Instrumental analysis of new listed POPs Dechlorane Plus and UV-328

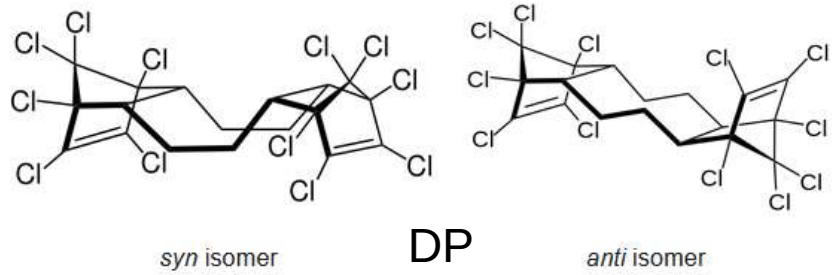
IPCP Webinar Series:
POPs in plastic and monitoring approaches
Part III: Extraction, clean-up, and analysis
of POPs in plastics
Tuesday, May 23, 2023

Ludwig Gruber

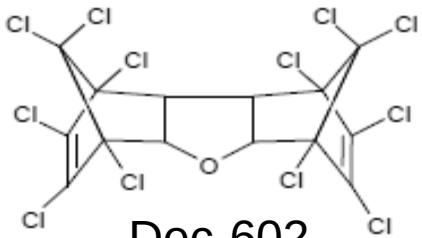
Head of Laboratory for Contaminants Analysis
ludwig.gruber@ivv.fraunhofer.de

Fraunhofer IVV

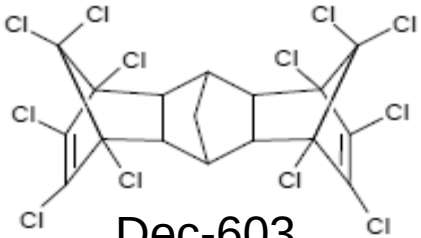
Dechlorane Plus



DP



Dec-602



Dec-603

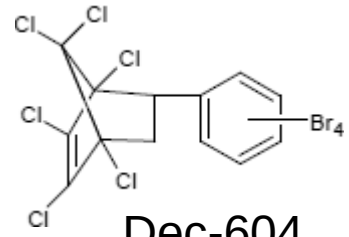
Dechlorane Plus® (abbrev. DP) is a polychlorinated flame retardant produced by Occidental Petroleum Corporation.

It is a substance of very high concern due to its very persistent and very bioaccumulating properties. The substance is widely detected in the global environment and some studies indicate increasing concentrations.

There is a restriction proposal by Norway (see Annex XV report).

There are also similar polychlorinated flame retardants called Dechlorane-602, -603 and Dechlorane-604.

<u>Native Standards</u>
Dechlorane-602
Dechlorane-604
Dechlorane-604 Component A
Dechlorane Plus® anti
Dechlorane Plus® syn
Dechlorane Plus® Technical Product



Dec-604

<u>Internal Standard</u>
Dechlorane Plus® anti (bis-cyclopentene-13C10,99%)

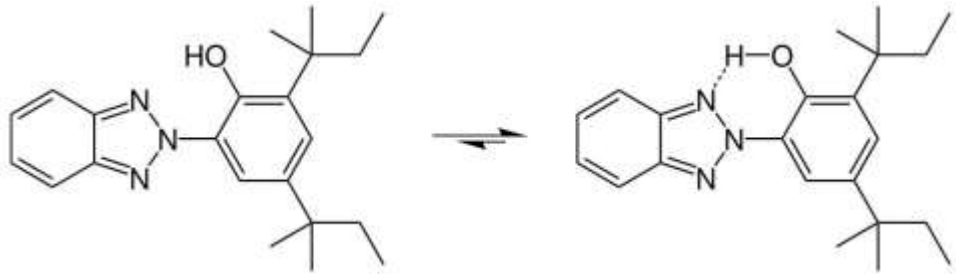
UV-328

UV-328
(2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol)

is a light or UV stabilizer for a variety of plastics like styrene based and acrylic polymers, unsaturated polyesters, polyvinyl chloride, polyolefins, polyurethanes, polyacetals, polyvinyl butyral, elastomers and adhesives.

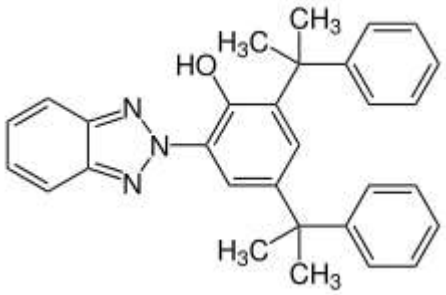
UV-328 has been identified as a Substance of Very High Concern (SVHC) in the EU.

Technical use is typically recommended concentration of UV-328 is between 1 and 3%.



Native Standard
Tinuvin 328

Internal Standard
Tinuvin 234



Fraunhofer IVV

Project with Norwegian Env. Agency

In support of ongoing regulatory processes for Dechlorane Plus (DP) under the *EU REACH legislation* and the *Stockholm Convention on POPs*, and in preparation for discussions on POPs waste by the Conference of the Parties to the Stockholm- and Basel Conventions, in the years 2020/2021 the Norwegian Environment Agency together with Ramboll and Fraunhofer IVV was starting a collaborative project.

We were collecting information on DP and other substances of concern in post-consumer waste destined for recycling and related secondary raw materials. Dechlorane Plus was only detected five times (in 26 investigated samples) with a maximum concentration of 16 mg/kg. Dechlorane Related Compounds were not found.

Analytical Instrumentation used

GC-Single quad-MS:
EI mode

PBDEs and Dechloranes

GC-ECD:
halogen screening,
TBBPA and BTBPE

LC-MS:
α-, β- and γ-HBCD

Sample preparation - 1

The sample material (0.5 – 1 gramm) is weighed into 50 ml centrifuge tubes together with **10 ml Toluene** (distilled quality).

The extraction is carried out for 15 h on an orbital shaker (175 rpm). After centrifugation for 10 min at 15000 rpm an aliquot of 1 ml of the supernatant is taken out and transferred into a 10 ml volumetric flask. The flask was filled beforehand with approximately **8 ml n-Hexane** (pesticide grade) to which the toluene extract was added dropwise for securing precipitation of solved polymers.

The flask is then filled completely with n-Hexane to the mark. The whole toluene/n-hexane mixture was then **filtrated through syringe filters** (PTFE membrane, 0.45 µm).

An aliquot of the filtrated extract is then taken for HBCD analysis via LC-MS (Thermo TSQ Quantum LC-MS-MS, neg mode, ESI, SRM; Column: EVO C18).

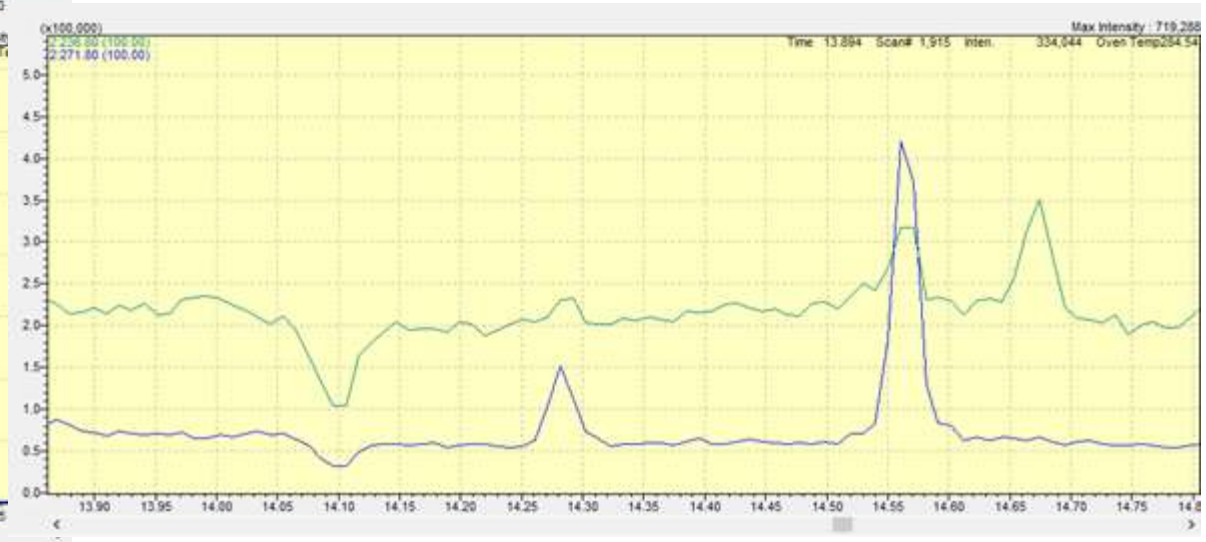
Sample preparation - 2

The rest of the toluene/n-hexane extract underwents a clean-up by adding **1 g of 44% sulfuric acid-impregnated silica gel**. For GC-MS analysis (PBDE, DBDPE and Dechloranes) an aliquot of 100 µl is taken after sedimentation of the silica gel, to which the internal standard substances (^{13}C-labeled anti-Dechlorane Plus and PBDEs) were added.

The used GC-MS-method was based on a simplified GC-MS-method for brominated flame retardants proposed by the National Institute for Environmental Studies, Japan (*Eguchi et al., 2021*). The instrument used was a quadrupole MS (Shimadzu QP2010 MS; Column DB-5HT (5 m x 0.25 mm, 0.1 µm, Agilent J&W). The detection was in single ion mode on specific mass fragments. The quantification was relying on both isotopes labelled internal standard substances and external calibration standards.

For determination of TBBPA and BTBPE an aliquot of the cleaned extract is analysed by GC-ECD. The instrument used was a Shimadzu GC-ECD with a 15 m DB-5 HT-column. External calibration was used for quantification.

Chromatogramms for Dechloranes



Dechlorane and anti-Dechlorane (standard solution)

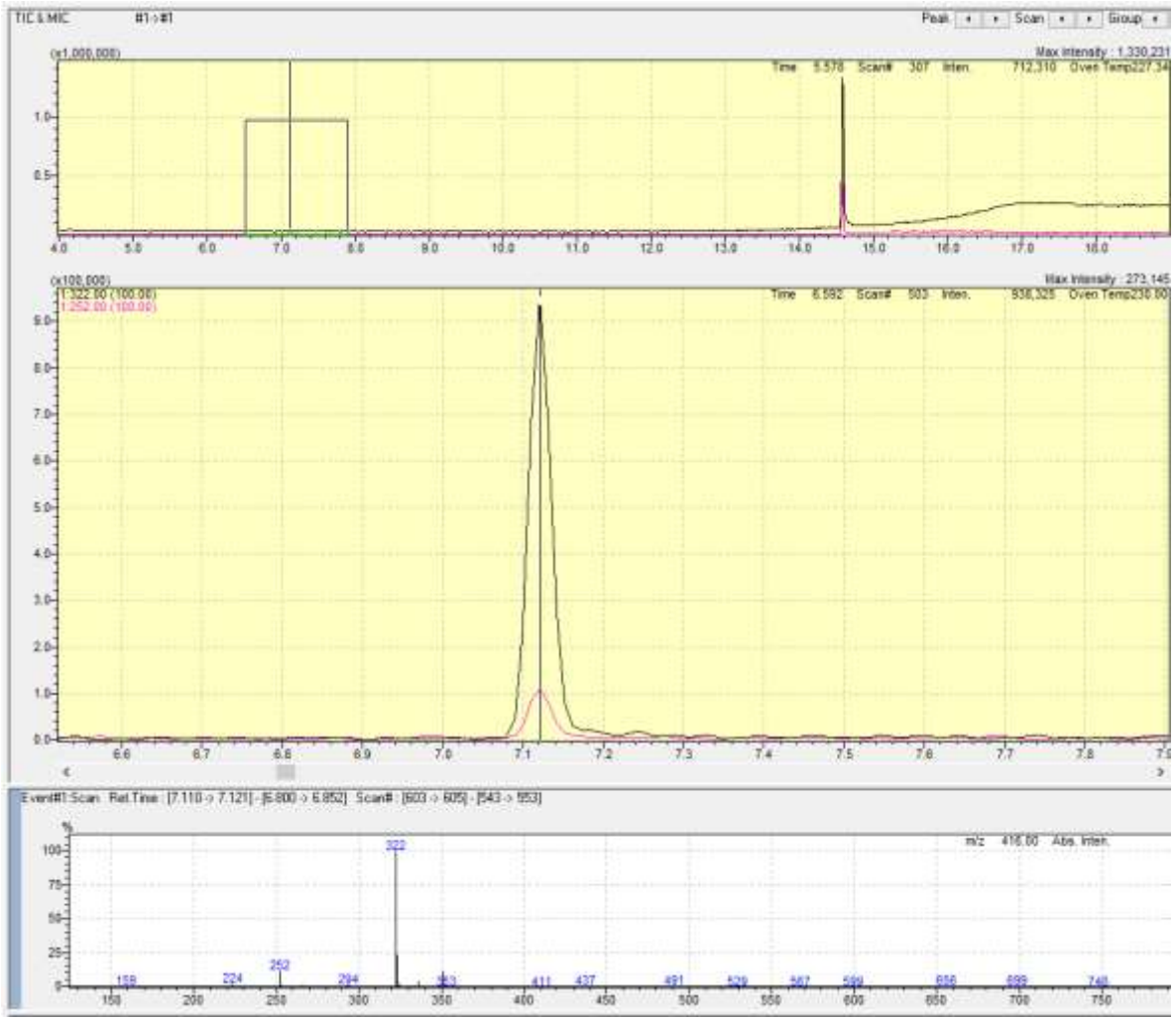
Project with UNEP

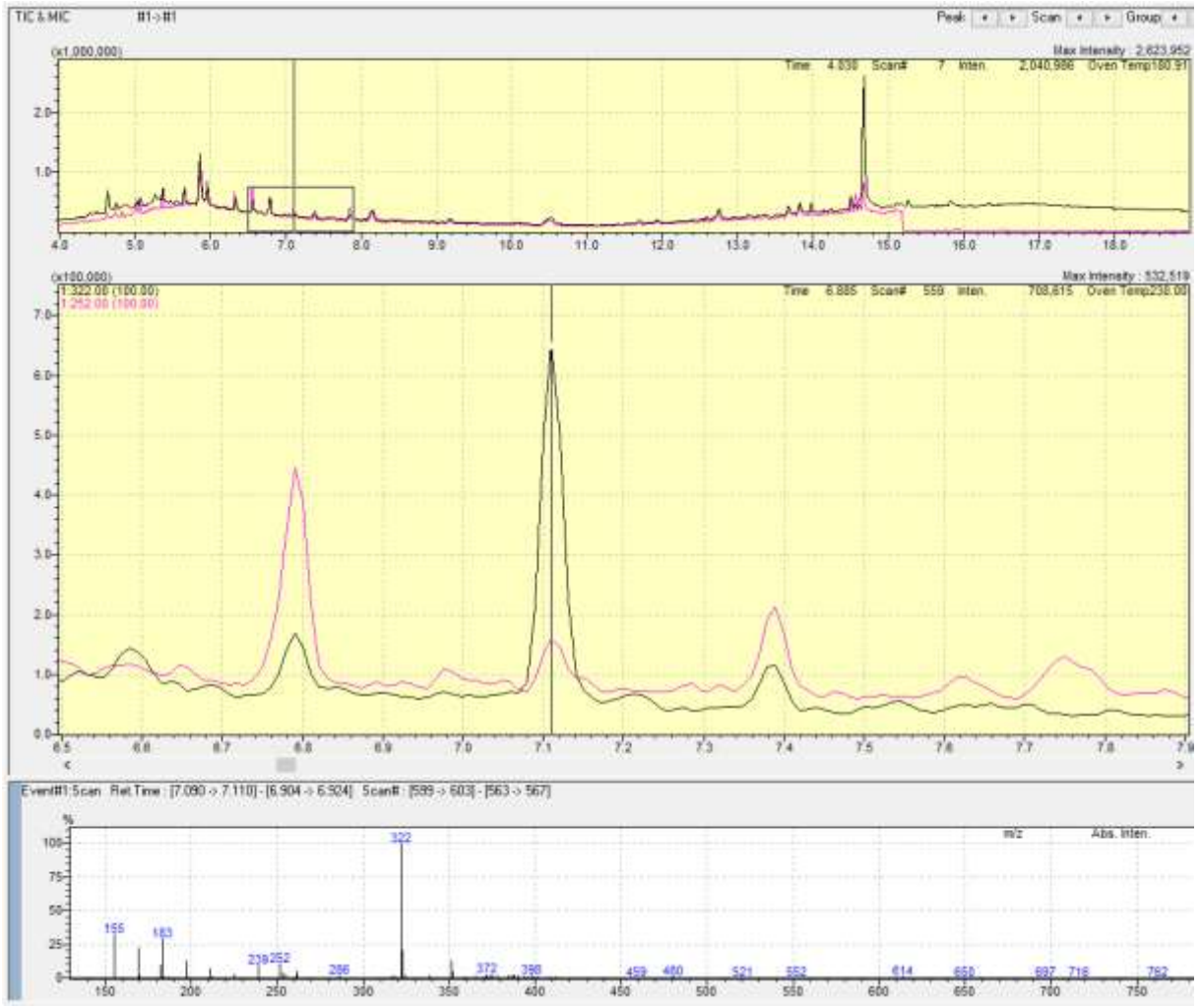
Plastics in their various applications contain a wide range of hazardous additives including several persistent organic pollutants (POPs) listed in the Stockholm Convention, such as HBCD, HBB, PBDEs, PCB, SCCP, Dechlorane Plus, and UV-328.

Environmental pollution from these POPs originates largely from the release from plastic (electronic products, vehicles, building materials, synthetic textiles) or plastic pellets. In developing countries, it is facilitated by open burning in end-of-life treatment and fires in dump sites. While a range of studies have been published on POPs in major product sectors, there is a lack of knowledge on POPs in plastic recyclates in developing countries. Therefore, activities are conducted with support from the UNEP/GEF POPs global monitoring plan projects from February to June 2023 and the International Panel on Chemical Pollution (IPCP) was tasked with the execution.

The main task of Fraunhofer IVV was the analysis of **Dechlorane Plus and UV-328**, but PBDEs will be analyzed on occasion.

Chromatogramms for UV-328





UV-328 (Standard solution and sample)

Work in progress

We modified the method from the NEA project to include UV-328:

- Use of a 15 m DB-5 HT column to make the analysis better comparable to GC-ECD
- Skip of the sulfuric acid step due to limited stability of UV-stabilizers
- Inclusion of UV-234 (Tinuvin 234) as internal standard
- Inclusion of the new chemical in a POP multimethod

First results show that the approach was successful.

Thank you for your attention !