Utilization of BFR plastics

in recovery of valuable metals during thermal treatment with solid wastes

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Brominated Flame Retardants (BFRs)

majority (38 %) of global production of bromine (Mehran et al., 2003)

Tetrabromobisphenol A (TBBPA)

59 % of global production of BFRs in 2001 (Sarah, 2005)

Reactive FR (90 %):

epoxy resins, polycarbonate resins

(20-25 wt % bromine)

(Alaee et al., 2003)

- **printed circuit boards (PCB)**
- **printed wire boards (PWB)**

Additive FR (10 %):

acrylonitrile -butadiene styrene resins (ABS), high-impact polystyrene

(6 -18 wt % bromine)

(Alaee et al. 2003, Maag et al., 2010)

- **PC and TV set housing,**
- **PC monitors, another electronics,**
- **paper, textiles**

Waste of Electronic and Electric Equipment **(WEEE)**

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Landfills disposal

Thermal processing

(co-combustion at MSWI, pyrolysis)

Advantages:
3R of organic and inorganic fractions

Disadvantages:
Hazardous Emissions: PBDD/Fs,PBP, PBBz

HBr (in flue gas)

main products of TBBPA decomposition (Luda et al., 2003)

May acts as bromination agent for selective volatilization of heavy metals from wastes (?)

THERMODYNAMIC CONSIDERATION

- Bromination reaction of metallic oxides by HBr gas -

$$\frac{1}{a}M_xO_y(s,l) + HBr(g) = \frac{1}{z}MBr_z(s,l) + \frac{1}{2}H_2O(g)$$

Where: (x/a = 1/z, y/a = 1/2)

$$\Delta G_r^o = -RT \ln \frac{P_{H2O}^{1/2}}{P_{HBr}}$$

ΔG_r^o - standard Gibbs energy change of reaction (J/mol)

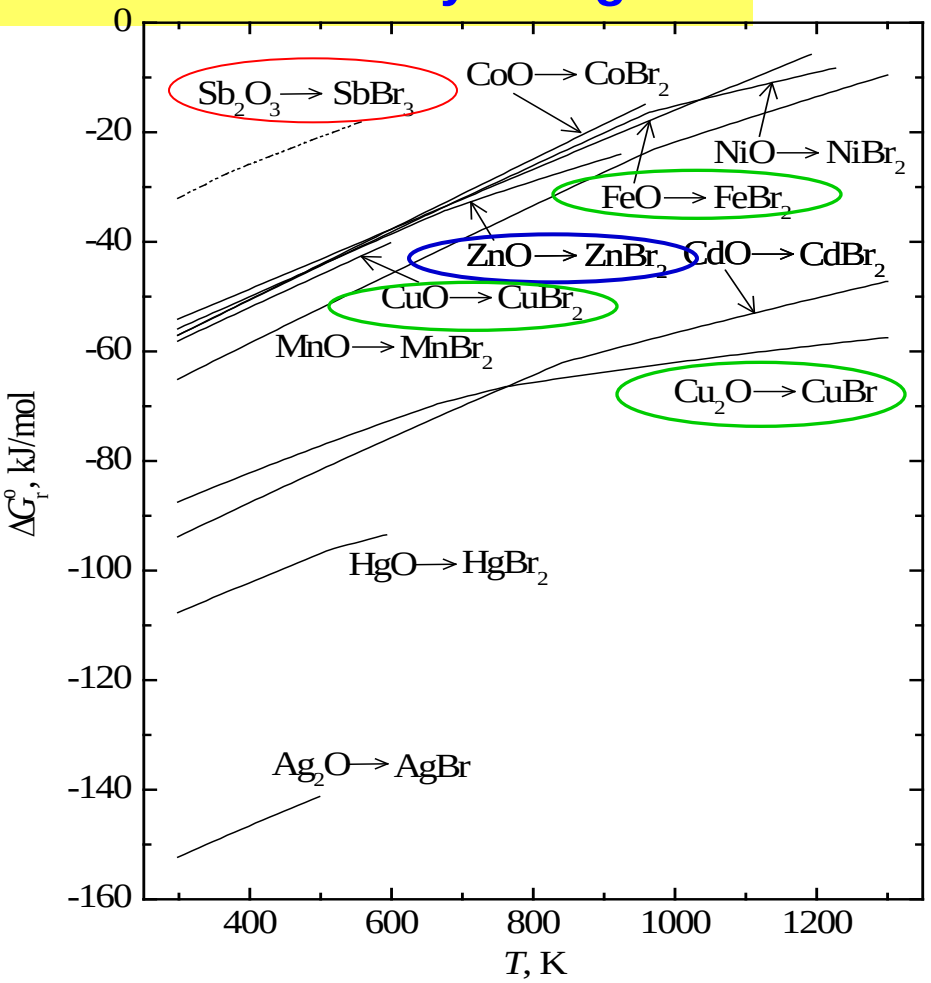
P - vapour pressure of the compound (atm)

R - gas constant (J/mol K)

T - temperature (K)

The order of reactivity of selected M_xO_y with HBr:

PbO > Cu_2O > CuO > ZnO > FeO > Sb_2O_3



Standard Gibbs free energy changes of bromination reaction of selected metal oxides

THERMODYNAMIC CONSIDERATION (II)

- Vapor Pressures of Metallic Bromides -

$$MBr_x\ (s,l) = MBr_x\ (g)$$

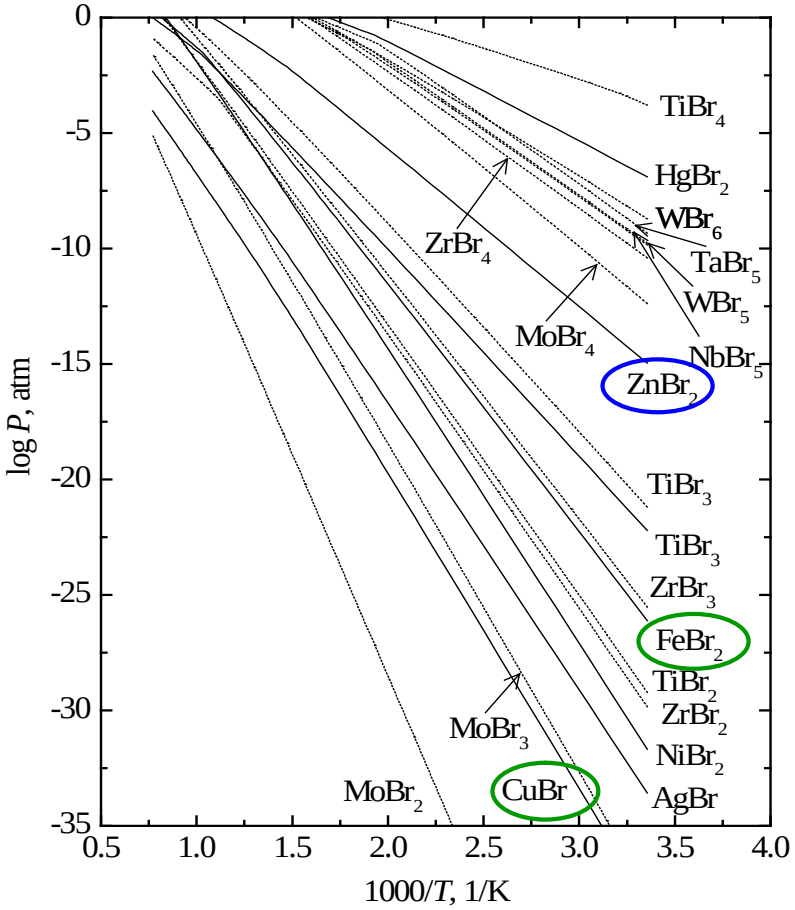
$$\Delta G_v^o = -RT \ln P_{MBrx}$$

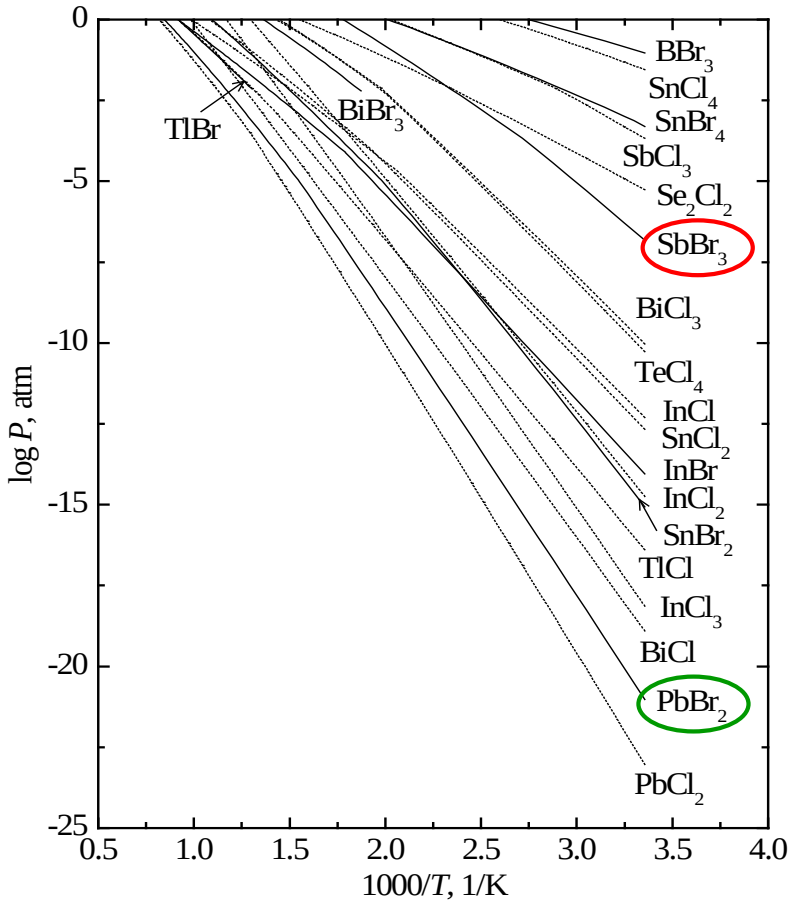
ΔG_v^o - is Gibbs energy changes (*J/mol*)

P - vapour pressure equilibrated with that of the pure compound (*atm*)

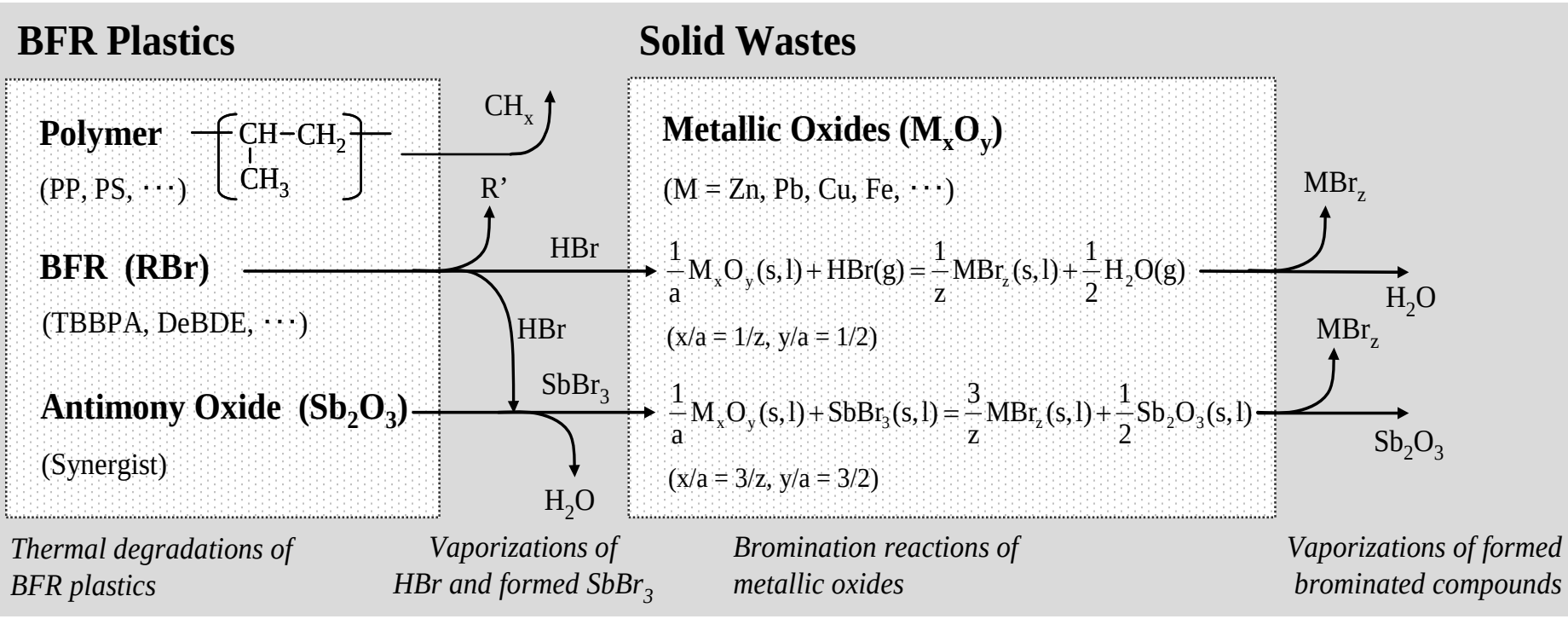
R - gas constant (*J/mol K*)

T - temperature (*K*)





Concept diagram of the thermal treatment of solid wastes containing metallic oxides with BFR plastics



If BFRs-containing plastics might be used in practical bromination-evaporation process could open technical possibility of :

- **recycling** of selectively volatilized heavy metals, metals-free ashes (WEEE, ASR)
- **simultaneous recycling** of WEEE and metal-rich metallurgical dusts (EAF dust, plating sludge)

Steel production in an electric arc furnace (EAF) generates **a flue by-product** called

Some 4.3–5.7 million tones of EAFD requiring disposal annually worldwide (*Mehran et al., 2003*)

EAFD chemical composition:

Element	Leclerc et al., 2002
Fe ($ZnFe_2O_4$, Fe_3O_4, Fe_2O_3)	16-44
Zn **(ZnO, $ZnFe_2O_4$)**	**7-28**
Pb (PbO)	0.2-8
Si, Mg, Ca, C, K, Na, Al, Cu, Cr, Cd, Mn, Cl, F…	

The worldwide generation of EAFD represents a possible recovery of 1.4 million tones of zinc (*ebfrip.org)*

There are two major methods for treatment of EAFD (Pickles, 2009):

1) chemical **fixation and stabilization** (CFS) for landfill,

2) recycling for metal **recovery** (pyrometallurgical (HTMR-Waelz), hydrometallurgical or hybrid pyro-hydro techniques))

PURPOSE OF THIS STUDY:

- recognize the reactivity of ZnO with HBr, main product of thermal decomposition of TBBPA

- recognize the behavior of the bromination reaction products

EXPERIMENTAL INVESTIGATION

- Reactivity of selected metallic oxides with bromine -

EXPERIMENTAL METHODS

Quartz-tube reactor heated by small furnace (Furnace)

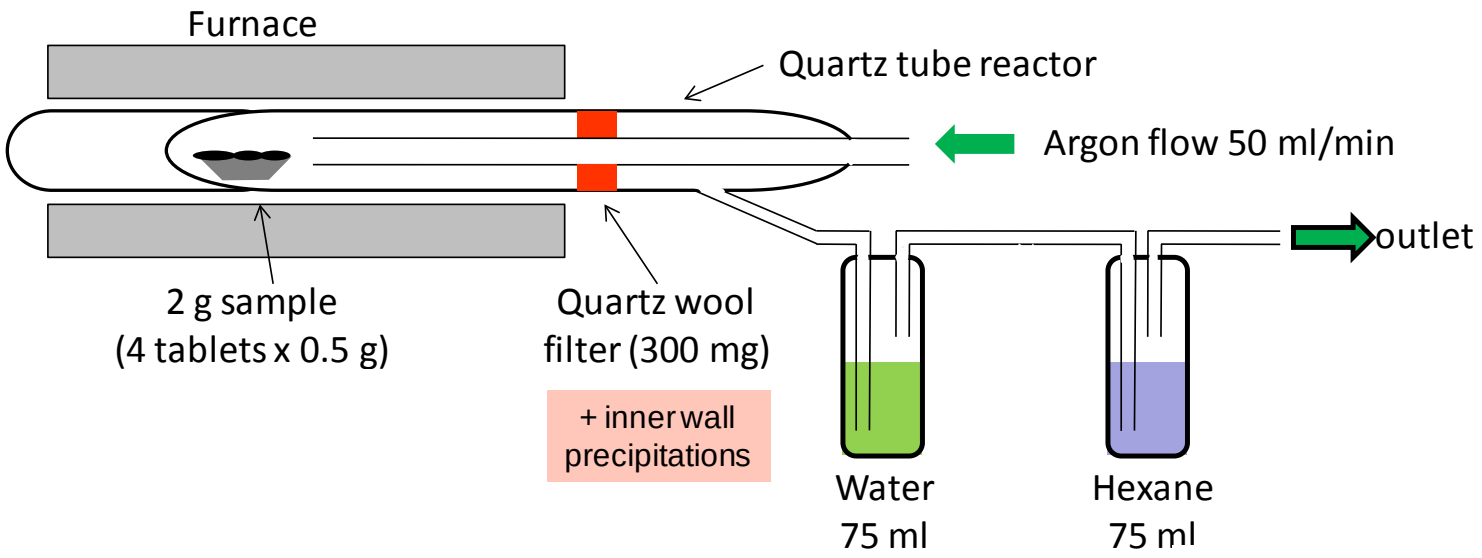
SAMPLES PREPARATION

Mixture of TBBPA with ZnO have been prepared according to stoichiometric mass ratio (3.34:1) (additionally: 5.17:1).

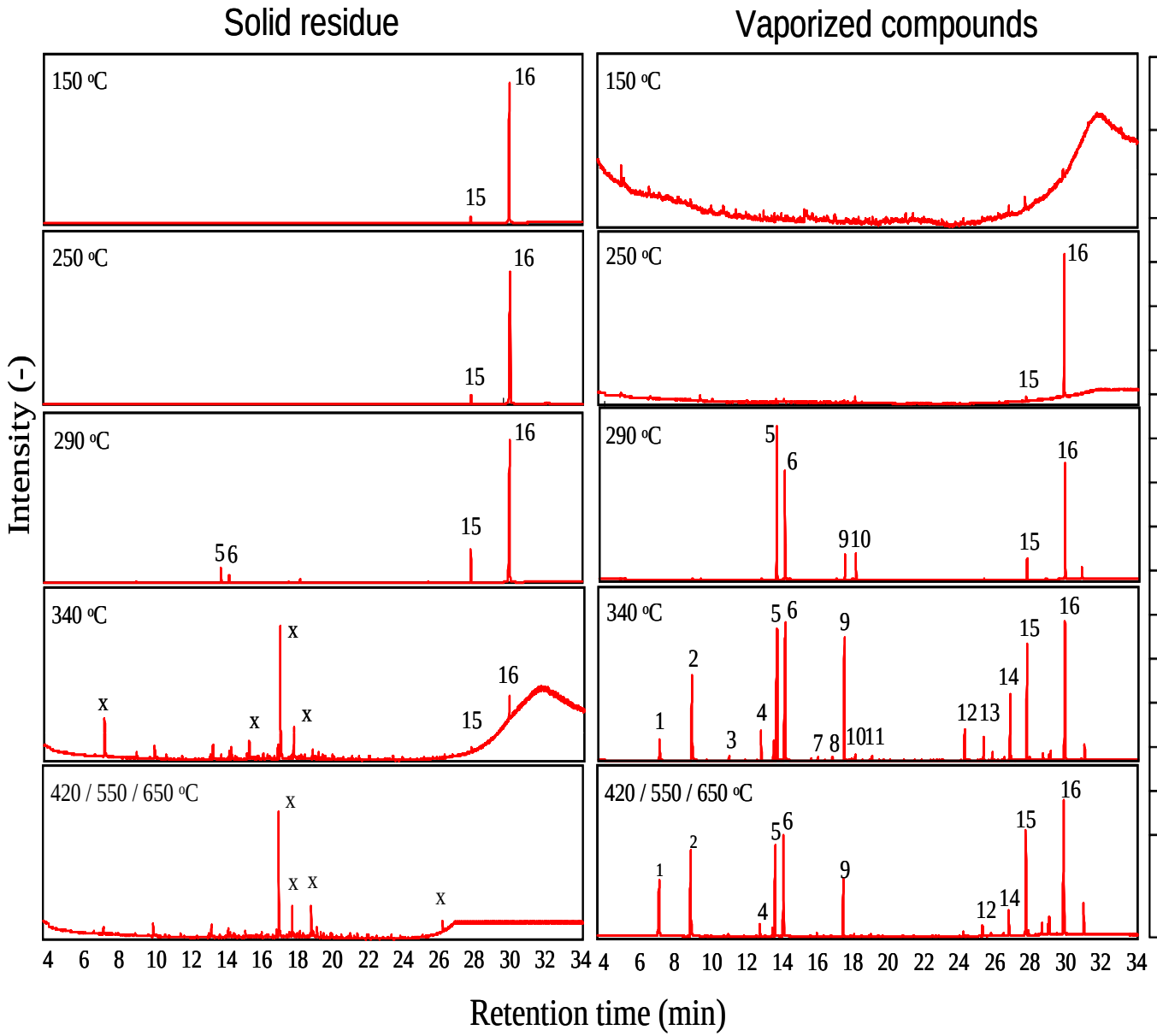
SAMPLES QUALIFICATION

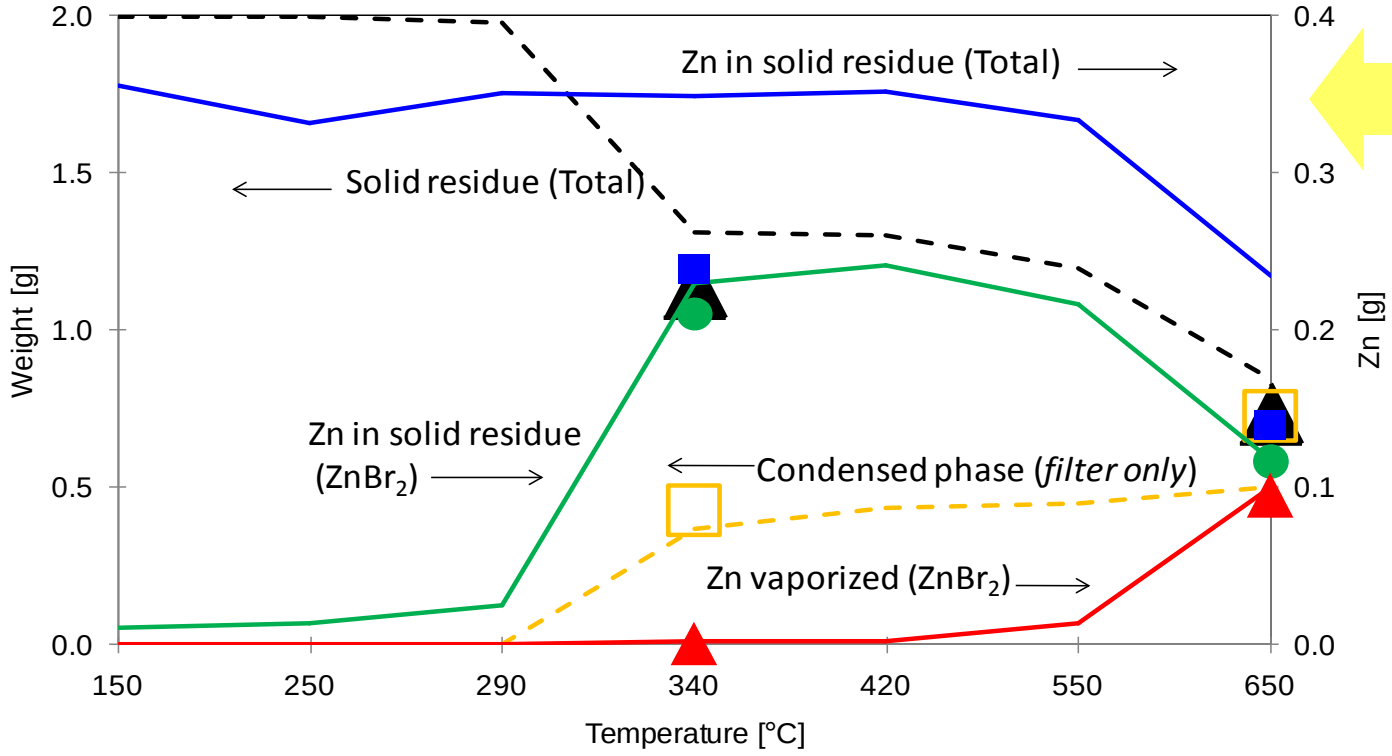
EPMA, XRD, IC, ICP, GC/MS analysis of products in solid residue and vaporized phase after thermal treatment.

Experimental set-up for quartz-tube reactor experiments



RESULTS: TIC of organic products from the thermal treatment of TBBPA:ZnO (3.34:1). No organic products were found in the hexane trap



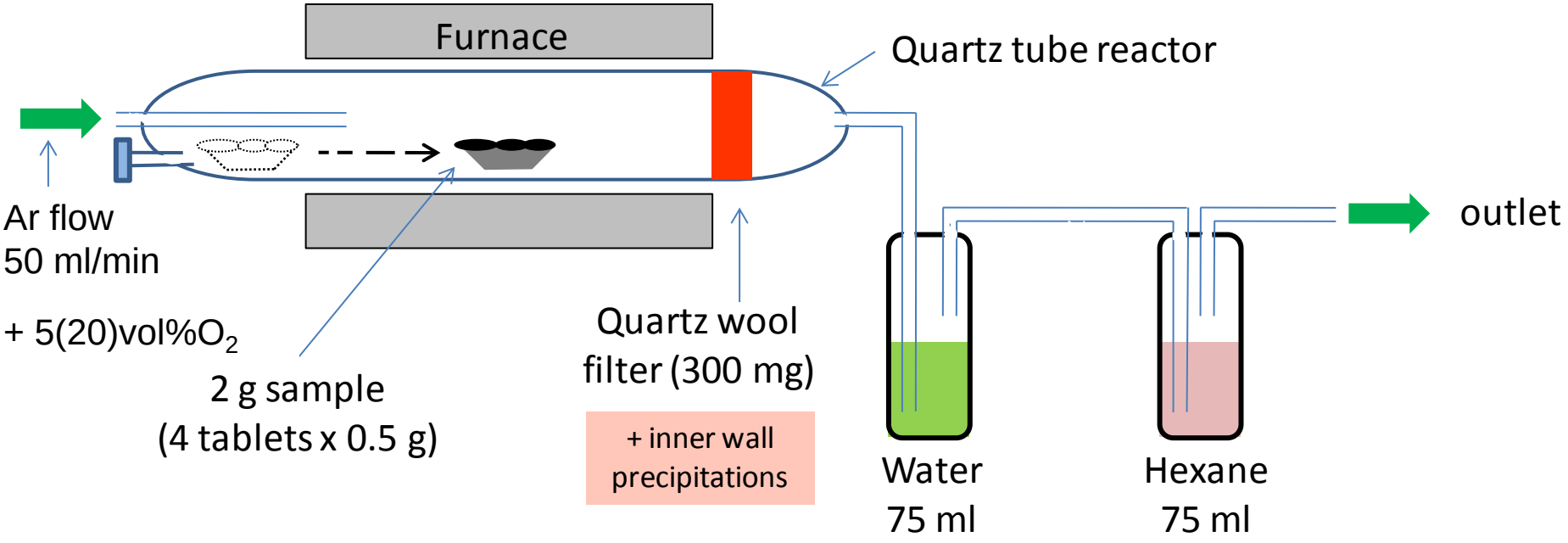


Weight change of solid residue and Zn Distribution during thermal treatment of TBBPA and ZnO

Fate of Bromine and Zinc at various temperature [%]

Temp. °C	TBBPA: ZnO	Br released %	Zn brominated of total Zn %	Zn vaporized of total Zn %	Zn vaporized of Zn brominated %	Zn loss %	Unreacted Br for Released Br %
150	**(3.34:1)**	0	3	0	0	2	0
250		0	4	0	0	9	0
290		5	7	0.	0	3	0
340		58 ± 1	64 ± 1	0 ±0	1 ± 0	4 ± 3	1 ± 1
420		61 ± 4	67 ± 1	0 ±0	1 ± 0	2 ± 2	1 ± 0
550		60 ± 3	63 ± 2	4 ±0	6 ± 1	4 ± 3	6 ± 5
650		62 ± 4	61 ± 0	28±1	45 ± 1	7 ± 2	9 ± 4
340	**(5.17:1)**	53	81	0	0	8	9
650		57	81	36	45	10	12

Experimental set-up for isothermal runs



Heating conditions:

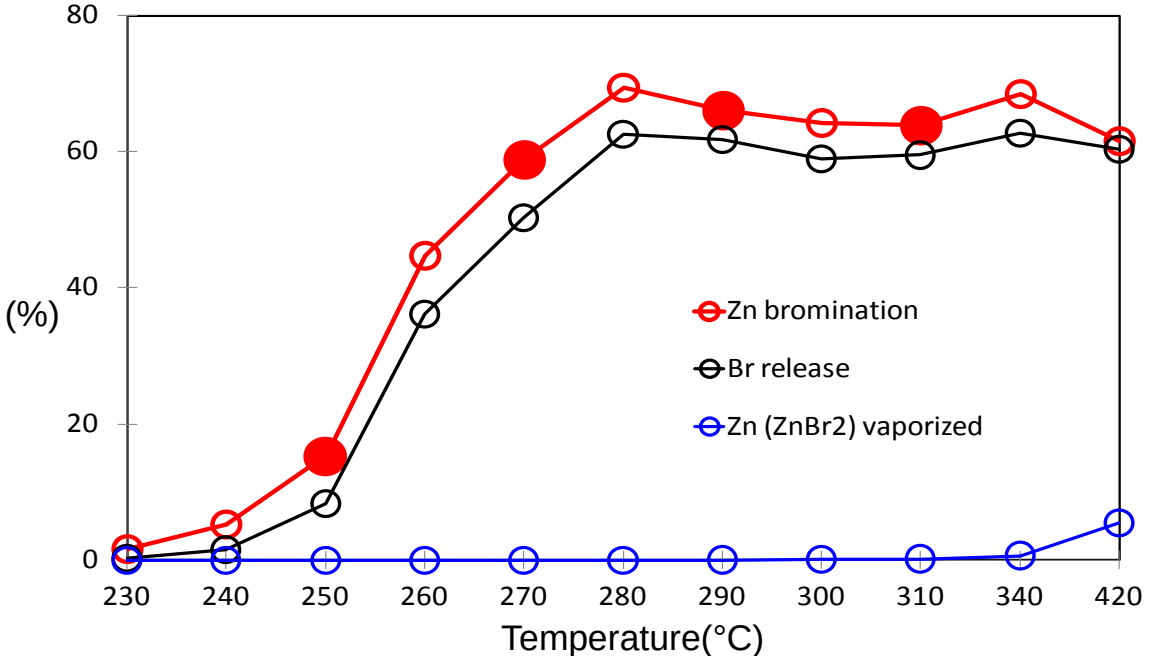
- ZnO bromination efficiency-

1. 230-310°C (every 10 °C), 340 and 420 °C – isothermal heating for 40 min (**temperature** effect)
2. 250, 270, 290, 310 °C – isothermal heating for (5) 10 – 100 (140) min (**time** effect)

- $ZnBr_2$ vaporization efficiency-

3. 490 – 950 °C – isothermal heating for 40 min (**temperature** effect)
4. 490, 550, 650 °C – isothermal heating for 10, 40, 80 min (**time** effect)

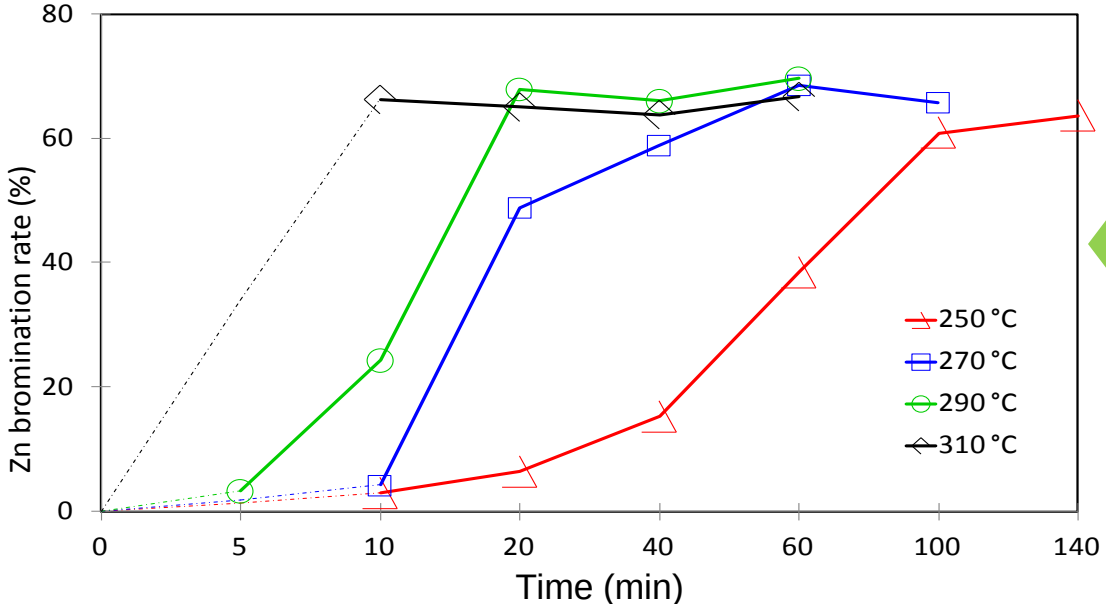
RESULTS: Effect of temperature (A) and time (B) on ZnO bromination rate



(A)

Effect of temperature

TBBPA:ZnO (3.34:1) 40 min

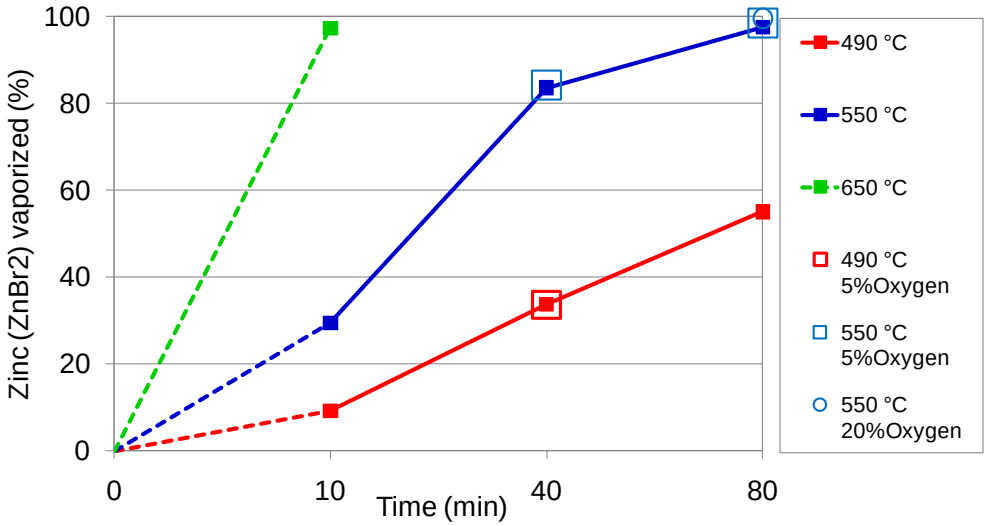


(B)

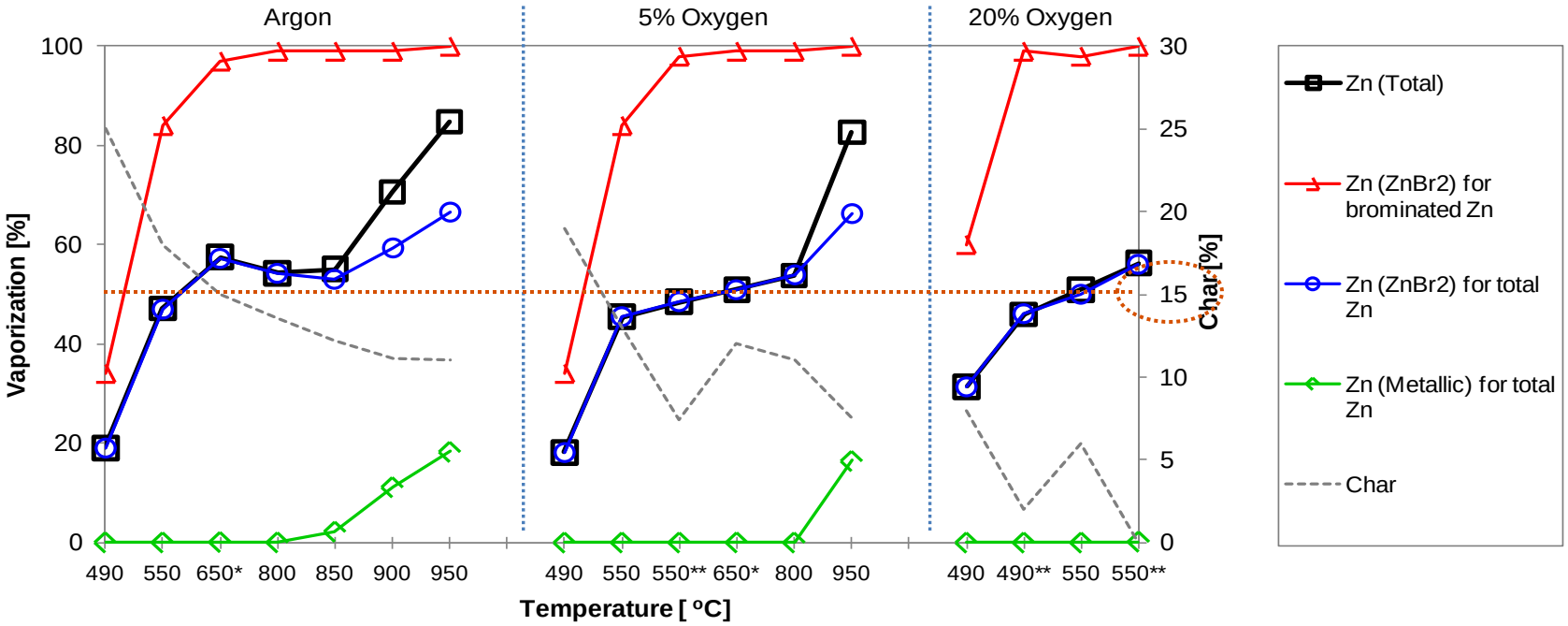
Effect of time

TBBPA:ZnO (3.34:1)

RESULTS: Effect of time (A), temperature and atmosphere (B) on $ZnBr_2$ vaporization yield



Char residue (%) at the following heating conditions			
	490 °C	550 °C	650 °C
10 min	30	21	15
40 min	25	18	-
80 min	19	15	-



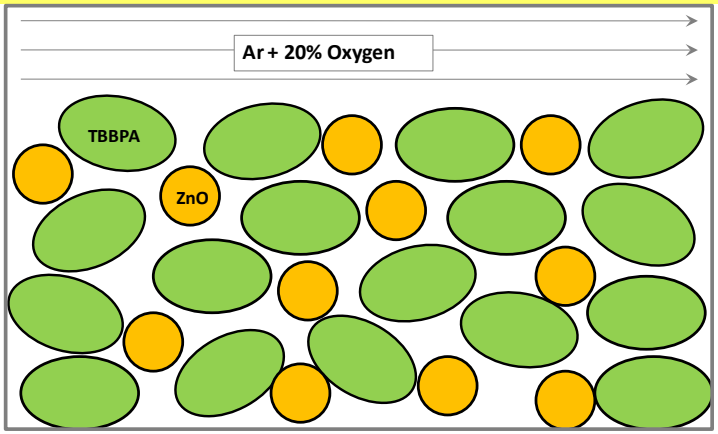
The temperatures marked by asterisks indicate different time of thermal treatment: * - 10 min.; ** - 80 min.

Concept of bromination-evaporation of ZnO during heating with TBBPA

1.

T < 180 °C

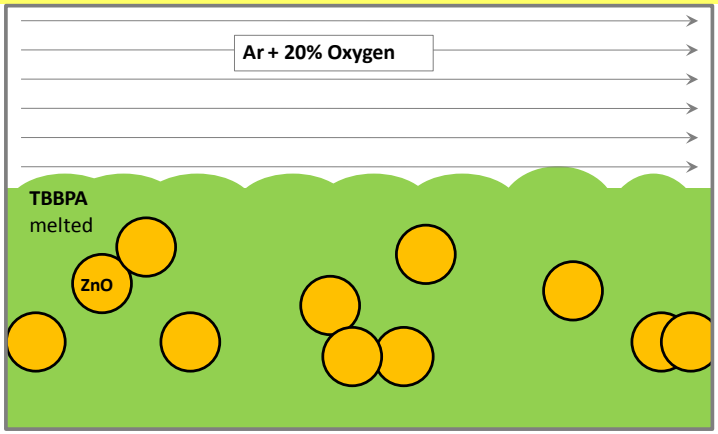
Compressed mixture of TBBPA + ZnO



2.

T = 180 - 240 °C

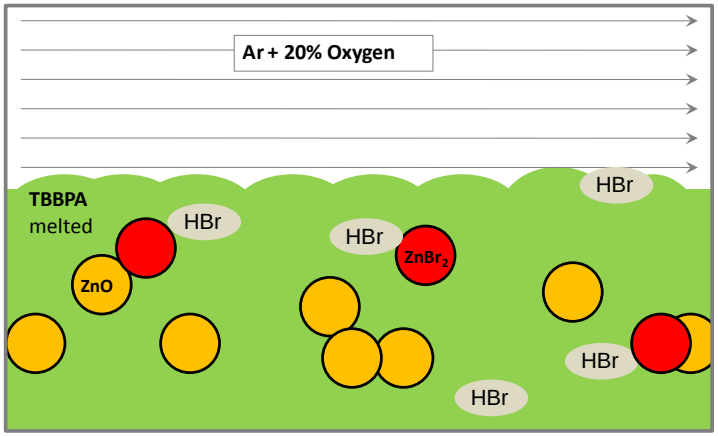
Zno covered by melted TBBPA



3.

T = 250 °C

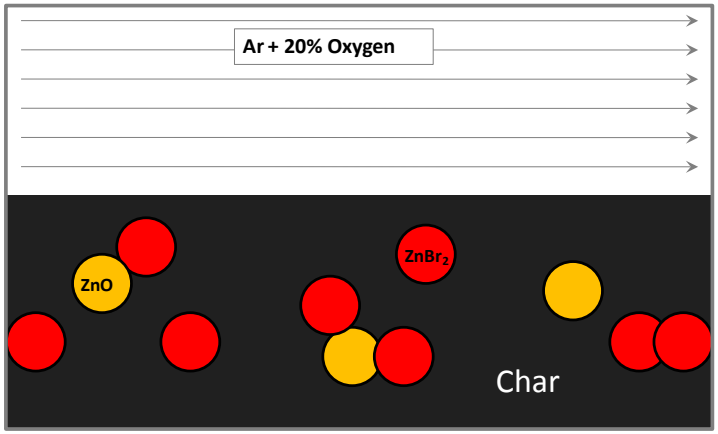
Initial decomposition of TBBPA, formation of $ZnBr_2$



4 .

T = 280 °C

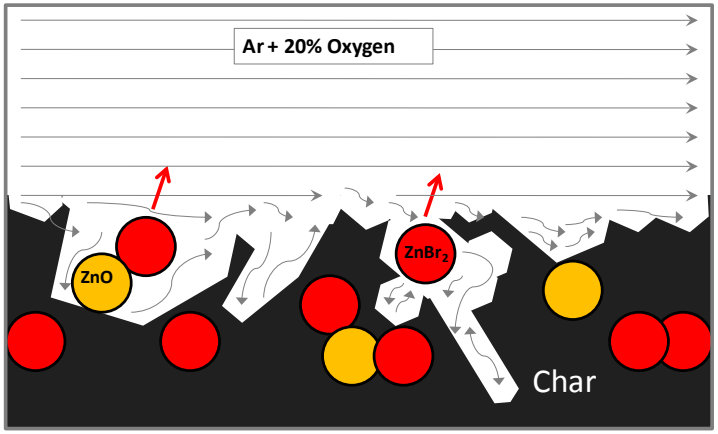
Char-bounded $ZnBr_2$ and remains of unreacted ZnO



5.

T = 490 - 550 °C

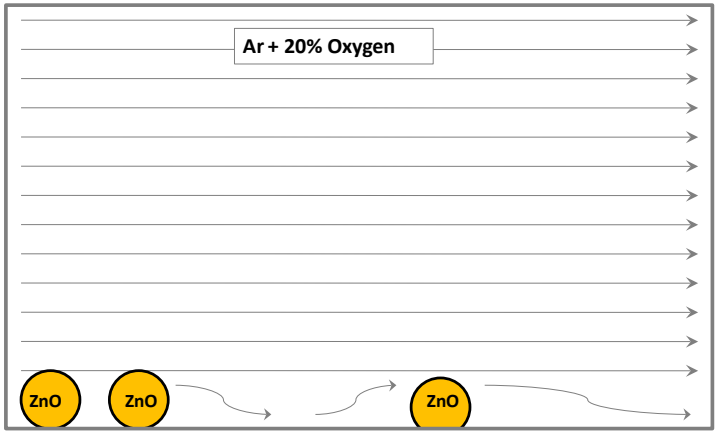
Oxidation of char and progresive vaporization of liberated $ZnBr_2$



6.

T = 550°C (80min)

Complete oxidation of char and vaporization of $ZnBr_2$. Remains of unreacted ZnO



CONCLUSIONS (I):

- **Decomposition of TBBPA in the presence of ZnO (3.34:1):**

  - proceeds between: 250 - 280 ^{o}C (isothermal heating)

    290 - 340 ^{o}C (heating 10 ^{o}C/min)

  - releases of 64% (270 ^{o}C) of the total amount of bromine present in TBBPA

- **Most of the inorganic bromine** (96 % at 250-650 ^{o}C) released from TBBPA is promptly utilized in the reaction with ZnO

CONCLUSIONS (II):

- **The bromination of ZnO occurrs at max yield of:**

dynamic heating (10 °C/min)

67 % for TBBPA:ZnO (3.34:1)

81 % for TBBPA:ZnO (5.17:1)

isothermal heating (60 min)

69 - 70 % for TBBPA:ZnO (3.34:1)

- **The bromination yield:**

- is dependent on quantity of HBr available around particles of ZnO

- increases with temperature below 280°C/340 °C (isothermal/dynamic)

- increases with time at temperatures below 310 °C (isothermal)

CONCLUSIONS (III):

- **Volatilization of the formed $ZnBr_2$**

  (at Argon atmosphere)

  - proceeds between: 420 - 950 ^{o}C (isothermal)

  - is affected by restraining impact of formed char; which decays when its concentration drops to 15% and lower

CONCLUSIONS (IV):

- **From 850 °C**, the char serves as a source of carbon for **carbothermic reduction** of remaining ZnO, which evaporates from solid residue in metallic form (completed at 950 °C)

CONCLUSIONS (V):

- **The presence of 5 vol % of oxygen**

  has no significant effect on:

  - bromination of ZnO
  - vaporization of formed $ZnBr_2$
  - carbothermic reduction of ZnO

- **The strong oxidizing conditions (20 vol % of oxygen):**

  - has no significant effect on bromination of ZnO;
  - prevents carbothermic reduction of remaining ZnO
  - boosts vaporization of $ZnBr_2$ together with amplifying influence on char degradation (vaporization of $ZnBr_2$ completed at 550 ^{o}C 80 min)

Details on the research can be found in:

Environ. Sci. Technol. 2009, 43(23), 8936-8941

Environ. Sci. Technol. 2009, 43(4), 1205-1210

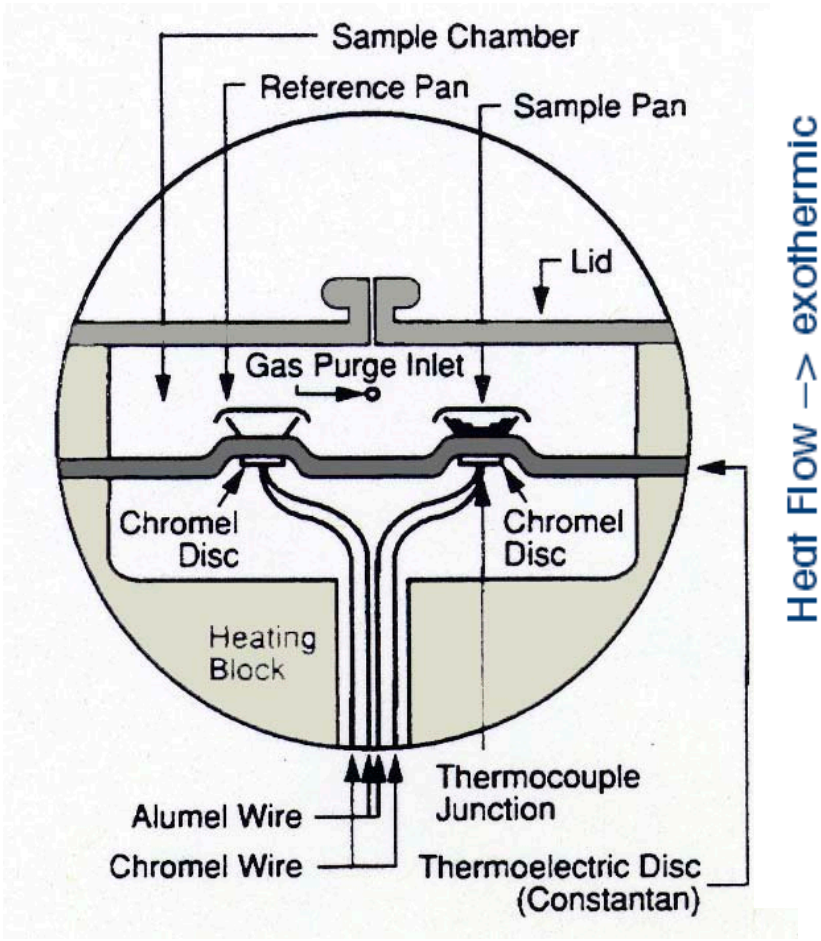
J. Anal. Appl. Pyrolysis. 2010, 88, 14-21

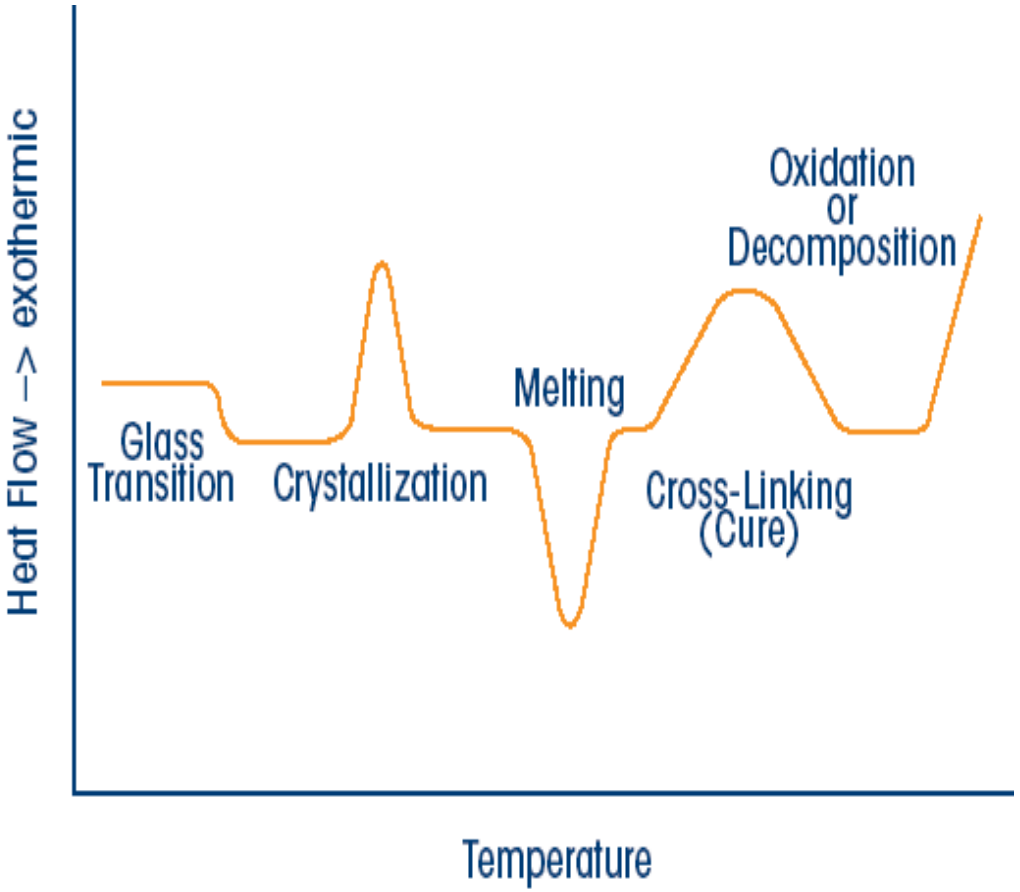
Thank you for your kind attention !

Additional Slides

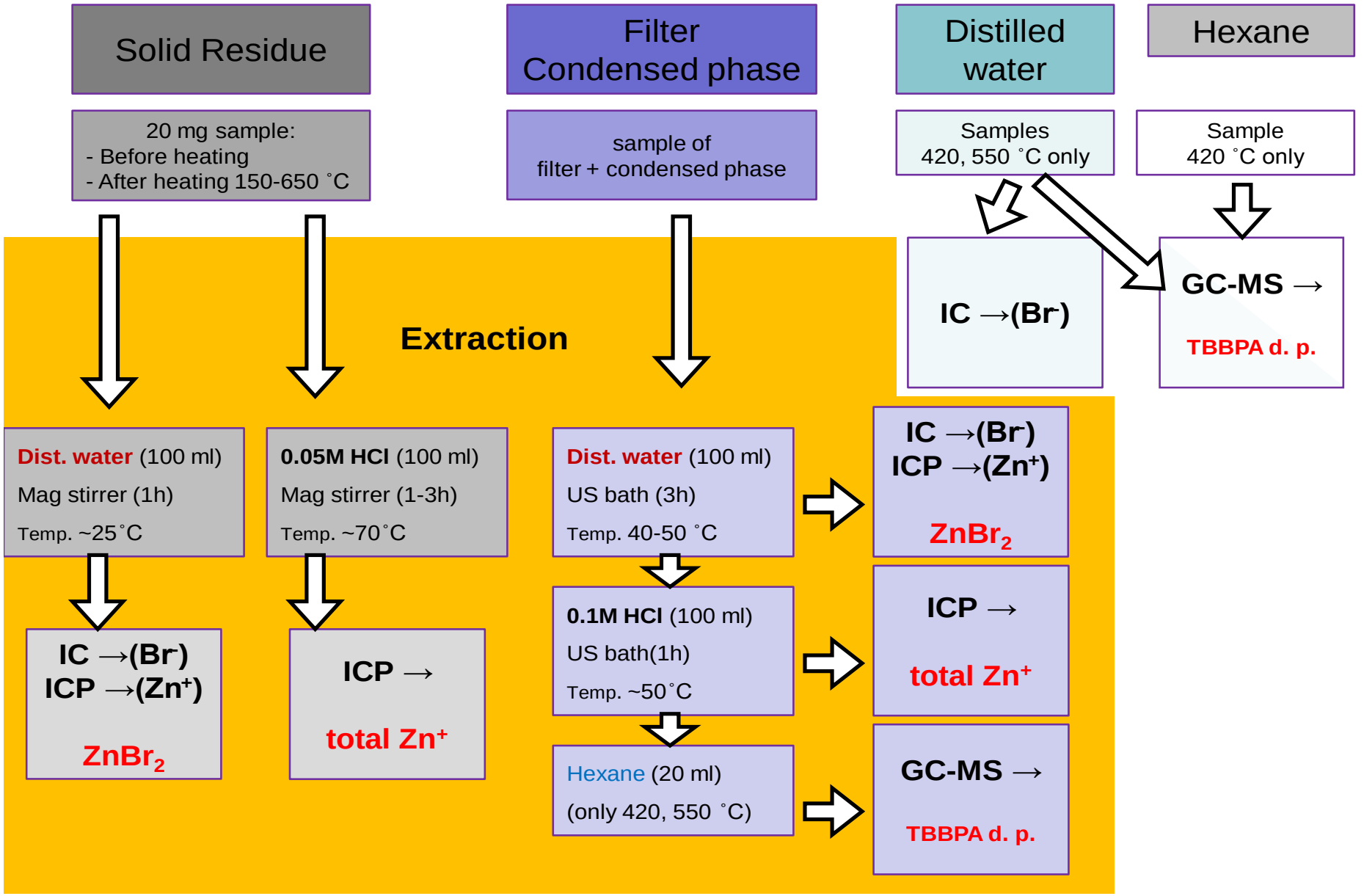
Differential Scanning Calorimeter DSC 2920

[*TA Instrument, New Castle, DE, 1997*]

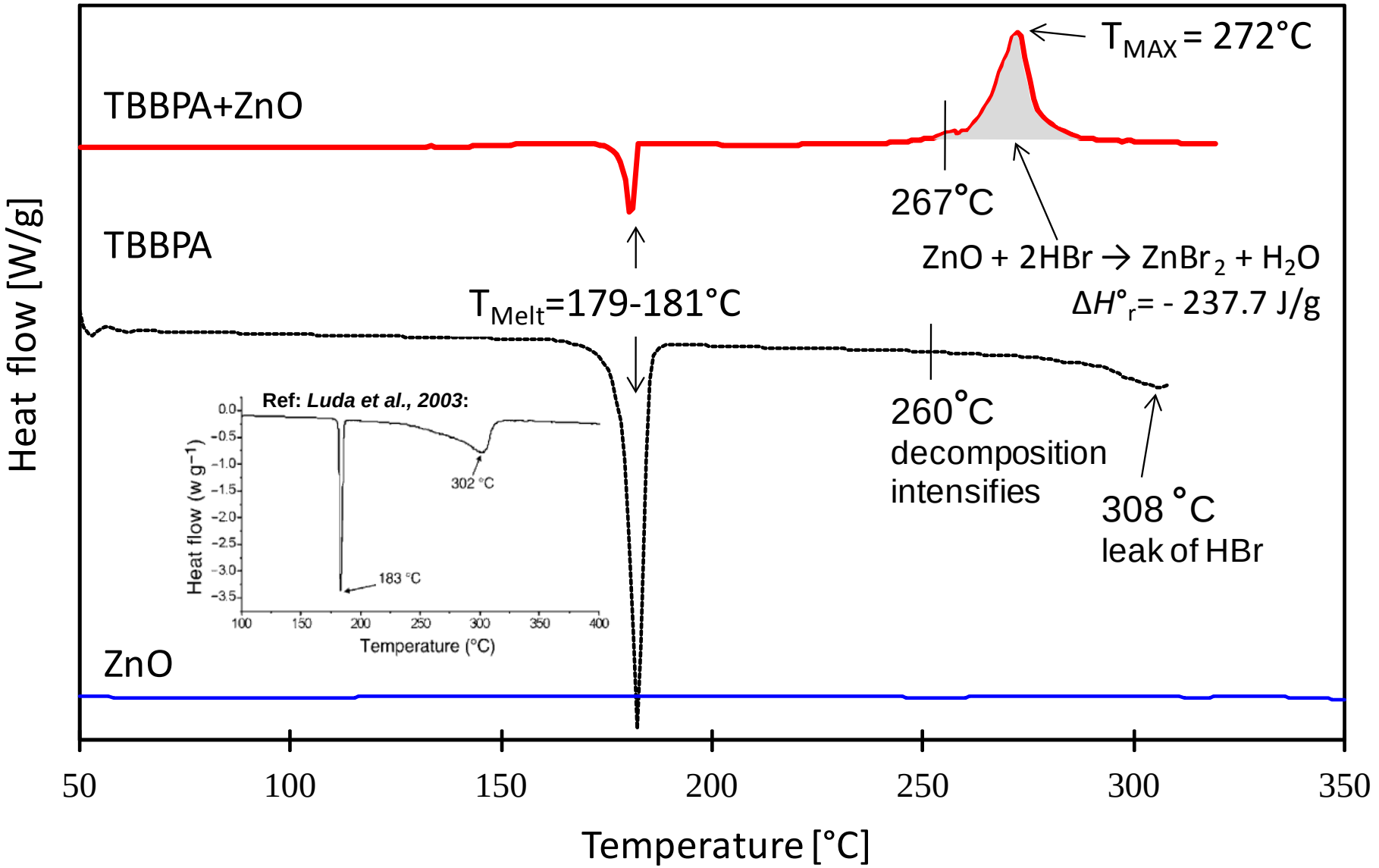


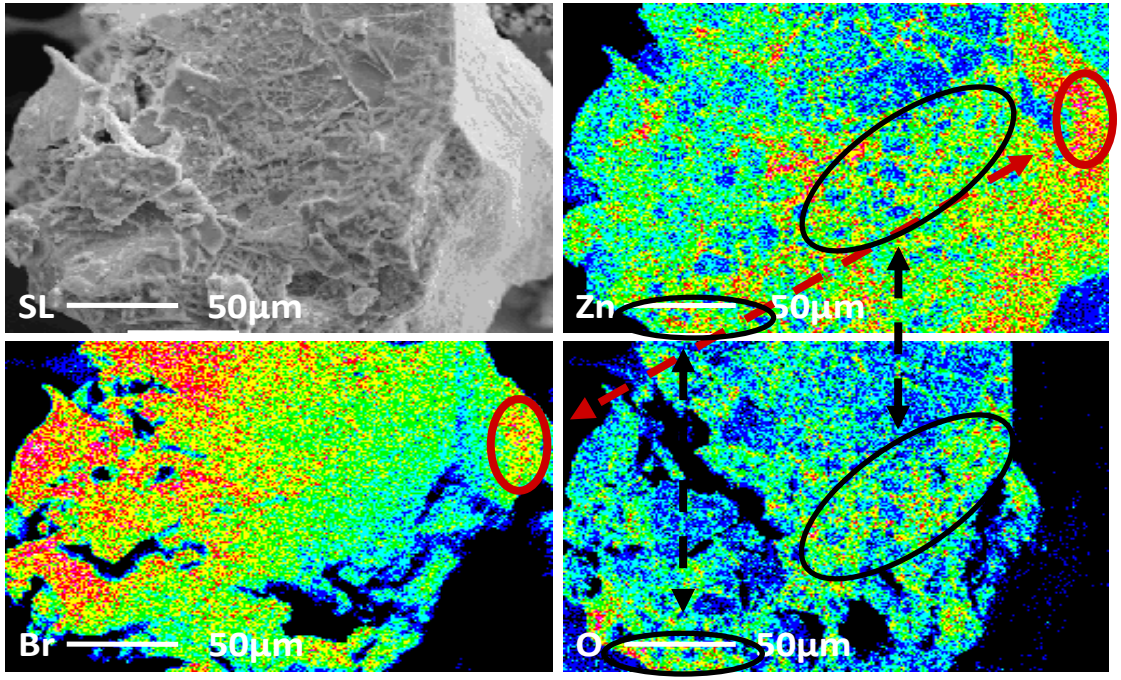


Analytical procedure



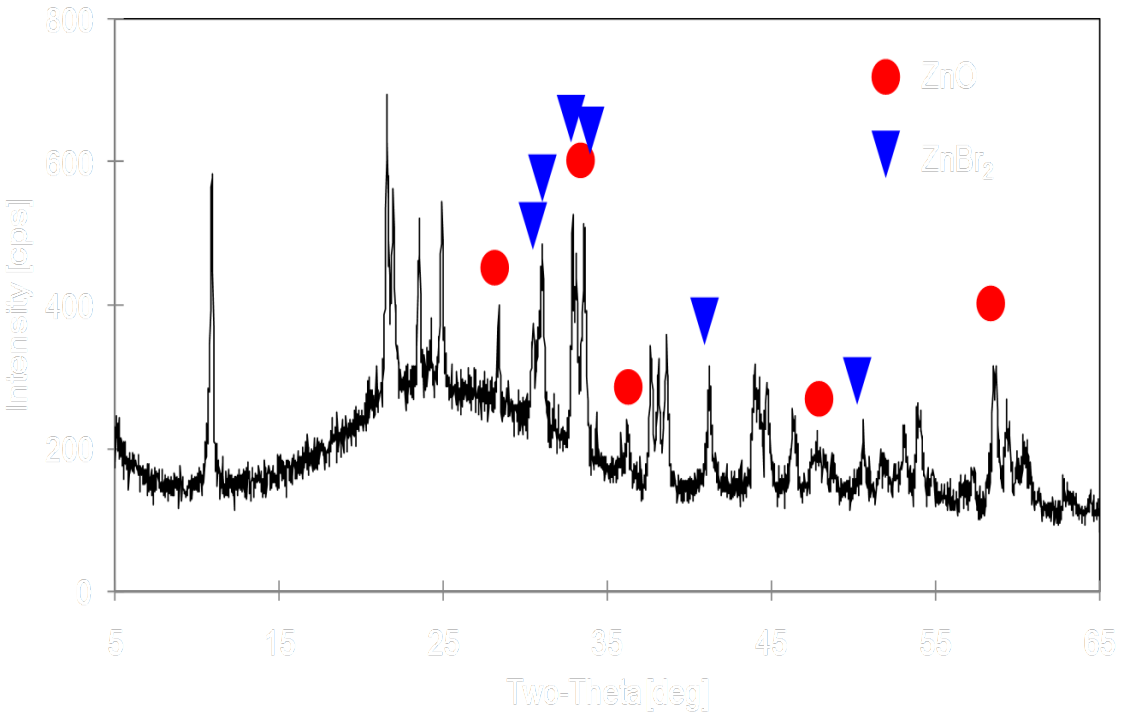
RESULTS: DSC curves for ZnO, TBBPA and TBBPA:ZnO (3.34:1) at a heating rate of 1 °C/min





RESULTS:

← EPMA pictures



← XRD patterns

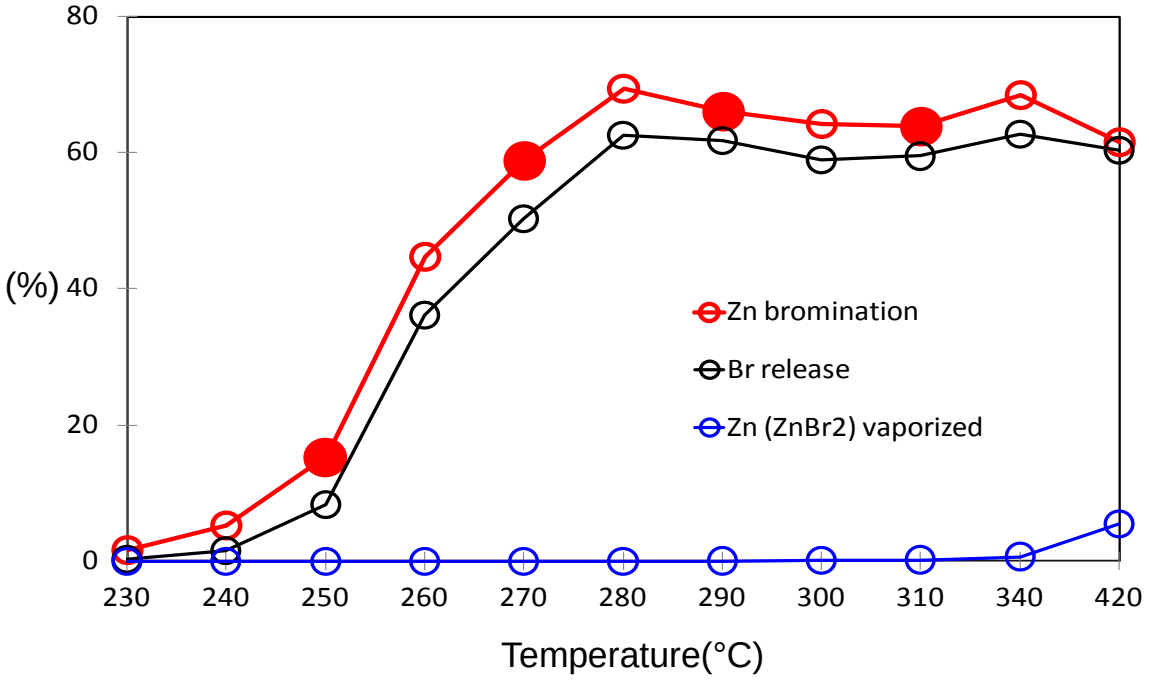
of solid residues

from thermal treatment of

TBBPA:ZnO (3.34:1)

by DSC at 272 °C.

RESULTS: Isothermal treatment of TBBPA:ZnO (3.34:1) for 40 min

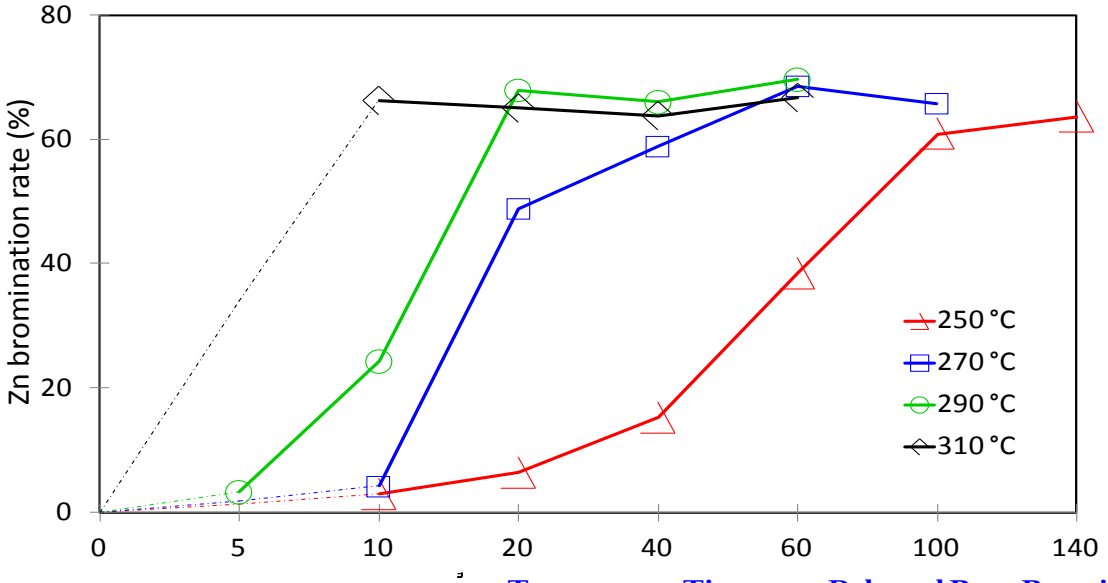


Zn and Br distribution (%) during thermal treatment of TBBPA:ZnO (3.34:1)

Fate of Bromine and Zinc at various temperature [%]

Temp.	Released Br	Brominated Zn for total Zn	Vaporized Zn for Brominated Zn	Zn loss	Unreacted Br for released Br
°C	%	%	%	%	%
230	0	2	0.0	24	2
240	2	5	0.0	4	1
250	8	15	0.0	6	0
260	36	45	0.0	4	7
270	50	59	0.0	5	6
280	63	69	0.0	5	2
290	62	66	0.1	3	5
300	59	64	0.2	2	5
310	59	64	0.2	3	7
340	63	68	0.7	3	5
420	60	62	5.4	6	11

RESULTS: Isothermal treatment of TBBPA:ZnO (3.34:1) for 5-140 min



Zn bromination rate (%) during thermal treatment of TBBPA:ZnO (3.34:1)

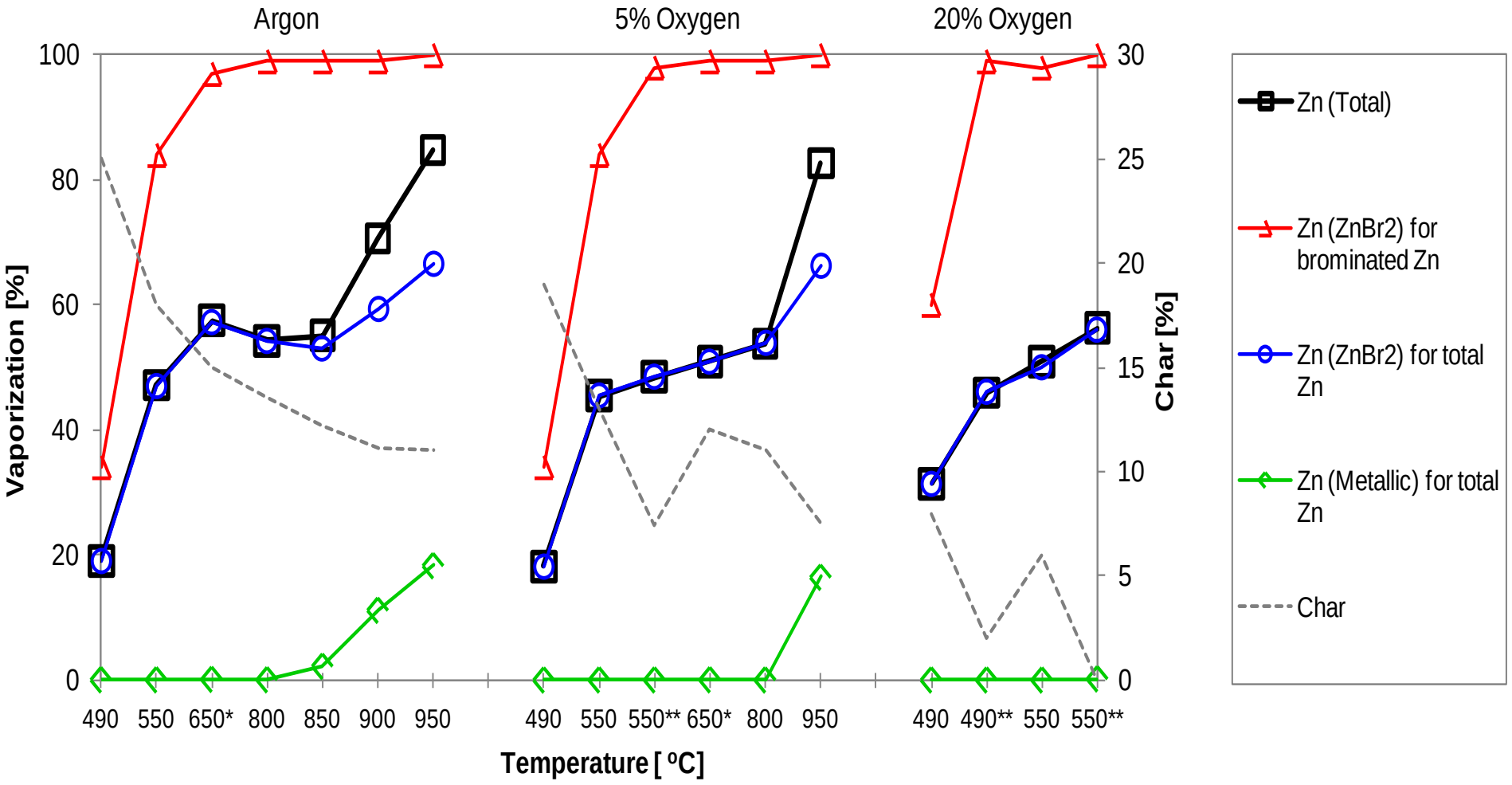
Fate of Bromine and Zinc for various conditions (%)

Temp.	Time	Released Br	Brominated Zn for total Zn	Vaporized Zn for Brominated Zn	Zn loss	Unreacted Br for released Br
° C	min	%	%	%	%	%
250	10	0	3	0.00	3	2
	20	2	6	0.00	5	0
	40	8	15	0.01	6	0
	60	35	38	0.01	3	6
	100	60	61	0.01	5	5
	140	63	64	0.01	7	8
270	10	1	4	0.00	7	4
	20	43	49	0.01	5	6
	40	50	59	0.01	5	2
	60	65	69	0.01	4	4
	100	64	66	0.01	8	4
290	5	0	3	0.00	-2	2
	10	18	24	0.01	0	2
	20	62	68	0.04	1	2
	40	62	66	0.07	3	5
	60	64	70	0.08	1	3
310	10	61	66	0.18	3	3
	20	60	65	0.11	5	3
	40	59	64	0.22	3	7
	60	64	67	0.25	1	2

RESULTS: Effect of ZnO on degradation of TBBPA

	TBBPA (Barontini et al., 2004)	TBBPA:ZnO (3.34:1) (This study)
Degradation products	no qualitative difference	
Released Br (Max, %)	52 (270 °C) 63-65 (270-310 °C)	63 (250°C) 64 (310°C) 75 (800°C) 77 (900°C) 81 (950°C)
Char (%)	20 (when conversion of TBBPA completed) 20 (310°C)	34 (250°C) 32 (270°C) 28-29 (290°C) 25-28 (310°C) 19-30 (490°C)

RESULTS: Effect inert and oxidizing conditions on vaporization of zinc during thermal treatment of TBBPA:ZnO (3.34:1) for 40 min



The temperatures marked by asterisks indicate different time of thermal treatment: single asterisk - 10 min.; double asterisks - 80 min.

Bromination and vaporization of zinc during isothermal treatment of TBBPA and ZnO at various conditions, expressed as percentages.

	Temp.	Time	Released Br / Br bounded to Zn for Br released	Brominated Zn for total Zn	Vapor pressure# of $ZnBr_2$	Vaporized Zn ($ZnBr_2$) for brominated Zn/total Zn	Vaporized Zn (metallic) for remaining/total Zn	Vaporized Zn (total) for total Zn	Zn loss	Char
	°C	min	%	%	Pa	%		%	%	%
Argon	490	10	41 / 100	59		9 / 5	0 / 0	5	6	30
		40	48 / 100	57	3,422	34 / 19	0 / 0	19	9	25
		80	53 / 100	53		55 / 29	0 / 0	29	13	19
	550	10	56 / 100	56	12,944	29 / 17	0 / 0	17	11	21
		40	54 / 100	56		84 / 47	0 / 0	47	7	18
		80	59 / 95	54		98 / 53	0 / 0	53	9	15
	650	10	53 / 100	59	75,517	97 / 57	0 / 0	57	8	15
	800	40	75 / 80	55	507,208	99 / 54	0 / 0	54	10	14
	850	40	74 / 79	53	830,506	99 / 53	4 / 2	55	14	12
	900	40	77 / 83	60	1,287,451	99 / 59	27 / 11	71	16	11
	950	40	81 / 86	67	1,903,222	100 / 66	53 / 18	85	15	11
5% Oxygen	490	40	53 / 100	54	3,422	34 / 18	0 / 0	18	13	19
	550	40	58 / 96	54	12,944	84 / 45	0 / 0	45	13	13
		80	51 / 98	49		98 / 48	0 / 0	48	14	7
	650	10	56 / 96	52	75,517	99 / 51	0 / 0	51	13	12
	800	40	80 / 74	54	507,208	99 / 54	0 / 0	54	9	11
	950	40	79 / 87	66	1,903,222	100 / 66	50 / 17	83	17	8
20% Oxygen	490	40	53 / 99	52	3,422	60 / 31	0 / 0	31	13	8
		80	49 / 97	46		99 / 46	0 / 0	46	17	2
	550	40	54 / 97	51	12,944	98 / 50	0 / 0	50	16	6
		80	58 / 98	56		100 / 56	0 / 0	56	9	0