IPCP Webinar Series: POPs in plastic and monitoring approaches

Part III: Extraction, clean-up, and analysis of POPs in plastics; 22/23 May 2023

# Analysing/Quantifying brominated Flame Retardants (BFRs) with GC-ECD in e-waste plastics


**Omotayo SINDIKU[1] and Roland WEBER[2]**

[1]Lead City University, Ibadan, Nigeria
https://www.researchgate.net/profile/Omotayo-Sindiku

[2]POPs Environmental Consulting, Scwäbisch Gmünd, Germany
https://www.researchgate.net/profile/Roland-Weber-2


STOCKHOLM CONVENTION

# Sampling of TV/PC CRT Plastic in WEEE Nigeria

- 382 samples (158 from TV CRT casings and 224 computer CRTs) have been sampled from eight locations in south west Nigeria.
- The samples were selected from waste storages, electronics workshops, roadsides, dumpsites and dismantling sites.


A


C


E


B


D


F

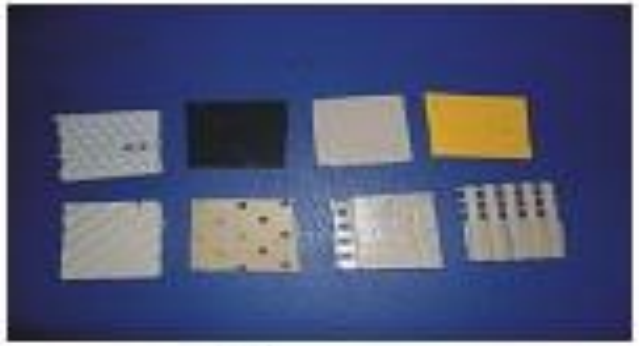
Sindiku et al. (2015)Environ Sci Pollut Res Int. 22, 14489-14501. DOI: 10.1007/s11356-014-3266-0

# Sample Preparation and Measurement

- Small pieces were cut of each polymer samples (approx. 100 x 50 mm) and sent to Fraunhofer Inst. (Freising/GER) for analysis.

A

C



E

B

D

F

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# Samples analysis for PBDE and other BFRs with GC/ECD

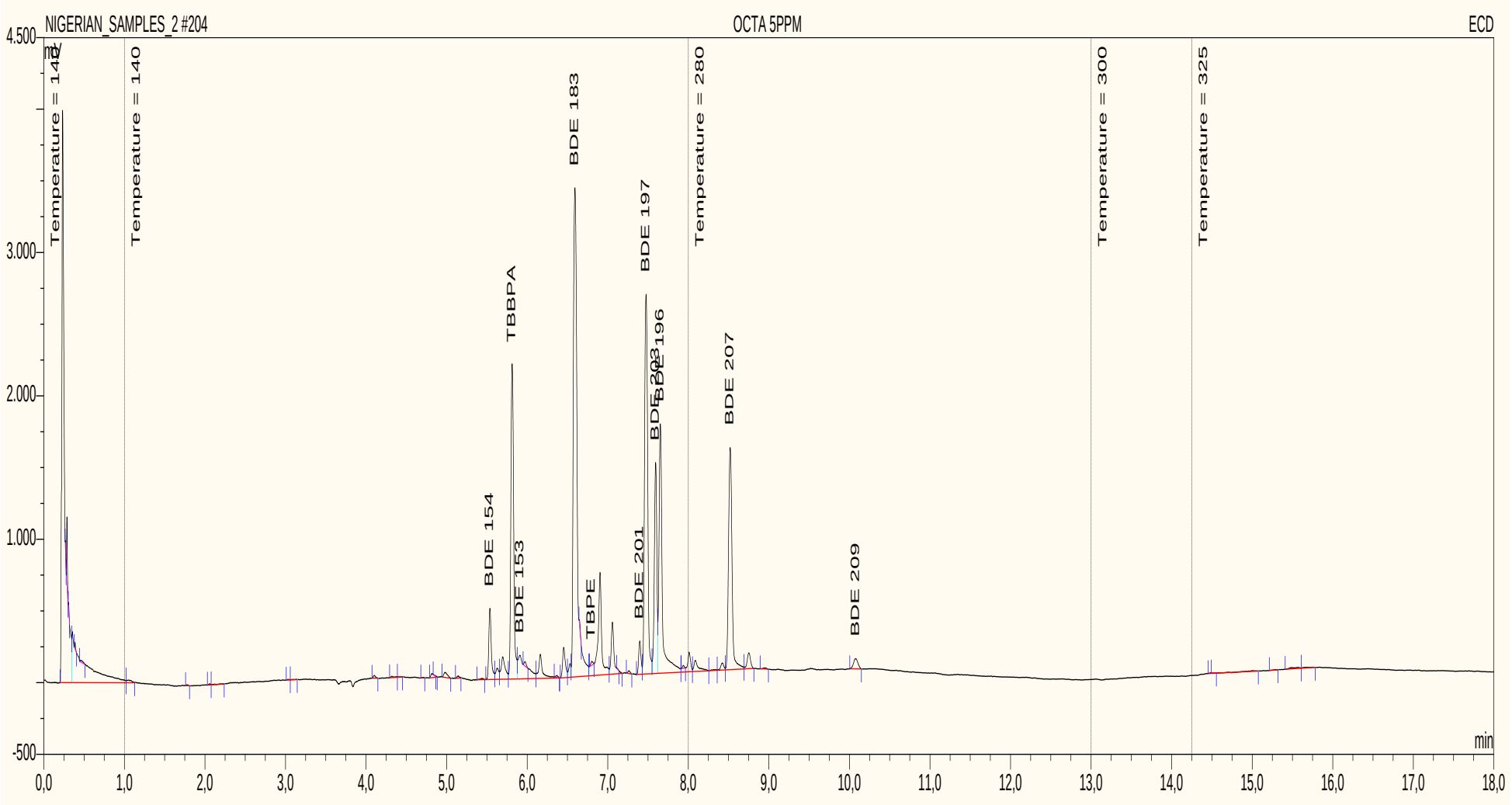
- The instrumental analysis was carried out using a gas chromatograph (TraceGC Ultra, Thermo, Dreieich, Germany) coupled with electron capture detection (ECD, $^{63}$Ni, 370 MBq).
- The GC was equipped with a ZB-5 HT inferno (15 m x 0.25 mm x 0.1 µm, Phenomenex, Aschaffenburg, Germany) as stationary phase.
- Temperatures of GC split/splitless injector and detector were set at 295 ˚C and 320 ˚C, respectively and the oven temperature was programmed as follows: 140 °C (1 min), 20 K/min (280 °C), 4 K/min (300 °C), 20 K/min (325 ˚C).

# Identification and Quantification by GC-ECD

- BFRs were identified by comparison of retention times with external technical standards of major  c-OctaBDE, commercial Decabromodiphenyl ether (c-DecaBDE), Tetrabromobisphenol A (TBBPA) and 1,2- bis-tribromophenoyethane (TBPE).
- This standards were used to quantify their amount in each plastic samples using external calibration with development of calibration curves.

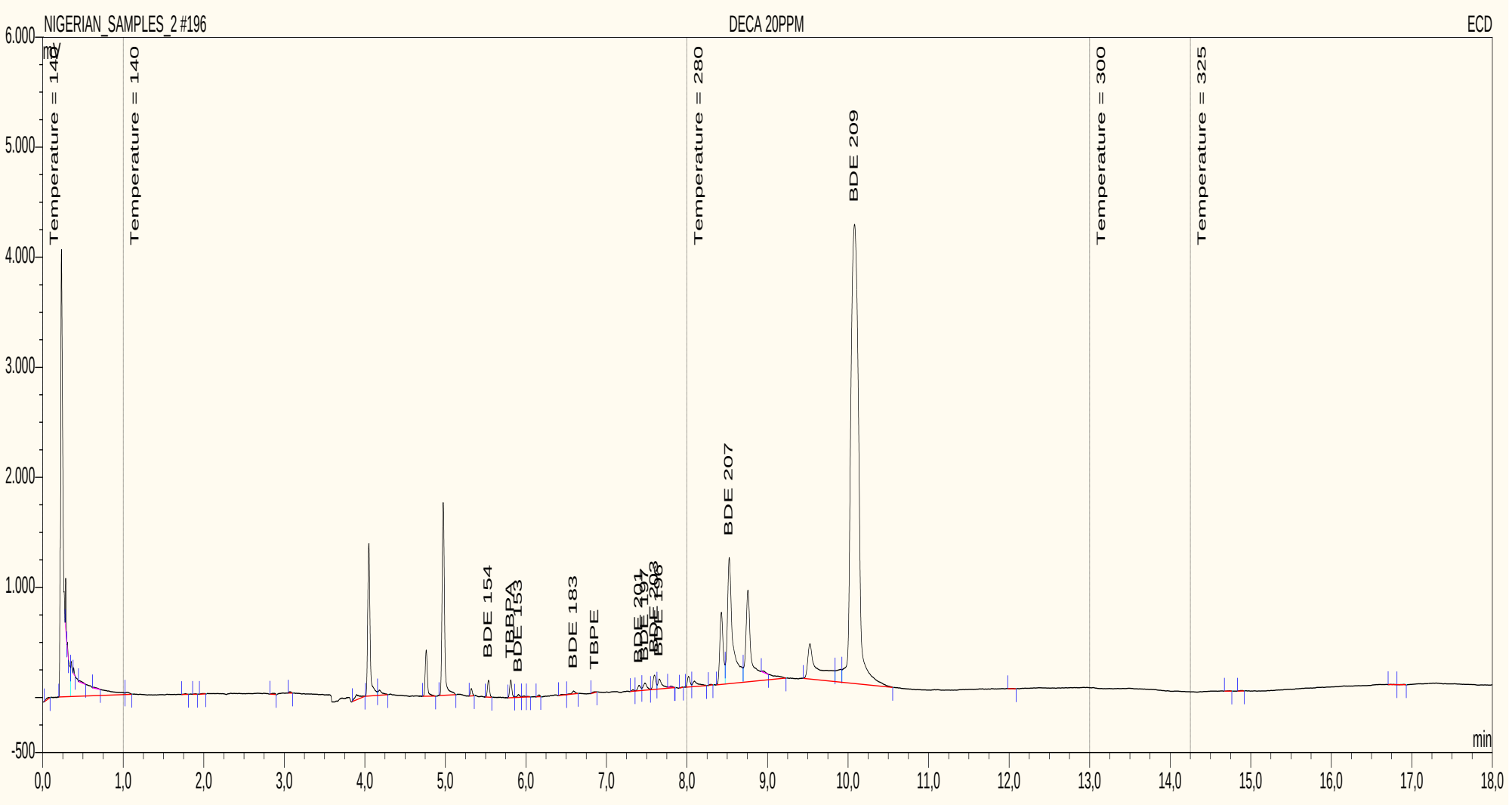
# GC-ECD Chromatogram of 10 ppm standard solution of OctaBDE

**The commercial OctaBDE standard** contains **hexaBDE (BDE-153, BDE-154), heptaBDE (BDE-183)** and **octaBDE (BDE-196; BDE197)** as major congeners. C-OctaBDE standard also contains **minor amount of nonaBDE (BDE-207)** and **very small amount DecaBDE.**



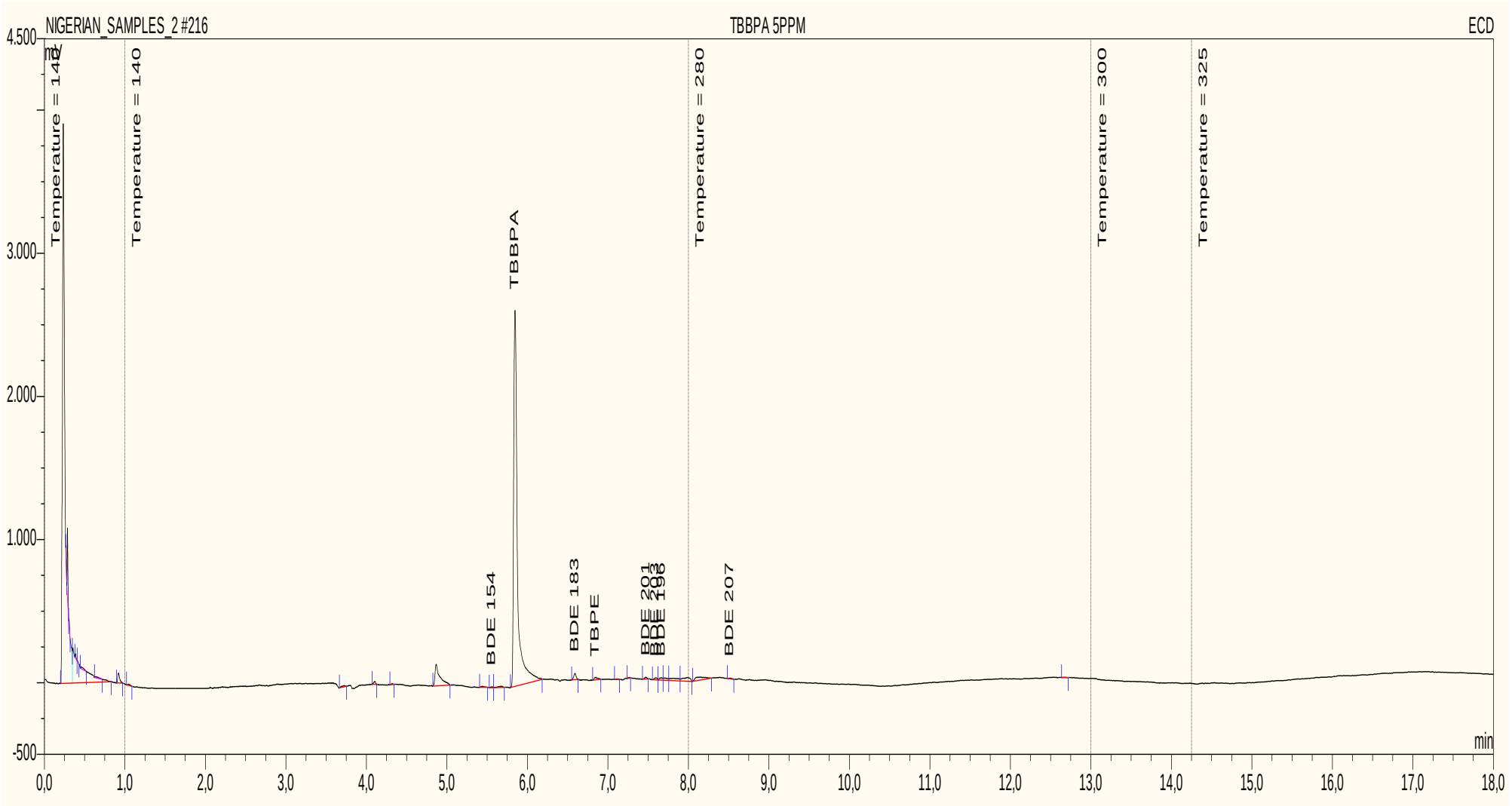
# GC-ECD Chromatogram of 10 ppm Standard solution of DecaBDE

**Commercial DecaBDE** contains largely **DecaBDE and some nonaBDE (BDE-206, 207, 208)**



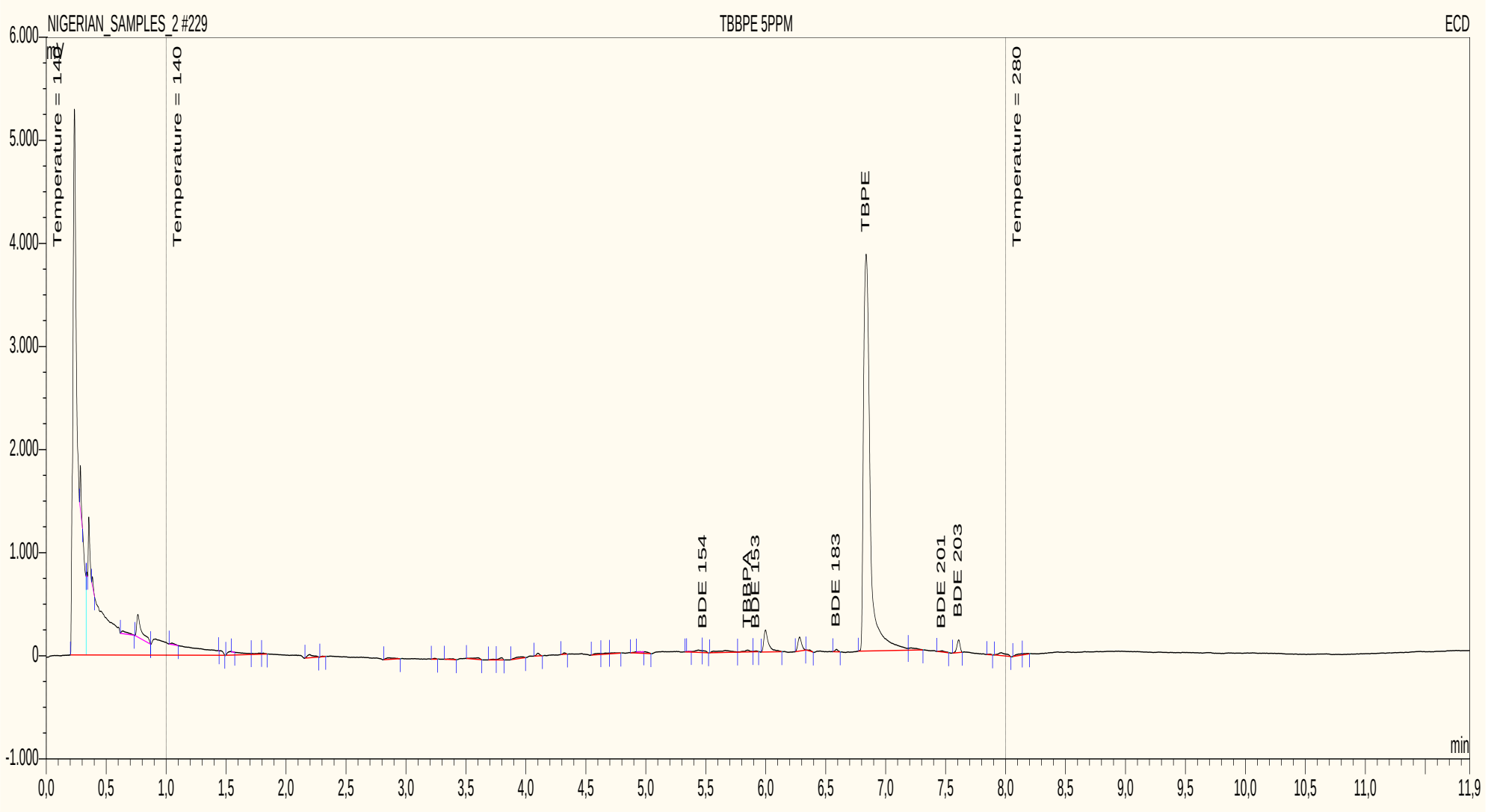
# GC-ECD Chromatogram of 10 ppm Standard solution of TBBPA

## These standards are also used to develop the calibration curves for quantification



# GC-ECD Chromatogram of 10 ppm Standard solution of TBPE

## These standards are also used to develop the calibration curves for quantification



# Quality Control (QA/QC) protocols for PBDEs analysis

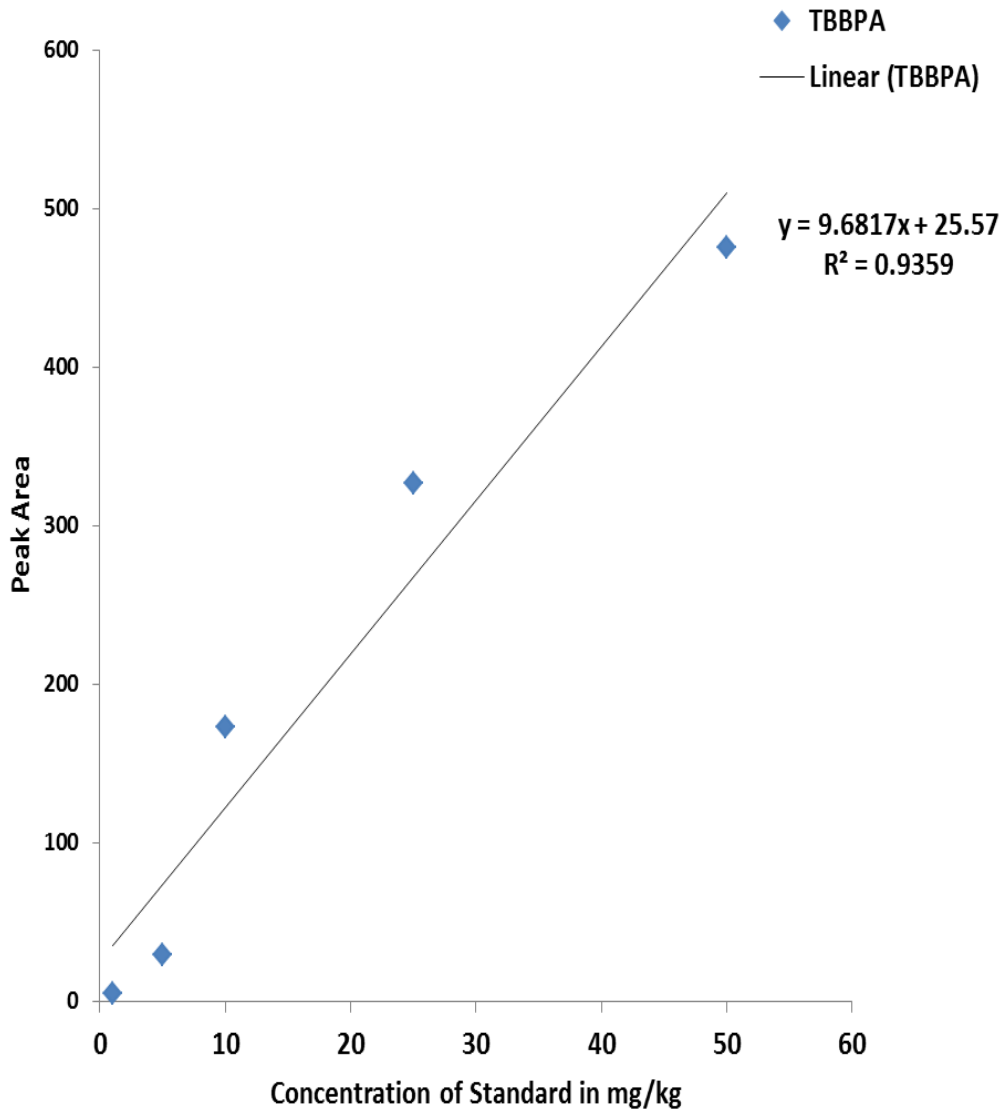
- The BFR analysis was performed according to Standard IEC-62321-2008 (Electrotechnical products - Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, and PBDEs))
- **The GC-ECD was calibrated each work day** in order to check the ECD for linearity and sensitivity.
- **Limits of quantifications (LOQs)** of BFR was calculated from the lowest calibration level and accounted for 10 to 25 mg/kg (10 to 25 ppm) polymer. **This levels are below the lowest provisional Basel Convention low POPs limit of 50 mg/kg for PBDEs or 100 mg/kg for HBCD. Therefore the method is able to quantify samples according Basel Convention requirements**

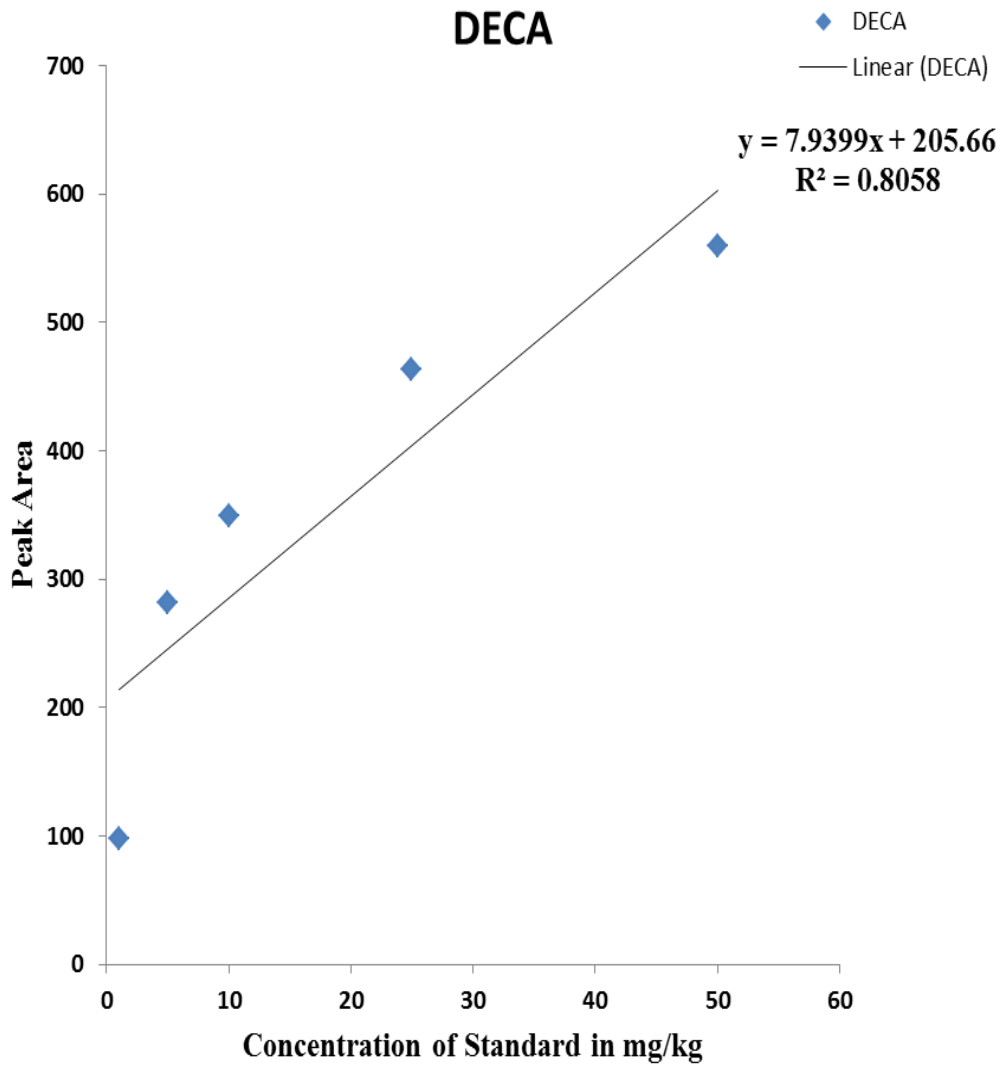
- **Blank injections were done to check for cross contaminations from plastic extract sample to sample.**

# Quantification of PBDEs/BFRs by external calibration

GC-ECD system was calibrated with standard mixtures of commercial BFR each work day.

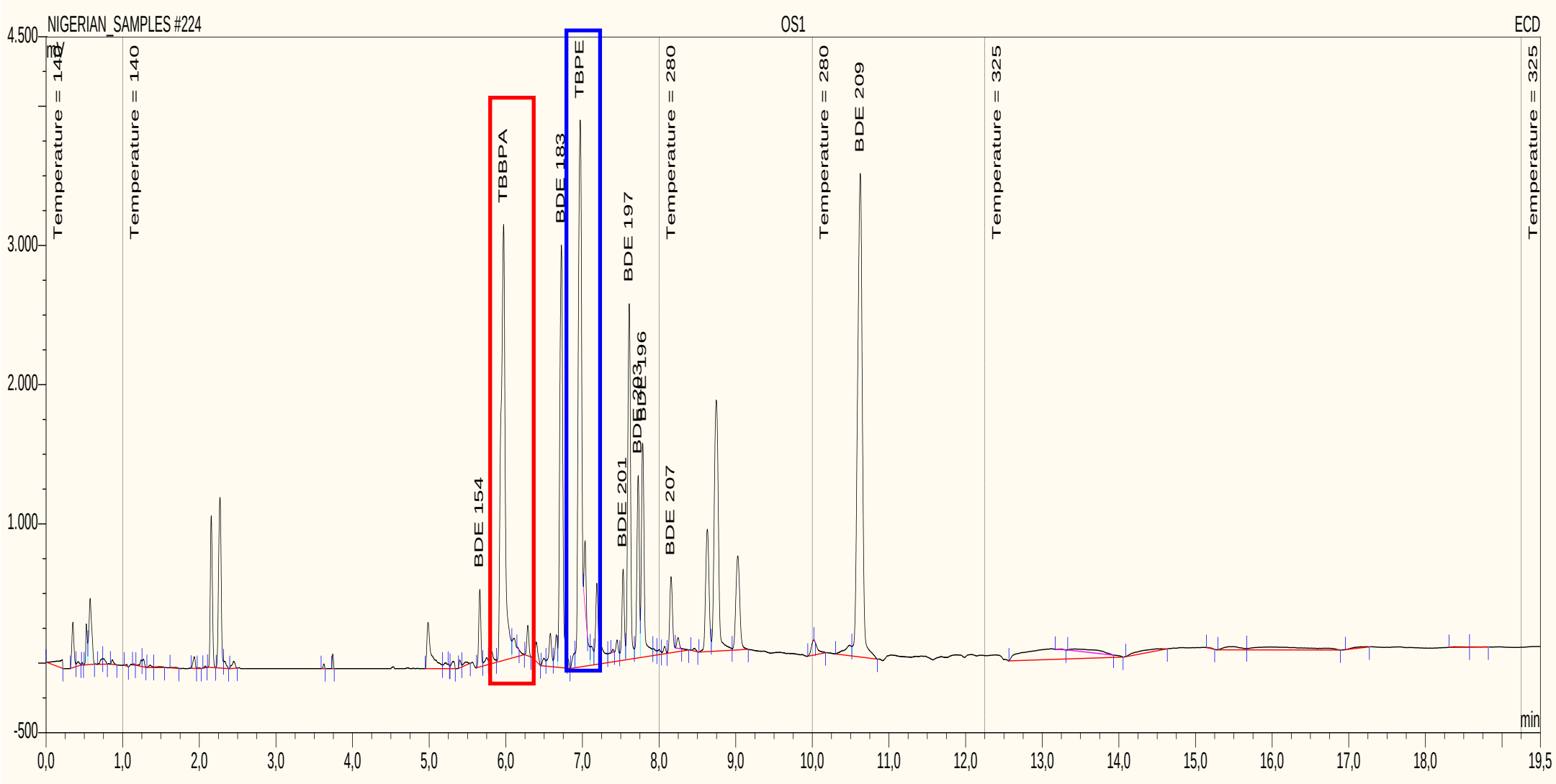
Here the calibration curves of DecaBDE and TBBPA



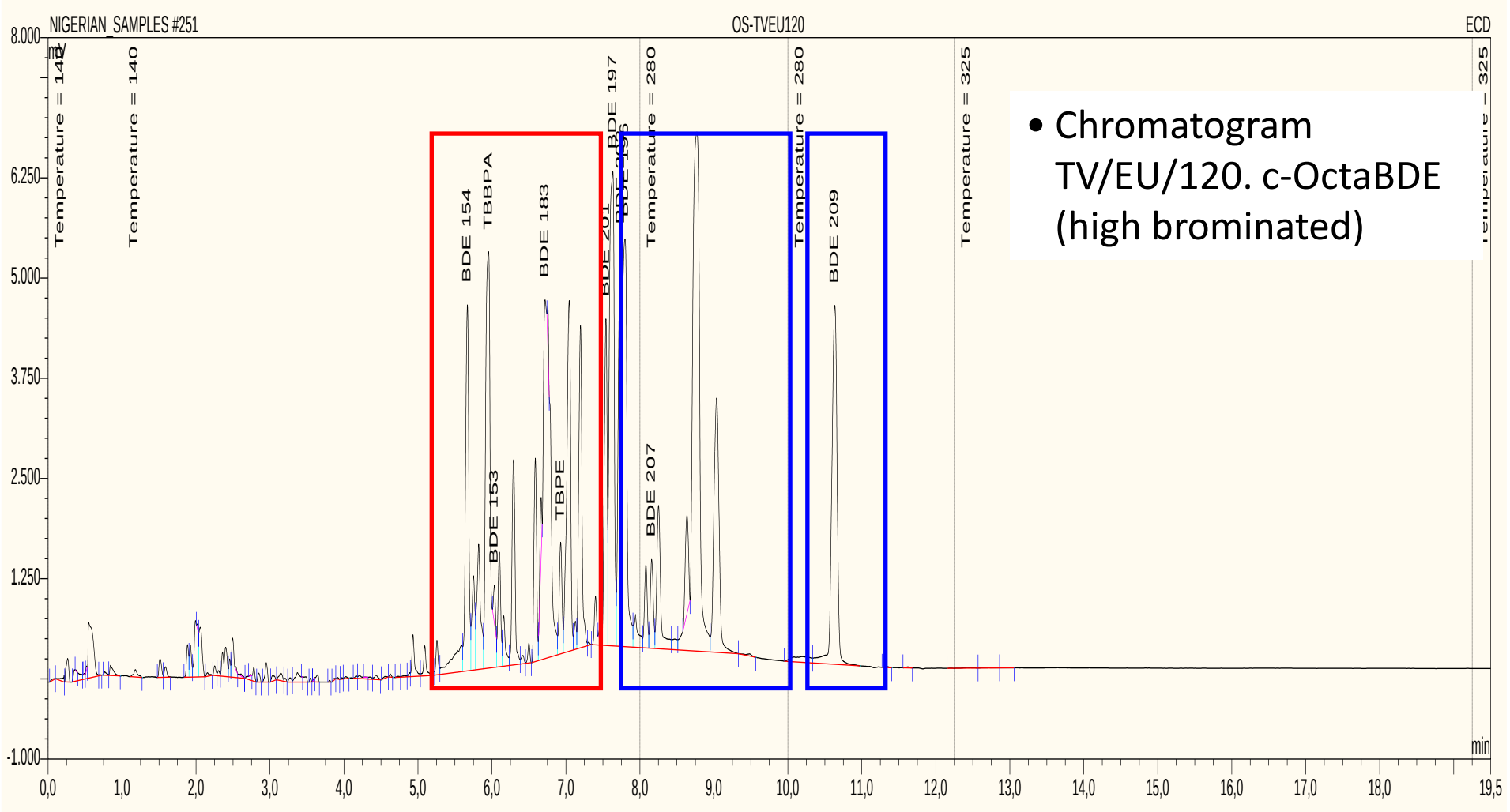
# GC-ECD Chromatogram of 50 ppm Standard mixture of TBBPA, TBPE, OctaBDE and DecaBDE

BFRs were identified by comparison of retention times with external technical standards of major isomers of **c-OctaBDE, DecaBDE, Tetrabromobisphenol A (TBBPA)** and 1,2- bis-tribromophenoyethane (TBPE).



# Samples analysis for BFRs of Nigerian CRT plastic casings with GC/ECD

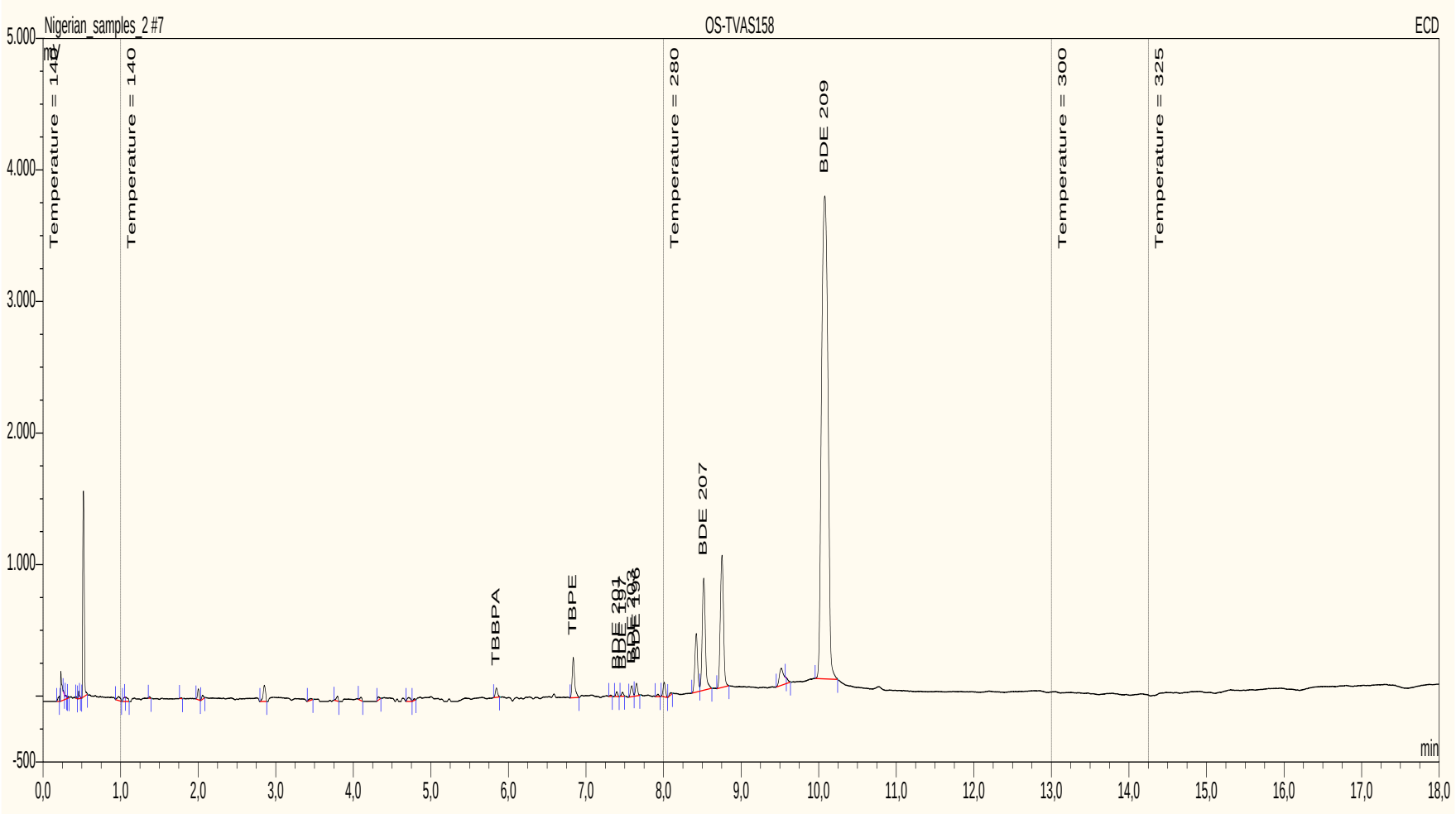
**Commercial OctaBDE detected in a CRT plastic with major hexaBDE (BDE-153, BDE-154), heptaBDE (BDE-183)** and **octaBDE (BDE-196; BDE197)** can also contains **relevant amount of nonaBDE (BDE-207)** and **DecaBDE.** Variation in production (see UNEP 2017)




- Chromatogram TV/EU/120. c-OctaBDE (high brominated)

# Samples analysis for BFRs of Nigerian CRT plastic casings with GC/ECD

## GC-ECD Chromatogram of a television from Europe (TV/AS/158) containing high levels of decaBE with low levels of nonaBDE as normally found in commercial decaBDE

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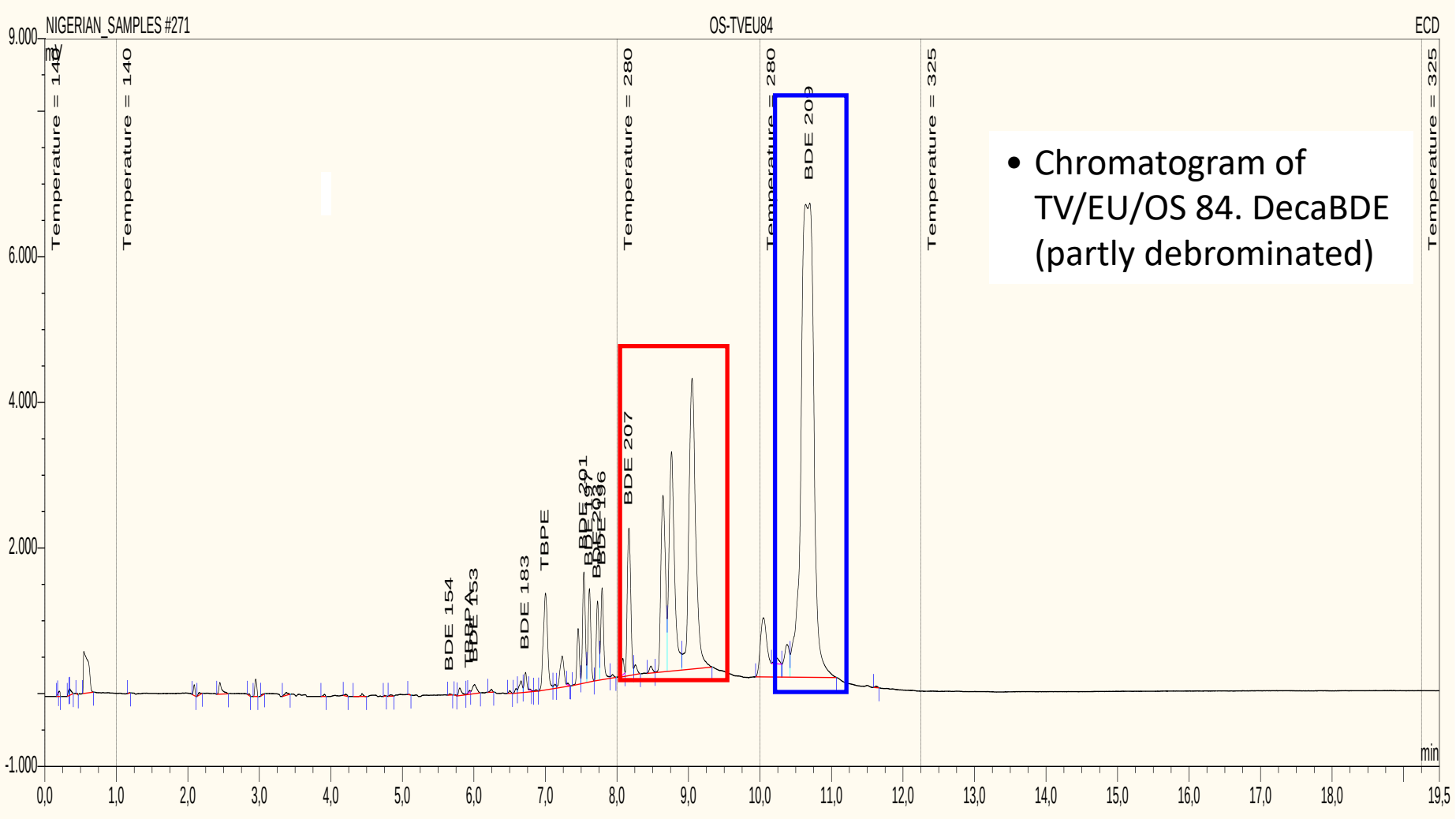
# Samples analysis for BFRs of Nigerian CRT plastic casings with GC/ECD

**But commercial decaBDE in CRT plastic samples were often associated with relative high levels of of nonaBDE (BDE-207)** which indicates that the original c-DecaBDE is partly dibrominated in the weathering CRT casings over the decades in the African sun.

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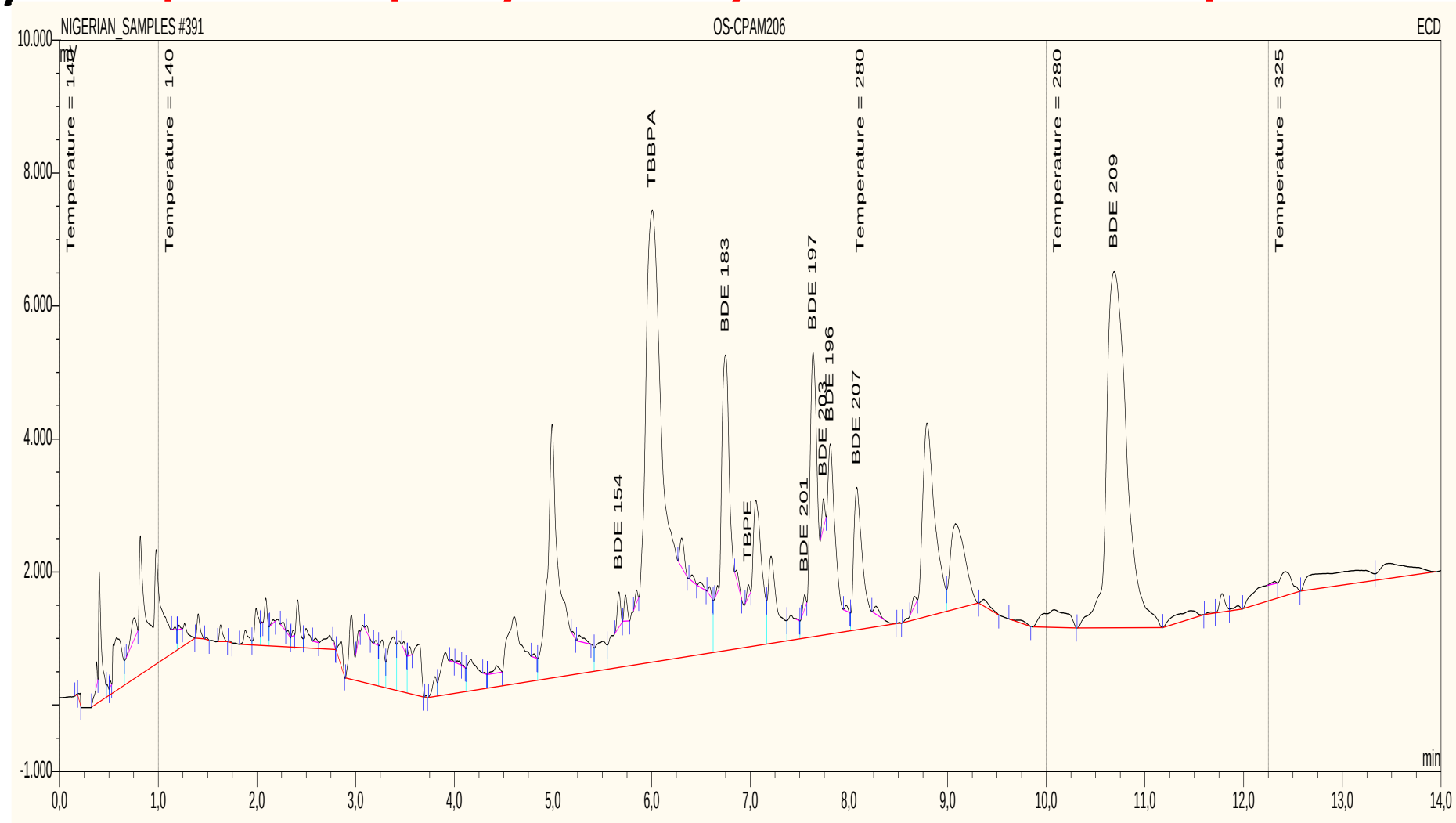
# Samples analysis for BFRs of Nigerian CRT plastic casings with GC/ECD

**GC-ECD Chromatogram of a CRT computer casing from America (CP/AM/206) containing mixture of BFRs (TBBPA, c-OctaBDE; DecaBDE) at lower levels indicating that it has likely been produced partly from recycled flame retarded plastic.**

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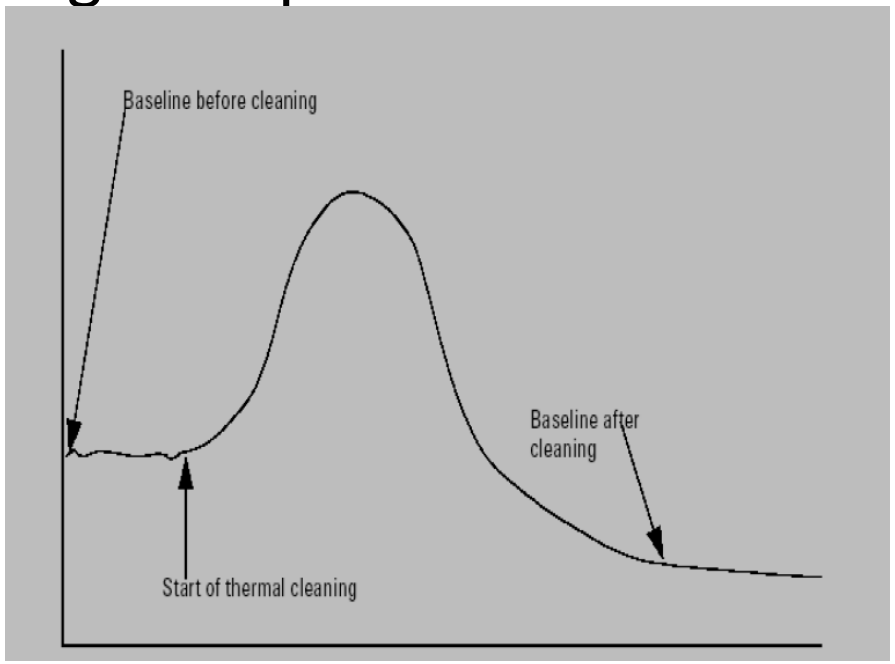
# Some Conclusions on using GC-ECD for PBDE/BFR analysis of WEEE (and other FR) plastic

- GC-ECD has excellent sensitivity for brominated flame retardants. Levels of BFRs in plastic are anyway high (ppm up to 25%) and easily detectable.
- The GC-ECD detect all BFRs injected. Therefore ECD is very suitable to monitoring recycled plastic products often containing multiple BFRs
- One advantage of the ECD is its robustness. The ECD can be heated to 350°C (and some up to 400°C) and a thermal cleaning can be performed (also called a “bakeout”). This is very beneficial for plastic samples.




- Due to their reasonable price and robustness, ECD are often available in developing countries and have lower maintenance cost. We have good experience with GC-ECD.


**HELP KEEP ELECTRONIC WASTE FROM GROWING!!!**