IPCP Webinar Series: POPs in plastic and monitoring approaches
Part III: Extraction, clean-up, and analysis of POPs in plastics

# Screening of specific brominated flame retardants (BFR) in WEEE plastic without extraction by FT-IR

Nudjarin Ramungul, Yot Boontongkong, Yawadee Temtanapat, Pavares Viwattanasittiphong, Nuengruthai Chuayrueng, Saisamorn Koonhorm, Arjaree Ausavanonkulporn

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Nudjarin Ramungul
(nudjarr@mtec.or.th)
Environment Research Group & MTEC's CE Team
National Metal and Materials Technology Center (MTEC)
National Science and Technology Development Agency (NSTDA)

# POPs BFR detection & monitoring challenges

- Lots of substances (BFRs) & lots of potentially relevant products
  - 5 BFRs currently in SC POPs List & likely more to come
- Lack of upstream data
  - Very limited data available from stakeholders & national database
- High costs of downstream monitoring
  - BFR detection typically involve materials extraction and clean-up followed by analysis of the extracted substances using highly sensitive equipment
    - Resource-intensive, time consuming & costly
- Results?
  - Limited number of testing & studies
  - Not enough data to predict FR usage patterns
  - Insufficient data/information for informed decision-making

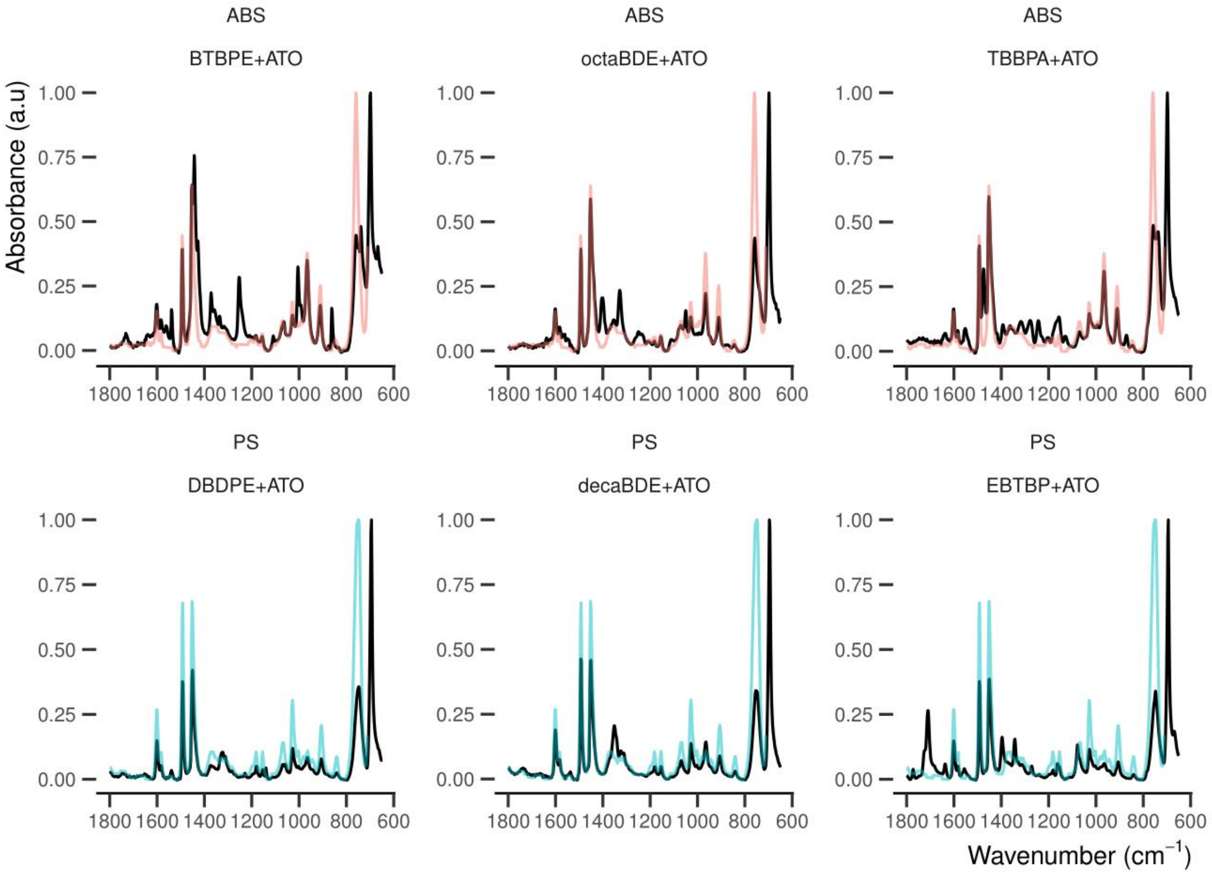
# ATR FT-IR can help filling the information gap

Attenuated total reflection (ATR) Fourier Transform Infrared Spectroscopy (FT-IR)

- FTIR can provide information on existing functional groups within materials
- Rapid and cost-effective
- FTIR spectra possess rich information
  - FT-IR is a non-targeted analysis technique – allowing for simultaneously detection and identification of various chemical compounds present in the sample.
- Non-destructive analysis
- Accessible
  - FT-IR spectroscopy are widely available in many laboratories
  - FT-IR does not require extensive training to operate and interpret results

# ATR-FTIR spectra exhibit distinct patterns

But it can be overwhelming if BFRs are to be identified manually




Actual WEEE samples consist of various constituents such as pigments, stabilizers, fillers, and more, leading to spectral overlaps.

Additionally, recycled pellets may contain degraded resins or constituents.

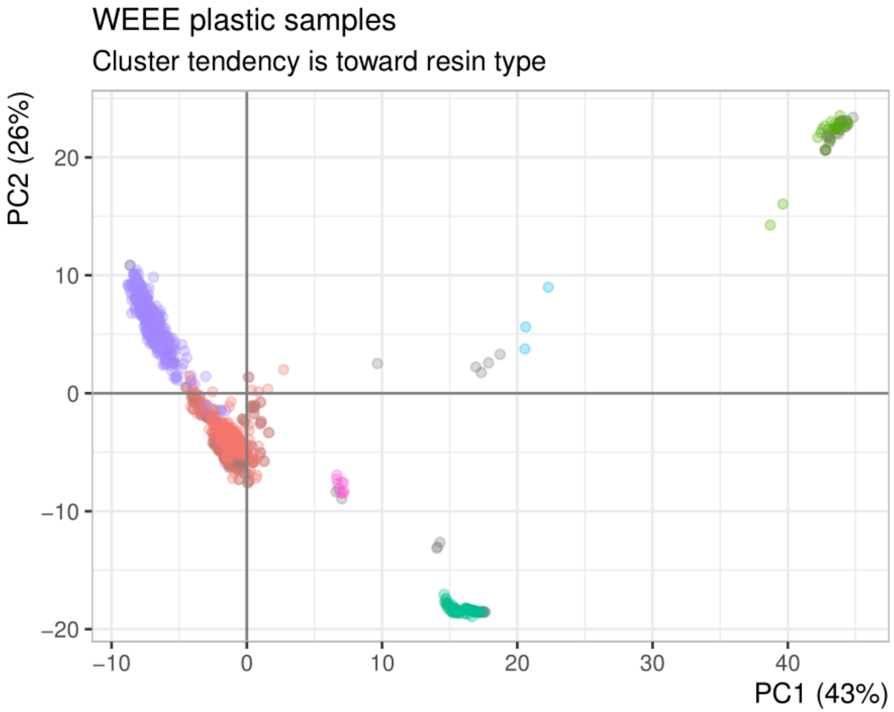
# Shortcomings of ATR FT-IR

## for identification of BFR in WEEE plastics

- Complications from spectral overlaps
- Limited sensitivity
  - – Difficulty detecting BFRs present in trace amount
    - LOD ~1-5%, depends on the type of the BFR and the underlying resins (and other constituents)
- Lack of specificity
  - – FT-IR detects functional group. Further analysis may be needed to confirm the presence of specific BFRs
  - – Challenges in identifying novel substances or substances that are not in the reference library
- Lack of quantitative accuracy

# Machine Learning (ML) assisted ATR-FTIR can be an effective tool

for effective classification of WEEE plastics



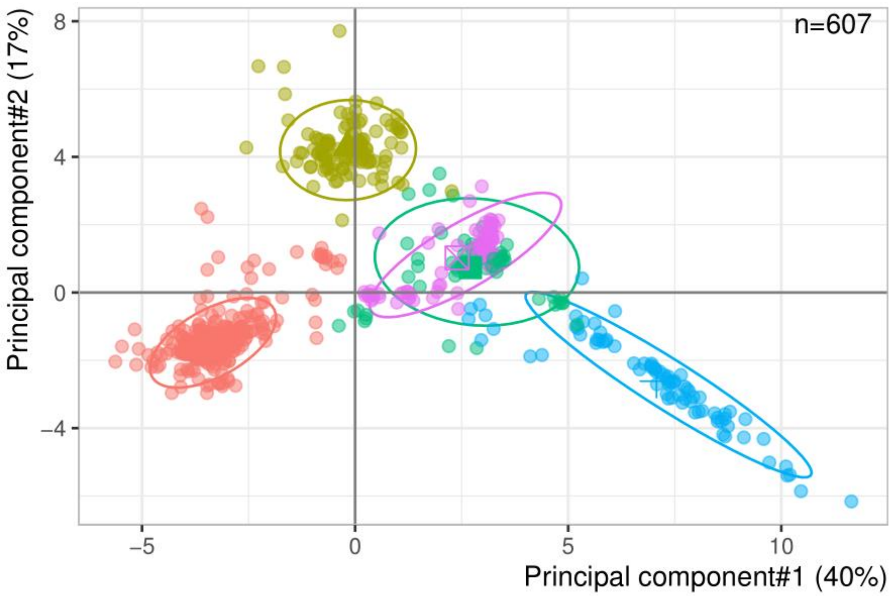

ML algorithms cluster spectra together based on their most distinctive features.

Relevant Factors (features):

- Materials related
  - Resins
  - Additives (Intentional & Non-intentional)
- Testing related
  - Equipment setup, resolutions etc.
  - Test methods & Operators

# Additive contents can be identified

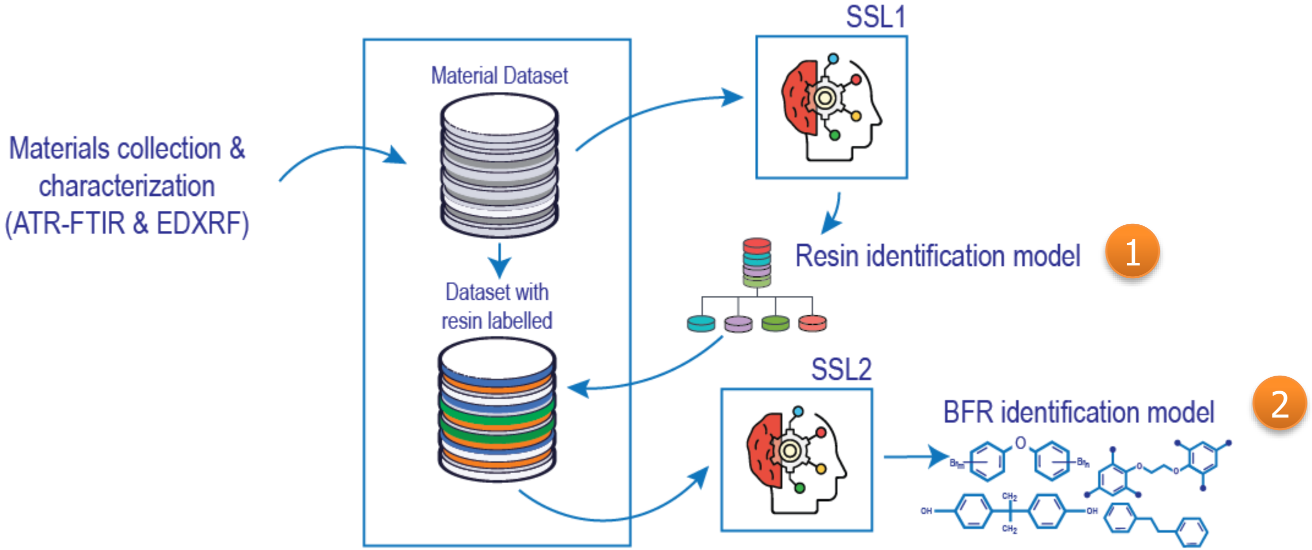
after removing unintended features from the dataset




PCA scores plot and associated cluster plot of ATR-FTIR spectra from 554 WEEE ABS samples and 53 impute spectra from "homemade" materials

# Our model framework

A **multi-stage semi-supervise learning (SSL)** framework for the identification of BFRs in ewaste plastics



# Process flow

FTIR & EDXRF

Shimadzu IR-Prestige-21
- PIKE technology MIRacle™ single-reflection ATR attachment
  - Diamond-coated ZnSe ATR Crystal
  - High pressure clamp

Pre-processing

Clustering

Sampling

Inhouse produced ("homemade") samples ($n = 27$)

Shimadzu QP2010 GC-MS
- Frontier Lab PY-2020iD Double-shot pyrolyzer
- Thermo-Dionex™ ASE™ 350 Accelerated Solvent Extractor

ID by GCMS ($n = 30$)

ID & label by experts

'Hard' labeling

Quasi-labeling

Semi-supervise learning model

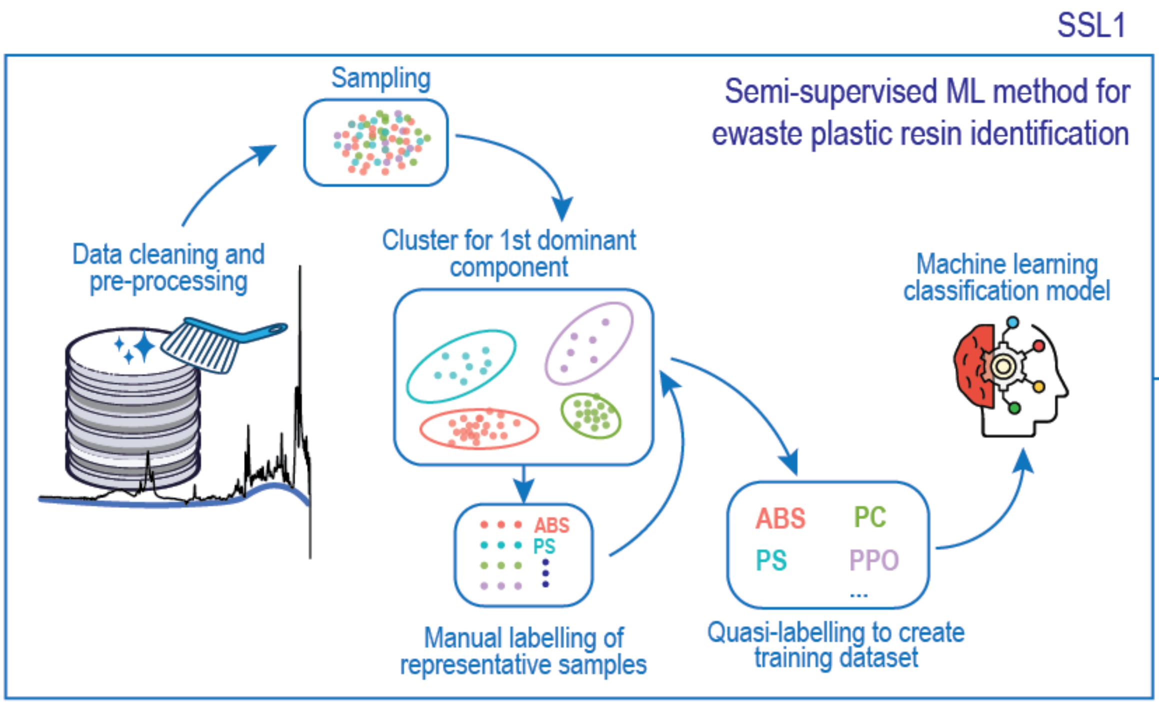
100% check by experts

Full machine learning dataset

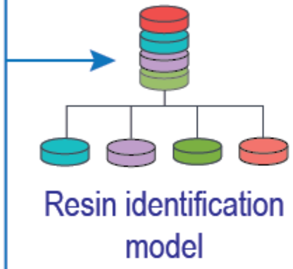
Predictive model

Performance check & tuning:
- Replicate samples
- Replicate spectrums
- Simulation (Repeated CV & Bootstrap)

# SSL1: Resin identification model




k-Nearest Neighbors (kNN) (with k=5) to classify 7 types of WEEE plastics (ABS, PS, PP, PC, PVC, PB, PPO)



# Resins classification model: kNN, k=5

Some problems with PVC, PB, PPO due to low number of (real) samples

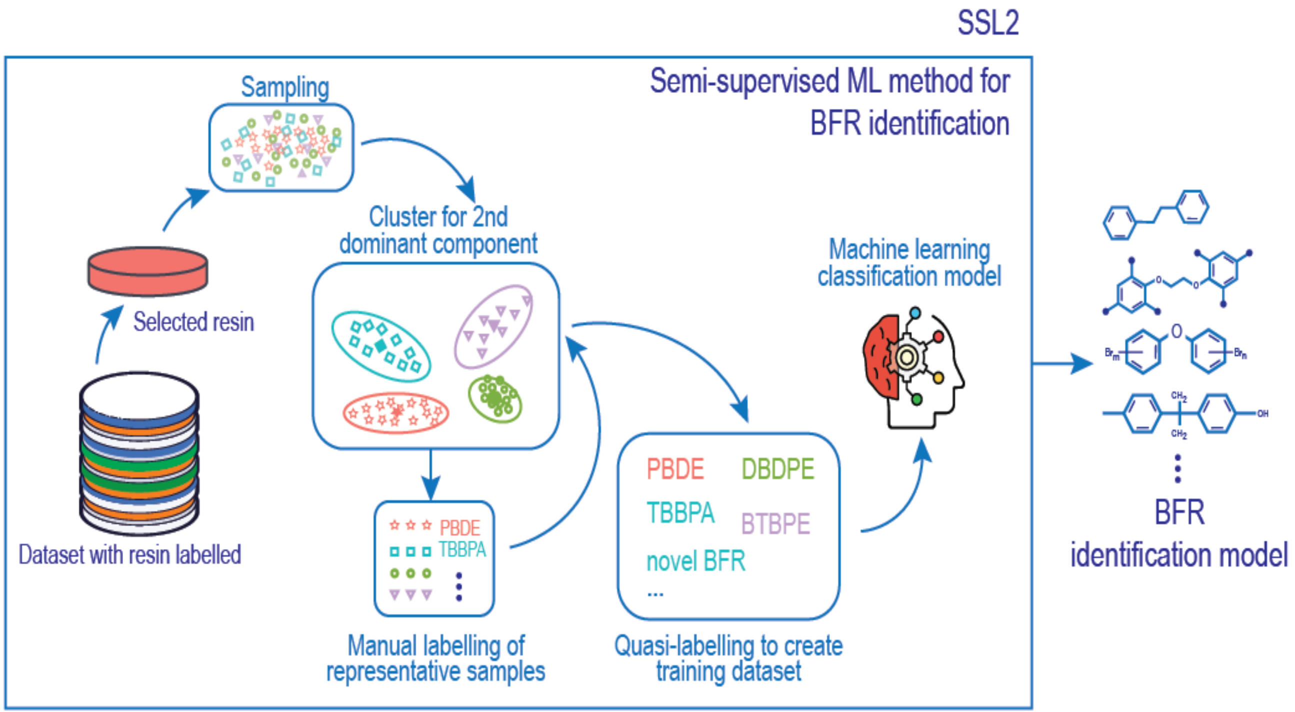
Test samples

```
## Confusion Matrix and Statistics
##
##            Reference
## Prediction ABS PB PC PP PPO PS PVC
##        ABS  37  0  0  0   0  1   0
##        PB    0  0  0  0   0  0   0
##        PC    0  0  2  0   0  0   0
##        PP    0  0  0  6   0  0   0
##        PPO   0  0  0  0   0  0   0
##        PS    0  0  0  0   0 35   0
##        PVC   0  0  0  0   0  0   2
##
## Overall Statistics
##
##                Accuracy : 0.988
##                  95% CI : (0.9347, 0.9997)
##     No Information Rate : 0.4458
##     P-Value [Acc > NIR] : < 2.2e-16
##
##                   Kappa : 0.9801
```

Validation samples

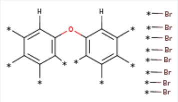
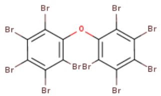
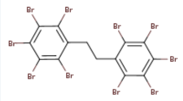
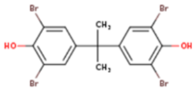
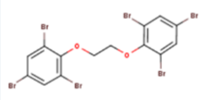
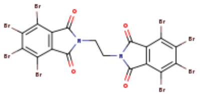
```
## Confusion Matrix and Statistics
##
##            Reference
## Prediction ABS PB PC PP PPO PS PVC
##        ABS  79  0  0  0   0  0   0
##        PB    0  0  0  0   0  0   0
##        PC    0  0  3  0   0  0   0
##        PP    0  0  0  0   0  0   0
##        PPO   0  0  0  0  15  0   0
##        PS    0  0  0  0   0 47   0
##        PVC   3  0  0  0   0  0   0
##
## Overall Statistics
##
##                Accuracy : 0.9796
##                  95% CI : (0.9415, 0.9958)
##     No Information Rate : 0.5578
##     P-Value [Acc > NIR] : < 2.2e-16
##
##                   Kappa : 0.9652
```

# SSL2: BFR identification model



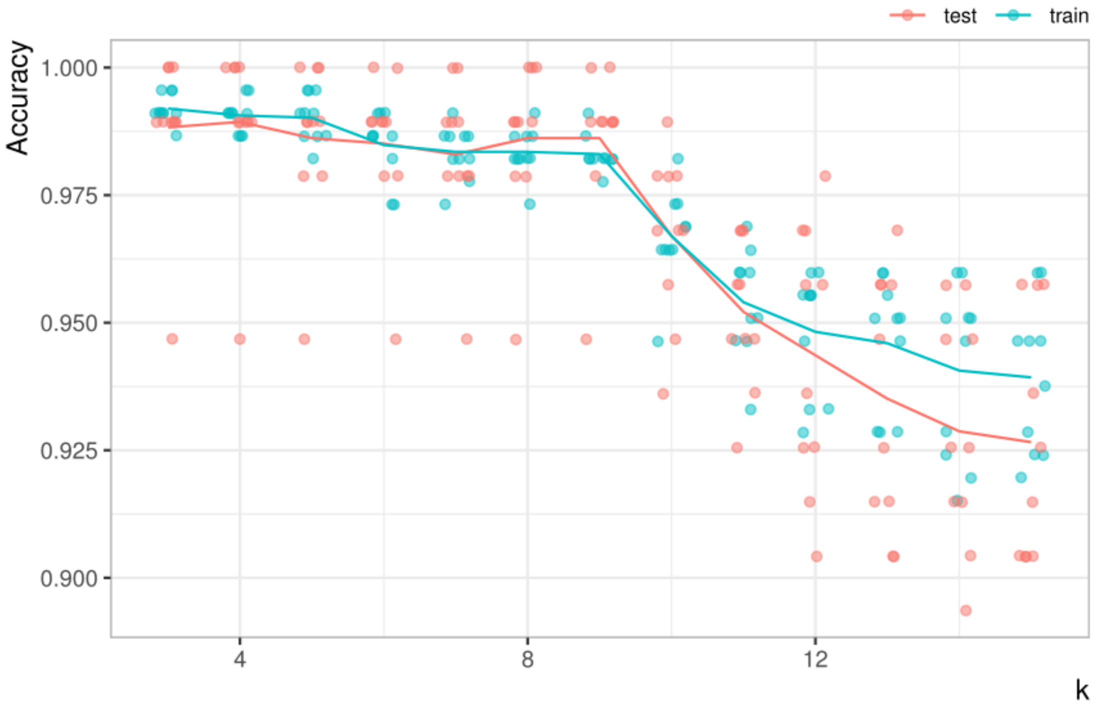

kNN to classify BFRs in targeted resins (ABS, PS)

# Types of BFR included in our ML model

| Abbreviation | | Substance | CAS No | Known Tradename |
|---|---|---|---|---|
| C-octaBDE |  | Octabromodiphenyl ether | 32536-52-0 | DE79, BDE 203, Saytex 105, FR1208 |
| C-decaBDE |  | Decabromodiphenyl ether | 1163-19-5 | FR 300BA, Saytex 102[E], Bromkal 83, PBDE 209, FR1210 |
| DBDPE |  | Decabromodiphenyl ethane | 84852-53-9 | Saytex 8010, FIREMASTER 2100 |
| TBBPA |  | Tetrabromobisphenol A | 79-94-7 | Firemaster BP4A, Saytex RB 100PC, FG 2000, FR-1524 |
| BTBPE |  | 1,2-Bis(2,4,6-tribromophenoxy)ethane | 37853-59-1 | FF680, FM680 |
| EBTBP |  | Ethylene Bis(Tetrabromophthalimide) | 32588-76-4 | Saytex BT93 |

# BFRs in ABS Training: Cross-validation

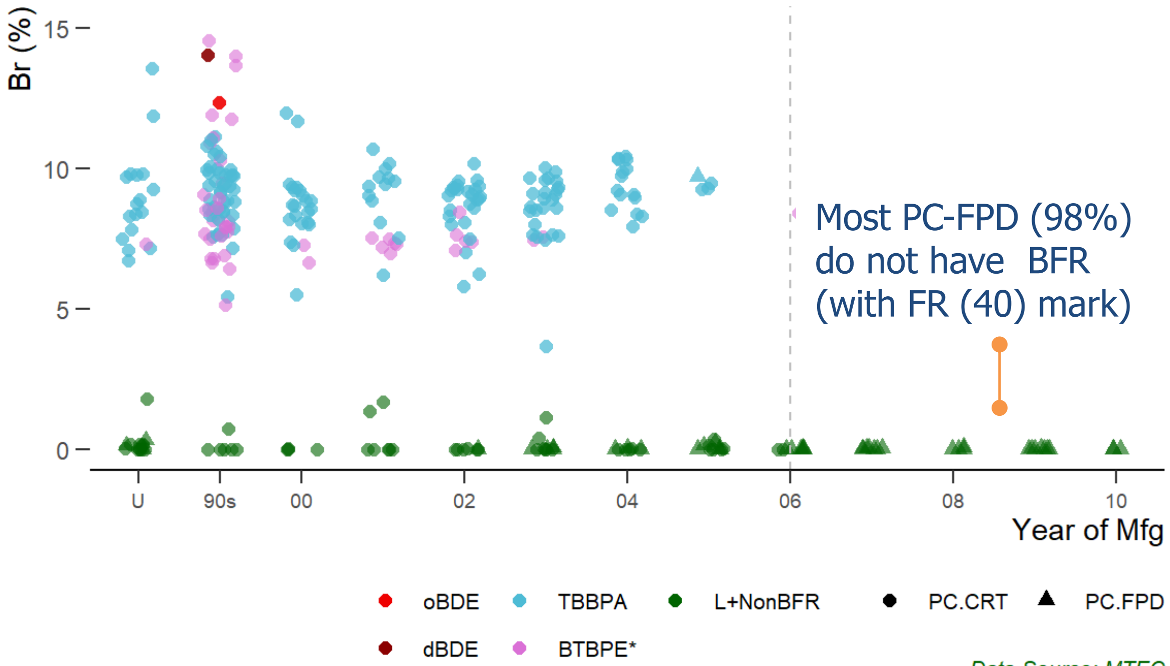
Train: Test = 70:30



# Apply the ML model to identify BFRs in WEEE ABS

ABS from EOL PC monitors

2 out of 316 unique PC monitor housings contain PBDEs




*Data Source: MTEC*

## BFR use pattern for ABS

Not PBDE but BTBPE → TBBPA

found only 2 samples w/ PBDE (from our dedicated attempt to find PBDE in WEEE-ABS)

1 octaBDE
- Unfamiliar brand
- Produced in 1994
- Unknown country of origin

1 decaBDE (also with high octaBDE)
- Hi-end brand (from mini/mainframe computer)
- Produced in 1995
- From an Asian country

# Summary

- ATR-FTIR coupled with ML classification algorithms can be used to help identify BFRs in WEEE plastics.
- The proposed method provides meaningful information for understanding the usage patterns of BFRs in Thai WEEE plastics.
- It can be useful for various applications, such as checking feedstocks, improving products, and developing data to inform decision-makers.
- The method is complementary to existing highly sensitive analysis techniques

MTEC
a member of NSTDA

# THANK YOU

## ศูนย์เทคโนโลยีโลหะและวัสดุแห่งชาติ

WWW.MTEC.OR.TH

### Contact information

**CE@MTEC**

114 Thailand Science Park, Phahonyothin road,
Klong Nueng, Klong Luang
Pathum Thani, 12120
DE4CE@mtec.or.th

SMART CIRCULAR www.mtec.or.th/smartcircular

# List of abbreviation

| Abbreviation | Explanation | Abbreviation | Explanation |
|---|---|---|---|
| ABS | Acrylonitrile butadiene styrene | HBCD | Hexabromocyclododecane |
| ATO | Antimony trioxide | HH-EDXRF | Hand-held Energy dispersive X-Ray fluorescent spectroscopy |
| BFR | Brominated flame retardants | MFA | Material flow analysis |
| BTBPE | 1,2-Bis(2,4,6-tribomophenoxy)ethane | PBB | Polybrominated biphenyls |
| CRT | Cathode ray tubes | PBDEs | Polybrominated diphenylethers |
| DBDPE | Decabromodiphenyl ethane | PCA | Principle component analysis |
| EBTBP | Ethylene Bis(Tetrabromophthalimide) | PS | Polystyrene |
| EOL | End-of-life | RoHS | Restriction of the use of certain hazardous substance |
| FPD | Flat panel display | TBBPA | Tetrabromobisphenol-A |
| FR | Flame retardants | WEEE | Waste of electrical and electronic equipment |