Going beyond six: altering the draft ASTM thermal desorption (TD) – GC/MS method to accommodate an expanded list of phthalates

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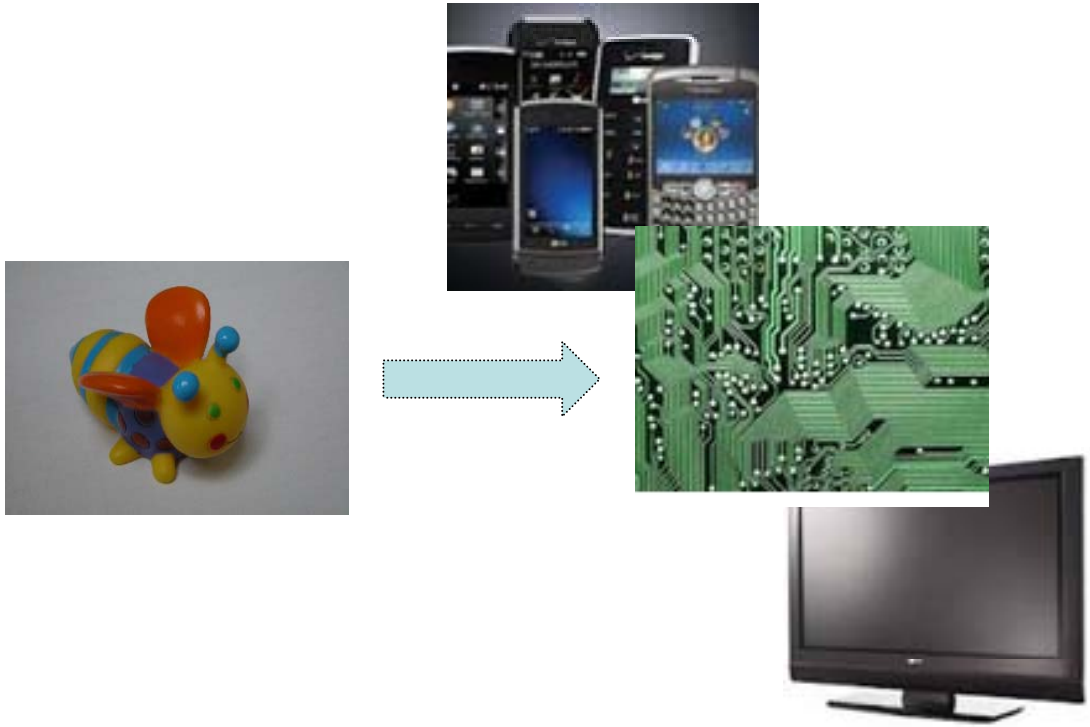
Introduction to the ASTM draft method for phthalates in PVC
Task Group 25759

Regulation of phthalates goes beyond “children’s toys”



Stakeholders:

Polymer formulators

Recyclers

Product manufacturing

Retailers

Consumers

Phthalates are restricted on a global scale

Regulation	Reference	Substances	Requirement
RoHS	Candidate of regulated substances	DBP, BBP, DEHP, DiBP	0.1 % (1000 mg/kg)
REACH	SVHC Candidate	DBP, BBP, DEHP, DiBP	0.1 % (1000 mg/kg)
CPSIA 1)	Section 108	DBP, BBP, DEHP, DNOP, DINP, DIDP	0.1 % (1000 mg/kg)
REACH	(EC) No. 1907/2006 Annex XVII items 51 & 52	DBP, BBP, DEHP, DNOP, DINP, DIDP	0.1 % (1000 mg/kg)
CA Prop 65	AB Package 21	DBP, BBP, DEHP, DnHP, DIDP	0.1 % (1000 mg/kg)
CCPSA 2)	SOR/2010-298	DBP, BBP, DEHP, DNOP, DINP, DIDP	0.1 % (1000 mg/kg)
KC 3)	Annex 35	DBP, BBP, DEHP, DNOP, DINP, DIDP	0.1 % (1000 mg/kg)

1) CPSIA : Consumer Products Safety Improvement Act 2) CCPSA : Canada Consumer Products Safety Act 3) KC : Korea Certification

Recent restrictions of phthalates in Europe

Denmark

Danish Environmental Protection Agency circulated the draft version of a law that prohibits the import and sales of any product containing phthalates which directly contact with skin.
(Effective date:
June 15, 2011)

Australia

Product Safety Agency announced via the Australia Consumer Act that child care articles and/or food containers containing phthalates are prohibiyed.
(Effective date:
January 1, 2011)

France

Prohibits the manufacture, import and sales of products containing phthalates
(Effective date: May 3, 2011)

ECHA

ECHA will hold Public Consultation to hear from interested parties on 4 phthalates (DEHP, BBP, DBP & DIBP). RAC/SEAC will review the Comments and the EU will determine if additional registration of these substances should be added to the REACH regulations.
(Effective date:
September, 2012)

Many “global” corporations have quality control guidelines for phthalates in place

Company	Substance	Business Dept.	Requirement
LG Electronics	DBP, BBP, DEHP, DNOP, DINP, DIDP, DiBP	Mobile Phone / PC	0.1 % (1000 mg/kg)
SAMSUNG ELECTRONICS	DBP, BBP, DEHP, DNOP, DINP, DIDP, DiBP & other phthalates	Wireless service	Low Detection Substance
NOKIA Connecting People	DBP, BBP, DEHP, DNOP, DINP, DIDP	All	Environment Control Substance
SONY make.believe	DBP, BBP, DEHP, DNOP, DINP, DIDP, DnHP	All	Environment Control Substance

Smart Phone
DEHP 1.5 %

Standard Practice for the Determination of Low Level Phthalates in Poly Vinyl Chloride by Thermal Desorption - Gas Chromatography/Mass Chromatography

- **Sample homogeneity**

  Cryo-milling

Red part ~ 40ppm DEHP
Blue part ~ 40ppm
Yellow part ~ 300ppm

- **Sample preparation**

  Two Solutions

  1. Quantitative solution of target compounds (300 µg/10 mL MeCl)
  2. THF solution of sample (200 mg/10 mL THF)

- **Injection**

  Thermal Desorption: 100 - 320˚C at 20˚C/min (5 min)
  Split ratio 1/20

- **Separation**

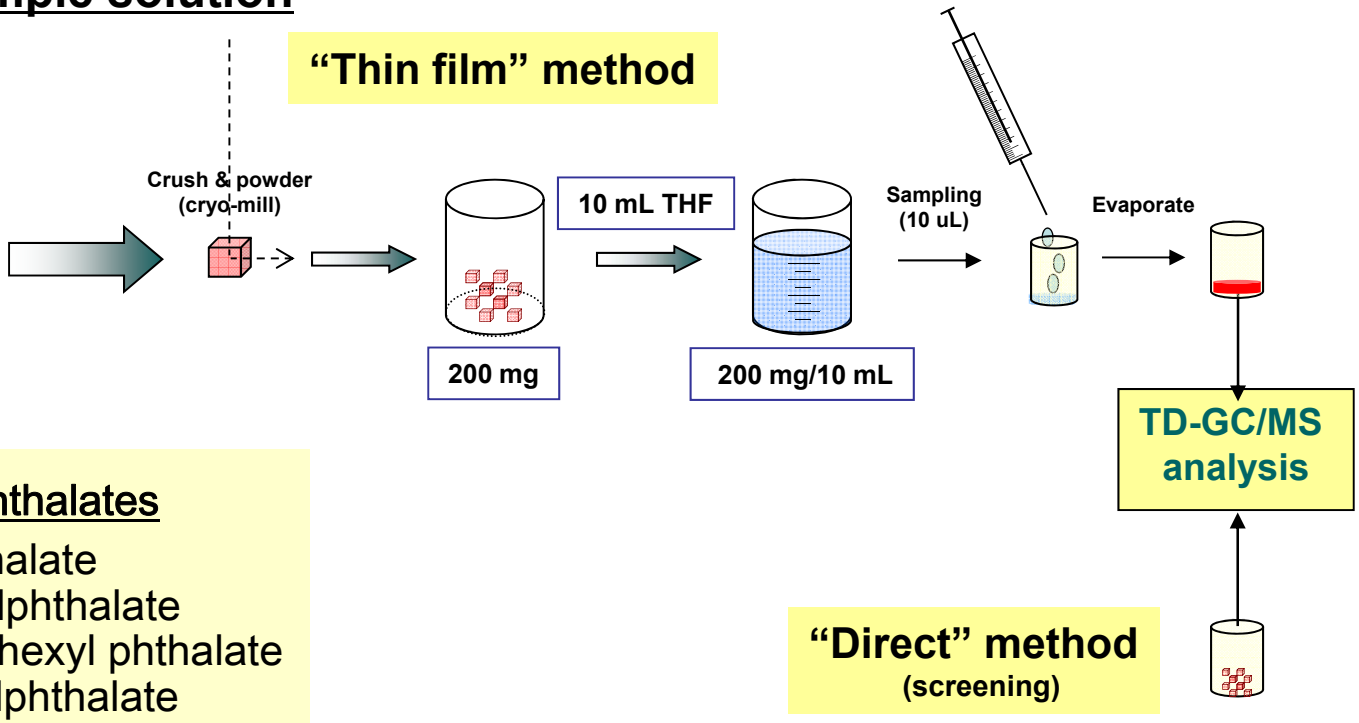
  Column: 5% phenyl – 30X 0.25 mm (0.25µm film)
  80 (1 min) - 200˚C @ 50˚C/min → 320˚C @ 15˚C/min (2 min)

- **Detection (GC/MS: scan or SIM mode)**

  Mass range 29 – 600 m/z, 2.57 scans/sec
  Transfer line 300˚C, ion source 230˚C

Quick, simple and "green" sample preparation

Solution 2: Sample solution

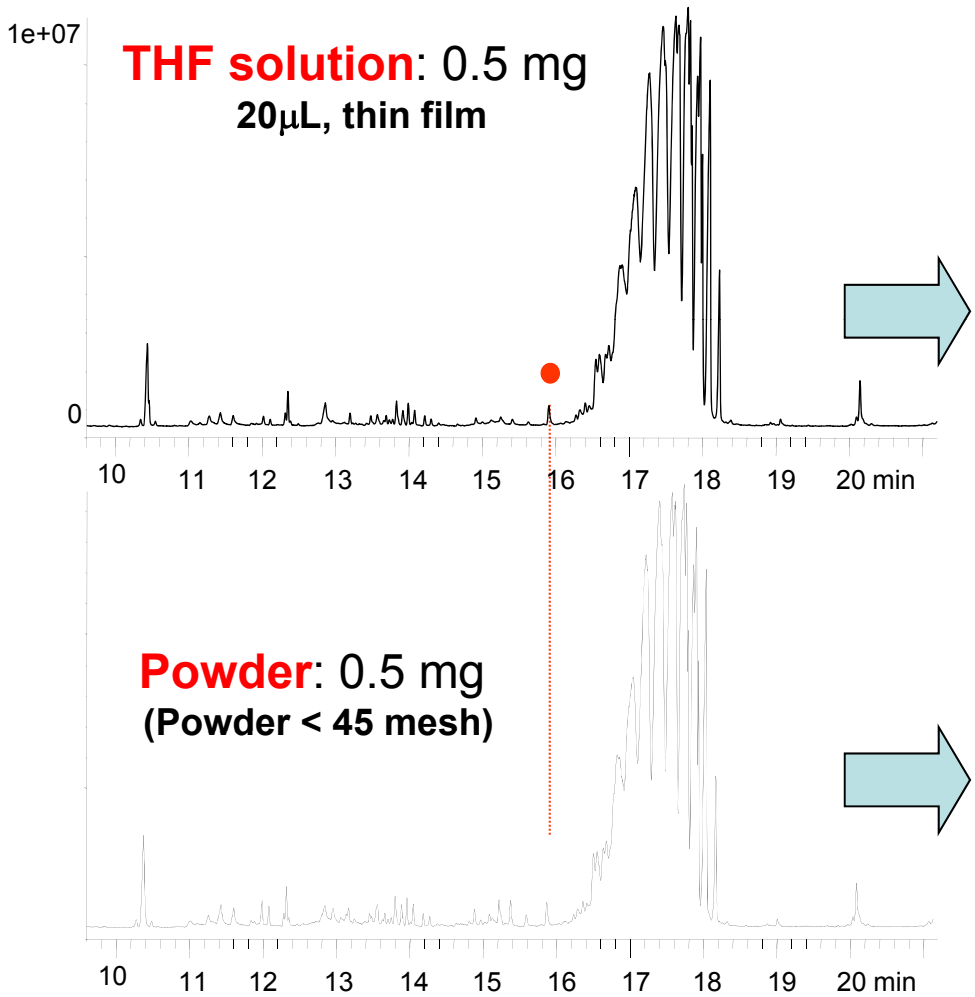


Restricted phthalates

DBP: Dibutylphthalate
BBP: Butylbenzylphthalate
DEHP: di-2-ethylhexyl phthalate
DNOP: di-n-octylphthalate
DINP: di-isononylphthalate
DIDP: di-isodecylphthalate

Influence of the sample state on analytical precision

Sample : Plastic Toy, TD: 100- 40ºC/min-350ºC (3 min)

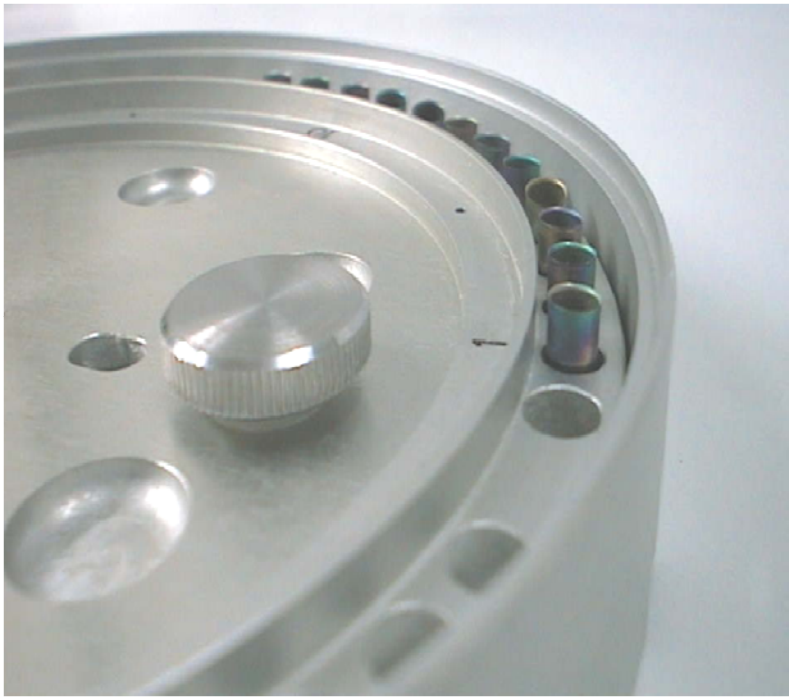


DEHP: %RSD = 1.15 (n=4)

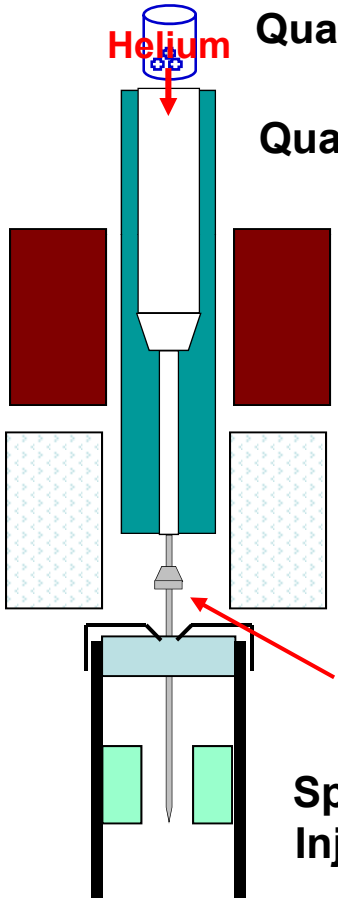
DEHP: %RSD = 4.79 (n=4)

One of the reasons for poor reproducibility comes from the inhomogeneity of DEHP in the fine particles.

Automated analysis of 1 samples/hour [analytical]
Automated analysis of 3 samples/hour [screening]



Injection



Analytical conditions

[Equipment]

Pyrolyzer : PY-2020iD (Frontier-Lab; Japan)
GC/MS : Agilent 6890+5973

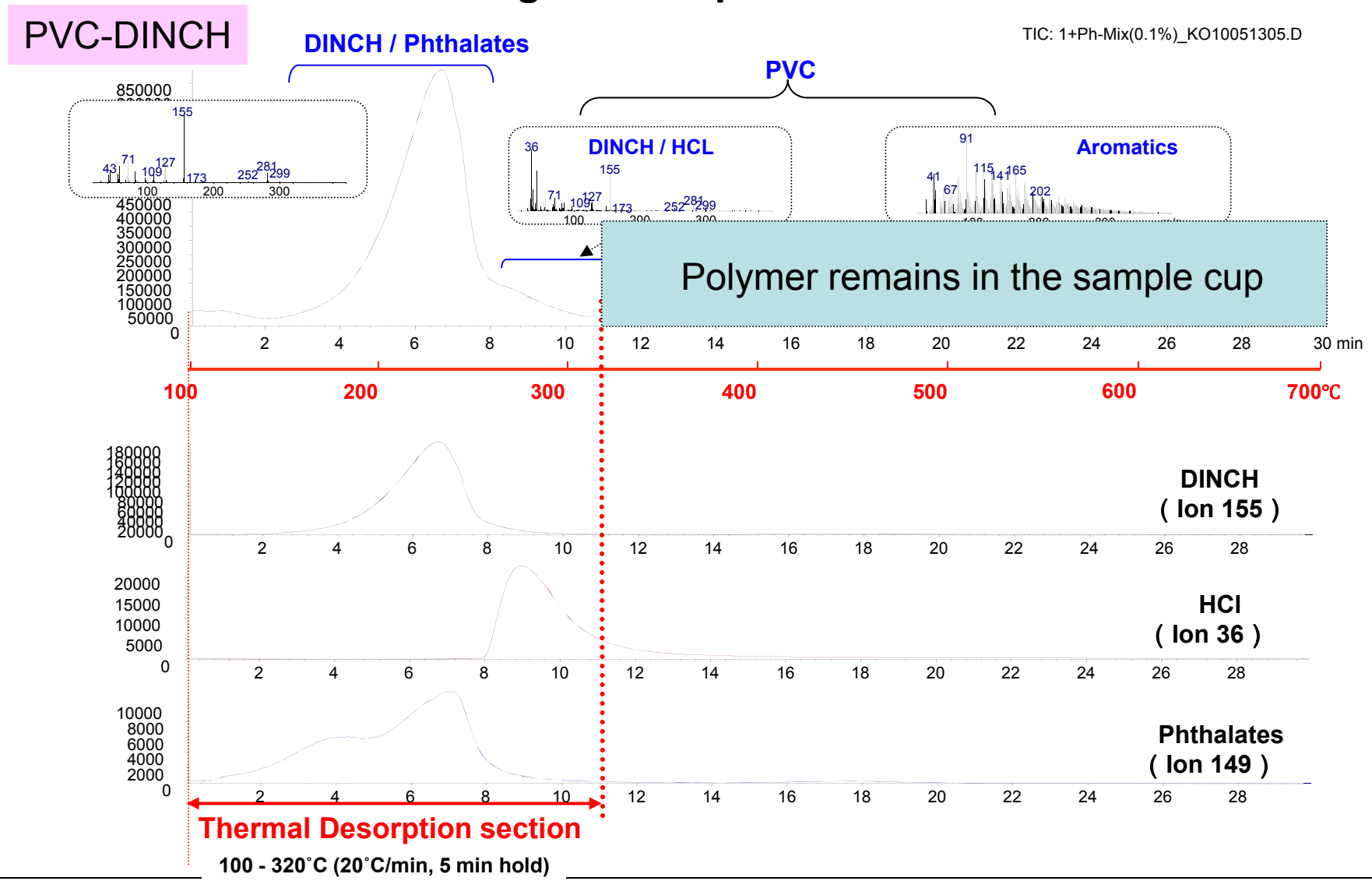
[EGA-MS analysis]

Py temperature : 100 → 700ºC (20ºC/min)
GC injection: 320ºC, GC Oven: 300ºC
EGA tube: Deactivated SS tube (2.5 m X 0.15 mm i.d.)
Column He flow: 1 mL/min, Split ratio: 1/50
Mass range: 29-600 m/z, Scan speed = 0.2 scans/sec, Threshold = 50
MS transfer line: 300ºC; Ion Source (EI) = 230ºC
Sample wt.: ca 200 μg

[Thermal Desorption (TD)-GC/MS analysis]

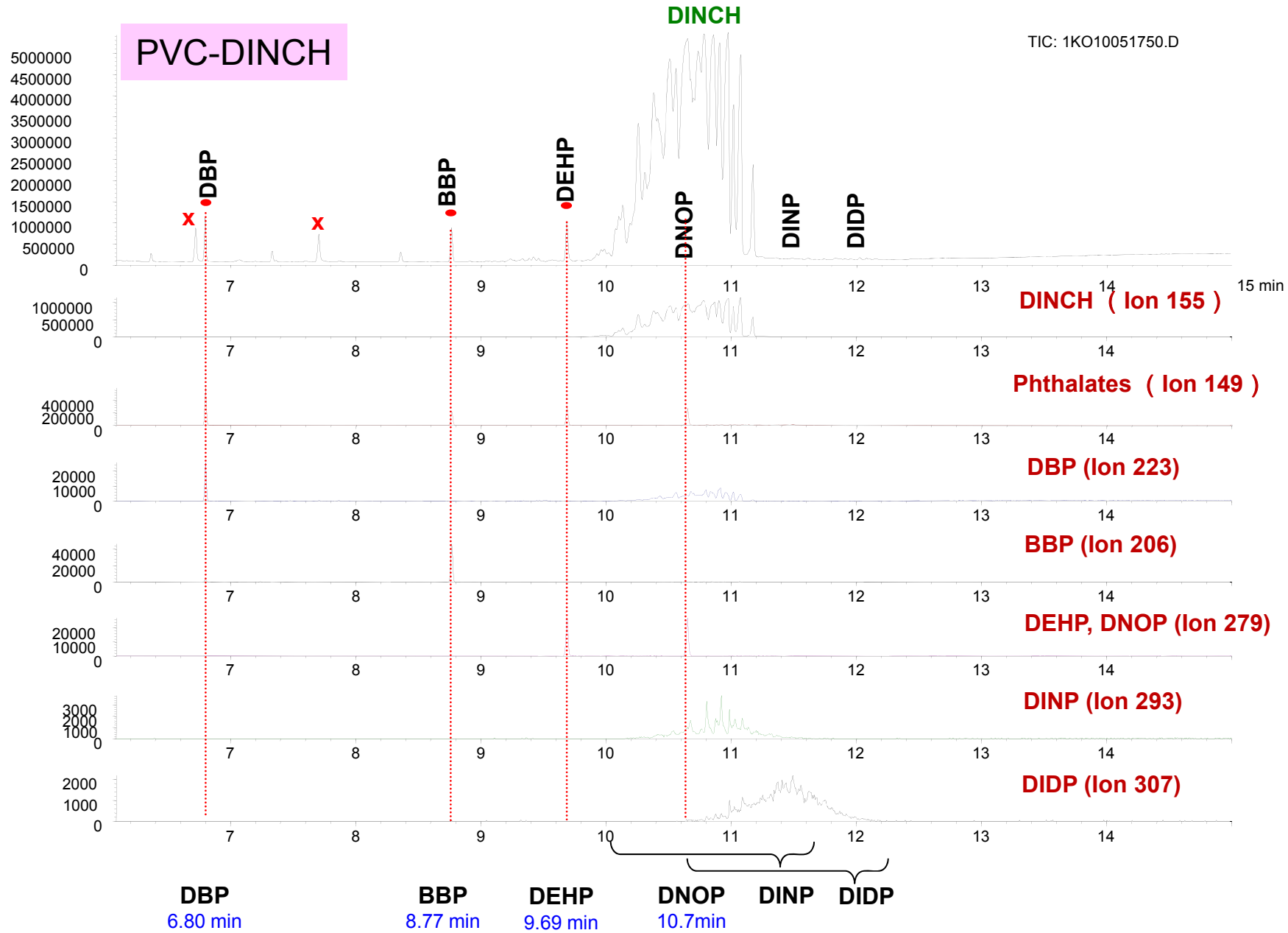
TD temperature: 100ºC → 320ºC (20ºC/min, 5 min hold) [[16 minutes]]
Py interface: 320ºC(Auto mode), GC injector : 300ºC
GC oven: 80 (1 min) - 200ºC (50ºC/min) - 350ºC (15ºC/min, 2 min hold)
Solvent delay: 6 min
Column: UA-5 (5% Diphenyl-95%dimethyl polysiloxane) 30 m x 0.25 mm i.d, 0.25 μm film
Column He flow: 1.2 mL/min, Split ratio: 1/20
Sample wt.: ca 200 μg

Determination of TD temperature range using EGA-MS thermogram and phthalate EIC

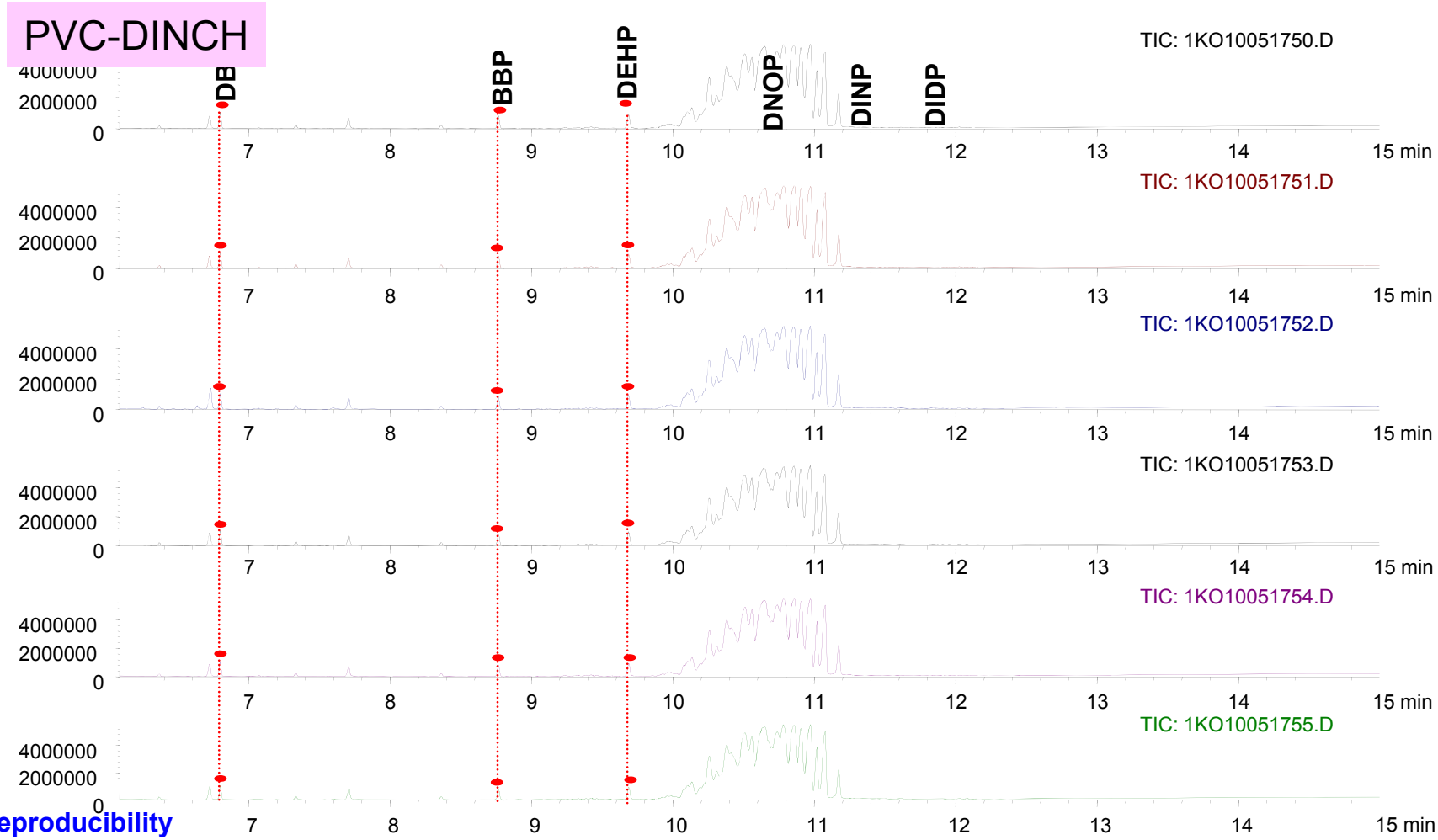


The small amount of HCl will not damage the liquid phase of the separation column. The polymeric material remains in the Eco-cup and will not contaminate the GC injector and column.

TD-GC/MS analysis of PVC-DINCH



Reproducibility of PVC-DINCH (n=6)

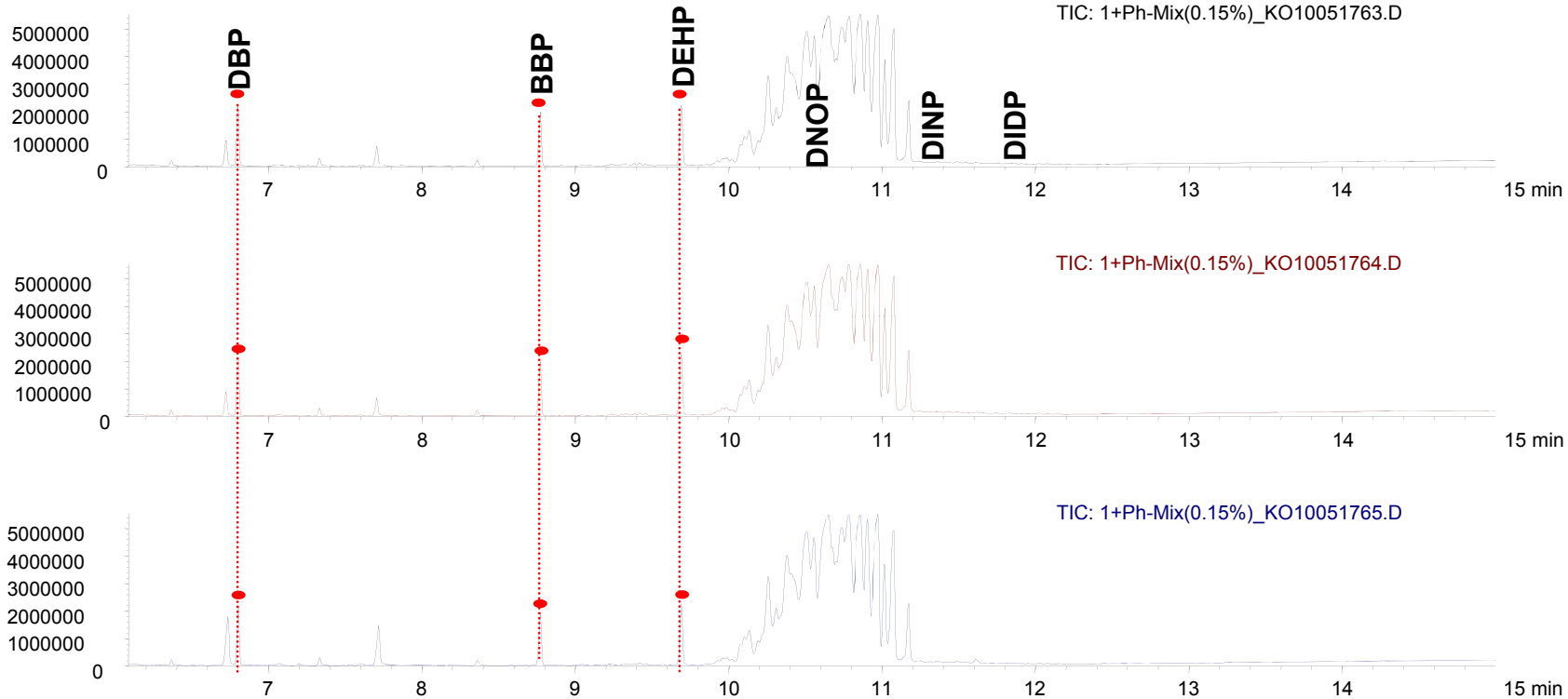


- **Reproducibility**

No	File name	DBP m/z=223	BBP m/z=206	DEHP m/z=279	DNOP m/z=279	DINP m/z=293	DIDP m/z=307
1	KO10051750	243,840	505,044	328,756	332,096	489,945	616,594
2	KO10051751	242,452	517,461	340,418	321,613	497,762	633,184
3	KO10051752	240,288	517,972	354,329	331,371	507,979	657,815
4	KO10051753	246,959	528,137	349,345	327,968	505,853	646,300
5	KO10051754	238,760	515,500	345,159	336,845	504,904	656,879
6	KO10051755	246,510	521,102	343,431	333,874	503,383	653,434
Averaged peak area		243,135	517,536	343,573	330,628	501,638	644,034
SD		3293.118547	7556.303832	8729.726158	5296.045748	6684.847213	16242.41879
RSD (%)		1.35	1.46	2.54	1.60	1.33	2.52

Standard addition method using Ph-Mix (0.15%)

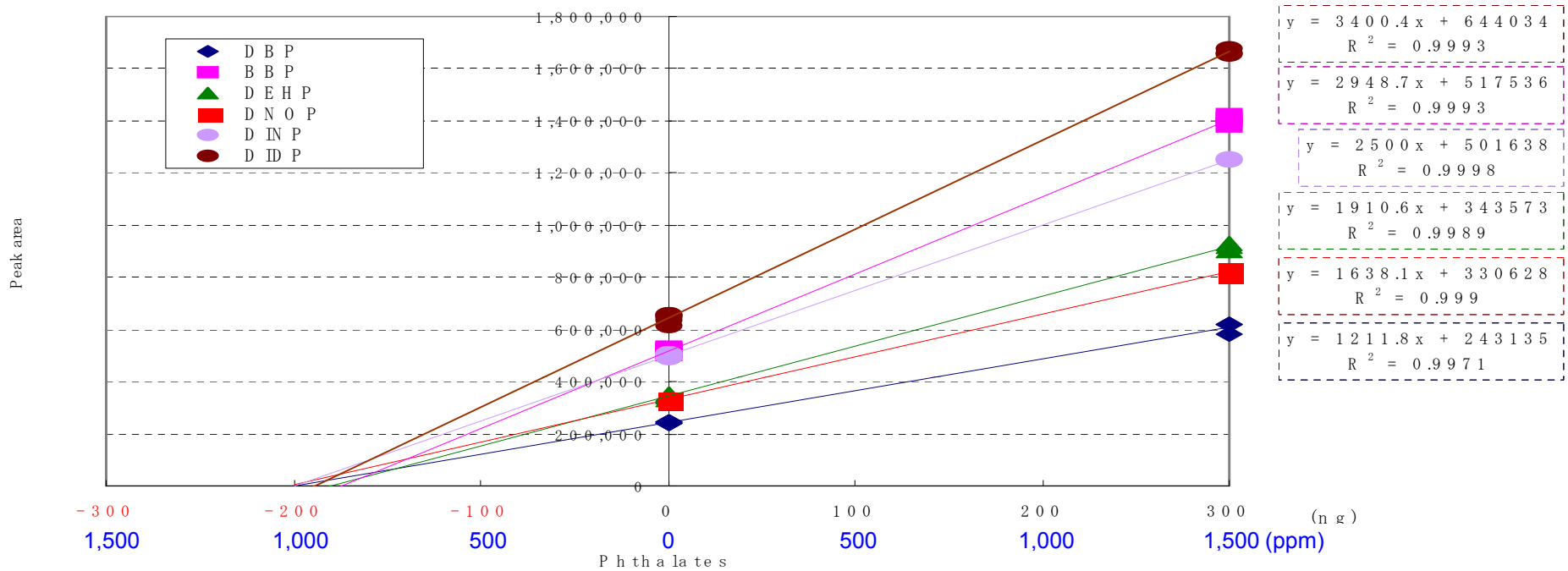
PVC-DINCH+Ph-Mix(0.15%)



- **Reproducibility**

No	File name	DBP m/z=223	BBP m/z=206	DEHP m/z=279	DNOP m/z=279	DINP m/z=293	DIDP m/z=307
1	KO10051763	617,676	1,404,496	916,464	808,100	1,249,390	1,655,684
2	KO10051764	617,692	1,420,341	929,940	824,984	1,254,874	1,674,483
3	KO10051765	584,653	1,381,582	903,893	833,106	1,250,645	1,662,251
Averaged peak area		606,674	1,402,140	916,766	822,063	1,251,636	1,664,139
SD		19070.45842	19486.64287	13026.12008	12756.28196	2873.259531	9540.699782
RSD (%)		3.14	1.39	1.42	1.55	0.23	0.57

Quantitative results using standard addition



DBP Calibration curve is given by: y = 1211.8 x + 243135 (R^2 = 0.9971)

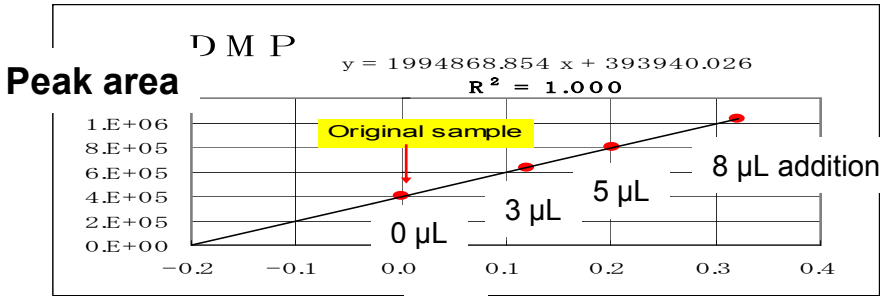
when y=0 then x = -243135/1211.8 = -200.6 ∴ 200.6 (ng)

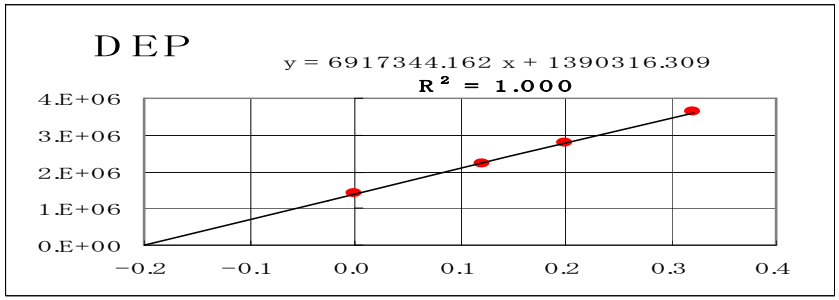
<u>Concentration in ppm is given by :</u>

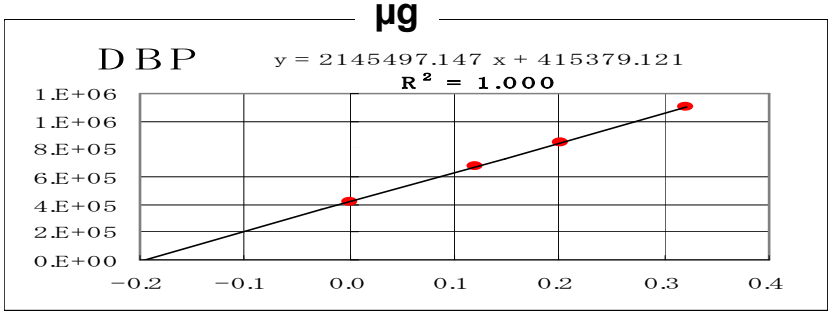
Value of DBP/Assumed content of PVC-DINCH = 200.6 (ng) /200 (μg) = 1003.2 (ppm)

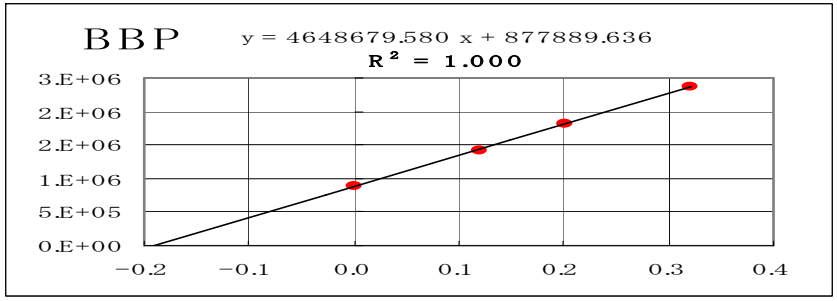
PVC-DINCH		DBP	BBP	DEHP	DNOP	DINP	DIDP
		m/z=223	m/z=206	m/z=279	m/z=279	m/z=293	m/z=307
Quantitative value	ng	200.6	175.5	179.8	201.8	200.7	189.4
	ppm	1,003.2	877.6	899.1	1,009.2	1,003.3	947.0
Reproducibility (n=6)	RSD (%)	1.35	1.46	2.54	1.60	1.33	2.52

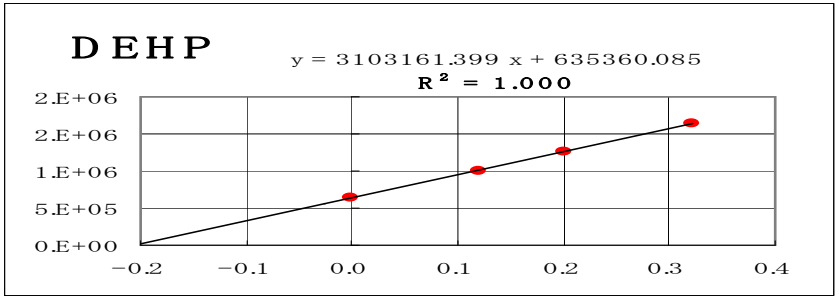
Calibration curves for 6 phthalates by standard addition

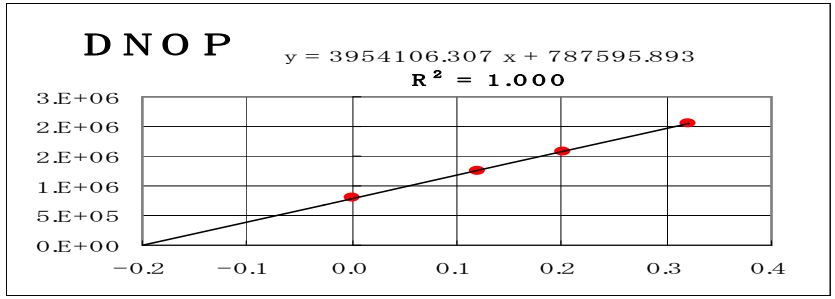












<u>% Recovery:</u>

DBP = 99.2 BBP = 101 DEHP = 97.3

DNOP = 94.9 DINP = 102.3 DIDP = 100

Method Validation Study: Summary

→ Thermal desorption temperature is system dependent.

→ EI or SIM comparable data quality; thin film columns preferred

→ Standard addition (1-point) calibration: R^2 >0.990

→ Intra-lab injection-to-injection reproducibility is <5 %RSD

→ Intra-lab sample-to-sample reproducibility (samples 3&4) is <10% error

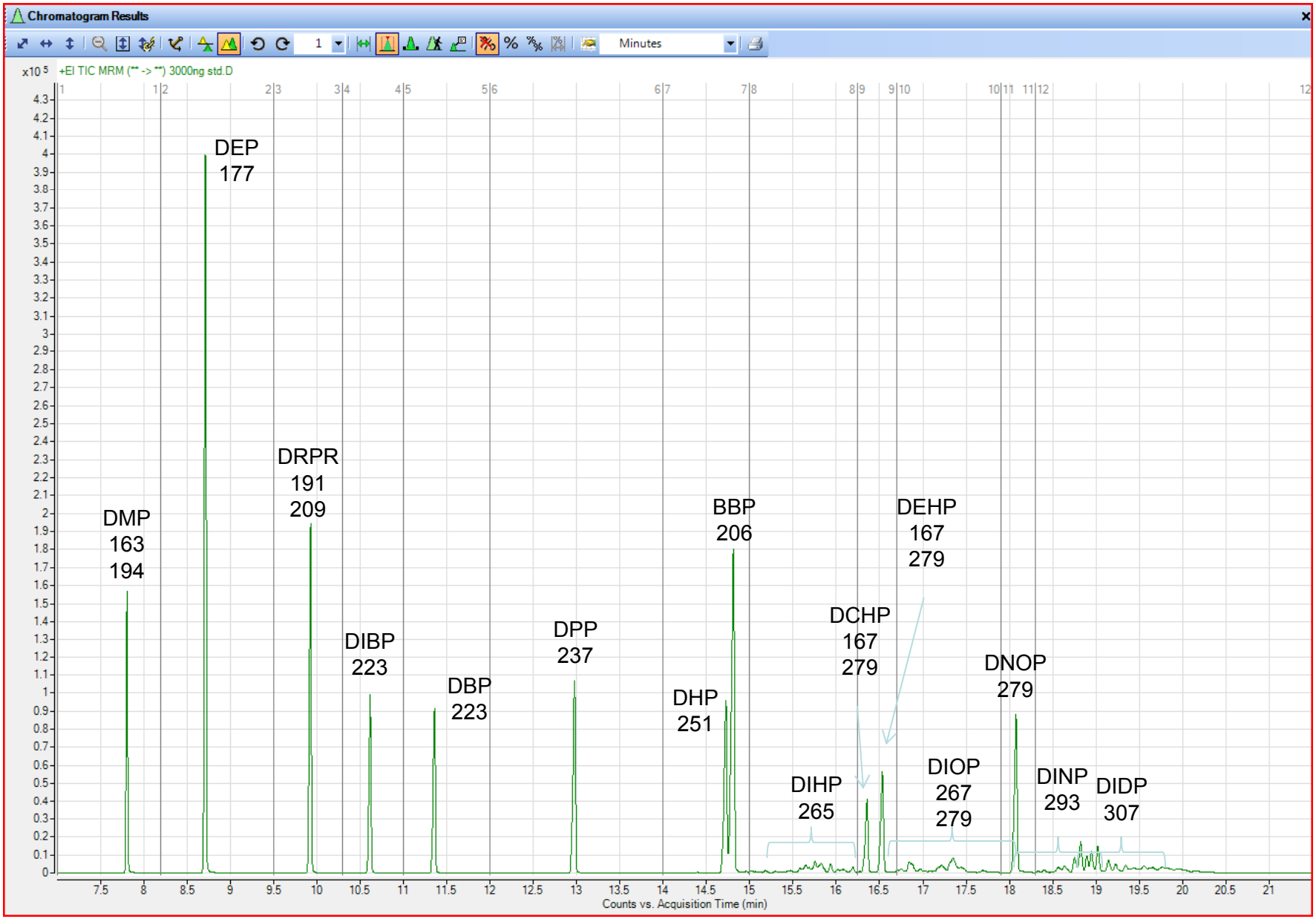
→ Laboratory-to-laboratory accuracy is ±25%

Extended target compound list

RT	Name	Acronym	CAS No.
7.805	Dimethyl phthalate	DMP	131-11-3
8.7	**Diethyl Phthalate**	DEP	84-66-2
9.915	Di-n-propyl phthalate	DRPR	131-16-8
10.6	Diisobutyl phthalate	DIBP	84-69-5
11.34	Dibutyl phthalate	DBP	84-74-2
12.957	Di-n-pentyl phthalate	DPP	131-18-0
14.686	di-n-Hexyl phthalate	DHP	84-75-3
14.778	**Benzyl butyl phthalate**	BBP	85-68-7
15.75	Diisoheptyl phthalate	DIHP	71888-89-6
16.328	Dicyclohexyl phthalate	DCHP	84-61-7
16.509	**Bis(2-ethylhexyl) phthalate**	DEHP	117-81-7
17.35	Diisooctyl phthalate	DIOP	27554-26-3
18.056	**Di-n-octyl phthalate**	DNOP	117-84-0
18.65	**Diisononyl phthalate**	DINP	68515-48-0
19.02	**Diisodecyl phthalate**	DIDP	26761-40-0

GC oven: 40 - 260ºC (10ºC/min) - 320ºC (20ºC/min, 4.5 min hold)

Extended target compound list



1. TD-GC/MS Method is easy, clean, green, and fully automated.

2. TD-GC/MS Method is precise and accurate.

3. TD-GC/MS accommodates an extended target compound list.

1. Run-to-run GC contamination must be eliminated or at least monitored.

2. Quant ions must be verified for each type of material tested.

3. Degree of difficulty increases when monitoring isomeric bends (DIDP).

Demanding more sensitivity, expanding the number of target phthalates and analyzing an ever increasing number of matrices places a significant burden on the laboratory to "get the right answer"

Method Validation Study: samples 3 & 4 (DINCH)

Samples dissolved in THF and solids dispersed prior to sampling

Summary of Data (Thermal Desorption Phthalate Analysis)

Sample #	DBP	BBP	DOP	DnOP	DINP	DIDP
#1	954	903	946	988	1185	1170
#2	1275	741	953	779	962	881
#3	1034	836	929	1078	1104	999
#4	997	859	942	1169	1165	1044

Samples dissolved in THF and solids allowed to settle and clear solution analyzed

Summary of Data- Average Duplicate Analyses(Thermal Desorption Phthalate Analysis)

Sample #	DBP	BBP	DOP	DnOP	DINP	DIDP
#1	871	834	956	967	1124	1046
#2	1006	901	946	946	1137	1190
#3	958	837	913	1174	1105	987
#4	846	772	876	1090	1130	1001

Method Validation Study: Average % Error: all Compounds

	LAB 1	LAB 2	LAB 3	FRONTIER
Sample 1	9	29	10	5
Sample 2	12	17	17	11
Sample 3	15	17	7	7
Sample 4	15	37	10	7