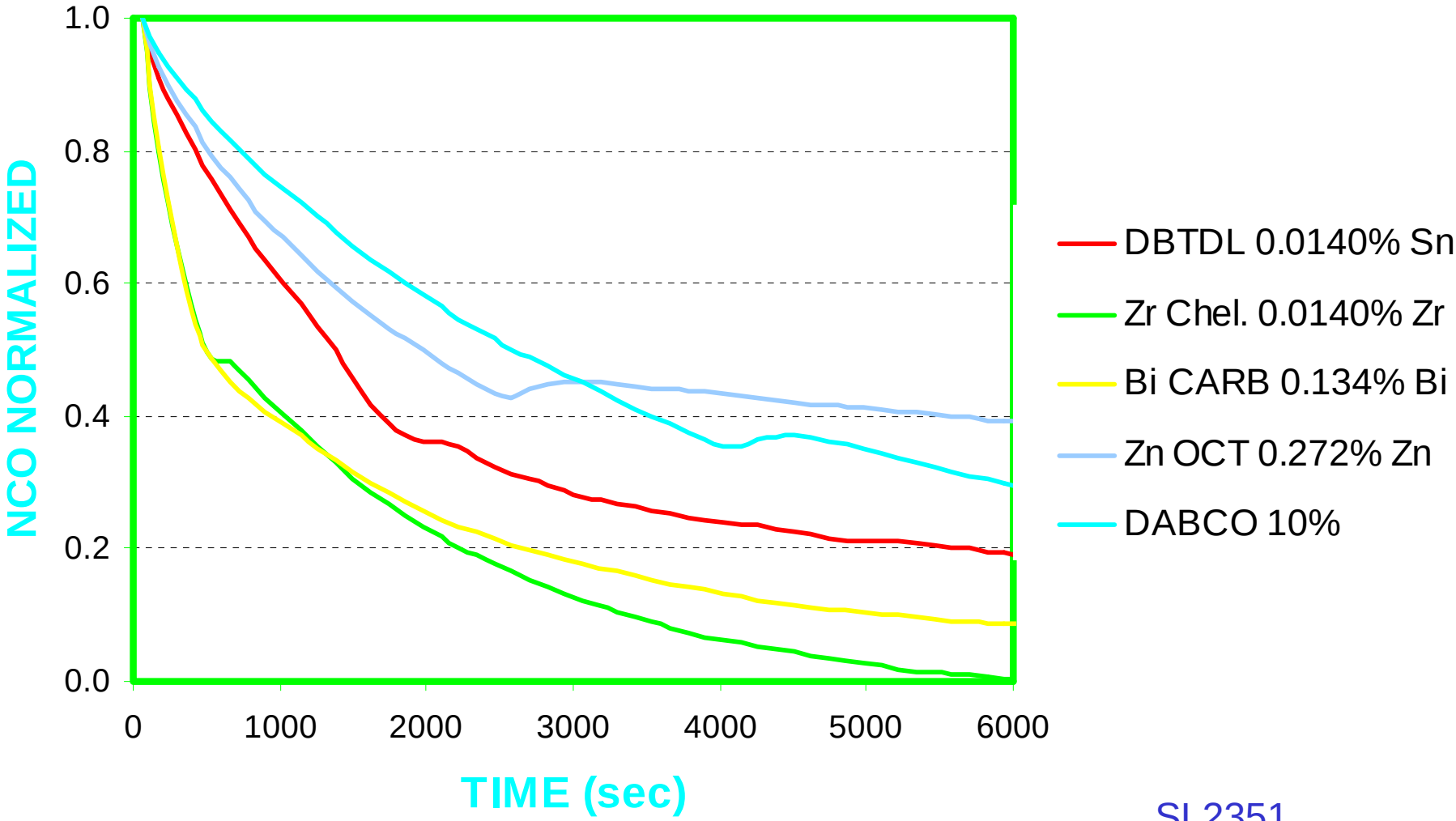
SL2349

HDI TRIMER / 2-HYDROXY ETHYL ESTER



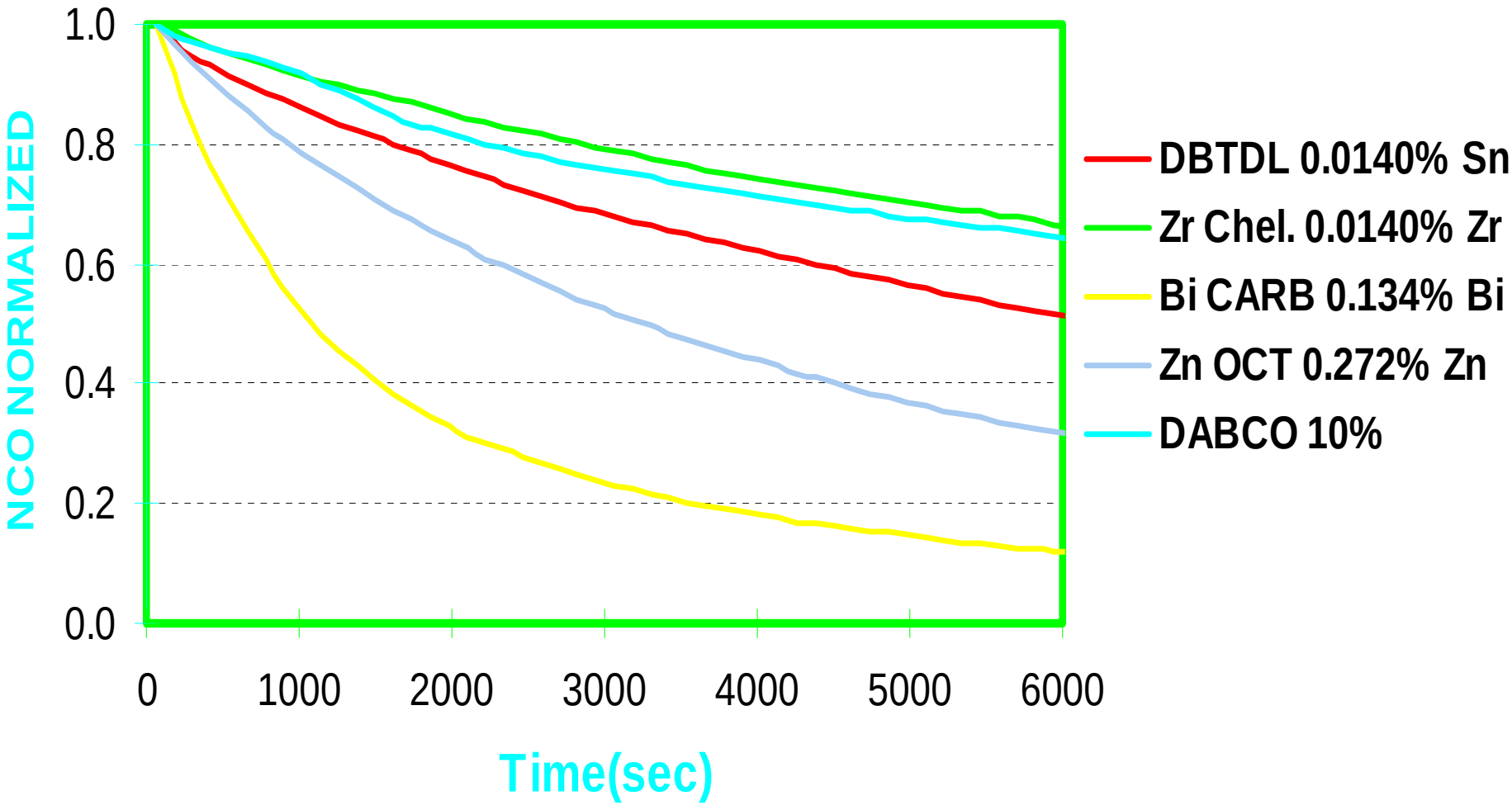
SL2350

HDI TRIMER / B-HYDROXY CARBAMATE



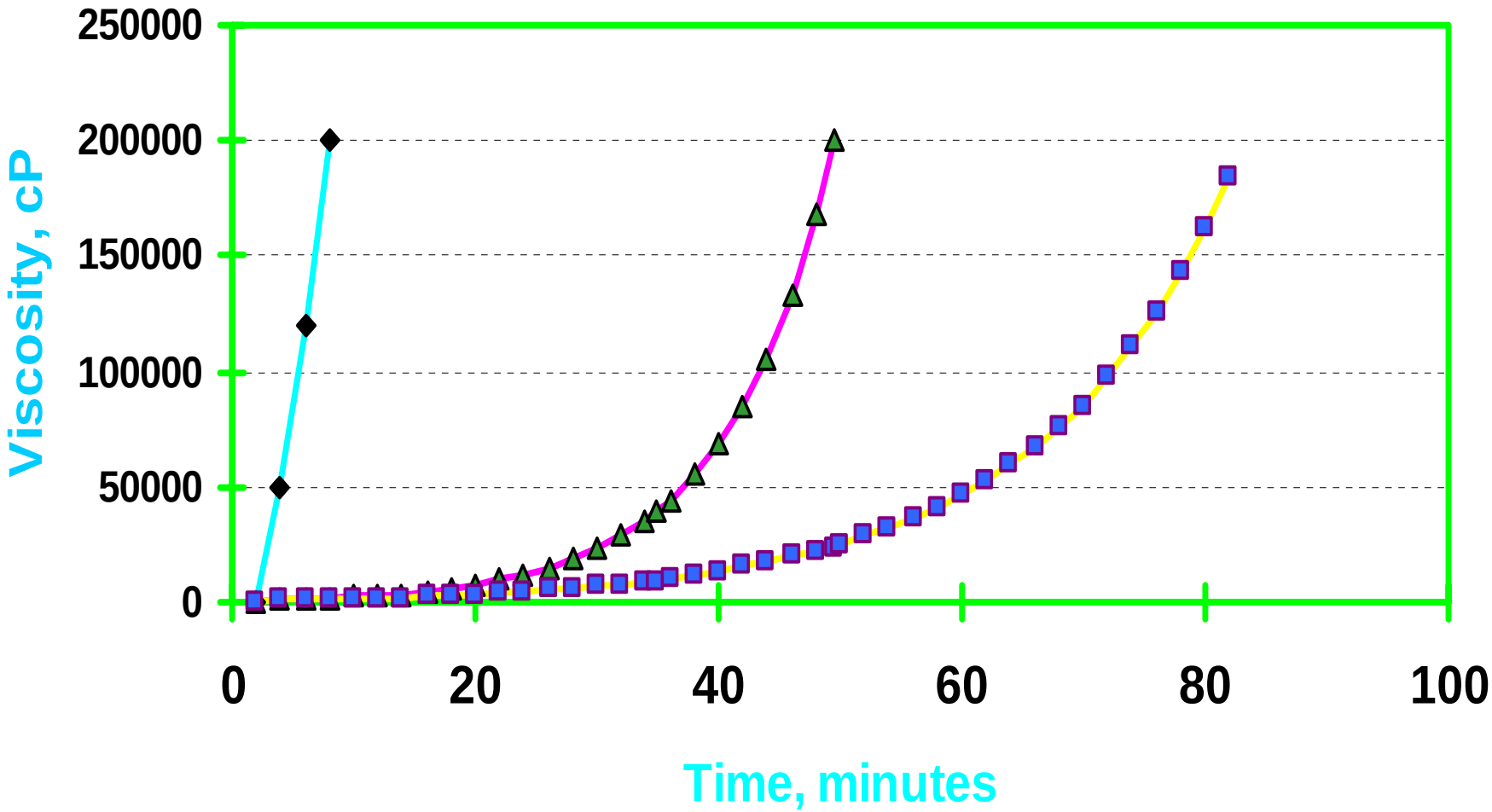
SL2351

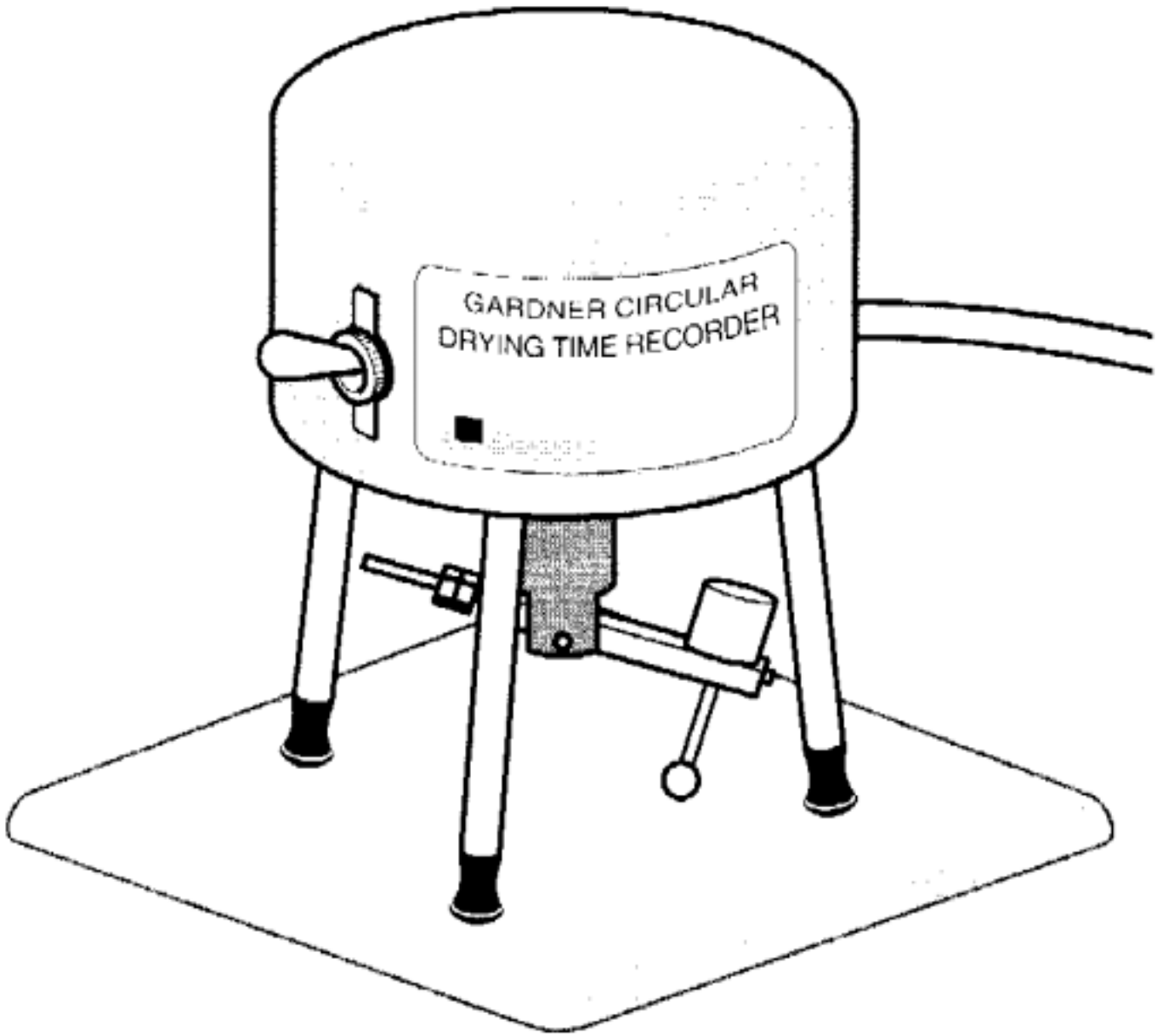
HDI TRIMER / TPG-O-Me

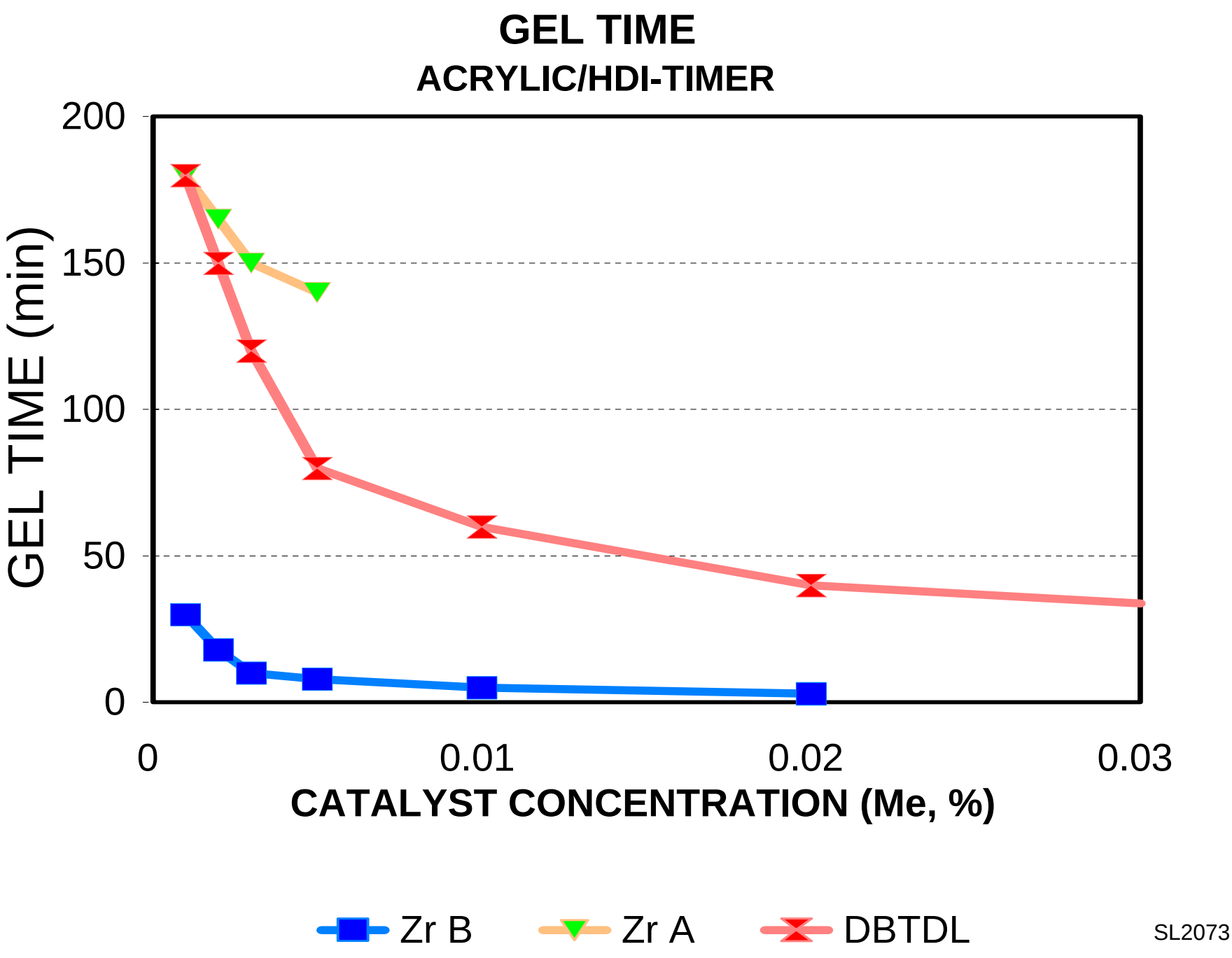


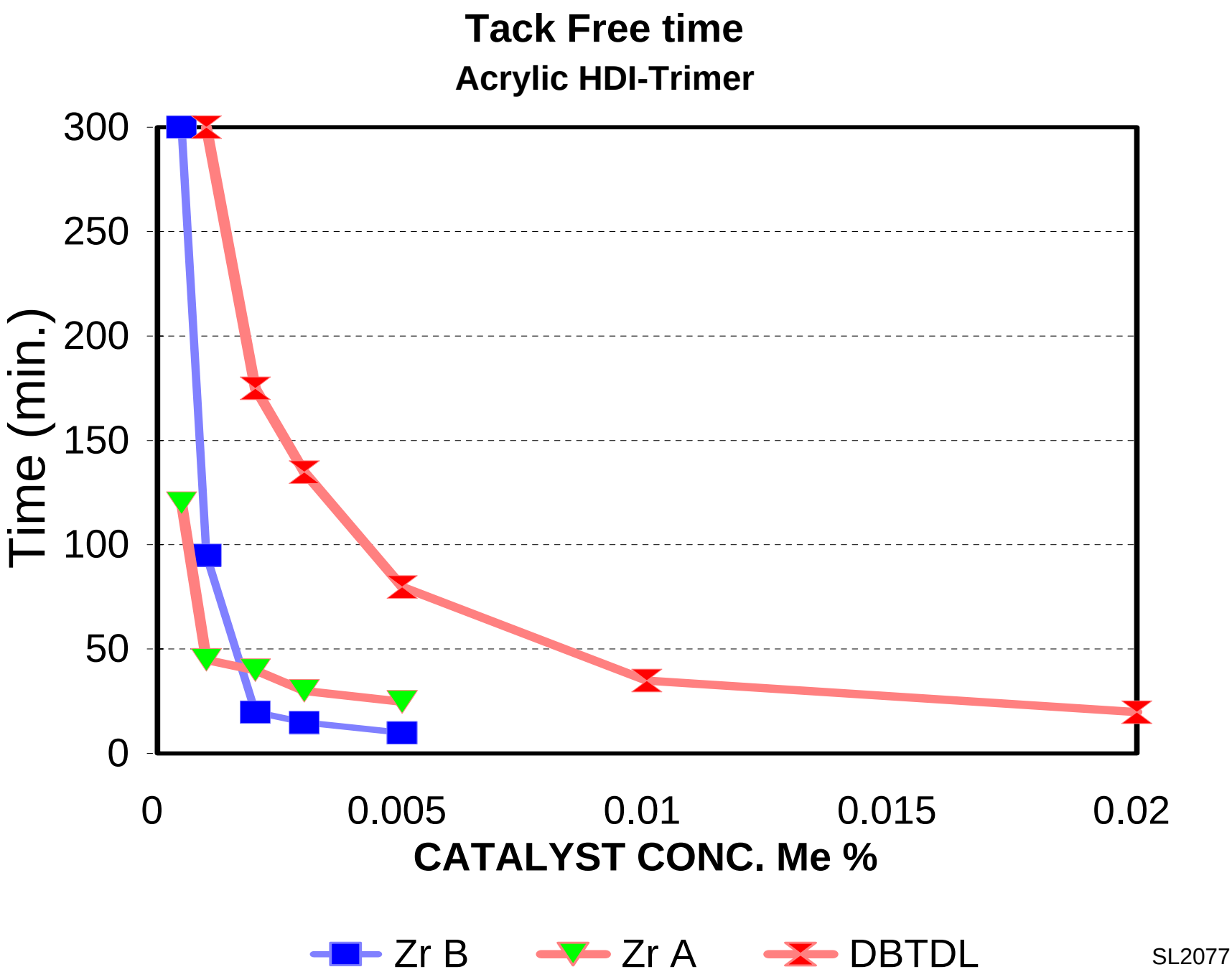
SL2352

Polyether MDI Elastomer
Bi Oct. 1/5 mol WATER



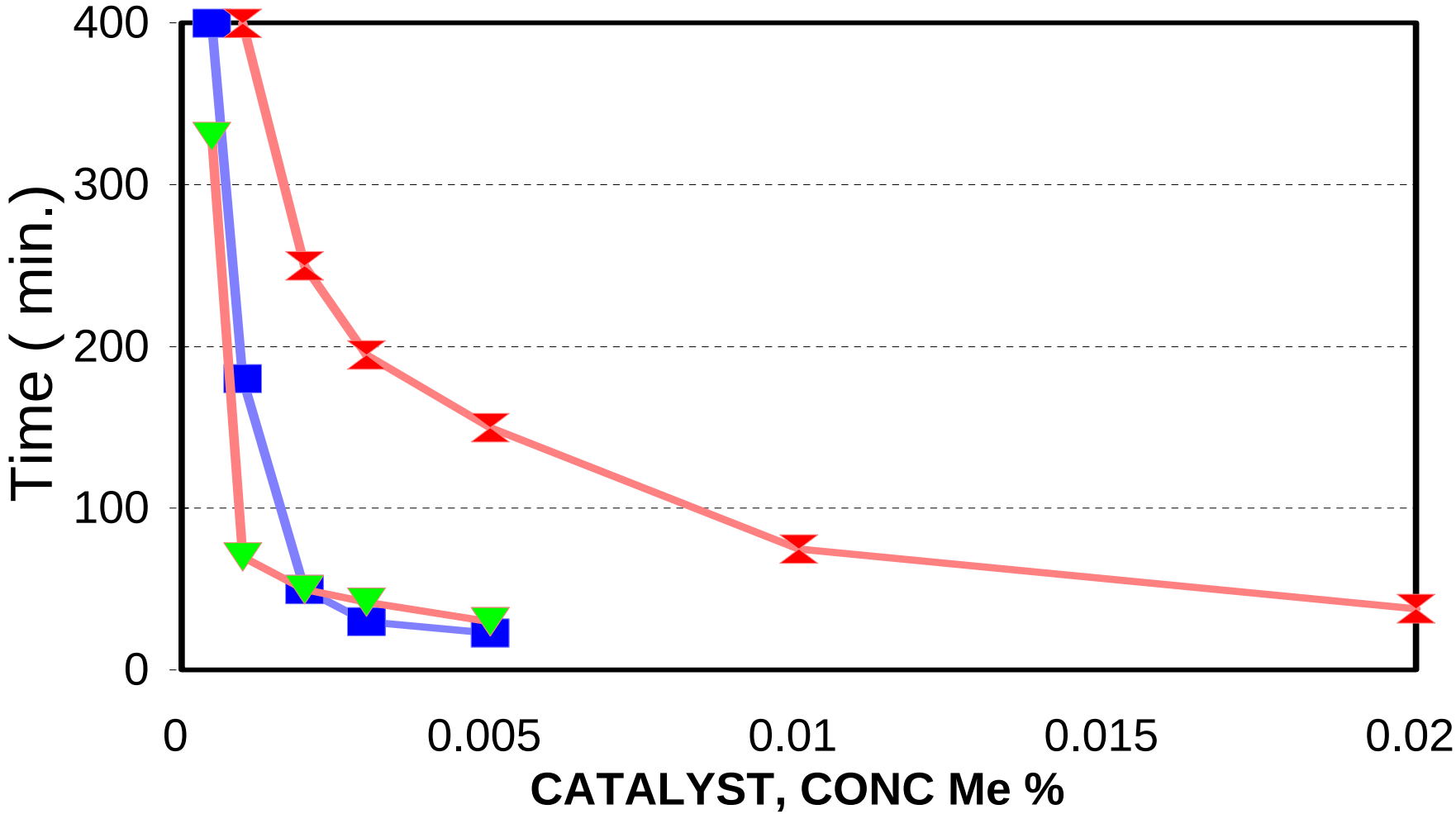

GARDNER CIRCULAR
DRYING TIME RECORDER


GEL TIME
ACRYLIC/HDI-TIMER
200
150
100
50
0
GEL TIME (min)
0
0.01
0.02
0.03
CATALYST CONCENTRATION (Me, %)
Zr B
Zr A
DBTDL
SL2073

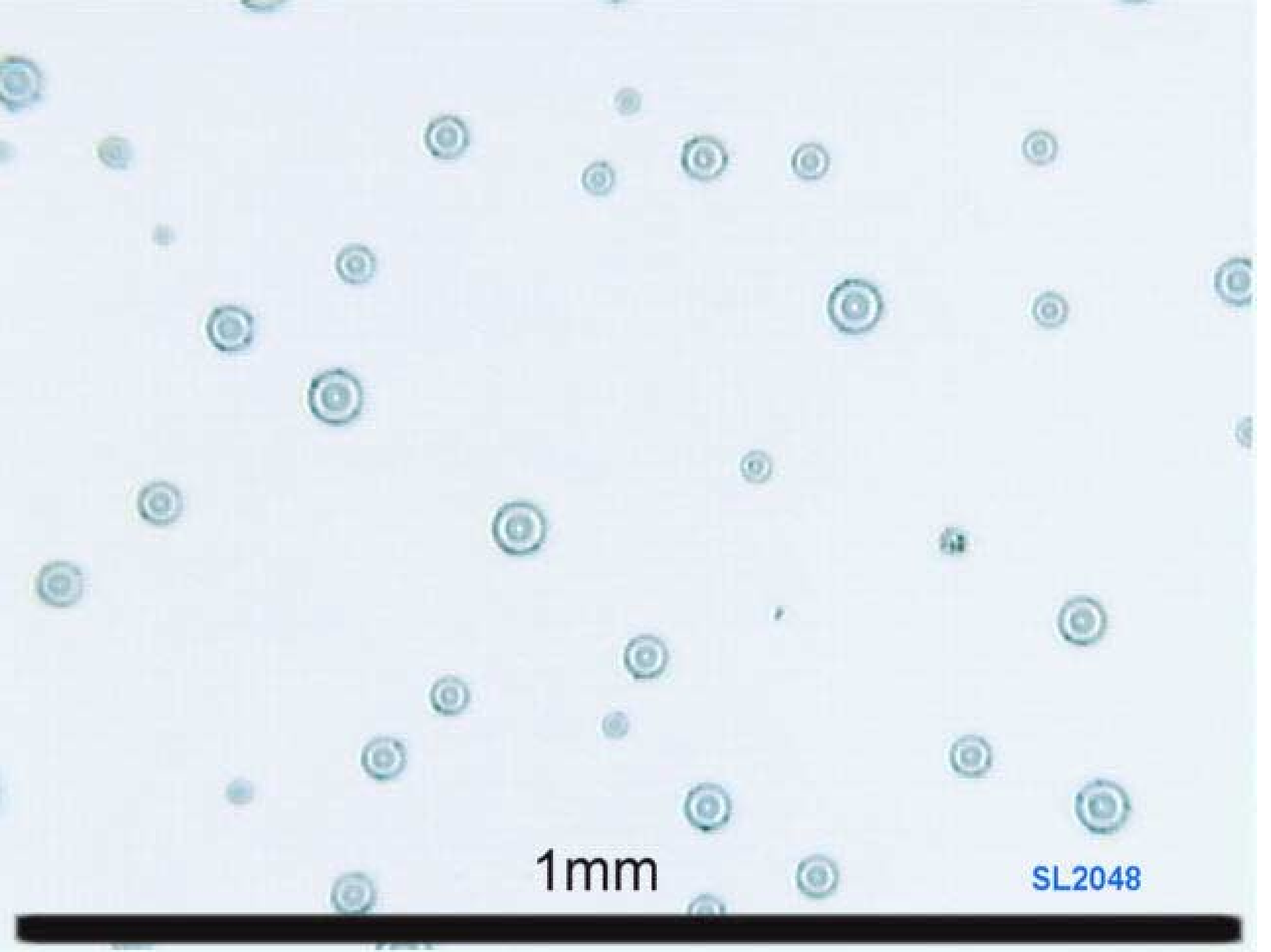

Tack Free time
Acrylic HDI-Trimer
Time (min.)
300
250
200
150
100
50
0
0
0.005
0.01
0.015
0.02
CATALYST CONC. Me %
Zr B
Zr A
DBTDL
SL2077

DRY THROUGH TIME

ACRYLIC/HDI-TRIMER, 30 µ,RT, 66 % RH



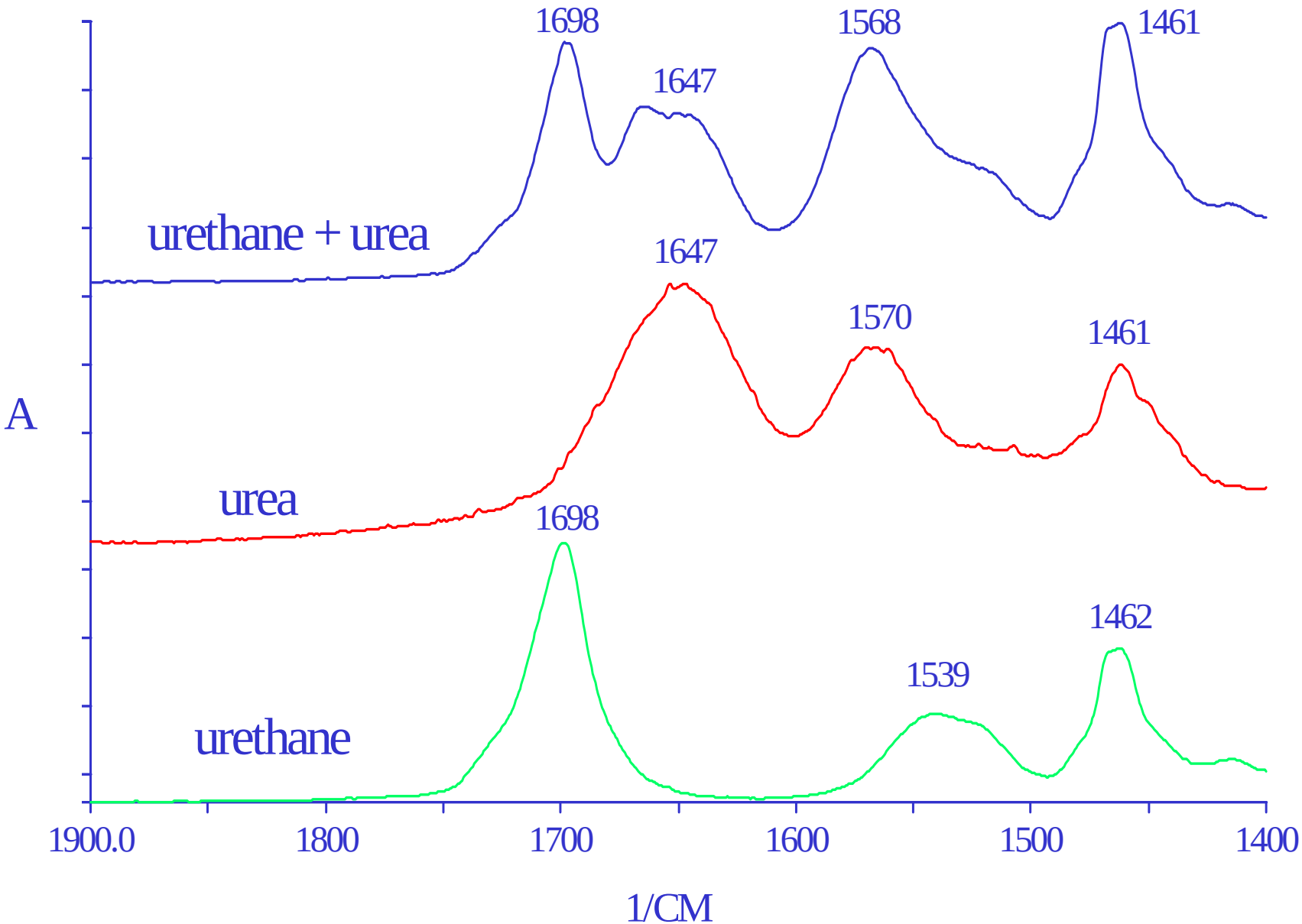
SL2075


1mm
SL2048

HDT-LV ISOCYANATE
WATER (2%) 0.0045 % Me

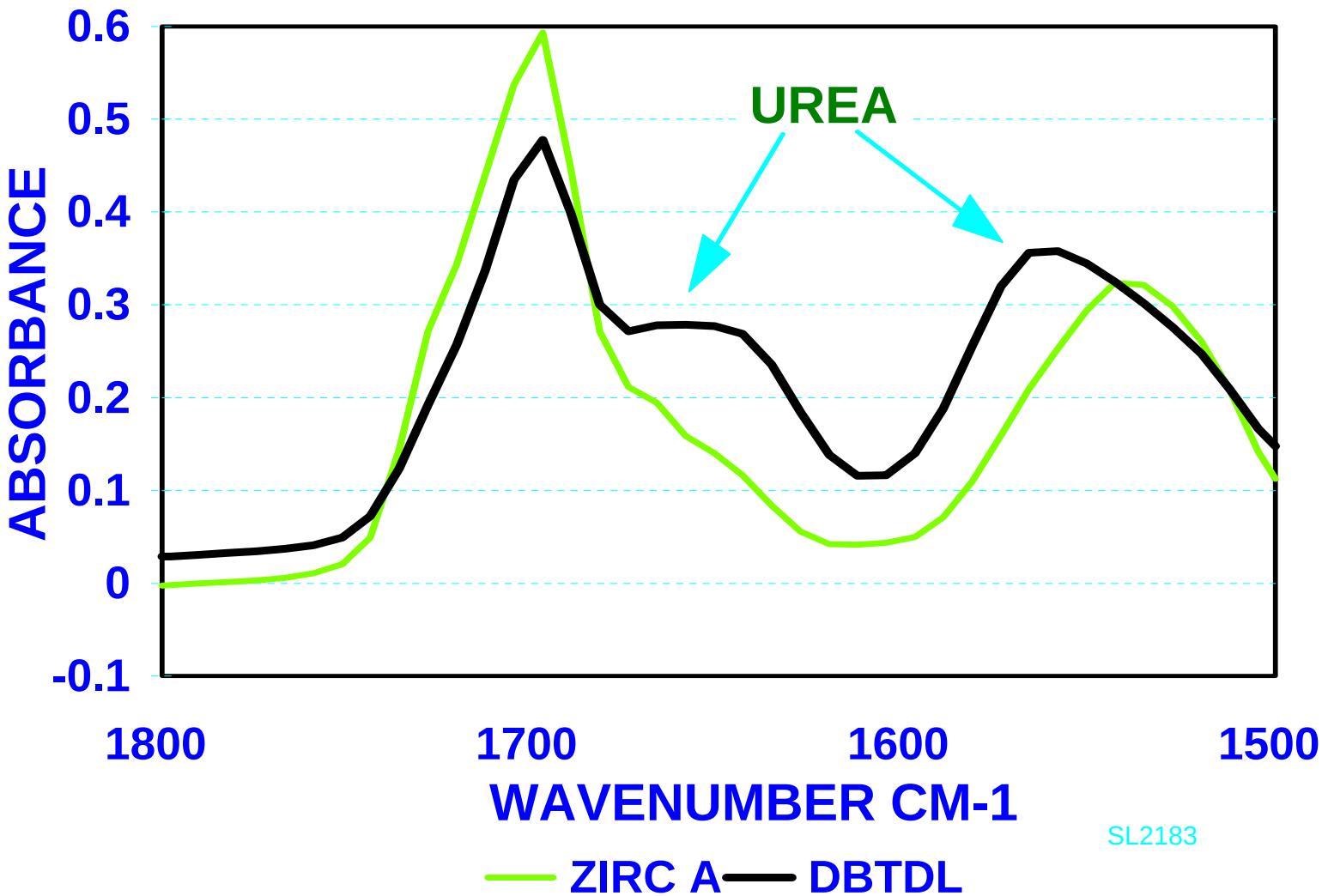
K-KAT XC-4205 DBTDL

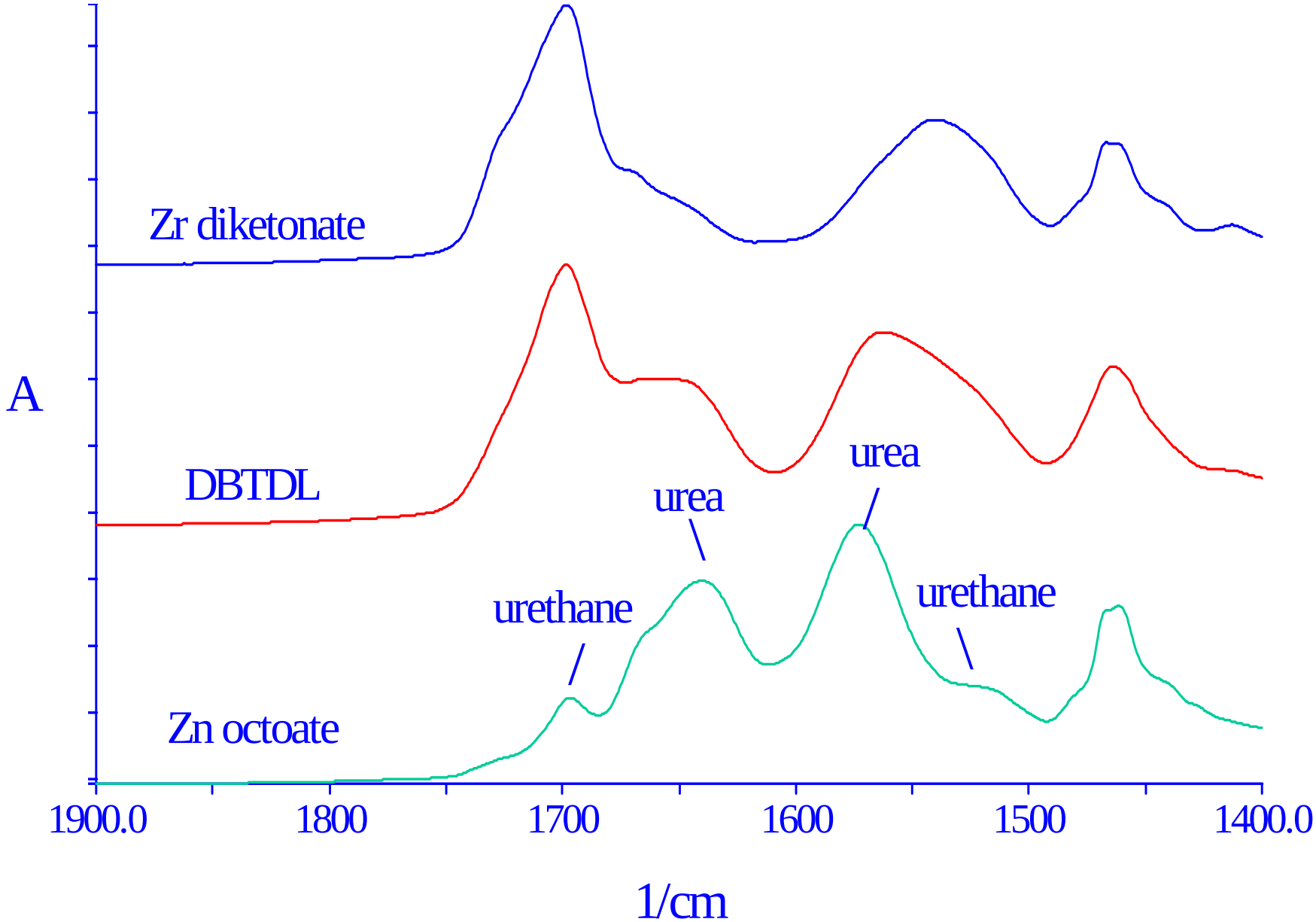
SL2014

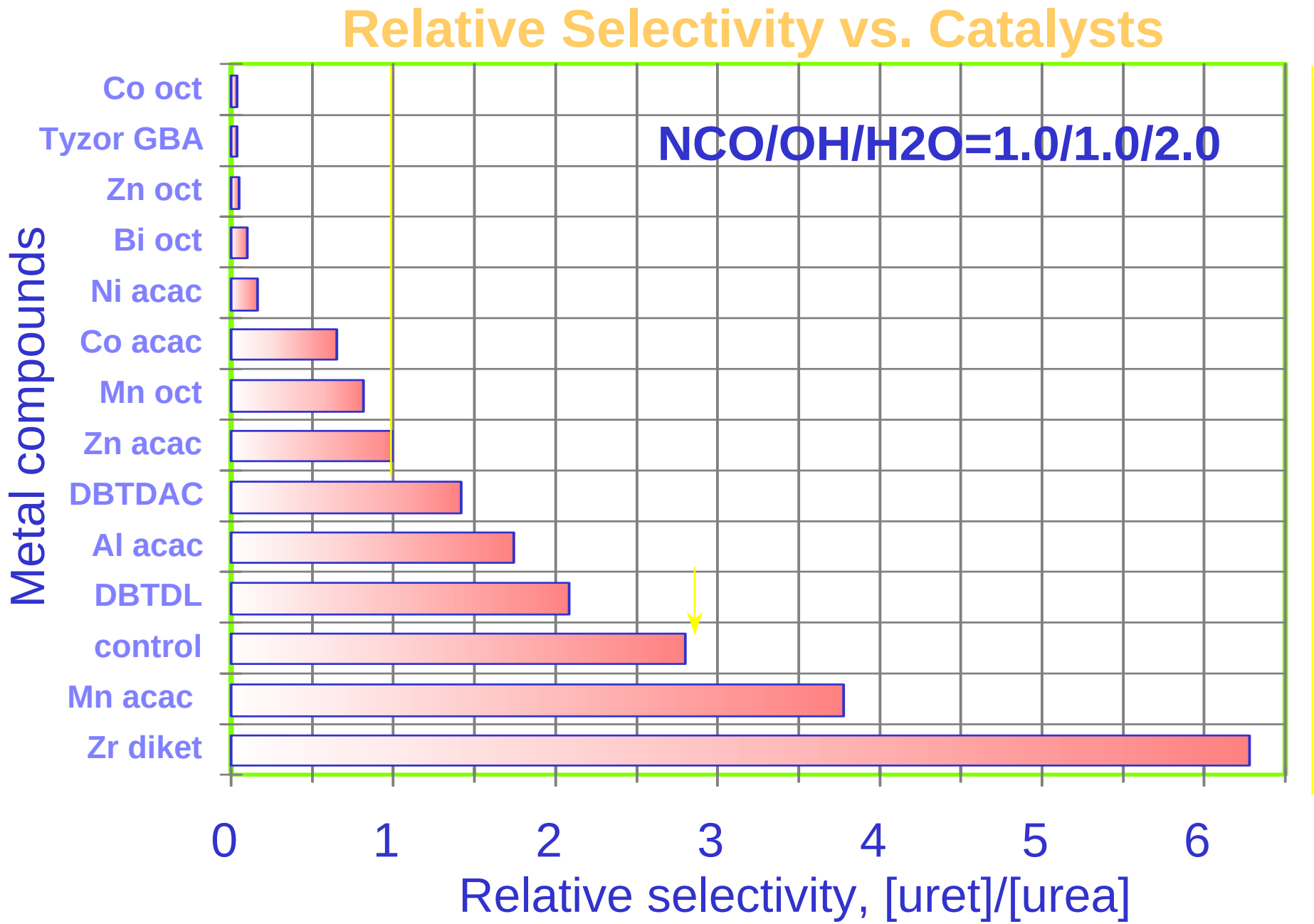

1698
1647
1568
1461
urethane + urea
1647
1570
1461
urea
1698
1462
1539
urethane
A
1900.0
1800
1700
1600
1500
1400
1/CM

SELECTIVITY OF CATALYSIS

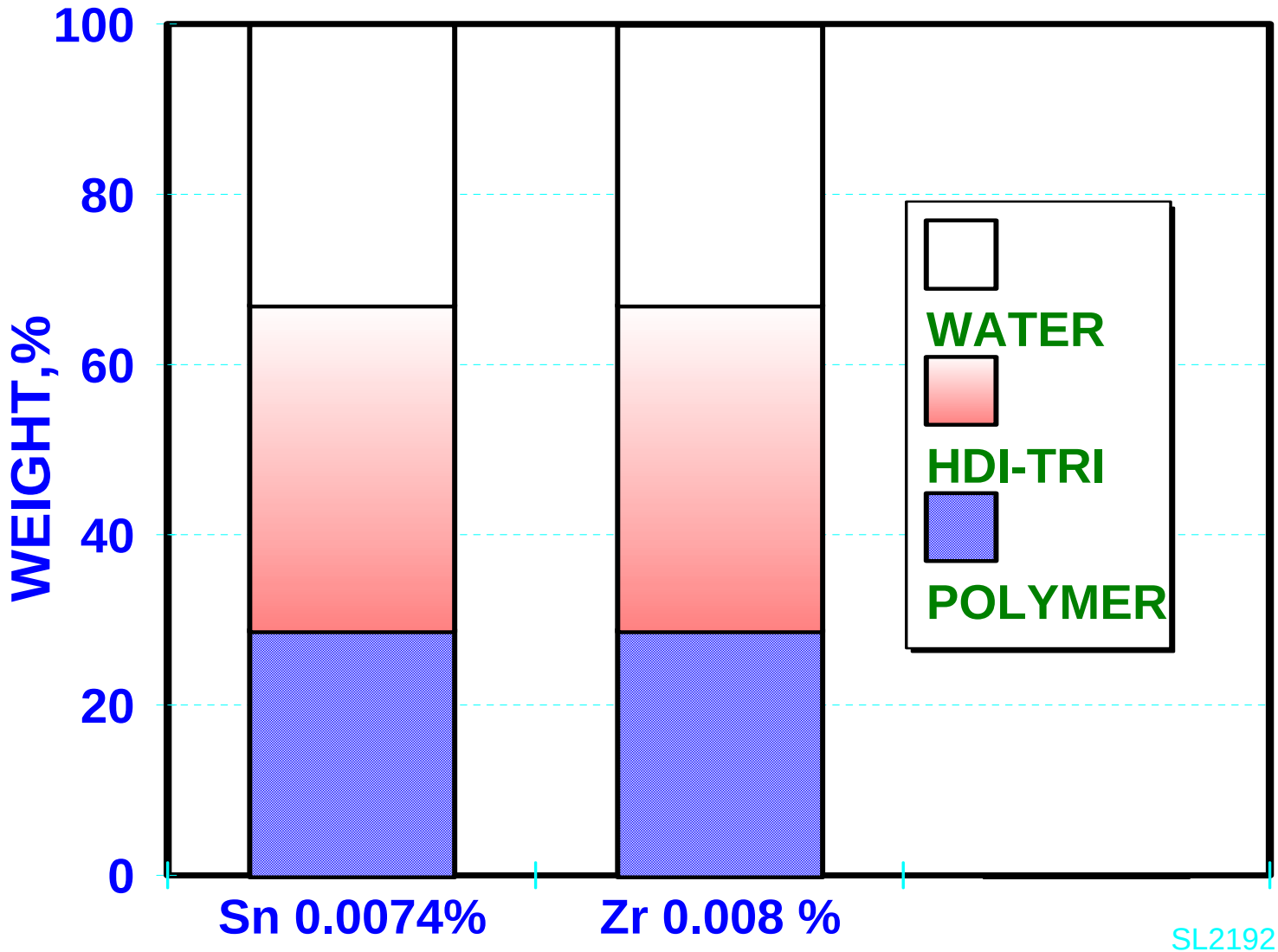
DBTDL & Zr CHELATE



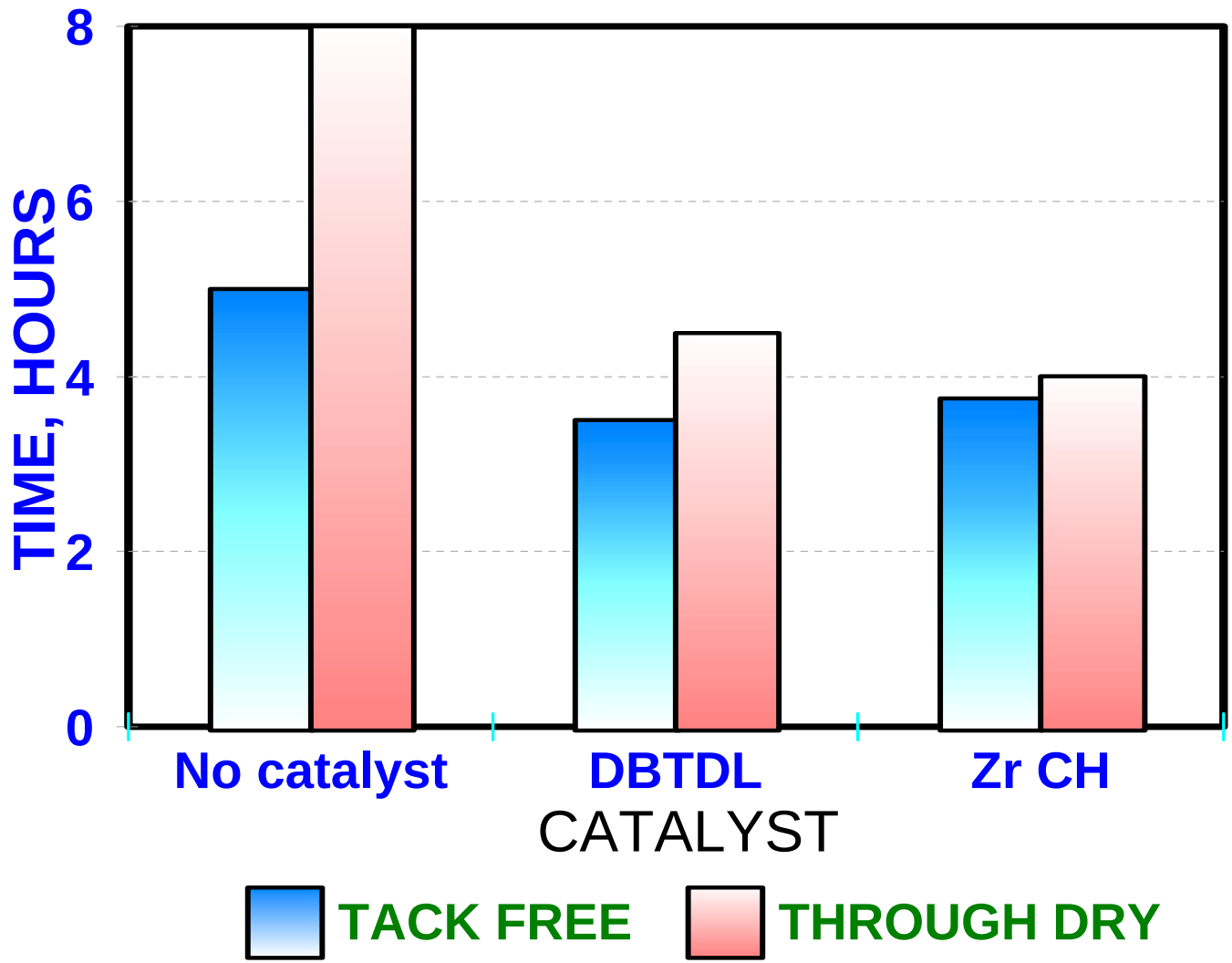

Zr diketonate
DBTDL
Zn octoate
A
urea
urea
urethane
urethane
1900.0
1800
1700
1600
1500
1400.0
1/cm


Relative Selectivity vs. Catalysts
NCO/OH/H2O=1.0/1.0/2.0
Metal compounds
Co oct
Tyzor GBA
Zn oct
Bi oct
Ni acac
Co acac
Mn oct
Zn acac
DBTDAC
Al acac
DBTDL
control
Mn acac
Zr diket
0
1
2
3
4
5
6
Relative selectivity, [uret]/[urea]

WATERBORNE TWO COMPONENT



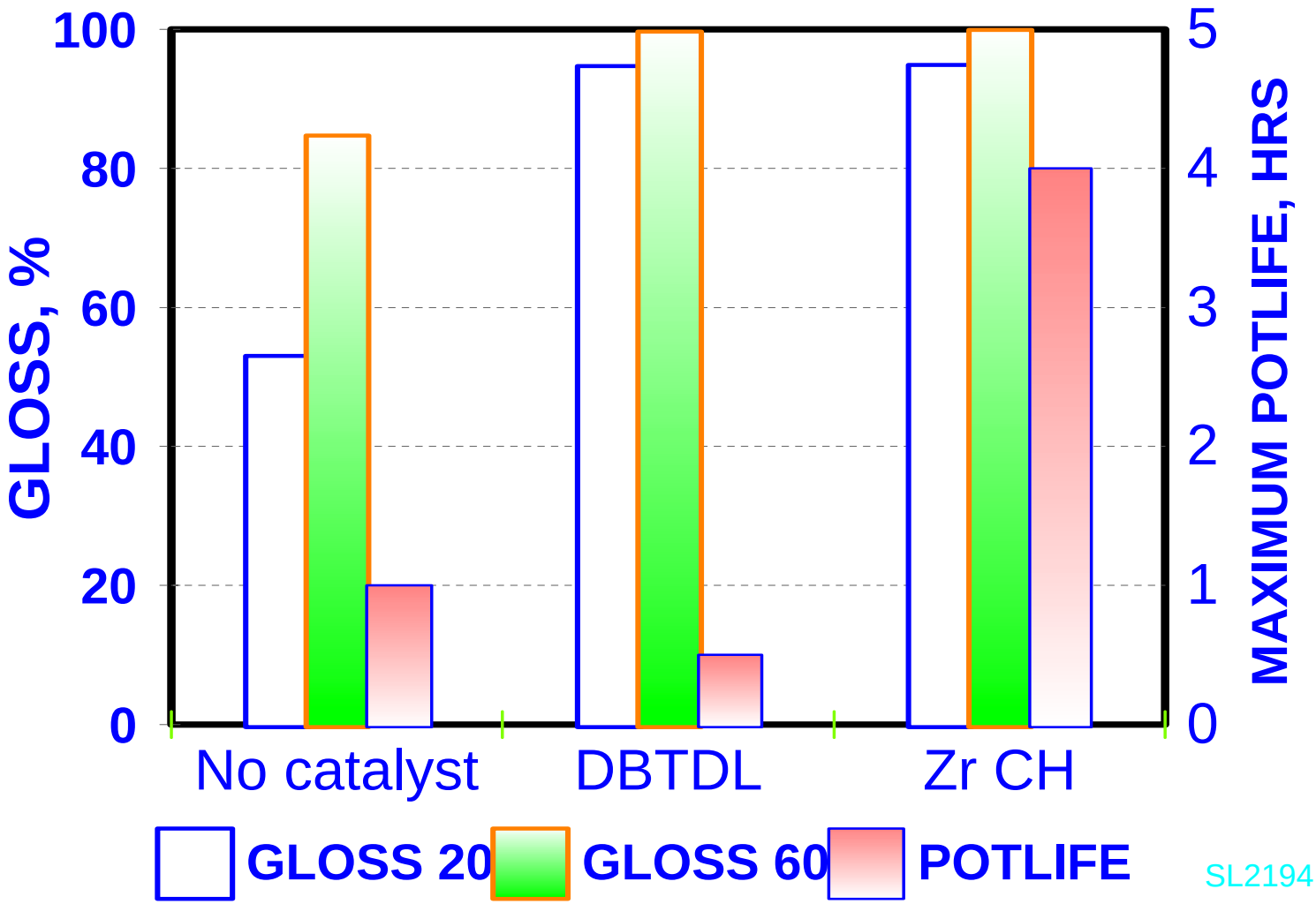
WATERBORNE TWO COMPONENT



SL2193

WATERBORNE TWO COMPONENT

CATALYST SELECTION



SL2194

WATERBORNE TWO COMPONENT

XC-6212

A100 XC6212 0H RT 496-10

0 HOUR

XC-6212

A107 XC6212 RT 496-10

4 HOURS

DBTDL

A111 DBTDL 0.5H RT 496-10

1/2 HOUR

SL2184

WATERBORNE TWO COMPONENT

XC-6212 XC-6212 XC-6212

A100 XC6212 OH RT 496-10

50 % RH

A108 XC6212 0H 70RT 496-10

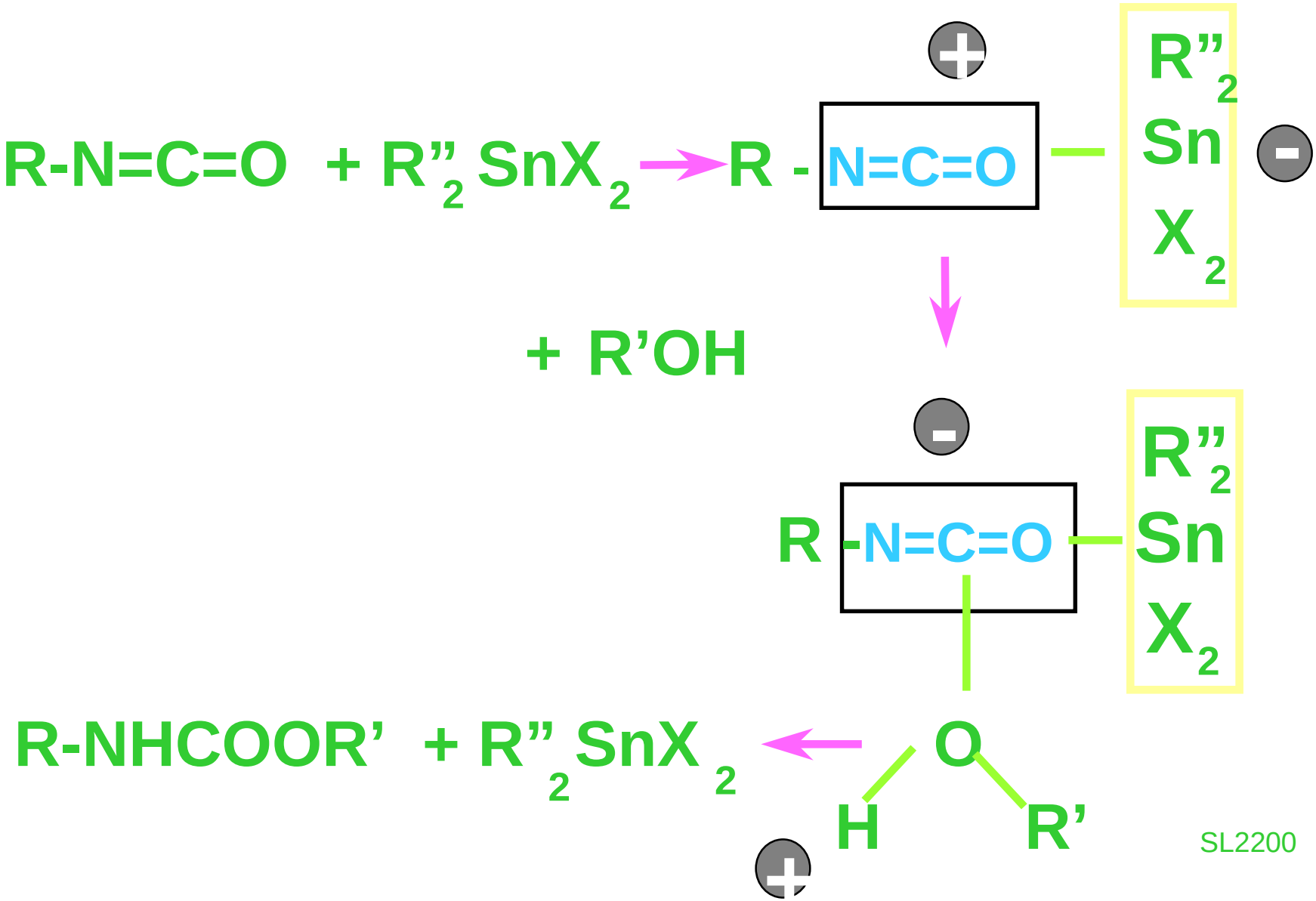
70 % RH

A100 XC6212 0H 90RT 496-10

90 % RH

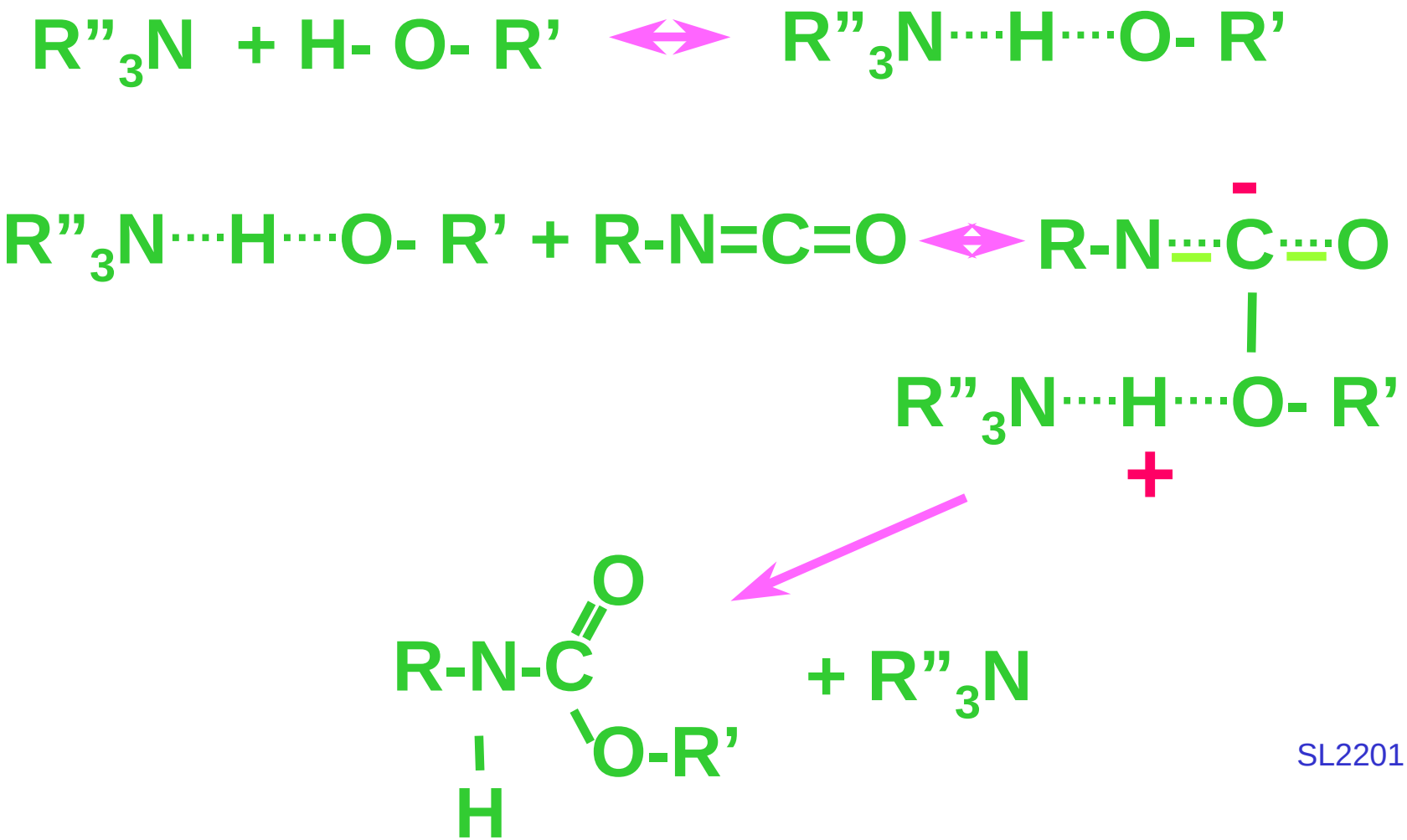
SL2185

LEWIS ACID CATALYSIS



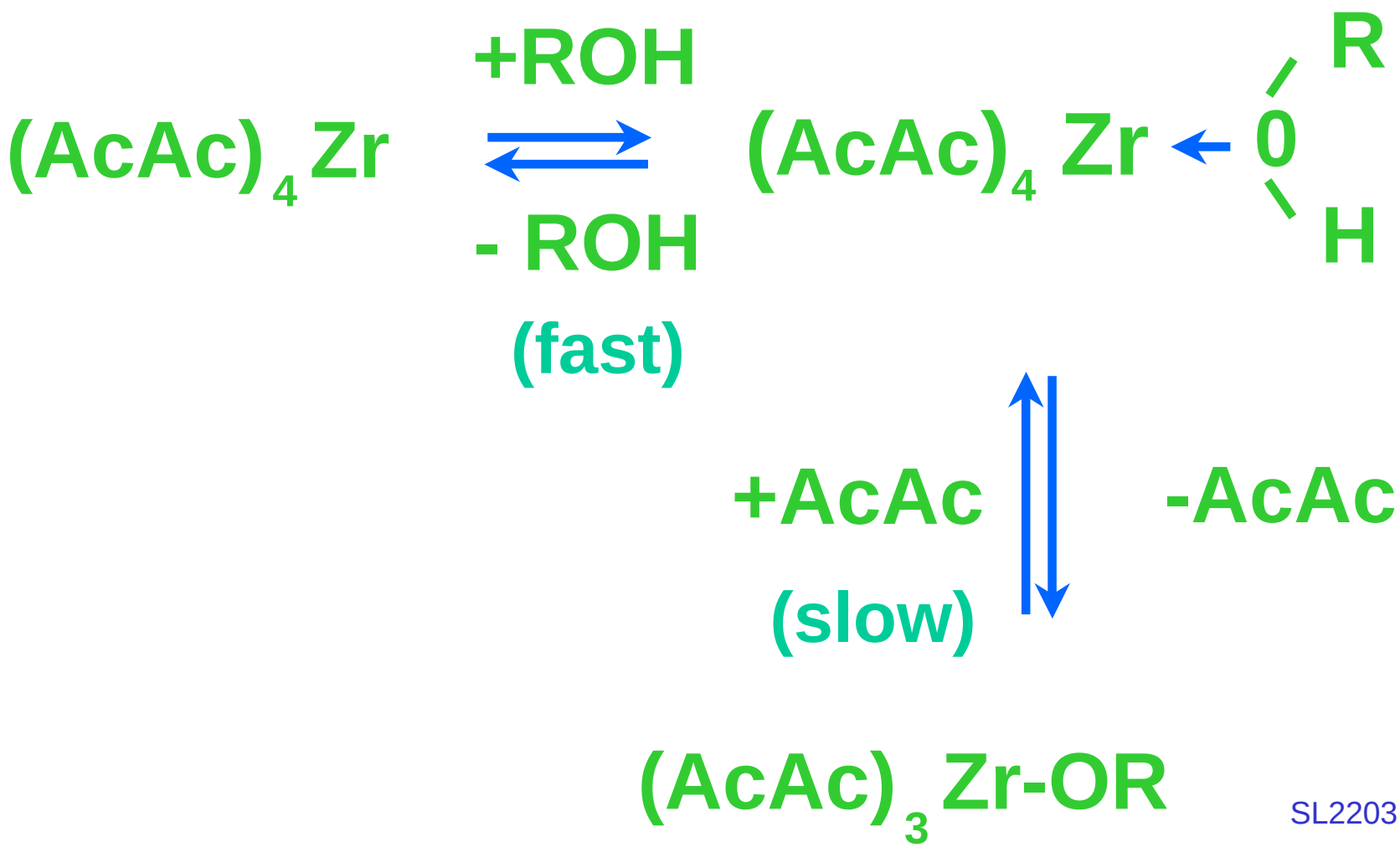
SL2200

AMINE CATALYSIS



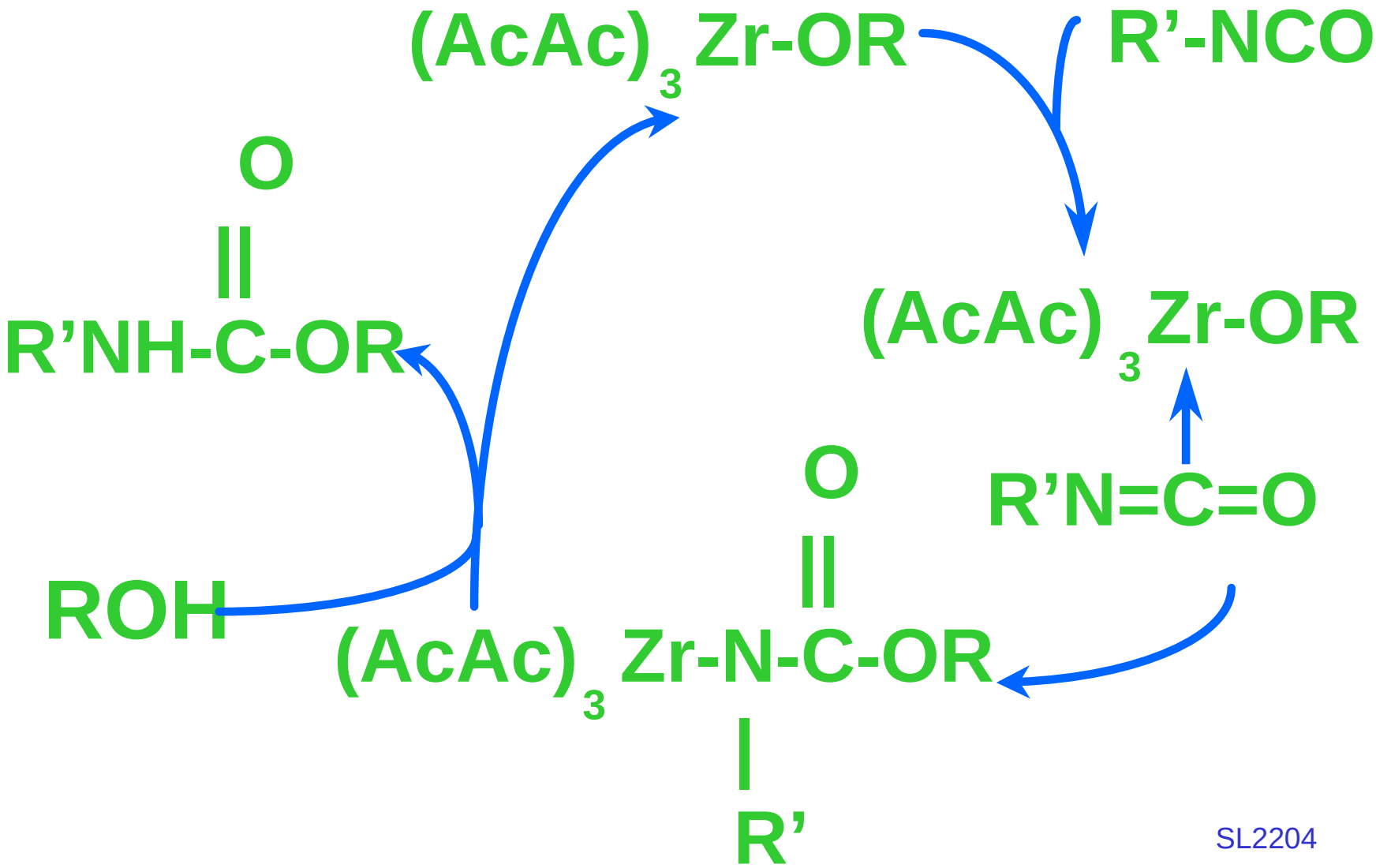
SL2201

ZIRCONIUM CHELATE CATALYSIS



SL2203

ZIRCONIUM CHELATE CATALYSIS



SL2204

HYDROLYSIS OF Zr CHELATE

DELAYED ACTION OF Bi CARBOXYLATE

DEACTIVATION

$$Bi(RCOO)_3 + H_2O \longleftrightarrow Bi_2O_3 + RCOOH$$

ACTIVATION

$$Bi_2O_3 + RCOOH \longrightarrow Bi(RCOO)_3 + H_2O$$

$$H_2O + RNCO \longrightarrow R\text{-}NHCOOH \rightarrow R\text{-}NH_2 + C0_2$$

$$R\text{-}NHCOOH + Bi_2O_3 \longrightarrow Bi(RNHCOO)_3$$

SUMMARY

ORGANO TIN FREE COATINGS POSSIBLE

CHOICE OF CATALYST DEPENDS ON APPLICATION

Zr CHELATE ACTIVATES HYDROXYL

Zr CHELATE CATALYSTS SELECTIVE FOR OH

HIGH REACTION RATES POSSIBLE

RELATIVE REACTIVITY OF HYDROXYLS DIFFERENT

CATALYSIS OF WATERBORNE COATINGS WITH Zr

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